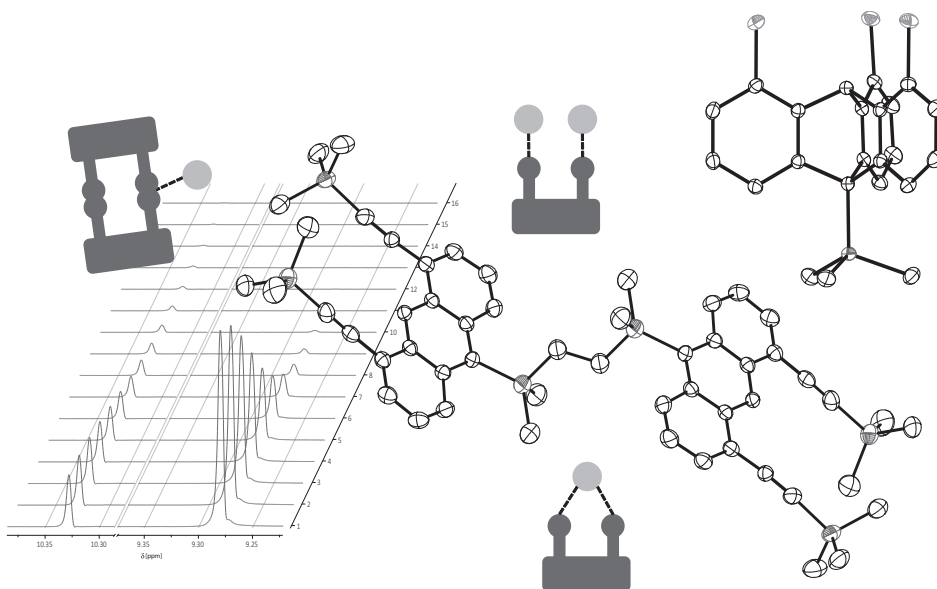


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# Anthracen-basierte Poly-Lewis-Säuren

Synthese, Charakterisierung und Wirt-Gast-Chemie

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Jan-Hendrik Lamm

–2014–

**Universität Bielefeld**  
Fakultät für Chemie  
Anorganische Chemie und Strukturchemie

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## **Kumulative Dissertation**

zur Erlangung des  
naturwissenschaftlichen Doktorgrades (Dr. rer. nat.)  
der Fakultät für Chemie  
der Universität Bielefeld

vorgelegt von  
**Jan-Hendrik Lamm**  
aus Bielefeld

–2014–

Dekan:	Prof. Dr. Norbert W. Mitzel
Erster Gutachter:	Prof. Dr. Norbert W. Mitzel
Zweiter Gutachter:	Prof. Dr. Berthold Hoge
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Diese Arbeit entstand in der Zeit von Oktober 2010 bis Mai 2014 unter der Anleitung von Herrn Prof. Dr. Norbert W. Mitzel in der Arbeitsgruppe Anorganische Chemie und Strukturchemie der Fakultät für Chemie an der Universität Bielefeld.

Meinem Doktorvater,

**Herrn Prof. Dr. Norbert W. Mitzel,**

danke ich herzlich für die Überlassung des interessanten Forschungsthemas, für sein stetes Interesse am Fortgang der Arbeit, für eine ausgezeichnete wissenschaftliche Betreuung in einer erstklassigen Arbeitsatmosphäre, für das mir entgegengebrachte Vertrauen und besonders für die vielen Freiheiten, die er mir bei der Bearbeitung der Aufgabe gewährt hat.



**I**ndes sie forschten, röntgten, filmten, funkten,  
entstand von selbst die köstlichste Erfindung:  
der Umweg als die kürzeste Verbindung zwischen zwei Punkten.

Erich Kästner (1899–1974), deutscher Schriftsteller

**Für meine Familie.**



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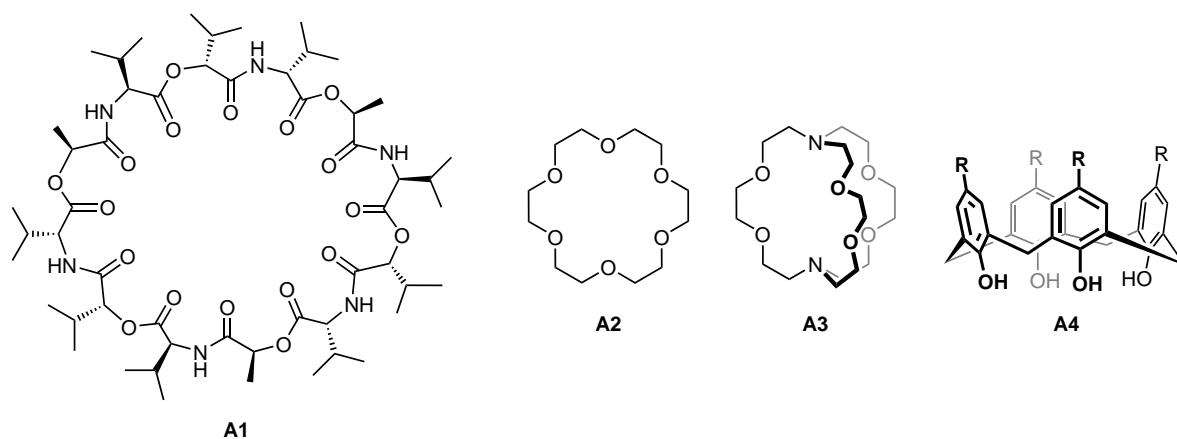


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# 1 Einleitung

In der Chemie der supramolekularen Systeme dominieren die nicht-kovalenten Wechselwirkungen, wie beispielsweise van der Waals-Wechselwirkungen, ionische Wechselwirkungen oder Wasserstoffbrückenbindungen. Neben den sich daraus ergebenden (synthetischen) Möglichkeiten zum Aufbau komplexer molekularer Systeme ("Molekulare Architektur") geriet die Supramolekulare Chemie auch deshalb verstärkt ins Blickfeld der chemischen Forschung, weil viele biologische und medizinische (Wirk-) Prozesse auf ebensolchen Wechselwirkungen beruhen.<sup>[1,2]</sup>

Die sogenannte *Wirt-Gast-Chemie*, bei der sich verschiedene Moleküle als *Gäste* in anderen *Wirtmolekülen* einlagern können, stellt dabei ein wichtiges Teilgebiet der Supramolekularen Chemie dar. Geprägt wurde der Begriff durch den US-amerikanischen Industriechemiker C. J. Pedersen, dem im Jahre 1967 die erstmalige Synthese cyclischer Polyether gelang, welche er als *Kronenether* bezeichnete.<sup>[3]</sup> Schema 1.1 zeigt mit [18]Krone-6 (**A2**) den bekanntesten Vertreter dieser Stoffklasse. Die Verbindung ist in der Lage, ebenso wie das natürlich vorkommende Antibiotikum Valinomycin (**A1**),<sup>[4]</sup> hochselektiv Kaliumkationen zu komplexieren.<sup>[2,5-7]</sup> In den darauf folgenden Jahren wurde eine Vielzahl unterschiedlichster Kronenverbindungen synthetisiert<sup>1</sup> und ihr erfolgreiches Prinzip der Gast-Komplexierung auf andere künstliche (dreidimensionale) Wirtssysteme, wie beispielsweise Kryptanden<sup>[8,9]</sup> (**A3**, von griech.: *Krypta* = Höhle) oder Calix[*n*]aren-Derivate<sup>[10,11]</sup> (**A4**, von lat.: *Calix* = Kelch) übertragen (Schema 1.1).



**Schema 1.1:** Beispiele für Wirtmoleküle: Das natürlich vorkommende Antibiotikum Valinomycin (**A1**) sowie die künstlichen Wirte [18]Krone-6 (**A2**), [2.2.2]Kryptand (**A3**) und ein Calix[4]aren-Derivat (**A4**).

<sup>1</sup>Bis zum Jahr 1989 waren über 5000 verschiedene Kronenverbindungen bekannt, die sich nicht nur in ihrer Ringgröße, sondern auch in der Art und Anzahl der enthaltenen Heteroatome unterscheiden.<sup>[6]</sup>

Wie aus den beispielhaft gezeigten Strukturformeln in Schema 1.1 hervorgeht, enthalten die Verbindungen mehrere N- und O-Heteroatome, die ihrerseits jeweils mindestens ein freies Elektronenpaar aufweisen. Gemäß der Lewis'schen Säure-Base-Definition<sup>[12]</sup> lassen sich solche Verbindungen entsprechend auch als *Poly-Lewis-Basen* bezeichnen, die in der Lage sind, Lewis-saure Gäste, also solche mit einem Elektronendefizit, zu binden.

Demzufolge stellen *Poly-Lewis-Säuren* die phänomenologischen Gegenstücke zu Poly-Lewis-Basen dar und sollten Lewis-basische, also Donoratom-haltige, Gastmoleküle komplexieren können. Die Untersuchung dieses zur Wirt-Gast-Chemie der Poly-Lewis-Basen inversen Gebietes gewann im Laufe der letzten drei Jahrzehnte stetig an Bedeutung, sodass es heute zu den wichtigen Bestandteilen der Supramolekularen Chemie zählt.<sup>[13,14]</sup> Allerdings sind die Kenntnisse in diesem Bereich im Vergleich zur Kationen- bzw. Lewis-Säuren-Erkennung durch polyfunktionale Lewis-Basen bis *dato* eher gering. Gründe hierfür liegen möglicherweise in der hohen Reaktivität der (metallorganischen) Lewis-aciden Wirtverbindungen aber auch im beschränkten Zugang zu geeigneten Donoratom-freien organischen Grundgerüsten, an denen die Lewis-sauren Atome fixiert werden können.

Die Erlangung neuer Erkenntnisse sowohl im Bezug auf die Synthese neuartiger, Donoratom-freier organischer Gerüste, ihre Funktionalisierung mit Lewis-aciden Substituenten als auch auf die Untersuchung der Wirt-Gast-Chemie von Poly-Lewis-Säuren soll Gegenstand dieser Arbeit sein.

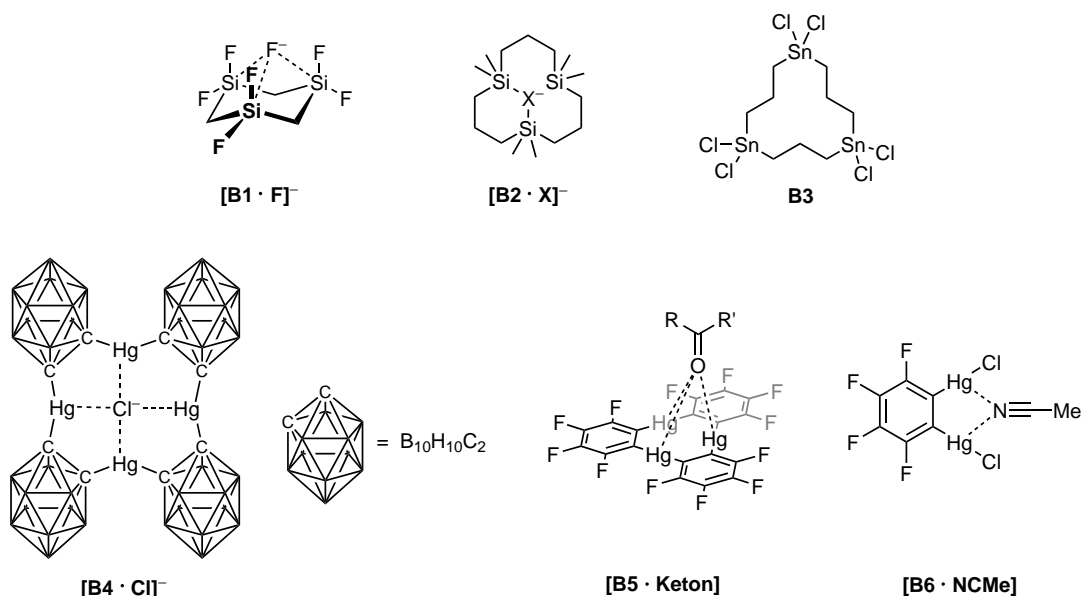
## 2 Kennnisstand

### 2.1 Poly-Lewis-Säuren und ihre Wirt-Gast-Chemie

#### 2.1.1 Silicium-, Zinn- und Quecksilber-basierte Wirtssysteme

Moleküle, bei denen mehrere Lewis-saure Atome an einem organischen Grundgerüst fixiert sind, werden, wie bereits erwähnt, als Poly-Lewis-Säuren bezeichnet. Die Chemie dieser Verbindungsklasse ist im Vergleich zur Chemie der sehr gut untersuchten komplementären Systeme, den Poly-Lewis-Basen verhältnismäßig wenig erforscht.

Gleichwohl sind einige Beispiele bekannt, wobei vornehmlich Silicium-,<sup>[15–18]</sup> Zinn-<sup>[19–22]</sup> oder Quecksilberatome<sup>[23–29]</sup> als Lewis-saure Funktionalitäten in den (Wirt-) Verbindungen eingesetzt werden. Schema 2.1 zeigt eine Auswahl prominenter Literaturbeispiele. Ihre Fähigkeit, als Lewis-saure Wirtssysteme einen Lewis-basischen Gast komplexieren zu können, wurde teilweise durch Umsetzung mit Anionen oder kleinen Lewis-basischen Molekülen nachgewiesen.



**Schema 2.1:** Beispiele einiger Poly-Lewis-Säuren mit Silicium- (**B1**<sup>[18]</sup> und **B2**<sup>[15]</sup>), Zinn- (**B3**<sup>[19]</sup>) und Quecksilberatomen (**B4**,<sup>[24,26]</sup> **B5**<sup>[28,29]</sup> und **B6**<sup>[25,27]</sup>) als Lewis-saure Funktionalitäten.

Das Trisilacyclohexan-Derivat **B1** kann Komplexe mit Fluorid-Ionen aus Kaliumfluorid bilden, wenn das Kalium-Kation von [18]Krone-6 koordiniert und so an der Salzbildung gehindert wird.<sup>[18]</sup> Die gezeigte [12]Silakrone-3 (**B2**) wurde bereits 1988 von Jung *et al.* synthetisiert und eignet sich ebenfalls zur Komplexierung von Halogenid-Ionen.<sup>[15]</sup>

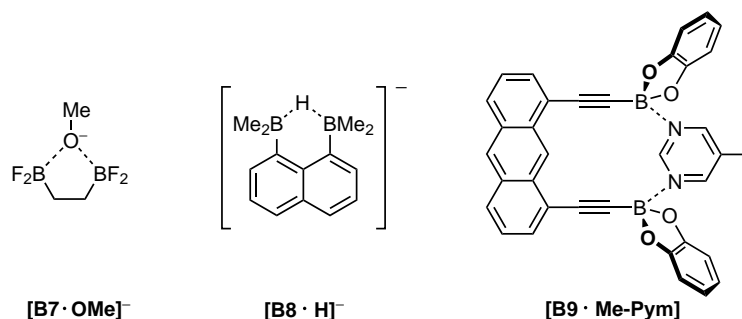
Der Zinn-Heterocyclus **B3** von Jurkschat und Mitarbeitern stellt ein Beispiel für die Zinn-basierten Poly-Lewis-Säuren dar, der Chlorid-Ionen komplexieren kann. Entsprechende Komplexe konnten mittels  $^{119}\text{Sn}$ -NMR-Spektroskopie nachgewiesen werden.<sup>[19]</sup>

Quecksilber-haltige Verbindungen, von denen eine kleine Auswahl im unteren Teil von Schema 2.1 gezeigt ist, sind in diesem Zusammenhang verhältnismäßig gut erforscht. Das Mercuracarboran **B4** stellten Hawthorne *et al.* im Jahr 1991 vor. Sie konnten zudem zeigen, dass **B4** in der Lage ist, Chlorid-Ionen zu umschließen.<sup>[24]</sup> Auch zwei Iodid-Ionen können von dem Rezeptor gebunden werden, wegen ihrer Größe allerdings nur ober- und unterhalb der  $\text{Hg}_4$ -Ebene.<sup>[26]</sup> Gabbaï und Mitarbeiter untersuchten das bekannte trimere *ortho*-Perfluorphenylen-Quecksilber (**B5**) bezüglich seiner Komplexbildung mit Aldehyden und Ketonen<sup>[28,29]</sup> sowie das 1,2-Bis(chloromercurio)tetrafluorbenzol (**B6**), von dem unter anderem die Kristallstruktur des Acetonitril-Komplexes aufgeklärt werden konnte.<sup>[25,27]</sup>

### 2.1.2 Erdmetall-basierte Wirtssysteme

Neben den vorstehend genannten Beispielen von Molekülen mit (Halb- oder Übergangs-) Metallatomen als Lewis-aciden Funktionalitäten sind auch einige Verbindungen bekannt, bei denen Elemente der Gruppe 13 zum Einsatz kommen. Bedingt durch das Elektronensextett an den (Halb-) Metallatomen eignen sich die Erdmetallelemente Bor, Aluminium, Gallium und Indium sehr gut, um polydentate Lewis-Säuren aufzubauen.

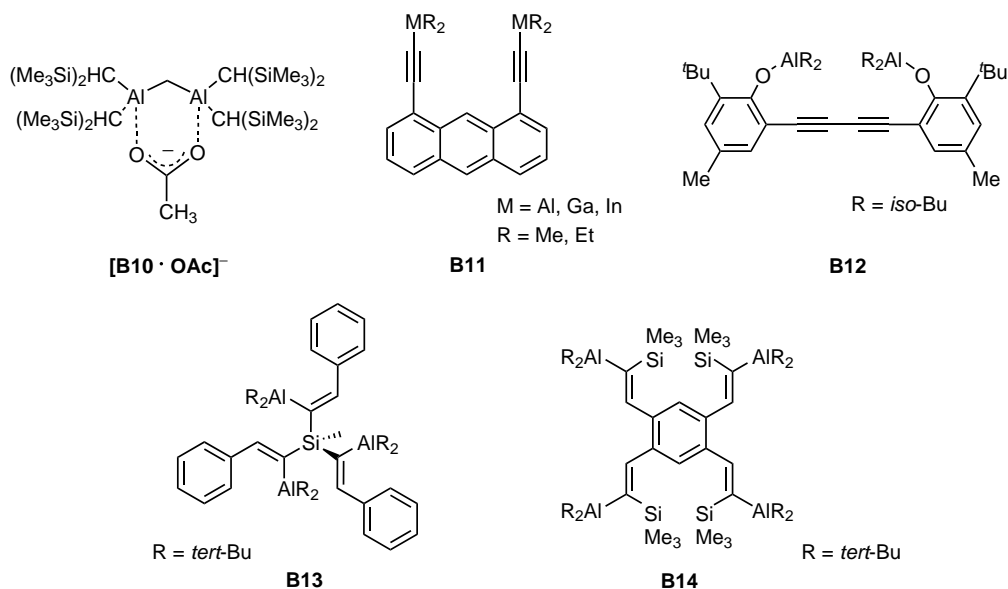
Eines der ersten Bor-basierten Wirtssysteme ist der in Schema 2.2 gezeigte zweizählige Ligand **B7**, dessen Boratome ein Methoxid-Ion komplexieren können.<sup>[30]</sup> Im Gegensatz zu dieser von Shriver und Biallas dargestellten flexiblen Verbindung synthetisierte Katz mit den in 1- und 8-Position substituierten Naphthalin- (**B8**) und Anthracen-Derivaten (**B9**) ebenfalls zwei bidentate Bor-Verbindungen, die sich jedoch durch ein verhältnismäßig starres organisches Rückgrat auszeichnen. Wie Schema 2.2 zeigt, sind beide Moleküle in der Lage, Lewis-basische Gäste komplexierend zu binden. So konnten von 1,8-Bis(dimethylboryl)naphthalin (**B8**) Komplexe mit Hydroxid-, Fluorid- und Chlorid-Ionen nachgewiesen werden. Die hohe Affinität zu Hydrid-Ionen brachte der Verbindung den Beinamen "Hydridschwamm" ein.<sup>[31-33]</sup>



**Schema 2.2:** Beispiele zweizähliger Bor-Lewis-Säuren von Shriver und Biallas (**B7**)<sup>[30]</sup> sowie von Katz (**B8**)<sup>[31-33]</sup> und **B9**)<sup>[34]</sup>.

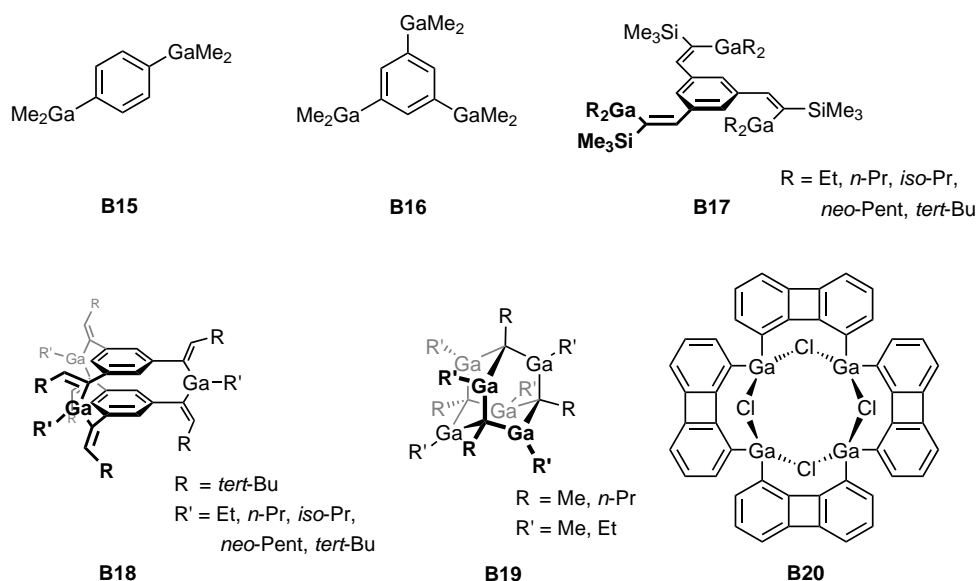
Im Falle des terminal Bor-substituierten Anthracen-Derivats **B9** weisen die beiden Lewis-aciden Atome einen Abstand von etwa 5 Å auf, was die gesamte Verbindung zu einem starren Rezeptor für größere Gastmoleküle macht. Den Nachweis dazu erbrachte Katz im Jahre 1989 in NMR-Titrationsexperimenten, indem er **B9** schrittweise mit kleinen Mengen verschiedener Methylpyrimidin-Derivate (Me-Pym) versetzte. Allerdings stützt er seine Aussagen zur Bildung des in Schema 2.2 gezeigten [**B9**·Me-Pym]-Komplexes auf geringfügige Änderungen der chemischen Verschiebung in <sup>1</sup>H-NMR-Experimenten von lediglich 0.1 ppm.<sup>[34]</sup>

Beispielhaft für Aluminium-basierte Poly-Lewis-Säuren sind in Schema 2.3 die zwei-, drei- und vierfach metallierten Verbindungen **B10** – **B14** abgebildet. Das Methylen-verbrückte Dialan **B10** wurde erstmals 1990 von Uhl *et al.* synthetisiert<sup>[35]</sup> und vermag Nitrit- und Nitrat-<sup>[36]</sup> sowie Azid- und Acetat-Ionen zu komplexieren.<sup>[37]</sup> Mitzel und Mitarbeitern gelang es, 1,8-Diethynylantracen terminal zu metallieren, indem das organische Grundgerüst in Alkaneliminierungsreaktionen mit verschiedenen Erdmetallalkylen umgesetzt wurde.<sup>[38,39]</sup> Die so erhaltenen Al-, Ga- und In-substituierten Verbindungen des Typs **B11** weisen eine strukturelle Ähnlichkeit zum zweifach Catecholboryl-substituierten Rezeptorsystem **B9** (Schema 2.2) auf, sollten jedoch aufgrund der zu  $\pi$ -Rückbindung unfähigen aliphatischen Reste am Erdmetallatom eine deutlich gesteigerte Lewis-Acidität zeigen. Ein starres Grundgerüst ist auch bei der von Wuest *et al.* dargestellten Dialuminiumverbindung **B12** gegeben, die durch Reaktion des entsprechenden Diols mit Tri-*iso*-butylaluminium generiert werden kann.<sup>[40]</sup> Die drei- und vierfach-Aluminium-funktionalisierten Verbindungen **B13** und **B14** konnten in der Arbeitsgruppe Uhl durch Hydroaluminierung von Methyl-tris(phenylethynyl)silan bzw. 1,2,4,5-Tetrakis[(trimethylsilyl)ethynyl]benzol mit Di-*tert*-butylalan erhalten werden.<sup>[41,42]</sup>



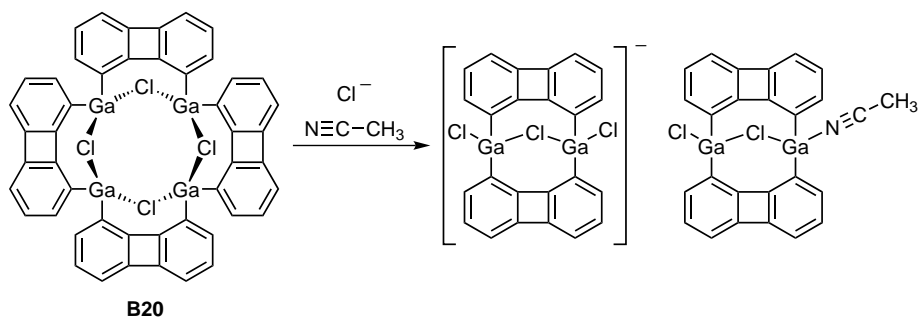
**Schema 2.3:** Literaturbeispiele einiger Aluminium-Poly-Lewis-Säuren mit zwei (**B10**,<sup>[35–37]</sup> **B11**<sup>[38,39]</sup> und **B12**<sup>[40]</sup>), drei (**B13**<sup>[41]</sup>) sowie vier Funktionalitäten (**B14**<sup>[42]</sup>).

Uhl *et al.* nutzten analog zu Hydroaluminierungs- auch Hydrogallierungsreaktionen zum Aufbau metallierter Gerüste. Dabei werden sowohl die einfachen Additionsprodukte wie beispielsweise **B17**,<sup>[43]</sup> oder, durch sich der Hydrometallierung anschließenden Eliminierungsprozesse, Käfig-artige Strukturen wie **B18**<sup>[44]</sup> oder **B19**<sup>[45]</sup> gebildet (Schema 2.4). Die 1,4-Bis- und 1,3,5-Tris(dimethylgallanylbenzol)-Derivate **B15** und **B16** konnten Jutzi und Mitarbeiter durch Hg-Ga-Austauschreaktionen gewinnen, indem die entsprechenden Chlormercuriobenzole ohne Lösungsmittel in Trimethylgallium umgesetzt wurden.<sup>[46]</sup>



**Schema 2.4:** Poly-Gallium-Verbindungen von Jutzi *et al.* (**B15** und **B16**<sup>[46]</sup>), Uhl *et al.* (**B17**,<sup>[43]</sup> **B18**<sup>[44]</sup> und **B19**<sup>[45]</sup>) sowie Jordan *et al.* (**B20**<sup>[47]</sup>).

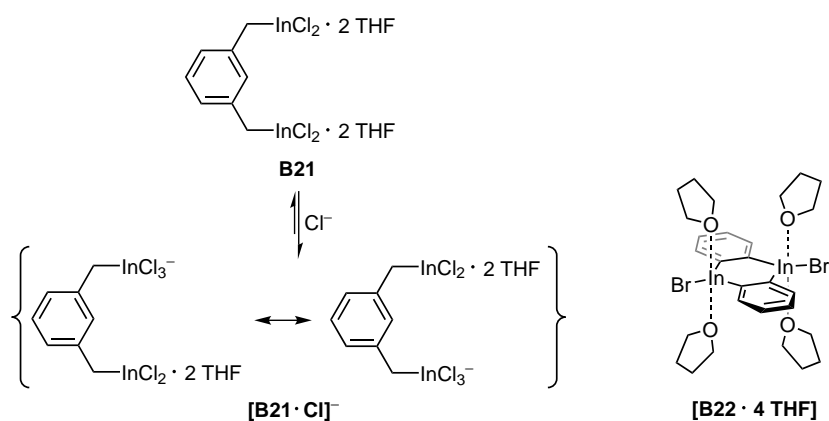
Die Arbeitsgruppe um Jordan nutzte ebenfalls Metall-Metall-Austauschreaktionen, um den Tetragallium-Makrocyclus **B20** aufzubauen. Die entsprechende Vorstufe, 1,8-Bis(trimethylstannyl)biphenylen, reagiert mit Gallium(III)-chlorid unter Eliminierung von Trimethylchlorstannan zur vierfach metallierten Wirtverbindung.<sup>[47]</sup>



**Schema 2.5:** Spaltung des Tetragallium-Macrocyclus' **B20** durch Reaktion mit Acetonitril und Chlorid-Ionen.<sup>[47]</sup>

Bei Zugabe einer Lewis-Base (Acetonitril oder THF) und von Halogenid-Ionen ( $\text{Br}^-$  oder  $\text{Cl}^-$ ) wurde eine Spaltung des Macrocyclus' **B20** und eine seitliche Koordination der Gastkomponenten beobachtet, wie sie in Schema 2.5 gezeigt ist.<sup>[47]</sup>

Neben dem bereits erwähnten InMe<sub>2</sub>-substituierten Diethinylanthracen-Derivat **B11**<sup>[38,39]</sup> sind auch weitere Indium-basierte polyfunktionale Lewis-saure Verbindungen bekannt. Gabbai *et al.* konnten durch eine Transmetallierungsreaktion von  $\alpha,\alpha'$ -*m*-Xyloldiylbis(quecksilber-chlorid) die entsprechende Indium-Spezies **B21** synthetisieren (Schema 2.6). Bedingt durch die beiden Lewis-sauren Indiumatome ist **B21** in der Lage, ein Lewis-basisches Chlorid-Anion zu komplexieren. Die mesomeren Grenzstrukturen des Adduktes können bei tiefen Temperaturen im <sup>1</sup>H-NMR-Spektrum unterschieden werden.<sup>[48]</sup> Die ebenfalls gezeigte Indium-Verbindung **B22**<sup>[49]</sup> stellt einen effizienten Rezeptor für neutrale Stickstoffbasen dar, wobei diese zwei THF-Einheiten aus dem Komplex verdrängen.<sup>[50]</sup>



**Schema 2.6:** Beispiele zweifach Indium-funktionalisierter Lewis-saurer Wirtverbindungen von Gabbai *et al.*<sup>[48-50]</sup>



## 2.2 Anthracene und Triptycene

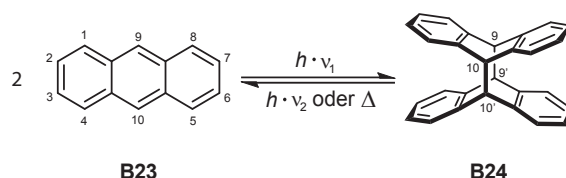
Bei vielen der in den vorangegangenen Abschnitten vorgestellten Poly-Lewis-Säuren sind die Lewis-aciden (Metall-) Atome an einem flexiblen organischen Grundgerüst fixiert und weisen deshalb keine definierte Ausrichtung auf. Für die (potentielle) Erkennung und Bindung Lewis-basischer Gastmoleküle können solche Wirtssysteme vorteilhaft sein, erlauben sie doch die Komplexierung von sich in Größe und Gestalt stark unterscheidender Verbindungen. Nachteilig hingegen ist, dass diese gesteigerte Flexibilität mit einer deutlich verringerten Selektivität bei der Gast-Erkennung einhergeht. Deshalb ist es sinnvoll, das Repertoire an unflexiblen, Donoratom-freien und gerichteten organischen Grundgerüsten zu erweitern, damit diese später zu starren Lewis-aciden Substraten umgesetzt werden können.

Da im Rahmen dieser Arbeit Anthracen- und Triptycen-basierte Grundkörper verwendet werden, wird im Folgenden eine kurze Einführung in beide Substanzklassen gegeben.

### 2.2.1 Anthracene – Allgemeines und Photochromie

Anthracen (von griech.: *Anthrax* = Kohle) wurde erstmals 1832 aus Steinkohleteer gewonnen und ist mit seinen 14  $\pi$ -Elektronen ein klassisches Beispiel für ein Hückel-aromatisches System, das sich zudem leicht funktionalisieren lässt. Heute sind diverse unterschiedlich-substituierte Anthracen-Derivate käuflich zu erwerben, oder lassen sich problemlos aus den entsprechend substituierten und ebenfalls kommerziell erhältlichen Anthrachinon-Derivaten darstellen. Da das planare organische Gerüst chemisch verhältnismäßig stabil ist und gegebenenfalls angebrachte Substituenten genau definierte Abstände zueinander aufweisen, finden sich Anthracensysteme oftmals als Synthesebausteine in (metall-) organischen Verbindungen.

Eine weitere überaus interessante Eigenschaft von Anthracen wurde bereits 1866 von Fritzsche beschrieben.<sup>[51]</sup> Er beobachtete, dass sich beim Bestrahlen einer gesättigten Anthracen-Lösung mit Sonnenlicht farblose Kristalle bildeten, die sich beim anschließenden Schmelzen, also durch Zufuhr von Wärme, wieder vollständig in die Ausgangssubstanz umwandelten.<sup>[52]</sup> Dass es sich bei dieser neuen Komponente um ein Dimer von Anthracen handelt, zeigten spätere Untersuchungen durch Bestimmung der Molmasse.<sup>[53,54]</sup> Die Aufklärung der Molekülstruktur im Kristall lieferte schließlich die genaue Struktur, das 9,10,9',10'-verbrückte Anthracen-Dimer **B24**,<sup>[55]</sup> das sich durch eine  $[4\pi + 4\pi]$ -Cycloadditionsreaktion gebildet haben muss.



**Schema 2.7:** Reversible Dimerisierung von Anthracen (**B23**, mit der Nummerierung potentieller Substituentenpositionen nach IUPAC) zum 9,10,9',10'-Photodimer **B24**.

In den folgenden Jahrzehnten wurde der Mechanismus dieser Reaktion ausgiebig studiert und die Einflüsse von Substituenten am Anthracengerüst auf die Dimerisierungs- bzw. Cycloeliminierungsreaktion<sup>1</sup> untersucht.

Das von Fritzsche beobachtete Phänomen der lichtinduzierten, reversiblen Umwandlung einer (chemischen) Spezies zwischen zwei Formen wird gemäß der IUPAC-Definition als *Photochromie* (von griech.: *phos* = Licht, *chroma* = Farbe) bezeichnet.<sup>[56]</sup> Bei einem solchen Vorgang kommt es zu einer Veränderung der physikalischen Eigenschaften der Substanz, die sich beispielsweise in unterschiedlichen Absorptionsspektren ausdrückt. Wie aus Schema 2.7 hervorgeht, kann die Cycloeliminierung, also die Rückreaktion, nicht nur durch Zuführen von Wärme ( $\Delta$ ), sondern auch unter Verwendung von Licht einer anderen Wellenlänge ( $h \cdot \nu_2$ ) erfolgen. Dementsprechend wird zwischen der thermischen *T-Typ*- und der photochemischen *P-Typ-Photochromie* unterschieden.

### 2.2.2 Photochromie (mehrfach) substituierter Anthracene

Bis auf sehr wenige Ausnahmen wird bei (mehrfach) substituierten Anthracenen bei der Bestrahlung mit UV-Licht das gleiche Dimerisierungsverhalten beobachtet, wie bei unsubstituierten Grundkörpern und es kommt durch eine  $[4\pi + 4\pi]$ -Cycloadditionsreaktion zur Ausbildung von 9,10,9',10'-Dimeren,<sup>[57]</sup> gegebenenfalls unter Bildung mehrerer Isomere, die sich in der Ausrichtung der Substituenten unterscheiden.<sup>2</sup>

Gleichwohl sind auch Beispiele anderer Anthracen-Dimerisierungen bekannt, die zu so genannten *nicht-klassischen Photodimeren* führen. Schema 2.8 zeigt davon eine kleine Auswahl,<sup>[58]</sup> wobei es unter Einbeziehung der ungesättigten Substituenten wie bei **B25** und **B27** zu  $[6\pi + 6\pi]$ - oder  $[4\pi + 2\pi]$ -Cycloadditionsreaktionen kommen kann.<sup>[59]</sup> Das in 2- und 6-Position mit Decyloxy-Substituenten funktionalisierte Anthracen-Derivat **B29** geht bei UV-Licht-Bestrahlung eine  $[4\pi + 4\pi]$ -Cycloaddition ein, wobei allerdings statt eines klassischen 9,10,9',10'- ein 9,10,1',4'-Photodimer entsteht.<sup>[57]</sup> Das [6](1,4)Anthracenophan (**B31**) reagiert unter UV-Bestrahlung zum  $[2\pi + 2\pi]$ -Cycloadditionsprodukt **B32**.<sup>[60]</sup>

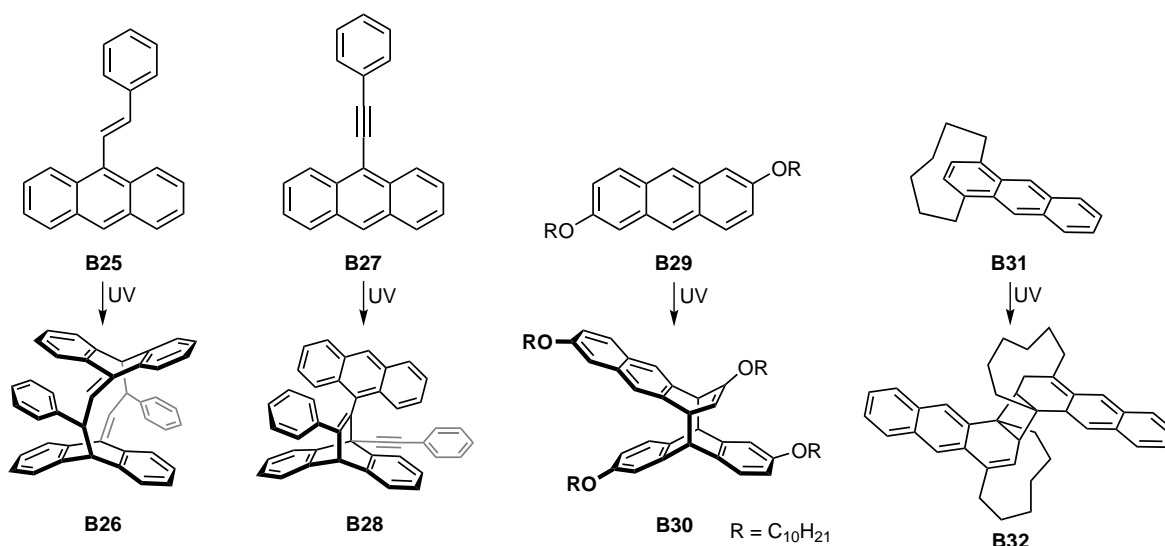
In der (jüngeren) Vergangenheit wurde die Photochemie unzähliger verschieden funktionalisierter Anthracen-Derivate ausführlichst – auch theoretisch – untersucht und verschiedentlich zusammengefasst,<sup>[52,58]</sup> sodass an dieser Stelle nicht weiter darauf eingegangen wird.<sup>3</sup> Zu erwähnen bleibt, dass der sterische Anspruch der Substituenten am Anthracengerüst offensichtlich Einfluss auf das (9,10,9',10'-) Dimerisierungsverhalten des gesamten Moleküls nimmt. So sind zwar einige 9,10,9',10'-Photodimere unsymmetrisch funktionalisierter Anthracene mit kleinen Substituenten in 9- und 10-Position bekannt, die sich aber durch eine teilweise starke Thermola-

<sup>1</sup>Die *Cycloeliminierung* ist auch unter der älteren Bezeichnung *Cycloreversion* bekannt.

<sup>2</sup>Im Falle 1,8-substituierter Anthracen-Derivate wird bei Dimerisierungsreaktionen in der Regel die Bildung zweier Isomere beobachtet: Das *head to head*-Isomer (*syn*), bei dem alle Substituenten in eine Richtung weisen sowie das *head to tail*-Isomer (*anti*), bei dem die Substituenten gegensinnig ausgerichtet sind.

<sup>3</sup>Zwischen 1967 und 1998 erschienen ca. 38000 Veröffentlichungen zu Anthracen-haltigen Verbindungen, von denen sich etwa 4000 zusätzlich mit der Untersuchung der Photochemie der Substanzen beschäftigten.<sup>[58]</sup>

bilität auszeichnen.<sup>[58,61,62]</sup> Hingegen gelten symmetrisch 9,10-substituierte Anthracene bis *dato* – mit Ausnahme von 9,10-Difluor-<sup>[63]</sup> und 9,10-Dimethylantracen<sup>[64]</sup> – als photostabil.<sup>[58]</sup>



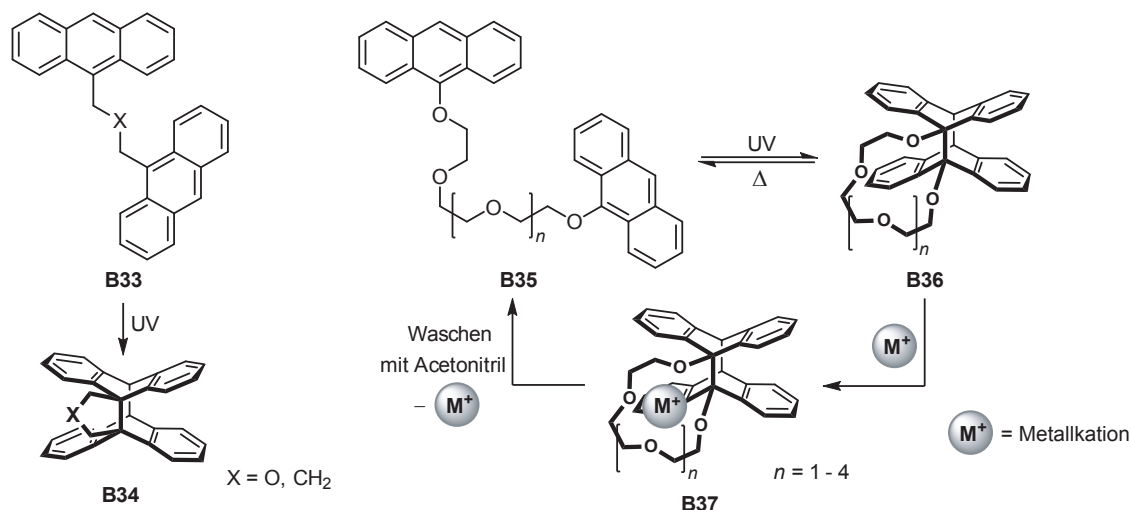
**Schema 2.8:** Beispiele nicht-klassischer Photodimerisierung einiger substituierter Anthracene in Form von  $[6\pi + 6\pi]$ - (**B25**  $\rightarrow$  **B26**),<sup>[59]</sup>  $[4\pi + 2\pi]$ - (**B27**  $\rightarrow$  **B28**),<sup>[59]</sup>  $[4\pi + 4\pi]$ - (**B29**  $\rightarrow$  **B30**)<sup>[57]</sup> und  $[2\pi + 2\pi]$ -Cycloadditionsreaktionen (**B31**  $\rightarrow$  **B32**).<sup>[60]</sup>

### 2.2.3 Photochromie verbrückter Anthracene

Neben der gezeigten intermolekularen Photodimerisierung zweier Anthracen-Monomere kann es auch zu einer intramolekularen Dimerisierung kommen, wenn zwei Anthraceneinheiten in einem Molekül vorhanden sind. Von besonderem (synthetischen) Interesse sind solche *bichromophoren Systeme* vor allem deshalb, weil sich durch eine Verbrückung zweier Anthracengerüste in vielen Fällen die Anzahl der entstehenden Photodimerisomere reduzieren lässt. Folgerichtig wurden bereits Arbeiten auf diesem Gebiet durchgeführt, von denen Schema 2.9 einige Beispiele zeigt.

Hervorzuheben sind in diesem Zusammenhang die eleganten Arbeiten zu photoschaltbaren Kronenethern, deren Ausgangsverbindungen zwei durch flexible Polyoxyethyleinheiten miteinander verbundene Anthracengerüste sind (**B35**). Wie in Schema 2.9 gezeigt, können bei UV-Licht-Bestrahlung die intramolekularen 9,10,9',10'-Photodimere **B36** gebildet werden. Diese zeigen sich extrem thermolabil und schalten sehr schnell wieder in die geöffnete Form **B35** zurück. Sind in der Lösung jedoch Metallkationen  $M^+$  zugegen (z. B.  $Li^+$  mit  $n=1$ ),<sup>4</sup> entsteht der entsprechende Metallkomplex **B37** und die Cycloeliminierungsreaktion wird unterbunden. Erst bei der Behandlung des Komplexes mit sehr polaren Lösungsmitteln, wie beispielsweise Acetonitril, kommt es zur Solvatation des Kations und die offenkettige Ausgangsspezies **B35** wird zurückerhalten.<sup>[62,65]</sup>

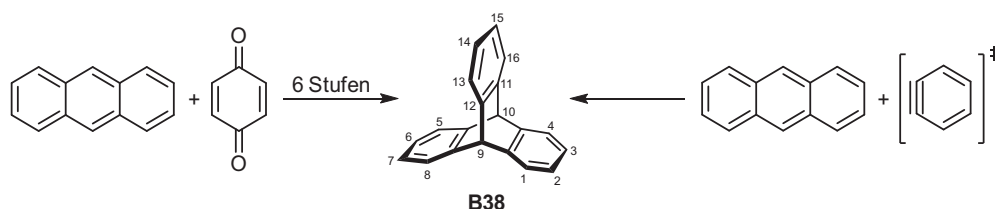
<sup>4</sup>Mit  $n=1$  handelt es sich bei **B35** *de facto* um ein Derivat von [12]Krone-4, das aufgrund des Hohlraumdurchmessers bevorzugt Lithium-Kationen komplexieren kann.<sup>[6]</sup>



Schema 2.9: Beispiele zur Photochromie verbrückter Anthracene. [58,62,65,66]

### 2.2.4 Triptycene – Allgemeines und Darstellung

Triptycenen (**B38**) ist ein  $D_{3h}$ -symmetrisches Molekül, das erstmalig 1942 durch Bartlett *et al.* in einer sechsstufigen Reaktion aus Anthracen und *p*-Benzochinon synthetisiert werden konnte. [67] Später gelang die einfachere und unkompliziertere Darstellung durch Umsetzung von Anthracen mit einem *in situ*-erzeugten Arin durch eine  $[4\pi + 2\pi]$ -Cycloadditionsreaktion (Schema 2.10). [68] Das Triptycenen ist der erste und einfachste Vertreter der Klasse der sogenannten *Iptycene*. [69] Nach einer Definition von Hart und Mitarbeitern zeichnen sich die polyaromatischen Verbindungen dadurch aus, dass die Aromaten an einem starren Bicyclo[2.2.2]octa-2,5,7-trien-Grundkörper<sup>5</sup> anelliert sind. [70]



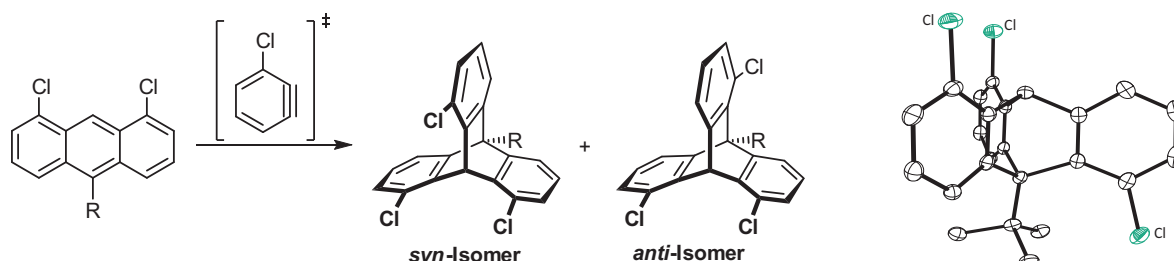
Schema 2.10: Unterschiedliche Möglichkeiten zur Synthese von Triptycenen (**B38**, mit Hellwinkel-Nomenklatur) nach Bartlett *et al.* (links) [67] bzw. nach Wittig und Ludwig (rechts). [68]

In den vergangenen Jahren und Jahrzehnten wurden auf dem Gebiet der Triptycenenchemie große Fortschritte verzeichnet, [69,71] sodass Triptycenen-Grundkörper heute unter anderem als Bausteine für (fluoreszierende) Makromoleküle und Flüssigkristalle, [72,73] oder als starre Spacereinheiten bei Pd-haltigen Kreuzkupplungskatalysatoren Anwendung finden. [74] Des Weiteren werden sie als Gerüstmoleküle in molekularen Maschinen eingesetzt, [75,76] oder in sogenannten Crystal-Engineering-Prozessen genutzt. [77]

<sup>5</sup>Auch *Barrelen* genannt.

### 2.2.5 Darstellung *syn*- und *anti*-substituierter Trichlortriptycene

Werden bei der in Schema 2.10 gezeigten Reaktion substituierte Anthracen- und/oder Arinkomponenten eingesetzt, können entsprechende (mehrfach-) funktionalisierte Triptycenen-Derivate erhalten werden.



**Schema 2.11:** Darstellung der 1,8,13- (*syn*-) und 1,8,16- (*anti*-) Chlor-funktionalisierten Triptycenen-Derivate (links) und Molekülstruktur des 10-*tert*-Butyl-substituierten *anti*-Trichlortriptycens (rechts).<sup>[39,78]</sup>

Wie in Schema 2.11 dargestellt, kommt es bei der Umsetzung unterschiedlicher 10-funktionalisierter 1,8-Dichloranthracen-Derivate mit Chlorarin zur Bildung eines Gemisches aus den entsprechenden *syn*- und *anti*-Isomeren, die sich in der Ausrichtung des ehemaligen Arin-Chloratoms relativ zu den anderen Chloratomen unterscheiden.<sup>[39,78,79]</sup> Zum Aufbau gerichteter Grundgerüste auf Triptycenen-Basis ist lediglich das *syn*-Isomer von Interesse, sodass es seit einiger Zeit Bestrebungen gibt, den *syn*-Anteil der Mischung gezielt zu erhöhen. Eine bedeutende Rolle spielen dabei die Eigenschaften des sich in 10-Position befindlichen Substituenten R.

In vorangegangenen Arbeiten wurde versucht, das *syn-anti*-Verhältnis der in Schema 2.11 gezeigten Reaktion durch das Einführen sterisch anspruchsvoller Substituenten R zu beeinflussen. Beabsichtigt war, durch eine repulsive Wechselwirkung zwischen R und dem dritten Chloratom den Anteil des *syn*-Isomers zu erhöhen. Allerdings zeigte sich eindrucksvoll am Beispiel des 10-*tert*-Butyl-substituierten 1,8-Dichloranthracens, dass allein ein großer räumlicher Anspruch des Restes R nicht zur selektiven *syn*-Ausrichtung führt, denn bei dessen Umsetzung mit einem *in situ*-erzeugten Chlorarin bildet sich mit 1,8,16-Trichlor-10-*tert*-butyltriptycenen ausschließlich das entsprechende *anti*-Isomer (Schema 2.11, rechts).<sup>[39,78]</sup> Tabelle 2.1 fasst die Ergebnisse dieser ausführlichen Untersuchungen zusammen.

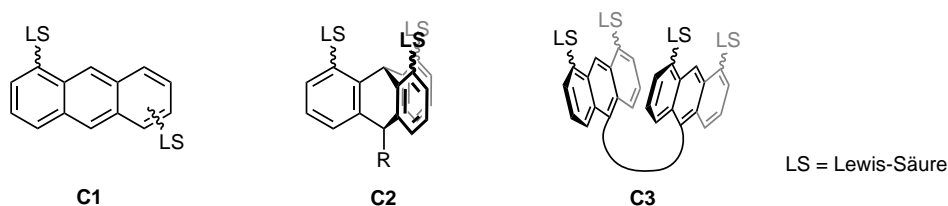
**Tabelle 2.1:** Ergebnisse zum Einfluss des Substituenten R in Position 10 auf das *syn-anti*-Isomerenverhältnis der in Schema 2.11 dargestellten Reaktion.<sup>[39,78]</sup>

R	<i>syn</i> -Isomer [%]	<i>anti</i> -Isomer [%]	R	<i>syn</i> -Isomer [%]	<i>anti</i> -Isomer [%]
H	21	79	<i>tert</i> -Bu	0	100
Me	37	63	Cy	21	79
<i>n</i> -Bu	40	60	Ph	25	75
<i>iso</i> -Pr	30	70			

### 3 Motivation und Aufgabenstellung

Wie einleitend bereits erwähnt, beschränkt sich ein Großteil der bis *dato* auf dem Gebiet der Wirt-Gast-Chemie erzielten Ergebnisse auf die Erkennung und Bindung Lewis-saurer Gäste, wie z. B. Kationen, durch poly-Lewis-basische Verbindungen. Auch der inverse Fall, die Komplexierung von Lewis-Basen durch Poly-Lewis-Säuren, wurde bereits untersucht und beschrieben, wenn auch in deutlich geringerem Umfang. Unter den verhältnismäßig wenigen Beispielen mehrfach Lewis-acid funktionalisierter Verbindungen finden sich nur wenige Moleküle, bei denen die Lewis-sauren (Metall-) Atome an einem Donoratom-freien und vor allem unflexiblen organischen Grundgerüst gebunden sind. Durch das Anbringen der Lewis-aciden Funktionalitäten an Gerüste mit starrem Rückgrat ist eine definierte räumliche Ausrichtung gegeben, was zu einer gesteigerten Selektivität bei der Komplexierung Lewis-basischer Gastmoleküle beitragen kann. In diese offensichtliche Lücke zielten bereits Vorarbeiten von Mitzel *et al.*, bei denen 1,8-funktionalisierte Dialkynylanthracene<sup>1</sup> als Rückgrat genutzt wurden.<sup>[38]</sup> Auch erste Versuche zur gezielten Darstellung 1,8,13-substituierte Triptycene<sup>2</sup> wurden unternommen.<sup>[78]</sup>

Motivation dieser Arbeit ist daher, die Kenntnisse auf diesem relativ unerforschten Gebiet der Wirt-Gast-Chemie in mehrerer Hinsicht zu erweitern. Hierzu sollen in einem ersten Schritt durch klassische organische Synthese weitere starre Anthracen- und Triptycen-basierte Gerüstmoleküle dargestellt werden. Eine weitere Funktionalisierung mit Lewis-sauren Atomen verschiedener Art soll nach Möglichkeit erfolgen, sodass die in Schema 3.1 gezeigten Verbindungen des Typs **C1** und **C2** erhalten werden.



**Schema 3.1:** Schematische Darstellung der angestrebten Lewis-Säuren: Auf Basis funktionalisierter Anthracene (**C1**), Triptycene (**C2**) und Anthracen-basierter Bichromophore (**C3**).

Durch ihre prinzipielle Fähigkeit zur Photodimerisierung bieten die verschieden substituierten Anthracen-Derivate Zugang zu einer Vielzahl neuer polydentater und gerichteter Verbindungen. Da die UV-Licht-induzierte Cycloaddition zweier Anthraceneinheiten prinzipiell auch immer reversibel ist, erweist sich die Untersuchung der photochromen Eigenschaften dieser neuen Systeme

<sup>1</sup>Zur Anthracen-Nomenklatur siehe Schema 2.7, Seite 8.

<sup>2</sup>Zur Triptycen-Nomenklatur siehe Schema 2.10, Seite 11.

als naheliegend. Um die Anzahl gerichteter Funktionalitäten zu erhöhen und gleichzeitig die Basis zur Darstellung mehrzähliger, gezielt photoschaltbarer Lewis-Säuren zu schaffen, sollen erste Versuche unternommen werden, zwei 1,8-substituierte Anthracene in 10-Position durch verschiedene Linkereinheiten zu verbrücken, wie mit **C3** in Schema 3.1 gezeigt.

Schließlich bedarf es auch einer genauen Verifizierung, ob diese Art der starren Lewis-sauren Verbindungen generell in der Lage sind, in Wirt-Gast-Chemie-Experimenten als Rezeptoren für Lewis-basische (Klein-) Moleküle zu fungieren. Untersuchungen dazu sollen anhand eines konkreten Beispielsystems, 1,8-Bis[(diethylgallanyl)ethinyl]anthracen, erfolgen. Durch Umsetzung dieser Lewis-aciden Digalliumspezies mit Lewis-basischen Molekülen soll die Wirt-Gast-Komplexbildung erstmals untersucht und der Mechanismus, welcher diesem Vorgang zu Grunde liegt, aufgeklärt werden.

## 4 Synthese, Struktur und Wirt-Gast-Chemie

In diesem Kapitel werden die Syntheserouten, die zur Darstellung der neuen Verbindungen führten, vorgestellt sowie ihre Charakterisierung und strukturellen Besonderheiten diskutiert.

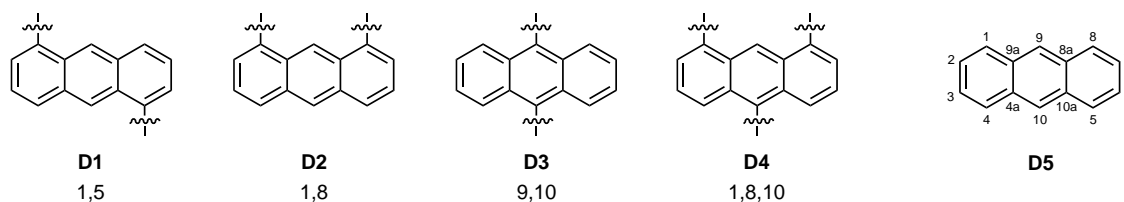
Dabei wird zunächst die Darstellung der Anthracen- bzw. Triptycen-basierten Grundgerüste präsentiert, die zwei-, drei-, vier- oder sechsfach mit Alkynyl- oder Chlorsubstituenten funktionalisiert sind. Im Anschluss daran steht die Umsetzung einiger Gerüste zu mehrzähligen Lewis-Säuren im Mittelpunkt, bevor zum Schluss am Beispiel einer bifunktionalen Gallium-Spezies Untersuchungen zur Dynamik von Wirt-Gast-Chemie-Experimenten erörtert werden.

Da viele Ergebnisse bereits veröffentlicht wurden oder sich entsprechende Publikationen im Begutachtungsprozess bzw. in Vorbereitung befinden, soll dieses Kapitel nur als Überblick über die erhaltenen Resultate dienen. Für Details sei an dieser Stelle auf die Veröffentlichungen im Anhang verwiesen.

### 4.1 Grundgerüste auf Basis substituierter Anthracene

Anthracen-Derivate eröffnen aufgrund der Tatsache, dass sie sich an vielen Positionen selektiv funktionalisieren lassen, die Möglichkeit, organische, Donoratom-freie Grundgerüste aufzubauen. Zudem weisen die Substituenten, bedingt durch das starre Molekülrückgrat, stets einen genau definierten Abstand zueinander auf, was zur späteren Generierung nicht-flexibler und somit selektiv komplexierender Wirtstrukturen von Vorteil ist.

Schema 4.1 zeigt die im Rahmen dieser Arbeit verwendeten Anthracen-Grundkörper, die in den Positionen 1 und 5 (**D1**), 1 und 8 (**D2**), 9 und 10 (**D3**) sowie 1, 8 und 10 (**D4**) zwei- bzw. dreifach funktionalisiert wurden. Die Arbeiten zu diesem Themenkomplex werden in Abschnitt 4.1.1 vorgestellt.



**Schema 4.1:** Verwendete Di- und Trialkynyl-substituierte Anthracen-Derivate **D1** – **D4** sowie das zur Veranschaulichung der IUPAC-Nomenklatur gezeigte Anthracen (**D5**).

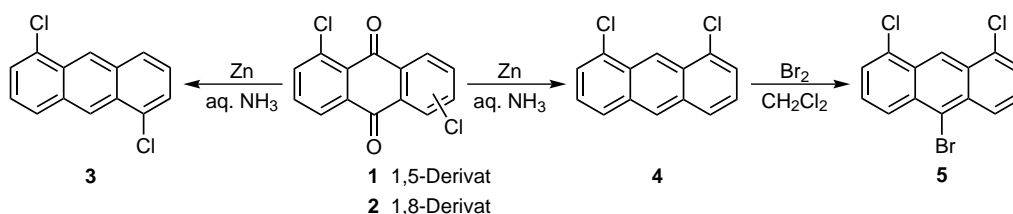
Da auch die verschiedenen zwei- und dreifach-substituierten Anthracen-Derivate photochrome Eigenschaften aufweisen, lassen sich prinzipiell auch alle gezeigten Verbindungen durch Bestrah-



lung mit UV-Licht dimerisieren, wobei dadurch weitere vier- und sechsfach-funktionalisierte Grundgerüste zugänglich gemacht werden können, was im darauf folgenden Abschnitt 4.1.2 näher erläutert wird.

#### 4.1.1 Alkynyl-substituierte Anthracene

Die Voraussetzung für die spätere Alkynyl-Funktionalisierung von Anthracenen durch verschiedene Arten von C–C-Kreuzkupplungsreaktionen ist der Zugang zu Br- und/oder Cl-funktionalisierten Anthracengerüsten. Dabei besteht die Möglichkeit, durch die unterschiedliche Reaktivität der Halogenatome in solchen Reaktionen die Alkynyl-Substitution selektiv zu steuern. Schema 4.2 zeigt die Darstellung von 1,5- (**3**) und 1,8-Dichloranthracen (**4**), die durch Reduktion der kommerziell erhältlichen Dichloranthrachinon-Derivate **1** und **2** erhalten werden können.<sup>[80,81]</sup> Verbindung **4** lässt sich durch Umsetzung mit elementarem Brom in Dichlormethan quantitativ in 10-Brom-1,8-dichloranthracen (**5**) überführen.<sup>[82]</sup>



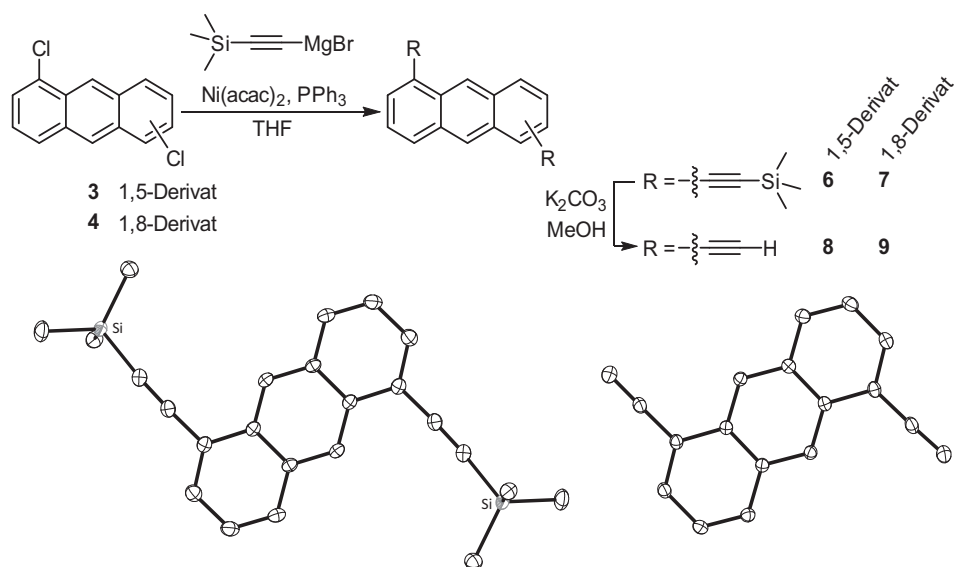
**Schema 4.2:** Darstellung der Halogenatom-substituierten Anthracen-Gerüste **3**, **4** und **5**.<sup>[80–82]</sup>

Die auf diese Weise erhaltenen Dichloranthracen-Derivate **3** und **4** lassen sich durch Nickel-katalysierte Kumada-Kreuzkupplungsreaktionen unter Verwendung von [(Trimethylsilyl)ethynyl]-magnesiumbromid in sehr guten Ausbeuten von über 90 % mit Alkynyleinheiten funktionalisieren (Schema 4.3).<sup>[83,84]</sup>

Die Abspaltung der SiMe<sub>3</sub>-Schutzgruppen gelingt problemlos mit Kaliumcarbonat in Methanol, sodass 1,5- (**8**) und 1,8-Diethynylanthracen (**9**) nach säulenchromatographischer Aufreinigung annähernd quantitativ erhalten werden können.

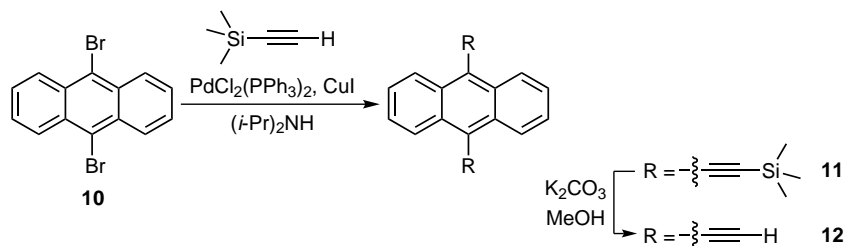
Wie aus dem unteren Teil von Schema 4.3 ersichtlich, gelang die röntgenkristallographische Aufklärung der Molekülstrukturen von 1,5-Bis[(trimethylsilyl)ethynyl]anthracen (**6**) und 1,5-Diethynylanthracen (**8**). Die Bindungslängen und -winkel beider Moleküle zeigen keine auffälligen Werte und sind sehr gut mit denen der analogen 1,8-substituierten Verbindungen<sup>1</sup> vergleichbar.<sup>[38,39,84]</sup>

<sup>1</sup>Die Aufklärung der Molekülstrukturen von 1,8-Bis[(trimethylsilyl)ethynyl]anthracen (**7**) und 1,8-Diethynylanthracen (**9**) im Kristall gelang bereits im Rahmen früherer Arbeiten.<sup>[38,39]</sup>



**Schema 4.3:** Darstellung der 1,5- und 1,8-Dialkyl-substituierten Anthracen-Derivate durch Kumada-Kreuzkupplungsreaktionen (**6** und **7**), bzw. durch Abspaltung der SiMe<sub>3</sub>-Schutzgruppen (**8** und **9**) sowie die Molekülstrukturen von **6** und **8** im Kristall.<sup>[83,84]</sup>

Das kommerziell erhältliche 9,10-Dibromanthracen (**10**) kann mittels Pd-katalysierter Sonogashira-Hagihara-Kreuzkupplung analog zu einer Vorschrift von Fudickar und Linker<sup>[85]</sup> zu 9,10-Bis[(trimethylsilyl)ethynyl]anthracen (**11**) umgesetzt werden (Schema 4.4).



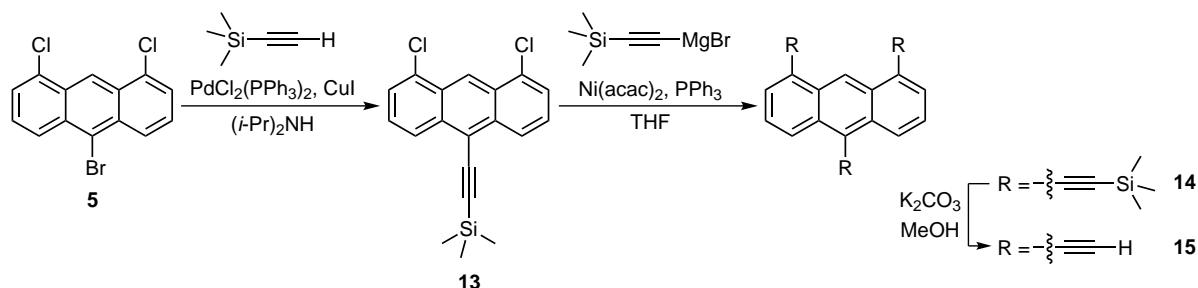
**Schema 4.4:** Darstellung der 9,10-Dialkyl-substituierten Verbindungen **11** und **12**.<sup>[84,85]</sup>

Wie bereits angedeutet, stellten auch 1,8,10-Trialkinyl-funktionalisierte Anthracengrundkörper ein lohnendes Synthesziel dar, die unter Verwendung von 10-Brom-1,8-dichloranthracen (**5**) in einer zweistufigen Synthese dargestellt werden konnten (Schema 4.5). Bedingt durch die unterschiedliche Nucleofugie der Brom- und Chlorsubstituenten, wurde zunächst selektiv die 10-Position durch eine Sonogashira-Hagihara-Kreuzkupplungsreaktion mit einer SiMe<sub>3</sub>-geschützten Alkinereinheit substituiert. Das so in 85 %iger Ausbeute erhaltene Produkt **13**<sup>2</sup> konnte im Folgenden erfolgreich einer zweifachen Kumada-Kreuzkupplungsreaktion unterworfen werden, was in einer guten Ausbeute von 83 % zur Isolierung von 1,8,10-Tris[(trimethylsilyl)ethynyl]anthracen

<sup>2</sup>Verbindung **13** kann auch auf einer anderen, literaturbekannten Syntheseroute durch Umsetzung von 1,8-Dichloranthracen-10-(9H)-on (**42**) mit [(Trimethylsilyl)ethynyl]magnesiumbromid dargestellt werden, jedoch mit geringerer Ausbeute; siehe auch Abschnitt 4.3.1.<sup>[39,78]</sup>

(**14**) führte.<sup>[84]</sup> Da prinzipiell auch Brom-substituierte aromatische Systeme in Kumada-Reaktionen Einsatz finden,<sup>[86]</sup> wurde versucht, die Syntheseroute abzukürzen und eine direkte Umsetzung von **5** zu **14** getestet. Jedoch erwies sich die Reaktion, zumindest unter den Bedingungen, die bei der Umsetzung von **13** zu **14** erfolgreich angewandt wurden, als nicht durchführbar.

Wie auch bei den anderen SiMe<sub>3</sub>-funktionalisierten Substraten lassen sich die Schutzgruppen im basischen Milieu abspalten und 1,8,10-Trialkynylanthracen (**15**) kann in einer Ausbeute von 86 % erhalten werden.<sup>[84]</sup>



**Schema 4.5:** Darstellung der 1,8,10-Trialkynyl-substituierten Verbindungen **14** und **15** über 1,8-Dichlor-10-[(trimethylsilyl)ethynyl]anthracen (**13**).<sup>[84]</sup>

#### 4.1.2 Photodimerisierungsreaktionen Alkynyl-substituierter Anthracene

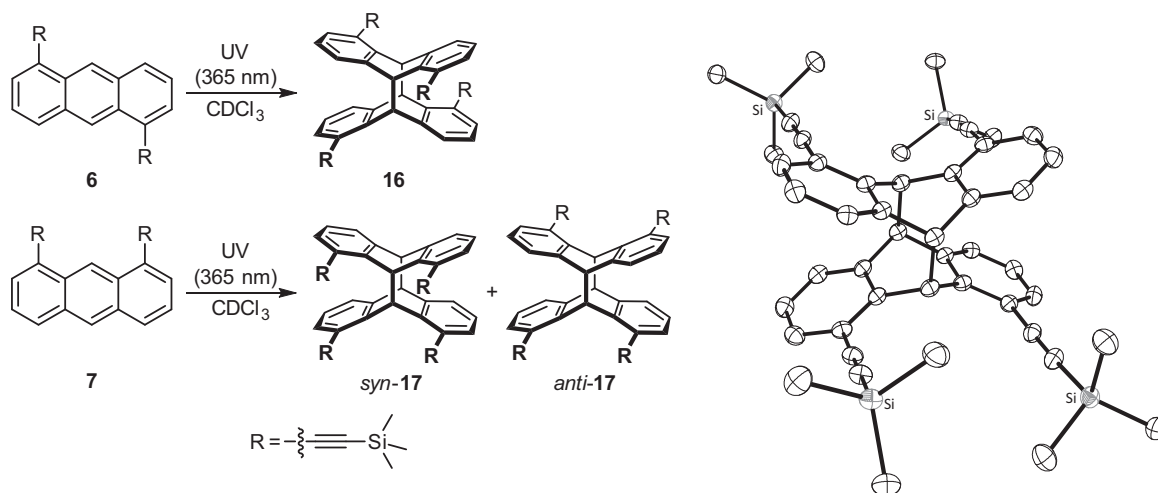
Mit der Absicht, durch photochemische Reaktionen weitere starre Grundgerüste zugänglich zu machen, wurden die synthetisierten ein-, zwei- und dreifach [(Trimethylsilyl)ethynyl]-substituierten Verbindungen **6**, **7**, **11**, **13** und **14** im Rahmen umfangreicher NMR-Studien auf ihr Dimerisierungsverhalten hin untersucht. Es stellte sich dabei die Frage, ob sich durch die UV-Licht-Bestrahlung der Verbindungen die jeweiligen  $[4\pi + 4\pi]$ -Cycloadditionsprodukte bilden und welchen Einfluss die Positionen der Alkynyleinheiten am Anthracengerüst gegebenenfalls auf das Verhältnis von *head to head*- (*syn*) und *head to tail*- (*anti*) Isomer ausüben.

Dazu wurden kleine Mengen der Substanzen in etwa 0.5 mL CDCl<sub>3</sub> gelöst und die Proben bei Raumtemperatur mit UV-Licht der Wellenlänge 365 nm bestrahlt. Der Reaktionsfortschritt wurde NMR-spektroskopisch verfolgt und die Bestrahlungen der Proben jeweils solange fortgesetzt, bis im <sup>1</sup>H-NMR-Spektrum keine Änderungen mehr auftraten.

Die Untersuchungen ergaben, dass sich mit Ausnahme von 9,10-Bis[(trimethylsilyl)ethynyl]anthracen (**11**) alle untersuchten Spezies innerhalb weniger Stunden durch UV-Bestrahlung vollständig in die Photodimere überführen lassen.

Beim Vergleich der Dimerisierung der zweifach [(Trimethylsilyl)ethynyl]-substituierten Verbindungen **6** und **7** zeigte sich deutlich, dass die Position der Alkynyleinheiten das Verhältnis der durch Photodimerisierung gebildeten Isomere beeinflusst. Während im Fall von 1,5-Bis[(trimethylsilyl)ethynyl]anthracen (**6**) selektiv das *head to tail*-Isomer entsteht, bildet sich beim analogen 1,8-Derivat **7** ein 49:51-Gemisch aus *syn*- und *anti*-Form (Schema 4.6). Weshalb *syn*-**17**

trotz der zu erwartenden repulsiven Wechselwirkungen der vier sterisch anspruchsvollen Reste zu etwa 50 % aus der Bestrahlungsreaktion hervorgeht, kann nur gemutmaßt werden.



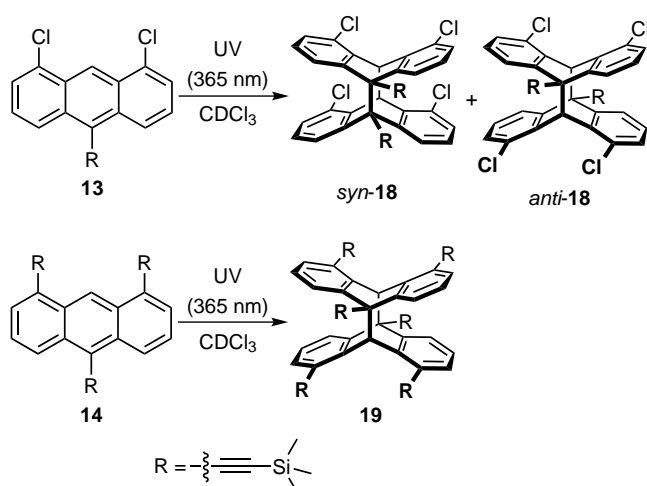
**Schema 4.6:** Darstellung der Photodimere **16** und **17** durch UV-Bestrahlung von 1,5- (**6**) und 1,8-Bis-[(trimethylsilyl)ethynyl]anthracen (**7**) sowie die Molekülstruktur von *anti-17* im Kristall. [84]

Im Rahmen der NMR-Messungen konnten Einkristalle von Verbindung *anti-17* erhalten und röntgenkristallographisch untersucht werden. Es handelt sich, wie im rechten Teil von Schema 4.6 gezeigt, um ein inversionssymmetrisches Molekül. Bindungslängen und -winkel der vier nunmehr isolierten aromatischen Ringsysteme weisen keine unerwarteten Werte auf. Die Alkinyleinheiten sind als Folge intramolekularer Abstoßungen leicht abgewinkelt. Eine signifikante Verlängerung erfährt hingegen die C(sp<sup>3</sup>)-C(sp<sup>3</sup>)-Bindung, welche die zentralen Ringe von *anti-17* verbindet. Mit 1.623(2) Å weicht sie deutlich vom Standardwert von 1.54 Å ab. [87]

Dass nicht nur die Position der Funktionalitäten am Anthracengerüst eine Rolle spielt, sondern auch die Art der Substituenten selbst das *syn-anti*-Verhältnis der Photoreaktion beeinflusst, wird am Beispiel der Dimerisierung der beiden dreifach-funktionalisierten Anthracen-Derivate **13** und **14** deutlich. Wie Schema 4.7 zeigt, wandelt sich bei Bestrahlung die dreifach Alkynyl-substituierte Verbindung **14** selektiv zum *anti*-Photodimer um, wohingegen sich bei 1,8-Dichlor-10-[(trimethylsilyl)ethynyl]anthracen (**13**) unter gleichen experimentellen Bedingungen eine Mischung aus *syn*- und *anti*-Isomer (32:68) bildet.

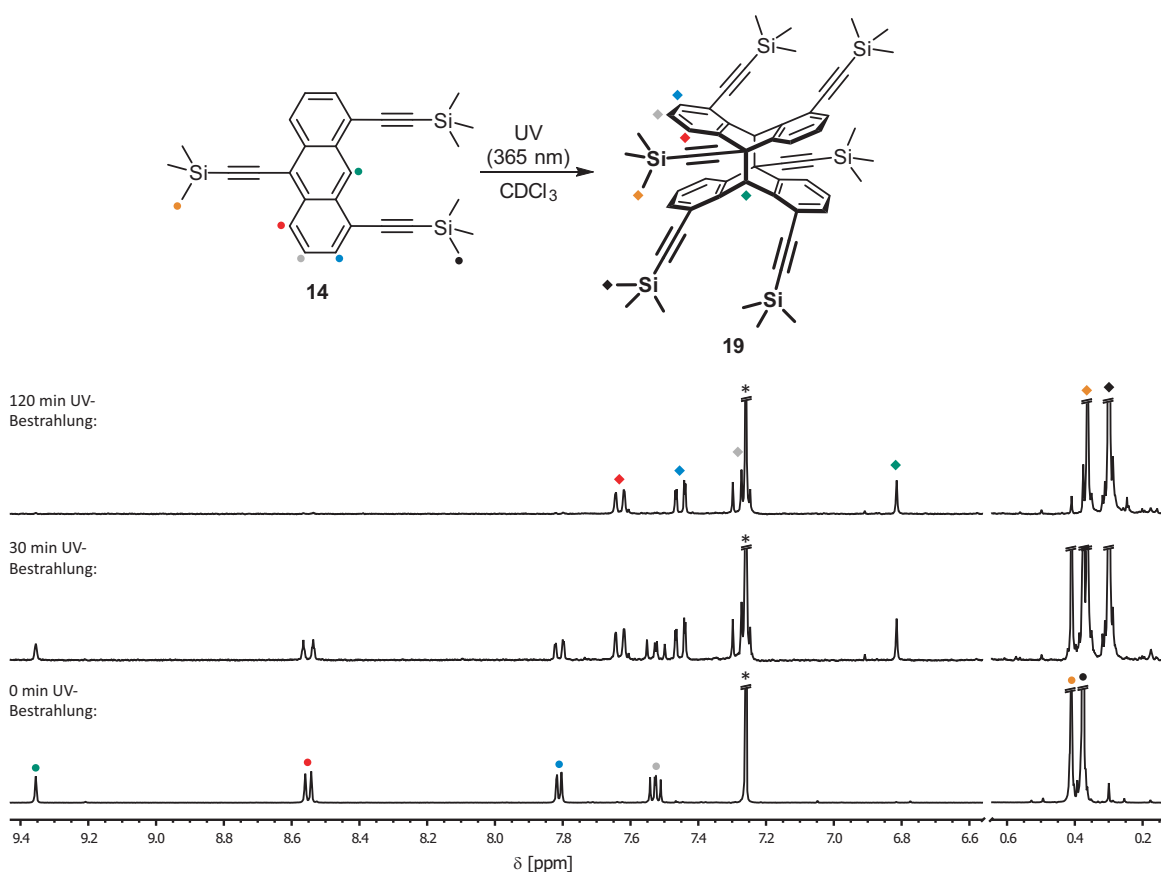
Aus früheren Arbeiten ist die Molekülstruktur des Photodimer-Isomers *anti-18* bekannt. [39] Auch hier zeigt sich, wie zuvor bei *anti-17* beschrieben, eine mit 1.634(2) Å in der gleichen Größenordnung verlängerte C(sp<sup>3</sup>)-C(sp<sup>3</sup>)-Bindung.

Tabelle 4.1 fasst die Ergebnisse der Bestrahlungsexperimente der 1,5- (**6**), 1,8- (**7**) sowie der beiden 1,8,10-substituierten Spezies **13** und **14** zusammen.



**Schema 4.7:** Darstellung der Photodimerspezies **18** und **19** durch UV-Bestrahlung von 1,8-Dichlor-10-[(trimethylsilyl)ethynyl]anthracen (**13**) bzw. 1,8,10-Tris[(trimethylsilyl)ethynyl]anthracen (**14**).<sup>[84]</sup>

Beispielhaft für die selektive und quantitative Umwandlung von **14** zum (*anti*-) Dimerisierungsprodukt **19** ist in Abbildung 4.1 der Verlauf der <sup>1</sup>H-NMR-Spektren gezeigt.



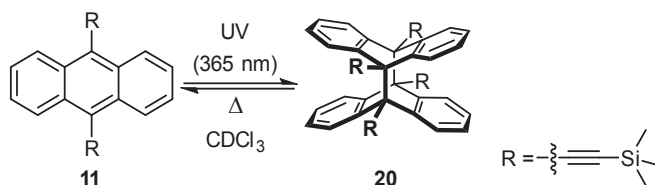
**Abbildung 4.1:** Ausschnitte aus den <sup>1</sup>H-NMR-Spektren (300 MHz, 298 K) der Photodimerisierung von **14** (unten) zu **19** (oben) in CDCl<sub>3</sub> (\*) mit Zuordnung der Resonanzen.

**Tabelle 4.1:** *syn-anti*-Isomerenverhältnis der Photodimerisierungsreaktionen verschiedener [(Trimethylsilyl)ethynyl]-substituierter Anthracen-Derivate. Bestrahlungsexperimente mit UV-Licht (365 nm) in CDCl<sub>3</sub> bei 298 K.

Monomer	Photodimer	<i>syn</i> -Isomer [%]	<i>anti</i> -Isomer [%]
<b>6</b>	<b>16</b>	0	100
<b>7</b>	<b>17</b>	49	51
<b>13</b>	<b>18</b>	32	68
<b>14</b>	<b>19</b>	0	100

Zusammenfassend lässt sich festhalten, dass in allen hier untersuchten Fällen eine – teilweise nur sehr geringe – Bevorzugung des *head to tail*-Isomers (*anti*) verzeichnet werden kann. Gründe hierfür mögen in der Abstoßung der sterisch anspruchsvollen Substituenten am Anthracengerüst zu suchen sein. Allerdings scheint, wie in der Literatur für beispielsweise 1,5- und 1,8-Dichloranthracen beschrieben,<sup>[88]</sup> auch die Wahl des Lösungsmittels das *syn-anti*-Verhältnis bei der Dimerisierung von Anthracen-Derivaten zu beeinflussen. So wurde in vorangegangenen Arbeiten im Falle von 1,8-Dichlor-10-[(trimethylsilyl)ethynyl]anthracen (**13**) bei Bestrahlung (350 nm) einer Dichlormethanolösung selektiv die Bildung des *head to tail*-Isomers *anti*-**18** beobachtet.<sup>[39]</sup> Alle bisher diskutierten Photodimerisierungsprodukte erwiesen sich als (bei Raumtemperatur) äußerst stabil, sodass auch nach mehreren Wochen keine Zersetzung bzw. Cycloeliminierungsreaktion festzustellen war.<sup>3</sup>

Ein gänzlich anderes Verhalten wird hingegen bei der UV-Licht-Bestrahlung einer Lösung von 9,10-Bis[(trimethylsilyl)ethynyl]anthracen (**11**) beobachtet. Auch bei diesem Substrat zeigt die <sup>1</sup>H-NMR-spektroskopische Reaktionskontrolle anhand eines neuen, Hochfeld-verschobenen Signalsatzes, dass die Dimerspezies entsteht. Durch das Substitutionsmuster am Anthracengerüst kann, zumindest unter der Voraussetzung, dass eine "klassische" 9,10,9',10'-Dimerisierung über eine [4π + 4π]-Cycloaddition stattfindet, nur ein Isomer entstehen (Schema 6.1).

**Schema 4.8:** Dimerisierung von 9,10-Bis[(trimethylsilyl)ethynyl]anthracen (**11**) zu **20** durch UV-Bestrahlung und thermisch induzierte Rückreaktion über eine Cycloeliminierungsreaktion.<sup>[84]</sup>

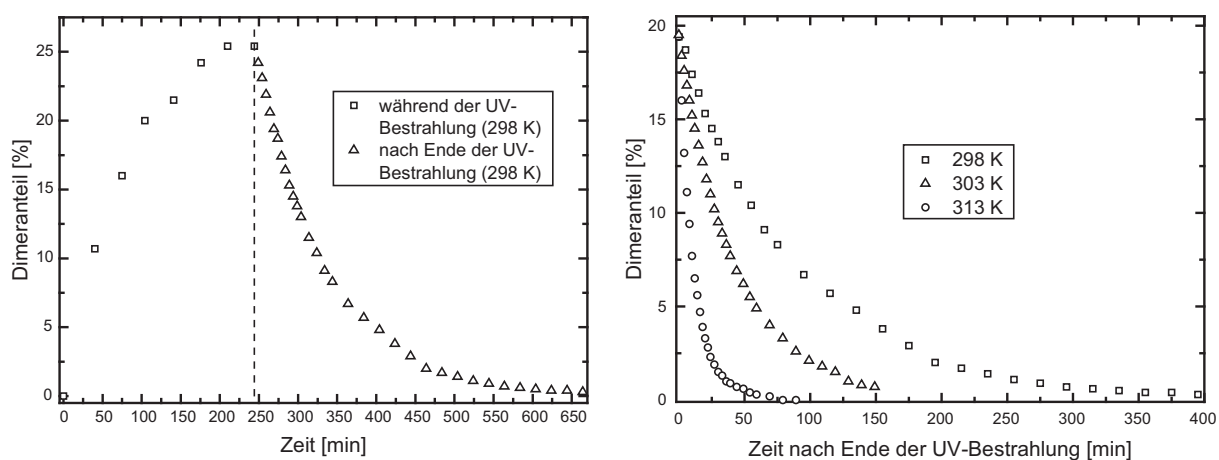
Während der Bestrahlungsexperimente wurde deutlich, dass sich Verbindung **11** im Gegensatz zu den oben beschriebenen 1,5- und 1,8- sowie 1,8,10-substituierten Derivaten nicht vollständig

<sup>3</sup>Am Beispiel einer Probe von *syn*-**17** und *anti*-**17** in C<sub>6</sub>D<sub>6</sub> wurde die thermische Stabilität der Dimerspezies gegenüber einer Cycloeliminierungsreaktion untersucht. Nach sieben Tagen bei 75 °C konnte NMR-spektroskopisch lediglich eine 1 %ige Verringerung des Dimeranteils festgestellt werden.

in das entsprechende Photodimer **20** überführen lässt. Trotz mehrstündigem Bestrahlen der Probe konnte in unterschiedlichen Experimenten lediglich ein Dimeranteil von etwa 25 % erreicht werden. Wird die UV-Bestrahlung abgebrochen und die Probe bei Raumtemperatur und Dunkelheit gelagert, kann bereits nach wenigen Stunden eine vollständige Rückreaktion zum Edukt **11** verzeichnet werden, wie Schema 6.1 zeigt.

Diese Cycloeliminierungsreaktion ist offensichtlich thermisch induziert und wurde im Folgenden ausführlich mittels  $^1\text{H}$ -NMR-Experimenten untersucht. Hierzu wurden etwa 8 mg von Verbindung **11** in 0.55 mL  $\text{CDCl}_3$  gelöst und die Probe mit UV-Licht (365 nm) bestrahlt. Im Abstand von ca. 30 Minuten wurde jeweils ein  $^1\text{H}$ -NMR-Spektrum der Mischung aufgenommen, sodass es zu Bestrahlungsunterbrechungen von knapp 3 Minuten kam.

In der linken Graphik in Abbildung 4.2 ist der Anteil der Photodimerkomponente **20** gegen die Bestrahlungsdauer aufgetragen. Zu erkennen ist, dass der Dimeranteil zunächst rasch ansteigt, jedoch nach etwa 210 Minuten keine weitere Zunahme zu erreichen ist. Nach 244 Minuten wird die Bestrahlung schließlich beendet und die Probe im NMR-Spektrometer belassen. In festgelegten Zeitabständen wird danach jeweils der Dimeranteil NMR-spektroskopisch ermittelt. Die linke Auftragung in Abbildung 4.2 zeigt, dass es bei 298 K zu einer exponentiellen Abnahme der Dimerkonzentration kommt und dass etwa 400 Minuten nach Beendigung der UV-Bestrahlung nur noch Spuren von Verbindung **20** nachweisbar sind.



**Abbildung 4.2:** Ergebnisse der NMR-Studien zur Kinetik der Photodimerisierung (**11**  $\rightarrow$  **20**, links) sowie zur Temperaturabhängigkeit der Cycloeliminierungsreaktion (**20**  $\rightarrow$  **11**, rechts).<sup>[84]</sup>

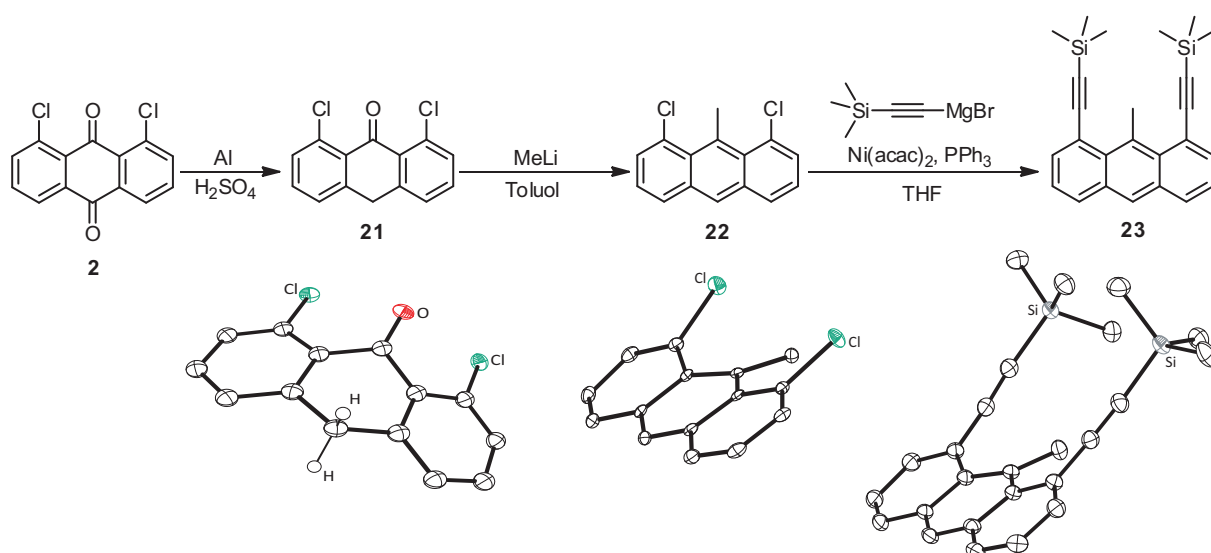
Um den Einfluss der Temperatur auf die Rückreaktion genauer zu studieren, wurden die Cycloeliminierungsreaktionen bei 298 K, 303 K und 313 K NMR-spektroskopisch verfolgt. Die rechte Graphik in Abbildung 4.2 zeigt vergleichend die Auftragungen der Dimeranteile bei den entsprechenden Temperaturen. Deutlich wird eine starke Abhängigkeit zwischen Temperatur und Reaktionsgeschwindigkeit. Ausgehend von einem Dimeranteil von 20 % verkürzt bereits eine Temperaturerhöhung um 15 K die Reaktionszeit der vollständigen Umwandlung zum Monomer **11** von ca. 400 Minuten (298 K) auf unter 90 Minuten (313 K).<sup>[84]</sup>

## 4.2 Grundgerüste auf Basis substituierter Triptycene

Wie bereits in Abschnitt 2.2.5 geschildert, bildet die gezielte Synthese funktionalisierter 1,8-Dichloranthracen-Substrate, welche in der Diels-Alder-Cycloadditionsreaktion als Dienophil mit dem Dien (Chlorarin) reagieren sollen, die Grundlage zur Darstellung verschieden funktionalisierter Triptycene. Da, wie bereits erwähnt, eine sterische Einflussnahme auf den Reaktionsausgang nicht erfolgreich war,<sup>[39,78]</sup> wurden verstärkt die elektronischen Eigenschaften der Anthracen-Substituenten in 9- und 10-Position untersucht. Dazu wurden im Vorfeld der experimentellen Arbeiten zunächst einfache quantenmechanische Berechnungen durchgeführt, welche die Auswahl der potentiell anzubringenden Funktionalitäten eingrenzen sollten. Da diese theoretischen Vorhersagen nicht in allen Fällen mit den später erhaltenen experimentellen *syn-anti*-Verhältnissen in Einklang zu bringen waren, wurden im Anschluss, basierend auf den synthetischen Ergebnissen, genauere quantenmechanische Rechnungen durchgeführt, mit denen die bevorzugte Bildung bestimmter Trichlortriptycenen-Isomere erklärt werden kann.

### 4.2.1 Synthese 1,8,9- und 1,8,10-funktionalisierter Anthracene

Die zunächst durchgeführten theoretischen Untersuchungen ergaben, dass 1,8-Dichloranthracen-Derivate, die in 9-Position eine Methylgruppe (bzw. generell eine Alkylgruppe) aufweisen, oder in Position 10 einen EMe<sub>3</sub>-Substituenten (mit E = Si, Ge, Sn) tragen, geeignet sein sollten, um bei der anschließenden Umsetzung mit der Chlorarin-Komponente bevorzugt das entsprechende *syn*-Trichlortriptycenen zu bilden. Unter Berücksichtigung dieser theoretischen Vorhersagen wurden die genannten Dichloranthracen-Derivate, deren Synthese und Charakterisierung im Folgenden kurz beschrieben wird, dargestellt, um sie im Anschluss zu den Triptycenen-Derivaten umzusetzen.

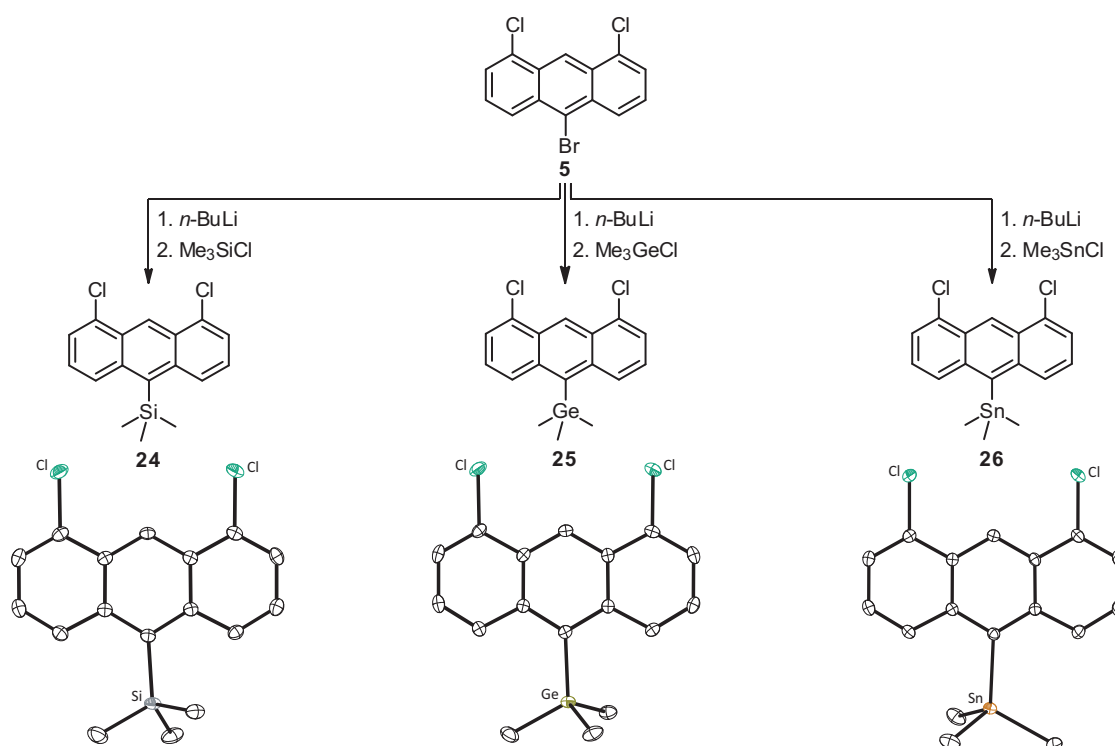


**Schema 4.9:** Syntheseroute zur Darstellung 1,8-funktionalisierter 9-Methylantracen-Derivate sowie die Molekülstrukturen von **21**, **22** und **23** im Kristall.<sup>[81,89,90]</sup>



Einen effizienten Zugang zu 1,8-funktionalisierten 9-Methylantracenen bietet das 1,8-Dichloranthracen-9-(10H)-on (**21**), das durch Reduktion von 1,8-Dichloranthrachinon (**2**) mit Aluminiumpulver in Schwefelsäure erhalten werden kann.<sup>[81]</sup> Die Umsetzung mit Methyllithium und anschließende Rearomatisierung liefert unter Wasserabspaltung 1,8-Dichlor-9-methylantracen (**22**), das sich durch Kumada-Kreuzkupplungsreaktionen mit Alkineinheiten weiter zu **23** funktionalisieren lässt (Schema 4.9).<sup>[89,90]</sup> Alle Produkte wurden vollständig NMR-spektroskopisch und massenspektrometrisch charakterisiert und die entsprechenden Molekülstrukturen im Kristall durch Röntgenbeugungsexperimente aufgeklärt. Bei den Anthracen-Derivaten **22** und **23** sind die repulsiven Wechselwirkungen zwischen den Methylgruppen und Substituenten in Position 1 und 8 bemerkenswert. Sie führen zu einer teilweise erheblichen Abweichung von der Planarität des aromatischen Systems und zu einer starken Abwinkelung der Chloratome und der Methyl- sowie Alkinylfunktionalitäten.

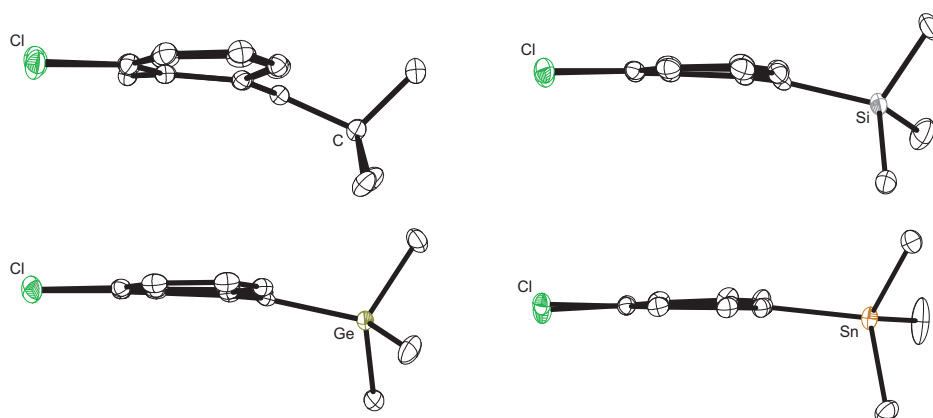
Als Schlüsselkomponente zur Darstellung von 1,8-Dichloranthracen-Derivaten, die in 10-Position mit einem Trimethylsilyl-, -germyl- oder -stannyl-Substituenten funktionalisiert sind, erwies sich das 10-Brom-1,8-dichloranthracen (**5**), das durch Umsetzung von 1,8-Dichloranthracen (**4**) mit elementarem Brom problemlos dargestellt werden konnte (Schema 4.2). Durch eine Halogenmetallaustausch-Reaktion bei  $-78\text{ }^{\circ}\text{C}$  mit *n*-Butyllithium in THF wurden die EMe<sub>3</sub>-substituierten Dichloranthracen-Derivate **24** (E = Si), **25** (E = Ge) und **26** (E = Sn) als Produkte einer Salzeliminierung erhalten und konnten eindeutig charakterisiert werden (Schema 4.10).<sup>[82]</sup>



**Schema 4.10:** Syntheseroute zur Darstellung 1,8-Dichlor-10-(trimethylelement)anthracene sowie die Molekülstrukturen von **24**, **25** und **26** im Kristall.<sup>[82]</sup>

Ein interessanter struktureller Aspekt bei diesen Verbindungen zeigt sich beim Vergleich der Seitenansichten der Kristallstrukturen von **24**, **25** und **26** mit der der *tert*-Butyl-substituierten Verbindung **27**.<sup>[39,78]</sup> Wie in Abbildung 4.3 gezeigt, wird in allen vier Fällen eine schmetterlingsartige Verzerrung des Anthracengerüsts sowie ein Abknicken des Substituenten in 10-Position beobachtet. Diese Deformation nimmt mit zunehmender Länge der C(10)–E-Bindung von der CMe<sub>3</sub>- (**27**, starke Deformation) zur SnMe<sub>3</sub>-substituierten Verbindung (**26**) ab. Die SiMe<sub>3</sub>- und die GeMe<sub>3</sub>-substituierten Spezies **24** und **25** weisen als Folge der d-Block-Kontraktion ähnliche C(10)–E-Bindungslängen auf [1.916(2) Å (**24**) und 1.986(3) Å (**25**)] und zeigen ein ähnliches Maß an Deformation der Molekülstruktur.<sup>[82]</sup>

Um Kristallpackungseffekte als Ursache für die gefundenen strukturellen Besonderheiten ausschließen zu können, wurden quantenmechanische Rechnungen durchgeführt. Die daraus resultierenden Strukturen der vier EMe<sub>3</sub>-substituierten 1,8-Dichloranthracen-Derivate (mit E = C, Si, Ge, Sn) zeigen ebenfalls die im Kristall beobachteten Abwinkelungen und Verzerrungen, sodass diese als Folge inhärenter Moleküleigenschaften angesehen werden können. In der Tat finden sich in allen vier Molekülstrukturen repulsive Wechselwirkungen zwischen den Methylgruppen und den Wasserstoffatomen in 4- und 5-Position des Anthracengerüsts,<sup>4</sup> die nachvollziehbar mit zunehmender Länge der C(10)–E-Bindung abnehmen.<sup>[82]</sup>



**Abbildung 4.3:** Seitenansichten der Kristallstrukturen der 10-EMe<sub>3</sub>-substituierten 1,8-Dichloranthracen-Derivate [mit E = C (**27**),<sup>[39,78]</sup> Si (**24**), Ge (**25**), Sn (**26**)]. Deutlich zu erkennen sind die Deformationen des Anthracengerüsts sowie ein Abknicken des EMe<sub>3</sub>-Substituenten.<sup>[82]</sup>

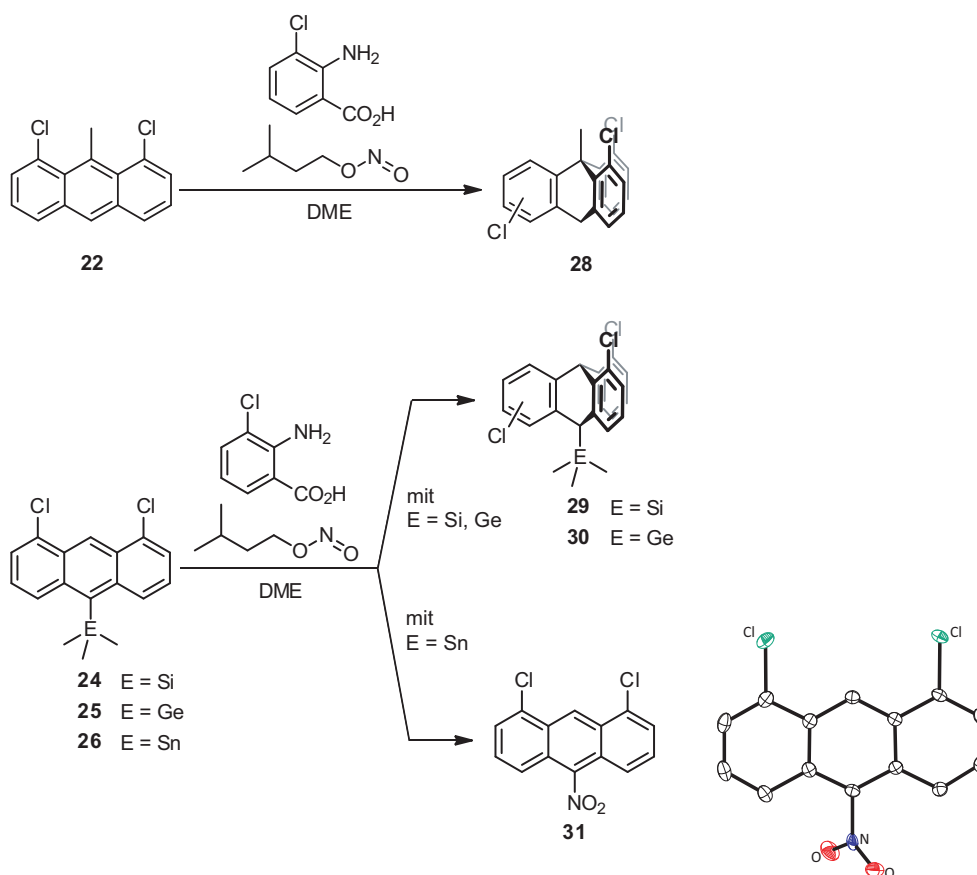
#### 4.2.2 Synthese funktionalisierter Triptycene

Um nun den Einfluss der Substituenten in 9- und 10-Position auf das *syn-anti*-Verhältnis bei der Trichlorotriptycenen-Synthese zu untersuchen, wurden die Dichloranthracen-Derivate **22**, **24**, **25** und **26** nach der Methode von Rogers und Averill mit *in situ* aus 3-Chloranthranilsäure und Isoamylnitrit erzeugtem Chlorarin umgesetzt.<sup>[79]</sup> Wie aus Schema 6.2 deutlich wird, konnten

<sup>4</sup>Die repulsiven Wechselwirkungen drücken sich in einer Aufweitung des C(10)–E–C<sub>Me</sub>-Tetraederwinkels und in einem (berechneten) *out-of-plane*-Winkel der Anthracenwasserstoffatome H4 und H5 (bis zu 4.1°) aus.

im Falle der 9-Methyl- sowie der 10-Trimethylsilyl- und 10-Trimethylgermyl-substituierten 1,8-Dichloranthracen-Derivate **22**, **24** und **25** die entsprechend funktionalisierten Trichlortriptycen-Spezies **28**, **29** und **30** generiert werden.

Beim Versuch, auf analoge Weise das SnMe<sub>3</sub>-substituierte 1,8-Dichloranthracen **26** mit dem Chlorarin zur Reaktion zu bringen, wurde statt der SnMe<sub>3</sub>-substituierten Trichlortriptycen-Derivate 1,8-Dichlor-10-nitroanthracen (**31**) erhalten. Bei der eindeutig durch NMR-Spektroskopie, Massenspektrometrie und Röntgenstrukturanalyse identifizierten Verbindung handelt es sich offensichtlich um das Produkt einer aromatischen Substitutionsreaktion, bei der eine Nitrogruppe vom Isoamylnitrit auf das Anthracengerüst übertragen wird.



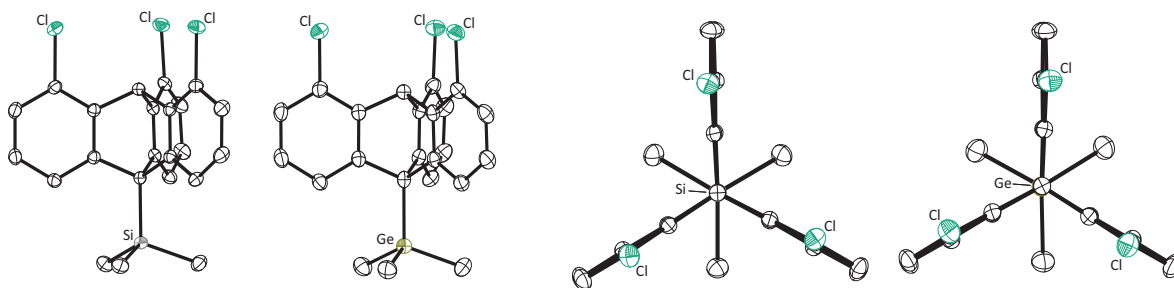
**Schema 4.11:** Syntheseveruche zur Darstellung 9- und 10-substituierter Trichlortriptycene sowie die Molekülstruktur von 1,8-Dichlor-10-nitroanthracen (**31**) im Kristall.<sup>[90]</sup>

Bei allen erfolgreich dargestellten Triptycenen wurde das Verhältnis der beiden durch Diels-Alder-Reaktion erhaltenen Konstitutionsisomere mittels Integration der entsprechenden Signale sowohl im <sup>1</sup>H-NMR- als auch im GC/MS-Spektrum bestimmt. Die Ergebnisse sind in Tabelle 4.2 zusammengefasst.

**Tabelle 4.2:** Einfluss des Substituenten R in Position 9 und 10 auf das *syn-anti*-Isomerenverhältnis der in Schema 6.2 dargestellten Reaktionen. a) Gesamtausbeute bezogen auf das *syn-anti*-Isomergemisch; b) Keine Reaktion zu den entsprechenden Trichlortriptycenen-Derivaten beobachtet.<sup>[90]</sup> Die Daten zur *tert*-Butyl-substituierten Verbindung sind zum Vergleich mit angegeben.<sup>[78]</sup>

	R-9	R-10	<i>anti</i> -Isomer [%]	<i>syn</i> -Isomer [%]	Ausbeute [%] <sup>a)</sup>
<b>22</b>	Me	H	66	34	45
<b>24</b>	H	SiMe <sub>3</sub>	16	84	55
<b>25</b>	H	GeMe <sub>3</sub>	30	70	15
<b>26</b>	H	SnMe <sub>3</sub>	–	–	0 <sup>b)</sup>
<b>27</b>	H	CMe <sub>3</sub>	100	0	41

Durch Röntgenbeugung an geeigneten Einkristallen der 10-SiMe<sub>3</sub>- und 10-GeMe<sub>3</sub>-substituierten Triptycene **29** und **30** konnten die Molekülstrukturen der entsprechenden *syn*-Isomere erfolgreich aufgeklärt werden (Abbildung 4.4). Beide Verbindungen kristallisieren isostrukturell wobei die Methylsubstituenten und die Phenylringe – wie die Aufsichten zeigen – eine gestaffelte Anordnung aufweisen.

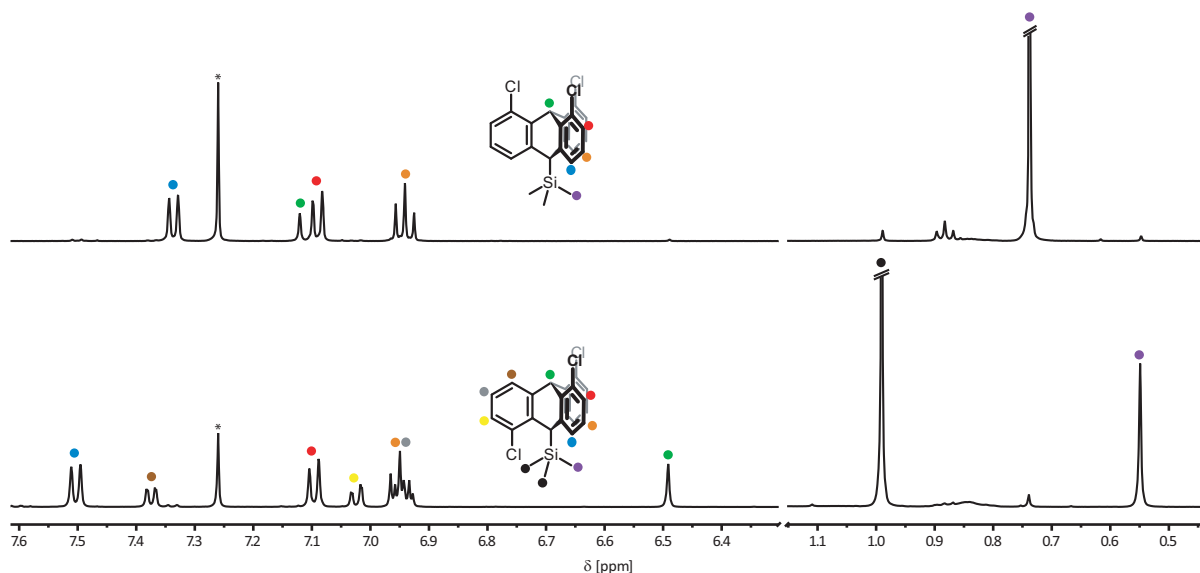


**Abbildung 4.4:** Seitenansichten (links) und Aufsichten (rechts) der Molekülstrukturen von 1,8,13-Trichlor-10-(trimethylsilyl)triptycenen (*syn*-**29**) und 1,8,13-Trichlor-10-(trimethylgermyl)triptycenen (*syn*-**30**) im Kristall.<sup>[90]</sup>

Die unterschiedlich hohe Symmetrie der SiMe<sub>3</sub>- und GeMe<sub>3</sub>-funktionalisierten Trichlortriptycenen-Verbindungen spiegelt sich auch in den NMR-Spektren beider Isomere wider. Abbildung 4.5 zeigt dies beispielhaft anhand der <sup>1</sup>H-NMR-Spektren des *syn*- und *anti*-Isomers, die durch Sublimation voneinander getrennt und so separat NMR-spektroskopisch charakterisiert werden konnten.

Augenfällig ist, dass das Spektrum des *anti*-Isomes (Abbildung 4.5, unten) eine größere Anzahl an Resonanzen zeigt, als das des C<sub>3</sub>-symmetrischen *syn*-Isomers. Die Zuordnung der Signale im aromatischen Bereich erfolgte durch eine Kombination aus NOESY- und H,H-COSY-NMR-Experimenten, wobei das Singulett des Brückenkopfprotons H-9 ( $\delta = 6.49$  ppm) als Ankerpunkt gewählt wurde. Im Hochfeldbereich des Spektrums sind bei 0.99 ppm und 0.55 ppm zwei Singulets mit einem relativen Integralverhältnis von 6:3 sichtbar, die den insgesamt neun Methylpro-

tonen zuzuordnen sind. Eine wie hier beobachtete Aufspaltung der Signale ist offensichtlich nur möglich, wenn die Rotation um die C(10)–Si-Bindung durch den dritten Chlorsubstituenten in Position 16 unterbunden ist.

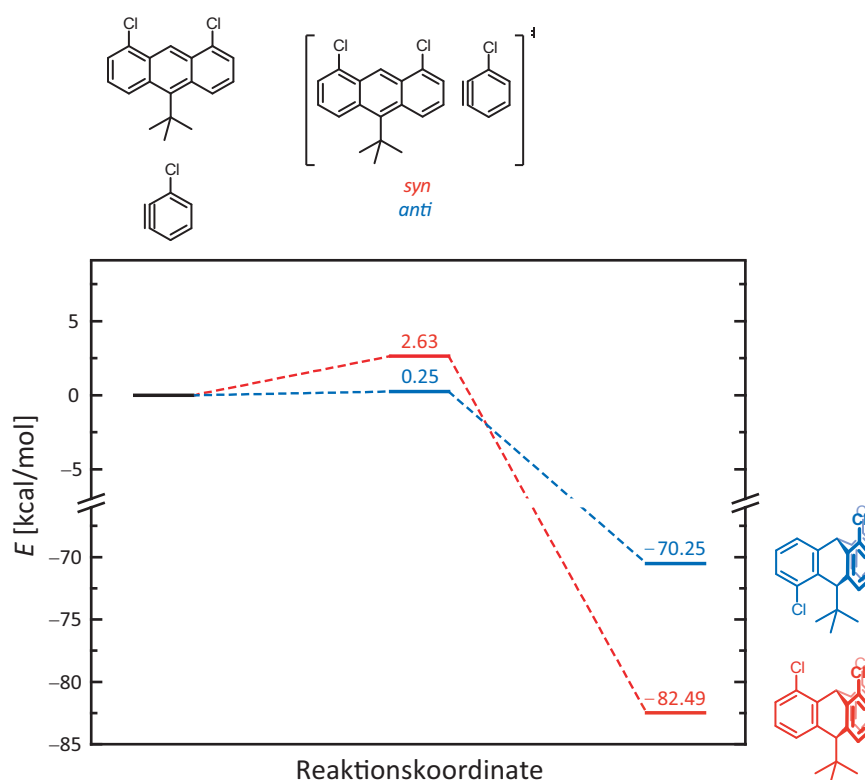


**Abbildung 4.5:** Vergleich der  $^1\text{H}$ -NMR-Spektren des *syn*- (oben) und *anti*-Trichlor-10-(trimethylsilyl)-tritypcens (unten) bei 298 K in  $\text{CDCl}_3$  (\*) mit Zuordnung der Signale.<sup>[90]</sup>

Ein vergleichbares Signalmuster wird erwartungsgemäß bei der  $^1\text{H}$ -NMR-spektroskopischen Untersuchung der analogen 10- $\text{GeMe}_3$ -Trichlortriptycens-Derivate beobachtet. Die Protonen der Germanium-gebundenen Methylgruppen des *syn*-Isomers verursachen ein Singulett bei 0.83 ppm, die magnetisch-inäquivalenten Methylprotonen der *anti*-substituierten Spezies zwei Singuletts bei 1.08 ppm und 0.59 ppm mit einem relativen Integralverhältnis von 6:3. Alle Signale sind im Vergleich zu den entsprechenden *syn*- und *anti*-Isomeren von Verbindung **29** leicht zu tiefem Feld verschoben.<sup>[90]</sup>

Die experimentell erhaltenen *syn-anti*-Verhältnisse zeigen, dass die eingangs erwähnten (einfachen) theoretischen Vorhersagen im Falle der  $\text{SiMe}_3$ - und  $\text{GeMe}_3$ -substituierten Dichloranthracene gut in Übereinstimmung zu bringen sind, während beim 9-Methyl-substituierten Dichloranthracen **22** das *anti*-Isomer erneut bevorzugt gebildet wird. Um die erhaltenen experimentellen Ergebnisse (auch theoretisch) erklären zu können, wurden detaillierte quantenmechanische Betrachtungen der  $[4\pi + 2\pi]$ -Cycloadditionsreaktionen angestellt. In diesem Zusammenhang wurde auch die Lage der Energieniveaus verschiedener Übergangszustände mit unterschiedlichen Methoden berechnet. Mit Hilfe der erhaltenen Ergebnisse, die im Folgenden beispielhaft für die Umsetzung des *tert*-Butyl-substituierten Dichloranthracens **27** mit Chlorarin erläutert werden, lassen sich die experimentellen Befunde dieser Arbeit und vorangegangener Untersuchungen<sup>[39,78]</sup> erstmals zusammenhängend erklären.<sup>[90]</sup>

Abbildung 4.6 zeigt am Beispiel der Umsetzung von 10-*tert*-Butyl-1,8-dichloranthracen (**27**) mit Chlorarin die Ergebnisse der quantenmechanischen Rechnungen. Aufgetragen sind jeweils die berechneten Energieniveaus der beiden Übergangszustände und der Trichlortriptycen-Derivate (rot: *syn*, blau: *anti*). Zu erkennen ist, dass das *tert*-Butyl-substituierte *syn*-Trichlortriptycyen wegen der nicht vorhandenen sterischen Abstoßung des Chloratoms mit dem *tert*-Butyl-Substituenten zwar das thermodynamisch stabilere Produkt ist ( $-82.49$  kcal/mol vs.  $-70.25$  kcal/mol), jedoch muss zu dessen Bildung im Vergleich zum (thermodynamisch leicht ungünstigeren) *anti*-Isomer im Übergangszustand eine höhere Energiebarriere überwunden werden ( $2.63$  kcal/mol vs.  $0.25$  kcal/mol). Folgerichtig handelt es sich bei dem im Experiment ausschließlich erhaltenen 10-*tert*-Butyl-1,8,16-trichlortriptycyen um das kinetische Produkt der Diels-Alder-Cycloaddition.



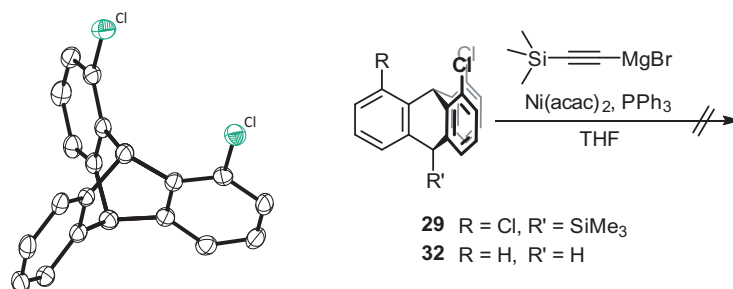
**Abbildung 4.6:** Darstellung der mittels DFT-Rechnungen ermittelten Energieniveaus der verschiedenen Übergangszustände und Endprodukte der Umsetzung von 10-*tert*-Butyl-1,8-dichloranthracen (**27**) mit Chlorarin (rot: *syn*, blau: *anti*).<sup>[90]</sup>

Vergleichbare Ergebnisse bezüglich der relativen energetischen Lage der Übergangszustände werden (mit unterschiedlichen Rechenmethoden) auch im Falle der anderen durchgeführten Triptycyen-Darstellungen erhalten. Zusammenfassend lässt sich deshalb festhalten, dass das *syn-anti*-Verhältnis der Diels-Alder-Cycloadditionsreaktion zu den Trichlortriptycyen-Derivaten mit großer Wahrscheinlichkeit von der Energie der entsprechenden Übergangszustände abhängig ist. Deren (relative) Lage zueinander lässt sich mit unterschiedlich großem Rechenaufwand ab-

schätzen, wobei jedoch eine genaue Vorhersage über das zu erwartende Verhältnis der *syn*- und *anti*-Isomere bisher nicht möglich ist.<sup>[90]</sup>

Die durchgeführten umfangreichen theoretischen und experimentellen Untersuchungen zur (selektiven) *syn*-Ausrichtung der Chloratome am Triptycengerüst stellten lediglich den ersten Schritt zum Aufbau gerichteter dreizähliger Lewis-Säuren dar. Hierauf folgen sollte eine Funktionalisierung der Substrate mit Alkineinheiten und anschließend die Umsetzung der Grundgerüste in verschiedenen (Hydro-) Metallierungsreaktionen.

Dazu wurde in Analogie zur bereits beschriebenen Alkynyl-Funktionalisierung von Dichloranthracen-Derivaten zunächst das *syn*-Trichlortriptycen *syn*-**29** in einer Kumada-Kreuzkupplungsreaktion mit [(Trimethylsilyl)ethinyl]magnesiumbromid zur Reaktion gebracht. Allerdings zeigte sich, dass es bei dieser Reaktion nicht zur Substitution der Chloratome des Triptycengerüsts kommt (Schema 4.12). Um einen wie auch immer gearteten negativen (sterischen) Einfluss der Cl- und gegebenenfalls des SiMe<sub>3</sub>-Substituenten auf die Kreuzkupplungsreaktion sicher ausschließen zu können, wurde durch Umsetzung von 1,8-Dichloranthracen mit *in situ*-erzeugtem Benzin das 1,8-Dichlortriptycen (**32**) als Testsubstrat dargestellt. Jedoch konnte auch bei der Umsetzung dieser zweifach Chlor-substituierten Triptycen-Spezies unter den gegebenen Bedingungen lediglich das Edukt reisoliert werden.<sup>[90]</sup>

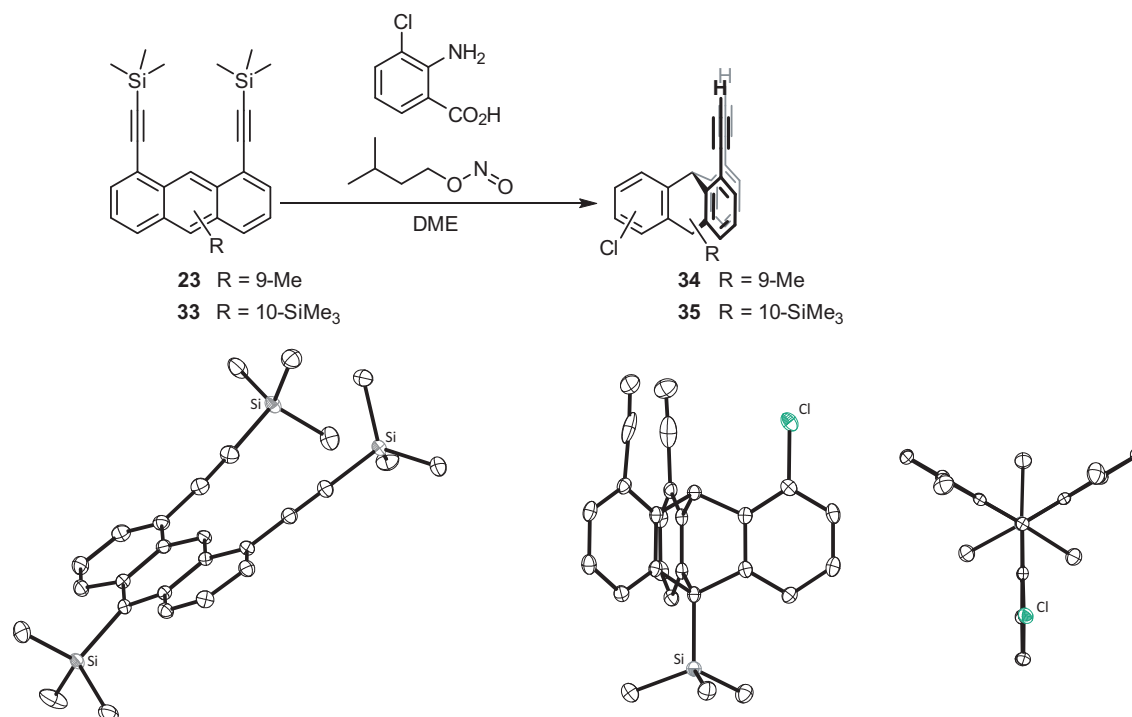


**Schema 4.12:** Versuche zur zwei- bzw. dreifachen Alkynyl-Funktionalisierung von 1,8-Dichlor- (**32**) und 1,8,13-Trichlor-10-(trimethylsilyl)triptycen (*syn*-**29**) durch Kumada-Kreuzkupplungsreaktionen (rechts) sowie die Molekülstruktur von **32** im Kristall (links).<sup>[90]</sup>

Um dennoch Alkynyl-funktionalisierte Triptycene zu erhalten, wurden 1,8-Bis[(trimethylsilyl)ethinyl]-9-methylantracen (**23**, siehe Schema 4.9) sowie das auf analoge Weise aus 1,8-Dichlor-10-(trimethylsilyl)anthracen (**24**) synthetisierte 1,8-Bis[(trimethylsilyl)ethinyl]-10-(trimethylsilyl)anthracen (**33**) mit Chlorarin umgesetzt.

Wie Schema 4.13 zeigt, wurden in beiden Fällen die entsprechenden zweifach Ethinyl-substituierten Chlortriptycendeivate **34** und **35** gebildet. Interessanterweise konnte nach Standardaufarbeitung bei der Umsetzung von **33** in der Diels-Alder-Cycloadditionen (in sehr geringen Ausbeuten) ausschließlich das *syn*-Derivat des entsprechenden Triptycens isoliert werden. Sowohl das *anti*-Produkt, als auch Nebenprodukte, die durch eine [2 $\pi$  + 2 $\pi$ ]-Cycloadditionen zwischen Alkin und Arin entstehen könnten, wurden – zumindest im ausfallenden Feststoff – nicht beobachtet.

Die Reaktion von 1,8-Bis[(trimethylsilyl)ethynyl]-9-methylantracen (**23**) mit dem entsprechenden Chlorarin brachte nach Aufarbeitung eine sehr geringe Menge (weniger als 1 mg) eines annähernd farblosen Feststoffs hervor, die für eine ausführliche NMR-spektroskopische Charakterisierung nicht ausreichend war. GC/MS-Untersuchungen der Probe zeigten jedoch ein Signal, das sich mit  $m/z = 350$  dem gewünschten (entschützten) Produkt **34** zuordnen ließe. Verlässliche Aussagen darüber, ob es sich dabei um das *syn*- oder *anti*-Isomer handelt, können bis *dato* allerdings nicht getroffen werden.



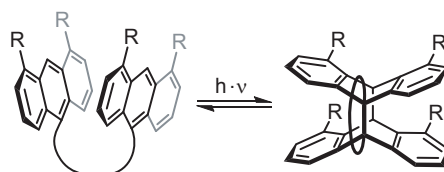
**Schema 4.13:** Umsetzung von 1,8-Bis[(trimethylsilyl)ethynyl]-9-methylantracen (**23**) und 1,8-Bis[(trimethylsilyl)ethynyl]-10-(trimethylsilyl)anthracen (**33**) zu den entsprechenden zweifach Ethynyl-substituierten Chlortriptycenen **34** und *syn*-**35** sowie die Molekülstrukturen von **33** und *syn*-**35** (Seitenansicht und Aufsicht) im Kristall.<sup>[90]</sup>

Anzumerken ist, dass die hier beobachtete Abspaltung der Trimethylsilyl-Alkylschutzgruppen eine Folge des standardmäßig durchgeführten Aufarbeitungsprozesses ist, bei dem das Reaktionsgemisch mit Methanol und wässriger Natriumhydroxidlösung versetzt wird.



### 4.3 Grundgerüste auf Basis verbrückter 1,8-funktionalisierter Anthracene

Wie bereits geschildert, kann es bei der durch UV-Licht-induzierten Dimerisierung 1,8-funktionalisierter Anthracen-Derivate zur Bildung zweier Isomere kommen: dem so genannten *head to head*-, oder auch *syn*-Isomer, bei dem alle vier Substituenten in eine Richtung weisen sowie dem *head to tail*-, oder auch *anti*-Isomer, bei dem eine gegensinnige Ausrichtung der Substituenten vorgefunden wird. Auch zu diesem Problem sollte in dieser Arbeit ein erster Lösungsansatz erarbeitet werden, der in Schema 4.14 schematisch dargestellt ist. Dabei werden zwei 1,8-funktionalisierte Anthracen-Derivate durch eine organische Verbrückungseinheit in 10-Position miteinander verknüpft, sodass bei Bestrahlung eine selektive *syn*-Photodimerisierung erzwungen wird.



**Schema 4.14:** Schematische Darstellung der durch Verbrückung in 10-Position erzwungenen *syn*-Photodimerisierung zweier 1,8-funktionalisierter Anthraceneinheiten.

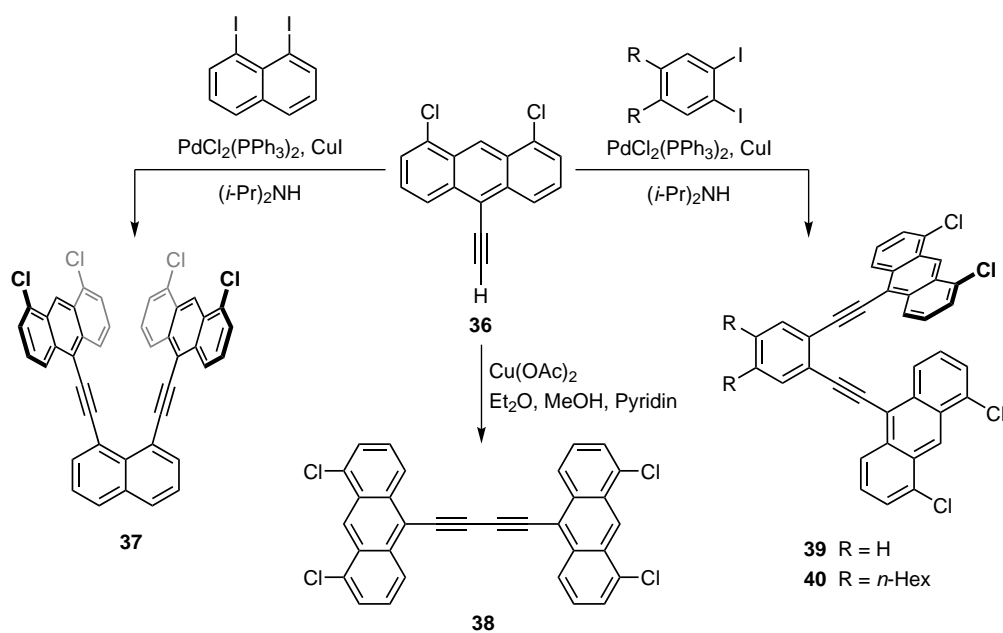
Die verwendeten Linker müssen dabei verschiedene Anforderungen erfüllen, welche die synthetischen Herausforderungen innerhalb dieses Teilprojektes ausmachen. So dürfen sie keine Heteroatome (in der Regel Donoratome) enthalten, da diese bei späteren Metallierungen zu Problemen führen könnten. Zudem muss die Brücke neben einer ausreichenden Länge auch ein gewisses Maß an Flexibilität und Vororientierung aufweisen, sodass eine Photodimerisierung der Anthraceneinheiten überhaupt möglich ist. Jedoch besteht bei einer zu langen und flexiblen Linkereinheit die Gefahr, dass es zu einer inter- statt der gewünschten intramolekularen Dimerisierung kommt.

In dieser Arbeit wurden dazu zwei unterschiedliche Synthesestrategien verfolgt, die in den folgenden Abschnitten vorgestellt werden sollen.

#### 4.3.1 Synthese und Struktur 1,8-funktionalisierter Anthracene mit starrer Verbrückung

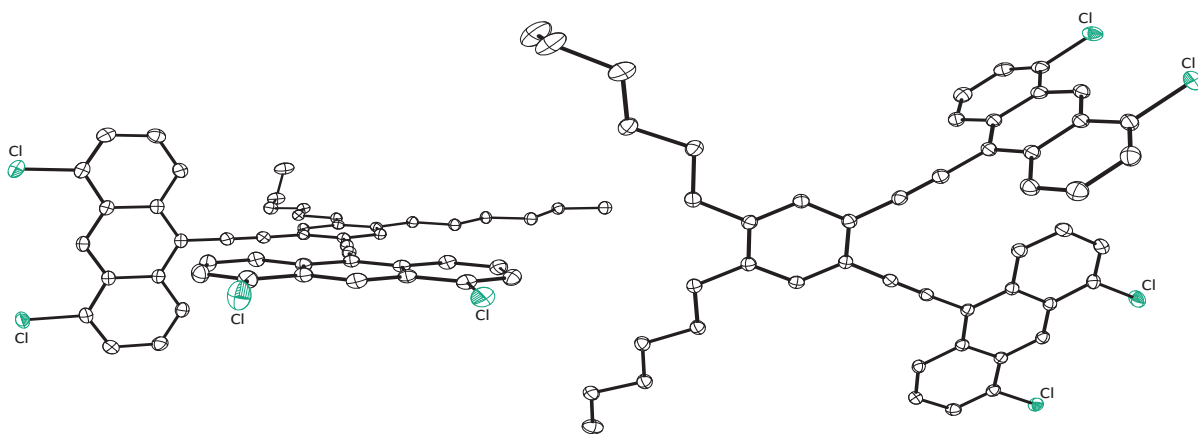
Durch den Einsatz der Schlüsselkomponente 1,8-Dichlor-10-(ethinyl)anthracen (**36**) in unterschiedlichen (Kreuz-) Kupplungsreaktionen lässt sich, wie Schema 4.15 zeigt, eine semiflexible Verbrückung zweier 1,8-funktionalisierter Anthraceneinheiten erreichen, wobei sich die Ausrichtung der jeweils zwei C-Cl-Funktionalitäten zwischen annähernd paralleler Orientierung (**37**) bis zu einem 180°-Winkel (**38**) variieren lässt.

Eine Kupfer-vermittelte oxidative Eglinton-Homokupplung<sup>[91]</sup> liefert mit einer sehr guten Ausbeute von 92 % die Butadiinyl-verbrückte Spezies **38**. Die Umsetzung von **36** mit 1,8-Diodnaphthalin und 1,2-Diodbenzol in Sonogashira-Hagihara-Kreuzkupplungsreaktionen bringt die Aryl-verbrückten Komponenten **37** und **39** hervor (Schema 4.15).<sup>[92]</sup>



**Schema 4.15:** Synthese semiflexibel-verbrückter Anthraceneinheiten durch Umsetzung von 1,8-Dichlor-10-ethynylantracen (**36**) in (Kreuz-) Kupplungsreaktionen.<sup>[92]</sup>

Alle drei Produkte zeichnen sich durch eine extrem geringe Löslichkeit in gängigen polaren und unpolaren organischen Lösungsmitteln aus, weshalb sie teilweise lediglich durch  $^1\text{H}$ -NMR-Spektroskopie und hochaufgelöste Massenspektrometrie identifiziert werden konnten. Aus demselben Grund konnte bei den Verbindungen bis *dato* keine weitere Funktionalisierung der starren Gerüste bzw. eine Photodimerisierung durchgeführt werden.

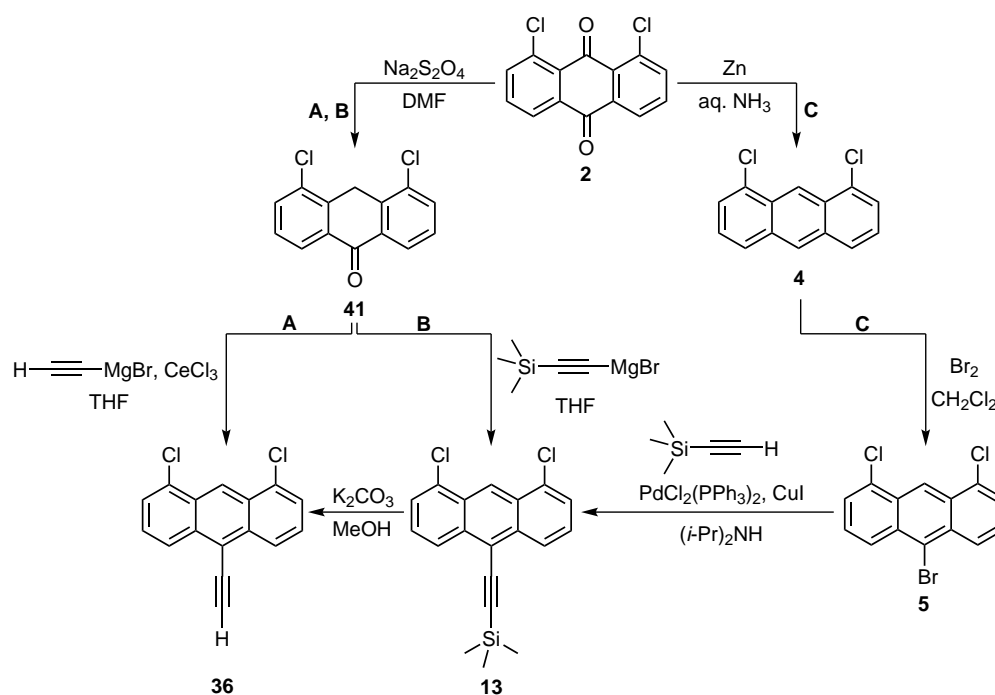


**Abbildung 4.7:** Verschiedene Ansichten der Molekülstruktur von Verbindung **40** im Kristall.<sup>[92]</sup>

Das Problem der geringen Löslichkeit von **39** konnte erfolgreich durch das Einführen zweier *n*-Hexylgruppen in 4- und 5-Position gelöst werden. Die erhaltene Verbindung **40** lässt sich leicht durch Säulenchromatographie aufreinigen, vollständig NMR-spektroskopisch und massenspek-

trometrisch charakterisieren sowie aus *n*-Pentan kristallisieren. Die röntgenkristallographische Untersuchung zeigt, dass im Kristall eine der Anthraceneinheiten komplanar mit dem Benzolring liegt, während die zweite orthogonal zur Benzolebene steht (Abbildung 4.7).<sup>[92]</sup> Um die für die intramolekulare Photodimerisierung benötigte Flexibilität des nun löslichen Grundgerüsts zu erreichen, wurden erste Ansätze zur Reduktion der Dreifachbindung mittels Wasserstoff und Pd/C in verschiedenen Lösungsmitteln durchgeführt, brachten jedoch bisher keinen Erfolg.

Wie erwähnt, stellt 1,8-Dichlor-10-(ethinyl)anthracen (**36**) die zentrale Komponente bei den semiflexibel-verbrückten 1,8-Dichloranthracenen dar, sodass im Rahmen dieses Teilprojektes auch ein effizienterer Zugang zu dieser Verbindung gefunden werden sollte. Zwar ist die dreistufige Darstellung von **36** ausgehend von 1,8-Dichloranthracen-10-(9H)-on (**41**)<sup>[93]</sup> in der Literatur bereits beschrieben (Route **B**, Schema 4.16),<sup>[78]</sup> jedoch muss hier zunächst das in der zweiten Stufe benötigte Grignardreagenz verhältnismäßig aufwendig synthetisiert werden. Zudem beinhaltet jeder Schritt eine säulenchromatographische Aufreinigung der Produkte. Ähnlich verhält es sich mit der vierstufigen Syntheseroute **C**, die sich nach der vorstehend beschriebenen einfachen Darstellung von 10-Brom-1,8-dichloranthracen (**5**) eröffnete.



**Schema 4.16:** Unterschiedliche Syntheserouten **A**, **B** und **C** zur Darstellung von 1,8-Dichlor-10-ethinylanthracen (**36**).<sup>[78,92,93]</sup>

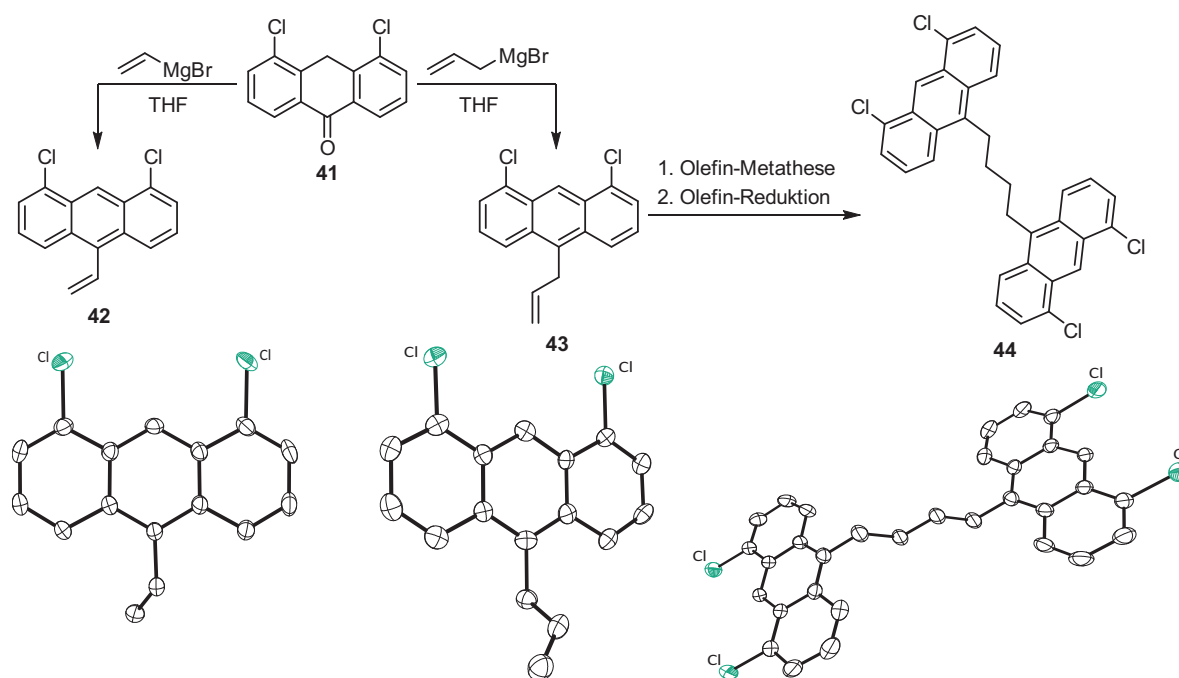
Als (zeit-) effizienteste Methode erwies sich schließlich die Cer(III)-vermittelte direkte Umsetzung des Anthrons **41** mit einer kommerziell erhältlichen Lösung aus Ethynylmagnesiumbromid in THF (Route **A**, Schema 4.16). Dabei wird zunächst Cer(III)-chlorid in THF suspendiert und bei 0 °C mit der Grignardkomponente versetzt, bevor das ebenfalls in THF gelöste Dichloran-

thron langsam zugegeben wird. Das gewünschte 1,8-Dichlor-10-(ethinyl)anthracen (**36**) kann auf diese Weise nach Säulenchromatographie mit einer guten Ausbeute erhalten werden.<sup>[92]</sup>

Die Zugabe von  $\text{CeCl}_3$  erfolgte in Anlehnung an eine Vorschrift von Imamoto und Mitarbeitern. Sie beschreiben bei Zusatz des Cersalzes eine signifikant gesteigerte Reaktivität von Carbonylsubstraten mit Grignardreagenzien,<sup>[94]</sup> die auch bei der Umsetzung von **41** zu **36** zu verzeichnen ist; ohne  $\text{CeCl}_3$  sinkt die Ausbeute deutlich von 65 % auf nur noch 14 %.<sup>[92]</sup>

#### 4.3.2 Synthese und Struktur 1,8-funktionalisierter Anthracene mit flexibler Verbrückung

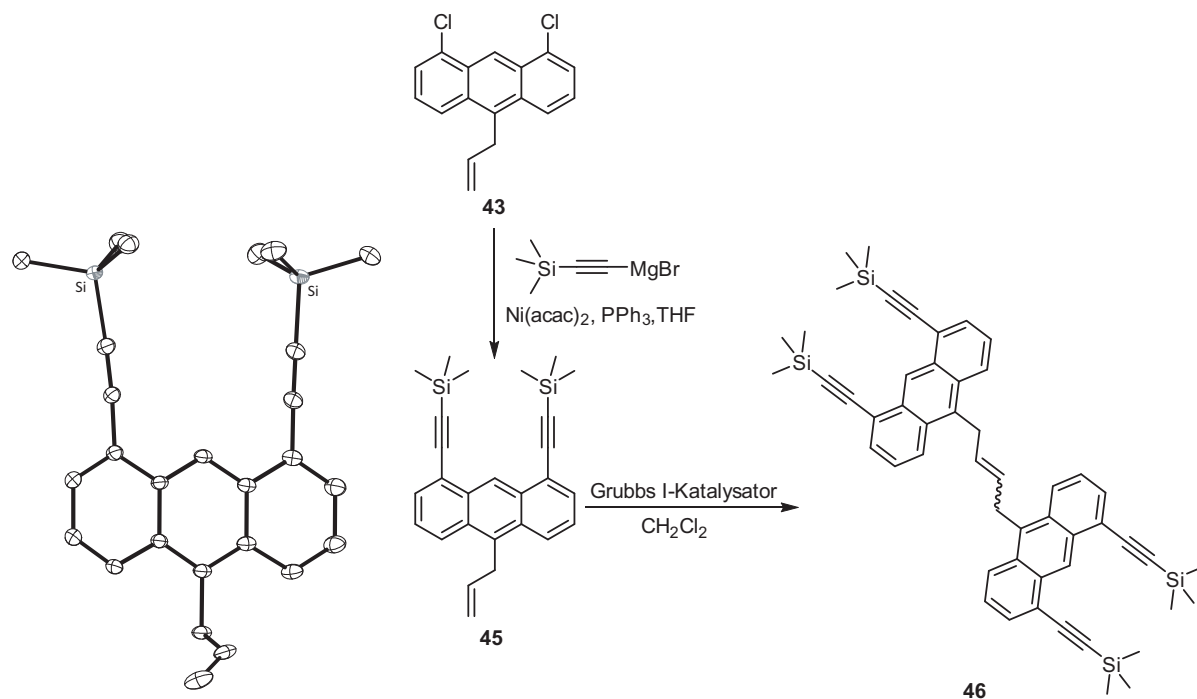
Da sich die nachträgliche Reduktion der eingeführten Brücke aufgrund der schlechten Löslichkeitseigenschaften als wenig praktikabel erwiesen hat, wurde in einer zweiten Synthesestrategie versucht, zwei 1,8-funktionalisierte Anthracen-Derivate direkt durch eine flexible Linkereinheit zu verbinden. Zu diesem Zweck bieten sich Olefinmetathese-Reaktionen an, wozu zunächst Anthraceneinheiten benötigt werden, die in 10-Position einen Substituenten mit terminaler Doppelbindung tragen.



**Schema 4.17:** Darstellung von 1,8-Dichlor-10-vinylanthracen (**42**) und 10-Allyl-1,8-dichloranthracen (**43**). Bei Letzterem gelang die Verbrückung zweier Anthracenmonomere durch Olefinmetathese-Reaktion mit anschließender Reduktion der Olefineinheit. Ebenfalls gezeigt sind die Molekülstrukturen von **42**, **43** und **44** im Kristall.<sup>[95]</sup>

Schema 4.17 zeigt einen (zumindest teilweise) gangbaren Synthesepfad, bei dem ausgehend von 1,8-Dichloranthracen-10(9H)-on (**41**) durch Umsetzung mit den entsprechenden Grignardreagenzien die in 10-Position mit Vinyl- und Allylsubstituenten funktionalisierten 1,8-Dichloranthracen-Derivate **42** und **43** dargestellt werden konnten. Die beiden vollständig charakterisier-

ten Verbindungen wurden in der Folge mit dem Grubbs-Katalysator der ersten Generation in Dichlormethan zur Reaktion gebracht, wobei lediglich im Falle der Umsetzung der Allyl-substituierten Spezies **43** eine Olefinmetathese-Reaktion beobachtet wurde. Jedoch erwies sich auch das But-2-enyl-verbrückte Metatheseprodukt als nahezu unlöslich in 23 getesteten Lösungsmitteln unterschiedlicher Polarität, sodass sich die Reduktion der Doppelbindung als kompliziert herausstellte. Nach Hydrierung mit *para*-Toluolsulfonsäurehydrazid in siedendem Xylol<sup>[96]</sup> konnten schließlich Spuren der Zielverbindung **44** erhalten werden, die sich mittels hochaufgelöster Massenspektrometrie und durch Bestimmung der Molekülstruktur im Kristall eindeutig identifizieren ließ. Versuche, die durch Reduktion flexibel-verbrückte Komponente **44** in handhabbaren Mengen zu erhalten, schlugen bis *dato* fehl, ebenso wie mehrere Ansätze, unter verschiedenen Bedingungen das Vinyl-substituierte Dichloranthracen-Derivat **42** in Olefinmetathese-Reaktionen in die entsprechende Ethenyl-verbrückte Spezies zu überführen.



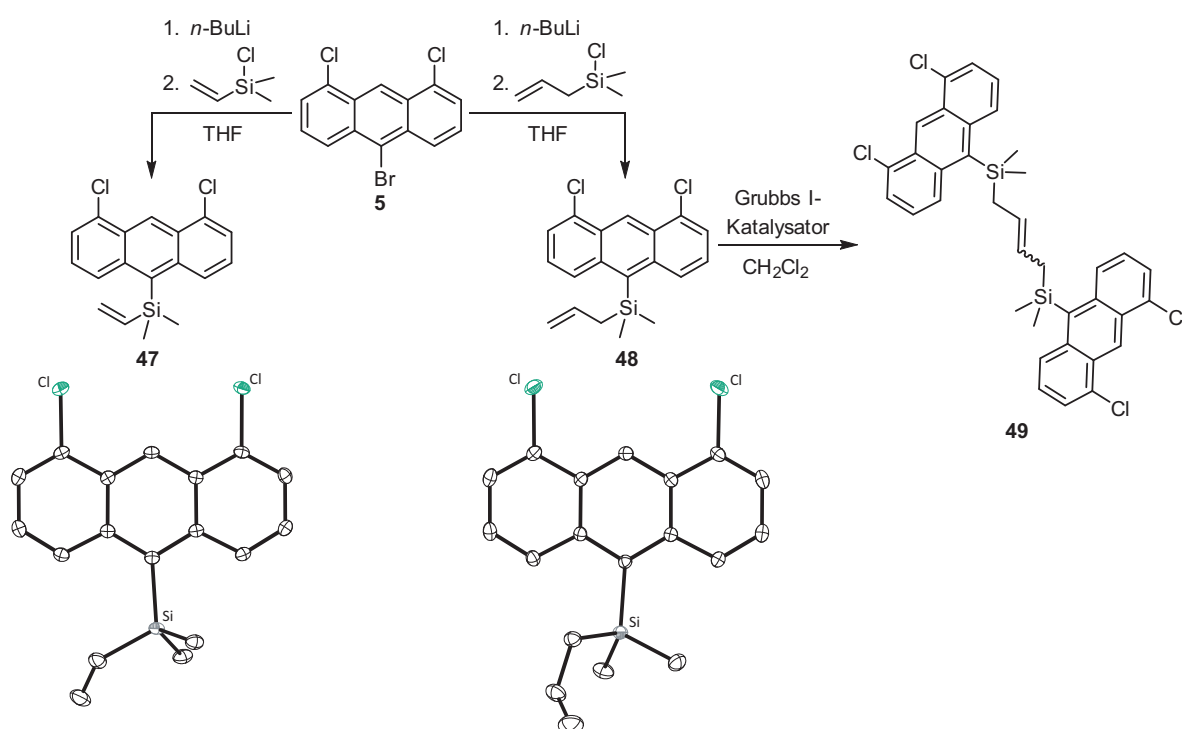
**Schema 4.18:** Darstellung von 10-Allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracen (**45**) mit anschließender Olefinmetathese-Reaktion zu **46** sowie die Molekülstruktur von **45** im Kristall.<sup>[95]</sup>

Als Folge der schlechten Löslichkeit von **44** war auch die weitere Funktionalisierung nicht möglich. Deshalb wurden in einem zweiten Ansatz zunächst die Chloratome von Verbindung **43** mittels Kumada-Kreuzkupplung durch Alkinyleinheiten substituiert und die auf diese Weise erhaltene Spezies **45** anschließend einer Olefinmetathese-Reaktion unterworfen (Schema 4.18).

Das Produkt **46** zeigt im Gegensatz zur analogen, vierfach Chlor-substituierten Verbindung **44** eine sehr gute Löslichkeit in vielen organischen Lösungsmitteln und konnte vollständig NMR-spektroskopisch und massenspektrometrisch charakterisiert werden.<sup>[95]</sup>

Ogleich das Problem der geringen Löslichkeit der durch Olefinmetathese-Reaktionen erhaltenen verbrückten Verbindungen durch den in Schema 4.18 gezeigten Syntheseweg erfolgreich umgangen wurde, gestaltet sich nun die selektive Reduktion der internen Doppelbindung als schwierig, da es stets auch zu einer Hydrierung der Alkinfunktionalitäten kommen würde. Dagehingehende Versuche wurden jedoch, ebenso wie auch UV-Bestrahlungsexperimente von Verbindung **46**, noch nicht durchgeführt.

Mit der Absicht, weiterhin die relativ unkompliziert verlaufende Olefinmetathese-Reaktion zum Aufbau der Linkereinheit nutzen zu können, aber gleichzeitig die Löslichkeit der vierfach Chlor-substituierten Produkte zu erhöhen, wurden, wie in Schema 4.19 gezeigt, die Dichloranthracen-Derivate **47** und **48** dargestellt. Die Methyl-Substituenten an den Siliciumatomen der Brücke sollten sich dabei löslichkeitsfördernd auswirken.

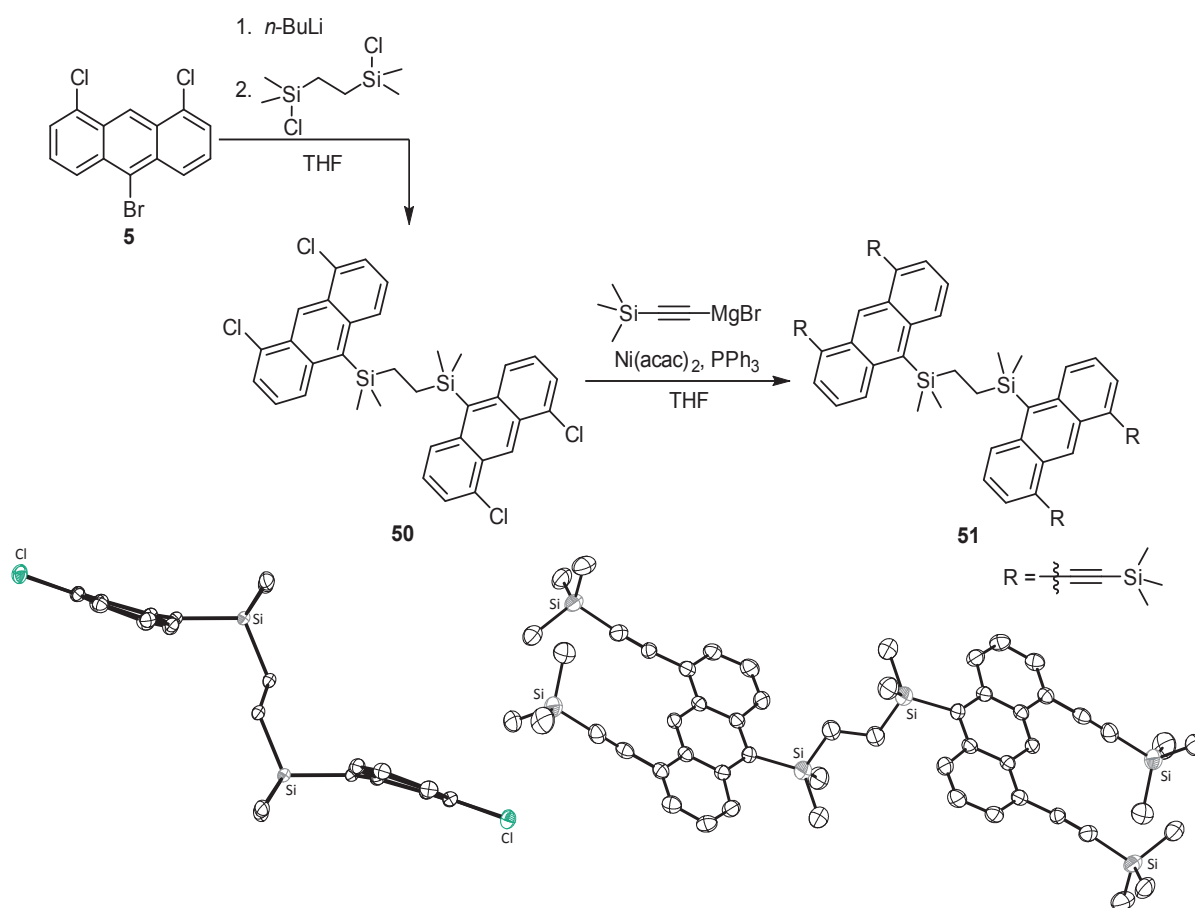


**Schema 4.19:** Synthese von 1,8-Dichlor-10-[dimethyl(vinyl)silyl]anthracen (**47**) und 10-[(Allyl)dimethylsilyl]-1,8-dichloranthracen (**48**) mit anschließender Olefinmetathese-Reaktion zu **49** sowie die Molekülstrukturen von **47** und **48** im Kristall.<sup>[95]</sup>

Ausgangsverbindung ist in beiden Fällen 10-Brom-1,8-dichloranthracen (**5**), das in einer Halogen-Metall-Austausch-Reaktion mit *n*-Butyllithium bei  $-78\text{ °C}$  in Position 10 lithiiert wurde. Nach dem Aufkondensieren von Chlordimethylvinylsilan bzw. Allylchlorodimethylsilan wurden die entsprechend in 10-Position funktionalisierten Verbindungen **47** und **48** nach wässriger Aufarbeitung und säulenchromatographischer Aufreinigung in moderaten Ausbeuten von 37 % bzw. 44 % isoliert.<sup>[95]</sup> Wie in Schema 4.19 bereits angedeutet, gelang auch im Falle von **42** und **43** nur mit der Allylsilyl-funktionalisierten Spezies **48** die erfolgreiche Umsetzung in der anschließenden

Olefinmetathese-Reaktion. Nach fünftägiger Reaktionszeit wurde mit einer Ausbeute von 71 % ein gelber Feststoff erhalten, der sich als gut löslich in vielen organischen Lösungsmitteln erwies. Die  $^1\text{H-NMR}$ -spektroskopischen und massenspektrometrischen Daten der Verbindung deuten auf die erfolgreiche Bildung von **49** hin.<sup>[95]</sup> Versuche zur Reduktion der internen C=C-Doppelbindung sowie zur Untersuchung der Photoschaltbarkeit stehen noch aus.

Ein ähnlicher Ansatz zur Verbrückung wurde mit der in Schema 4.20 gezeigten Syntheseroute verfolgt. Hierbei folgt dem Halogen-Metall-Austausch die direkte Umsetzung mit einem halben Äquivalent 1,2-Bis(chlordimethylsilyl)ethan. Unter Eliminierung von Lithiumchlorid entsteht mit einer Ausbeute von 16 % die flexibel verbrückte vierfach Chlor-substituierte Spezies **50**, die sich gut in organischen Lösungsmitteln lösen lässt. Durch eine vierfache Kumada-Kreuzkupplungsreaktion gelang die Substitution der Chloratome durch (Trimethylsilyl)ethinyl-Funktionalitäten, wodurch Verbindung **51** erhalten werden konnte.<sup>[95]</sup>

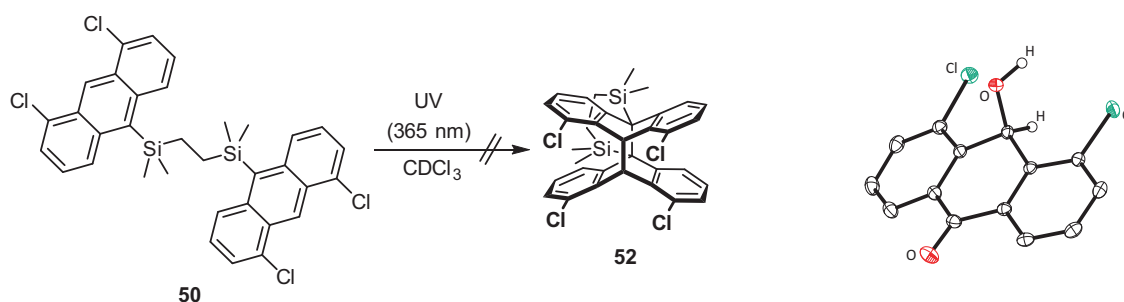


**Schema 4.20:** Darstellung der flexibel verbrückten Verbindung **50** und weitere Funktionalisierung zu **51** sowie die Molekülstrukturen beider Verbindungen im Kristall.<sup>[95]</sup>

Neben der Charakterisierung der flexibel verbrückten Komponenten **50** und **51** durch NMR-Spektroskopie und Massenspektrometrie gelang in beiden Fällen die Aufklärung der Molekül-

struktur im Kristall (Schema 4.20). Bei 1,2-Bis[(1,8-dichloranthracen-10-yl)dimethylsilyl]ethan (**50**) kann, wie zuvor auch schon im Fall von 1,8-Dichlor-10-(trimethylsilyl)anthracen (**24**) beschrieben,<sup>[82]</sup> ein Abknicken des Silylsubstituenten beobachtet werden.<sup>[95]</sup>

Die UV-Licht-Bestrahlung einer CDCl<sub>3</sub>-Lösung der verbrückten vierfach Chlor-substituierten Spezies **50** erfolgte mit dem Ziel, eine intramolekulare *syn*-Dimerisierung, in diesem Falle also eine gleichsinnige Ausrichtung aller vier Chloratome, zu erreichen (Schema 4.21). Tatsächlich zeigten <sup>1</sup>H-NMR-Reaktionskontrollen bereits nach kurzer Zeit eine vollständige und selektive Umwandlung von **50** in eine neue Verbindung. Allerdings handelt es sich bei dieser neuen Komponente nicht um das Zielprodukt **52**. Erhalten wurde – vermutlich durch Reaktion von **50** mit Spuren von Sauerstoff und/oder Wasser aus dem Lösungsmittel – das 1,8-Dichlor-9-hydroxyanthracen-9-(10H)-on (**53**)<sup>5</sup> dessen Molekülstruktur im Kristall im rechten Teil von Schema 4.21 gezeigt ist.<sup>[95]</sup> Genauere Untersuchungen zur Bildung des Anthronols **53** wurden im Rahmen dieser Arbeit nicht angestellt.



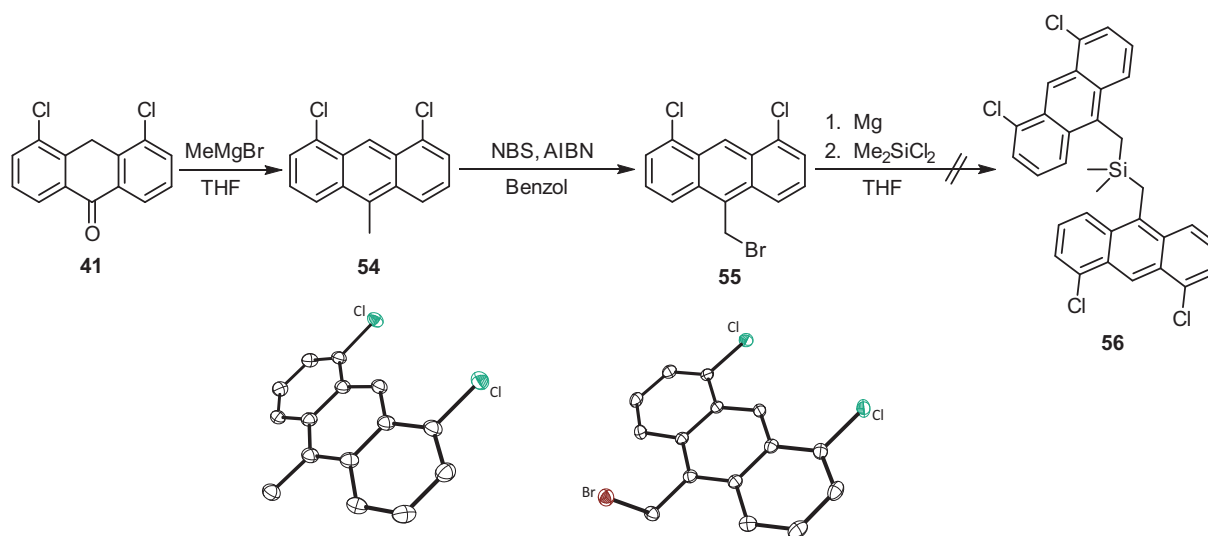
**Schema 4.21:** Versuch zur selektiven *syn*-Photodimerisierung der vierfach Chlor-substituierten Spezies **50** zu **52** sowie die Molekülstruktur von **53** im Kristall.<sup>[95]</sup>

Mit dem in Schema 4.22 gezeigten Ziel, zwei 1,8-Dichloranthraceneinheiten über eine flexible CH<sub>2</sub>Si(Me)<sub>2</sub>CH<sub>2</sub>-Einheit zu verbrücken, wurde aus dem Dichloranthron **41** durch Umsetzung mit Methylmagnesiumbromid und anschließender Rearomatisierung 1,8-Dichlor-10-methylanthracen (**54**) synthetisiert.<sup>[39]</sup> Die anschließende radikalische Bromierung in Benzylposition gelingt in guten Ausbeuten mit *N*-Bromsuccinimid (NBS) und Azo-bis(isobutyronitril) (AIBN) als Radikalstarter in Benzol.<sup>[97]</sup> Bei beiden Verbindungen konnte durch Röntgenbeugungsexperimente an Einkristallen die jeweilige Molekülstruktur im Festkörper bestimmt werden. Um die Brommethyl-substituierte Verbindung **55** zur verbrückten Spezies **56** umzusetzen, wurde eine THF-Lösung des Anthracen-Derivates zu einem halben Äquivalent Dichlordimethylsilan und Magnesiumspänen getropft. Wie aus Schema 4.22 hervorgeht, gelang es jedoch nicht, das Zielprodukt **56** zu isolieren.<sup>6</sup>

<sup>5</sup>Die Identität von Verbindung **53** wurde ebenfalls durch NMR-spektroskopische und massenspektrometrische Untersuchungen bestätigt.<sup>[95]</sup>

<sup>6</sup>Bei der Umsetzung (substituierter) Anthracene mit elementarem Magnesium in THF kann sich in einer Nebenreaktion auch Magnesiumanthracen · 3 THF bilden,<sup>[98]</sup> was aber bei der hier durchgeführten Reaktion nicht beobachtet wurde.





**Schema 4.22:** Syntheseroute zur Darstellung von 1,8-Dichlor-10-(brommethyl)anthracen (**55**) und Versuch der Verbrückung zu **56** sowie die Molekülstrukturen von **54** und **55** im Kristall.

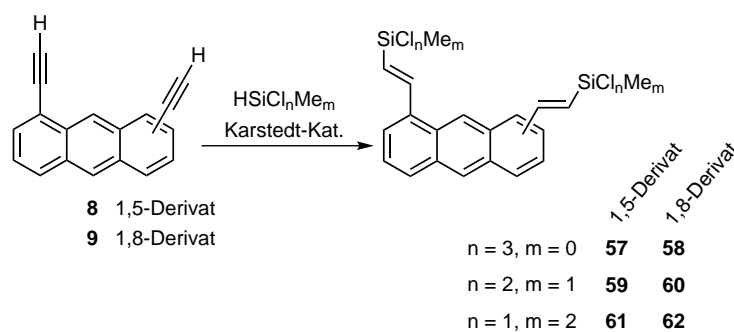
## 4.4 Metallierungsreaktionen an Alkynyl-substituierten Anthracengerüsten

Im Rahmen dieser Arbeit wurden, wie bereits beschrieben, verschiedene Alkynyl-substituierte Anthracen-Derivate synthetisiert und (strukturell) charakterisiert. In diesem Abschnitt werden nun die Reaktionen vorgestellt, die zur weiteren Funktionalisierung der organischen Grundgerüste mit Lewis-sauren Atomen durchgeführt wurden.

### 4.4.1 Hydrosilylierungsreaktionen

Bei der Hydrosilylierung handelt es sich formal um die Addition eines Silans an eine interne oder terminale C–C-Mehrfachbindung, bei der die entsprechenden Si-substituierten Alkane oder Alkene entstehen. Im Gegensatz zu den später diskutierten Hydroborierungs- und Hydrogallierungsreaktionen werden Hydrosilylierungsreaktionen in der Regel unter Einsatz eines Übergangsmetall-Katalysators durchgeführt.<sup>7</sup> Eines der prominentesten und inzwischen auch kommerziell erhältlichen Katalysatorsysteme ist der 1,3-Divinyl-1,1,3,3-tetramethyldisiloxan-Komplex von Platin(0), auch als *Karstedt-Katalysator* bekannt, der in sehr guten Ausbeuten die selektive *syn*-Addition des Silans zum *anti*-Markownikow-Produkt fördert.<sup>[99]</sup>

Die Hydrosilylierung terminaler Aryl-gebundener Alkine liefert die entsprechenden Si-funktionalisierten Vinylaryle. Schema 4.23 zeigt die im Rahmen dieser Arbeit durchgeführten Hydrosilylierungsreaktionen. Dabei wurden 1,5- (**8**) und 1,8-Diethinylanthracen (**9**) in Trichlorsilan, Dichlormethylsilan, bzw. Chlordimethylsilan gelöst und bei Raumtemperatur mit jeweils einem Tropfen einer Xylol-Lösung des Karstedt-Katalysators versetzt. Nach Entfernen des überschüssigen Silans wurden alle Verbindungen **57** – **62** in quantitativer Ausbeute als gelbe Feststoffe isoliert und eindeutig mittels NMR-Spektroskopie und Massenspektrometrie identifiziert.<sup>[100]</sup>



**Schema 4.23:** Synthese der zweifach hydrosilylierten Verbindungen **57** – **62** durch Pt-katalysierte Hydrosilylierungsreaktionen von 1,5- (**8**) und 1,8-Diethinylanthracen (**9**).<sup>[100]</sup>

Bei den auf diese Weise erhaltenen zweifach  $\text{SiCl}_3$ -,  $\text{SiCl}_2\text{Me}$ - und  $\text{SiClMe}_2$ -funktionalisierten Verbindungen sollte durch die Substitution eines (elektronenziehenden) Chloratoms durch eine

<sup>7</sup>Auch radikalische Hydrosilylierungen sind bekannt, im Vergleich zur Übergangsmetall-katalysierten Reaktionsführung aber weitaus weniger verbreitet.<sup>[99]</sup>

(elektronenschiebende) Methylgruppe in der genannten Reihenfolge eine Abnahme der Lewis-Acidität des Siliciumatoms zu verzeichnen sein.

Da sich die Hydrosilylierungsprodukte als schwer- bis unlöslich in donorfreen Lösungsmitteln erwiesen, wurde versucht, die Verbindungen aus Diethylether zu kristallisieren, gegebenenfalls unter Inkaufnahme der Bildung der entsprechenden Ether-Addukte. Lediglich in einem Fall, dem  $\text{SiCl}_3$ -substituierten 1,8-Derivat **58**, konnten Kristalle erhalten werden, die sich zur röntgenkristallographischen Untersuchung eigneten. Abbildung 4.8 zeigt die Molekülstruktur von Verbindung **63** im Kristall,<sup>8</sup> bei der es sich offensichtlich um das Produkt einer Etherspaltungsreaktion handelt.<sup>[100]</sup>

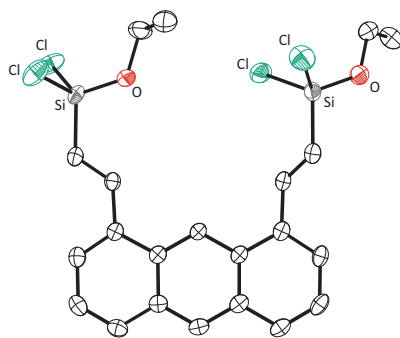
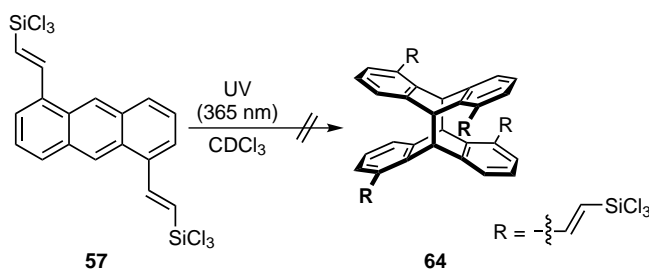


Abbildung 4.8: Molekülstruktur von Verbindung **63** im Kristall.<sup>[100]</sup>

Bei den Verbindungen **57**, **59** und **61** sind die Lewis-sauren Funktionalitäten in entgegengesetzte Richtung orientiert. Allerdings bietet sich, wie in Abschnitt 4.1.2 beschrieben, potentiell die Möglichkeit, die 1,5-substituierten Anthracen-Derivate durch UV-Licht-Bestrahlung in Janus-artige, gerichtete Verbindungen zu überführen.<sup>[84]</sup> Anhand von 1,5-Bis[2-(trichlorsilyl)vinyl]anthracen (**57**) wurde eine derartige Reaktivität getestet (Schema 4.24). Jedoch führte die Bestrahlung der in  $\text{CDCl}_3$ -gelösten Probe nicht zur Bildung eines *syn*- oder *anti*-Photodimers, sondern zu einer vollständigen Zersetzung der Substanz, die allerdings nicht näher untersucht wurde.



Schema 4.24: Versuch der Photodimerisierung von 1,5-Bis[2-(trichlorsilyl)vinyl]anthracen (**57**) zum *anti*-Photodimer **64**.

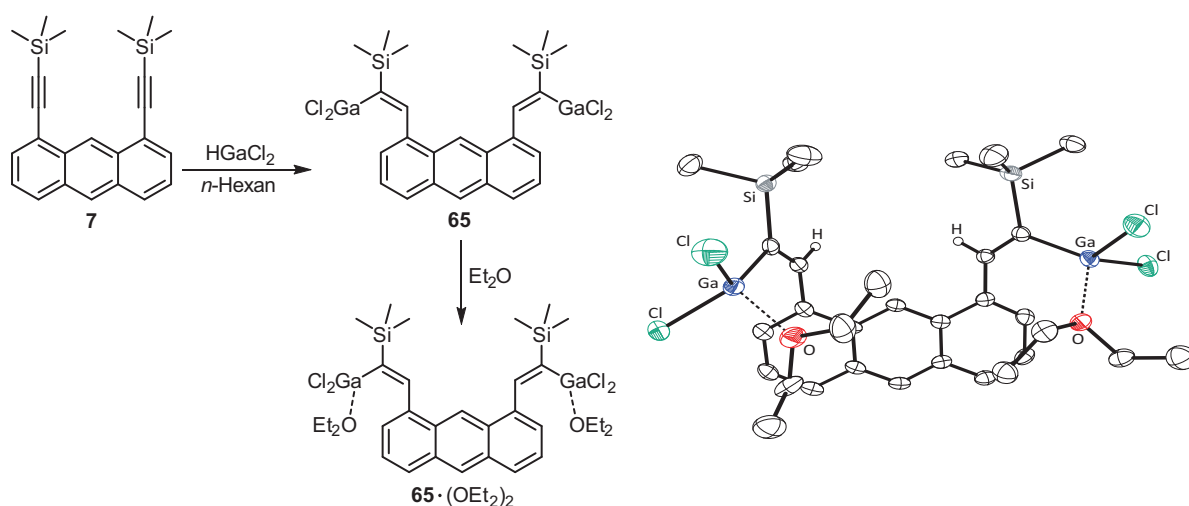
<sup>8</sup>Bei dem untersuchten Kristall handelt es sich um ein Mischkristallsystem, bei dem an den Siliciumatomen der Ethoxy- und der (in Abbildung 4.8 nicht gezeigte) dritte Chlorsubstituent im Verhältnis 89:11 bzw. 95:5 nebeneinander vorliegen.<sup>[100]</sup>

## 4.4.2 Hydrogallierungsreaktionen

Die Addition von Gallanen an C–C-Mehrfachbindung wird als *Hydrogallierung* bezeichnet, die, wie bereits erwähnt, ohne Zusatz eines Katalysators ablaufen kann. Umfangreiche Arbeiten zur vielfältigen Anwendbarkeit von Hydrogallierungsreaktionen an Alkinen, insbesondere zum Aufbau von Poly-Lewis-Säuren, stammen von Uhl und Mitarbeitern. Zum Einsatz kommen vornehmlich diverse Dialkylgallane,  $\text{HGaR}_2$ ,<sup>[41,43–45]</sup> oder das Dichlorgallan,  $\text{HGaCl}_2$ ,<sup>[101–104]</sup> wobei in beiden Fällen sowohl eine einfache als auch eine doppelte Addition des Gallans an die Dreifachbindung beobachtet werden kann.

Dichlorgallan lässt sich nach einer Methode von Schmidbaur *et al.* sehr einfach durch eine Reaktion äquimolarer Mengen von Gallium(III)-chlorid und Triethylsilan unter Freisetzung von Chlortriethylsilan gewinnen.<sup>[105]</sup> Die anschließende Umsetzung mit dem  $\text{SiMe}_3$ -geschützten Anthracensubstrat **7** erfolgte in *n*-Hexan bei etwa 60 °C und lieferte die zweifach  $\text{GaCl}_2$ -funktionalisierte Spezies **65** in 62 %iger Ausbeute (Schema 4.25). Interessanterweise konnte trotz Verwendung eines großen Überschusses an  $\text{HGaCl}_2$  keine vierfache Addition des Gallans an **7** beobachtet werden. Versuche zur analogen Umsetzung von 1,5- (**6**) und 9,10-Bis[(trimethylsilyl)ethynyl]anthracen (**11**) schlugen bis *dato* fehl.

Da sich auch dieses Produkt als nahezu unlöslich in gängigen unpolaren Lösungsmitteln zeigte, konnten Einkristalle, die sich zu Röntgendiffraktionsexperimenten eigneten, nur aus Diethylether erhalten werden. Schema 4.25 zeigt die Molekülstruktur des zweifachen Diethylether-Addukts **65**·( $\text{Et}_2\text{O}$ )<sub>2</sub> im Kristall. Beide  $\text{GaCl}_2$ -Einheiten sind zur selben Seite des Anthracensystems hin orientiert und die C=C-Doppelbindungsgeometrie ist mit C=C–C<sub>Ar</sub>-Winkeln von etwa 130° verzerrt.<sup>[100]</sup> Die gefundenen Ga–O-Abstände sind mit 1.98 Å bzw. 2.00 Å vergleichbar mit Literaturdaten und liegen im Bereich typischer Donor-Akzeptor-Komplexe.<sup>[102]</sup>



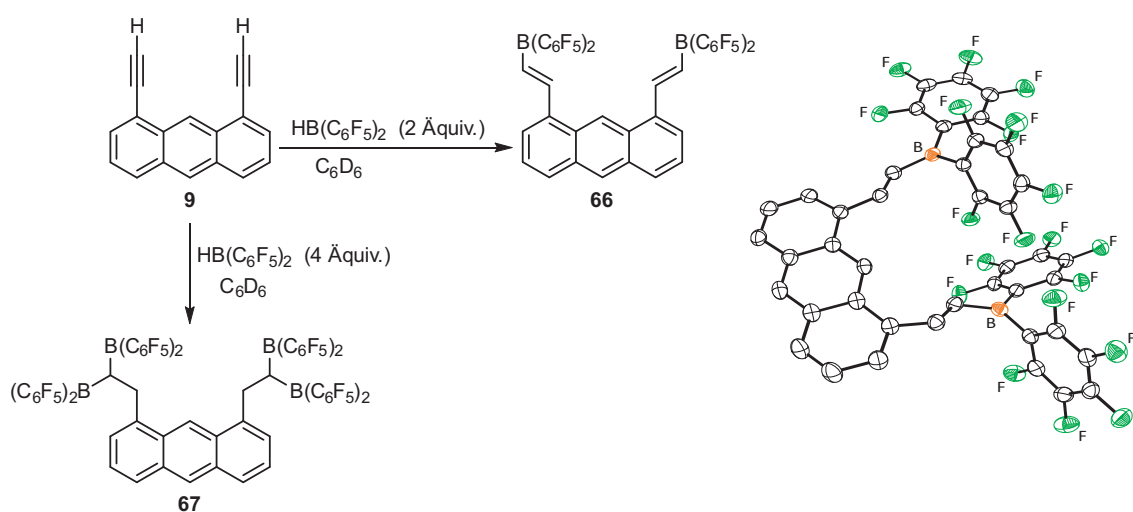
**Schema 4.25:** Hydrogallierung von 1,8-Bis[(trimethylsilyl)ethynyl]anthracen (**7**) zu **65** und Umsetzung mit Diethylether zum Etherat **65**·( $\text{Et}_2\text{O}$ )<sub>2</sub> (links) sowie dessen Molekülstruktur im Kristall (rechts).<sup>[100]</sup>

### 4.4.3 Hydroborierungsreaktionen

Die *Hydroborierung* von C–C-Mehrfachbindungen hat sich seit ihrer Entdeckung durch H. C. Brown in den 1960er Jahren zu einem extrem vielseitigen Werkzeug in der Synthesechemie entwickelt.<sup>[106]</sup> Neben dem einfachen Boran,  $\text{BH}_3$ , wurde im Laufe der Zeit eine große Anzahl an Hydroborierungsreagenzien entwickelt, die sich hinsichtlich des sterischen Anspruchs oder der elektronischen Eigenschaften der Substituenten an der B–H-Einheit unterscheiden.

Mit dem von W. E. Piers 1995 erstmals vorgestellten Bis(pentafluorphenyl)boran,  $\text{HB}(\text{C}_6\text{F}_5)_2$ , auch *Piers' Boran* genannt,<sup>[107]</sup> steht ein potentes Hydroborierungsreagenz zur Verfügung, mit dem sich in hoher Ausbeute diverse sowohl interne als auch terminale Alkine mit stark elektronegativ substituierten Boratomen funktionalisieren lassen. Bei der Umsetzung von Phenylacetylen mit Bis(pentafluorphenyl)boran beobachteten Piers und Mitarbeiter sowohl eine ein- als auch eine zweifache Hydroborierung, je nachdem, ob sie das Substrat mit einem oder zwei Äquivalenten des Borans umsetzten. In beiden Fällen erfolgt die Addition des  $\text{B}(\text{C}_6\text{F}_5)_2$ -Substituenten an das  $\beta$ -Kohlenstoffatom.<sup>[107,108]</sup>

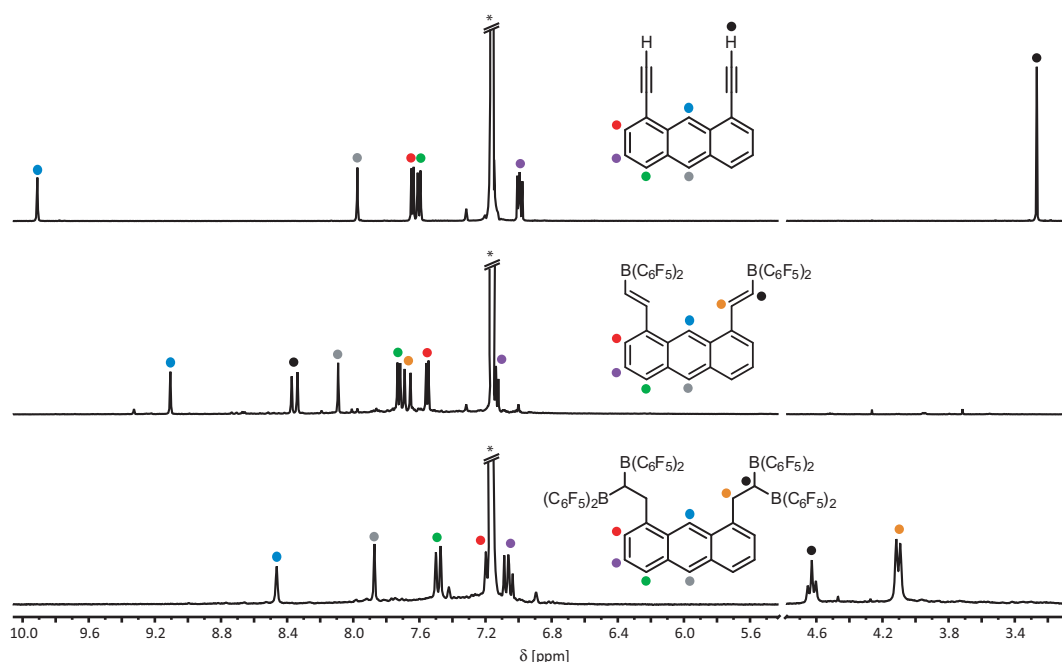
In Anlehnung an diese Experimente wurde im Rahmen dieser Arbeit auch 1,8-Diethinylanthracen (**9**) mit zwei und vier Äquivalenten Piers' Boran umgesetzt (Schema 4.26). Die entsprechenden Additionsprodukte **66** und **67** wurden quantitativ erhalten und konnten NMR-spektroskopisch eindeutig nachgewiesen werden.<sup>[100]</sup>



**Schema 4.26:** Synthese der zwei- (**66**) und vierfach hydroborierten Spezies (**67**) durch Umsetzung von 1,8-Diethinylanthracen (**9**) mit Piers' Boran,  $\text{HB}(\text{C}_6\text{F}_5)_2$ , sowie Molekülstruktur von 1,8-Bis{2-[bis(pentafluorphenyl)boranyl]ethinyl}anthracen (**66**) im Kristall.<sup>[100]</sup>

Im Falle von 1,8-Bis{2-[bis(pentafluorphenyl)boranyl]ethinyl}anthracen (**66**) gelang die Aufklärung der Molekülstruktur im Kristall durch Röntgenbeugungsexperimente, wie Schema 4.26 zeigt. Im Gegensatz zum oben beschriebenen Etheraddukt der zweifach hydrogallierten Spezies **65**· $(\text{Et}_2\text{O})_2$  sind im Falle von **66** die beiden Lewis-sauren Atome nicht zu einer Seite der

Anthracenebene geneigt, sondern weisen (mit unterschiedlicher Ausprägung) zu verschiedenen Seiten, was auf den hohen sterischen Anspruch der  $B(C_6F_5)_2$ -Einheiten zurückgeführt werden kann.<sup>[100]</sup> Obwohl die Bildung des vierfach hydroborierten Produktes **67** nicht durch Röntgenstrukturanalyse belegt werden kann,<sup>9</sup> zeigen die aufgenommenen  $^1H$ -NMR-Spektren eindeutig die erfolgreiche Umsetzung zum Zielprodukt (Abbildung 4.9). Bei der zweifach hydroborierten Verbindung **66** weisen die Tieffeld-verschobenen Dubletts bei 8.36 ppm und 7.67 ppm mit einer  $^3J_{H,H}$ -Kopplungskonstante von 17.5 Hz auf die ausschließliche Bildung des *trans*-substituierten Produktes hin. Im Falle der Umsetzung von **9** mit vier Äquivalenten Piers' Boran können das Dublett 4.10 ppm und das Triplet bei 4.63 ppm mit  $^3J_{H,H}$ -Kopplungskonstanten von jeweils 7.4 Hz den  $CH_2-CHB(C_6F_5)_2$ -Einheiten von Verbindung **67** zugeordnet werden.<sup>[100]</sup>



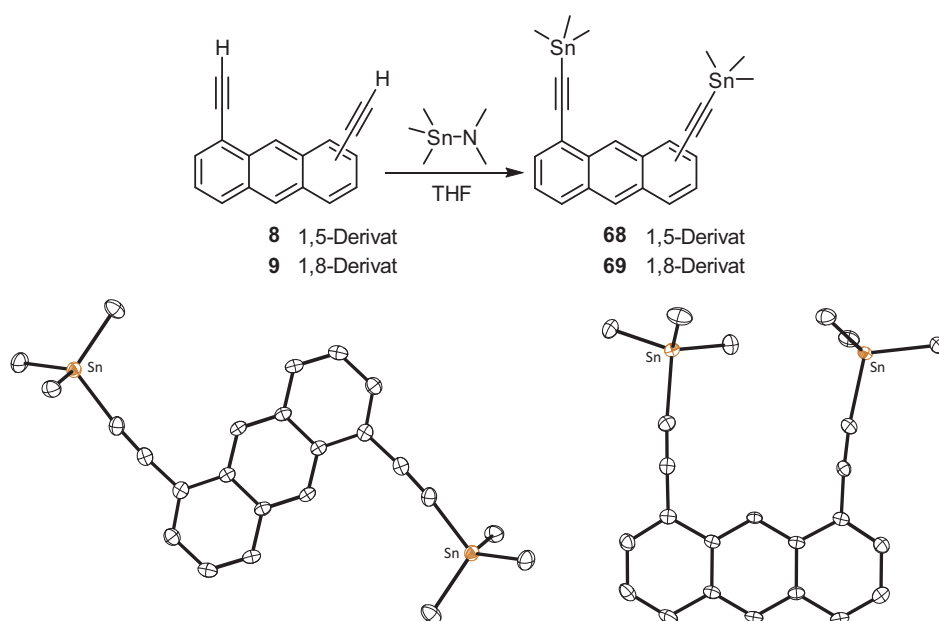
**Abbildung 4.9:** Ausschnitte der  $^1H$ -NMR-Spektren von **9** (oben, 500 MHz), **66** (Mitte, 500 MHz) und **67** (unten, 300 MHz) bei 298 K in  $C_6D_6$  (\*) mit Zuordnung der Signale.

Zu erwähnen bleibt, dass auch 1,5-Diethynylanthracen (**8**) auf analoge Weise mit zwei und vier Äquivalenten  $HB(C_6F_5)_2$  umgesetzt wurde, wobei auch hier instantan eine rotorange Lösung entstand. Allerdings wurde auch die Bildung eines tiefroten bis schwarzen Feststoffs beobachtet, der sich als unlöslich in  $C_6D_6$  erwies. Lösungs- und Analytikversuche in deuteriertem THF scheiterten bis *dato* an der sofortigen Polymerisation des Lösungsmittels, offensichtlich bedingt durch eine Etherspaltungsreaktion.

<sup>9</sup>Die in der Glovebox bei  $-30$  °C durch Kristallisation aus *n*-Pentan erhaltenen Kristalle zersetzten sich innerhalb kürzester Zeit im zur Kristallpräparation erforderlichen (ebenfalls vorgekühlten) inerten Öl.

## 4.4.4 Stannylierungsreaktionen

Terminale Alkine können nach einer Methode von Wrackmeyer *et al.* durch Umsetzung mit (Dimethylamino)trimethylstannan in THF bei etwa 60 °C zu den entsprechenden SnMe<sub>3</sub>-substituierten Alkinspezies umgesetzt werden.<sup>[109]</sup> Wie Schema 4.27 zeigt, gelang im Rahmen dieser Arbeit auch die Übertragung der Reaktion auf Ethinyl-substituierte Anthracen-Derivate. 1,5- (**8**) bzw. 1,8-Diethinylanthracen (**9**) konnten quantitativ in 1,5- (**68**) und 1,8-Bis[(trimethylstannyl)ethinyl]anthracen (**69**) überführt werden. Die Produkte wurden eindeutig durch multinukleare NMR-Spektroskopie, Massenspektrometrie und Röntgenstrukturanalyse charakterisiert.<sup>[84]</sup>



**Schema 4.27:** Synthese von 1,5- (**68**) und 1,8-Bis[(trimethylstannyl)ethinyl]anthracen (**69**) durch Umsetzung von 1,5- (**8**) bzw. 1,8-Diethinylanthracen (**9**) mit (Dimethylamino)trimethylstannan (oben) sowie die Molekülstrukturen beider Produkte im Kristall (unten).<sup>[84]</sup>

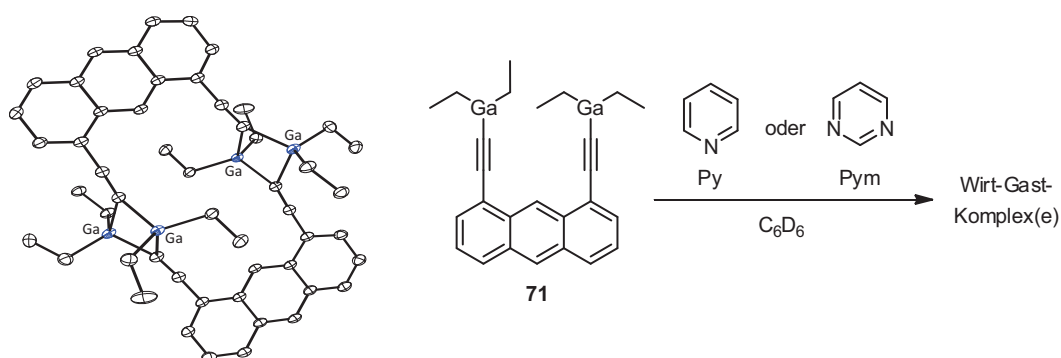
Auch 1,8,10-Triethinylanthracen (**15**) konnte mit (Dimethylamino)trimethylstannan zur dreifach SnMe<sub>3</sub>-funktionalisierten Anthracenspezies **70** umgesetzt werden. Die <sup>1</sup>H-NMR-spektroskopische Untersuchung zeigt neben dem erwarteten Signalmuster 1,8,10-trisubstituierter Anthracene anhand zweier Hochfeld-verschobener Singulets mit den typischen <sup>117</sup>Sn- und <sup>119</sup>Sn-Satelliten im Verhältnis 1:2 eindeutig die Bildung der gewünschten Zielverbindung an. Allerdings erwies sich **70** im Gegensatz zu den zweifach metallierten Derivaten **68** und **69** als verhältnismäßig instabil, sodass nach kürzester Zeit lediglich das Edukt **15** reisoliert werden konnte.

Mit dem Ziel, unter Freisetzung von Trimethylchlorstannan die Alkineinheiten von Bis[(trimethylstannyl)ethinyl]anthracen-Derivate terminal mit B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-Gruppen zu funktionalisieren, wurde **68** testweise mit Bis(pentafluorphenyl)chlorboran zur Reaktion gebracht, was allerdings zu keinerlei Reaktion führte.

## 4.5 Untersuchungen zur Wirt-Gast-Chemie

Neben der Synthese und Charakterisierung neuartiger Lewis-saurer Wirtverbindungen lag ein wesentliches Ziel dieser Arbeit auf der erstmaligen Untersuchung der Wirt-Gast-Chemie entsprechender Moleküle. Im Gegensatz zu vielen anderen Wirt-Gast-Experimenten sollte bei diesen Versuchen die Dynamik der Komplexierungsprozesse und der Mechanismus zur Bildung der Wirt-Gast-Komplexe im Vordergrund stehen.

Als geeignete Modellsysteme wurde 1,8-Bis[(diethylgallanyl)ethinyl]anthracen (**71**)<sup>[38,39]</sup> als bidentater Lewis-saurer Wirt sowie die *N*-heterocyclischen Aromaten Pyridin (Py) und Pyrimidin (Pym) als mono- bzw. bifunktionale Lewis-basische Gastkomponenten gewählt (Schema 4.28).<sup>[110]</sup>



**Schema 4.28:** Umsetzung von 1,8-Bis[(diethylgallanyl)ethinyl]anthracen (**71**) als Wirt- mit Pyridin (Py) und Pyrimidin (Pym) als Gastkomponenten (rechts).<sup>[110]</sup> Im Festkörper liegt **71** als dimere Struktur mit verbrückenden Dimetallacyclobutan-Einheiten vor (links).<sup>[38,39]</sup>

In einer Kombination aus NMR-Titration und Diffusions-NMR-Experimenten wurde der Wirt **71** in kleinen Portionen mit den entsprechenden Gastmolekülen versetzt und anschließend die Diffusionskoeffizienten  $D$  der sich in Lösung befindlichen Spezies mittels  $^1\text{H}$ -NMR-Diffusometrie bestimmt. Die Diffusions-NMR-Spektroskopie stellt eine potente Methode dar, aus einem Gemisch verschiedener Komponenten in Lösung den Diffusionskoeffizienten  $D$  über den exponentiellen Abfall der Signalintensitäten mehrerer NMR-Experimente zu berechnen (Gleichung 4.1).<sup>[111–114]</sup>

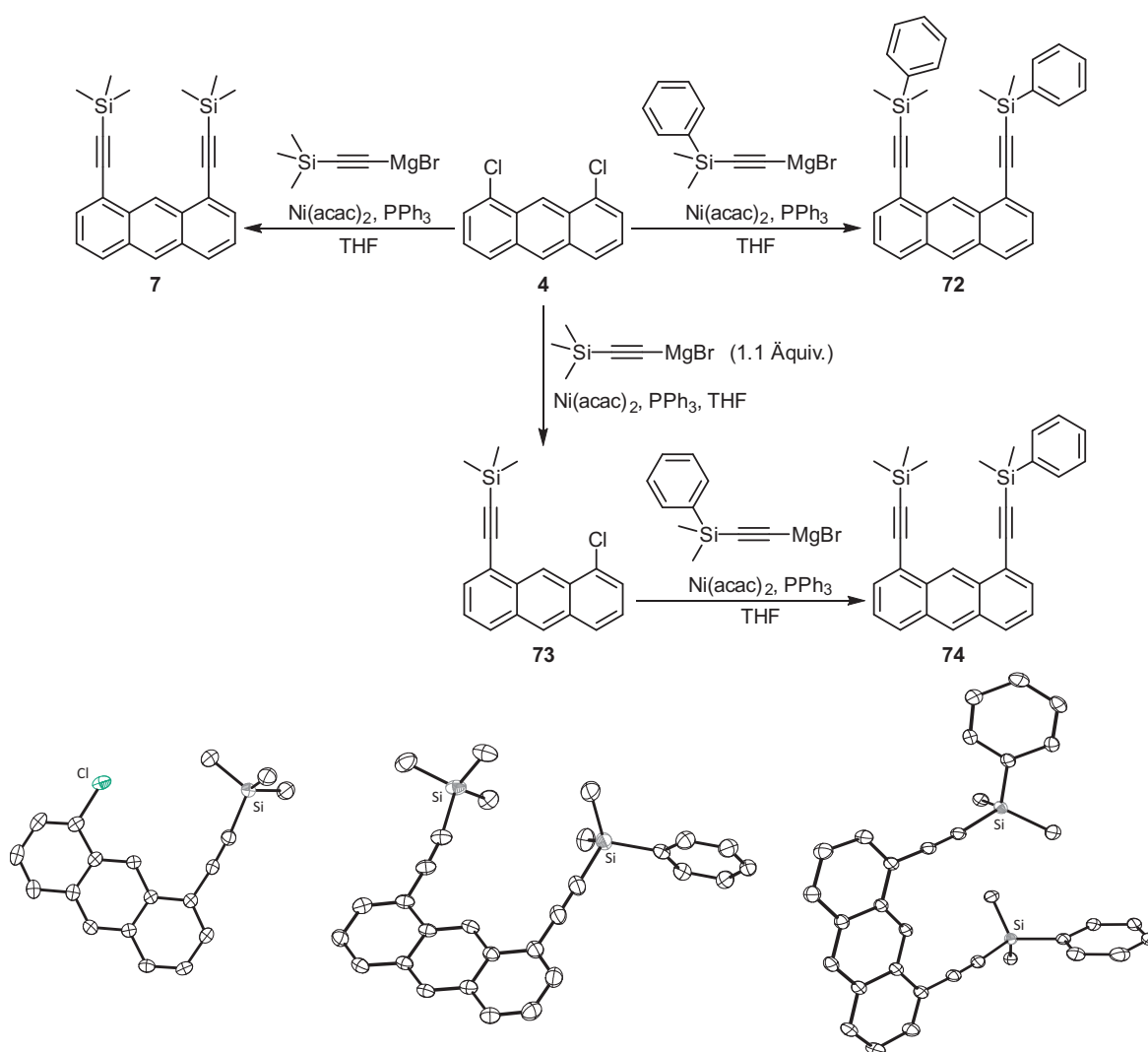
$$I = I_0 \cdot \exp \left[ -D \cdot \gamma^2 \cdot g^2 \cdot \delta^2 \cdot \left( \Delta - \frac{\delta}{3} \right) \right] \quad (4.1)$$

Gemäß der Stokes-Einstein-Beziehung (Gleichung 4.2) ist der so erhaltene Diffusionskoeffizient umgekehrt proportional zum hydrodynamischen Radius  $r_s$  der untersuchten Spezies, und stellt somit ein Maß für deren Größe und geometrische Gestalt in Lösung dar. Entsprechend werden für kleine Moleküle oder Addukte tendenziell größere Werte für  $D$  erwartet.

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot r_s} \quad (4.2)$$



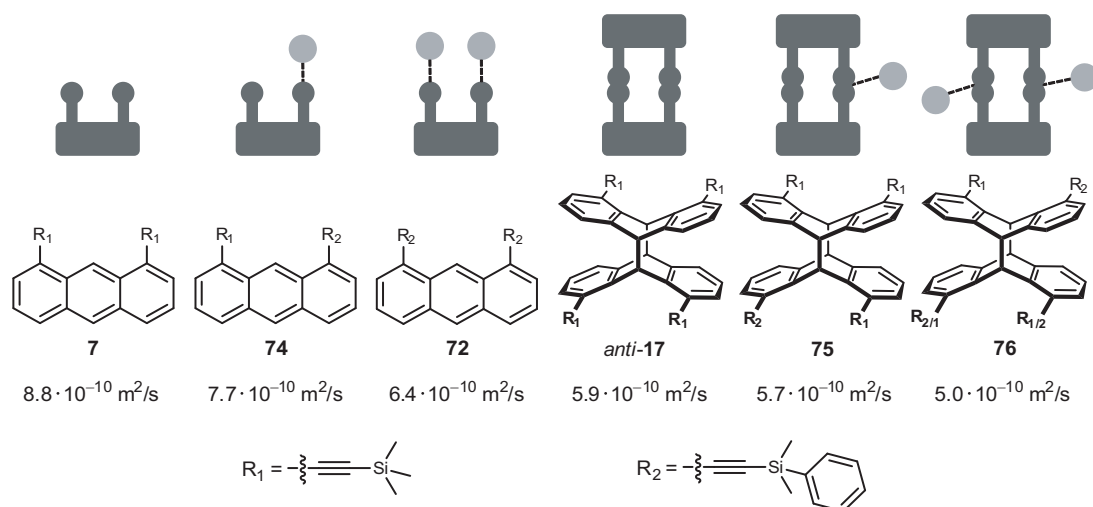
Die auf diese Weise erhaltenen Ergebnisse liefern lediglich eine relative Information über die untersuchten Teilchen, erlauben jedoch keine absolute Aussage über die Zusammensetzung möglicher Wirt-Gast-Aggregate. Aus diesem Grund ist zur Identifizierung der in Lösung vorliegenden Spezies ein Vergleich der aus den NMR-Titrations gewonnenen Diffusionskoeffizienten mit denen von Referenzverbindungen nötig und sinnvoll, die in Größe und Gestalt mit den potentiellen Wirt-Gast-Spezies in Lösung übereinstimmen sollen. Ein wesentlicher Teil der Arbeit in diesem Teilprojekt bestand folglich aus der Synthese und Charakterisierung ebensolcher Verbindungen, wobei ausgehend von 1,8-Dichloranthracen (**4**) unterschiedliche Kumada-Kreuzkupplungsreaktionen zum Aufbau der Anthracen-basierten Systeme genutzt wurden.



**Schema 4.29:** Synthese verschiedener Referenzverbindungen ausgehend von 1,8-Dichloranthracen (**4**) durch Kumada-Kreuzkupplungsreaktionen: **7** ( $\text{W}_1$ ), **74** ( $\text{W}_1\text{G}_1$ ) und **72** ( $\text{W}_1\text{G}_2$ ); mit W = Wirt: **71** und G = Gast: Py oder Pym sowie die Molekülstrukturen im Kristall von Verbindung **72**, **73** und **74**.<sup>[110]</sup>

Schema 4.29 zeigt die Referenzverbindungen für den Fall, dass der reine Wirt in Lösung als Monomer vorliegt ( $W_1$ -Struktur, **7**) sowie für die Fälle, dass ein ( $W_1G_1$ -Struktur, **74**) oder zwei Gastmoleküle koordinierend an ein Wirt-Monomer binden ( $W_1G_2$ -Struktur, **72**). Bei der Synthese der Wirt-Dimer-basierten Referenzverbindungen wurden, wie in Abschnitt 4.1.2 bereits erwähnt, die photochromen Eigenschaften der Anthracen-Derivate ausgenutzt und die  $W_2$ - (*anti*-**17**),  $W_2G_1$ - (**75**) und  $W_2G_2$ -Verbindungen (**76**) durch UV-Licht-Bestrahlung von  $C_6D_6$ -Lösungen von **7** ( $\rightarrow$  *anti*-**17**), **74** ( $\rightarrow$  **76**) sowie einer 1:1-Mischung aus **7** und **74** ( $\rightarrow$  **75**) erhalten.

Bei der Bestimmung der entsprechenden Diffusionskoeffizienten  $D$  der sechs synthetisierten Referenzverbindungen zeigte sich wie erwartet einen Abfall der  $D$ -Werte mit steigender Molekülgröße (Schema 4.30).



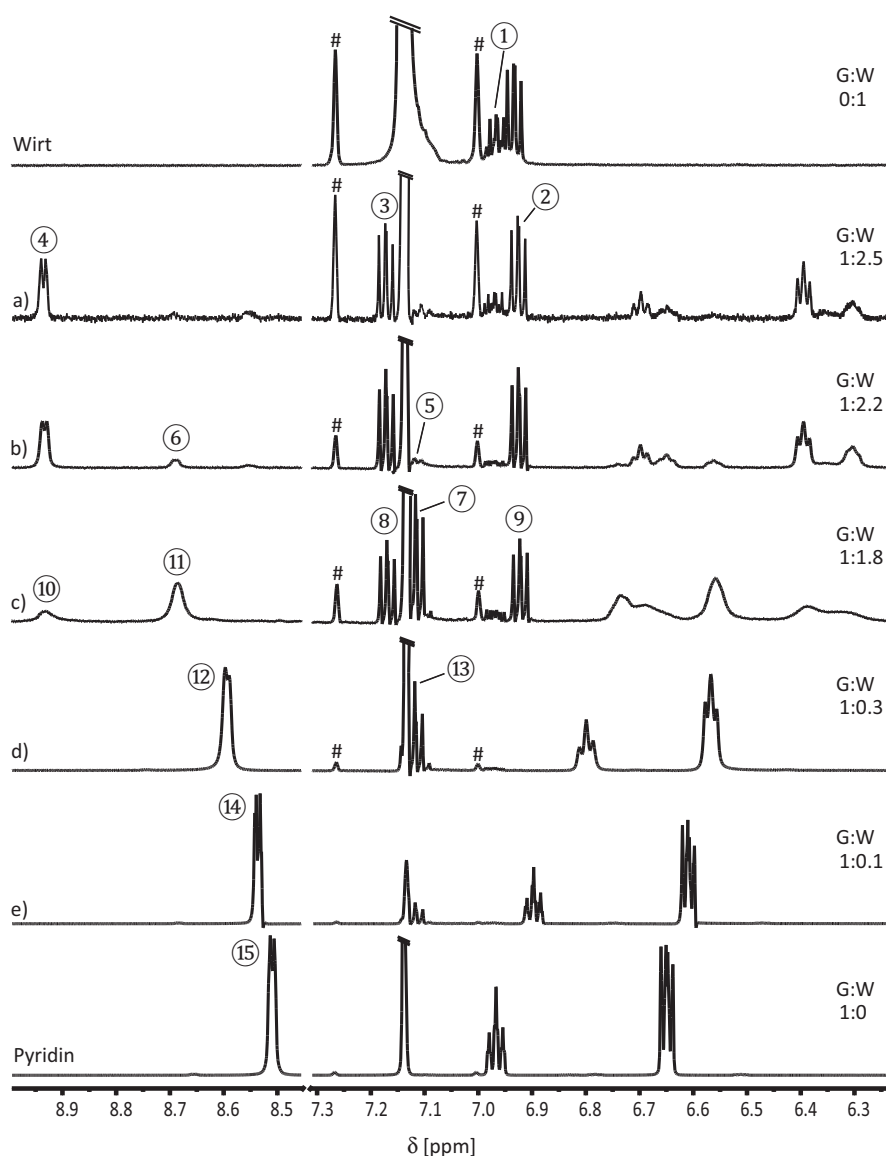
**Schema 4.30:** Schematische Darstellung möglicher Wirt-Aggregate und Wirt-Pyridin-Komplexe (oben) sowie die entsprechenden Referenzverbindungen mit den gemessenen Diffusionskoeffizienten  $D$  in  $C_6D_6$  bei 294 K (unten). Von links nach rechts:  $W_1$ ,  $W_1G_1$ ,  $W_1G_2$ ,  $W_2$ ,  $W_2G_1$  und  $W_2G_2$ .<sup>[110]</sup>

Wird nun die Digallium-Wirtverbindung **71** schrittweise mit kleinen Mengen der Lewis-basischen Gast-Komponenten versetzt, kann bei Pyridin und Pyrimidin jeweils ein unterschiedliches Komplexierungsverhalten beobachtet werden, wobei es in beiden Fällen gelang, nicht nur die dynamischen Prozesse NMR-spektroskopisch zu verfolgen, sondern erstmals auch die sich (intermediär) bildenden Komplexe eindeutig zu identifizieren.

Abbildung 4.10 zeigt eine Auswahl von  $^1H$ -NMR-Spektren der Umsetzung von **71** mit Pyridin in  $C_6D_6$ . Zur besseren Übersicht sind nur die Ausschnitte der H3/H6-Protonenresonanzen der Anthracen-Spezies<sup>10</sup> sowie die Signale der Gast-Komponente Pyridin gezeigt. Zu erkennen ist, dass die Wirtverbindung Spuren ( $< 1\%$ ) von nicht- und mono-metalliertem 1,8-Diethynylanthracen enthält (**①**). Bei Zugabe einer kleinen Menge Pyridin (W:G = 2.5:1) befindet sich neben der reinen Wirt-Komponente (**②**) eine weitere Anthracen-haltige Spezies in Lösung

<sup>10</sup>H3/H6 erzeugen ein Dublett von Dubletts auf Grund der unterschiedlichen Kopplungen zu H2/H7 bzw. H4/H5.

(③). Durch Vergleich der aus den NMR-Titrationsexperimenten erhaltenen Diffusionskoeffizienten mit denen der Referenzverbindungen (Schema 4.30) kann ein monomeres Vorliegen der reinen Wirtverbindung ausgeschlossen und ③ als Addukt des Wirt-Dimers und eines Pyridin-Moleküls identifiziert werden. Die Resonanz der *ortho*-ständigen Pyridin-Protonen (④) erfährt im Vergleich zum reinen Pyridin (⑮) einen Tieffeld-Shift von etwa 0.5 ppm, was, zusammen mit einem extrem unterschiedlichen  $D$ -Wert [ $6.0 \cdot 10^{-10} \text{ m}^2/\text{s}$  (④) vs.  $22.1 \cdot 10^{-10} \text{ m}^2/\text{s}$  (⑮)] für eine relativ starke Bindung des Pyridins durch den Wirt spricht.

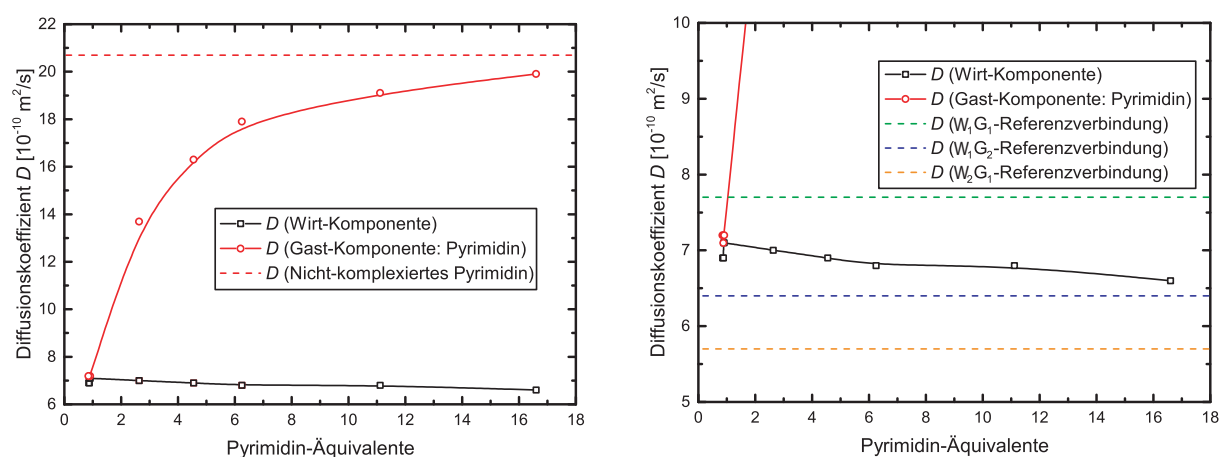


**Abbildung 4.10:** Ausschnitte ausgewählter  $^1\text{H}$ -NMR-Spektren (600 MHz) der reinen Wirtverbindung **71**, verschiedenen Wirt-Gast-Mischungen [a) – e)] und von reinem Pyridin bei 294 K in  $\text{C}_6\text{D}_6$  ( $\delta = 7.13 \text{ ppm}$ ). Die  $^{13}\text{C}$ -Satelliten des Lösungsmittels sind durch # gekennzeichnet. <sup>[110]</sup>

Eine weitere Erhöhung der Pyridin-Konzentration ( $W:G = 2.2:1$ ) führt zur Bildung eines weiteren Wirt-Gast-Komplexes, angezeigt durch die mit ⑤ (Wirt) und ⑥ (Gast) gekennzeichneten Signale in Spektrum b). Diese neu entstandene Spezies, bei der es sich um einen  $W_1G_2$ -Komplex handelt, ist bei einem Wirt-Gast-Verhältnis von 1.8:1 [Spektrum c)] bereits die dominierende Komponente im Gemisch. Interessanterweise liegen bei diesem Wirt-Gast-Mischungsverhältnis sowohl die reine Wirtverbindung (⑨), als auch die beiden unterschiedlichen Wirt-Gast-Komplexe ( $W_2G_1$ : ⑧ und ⑩ sowie  $W_1G_2$ : ⑦ und ⑪) nebeneinander in der Lösung vor. Die teilweise starke Verbreiterung der Gastsignale deutet bei diesem Konzentrationsbereich auf eine starke Dynamik in der Lösung hin.

Bei einem Überschuss der Gast-Komponente [Spektrum d) und folgende] ist mit ⑬ lediglich noch eine Anthracen-haltige Spezies in Lösung zu finden. Erwartungsgemäß handelt es sich dabei um jenen Komplex, bei welchem beide Galliumatome des Wirtes durch jeweils eine Pyridin-Einheit abgesättigt sind ( $W_1G_2$ ). Die Tatsache, dass beispielsweise mit ⑭ oder ⑮ einzig ein Signal für die Gast-Komponente erkennbar ist, spricht für einen Austauschprozess zwischen Wirt und Pyridin, der schneller als die NMR-Zeitskala abläuft. Wird der Pyridin-Anteil weiter stetig erhöht, nähern sich die chemischen Verschiebungen und die durch NMR-Diffusometrie bestimmten  $D$ -Werte der Pyridin-Resonanzen der verschiedenen Wirt-Gast-Mischungen denen des reinen Pyridins (⑮) an, was die angestellten Überlegungen zu bestätigen scheint.

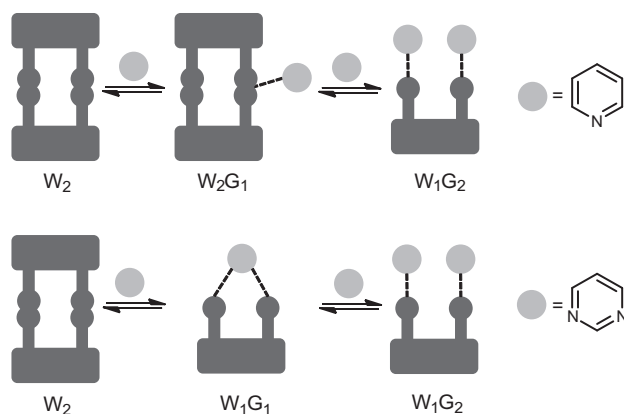
Gänzlich anders verhält es sich bei der Umsetzung der Digallium-Wirtverbindung **71** mit Pyrimidin, einer Gast-Komponente mit zwei Lewis-basischen Funktionalitäten. In Analogie zu den von Katz im Jahre 1989 durchgeführten Experimenten mit einer zweizähligen Bor-Lewis-Säure auf 1,8-Diethynylanthracen-Basis,<sup>[34]</sup> deuten die ermittelten Diffusionskoeffizienten bei einem Pyrimidin-Unterschuss das Entstehen eines  $W_1G_1$ -Komplexes hin.



**Abbildung 4.11:** Auftragung der gemessenen Diffusionskoeffizienten  $D$  gegen die Pyrimidin-Äquivalente in Lösung. Links: Gesamtansicht, rechts: vergrößerte Darstellung mit den Diffusionskoeffizienten der  $W_1G_1$ -,  $W_1G_2$ - und der  $W_2G_1$ -Referenzverbindungen.<sup>[110]</sup>

Offenbar wird der bifunktionale Gast ideal zwischen den beiden Lewis-aciden Galliumatomen chelatisierend gebunden. Der entstehende Komplex scheint sehr stabil und seine Bildung deshalb bevorzugt zu sein, da über weite Konzentrationsbereiche lediglich ein Satz an Wirt- und Gast-Resonanzen beobachtet werden kann, deren Diffusionskoeffizienten in beiden Fällen im Bereich der  $W_1G_1$ -Referenzverbindung **74** liegen. Erst bei einem Pyrimidin-Überschuss in Lösung steigt der  $D$ -Wert der Gast-Komponente stark an und strebt gegen den des unkomplexierten Pyrimidins (Abbildung 4.11, links). Der entsprechende Wert der Anthracen-haltigen Spezies hingegen sinkt leicht ab und nähert sich bei weiterer Erhöhung der Pyrimidin-Konzentration dem Diffusionskoeffizienten der  $W_1G_2$ -Referenzverbindung **72** an (Abbildung 4.11, rechts).

Es lässt sich zusammenfassen, dass bei der Umsetzung der bidentaten Gallium-Lewis-Säure **71** mit Pyridin bzw. Pyrimidin ein unterschiedliches Komplexierungsverhalten beobachtet werden kann, das in Schema 4.31 vergleichend dargestellt ist.



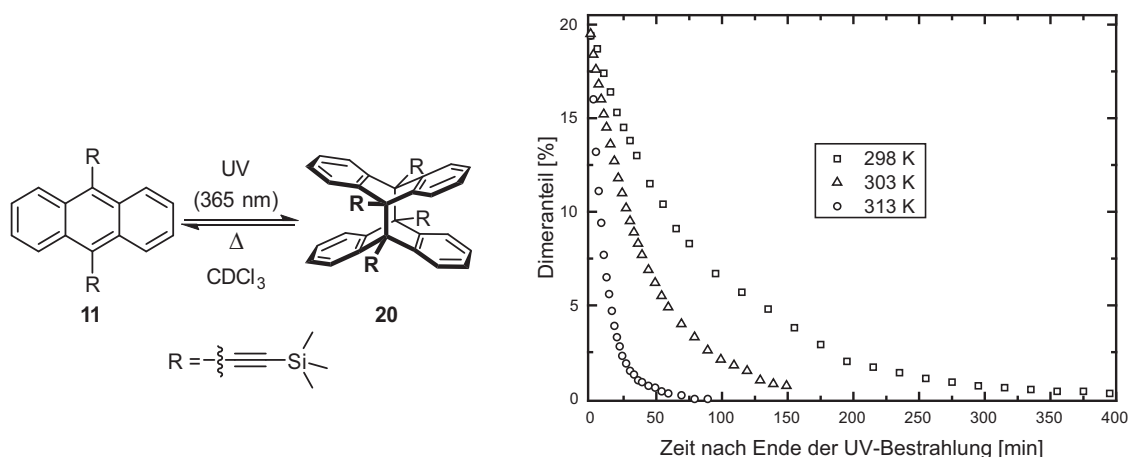
**Schema 4.31:** Schematische Darstellung der unterschiedlichen Komplexierungsverhalten von **71** gegenüber Pyridin (oben) und Pyrimidin (unten).<sup>[110]</sup>

Während mit der monofunktionalen Gastkomponente Pyridin zunächst Komplexe bestehend aus einem Wirt-Dimer und einem Gastmolekül ( $W_2G_1$ -Komplex) beobachtet wurden, war ein Nachweis eines analogen Pyrimidin-Addukts nicht möglich. Stattdessen bildete sich mit großer Wahrscheinlichkeit eine  $W_1G_1$ -Spezies, bei der die beiden Galliumatome eines Wirt-Monomers chelatisierend an je ein Stickstoffatom eines Pyrimidin-Moleküls binden.<sup>[110]</sup>

## 5 Zusammenfassung

Im Hinblick auf die Tatsache, dass sich ein Großteil der bisher erzielten Ergebnisse in der Wirt-Gast-Chemie auf die Entwicklung Lewis-basischer Wirtverbindungen und deren Einsatz in der Komplexierung Lewis-saurer Gäste beschränkt, birgt die Erforschung der inversen Situation ein erhebliches Potential. Im Rahmen dieser Arbeit konnten dazu in mehreren wichtigen Bereichen neue Erkenntnisse gewonnen werden, indem neben der Synthese neuartiger, starrer organischer Grundgerüste und ihrer Funktionalisierung mit Lewis-sauren Atomen auch die Wirt-Gast-Chemie erstmals detailliert untersucht wurde.

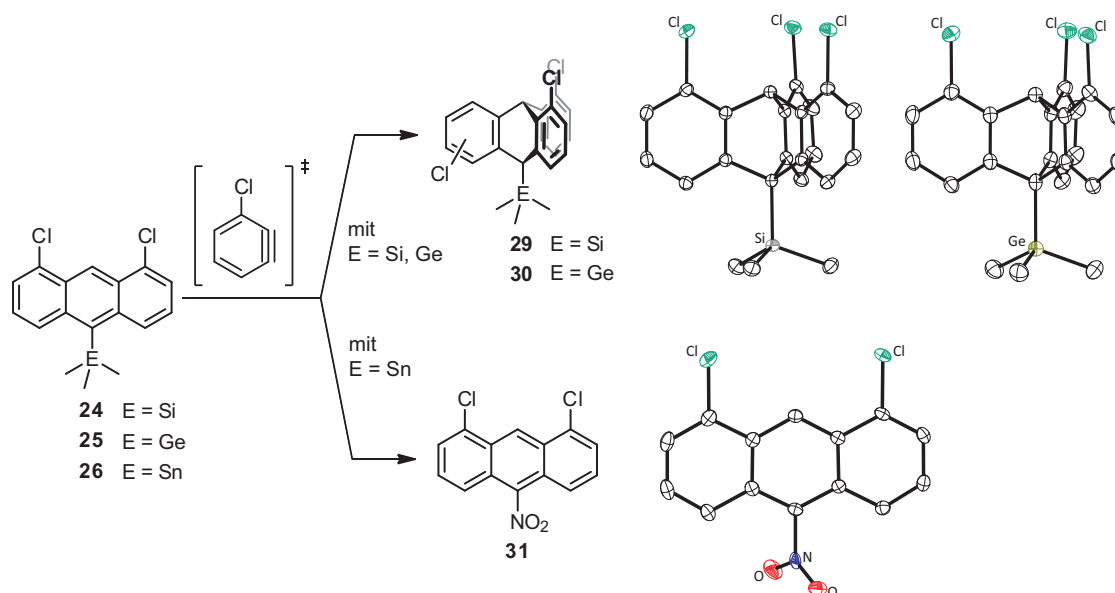
So wurden zunächst durch Kreuzkupplungsreaktionen diverse zwei- und dreifach Alkynyl-substituierte Anthracen-Derivate synthetisiert. Die photochromen Verbindungen ließen sich durch photochemische Reaktionen in die entsprechenden *syn*- und/oder *anti*-Photodimere überführen, wodurch neue gerichtete und vielseitig funktionalisierbare Verbindungen generiert werden konnten. Ein besonders interessantes Verhalten zeigte sich dabei bei 9,10-Bis[(trimethylsilyl)ethynyl]-anthracen (**11**) zum Photodimer **20**. Die Dimerspezies erweist sich als verhältnismäßig thermolabil und wandelt sich bereits nach wenigen Stunden bei Raumtemperatur unter vollständiger Cycloeliminiierung zum Edukt zurück (Schema 5.1). **11** ist nach 9,10-Difluor- und 9,10-Dimethylantracen erst das dritte bekannte Beispiel eines photoschaltbaren symmetrisch 9,10-funktionalisierten Anthracens.



**Schema 5.1:** Darstellung der Temperaturabhängigkeit der Cycloeliminierungsreaktion (**20**  $\rightarrow$  **11**).

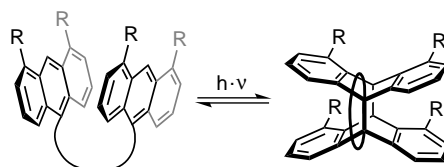
Während der Arbeiten zur Darstellung gerichteter dreizähliger Grundgerüste auf Triptycyl-Basis galt es, die Einflüsse der 1,8-Dichloranthracen-Substituenten in 9- und 10-Position auf das *syn-anti*-Verhältnis der durch Reaktion mit einer Chlorarin-Komponente entstehenden Trichlor-

tritycene zu untersuchen. Quantenmechanische Rechnungen prognostizierten einen erhöhten *syn*-Anteil, wenn 1,8-Dichloranthracen-Derivate mit SiMe<sub>3</sub>-, GeMe<sub>3</sub>- oder SnMe<sub>3</sub>-Substituenten in 10-Position umgesetzt werden. Tatsächlich konnten 1,8,13-Trichlor-10-(trimethylsilyl)- (*syn*-**29**) sowie 1,8,13-Trichlor-10-(trimethylgermyl)tritycenen (*syn*-**30**) als eindeutige Hauptprodukte der Synthesen erhalten werden, wohingegen sich bei der Umsetzung des 10-SnMe<sub>3</sub>-funktionalisierten Substrates durch aromatische Substitution 1,8-Dichlor-10-nitroanthracen (**31**) bildete (Schema 5.2).



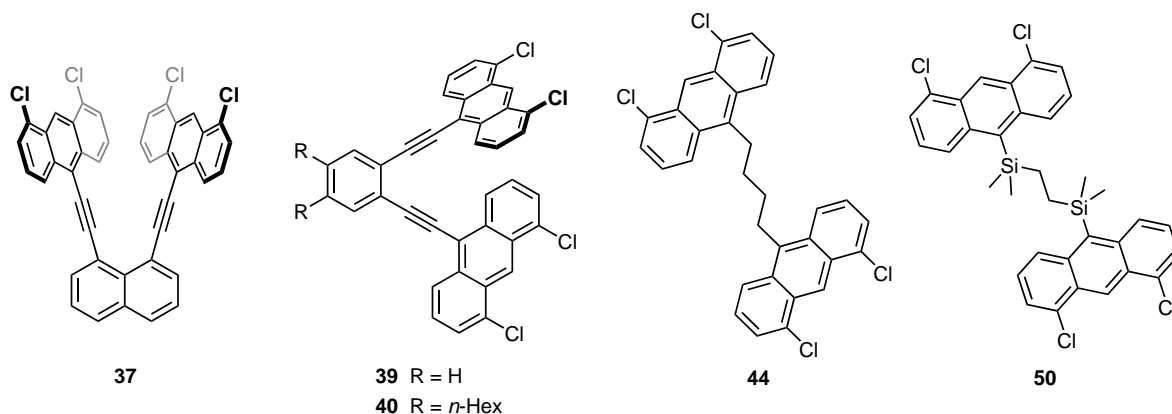
**Schema 5.2:** Reaktionen zur Darstellung von Trichlortritycenen aus den 10-EMe<sub>3</sub>-substituierten 1,8-Dichloranthracen-Derivaten **24** (E = Si), **25** (E = Ge) und **26** (E = Sn).

Bei der UV-Licht-Bestrahlung funktionalisierter Anthracene kann es zur Bildung unterschiedlicher Photodimer-Isomere kommen, die sich hinsichtlich der Ausrichtung der Substituenten unterscheiden. Dieses auch bei 1,8-substituierten Anthracen-Derivaten auftretende Problem war Gegenstand eines weiteren Projektes. Der in dieser Arbeit gewählte Lösungsansatz bestand in der Verbrückung zweier 1,8-funktionalisierter Anthracen-Monomere, sodass, wie in Schema 5.3 gezeigt, das System bei der Dimerisierung zu einer gleichsinnigen Ausrichtung der Substituenten gezwungen wird.



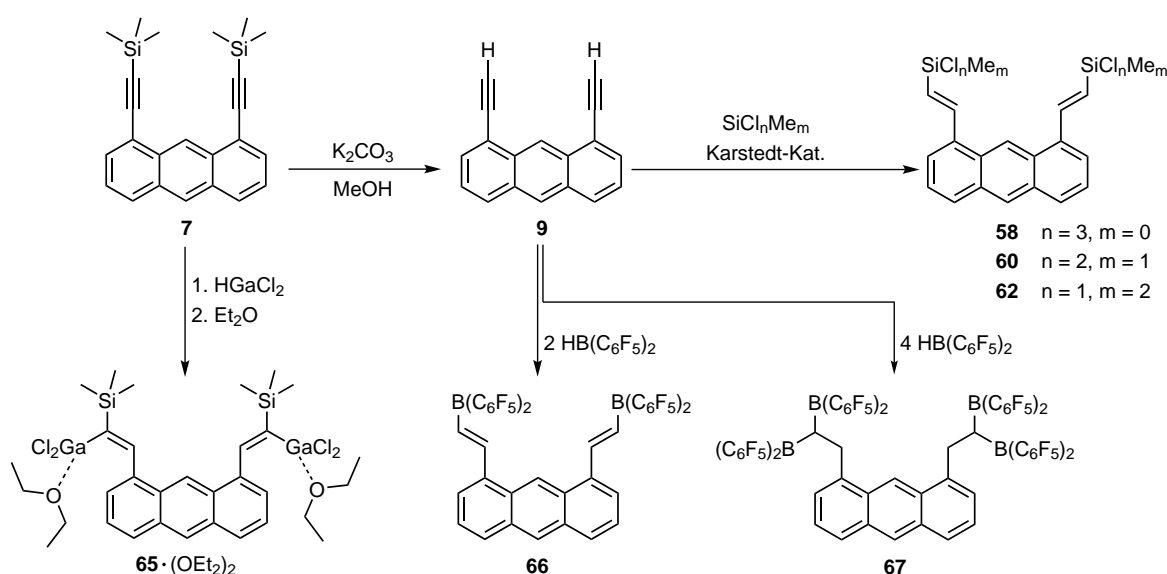
**Schema 5.3:** Konzept zur selektiven *syn*-Ausrichtung der 1,8-Substituenten bei der Photodimerisierung verbrückter Anthracene.

Die Linkereinheit muss dabei mehrere Eigenschaften aufweisen. Sie darf im Hinblick auf die potentielle weitere Funktionalisierung mit Lewis-Säuren keine Donor-Atome enthalten. Sie sollte ferner von ausreichender Länge und Flexibilität sein, sodass es zu einer intramolekularen Dimerisierung kommen kann, wobei eine gewisse Vororientierung der photochromen Anthraceneinheiten wünschenswert wäre. Aufgebaut wurde eine Vielzahl solcher verbrückten Systeme, von denen Schema 6.3 eine kleine Auswahl zeigt, durch unterschiedliche (Kreuz-) Kupplungsreaktionen sowie durch Olefin- und/oder Salzmetathese-Reaktionen.



**Schema 5.4:** Beispiele unterschiedlich verbrückter 1,8-Dichloranthraceneinheiten.

Neben der Darstellung mehrzähliger und potentiell photoschaltbarer organischer Gerüste war auch deren Funktionalisierung mit Lewis-sauren (Metall-) Atomen Gegenstand dieser Arbeit.



**Schema 5.5:** Beispiele unterschiedlicher durch Hydrogallierungs-, Hydrosilylierungs- und Hydroborierungsreaktionen erhaltene zwei- und vierzählige Lewis-Säuren.



Aus Schema 5.5 wird deutlich, dass unter anderem 1,8-Dialkinylanthracen-Derivate in verschiedenen (Hydro-) Metallierungsreaktionen eingesetzt wurden und auf diese Weise eine Vielzahl neuer zwei- und vierzähliger Lewis-Säuren generiert werden konnte.

Einige dieser gerichteten Verbindungen wurden mit Diethylether umgesetzt, wobei unterschiedliche Reaktivitäten zwischen den Lewis-sauren Wirtverbindungen und der Lewis-basischen Gastkomponente beobachtet werden konnten. Wie Abbildung 5.1 zeigt, kommt es bei der zweifach GaCl<sub>2</sub>-funktionalisierten Spezies **65** zu einer einfachen Anlagerung bzw. Adduktbildung, während bei der zweifach SiCl<sub>3</sub>-substituierte Verbindung **58** offensichtlich eine Etherspaltungsreaktion stattfindet, die zur Bildung von **63** führt.

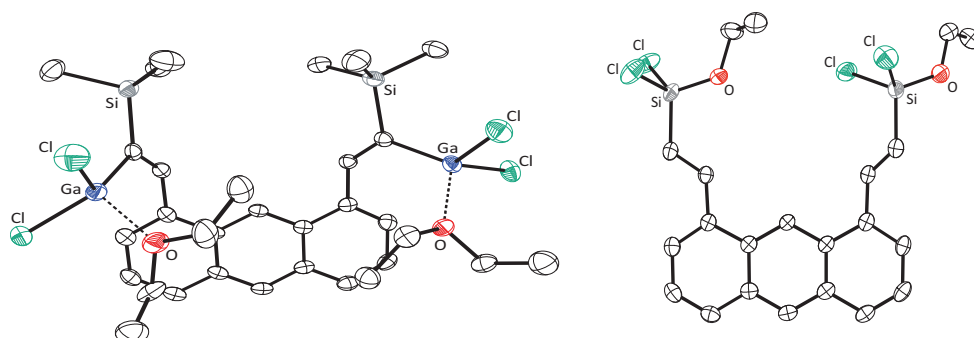
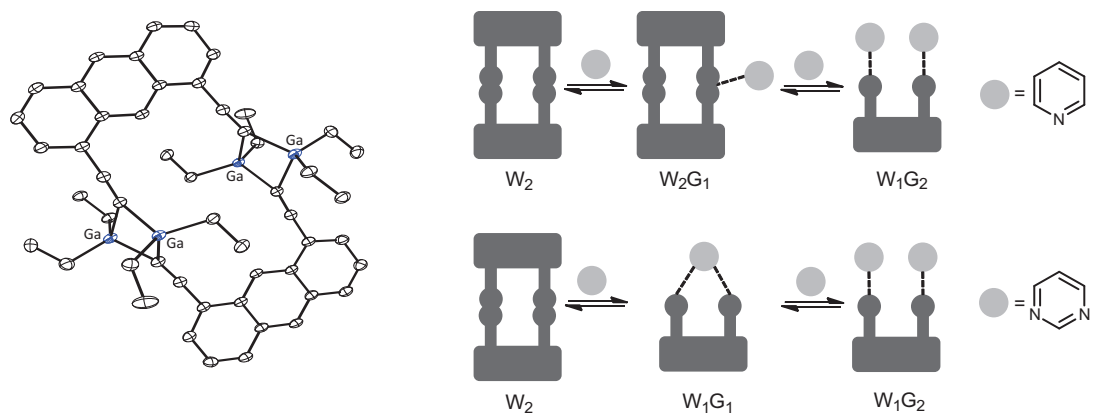


Abbildung 5.1: Molekülstrukturen von Verbindung **65**·(Et<sub>2</sub>O)<sub>2</sub> (links) und **63** (rechts) im Kristall.

Schließlich gelang es in einem weiteren Teilprojekt der Arbeit, die Wirt-Gast-Chemie starrer, zweizahliger Lewis-Säuren erstmals eingehend zu untersuchen. Im Gegensatz zu Lewis-aciden Rezeptorsystemen mit flexiblem Rückgrat liegt der Vorteil starrer Verbindungen in der potentiell höheren Selektivität bei der Erkennung und Bindung Lewis-basischer Gastmoleküle. Für die entsprechenden Untersuchungen wurde ein System bestehend aus 1,8-Bis[(diethylgallanyl)ethinyl]-anthracen (**71**) als Wirt sowie Pyridin und Pyrimidin als Gastkomponenten mit einer bzw. zwei Lewis-basischen Funktionalitäten gewählt.

Durch einen neuartigen analytischen Ansatz konnten die Dynamiken bei der Bildung entsprechender Wirt-Gast-Komplexe in Lösung studiert werden. Die Kombination aus NMR-Titration und NMR-Diffusionsexperimenten erlaubt bei der Umsetzung von Wirt- und Gastmolekülen die sich (intermediär) bildenden Komplexe anhand ihrer NMR-chemischen Verschiebung sowie ihrer Diffusionskoeffizienten zu unterscheiden. Durch die gezielte Synthese zahlreicher organischer Referenzverbindungen, deren Strukturen mit denen potentieller Wirt-Gast-Aggregate vergleichbar ist, gelang es, die unterschiedlichen Komplexe zu identifizieren. Aus Schema 5.6 wird ersichtlich, dass bei der Umsetzung der Digalliumverbindung **71** mit Pyridin oder Pyrimidin jeweils unterschiedliche Zwischenstufen beobachtet werden. Während kleine Mengen an Pyridin zur Ausbildung eines Komplexes bestehend aus einem Wirt-Dimer und einem Gastmolekül führen, entsteht bei Pyrimidin ein Komplex, bei dem der bifunktionale Gast chelatisierend durch den Digalliumrezeptor gebunden wird. Wird die Gastverbindung im Überschuss zugesetzt, kommt

es in beiden Fällen zu einer Absättigung beider Lewis-aciden Galliumatome durch jeweils ein koordinierend angelagertes Gastmolekül.



**Schema 5.6:** Schematische Darstellung des unterschiedlichen Komplexierungsverhaltens der Wirtkomponente **71** gegenüber Pyridin (oben) und Pyrimidin (unten) sowie Molekülstruktur von 1,8-Bis[(diethylgallanyl)ethinyl]anthracen (**71**) im Kristall (links).

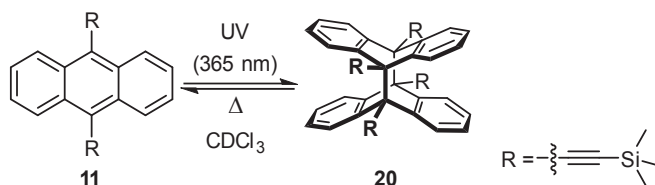
Mit der Anwendung dieser Methodik – dem Vergleich der NMR-Diffusometrie-Daten aus Wirt-Gast-Experimenten mit denen gezielt synthetisierter Referenzverbindungen – konnten erstmalig detaillierte Einblicke in den Bildungsmechanismus und die Dynamik der Wirt-Gast-Komplexbildung in Lösung erhalten werden. Die Bildung der entsprechenden (intermediären) Aggregate ließ sich direkt NMR-spektroskopisch verfolgen. Eine Übertragung dieses Ansatzes auf andere Wirt-Gast-Systeme bietet sich an und wird zur Aufklärung ähnlicher Problemstellungen beitragen können.



## 6 Summary

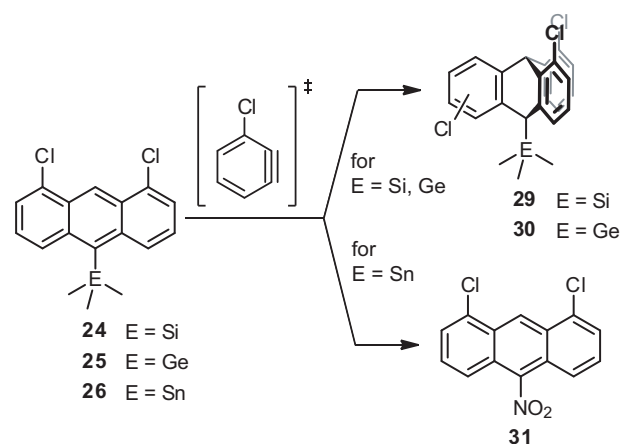
Host-guest chemistry became a well-established part in supramolecular chemistry since Pedersen reported the formation of crown ether-potassium complexes in 1967. Most results achieved in this field relate to the development of poly-Lewis bases (e.g. crown ethers, cryptands) and their complexation behaviour towards Lewis-acidic guest compounds. Regarding to this fact, a detailed investigation of the inverse situation, the host-guest chemistry of poly-Lewis acids, is a desirable goal and object of the present work.

In order to increase the selectivity of Lewis-base complexation, rigid organic frameworks, containing no donor atoms and allowing further functionalisations are needed. Therefore, a series of substituted anthracene and triptycene derivatives have been synthesised and characterised by various methods. The photochromism of the anthracene species was used to generate the corresponding *syn*- and *anti*-isomers by UV-irradiation. An interesting behaviour was observed, when 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**11**) was irradiated with UV light (Scheme 6.1). The thermolabile photodimer **20** was obtained and the kinetics of the cycloelimination reaction was investigated in detail by NMR spectroscopy.



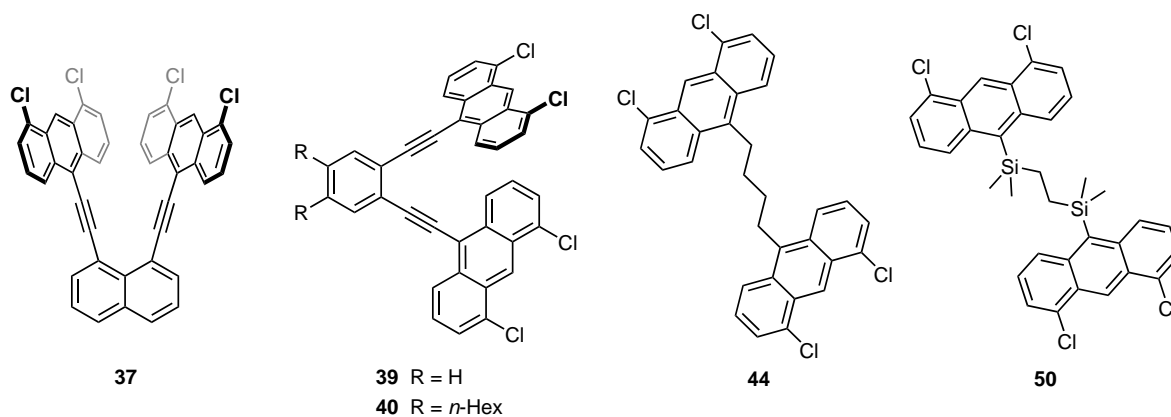
**Scheme 6.1:** Photochromism of 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**11**).

Triptycenes bearing functionalisable substituents (e.g. chlorine atoms) in positions 1, 8 and 13 (*syn*-triptycenes) are useful organic species for building up symmetrical tridentate backbones. These molecules can be synthesised by converting *in situ*-generated chloroarynes with (substituted) 1,8-dichloroanthracenes. The *syn-anti* ratio of the Diels-Alder reaction is significantly influenced by the electronic properties of the substituents in 9- and 10-position of the latter compounds. In consideration of preliminary quantum chemical calculations, different 9- and 10-substituted anthracene derivatives have been synthesised and characterised. In the cases of 1,8-dichloro-10-(trimethylsilyl)- (**24**) and 1,8-dichloro-10-(trimethylgermyl)anthracene (**25**) the corresponding *syn*-trichlorotriptycenes *syn*-**29** and *syn*-**30** were obtained as the unambiguous main products (Scheme 6.2). Conversion of the 10-SnMe<sub>3</sub>-substituted 1,8-dichloroanthracene (**26**) led to the unexpected formation of 1,8-dichloro-10-nitroanthracene (**31**).



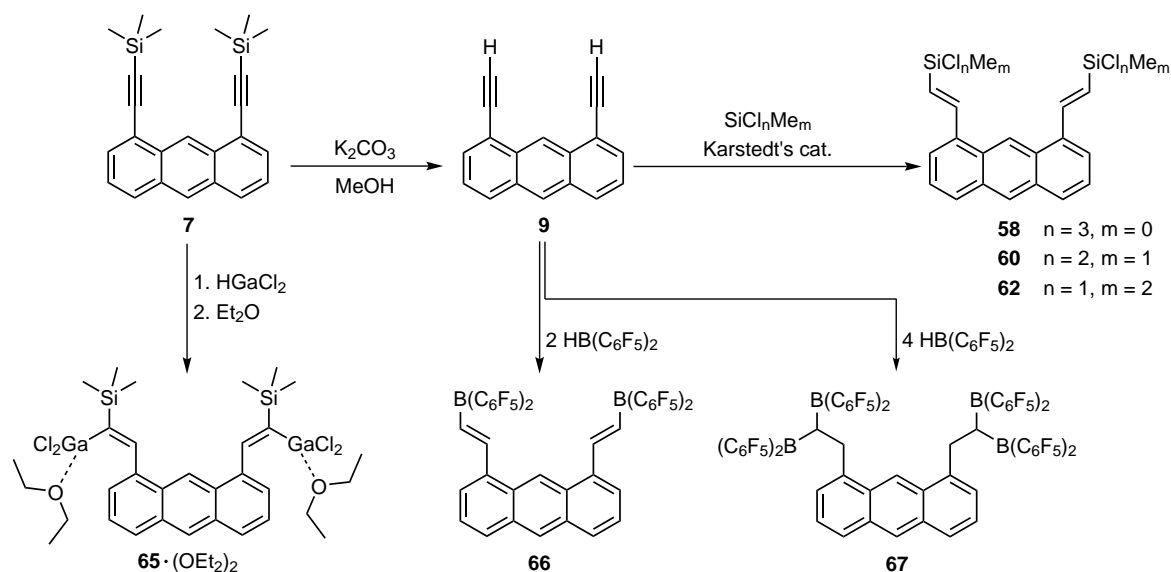
**Scheme 6.2:** Conversions of 10- $\text{EMe}_3$ -substituted 1,8-dichloroanthracenes **24**, **25** and **26** with *in situ*-generated chloroaryne.

In general, UV light irradiation of functionalised anthracenes leads to the formation of diverse photodimer isomers differing in the orientation of their substituents. In the case of 1,8-substituted anthracenes a mixture of *syn*- and *anti*-photodimers is obtained. One aim of this work was the suppression of the *anti*-isomer formation by linking two 1,8-functionalised anthracene backbones. Consequently, several bichromophoric species were synthesised by using (cross-) coupling reactions as well as olefin- or salt metathesis reactions (Scheme 6.3).



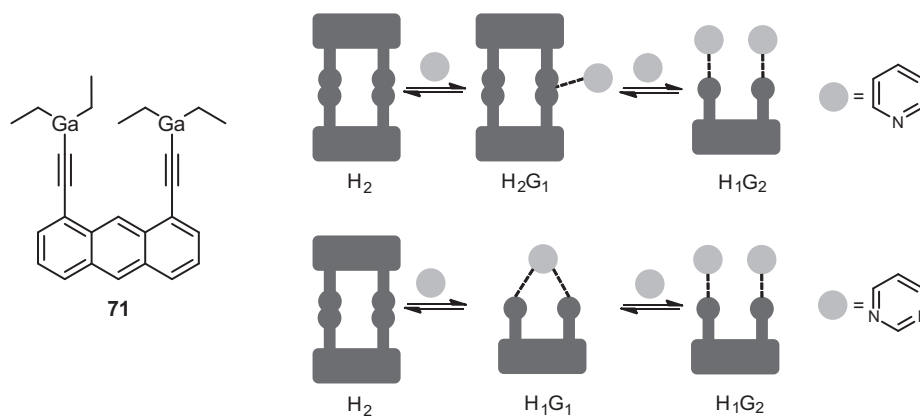
**Scheme 6.3:** Some examples of linked 1,8-dichloroanthracene derivatives.

Besides the syntheses of new and potentially photoswitchable rigid organic frameworks, polydentate Lewis acids were prepared by the conversion of 1,5- and 1,8-dialkynylanthracenes in various (hydro-) metallation reactions (Scheme 6.4). Some of these compounds were treated with diethyl ether demonstrating the different reactivity of the Lewis-acidic species towards the Lewis-basic (guest-) molecule. In the case of the  $\text{GaCl}_2$ -substituted compound **65** the formation of an adduct was observed, whereas the conversion of the twofold  $\text{SiCl}_3$ -functionalised species **58** led to the ether cleavage product **63**.



**Scheme 6.4:** Some examples of anthracene-based bi- and tetradentate Lewis acids by hydrometallation reactions.

Furthermore, the host-guest chemistry of the rigid digallium Lewis acid **71** was investigated in detail for the first time to proof the principle of Lewis base complexation of these receptor systems. Therefore, the host compound was treated stepwise with increasing amounts of pyridine and pyrimidine, respectively. The resulting (intermediately formed) host-guest complexes were identified by comparison of their diffusion coefficients with those of suitable tailor-made model systems. These compounds were of well-known shape and geometry similar to that of expected host aggregates and host-guest complexes. As shown in Scheme 6.5, a different behaviour was observed when **71** was converted with pyridine (above) instead of pyrimidine (below).



**Scheme 6.5:** Host-guest complex formation of **71** with pyridine (above) and pyrimidine (below).



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Bielefeld, im Mai 2014  
Jan-Hendrik Lamm

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## Anhang

Auf den folgenden Seiten finden sich einige der bisher aus dieser Arbeit hervorgegangenen Publikationen, die bereits veröffentlicht, von den Verlagen akzeptiert, sich zur Zeit im Begutachtungsprozess befinden, bzw. kurz davor stehen.

### Publikationen und Manuskripte

#### **1 Syntheses and Structures of 10-Trimethylelement-Substituted 1,8-Dichloroanthracenes**

Jan-Hendrik Lamm, Yury V. Vishnevskiy, Eric Ziemann, Timo A. Kinder, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Eur. J. Inorg. Chem.* **2014**, 941–947.

#### **2a Aufklärung des Bildungsmechanismus von Wirt-Gast-Komplexen und Identifizierung von Intermediaten mithilfe von NMR-Titration und Diffusions-NMR-Spektroskopie**

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Angew. Chem.* **2014**, *126*, 8072–8076.

#### **2b Mechanism of Host-Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy**

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Angew. Chem. Int. Ed.* **2014**, *53*, 7938–7942.

#### **3 Improved Access to 1,8-Dichloro-10-(ethynyl)anthracene – A Building Block for Rigid Organic Frameworks**

Jan-Hendrik Lamm, Leif Arne Körte, Lisa Kuhlmann, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Eur. J. Org. Chem.* **2014**, Manuskript in Begutachtung.



#### **4 Polyalkynylanthracenes – Syntheses, Structures and their Behaviour towards UV Irradiation**

Jan-Hendrik Lamm, Johanna Glatthor, Jan-Henrik Weddeling, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

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#### **5 Poly-Boron, -Silicon and -Gallium Lewis Acids by Hydrometallation of 1,5- and 1,8-Dialkynylanthracenes**

Jan-Hendrik Lamm, Jan Horstmann, Jan Hendrick Nissen, Jan-Henrik Weddeling, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Eur. J. Inorg. Chem.* **2014**, akzeptiert.

#### **6 A Rational Approach to Improve Stereochemical Control in Triptycene Formation – An Exercise in Subtle Balancing Multiple Factors**

Jan-Hendrik Lamm, Yury V. Vishnevskiy, Eric Ziemann, Timo A. Kinder, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

vorgesehen für *Chem. Eur. J.*

#### **7 Syntheses of Donor-free Linked 1,8-functionalised Anthracene Derivatives**

Jan-Hendrik Lamm, Marvin Linnemannstöns, Sven Solyntjes, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

vorgesehen für *Eur. J. Org. Chem.*

#### **8 Alkynyl compounds of the rare earth metals**

Anja Nieland, Jan-Hendrik Lamm, Andreas Mix, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Z. Anorg. Allg. Chem.* **2014**, Manuskript in Begutachtung.

## **Publikation 1**

### **Syntheses and Structures of 10-Trimethylelement-Substituted 1,8-Dichloroanthracenes**

Jan-Hendrik Lamm, Yury V. Vishnevskiy, Eric Ziemann, Timo A. Kinder, Beate Neumann, Hans-Georg Stammer, Norbert W. Mitzel

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## Syntheses and Structures of 10-Trimethylelement-Substituted 1,8-Dichloroanthracenes

Jan-Hendrik Lamm,<sup>[a]</sup> Yury V. Vishnevskiy,<sup>[a]</sup> Eric Ziemann,<sup>[a]</sup>  
Timo A. Kinder,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammer,<sup>[a]</sup> and  
Norbert W. Mitzel\*<sup>[a]</sup>

**Keywords:** Arenes / Fused-ring systems / Germanium / Silicon / Tin / Solid-state structures / Quantum chemistry

1,8-Dichloroanthracenes bearing EMe<sub>3</sub> substituents at the 10-position (E = Si, Ge, Sn) have been synthesised by salt elimination reactions. The key compound, 10-bromo-1,8-dichloroanthracene (**2**), was quantitatively obtained by conversion of 1,8-dichloroanthracene with elemental bromine in dichloromethane. The EMe<sub>3</sub>-substituted anthracene compounds 1,8-dichloro-10-(trimethylsilyl)- (**3**), 1,8-dichloro-10-(trimethylgermyl)- (**4**) and 1,8-dichloro-10-(trimethylstannyl)anthracene (**5**) were completely characterised by multinuclear NMR spectroscopy and mass spectrometry. Their mo-

lecular structures in the crystalline state were analysed by X-ray diffraction experiments and compared with the crystal structure of 10-*tert*-butyl-1,8-dichloroanthracene (**1**). It was found that the level of deformation of the anthracene backbone continuously increases along the series of anthracene substituents SnMe<sub>3</sub> < GeMe<sub>3</sub> < SiMe<sub>3</sub> < CMe<sub>3</sub>. Owing to the good agreement of experimental structural parameters with the results of quantum chemical calculations, the molecular deformations can be regarded as inherent molecular properties.

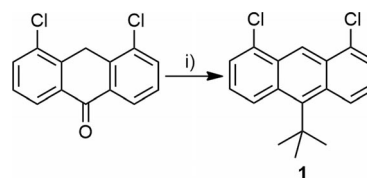
### Introduction

Substituted anthracenes are useful building blocks and are widely utilised in many fields of (metal)organic chemistry. Anthracenes are known to undergo a cycloaddition upon UV irradiation.<sup>[1]</sup> In this way they can be essential components in many photoswitchable compounds. Owing to the rigidity of their skeletons, anthracene units are often used when defined distances between substituents are intended.<sup>[2]</sup> Therefore, it is necessary to study circumstances that might lead to a deformation of the well-defined anthracene backbone.

During our investigations in the field of poly-Lewis acids with rigid organic frameworks,<sup>[2a]</sup> we became interested in the synthesis of 1,8-dichloroanthracenes bearing sterically demanding substituents such as *tert*-butyl in the 10-position (**1**) (Scheme 1).

We determined its molecular structure in the crystalline state and observed a butterfly-like deformation of the anthracene backbone as well as a bending of the *tert*-butyl substituent in the 10-position. For further explorations in this field, we synthesised the higher homologues of 10-*tert*-butyl-1,8-dichloroanthracene (Ant-CMe<sub>3</sub>, with Ant = 1,8-dichloroanthracen-10-yl, **1**).

Herein we report an efficient preparative route to Ant-Br (**2**) and the syntheses of Ant-SiMe<sub>3</sub> (**3**), Ant-GeMe<sub>3</sub> (**4**)



Scheme 1. Synthesis of the 10-*tert*-butyl-1,8-dichloroanthracene (**1**). Reagents and conditions: (i) 1. *t*BuMgBr, THF, Et<sub>2</sub>O, 0 °C; 2. aqueous HCl, 0 °C; 3. P<sub>2</sub>O<sub>5</sub>, toluene, 80 °C, 12%.<sup>[3]</sup>

and Ant-SnMe<sub>3</sub> (**5**) by salt elimination reactions. We discuss their crystal structures to determine the influence of the moiety in the 10-position and compare them with the results of quantum chemical calculations.

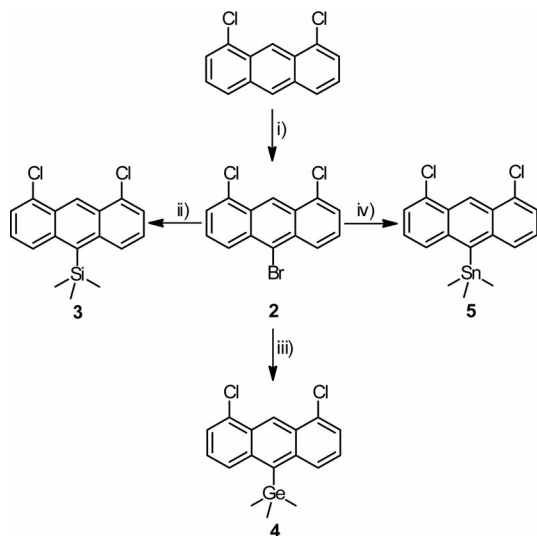
### Results and Discussion

#### Syntheses and Characterisation of the Anthracene Derivatives

To investigate the influence of the sterically demanding substituents in the 10-position, we synthesised the SiMe<sub>3</sub>-, GeMe<sub>3</sub>- and SnMe<sub>3</sub>-functionalised 1,8-dichloroanthracenes **3**, **4** and **5**, respectively. As shown in Scheme 2, 10-bromo-1,8-dichloroanthracene (**2**) is the key compound for the following salt elimination reactions. According to the literature, it can be prepared by the reaction of 1,8-dichloroanthracene with *N*-bromosuccinimide in chloroform (yield 30%<sup>[4]</sup>) or by conversion with PBr<sub>5</sub> (yield 66%<sup>[5]</sup>). However,

[a] Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie, Universität Bielefeld, Universitätsstrasse 25, 33615 Bielefeld, Germany  
E-mail: mitzel@uni-bielefeld.de  
http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/

we found that the brominated species **2** can easily be synthesised by the reaction of 1,8-dichloroanthracene with elemental bromine, essentially in quantitative yield. The  $^1\text{H}$  NMR spectrum of compound **2** recorded at ambient temperature (298 K) in  $\text{CDCl}_3$  shows one singlet at  $\delta = 9.38$  ppm (H9), two doublets at  $\delta = 8.49$  (H4/H5) and 7.69 ppm (H2/H7) and one doublet of doublets at  $\delta = 7.55$  ppm (H3/H6). In contrast to the spectrum of 1,8-dichloroanthracene, the signals are slightly shifted and no singlet for the proton in the 10-position is detected. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** contains eight signals at  $\delta = 132.96$ – $121.83$  ppm and mass spectrometric investigations further confirm its identity.



Scheme 2. Syntheses of the 10-substituted 1,8-dichloroanthracenes **3**, **4** and **5** using the brominated species **2**. Reagents and conditions: (i)  $\text{Br}_2$ ,  $\text{CH}_2\text{Cl}_2$ , 0 °C to room temp., 14 h, quant.; (ii) 1. *n*BuLi, THF,  $-78$  °C, 2 h; 2.  $\text{Me}_3\text{SiCl}$ , 72%; (iii) 1. *n*BuLi, THF,  $-78$  °C, 2 h; 2.  $\text{Me}_3\text{GeCl}$ , 62%; (iv) 1. *n*BuLi, THF,  $-78$  °C, 2 h; 2.  $\text{Me}_3\text{SnCl}$ , 74%.

After bromine–lithium exchange with *n*-butyllithium in THF at  $-78$  °C, chlorotrimethylsilane or chlorotrimethylgermane was condensed onto the frozen mixtures and warmed to form Ant-SiMe<sub>3</sub> (**3**) and Ant-GeMe<sub>3</sub> (**4**), respectively. Ant-SnMe<sub>3</sub> (**5**) was obtained after conversion of the in situ generated lithiated species in THF by the addition of solid trimethyltin chloride.

The new anthracene compounds were purified by column chromatography (**3**) or sublimation (**4** and **5**) and identified by multinuclear NMR spectroscopy as well as (high-resolution) mass spectrometry. The  $^1\text{H}$  NMR spectroscopic shifts of compounds **3**, **4** and **5** are listed in Table 1; the shifts of the *tert*-butyl-substituted species **1**<sup>[3]</sup> are given for comparison.

In all cases, nine different signals were observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (ten signals for compound **1**). In the  $^{29}\text{Si}$  NMR spectrum of compound **3** the signal for the SiMe<sub>3</sub> group was detected at  $\delta = 4.39$  ppm. The  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of compound **5** shows a singlet at  $\delta = -42.23$  ppm. *J* couplings of the tin nucleus to the methyl protons as well as to the protons at the 4-, 5- and 9-positions

Table 1.  $^1\text{H}$  NMR spectroscopic shifts of the EM<sub>3</sub>-substituted compounds **1**,<sup>[3]</sup> **3**, **4** and **5** in  $\text{CDCl}_3$  (500 MHz, 298 K). For NMR spectroscopic assignments, see Scheme 3 in the Exp. Section.

	E	H9	H4/H5	H2/H7	H3/H6	E(CH <sub>3</sub> ) <sub>3</sub>
<b>3</b>	Si	9.44	8.37	7.62	7.40	0.70
<b>4</b>	Ge	9.38	8.28	7.60	7.40	0.84
<b>5</b>	Sn	9.37	8.11	7.63	7.42	0.64
<b>1</b>	C	9.28	8.46	7.57	7.26	1.90

of the anthracene unit are observable. The corresponding coupling constants  $^4J_{\text{Sn,H}} = 8.8$  Hz (H4/H5),  $^5J_{\text{Sn,H}} = 6.6$  Hz (H9) and the  $^2J$  couplings of the methyl protons to  $^{117}\text{Sn}$  ( $J = 52.0$  Hz) and  $^{119}\text{Sn}$  ( $J = 54.1$  Hz) can be obtained from the  $^1\text{H}$  NMR spectrum.

### Molecular Structures of the Anthracene Derivatives

The molecular structures of the substituted 1,8-dichloroanthracene derivatives **3**, **4** and **5** (displayed in Figures 1, 3 and 4) were determined by X-ray diffraction experiments of single crystals, which were grown from solutions by slow evaporation of the solvent. Owing to the fact that similar structural parameter values are observed for compounds **3** and **4**, their molecular structures in the crystalline state are described together.

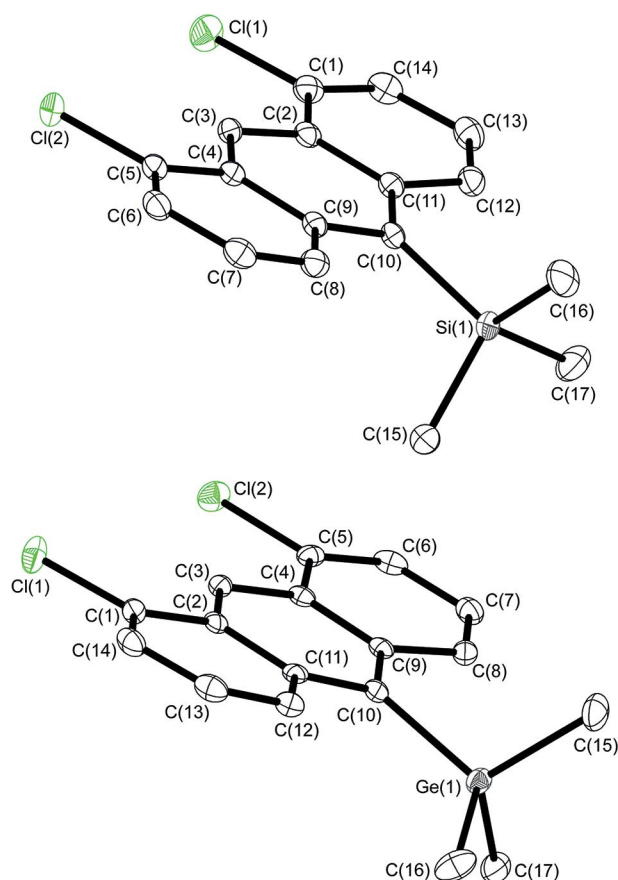


Figure 1. Molecular structures of Ant-SiMe<sub>3</sub> (**3**, above) and Ant-GeMe<sub>3</sub> (**4**, below) in the crystalline state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 2.

Ant-SiMe<sub>3</sub> (**3**) and Ant-GeMe<sub>3</sub> (**4**) crystallise in the monoclinic space group *P2<sub>1</sub>/c* with four molecules per unit cell. Both chlorine atoms of **3** and **4** are found in-plane with the almost planar side rings they are bonded to. The C–Cl distances in the SiMe<sub>3</sub>-substituted species **3** {1.745(2) Å [C(1)–Cl(1)] and 1.744(2) Å [C(5)–Cl(2)]} agree well with the corresponding C–Cl distances in **4** [1.745(3) Å for C(1)–Cl(1) and C(5)–Cl(2)]. They are identical within experimental error with the values reported for other 1,8-dichloroanthracenes that bear alkyl or aryl substituents in the 10-position [e.g., 1.745(3) Å (Ant-Cy) and 1.748(2) Å (Ant-Ph)].<sup>[3]</sup> The C–C bond lengths in the anthracene unit of **3** {1.353(2) Å [C(1)–C(14)] to 1.445(2) Å [C(2)–C(11)]} differ just slightly from those in the GeMe<sub>3</sub>-substituted compound **4** {1.353(4) Å [C(1)–C(14)] to 1.439(4) Å [C(2)–C(11)]} and from our previously published results for *n*-butyl-, cyclohexyl-, phenyl- or (trimethylsilyl)ethynyl-substituted 1,8-dichloroanthracenes.<sup>[3]</sup>

The C(10)–Si(1) distance in **3** at 1.916(2) Å is remarkably long and very comparable to the C<sub>aryl</sub>–Si bond in 9,10-bis-(trimethylsilyl)anthracene [1.913(2) and 1.916(2) Å<sup>[6]</sup>] and 9,10-bis(diisopropylsilyl)anthracene [1.906(4)<sup>[7a]</sup> and 1.904(2) Å,<sup>[7b]</sup> respectively]. In general, these C–Si bond elongations in **3** and the other mentioned alkylsilyl-substituted compounds seem to be caused by repulsive interactions of the aryl-bound hydrogen atoms with the silyl substituents. Without sterically demanding groups at the silicon atom, such long C<sub>aryl</sub>–Si distances are not observed, neither in solid-state structures [e.g., 1.878(2) Å<sup>[8]</sup> (9,10-disilyl-anthracene)] nor in gas-phase structures [e.g., 1.863(3) Å<sup>[9]</sup> in silylbenzene or 1.892(2) Å<sup>[10]</sup> in hexasilylbenzene].

In the case of Ant-GeMe<sub>3</sub> (**4**) the C(10)–Ge(1) bond of 1.986(3) Å is also longer than the C<sub>aryl</sub>–Ge distances found in 1,8-bis(trimethylgermyl)naphthalene (1.973 and 1.975 Å).<sup>[11]</sup>

Related to the structure of Ant-CMe<sub>3</sub> (**1**; see Figure 2),<sup>[3]</sup> a steric repulsion of the hydrogen atoms in the 4- and 5-

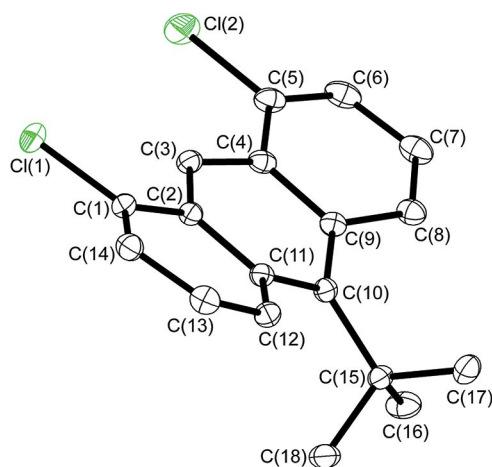


Figure 2. Molecular structure of Ant-CMe<sub>3</sub> (**1**) in the crystalline state, which is shown for comparison. For a detailed discussion of the structure, see the literature.<sup>[3]</sup> Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 2.

position of the anthracene system and those of the trimethylsilyl- and trimethylgermyl group is indicated, thus leading to a deformation of the anthracene unit and the bending of the SiMe<sub>3</sub> and GeMe<sub>3</sub> substituents, respectively (see Figure 4).

Owing to the steric bulk of the EMe<sub>3</sub> substituents (E = C, Si, Ge), the anthracene backbones of the corresponding compounds **1**, **3** and **4** show a butterfly-like deformation, which can also be observed in the crystal structure of 9-*tert*-butylantracene.<sup>[12]</sup>

The dihedral angles C(1)–C(2)–C(3)–C(4) and C(9)–C(10)–C(11)–C(12) can be used to describe the anthracene deformation at the “upper rim” and the “lower rim”, respectively. As shown in Table 2, the C(9)–C(10)–C(11)–C(12) torsion angles are 155.8(1)° (CMe<sub>3</sub>), 171.5(1)° (SiMe<sub>3</sub>) and 172.2(2)° (GeMe<sub>3</sub>), which are far from planarity. The C(1)–C(2)–C(3)–C(4) angles are closer to 180°, thus indicating a weaker influence of the substituent in the 10-position on the deformation of the “upper rim” of the anthracene unit.

The deformation of the anthracene backbone also results in an elongation of the C(9)–C(10) and C(10)–C(11) bonds (see Table 2). C(10)–C(11) distances of 1.425(2) (**1**), 1.423(2) (**3**) and 1.416(4) Å (**4**) are found, which are longer than the corresponding C–C bonds reported, for example, for the *n*-butyl- [1.409(3) Å] or the phenyl-substituted 1,8-dichloroanthracene [1.407(2) Å].<sup>[3]</sup>

In contrast to the structural parameters of compounds **1**, **3** and **4**, such a strong anthracene deformation cannot be observed in the case of the 1,8-dichloro-10-(trimethylstannyl)anthracene (**5**). The compound crystallises in the monoclinic space group *P2<sub>1</sub>/n* with four molecules per unit cell and its molecular structure in the crystalline state is depicted in Figures 3 and 4.

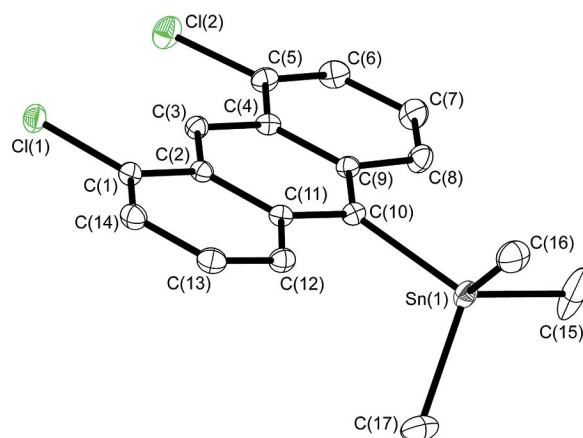


Figure 3. Molecular structure of Ant-SnMe<sub>3</sub> (**5**) in the crystalline state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 2.

The anthracene backbone of compound **5** is clearly more planar than in compounds **1**, **3** and **4**, and the out-of-plane bending of its substituent is remarkably smaller. As both chloro functions of the different molecules are not influ-

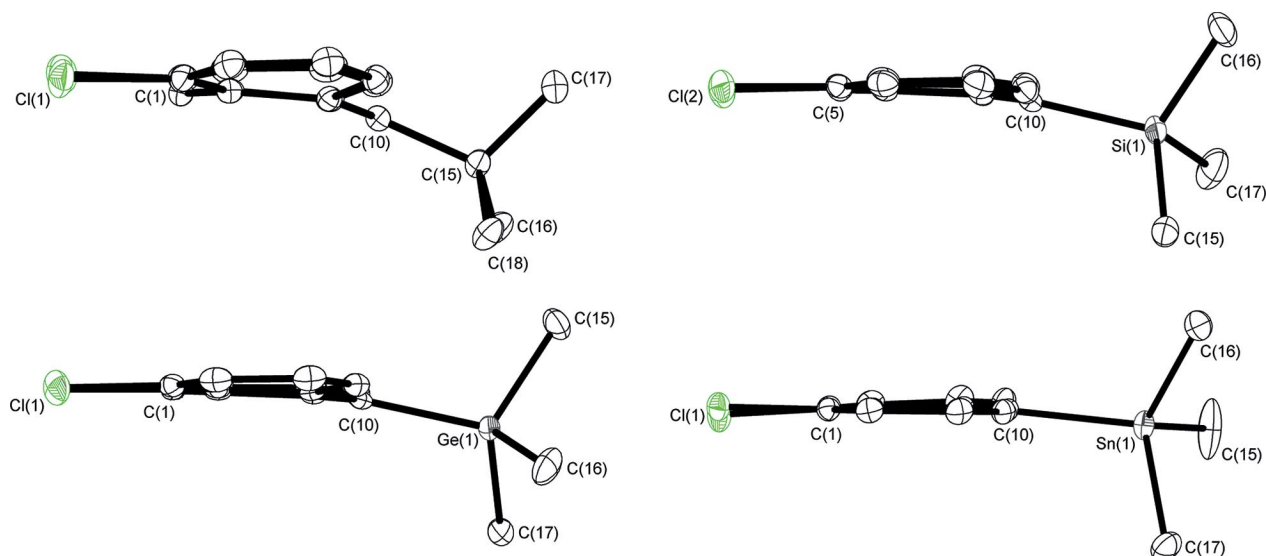


Figure 4. Side views of the molecular structures of compounds Ant-CMe<sub>3</sub> (**1**), Ant-SiMe<sub>3</sub> (**3**), Ant-GeMe<sub>3</sub> (**4**) and Ant-SnMe<sub>3</sub> (**5**) in the crystalline state to illustrate the substituent bendings.

Table 2. Selected measured and calculated bond lengths [Å] and angles [°] of compounds **1**,<sup>[3]</sup> **3**, **4** and **5**.

	1, E = C(15)		3, E = Si(1)		4, E = Ge(1)		5, E = Sn(1)	
	XRD	calcd.	XRD	calcd.	XRD	calcd.	XRD	calcd.
Cl(1)–C(1)	1.741(1)	1.735	1.745(2)	1.736	1.745(3)	1.735	1.744(2)	1.736
Cl(2)–C(5)	1.739(2)	1.735	1.744(2)	1.735	1.745(3)	1.735	1.739(2)	1.736
C(1)–C(14)	1.359(2)	1.358	1.353(2)	1.358	1.353(4)	1.359	1.358(2)	1.359
C(2)–C(3)	1.393(2)	1.385	1.388(2)	1.385	1.394(4)	1.386	1.391(2)	1.387
C(2)–C(11)	1.440(2)	1.440	1.445(2)	1.440	1.439(4)	1.439	1.439(2)	1.440
C(9)–C(10)	1.420(2)	1.415	1.424(2)	1.414	1.425(4)	1.408	1.412(2)	1.406
C(10)–C(11)	1.425(2)	1.418	1.423(2)	1.412	1.416(4)	1.410	1.415(2)	1.408
C(10)–E	1.561(2)	1.551	1.916(2)	1.922	1.986(3)	2.009	2.175(2)	2.198
C(15)–C(16) <sup>[a]</sup>	1.549(2)	1.544	–	–	–	–	–	–
C(15)–C(17) <sup>[a]</sup>	1.542(2)	1.534	–	–	–	–	–	–
C(15)–C(18) <sup>[a]</sup>	1.549(2)	1.545	–	–	–	–	–	–
E–C(15) <sup>[b]</sup>	–	–	1.887(3)	1.887	1.954(3)	1.975	2.154(2)	2.165
E–C(16) <sup>[b]</sup>	–	–	1.872(3)	1.884	1.960(3)	1.977	2.143(2)	2.164
E–C(17) <sup>[b]</sup>	–	–	1.878(3)	1.888	1.965(3)	1.976	2.147(2)	2.164
H(8)⋯H <sub>methyl</sub> <sup>[c]</sup>	–	1.820	–	2.131	–	2.085	–	2.244
H(8)⋯H <sub>methyl</sub> <sup>[c]</sup>	–	2.484	–	2.161	–	2.275	–	2.248
H(12)⋯H <sub>methyl</sub> <sup>[c]</sup>	–	1.929	–	2.022	–	2.194	–	2.322
H(12)⋯H <sub>methyl</sub> <sup>[c]</sup>	–	1.950	–	2.280	–	2.198	–	2.338
Cl(1)–C(1)–C(14)	118.3(1)	118.3	118.3(2)	118.4	118.5(2)	118.4	118.8(2)	118.4
C(1)–C(2)–C(3)	121.9(2)	121.4	122.3(2)	121.9	122.4(3)	122.1	122.1(2)	122.1
C(2)–C(3)–C(4)	119.9(2)	120.4	120.9(2)	121.2	120.7(3)	121.2	120.9(2)	121.3
C(9)–C(10)–C(11)	116.9(2)	117.2	118.1(2)	118.5	118.3(3)	119.1	119.2(2)	119.4
C(9)–C(10)–E	122.1(1)	122.4	117.4(2)	123.8	117.3(2)	123.3	123.1(1)	123.3
C(11)–C(10)–E	120.9(1)	120.4	124.2(2)	117.5	124.1(2)	117.4	117.5(2)	117.6
C(10)–C(15)–C(16) <sup>[a]</sup>	112.0(1)	114.1	–	–	–	–	–	–
C(10)–C(15)–C(17) <sup>[a]</sup>	111.6(1)	111.8	–	–	–	–	–	–
C(10)–C(15)–C(18) <sup>[a]</sup>	110.9(1)	109.7	–	–	–	–	–	–
C(10)–E–C(15) <sup>[b]</sup>	–	–	106.7(1)	108.3	111.0(2)	110.1	116.3(1)	117.3
C(10)–E–C(16) <sup>[b]</sup>	–	–	110.9(2)	110.6	117.0(2)	116.8	110.4(1)	108.4
C(10)–E–C(17) <sup>[b]</sup>	–	–	117.0(1)	116.8	106.3(2)	108.1	106.2(1)	107.9
C(1)–C(2)–C(3)–C(4) <sup>[d]</sup>	169.9(1)	171.5	178.3(1)	176.7	178.2(3)	177.0	178.4(1)	179.6
C(9)–C(10)–C(11)–C(12) <sup>[d]</sup>	155.8(1)	159.9	171.5(1)	172.3	172.2(2)	173.3	178.5(1)	179.4
C(8)–C(9)–C(10)–E <sup>[d]</sup>	26.3(2)	25.2	13.1(2)	14.1	12.4(3)	12.6	8.5(2)	1.3
C(12)–C(11)–C(10)–E <sup>[d]</sup>	27.3(2)	23.4	14.4(2)	13.1	13.6(4)	11.9	6.9(2)	1.5
H(12)–C(11)–C(12)–C(13) <sup>[e]</sup>	–	3.3	–	1.6	–	1.5	–	0.1
H(8)–C(7)–C(8)–C(9) <sup>[e]</sup>	–	4.1	–	1.7	–	1.5	–	0.1

[a] For **1** only. [b] For **3**, **4** and **5** only. [c] Only the two shortest calculated H(8)⋯H<sub>methyl</sub> and H(12)⋯H<sub>methyl</sub> distances are given. [d] Torsion angles, given in absolute values. [e] Calculated out-of-plane angles of hydrogen atoms.

enced by the substituent in the 10-position, the C–Cl distances of Ant-SnMe<sub>3</sub> (**5**) are comparable to those mentioned above for **1**, **3** and **4**. The C–C bond lengths in the anthracene backbone are in a similar range.

Expectedly, the C(10)–EMe<sub>3</sub> distance elongates from 1.561(2) Å (CMe<sub>3</sub>), through 1.916(2) (SiMe<sub>3</sub>) and 1.986(3) Å (GeMe<sub>3</sub>) up to 2.175(2) Å (SnMe<sub>3</sub>). Relative to **1**, **3** and **4**, the longer C–Sn bond leads to a weaker repulsive interaction of the hydrogen atoms in the 4- and 5-position of the anthracene unit with the methyl groups in compound **5** and a weaker deformation of the central anthracene ring, as is indicated in the dihedral angles C(1)–C(2)–C(3)–C(4) [178.4(1)°] and C(9)–C(10)–C(11)–C(12) [178.5(1)°].

Owing to the (strong) deformation of the central anthracene ring in compounds **1**, **3** and **4**, the dihedral angles C(8)–C(9)–C(10)–E and C(12)–C(11)–C(10)–E (with E = C, Si, Ge, Sn) are particularly suitable for describing and comparing the substituent bendings. As given in Table 2, the torsion angles increase with decreasing E–C(10) distances from 6.9(2) and 8.5(2)° (SnMe<sub>3</sub>, **5**) to 26.3(2) and 27.3(2)° (CMe<sub>3</sub>, **1**). Owing to d-block contraction, the C(10)–Ge(1) bond length in Ant-GeMe<sub>3</sub> (**4**) [1.986(3) Å] is just marginally longer than the C(10)–Si(1) bond [1.916(2) Å] found in Ant-SiMe<sub>3</sub> (**3**) relative to compounds **1** and **5**. As a consequence, the corresponding dihedral angles of compounds **3** and **4** [13.1(2) and 14.4(2)° (SiMe<sub>3</sub>) versus 12.4(3) and 13.6(4)° (GeMe<sub>3</sub>)] are only slightly different. Side views of all compounds are pictured in Figure 4, thus illustrating the anthracene deformation and the bending of the EMe<sub>3</sub> substituents. Nevertheless, all EMe<sub>3</sub> substituents are barely affected, which is indicated by the C(10)–E–CH<sub>3</sub> angles. In all crystal structures at least two of them are found to be larger than 109.5° (see Table 2). The EMe<sub>3</sub> groups themselves exhibit average E–CH<sub>3</sub> bond lengths of 1.55 [**1**, lit. (C–C): 1.52 Å<sup>[13]</sup>], 1.88 [**3**, lit. (Si–C): 1.87 Å<sup>[13]</sup>], 1.96 [**4**, lit. (Ge–C): 1.96 Å<sup>[13]</sup>] and 2.15 Å [**5**, lit. (Sn–C): 2.15 Å<sup>[13]</sup>], respectively, which differ slightly from the sum of the corresponding covalent radii values given in the literature.

### Quantum Chemical Calculations

To confirm the effects concluded from the experimentally determined crystal structures and to exclude the effect of intermolecular interactions upon the deformation of the anthracene backbone as well as the bending of the substituent in the 10-position, quantum chemical calculations were performed (see Exp. Section for details). Our theoretical predictions of structures for free molecules are in good agreement with the experimental data for the solid state, thus indicating that the deformation of the anthracene units and the bending of the EMe<sub>3</sub> substituents is likely a consequence of intramolecular interactions (i.e., an inherent molecular property).

For the CMe<sub>3</sub>-, SiMe<sub>3</sub>- and GeMe<sub>3</sub>-substituted species, the calculated torsion angles are in good agreement with

the measured values (see Table 2). The Sn(1)–C(10)–C(9)–C(8) and the Sn(1)–C(10)–C(11)–C(12) angles calculated for Ant-SnMe<sub>3</sub> (**5**) show a larger deviation [experimental 8.5(2)/6.9(2)° versus theoretical 1.3/1.5°].

As stated above, the bending of the substituent in the 10-position seems to be a consequence of the repulsive interaction of the methyl groups with the hydrogen atoms located at the 4- and 5-position of the anthracene backbone. This is denoted by the calculated out-of-plane angles H(12)–C(11)–C(12)–C(13) and H(8)–C(7)–C(8)–C(9), respectively. In the case of the CMe<sub>3</sub>-substituted species **1**, which is displayed as an example in Figure 5, the out-of-plane angles are 3.3 and 4.1°, thus indicating a remarkable intramolecular repulsion. However, in Ant-SiMe<sub>3</sub> (**3**) and Ant-GeMe<sub>3</sub> (**4**) the corresponding angles are 1.6 and 1.7° (**3**) and twice 1.5° (**4**), thereby suggesting a slight interaction of the hydrogen atoms, whereas weak interactions are calculated for the SnMe<sub>3</sub>-substituted compound **5** (out-of-plane angles: 0.1°). Short H<sub>aryl</sub>⋯H<sub>methyl</sub> distances, which are within the van der Waals radii, are calculated between H(8) and the methyl protons. The shortest distances increase from 1.820 Å (CMe<sub>3</sub>) through 2.131 (SiMe<sub>3</sub>) and 2.085 Å (GeMe<sub>3</sub>) up to 2.244 Å (SnMe<sub>3</sub>). The calculated H(12)⋯H<sub>methyl</sub> distances take a similar course (see Table 2). For Ant-CMe<sub>3</sub> (**1**) short H<sub>aryl</sub>⋯H<sub>methyl</sub> distances are found in the case of H(8)⋯H(16a) (1.820 Å) and H(8)⋯H(17c) (2.484 Å) as well as in the case of H(12)⋯H(17a) (1.950 Å) and H(12)⋯H(18a) (1.929 Å), respectively (see Figure 5). The different H(8)⋯H(17c) and H(12)⋯H(17a) distances are caused by a torsion of the CMe<sub>3</sub> substituent [C(11)–C(10)–C(15)–C(17) 83.1° versus C(9)–C(10)–C(15)–C(17) 100.3°].

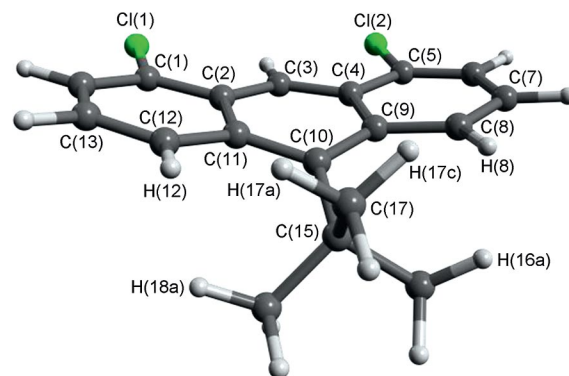


Figure 5. Calculated structure of Ant-CMe<sub>3</sub> (**1**).

### Conclusion

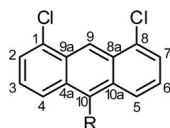
Starting from 1,8-dichloroanthracene, 10-bromo-1,8-dichloroanthracene (**2**) was quantitatively afforded by conversion with elemental bromine in dichloromethane. By using this versatile, applicable key compound, Ant-SiMe<sub>3</sub> (**3**), Ant-GeMe<sub>3</sub> (**4**) and Ant-SnMe<sub>3</sub> (**5**) have been synthesised by salt elimination reactions and their structures in the crystalline state have been determined by X-ray diffraction experiments. Comparing the results to the previously published crystal structure of Ant-CMe<sub>3</sub> (**1**),<sup>[3]</sup> a remarkably



weaker bending of the moiety in the 10-position can be observed for the CMe<sub>3</sub>- to the SnMe<sub>3</sub>-substituted compounds. Quantum chemical calculations revealed that the structural distortions that the anthracene skeleton and the adjacent EMe<sub>3</sub> groups experience are inherent molecular properties and are not due to intermolecular forces.

## Experimental Section

**General:** The syntheses of 1,8-dichloroanthracene<sup>[14]</sup> and Ant-CMe<sub>3</sub> (**1**)<sup>[3]</sup> are described elsewhere. *n*-Butyllithium (1.6 M solution in hexanes) was purchased from Acros Organics. Chlorotrimethylsilane (from Alfa Aesar), chlorotrimethylgermane (from Sigma Aldrich) and trimethyltin chloride (from Strem Chemicals) were used without further purification. All metallation reactions were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried with potassium and freshly distilled before use in the reactions). Column chromatography was performed on silica gel 60 (0.04–0.063 mm mesh). NMR spectra were recorded with a Bruker DRX 500 and a Bruker Avance III 500 instrument at room temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm; <sup>13</sup>C NMR  $\delta$  = 77.16 ppm) or referenced externally (<sup>29</sup>Si: SiMe<sub>4</sub>; <sup>119</sup>Sn: SnMe<sub>4</sub>). EI mass spectra were recorded with an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV. The numbering scheme for NMR spectroscopic assignments (Scheme 3) is based on IUPAC guidelines.



Scheme 3. Numbering scheme for NMR spectroscopic assignments.

**10-Bromo-1,8-dichloroanthracene (2):** 1,8-Dichloroanthracene (550 mg, 2.23 mmol) was dissolved in dry dichloromethane (20 mL) and bromine (0.12 mL, 2.3 mmol) dissolved in dichloromethane (10 mL), was added dropwise at 0 °C. After the pale orange solution was stirred overnight at ambient temperature, all volatile compounds were removed under vacuum and the desired product was quantitatively obtained as a bright yellow solid, which was used for further syntheses without additional purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.38 (s, 1 H, H<sub>9</sub>), 8.49 (d, <sup>3</sup>J<sub>H,H</sub> = 8.9 Hz, 2 H, H<sub>4</sub>/H<sub>5</sub>), 7.69 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2 H, H<sub>2</sub>/H<sub>7</sub>), 7.55 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.9 Hz, 2 H, H<sub>3</sub>/H<sub>6</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.96, 131.78, 129.92, 127.42 (C<sub>3</sub>/C<sub>6</sub>), 127.35 (C<sub>4</sub>/C<sub>5</sub>), 126.55 (C<sub>2</sub>/C<sub>7</sub>), 123.81, 121.83 (C<sub>9</sub>) ppm. EI-MS (70 eV):  $m/z$  = 325.8 [M]<sup>+</sup>, 290.8 [M – Cl]<sup>+</sup>, 244.9 [M – Br]<sup>+</sup>, 209.9 [M – Br–Cl]<sup>+</sup>. HRMS (EI, 70 eV): calcd. for C<sub>14</sub>H<sub>7</sub>BrCl<sub>2</sub><sup>+</sup>: 323.91027; found 323.90986.

**1,8-Dichloro-10-(trimethylsilyl)anthracene (3):** 10-Bromo-1,8-dichloroanthracene (400 mg, 1.23 mmol) was dissolved in dry THF (15 mL). *n*-Butyllithium solution (1.6 M in hexanes, 0.77 mL, 1.2 mmol) was added dropwise at –78 °C, then the mixture was stirred for 2 h at this temperature and degassed by three freeze/pump/thaw cycles. Chlorotrimethylsilane (3.6 mmol, 2.9 equiv.) was condensed onto the frozen solution, then the mixture was warmed to ambient temperature and stirred overnight. After quenching

with saturated aqueous NH<sub>4</sub>Cl (20 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (4 × 25 mL). The combined organic solution was washed with saturated aqueous NaCl, dried with MgSO<sub>4</sub> and the solvent was evaporated. The orange-yellow crude product was purified by column chromatography ( $\phi$  = 3 cm,  $l$  = 25 cm, eluent: *n*-pentane) and the product was obtained as a bright yellow solid.  $R_f$  = 0.70 (*n*-pentane), yield 285 mg (72%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.44 (s, 1 H, H<sub>9</sub>), 8.37 (d, <sup>3</sup>J<sub>H,H</sub> = 9.0 Hz, 2 H, H<sub>4</sub>/H<sub>5</sub>), 7.62 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2 H, H<sub>2</sub>/H<sub>7</sub>), 7.40 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.1, 9.0 Hz, 2 H, H<sub>3</sub>/H<sub>6</sub>), 0.70 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.38, 138.06, 133.40, 129.30 (C<sub>4</sub>/C<sub>5</sub>), 127.98, 125.47 (C<sub>2</sub>/C<sub>7</sub>), 124.92 (C<sub>3</sub>/C<sub>6</sub>), 124.07 (C<sub>9</sub>), 4.74 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.39 ppm. EI-MS (70 eV):  $m/z$  = 318.0 [M]<sup>+</sup>, 303.0 [M – CH<sub>3</sub>]<sup>+</sup>, 268.0 [M – CH<sub>3</sub> – Cl]<sup>+</sup>. HRMS (EI, 70 eV): calcd. for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>Si<sup>+</sup>: 318.03928; found 318.03898.

**1,8-Dichloro-10-(trimethylgermyl)anthracene (4):** 10-Bromo-1,8-dichloroanthracene (250 mg, 0.77 mmol) was dissolved in dry THF (20 mL). *n*-Butyllithium solution (1.6 M in hexanes, 0.5 mL, 0.8 mmol) was added dropwise at –78 °C, then the mixture was stirred for 2 h at this temperature and was degassed by three freeze/pump/thaw cycles. Chlorotrimethylgermane (0.94 mmol, 1.2 equiv.) was condensed onto the frozen solution, then the mixture was warmed to ambient temperature and stirred overnight. After quenching with saturated aqueous NH<sub>4</sub>Cl (20 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic solution was washed with saturated aqueous NaCl, dried with MgSO<sub>4</sub> and the solvent was evaporated. Byproducts were removed by sublimation (27 °C, 7 × 10<sup>–3</sup> mbar) and the desired product was obtained as a yellow solid, yield 173 mg (62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.38 (s, 1 H, H<sub>9</sub>), 8.28 (d, <sup>3</sup>J<sub>H,H</sub> = 8.9 Hz, 2 H, H<sub>4</sub>/H<sub>5</sub>), 7.60 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2 H, H<sub>2</sub>/H<sub>7</sub>), 7.40 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.9 Hz, 2 H, H<sub>3</sub>/H<sub>6</sub>), 0.84 [s, 9 H, Ge(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.03, 137.40, 133.22, 127.93 (C<sub>4</sub>/C<sub>5</sub>), 129.21, 125.46 (C<sub>2</sub>/C<sub>7</sub>), 124.98 (C<sub>3</sub>/C<sub>6</sub>), 123.11 (C<sub>9</sub>), 4.84 [Ge(CH<sub>3</sub>)<sub>3</sub>] ppm. EI-MS (70 eV):  $m/z$  = 363.9 [M]<sup>+</sup>, 348.9 [M – CH<sub>3</sub>]<sup>+</sup>, 364.9 [M – (CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 246.0 [M – Ge(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. HRMS (EI, 70 eV): calcd. for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>Ge<sup>+</sup>: 363.98408; found 363.98192.

**1,8-Dichloro-10-(trimethylstannyl)anthracene (5):** 10-Bromo-1,8-dichloroanthracene (130 mg, 0.40 mmol) was dissolved in dry THF (10 mL). *n*-Butyllithium solution (1.6 M in hexanes, 0.26 mL, 0.42 mmol) was added dropwise at –78 °C and the mixture was stirred for 2 h at this temperature. Solid trimethyltin chloride (100 mg, 0.50 mmol, 1.25 equiv.) was added and the mixture was stirred overnight at ambient temperature. After quenching with water (20 mL) the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic solution was washed with saturated aqueous NaCl, dried with MgSO<sub>4</sub> and the solvent was evaporated. Byproducts were removed by sublimation (27 °C, 7 × 10<sup>–3</sup> mbar) and the desired product was obtained as a yellow solid, yield 121 mg (74%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.37 (s, 1 H, H<sub>9</sub>), 8.11 (d, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, 2 H, H<sub>4</sub>/H<sub>5</sub>), 7.63 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2 H, H<sub>2</sub>/H<sub>7</sub>), 7.42 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.8 Hz, 2 H, H<sub>3</sub>/H<sub>6</sub>), 0.64 [s, 9 H, Sn(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.01, 139.16, 133.31, 129.44 (C<sub>4</sub>/C<sub>5</sub>), 129.32, 125.58 (C<sub>3</sub>/C<sub>6</sub>), 125.38 (C<sub>2</sub>/C<sub>7</sub>), 122.87 (C<sub>9</sub>), –3.98, [Sn(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (112 MHz, CDCl<sub>3</sub>):  $\delta$  = –42.23 ppm. EI-MS (70 eV):  $m/z$  = 410.0 [M]<sup>+</sup>, 395.0 [M – CH<sub>3</sub>]<sup>+</sup>, 364.9 [M – (CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 246.0 [M – Sn(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 210.0 [M – Sn(CH<sub>3</sub>)<sub>3</sub> – Cl]<sup>+</sup>. HRMS (EI, 70 eV): calcd. for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>Sn<sup>+</sup>: 409.96455; found 409.96486.

**Quantum Chemical Calculations:** Structures of all molecules were optimised using the PBE0<sup>[15]</sup> functional of the DFT theory<sup>[16]</sup> with D3 dispersion correction<sup>[17]</sup> as implemented in the Firefly program.<sup>[18]</sup> Dunning's triple- $\zeta$  cc-pVTZ basis set<sup>[19]</sup> was used for H, C, Si and Cl atoms. For heavy atoms Ge and Sn the SDB-cc-pVTZ basis set<sup>[20]</sup> with pseudopotential was utilised. The results of structure optimisations are listed in Table 2.

**Crystal Structure Determination:** Suitable crystals of the compounds **3**, **4** and **5** were obtained by slow evaporation of saturated solutions of *n*-pentane (for **3**), THF/dichloromethane (for **4**) and dichloromethane/*n*-hexane (for **5**). They were selected, coated with paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. Data collection was performed at 100(1) K with a SuperNova Atlas diffractometer using monochromated Cu- $K_{\alpha}$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) for compound **3** or monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for compound **5**, whereas the data for compound **4** were collected with a SuperNova Eos diffractometer with monochromated Mo- $K_{\alpha}$  radiation.

The structures were solved by direct methods and refined by full-matrix least-squares cycles with the SHELX-97 program.<sup>[21]</sup> Crystal and refinement details as well as CCDC numbers are provided in Table 3.

Table 3. Crystallographic data for **3**, **4** and **5**.

	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>17</sub> H <sub>16</sub> Cl <sub>2</sub> Si	C <sub>17</sub> H <sub>16</sub> Cl <sub>2</sub> Ge	C <sub>17</sub> H <sub>16</sub> Cl <sub>2</sub> Sn
$M_r$	319.29	363.79	409.89
$F(000)$	664	736	808
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
$a$ [Å]	11.01140(11)	11.07376(15)	12.3624(2)
$b$ [Å]	11.31153(19)	11.37318(15)	10.82236(13)
$c$ [Å]	13.1231(2)	13.07639(18)	13.1020(2)
$\beta$ [°]	107.1819(18)	107.1112(15)	115.756(2)
$V$ [Å <sup>3</sup> ]	1561.62(4)	1573.99(4)	1578.77(5)
$Z$	4	4	4
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.358	1.535	1.724
$\mu$ [mm <sup>-1</sup> ]	4.352	2.272	1.944
$\theta_{\text{max}}$ [°]	71.98	26.02	30.00
Index ranges	$-13 \leq h \leq 13$ $-13 \leq k \leq 13$ $-16 \leq l \leq 16$	$-13 \leq h \leq 13$ $-14 \leq k \leq 14$ $-16 \leq l \leq 16$	$-17 \leq h \leq 17$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$
Reflns. collected	16085	96496	36126
Indep. reflns.	3059	8017	4595
$R_{\text{int}}$	0.0414	–	0.0233
Observed reflns.	2853	6111	4410
$[I > 2\sigma(I)]$			
Parameters	184	185	184
$R_1 [I > 2\sigma(I)]$	0.0342	0.0344	0.0160
$wR_2 [I > 2\sigma(I)]$	0.0939	0.0887	0.0384
$R_1$ (all data)	0.0362	0.0514	0.0171
$wR_2$ (all data)	0.0964	0.0932	0.0389
GoF	1.052	1.082	1.090
$\rho_{\text{max}}/\rho_{\text{min}}$ [e Å <sup>-3</sup> ]	0.36/–0.29	0.89/–0.46	0.54/–0.73

[a] Refined as a two-component twin (BASF 0.06630).

CCDC-968500 (for **3**), -968501 (for **4**) and -968502 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

For data for compound **1**, see ref.<sup>[3]</sup> or CCDC-768540.

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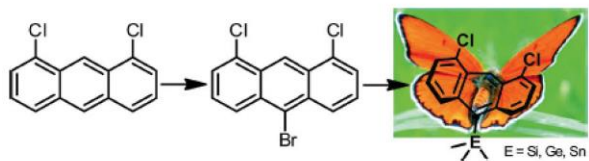
## Entry for the Table of Contents

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Syntheses and Structures of 10-Tri-  
methylelement-Substituted 1,8-Dichloro-  
anthracenes

**Keywords:** Arenes / Fused-ring systems /  
Germanium / Silicon / Tin / Solid-state  
structures / Quantum chemistry



10-Bromo-1,8-dichloroanthracene was quantitatively obtained by bromination of 1,8-dichloroanthracene and converted into 1,8-dichloro-10-(trimethylelement)-anthracenes (with E = Si, Ge, Sn). Their

crystal structures show a butterfly-like deformation of the molecules, which is also observed in case of the *tert*-butyl compound (E = C).

## **Publikation 2a**

### **Aufklärung des Bildungsmechanismus von Wirt-Gast-Komplexen und Identifizierung von Intermediaten mithilfe von NMR-Titration und Diffusions-NMR-Spektroskopie**

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin  
Chmiel, Beate Neumann, Hans-Georg Stammer, Norbert W. Mitzel

*Angew. Chem.* **2014**, *126*, 8072–8076.



# Aufklärung des Bildungsmechanismus von Wirt-Gast-Komplexen und Identifizierung von Intermediaten mithilfe von NMR-Titration und Diffusions-NMR-Spektroskopie\*\*

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler und Norbert W. Mitzel\*

Professor Lothar Weber zum 70. Geburtstag gewidmet

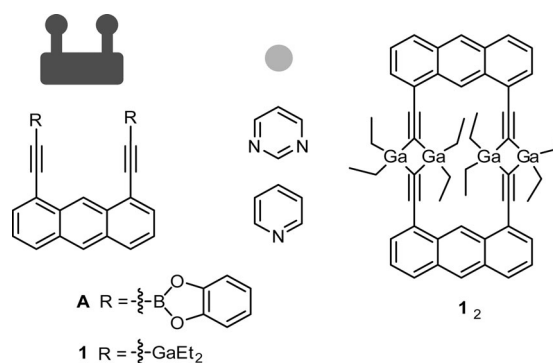
**Abstract:** Die Bildung von Wirt(W)-Gast(G)-Komplexen aus 1,8-Bis[(diethylgallanyl)ethinyl]anthracen (W) und den N-heterocyclischen Arenen Pyridin und Pyrimidin (G) wurde in Lösung durch Kombination von NMR-Titration und Diffusions-NMR-Spektroskopie untersucht. Bei Letzterer wurden die Diffusionskoeffizienten der potenziell in Lösung vorliegenden Wirt-Gast-Strukturen mit denen speziell synthetisierter Referenzverbindungen (vollständig durch NMR, HRMS und – teilweise – XRD charakterisiert) verglichen. Beide Umsetzungen zeigen ein hochdynamisches Verhalten mit verschiedenen (intermediär) gebildeten W-G-Spezies und Gleichgewichten. Mit ansteigender Gast-Konzentration wird im Fall von Pyridin die Bildung eines  $W_3 \rightleftharpoons W_2 \kappa^1 \cdot G \rightleftharpoons W G_2$ -Gleichgewichtes (im zweiten Schritt koordiniert ein Gast-Molekül an ein Wirt-Dimer) und bei Pyrimidin eines Gleichgewichtes  $W_2 \rightarrow W_1 \kappa^2 \cdot G \rightleftharpoons W G_2$  (intermediär entsteht ein 1:1-Komplex) beobachtet.

Seit Pedersens ersten Berichten über Kronenether-komplexierte Kalium-Kationen aus dem Jahre 1967 ist die Wirt-Gast-Chemie ein fester Bestandteil der supramolekularen Chemie.<sup>[1]</sup> Heute sind über 5000 verschiedenartige Kronenverbindungen bekannt, und das Prinzip ihrer Gast-Komplexierung wurde auf dreidimensionale Wirt-Systeme wie Cryptanden übertragen.<sup>[2,3]</sup> Im Unterschied zur sehr gut untersuchten und entwickelten Kationen-Erkennung (Lewis-Säuren) durch Poly-Lewis-Basen ist der inverse Fall, die Bindung Lewis-basischer Gäste durch poly-Lewis-acide Wirt-Substrate, verhältnismäßig wenig untersucht. Gründe hierfür liegen möglicherweise in der hohen Reaktivität vieler Lewis-acider Verbindungen oder im beschränkten Zugang zu do-

norfreien organischen Grundgerüsten, an denen die Lewis-aciden Atome fixiert werden können. Einige bekannte Beispiele solcher Wirt-Systeme basieren auf Silicium,<sup>[4]</sup> Zinn,<sup>[5]</sup> Quecksilber<sup>[6]</sup> sowie den Erdmetallen Bor,<sup>[6d,7]</sup> Aluminium,<sup>[8]</sup> Gallium<sup>[8c,d,9]</sup> und Indium<sup>[10]</sup> als Lewis-aciden Funktionen.

In vielen der Beispiele sind die Lewis-aciden Atome an einem verhältnismäßig flexiblen organischen Grundgerüst gebunden, was eine große Bandbreite an Gast-Komplexierungen ermöglicht, aber auch mit einer verringerten Selektivität der Gast-Erkennung einhergeht. Gleichwohl sind auch starre Rezeptorsysteme bekannt, z.B. die 1,2-Bis(organo-stannyl)benzole,<sup>[11]</sup> die eine weit höhere Affinität für die Bindung von Fluoridionen aufweisen als die flexibleren Methylen- und Dimethylen-verbrückten Bisstannane.<sup>[12]</sup> Ein vergleichbares Verhalten zeigen 1,2-Disilylbenzol<sup>[13]</sup> oder 1,8-Naphthalindiboran-Derivate.<sup>[14]</sup> Als weitere Beispiele starrer Di-Lewis-Säuren können 1,2-Dimercuriobenzole<sup>[15]</sup> oder ein 1,8-Biphenylen-basierter Tetragallium-Makrocyclus genannt werden.<sup>[9e]</sup>

Vor einiger Zeit gelang uns durch Umsetzung mit  $ER_3$  [mit E = Al, Ga (1), In; R = Me, Et] in Alkaneliminierungsreaktionen die zweifache terminale Metallierung von 1,8-Diethinylanthracen. Die erhaltenen metallierten Produkte zeigen im Festkörper eine dimere Struktur mit einer Verbrückung über  $[\equiv C(E)_2 C \equiv]$ -Einheiten (Schema 1).<sup>[16]</sup> Generell besteht bei 1,8-substituierten Anthracenen die Möglich-



**Schema 1.** Anthracen-basierte zweizählige Bor-Lewis-Säure **A**<sup>[7a]</sup> und Digallium-Verbindung **1**<sup>[16]</sup> sowie schematische Darstellungen von Wirt- und Gast-Komponenten und die im Festkörper gefundene dimere Struktur der Wirt-Verbindung 1,8-Bis[(diethylgallanyl)ethinyl]anthracen (1; rechts).

[\*] M. Sc. J.-H. Lamm, B. Sc. P. Niermeier, Dr. A. Mix, Dr. J. Chmiel, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. N. W. Mitzel  
Lehrstuhl für Anorganische Chemie und Strukturchemie  
Universität Bielefeld, Fakultät für Chemie  
Universitätsstraße 25, 33615 Bielefeld (Deutschland)  
E-Mail: mitzel@uni-bielefeld.de  
Homepage: <http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/>

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keit, reaktive funktionelle Gruppen an einem starren organischen Grundgerüst gerichtet zu fixieren.

Erste Wirt-Gast-Untersuchungen mit Lewis-aciden Rezeptoren auf Basis von 1,8-Dialkylanthracenen wurden 1989 von Katz durchgeführt. Die von ihm verwendete zwei-zählige Bor-Lewis-Säure **A** (Schema 1, B...B-Abstand ca. 5 Å) bildet mit Methylpyrimidin-Derivaten Komplexe, deren Bildung in NMR-Titrationsexperimenten nachgewiesen wurde. Die Ergebnisse stützen sich dabei auf kleine Veränderungen in der  $^1\text{H}$ -NMR-Verschiebung der Wirt-Verbindung von maximal  $\delta = 0.08$  ppm.<sup>[7a]</sup>

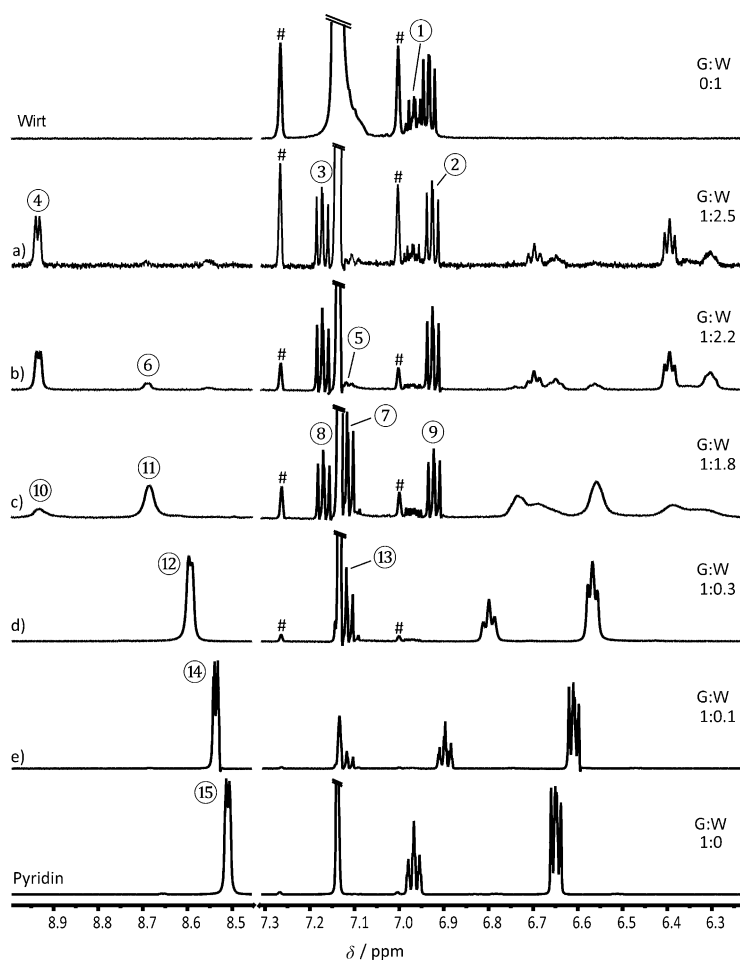
Im Rahmen unserer Untersuchungen zur Wirt-Gast-Komplex-Bildung der Digallium-Verbindung **1** beobachteten wir bei ähnlichen Experimenten oftmals komplexe  $^1\text{H}$ -NMR-Spektren wie solche, die in Abbildung 1 c gezeigt sind. Diese auf den ersten Blick wenig aussagekräftigen Resultate ließen uns daran zweifeln, dass die Bindung N-heterocyclischer Gäste durch den Wirt **1** ähnlich unkompliziert abläuft, wie sie für die Dibor-Verbindung **A** beschrieben wurde, nämlich in Form einer einfachen, chelatisierenden Komplexierung. Auch wenn eine Identifizierung der Wirt-Gast-Addukte durch eine röntgenkristallographische Analyse von Einkristallen in

diesem Zusammenhang erstrebenswert wäre, könnte es sein, dass sich die Ergebnisse nicht direkt auf die offensichtlich komplexeren Abläufe in Lösung übertragen lassen. Da auch einfache NMR-Titrationsexperimente (mit Pyridin; Abbildung 1) die Vorgänge nicht zufriedenstellend aufklären konnten, bedurfte es einer anspruchsvolleren Herangehensweise an das Problem, die wir in einer Kombination von NMR-Titration und Diffusions-NMR-spektroskopischen Experimenten fanden. Die NMR-Diffusometrie ist eine potente Methode, um in Lösung befindliche Gemische mehrerer Komponenten durch eine gepulste Feldgradienten-Technik zu untersuchen. Anwendung findet diese Methode beispielsweise bei der Größenbestimmung von Molekülen,<sup>[17]</sup> der Aufklärung von Reaktionsmechanismen,<sup>[18]</sup> zum Nachweis von Natriumdodecylsulfat-Micellen-Peptid-Assoziationen<sup>[19]</sup> oder zur Untersuchung von Komplexierungsphänomenen in Lösung.<sup>[20]</sup> Während der Diffusions-NMR-spektroskopischen Experimente sorgen entlang der  $z$ -Achse angelegte Feldgradienten für eine Spinmarkierung der Moleküle und liefern, nach zeitaufgelöster Detektion, die Diffusionskoeffizienten  $D$  der einzelnen Komponenten des untersuchten Gemisches. Diese sind gemäß der Stokes-Einstein-Gleichung umgekehrt proportional zum entsprechenden hydrodynamischen Radius  $r_s$ , sind also ein Maß für die Größe des Moleküls in Lösung.<sup>[21]</sup>

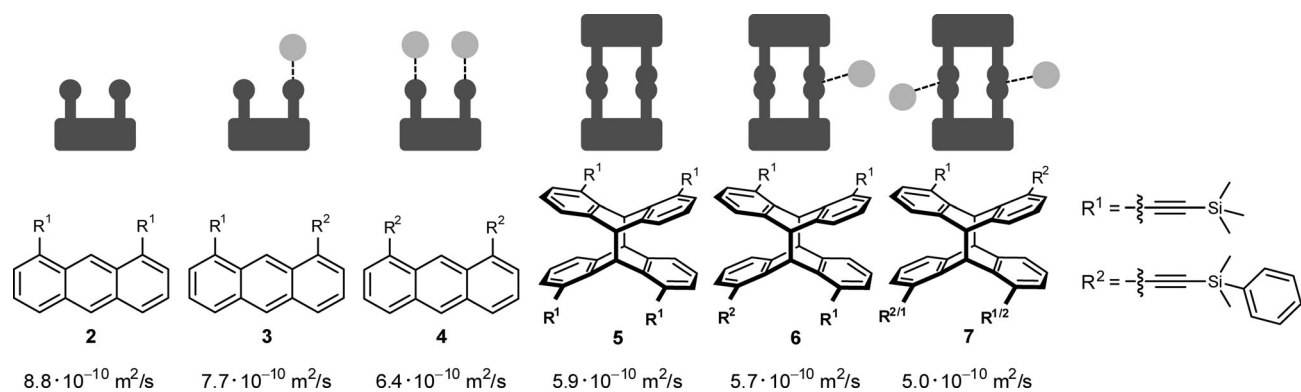
Da die auf diese Weise erhaltenen Diffusionskoeffizienten  $D$  sehr stark von Größe und Gestalt der untersuchten Systeme in Lösung abhängen, ist eine zuverlässige Interpretation der erhaltenen Daten nur durch Vergleich mit denjenigen geeigneter Referenzverbindungen möglich. Deren Strukturen sollten sicher bekannt und ähnlich zu denen der zu untersuchenden Spezies sein. Außerdem ist es zwingend erforderlich, dass alle Werte für  $D$  unter gleichen äußeren Bedingungen (Lösungsmittel, Temperatur) aufgenommen werden. Folglich bestand ein Großteil dieser Arbeit aus der Synthese diverser Referenzverbindungen, die in Größe und Gestalt annähernd mit möglichen Wirt-Aggregaten und Wirt-Gast-Strukturen übereinstimmen. In Schema 2 sind die entsprechenden Referenzverbindungen dargestellt, deren Synthesen kurz unter Lit. [22] und ausführlich in den Hintergrundinformationen beschrieben werden.

Abbildung 1 zeigt die  $^1\text{H}$ -NMR-Spektren verschiedener Gemische der Digallium-Wirt-Verbindung **1** (W) mit zunehmendem Anteil an Pyridin (G; Abbildung 1 a–c) sowie die Spektren von jeweils reinem W und G. Bedingt durch die geringe Löslichkeit des Wirtes **1** in  $\text{C}_6\text{D}_6$  wurden die Verhältnisse von Wirt und Gast durch Integration der NMR-Signale ermittelt. Eine Zuordnung der Resonanzen verschiedener Wirt-Gast-Addukte erfolgte durch die Bestimmung der jeweiligen Diffusionskoeffizienten  $D$  mit NMR-Diffusometrie und den Vergleich der so erhaltenen Werte mit denen der in Schema 2 gezeigten Referenzverbindungen.

Das  $^1\text{H}$ -NMR-Spektrum der Wirt-Verbindung **1** zeigt für die Anthracenprotonen H3 und H6 ein



**Abbildung 1.**  $^1\text{H}$ -NMR-Spektren (600 MHz, 294 K) der Wirt-Verbindung **1**, verschiedener Wirt-Pyridin-Mischungen und von reinem Pyridin in  $\text{C}_6\text{D}_6$  ( $\delta = 7.13$  ppm); # kennzeichnet die  $^{13}\text{C}$ -Satelliten von  $\text{C}_6\text{D}_6$  (abgeschnittenes Signal).



**Scheme 2.** Mögliche Wirt-Aggregate und Wirt-Pyridin-Strukturen in Lösung (oben) sowie die speziell synthetisierten Referenzverbindungen mit ihren entsprechenden Diffusionskoeffizienten  $D$ , gemessen in  $\text{C}_6\text{D}_6$  bei 294 K (unten). Von links nach rechts:  $\text{W}_1$ ,  $\text{W}_1\text{G}_1$ ,  $\text{W}_1\text{G}_2$ ,  $\text{W}_2$ ,  $\text{W}_2\text{G}_1$ ,  $\text{W}_2\text{G}_2$  mit W: 1; G: Pyridin. Die Referenzverbindungen können analog auch zur Untersuchung der Pyrimidin-Komplexierung herangezogen werden.

Dublett von Dubletts bei  $\delta = 6.92$  ppm (in Abbildung 1 mit ② gekennzeichnet). Die Probe enthält jedoch auch sehr geringe Verunreinigungen durch nicht- und monometalliertes 1,8-Diethinylanthracen [Signale bei  $\delta = 6.97$  ppm (①)], die sich im Unterschied zur zweifach metallierten Spezies **1** sehr gut in  $\text{C}_6\text{D}_6$  lösen lassen; die über 99-prozentige Reinheit der Wirt-Verbindung wurde durch  $^1\text{H-NMR}$ -Spektroskopie in  $[\text{D}_8]\text{THF}$  bestätigt. Der Diffusionskoeffizient von **1** wurde mit  $D = 5.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  bestimmt und ist somit identisch mit dem der  $\text{W}_2$ -Referenzverbindung **5** ( $D = 5.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), aber nicht vergleichbar mit dem von **2** ( $D = 8.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), der Modellverbindung einer monomeren Wirt-Struktur. Die Befunde lassen folglich darauf schließen, dass der Wirt **1** in Benzol wie im Festkörper als Dimer vorliegt.<sup>[16]</sup>

Die Zugabe einer kleinen Menge der Gast-Komponente Pyridin (G/W-Verhältnis = 1:2.5) führt zur Entstehung eines neuen Dubletts von Dubletts bei  $\delta = 7.17$  ppm (③) und zu einer deutlichen Verschiebung der Pyridin-Signale, was auf die Bildung eines neuen Anthracen-haltigen Pyridin-Komplexes hindeutet. Dieser weist einen Diffusionskoeffizienten von  $D = 5.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  auf, der in der gleichen Größenordnung liegt wie jener des Wirt-Dimers  $\text{W}_2$ . Auch wenn der bei den  $D$ -Messungen auftretende Fehler mit  $0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  angenommen wird, lässt die Tatsache, dass sich eine neue Spezies mit einem tendenziell kleineren Diffusionskoeffizienten gebildet hat, den Schluss zu, dass der neu entstandene Komplex geringfügig größer sein muss als das Wirt-Dimer  $\text{W}_2$ . Ein Vergleich mit den  $D$ -Werten der  $\text{W}_1\text{G}_1$ - (**3**;  $D = 7.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ),  $\text{W}_1\text{G}_2$ - (**4**;  $D = 6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) und  $\text{W}_2\text{G}_2$ -Referenzverbindungen (**7**;  $D = 5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) lässt die Bildung eines Adduktes aus einem Wirt-Dimer und einem Pyridin-Molekül ( $\text{W}_2\text{G}_1$ -Struktur) als am wahrscheinlichsten erscheinen. Gestützt wird diese Annahme durch den Diffusionskoeffizienten der entsprechenden  $\text{W}_2\text{G}_1$ -Referenzverbindung **6** ( $D = 5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), der mit dem des Wirt-Gast-Komplexes die beste Übereinstimmung zeigt. Ebenso deutet der  $D$ -Wert, der über das mit ④ gekennzeichnete Signal der *ortho*-Protonen der Gast-Komponente bestimmt wurde, auf eine Komplexierung des Pyridins hin. Er weicht mit  $D = 6.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  erheblich vom Wert der ungebundenen Gast-Verbindung ⑬ ab ( $D = 22.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), ist aber ver-

gleichbar mit dem  $D$ -Wert von ③ ( $D = 5.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) und dem der  $\text{W}_2\text{G}_1$ -Referenzverbindung **6**. Der geringfügig größere Diffusionskoeffizient kann durch schnelle Dissoziationsprozesse erklärt werden. Dabei führt der Wirt-Überschuss im System dazu, dass stets ein Großteil des Gastes komplexiert vorliegt und der  $D$ -Wert des ungebundenen Pyridins nur zu einem geringen Maße zum messbaren gemittelten Diffusionskoeffizienten beiträgt. Die dynamischen Prozesse bei der Komplexierung der N-heterocyclischen Gast-Verbindungen wurden beispielhaft bei einer 1:4-Mischung von **1** und Pyrimidin durch VT-NMR-spektroskopische Experimente (VT = variable Temperatur) in  $[\text{D}_8]\text{Toluol}$  nachgewiesen, indem auch bei 203 K kein zweiter Satz an Gast-Signalen beobachtet werden konnte (Details siehe Hintergrundinformationen).

Bei einer leichten Erhöhung der Gast-Konzentration auf ein G/W-Verhältnis von 1:2.2 ist außer einem Signal einer neuen Wirt-Komponente ⑤ auch ein neues Pyridin-Signal (⑥) zu verzeichnen, das gegenüber dem von freiem Pyridin zu tiefem Feld verschoben ist. Die Intensitäten dieser Signale nehmen stark zu, wenn der Gast-Anteil auf G/W = 1:1.8 weiter erhöht wird, sodass Signal ⑦ bei  $\delta = 7.12$  ppm ( $D = 6.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) unter diesen Umständen von der dominierenden Spezies in Lösung hervorgerufen wird. Interessanterweise liegen bei diesem Wirt-Gast-Verhältnis ebenfalls nicht unbedeutende Mengen an  $\text{W}_2\text{G}_1$ -Komplex (⑧) und  $\text{W}_2$ -Dimer  $\text{W}_2$  (⑨) vor. Der für das neue Signal ⑦ bestimmte Diffusionskoeffizient ist mit dem der Referenzverbindung **4** ( $D = 6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) gut vergleichbar und macht die Bildung eines  $\text{W}_1\text{G}_2$ -Komplexes wahrscheinlich. Bei einem Überschuss an Gast (Abbildung 1 d,e) verbleibt einzig der  $\text{W}_1\text{G}_2$ -Komplex in Lösung (⑬).

Die bis hier getroffenen Aussagen stützen sich vornehmlich auf die Auswertung der Wirt-Signale, lassen sich aber durch die Analyse der Gast-Signale bestätigen. So ist zu beobachten, dass die gemessenen Gast-Diffusionskoeffizienten mit steigender Pyridin-Konzentration stetig ansteigen. Während für Signal ⑩ in der W/G-Mischung von 1:1.8 (Abbildung 1 c) ein Wert von  $D = 6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  gemessen wird (vergleichbar mit dem entsprechenden Wert aus Abbildung 1 a), kann aus dem bei  $\delta = 8.69$  ppm neu entstandenen



Signal ⑩ ein Wert von  $D = 7.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  ermittelt werden, was für die Bildung einer Spezies mit einem geringeren hydrodynamischen Radius  $r_s$  spricht. Bei weiterer Erhöhung des Pyridin-Anteils ist lediglich ein Satz an Pyridin-Signalen zu erkennen (Abbildung 1 d,e), wobei die entsprechenden Diffusionskoeffizienten von  $D = 10.5 \times 10^{-10}$  (⑫) zu  $18.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (⑭) ansteigen und gegen den Wert von nicht komplexiertem Pyridin (⑮;  $D = 22.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) streben. Dies ist wiederum mit einem Austausch der gebundenen und freien Gast-Moleküle zu erklären, der schneller abläuft als die Zeitskala des NMR-spektroskopischen Experimentes.

Zusätzlich zur Umsetzung von **1** mit Pyridin untersuchten wir in analoger Weise auch die Komplexbildung von Pyrimidin, einer Lewis-Base mit zwei N-Donoratomen. Im Unterschied zur Umsetzung mit Pyridin erwarteten wir hier die Bildung eines  $W_1G_1$ -Komplexes (Schema 2). Dabei sollte es über zwei Ga-N-Bindungen zu einer chelatisierenden Koordination eines Gast-Moleküls an ein Wirt-Monomer kommen, wie es Katz bereits 1989 postuliert hatte.<sup>[7a]</sup> Tatsächlich wird ein vollständig anderes Verhalten beobachtet, wenn **1** anstelle von Pyridin mit Pyrimidin umgesetzt wird (Tabelle 1).

**Tabelle 1:** Ausgewählte Diffusions-NMR-spektroskopische Daten der Umsetzung von **1** mit Pyrimidin.<sup>[a]</sup>

G/W	$D$ (Wirt) <sup>[b]</sup>	$D$ (Gast) <sup>[b]</sup>
1:1.17	6.9	7.2
1:1.14	6.9	7.1
1:1.10	7.1	7.2
1:0.38	7.0	13.7
1:0.16	6.8	17.9
1:0.06	6.6	19.9

[a] Vollständige Daten in Tabelle S5 der Hintergrundinformationen.

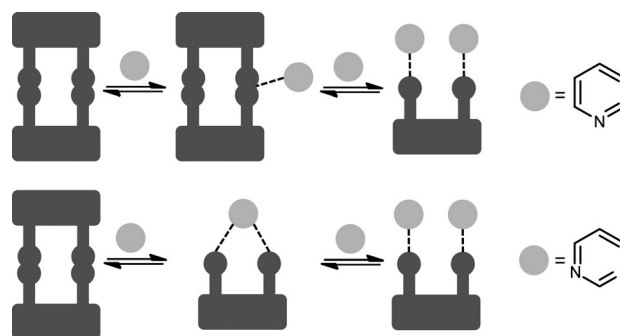
[b]  $D$  [ $10^{-10} \text{ m}^2 \text{ s}^{-1}$ ], gemessen in  $C_6D_6$  bei 294 K.

Bei Versetzen mit einer substöchiometrischen Menge an Pyrimidin (G/W-Verhältnis 1:1.17) wird die Bildung eines Anthracen-haltigen Komplexes mit einem Diffusionskoeffizienten von  $D = 7.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  beobachtet. Ein Vergleich mit den  $D$ -Werten der Referenzverbindungen  $W_1G_1$  (**3**;  $D = 7.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ),  $W_2G_1$  (**6**;  $D = 5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , der intermediär gebildeten Spezies bei der substöchiometrischen Umsetzung von **1** mit Pyridin) und  $W_2G_2$  (**7**;  $D = 5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) lässt vermuten, dass ein Addukt aus einem Wirt-Monomer und einem Pyrimidin-Molekül ( $W_1G_1$ -Struktur mit einem chelatisierend gebundenen Pyrimidin) entstanden sein muss. Die geringe Abweichung vom Diffusionskoeffizienten der Referenzverbindung **3** erklärt sich durch die Tatsache, dass sich **3** besser zur Beschreibung eines einzähnig gebundenen Gastes an ein Wirt-Monomer eignet. Der erhaltene Wirt-Gast-Komplex ist offensichtlich sehr stabil, da auch bei einer Erhöhung des Pyrimidinanteils keine neuen Anthracen-haltigen Spezies in Lösung nachweisbar sind. Die Diffusionskoeffizienten, die für den einfachen Signalsatz der Gast-Komponente bestimmt wurden, befinden sich, solange der Wirt im Überschuss vorliegt, in derselben Größenordnung wie die der entsprechenden Wirt-Signale. Erst ab einem G/W-Verhältnis von 1:0.38 (und höher) steigt der Diffusionskoeffizient der Gast-Komponente stark an (Tabelle 1). Ähnlich

wie im bereits beschriebenen Fall der Pyridin-Komplexierung nähern sich auch hier die  $D$ -Werte denen von freiem Pyrimidin ( $D = 20.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), was auf einen schnellen Austausch von gebundenem und freiem Gast schließen lässt.

Wird **1** mit einem Überschuss an Pyrimidin versetzt, werden tendenziell kleinere Diffusionskoeffizienten für die Wirt-Verbindung gemessen, was auf die Bildung eines  $W_1G_2$ -Komplexes in Lösung hindeutet (Referenzverbindung **4**;  $D = 6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). In diesem Fall würde jedes der beiden Pyrimidin-Moleküle über ein Stickstoffatom an die Wirt-Komponente binden.

Die zweizähnige Gallium-Lewis-Säure **1** zeigt bei der Komplexbildung der mono- und difunktionellen N-heterocyclischen Gast-Moleküle Pyridin und Pyrimidin ein stark unterschiedliches Verhalten. Die Umsetzung mit Pyridin erwies sich als deutlich komplizierter als zunächst angenommen und führte intermediär zur Bildung unvorhergesehener Wirt-Gast-Komplexe. Obwohl die hier verwendete Kombination aus NMR-Titration und NMR-Diffusometrie keine direkten Aussagen über die exakten Strukturen in den dynamischen Systemen ermöglicht, können aus den experimentellen Daten durch Vergleich mit den Diffusionskoeffizienten der entsprechenden Referenzverbindungen Rückschlüsse auf das Verhalten in Lösung gezogen werden. Schema 3 fasst die Ergebnisse in graphischer Form zusammen.



**Schema 3.** Verschiedene beobachtete Komplexbildungsphänomene im Fall von Pyridin (oben) und Pyrimidin (unten) als Lewis-basische Gast-Komponenten.

Pyridin koordiniert zunächst an ein Wirt-Dimer, bevor das Aggregat aufbricht und sich ein Komplex aus einem Wirt-Monomer und zwei Pyridin-Molekülen bildet. In einem gewissen Konzentrationsverhältnis stehen alle drei Spezies ( $W_2$ ,  $W_2G_1$  und  $W_1G_2$ ) in einem dynamischen Gleichgewicht miteinander. Im Unterschied dazu konnte bei der Umsetzung mit Pyrimidin kein experimenteller Hinweis für das Entstehen eines Wirt-Dimer-Pyrimidin-Aggregates gefunden werden. Stattdessen wurde die direkte intermediäre Bildung eines – möglicherweise – chelatisierend gebundenen Komplexes aus einer jeweils difunktionellen Wirt- und Gast-Komponente beobachtet. Diese  $W_1G_1$ -Struktur ist auch bei ansteigenden Gast-Konzentrationen noch die dominierende Spezies in der Lösung, wobei die experimentellen Befunde bei einem größeren Pyrimidin-Überschuss (wie auch im Fall von Pyridin als Gast) auf das Entstehen von Komplexen schließen lassen, bei

denen zwei Gast-Moleküle an einem Wirt-Monomer gebunden sind ( $W_1G_2$ -Spezies).

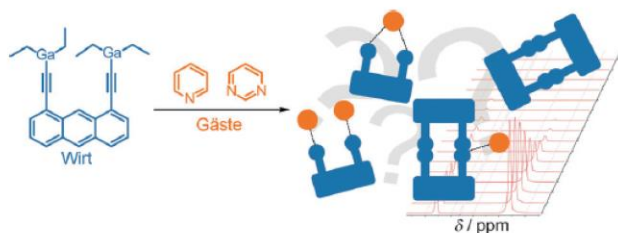
Generell liefert die in dieser Arbeit erstmals durchgeführte Kombination aus NMR-Titration und Diffusions-NMR-Spektroskopie neuartige und detaillierte Einblicke in die Chemie der molekularen Erkennung chelatisierender Lewis-Säuren. In Verbindung mit der gezielten Synthese maßgeschneiderter Referenzverbindungen gelang es, durch Vergleich der Diffusionskoeffizienten den Bildungsmechanismus von Wirt-Gast-Komplexen aufzuklären und die sich intermediär bildenden Komplexe zu identifizieren. Eine Übertragung dieser Methode auf andere Systeme verspricht, besonders unter Zuhilfenahme geeigneter Referenzverbindungen, genauere Erkenntnisse zum Ablauf von (Komplexierungs-)Phänomenen in Lösung.

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**Stichwörter:** Anthracene · Diffusions-NMR-Spektroskopie · Gallium · Poly-Lewis-Säuren · Wirt-Gast-Systeme

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- [22] Die Referenzverbindungen **2–4** (Schema 2) wurden in guten bis moderaten Ausbeuten durch Nickel-katalysierte Kumada-Kreuzkupplung erhalten, wobei [(Trimethylsilyl)ethynyl]magnesiumbromid oder {[Dimethyl(phenyl)silyl]ethynyl}magnesiumbromid<sup>[23]</sup> zur Funktionalisierung von 1,8-Dichloranthracen genutzt wurde.<sup>[16,24]</sup> **2–4** wurden mit NMR-Spektroskopie, Massenspektrometrie und teilweise durch Röntgenstrukturanalyse eindeutig charakterisiert. Die Wirt-Dimer-Referenzverbindung **5** wurde durch Photodimerisierung (365 nm) einer Lösung von **2** in  $C_6D_6$  hergestellt, während die  $W_2G_2$ - (**7**) und  $W_2G_1$ -Referenzverbindung (**6**) durch Bestrahlung von NMR-Proben von **3** bzw. einer 1:1-Mischung von **2** und **3** erhalten wurden. **5–7** wurden nicht als reine Substanzen isoliert, sondern einzig zur Bestimmung der jeweiligen Diffusionskoeffizienten generiert. In diesem Fall kann der Diffusionskoeffizient des asymmetrisch substituierten **3** mit der  $W_1G_1$ -Struktur (ein N-heterocyclisches Gast-Molekül, koordiniert an ein Wirt-Monomer **1**) verglichen werden. **4** ist ein ideales Referenzsystem für eine  $W_1G_2$ -Struktur. **2** repräsentiert die monomere Wirt-Struktur ( $W_1$ ), und **5** (durch UV-Bestrahlung von **2** erhalten) kann als Referenz für ein Wirt-Dimer ( $W_2$ ) angesehen werden, das auch im Festkörper angegriffen wird.<sup>[16]</sup>
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Die dynamische Wirt-Gast-Komplex-Bildung wurde unter Verwendung einer neuartigen Kombination aus NMR-Titration und Diffusions-NMR-Spektroskopie untersucht. Der Wirt war hierbei das zweizählige 1,8-Bis[(diethylgallanyl)ethi-

nyl]anthracen, und als Gast-Komponenten wurden Pyridin und Pyrimidin verwendet. Die genaue Auswertung der Diffusions-NMR-spektroskopischen Experimente erforderte die gezielte Synthese maßgeschneiderter Referenzverbindungen.

#### Wirt-Gast-Chemie

J.-H. Lamm, P. Niermeier, A. Mix,  
J. Chmiel, B. Neumann, H.-G. Stammer,  
N. W. Mitzel\* \_\_\_\_\_ 8072–8076

Aufklärung des Bildungsmechanismus von Wirt-Gast-Komplexen und Identifizierung von Intermediaten mithilfe von NMR-Titration und Diffusions-NMR-Spektroskopie



## **Publikation 2b**

# **Mechanism of Host-Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy**

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin  
Chmiel, Beate Neumann, Hans-Georg Stammer, Norbert W. Mitzel

*Angew. Chem. Int. Ed.* **2014**, *53*, 7938–7942.



# Mechanism of Host–Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy\*\*

Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, and Norbert W. Mitzel\*

Dedicated to Professor Lothar Weber on the occasion of his 70th birthday

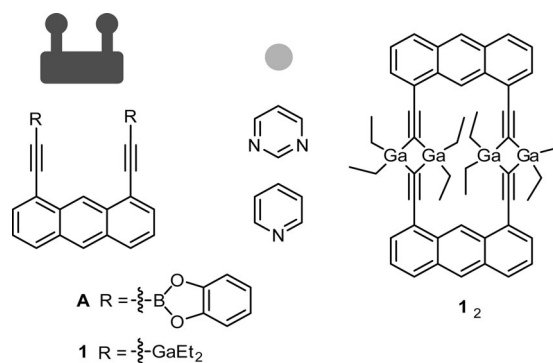
**Abstract:** The formation of host–guest (H–G) complexes between 1,8-bis[(diethylgallanyl)ethynyl]anthracene (H) and the N-heterocycles pyridine and pyrimidine (G) was studied in solution using a combination of NMR titration and diffusion NMR experiments. For the latter, diffusion coefficients of potential host–guest structures in solution were compared with those of tailor-made reference compounds of similar shape (synthesized and characterized by NMR, HRMS, and in part XRD). Highly dynamic behavior was observed in both cases, but with different host–guest species and equilibria. With increasing concentrations of the pyridine guest, the equilibrium  $H_3 \rightleftharpoons H_2 \kappa^1-G_1 \rightleftharpoons HG_2$  is observed (in the second step a host dimer coordinates one guest molecule); for pyrimidine the equilibrium  $H_2 \rightarrow H_1 \kappa^2-G_1 \rightleftharpoons HG_2$  is observed (the formation of a 1:1 aggregate is the second step).

Host–guest chemistry has become a well-established part of macromolecular chemistry since Pedersen reported the formation of potassium crown ether complexes in 1967.<sup>[1]</sup> Today more than 5000 crown compounds are known.<sup>[2]</sup> Their complexation principle was extended to three-dimensional host systems such as cryptands.<sup>[3]</sup> In contrast to this well-understood and extensively studied cation complexation (Lewis acids) by poly-Lewis bases, the inverse situation with poly-Lewis acids as host compounds is less well explored. This might be due to the high reactivity of many Lewis acidic compounds and a distinct paucity of donor-free frameworks to carry suitable Lewis acid functions. Known examples of such host systems include species based on silicon,<sup>[4]</sup> tin,<sup>[5]</sup>

mercury<sup>[6]</sup> as well as boron,<sup>[6d,7]</sup> aluminum,<sup>[8]</sup> gallium,<sup>[8c,d,9]</sup> and indium<sup>[10]</sup> as Lewis acid functions.

Common to most examples are acid functions attached to a more or less flexible organic framework. Flexible receptors are capable of binding a wide range of guest species, but this flexibility is equipollent to low selectivity. However, there are also some systems with rigid frameworks. For instance the rigid 1,2-bis(organostannyl)benzene hosts have been demonstrated to be superior fluoride acceptors<sup>[11]</sup> than the less rigid methylene- and dimethylene-bridged bisstannanes.<sup>[12]</sup> Similar results exist for 1,2-disilylbenzenes<sup>[13]</sup> and 1,8-naphthalene-diboranes.<sup>[14]</sup> Other examples of rigid bis-Lewis acids are the 1,2-dimercuriobenzenes<sup>[15]</sup> and a 1,8-biphenylene-based tetragallium compound.<sup>[9e]</sup>

Recently, we reported the double metalation of 1,8-diethynylantracene through alkane-elimination reactions by conversion of the corresponding dialkynes with  $ER_3$  [with E = Al, Ga (1), In; R = Me, Et]. In their crystals these metalated compounds are dimers linked by  $[C(E)_2C(E)]$  units (Scheme 1).<sup>[16]</sup>



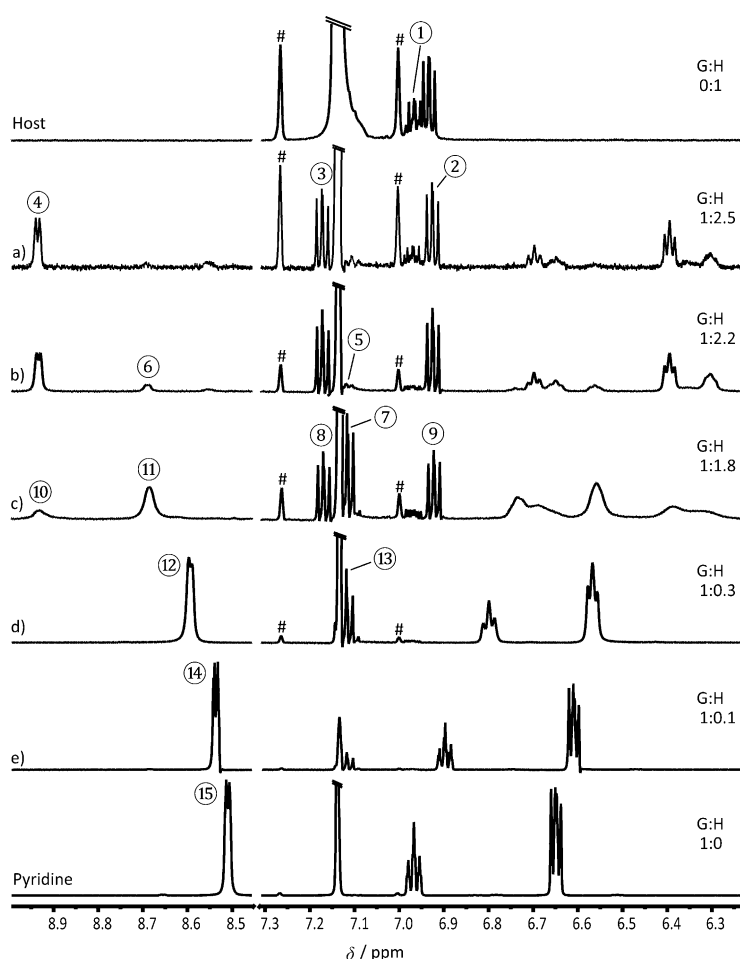
**Scheme 1.** The anthracene-based bidentate boron Lewis acid **A**<sup>[7a]</sup> and the digallium compound **1**,<sup>[16]</sup> as well as schematic representations of host and guest molecules and the dimeric structure of host compound **1** in the solid state (right).

1,8-Substituted anthracenes provide rigid organic frameworks with the opportunity to orientate reactive sites in a defined direction. Their use as receptor molecules in host–guest experiments was first explored by Katz in 1989.<sup>[7a]</sup> His bidentate boron Lewis acid **A** (Scheme 1, B···B distance ca.

[\*] M. Sc. J.-H. Lamm, B. Sc. P. Niermeier, Dr. A. Mix, Dr. J. Chmiel, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. N. W. Mitzel  
Lehrstuhl für Anorganische Chemie und Strukturchemie  
Universität Bielefeld, Fakultät für Chemie  
Universitätsstrasse 25, 33615 Bielefeld (Germany)  
E-mail: mitzel@uni-bielefeld.de  
Homepage: <http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/>

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**Figure 1.**  $^1\text{H}$  NMR spectra (600 MHz, 294 K) of host compound **1**, different host-pyridine mixtures, and pure pyridine in  $\text{C}_6\text{D}_6$  ( $\delta = 7.13$  ppm); # denotes  $^{13}\text{C}$  satellites of  $\text{C}_6\text{D}_6$  (cut-off signal).

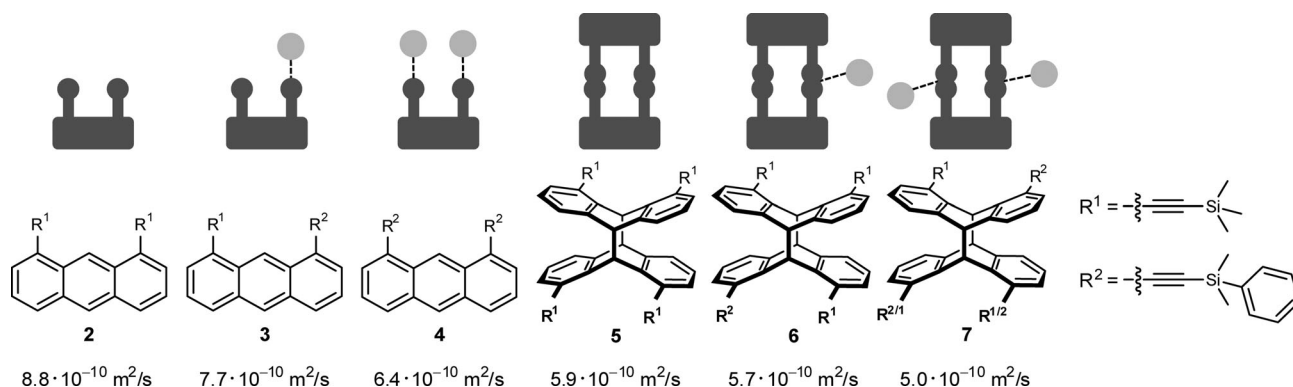
$5 \text{ \AA}$ ) forms complexes with methylpyrimidine derivatives and has been studied by NMR titration experiments, but the results were derived from very small changes in  $^1\text{H}$  NMR shifts (max.  $\Delta\delta = 0.08$  ppm) of the host component.<sup>[7a]</sup>

During our studies of the formation of host-guest complexes with the digallium compound **1** we regularly observed

complex  $^1\text{H}$  NMR spectra like those shown in Figure 1c). On first glance these seemed to be poor in information. This raised doubts that the adduct formation proceeded as simply as previously assumed and that **1** behaved as a chelating Lewis acid as described for compound **A**. Though the isolation of a product by crystallization might be desirable for structure elucidation in this context, it would not inevitably be a good model for the solution state, the most relevant for molecular recognition. Because simple titration experiments (with pyridine: Figure 1) were not conclusive, the situation demanded a more sophisticated approach of analysis.

We found that the combination of NMR titration with diffusion NMR experiments is a novel methodological approach to characterize host-guest complexes in solution. Diffusion NMR methods are powerful tools for the analysis of compound mixtures in solution by pulsed field gradient techniques. They are applied in areas such as molecular-size determination<sup>[17]</sup> and for elucidating reaction mechanisms,<sup>[18]</sup> sodium dodecylsulfate micelle-peptide association,<sup>[19]</sup> and other complexation phenomena in solution.<sup>[20]</sup> During diffusion NMR experiments field gradients along the  $z$ -axis allow for spatially selective spin-labeling and after time-dependent detection, diffusion coefficients  $D$  can be extracted individually for every compound in a mixture. According to the Stokes-Einstein equation,  $D$  is reciprocally proportional to the hydrodynamic radius  $r_s$ , that is, the size of the molecule in solution.<sup>[21]</sup>

However, the self-translational diffusion coefficients  $D$  are strongly dependent on the shape and size of the investigated systems. For a thorough interpretation of the hydrodynamic radius value it is therefore necessary to compare the results with values of suitable model systems, preferably of well-known shape similar to that of the analytes and under the same experimental conditions. Consequently, the most time-consuming part of this work was the syntheses of such reference compounds with suitable geometry to model a couple of possible host aggregates and host-guest complexes. They are



**Scheme 2.** Possible host aggregates and host-pyridine structures in solution (top) and the corresponding reference compounds with their diffusion coefficients  $D$ , measured in  $\text{C}_6\text{D}_6$  at 294 K (bottom). From left to right:  $\text{H}_1$ ,  $\text{H}_1\text{G}_1$ ,  $\text{H}_1\text{G}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{G}_1$ ,  $\text{H}_2\text{G}_2$  with  $\text{H}$ : **1**;  $\text{G}$ : pyridine. The models also serve for the complexation of pyrimidine.

shown in Scheme 2; their syntheses are briefly outlined in reference [22] and in detail in the Supporting Information.

Figure 1 shows the changes in the  $^1\text{H}$  NMR spectra of mixtures of the digallium compound **1** (host, H) with increasing concentrations of pyridine (guest, G) as well as spectra of pure H and G solutions. Due to the poor solubility of **1** in  $[\text{D}_6]$ benzene the reactant ratios in solution were measured by integration of the NMR signals. An assignment of resonances to host–guest complexes was undertaken by determination of the diffusion coefficients  $D$  associated with each signal. Scheme 2 provides a correlation of these diffusion coefficients with reference structures. The following description starts with host compound **1** and follows the changes in the spectra upon addition of increasing amounts of pyridine.

The  $^1\text{H}$  NMR spectrum of the pure host **1** shows doublets of doublets, induced by the anthracene protons H3 and H6 at  $\delta = 6.92$  ppm (signal labeled ②). Note that this spectrum of the sparingly soluble **1** contains enriched traces of non- and monometalated 1,8-diethynylanthracene [signals at  $\delta = 6.97$  ppm (①)] due to their better solubility; the purity of **1** determined by  $^1\text{H}$  NMR analysis in  $[\text{D}_8]$ THF solution was better than 99%. The diffusion coefficient of **1**,  $D = 5.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , is the same as that of reference compound **5** ( $D = 5.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), but markedly deviates from that of **2** ( $D = 8.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), the reference for a monomeric host structure. This proves that host **1** exists as dimers in benzene solution as well as in the solid state.<sup>[16]</sup>

The addition of a small amount of the guest pyridine (molar ratio G/H = 1:2.5) leads to a new doublet of doublets at  $\delta = 7.17$  ppm (③) and to significantly shifted pyridine resonances. This corresponds to the formation of a new anthracene-containing pyridine complex. Its diffusion coefficient measured at signal ③ at  $D = 5.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  is almost identical to that of host dimer  $\text{H}_2$  (note that the estimated error in  $D$  is about  $0.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). The fact that it is a new compound and the tendency to a smaller  $D$  indicates that this species should be slightly larger than that of the host dimer  $\text{H}_2$ . If one compares this value to the diffusion coefficients of reference compounds  $\text{H}_1\text{G}_1$  (**3**,  $7.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ),  $\text{H}_1\text{G}_2$  (**4**,  $6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), and  $\text{H}_2\text{G}_2$  (**7**,  $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) this adduct is likely to consist of one pyridine guest molecule associated with a host dimer ( $\text{H}_2\text{G}_1$  structure). Further support for this argument is the  $D$  value of reference **6** ( $5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), which is the closest match. Additional confirmation stems from the diffusion coefficient of signal ④ ( $6.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) belonging to the *ortho*-protons of pyridine. It is significantly different from that of free pyridine (⑤ ( $22.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ )), but in good agreement with that of ③ ( $5.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and that of  $\text{H}_2\text{G}_1$  reference **6**. It demonstrates that this pyridine unit belongs to the  $\text{H}_2\text{G}_1$  structure. The slightly higher  $D$  value measured at resonance ④ is explicable by rapid dissociation. Due to the excess of host, the majority of pyridine is present in a bound state on time average so that the diffusion coefficient of the free pyridine contributes only to a small extent. The presence of this complexation dynamics was proven by variable-temperature (VT) NMR measurements of a 1:4 mixture of **1** and pyrimidine in  $[\text{D}_8]$ toluene with no indication of a second set of guest resonances at temperatures as low as 203 K (for details see the Supporting Information).

In Figure 1b the G/H ratio is slightly increased to 1:2.2. Under these conditions resonance ⑤ of a new host–guest species is observed. Also observed is a new set of pyridine resonances (⑥), which again shifted far downfield relative to that of free pyridine. These new resonances become much more intense when the G/H ratio is increased to 1:1.8 (Figure 1c). Under these conditions signal ⑦ at  $\delta = 7.12$  ppm ( $D = 6.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) belongs to the main component in the mixture besides  $\text{H}_2\text{G}_1$  (⑧ and ⑩) and the host dimer  $\text{H}_2$  (⑨). The  $D$  value of signal ⑦ is similar to that determined for reference **4** ( $6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and makes an  $\text{H}_1\text{G}_2$  structure the most likely assignment. The addition of an excess of pyridine (Figure 1d,e) leaves the  $\text{H}_1\text{G}_2$  complex as the only remaining host-containing species in solution (⑬).

Up to this point the analysis has been based primarily on the host signals; further support is gained by analysis of the guest signals. Thus we observed that with increasing pyridine content in the mixture, the  $D$  values of the guest increase continuously. For signal ⑩ in the mixture with G/H = 1:1.8 (Figure 1c) a value of  $6.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  was measured, similar to that in Figure 1a. The new pyridine signal ⑪ occurring at  $\delta = 8.69$  ppm at higher concentrations has a larger  $D$  value of  $7.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . This indicates the formation of a species with smaller hydrodynamic radius  $r_s$ . Upon further addition of pyridine, just one set of guest signals remains observable (Figure 1d,e). The corresponding diffusion coefficients increase from  $10.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (⑫) to  $18.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  (⑬) and approach the value of noncomplexed pyridine (⑭,  $22.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). As there is still rapid exchange between the host–guest complex and free pyridine, the unbound pyridine available in the mixture contributes increasingly to the measured diffusion coefficient. This is because only a mean value weighted by the molar fractions is observable on the timescale of the NMR experiment.

We also used pyrimidine as a guest exhibiting two donor atoms to investigate the Lewis base complexation of host **1**. In contrast to the addition of pyridine and in analogy to the results postulated by Katz in 1989,<sup>[7a]</sup> we expected the formation of an  $\text{H}_1\text{G}_1$  structure (Scheme 2) with pyrimidine bound in a chelating fashion through two Ga–N bonds. This should particularly be the case, when small amounts of pyrimidine are added to the bidentate host molecule **1**. In fact, completely different behavior was observed when pyrimidine was added instead of pyridine (see Table 1).

Upon addition of a substoichiometric amount of pyrimidine (molar ratio G/H = 1:1.17) the formation of only one anthracene-containing complex with a diffusion coefficient of  $7.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  was observed. If one compares this to the  $D$  values of the reference compounds  $\text{H}_1\text{G}_1$  (**3**,  $7.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ),  $\text{H}_2\text{G}_1$  (**6**,  $5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , the intermediate analogue to substoichiometric conversion of **1** with pyridine), and  $\text{H}_2\text{G}_2$  (**7**,  $5.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), the formation of a complex consisting of a host monomer and one pyrimidine molecule ( $\text{H}_1\text{G}_1$  structure with chelating bound pyrimidine) is most likely (the small deviation of the  $D$  value from that of reference **3** may be due to the fact that **3** represents a monodentate-bound pyrimidine aggregate). This complex is apparently very stable, because we do not observe any other anthracene-containing species when the pyrimidine concen-



**Table 1:** Selected results from diffusion NMR experiments for various mixtures of **1** and pyrimidine.<sup>[a]</sup>

G/H	<i>D</i> (host) <sup>[b]</sup>	<i>D</i> (guest) <sup>[b]</sup>
1:1.17	6.9	7.2
1:1.14	6.9	7.1
1:1.10	7.1	7.2
1:0.38	7.0	13.7
1:0.16	6.8	17.9
1:0.06	6.6	19.9

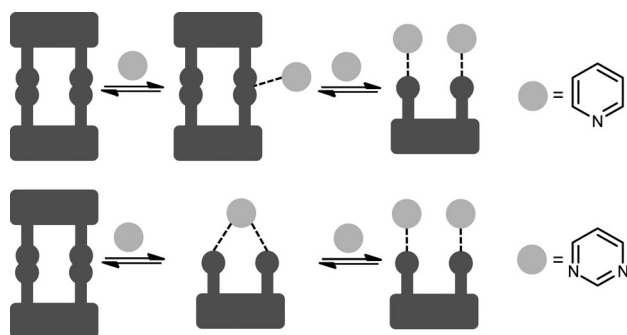
[a] For complete data see Table S5 in the Supporting Information. [b] *D* [ $10^{-10} \text{ m}^2 \text{ s}^{-1}$ ] measured in  $\text{C}_6\text{D}_6$  at 294 K.

tration is increased. The diffusion coefficients measured for the single set of guest  $^1\text{H}$  NMR resonances are very similar to those determined for the host signals, when the mixture contains an excess of host. Addition of further quantities of pyrimidine ( $G/H = 1:0.38$  and higher) leads to an increase of the guest's diffusion coefficients (see Table 1). Like in case of pyridine complexation described above, the *D* values continuously approach the value of free pyrimidine ( $D = 20.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), again reflecting the exchange of free and bound guest.

However, the diffusion coefficients for the host compound tend to decrease when an excess of pyrimidine is used; this is possibly due to formation of some  $\text{H}_1\text{G}_2$  structure (reference compound **4**:  $D = 6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ), whereby each pyrimidine would use only one nitrogen atom for binding to the host.

In summary, the bidentate Lewis acid **1** behaves very differently in the complexation of the mono- and difunctional N-heterocyclic guest molecules pyridine and pyrimidine. The complexation by pyridine turned out to be far more complex than anticipated and involves previously unpredicted species. Although the use of a combination of NMR titration and diffusion NMR spectroscopy in a dynamic system does not allow determining exact structures, the composition and tentative structure assignment can be extracted from the experimental data. Scheme 3 compiles the results in graphical form.

Pyridine is first complexed to the host dimer, then this aggregate is cleaved to give a complex of one host and two pyridine units; in a certain regime of concentrations these species are found to coexist. For pyrimidine, there is no experimental proof for a similar aggregate consisting of a host



**Scheme 3.** Different complexation phenomena when pyridine (top) and pyrimidine (bottom) are used as guest compounds.

dimer and one pyrimidine molecule. Instead almost immediate formation of a (possible) chelate between the difunctional host and one guest is observed. This  $\text{H}_1\text{G}_1$  species remains the dominant species even under higher guest concentrations, while there is some evidence for the formation of small amounts of a complex of two pyrimidine units bound to one host molecule ( $\text{H}_1\text{G}_2$  species).

In general, the combination of titration and diffusion NMR experiments allows new insights in the chemistry of molecular recognition by chelating Lewis acids, provided one is able to compare diffusion coefficients with those of suitable tailor-made reference compounds. The method combination can be transferred to other complex aggregation phenomena.

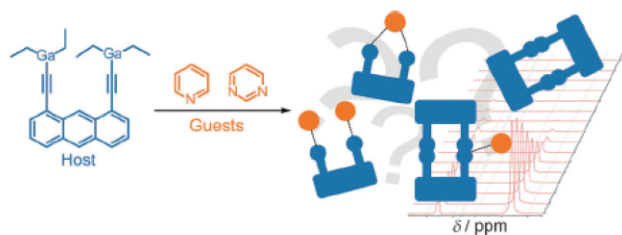
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- [22] Reference compounds **2–4** (Scheme 2) were synthesized in good to moderate yields by Ni-catalyzed Kumada cross-coupling reactions using [(trimethylsilyl)ethynyl]magnesium bromide and [[dimethyl(phenyl)silyl]ethynyl]magnesium bromide,<sup>[23]</sup> respectively, to functionalize 1,8-dichloroanthracene.<sup>[16,24]</sup> Compounds **2–4** were characterized by multinuclear NMR spectroscopy as well as mass spectrometry and in part by X-ray diffraction experiments. The host dimer reference **5** was obtained by photodimerization (365 nm) of **2** in C<sub>6</sub>D<sub>6</sub> solution, whereas H<sub>2</sub>G<sub>2</sub> (**7**) and H<sub>2</sub>G<sub>1</sub> (**6**) compounds were generated by irradiating NMR samples of pure **3** and a 1:1 mixture of **2** and **3**, respectively. Compounds **5–7** were not isolated in pure form, and solely generated to determine their diffusion coefficients. In this case, the diffusion coefficient of the asymmetrically substituted **3** can be compared with the H<sub>1</sub>G<sub>1</sub> structure (one N-heterocyclic guest molecule coordinates to one host monomer **1**), whereas **4** serves as a model system for the H<sub>1</sub>G<sub>2</sub> structure. Compound **2** represents a monomeric host structure (H<sub>1</sub>) and **5** (obtained by UV irradiation of **2**) is used as a reference for a dimeric host structure (H<sub>2</sub>) which has been observed in the solid state (see Ref. [16]).
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Dynamic host-guest complexation was studied using a new combination of NMR titration and diffusion NMR experiments. The host is the bidentate 1,8-bis[(diethylgallanyl)ethynyl]anthracene, the guests

are pyrimidine and pyridine. The analysis of the diffusion NMR experiments requires tailor-made reference compounds of the same shape for comparison.

### Host-Guest Chemistry

J.-H. Lamm, P. Niermeier, A. Mix,  
J. Chmiel, B. Neumann, H.-G. Stammer,  
N. W. Mitzel\* \_\_\_\_\_ 7938–7942

Mechanism of Host-Guest Complex  
Formation and Identification of  
Intermediates through NMR Titration and  
Diffusion NMR Spectroscopy



Supporting Information

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**Mechanism of Host–Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy\*\***

*Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, and Norbert W. Mitzel\**

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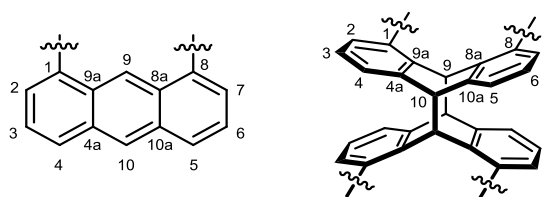
## Experimental Section

### General Remarks

Syntheses of 1,8-bis[(diethylgallanyl)ethynyl]anthracene (**1**),<sup>[S1]</sup> 1,8-dichloroanthracene<sup>[S2]</sup> and 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**2**)<sup>[S3]</sup> have been described elsewhere. The reactions were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried over potassium and freshly distilled before being used for the reactions). Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). Pyrimidine and pyridine were dried over CaH<sub>2</sub>, distilled and degassed before being used for the NMR experiments.

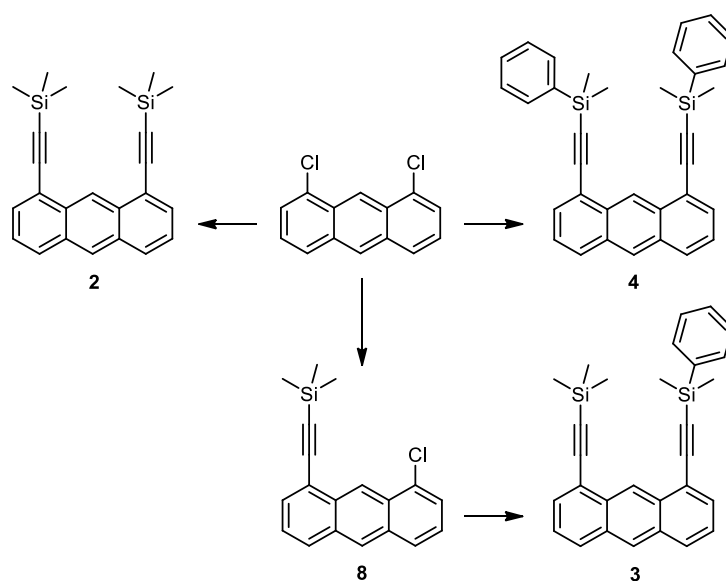
NMR spectra were recorded on a Bruker *DRX 500*, a Bruker *Avance III 500* and a Bruker *Avance 600* instrument at ambient temperature (298 K); the chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C NMR  $\delta$  = 77.13 ppm; C<sub>6</sub>D<sub>6</sub>: <sup>1</sup>H NMR  $\delta$  = 7.16 ppm, <sup>13</sup>C NMR  $\delta$  = 128.06 ppm; toluene-d<sub>8</sub>: <sup>1</sup>H NMR  $\delta$  = 7.00 ppm) or referenced externally (<sup>29</sup>Si NMR: SiMe<sub>4</sub>). The deuterated solvents used for the host-guest experiments (benzene-d<sub>6</sub> and toluene-d<sub>8</sub>) were dried over Na/K alloy, degassed and condensed before being used. EI mass spectra were recorded using an *Autospec X* magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV.

The numbering scheme for NMR assignments (Scheme S1) is based on IUPAC guidelines.



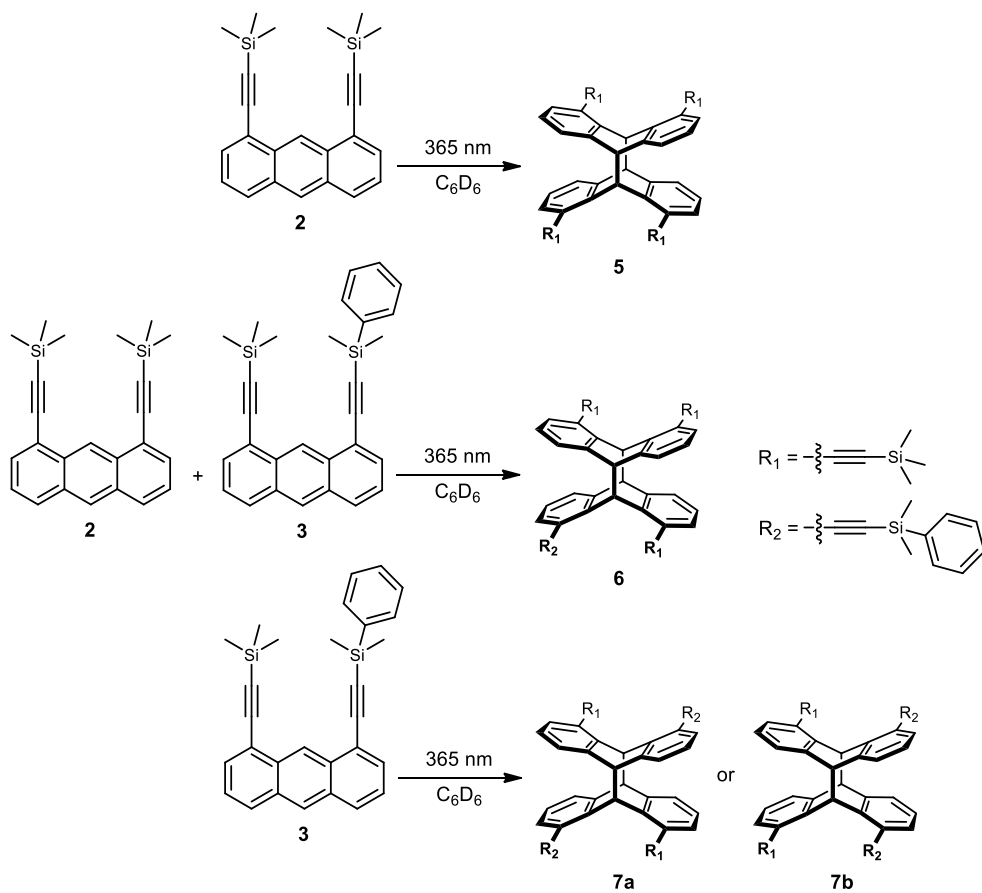
**Scheme S1.** Numbering scheme for NMR assignments.

**General Scheme for the Syntheses of the Reference Compounds 2, 3 and 4:**



**Scheme S2.** Syntheses of reference compounds 2, 3 (via 8) and 4.

**General Scheme for the Syntheses of the Reference Compounds 5, 6 and 7:**



**Scheme S3.** Syntheses of reference compounds 5, 6 and 7.

### Synthesis of ethynyldimethyl(phenyl)silane

Ethynyldimethyl(phenyl)silane was synthesised by a modified literature procedure.<sup>[S4]</sup>

Chlorodimethyl(phenyl)silane (11.5 mL, 68.5 mmol) in THF (10 mL) was added dropwise to a slurry of sodium acetylide (18 wt% in xylene/mineral oil, 17.7 g, 66.3 mmol) in THF (20 mL) at 0 °C. After stirring overnight at room temperature, the orange-red suspension was quenched with water and the aqueous layer was extracted with diethyl ether (5 × 30 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (100 mL) and dried over MgSO<sub>4</sub>. The solvent was evaporated and vacuum distillation (31 °C, 1 Torr) of the dark orange residue afforded the pure product as a colorless liquid. Yield 5.47 g, 52%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.64 (m, 2H, *o*-PhH), 7.39 (m, 3H, *m*-/*p*-PhH), 2.52 (s, 1H, C≡C-H), 0.45 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 136.31 (C<sub>q</sub>), 133.77 (*o*-PhC), 129.75 (*p*-PhC), 128.10 (*m*-PhC), 94.94 (C≡C-H), 88.31 (C≡C-H), -0.96 (SiCH<sub>3</sub>) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>): δ = -21.22 ppm.

For (high resolution) mass spectrometric data of this compound see ref. S4.

### General Procedure for Kumada Cross Coupling Reactions

The silylethynyl compound (Me<sub>3</sub>SiC≡CH or PhMe<sub>2</sub>SiC≡CH) was added dropwise to a solution of ethylmagnesium bromide (1 M in THF) at 0 °C. The mixture was stirred at room temperature for 2 h and gas evolution was observed. The formed ethynylmagnesium bromide compounds were slowly added to a solution of (di-)chloroanthracene, Ni(acac)<sub>2</sub> and PPh<sub>3</sub> in THF at room temperature, while the color of the solution changed from yellow to dark red. The mixture was heated to reflux for at least 43 h and then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with a saturated aqueous solution of NaCl and

dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography using different eluents (see below).

### Synthesis of 1-chloro-8-[(trimethylsilyl)ethynyl]anthracene (**8**)

Synthesis according to the general procedure using 1,8-dichloroanthracene (0.40 g, 1.62 mmol), ethynyltrimethylsilane (0.25 mL, 0.17 g, 1.77 mmol), ethylmagnesium bromide solution (1.8 mL, 1.8 mmol), Ni(acac)<sub>2</sub> (2 mg, 0.006 mol%), PPh<sub>3</sub> (4 mg, 0.01 mol%); reflux for 61 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 15$  cm, eluent: *n*-pentane) afforded **8** as a bright yellow solid.  $R_f = 0.34$  (*n*-pentane). Yield 224 mg, 45%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.38$  (s, 1H, *H9*), 8.44 (s, 1H, *H10*), 7.99 (d, <sup>3</sup> $J_{H,H} = 8.8$  Hz, 1H, *H5*), 7.94 (d, <sup>3</sup> $J_{H,H} = 8.9$  Hz, 1H, *H4*), 7.75 (dd, <sup>3</sup> $J_{H,H} = 6.9$  Hz, <sup>4</sup> $J_{H,H} = 0.7$  Hz, 1H, *H7*), 7.62 (dd, <sup>3</sup> $J_{H,H} = 7.1$  Hz, <sup>4</sup> $J_{H,H} = 0.6$  Hz, 1H, *H2*), 7.45 (dd, <sup>3</sup> $J_{H,H} = 6.9$ , 8.5 Hz, 1H, *H6*), 7.39 (dd, <sup>3</sup> $J_{H,H} = 7.2$ , 8.5 Hz, 1H, *H3*), 0.41 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 9.81$  (s, 1H, *H9*), 7.93 (s, 1H, *H10*), 7.66 (d, <sup>3</sup> $J_{H,H} = 6.8$  Hz, <sup>4</sup> $J_{H,H} = 0.6$  Hz, 1H, *H7*), 7.56 (d, <sup>3</sup> $J_{H,H} = 8.6$  Hz, 1H, *H5*), 7.49 (dd, <sup>3</sup> $J_{H,H} = 8.5$  Hz, 1H, *H4*), 7.32 (dd, <sup>3</sup> $J_{H,H} = 6.7$  Hz, <sup>4</sup> $J_{H,H} = 0.5$  Hz, 1H, *H2*), 6.99 (dd, <sup>3</sup> $J_{H,H} = 6.9$ , 8.5 Hz, 1H, *H6*), 6.89 (dd, <sup>3</sup> $J_{H,H} = 7.3$ , 8.4 Hz, 1H, *H3*), 0.39 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 132.74$ , 132.62, 131.90, 131.59, 130.78 (*C7*), 129.61, 129.14 (*C5*), 127.58 (*C10*), 127.53 (*C4*), 125.92 (*C2*), 125.53 (*C6*), 125.46 (*C3*), 122.92 (*C9*), 121.60, 103.05 (C≡C–Si), 101.10 (C≡C–Si), 0.26 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 132.95$ , 132.74, 132.33, 131.80, 130.92 (*C7*), 129.92, 129.22 (*C5*), 127.97 (*C10*), 127.62 (*C4*), 126.17 (*C2*), 125.56 (*C6*), 125.44 (*C3*), 123.20 (*C9*), 122.15, 103.78 (C≡C–Si), 101.31 (C≡C–Si), 0.16 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -17.19$  ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -17.41$  ppm. MS (EI, 70 eV):  $m/z$  (%) [assignment] = 308.1 (100) [M]<sup>+</sup>, 293.0 (88) [M–Me]<sup>+</sup>, 263.0 (5) [M–3Me]<sup>+</sup>. HRMS:



calculated for  $C_{19}H_{17}ClSi^+$ : 308.07826, measured: 308.07730, deviation [mmu]: 0.96, [ppm]: 3.10.

### Synthesis of 1-[[dimethyl(phenyl)silyl]ethynyl]-8-[[trimethylsilyl]ethynyl]anthracene (**3**)

Synthesis according to the general procedure using 1-chloro-8-[[trimethylsilyl]ethynyl]-anthracene (**8**) (0.56 g, 1.83 mmol), ethynyldimethyl(phenyl)silane (1.3 mL, 1.2 g, 7.4 mmol), ethylmagnesium bromide solution (7.4 mL, 7.4 mmol), Ni(acac)<sub>2</sub> (6 mg, 0.012 mol%), PPh<sub>3</sub> (10 mg, 0.03 mol%); reflux for 84 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 15$  cm, eluent: *n*-pentane/dichloromethane 8:1) afforded **3** as bright yellow crystals.  $R_f = 0.19$  (*n*-pentane/DCM 8:1). Yield 571 mg, 72%.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.38$  (s, 1H, *H*<sub>9</sub>), 8.44 (s, 1H, *H*<sub>10</sub>), 8.00 (m, 2H, *H*<sub>4</sub>/*H*<sub>5</sub>), 7.81 (m, 4H, *H*<sub>2</sub>/*H*<sub>7</sub>/*o*-Ph*H*), 7.42 (m, 5H, *H*<sub>3</sub>/*H*<sub>6</sub>/*m*-/*p*-Ph*H*), 0.62 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>Ph], 0.26 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 9.92$  (s, 1H, *H*<sub>9</sub>), 7.98 (s, 1H, *H*<sub>10</sub>), 7.89 (m, 2H, *o*-Ph*H*), 7.74 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.8 Hz, 1H, *H*<sub>7</sub>), 7.73 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.8 Hz, 1H, *H*<sub>2</sub>), 7.61 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.4 Hz, 1H, *H*<sub>4</sub>), 7.60 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.4 Hz, 1H, *H*<sub>5</sub>), 7.26 (m, 3H, *m*-/*p*-Ph*H*), 7.01 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 7.0, 8.5 Hz, 1H, *H*<sub>3</sub>), 7.00 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 7.0, 8.5 Hz, 1H, *H*<sub>6</sub>), 0.66 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>Ph], 0.31 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 137.23$ , 134.04, 132.81, 132.47, 131.56, 131.51, 131.47, 131.36, 129.64, 129.60 (*C*<sub>4</sub> or *C*<sub>5</sub>), 129.38 (*C*<sub>4</sub> or *C*<sub>5</sub>), 128.12, 127.87 (*C*<sub>10</sub>), 125.15, 125.09, 124.03 (*C*<sub>9</sub>), 121.49, 121.29, 105.49, 103.53, 100.13 [C≡C–Si(CH<sub>3</sub>)<sub>3</sub>], 97.75 [C≡C–Si(CH<sub>3</sub>)<sub>2</sub>Ph], 0.41 [Si(CH<sub>3</sub>)<sub>3</sub>], –0.10 [Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm (due to similar NMR shifts, no further assignments are possible). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 137.41$ , 134.39, 133.09, 132.64, 132.00, 131.86, 131.80, 129.84, 129.81, 129.53, 128.42, 128.35, 128.32, 125.21, 125.14, 124.40 (*C*<sub>9</sub>), 122.04, 121.72, 106.31, 104.38, 100.28, 98.08, 0.45, 0.04 ppm (due to similar NMR shifts, no further assignments are possible). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -17.49$  [Si(CH<sub>3</sub>)<sub>3</sub>], –21.11 [Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR

(99 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -17.78$  [Si(CH<sub>3</sub>)<sub>3</sub>],  $-21.11$  [Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. MS (EI, 70 eV):  $m/z$  (%) [assignment] = 431.9 (100) [M]<sup>+</sup>, 416.9 (10) [M–Me]<sup>+</sup>, 359.9 (32) [M–SiMe<sub>3</sub>]<sup>+</sup>, 135.0 (86) [SiMe<sub>2</sub>Ph]<sup>+</sup>, 73.0 (57) [SiMe<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>29</sub>H<sub>28</sub>Si<sub>2</sub><sup>+</sup>: 432.17241, measured: 432.97285, deviation [mmu]: 0.67, [ppm]: 1.56.

#### Synthesis of 1,8-bis{[dimethyl(phenyl)silyl]ethynyl}anthracene (**4**)

Synthesis according to the general procedure using 1,8-dichloroanthracene (0.30 g, 1.21 mmol), ethynyldimethyl(phenyl)silane (1.0 mL, 0.91 g, 5.7 mmol), ethylmagnesium bromide solution (6.0 mL, 6.0 mmol), Ni(acac)<sub>2</sub> (6 mg, 0.02 mol%), PPh<sub>3</sub> (5 mg, 0.02 mol%); reflux for 43 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 15$  cm, eluent: *n*-pentane/dichloromethane 8:1) afforded **4** as bright yellow crystals.  $R_f = 0.10$  (*n*-pentane/DCM 8:1). Yield 408 mg, 68%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.44$  (s, 1H, *H*<sub>9</sub>), 8.45 (s, 1H, *H*<sub>10</sub>), 8.02 (d, <sup>3</sup> $J_{\text{H,H}} = 8.6$  Hz, 2H, *H*<sub>4</sub>/*H*<sub>5</sub>), 7.84 (dd, <sup>3</sup> $J_{\text{H,H}} = 6.9$  Hz, <sup>4</sup> $J_{\text{H,H}} = 0.8$  Hz, 2H, *H*<sub>2</sub>/*H*<sub>7</sub>), 7.76 (m, 4H, *o*-Ph*H*), 7.44 (dd, <sup>3</sup> $J_{\text{H,H}} = 6.9$ , 8.5 Hz, 2H, *H*<sub>3</sub>/*H*<sub>6</sub>), 7.39 (m, 6H, *m*-/*p*-Ph*H*), 0.50 [s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 9.94$  (s, 1H, *H*<sub>9</sub>), 7.97 (s, 1H, *H*<sub>10</sub>), 7.84 (m, 4H, *o*-Ph*H*), 7.71 (d, <sup>3</sup> $J_{\text{H,H}} = 6.9$  Hz, 2H, *H*<sub>2</sub>/*H*<sub>7</sub>), 7.60 (d, <sup>3</sup> $J_{\text{H,H}} = 8.6$  Hz, 2H, *H*<sub>4</sub>/*H*<sub>5</sub>), 7.24 (m, 6H, *m*-/*p*-Ph*H*), 7.00 (dd, <sup>3</sup> $J_{\text{H,H}} = 8.5$ , 7.0 Hz, 2H, *H*<sub>3</sub>/*H*<sub>6</sub>), 0.54 [s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 137.22$  (*i*-PhC), 134.01 (*o*-PhC), 133.90, 132.80 (*C*<sub>2</sub>/*C*<sub>7</sub>), 131.52, 131.42, 129.63 (*C*<sub>4</sub>/*C*<sub>5</sub>), 129.57 (*p*-PhC), 128.09 (*m*-PhC), 127.93 (*C*<sub>10</sub>), 125.14 (*C*<sub>3</sub>/*C*<sub>6</sub>), 124.00 (*C*<sub>9</sub>), 121.30, 105.35 (*C* $\equiv$ C–Si), 97.89 (*C* $\equiv$ C–Si),  $-0.30$  [Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 137.41$  (*i*-PhC), 134.35 (*o*-PhC), 133.03 (*C*<sub>2</sub>/*C*<sub>7</sub>), 131.92, 131.80, 129.80 (*C*<sub>4</sub>/*C*<sub>5</sub>), 129.77 (*p*-PhC), 128.38 (*m*-PhC), 128.36 (*C*<sub>10</sub>), 125.19 (*C*<sub>3</sub>/*C*<sub>6</sub>), 124.34 (*C*<sub>9</sub>), 121.73, 106.12 (*C* $\equiv$ C–Si), 98.28 (*C* $\equiv$ C–Si),  $-0.14$  [Si(CH<sub>3</sub>)<sub>2</sub>Ph] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -21.17$  ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -21.05$  ppm. MS (EI, 70 eV):  $m/z$  (%) [assignment] = 494.2 (100) [M]<sup>+</sup>, 401.1 (8) [M–Ph–Me]<sup>+</sup>, 360.1 (7)

[M-(SiMe<sub>2</sub>Ph)]<sup>+</sup>. HRMS: calculated for C<sub>34</sub>H<sub>30</sub>Si<sub>2</sub><sup>+</sup>: 494.18806, measured: 494.18916, deviation [mmu]: 1.10, [ppm]: 2.24.

### Syntheses of the photo-dimer reference compounds **5**, **6** and **7**

NMR samples of **2** (to afford **5**) and **3** (to afford **7**), dissolved in C<sub>6</sub>D<sub>6</sub> (0.5 mL), were irradiated with UV light (365 nm) for several hours. The solutions of the corresponding reference compounds were used for diffusion NMR experiments without further purification.

Data of reference compound **5**: <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 7.17 (d, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 4H, H4/H5), 7.04 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 4H, H2/H7), 6.57 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.6, 7.6 Hz, 4H, H3/H6), 5.99 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz, 2H, H9), 4.81 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz, 2H, H10), 0.42 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.

Data of reference compound **7**: <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): 7.93 (m, 4H, H4/H5), 7.35 (m, 4H, H2/H7), 7.27 (m, 4H, PhH), 7.20 (m, 2H, PhH), 7.05 (m, 4H, PhH), 6.56 (m, 4H, H3/H6), 6.07 (d, <sup>3</sup>J<sub>H,H</sub> = 11.1 Hz, 2H, H9), 4.87 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz, 2H, H10), 0.65 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>Ph], 0.62 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>Ph], 0.30 [m, 18H, Si(CH<sub>3</sub>)<sub>3</sub>].

In case of the photo-dimerisation of monomer **3** the formation of two dimer isomers **7a** and **7b** is possible (see Scheme S3). We observe the formation of just one *anti* isomer, but we were not able to differentiate between **7a** and **7b** by NMR spectroscopy. However, we assume the diffusion coefficients to be similar for both isomers.

UV irradiation of a 1:1 mixture of **2** and **3**, dissolved in C<sub>6</sub>D<sub>6</sub> (0.5 mL), was performed to afford the asymmetrically substituted reference compound **6**. After irradiation a 1:2:1 mixture of the photo-dimer species **5**, **6** and **7** was observed, exhibiting very similar and overlapping <sup>1</sup>H NMR resonances except two signals [<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 6.00 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz), 4.82 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz), no assignments possible], which were used to determine the diffusion coefficient of **6** ( $D = 5.7 \cdot 10^{-10} \text{ m}^2/\text{s}$ ).

## Crystal Structure Determination

Suitable crystals of the compounds **3**, **4** and **8** were obtained by slow evaporation of saturated solutions of an 8:1 mixture of *n*-pentane/dichloromethane (**3** and **4**) and *n*-hexane/dichloromethane (**8**). They were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen-gas cold-stream solidifying the oil. Data collection was performed on a *Nonius KappaCCD* diffractometer (**4**) and a *SuperNova, Dual, Cu at zero, Atlas* diffractometer (**3** and **8**).

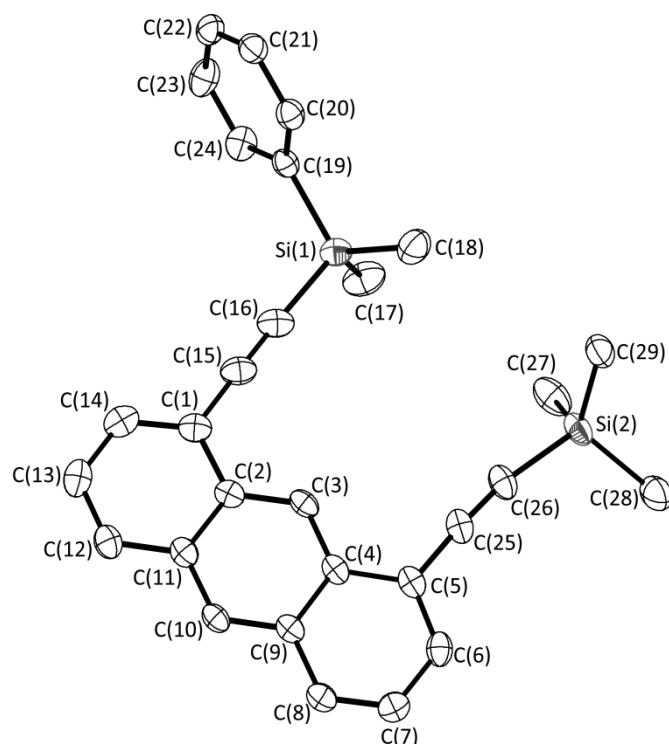
The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>[S5]</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table S1. CCDC 984387–984389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.ac.uk/data\\_request/cif](http://www.ccdc.ac.uk/data_request/cif).

The bond lengths and angles determined for (the reference) compounds **3**, **4** and **8** by X-ray diffraction experiments are found to be in the expected range.<sup>[S6]</sup> They are comparable with the corresponding values in 1,8- or 1,8,10-substituted anthracene derivatives.<sup>[S7]</sup> The molecular structures of compounds **2** and **5** will be published soon in a different context.<sup>[S8]</sup>

**Table S1.** Crystallographic data for **3**, **4** and **8**.

	<b>3</b>	<b>4</b>	<b>8</b>
Empirical formula	C <sub>29</sub> H <sub>28</sub> Si <sub>2</sub>	C <sub>34</sub> H <sub>30</sub> Si <sub>2</sub>	C <sub>19</sub> H <sub>17</sub> ClSi
$M_r$	432.69	494.76	308.86
$\lambda$ [Å]	1.54184	0.71073	1.54184
$T$ [K]	99.96(13)	100(2)	150(1)
$F(000)$	460	524	324
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ [Å]	8.7318(3)	10.3832(4)	7.3140(4)
$b$ [Å]	12.3637(5)	11.9334(4)	10.4081(7)
$c$ [Å]	12.8339 (5)	12.1770(4)	11.7291(6)
$\alpha$ [°]	69.766(4)	108.248(2)	70.394(5)
$\beta$ [°]	75.068(3)	103.561(2)	86.639(4)
$\gamma$ [°]	81.196(3)	92.423 (2)	78.460(5)
$V$ [Å <sup>3</sup> ]	1252.98(9)	1382.00(8)	824.07(9)
$Z$	2	2	2
$\rho_{\text{calcd.}}$ [g cm <sup>-3</sup> ]	1.147	1.189	1.245
$\mu$ [mm <sup>-1</sup> ]	1.367	0.149	2.652
$\theta_{\text{max}}$ [°]	72.12	30.00	72.12
Index ranges $h$	$-10 \leq h \leq 10$	$-14 \leq h \leq 14$	$-9 \leq h \leq 9$
Index ranges $k$	$-15 \leq k \leq 15$	$-16 \leq k \leq 16$	$-12 \leq k \leq 11$
Index ranges $l$	$-15 \leq l \leq 14$	$-15 \leq l \leq 17$	$-14 \leq l \leq 14$
Reflexes collected	23044	29110	13087
Independent reflexes	4929	8003	3228
$R_{\text{int}}$	0.0311	0.041	0.0243
Observed refl., $I > 2\sigma(I)$	4442	5885	2916
Parameters	285	329	193
$R_1$ , $I > 2\sigma(I)$	0.0390	0.0422	0.0344
$wR_2$ , $I > 2\sigma(I)$	0.1033	0.1041	0.0971
$R_1$ (all data)	0.0434	0.0675	0.0384
$wR_2$ (all data)	0.1071	0.1155	0.1007
$GoF$ on $F^2$	1.051	1.047	1.058
$\rho_{\text{max}}/\rho_{\text{min}}$ [ $e \text{ \AA}^{-3}$ ]	0.44/-0.30	0.31832/-0.312	0.30/-0.20
CCDC number	984388	984387	984389

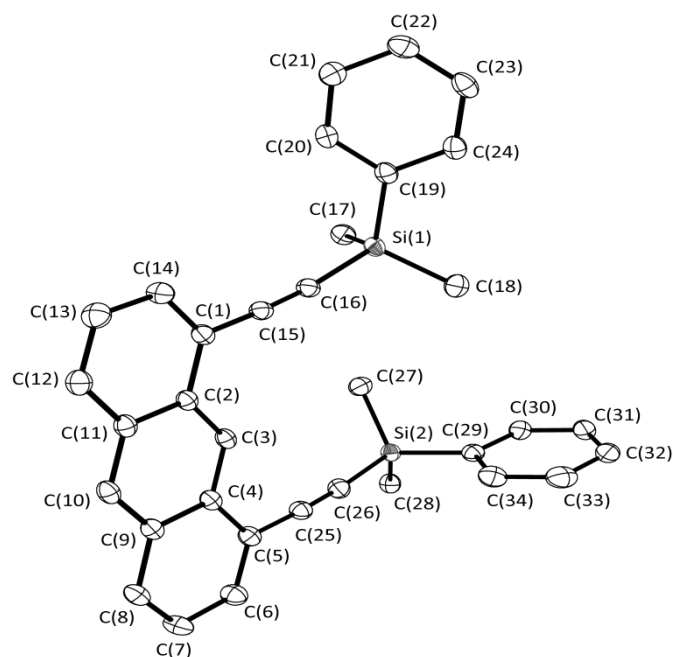
### Crystal Structure of 1-[[Dimethyl(phenyl)silyl]ethynyl]-8-[(trimethylsilyl)ethynyl]anthracene (**3**)



**Figure S1.** Molecular structure of 1-[[dimethyl(phenyl)silyl]ethynyl]-8-[(trimethylsilyl)ethynyl]anthracene (**3**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: C(1)–C(2) 1.445(2), C(1)–C(14) 1.375(2), C(1)–C(15) 1.436(2), C(2)–C(3) 1.396(2), C(2)–C(11) 1.438(2), C(5)–C(25) 1.436(2), C(15)–C(16) 1.207(2), C(16)–Si(1) 1.836(2), C(17)–Si(1) 1.858(2), C(19)–Si(1) 1.876(2), C(19)–C(20) 1.393(2), C(25)–C(26) 1.208(2), C(26)–Si(2) 1.844(2); C(1)–C(2)–C(3) 122.8(2), C(1)–C(2)–C(11) 117.6(2), C(1)–C(15)–C(16) 179.0(2), C(2)–C(1)–C(15) 119.1(2), C(4)–C(5)–C(25) 120.9(2), C(5)–C(25)–C(26) 176.5(2), C(15)–C(16)–Si(1) 176.6(2), C(25)–C(26)–Si(2) 170.1(2).

The angle between the planes spanned by C(20), C(21), C(23) and C(24) and the anthracene carbon atoms C(6), C(7), C(13) and C(14) is  $79.1(1)^\circ$ .

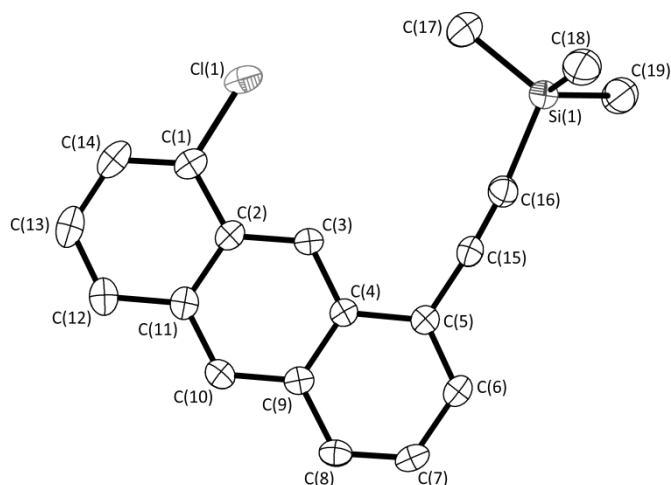
## Crystal Structure of 1,8-Bis{[dimethyl(phenyl)silyl]ethynyl}anthracene (4)



**Figure S2.** Molecular structure of 1,8-bis{[dimethyl(phenyl)silyl]ethynyl}anthracene (4). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.445(2), C(1)–C(14) 1.370(2), C(1)–C(15) 1.435(2), C(2)–C(3) 1.395(2), C(2)–C(11) 1.434(2), C(5)–C(25) 1.435(2), C(15)–C(16) 1.208(2), C(16)–Si(1) 1.835(2), C(25)–C(26) 1.206(2), C(26)–Si(2) 1.837(2); C(1)–C(2)–C(3) 122.1(1), C(1)–C(2)–C(11) 118.3(1), C(1)–C(15)–C(16) 173.9(1), C(2)–C(1)–C(15) 121.5(1), C(4)–C(5)–C(25) 119.6(1), C(5)–C(25)–C(26) 177.7(2), C(15)–C(16)–Si(1) 171.9(1), C(16)–Si(1)–C(18) 110.5(1), C(16)–Si(1)–C(19) 106.9(1), C(25)–C(26)–Si(2) 175.1(1).

The phenyl carbon atoms C(30), C(31), C(33) and C(34) and the anthracene carbon atoms C(6), C(7), C(13) and C(14) form planes, which are nearly orthogonal to each other [91.0(6)°], whereas the angle between the anthracene-plane and the plane spanned by the second phenyl group [C(20)–C(21)–C(23)–C(24)] is remarkable smaller [54.3(1)°]. The angle between the two planes of the phenyl substituents are at an 82.8(1)° angle to each other.

## Crystal Structure of 1-Chloro-8-[(trimethylsilyl)ethynyl]anthracene (**8**)



**Figure S3.** Molecular structure of 1-chloro-8-[(trimethylsilyl)ethynyl]anthracene (**8**). Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: C(1)–C(2) 1.434(2), C(1)–C(14) 1.356(2), C(1)–Cl(1) 1.743(2), C(2)–C(3) 1.397(2), C(2)–C(11) 1.435(2), C(5)–C(15) 1.438(2), C(15)–C(16) 1.200(2), C(16)–Si(1) 1.836(2), C(17)–Si(1) 1.862(2); C(1)–C(2)–C(3) 123.6(1), C(1)–C(2)–C(11) 116.8(1), C(2)–C(1)–C(14) 122.4(2), C(2)–C(1)–Cl(1) 118.8(1), C(4)–C(5)–C(15) 118.3(1), C(5)–C(15)–C(16) 175.3(2), C(15)–C(16)–Si(1) 174.2(1), C(16)–Si(1)–C(17) 106.3(2).



## Diffusion NMR Experiments

### a) General Remarks

$^1\text{H}$  Diffusion NMR measurements have been performed on a Bruker *Avance 600* instrument in  $\text{C}_6\text{D}_6$  (294 K,  $\delta = 7.13$  ppm) using the LED sequence with bipolar gradients (ledbpgp2s) delivered by the manufacturer. The probe was disconnected from the gas supply and the sample was allowed to equilibrate for at least three hours within the probe/magnet prior to data recording. The duration of the gradients was incremented linearly in 16 steps. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN<sup>®</sup>.

### b) Diffusion Coefficients of the Guest Molecules

Small amounts of the *N*-heterocyclic guest molecules were dissolved in  $\text{C}_6\text{D}_6$ . Their diffusion coefficients were determined according to the procedure described above. Results are listed in Table S2.

**Table S2.** Results of the diffusion NMR measurements of the pure guest molecules.

	$\delta$ [ms]	$\Delta$ [ms]	$D$ [ $10^{-10}$ m <sup>2</sup> /s]
Pyridine	2.40	50.00	22.1
Pyrimidine	2.00	50.00	20.7

### c) Diffusion Coefficients of the Reference Compounds

Small amounts of the reference compounds **2**, **3**, **4**, **5**, **6** and **7** were dissolved in C<sub>6</sub>D<sub>6</sub>. Their diffusion coefficients were determined according to the procedure described above. Results are listed in Table S3.

**Table S3.** Results of the diffusion NMR measurements of the reference compounds.

Reference compound	$\delta$ [ms]	$\Delta$ [ms]	$D$ [ $10^{-10}$ m <sup>2</sup> /s]
<b>2</b> (H <sub>1</sub> )	4.00	60.00	8.8
<b>3</b> (H <sub>1</sub> G <sub>1</sub> )	4.00	60.00	7.7
<b>4</b> (H <sub>1</sub> G <sub>2</sub> )	4.20	60.00	6.4
<b>5</b> (H <sub>2</sub> )	4.40	60.00	5.9
<b>6</b> (H <sub>2</sub> G <sub>1</sub> )	4.40	60.00	5.7
<b>7</b> (H <sub>2</sub> G <sub>2</sub> )	4.40	60.00	5.0

### d) Conversion of 1,8-Bis[(diethylgallanyl)ethynyl]anthracene (**1**) with Pyridine

**1**: 4.9 mg (10.2  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub> (0.50 mL); small amounts of pyridine were added using a 10 and a 50  $\mu$ L syringe (ITO CORPORATION, Fuji, Japan). The diffusion coefficients were determined according to the procedure described above. Data are listed in Table S4.

**Table S4.** Data of the diffusion NMR measurements of the conversion of **1** with pyridine. The spectra are displayed in the paper (Figure 3).

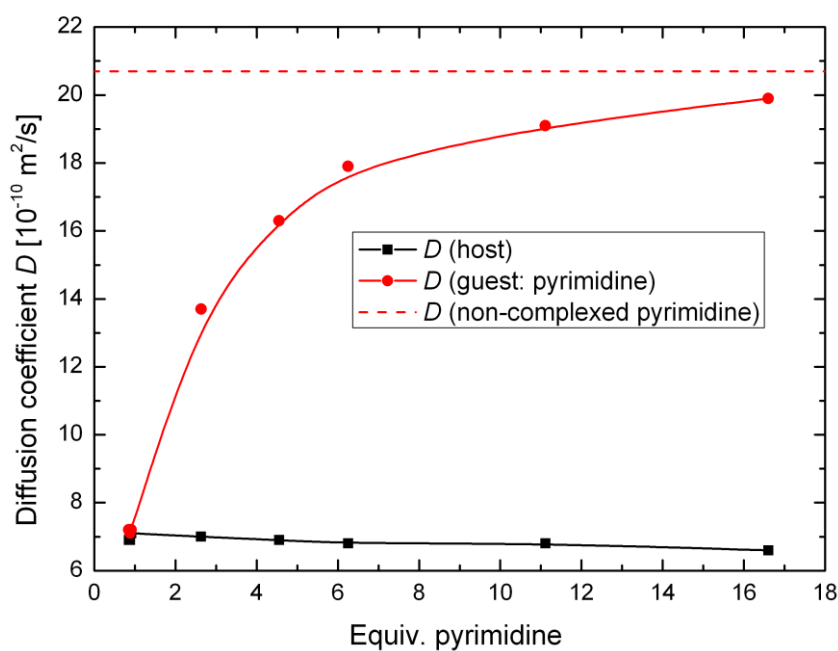
Molar ratio G:H	$\delta$ [ms]	$\Delta$ [ms]
1:2.5	4.00	60.00
1:2.2	4.60	60.00
1:1.8	4.60	60.00
1:0.3	4.60	60.00
1:0.1	4.20	60.00

### e) Conversion of 1,8-Bis[(diethylgallanyl)ethynyl]anthracene (**1**) with Pyrimidine

**1**: 5.6 mg (10.2  $\mu\text{mol}$ ) in  $\text{C}_6\text{D}_6$  (0.50 mL); small amounts of pyrimidine were added using a 10 and a 50  $\mu\text{L}$  syringe (ITO CORPORATION, Fuji, Japan). The diffusion coefficients were determined according to the procedure described above. Results are listed in Table S5 and plotted in Figures S4, S5 and S6.

**Table S5.** Results of the diffusion NMR measurements of the conversion of **1** with pyrimidine.

Molar ratio G:H	$\delta$ [ms]	$\Delta$ [ms]	$D$ (Host) [ $10^{-10} \text{ m}^2/\text{s}$ ]	$D$ (Guest) [ $10^{-10} \text{ m}^2/\text{s}$ ]
1:1.17	4.00	60.00	6.9	7.2
1:1.14	4.00	60.00	6.9	7.1
1:1.12	4.00	60.00	7.1	7.2
1:1.10	4.60	60.00	7.1	7.2
1:0.38	4.60	60.00	7.0	13.7
1:0.22	4.20	60.00	6.9	16.3
1:0.16	4.20	60.00	6.8	17.9
1:0.95	4.20	60.00	6.8	19.1
1:0.06	4.20	60.00	6.6	19.9



**Figure S4.**

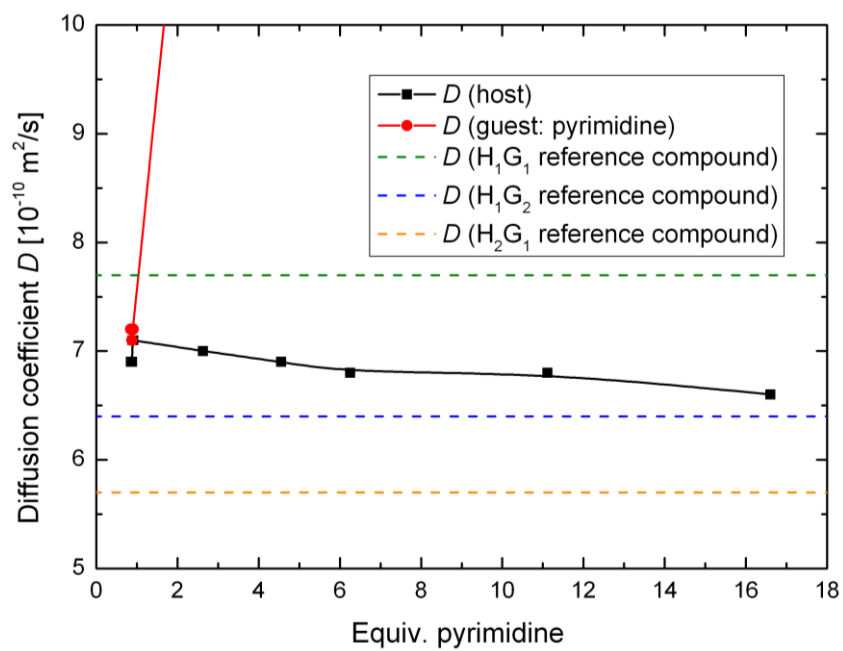


Figure S5. Detail of Figure S4.

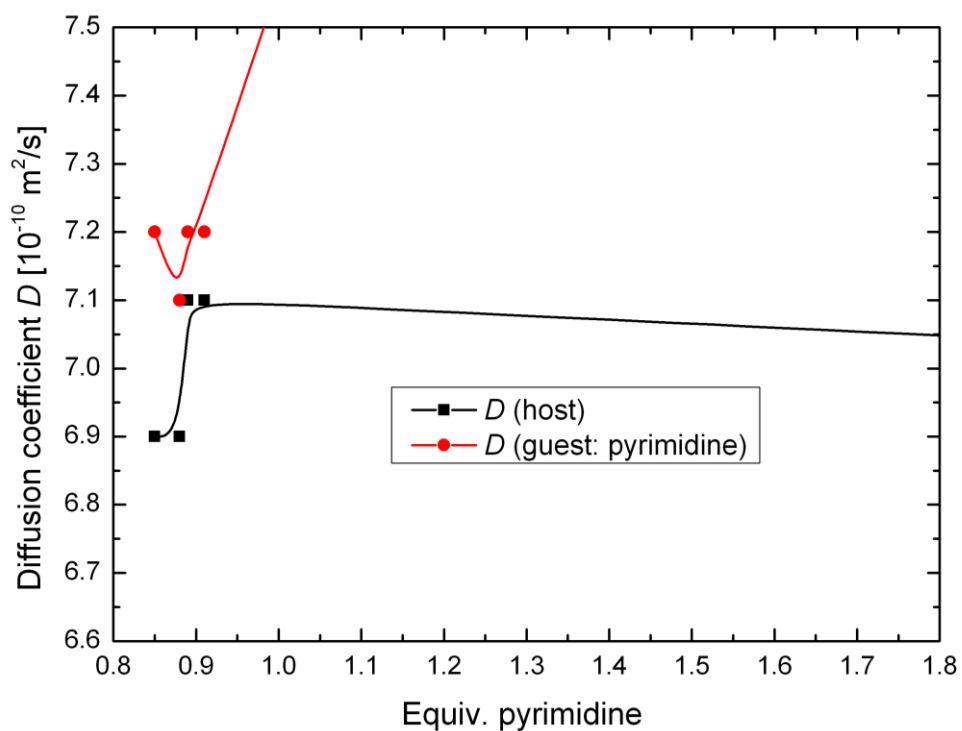
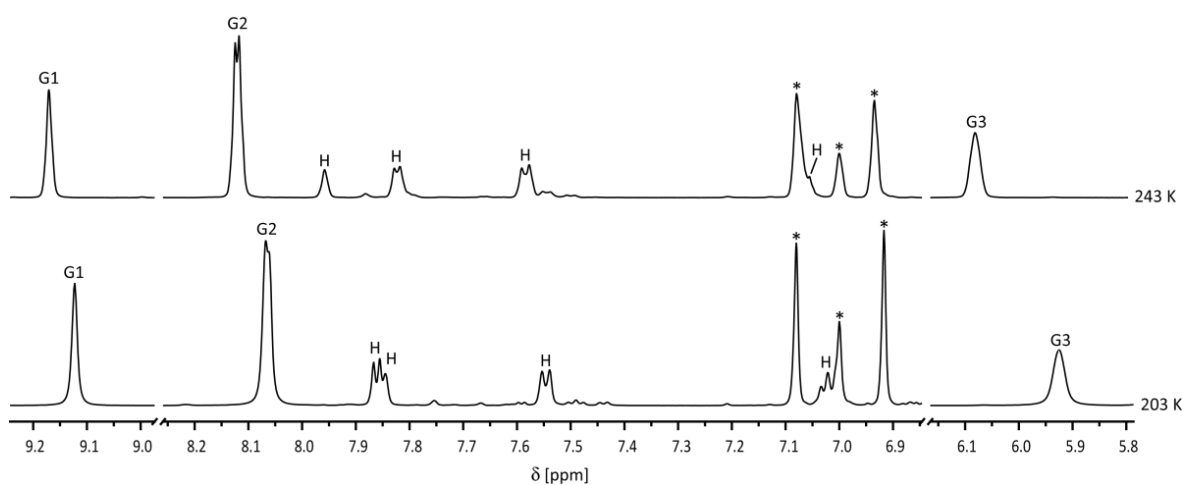


Figure S6. Detail of Figure S5.

## VT NMR Experiments

$^1\text{H}$  VT NMR experiments have been performed on a Bruker *Avance 600* instrument using a 1:4 mixture of the digallium host-compound **1** and pyrimidine in toluene- $d_8$  (\*, reference: 7.00 ppm) at 243 K and 203 K. The spectra are displayed in Figure S7. At 203 K the resonances of the guest-component (G1 – G3) are significantly shifted to higher field, but no second set of signals is observed, indicating a highly dynamic exchange process in solution.



**Figure S7.**  $^1\text{H}$  NMR spectra of a 1:4-mixture of the host compound (H, **1**) and pyrimidine (G1 – G3) at 243 and 203 K in toluene- $d_8$  (\*).

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## **Publikation 3**

### **Improved Access to 1,8-Dichloro-10-(ethynyl)anthracene – A Building Block for Rigid Organic Frameworks**

Jan-Hendrik Lamm, Leif Arne Körte, Lisa Kuhlmann,  
Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Eur. J. Org. Chem.* **2014**, Manuskript in Begutachtung.





## Improved Access to 1,8-Dichloro-10-(ethynyl)anthracene – A Building Block for Rigid Organic Frameworks

Jan-Hendrik Lamm,<sup>[a]</sup> Leif A. Körte,<sup>[a]</sup> Lisa Kuhlmann,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammer,<sup>[a]</sup> and Norbert W. Mitzel\*<sup>[a]</sup>

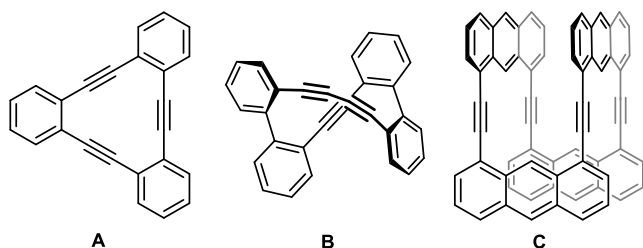
**Keywords:** Anthracenes / Alkynes / Rigid Organic Backbones / Solid-State Structures

An easy access to 1,8-dichloro-10-(ethynyl)anthracene (**4**) is reported, which is widely applicable for building up rigid linkers between two 1,8-dichloroanthracene units. For this 1,8-dichloroanthracene is reacted with ethynylmagnesium bromide in the presence of CeCl<sub>3</sub>; the yield is 65%. **4** is used as a substrate in (cross) coupling reactions and some examples of linked 1,8-dichloroanthracene-10-yls (e.g. 1,8-diethynylanthracenyl- or 1,2-di-

ethynylbenzyl-) are synthesised in good to moderate yields. Linkers between the 1,8-dichloroanthracene units are: butadiynediyl, 1,8-diethynylanthracene and 1,2-bisdiethynylbenzene. The new anthracene compounds were characterised by NMR spectroscopy, high resolution mass spectrometry and – in part – by X-ray diffraction experiments.

### Introduction

Rigid organic frameworks consisting of alkyne-linked aryl units are widely utilised in nearly all fields of (synthetic) chemistry. The corresponding molecules are of structural interests, like those shown in Scheme 1.<sup>[1–3]</sup>



Scheme 1. Examples of rigid organic frameworks consisting of alkyne-linked aryls by Eglinton (A),<sup>[1a]</sup> Tobe (B)<sup>[2]</sup> and Toyota (C).<sup>[3]</sup>

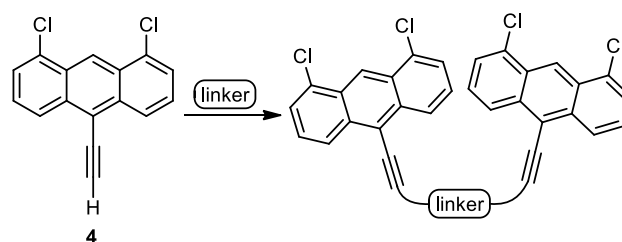
They are also versatily applied in supramolecular chemistry, e.g. as host-structures in host-guest chemistry,<sup>[4]</sup> in creating nano-scale 3D structures with large interior space,<sup>[5]</sup> as building blocks in shape-persistent, fluorescent or through-space conjugated polymers,<sup>[6]</sup> in sensors<sup>[7]</sup> or in Light-Emitting Diodes (LEDs).<sup>[8]</sup> Wider applications of these (conjugated) backbones are conceivable, especially when the aryl rings are substituted with atoms or groups allowing further functionalisations.

[a] Universität Bielefeld, Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie, Universitätsstraße 25, D-33615 Bielefeld, Germany  
Fax: +49(0)521 106-6026  
E-mail: mitzel@uni-bielefeld.de  
http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.xxxxxxxx>.

In the course of our investigations in the field of poly-Lewis acids with rigid organic frameworks,<sup>[9a]</sup> we are searching and constructing donor-free organic backbones with directed functionalities. Lastly, we have used 1,8-substituted anthracene derivatives and synthesised bidentate Al, Ga and In Lewis acids with almost parallel oriented earth metal acceptor functions. Their use as Lewis-acidic receptor molecules in host-guest chemistry has been demonstrated.<sup>[9,11]</sup> In order to increase the number of oriented functionalities, we found that systems with two 1,8-dichloroanthracene units donor-freely linked in 10-position are desirable synthetic targets (Scheme 2).



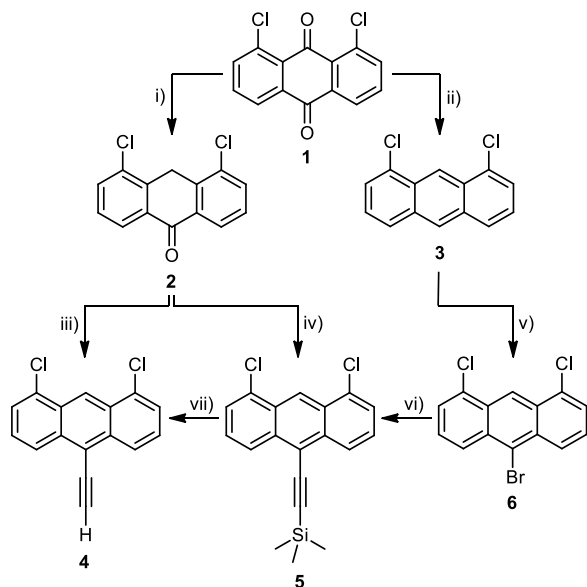
Scheme 2. Schematic drawing of two linked 1,8-dichloro-10-(ethynyl)anthracene units.

Herein we report an efficient route to 1,8-dichloro-10-(ethynyl)anthracene (**4**) and demonstrate some examples to join two of these units using different linker systems (Scheme 2). These systems allow the variation of the orientation of the C–Cl functions from 180° to almost parallel orientation. Further functionalisation of the backbones is optional but not provided in this work.

## Results and Discussion

As shown in Scheme 3, 1,8-dichloro-10-(ethynyl)anthracene (**4**) can be synthesised using various routes starting from the commercially available 1,8-dichloroanthraquinone (**1**). We recently reported the synthesis of 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**5**), the SiMe<sub>3</sub>-protected form of the desired species **4**, by conversion of the 1,8-dichloroanthrone **2** with [(trimethylsilyl)ethynyl]magnesium bromide.<sup>[12]</sup> This compound has also been obtained by a Sonogashira-Hagihara cross-coupling reaction using 10-bromo-1,8-dichloroanthracene (**6**).<sup>[13]</sup> The latter can be prepared from 1,8-dichloroanthracene (**3**) with elemental bromine in quantitative yield.<sup>[14]</sup> Cleaving off the TMS group by a standard protocol gives 1,8-dichloro-10-(ethynyl)anthracene (**4**) in an overall yield of 38% starting from **2** and 58% starting from **3**, respectively.<sup>[15]</sup>

A new and efficient access to compound **4** is provided by a CeCl<sub>3</sub> promoted conversion of anthrone **2** with ethynylmagnesium bromide in THF (yield: 65% starting from **2**). Imamoto and co-workers demonstrated in 1989 that the addition of CeCl<sub>3</sub> improves the addition of Grignard reagents to ketones by suppressing side reactions.<sup>[16]</sup> The presence of the cerium salt seems to be important, since the yield of **4** is remarkably lower (14%), when the reaction is carried out under the same conditions in absence of CeCl<sub>3</sub>.



Scheme 3. Various synthetic routes for 1,8-dichloro-10-(ethynyl)anthracene (**4**). Reagents and conditions: i) Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, DMF, H<sub>2</sub>O, 90 °C, 4 h, 92%;<sup>[17]</sup> ii) 1. Zn, aq. NH<sub>3</sub>; 2. HCl, *i*-PrOH, 85%;<sup>[18]</sup> iii) HC≡C-MgBr, CeCl<sub>3</sub>, THF, 0 °C to r.t., overnight, 65%; iv) 1. Me<sub>3</sub>SiC≡C-MgBr (3 eq.), Et<sub>2</sub>O, r.t. overnight; 2. aq. workup, 56%;<sup>[12]</sup> v) Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C to r.t., quant.;<sup>[14]</sup> vi) 1. Me<sub>3</sub>SiC≡CH (2 eq.), CuI (10 mol%), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol%), (*i*-Pr)<sub>2</sub>NH, reflux, 3d; 2. aq. workup, 85%; vii) K<sub>2</sub>CO<sub>3</sub>, MeOH, r.t., 68%.<sup>[15]</sup>

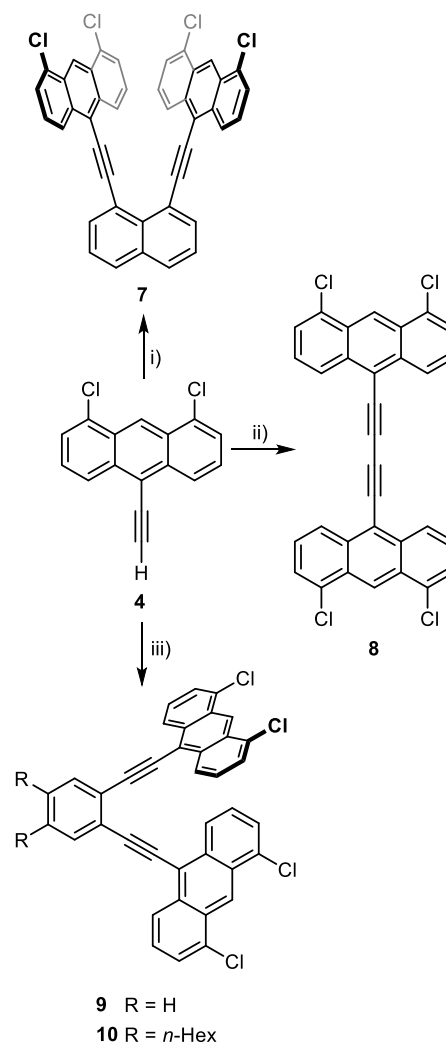
Compound **4** was identified by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, as well as by (high resolution) mass spectrometry. Its <sup>1</sup>H NMR spectrum recorded at ambient temperature (298 K) in CDCl<sub>3</sub> shows the typical set of resonances for 1,8,10-substituted anthracene derivatives, containing one singlet at δ = 9.35 ppm (H9), two doublets at 8.53 ppm (H4/H5) and 7.68 ppm (H2/H7) and one doublet of doublets at 7.53 ppm (H3/H6). The singlet at δ = 4.03 ppm is caused by the ethynyl proton.

As described above, the deprotected species **4** can be used to build up rigid organic frameworks with directed chloro substituents, allowing further functionalisation. As displayed in Scheme 4, we used (cross) coupling reactions to synthesise such fourfold chlorine-substituted organic backbones, whereby the direction of

the C–Cl functions can be varied from nearly parallel orientation (**7**) to ca. 180° (**8**).

The 1,3-butadiynyl-linked species **8** was obtained in excellent yield by a Cu mediated oxidative Eglinton coupling reaction using copper(II) acetate and a mixture of diethyl ether, methanol and pyrimidine as a solvent.<sup>[19]</sup>

Compounds **7** and **9** were synthesised in good to moderate yields by Sonogashira-Hagihara cross-coupling reactions with 1,2-diiodobenzene and 1,8-diiodonaphthalene as arylhalide species. In all cases, the extreme low solubility of the obtained products **7** and **8** in common organic solvents – polar as well as non-polar ones – caused serious problems in recording NMR spectra. Notwithstanding, the compounds were identified and their successful synthesis was proven by at least <sup>1</sup>H NMR spectroscopy and (high resolution) mass spectrometry.



Scheme 4. Use of 1,8-dichloro-10-(ethynyl)anthracene (**4**) as a precursor for rigid organic frameworks. Reagents and conditions: i) 1,8-diiodonaphthalene, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, (*i*-Pr)<sub>2</sub>NH, r.t., 15 h; 2. aq. workup, 63%; ii) Cu(OAc)<sub>2</sub>, Et<sub>2</sub>O/MeOH/pyridine [4:1:1 (v/v/v)], reflux, 2 h, 92%; iii) Synthesis of **9**: 1,2-diiodobenzene, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, (*i*-Pr)<sub>2</sub>NH, r.t., 15 h; 2. aq. workup, 83%; Synthesis of **10**: 1,2-di-*n*-hexyl-4,5-diiodobenzene, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, (*i*-Pr)<sub>2</sub>NH, r.t., 18 h; 2. aq. workup, 60%.

To increase the solubility compared to that of **9**, we used the twofold *n*-hexyl-substituted *ortho*-diiodobenzene (Scheme 4) to link two 1,8-dichloro-10-(ethynyl)anthracene units. Starting from 1,2-dichlorobenzene, the diiodoaryl linker was synthesised in analogy to a literature protocol in a two-step reaction *via* 1,2-di-*n*-

hexylbenzene.<sup>[20]</sup> In fact, **10** shows a much better solubility than **9** and can be purified by column chromatography. The <sup>1</sup>H NMR spectrum recorded at ambient temperature (298 K) in CDCl<sub>3</sub> shows an anthracene signal pattern being comparable with that of compound **4**, whereby the anthracene resonances are slightly shifted. Besides these signals a singlet at  $\delta = 7.66$  ppm can be assigned to the two protons at the benzene unit and broad multiplet signals at  $\delta = 2.74$  ppm, 1.70 ppm, 1.50 ppm and 0.94 ppm are observed for the overall 26 protons of the *n*-hexyl substituents. In case of the conversion of 1,8-dichloro-10-(ethynyl)anthracene (**4**) with the diiodobenzene derivatives we were capable of isolating the corresponding mono-substituted species **9a** and **10a** (Figure 2) by sublimation.

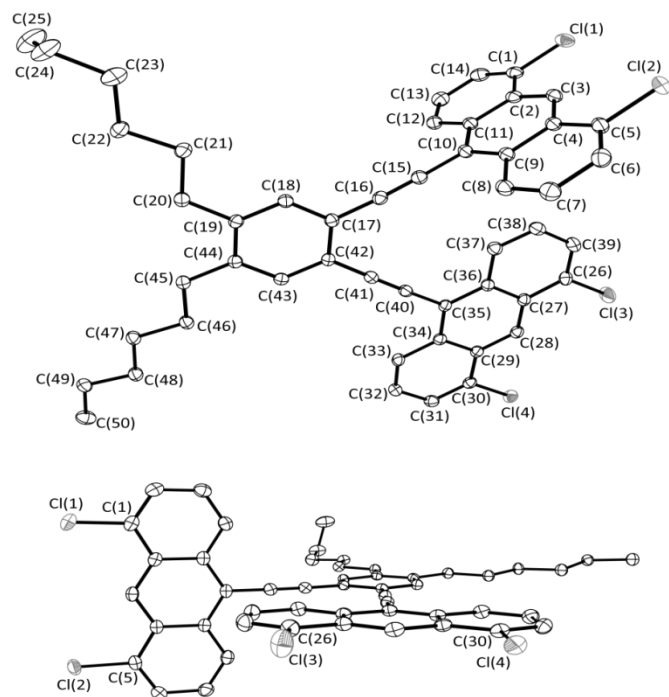


Figure 1. Different views of the molecular structure of **10** in crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. The side view (below) illustrates the orthogonality of the anthracene units. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.433(2), C(1)–C(14) 1.354(2), C(1)–Cl(1) 1.742(1), C(2)–C(3) 1.396(2), C(2)–C(11) 1.438(2), C(10)–C(11) 1.411(2), C(10)–C(15) 1.434(2), C(15)–C(16) 1.200(2), C(16)–C(17) 1.429(2), C(17)–C(18) 1.401(2), C(17)–C(42) 1.407(2), C(18)–C(19) 1.388(2), C(19)–C(20) 1.509(2), C(19)–C(44) 1.416(2); C(1)–C(2)–C(3) 123.5(1), C(1)–C(2)–C(11) 116.9(1), C(2)–C(1)–Cl(1) 118.8(1), C(9)–C(10)–C(11) 121.2(1), C(9)–C(10)–C(15) 119.4(1), C(10)–C(15)–C(16) 177.6(1), C(15)–C(16)–C(17) 177.0(1), C(16)–C(17)–C(18) 119.9(1), C(17)–C(18)–C(19) 121.9(1), C(18)–C(19)–C(20) 121.8(1), C(18)–C(19)–C(44) 119.0(1).

Single crystals of 1,2-di-*n*-hexyl-4,5-bis[(1,8-dichloroanthracene-10-yl)ethynyl]benzene (**10**) were obtained by slow evaporation of the solvent after column chromatography. Its molecular structure was determined by X-ray diffraction and is depicted in Figure 1. Compound **10** crystallises in the triclinic space group *P* $\bar{1}$  with two molecules per unit cell. As illustrated in the structure side view (Figure 1, below), one anthracene unit is almost coplanar with the central benzene ring [angle between their mean-planes: 2.4(1)°], whereas the second anthracene substituent is found to be nearly orthogonal to the other benzene ring as is indicated by the 86.8(1)° angle between their mean-planes. The four chlorine atoms are found to be in-plane with the adjacent anthracene units. The anthracene units themselves exhibit the expected bond lengths and angles, the structural parameters being well comparable with those of the

previously reported SiMe<sub>3</sub>-derivative **5**.<sup>[12]</sup> The bonds C(15)–C(16) and C(40)–C(41) are 1.200(2) Å and 1.203(2) Å in length, respectively. They are identical within experimental error, well comparable with the corresponding C≡C triple bond length in **5** [1.208(3) Å<sup>[12]</sup>] and conform to the standard C≡C triple bond length (1.20 Å<sup>[21]</sup>). The alkynyl group of the orthogonally twisted anthracene substituent is slightly more distorted from linearity as is indicated in the corresponding angles {177.6(1)° [C(10)–C(15)–C(16)] vs. 179.0(1)° [C(35)–C(40)–C(41)]} and {177.0(1)° [C(15)–C(16)–C(17)] vs. 178.9(1)° [C(40)–C(41)–C(42)]}. Distances and angles at the central benzene ring are not markedly influenced by the substituents in 1-, 2-, 4- and 5-position as the C–C distances vary just marginally from that of benzene (1.395 Å<sup>[22]</sup>). With C–C–C angles ranging from 119.0(1)° [C(18)–C(19)–C(44)] to 121.8(1)° [C(18)–C(19)–C(20)] all quaternary benzene carbon atoms are trigonal-planar coordinated.

We also determined the molecular structures of the mono-substituted compounds **9a** and **10a** by X-ray crystallography, which are displayed in Figures 2 and 3. Owing to the fact, that similar structural parameter values are observed for **9a** and **10a**, their molecular structures are described together.

In contrast to the molecular structure of **10** described above, the two aromatic ring systems of the mono-substituted species **9a** and **10a** are found to be not exactly coplanar. The angles between the corresponding mean-planes are 9.4(1)° (**9a**) and 5.1(1)° (**10a**), obviously differing from that of **10** [2.4(1)°]. As observed in case of **10**, the chlorine atoms of **9a** and **10a** (as well as the iodine atoms) are in-plane with the aromatic ring systems. Due to the fact that all bond lengths and angles are within the expected range (Table 1), only two selected structural parameters deserve detailed comment. As is exemplarily indicated in the C(19)–C(20) distances [1.368(6) Å (**9a**) vs. 1.393(2) Å (**10a**)] and C(17)–C(22) distances [1.446(6) Å (**9a**) vs. 1.410(2) Å (**10a**)], the geometry of the central benzene ring seem to be affected by the *n*-hexyl substituents, whereby a significant aberration is observed in the latter case. The dichloroanthracene and alkyne values are found to be identical within experimental error. All mentioned distances and angles of the (alkynyl-) dichloroanthracene unit are well comparable with those observed in various other 10-substituted 1,8-dichloroanthracene derivatives.<sup>[12,14]</sup>

Table 1. Selected bond lengths [Å] and angles [°] of the mono-substituted compounds **9a** and **10a**.

	<b>9a</b>	<b>10a</b>
C(1)–C(2)	1.428(5)	1.429(2)
C(1)–C(14)	1.354(6)	1.361(2)
C(1)–Cl(1)	1.743(4)	1.741(2)
C(2)–C(3)	1.411(6)	1.396(2)
C(2)–C(11)	1.427(6)	1.435(2)
C(9)–C(10)	1.415(6)	1.413(2)
C(10)–C(15)	1.431(6)	1.429(2)
C(15)–C(16)	1.201(6)	1.202(2)
C(16)–C(17)	1.428(6)	1.428(2)
C(17)–C(18)	1.410(5)	1.396(2)
C(17)–C(22)	1.446(6)	1.410(2)
C(18)–I(1)	2.091(4)	2.092(2)
C(19)–C(20)	1.368(6)	1.393(2)
C(1)–C(2)–C(3)	123.4(4)	122.8(1)
C(1)–C(2)–C(11)	117.2(4)	117.0(1)
C(9)–C(10)–C(15)	119.4(4)	119.7(1)
C(10)–C(15)–C(16)	175.4(4)	178.4(2)
C(15)–C(16)–C(17)	175.4(4)	176.0(2)
C(16)–C(17)–C(18)	122.4(4)	123.5(1)
C(17)–C(18)–I(1)	120.6(3)	121.0(1)

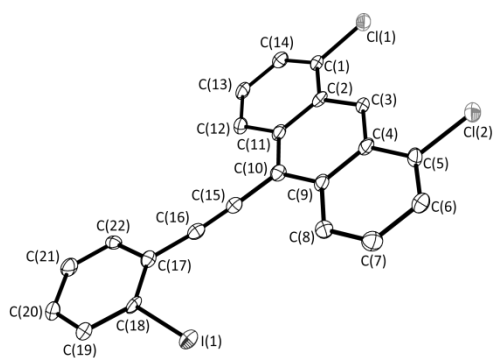


Figure 2. Molecular structure of the mono-substituted compound **9a** in the crystal. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 1.

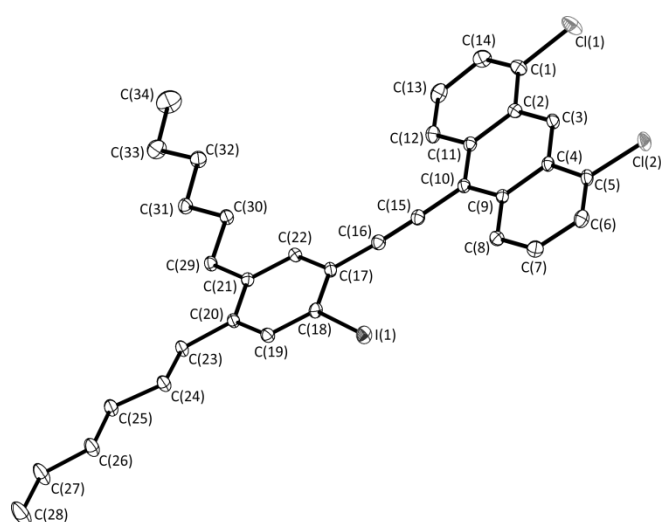


Figure 3. Molecular structure of the mono-substituted compound **10a** in the crystal. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 1.

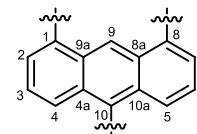
## Conclusions

1,8-Dichloro-10-(ethynyl)anthracene (**4**), a highly conjugated anthracene containing species, was afforded by the reaction of 1,8-dichloroanthrone **2** with ethynylmagnesium bromide in one-step, whereby addition of cerium(III) chloride led to a remarkable increase in yield. Compound **4** was demonstrated to be a useful building block in the formation of rigid organic backbones for (cross) coupling reactions. A serious restriction in applicability of most of these linked products is their (extreme) low solubility in organic solvents. This problem was exemplarily solved in one case by introduction of long-chain alkyl groups. Further functionalisation of the chloro substituents, are presently under investigation in a broader context.

## Experimental Section

**General:** 1,8-Dichloroanthracen-10-(9H)-one (**2**),<sup>[17]</sup> 1,8-diiodonaphthalene<sup>[23]</sup> and 1,2-di-*n*-hexyl-4,5-diiodobenzene<sup>[20]</sup> were synthesised according to the literature. Ethynylmagnesium bromide solution (0.5 M in THF) was purchased from Sigma Aldrich, anhydrous CeCl<sub>3</sub> (purchased from Strem

Chemicals) was used without further purification. All reactions using metal organic reagents were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried over potassium and freshly distilled before being used for the reactions). Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). NMR spectra were recorded on a Bruker *Avance III 300*, a Bruker *DRX 500* and a Bruker *Avance III 500* instrument at room temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C NMR  $\delta$  = 77.16 ppm). EI mass spectra were recorded using an *Autospec X* magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. MALDI TOF mass spectra were recorded with a Voyager DE Instrument (PE Biosystems GmbH, Weiterstadt, Germany) and ESI/APCI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. The numbering scheme for NMR assignments (Scheme 4) is based on IUPAC guidelines.



Scheme 4. Anthracene numbering scheme, exemplarily shown for a 1,8,10-substituted anthracene derivative.

**1,8-Dichloro-10-(ethynyl)anthracene (4):** Dry THF (25 mL) was added to cerium(III) chloride (2.11 g, 8.6 mmol) at 0 °C under vigorous stirring and the grey suspension was stirred for another 3.5 h at ambient temperature. After ethynylmagnesium bromide (0.5 M in THF, 17.0 mL, 8.5 mmol) was added dropwise at 0 °C, a solution of 1,8-dichloroanthracen-10-(9H)-one (1.50 g, 5.7 mmol), dissolved in dry THF (20 mL), was added to the black solution at the same temperature. The mixture was stirred overnight and allowed to warm to ambient temperature. The mixture was quenched with a saturated aqueous solution of NH<sub>4</sub>Cl (20 mL) and the aqueous layer was extracted with THF (4 × 50 mL). The combined organic phases were washed with brine and dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow brownish solid was purified by flash column chromatography. ( $\varnothing$  = 3 cm,  $l$  = 5 cm, eluent: *n*-pentane) affording **4** as a yellow solid. Yield: 1.01 g (65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.35 (s, 1H, H<sub>9</sub>), 8.53 (d, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.68 (d, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.53 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.7 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 4.03 (s, 2H, C≡C–H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.26, 133.16, 129.08, 127.14 (C<sub>3</sub>/C<sub>6</sub>), 126.57 (C<sub>2</sub>/C<sub>7</sub>), 126.03 (C<sub>4</sub>/C<sub>5</sub>), 122.66 (C<sub>9</sub>), 120.87, 89.49 (C≡C–H), 79.89 (C≡C–H) ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 270.0 [M]<sup>+</sup>, 235.0 [M–Cl]<sup>+</sup>, 200.0 [M–2Cl]<sup>+</sup> HRMS: calculated for C<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub><sup>+</sup>: 270.00031; measured: 269.99416.

### 1,4-Bis(1,8-dichloroanthracene-10-yl)buta-1,3-diyne (8):

1,8-Dichloro-10-(ethynyl)anthracene (130 mg, 0.48 mmol) was added to a blue solution of Cu(OAc)<sub>2</sub> (0.30 g, 1.67 mmol) in a 4:1:1 (v/v/v) mixture of diethyl ether/methanol/pyridine and heated to reflux for 2 h. A red solid precipitated which was filtered off and washed with small amounts of diethyl ether. Yield: 119 mg (92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.40 (s, 2H, H<sub>9</sub>), 8.63 (d, <sup>3</sup>J<sub>H,H</sub> = 9.1 Hz, 4H, H<sub>4</sub>/H<sub>5</sub>), 7.73 (d, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 4H, H<sub>2</sub>/H<sub>7</sub>), 7.62 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5, 8.4 Hz, 4H, H<sub>3</sub>/H<sub>6</sub>) ppm. Due to extreme low solubility, no <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could be recorded. MS (EI, 70 eV):  $m/z$  [assignment] = 540.0 [M]<sup>+</sup>, 504.0 [M–Cl]<sup>+</sup>, 468.0 [M–2Cl]<sup>+</sup>, 432.0 [M–3Cl]<sup>+</sup>, 396.0 [M–4Cl]<sup>+</sup>, 269.9 [M–(C<sub>16</sub>H<sub>7</sub>Cl<sub>2</sub>)]<sup>+</sup>. MS (MALDI-TOF, positive ions, DHB):  $m/z$  [assignment] = 541.0 [M+H]<sup>+</sup>, 468.5 [M–2Cl]<sup>+</sup>. HRMS (MALDI-TOF): calculated for C<sub>32</sub>H<sub>14</sub>Cl<sub>4</sub><sup>+</sup>: 537.98441; measured: 537.98453.

### General Procedure for Sonogashira-Hagihara Coupling Reactions:

The diiodoaryls and 1,8-dichloro-10-(ethynyl)anthracene (**4**) were dissolved in diisopropylamine, the solutions were degassed by at least two freeze-pump-thaw cycles and CuI and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (one spatula tip of each compound) were added to the mixtures which were stirred overnight at ambient temperature. A saturated aqueous solution of NH<sub>4</sub>Cl was added to quench the reaction and the solid was filtered off. In case of compounds **7** and **9** the desired products were obtained as hardly soluble solids after washing with water and cold *n*-pentane. The di-*n*-hexyl-substituted species **10** was afforded after extracting the aqueous layer with dichloromethane (3 × 15 mL), washing the combined organic phases with brine and drying over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow-orange solid was purified by column chromatography ( $\varnothing$  = 3 cm, *l* = 20 cm, eluent: *n*-pentane).

### 1,8-Bis[(1,8-dichloroanthracene-10-yl)ethynyl]naphthalene (7):

Synthesis according to the General Procedure using 1,8-diiodonaphthalene (70 mg, 0.19 mmol), 1,8-dichloro-10-(ethynyl)anthracene (100 mg, 0.37 mmol) and diisopropylamine (10 mL). Yellow-brownish solid. Yield: 80 mg (63%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.33 (s, 2H, H<sub>9</sub>), 8.78 (d, <sup>3</sup>J<sub>H,H</sub> = 8.3 Hz, 4H, H<sub>4</sub>/H<sub>5</sub>), 8.33 (m, 2H, NaphH), 8.16 (m, 2H, NaphH), 7.92 (d, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 4H, H<sub>2</sub>/H<sub>7</sub>), 7.69 (m, 4H, H<sub>3</sub>/H<sub>6</sub>) 7.54 (m, 2H, NaphH) ppm. Due to extreme low solubility, no <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could be recorded. MS (MALDI-TOF, positive ions, DHB): *m/z* [assignment] = 667.0 [M+H]<sup>+</sup>, 524.0 [M-4Cl]<sup>+</sup>. HRMS (MALDI-TOF): calculated for C<sub>42</sub>H<sub>20</sub>Cl<sub>4</sub><sup>+</sup>: 664.03136; measured: 664.03177.

### 1,2-Bis[(1,8-dichloroanthracene-10-yl)ethynyl]benzene (9):

Synthesis according to the General Procedure using 1,2-diiodobenzene (0.27 g, 0.82 mmol), 1,8-dichloro-10-(ethynyl)anthracene (0.46 g, 1.71 mmol) and diisopropylamine (20 mL). Traces of the mono-substituted by-product **9a** (analytical data see below) were removed by sublimation (170 °C, 7·10<sup>-3</sup> mbar). Yellow-brownish solid. Yield: 0.42 g (83%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.30 (s, 2H, H<sub>9</sub>), 8.59 (d, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz, 4H, H<sub>4</sub>/H<sub>5</sub>), 7.91 (m, 2H, PhH), 7.54 (m, 2H, PhH), 7.49 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 4H, H<sub>2</sub>/H<sub>7</sub>), 6.88 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.7 Hz, 4H, H<sub>3</sub>/H<sub>6</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 133.78, 132.92, 132.62, 129.06, 128.99, 126.75, 126.50, 126.30, 125.78, 122.34, 118.80, 100.62, 90.22 ppm. MS (ESI, positive mode, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, AgBF<sub>4</sub>): *m/z* [assignment] = 639.4 [M+Na]<sup>+</sup>, 581.3 [M-Cl]<sup>+</sup>. MS (MALDI-TOF, positive ions, DHB): *m/z* [assignment] = 614.2 [M]<sup>+</sup>, 472.2 [M-4Cl]<sup>+</sup>. HRMS (MALDI-TOF): calculated for C<sub>38</sub>H<sub>18</sub>Cl<sub>4</sub><sup>+</sup>: 614.01571; measured: 614.01569.

Analytical data for **9a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.34 (s, 1H, H<sub>9</sub>), 8.78 (d, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.98 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, PhH), 7.79 (dd, <sup>3</sup>J<sub>H,H</sub> = 1.4, 7.7 Hz, 1H, PhH), 7.69 (d, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.55 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.3, 8.6 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 7.45 (td, <sup>3</sup>J<sub>H,H</sub> = 1.0, 7.6 Hz, 1H, PhH), 7.12 (td, <sup>3</sup>J<sub>H,H</sub> = 1.6, 7.9 Hz, 1H, PhH) ppm. MS (EI, 70 eV): *m/z* [assignment] = 471.7 [M]<sup>+</sup>, 436.8 [M-Cl]<sup>+</sup>, 343.8 [M-I]<sup>+</sup>, 309.9 [M-I-Cl]<sup>+</sup>, 274.1 [M-I-2Cl]<sup>+</sup>.

### 1,2-Di-*n*-hexyl-4,5-bis[(1,8-dichloroanthracene-10-yl)ethynyl]benzene (10):

Synthesis according to the General Procedure using 1,2-di-*n*-hexyl-4,5-diiodobenzene (55 mg, 0.11 mmol), 1,8-dichloro-10-(ethynyl)anthracene (65 mg, 0.24 mmol) and diisopropylamine (10 mL). Bright yellow solid. Yield: 52 mg (60%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.27 (s, 2H, H<sub>9</sub>), 8.60 (d, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz, 4H, H<sub>4</sub>/H<sub>5</sub>), 7.66 (s, 2H, PhH), 7.47 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 4H, H<sub>2</sub>/H<sub>7</sub>), 6.87 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.3, 8.7 Hz, 4H, H<sub>3</sub>/H<sub>6</sub>), 2.74 {m, 4H, [Ph-CH<sub>2</sub>-(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>], 1.70 {m, 4H, [Ph-CH<sub>2</sub>-CH<sub>2</sub>-(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>], 1.42 {m, 12H, [Ph-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>3</sub>H<sub>6</sub>)-CH<sub>3</sub>]<sub>2</sub>}, 0.94 {m, 6H, [Ph-(C<sub>5</sub>H<sub>10</sub>)-CH<sub>3</sub>]<sub>2</sub>} ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.51, 133.72, 133.11, 132.86 (PhCH), 129.08, 126.60, 126.46, 123.04, 121.98 (C<sub>9</sub>), 119.22, 101.15, 89.12, 32.87 (Ph-CH<sub>2</sub>-C<sub>5</sub>H<sub>11</sub>), 31.92, 31.32, 29.87, 22.83, 14.30 (CH<sub>3</sub>) ppm. One signal missing due to overlap or line broadening. Owing to similar NMR shifts, no further assignments are possible. MS (MALDI-TOF, positive ions, DHB):

*m/z* [assignment] = 784.3 [M+H]<sup>+</sup>. HRMS (MALDI-TOF): calculated for C<sub>50</sub>H<sub>42</sub>Cl<sub>4</sub><sup>+</sup>: 782.20351; measured: 782.20291.

Analytical data for **10a**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.31 (s, 1H, H<sub>9</sub>), 8.79 (d, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.72 (s, 1H, PhH), 7.68 (d, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.55 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.4, 8.5 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 7.52 (s, 1H, PhH), 2.61 {m, 4H, [Ph-CH<sub>2</sub>-(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>], 1.61 {m, 4H, [Ph-CH<sub>2</sub>-CH<sub>2</sub>-(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>], 1.39 {m, 12H, [Ph-(CH<sub>2</sub>)<sub>2</sub>-(C<sub>3</sub>H<sub>6</sub>)-CH<sub>3</sub>]<sub>2</sub>}, 0.92 {m, 6H, [Ph-(C<sub>5</sub>H<sub>10</sub>)-CH<sub>3</sub>]<sub>2</sub>} ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.10, 141.29, 139.52, 133.92, 133.86, 133.06, 129.28, 127.07, 126.85, 126.69, 126.59, 122.08, 119.26, 103.66, 97.06, 88.31, 32.51, 32.46, 31.87, 31.84, 31.25, 31.15, 29.53, 29.50, 22.80, 22.77, 14.27. One signal missing due to overlap or line broadening. MS (EI, 70 eV): *m/z* [assignment] = 640.1 [M]<sup>+</sup>, 514.2 [M-I]<sup>+</sup>, 498.9 [M-I-CH<sub>3</sub>]. HRMS (EI): calculated for C<sub>34</sub>H<sub>35</sub>Cl<sub>2</sub>I<sup>+</sup>: 640.11550; measured: 640.11565.

Table 2: Crystallographic data for **9a**, **10** and **10a**.

	<b>9a</b>	<b>10</b>	<b>10a</b>
Emp. formula	C <sub>22</sub> H <sub>11</sub> Cl <sub>2</sub> I	C <sub>50</sub> H <sub>42</sub> Cl <sub>4</sub>	C <sub>34</sub> H <sub>35</sub> Cl <sub>2</sub> I
<i>M<sub>r</sub></i>	473.11	784.64	641.42
$\lambda$ [Å]	1.54178	0.71073	0.71073
<i>T</i> [K]	100(2)	100(2)	100(2)
<i>F</i> (000)	460	820	652
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	13.6438(3)	9.5969(1)	7.0151(1)
<i>b</i> [Å]	3.9082(1)	12.7474(1)	8.2307(1)
<i>c</i> [Å]	16.6992(4)	16.4508(2)	25.9424(3)
$\alpha$ [°]	90	82.4109(8)	95.178(1)
$\beta$ [°]	105.311(2)	85.6854(7)	90.410(1)
$\gamma$ [°]	90	88.5133(7)	91.970(1)
<i>V</i> [Å <sup>3</sup> ]	858.84(4)	1988.97(4)	1490.83(3)
<i>Z</i>	2	2	2
$\rho_{\text{calcd}}$ [gcm <sup>-3</sup> ]	1.829	1.310	1.429
$\mu$ [mm <sup>-1</sup> ]	17.504	0.333	1.274
$\theta_{\text{max}}$ [°]	70.00	30.00	30.00
Index ranges <i>h</i>	-16 ≤ <i>h</i> ≤ 16	-13 ≤ <i>h</i> ≤ 13	-9 ≤ <i>h</i> ≤ 9
Index ranges <i>k</i>	-4 ≤ <i>k</i> ≤ 4	-17 ≤ <i>k</i> ≤ 17	-11 ≤ <i>k</i> ≤ 11
Index ranges <i>l</i>	-20 ≤ <i>l</i> ≤ 20	-23 ≤ <i>l</i> ≤ 23	-36 ≤ <i>l</i> ≤ 36
Refl. collected	16193	80924	173568
Indep. refl.	3156	11562	8687
<i>R</i> <sub>int</sub>	0.040	0.054	0.047
Observed refl., <i>I</i> > 2 $\sigma$ ( <i>I</i> )	3070	8691	8522
Parameters	226	489	336
<i>R</i> <sub>1</sub> , <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0254	0.0388	0.0251
<i>wR</i> <sub>2</sub> , <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0658	0.0964	0.0612
<i>R</i> <sub>1</sub> (all data)	0.0264	0.0594	0.0257
<i>wR</i> <sub>2</sub> (all data)	0.0664	0.1056	0.0615
<i>GoF</i>	1.068	1.036	1.226
$\rho_{\text{max}}/\rho_{\text{min}}$ [e Å <sup>-3</sup> ]	1.00/-0.64	0.36/-0.35	0.90/-0.54
CCDC number	987865	987866	987867

### Crystal Structure Determination

Suitable crystals of compounds **9a**, **10** and **10a** were obtained by slow evaporation of saturated solutions in chloroform (**9a**) and *n*-pentane (**10** and **10a**), respectively. Crystals were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen cold stream solidifying the oil. Data collection was performed on a Bruker AXS X8 Prospecor Ultra with APEX II diffractometer (**9a**), a Nonius Kappa CCD diffractometer (**10**) and a Super Nova, Dual, Cu at zero, Atlas diffractometer (**10a**).

The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>[24]</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table 2. CCDC 987865 – 987867 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.ac.uk/data\\_request/cif](http://www.ccdc.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): NMR spectra of all new compounds and X-ray data in CIF format for compounds **9a**, **10** and **10a**.

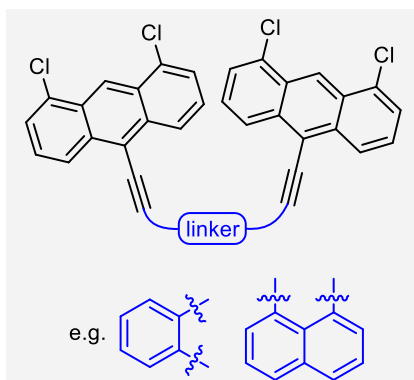
## Acknowledgments

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A useful building block for the synthesis of linked di-anthracenene compounds with four oriented C–Cl functions is 1,8-dichloro-10-(ethynyl)anthracene; it is accessible by an improved cerium mediated protocol.



### Anthracene Linking

**J.-H. Lamm, L. A. Körte,  
L. Kuhlmann, B. Neumann,  
H.-G. Stammler,  
N. W. Mitzel\*** .... Page No. – Page No.

Improved Access to 1,8-Dichloro-10-(ethynyl)anthracene – A Building Block for Rigid Organic Frameworks

**Keywords:** Anthracenes / Alkynes / Rigid Organic Backbones / Solid-State Structures





## **Publikation 4**

### **Polyalkynylanthracenes – Syntheses, Structures and their Behaviour towards UV Irradiation**

Jan-Hendrik Lamm, Johanna Glatthor, Jan-Henrik Weddeling, Andreas Mix,  
Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

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## ARTICLE

# Polyalkynylanthracenes – Syntheses, Structures and their Behaviour towards UV Irradiation

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Jan-Hendrik Lamm,<sup>a</sup> Johanna Glatthor,<sup>a</sup> Jan-Henrik Weddeling,<sup>a</sup> Andreas Mix,<sup>a</sup> Jasmin Chmiel,<sup>a</sup> Beate Neumann,<sup>a</sup> Hans-Georg Stammer<sup>a</sup> and Norbert W. Mitzel<sup>\*a</sup>

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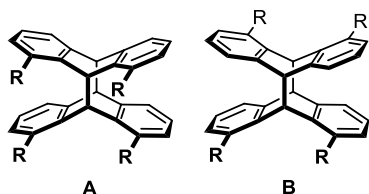
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A series of bis- and tris[(trimethylsilyl)ethynyl]anthracenes (1,5-, 1,8-, 9,10- and 1,8,10-) has been synthesised by multistep (cross coupling) reactions and the behaviour of the SiMe<sub>3</sub>-functionalised alkynylanthracene derivatives towards UV irradiation was qualitatively studied by NMR spectroscopy. In case of 9,10-bis[(trimethylsilyl)ethynyl]anthracene we observed a photodimerisation upon UV irradiation; the third example reported for a symmetrically 9,10-difunctionalised anthracene derivative, besides those with small fluorine- and methyl-substituents. The anthracene dimerisation is completely thermally reversible and the temperature dependency of the cycloelimination reaction was studied using <sup>1</sup>H VT-NMR experiments. The (deprotected) 1,5- and 1,8-diethynylanthracenes were converted with (dimethylamino)trimethylstannane to gain the corresponding SnMe<sub>3</sub>-functionalised alkynes, potentially useful as highly conjugated building blocks in Stille cross coupling reactions. The new anthracene compounds were completely characterised by multinuclear NMR spectroscopy, (high resolution) mass spectrometry and –in most cases– by X-ray diffraction experiments.

## Introduction

Anthracenes and their substituted derivatives undergo cycloaddition reactions upon irradiation with UV light.<sup>1</sup> In case of functionalised anthracenes, like 1,8-substituted ones, a mixture of so-called *head to head*- (**A**) and *head to tail*- (**B**) photodimers is obtained. Owing to steric interactions of the substituents, the *head to tail* isomer is the preferred product in most cases.<sup>2</sup>



**Scheme 1** Photodimerisation products of 1,8-substituted anthracene derivatives.

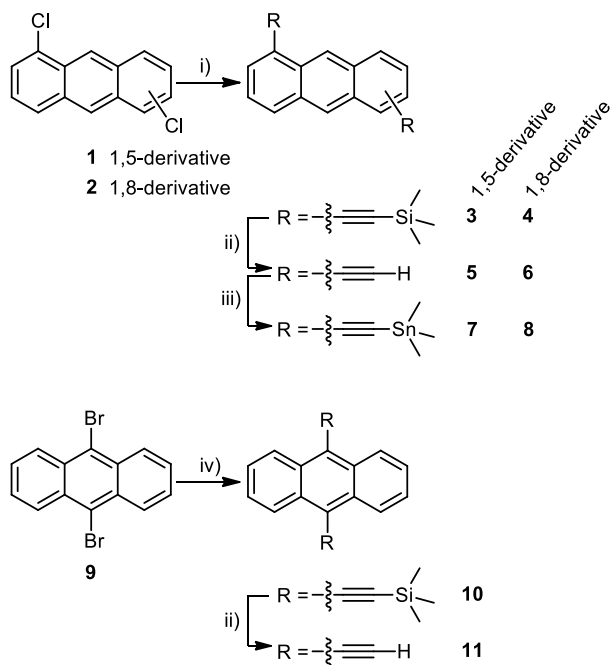
(Di-) Substituted anthracenes find various applications as photoswitchable units e.g. in supramolecular systems,<sup>3</sup> as their photodimerisation reactions are mostly found to be similar to unsubstituted anthracene, i.e. [4+4] cycloaddition leading to the 9,10:9',10' photodimer.<sup>4</sup> However, other types of (mono-) substituted anthracene dimerisation, called *non-classical photodimers*, have been observed, e.g. in the case of 9-(phenylethynyl)anthracene ([4+2] cycloaddition) or *trans*-1-(9-anthryl)-2-phenylethylene ([6+6] cycloaddition).<sup>1b,5</sup>

Due to steric repulsion of the substituents, the photodimerisation of 9,10-disubstituted anthracenes is scarcely explored. Nevertheless, some examples are known. Some unsymmetrically substituted anthracene derivatives have been found to undergo photodimerisation yielding [4+4] cycloaddition products, which are thermally labile in most cases.<sup>1b</sup> Until now, symmetrically 9,10-disubstituted anthracenes are known to be unwilling to dimerise, except 9,10-difluoro<sup>6</sup> and 9,10-dimethylantracene.<sup>7</sup>

## Results and discussion

### Syntheses and Characterisations of the Anthracene Derivatives

The bis[(trimethylsilyl)ethynyl]-functionalised anthracenes **3**, **4** and **10** were obtained by Kumada and Sonogashira-Hagihara cross coupling reactions using 1,5- (**1**) and 1,8-dichloroanthracene (**2**) as well as 9,10-dibromoanthracene (**9**), respectively (Scheme 2).<sup>8,9</sup> After cleaving the SiMe<sub>3</sub> groups, the deprotected dialkynes **5** and **6** were converted with (dimethylamino)trimethylstannane and the SnMe<sub>3</sub>-functionalised compounds **7** and **8** were obtained in quantitative yield. These terminally SnMe<sub>3</sub>-functionalised dialkynyl anthracenes might be applicable as highly conjugated (photoswitchable) building blocks e.g. when two functionalities should be linked by Stille cross coupling reactions.<sup>10</sup> All compounds were characterised by multinuclear NMR spectroscopy as well as (high resolution) mass spectrometry. Tables 1 and 2 provide the <sup>1</sup>H NMR spectroscopic shifts of the 1,5- and 1,8-substituted derivatives for comparison.



**Scheme 2** Syntheses of the 1,5-, 1,8- and 9,10-dialkynylsubstituted anthracene derivatives. Reagents and conditions: i) 1.  $\text{Me}_3\text{SiC}\equiv\text{CMgBr}$  (7 eq.),  $\text{Ni}(\text{acac})_2$ ,  $\text{PPh}_3$ , THF, reflux; 2. aq. workup, 82% (**3**), 92% (**4**); ii)  $\text{K}_2\text{CO}_3$ , MeOH, r.t., 93% (**5**), 82% (**6**), 25% (**11**); iii)  $\text{Me}_3\text{SnNMe}_2$ , THF, 60 °C, 4h, quant. (**7** and **8**); iv) 1.  $\text{Me}_3\text{SiC}\equiv\text{CH}$  (2 eq.),  $\text{CuI}$  (10 mol%),  $\text{PdCl}_2(\text{PPh}_3)_2$  (5 mol%), (*i*-Pr) $_2\text{NH}$ , reflux, 3d; 2. aq. workup, 38%.

**Table 1**  $^1\text{H}$  NMR shifts of the 1,5-dialkynylsubstituted compounds **3** (E = Si), **5** and **7** (E = Sn) in  $\text{CDCl}_3$  (500 MHz, 298 K). For NMR spectroscopic assignments see Scheme 7.

	H9/H10	H4/H8	H2/H6	H3/H7	C $\equiv$ C–H	E(CH $_3$ ) $_3$
<b>3</b>	8.88	8.06	7.74	7.44	-	0.39
<b>5</b>	8.93	8.10	7.79	7.46	3.60	-
<b>7</b>	8.93	8.04	7.72	7.42	-	0.48

**Table 2**  $^1\text{H}$  NMR shifts of the 1,8-dialkynylsubstituted compounds **4** (E = Si), **6** and **8** (E = Sn) in  $\text{CDCl}_3$  (500 MHz, 298 K). For NMR spectroscopic assignments see Scheme 7.

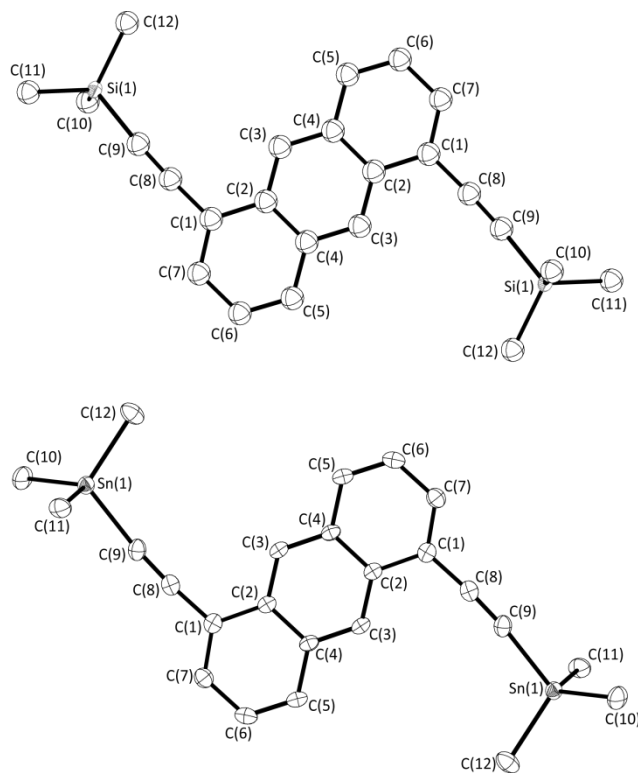
	H9	H10	H4/H5	H2/H7	H3/H6	C $\equiv$ C–H	E(CH $_3$ ) $_3$
<b>4</b>	9.32	8.42	7.98	7.79	7.42	-	0.39
<b>6</b>	9.44	8.45	8.03	7.80	7.45	3.62	-
<b>8</b>	9.43	8.40	8.95	7.76	7.40	-	0.46

We also tried to convert 9,10-diethynylantracene (**11**) into the corresponding  $\text{SnMe}_3$  substituted species. However, the brownish product was found to be insoluble in common organic solvents and could not be analysed so far.

The molecular structures in the crystalline state of compounds **3**, **4**, **5**, **7** and **8** are displayed in Figures 1, 2, 3 and 4 (the structure of **6** was previously published by us<sup>11</sup>). They were determined by X-ray diffraction experiments of single crystals grown from solutions by slow evaporation of the solvent (see Experimental Section for details). Due to the fact that similar structural parameter values are observed for compounds **3** and

**7**, as well as for compounds **4** and **8**, their molecular structures are described together.

The terminally  $\text{SiMe}_3$ - and  $\text{SnMe}_3$ -substituted 1,5-diethynylantracenes **3** and **7** exhibit an inversion centre in the middle of the central anthracene ring. The aromatic systems are planar with C–C distances ranging from 1.367(2) Å [C(5)–C(6), **3**] and 1.364(3) Å [C(5)–C(6), **7**] to 1.447(1) Å [C(1)–C(2), **3**] and 1.452(3) Å [C(1)–C(2), **7**], respectively. The alkynyl substituents are nearly in the same plane as the anthracene backbone; this is manifest from the surrounding angles of C(1), which are close to 120° [maximum deviations are 0.9° (**3**) and 1.7° (**7**)]. The angles C(1)–C(8)–C(9) [175.5(2)° (**3**) and 175.2(2)° (**7**)] and C(8)–C(9)–E(1) [171.9(2)° (**3**) and 166.2(2)° (**7**)] show the (trimethylelement)ethynyl groups to be slightly bent out of linearity and they are found to be not in-plane with the anthracene units as is indicated in the dihedral angles C(6)–C(7)–C(1)–C(8) at 175.3(1)° (**3**) and 177.0(2)° (**7**), respectively. The silicon and tin atoms are tetrahedrally coordinated with E(1)–C $_M$ e distances in the expected range.<sup>12</sup> The C $\equiv$ C bond lengths of compounds **3** [1.209(2) Å] and **7** [1.210(3) Å] are identical within experimental error and with the standard triple bond length of 1.20 Å.<sup>12</sup>

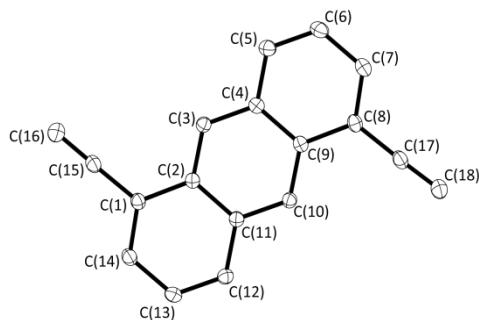


**Fig. 1** Molecular structures of compounds **3** (above) and **7** (below) in crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 3.

**Table 3** Selected bond lengths [Å] and angles [°] of compounds **3** and **7**.

	<b>3</b> (E = Si)	<b>7</b> (E = Sn)
C(1)–C(2)	1.447(1)	1.452(3)
C(1)–C(7)	1.376(1)	1.380(3)
C(1)–C(8)	1.437(1)	1.434(3)
C(2)–C(3)	1.397(1)	1.393(3)
C(2)–C(4)	1.436(1)	1.433(3)
C(8)–C(9)	1.209(2)	1.210(3)
C(9)–E(1)	1.844(1)	2.113(2)
C(10)–E(1)	1.866(1)	2.131(2)
C(1)–C(2)–C(3)	122.4(1)	122.4(2)
C(1)–C(2)–C(4)	118.5(1)	118.6(2)
C(1)–C(8)–C(9)	175.5(1)	175.2(2)
C(2)–C(1)–C(7)	120.0(1)	119.7(2)
C(2)–C(1)–C(8)	119.1(1)	118.6(2)
C(8)–C(9)–E(1)	171.9(1)	166.2(2)

The molecular structure of the deprotected 1,5-diethynylantracene (**5**) depicted in Figure 2 exhibits no unexpected bond lengths and angles. Carbon atoms C(1) and C(8) are trigonal-planar coordinated with the three surrounding angles being close to 120°. The alkynyl substituents are found to be in-plane with the planar anthracene skeleton. With “aromatic” C–C distances between 1.367(1) Å [C(5)–C(6)] and 1.436(1) Å [C(4)–C(9)], the structural parameters are well comparable with those of 1,8-diethynylantracene (**6**).<sup>11</sup>



**Fig. 2** Molecular structure of compound **5** in crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.445(1), C(1)–C(14) 1.378(1), C(1)–C(15) 1.435(1), C(2)–C(3) 1.396(1), C(2)–C(11) 1.436(1), C(15)–C(16) 1.195(1); C(1)–C(2)–C(3) 122.3(1), C(1)–C(2)–C(11) 118.4(1), C(1)–C(15)–C(16) 178.5(1), C(2)–C(1)–C(14) 120.2(1), C(2)–C(1)–C(15) 119.5(1).

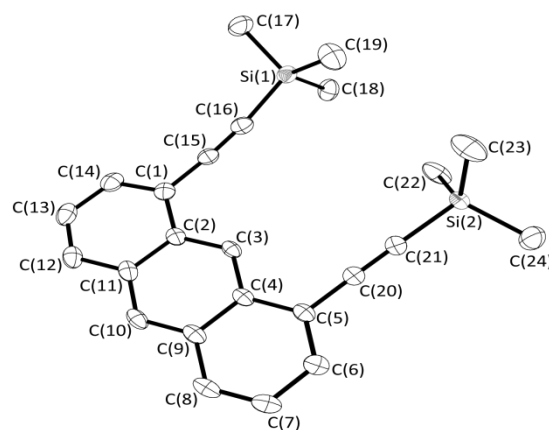
The SiMe<sub>3</sub>-substituted 1,8-dialkynylantracene **4** is depicted in Figure 3 and important structural parameters of both molecules are listed in Table 4.

After recrystallisation from *n*-hexane, the molecular structure of the SnMe<sub>3</sub> derivative **8** was also determined by X-ray diffraction experiments (Figure 4). In contrast to the corresponding 1,5-substituted compound **7**, four molecules of 1,8-bis[(trimethylstannyl)ethynyl]anthracene (**8**) and one *n*-hexane molecule are found in the asymmetric unit. Selected value ranges of the corresponding bond lengths and angles of **4** and **8** are listed in Table 4 for comparison. A few remarkably different values were measured demonstrating the variability of structural parameters of independent molecules for the same compound, a

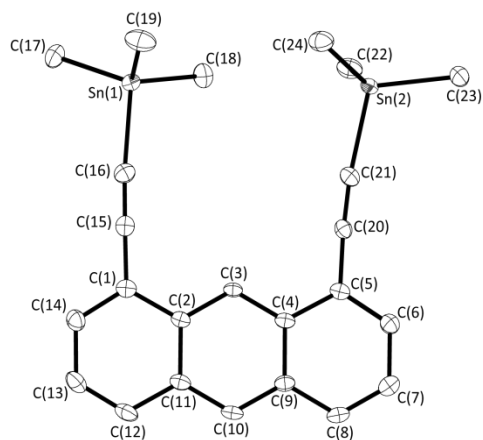
fact, that has also been observed in the X-ray diffraction results of 1,8-diethynylantracene (**6**).<sup>11</sup> Nevertheless, the bond lengths and angles determined for compounds **4** and **8** are in the expected ranges and the values are comparable to those of the corresponding 1,5-substituted derivatives **3** and **7** described above in more details. Exact values for certain molecules are given in the captures of Figures 3 and 4.

**Table 4** Selected value ranges (minimum and maximum) of bond lengths [Å] and angles [°] of compounds **4** and **8**.

	<b>4</b> (E = Si)		<b>8</b> (E = Sn)	
	min.	max.	min.	max.
C <sub>Ar</sub> –C≡	1.437(2)	1.440(2)	1.427(3)	1.438(3)
–C≡C–	1.205(2)	1.209(2)	1.200(3)	1.210(3)
≡C–E	1.842(1)	1.847(1)	2.105(2)	2.123(2)
E–C <sub>Me</sub>	1.849(2)	1.864(2)	2.126(2)	2.137(2)
C <sub>Ar</sub> –C <sub>Ar</sub>	1.356(2)	1.443(2)	1.355(3)	1.449(2)
C <sub>Ar</sub> –C <sub>Ar</sub> –C <sub>Ar</sub>	117.9(1)	122.6(1)	118.0(2)	122.4(2)
C <sub>Ar</sub> –C <sub>Ar</sub> –C≡	118.9(1)	121.1(1)	119.2(2)	121.5(2)
C <sub>Ar</sub> –C≡C	174.4(1)	178.5(1)	174.9(2)	179.6(2)
C≡C–E	173.9(1)	177.1(1)	170.2(2)	176.3(2)
≡C–E–C <sub>Me</sub>	106.3(1)	109.4(1)	103.1(1)	109.0(1)
C <sub>Me</sub> –E–C <sub>Me</sub>	109.5(2)	112.1(1)	108.9(1)	117.7(1)

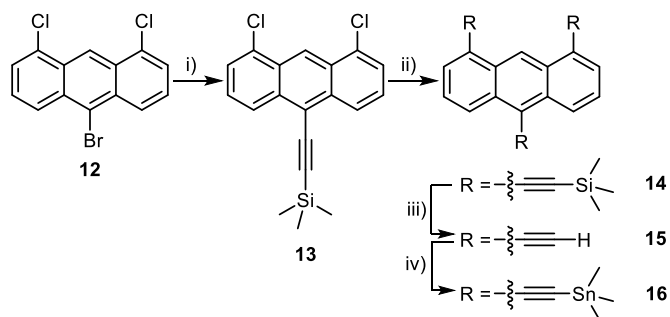


**Fig. 3** Molecular structure of compound **4** in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted and only one molecule is shown for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.443(2), C(1)–C(14) 1.377(2), C(1)–C(15) 1.440(2), C(2)–C(3) 1.396(2), C(2)–C(11) 1.438(2), C(5)–C(20) 1.437(2), C(6)–C(7) 1.416(2), C(16)–Si(1) 1.842(1), C(17)–Si(1) 1.864(2); C(1)–C(2)–C(3) 122.6(1), C(1)–C(2)–C(11) 118.3(1), C(1)–C(15)–C(16) 176.0(1), C(2)–C(1)–C(15) 120.5(1), C(5)–C(20)–C(21) 178.5(1), C(15)–C(16)–Si(1) 173.9(1), C(20)–C(21)–Si(2) 177.1(1).



**Fig. 4** Molecular structure of compound **8** in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted and only one molecule is shown for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.448(2), C(1)–C(14) 1.381(2), C(1)–C(15) 1.431(3), C(2)–C(3) 1.400(2), C(2)–C(11) 1.430(2), C(5)–C(20) 1.433(3), C(6)–C(7) 1.415(3), C(16)–Sn(1) 2.114(2), C(17)–Sn(1) 2.127(2); C(1)–C(2)–C(3) 122.1(2), C(1)–C(2)–C(11) 118.6(2), C(1)–C(15)–C(16) 177.5(2), C(2)–C(1)–C(15) 120.1(2), C(5)–C(20)–C(21) 176.0(2), C(15)–C(16)–Sn(1) 171.5(2), C(20)–C(21)–Sn(2) 174.7(2).

Starting from 10-bromo-1,8-dichloroanthracene (**12**),<sup>13</sup> the tris-[(trimethylsilyl)ethynyl]-substituted species **14** was synthesised in a two-step reaction *via* 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**), as displayed in Scheme 3. **13** can also be prepared (in lower yields) by conversion of 1,8-dichloroanthracene-10-(9H)-one with [(trimethylsilyl)ethynyl]magnesium bromide in THF.<sup>14</sup> Deprotection of the alkynyl units of **14** led to the formation of **15** which was converted with (dimethylamino)trimethylstannane to afford 1,8,10-tris[(trimethylstannyl)ethynyl]anthracene (**16**).



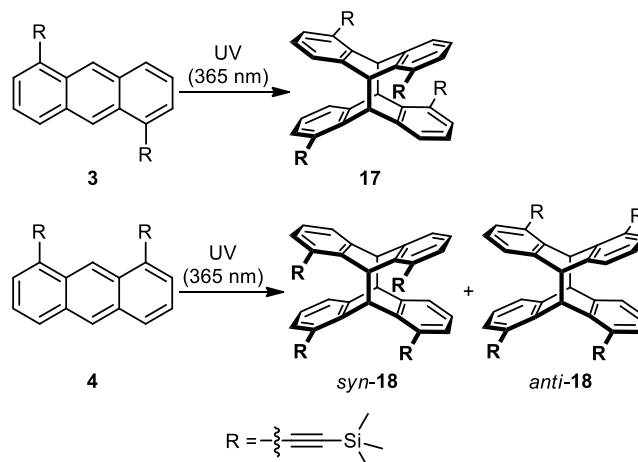
**Scheme 3** Syntheses of the 1,8,10-trialkynylsubstituted anthracene derivatives. Reagents and conditions: i) 1.  $\text{Me}_3\text{SiC}\equiv\text{CH}$  (2 eq.),  $\text{CuI}$  (10 mol%),  $\text{PdCl}_2(\text{PPh}_3)_2$  (5 mol%),  $(i\text{-Pr})_2\text{NH}$ , reflux, 3d; 2. aq. workup, 85%; ii) 1.  $\text{Me}_3\text{SiC}\equiv\text{CMgBr}$  (10 eq.),  $\text{Ni}(\text{acac})_2$ ,  $\text{PPh}_3$ , THF, reflux; 2. aq. workup, 83%; iii)  $\text{K}_2\text{CO}_3$ , MeOH, r.t., 86%; iv)  $\text{Me}_3\text{SnMe}_2$ , THF, 60 °C, 4h.

However, compared to the 1,5- and 1,8-disubstituted compounds **7** and **8**, the obtained product was found to be unstable towards air and moisture. Anyway, we found some evidence for the successful synthesis of the desired threefold  $\text{SnMe}_3$ -substituted compound **16** stemming from  $^1\text{H}$  NMR data of the raw product. As expected for 1,8,10-trisubstituted anthracenes, the

$^1\text{H}$  NMR spectrum recorded at ambient temperature (298 K) in  $\text{CDCl}_3$  shows one downfield-shifted singlet at  $\delta = 9.44$  ppm (H9), two doublets at 8.58 ppm (H4/H5) and 7.78 ppm (H2/H7), as well as one doublet of doublets at 7.50 ppm (H3/H6). Two singlets at 0.49 ppm and 0.46 ppm (integral ratio 9:18) show typical  $^{117}\text{Sn}$ - and  $^{119}\text{Sn}$ -satellites, indicating the availability of two different trimethylstannyl groups.

### Photodimerisation Reactions

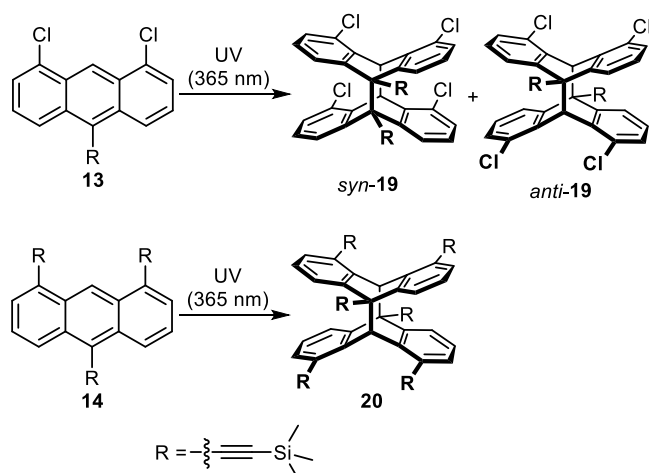
To investigate the influence of the (trimethylsilyl)ethynyl substituent positions on the *syn-anti* ratio of the anthracene dimerisation, the corresponding compounds were irradiated with UV light (365 nm) at ambient temperature in  $\text{CDCl}_3$ . For an exploratory qualitative assessment of the kinetics of these reactions simple NMR spectroscopic investigations were performed and one example was explored in more detail (see below). For this purpose, small amounts of compounds **3**, **4**, **10**, **13** and **14** were dissolved in  $\text{CDCl}_3$  and irradiated in an NMR tube for several hours, so that the reaction progress could be easily monitored by  $^1\text{H}$  NMR spectroscopy. UV irradiation of the 1,5- (**3**), 1,8- (**4**) led to a complete conversion into the corresponding [4+4] cycloaddition products **17** and **18**, respectively. In the case of **3** only one photodimerised species was observed and  $^1\text{H}$  NMR spectroscopically identified as the *head to tail*-isomer, whereas a 49:51-mixture of the *head to head* (*syn*) and *head to tail* (*anti*) photodimers was obtained, when a  $\text{CDCl}_3$  solution of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**4**) was irradiated with UV light (Scheme 4). This is in accordance with the literature for the photodimerisation of 1,8-dichloroanthracene (**2**) in various solvents.<sup>2</sup> We did not observe the formation of a *syn-anti* mixture of photodimers, when the corresponding 1,5-substituted species **3** was irradiated, although a *syn-anti* mixture was reported for 1,5-dichloroanthracene (**1**).<sup>2</sup>



**Scheme 4** Photodimerisation of the monomers **3** and **4** to the dimeric species **17** and **18** by UV irradiation in  $\text{CDCl}_3$ .

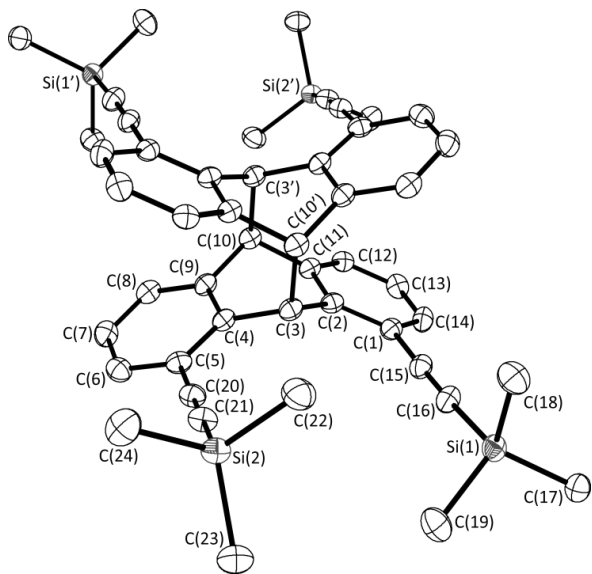
As expected, UV irradiation of the 1,8,10-substituted compound **14** led to a complete conversion into the corresponding *anti*-[4+4] cycloaddition products **20** (Scheme 5). An increased repulsive interaction of the bulky (trimethylsilyl)ethynyl substituents might be the reason for the selective *anti*-dimerisation reaction. In contrast to that, a *syn-anti* mixture (32:68) of **19** was obtained when a solution of 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**) was irradiated under the same

conditions indicating a weaker interaction of the substituents in positions 1, 8 and 10 of the *syn*-**19** isomer.



**Scheme 5** Photodimerisation of the monomers **13** and **14** to the dimeric species **19** and **20** by UV irradiation in  $\text{CDCl}_3$ .

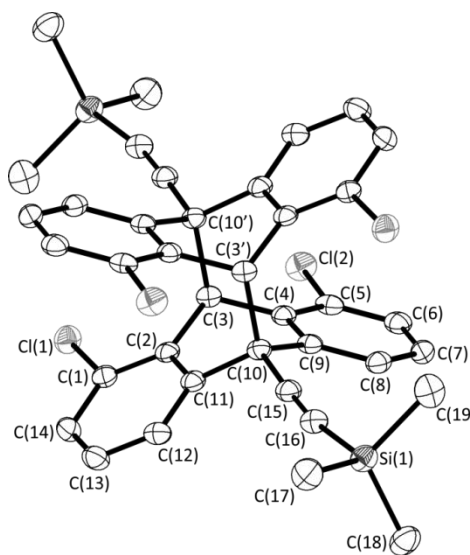
In the case of the photodimerisation of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**4**), as well as 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**), we determined the molecular structures in crystalline state of the corresponding *head-to-tail* isomers *anti*-**18** (Figure 5) and *anti*-**19** (Figure 6), respectively.



**Fig. 5** Molecular structure of the *anti*-photo dimer of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (*anti*-**18**). Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.398(2), C(1)–C(14) 1.406(2), C(1)–C(15) 1.445(2), C(2)–C(3) 1.517(2), C(2)–C(11) 1.407(2), C(3)–C(4) 1.519(2), C(3)–C(10') 1.623(2), C(5)–C(20) 1.443(3), C(15)–C(16) 1.207(2), C(16)–Si(1) 1.845(2), C(20)–C(21) 1.208(2), C(21)–Si(2) 1.842(2); C(1)–C(2)–C(3) 122.4(1), C(1)–C(2)–C(11) 119.6(1), C(1)–C(15)–C(16) 179.0(1), C(2)–C(1)–C(15) 121.0(1), C(2)–C(3)–C(4) 108.3(1), C(2)–C(3)–C(10') 112.2(1), C(4)–C(5)–C(20) 119.8(1), C(5)–C(20)–C(21) 173.4(1), C(15)–C(16)–Si(1) 175.4(1), C(20)–C(21)–Si(2) 173.9(1).

Due to the [4+4] cycloaddition reaction, *anti*-**18** contains four isolated aromatic rings and an aliphatic tricyclic system. The aromatic rings are planar and the dihedral angle between their mean planes is  $137.6(1)^\circ$ . The phenyl C–C bond lengths and angles are ranging from 1.390(2) Å [C(6)–C(7)] to 1.407(2) Å [C(2)–C(11)] and from  $119.2(2)^\circ$  [C(5)–C(4)–C(9)] to  $120.6(2)^\circ$  [C(2)–C(11)–C(12)], respectively. As expected for  $\text{sp}^3$  carbon atoms, the angles around C(3) and C(10) are close to tetrahedral geometry { $107.9(2)^\circ$  [C(9)–C(10)–C(11)] to  $112.2(2)^\circ$  [C(2)–C(3)–C(10')]}]. The C( $\text{sp}^3$ )–C<sub>Ph</sub> distances are between 1.512(2) Å [C(10)–C(11)] and 1.519(2) Å [C(3)–C(4)], which is slightly longer than a standard C( $\text{sp}^3$ )–C( $\text{sp}^2$ ) bond (1.50 Å<sup>12</sup>). The C(3)–C(10') [1.623(2) Å] bond is found to be remarkably longer than a standard C( $\text{sp}^3$ )–C( $\text{sp}^3$ ) bond (1.54 Å<sup>1</sup>). A repulsive interaction between the TMS-substituted alkynyl units results in an angle between the C(1)–Si(1)- and C(5)–Si(2)-vectors [ $15.5(1)^\circ$ ]. Like in case of **4** and **8**, one of the alkynyl substituents is nearly in plane with the aryl ring it is bonded to [the C(1)-bonded in *anti*-**18**], whereas the second alkynyl unit is slightly bended, as denoted by the torsion angles C(5)–C(20)–C(21) [ $173.4(2)^\circ$ ] and C(20)–C(21)–Si(1) [ $173.9(2)^\circ$ ].

Like in case of *anti*-**18**, the photodimer of the 10-(trimethylsilyl)ethynyl-substituted 1,8-dichloroanthracene (*anti*-**19**) crystallises in the triclinic space group  $P\bar{1}$  with one centrosymmetric molecule in the unit cell.



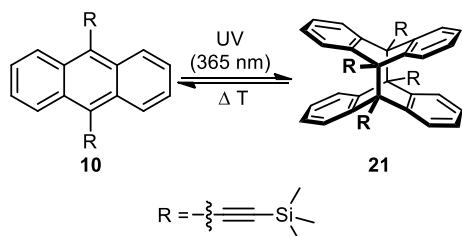
**Fig. 6** Molecular structure of the *anti*-photo dimer of 1,8-bis[(trimethylsilyl)ethynyl]anthracene (*anti*-**19**). Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.391(3), C(1)–C(14) 1.391(3), C(1)–Cl(1) 1.746(2), C(2)–C(3) 1.512(2), C(2)–C(11) 1.398(3), C(3)–C(4) 1.512(3), C(3)–C(10') 1.643(2), C(10)–C(15) 1.471(3), C(15)–C(16) 1.209(3), C(16)–Si(1) 1.840(2), C(18)–Si(1) 1.864(2); C(1)–C(2)–C(3) 123.1(2), C(1)–C(2)–C(11) 117.9(2), C(2)–C(1)–Cl(1) 120.2(1), C(2)–C(3)–C(4) 109.1(1), C(2)–C(3)–C(10') 112.2(1), C(10)–C(15)–C(16) 176.7(2), C(11)–C(10)–C(15) 112.3(2), C(15)–C(16)–Si(1) 171.2(2).

The former anthracene units are linked by their central rings, whereby the C(3)–C(10')/C(10)–C(3') bonds measure 1.634(2) Å, slightly longer than the corresponding ones in *anti*-**18** [1.623(2) Å] and remarkably longer than the standard C–C bond (1.54 Å<sup>12</sup>). The quaternary carbon atom C(10) adopts a somewhat distorted tetrahedral coordination geometry, as is in-



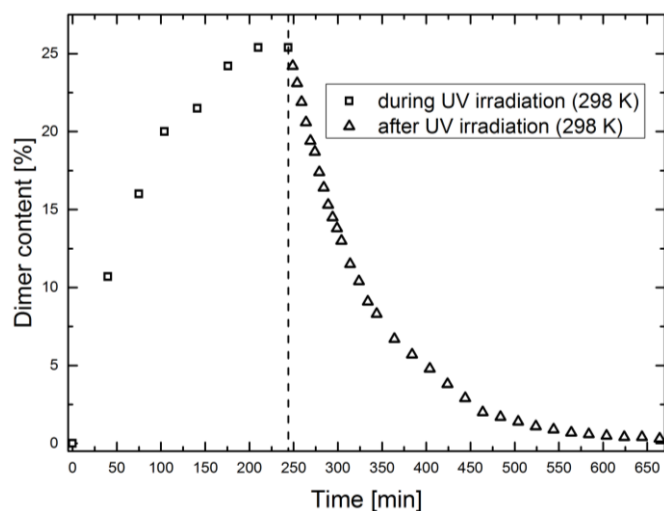
indicated by its surrounding angles ranging from  $106.5(2)^\circ$  [C(15)–C(10)–C(3')] to  $112.3(2)^\circ$  [C(15)–C(10)–C(11)]. As is indicated by the angles C(10)–C(15)–C(16) [ $176.7(2)^\circ$ ] and C(15)–C(16)–Si(1) [ $171.2(2)^\circ$ ], the alkynyl substituents deviate little from linearity. The chlorine atoms are found to be in-plane with the aromatic rings they are bonded to. The dihedral angle between these aromatic mean planes is  $135.5(1)^\circ$ , slightly smaller than the corresponding one in compound *anti-18* [ $137.6(1)^\circ$ ].

In all cases mentioned above, a quantitative conversion into the photodimers **17**, **18**, **19** and **20** was observed and they are found to be thermally stable at ambient temperature for several weeks. A completely different behaviour was observed, when 9,10-bis-[(trimethylsilyl)ethynyl]anthracene (**10**) was irradiated under the same conditions. Although a [4+4] cycloaddition reaction occurs (indicated in a new set of resonances in the  $^1\text{H}$  NMR spectra), a quantitative conversion of **10** into its photodimer **21** could not be achieved (Scheme 6). Solely a maximum of 25% dimer **21** was formed after the sample was irradiated with UV light for ca. 4 h at ambient temperature. Anyhow, a proceeding irradiation (up to 5 hours) did not lead to an increase of the dimer-to-monomer ratio under the given circumstances.



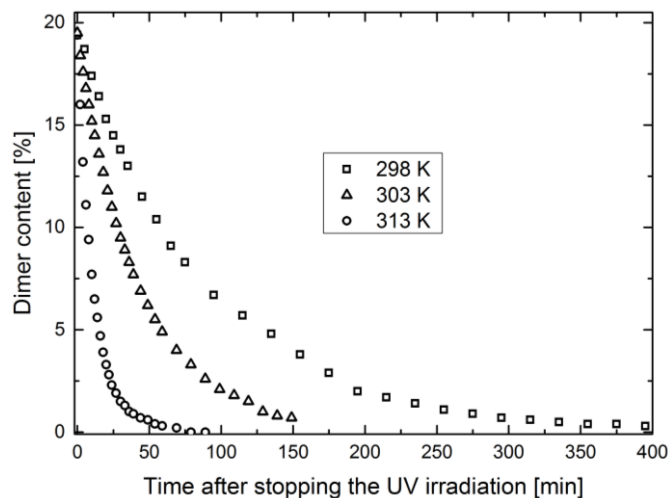
**Scheme 6** Photodimerisation of 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) to the thermally (r.t.) unstable compound **21** by UV irradiation in  $\text{CDCl}_3$ .

Interestingly, we found that dimer compound **21** is much more thermally labile, compared to the other (trimethylsilyl)ethynyl-substituted photodimers **17**, **18**, **19** and **20**, which were synthesised in this work. We investigated the kinetics of this cycloelimination reaction by a series of  $^1\text{H}$  NMR experiments. Therefore, a NMR sample of 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) in  $\text{CDCl}_3$  was irradiated with UV light for at least 3.5 hours at ambient temperature (298 K), only interrupted for ca. 3 minutes by recording proton NMR spectra. After irradiation, the sample was left in the magnet at that temperature and the decay of the dimer concentration was monitored by recording  $^1\text{H}$  NMR spectra. As shown in Figure 7, a complete cycloelimination reaction of **21** into the corresponding monomer **10** was observed after ca. 6.5 hours, when the sample was exposed to ambient temperature without further UV irradiation.



**Fig. 7** Content of the photodimer **21** [%] vs. (irradiation-) time [min] at 298 K.

In order to monitor the influence of the temperature on the monomerisation (**21**  $\rightarrow$  **10**) we performed kinetic NMR experiments at 298 K, 303 K and 313 K. As can be concluded from Figure 8, a faster decay of the dimer concentration can be observed at higher temperatures.



**Fig. 8** Content of the photodimer **21** [%] vs. time after stopping the UV irradiation [min] at 298 K, 303 K and 313 K.

Starting with a photodimer-to-monomer ratio of 19.5%, a complete conversion into the monomer **10** was observed after more than 6 hours at 298 K. However, the reaction rate is remarkably increased, when the sample is held at 303 K (ca. 2.5 hours) or 313 K (ca. 1.5 hours), respectively (Figure 8). From the data shown in Figure 8 we could calculate an estimate for the barrier of activation  $E_A$  of  $94 \text{ kJ mol}^{-1}$ . These results suggest, that 9,10-dialkynylanthracene derivatives might be applicable as molecular thermo-reversible photo switching units.

Due to this interesting behaviour in solution we further assumed to dimerise 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) in the solid state, according to experiments with e.g. di-

arylethene derivatives performed by Irie and coworkers.<sup>15</sup> For this purpose, we fixed a single crystal of **10** on a glass fibre onto the goniometer of the diffractometer. After collecting the monomer data, we used a blue-violet laser (402 nm) to irradiate the crystal (the ability of this light source for dimerisation reactions was tested by irradiating a NMR sample of **10** in CDCl<sub>3</sub>). However, no photoreaction was observed by X-ray diffraction investigations, also not when the irradiation experiments were repeated several times between 243 K and 363 K. This might be due to the fact that the 9,10-disubstituted anthracenes **10** are perpendicularly orientated to each other and no  $\pi$ - $\pi$  interaction are found in its molecular structure in the solid state.<sup>16</sup>

## Conclusions

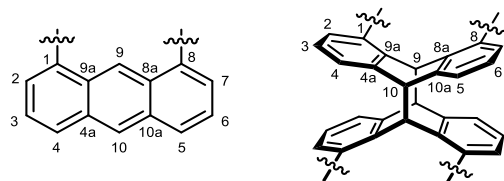
Anthracenes with (trimethylsilyl)ethynyl substituents in 1,5- (**3**), 1,8- (**4**) and 9,10-positions (**10**), as well as 1,8-dichloro-10-[(trimethylsilyl)ethynyl]- (**13**) and 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (**14**) were synthesised by cross coupling reactions. In addition, 1,5- (**7**) and 1,8-bis[(trimethylstannyl)ethynyl]anthracene (**8**) have been quantitatively synthesised by conversion of the corresponding ethynyl-substituted anthracene derivatives with (dimethylamino)trimethylstannane. The SnMe<sub>3</sub>-substituted dialkynes might be useful substrates in Stille type cross coupling reactions.

CDCl<sub>3</sub> solutions of the highly conjugated SiMe<sub>3</sub>-substituted systems were irradiated with UV light whereby [4+4] cycloaddition reactions were observed. The *anti*-isomers were selectively and quantitatively formed in case of **3** and **14**. Irradiation of the 1,8- and 1,8,10-substituted species **4** and **13** gave *syn-anti* mixtures [49:51 (**4**); 32:68 (**13**)] of the photodimerised products. Interestingly, 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**) was found to dimerise to afford **21**, although symmetrically 9,10-substituted anthracenes with substituents, except fluorine atoms or methyl groups, are known for 28 years to be stable towards UV irradiation.<sup>1b,6</sup> The influence of the temperature upon monomerisation (cycloelimination) was qualitatively investigated by NMR experiments. Due to the fact that ambient temperature is sufficient for the thermally induced reaction of the photodimer **21**, 9,10-dialkynylanthracenes might be interesting objects of study e.g. for detailed kinetic investigations.

## Experimental

**General.** 1,5- (**1**)<sup>17</sup> and 1,8-dichloroanthracene (**2**),<sup>18</sup> as well as 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**4**),<sup>8</sup> 1,8-diethynylanthracene (**6**),<sup>8</sup> 9,10-bis[(trimethylsilyl)ethynyl]anthracene (**10**)<sup>9</sup> and 10-bromo-1,8-dichloroanthracene (**12**)<sup>13</sup> were synthesised according to literature protocols. All reactions using organometallic reagents were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried over potassium) or *n*-hexane (dried over LiAlH<sub>4</sub>). The solvents were freshly distilled before being used for the reactions. Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). NMR spectra were recorded on a Bruker Avance III 300, a Bruker DRX 500, a Bruker Avance III 500 and a Bruker Avance 600 instrument at room temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>): <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C NMR  $\delta$  = 77.16 ppm) or referenced externally (<sup>29</sup>Si: SiMe<sub>4</sub>, <sup>119</sup>Sn: SnMe<sub>4</sub>). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE

geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV. The numbering scheme for NMR assignments (Scheme 7) is based on IUPAC guidelines.



**Scheme 7** Numbering scheme exemplarily shown for a 1,8-substituted anthracene derivative and its corresponding *anti*-photodimer.

**1,8-Dichloro-10-[(trimethylsilyl)ethynyl]anthracene (**13**).** 10-Bromo-1,8-dichloroanthracene (200 mg, 0.61 mmol) and (trimethylsilyl)acetylene (0.7 mL, 1.22 mmol) were dissolved in diisopropylamine (40 mL). The solution was degassed by three freeze-pump-thaw cycles and CuI (12 mg, 10 mol%) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (22 mg, 5 mol%) were added. After heating to reflux for 3 d, the dark brownish mixture was filtered, washed with *n*-pentane and added to water (50 mL). The aqueous layer was extracted with *n*-pentane (3 × 25 mL) and the combined organic phases were washed with brine and dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography ( $\varnothing$  = 3 cm, *l* = 20 cm, eluent: *n*-pentane). Yield: 147 mg (71%). For analytical data see ref. 14 (different synthetic protocol).

**9,10-Bis[(trimethylsilyl)ethynyl]anthracene (**10**).** Synthesis according to ref. 9; for <sup>1</sup>H and <sup>13</sup>C NMR data see ref. 9. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = -17.17 ppm. MS (EI, 70 eV): *m/z* [assignment] = 370 [M]<sup>+</sup>, 355 [M-CH<sub>3</sub>]<sup>+</sup>, 297 [M-Si(CH<sub>3</sub>)<sub>3</sub>]. HRMS: calculated for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub><sup>+</sup>: 370.15676; measured: 370.15800.

**General Procedure for Kumada Coupling Reactions.** Trimethylsilyl acetylene (Me<sub>3</sub>SiC≡CH, ca. 7 eq.) was added dropwise to a freshly prepared solution of ethylmagnesium bromide in THF at 0 °C. The mixture was stirred at room temperature for 2 h and gas evolution was observed. The [(trimethylsilyl)ethynyl]magnesium bromide suspension was transferred into a dropping funnel, fitted with glass wool for simultaneous filtering and slowly added to a solution of the dichloroanthracene derivative, Ni(acac)<sub>2</sub> and PPh<sub>3</sub> in THF at room temperature, whereby the colour of the solution changed from yellow to dark red. The mixture was heated to reflux and then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with brine and dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography using different eluents (see below).

**1,5-Bis[(trimethylsilyl)ethynyl]anthracene (**3**).** Synthesis according to the general procedure for Kumada coupling reactions using 1,5-dichloroanthracene (1.60 g, 6.47 mmol), PPh<sub>3</sub> and Ni(acac)<sub>2</sub> (one spatula tip of each compound), reflux for 113 h. Column chromatography ( $\varnothing$  = 3 cm, *l* = 25 cm, eluent: *n*-pentane/dichloromethane 8:1) afforded **3** as bright yellow crystals. Yield: 1.96 g (82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.88 (s, 2H, H<sub>9</sub>/H<sub>10</sub>), 8.06 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 2H, H<sub>4</sub>/H<sub>8</sub>), 7.74 (d,

$^3J_{\text{H,H}} = 6.8$  Hz, 2H, *H2/H6*), 7.44 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.5 Hz, 2H, *H3/H7*), 0.39 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 131.65$ , 131.45, 131.20 (*C2/C6*), 130.01 (*C4/C8*), 125.94 (*C9/C10*), 125.12 (*C3/C7*), 120.87, 103.27 (*C≡C-Si*), 100.34 (*C≡C-Si*), 0.30 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -17.36$  ppm. MS (EI, 70 eV): *m/z* [assignment] = 370 [M]<sup>+</sup>, 355 [M-CH<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub><sup>+</sup>: 370.15676; measured: 370.15590.

**1,8-Bis[(trimethylsilyl)ethynyl]anthracene (4).** Synthesis according to ref. 8. Complete analytical data:  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.32$  (s, 1H, *H9*), 8.42 (s, 1H, *H10*), 7.98 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2H, *H4/H5*), 7.79 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2H, *H2/H7*), 7.42 (dd,  $^3J_{\text{H,H}} = 7.0$ , 9.0 Hz, 2H, *H3/H6*), 0.39 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 132.48$  (*C2/C6*), 131.50, 131.37, 129.40 (*C4/C5*), 127.80 (*C10*), 125.09 (*C3/C6*), 124.02 (*C9*), 121.43, 103.67 (*C≡C-Si*), 99.94 (*C≡C-Si*), 0.56 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -17.47$  ppm. MS (EI, 70 eV): *m/z* [assignment] = 370 [M]<sup>+</sup>, 355 [M-CH<sub>3</sub>]<sup>+</sup>, 267 [M-Si(CH<sub>3</sub>)<sub>3</sub>-2CH<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub><sup>+</sup>: 370.15676; measured: 370.15651.

**1,8,10-Tris[(trimethylsilyl)ethynyl]anthracene (14).** Synthesis according to the general procedure for Kumada coupling reactions using 1,8-dichloro-10-[(trimethylsilyl)ethynyl]anthracene (210 mg, 0.62 mmol), PPh<sub>3</sub> and Ni(acac)<sub>2</sub> (one spatula tip of each compound), reflux for 5 d. Column chromatography ( $\varnothing = 3$  cm, *l* = 25 cm, eluent: *n*-pentane) afforded **14** as bright yellow crystals. Yield: 217 mg (83%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.35$  (s, 1H, *H9*), 8.55 (d,  $^3J_{\text{H,H}} = 8.7$  Hz, 2H, *H4/H5*), 7.81 (dd,  $^3J_{\text{H,H}} = 6.9$  Hz,  $^3J_{\text{H,H}} = 0.7$  Hz, 2H, *H2/H7*), 7.53 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.7 Hz, 2H, *H3/H6*), 0.41 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.38 [s, 18H, [Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 132.82$  (*C2/C7*), 132.70, 130.80, 128.01 (*C4/C5*), 126.34 (*C3/C6*), 125.40 (*C9*), 121.95, 118.69, 107.37 [*C≡C-Si(CH<sub>3</sub>)<sub>3</sub>*], 103.47 [[*C≡C-Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>], 101.28 [*C≡C-Si(CH<sub>3</sub>)<sub>3</sub>*], 100.52 [[*C≡C-Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>], 0.52 [Si(CH<sub>3</sub>)<sub>3</sub>], 0.34 [[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, CDCl<sub>3</sub>):  $\delta = -17.18$  [Si(CH<sub>3</sub>)<sub>3</sub>], -17.35 [[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] ppm. MS (EI, 70 eV): *m/z* [assignment] = 466 [M]<sup>+</sup>, 451 [M-CH<sub>3</sub>]<sup>+</sup>, 394 [M-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>29</sub>H<sub>34</sub>Si<sub>3</sub><sup>+</sup>: 466.19628; measured: 466.19757.**

**General Procedure for the Syntheses of the Ethynyl-Substituted Compounds 5, 6, 11 and 15.** The (trimethylsilyl)ethynyl substituted compounds were dissolved in an adequate amount of boiling methanol. After cooling to ambient temperature, K<sub>2</sub>CO<sub>3</sub> (ca 1.2 eq./alkyne unit) was added to the mixture stirred overnight. The solvent was evaporated and the crude products were purified by column chromatography.

**1,5-Diethynylanthracene (5).** Synthesis according to the general procedure using 1,5-bis[(trimethylsilyl)ethynyl]anthracene (1.70 g, 4.59 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.14 g, 8.25 mmol) in MeOH (450 mL). Column chromatography ( $\varnothing = 3$  cm, *l* = 11 cm, eluent: *n*-pentane) afforded **5** as bright yellow crystals. Yield: 0.96 g (93%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.93$  (s, 2H, *H9/H10*), 8.10 (d,  $^3J_{\text{H,H}} = 8.6$  Hz, 2H, *H4/H8*), 7.79 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 2H, *H2/H6*), 7.46 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.4 Hz, 2H, *H3/H7*), 3.60 (s, 2H, *C≡C-H*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 131.74$  (*C2/C6*), 131.70, 131.51, 130.20 (*C4/C8*), 125.78 (*C9/C10*), 125.15 (*C3/C7*), 119.92, 82.72 (*C≡C-H*), 81.94 (*C≡C-H*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 226 [M]<sup>+</sup>, 200 [M-CCH]<sup>+</sup>. HRMS: calculated for C<sub>18</sub>H<sub>10</sub><sup>+</sup>: 226.07770; measured: 226.07662.

**1,8-Diethynylanthracene (6).** Synthesis according to ref. 8. Complete analytical data:  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.44$  (s, 1H, *H9*), 8.45 (s, 1H, *H10*), 8.03 (d,  $^3J_{\text{H,H}} = 8.6$  Hz, 2H, *H4/H5*), 7.80 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 2H, *H2/H7*), 7.45 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.5 Hz, 2H, *H3/H6*), 3.62 (s, 2H, *C≡C-H*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 131.72$  (*C2/C6*), 131.47, 129.61 (*C4/C5*), 127.67 (*C10*), 125.14 (*C3/C6*), 123.90 (*C9*), 120.49, 82.78 (*C≡C-H*), 81.81 (*C≡C-H*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 226 [M]<sup>+</sup>. HRMS: calculated for C<sub>18</sub>H<sub>10</sub><sup>+</sup>: 226.07770; measured: 226.07599.

**9,10-Diethynylanthracene (11).** Synthesis according to the general procedure using 9,10-bis[(trimethylsilyl)ethynyl]anthracene (0.45 g, 1.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.42 g, 3.0 mmol) in MeOH (250 mL). Column chromatography ( $\varnothing = 3$  cm, *l* = 9 cm, eluent: *n*-pentane) afforded **11** as a yellow-brownish solid. Yield: 71 mg (25%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.62$  (m, 6H, *H1/H4/H5/H8*), 7.63 (m, 6H, *H2/H3/H6/H7*), 4.07 (s, 2H, *C≡C-H*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 132.62$ , 127.19, 127.17, 117.96, 90.01 (*C≡C-H*), 80.35 (*C≡C-H*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 226 [M]<sup>+</sup>, 198 [M-CCH]<sup>+</sup>. HRMS: calculated for C<sub>18</sub>H<sub>10</sub><sup>+</sup>: 226.07770; measured: 226.07663.

**1,8,10-Triethynylanthracene (15).** Synthesis according to the general procedure using 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (0.48 g, 1.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.24 g, 1.75 mmol) in MeOH (80 mL). Column chromatography ( $\varnothing = 3$  cm, *l* = 8 cm, eluent: *n*-pentane) afforded **15** as a bright yellow solid. Yield: 0.22 g (86%).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 9.52$  (s, 1H, *H9*), 8.61 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 2H, *H4/H5*), 7.83 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 2H, *H2/H7*), 7.56 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.7 Hz, 2H, *H3/H6*), 4.02 (s, 1H, *C≡C-H*), 3.63 [s, 2H, (*C≡C-H*)<sub>2</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 132.79$ , 131.80 (*C2/C7*), 127.94 (*C4/C5*), 126.18 (*C3/C6*), 125.80 (*C9*), 120.74, 89.04 (*C≡C-H*), 83.10 [(*C≡C-H*)<sub>2</sub>], 81.32 [(*C≡C-H*)<sub>2</sub>], 79.86 (*C≡C-H*) ppm. MS (EI, 70 eV): *m/z* [assignment] = 250 [M]<sup>+</sup>, 224 [M-CCH]<sup>+</sup>. HRMS: calculated for C<sub>20</sub>H<sub>10</sub><sup>+</sup>: 250.07770; measured: 250.07795.

**General Procedure for the Syntheses of the Trimethylstannyl-Substituted Compounds 7, 8 and 16.** The SnMe<sub>3</sub> functionalisation of the ethynyl substituted compounds was carried out analogous to a procedure described by Wrackmeyer and coworkers.<sup>19</sup> The corresponding ethynylanthracene derivatives were dissolved in a small amount of dry THF. (Dimethylamino)trimethylstannane (ca. 2 eq./alkyne unit) was added dropwise to the solution and the mixture was heated to 60 °C for 4 h. After cooling to ambient temperature, all volatile compounds were removed in vacuo and the desired species were quantitatively obtained as yellow solids. Single crystals of **7** and **8**, suitable for X-ray diffraction experiments were afforded after recrystallisation from dry *n*-hexane.

**1,5-Bis[(trimethylstannyl)ethynyl]anthracene (7).** Synthesis according to the general procedure using 1,5-diethynylanthracene (20 mg, 0.09 mmol), (dimethylamino)trimethylstannane (0.08 mL, 0.49 mmol) and THF (6 mL).  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.93$  (s, 2H, *H9/H10*), 8.04 (d,  $^3J_{\text{H,H}} = 8.7$  Hz, 2H, *H4/H8*), 7.72 (m, 2H, *H2/H6*), 7.42 (dd,  $^3J_{\text{H,H}} = 6.9$ , 8.5 Hz, 2H, *H3/H7*), 0.48 [s, 18H, Sn(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 131.69$ , 131.53, 130.84 (*C2/C6*), 129.54 (*C4/C8*), 126.04 (*C9/C10*), 125.11 (*C3/C7*), 121.36, 107.04 (*C≡C-Sn*), 99.77 (*C≡C-Sn*), -7.30 [Sn(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (186 MHz, CDCl<sub>3</sub>):  $\delta = -63.15$  ppm. MS (EI, 70 eV): *m/z* [assignment] = 552 [M]<sup>+</sup>, 537 [M-CH<sub>3</sub>]<sup>+</sup>, 226 [M-2(SnCH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>24</sub>H<sub>26</sub>Sn<sub>2</sub><sup>+</sup>: 554.00730; measured: 554.00711.

**1,8-Bis[(trimethylstannyl)ethynyl]anthracene (8).** Synthesis according to the general procedure using 1,8-diethynylanthracene (26 mg, 0.11 mmol), (dimethylamino)trimethylstannane (0.11 mL, 0.70 mmol) and THF (6 mL).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.43 (s, 1H, H9), 8.40 (s, 1H, H10), 7.95 (d,  $^3J_{\text{H,H}} = 8.4$  Hz, 2H, H4/H5), 7.76 (dd,  $^3J_{\text{H,H}} = 6.9$  Hz,  $^4J_{\text{H,H}} = 1.0$  Hz, 2H, H2/H7), 7.40 (dd,  $^3J_{\text{H,H}} = 6.9$ , 8.5 Hz, 2H, H3/H6), 0.46 [s, 18H, Sn(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 131.77 (C2/C7), 131.57, 131.51, 128.92 (C4/C5), 127.58 (C10), 125.10 (C3/C6), 124.44 (C9), 107.43 (C≡C–Sn), 99.27 (C≡C–Sn), –6.99 [Sn(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (186 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –63.98 ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 552 [M]<sup>+</sup>, 537 [M–CH<sub>3</sub>]<sup>+</sup>, 390 [M–Sn(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 345 [M–Sn(CH<sub>3</sub>)<sub>3</sub>–3CH<sub>3</sub>]<sup>+</sup>, 224 [M–2(SnCH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. HRMS: calculated for C<sub>24</sub>H<sub>26</sub>Sn<sub>2</sub>: 554.00730; measured: 554.00760.

**1,8,10-Tris[(trimethylstannyl)ethynyl]anthracene (16).** Synthesis according to the general procedure using 1,8,10-triethynylanthracene (20 mg, 0.08 mmol), (dimethylamino)trimethyltin (0.1 mL, 0.6 mmol) and THF (19 mL).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.44 (s, 1H, H9), 8.58 (d,  $^3J_{\text{H,H}} = 8.7$  Hz, 2H, H4/H5), 7.78 (d,  $^3J_{\text{H,H}} = 6.5$  Hz, 2H, H2/H7), 7.49 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.7 Hz, 2H, H3/H6), 0.49 [s, 9H, Sn(CH<sub>3</sub>)<sub>3</sub>], 0.46 [s, 18H, [Sn(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>] ppm. Due to rapid decomposition to the reactant **15** under the experimental conditions, no further characterisation of the product could be performed.

**General Procedure for Photodimerisation Reactions.** Small amounts of the (trimethylsilyl)ethynyl substituted compounds **3**, **4**, **10**, **13** and **14** were dissolved in  $\text{CDCl}_3$  (ca. 0.55 mL) and irradiated with UV light (365 nm, UVP, UVGL-25 Compact UV Lamp 254/365 nm, 4 W) in an NMR tube for several hours.

**Photodimerisation of 1,5-Bis[(trimethylsilyl)ethynyl]anthracene.** Synthesis according to the general procedure. Analytical data:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38 (m, 8H, H4/H8/H2/H6), 7.44 (dd,  $^3J_{\text{H,H}} = 7.2$ , 8.1 Hz, 4H, H3/H7), 6.38 (s, 4H, H9/H10), 0.31 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.93, 137.81, 131.17, 127.80 (C3/C7), 124.03, 118.87, 100.74 (C≡C–Si), 99.81 (C≡C–Si), 77.00 (C9/C10), 0.12 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –17.03 ppm.

**Photodimerisation of 1,8-Bis[(trimethylsilyl)ethynyl]anthracene.** Synthesis according to the general procedure gives a *syn-anti* mixture (49:51) of the photodimerised species. Analytical data for the *syn* isomer:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.43 (d,  $^3J_{\text{H,H}} = 7.9$  Hz, 4H, H2/H7), 7.35 (d,  $^3J_{\text{H,H}} = 7.2$  Hz, 4H, H4/H5), 7.22 (m, 4H, H3/H6), 6.79 (s, 2H, H9), 5.96 (s, 2H, H10), 0.38 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.30, 132.78 (C2/C7), 127.78 (C3/C6), 123.66 (C4/C5), 119.49, 101.28 (C≡C–Si), 98.14 (C≡C–Si), 78.95 (C10), 75.27 (C9), 0.63 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. One signal missing due to overlap or line broadening.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –17.08 ppm. Analytical data for the *anti*-isomer:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.03 (d,  $^3J_{\text{H,H}} = 7.3$  Hz, 4H, H4/H5), 6.97 (dd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^4J_{\text{H,H}} = 0.8$  Hz, 4H, H2/H7), 6.80 (m, 4H, H3/H6), 5.54 (d,  $^3J_{\text{H,H}} = 11.0$  Hz, 2H, H9), 4.54 (d,  $^3J_{\text{H,H}} = 10.9$  Hz, 2H, H10), 0.31 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.14, 143.37, 130.25 (C2/C7), 126.40 (C4/C5), 125.74 (C3/C6), 121.83, 104.52 (C≡C–Si), 99.67 (C≡C–Si), 52.23 (C9), 48.74 (C10), 0.35 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. One signal missing due to overlap or line broadening.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –17.83 ppm.

**Photodimerisation of 9,10-Bis[(trimethylsilyl)ethynyl]anthracene.** Synthesis according to the general procedure. Analytical data:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.69 (m, 8H,

H1/H4/H5/H8), 7.37 (m, 8H, H2/H3/H6/H7), 0.38 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm; Due to the fast cycloelimination reaction,  $^{13}\text{C}$  NMR shifts of the photodimerised compound **21** were determined using  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC and HSQC experiments at 278 K in  $\text{CDCl}_3$ .  $\delta$  = 136.86, 128.06, 122.82, 101.53, 79.08 (C9/C10) ppm. Signals missing due to overlap or line broadening.

**Photodimerisation of 1,8-Dichloro-10-[(trimethylsilyl)ethynyl]anthracene.** Synthesis according to the general procedure gives a *syn-anti* mixture (32:68) of the photodimerised species. Analytical data for the *syn* isomer:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.59 (d,  $^3J_{\text{H,H}} = 7.3$  Hz, 4H, H4/H5), 7.35 (d,  $^3J_{\text{H,H}} = 7.5$  Hz, 4H, H2/H7), 7.29 (m, 4H, H3/H6), 6.89 (s, 2H, H9), 0.37 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>].  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.97, 134.66, 129.48, 129.22 (C3/C6), 129.05 (C2/C7), 121.56 (C4/C5), 102.52 (C≡C–Si), 92.58 (C≡C–Si), 73.61 (C9), –0.13 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. C10 signal missing due to overlap or line broadening.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –15.21 ppm. Analytical data for the *anti*-isomer:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.70 (dd,  $^3J_{\text{H,H}} = 7.4$  Hz,  $^4J_{\text{H,H}} = 1.0$  Hz, 4H, H4/H5), 6.95 (dd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^4J_{\text{H,H}} = 1.2$  Hz, 4H, H2/H7), 6.91 (m, 4H, H3/H6), 5.99 (s, 2H, H9), 0.38 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>].  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.74, 136.89, 133.33, 127.68 (C3/C6), 127.52 (C2/C7), 124.04 (C4/C5), 106.61 (C≡C–Si), 94.96 (C≡C–Si), 56.08 (C9), 53.75 (C10), 0.26 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –17.18 ppm.

**Photodimerisation of 1,8,10-Tris[(trimethylsilyl)ethynyl]anthracene.** Synthesis according to the general procedure. Analytical data:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 7.63 (d,  $^3J_{\text{H,H}} = 7.2$  Hz, 4H, H2/H7), 7.45 (dd,  $^3J_{\text{H,H}} = 1.1$ , 7.9 Hz, 4H, H4/H5), 7.27 (m, 4H, H3/H6), 6.81 (s, 2H, H10), 0.36 [s, 18H, [Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>], 0.30 [s, 36H, [Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.37, 137.50, 133.16 (C4/C5), 127.72 (C3/C6), 122.83 (C2/C7), 119.22, 101.24 {[C≡C–Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}, 99.74 {[C≡C–Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>}, 75.72 (C10), 0.35 {[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>}, 0.09 {[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>} ppm. Signals missing due to overlap or line broadening.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –15.45 [Si(CH<sub>3</sub>)<sub>3</sub>], –17.08 {[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>} ppm.

**Crystal Structure Determination.** Suitable crystals of the compounds **3**, **4**, **5**, **7**, **8**, *anti*-**18**, and *anti*-**19** were obtained by recrystallisation of dry *n*-hexane (**7** and **8**), by slow evaporation of saturated solutions of *n*-pentane (**5** and *anti*-**19**), *n*-pentane/dichloromethane (**3** and **4**) and chloroform (*anti*-**18**). They were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a *SuperNova, Dual, Cu at zero, Atlas* diffractometer (**3**, **7** and **8**), a *SuperNova, Single Source at Offset, Eos* diffractometer (**5**), a *Nonius KappaCCD* diffractometer (**4** and *anti*-**19**) and a *Bruker AXS X8 ProspectorUltra with APEX II* diffractometer (*anti*-**18**).

The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>20</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table 5. CCDC 994028 – 994034 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.ac.uk/data\\_request/cif](http://www.ccdc.ac.uk/data_request/cif).

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The authors thank Klaus-Peter Mester and Gerd Lipinski for recording NMR spectra, as well as Jens Sproß and Heinz-Werner Patruck for measuring mass spectra. We gratefully acknowledge financial support from Deutsche Forschungsgemeinschaft (DFG).

**Table 5** Crystallographic data for **3**, **4**, **5**, **7**, **8**, *anti-18* and *anti-19*.

	<b>3</b>	<b>4</b>	<b>5</b>	<b>7</b>	<b>8</b>	<i>anti-18</i>	<i>anti-19</i>
Emp. formula	C <sub>24</sub> H <sub>26</sub> Si <sub>2</sub>	C <sub>24</sub> H <sub>26</sub> Si <sub>2</sub>	C <sub>18</sub> H <sub>10</sub>	C <sub>24</sub> H <sub>26</sub> Sn <sub>2</sub>	C <sub>102</sub> H <sub>118</sub> Sn <sub>8</sub>	C <sub>48</sub> H <sub>52</sub> Si <sub>4</sub>	C <sub>38</sub> H <sub>32</sub> Cl <sub>4</sub> Si <sub>2</sub>
<i>M<sub>r</sub></i>	370.63	370.63	226.26	551.83	2293.48	741.26	686.62
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	1.54178	0.71073
<i>T</i> [K]	100.0	100(2)	100.0(2)	100.0(1)	100.0(1)	100(2)	100(2)
<i>F</i> (000)	396	1584	472	540	2260	396	356
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.26970(2)	23.6928(2)	10.93715(2)	11.4064(2)	15.3809(3)	8.564(3)	7.5761(6)
<i>b</i> [Å]	5.81937(7)	8.6313(1)	11.26203(2)	6.07068(1)	15.4149(3)	10.244(4)	10.0339(8)
<i>c</i> [Å]	16.56046(2)	24.1592(2)	9.96535(2)	16.7481(4)	21.7315(4)	12.957(5)	12.7454(8)
$\alpha$ [°]	90	90	90	90	80.698(2)	79.45(3)	110.973(5)
$\beta$ [°]	99.6391(1)	117.0424(5)	105.9353(2)	94.669(2)	74.637(2)	82.01(2)	99.303(5)
$\gamma$ [°]	90	90	90	90	86.960(2)	76.34(1)	101.673(4)
<i>V</i> [Å <sup>3</sup> ]	1070.74(2)	4400.40(7)	1180.31(3)	1122.46(4)	4902.7(2)	1080.5(7)	856.5(1)
<i>Z</i>	2	8	4	2	2	1	1
$\rho_{\text{calcd.}}$ [gcm <sup>-3</sup> ]	1.150	1.119	1.273	1.633	1.554	1.139	1.331
$\mu$ [mm <sup>-1</sup> ]	0.170	0.166	0.072	2.229	2.045	1.502	0.442
$\theta_{\text{max}}$ [°]	30.30	27.49	30.03	30.00	30.00	72.42	25.00
Index ranges <i>h</i>	-15 ≤ <i>h</i> ≤ 15	-30 ≤ <i>h</i> ≤ 30	-15 ≤ <i>h</i> ≤ 15	-16 ≤ <i>h</i> ≤ 16	-21 ≤ <i>h</i> ≤ 21	-10 ≤ <i>h</i> ≤ 10	-9 ≤ <i>h</i> ≤ 9
Index ranges <i>k</i>	-8 ≤ <i>k</i> ≤ 8	-11 ≤ <i>k</i> ≤ 11	-15 ≤ <i>k</i> ≤ 15	-8 ≤ <i>k</i> ≤ 8	-21 ≤ <i>k</i> ≤ 21	-12 ≤ <i>k</i> ≤ 12	-11 ≤ <i>k</i> ≤ 11
Index ranges <i>l</i>	-23 ≤ <i>l</i> ≤ 23	-31 ≤ <i>l</i> ≤ 31	-14 ≤ <i>l</i> ≤ 14	-23 ≤ <i>l</i> ≤ 23	-30 ≤ <i>l</i> ≤ 30	-15 ≤ <i>l</i> ≤ 15	-15 ≤ <i>l</i> ≤ 14
Refl. collected	59469	93358	67142	47899	85614	20419	11464
Indep. refl.	3116	10078	3436	3274	28567	4051	2930
<i>R</i> <sub>int</sub>	0.0343	0.034	0.0433	0.0393	0.0256	0.0300	0.044
Observed refl., <i>I</i> > 2σ( <i>I</i> )	2870	8795	2987	2966	24838	3821	2605
Parameters	121	481	163	121	1017	241	202
<i>R</i> <sub>1</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0327	0.0335	0.0428	0.0225	0.0238	0.0335	0.0347
<i>wR</i> <sub>2</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0937	0.0936	0.1229	0.0532	0.0465	0.0901	0.0876
<i>R</i> <sub>1</sub> (all data)	0.0352	0.0395	0.0489	0.0260	0.0311	0.0350	0.0398
<i>wR</i> <sub>2</sub> (all data)	0.0963	0.0980	0.1277	0.0558	0.0490	0.0912	0.0915
<i>GoF</i>	1.063	1.039	1.068	1.068	1.032	1.062	1.039
$\rho_{\text{max}}/\rho_{\text{min}}$ [e Å <sup>-3</sup> ]	0.43/-0.19	0.33/-0.30	0.43/-0.18	1.07/-0.60	0.53/-0.54	0.41/-0.20	0.28/-0.33
Remarks	-	-	-	-	a)	-	-
CCDC number	994028	994029	994030	994031	994032	994033	994034

Remarks: a) Four molecules of **8** and one molecule of *n*-hexane are found in the asymmetric unit.

## Notes and references

<sup>a</sup> Universität Bielefeld, Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie, Universitätsstraße 25, D-33615 Bielefeld, Germany. E-mail: mitzel@uni-bielefeld.de; Fax: +49 521 106 6026; Tel: +49 521 106 6128  
 † CCDC 994028–994034.

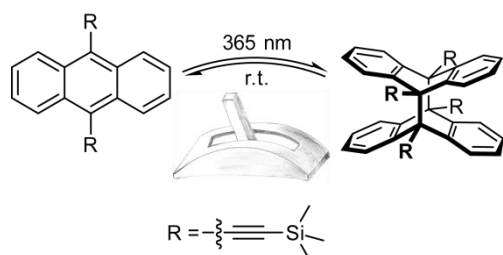
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## Entry for the table of contents:

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**Polyalkynylanthracenes – Syntheses, Structures and their Behaviour towards UV Irradiation**

Jan-Hendrik Lamm, Johanna Glatthor, Jan-Henrik Weddeling, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler and Norbert W. Mitzel\*

A series of 1,5-, 1,8-, 9,10- and 1,8,10-alkynyl-substituted anthracenes has been synthesised and characterised. Amongst others, 9,10-bis[(trimethylsilyl)ethynyl]anthracene could be dimerised upon UV irradiation, the third example of symmetrically 9,10-substituted anthracenes besides the corresponding difluoro- and dimethyl-derivatives. The photodimer was found to be thermally instable and the cycloelimination reaction was investigated by VT NMR spectroscopy.

## **Publikation 5**

### **Poly-Boron, -Silicon and -Gallium Lewis Acids by Hydrometallation of 1,5- and 1,8-Dialkynylanthracenes**

Jan-Hendrik Lamm, Jan Horstmann, Jan Hendrick Nissen, Jan-Henrik  
Weddeling, Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

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# Poly-Boron, -Silicon, and -Gallium Lewis Acids by Hydrometallation of 1,5- and 1,8-Dialkynylanthracenes

Jan-Hendrik Lamm,<sup>[a]</sup> Jan Horstmann,<sup>[a]</sup> Jan H. Nissen,<sup>[a]</sup>  
Jan-Henrik Weddeling,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-  
Georg Stammler,<sup>[a]</sup> and Norbert W. Mitzel\*<sup>[a]</sup>

**Keywords:** Polycycles / Lewis acids / Hydrosilylation / Hydroboration / Hydrogallation / Solid-state structures

1,5-Dialkynylanthracenes and 1,8-dialkynylanthracenes have been functionalised by a series of hydrometallation reactions, namely, hydrosilylation, hydroboration and hydrogallation. Nine anthracene-based Lewis acidic compounds with a semiflexible organic framework bearing SiCl<sub>3</sub>, SiCl<sub>2</sub>Me, SiClMe<sub>2</sub>, B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and GaCl<sub>2</sub> substituents were obtained. In all cases, the substrate could be functionalised

twice, and bidentate Lewis acids were obtained. By using Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>], a fourfold-substituted anthracene species functionalised with four extremely electronegatively substituted boron atoms could be generated in quantitative yield. All of the poly-Lewis acids were characterised by multinuclear NMR spectroscopy and, in part, by mass spectrometry and X-ray diffraction experiments.

## Introduction

Compared to the manifold knowledge on poly-Lewis bases (crown ethers, cryptands, etc.), the chemistry of poly-Lewis acids is less explored. Some of these compounds have been reported, and the known examples comprise mostly flexible (organic) frameworks functionalised with Lewis acidic atoms. Prominent examples include mercury,<sup>[1]</sup> tin<sup>[2]</sup> and silicon,<sup>[3]</sup> for example, the trisilacyclohexane derivative reported by Brondani et al.<sup>[3a]</sup> or the Si-based crown ether analogue reported by Jung and Xia.<sup>[3b]</sup> Remarkable progress in the field of poly-Lewis acids based on aluminium<sup>[4]</sup> and gallium<sup>[4c–4g,5]</sup> has been achieved by Uhl and co-workers with hydroalumination<sup>[4d–4f]</sup> and hydrogallation reactions employing dialkylgallanes<sup>[4e,4f,5a–5c]</sup> and dichlorogallane as reagents,<sup>[5d–5g]</sup> respectively. The synthesis of dichlorogallane (HGaCl<sub>2</sub>)<sub>2</sub><sup>[6]</sup> and its application in the hydrogallation of unsaturated substrates<sup>[7]</sup> was first investigated by Schmidbaur and co-workers.

Molecules containing multiple boron atoms as Lewis acidic functions are also known. Many have been reported by Gabbai et al.<sup>[1d,8,9]</sup> in the context of fluoride ion sensing. Jäkle reviewed polymeric organoboron Lewis acids.<sup>[10]</sup> The 9,10-dihydro-9,10-diboraanthracene reported by Wagner et al.<sup>[11]</sup> and the anthracenes with boron functions reported by Katz are also interesting,<sup>[12]</sup> as are the applications of such systems (as catalysts) in organic synthesis.<sup>[13]</sup> As mentioned

above, most of the poly-Lewis acids exhibit a flexible organic framework and are potentially capable of complexing a wide range of guest species such as anions or (small) Lewis basic molecules. Just a few examples of polydentate Lewis acids with a rigid organic backbone have been synthesised, for example, by Gabbai et al.,<sup>[1a,1c]</sup> Jurkschat and co-workers<sup>[2b]</sup> or Katz.<sup>[12]</sup>

During an ongoing project, we synthesised a series of bidentate earth metal Lewis acids.<sup>[4g]</sup> We used 1,8-diethynylanthracene as a rigid organic backbone, as we considered that nonflexible receptor molecules might increase the selectivity of the binding of Lewis basic guest species. Recently, we published some investigations concerning the mechanism of the formation of host–guest complexes of 1,8-bis[(diethylgallanyl)ethynyl]anthracene with pyridine or pyrimidine, and the Lewis acid demonstrated different reactivity towards both substrates.<sup>[14]</sup>

Herein, we report efficient preparative routes to a series of electronegatively substituted Si-, B- and Ga-containing bi- and tetradentate Lewis acids. These semiflexible systems were generated by hydrometallation of 1,5- and 1,8-dialkynyl-functionalised anthracenes.

## Results and Discussion

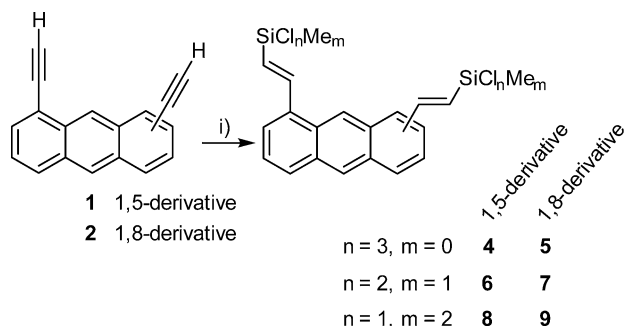
### Hydrosilylation Reactions

The required organic substrates 1,5-diethynylanthracene (**1**), 1,8-diethynylanthracene (**2**) and 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**3**) were synthesised according to modified literature protocols.<sup>[4g,15,16]</sup> The trimethylsilyl-substituted compound **3** was used for hydrogallation reactions,

[a] Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie, Centrum für Molekulare Materialien CM2, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany  
E-mail: mitzel@uni-bielefeld.de  
<http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/>

whereas the deprotected species **1** and **2** were converted in hydrosilylation and hydroboration reactions, respectively.

As shown in Scheme 1, the hydrosilylated compounds **4–9** were afforded by conversion of **1** and **2** with the corresponding neat chloro(methyl)silanes in the presence of Karstedt's platinum(0) catalyst.



Scheme 1. Hydrosilylation of **1** and **2**. Reagents and conditions: i)  $\text{HSiCl}_3$ ,  $\text{HSiCl}_2\text{Me}$  or  $\text{HSiClMe}_2$  (neat), Karstedt's catalyst, room temp., overnight, quantitative.

All products were quantitatively obtained as yellow solids and characterised by multinuclear NMR spectroscopy as well as by EI mass spectrometry. The  $^1\text{H}$  NMR chemical shifts of the compounds in  $\text{CDCl}_3$  at ambient temperature are listed in Tables 1 and 2. In all cases, the  $\text{C}=\text{C}$  double bond is selectively *trans*-substituted as indicated by the coupling constants of the vinyl proton resonances ( $^3J_{\text{H,H}} \approx 18.5$  Hz).

Table 1.  $^1\text{H}$  NMR shifts of the twofold-hydrosilylated compounds **4**, **6** and **8** in  $\text{CDCl}_3$  (500 MHz, 298 K). For NMR spectroscopic assignments, see Scheme 4.

Compound (substituent)	<b>4</b> ( $\text{SiCl}_3$ )	<b>6</b> ( $\text{SiCl}_2\text{Me}$ )	<b>8</b> ( $\text{SiClMe}_2$ )
9-H/10-H	8.70	8.68	8.69
Ar-CH=	8.36	8.21	8.02
4-H/8-H	8.16	8.10	8.06
2-H/6-H	7.81	7.75	7.71
3-H/7-H	7.55	7.52	7.49
SiCH=	6.65	6.63	6.64
SiCH <sub>3</sub>	–	1.06	0.70

Table 2.  $^1\text{H}$  NMR shifts of the twofold-hydrosilylated compounds **5**, **7** and **9** in  $\text{CDCl}_3$  (500 MHz, 298 K). For NMR spectroscopic assignments, see Scheme 4.

Compound (substituent)	<b>5</b> ( $\text{SiCl}_3$ )	<b>7</b> ( $\text{SiCl}_2\text{Me}$ )	<b>9</b> ( $\text{SiClMe}_2$ )
9-H	8.87	8.93	8.96
10-H	8.50	8.49	8.46
Ar-CH=	8.37	8.24	8.06
4-H/5-H	8.07	8.04	7.99
2-H/7-H	7.79	7.75	7.71
3-H/6-H	7.53	7.51	7.49
SiCH=	6.65	6.63	6.64
SiCH <sub>3</sub>	–	1.05	0.70

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra show the anticipated number of resonances, and the  $^{29}\text{Si}\{^1\text{H}\}$  NMR shifts of the hydrosilylated 1,5-derivatives increase from  $\delta = -3.0$  (**4**) to 17.1 (**6**) and 18.8 ppm (**8**). The corresponding shifts of the 1,8-disubstituted anthracenes **5**, **7** and **9** take a similar course.

In consideration of our recently published results concerning the selective *anti*-[4+4] photodimerisation of 1,5-dialkynyl-substituted anthracenes,<sup>[15]</sup> the silylated anthracene derivatives **4**, **6** and **8** might be used in photoreactions under UV irradiation to afford the corresponding bidentate Janus-like Lewis acidic compounds.

Owing to solubility issues, we attempted to crystallise the hydrosilylated species from saturated *n*-pentane/diethyl ether mixtures. Single crystals suitable for X-ray diffraction experiments could be obtained only for **5** by slow evaporation of the solvent mixture. Instead of the expected diethyl ether adduct of the bis(trichlorosilane) **5**, the ether cleavage product **5a** (Figure 1) was obtained as the main component of a mixed crystal system in addition to the corresponding  $\text{SiCl}_3$  derivative **5** (see the Crystal Structure Determination subsection for details). This may indicate the high reactivity and Lewis acidity of the twofold  $\text{SiCl}_3$ -substituted species. As no useful quantities of **5a** could be produced, the compound was solely characterised by X-ray diffraction experiments.

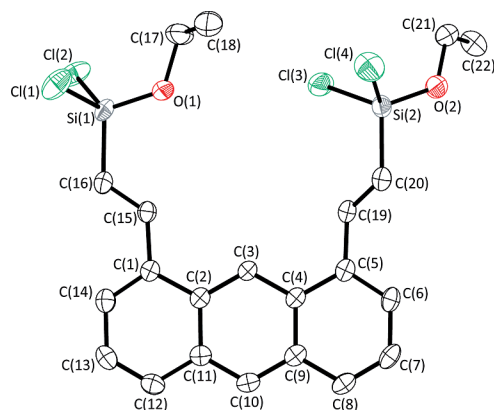


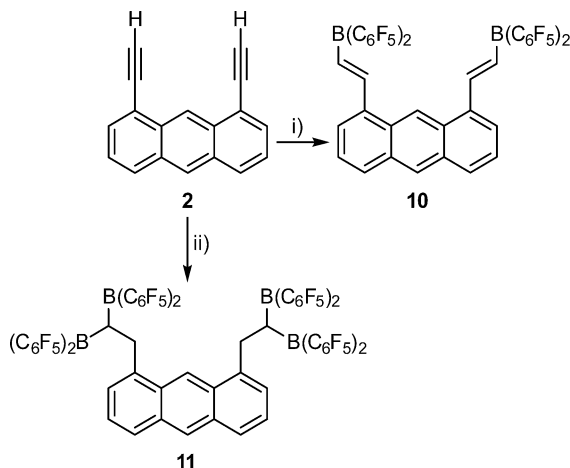
Figure 1. Molecular structure of **5a** in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. For clarity, the main component of the mixed crystal system is shown, and hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.451(3), C(1)–C(14) 1.371(3), C(1)–C(15) 1.470(3), C(2)–C(3) 1.395(3), C(2)–C(11) 1.434(3), C(5)–C(19) 1.467(3), C(15)–C(16) 1.331(3), C(16)–Si(1) 1.811(2), C(19)–C(20) 1.335(3), C(20)–Si(2) 1.821(2), Si(1)–Cl(1) 2.044(1), Si(1)–Cl(2) 2.052(1), Si(1)–O(1) 1.588(3), Si(2)–Cl(3) 2.048(1), Si(2)–Cl(4) 2.041(1), Si(2)–O(2) 1.595(3); C(1)–C(2)–C(3) 123.3(2), C(1)–C(2)–C(11) 118.3(2), C(1)–C(15)–C(16) 126.6(2), C(2)–C(1)–C(15) 120.6(2), C(4)–C(5)–C(19) 120.0(2), C(5)–C(19)–C(20) 127.1(2), C(15)–C(16)–Si(1) 122.8(2), C(16)–Si(1)–Cl(1) 110.2(1), C(16)–Si(1)–O(1) 109.2(1), C(19)–C(20)–Si(2) 123.2(2), C(20)–Si(2)–Cl(3) 110.0(1), C(20)–Si(2)–O(2) 110.5(1), Si(1)–O(1)–C(17) 124.6(2), Si(2)–O(2)–C(21) 126.5(2).

1,8-Bis{2-[dichloro(ethoxy)silyl]vinyl}anthracene (**5a**) crystallises in the monoclinic space group  $P2_1/c$  with four molecules per unit cell. The bond lengths {from 1.363(3) [C(12)–C(13)] to 1.451(3) Å [C(1)–C(2)]} and angles in the aromatic system {from 118.3(2) [C(1)–C(2)–C(11)] to 123.3(2)° [C(1)–C(2)–C(3)]} exhibit no unexpected values and compare well with the corresponding values for other 1,8-disubstituted anthracenes.<sup>[4g,14,15]</sup> The  $\text{C}=\text{C}$  double bonds are not in the plane with the anthracene unit as is indicated by the torsion angles C(16)–C(15)–C(1)–

C(14) [13.3(4)°] and C(20)–C(19)–C(5)–C(6) [–30.9(4)°]. Both C–C angles at C(15) and C(19) [126.6(2)° for C(1)–C(15)–C(16) and 127.1(2)° for C(5)–C(19)–C(20)] are widened as is typically found for substituted ethylenes.<sup>[17]</sup> The Si atoms are nearly tetrahedrally coordinated; the Si–O {1.588(3) [Si(1)–O(1)] and 1.595(3) Å [Si(2)–O(2)]} and Si–C bond lengths {1.811(2) [Si(1)–C(16)] and 1.821(2) Å [Si(2)–C(20)]} are remarkably shortened compared to the sum of the corresponding covalent radii in the crystalline state [Si–O 1.77 Å and Si–C(sp<sup>2</sup>) 1.84 Å].<sup>[18]</sup> The Si–O–C angles are 124.6(2) [Si(1)–O(1)–C(17)] and 126.5(2)° [Si(2)–O(2)–C(21)].

### Hydroboration Reactions

As shown in Scheme 2, the two- and fourfold boron-substituted species **10** and **11** have been successfully synthesised in quantitative yield by conversion of the dialkyne **2** with 2 and 4 equiv. of HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (Piers' borane)<sup>[19]</sup> in benzene. We also tried to functionalise 1,5-diethynylantracene in the same manner as described for the 1,8-derivative. However, the dark red precipitate that formed immediately was found to be insoluble in common (NMR) solvents; therefore, it has not yet been analysed (when [D<sub>8</sub>]THF was used, rapid polymerisation of the solvent was observed).



Scheme 2. Hydroboration of **2**. Reagents and conditions: i) 2HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, 1 min, room temp., quantitative; ii) 4HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, 1 min, room temp., quantitative.

The deep red compounds **10** and **11** were identified by <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C and <sup>19</sup>F NMR spectroscopy. The <sup>1</sup>H NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub> at ambient temperature and show the typical signal pattern of 1,8-disubstituted anthracenes, which consists of two singlets for 9-H and 10-H, two doublets for 2-H/7-H and 4-H/5-H and one doublet of doublets for the protons at the 3- and 6-positions of the aromatic backbone. For the twofold-functionalised species **10**, two further doublets detected at  $\delta = 8.36$  and 7.67 ppm were attributed to the olefinic protons. Their coupling constants of 17.5 Hz indicate the exclusive formation of the *trans* product. In contrast, the conversion of **2** with 4 equiv. of Piers' borane afforded **11**, which bears four extremely elec-

tronegatively substituted boron atoms. In the <sup>1</sup>H NMR spectrum of **11** in C<sub>6</sub>D<sub>6</sub>, its CHCH<sub>2</sub> groups induce a triplet ( $\delta = 4.63$  ppm) and a doublet ( $\delta = 4.10$  ppm) with coupling constants of 7.5 Hz. For both compounds, the <sup>19</sup>F NMR spectroscopic signals can be observed in the typical range for C<sub>6</sub>F<sub>5</sub> groups at  $\delta \approx -130$ ,  $-147$  and  $-160$  ppm.

The NMR spectroscopic data of **10** described above are consistent with the structure obtained by X-ray diffraction experiments (Figure 2). Single crystals of the compound were obtained by cooling a concentrated *n*-pentane solution to  $-30$  °C for at least one week.

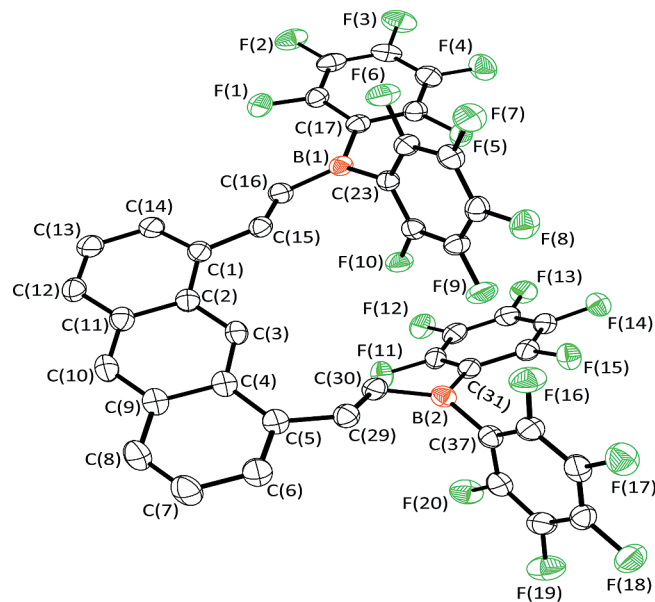


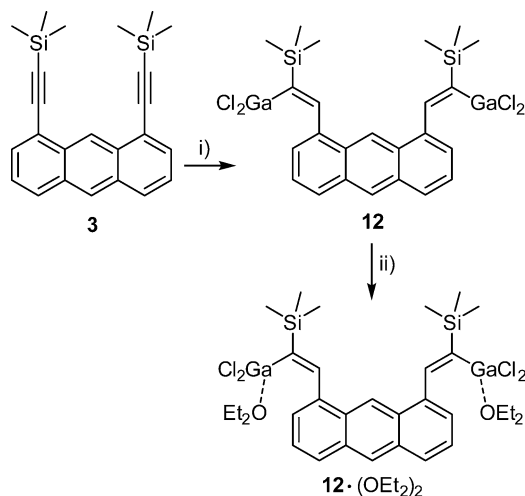
Figure 2. Molecular structure of **10** in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.447(4), C(1)–C(14) 1.376(4), C(1)–C(15) 1.469(3), C(2)–C(3) 1.403(3), C(2)–C(11) 1.440(3), C(5)–C(29) 1.467(3), C(15)–C(16) 1.344(4), C(16)–B(1) 1.533(4), C(23)–B(1) 1.583(4), C(29)–C(30) 1.338(4), C(30)–B(2) 1.533(4), C(37)–B(2) 1.587(4); C(1)–C(2)–C(3) 124.0(2), C(1)–C(2)–C(11) 117.8(2), C(1)–C(15)–C(16) 126.6(2), C(2)–C(1)–C(15) 121.4(2), C(4)–C(5)–C(29) 126.7(2), C(5)–C(29)–C(30) 131.1(2), C(15)–C(16)–B(1) 123.0(2), C(16)–B(1)–C(17) 123.5(2), C(16)–B(1)–C(23) 117.8(2), C(17)–B(1)–C(23) 118.6(2), C(29)–C(30)–B(2) 121.5(2), C(30)–B(2)–C(31) 120.6(2), C(30)–B(2)–C(37) 122.6(2), C(31)–B(2)–C(37) 116.7(2).

Compound **10** crystallises in the triclinic space group *P* $\bar{1}$  with two molecules per unit cell. The C–C bond lengths in the anthracene unit of **10** {1.349(4) [C(7)–C(8)] to 1.452(4) Å [C(4)–C(5)]} are identical within experimental error to the values found in **2**<sup>[4g]</sup> and are comparable to those of **5a** and to those reported for other 1,8-disubstituted anthracene derivatives.<sup>[4g,14,15]</sup> The “upper rim” of the aromatic system itself is slightly distorted as is indicated by the C(14)–C(1)–C(2)–C(3) [172.9(2)°] and C(3)–C(4)–C(5)–C(6) torsion angles [172.2(2)°], whereas the torsion angles of the “lower rim” of the backbone are close to the expected 180° [C(7)–C(8)–C(9)–C(10) 179.0(3)°, C(10)–C(11)–C(12)–C(13) 178.1(3)°]. The B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-substituted vinyl moieties at the 1- and 8-position are not in-plane with the aromatic rings they are bonded to. Owing to the steric interactions

of the fluorine atoms, the substituents of **10** are bent to different sides of the anthracene system as indicated by the torsion angles C(11)–C(2)–C(1)–C(15) [170.2(2)°] and C(16)–C(15)–C(1)–C(14) [–24.9(4)°] as well as C(9)–C(4)–C(5)–C(29) [167.8(2)°] and C(30)–C(29)–C(5)–C(6) [150.0(3)°]. The C(15)–C(1)–C(5)–C(29) angle is –22.1(2)°. The lengths of the C=C bonds are identical within experimental error {1.344(4) [C(15)–C(16)] and 1.338(4) Å [C(29)–C(30)]}. The C–C–C angles at the corresponding carbon atoms {e.g., 131.1(2) [C(5)–C(29)–C(30)] and 123.0(2)° [C(15)–C(16)–B(1)]} deviate from one another, and the first one is widened compared to the standard values. With angles close to 120°, the boron atoms are nearly trigonal planar. The angles between the mean plane through the anthracene carbon atoms (A) and the mean planes through the phenyl-bound fluorine atoms (labelled by the phenyl *ipso* C atom) range from 4.9(6) [A–C(17)] to 43.3(1) [A–C(31)], 69.5(1) [A–C(37)] and 72.0(1)° [A–C(23)].

### Hydrogallation Reactions

The conversion of the TMS-protected dialkyne compound **3** with dichlorogallane [(HGaCl<sub>2</sub>)<sub>2</sub>]<sup>[6b]</sup> affords the twofold-hydrogallated compound **12** (Scheme 3). In contrast to the results published by Uhl et al.<sup>[5d]</sup> we did not observe the formation of a fourfold GaCl<sub>2</sub>-substituted species, although more than 4.5 equiv. of HGaCl<sub>2</sub> were used. Compound **12** is insoluble in *n*-hexane and other non-coordinating solvents and was, therefore, identified by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectroscopy in [D<sub>8</sub>]THF at ambient temperature.



Scheme 3. Hydrogallation of **3** with dichlorogallane to afford **12** and its diethyl ether adduct **12**·(OEt<sub>2</sub>). Reagents and conditions: i) 4.6HGaCl<sub>2</sub>, *n*-hexane, 70 °C, 7 h, 62%; ii) Et<sub>2</sub>O.

The <sup>1</sup>H NMR spectrum of **12** shows two singlets for 9-H and 10-H, two doublets for 2-H/7-H and 4-H/5-H and one doublet of doublets for the protons at the 3- and 6-position of the aromatic system. A downfield-shifted singlet ( $\delta$  = 8.46 ppm) is induced by the two vinyl protons.

The treatment of the brownish solid with diethyl ether afforded the adduct **12**·(OEt<sub>2</sub>)<sub>2</sub> as bright yellow crystals. The compound crystallises in the orthorhombic space group *Pbca* with eight molecules per unit cell. The molecular structure in the solid state is depicted in Figure 3, which illustrates the coordination of one diethyl ether molecule to each gallium atom.

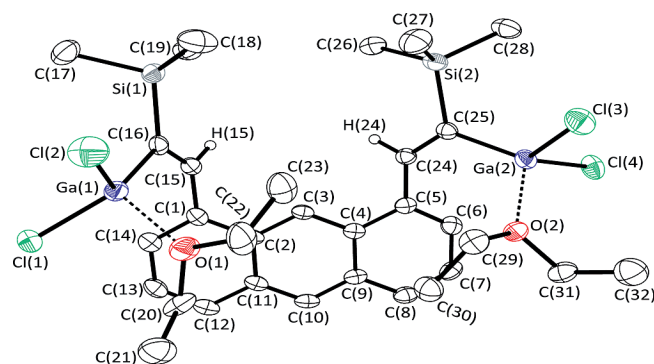


Figure 3. Molecular structure of the twofold diethyl ether adduct **12**·(OEt<sub>2</sub>)<sub>2</sub> in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except those at C(15) and C(24), and the disordered C(32) are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.439(3), C(1)–C(14) 1.374(3), C(1)–C(15) 1.486(3), C(2)–C(3) 1.402(3), C(2)–C(11) 1.436(3), C(5)–C(24) 1.479(3), C(15)–C(16) 1.344(3), C(16)–Ga(1) 1.960(2), C(16)–Si(1) 1.870(2), C(24)–C(25) 1.346(3), C(25)–Ga(2) 1.957(2), C(25)–Si(2) 1.879(2), Cl(1)–Ga(1) 2.183(1), Cl(3)–Ga(2) 2.193(1), O(1)–Ga(1) 2.009(2), O(2)–Ga(2) 1.975(2); C(1)–C(2)–C(3) 121.9(2), C(1)–C(2)–C(11) 119.2(2), C(1)–C(15)–C(16) 127.7(2), C(2)–C(1)–C(15) 120.3(2), C(4)–C(5)–C(24) 119.0(2), C(5)–C(24)–C(25) 129.3(2), C(15)–C(16)–Ga(1) 119.2(2), C(15)–C(16)–Si(1) 120.4(2), C(20)–O(1)–C(22) 114.3(2), C(29)–O(2)–C(31) 116.3(2), Si(1)–C(16)–Ga(1) 120.3(1), Si(2)–C(25)–Ga(2) 117.0(1), Cl(1)–Ga(1)–Cl(2) 106.1(1), Cl(3)–Ga(2)–Cl(4) 107.2(1).

As already observed for **5a** and **10** (as well as other literature examples),<sup>[4g,14,15]</sup> the bond lengths and angles of the aromatic backbone are not significantly influenced by the substituents at the 1- and 8-position. The values compare well with the corresponding ones of **3**.<sup>[15]</sup> The C=C double bonds are 1.344(3) [C(15)–C(16)] and 1.346(3) Å [C(24)–C(25)]. They are identical within experimental error to those of **5a** and **10** and the C=C bond lengths of the diethyl ether adducts of the two- and threefold-hydrogallated 1,4-bis- [1.341(3) Å] and 1,3,5-tris[(trimethylsilyl)ethynyl]benzenes [1.331(4) Å] reported by Uhl and Claesener.<sup>[5c]</sup> The alkenylgallium moieties are orientated to the same side of the anthracene system but are bent differently as is indicated by the torsion angles C(14)–C(1)–C(15)–C(16) [60.5(3)°] and C(6)–C(5)–C(24)–C(25) [–43.7(4)°]. Compared to those of **10**, both substituents are less influenced by steric interactions as is indicated by the torsion angle C(15)–C(1)–C(5)–C(24) [2.1(2)°]. As in **5a**, **10** and similar molecules from the literature,<sup>[5c]</sup> the trigonal planar surrounding of the atoms that form the double bond is slightly distorted [e.g., C(1)–C(15)–C(16) 127.7(2)° and C(5)–C(24)–C(25) 129.3(2)°]. The Ga–Cl bond lengths range from 2.183(1) [Ga(1)–Cl(1)] to 2.193(1) Å [Ga(1)–Cl(2)] and

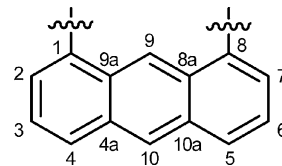
are shorter than the sum of the covalent radii (2.24 Å).<sup>[18]</sup> The Ga(1)–O(1) and Ga(2)–O(2) distances [2.009(2) and 1.975(2) Å, respectively] are consistent with the corresponding data of Uhl and Claesener and they are in the expected range for donor–acceptor complexes.<sup>[5e]</sup> The C–O–C angles of the coordinated diethyl ether molecules are 114.3(2) [C(20)–O(1)–C(22)] and 116.3(2)° [C(29)–O(2)–C(31)] and are comparable to the corresponding value for non-coordinated diethyl ether (112°).<sup>[20]</sup>

## Conclusions

Starting from 1,5- and 1,8-dialkynyl-substituted anthracenes, a series of twofold Lewis acidic functionalised compounds can be synthesised by hydrosilylation, hydroboration and hydrogallation reactions. Different (methyl)chlorosilanes (HSiCl<sub>3</sub>, HSiCl<sub>2</sub>Me and HSiClMe<sub>2</sub>) in the quantitative hydrosilylation reactions afforded products with varying Lewis acidity. The SiMe<sub>3</sub>-substituted substrate 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**3**) can be converted with HGaCl<sub>2</sub> to a di-Lewis acid with two GaCl<sub>2</sub> units. Whereas the cleavage of diethyl ether was shown to be a possible reaction for the di-silicon Lewis acids, a stable diethyl ether adduct of the di-gallium Lewis acid was crystallised and characterised by X-ray diffraction. A tetradentate boron Lewis acid, that is, an anthracene derivative bearing two CH<sub>2</sub>(H)C[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub> substituents at the 1- and 8-position, was obtained by the reaction of 1,8-diethynylanthracene (**2**) with 4 equiv. of Piers' borane.

## Experimental Section

**General:** The syntheses of **1**,<sup>[14]</sup> **2**<sup>[4g,15]</sup> and **3**<sup>[16]</sup> have been described elsewhere. Dichlorogallane, HGaCl<sub>2</sub>,<sup>[6b]</sup> and HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub><sup>[19a]</sup> were synthesised according to literature protocols. Chlorodimethylsilane, dichloromethylsilane (both from ABCR) and trichlorosilane (from Sigma–Aldrich) were dehydrochlorinated over Mg turnings, distilled and degassed before use in the reactions. Karstedt's catalyst (2% Pt in xylene) was purchased from ABCR. All reactions were performed under an anhydrous, inert atmosphere of nitrogen or argon by using standard Schlenk or glovebox techniques and freshly dried and degassed solvents (benzene dried with Na/K alloy, *n*-hexane and Et<sub>2</sub>O dried with LiAlH<sub>4</sub>). NMR spectra were recorded with Bruker DRX 500 and Bruker Avance III 500 instruments at room temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm and referenced to the solvent signals (C<sub>6</sub>D<sub>6</sub>: <sup>1</sup>H NMR  $\delta$  = 7.16 ppm, <sup>13</sup>C NMR  $\delta$  = 128.06 ppm; CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C NMR  $\delta$  = 77.16 ppm; [D<sub>8</sub>]THF: <sup>1</sup>H NMR  $\delta$  = 3.58 ppm, <sup>13</sup>C NMR  $\delta$  = 67.57 ppm) or referenced externally (<sup>11</sup>B: BF<sub>3</sub>·OEt<sub>2</sub>; <sup>19</sup>F: CFCl<sub>3</sub>; <sup>29</sup>Si: SiMe<sub>4</sub>). EI mass spectra were recorded with an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. The samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV. The numbering scheme for NMR assignments (Scheme 4) is based on IUPAC guidelines.



Scheme 4. Numbering scheme for NMR assignments, exemplarily shown for a 1,8-disubstituted anthracene derivative.

**General Procedure for Hydrosilylation Reactions:** **1** or **2** was dissolved in a small amount of the corresponding chloro(methyl)silane, and one drop of Karstedt's catalyst (2% Pt in xylene) was added at ambient temperature. After the mixture was stirred overnight, the chloro(methyl)silanes were removed by condensation, and the desired products were obtained regioselectively and in almost quantitative yield (>98%); no further purification was necessary.

**1,5-Bis[2-(trichlorosilyl)vinyl]anthracene (4):** Synthesised according to the general procedure with 1,5-diethynylanthracene (22 mg, 0.10 mmol) and trichlorosilane (5.7 mL). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.70 (s, 2 H, 9-H/10-H), 8.36 (d, <sup>3</sup>J<sub>H,H</sub> = 18.4 Hz, 2 H, Ar-CH=CH), 8.16 (d, <sup>3</sup>J<sub>H,H</sub> = 8.5 Hz, 2 H, 4-H/8-H), 7.81 (d, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 2 H, 2-H/6-H), 7.55 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.2, 8.3 Hz, 2 H, 3-H/7-H), 6.65 (d, <sup>3</sup>J<sub>H,H</sub> = 18.4 Hz, 2 H, Ar-CH=CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.5 (Ar-CH=CH), 133.4, 132.2, 131.5 (C-4/C-8), 129.4, 125.6 (C-3/C-7), 125.4 (C-2/C-6), 123.2 (Ar-CH=CH), 123.0 (C-9/C-10) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = -3.0 ppm. EI-MS (70 eV): *m/z* = 495.8 [M]<sup>+</sup>, 360.9 [M - SiCl<sub>3</sub>]<sup>+</sup>, 227.1 [M - 2SiCl<sub>3</sub>]<sup>+</sup>.

**1,5-Bis[2-(dichloromethylsilyl)vinyl]anthracene (6):** Synthesised according to the general procedure with 1,5-diethynylanthracene (46 mg, 0.20 mmol) and dichloromethylsilane (5.0 mL). Bright yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.68 (s, 2 H, 9-H/10-H), 8.21 (d, <sup>3</sup>J<sub>H,H</sub> = 18.6 Hz, 2 H, Ar-CH=CH), 8.10 (d, <sup>3</sup>J<sub>H,H</sub> = 8.6 Hz, 2 H, 4-H/8-H), 7.75 (d, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 2 H, 2-H/6-H), 7.52 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.1, 8.3 Hz, 2 H, 3-H/7-H), 6.63 (d, <sup>3</sup>J<sub>H,H</sub> = 18.6 Hz, 2 H, Ar-CH=CH), 1.06 [s, 6 H, Si(CH<sub>3</sub>)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.4 (Ar-CH=CH), 134.3, 132.1, 130.7 (C-4/C-8), 129.4, 125.5 (Ar-CH=CH, C-3/C-7), 124.7 (C-2/C-6), 123.1 (C-9/C-10), 6.0 [Si(CH<sub>3</sub>)] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.1 ppm. EI-MS (70 eV): *m/z* = 455.7 [M]<sup>+</sup>, 340.9 [M - SiCl<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>, 227.0 [M - 2 SiCl<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>.

**1,5-Bis[2-(chlorodimethylsilyl)vinyl]anthracene (8):** Synthesised according to the general procedure with 1,5-diethynylanthracene (29 mg, 0.13 mmol) and chlorodimethylsilane (6.0 mL). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.69 (s, 2 H, 9-H/10-H), 8.06 (d, <sup>3</sup>J<sub>H,H</sub> = 8.7 Hz, 2 H, 4-H/8-H), 8.02 (d, <sup>3</sup>J<sub>H,H</sub> = 18.8 Hz, 2 H, Ar-CH=CH), 7.71 (d, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 2 H, 2-H/6-H), 7.49 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.1, 8.3 Hz, 2 H, 3-H/7-H), 6.64 (d, <sup>3</sup>J<sub>H,H</sub> = 18.8 Hz, 2 H, Ar-CH=CH), 0.70 [s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.9 (Ar-CH=CH), 135.4, 132.1, 129.9 (C-4/C-8), 129.4, 129.1 (Ar-CH=CH), 125.5 (C-3/C-7), 124.1 (C-2/C-6), 123.1 (C-9/C-10), 2.4 [Si(CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = 18.8 ppm. EI-MS (70 eV): *m/z* = 413.8 [M]<sup>+</sup>, 320.9 [M - SiCl(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 285.1 [M - SiCl(CH<sub>3</sub>)<sub>2</sub> - Cl]<sup>+</sup>, 226.9 [M - 2SiCl(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.

**1,8-Bis[2-(trichlorosilyl)vinyl]anthracene (5):** Synthesised according to the general procedure with 1,8-diethynylanthracene (23 mg, 0.10 mmol) and trichlorosilane (6.0 mL). Bright yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.87 (s, 1 H, 9-H), 8.50 (s, 1 H, 10-H), 8.37 (d, <sup>3</sup>J<sub>H,H</sub> = 18.5 Hz, 2 H, Ar-CH=CH), 8.07 (d, <sup>3</sup>J<sub>H,H</sub> =

8.5 Hz, 2 H, 4-H/5-H), 7.79 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2 H, 2-H/7-H), 7.53 (dd,  $^3J_{\text{H,H}} = 7.2$ , 8.3 Hz, 2 H, 3-H/6-H), 6.65 (d,  $^3J_{\text{H,H}} = 18.5$  Hz, 2 H, Ar-CH=CH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.5$  (Ar-CH=CH), 133.6, 131.7, 130.9 (C-4/C-5), 129.6, 128.4 (C-10), 125.5 (C-3/C-6), 125.3 (C-2/C-7), 123.1 (Ar-CH=CH), 117.4 (C-9) ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = -2.9$  ppm. EI-MS (70 eV):  $m/z = 495.6$   $[\text{M}]^+$ , 362.8  $[\text{M} - \text{SiCl}_3]^+$ , 226.9  $[\text{M} - 2\text{SiCl}_3]^+$ .

**1,8-Bis[2-(dichloromethylsilyl)vinyl]anthracene (7):** Synthesised according to the general procedure with 1,8-diethynylanthracene (50 mg, 0.22 mmol) and dichloromethylsilane (5.5 mL). Yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.93$  (s, 1 H, 9-H), 8.49 (s, 1 H, 10-H), 8.24 (d,  $^3J_{\text{H,H}} = 18.6$  Hz, 2 H, Ar-CH=CH), 8.04 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2 H, 4-H/5-H), 7.75 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2 H, 2-H/7-H), 7.51 (dd,  $^3J_{\text{H,H}} = 7.2$ , 8.3 Hz, 2 H, 3-H/6-H), 6.63 (d,  $^3J_{\text{H,H}} = 18.5$  Hz, 2 H, Ar-CH=CH), 1.05 [s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.5$  (Ar-CH=CH), 134.7, 131.8, 130.1 (C-4/C-5), 129.6, 128.1 (C-10), 125.7 (Ar-CH=CH), 125.5 (C-3/C-6), 124.7 (C-2/C-7), 117.8 (C-9), 5.9 [Si(CH<sub>3</sub>)<sub>2</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.2$  ppm. EI-MS (70 eV):  $m/z = 455.8$   $[\text{M}]^+$ , 340.9  $[\text{M} - \text{SiCl}_2\text{CH}_3]^+$ , 226.9  $[\text{M} - 2(\text{SiCl}_2\text{CH}_3)]^+$ .

**1,8-Bis[2-(chlorodimethylsilyl)vinyl]anthracene (9):** Synthesised according to the general procedure with 1,8-diethynylanthracene (29 mg, 0.13 mmol) and chlorodimethylsilane (4.0 mL). Bright yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.96$  (s, 1 H, 9-H), 8.46 (s, 1 H, 10-H), 8.06 (d,  $^3J_{\text{H,H}} = 18.8$  Hz, 2 H, Ar-CH=CH), 7.99 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2 H, 4-H/5-H), 7.71 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2 H, 2-H/7-H), 7.49 (dd,  $^3J_{\text{H,H}} = 7.3$ , 8.2 Hz, 2 H, 3-H/6-H), 6.64 (d,  $^3J_{\text{H,H}} = 18.5$  Hz, 2 H, Ar-CH=CH), 0.70 [s, 12 H, Si(CH<sub>3</sub>)<sub>2</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.0$  (Ar-CH=CH), 135.8, 131.7, 129.6, 129.3 (C-4/C-5), 129.2 (Ar-CH=CH), 127.8 (C-10), 125.5 (C-3/C-6), 124.0 (C-2/C-7), 118.0 (C-9), 2.4 [Si(CH<sub>3</sub>)<sub>2</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = 18.3$  ppm. EI-MS (70 eV):  $m/z = 414.0$   $[\text{M}]^+$ , 321.0  $[\text{M} - \text{SiCl}(\text{CH}_3)_2]^+$ , 227.0  $[\text{M} - 2\text{SiCl}(\text{CH}_3)_2]^+$ .

**1,8-Bis[2-[bis(pentafluorophenyl)boryl]vinyl]anthracene (10):** In an NMR tube fitted with a polytetrafluoroethylene (PTFE) tap, bis(pentafluorophenyl)borane (31 mg, 0.08 mmol) and 1,8-diethynylanthracene (10 mg, 0.04 mmol) were dissolved in  $\text{C}_6\text{D}_6$  (1 mL). The treatment of the mixture in an ultrasonic bath for ca. 1 min. afforded the product as a dark red solid in quantitative yield. Dark red crystals suitable for X-ray diffraction experiments were obtained after removal of the solvent in vacuo and recrystallisation from *n*-pentane.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 9.11$  (s, 1 H, 9-H), 8.36 [d,  $^3J_{\text{H,H}} = 17.5$  Hz, 2 H, (R<sup>F</sup>)<sub>2</sub>B-CH=CH], 8.09 (s, 1 H, 10-H), 7.72 (d,  $^3J_{\text{H,H}} = 8.4$  Hz, 2 H, 4-H/5-H), 7.67 [d,  $^3J_{\text{H,H}} = 17.5$  Hz, 2 H, (R<sup>F</sup>)<sub>2</sub>B-CH=CH], 7.55 (d,  $^3J_{\text{H,H}} = 7.0$  Hz, 2 H, 2-H/7-H), 7.14 (dd,  $^3J_{\text{H,H}} = 7.0$ , 8.4 Hz, 2 H, 3-H/6-H) ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 40.2$  ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 160.6$  [(R<sup>F</sup>)<sub>2</sub>B-CH=CH], 148.0 (*m*-C), 143.5 (*p*-C), 137.8 (*o*-C), 136.5, 135.8 [(R<sup>F</sup>)<sub>2</sub>B-CH=CH], 132.2, 132.2 (C-2/C-7), 130.1, 129.2 (C-10), 128.9 (C-4/C-5), 125.7 (C-3/C-6), 119.8 (C-9), 114.1 ppm.  $^{19}\text{F}$  NMR (282 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -129.5$  (m, 2 F, *o*-F), -147.6 (tt,  $^3J_{\text{F,F}} = 20.6$  Hz,  $^4J_{\text{F,F}} = 2.5$  Hz, 1 F, *p*-F), -160.9 (m, 2 F, *m*-F) ppm.

**1,8-Bis[2,2-[bis(pentafluorophenyl)boryl]ethyl]anthracene (11):** In an NMR tube fitted with a PTFE tap, bis(pentafluorophenyl)borane (31 mg, 0.08 mmol) and 1,8-diethynylanthracene (5.0 mg, 0.02 mmol) were dissolved in  $\text{C}_6\text{D}_6$  (1 mL). The treatment of the mixture in an ultrasonic bath for ca. 1 min. afforded the product as a dark red solid in quantitative yield.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 8.46$  (s, 1 H, 9-H), 7.87 (s, 1 H, 10-H), 7.49 (d,  $^3J_{\text{H,H}} = 8.6$  Hz, 2 H, 4-H/

5-H), 7.19 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2 H, 2-H/7-H), 7.06 (dd,  $^3J_{\text{H,H}} = 6.9$ , 8.4 Hz, 2 H, 3-H/6-H), 4.63 {t,  $^3J_{\text{H,H}} = 7.5$  Hz, 2 H, [(R<sup>F</sup>)<sub>2</sub>B]<sub>2</sub>-CHCH<sub>2</sub>}, 4.10 {d,  $^3J_{\text{H,H}} = 7.5$  Hz, 4 H, [(R<sup>F</sup>)<sub>2</sub>B]<sub>2</sub>-CH-CH<sub>2</sub>} ppm.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 44.0$  ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 147.4$  (*m*-C), 143.4 (*p*-C), 137.8, 137.6 (*o*-C), 131.7, 129.8, 128.5 (C-10), 127.6 (C-2/C-7), 126.3 (C-4/C-5), 125.5 (C-3/C-6), 116.9 (C-9), 113.6, 54.9 {[(R<sup>F</sup>)<sub>2</sub>B]<sub>2</sub>CHCH<sub>2</sub>}, 30.2 {[(R<sup>F</sup>)<sub>2</sub>B]<sub>2</sub>-CH-CH<sub>2</sub>} ppm.  $^{19}\text{F}$  NMR (282 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -130.0$  (m, 2 F, *o*-F), -146.5 (tt,  $^3J_{\text{F,F}} = 20.6$  Hz,  $^4J_{\text{F,F}} = 2.5$  Hz, 1 F, *p*-F), -160.4 (m, 2 F, *m*-F) ppm.

**1,8-Bis[2-(dichlorogallyl)-2-(trimethylsilyl)vinyl]anthracene (12):** 1,8-Diethynylanthracene (35 mg, 0.09 mmol) was dissolved in *n*-hexane (18 mL), and dichlorogallane (55 mg, 0.41 mmol) was added to the yellow solution at ambient temperature. The mixture was heated to reflux for 7 h, and the formation of a brownish precipitate was observed. The precipitate was collected by filtration, washed with *n*-hexane (3 × 5 mL) and dried in vacuo, yield 37 mg (62%).  $^1\text{H}$  NMR (500 MHz, [D<sub>8</sub>]THF):  $\delta = 8.63$  (s, 1 H, 9-H), 8.52 (s, 1 H, 10-H), 8.46 [s, 2 H, Ar-CH=C(Si)], 7.99 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2 H, 4-H/5-H), 7.67 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 2 H, 2-H/7-H), 7.46 (dd,  $^3J_{\text{H,H}} = 6.9$ , 8.4 Hz, 2 H, 3-H/6-H), 0.38 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, [D<sub>8</sub>]THF):  $\delta = 153.9$  [CH=C(Si)Ga], 152.5 [CH=C(Si)Ga], 141.5, 132.6, 130.8, 129.3 (C-4/C-5), 128.4 (C-10), 126.6 (C-3/C-6), 126.4 (C-2/C-7), 120.7 (C-9), 0.4 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, [D<sub>8</sub>]THF):  $\delta = -3.0$  ppm.

**Diethyl Ether Adduct of 1,8-Bis[2-(dichlorogallyl)-2-(trimethylsilyl)vinyl]anthracene [12·(OEt<sub>2</sub>)<sub>2</sub>]:** A small quantity of the twofold-hydrogallated species **12** was dissolved in diethyl ether. After the yellow solution was cooled to -30 °C for at least one week, **12·(OEt<sub>2</sub>)<sub>2</sub>** was obtained as yellow crystals, yield not determined.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 8.69$  (s, 1 H, 9-H), 8.54 [s, 2 H, Ar-CH=C(Si)], 8.17 (s, 1 H, 10-H), 7.91 (d,  $^3J_{\text{H,H}} = 6.7$  Hz, 2 H, 2-H/7-H), 7.72 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2 H, 4-H/5-H), 7.27 (dd,  $^3J_{\text{H,H}} = 7.1$ , 8.2 Hz, 2 H, 3-H/6-H), 3.23 [br, 8 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 0.58 [br, 12 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>] 0.56 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 154.1$  [CH=C(Si)Ga], 152.0 [CH=C(Si)Ga], 140.5, 131.8, 129.7, 128.5 (C-4/C-5), 127.8 (C-10), 126.4 (C-2/C-7), 126.0 (C-3/C-6), 120.1 (C-9), 67.6 [O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 13.7 [O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>], 0.2 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = -0.2$  ppm.

**Crystal Structure Determination:** Suitable crystals of **5a**, **10** and **12·(OEt<sub>2</sub>)<sub>2</sub>** were obtained by cooling saturated solutions of *n*-pentane (**10**) or diethyl ether [**5a** and **12·(OEt<sub>2</sub>)<sub>2</sub>**] to -30 °C for at least one week. The crystals were selected inside a glovebox, coated with Paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream to solidify the oil. Data collection was performed with an Agilent SuperNova (Dual source, Cu at zero, Atlas CCD) diffractometer (**5a**), a Bruker AXS X8 Prospector Ultra with APEX II diffractometer (**10**) and a Nonius KappaCCD diffractometer [**12·(OEt<sub>2</sub>)<sub>2</sub>**].

The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>[21]</sup> The crystal and refinement details are listed in Table 3.

CCDC-999999 (for **5a**), -1000000 (for **10**) and -1000001 [for **12·(OEt<sub>2</sub>)<sub>2</sub>**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Table 3. Crystallographic data for **5a**, **10** and **12**·(OEt)<sub>2</sub>.

	<b>5a</b> <sup>[a]</sup>	<b>10</b>	<b>12</b> ·(OEt) <sub>2</sub> <sup>[b]</sup>
Empirical formula	C <sub>21.68</sub> H <sub>21.19</sub> Cl <sub>4.16</sub> O <sub>1.84</sub> Si <sub>2</sub>	C <sub>42</sub> H <sub>12</sub> B <sub>2</sub> F <sub>20</sub>	C <sub>32</sub> H <sub>48</sub> Cl <sub>4</sub> Ga <sub>2</sub> O <sub>2</sub> Si <sub>2</sub>
<i>M</i> <sub>r</sub>	514.82	918.14	802.12
$\lambda$ [Å]	1.54178	1.54178	0.71073
<i>T</i> [K]	99.9(2)	100(2)	100(2)
<i>F</i> (000)	1059	908	3312
Crystal system	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	13.4814(3)	11.0754(9)	11.7673(2)
<i>b</i> [Å]	26.1382(6)	12.4946(11)	20.6574(4)
<i>c</i> [Å]	6.93139(18)	13.7581(12)	32.6589(5)
$\alpha$ [°]	90	102.821(6)	90
$\beta$ [°]	98.692(2)	90.107(6)	90
$\gamma$ [°]	90	108.233(5)	90
<i>V</i> [Å <sup>3</sup> ]	2414.42(10)	1758.0(3)	7938.8(2)
<i>Z</i>	4	2	8
$\rho$ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.416	1.734	1.342
$\mu$ [mm <sup>-1</sup> ]	5.705	1.573	1.713
$\theta$ <sub>max</sub> [°]	72.12	66.69	27.48
Index ranges <i>h</i>	-16 ≤ <i>h</i> ≤ 16	-12 ≤ <i>h</i> ≤ 12	-15 ≤ <i>h</i> ≤ 15
Index ranges <i>k</i>	-32 ≤ <i>k</i> ≤ 32	-14 ≤ <i>k</i> ≤ 14	-26 ≤ <i>k</i> ≤ 26
Index ranges <i>l</i>	-8 ≤ <i>l</i> ≤ 8	-16 ≤ <i>l</i> ≤ 15	-42 ≤ <i>l</i> ≤ 42
Reflections collected	42388	17500	73514
Independent reflections	4765	5770	9081
<i>R</i> <sub>int</sub>	0.0563	0.0326	0.067
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	3885	4742	6843
Parameters	283	577	390
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0380	0.0448	0.0355
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0909	0.1268	0.0824
<i>R</i> <sub>1</sub> (all data)	0.0523	0.0550	0.0570
<i>wR</i> <sub>2</sub> (all data)	0.0993	0.1363	0.0896
GoF	1.024	1.033	1.046
$\rho$ <sub>max</sub> / $\rho$ <sub>min</sub> [e Å <sup>-3</sup> ]	0.41/-0.45	0.33/-0.29	0.81/-0.55

[a] Mixed crystal, O(1), C(17), C(18) and Cl(5) share the same site with a 89:11 distribution; O(2), C(21), C(22) and Cl(6) share the same site with a 95:5 distribution. [b] Disorder of C(32) at two positions (57:43).

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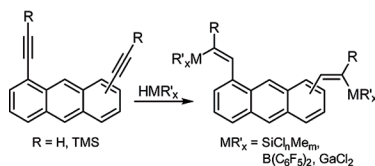
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## Lewis Acids

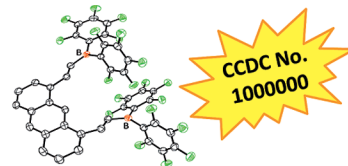
J.-H. Lamm, J. Horstmann, J. H. Nissen,  
J.-H. Weddeling, B. Neumann,  
H.-G. Stammler, N. W. Mitzel\* ..... 1–9

Poly-Boron, -Silicon, and -Gallium Lewis  
Acids by Hydrometallation of 1,5- and 1,8-  
Dialkynylantracenes

**Keywords:** Polycycles / Lewis acids / Hydro-  
silylation / Hydroboration / Hydrogall-  
ation / Solid-state structures



A series of B-, Si- and Ga-containing poly-  
Lewis acids were synthesised by converting  
1,5- and 1,8-dialkynylantracene deriva-  
tives in hydrometallation reactions. Some



of the compounds reacted with diethyl  
ether, which demonstrates the variable be-  
haviour of the Lewis acidic compounds  
towards Lewis basic molecules.



## **Publikation 6**

### **A Rational Approach to Improve Stereochemical Control in Triptycene Formation – An Exercise in Subtle Balancing Multiple Factors**

Jan-Hendrik Lamm, Yury V. Vishnevskiy, Eric Ziemann, Timo A. Kinder, Beate Neumann, Hans-Georg Stammer, Norbert W. Mitzel

vorgesehen für *Chem. Eur. J.*



## Triptycene Chemistry

## A Rational Approach to Improve Stereochemical Control in Triptycene Formation – An Exercise in Subtle Balancing Multiple Factors

Jan-Hendrik Lamm,<sup>[a]</sup> Yury V. Vishnevskiy,<sup>[a]</sup> Eric Ziemann,<sup>[a]</sup> Timo A. Kinder,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammler,<sup>[a]</sup> and Norbert W. Mitzel<sup>\*[a]</sup>

**Abstract:** Reactions of 1,8-dichloroanthracenes with substituents in position 9 or 10 with *ortho*-chloroaryne give mixtures of 1,8,13- (*syn*) and 1,8,16-trichlorotriptycenes (*anti*), whereupon the *syn/anti* ratio is dependent on the nature of the anthracene substituents in positions 9 and 10. Using quantum chemical calculations, transition states for the formation of the *anti*- and *syn*-isomers were computed. The calculations show the importance of dispersive forces for a correct at least qualitative prediction of results, a series of 1,8,9- and 1,8,10-functionalised anthracene regiochemical preference. Based on

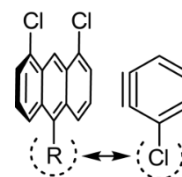
these theoretical results, a series of 1,8,9- and 1,8,10-functionalised anthracene derivatives has been synthesised and reacted with *ortho*-chloroaryne. In the case of 1,8-dichloro-10-(trimethylsilyl)anthracene and 1,8-dichloro-10-(trimethylgermyl)anthracene the *syn*-isomer of the corresponding trichlorotriptycene was found to be the main product. The anthracene and triptycene compounds were completely characterised by NMR spectroscopy, mass spectrometry and by X-ray diffraction experiments.

## Introduction

Triptycene represents one of a few molecules of  $C_3$  symmetry exhibiting a rigid organic framework without Lewis-basic heteroatom functionalities. It was first synthesised by Bartlett *et al.* in 1942 by a multi-step procedure starting with anthracene and *p*-benzoquinone.<sup>[1]</sup> In 1956, Wittig and Ludwig reported a more efficient access to triptycene by a one-step reaction of anthracene with *in situ*-formed benzyne.<sup>[2]</sup> Substituted triptycenes are widely used e.g. as building blocks for fluorescent or non-fluorescent organic macromolecules, polymers and liquid crystals,<sup>[3,4]</sup> as rigid spacers in several palladium complexes used for cross coupling reactions,<sup>[5]</sup> as devices in molecular machines<sup>[6]</sup> or are utilised in crystal engineering processes.<sup>[7,8]</sup>

In an ongoing project, we want to use 1,8,13-trialkynylsubstituted triptycenes as rigid organic frameworks to build up tridentate earth metal poly-Lewis acids.<sup>[9,10]</sup> 1,8,13-trisubstituted triptycenes (*syn*-isomers) can be obtained by Diels-Alder reaction of 1,8-disubstituted anthracenes with *ortho*-substituted arynes, as

shown by Rogers and Averill in 1986.<sup>[11]</sup> However, the corresponding 1,8,16-trisubstituted *anti*-isomer is always formed and is obtained unambiguously as the main product, when e.g. Cl-functionalisated anthracenes and arynes are used.<sup>[9,11]</sup> In 2010, we reported attempts to increase the ratio of 1,8,13-trichlorosubstituted (*syn*) triptycenes.<sup>[9]</sup> A steric interference of the (bulky) anthracene substituent at C-10 with the chlorine moiety of the chloroaryne (Scheme 1) was expected to lead to an increased formation of the *syn*-isomer. Interestingly, the influence of the steric demand of the C-10 substituent was clearly overruled by electronic properties.<sup>[9]</sup>



**Scheme 1.** Expected steric interference of a bulky-substituted 1,8-dichloroanthracene derivative and a chloroaryne unit.

[a] M.Sc. J.-H. Lamm, Dr. Yu. V. Vishnevskiy, B.Sc. E. Ziemann, B.Sc. Timo A. Kinder, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. N. W. Mitzel  
Universität Bielefeld, Fakultät für Chemie  
Lehrstuhl für Anorganische Chemie und Strukturchemie  
Universitätsstraße 25, D-33615 Bielefeld, Germany  
Fax: (+) 49 (0)521 106-6026  
E-mail: mitzel@uni-bielefeld.de

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Herein we describe the syntheses and characterisation of a series of substituted anthracenes and their reaction with *in situ*-generated arynes or chloroarynes to form the corresponding *syn*- and *anti*-substituted triptycenes. The influences of the substituents in positions 9 and 10 are determined and compared with the results of quantum chemical calculations.

## Results and Discussion

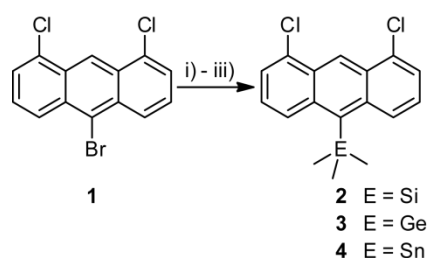
### Preceding Remarks

Taking previous results into account,<sup>[9]</sup> we performed preliminary quantum chemical calculations on the B3LYP/6-31G(d,p) level to obtain partial charges of the carbon atoms C-9 and C-10 of the 9- and 10-substituted 1,8-dichloroanthracenes as well as those of C-2 and C-3 of the chloroaryne component. We expected to be able to use these to predict the preferred orientation of the arylene in the [4+2] cycloadditions. Interestingly, the results of these investigations (listed in Table S1 and S2, S.I.) revealed NBO<sup>[12]</sup> and AIM<sup>[13]</sup> charges in contradiction, especially for the chloroaryne molecule. The NBO charges indicated that a SiMe<sub>3</sub> substituent in 10-position as well as a methyl group in 9-position would change the charge distribution in a way that the reaction would preferably proceed to the corresponding *syn*-isomer of the trichlorotriptycenes.

### Anthracene Derivatives: Syntheses and Characterisation

Considering the preliminary quantum chemical calculation results described above, we synthesised a series of 1,8,9- and 1,8,10-substituted anthracene derivatives to convert them with *in situ*-generated chloroaryne.

The SiMe<sub>3</sub>-, GeMe<sub>3</sub>- and SnMe<sub>3</sub>-functionalised 1,8-dichlorotriptycenes **2**, **3** and **4** were obtained by salt-elimination reactions according to previously published results (Scheme 2).<sup>[14]</sup>

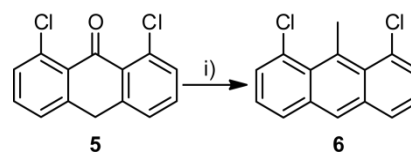


**Scheme 2.** Syntheses of the 10-substituted 1,8-dichloroanthracenes **2**, **3** and **4** via the brominated species **1**. Reagents and conditions: i) 1. *n*-BuLi, THF, -78 °C, 2 h; 2. Me<sub>3</sub>SiCl, 72%; ii) 1. *n*-BuLi, THF, -78 °C, 2 h; 2. Me<sub>3</sub>GeCl, 62%; iii) 1. *n*-BuLi, THF, -78 °C, 2 h; 2. Me<sub>3</sub>SnCl, 74%.<sup>[14]</sup>

In general, 9-alkyl-substituted 1,8-dichloroanthracenes can be synthesised by a nucleophilic addition of Grignard or alkyl lithium compounds to 1,8-dichloro-9-anthrone **5** (Scheme 3), which can be easily prepared by reduction of the commercially available 1,8-dichloroanthraquinone with aluminium chips in sulphuric acid.<sup>[15]</sup> 9-Methyl-substituted 1,8-dichloroanthracene **6** was prepared by converting anthrone **5** with methyl lithium. Contrary to literature reports<sup>[16]</sup> we found that using methyl lithium instead of methyl magnesium bromide solution leads to improved yields of **6**. After rearomatisation with aqueous HCl and purification by column chromatography, 1,8-dichloro-9-methylanthracene (**6**) was isolated as yellow crystals.

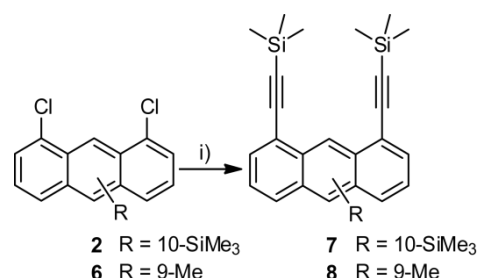
The molecular structures of 1,8-dichloroanthracen-9-(10*H*)-one (**5**) and 1,8-dichloro-9-methylanthracene (**6**) were determined by X-ray diffraction experiments (see Figures S1 and S2, S.I.). In the case of the 9-methyl substituted 1,8-dichloroanthracene **6** (Figure S2) steric repulsion between the chlorine- and methyl-

substituents leads to a remarkable distortion from planarity of the anthracene unit.



**Scheme 3.** Synthesis of 1,8-dichloro-9-methylanthracene (**6**) via 1,8-dichloroanthracen-9-(10*H*)-one (**5**). Reagents and conditions: i) 1. MeLi, Et<sub>2</sub>O, toluene, -50 °C; 2. aq. HCl (10%), reflux, 0.5 h, 50%.

The 10- and 9-substituted 1,8-dichloroanthracene derivatives **2** and **6** were further functionalised with (trimethylsilyl)ethynyl units by using Ni-catalysed Kumada cross coupling reactions (Scheme 4).<sup>[10,17]</sup>



**Scheme 4.** Syntheses of the 9- and 10-substituted 1,8-bis(trimethylsilyl)ethynylanthracene derivatives **7** and **8** by Kumada cross coupling reactions. Reagents and conditions: i) 1. Me<sub>3</sub>SiC≡CMgBr (7 eq.), Ni(acac)<sub>2</sub>, PPh<sub>3</sub>, THF, reflux; 2. aq. workup, 58% (**7**), 60% (**8**).

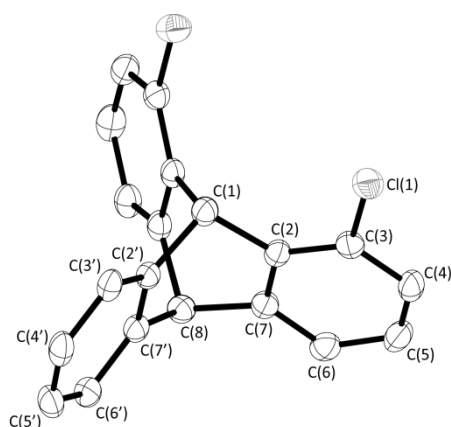
The TMS-alkynyl-functionalised compounds were purified by column chromatography and characterised by multinuclear NMR spectroscopy as well as high resolution mass spectrometry. The <sup>1</sup>H NMR spectra of the compounds show typical patterns of substituted anthracenes consisting of two doublets (induced by protons H2/H7 and H4/H5, respectively), one doublet of doublets (H3/H6) and one singlet for the proton in position 9 or 10. In CDCl<sub>3</sub> at ambient temperature (298 K) the <sup>1</sup>H resonance of the methyl protons of **8** at δ = 3.79 ppm is slightly shifted compared to the dichloro compound **6** (δ = 3.39 ppm). The <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra show the anticipated number of resonances. For crystal structures of compounds **7** and **8** see S.I., Figures S3 and S4.

### Triptycene Derivatives: Syntheses and Characterisation

Following the procedure described by Rogers and Averill,<sup>[11]</sup> we synthesised 1,8-dichlorotriptycene (**9**) as a test-compound for further functionalisations (see below) by reaction of 1,8-dichloroanthracene with *in situ*-generated benzyne. The product was characterised by high resolution mass spectrometry as well as <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

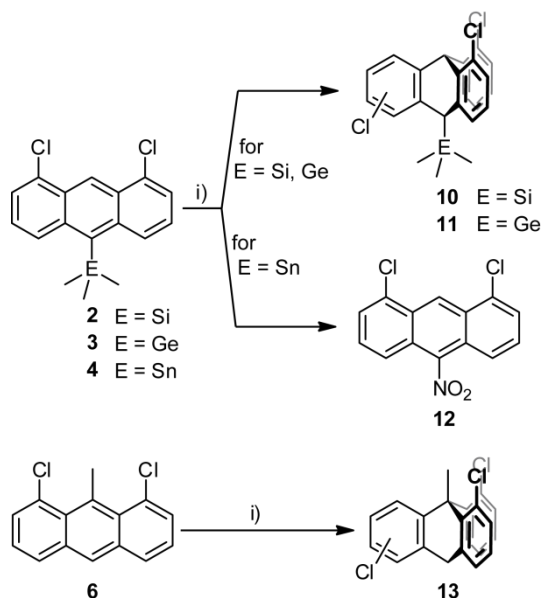
Its molecular structure in the crystalline state was determined by X-ray diffraction experiments and is depicted in Figure 1. In the crystal the two chlorine atoms are statistically distributed over the three possible *syn*-positions at the triptycene backbone, which

resides on a three-fold rotation axis. All average bond lengths and angles exhibit expected values and are not discussed in detail.



**Figure 1.** Molecular structure of 1,8-dichlorotriptycene (**9**) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.530(3), C(2)–C(3) 1.381(3), C(2)–C(7) 1.393(3), C(3)–Cl(1) 1.709(3), C(7)–C(8) 1.530(3); C(1)–C(2)–C(3) 127.2(2), C(1)–C(2)–C(7) 113.3(2), C(2)–C(1)–C(2') 105.4(2), C(2)–C(3)–C(4) 120.3(2), C(2)–C(3)–Cl(1) 121.2(2), C(2)–C(7)–C(6) 121.0(2), C(2)–C(7)–C(8) 113.4(2), C(7)–C(8)–C(7') 105.3(2).

To investigate the influence of substituents in positions 10 and 9, the 1,8-dichloroanthracene derivatives **2**, **3**, **4** and **6** were converted with *in situ*-generated chloroaryne, to obtain the corresponding trichlorotriptycenes (Scheme 5).



**Scheme 5.** Conversion of the 10-trimethylelement-substituted 1,8-dichloroanthracenes **2**, **3**, **4** and **6** with *in situ*-generated chloroaryne to give the trichlorotriptycenes **10**, **11** and **13** as well as 1,8-dichloro-10-nitroanthracene (**12**). Reagents and conditions: i) 1. 3-chloroanthranilic acid, isoamyl nitrite, DME, reflux, 4 h; 2. aq. NaOH, MeOH, 55% (**10**), 45% (**11**), 45% (**13**).

In the case of the 10-SiMe<sub>3</sub>-, the 10-GeMe<sub>3</sub>- and the 9-Me-substituted anthracenes we observed a mixture of the *syn*- and *anti*-trichlorotriptycene derivatives **10**, **11** and **13**. Expectedly, the *syn:anti* ratio of the triptycene formation reaction depends on the substituents in positions 9 and 10 (Table 1).

**Table 1.** Results of the trichlorotriptycene syntheses by conversion of the corresponding 1,8-dichloroanthracene derivatives **2**, **3** and **6** with *in situ*-generated chloroaryne. The data for other 10-substituted 1,8-dichloroanthracenes (R-10 = CMe<sub>3</sub>, Ph, Me, H) are given for comparison.<sup>[9]</sup> The reactions have been also investigated by quantum-chemical calculations (see below and in S.I.).

anthracene derivative	R-9	R-10	<i>syn</i> [%]	<i>anti</i> [%]	Yield [%] <sup>[a]</sup>
<b>6</b>	Me	H	34	66	45
<b>3</b>	H	GeMe <sub>3</sub>	70	30	45
<b>2</b>	H	SiMe <sub>3</sub>	84	16	55
	H	CMe <sub>3</sub>	0	100	43
	H	Ph	25	75	28
	H	Me	37	63	42
	H	H	21	79	16

[a] All yields are given for a mixture of *syn*- and *anti*-trichlorotriptycenes.

In accordance with the results of the preliminary quantum chemical calculations described above, we obtained a marked excess of the *syn*-trichlorotriptycene isomer in the case of the conversion of 1,8-dichloro-10-(trimethylsilyl)anthracene (**2**) with chloroaryne. The isomers could be separated by sublimation and were characterised by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectroscopy as well as high resolution mass spectrometry.

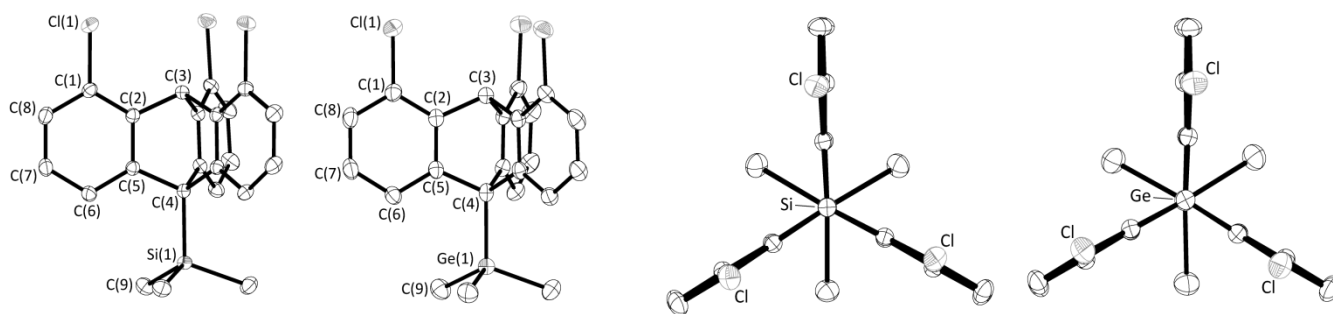
In the case of 1,8,16-trichloro-10-(trimethylsilyl)triptycene (*anti*-**10**) a hindrance of the rotation about the C<sub>Ar</sub>-Si axis can be observed as is indicated by two resonances at δ = 0.99 ppm (6H) and 0.55 ppm (3H) induced by the protons of the SiMe<sub>3</sub> substituent. This signal splitting is also observed in the case of 10-*tert*-butyl-1,8,16-trichlorotriptycene, the carbon analogon of *anti*-**10**.<sup>[9]</sup> The singlet generated by the bridgehead proton H9 of the *syn*-isomer (*syn*-**10**) experiences a larger downfield shift than that of the *anti*-isomer (*anti*-**10**) (δ = 7.12 ppm vs. 6.49 ppm).

In the case of the conversion of 1,8-dichloro-10-(trimethylgermyl)anthracene (**3**) with chloroaryne we observed the same reactivity as described for the SiMe<sub>3</sub> derivative and a *syn:anti* mixture (70:30) of the GeMe<sub>3</sub>-substituted trichlorotriptycene **11** was obtained.

The molecular structures of *syn*-**10** and *syn*-**11** in the crystalline state were determined by single-crystal X-ray diffraction experiments and are depicted in Figure 2. Selected bond lengths and angles are listed in Table 2.

The *syn*-isomers of compounds **10** and **11** crystallise in the trigonal space group *R* $\bar{3}$  with six molecules per unit cell. The molecules exhibit a paddlewheel configuration with the benzene- and methyl substituents being arranged in a staggered conformation (Figure 2). The molecule is of crystallographic C<sub>3</sub> symmetry and close to C<sub>3v</sub> symmetry.





**Figure 2.** Side view (left) and view along the C(3)–C(4)–E(1) axis (right) of the molecular structures of *syn*-**10** and *syn*-**11** in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 2.

**Table 2.** Selected bond lengths [Å] and angles [°] of *syn*-**10** and *syn*-**11**.

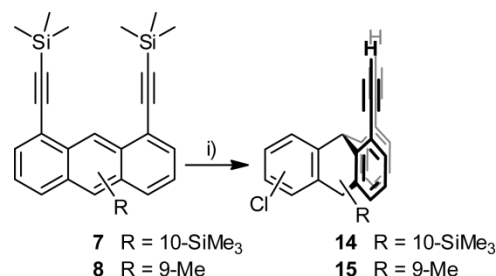
	<i>syn</i> - <b>10</b> (E = Si)	<i>syn</i> - <b>11</b> (E = Ge)
C(1)–C(2)	1.386(2)	1.382(2)
C(1)–C(8)	1.393(2)	1.399(3)
C(1)–Cl(1)	1.744(1)	1.742(2)
C(2)–C(3)	1.517(1)	1.519(2)
C(2)–C(5)	1.408(1)	1.402(2)
C(4)–C(5)	1.548(1)	1.545(2)
C(4)–E(1)	1.922(2)	1.994(3)
C(9)–E(1)	1.879(1)	1.954(2)
Cl(1)–C(1)–C(2)	119.8(1)	120.0(1)
Cl(1)–C(1)–C(8)	118.9(1)	118.9(1)
C(1)–C(2)–C(3)	126.4(1)	126.6(2)
C(2)–C(1)–C(8)	121.2(1)	121.0(2)
C(2)–C(3)–C(2')	105.6(1)	105.5(1)
C(3)–C(2)–C(5)	113.8(1)	113.8(2)
C(4)–C(5)–C(6)	127.2(1)	126.8(2)
C(5)–C(4)–E(1)	114.2(1)	114.0(1)

The bond lengths in the benzene rings are found to be in a normal range, partly varying about 0.03 Å from the standard bond length of benzene (1.395 Å<sup>[18]</sup>). As expected, the C(2)–C(3) and C(4)–C(5) distances are found to be longer [1.517(2) Å and 1.548(2) Å (*syn*-**10**), 1.519(2) Å and 1.545(2) Å (*syn*-**11**)]. The C(4)–E(1) bond lengths are significantly elongated compared to the corresponding standard C(sp<sup>3</sup>)–E distances given in the literature [1.922(2) Å (*syn*-**10**) vs. 1.87 Å<sup>[19]</sup> and 1.994(3) Å (*syn*-**11**) vs. 1.96 Å<sup>[19]</sup>]. This might be due to intramolecular repulsion of the hydrogen atoms at C(6) and symmetry equivalents of the triptycene backbone and those of the methyl groups.

The conversion of the SnMe<sub>3</sub> substituted anthracene derivative **4** under the same conditions afforded 1,8-dichloro-10-nitroanthracene (**12**) instead of the SnMe<sub>3</sub>-substituted trichlorotriptycene (Scheme 5). **12** seems to be the product of an aromatic substitution of **4** with isoamyl nitrite, which is needed to generate the aryne species indicating a weak Sn–C<sub>Ar</sub> bond in compound **4**.

In attempt to prepare 1,8,13-trialkyne-substituted triptycenes, we converted the di- and trichlorotriptycenes **9** and *syn*-**10** with [(trimethylsilyl)ethynyl]magnesium bromide under Kumada conditions. However, no alkyne functionalisations of the triptycene derivatives were observed although the cross coupling reactions were carried out according to a well-established protocol.<sup>[10,17,20]</sup>

Following an alternative synthetic strategy, we used the alkyne-substituted anthracene compounds **7** and **8** as starting materials to prepare the triptycene derivatives (Scheme 6).

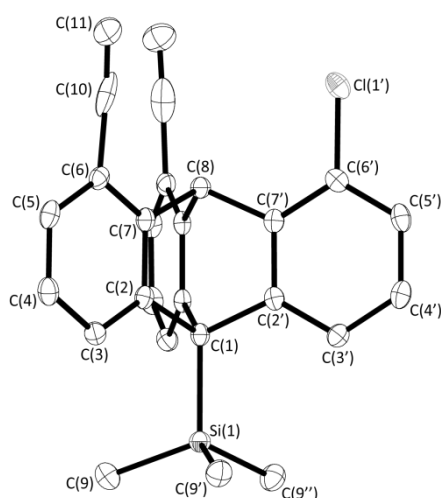


**Scheme 6.** Conversion of the alkyne-substituted anthracene derivatives **7** and **8** with *in situ*-generated chloroaryne to give the triptycenes *syn*-**14** and **15**. Reagents and conditions: i) 1. 3-chloroanthranilic acid, isoamyl nitrite, DME, reflux, 4 h; 2. aq. NaOH, MeOH, 9% (*syn*-**14**), < 1% (**15**).

The reaction between the 10-SiMe<sub>3</sub>-substituted dialkynylantracenes **7** and **8** afforded the corresponding chlorotriptycenes **14** and **15**, respectively (Scheme 6). Owing to the standard work-up procedure for triptycenes using methanol and an aqueous solution of sodium hydroxide, the alkyne-bound SiMe<sub>3</sub> groups were cleaved off to give directly the deprotected species. The conversion of **7** with the chloroaryne species exclusively afforded the *syn*-isomer 1-chloro-8,13-diethynyl-10-(trimethylsilyl)triptycene (*syn*-**14**) in 9% yield. Conversion of the 9-methyl-substituted dichloroanthracene **8** with chloroaryne gave less than 1 mg of a colourless solid, which could not be sufficiently characterised by NMR spectroscopy. However, the formation of the desired chloro-diethynyl-substituted triptycene compound **15** is indicated by mass spectrometric investigations of the product (*m/z* = 350; see Experimental Section for fragmentation pattern).

The <sup>1</sup>H NMR spectrum of *syn*-**14** in CDCl<sub>3</sub> shows the characteristic signal pattern for *syn*-substituted triptycenes as well as one singlet at δ = 3.49 ppm (2H) induced by the alkynyl protons. The molecular structure of *syn*-**14** was determined by X-ray diffraction experiments (Figure 3). Like in the structure of 1,8-dichlorotriptycene (**9**), the substituents of the triptycene are statistically distributed among the three *syn*-positions of the molecule, which is situated at a three-fold rotation axis. The phenyl rings and the Si-bound methyl substituents are arranged in a staggered conformation as it is already observed in the crystal structures of

*syn-10* and *syn-11*. All average bond lengths and angles exhibit expected values, so they are not discussed in detail.

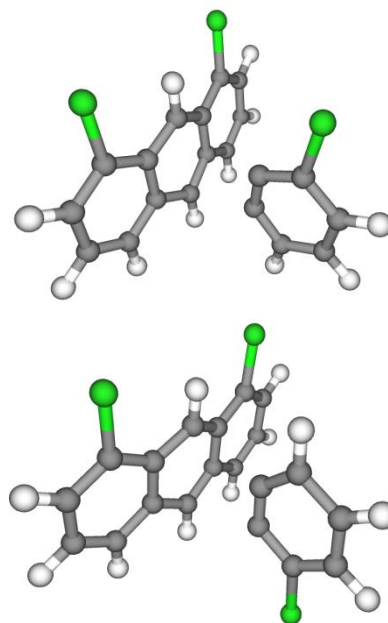


**Figure 3.** Molecular structure of 1-chloro-8,13-diethynyl-10-(trimethylsilyl)tritycene (*syn-14*) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.550(2), C(1)–Si(1) 1.921(2), C(2)–C(3) 1.391(2), C(2)–C(7) 1.398(2), C(4)–C(5) 1.381(2), C(5)–C(6) 1.399(2), C(6)–C(7) 1.391(2), C(6)–C(10) 1.51(2), C(6')–Cl(1') 1.698(8), C(9)–Si(1) 1.878(2), C(10)–C(11) 1.13(2); C(1)–C(2)–C(3) 126.7(2), C(1)–C(2)–C(7) 113.9(2), C(1)–Si(1)–C(9) 108.9(1), C(2)–C(1)–C(2') 104.0(1), C(2)–C(7)–C(6) 120.8(1), C(2)–C(7)–C(8) 113.9(2), C(5)–C(6)–Cl(1) 119.0(3), C(6)–C(10)–C(11) 174.7(16), C(7)–C(8)–C(7') 105.3(1), C(7)–C(6)–C(10) 117.8(7).

### Quantum Chemical Calculations

The calculated AIM and NBO charges (Tables S1 and S2) of relevant atoms in the anthracene derivatives and the chloroaryne molecule deviate strongly, contradict one another regarding sign and cannot explain the obtained fractions of *syn*- and *anti*-trichlorotriptycenes in the corresponding reactions. To explore further the importance of charge distributions in the reagents the electrostatic potentials (ESP) have been calculated for the chloroaryne and anthracene molecules. Figures S5 and S6 (see S.I.) demonstrate the total ESPs for 1,8-dichloro-10-methylanthracene and chlorobenzene. On the basis of these calculations it can be concluded that the benzyne molecules should preferably attack anthracene molecules so that the *anti*-isomer is formed. However, ESPs are giving only a qualitative picture of the process and cannot be used for a detailed prediction of these reactions.

The most direct way of theoretical investigation of reactions and explanation of their product compositions is the calculation of structures and energies of the corresponding transition states. We performed such calculations for a series of reactions using different approximations. As the first step the activation barriers for the reaction of 1,8-dichloroanthracene with chlorobenzene were calculated using different approximations (Table S3). It turned out that the best and still affordable method is DFT theory using the B3LYP functional with a 6-31G(d,p) basis set including accounting for the contributions of basis-set superposition error. The optimised transition state structures are shown in Figure 4.

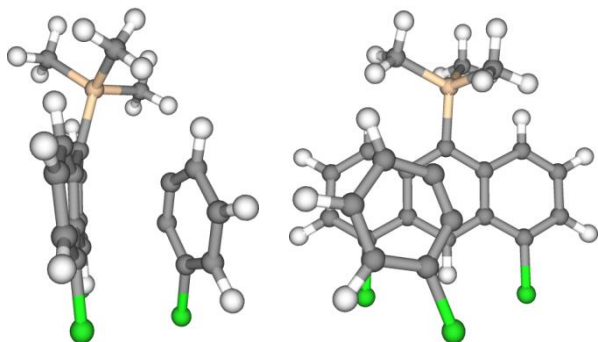


**Figure 4.** Optimised [B3LYP/6-31G(d,p)] structure of the transition state for the formation reaction of 1,8,13-trichlorotriptycene (*syn*, above) and 1,8,16-trichlorotriptycene (*anti*, below).

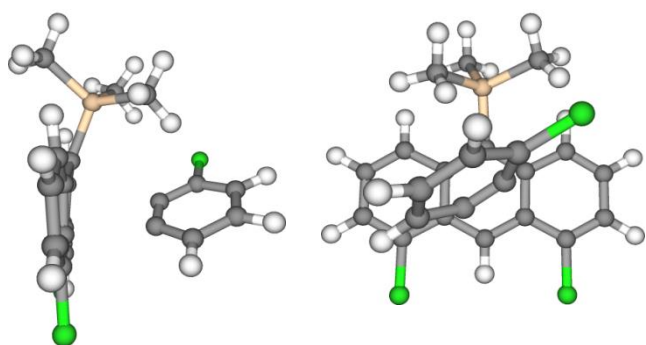
Interesting aspects could be obtained from analyses of these structures with AIM and Interacting Quantum Atoms (IQA) techniques.<sup>[21]</sup> The corresponding AIM molecular graphs (Figures S8 and S9, S.I.) show the existence of bond critical points (BCP) for the bonds forming during the reactions. The properties of these BCPs (Table S4) are those of weak stabilising closed-shell interactions between atoms participating in formation of bonds. Another useful possibility to analyse the energies of transition states is the Natural Energy Decomposition Analysis (NEDA) in NBO theory.<sup>[22]</sup> The calculated energy components (Table S5, S.I.) for the transition states of the *syn*- and *anti*-trichlorotriptycene show better stabilisation of the latter. As the result, the activation barrier to the *anti*-trichlorotriptycene is lower and is therefore the dominant product in the corresponding reaction. Detailed analysis reveals the importance of the electronic component (sum of electrostatic, polarisation and self-energies)<sup>[22]</sup> in stabilisation of the *anti*-trichlorotriptycene transition state.

The above discussed theoretical results were obtained by using the B3LYP/6-31G(d,p) approximation, which – if compared with the experimental results (Table 1) – gives at least qualitatively correct relative energies for the transition states in reactions of chlorobenzene with 1,8-dichloroanthracene derivatives, however, except for the case R = SiMe<sub>3</sub>. Consequently, a series of additional calculations has been performed (Table S6) in order to find correct transition states and their energies for this reaction. Expanding the basis set and the use of different DFT functionals did not improve the calculated energies. The barriers to the formation of the *syn*-isomer (with R = SiMe<sub>3</sub>) were still higher than those for the corresponding *anti*-isomer. Attempts to account for static correlation with the CASSCF method did not give correct results either. However, single-point MP2<sup>[23]</sup> and XMCQDPT2-energies<sup>[24]</sup> for the transition state structures from the respective

RHF and CASSCF calculations indicated that dynamic correlation can play a significant role in these reactions. In order to test this hypothesis further, we carried out MP2/def2-SV(P) optimisations for the transition states. These revealed that the transition states for the formation of *syn*- and *anti*-trichloro-10-(trimethylsilyl)triptycene have completely different structures (Figures 5 and 6) from those according DFT calculations.



**Figure 5.** Different views of the optimised [MP2/def2-SV(P)] transition state structure of the reaction forming 1,8,13-trichloro-10-(trimethylsilyl)triptycene (*syn*-isomer).



**Figure 6.** Different views of the optimised [MP2/def2-SV(P)] transition state structure of the reaction forming 1,8,16-trichloro-10-(trimethylsilyl)triptycene (*anti*-isomer).

On this level of theory, the energy of the transition state to the *anti*-isomer is 1.48 kcal mol<sup>-1</sup> higher than that for the *syn*-isomer, which agrees with the experimental observations of a preferred formation of the latter compound. As shown in Figure 5, the structure of the transition state to 1,8,13-trichloro-10-(trimethylsilyl)triptycene (*syn*-isomer) is probably stabilised due to  $\pi$ -stacking of the benzyne ring with the anthracene molecule. In the transition state to the *anti*-isomer this is impossible due to steric repulsion between SiMe<sub>3</sub> group and the Cl atom in chlorobenzene (Figure 6).

## Conclusion

A series of new trichlorotriptycenes has been synthesised by conversion of *in situ*-generated chloroarynes with 1,8-dichloroanthracenes, bearing different substituents in positions 9 and 10. The influence of these anthracene substituents upon the *syn:anti* ratio of the trichlorotriptycene formation was investigated. In accordance with quantum chemical calculations, we found that

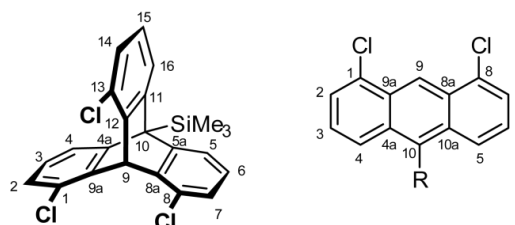
SiMe<sub>3</sub> and GeMe<sub>3</sub> substituents in position 10 leads to an excess of the corresponding *syn*-isomers 1,8,13-trichloro-10-(trimethylsilyl)anthracene (*syn*-**10**) and 1,8,13-trichloro-10-(trimethylgermyl)anthracene (*syn*-**11**) (84% and 70%, respectively). Owing to the fact that in the case of a 10-*tert*-butyl-1,8-dichloroanthracene the *anti*-isomer is exclusively formed, the electronic properties of the substituents remain of dominant importance and seem to override steric repulsion effects during the [4+2] cycloaddition reactions.

A large series of quantum-chemical calculations have shown that many methods fail to describe the experimentally observed regiochemistry and that only methods taking dynamic correlation or dispersive forces into account are able to describe the situation appropriately. The transition states calculated by these relatively costly methods demonstrate the importance of secondary interactions like  $\pi$ -stacking for regiochemistry.

Further attempts to functionalise 1,8-dichlorotriptycene (**9**) and 1,8,13-trichloro-10-(trimethylsilyl)triptycene (*syn*-**10**) with alkyne units in Kumada type reactions failed so far. However, *syn*-chlorodiethynyltriptycenes were synthesised in the reaction of two-fold alkynyl substituted anthracene units with chloroaryne.

## Experimental Section

**General:** The SiMe<sub>3</sub>- (**2**),<sup>[14]</sup> GeMe<sub>3</sub>- (**3**)<sup>[14]</sup> and SnMe<sub>3</sub>-substituted 1,8-dichloroanthracenes (**4**),<sup>[14]</sup> as well as anthrone **5**<sup>[15]</sup> and 1,8-dichloroanthracene<sup>[15]</sup> were synthesised according to literature protocols. Methyl lithium solution (1.6 M in Et<sub>2</sub>O) was purchased from Acros Organics. Anthranilic acid, 3-chloroanthranilic acid (both from Sigma Aldrich) and isoamyl nitrite (from Alfa Aesar) were used without further purification. All reactions using metal organic reagents were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF or toluene (dried over potassium and freshly distilled before being used for the reactions). Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). NMR spectra were recorded on a Bruker DRX 500 and a Bruker Avance III 500 instrument at room temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  = 77.16 ppm; THF-d<sub>6</sub>: <sup>1</sup>H NMR  $\delta$  = 3.58 ppm) or referenced externally (<sup>29</sup>Si{<sup>1</sup>H}: SiMe<sub>4</sub>). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by a push rod in aluminium crucibles. Ions were accelerated by 8 kV. The numbering scheme for NMR assignments (Scheme 7) is based on IUPAC (anthracenes) and Hellwinkel guidelines (triptycenes).



**Scheme 7.** Numbering scheme for NMR spectroscopic assignments.

**1,8-Dichloro-9-methylanthracene (6):** 1,8-Dichloroanthracen-9-(10*H*)-one (501 mg, 1.9 mmol) was dissolved in dry toluene (12 mL) and cooled to -50 °C. Methyl lithium solution (1.6 M in Et<sub>2</sub>O, 2.5 mL, 4.0 mmol) was added dropwise. The mixture was stirred overnight at ambient temperature, quenched with aq. HCl (10%, 7 mL) and heated to reflux for 0.5 h. The organic layer was separated and the aqueous layer was extracted with toluene (3 x 25 mL). The combined organic solution was washed with aq. NaCl, dried with MgSO<sub>4</sub> and the

solvent was evaporated. The pale orange crude product was purified by column chromatography ( $\varnothing = 3$  cm,  $l = 12$  cm, eluent: *n*-pentane) and the product was obtained as bright yellow crystals. Yield: 317 mg (64%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.22$  (s, 1H, H10), 7.83 (d,  $^3J_{\text{H,H}} = 8.4$  Hz, H4/H5), 7.59 (d,  $^3J_{\text{H,H}} = 7.0$  Hz, H2/H7), 7.30 (dd,  $^3J_{\text{H,H}} = 7.3$ , 8.2 Hz, H3/H6), 3.39 (s, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 134.17$ , 133.44, 131.70, 131.53, 129.56 (C2/C7), 128.29 (C4/C5), 126.52 (C10), 125.13 (C3/C6), 27.00 ( $\text{CH}_3$ ) ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 260.0 [ $\text{M}^+$ ], 225.1 [ $\text{M}-\text{Cl}^+$ ], 189.1 [ $\text{M}-2\text{Cl}^+$ ]. HRMS: calculated for  $\text{C}_{15}\text{H}_{10}\text{Cl}_2^+$ : 260.01541; measured: 260.01162.

**General Procedure for Kumada Coupling Reactions:** Trimethylsilyl acetylene ( $\text{Me}_3\text{SiC}\equiv\text{CH}$ , ca. 7 eq.) was added dropwise to a freshly prepared solution of ethylmagnesium bromide in THF at  $0^\circ\text{C}$ . The mixture was stirred at room temperature for 2 h and gas evolution was observed. The formed ((trimethylsilyl)ethynyl)magnesium bromide suspension was transferred into a dropping funnel, fitted with glass wool for simultaneous filtering and slowly added to a solution of the 1,8-dichloroanthracene derivative,  $\text{Ni}(\text{acac})_2$  and  $\text{PPh}_3$  in THF at room temperature, whereby the colour of the solution changed from yellow to dark red. The mixture was heated to reflux for several hours and then quenched with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with a saturated aqueous solution of  $\text{NaCl}$  and dried over  $\text{MgSO}_4$ . The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography using different eluents (see below).

**1,8-Bis((trimethylsilyl)ethynyl)-10-(trimethylsilyl)anthracene (7):** Synthesis according to the general procedure using 1,8-dichloro-10-(trimethylsilyl)anthracene (360 mg, 1.08 mmol),  $\text{PPh}_3$  and  $\text{Ni}(\text{acac})_2$  (one spatula tip of each compound), reflux for 89 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 40$  cm, eluent: *n*-pentane) afforded **7** as bright yellow crystals. Yield: 280 mg (58%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.46$  (s, 1H, H9), 8.40 (d,  $^3J_{\text{H,H}} = 9.0$  Hz, 2H, H4/H5), 7.76 (d,  $^3J_{\text{H,H}} = 6.9$  Hz, 2H, H2/H7), 7.39 (dd,  $^3J_{\text{H,H}} = 6.9$ , 9.0 Hz, 2H, H3/H6), 0.67 [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ], 0.37 [s, 18H,  $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 137.67$ , 136.75, 131.83, 130.99, 129.89, 127.01, 124.23, 122.36, 104.09 (C=C-Si), 99.89 (C=C-Si), 4.60 [ $\text{Ar}-\text{Si}(\text{CH}_3)_3$ ], 0.38 [C=C-Si( $\text{CH}_3$ ) $_3$ ] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = -17.69$  [C=C-Si( $\text{CH}_3$ ) $_3$ ],  $-5.22$  [ $\text{Ar}-\text{Si}(\text{CH}_3)_3$ ] ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 442.2 [ $\text{M}^+$ ], 427.1 [ $\text{M}-\text{Me}^+$ ], 370.1 [ $\text{M}-\text{SiMe}_3^+$ ], 339.1 [ $\text{M}-\text{SiMe}_3-2\text{Me}^+$ ]. HRMS: calculated for  $\text{C}_{24}\text{H}_{37}\text{Si}_3^+$ : 442.19628; measured: 442.19593.

**1,8-Bis((trimethylsilyl)ethynyl)-9-methylanthracene (8):** Synthesis according to the general procedure using 1,8-dichloro-9-methylanthracene (330 mg, 1.26 mmol),  $\text{PPh}_3$  and  $\text{Ni}(\text{acac})_2$  (one spatula tip of each compound), reflux for 160 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 40$  cm, eluent: *n*-pentane/dichloromethane 8:1) afforded **8** as bright yellow crystals. Yield: 290 mg (60%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.23$  (s, 1H, H10), 7.90 (d,  $^3J_{\text{H,H}} = 8.3$  Hz, 2H, H4/H5), 7.81 (d,  $^3J_{\text{H,H}} = 6.8$  Hz, 2H, H2/H7), 7.34 (dd,  $^3J_{\text{H,H}} = 6.9$ , 8.4 Hz, 2H, H3/H6), 3.79 (s, 3H,  $\text{CH}_3$ ), 0.32 [s, 18H,  $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 135.87$ , 134.96, 132.02, 131.95, 130.43, 127.10, 124.38, 120.37, 108.06 (C=C-Si), 101.02 (C=C-Si), 24.68 ( $\text{CH}_3$ ), 0.02 [ $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = -18.02$  ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 384.1 [ $\text{M}^+$ ], 311.1 [ $\text{M}-\text{Si}(\text{CH}_3)_3^+$ ], 295.0 [ $\text{M}-\text{Si}(\text{CH}_3)_3-\text{CH}_3^+$ ]. HRMS: calculated for  $\text{C}_{25}\text{H}_{28}\text{Si}_2^+$ : 384.17241; measured: 384.17101.

**General Procedure for the Syntheses of Triptycenes:** All triptycene derivatives were synthesised according to literature protocols.<sup>[9,11]</sup>

**1,8-Dichlorotriptycene (9):** Synthesis according to the general procedure using 1,8-dichloroanthracene (1.62 g, 6.56 mmol), isoamyl nitrite ( $2 \times 1.8$  mL,  $2 \times 13.0$  mmol), anthranilic acid ( $2 \times 1.80$  g,  $2 \times 13.1$  mmol) in DME (60 mL), reflux for 1.5 h. Sublimation ( $120^\circ\text{C}$ ,  $7 \cdot 10^{-3}$  mbar) and recrystallisation from *n*-hexane afforded **9** as a pale beige solid. Yield: 1.74 g, 82%.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.51$  (m, 1H, H13), 7.40 (m, 1H, H16), 7.28 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 2H, H4/H5), 7.05 (m, 4H, H2/H7/H14/H15), 6.93 (dd,  $^3J_{\text{H,H}} = 7.6$ , 8.1 Hz, 2H, H3/H6), 6.44 (s, 1H, H9), 5.45 (s, 1H, H10) ppm. Separated  $^1\text{H NMR}$  resonances are observed in  $d_8$ -THF:  $^1\text{H NMR}$  (500 MHz,  $d_8$ -THF):  $\delta = 7.48$  (m, 1H, H13), 7.41 (m, 1H, H16), 7.34 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 2H, H4/H5), 7.05 (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 2H, H2/H7), 7.01 (m, 2H, H14/H15), 6.97 (dd,  $^3J_{\text{H,H}} = 7.3$ , 8.0 Hz, 2H, H3/H6), 6.43 (s, 1H, H9), 5.61 (s, 1H, H10) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 147.69$ , 145.00, 143.35, 142.00, 130.10, 126.26 (C3/C6), 126.14 (C2/C7), 125.91 (C14), 125.71 (C15), 124.73 (C13), 123.92 (C16), 122.12 (C4/C5), 54.47 (C10), 47.16 (C9) ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 322.0 [ $\text{M}^+$ ], 287.0 [ $\text{M}-\text{Cl}^+$ ], 252.1 [ $\text{M}-2\text{Cl}^+$ ]. HRMS: calculated for  $\text{C}_{20}\text{H}_{12}\text{Cl}_2^+$ : 322.03106; measured: 322.03039.

**1,8,13-Trichloro-10-(trimethylsilyl)triptycene (syn-10) and 1,8,16-Trichloro-10-(trimethylsilyl)triptycene (anti-10):** Synthesis according to the general procedure using 1,8-dichloro-10-(trimethylsilyl)anthracene (190 mg, 0.59 mmol), isoamyl nitrite ( $2 \times 0.28$  mL,  $2 \times 2.08$  mmol), 3-chloroanthranilic acid ( $2 \times 207$  mg, 1.21 mmol) in DME (30 mL), reflux for 1.5 h. Byproducts were removed by sublimation ( $50^\circ\text{C}$ ,  $7 \cdot 10^{-3}$  mbar) affording a mixture of *syn-10* (84%) and *anti-10* (16%) as a beige solid. Yield: 135 mg, 55%. The *anti*-trichlorotriptycene can be removed by further sublimation ( $85^\circ\text{C}$ ,  $7 \cdot 10^{-3}$  mbar). **NMR data for *syn-10*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.64$  (d,  $^3J_{\text{H,H}} = 7.8$  Hz, 3H, H4/H5/H16), 7.12 (s, 1H, H9), 7.09 (d,  $^3J_{\text{H,H}} = 8.0$  Hz, 3H, H2/H7/H14), 6.94 (m, 3H, H3/H6/H15), 0.74 [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.22$ , 144.02, 130.78, 126.02 (C2/C7/C14), 125.99 (C3/C6/C15), 123.75 (C4/C5/C16), 49.20 (C10), 43.98 (C9), 2.01 [ $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.02$  ppm. **NMR data for *anti-10*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.50$  (d,  $^3J_{\text{H,H}} = 7.8$  Hz, 2H, H4/H5), 7.38 (m, 1H, H13), 7.10 (d,  $^3J_{\text{H,H}} = 8.1$  Hz, 2H, H2/H7), 7.02 (m, 1H, H15), 6.95 (m, 3H, H3/H6/H14), 6.49 (s, 1H, H9), 0.99 [s, 6H,  $\text{Si}(\text{CH}_3)_2$ ], 0.55 [s, 3H,  $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.87$ , 144.84, 144.44, 130.36, 129.53, 128.57 (C13), 126.84 (C14), 126.07 (C2/C7), 125.63 (C3/C6), 125.25 (C4/C5), 123.70 (C15), 49.94 (C10), 48.38 (C9), 7.54 [ $\text{Si}(\text{CH}_3)_2$ ], 5.35 [ $\text{Si}(\text{CH}_3)_3$ ] ppm.  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.27$  ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 430.0 [ $\text{M}^+$ ], 415.0 [ $\text{M}-\text{CH}_3^+$ ], 320.0 [ $\text{M}-\text{Si}(\text{CH}_3)_3-\text{Cl}^+$ ]. HRMS: calculated for  $\text{C}_{23}\text{H}_{19}\text{Cl}_3\text{Si}^+$ : 428.03161; measured: 428.03124.

**1,8,13-Trichloro-10-(trimethylgermyl)triptycene (syn-11) and 1,8,16-Trichloro-10-(trimethylgermyl)triptycene (anti-11):** Synthesis according to the general procedure using 1,8-dichloro-10-(trimethylgermyl)anthracene (40 mg, 0.11 mmol), isoamyl nitrite ( $2 \times 0.03$  mL,  $2 \times 2.08$  mmol), 3-chloroanthranilic acid ( $2 \times 34$  mg, 0.20 mmol) in DME (5 mL), reflux for 1.5 h. A mixture of *syn-11* (70%) and *anti-11* (30%) was afforded as a colourless solid. Yield: 24 mg, 45%. **NMR data for *syn-11*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.22$  (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 3H, H4/H5/H16), 7.10 (s, 1H, H9), 7.09 (d,  $^3J_{\text{H,H}} = 8.1$  Hz, 3H, H2/H7/H14), 6.95 (m, 3H, H3/H6/H15), 0.83 [s, 9H,  $\text{Ge}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.37$ , 144.01, 130.79, 126.18 (C3/C6/C15), 126.08 (C2/C7/C14), 123.46 (C4/C5/C16), 51.89 (C10), 43.90 (C9), 2.24 [ $\text{Ge}(\text{CH}_3)_3$ ] ppm. **NMR data for *anti-11*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.38$  (m, 3H, H4/H5/H13), 7.10 (m, 2H, H2/H7), 7.02 (dd,  $^3J_{\text{H,H}} = 8.0$  Hz,  $^4J_{\text{H,H}} = 1.3$  Hz, 1H, H15), 6.95 (m, 3H, H3/H6/H14), 6.48 (s, 1H, H9), 1.08 [s, 6H,  $\text{Ge}(\text{CH}_3)_2$ ], 0.59 [s, 3H,  $\text{Ge}(\text{CH}_3)_3$ ] ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.61$ , 148.98, 144.33, 130.20, 128.42 (C15), 126.83, 126.11, 125.86, 124.93 (C4/C5), 123.63 (C13), 51.89 (C10), 48.28 (C9), 8.39 [ $\text{Ge}(\text{CH}_3)_2$ ], 5.77 [ $\text{Ge}(\text{CH}_3)_3$ ] ppm (two signals missing due to overlap or line broadening). MS (EI, 70 eV):  $m/z$  [assignment] = 473.8 [ $\text{M}^+$ ], 458.8 [ $\text{M}-\text{CH}_3^+$ ], 319.9 [ $\text{M}-\text{Ge}(\text{CH}_3)_3-\text{Cl}^+$ ], 250.0 [ $\text{M}-\text{Ge}(\text{CH}_3)_3-3\text{Cl}^+$ ]. HRMS: calculated for  $\text{C}_{23}\text{H}_{19}\text{Cl}_3\text{Ge}^+$ : 473.97586; measured: 473.97545.

**1,8,13-Trichloro-9-methyltriptycene (syn-13) and 1,8,16-Trichloro-9-methyltriptycene (anti-13):** Synthesis according to the general procedure using 1,8-dichloro-9-methylanthracene (200 mg, 0.77 mmol), isoamyl nitrite ( $2 \times 0.35$  mL,  $2 \times 2.60$  mmol), 3-chloroanthranilic acid ( $2 \times 300$  mg, 1.75 mmol) in DME (30 mL), reflux for 1.5 h. Byproducts were removed by sublimation ( $50^\circ\text{C}$ ,  $7 \cdot 10^{-3}$  mbar) affording a mixture of *syn-13* (34%) and *anti-13* (66%) as a colourless solid. Yield: 131 mg, 45%. **NMR data for *syn-13*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.25$  (m, 3H, H4/H5/H16), 7.04 (m, 3H, H2/H7/H14), 6.94 (m, 3H, H3/H6/H15), 5.24 (s, 1H, H10), 3.47 (s, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.87$ , 141.25, 130.96, 130.57 (C2/C7/C14), 127.28 (C3/C6/C15), 122.56 (C4/C5/C16), 56.66 (C10), 25.49 ( $\text{CH}_3$ ) ppm (one signal missing due to overlap or line broadening). **NMR data for *anti-13*:**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.40$  (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H, H13), 7.32 (d,  $^3J_{\text{H,H}} = 7.1$  Hz, 2H, H2/H7), 7.10 (d,  $^3J_{\text{H,H}} = 7.9$  Hz, 1H, H15), 7.04 (m, 3H, H4/H5/H14), 6.94 (m, 2H, H3/H6), 5.82 (s, 1H, H10), 3.08 (s, 3H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.81$ , 148.61, 142.34, 141.41, 130.53 (C14), 130.05 (C4/C5), 129.26, 127.09 (C3/C6), 126.24, 126.29 (C15), 123.08 (C2/C7), 121.33 (C13), 51.75 (C10), 21.68 ( $\text{CH}_3$ ) ppm (one signal missing due to overlap or line broadening). MS (EI, 70 eV):  $m/z$  [assignment] = 370.0 [ $\text{M}^+$ ], 335.0 [ $\text{M}-\text{Cl}^+$ ], 320.0 [ $\text{M}-\text{Cl}-\text{CH}_3^+$ ], 301.0 [ $\text{M}-2\text{Cl}^+$ ], 286.0 [ $\text{M}-2\text{Cl}-\text{CH}_3^+$ ], 265.1 [ $\text{M}-3\text{Cl}^+$ ], 250.0 [ $\text{M}-3\text{Cl}-\text{CH}_3^+$ ]. HRMS: calculated for  $\text{C}_{21}\text{H}_{13}\text{Cl}_3^+$ : 370.00773; measured: 370.00574.

**1-Chloro-8,13-diethynyl-10-(trimethylsilyl)triptycene (syn-14):** Synthesis according to the general procedure using 1,8-bis((trimethylsilyl)ethynyl)-10-(trimethylsilyl)anthracene (280 mg, 0.63 mmol), isoamyl nitrite ( $2 \times 0.16$  mL,  $2 \times 1.27$  mmol), 3-chloroanthranilic acid ( $2 \times 163$  mg, 0.96 mmol) in DME (15 mL), reflux for 3 h affording *syn-14* as a pale beige solid. Yield: 23 mg, 9%.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.42$  (d,  $^3J_{\text{H,H}} = 7.7$  Hz, 2H, H5/H16), 7.32 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H, H4), 7.22 (s, 1H, H9), 7.19 (d,  $^3J_{\text{H,H}} = 7.9$  Hz, 2H, H7/H14), 7.07 (d,  $^3J_{\text{H,H}}$

= 8.1 Hz, 1H, *H*<sub>2</sub>), 6.93 (m, 3H, *H*<sub>3</sub>/*H*<sub>6</sub>/*H*<sub>15</sub>), 3.49 (s, 2H, C≡CH), 0.74 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 149.74, 149.04, 147.97, 144.86, 128.93, 128.72 (C7/C14), 125.95 (C3), 125.72 (C2), 125.67 (C5/C16), 124.67 (C6/C15), 123.59 (C4), 119.01, 81.13 (C≡CH), 80.74 (C≡CH), 48.44 (C10), 46.43 (C9), 2.00 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>): δ = -0.24 ppm. MS (EI, 70 eV): *m/z* [assignment] = 408.3 [M]<sup>+</sup>, 393.2 [M-CH<sub>3</sub>]<sup>+</sup>, 300.2 [M-Si(CH<sub>3</sub>)<sub>3</sub>-Cl]<sup>+</sup>. HRMS: calculated for C<sub>27</sub>H<sub>21</sub>SiCl<sup>+</sup>: 408.10956; measured: 408.11117.

**1-Chloro-8,13-diethynyl-9-methyltriptycene (syn-15) and 1-Chloro-8,16-diethynyl-9-methyltriptycene (anti-15):** Synthesis according to the general procedure using 1,8-bis[(trimethylsilyl)ethynyl]-9-methylanthracene (20 mg, 0.63 mmol), isoamyl nitrite (2 × 0.03 mL, 2 × 1.27 mmol), 3-chloroanthranilic acid (2 × 36 mg, 0.96 mmol) in DME (4 mL), reflux for 3.5 h affording a beige solid. Yield: < 1 mg, < 1%. Due to low yields, the product could not be completely characterised by NMR spectroscopy. However, mass spectrometric investiga-

tions indicate the formation of the product. MS (EI, 70 eV): *m/z* [assignment] = 350.1 [M]<sup>+</sup>, 315.1 [M-Cl]<sup>+</sup>, 300.2 [M-Cl-CH<sub>3</sub>]<sup>+</sup>, 274.6 [M-Cl-CH<sub>3</sub>-(CCH)]<sup>+</sup>.

**Synthetic Attempt for 1,8-Dichloro-10-nitroanthracene (12):** The nitro compound **12** was obtained after converting 1,8-dichloro-10-(trimethylstannyl)anthracene (**4**) with 3-chloroanthranilic acid and isoamyl nitrite according to the general procedure for the syntheses of triptycenes. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 9.54 (s, 1H, *H*<sub>9</sub>), 7.84 (d, <sup>3</sup>J<sub>H,H</sub> = 8.9 Hz, 2H, *H*<sub>4</sub>/*H*<sub>5</sub>), 7.74 (d, <sup>3</sup>J<sub>H,H</sub> = 7.2 Hz, 2H, *H*<sub>2</sub>/*H*<sub>7</sub>), 7.60 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.5, 8.6 Hz, 2H, *H*<sub>3</sub>/*H*<sub>6</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 133.33, 129.15 (C3/C6), 128.90, 127.09 (C2/C7), 124.88 (C9), 123.81, 120.70 (C4/C5) ppm (one signal missing due to overlap or line broadening). MS (EI, 70 eV): *m/z* [assignment] = 291.0 [M]<sup>+</sup>, 245.0 [M-NO<sub>2</sub>]<sup>+</sup>, 210.0 [M-NO<sub>2</sub>-Cl]<sup>+</sup>. HRMS: calculated for C<sub>14</sub>H<sub>7</sub>NO<sub>2</sub>Cl<sub>2</sub><sup>+</sup>: 290.98484; measured: 290.98418. In addition, we determined the crystal structure of compound **12**. Due to incomplete data set, the structure is not presented here.

**Table 3.** Crystallographic data for compounds **5**, **6**, **7**, **8**, **9**, *syn-10*, *syn-11* and *syn-14*. The molecular structures in crystalline state of compounds **5**, **6** and **8** are depicted in Figures S1 – S4 (S.I.).

	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<i>syn-10</i>	<i>syn-11</i>	<i>syn-14</i>
Empirical formula	C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub> O	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub>	C <sub>27</sub> H <sub>34</sub> Si <sub>3</sub>	C <sub>25</sub> H <sub>28</sub> Si <sub>2</sub>	C <sub>20</sub> H <sub>12</sub> Cl <sub>2</sub> 0.5 CHCl <sub>3</sub>	C <sub>23</sub> H <sub>19</sub> Cl <sub>3</sub> Si	C <sub>23</sub> H <sub>19</sub> Cl <sub>3</sub> Ge	C <sub>27</sub> H <sub>21</sub> ClSi 2 H <sub>2</sub> O
<i>M<sub>r</sub></i>	263.10	261.13	442.81	384.65	382.88	429.82	474.32	408.98/445
<i>λ</i> [Å]	1.54178	1.54178	1.54178	1.54178	0.71073	0.71073	0.71073	1.54178
<i>T</i> [K]	100(2)	100.01(10)	100.01(10)	99.99(10)	100(2)	100.00(10)	100.00(12)	100.01(10)
<i>F</i> (000)	1072	1072	952	412	780	1332	1440	1404
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	trigonal	trigonal	trigonal	trigonal
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{3}$ <i>c</i> 1	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$
<i>a</i> [Å]	17.8947(6)	10.15040(18)	9.19229(9)	8.9556(5)	11.7471(4)	12.27330(14)	12.3697(2)	11.9967(3)
<i>b</i> [Å]	7.2411(2)	8.46384(14)	36.1562(3)	9.2843(7)	11.7471(4)	12.27330(14)	12.3697(2)	11.9967(3)
<i>c</i> [Å]	17.8973(6)	26.8184(5)	8.26198(9)	14.7724(5)	14.3629(4)	23.9782(3)	24.1358(5)	26.6398(8)
<i>α</i> [°]	90	90	90	104.941(5)	90	90	90	90
<i>β</i> [°]	108.964(2)	94.3324(17)	109.9739(11)	94.669(4)	90	90	90	90
<i>γ</i> [°]	90	90	90	107.598(6)	120	120	120	120
<i>V</i> [Å <sup>3</sup> ]	2193.21(12)	2297.42(7)	2580.76(5)	1114.16(11)	1716.46(10)	3128.02(6)	3198.22(13)	3320.38(19)
<i>Z</i>	8	8	4	2	4	6	6	6
<i>ρ</i> <sub>calcd.</sub> [gcm <sup>-3</sup> ]	1.594	1.510	1.140	1.147	1.482	1.369	1.478	1.335
<i>μ</i> [mm <sup>-1</sup> ]	5.124	4.818	1.761	1.473	0.610	0.503	1.818	2.216
<i>θ</i> <sub>max</sub> [°]	69.46	67	71.989	67.11	27.45	32.36	32.28	72.09
Index ranges <i>h</i>	-20 ≤ <i>h</i> ≤ 21	-9 ≤ <i>h</i> ≤ 12	-11 ≤ <i>h</i> ≤ 11	-10 ≤ <i>h</i> ≤ 9	-15 ≤ <i>h</i> ≤ 15	-17 ≤ <i>h</i> ≤ 18	-18 ≤ <i>h</i> ≤ 18	-14 ≤ <i>h</i> ≤ 11
Index ranges <i>k</i>	-8 ≤ <i>k</i> ≤ 8	-10 ≤ <i>k</i> ≤ 7	-44 ≤ <i>k</i> ≤ 44	-11 ≤ <i>k</i> ≤ 11	-12 ≤ <i>k</i> ≤ 12	-18 ≤ <i>k</i> ≤ 17	-18 ≤ <i>k</i> ≤ 18	-8 ≤ <i>k</i> ≤ 14
Index ranges <i>l</i>	-21 ≤ <i>l</i> ≤ 21	-31 ≤ <i>l</i> ≤ 32	-10 ≤ <i>l</i> ≤ 10	-17 ≤ <i>l</i> ≤ 12	-17 ≤ <i>l</i> ≤ 18	-35 ≤ <i>l</i> ≤ 35	-35 ≤ <i>l</i> ≤ 35	-32 ≤ <i>l</i> ≤ 31
Refl. collected	76716	7854	47279	7158	14366	128031	65255	4830
Indep. refl.	8015	4057	5075	3979	1313	2026	2080	1318
<i>R</i> <sub>int</sub>	0.0402	0.0232	0.0261	0.0277	0.063	0.0358	0.0369	0.0149
Observed refl., <i>I</i> > 2σ( <i>I</i> )	7662	3937	4808	3370	1233	1888	1908	1211
Parameters	617	309	280	251	88	83	83	101
<i>R</i> <sub>1</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0394	0.0396	0.0272	0.0367	0.0537	0.0299	0.0322	0.0320
<i>wR</i> <sub>2</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0977	0.1056	0.0777	0.0935	0.1319	0.0918	0.0850	0.0864
<i>R</i> <sub>1</sub> (all data)	0.0418	0.0406	0.0287	0.0463	0.0567	0.0314	0.0351	0.0342
<i>wR</i> <sub>2</sub> (all data)	0.0999	0.1065	0.0791	0.1006	0.1338	0.0930	0.0869	0.0875
<i>GoF</i>	1.067	1.093	1.034	1.047	1.101	1.104	1.078	1.093
<i>ρ</i> <sub>max</sub> / <i>ρ</i> <sub>min</sub> [e Å <sup>-3</sup> ]	1.11/-0.28	0.42/-0.33	0.30/-0.29	0.35/-0.25	0.30/-0.32	0.41/-0.35	1.87/-0.65	0.25/-0.32
Remarks	[a]	–	–	–	[b]	[c]	–	[d]
CCDC number	1002159	1002160	1002161	1002162	1002163	1002356	1002357	1002358

[a] pseudo-merohedral and racemic twin, TWIN 0 0 1 0 1 0 1 0 0 -4 BASF 0.36471 0.13648 0.14213, U<sub>ij</sub> of all carbon atoms were restrained to be similar (Shelxl-Card "SIMU"); [b] The two chlorine atoms of the triptycene are statistically distributed among the three *syn*-positions of the molecule, which is situated at a three-fold rotation axis. The chloroform is disordered at a three-fold rotoinversion axis; [c] The electron density of disordered CH<sub>2</sub>Cl<sub>2</sub> on a three-fold axis was masked with OLEX2 program.<sup>[25]</sup> [d] The electron density of two highly disordered H<sub>2</sub>O on a three-fold axis was accounted for by the SQUEEZE procedure.

**Crystal Structure Determination:** Suitable crystals of the compounds **5**, **6**, **7**, **8**, **9**, *syn-10*, *syn-11* and *syn-14* were obtained by slow evaporation of saturated solutions of an *n*-hexane/dichloromethane mixture (**5**, *syn-11*), *n*-pentane (**6**, **7**), an *n*-pentane/dichloromethane mixture (**8**) and chloroform (**9**, *syn-10*, *syn-14*). They were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a *SuperNova, Dual, Cu at zero, Atlas* diffractometer (**6**, **7**, **8**, *syn-14*), a *SuperNova, Single Source at Offset, Eos* diffractometer (*syn-10*, *syn-11*), a *Nonius KappaCCD* diffractometer (**9**) and a *Bruker AXS X8 ProspectorUltra with APEX II* diffractometer (**5**). The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>[26]</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table 3. CCDC 1002159 – 1002163 and 1002356 – 1002358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.ac.uk/data\\_request/cif](http://www.ccdc.ac.uk/data_request/cif).

## Acknowledgements

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**Keywords:** Anthracenes • Triptycenes • Cycloaddition • Quantum Chemical Calculations • Solid-State Structures

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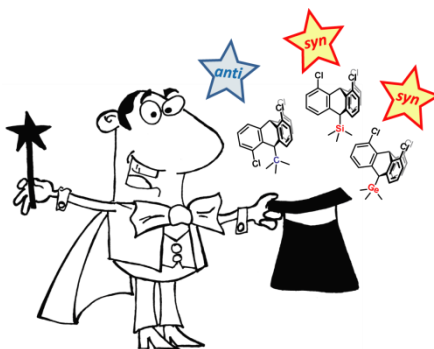
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Entry for the Table of Contents

FULL PAPER

**Hocus Pocus *syn*-Salabim:** The conversion of 10-EMe<sub>3</sub>-substituted 1,8-dichloroanthracenes with chloroaryne leads to the formation of the corresponding *syn*- or *anti*-trichlorotriptycenes. In the case of 10-*tert*-butyl-dichloroanthracene (E = C) the *anti*-isomer is exclusively afforded. Using SiMe<sub>3</sub>- or GeMe<sub>3</sub>-functionalised 1,8-dichloroanthracenes, the corresponding *syn*-trichlorotriptycenes are found to be the unambiguous main products of the [4+2] cycloaddition reactions.



Triptycene Chemistry

J.-H. Lamm, Yu. V. Vishnevskiy,  
E. Ziemann, T. A. Kinder,  
B. Neumann, H.-G. Stammer,  
N. W. Mitzel\*



**A Rational Approach to Improve  
Stereochemical Control in  
Triptycene Formation – An  
Exercise in Subtle Balancing  
Multiple Factors**

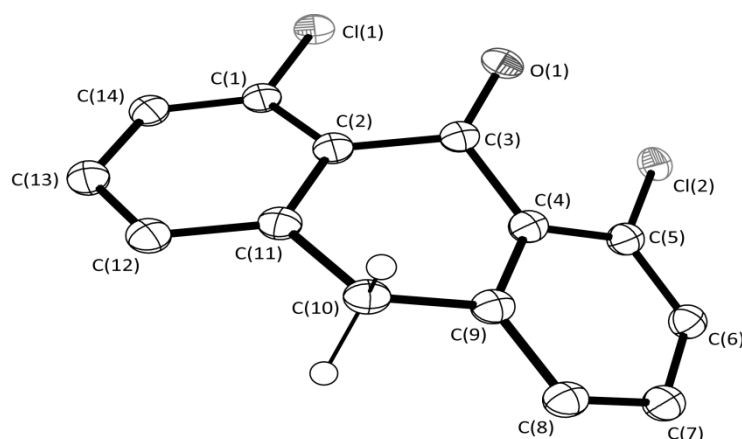
# Supporting Information

## **A Rational Approach to Improve Stereochemical Control in Triptycene Formation – An Exercise in Subtle Balancing Multiple Factors**

Jan-Hendrik Lamm,<sup>[a]</sup> Yury V. Vishnevskiy,<sup>[a]</sup> Eric Ziemann,<sup>[a]</sup> Timo A. Kinder,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammler,<sup>[a]</sup> and Norbert W. Mitzel\*<sup>[a]</sup>



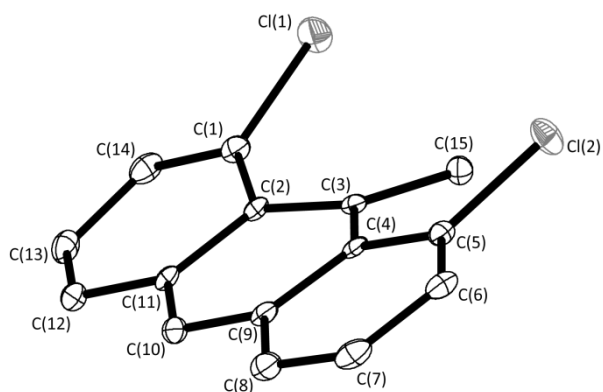
## Crystal Structure of 1,8-Dichloroanthracen-9-(10*H*)-one (**5**)



**Figure S1.** Molecular structure of 1,8-dichloroanthracen-9-(10*H*)-one (**5**) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Only two selected hydrogen-atoms are pictured for a better overview. Selected bond lengths [Å] and angles [°]: C(1)–Cl(1) 1.740(4), C(1)–C(2) 1.416(6), C(1)–C(14) 1.376(7), C(2)–C(3) 1.488(6), C(2)–C(11) 1.414(6), C(3)–C(4) 1.495(7), C(3)–O(1) 1.201(5), C(9)–C(10) 1.501(6), C(10)–C(11) 1.511(7); C(1)–C(2)–C(3) 123.7(4), C(1)–C(2)–C(11) 117.8(4), C(2)–C(3)–C(4) 114.6(4), C(2)–C(1)–C(14) 122.5(4), C(2)–C(3)–O(1) 122.8(4), C(4)–C(9)–C(10) 118.7(4), C(6)–C(5)–Cl(2) 117.1(3), C(8)–C(9)–C(10) 121.6(4), C(9)–C(10)–C(11) 113.7(4), C(14)–C(1)–Cl(1) 116.8(4).

The molecule adopts a butterfly-like deformation as is indicated by the 32.1(2)° angle between the planes spanned by the carbon atoms C(2), C(11), C(13) and C(14) as well as by C(4), C(6), C(7) and C(9). Owing to steric interactions of the chlorine and the oxygen atoms, all substituents at the “upper rim” of the molecule are distorted as is indicated by the (torsion) angles Cl(1)–C(1)–C(14) [116.8(4)°], Cl(2)–C(5)–C(6) [117.1(3)°] and C(1)–C(2)–C(3)–O(1) [31.9(7)°].

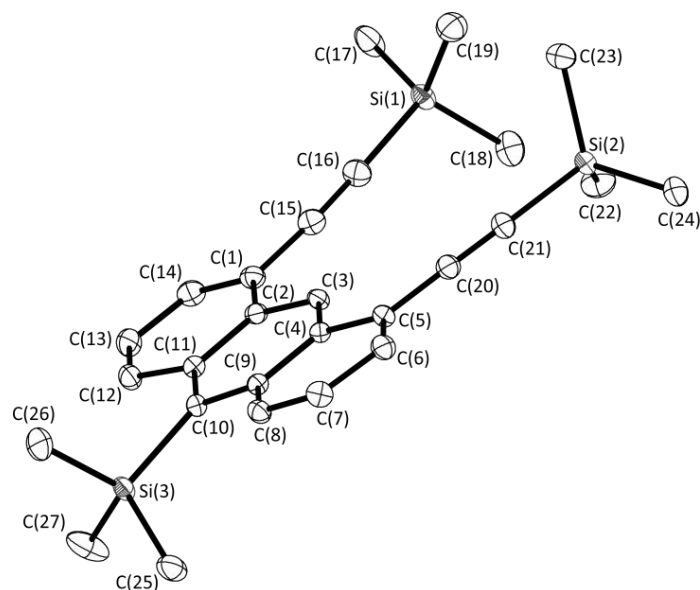
## Crystal Structure of 1,8-Dichloro-9-methylanthracene (6)



**Figure S2.** Molecular structure of 1,8-dichloro-9-methylanthracene (**6**) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–Cl(1) 1.747(2), C(1)–C(2) 1.442(3), C(1)–C(14) 1.363(3), C(2)–C(3) 1.419(3), C(2)–C(11) 1.442(3), C(3)–C(15) 1.518(3), C(9)–C(10) 1.397(3); C(1)–C(2)–C(3) 125.2(2), C(1)–C(2)–C(11) 114.9(2), C(2)–C(3)–C(4) 118.9(2), C(2)–C(1)–C(14) 122.7(2), C(2)–C(3)–C(15) 119.4(2), C(6)–C(5)–Cl(2) 115.1(2), C(9)–C(10)–C(11) 121.8(2), C(14)–C(1)–Cl(1) 115.3(2).

A steric repulsion of the chlorine- and the methyl-substituents leads to a remarkable distortion of the planarity of the anthracene unit [C(14)–C(1)–C(2)–C(3) 170.6(2)°, C(1)–C(2)–C(11) 114.9(2)°] and a bending of the substituents as is indicated by the torsion angles Cl(1)–C(1)–C(14)–C(13) [–169.8(2)°], Cl(2)–C(5)–C(6)–C(7) [171.7(1)°] and C(11)–C(2)–C(3)–C(15) [156.3(2)°].

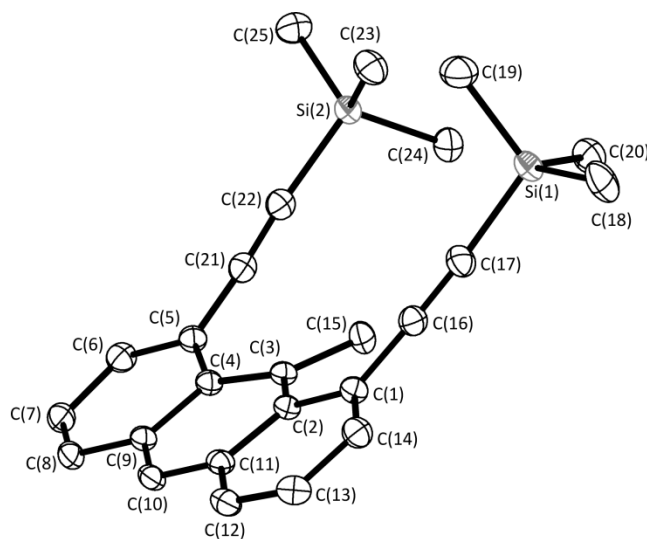
### Crystal Structure of 1,8-Bis[(trimethylsilyl)etynyl]-10-(trimethylsilyl)anthracene (7)



**Figure S3.** Molecular structure of 1,8-bis[(trimethylsilyl)etynyl]-10-(trimethylsilyl)anthracene (7) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.446(2), C(1)–C(14) 1.374(2), C(1)–C(15) 1.437(2), C(2)–C(3) 1.393(2), C(2)–C(11) 1.443(2), C(9)–C(10) 1.422(2), C(10)–Si(3) 1.922(1), C(15)–C(16) 1.208(2), C(16)–Si(1) 1.843(1), C(17)–Si(1) 1.865(1), C(27)–Si(3) 1.880(1); C(1)–C(2)–C(3) 121.3(1), C(1)–C(2)–C(11) 119.1(1), C(1)–C(15)–C(16) 175.4(1), C(2)–C(3)–C(4) 121.1(1), C(2)–C(1)–C(14) 120.4(1), C(2)–C(1)–C(15) 121.0(1), C(6)–C(5)–C(20) 119.4(1), C(9)–C(10)–C(11) 117.9(1), C(10)–Si(3)–C(27) 113.5(1), C(14)–C(1)–C(15) 118.6(1), C(15)–C(16)–Si(1) 177.4(1), C(16)–Si(1)–C(17) 108.3(1), C(25)–Si(3)–C(27) 102.6(1).

The substituent in 10-position is slightly bent and the anthracene backbone is not planar as is indicated by the torsion angles C(8)–C(9)–C(10)–Si(3) [–12.4(1)°] and C(8)–C(9)–C(10)–C(11) [171.4(1)°], respectively. These effects were also observed in all crystal structures of 10-EMe<sub>3</sub>-substituted 1,8-dichloroanthracenes (with E = C, Si, Ge, Sn) and can be regarded to be an inherent molecular property.<sup>[S1]</sup> Steric interactions of the substituents in 1- and 8-position are observed reflected by the aberration from linearity of the alkyne units.

## Crystal Structure of 1,8-Bis[(trimethylsilyl)etynyl]-9-methylanthracene (**8**)



**Figure S4.** Molecular structure of 1,8-bis[(trimethylsilyl)etynyl]-9-methylanthracene (**8**) in crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: C(1)–C(2) 1.455(2), C(1)–C(14) 1.375(2), C(1)–C(16) 1.441(2), C(2)–C(11) 1.444(2), C(2)–C(3) 1.411(2), C(3)–C(15) 1.517(2), C(9)–C(10) 1.388(2), C(16)–C(17) 1.206(2), C(17)–Si(1) 1.839(2), C(18)–Si(1) 1.861(2); C(1)–C(2)–C(3) 124.4(1), C(1)–C(2)–C(11) 116.0(2), C(1)–C(16)–C(17) 172.0(2), C(2)–C(3)–C(4) 119.9(1), C(2)–C(1)–C(14) 120.6(2), C(2)–C(1)–C(16) 123.6(2), C(2)–C(3)–C(15) 119.5(2), C(6)–C(5)–C(21) 116.8(2), C(9)–C(10)–C(11) 122.1(2), C(14)–C(1)–C(16) 115.2(2), C(16)–C(17)–Si(1) 176.5(2), C(17)–Si(1)–C(18) 108.2(1).

In case of the 1,8,9-substituted anthracene derivative **8** the steric demand at the “upper rim” of the backbone is increased leading to a stronger bending of the methyl substituent [C(5)–C(4)–C(3)–C(15)  $-18.4(2)^\circ$ ] and distortion of the planarity of the anthracene unit [C(2)–C(3)–C(4)–C(5)  $169.2(2)^\circ$ ].

## Quantum Chemical Calculations

**Table S1.** Calculated charges of the carbon atoms C9 and C10 of the 9-/10-substituted 1,8-dichloroanthracenes.

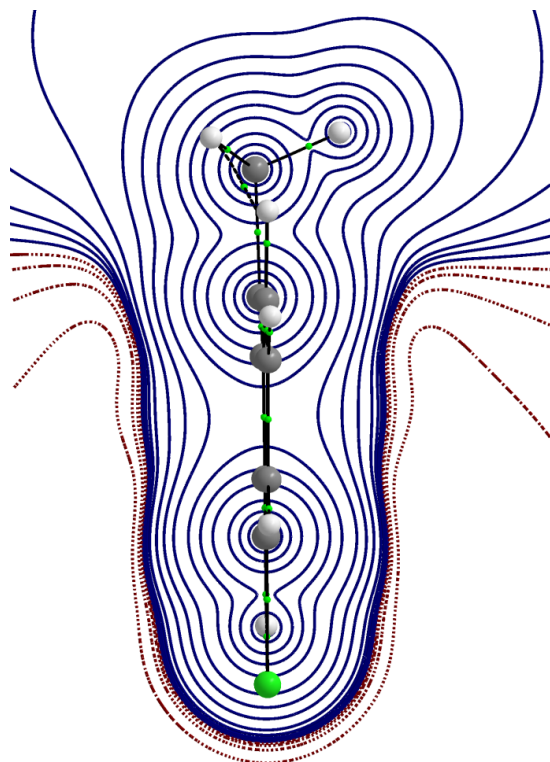
Anthracene Substituents		NBO charges <sup>[a]</sup>		AIM charges <sup>[a]</sup>	
R9	R10	<i>q</i> (C9)	<i>q</i> (C10)	<i>q</i> (C9)	<i>q</i> (C10)
Me	H	+0.04	-0.18	+0.01	-0.00
H	SiMe <sub>3</sub>	-0.17	-0.44	+0.01	-0.65
H	CMe <sub>3</sub>	-0.18	+0.04	+0.01	-0.02
H	Ph	-0.18	+0.01	+0.01	-0.01
H	Cy	-0.18	+0.03	+0.01	-0.01
H	<i>n</i> -Bu	-0.18	+0.03	+0.01	-0.01
H	<i>iso</i> -Pr	-0.18	+0.03	+0.01	-0.01
H	Me	-0.18	+0.03	+0.01	-0.00
H	H	-0.18	-0.18	+0.01	-0.00

[a] Calculated on B3LYP/6-31G(d,p) level.

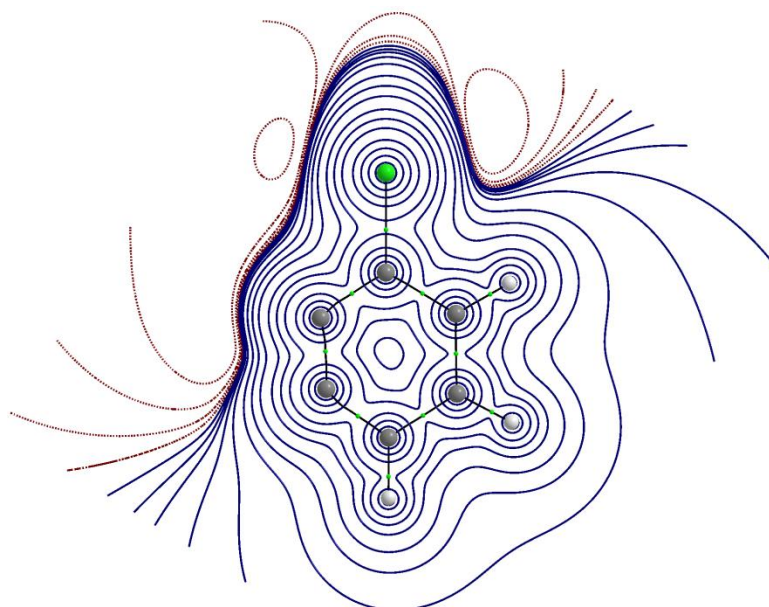
**Table S2.** Calculated charges of the carbon atoms C2 and C3 of the chloroaryne unit.

NBO charges <sup>a)</sup>		AIM charges <sup>[a]</sup>	
<i>q</i> (C2)	<i>q</i> (C3)	<i>q</i> (C2)	<i>q</i> (C3)
-0.02	+0.10	+0.01	-0.21

[a] Calculated on B3LYP/6-31G(d,p) level.



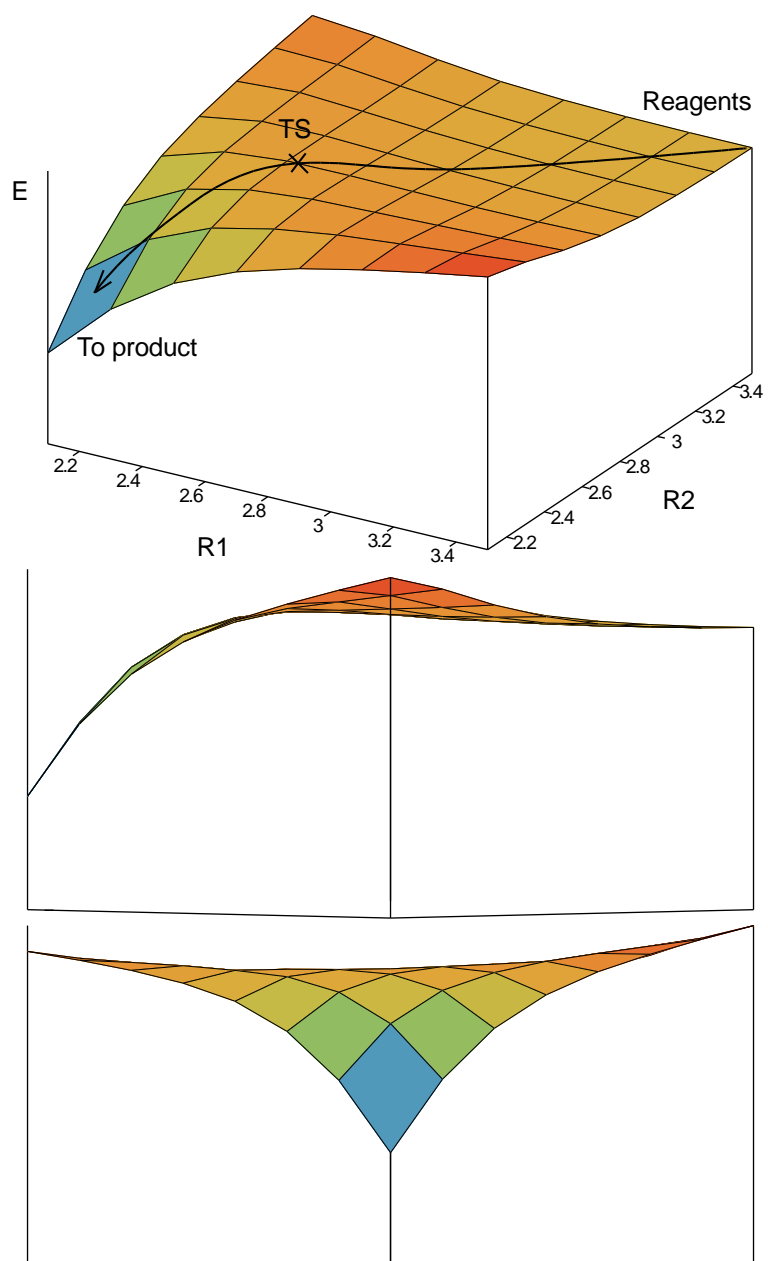
**Figure S5.** Total electrostatic potential of the 1,8-dichloro-10-methylantracene calculated on B3LYP/6-31G(d,p) level in the plane perpendicular to the molecular skeleton and going through atoms C(9) and C(10). Blue lines correspond to positive values; dashed red lines correspond to negative values.



**Figure S6.** Total electrostatic potential of the chlorobenzynes molecule calculated on B3LYP/6-31G(d,p) level in the plane of molecule. Blue lines correspond to positive values; dashed red lines correspond to negative values.

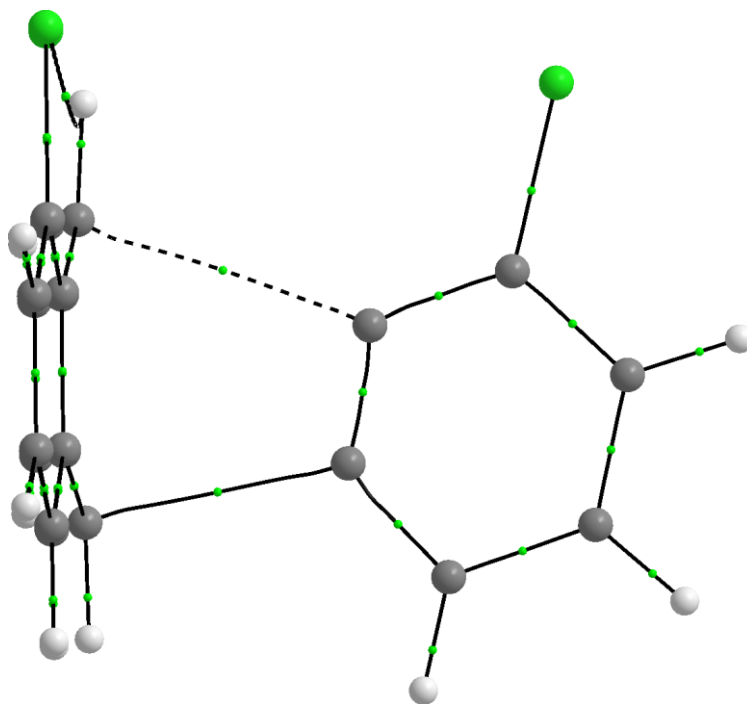
**Table S3.** Calculated activation barriers for the reaction of 1,8-dichloroanthracene with chlorobenzene using different approximations.

Method	Barrier to trichlorotriptycene [kcal/mol]		
	1,8,13-isomer ( <i>syn</i> )	1,8,16-isomer ( <i>anti</i> )	
B3LYP/6-31G(d,p)	1.79	0.79	Agreement with experiment
B3LYP/6-31G(d,p) BSSE	4.76	3.78	Agreement with experiment
B3LYP/6-31+G(d,p)	–	–	SCF or geometry optimization did not converge
B3LYP/6-31+G(d,p) BSSE	–	–	SCF or geometry optimization did not converge
B3LYP/6-31++G(d,p)	2.82	1.91	Agreement with experiment
B3LYP/6-31++G(d,p) BSSE	4.17	–	SCF or geometry optimization did not converge
B3LYP/cc-pVTZ	4.22	3.35	Agreement with experiment
B3LYP/cc-pVTZ BSSE	4.81	3.98	Agreement with experiment
PBE0/cc-pVTZ	0.39	–	Too small barrier
PBE0/cc-pVTZ BSSE	0.90	0.03	Agreement with experiment
PBE0/pc-2	0.35	–	Too small barrier
PBE0/pc-2 BSSE	0.76	–	Too small barrier
PBE0-D3/cc-pVTZ	–	–	Too small barrier
PBE0-D3/cc-pVTZ BSSE	–	–	Too small barrier
M11/cc-pVTZ	–	–	Too small barrier
M11/cc-pVTZ BSSE	–	–	Too small barrier

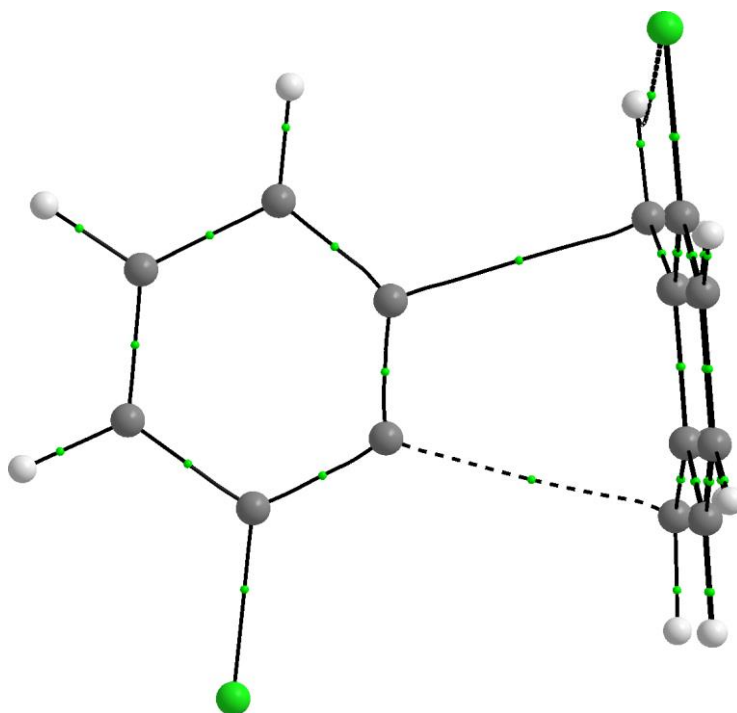


**Figure S7.** Potential energy surface [B3LYP/6-31G(d,p)] around transition state of the reaction forming 1,8,13-trichlorotriptycene. Coordinates R1 and R2 correspond to distances C9...C2 and C10...C3, respectively.





**Figure S8.** AIM molecular graph [B3LYP/6-31G(d,p)] for transition state of 1,8,13-trichlorotriptycene (*syn*-isomer).



**Figure S9.** AIM molecular graph [B3LYP/6-31G(d,p)] for transition state of 1,8,16-trichlorotriptycene (*anti*-isomer).

**Table S4.** Calculated [B3LYP/6-31G(d,p)] AIM and IQA parameters (electron density, Laplacian of electron density, ellipticity and atomic interaction energy) for bond critical points C9...C<sub>aryne</sub> and C10...C<sub>aryne</sub> in transition states of 1,8,13- (*syn*) and 1,8,16-trichlorotriptycene (*anti*).

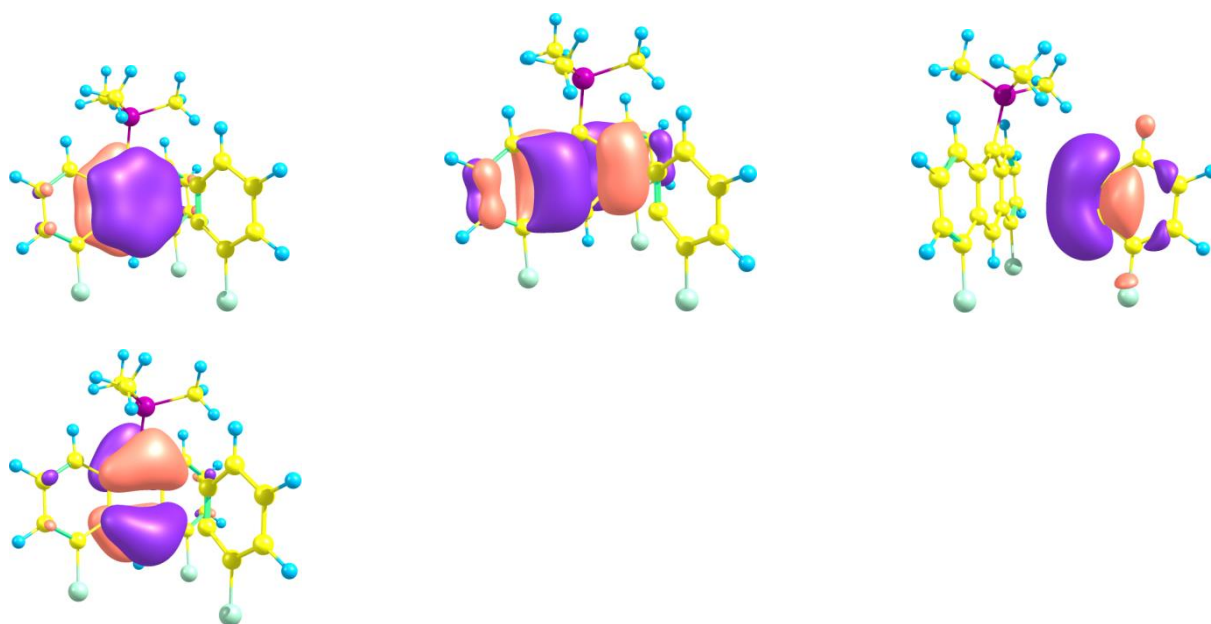
Parameter	TS 1,8,13- trichlorotriptycene ( <i>syn</i> )		TS 1,8,16- trichlorotriptycene ( <i>anti</i> )	
	C9...C2	C10...C3	C9...C3	C10...C2
$\rho$ , a.u.	0.018	0.035	0.032	0.021
$\Delta\rho$ , a.u.	0.039	0.053	0.052	0.044
$\varepsilon$	0.32	0.15	0.16	0.28
$E_{\text{IQA}}$ , a.u.	-0.021	-0.041	-0.039	-0.024

**Table S5.** Calculated by NEDA [using B3LYP/6-31G(d,p)] interaction energies [kcal mol<sup>-1</sup>] and their components (EL – electric, CT – charge transfer, core and XC – Pauli exchange) for transition states of 1,8,13- (*syn*) and 1,8,16-trichlorotriptycene (*anti*).

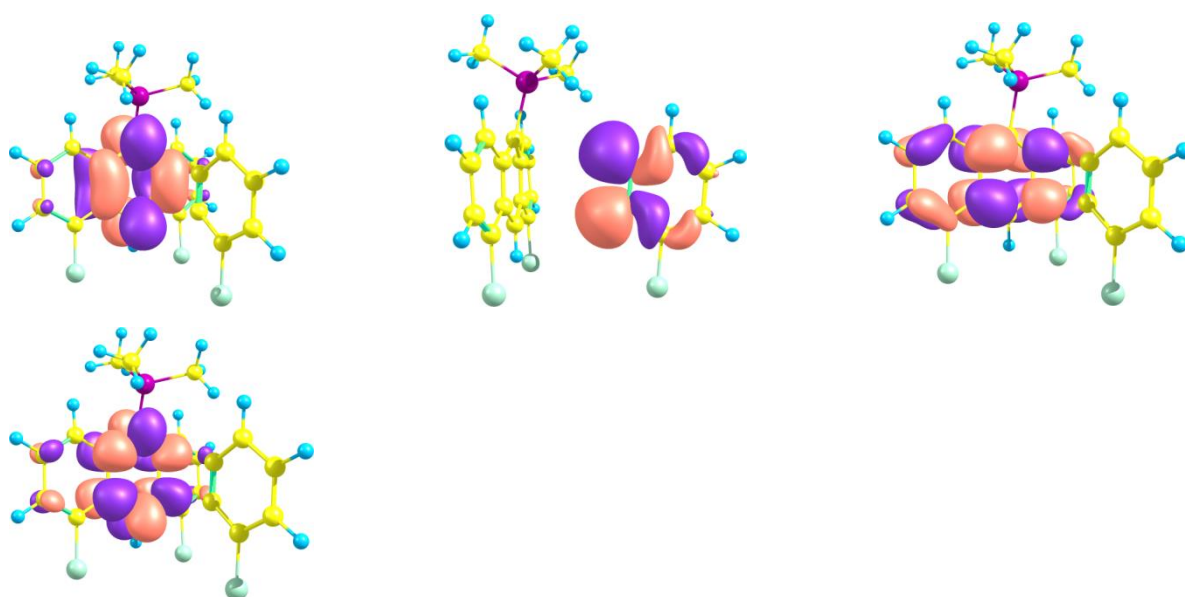
Component	TS 1,8,13-trichlorotriptycene ( <i>syn</i> )	TS 1,8,16-trichlorotriptycene ( <i>anti</i> )
$E^{\text{EL}}$	-39.39	-40.30
$E^{\text{CT}}$	-50.26	-49.45
$E^{\text{CORE}} (E^{\text{XC}})$	88.55 (-20.46)	87.72 (-20.53)
$E^{\text{NEDA}}$ , Total	-1.10	-2.03

**Table S6.** Results of calculations of relative energies for transition states of 1,8,13- (*syn*) and 1,8,16-trichloro-10-(trimethylsilyl)tritycene (*anti*).

Approximation	$\Delta E$ (TS), kcal/mol	
	<i>syn</i> (86%)	<i>anti</i> (14%)
B3LYP/6-31G(d,p)	1.78	0.0
B3LYP/cc-pVTZ	1.57	0.0
B3LYP/6-31+G(d,p)	1.73	0.0
B3LYP/6-31G(d,p) in Solution (SMD)	1.68	0.0
M06-2X/cc-pVTZ	1.58	0.0
RHF/6-311G(d,p)	3.55	0.0
RHF/cc-pVTZ	3.62	0.0
MP2/cc-pVTZ // RHF/cc-pVTZ	-5.05	0.0
CISD/6-31G(d,p) // B3LYP/cc-pVTZ	0.46	0.0
CASSCF(4,4)/6-31G(d)	0.11	0.0
XMCQDPT2(4,4)/6-31G(d) // CASSCF(4,4)/6-31G(d)	0.52	0.0
CASSCF(8,8)/6-31G(d)	0.97	0.0
XMCQDPT2(8,8)/6-31G(d) // CASSCF(8,8)/6-31G(d)	-0.08	0.0



**Figure S10.** Optimised occupied natural orbitals from active space in CASSCF(8,8)/6-31G(d) calculation.



**Figure S11.** Optimised vacant natural orbitals from active space in CASSCF(8,8)/6-31G(d) calculation.

## References

[S1] J.-H. Lamm, Yu. V. Vishnevskiy, E. Ziemann, T. A. Kinder, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Eur. J. Inorg. Chem.* **2014**, 941–947.



## **Publikation 7**

# **Syntheses of Donor-free Linked 1,8-functionalised Anthracene Derivatives**

Jan-Hendrik Lamm, Marvin Linnemannstöns, Sven Solyntjes,  
Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

vorgesehen für *Eur. J. Org. Chem.*



## Syntheses of Donor-free Linked 1,8-functionalised Anthracene Derivatives

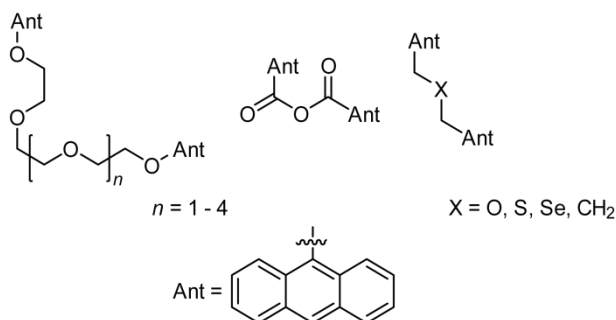
Jan-Hendrik Lamm,<sup>[a]</sup> Marvin Linnemannstös,<sup>[a]</sup> Sven Solyntjes,<sup>[a]</sup> Beate Neumann,<sup>[a]</sup> Hans-Georg Stammler,<sup>[a]</sup> and Norbert W. Mitzel<sup>[a]\*</sup>**Keywords:** Anthracenes / Metathesis Reactions / Solid-State Structures

Starting from 1,8-dichloroanthracen-10(9*H*)-one and 10-bromo-1,8-dichloroanthracene, a series of 1,8-difunctionalised anthracene derivatives linked in position 10 has been synthesised. The anthracene systems are connected by linker units containing no donor atoms, namely Me<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>, CH<sub>2</sub>CH=CHCH<sub>2</sub> and Me<sub>2</sub>SiCH<sub>2</sub>CH=CHCH<sub>2</sub>SiMe<sub>2</sub>. The latter ones were built up by converting allyl(silyl)-substituted anthracenes in olefin- and/or salt-

elimination reactions. However, the corresponding vinyl(silyl)-functionalised anthracenes were used, but only in the cases of 10-allyl- and 10-(allyldimethylsilyl)-substituted anthracenes, a metathesis reactivity was observed. The new anthracene compounds were characterised by NMR spectroscopy, mass spectrometry and – in most cases – by X-ray diffraction experiments.

## Introduction

Functionalised anthracenes provide a non-flexible framework with well-defined distances and orientation of the substituents (e.g. in position 1 and 8). Therefore, such systems are useful building blocks and they are widely used in many fields of (metal-) organic chemistry.<sup>[1,2]</sup> The number of directed functionalities for further modification can be increased by linking two anthracene units, e.g. in position 10. Some examples of such bichromophoric systems are known. In most cases, non-substituted anthracenes are connected by (donor atom-containing) linker units, e.g. polyoxyethylene yielding photoswitchable crown ether molecules (Scheme 1).<sup>[3]</sup>



Scheme 1. Examples of anthracene-containing bichromophoric systems connected by flexible linker units.<sup>[3-7]</sup>

During our investigations in the field of poly-Lewis acids, we became interested in rigid frameworks based on anthracene (dimers) strictly avoiding donor functions.<sup>[2b]</sup> However, the field of anthracene derivatives linked in this manner is only scarcely

explored. Recently, we connected two 1,8-dichloroanthracene systems by rigid linker units. We utilised 1,8-dichloro-10-ethynylanthracene and used (cross-) coupling reactions to construct non-flexible frameworks bearing four directed chlorine functions.<sup>[8]</sup> However, most of these products are barely soluble and therefore not useful for further functionalisations.

Herein we report an efficient preparative route to a series of 1,8-disubstituted anthracene backbones which are interconnected in position 10. The linker units, built up by using olefin and/or salt metathesis reactions, do not contain any donor function. Most of the products are soluble in common organic solvents and some were functionalised with alkyne units.

## Results and Discussion

## Hydrocarbon-linked Anthracene Derivatives

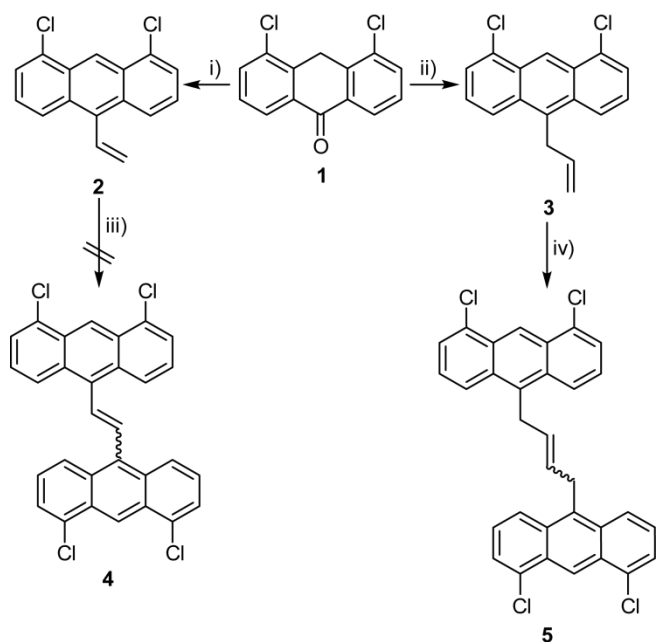
As shown in Scheme 2, the vinyl- and allyl-substituted 1,8-dichloroanthracenes **2** and **3** were synthesised by reacting 4,5-dichloro-9-anthrone (**1**) with vinyl- and allylmagnesium bromide, respectively. Anthrone **1** is easily available by reduction of 1,8-dichloroanthraquinone with sodium dithionite in DMF.<sup>[9]</sup> After aqueous workup, rearomatisation and purification by column chromatography, the alkenyl-substituted anthracenes were obtained as bright yellow crystals.

Compounds **2** and **3** were completely characterised by NMR spectroscopy and mass spectrometry. The <sup>1</sup>H NMR spectra recorded at ambient temperature (298 K) in CDCl<sub>3</sub> show the typical patterns for aromatic protons: one downfield shifted singlet (H9), one doublet of doublets for the protons in positions 3 and 6 as well as two doublets for H2/H7 (<sup>3</sup>J<sub>H,H</sub> ≈ 7 Hz) and H4/H5 (<sup>3</sup>J<sub>H,H</sub> ≈ 9 Hz), respectively. Characteristic doublets of doublets for the vinyl groups can be observed at δ = 7.41 ppm, 6.05 ppm and 5.59 ppm. The allyl substituent causes signals at δ = 6.16 ppm (ddt), 5.08 ppm (dd), 4.86 ppm (dd) and 4.31 ppm (d) with relative integrals of 1:1:1:2.

[a] Universität Bielefeld, Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie, Universitätsstraße 25, D-33615 Bielefeld, Germany  
 Fax: +49(0)521 106-6026  
 E-mail: mitzel@uni-bielefeld.de  
 http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.xxxxxxxx>.





Scheme 2. Syntheses of 1,8-dichloro-10-vinylanthracene (**2**) and 10-allyl-1,8-dichloroanthracene (**3**) by reaction of 4,5-dichloro-9-anthrone (**1**) with Grignard compounds and their conversion in olefin metathesis reactions. Reagents and conditions: i) vinyl-MgBr, THF, r.t., 16 h, 33%; ii) allyl-MgBr, THF, r.t., 16 h, 80%; iii) Grubbs' I cat. (5mol%), CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, overnight, no reaction; iv) Grubbs' I cat. (5mol%), CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, overnight, 95%.

Single crystals of both compounds suitable for X-ray diffraction experiments were obtained upon slow evaporation of the solvent of concentrated *n*-hexane/dichloromethane (**2**) and *n*-pentane solutions (**3**), respectively. Their molecular structures are displayed in Figure 1. All bond lengths and angles are found to be in the expected ranges (see Table 1). The values of the aromatic ring systems are identical within experimental error and they are comparable with other 10-substituted 1,8-dichloroanthracenes described in the literature.<sup>[10,11]</sup>

Compounds **2** and **3** were reacted in olefin metathesis reactions to afford the corresponding ethenyl- or but-2-enyl-linked 1,8-dichloroanthracenes **4** and **5**, respectively (Scheme 2). However, only in the case of the allyl-functionalised compound **3** the alkenyl-linked 1,4-bis(1,8-dichloroanthracen-10-yl)but-2-ene (**5**) was obtained in nearly quantitative yield. No reaction was observed when 1,8-dichloro-10-vinylanthracene (**2**) was treated under the same conditions. Compound **5** was obtained as a bright yellow solid which was found to be nearly insoluble in common polar and non-polar solvents (23 different solvents were tested). For this reason, **5** could only be identified by <sup>1</sup>H NMR spectroscopy and high resolution mass spectrometry. Its <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> at ambient temperature (298 K) shows the four characteristic signals for 1,8,10-trisubstituted anthracene derivatives, which are slightly shifted compared to the 10-allyl-1,8-dichloroanthracene (**3**). The but-2-ene linker causes multiplet signals at  $\delta$  = 5.63 ppm (2H) and 4.21 ppm (4H).

Due to the extremely low solubility, the reduction of the unsaturated linker unit of compound **5** caused serious problems. Anyhow, very small amounts of the reduced species **6** were obtained after converting **5** with an excess of *para*-toluolsulfonhydrazide in boiling xylene. 1,4-bis(1,8-dichloroanthracen-10-yl)butane (**6**) was identified by high resolution mass spectrometry and X-ray diffraction experiments. Figure 2 shows the molecular structure in crystalline state. Unusual bond lengths and angles were not observed.

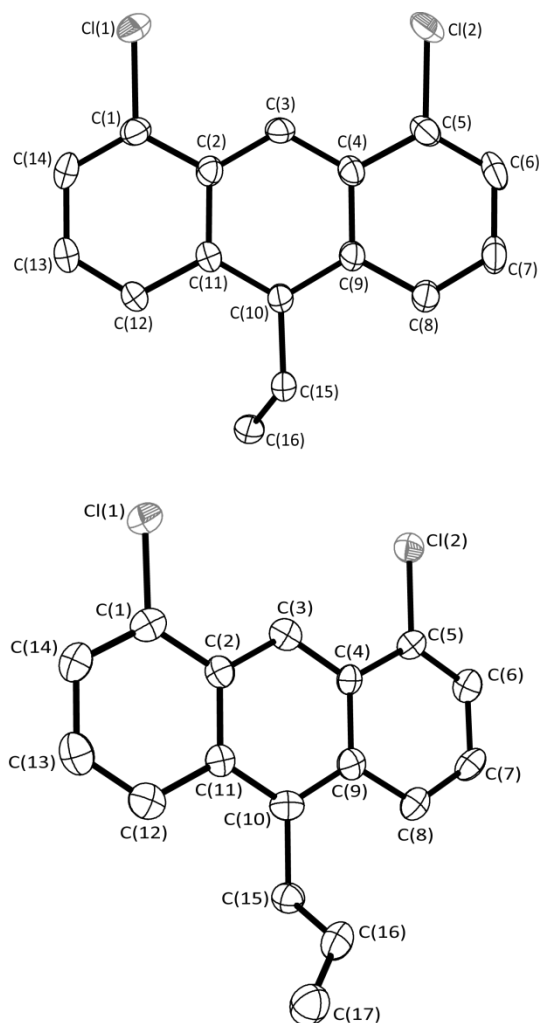


Figure 1. Molecular structures of 1,8-dichloro-10-vinylanthracene (**2**, above) and 10-allyl-1,8-dichloroanthracene (**3**, below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] of compounds **2** and **3**.

	<b>2</b>	<b>3</b>
C(1)–C(2)	1.426(5)	1.418(8)
C(1)–C(14)	1.359(6)	1.375(8)
C(1)–Cl(1)	1.749(4)	1.743(6)
C(2)–C(3)	1.390(5)	1.404(8)
C(2)–C(11)	1.446(6)	1.445(7)
C(10)–C(11)	1.412(6)	1.418(8)
C(10)–C(15)	1.483(6)	1.507(7)
C(15)–C(16)	1.317(6)	1.502(8)
C(16)–C(17)	–	1.294(8)
C(1)–C(2)–C(3)	122.6(4)	121.4(5)
C(1)–C(2)–C(11)	117.3(3)	118.7(5)
C(2)–C(1)–Cl(1)	118.7(3)	119.6(4)
C(2)–C(3)–C(4)	121.3(4)	120.8(5)
C(2)–C(11)–C(10)	119.1(3)	119.9(5)
C(10)–C(15)–C(16)	125.9(5)	113.4(5)
C(11)–C(10)–C(15)	121.7(3)	121.1(5)
C(15)–C(16)–C(17)	–	125.7(6)

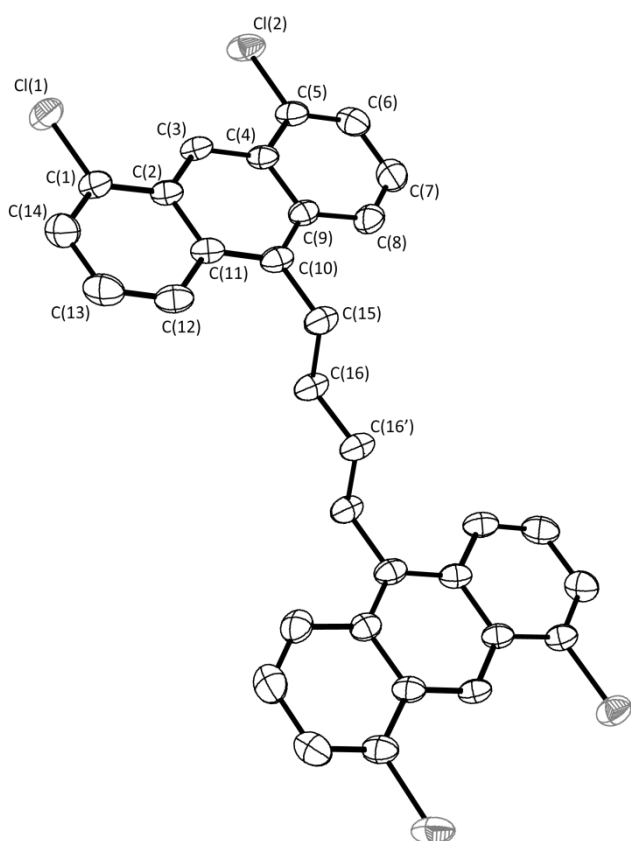
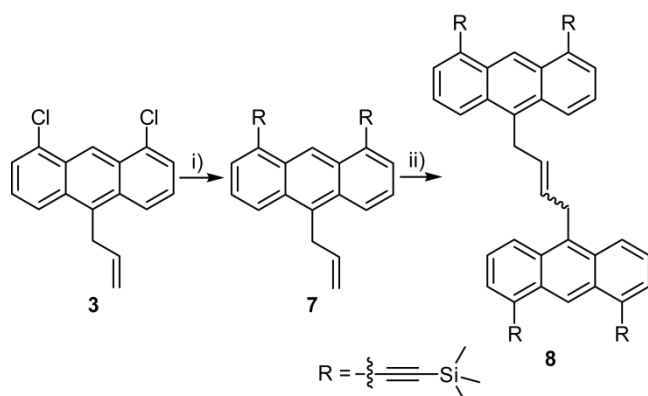


Figure 2. Molecular structure of 1,4-bis(1,8-dichloroanthracen-10-yl)butane (**6**) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.423(2), C(1)–C(14) 1.353(2), C(1)–Cl(1) 1.743(2), C(2)–C(3) 1.387(2), C(2)–C(11) 1.438(2), C(10)–C(11) 1.405(2), C(10)–C(15) 1.512(2), C(15)–C(16) 1.523(2), C(16)–C(16') 1.516(3); C(1)–C(2)–C(3) 122.8(2), C(1)–C(2)–C(11) 117.6(1), C(2)–C(1)–Cl(1) 118.7(1), C(2)–C(3)–C(4) 121.5(2), C(2)–C(11)–C(10) 119.7(2), C(10)–C(15)–C(16) 113.9(1), C(11)–C(10)–C(15) 120.1(2), C(15)–C(16)–C(16') 113.2(2).

In order to increase the solubility of the metathesis product, substrate **3** was functionalised with (trimethylsilyl)ethynyl substituents by using a Kumada type cross-coupling reaction (Scheme 3).



Scheme 3. Synthesis of 1,4-bis[1,8-bis((trimethylsilyl)ethynyl)anthracen-10-yl]but-2-ene (**8**) via 1,8-bis((trimethylsilyl)ethynyl)anthracene (**7**). Reagents and conditions: i)  $\text{Me}_3\text{Si}-\text{C}\equiv\text{CMgBr}$ , THF,  $\text{Ni}(\text{acac})_2$ ,  $\text{PPh}_3$ , reflux, 4 d, 55%; ii) Grubbs' I catalyst (20mol%),  $\text{CH}_2\text{Cl}_2$ , 40 °C, overnight, 39%.

In fact, compound **8**, obtained as the product of the conversion of 10-allyl-1,8-bis((trimethylsilyl)ethynyl)anthracene (**7**) with first generation Grubbs' catalyst, shows a good solubility in organic solvents and was completely characterised by NMR spectroscopy of the nuclei  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  as well as by mass spectrometry.

The molecular structure of compound **7** in crystalline state was determined by X-ray diffraction experiments and is depicted in Figure 3. One of the alkynyl substituents is slightly bent as is indicated by the angles C(1)–C(15)–C(16) [175.4(1)°] and C(15)–C(16)–Si(1) [176.2(1)°]. This effect was also observed for 1,8-bis((trimethylsilyl)ethynyl)anthracene and its corresponding trimethylstannyl derivative,<sup>[12]</sup> as well as in 1,8-bis((trimethylsilyl)ethynyl)-10-(trimethylsilyl)anthracene.<sup>[13]</sup>

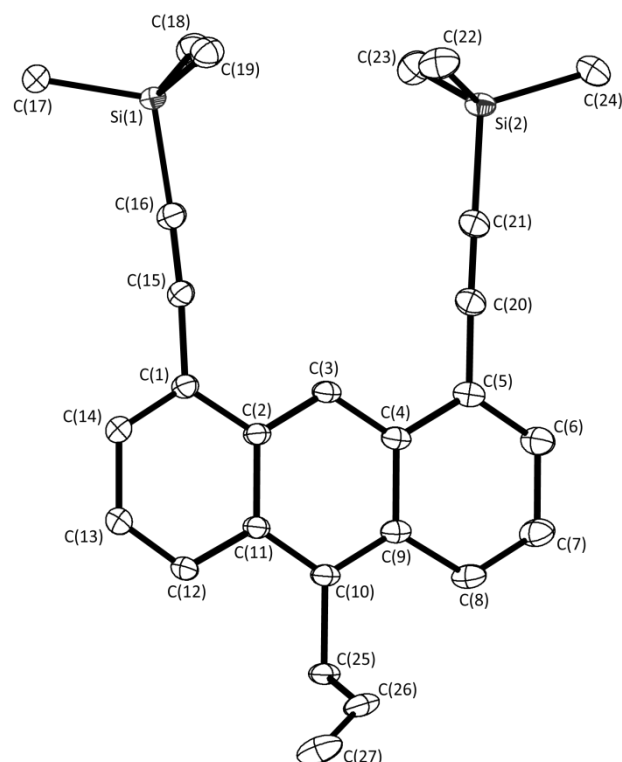
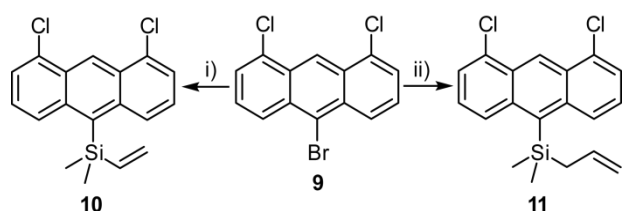


Figure 3. Molecular structure of 10-allyl-1,8-bis((trimethylsilyl)ethynyl)anthracene (**7**) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.443(1), C(1)–C(14) 1.372(1), C(1)–C(15) 1.439(1), C(2)–C(3) 1.393(1), C(2)–C(11) 1.440(1), C(10)–C(11) 1.411(1), C(10)–C(25) 1.522(1), C(15)–C(16) 1.210(1), C(16)–Si(1) 1.840(1), C(17)–Si(1) 1.863(1), C(25)–C(26) 1.505(1), C(26)–C(27) 1.322(2); C(1)–C(2)–C(3) 121.4(1), C(1)–C(2)–C(11) 119.0(1), C(1)–C(15)–C(16) 175.4(1), C(2)–C(1)–C(15) 121.4(1), C(2)–C(3)–C(4) 121.2(1), C(2)–C(11)–C(10) 119.8(1), C(5)–C(20)–C(21) 178.2(1), C(10)–C(25)–C(26) 111.2(1), C(11)–C(10)–C(25) 119.6(1), C(15)–C(16)–Si(1) 176.2(1), C(20)–C(21)–Si(2) 178.5(1), C(25)–C(26)–C(27) 124.9(1).

### Silylalkenyl-linked Anthracene Derivatives

In addition to the vinyl- and allyl-substituted 1,8-dichloroanthracenes **2** and **3**, we synthesised the 1,8-dichloro-10-(dimethylvinylsilyl)anthracene (**10**) and its corresponding allyl derivative **11**. Starting from 10-bromo-1,8-dichloroanthracene (**9**),<sup>[11]</sup> both compounds were obtained by salt elimination reactions in moderate yields (Scheme 4).



Scheme 4. Syntheses of 1,8-dichloro-10-(dimethylvinylsilyl)anthracene (**10**) and 10-(allyldimethylsilyl)-1,8-dichloroanthracene (**11**). Reagents and conditions: i) 1. *n*-BuLi, THF,  $-78\text{ }^\circ\text{C}$ , 1 h; 2.  $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ ,  $-78\text{ }^\circ\text{C}$  to r.t., 37%; ii) 1. *n*-BuLi, THF,  $-78\text{ }^\circ\text{C}$ , 1 h; 2.  $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ ,  $-78\text{ }^\circ\text{C}$  to r.t., 44%.

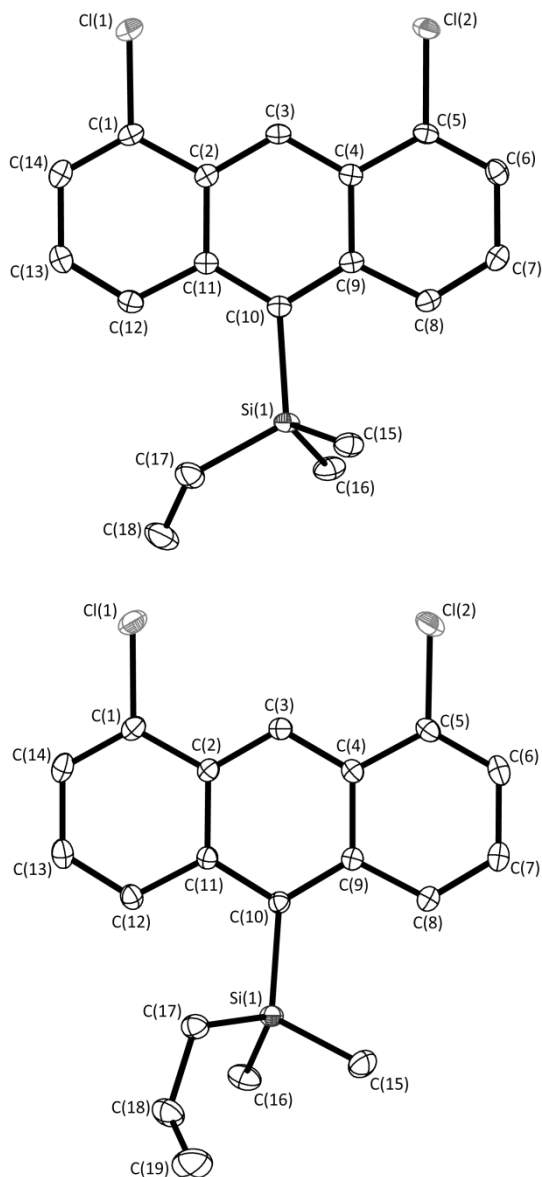


Figure 4. Molecular structures of 1,8-dichloro-10-(dimethylvinylsilyl)anthracene (**10**, above) and 10-(allyldimethylsilyl)-1,8-dichloroanthracene (**11**, below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 2.

Besides the NMR spectroscopic and mass spectrometric characterisation of the silyl-substituted dichloroanthracenes **10** and **11**, their molecular structures in crystalline state (depicted in Figure 4)

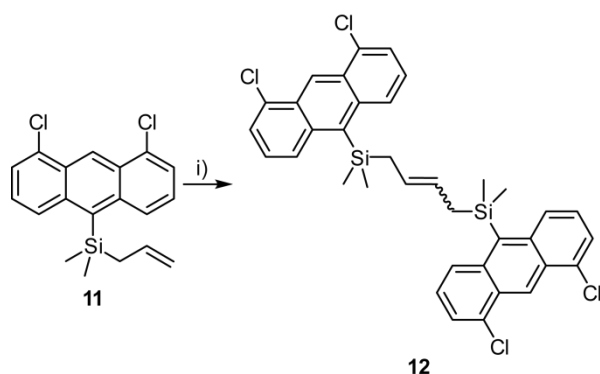
were determined by X-ray diffraction experiments. Owing to the fact, that no unexpected structural parameters are observed, the bond lengths and angles are not discussed in detail (selected values are listed in Table 2).

Table 2. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of compounds **10** and **11**.

	<b>10</b>	<b>11</b>
C(1)–C(2)	1.437(2)	1.434(1)
C(1)–C(14)	1.353(2)	1.358(1)
C(1)–Cl(1)	1.744(1)	1.740(1)
C(2)–C(3)	1.391(2)	1.395(1)
C(2)–C(11)	1.446(2)	1.439(1)
C(10)–C(11)	1.423(2)	1.425(1)
C(10)–Si(1)	1.916(1)	1.913(1)
C(16)–Si(1)	1.871(2)	1.867(1)
C(17)–C(18)	1.327(2)	1.492(2)
C(17)–Si(1)	1.874(2)	1.905(1)
C(18)–C(19)	–	1.318(2)
C(1)–C(2)–C(3)	122.1(1)	122.1(1)
C(1)–C(2)–C(11)	117.9(1)	118.0(1)
C(2)–C(1)–Cl(1)	118.9(1)	118.9(1)
C(2)–C(3)–C(4)	121.0(1)	120.8(1)
C(2)–C(11)–C(10)	120.0(1)	120.5(1)
C(10)–Si(1)–C(17)	114.8(1)	107.1(1)
C(11)–C(10)–Si(1)	124.2(1)	118.1(1)
C(17)–C(18)–C(19)	–	126.0(1)
C(18)–C(17)–Si(1)	124.2(1)	111.7(1)

The “lower rims” of both aromatic systems are slightly distorted from planarity as is indicated by the torsion angles C(9)–C(10)–C(11)–C(12) [ $-171.9(1)^\circ$  (**10**) and  $170.4(1)^\circ$  (**11**)], whereas the “upper rims” are found to be nearly undistorted [C(1)–C(2)–C(3)–C(4)  $178.8(1)^\circ$  (**10**) and  $-177.3(1)^\circ$  (**11**)]. These distortions are well comparable with the corresponding values of the similarly distorted 1,8-dichloro-10-(trimethylsilyl)anthracene [ $171.5(1)^\circ$  and  $178.3(1)^\circ$ ].<sup>[11]</sup> The substituents in position 10 are out of the plane of the anthracene backbone they are bonded to. The torsion angles C(8)–C(9)–C(10)–Si(1) [ $-12.0(2)^\circ$  (**10**) and  $16.7(1)^\circ$  (**11**)] as well as C(12)–C(11)–C(10)–Si(1) [ $-13.4(2)^\circ$  (**10**) and  $-16.1(1)^\circ$  (**11**)], demonstrate the bending of the substituents and are consequences of intramolecular repulsive interactions between Si-bound methyl / vinyl / allyl groups and the hydrogen atoms located at positions 4 and 5 of the anthracene skeleton. Due to these interactions, the bonds C(10)–Si(1) are remarkable elongated [1.916(1)  $\text{\AA}$  (**10**) and 1.913(1)  $\text{\AA}$  (**11**)] compared to the standard C–Si bond length (1.87  $\text{\AA}$ )<sup>[14]</sup>. Both effects – the bending of the substituents and elongation of the C(10)–Si bond – are also observed in the case of 1,8-dichloro-10-(trimethylsilyl)anthracene [e.g. C(10)–Si(1) 1.916(2)  $\text{\AA}$ ], which was found to be an inherent molecular property.<sup>[11]</sup>

Both silyl-substituted compounds were converted in olefin metathesis reactions using Grubbs’ I catalyst in dichloromethane. Like in the case of the reaction of 1,8-dichloro-10-vinylanthracene (**2**) described above, no metathesis reactivity was observed when 1,8-dichloro-10-(dimethylvinylsilyl)anthracene (**10**) was used. Anyhow, after converting 10-(allyldimethylsilyl)-1,8-dichloroanthracene (**11**) under the same conditions, a bright yellow solid was obtained in 71% yield (Scheme 5). Compared to the  $^1\text{H}$  NMR data of compound **11**, its aromatic-H and methyl resonances are slightly shifted indicating the formation of the corresponding olefin metathesis product **12**. The  $^1\text{H}$  NMR resonances caused by the linking  $(\text{CH}_2\text{--CH})_2$  unit could not be observed. However, further confirmation of its identity stem from mass spectrometric investigations.



Scheme 5. Synthesis of 1,4-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]but-2-ene (**12**). Reagents and conditions: i) Grubbs' I catalyst (20mol%), CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 120 h, 71%.

### Silylalkenyl-linked Anthracene Derivatives

Starting from 10-bromo-1,8-dichloroanthracene (**9**) the 1,2-bis-(dimethylsilyl)ethane-linked compound **13** was synthesised which can be further functionalised with (trimethylsilyl)ethynyl substituents in a four-fold Kumada cross-coupling reaction yielding **14** (Scheme 6). Both species were characterised by NMR spectroscopy, mass spectrometry and X-ray diffraction experiments.

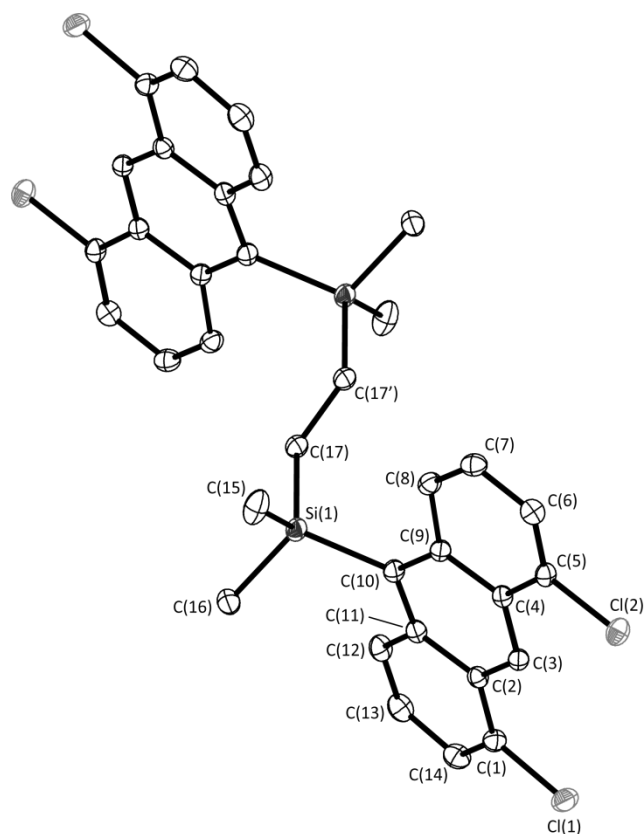


Figure 5. Molecular structure of 1,2-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (**13**) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.432(2), C(1)–C(14) 1.360(2), C(1)–Cl(1) 1.738(1), C(2)–C(3) 1.392(2), C(2)–C(11) 1.440(2), C(10)–C(11) 1.422(2), C(10)–Si(1) 1.919(1), C(15)–Si(1) 1.881(1), C(17)–C(17') 1.544(2), C(17)–Si(1) 1.886(1); C(1)–C(2)–C(3) 122.1(1), C(1)–C(2)–C(11) 118.2(1), C(2)–C(1)–Cl(1) 119.2(1), C(2)–C(3)–C(4) 120.9(1), C(2)–C(11)–C(10) 120.6(1), C(9)–C(10)–Si(1) 121.1(1), C(10)–Si(1)–C(15) 109.8(1), C(10)–Si(1)–C(17) 120.6(1), Si(1)–C(17)–C(17') 117.4(1).

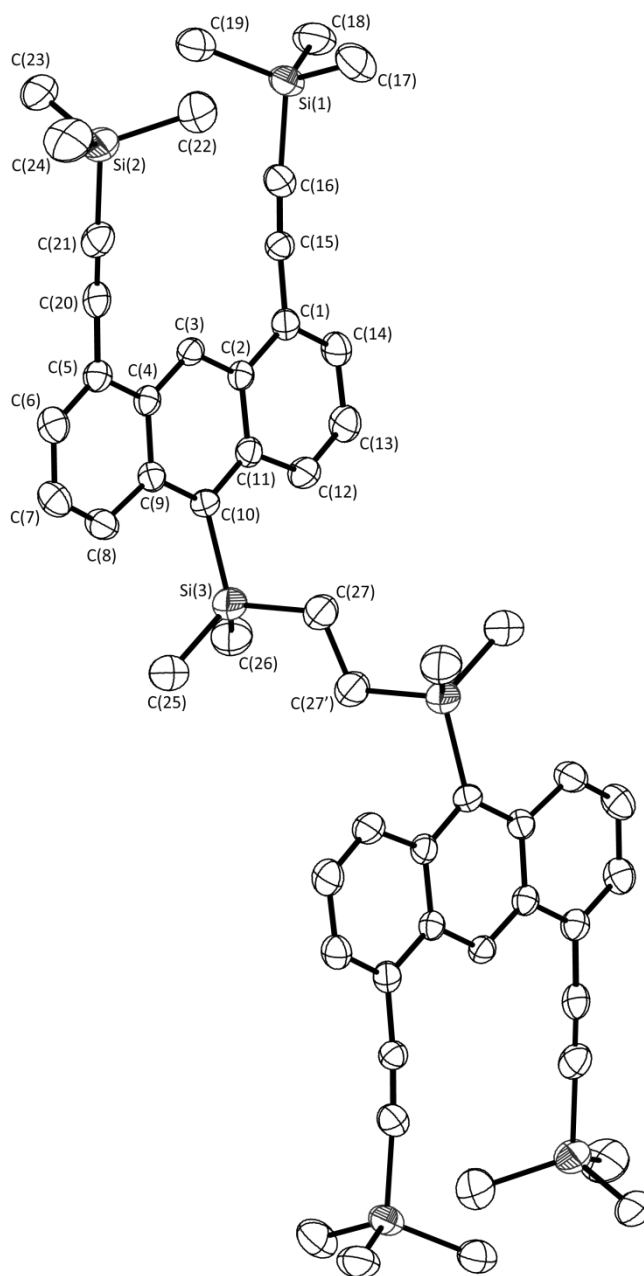
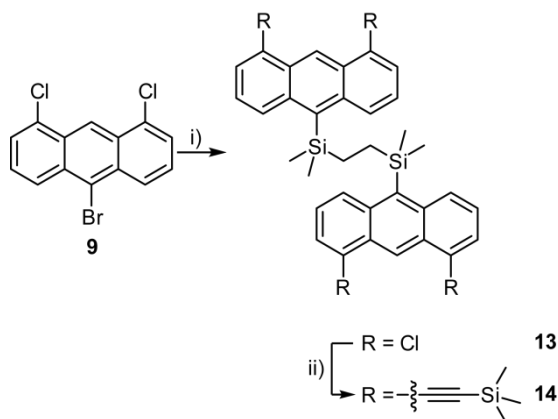


Figure 6. Molecular structure of 1,2-bis[{1,8-bis[(trimethylsilyl)ethynyl]anthracen-10-yl}dimethylsilyl]ethane (**14**) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.443(4), C(1)–C(14) 1.376(4), C(1)–C(15) 1.463(5), C(2)–C(3) 1.397(4), C(2)–C(11) 1.436(4), C(10)–C(11) 1.414(4), C(10)–Si(3) 1.919(3), C(15)–C(16) 1.205(5), C(16)–Si(1) 1.856(4), C(17)–Si(1) 1.858(5), C(26)–Si(3) 1.890(4), C(27)–Si(3) 1.876(4), C(27)–C(27') 1.543(7); C(1)–C(2)–C(3) 120.7(3), C(1)–C(2)–C(11) 120.0(3), C(1)–C(15)–C(16) 175.2(4), C(2)–C(1)–C(15) 121.4(3), C(2)–C(3)–C(4) 120.8(3), C(2)–C(11)–C(10) 121.2(3), C(4)–C(5)–C(20) 119.8(3), C(5)–C(20)–C(21) 174.8(3), C(9)–C(10)–Si(3) 122.7(2), C(10)–Si(3)–C(26) 111.6(2), C(10)–Si(3)–C(27) 105.7(2), C(15)–C(16)–Si(1) 176.3(4), C(16)–Si(1)–C(17) 107.4(2), C(20)–C(21)–Si(2) 178.1(3), C(25)–Si(3)–C(26) 103.1(2), Si(3)–C(27)–C(27') 113.9(3).

The molecular structures in crystalline state are depicted in Figures 5 (**13**) and 6 (**14**). All bond lengths and angles are found to be in the expected ranges. As already observed in the cases of the allyldimethylsilyl- and dimethylvinylsilyl-substituted dichloroanthracenes **10** and **11**, the chlorine atoms are in-plane with the aromatic system they are bonded to. The silyl substituent in position 10 is bent relative to the anthracene skeleton as is indicated

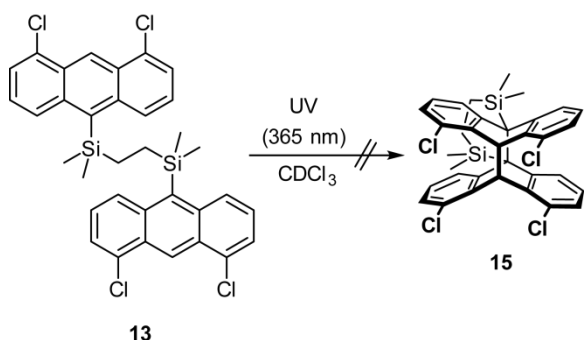
by the torsion angle C(8)–C(9)–C(10)–Si(1) [20.1(1)°]. This is remarkable larger than the corresponding ones in compounds **10** [–12.0(2)°], **11** [16.7(1)°] and in 1,8-dichloro-10-(trimethylsilyl)anthracene [13.1(2)°<sup>[11]</sup>]. The same bending-effect can be observed, when the (dimethylsilyl)ethane-linked anthracenes are functionalised with (trimethylsilyl)ethynyl units in positions 1 and 8. The torsion angle C(8)–C(9)–C(10)–Si(1) is at –13.4(3)°, remarkably smaller than in compound **13** [20.1(1)°] but in good agreement with the corresponding angle found in 1,8-bis[(trimethylsilyl)ethynyl]-10-(trimethylsilyl)anthracene [–12.4(1)°<sup>[13]</sup>]. As already observed in the cases of 10-allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (**7**) and similar 1,8-disubstituted compounds,<sup>[2c,12,13]</sup> one of the alkynyl units is distorted from linearity as is indicated by the angles C(1)–C(15)–C(16) [175.2(4)°] and C(15)–C(16)–Si(1) [176.3(4)°].



Scheme 6. Syntheses of the 1,2-bis(dimethylsilyl)ethane-linked species **13** and **14**. Reagents and conditions: i) 1. *n*-BuLi, THF, –78 °C, 1 h; 2. [(CH<sub>3</sub>)<sub>2</sub>ClSiCH<sub>2</sub>]<sub>2</sub>, –78 °C to r.t., 16%; ii) Me<sub>3</sub>Si–C≡CMgBr, THF, Ni(acac)<sub>2</sub>, PPh<sub>3</sub>, reflux, 4 d, 29%.

### Silylalkenyl-linked Anthracene Derivatives

In attempts to demonstrate the principle applicability of such like linked anthracene bichromophors, preliminary UV light (365 nm) irradiation experiments were performed using 1,2-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (**13**) in CDCl<sub>3</sub>. In accordance to some literature examples, e.g. those shown in Scheme 1,<sup>[3–5]</sup> we expected the formation of the directed and four-fold chloro-substituted species **15** (Scheme 7).



Scheme 7. UV light irradiation of compound **13**.

Interestingly, we did not observe any inter- or intramolecular cycloaddition reactions of compound **13**. Instead, 1,8-dichloro-9-hydroxyanthracen-10(9*H*)-one (**16**) was quantitatively obtained, probably by UV light induced reaction of the linked substrate with traces of water and/or oxygen from the solvent. However, this reac-

tion was not investigated in more detail and further “dimerisation” studies (also under inert conditions) are now in progress.

Compound **16** was clearly identified by NMR spectroscopy, mass spectrometry and X-ray diffraction experiments. Its molecular structure in crystalline state is depicted in Figure 7. No unexpected structural parameters are found in the molecule. The C–C, C–Cl and C=O bond lengths of **16** are identical within experimental error with those of 1,8-dichloroanthracen-9(10*H*)-one<sup>[13]</sup> and 1,8-dichloroanthracen-10(9*H*)-one.<sup>[15]</sup>

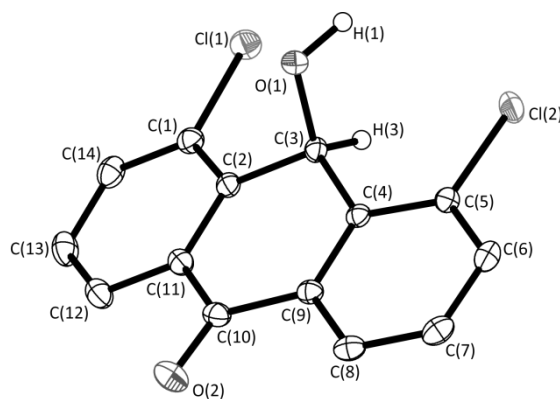


Figure 7. Molecular structure of 1,8-dichloro-9-hydroxyanthracen-10(9*H*)-one (**16**) in the crystalline state. Displacement ellipsoids of carbon, oxygen and chlorine atoms are drawn at 50% probability level. Hydrogen atoms except H(1) and H(3) are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.401(2), C(1)–C(14) 1.385(2), C(1)–Cl(1) 1.740(1), C(2)–C(3) 1.508(2), C(2)–C(11) 1.402(2), C(3)–O(1) 1.440(2), C(10)–C(11) 1.485(2), C(10)–O(2) 1.228(2); C(1)–C(2)–C(3) 120.6(1), C(1)–C(2)–C(11) 117.2(1), C(2)–C(1)–C(14) 122.2(1), C(2)–C(1)–Cl(1) 120.1(1), C(2)–C(3)–C(4) 114.2(1), C(2)–C(3)–O(1) 107.0(1), C(2)–C(11)–C(10) 120.7(1), C(9)–C(10)–O(2) 121.2(1).

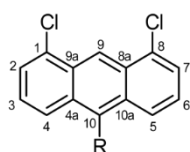
### Conclusions

Using nucleophilic additions or salt elimination reactions, a series of 1,8-difunctionalised anthracene derivatives bearing vinyl or allyl containing substituents in position 10 has been synthesised. These “anthracene monomers” were converted in olefin metathesis reactions. The corresponding linked anthracene systems were only obtained in the case of the allyl-functionalised anthracenes. In addition, two 1,8-dichloroanthracene units were directly linked by a 1:2 conversion of 1,2-bis(chlorodimethylsilyl)ethane and the lithiated anthracene species. The product, 1,2-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (**13**), was further functionalised with rigid alkyne units and preliminary UV irradiation reactions were performed. Instead of the *syn*-tetrachloro compound **15**, its decomposition product 1,8-dichloro-9-hydroxyanthracen-10(9*H*)-one (**16**) was quantitatively afforded.

### Experimental Section

**General:** 1,8-dichloroanthracene-10(9*H*)-one (**1**)<sup>[9]</sup> and 10-bromo-1,8-dichloroanthracene (**9**)<sup>[11]</sup> were synthesised according to literature protocols. Vinylmagnesium bromide (1.0 M in THF) and allylmagnesium bromide (1.0 M in Et<sub>2</sub>O) and *n*-butyllithium (1.6 M in hexanes; all purchased from Sigma Aldrich), dimethylvinylchlorosilane, 1,2-bis(chlorodimethylsilyl)ethane (both from abcr), allyldimethylchlorosilane (from Alfa Aesar) were used without further purification. First generation Grubbs catalyst was purchased from Strem Chemicals. All reactions using metal organic reagents were carried out under an anhydrous, inert atmosphere of nitrogen using standard Schlenk techniques in dry THF (dried over potassium) or dichloromethane (dried over LiAlH<sub>4</sub>). The solvents were freshly distilled

before being used for the reactions. Column chromatography was performed on silica gel 60 (0.04 – 0.063 mm mesh). NMR spectra were recorded on a Bruker *Avance III 300*, a Bruker *DRX 500* and a Bruker *Avance III 500* at ambient temperature (298 K). The chemical shifts ( $\delta$ ) were measured in ppm with respect to the solvent (CDCl<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  = 7.26 ppm, <sup>13</sup>C NMR  $\delta$  = 77.16 ppm) or referenced externally (<sup>29</sup>Si: SiMe<sub>4</sub>). EI mass spectra were recorded using an *Autospec X* magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. MALDI-TOF experiments were performed using a Voyager DE Instrument (PE Biosystems GmbH, Weiterstadt, Germany). High resolution MALDI-TOF mass spectra were recorded with a Fourier Transform Ion Cyclotron resonance (FT-ICR) mass spectrometer *APEX III* (Bruker Daltonik GmbH, Bremen, Germany). ESI mass spectra were recorded using an *Esquire 3000* ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI source. The numbering scheme for NMR assignments of the anthracenes (Scheme 8) is based on IUPAC guidelines.



Scheme 8. Numbering scheme for NMR spectroscopic assignments.

**General Procedure for the Synthesis of 2 and 3:** A THF solution of 1,8-dichloroanthracen-10(9*H*)-one (**1**) was added dropwise to a solution of vinyl- or allylmagnesium bromide at ambient temperature. The reaction mixture was stirred overnight and then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with a saturated aqueous solution of NaCl, dried over MgSO<sub>4</sub> and the solvent was evaporated. For the complete elimination of water the residue was dissolved in dry toluene (25 mL) and P<sub>2</sub>O<sub>5</sub> (approx. 30 mg) was added. After heating to 80 °C for at least 1.5 h the mixture was filtered and the solid was washed with small amounts of toluene. The brownish crude product was purified by column chromatography on silica gel using *n*-pentane as eluent.

**1,8-Dichloro-10-vinylanthracene (2):** Synthesis according to the general procedure using 1,8-dichloroanthracen-10(9*H*)-one (**1**; 1.00 g, 3.80 mmol) and vinyl magnesium bromide (1.0 M in THF, 7.6 mL, 7.6 mmol). Column chromatography ( $\varnothing$  = 3 cm, *l* = 20 cm) afforded **2** as bright yellow crystals. *R<sub>f</sub>* = 0.9 (*n*-pentane). Yield 342 mg (33%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.28, (s, 1H, H<sub>9</sub>), 8.24 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.9 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.63 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.1 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.41 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 17.5, 11.7 Hz, 1H, CH=CH<sub>2</sub>), 7.40 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 8.8, 7.2 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 6.05 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 11.5, <sup>2</sup>*J*<sub>H,H</sub> = 1.8 Hz, 1H, CH=CH<sub>cis</sub>H), 5.59 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 17.9, <sup>2</sup>*J*<sub>H,H</sub> = 1.8 Hz, 1H, CH=CHH<sub>trans</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 135.4, 133.4 (CH=CH<sub>2</sub>), 132.9, 130.5, 129.3, 126.0 (C<sub>2</sub>/C<sub>7</sub>), 125.6 (C<sub>3</sub>/C<sub>6</sub>), 125.5 (C<sub>4</sub>/C<sub>5</sub>), 124.0 (CH=CH<sub>2</sub>), 120.7 (C<sub>9</sub>) ppm. MS (EI, 70 eV): *m/z* [assignment] = 272.0 [M]<sup>+</sup>, 239.0 [M–Cl]<sup>+</sup>, 202.1 [M–2Cl]<sup>+</sup>. HRMS (EI): calculated for C<sub>16</sub>H<sub>10</sub>Cl<sub>2</sub><sup>+</sup>: 272.01596; measured: 272.01480; dev. [ppm]: 4.25, dev. [mmu]: 1.16.

**10-Allyl-1,8-dichloroanthracene (3):** Synthesis according to the general procedure using 1,8-dichloroanthracen-10(9*H*)-one (**1**; 400 mg, 1.52 mmol) and allylmagnesium bromide (1.0 M in Et<sub>2</sub>O, 7.6 mL, 7.6 mmol). Column chromatography ( $\varnothing$  = 3 cm, *l* = 17 cm) afforded **3** as bright yellow crystals. *R<sub>f</sub>* = 0.9 (*n*-pentane). Yield 352 mg (80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.26 (s, 1H, H<sub>9</sub>), 8.11 (d, <sup>3</sup>*J*<sub>H,H</sub> = 8.9 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.61 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.1 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.41 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 8.7, 7.4 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 6.16 (ddt, <sup>3</sup>*J*<sub>H,H</sub> = 16.1, 10.7, 5.5 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.08 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 10.2 Hz,

<sup>2</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, CH<sub>2</sub>CH=CH<sub>cis</sub>H), 4.86 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 17.2 Hz, <sup>2</sup>*J*<sub>H,H</sub> = 1.2 Hz, 1H, CH<sub>2</sub>CH=CHH<sub>trans</sub>), 4.31 (d, <sup>3</sup>*J*<sub>H,H</sub> = 5.4 Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.0 (CH<sub>2</sub>CH=CH<sub>2</sub>), 133.3, 133.3, 131.1, 129.3, 125.8 (C<sub>3</sub>/C<sub>6</sub>), 125.8 (C<sub>2</sub>/C<sub>7</sub>), 123.9 (C<sub>4</sub>/C<sub>5</sub>), 120.6 (C<sub>9</sub>), 116.7 (CH<sub>2</sub>CH=CH<sub>2</sub>), 32.7 (CH<sub>2</sub>CH=CH<sub>2</sub>) ppm. MS (EI, 70 eV): *m/z* [assignment] = 286.1 [M]<sup>+</sup>, 251.1 [M–Cl]<sup>+</sup>, 215.1 [M–2Cl]<sup>+</sup>. HRMS (EI): calculated for C<sub>17</sub>H<sub>12</sub>Cl<sub>2</sub><sup>+</sup>: 286.03161; measured: 286.02950; dev. [ppm]: 7.36, dev. [mmu]: 2.11.

**General Procedure for Kumada Coupling Reactions:** Trimethylsilylacetylene (Me<sub>3</sub>SiC≡CH, ca. 7 eq.) was added dropwise to a freshly prepared solution of ethylmagnesium bromide in THF at 0 °C. The mixture was stirred at room temperature for 2 h and gas evolution was observed. The formed [(trimethylsilyl)ethynyl]magnesium bromide suspension was transferred into a dropping funnel, fitted with glass wool for simultaneous filtering and slowly added to a solution of the 10-substituted 1,8-dichloroanthracene, Ni(acac)<sub>2</sub> and PPh<sub>3</sub> in THF at room temperature. The colour of the solution changed from yellow to dark red and the mixture was heated to reflux. After quenching with a saturated aqueous solution of NH<sub>4</sub>Cl, the aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with brine and dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude yellow brownish solid was purified by column chromatography on silica gel using a mixture of *n*-pentane/dichloromethane (8:1) as eluent.

**10-Allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (7):** Synthesis according to the general procedure for Kumada coupling reactions using 10-allyl-1,8-dichloroanthracene (**3**; 300 mg, 1.04 mmol), PPh<sub>3</sub> and Ni(acac)<sub>2</sub> (one spatula tip of each compound), reflux for 96 h. Column chromatography ( $\varnothing$  = 3 cm, *l* = 22 cm) afforded **7** as bright yellow crystals. *R<sub>f</sub>* = 0.8 [*n*-pentane/dichloromethane (8:1)]. Yield 236 mg (55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.40 (s, 1H, H<sub>9</sub>), 8.22 (d, <sup>3</sup>*J*<sub>H,H</sub> = 9.0 Hz, 2H, H<sub>4</sub>/H<sub>5</sub>), 7.81 (d, <sup>3</sup>*J*<sub>H,H</sub> = 6.5 Hz, 2H, H<sub>2</sub>/H<sub>7</sub>), 7.46 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 9.0 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 6.9 Hz, 2H, H<sub>3</sub>/H<sub>6</sub>), 6.20 (ddt, <sup>3</sup>*J*<sub>H,H</sub> = 17.0 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 10.5 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 5.4 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.08 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 10.2 Hz, <sup>2</sup>*J*<sub>H,H</sub> = 1.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>cis</sub>), 4.85 (dd, <sup>3</sup>*J*<sub>H,H</sub> = 17.2 Hz, <sup>2</sup>*J*<sub>H,H</sub> = 1.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>trans</sub>), 4.36 (d, <sup>3</sup>*J*<sub>H,H</sub> = 5.4 Hz, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 0.42 [s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.4 (CH<sub>2</sub>CH=CH<sub>2</sub>), 132.8, 132.2 (C<sub>2</sub>/C<sub>7</sub>), 131.2, 129.9, 125.8 (C<sub>4</sub>/C<sub>5</sub>), 125.2 (C<sub>3</sub>/C<sub>6</sub>), 123.6 (C<sub>9</sub>), 122.2, 116.5 (CH<sub>2</sub>CH=CH<sub>2</sub>), 104.0 (C≡C–Si), 100.0 (C≡C–Si), 32.3 (CH<sub>2</sub>CH=CH<sub>2</sub>), 0.6 [Si(CH<sub>3</sub>)<sub>3</sub>] ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  = –17.5 ppm. MS (EI, 70 eV): *m/z* [assignment] = 410.2 [M]<sup>+</sup>, 337.1 [M–Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 307.1 [M–Si(CH<sub>3</sub>)<sub>3</sub>–2 (CH<sub>3</sub>)]<sup>+</sup>. HRMS (EI): calculated for C<sub>34</sub>H<sub>30</sub>Cl<sub>4</sub>Si<sub>2</sub>: 410.18806, measured: 410.18712, dev. [ppm]: 2.28, dev. [mmu]: 0.94.

**General Procedure for the Synthesis of 10 and 11:** A solution of *n*-butyllithium (1.6 M in hexanes) was added dropwise to a THF solution of 10-bromo-1,8-dichloroanthracene (**9**) at –78 °C. The dark red mixture was stirred for 1.5 h at this temperature and degassed by two freeze-pump-thaw cycles. After warming to –78 °C, the chlorosilane compound was condensed onto the mixture. The solution was allowed to warm to ambient temperature overnight and then quenched with a saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with dichloromethane for several times. The combined organic phases were washed with a saturated aqueous solution of NaCl, dried over MgSO<sub>4</sub> and the solvent was evaporated. The brownish yellow crude product was purified by column chromatography on silica gel using *n*-pentane as eluent.

**1,8-Dichloro-10-(dimethylvinylsilyl)anthracene (10):** Synthesis according to the general procedure using 10-bromo-1,8-dichloroanthracene (**9**; 400 mg, 1.23 mmol), *n*-butyllithium solution (0.77 mL, 1.23 mmol) and dimethylvinylchlorosilane (2.42 mmol). Column chromatography ( $\varnothing$  = 3 cm, *l* = 26 cm) afforded **10** as bright yellow crystals. *R<sub>f</sub>* = 0.7 (*n*-pentane). Yield 149 mg (37%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.47 (s, 1H, H<sub>9</sub>), 8.42 (d, <sup>3</sup>*J*<sub>H,H</sub> = 9.0 Hz, H<sub>4</sub>/H<sub>5</sub>), 7.61 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.1 Hz, H<sub>2</sub>/H<sub>7</sub>), 7.38 (dd, <sup>3</sup>*J*<sub>H,H</sub> =

8.9, 7.2 Hz,  $H3/H6$ ), 6.62 (dd,  $^3J_{HH} = 20.3, 14.5$  Hz, 1H,  $SiCH=CH_2$ ), 6.10 (dd,  $^3J_{HH} = 14.5, ^2J_{HH} = 3.2$  Hz, 1H,  $SiCH=CH_{cisH}$ ), 5.86 (dd,  $^3J_{HH} = 20.3, ^2J_{HH} = 3.2$  Hz, 1H,  $SiCH=CH_{transH}$ ), 0.74 [s, 6H,  $Si(CH_3)_2$ ] ppm.  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta = 141.1$  ( $SiCH=CH_2$ ), 138.3, 136.2, 133.3, 131.7 ( $SiCH=CH_2$ ), 129.3, 128.2 ( $C4/C5$ ), 125.5 ( $C2/C7$ ), 125.0 ( $C3/C6$ ), 124.4 ( $C9$ ), 2.8 [ $Si(CH_3)_2$ ] ppm.  $^{29}Si\{^1H\}$  NMR (99 MHz,  $CDCl_3$ ):  $\delta = -11.7$  ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 330.0 [ $M]^+$ ], 315.0 [ $M-CH_3]^+$ ], 295.1 [ $M-Cl]^+$ ]. HRMS (EI): calculated for  $C_{18}H_{16}Cl_2Si^+$ : 330.03928; measured: 330.03863; dev. [ppm]: 1.98, dev. [mmu]: 0.65.

**10-(Allyldimethylsilyl)-1,8-dichloroanthracene (11):** Synthesis according to the general procedure using 10-bromo-1,8-dichloroanthracene (**9**; 400 mg, 1.23 mmol), *n*-butyllithium solution (0.77 mL, 1.23 mmol) and allyldimethylchlorosilane (2.45 mmol). Traces of 1,8-dichloroanthracene were removed by sublimation (40 °C, 0.005 mbar). Column chromatography ( $\varnothing = 3$  cm,  $l = 36$  cm) afforded **11** as bright yellow crystals.  $R_f = 0.8$  (*n*-pentane). Yield 193 mg (44%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta = 9.45$  (s, 1H,  $H9$ ), 8.33 (d,  $^3J_{HH} = 9.0$  Hz,  $H4/H5$ ), 7.62 (d,  $^3J_{HH} = 7.1$  Hz,  $H2/H7$ ), 7.40 (dd,  $^3J_{HH} = 9.0, 7.2$  Hz,  $H3/H6$ ), 5.79 (ddt,  $^3J_{HH} = 16.3, 10.0, 8.1$  Hz, 1H,  $SiCH_2CH=CH_2$ ), 4.92 (dd,  $^3J_{HH} = 17.0$  Hz,  $^2J_{HH} = 1.8$  Hz, 1H,  $SiCH_2CH=CH_{transH}$ ), 4.85 (dd,  $^3J_{HH} = 10.1$  Hz,  $^2J_{HH} = 1.0$  Hz, 1H,  $SiCH_2CH=CH_{cisH}$ ), 2.17 (s,  $^3J_{HH} = 8.0$  Hz, 2H,  $SiCH_2CH=CH_2$ ), 0.70 [s, 6H,  $Si(CH_3)_2$ ] ppm.  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta = 138.3, 136.9, 134.4$  ( $CH_2CH=CH_2$ ), 132.1 ( $C2/C7$ ), 133.4, 127.9 ( $C4/C5$ ), 125.5 ( $C2/C7$ ), 125.1 ( $C3/C6$ ), 124.3 ( $C9$ ), 114.5 ( $CH_2CH=CH_2$ ), 26.8 ( $CH_2CH=CH_2$ ), 3.2 [ $Si(CH_3)_2$ ] ppm.  $^{29}Si\{^1H\}$  NMR (99 MHz,  $CDCl_3$ ):  $\delta = -4.6$  ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 344.1 [ $M]^+$ ], 303.1 [ $M-C_3H_5]^+$ ], 268.1 [ $M-C_3H_5-Cl]^+$ ]. HRMS (EI): calculated for  $C_{19}H_{18}Cl_2Si^+$ : 344.05493; measured: 344.05600; dev. [ppm]: 3.10, dev. [mmu]: 1.07.

**General Procedure for Olefin Metathesis Reactions:** In an argon filled glove-box bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (first generation Grubbs' catalyst) was added to a solution of the allyl- or vinyl(silyl)-substituted anthracenes in dichloromethane. The mixtures were stirred for several hours at different temperatures (see below). Only in the cases of the allyl-substituted species **3**, **7** and **11** olefin metathesis reactivity is observed. No reaction takes place in the cases of the vinyl-substituted compounds **2** and **10** (even if the reaction time is extended or the reaction temperature is increased), so the experimental procedure is not described here.

**1,4-Bis(1,8-dichloroanthracen-10-yl)but-2-ene (5):** Synthesis according to the general procedure for olefin metathesis reactions using 10-allyl-1,8-dichloroanthracene (**3**; 114 mg, 0.40 mmol) and Grubbs' I catalyst (5mol%). Stirring overnight at ambient temperature, filtration and washing with small amounts of cold dichloromethane afforded **5** as a bright yellow solid. Yield 102 mg (95%).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 9.30$  (s, 1H,  $H9$ ), 8.04 (d,  $^3J_{HH} = 9.0$  Hz,  $H4/H5$ ), 7.62 (d,  $^3J_{HH} = 7.9$  Hz,  $H2/H7$ ), 7.37 (dd,  $^3J_{HH} = 9.0, 7.1$  Hz,  $H3/H6$ ), 5.63 (m, 2H,  $=CHCH_2$ ), 4.20 (m, 4H,  $=CHCH_2$ ) ppm. Due to the extreme low solubility of the compound, a  $^{13}C\{^1H\}$  NMR spectra could not be recorded. MS (EI, 70 eV):  $m/z$  [assignment] = 546.1 [ $M]^+$ ], 510.1 [ $M-Cl]^+$ ], 259.0 [ $C_{15}H_9Cl_2]^+$ ]. HRMS (EI): calculated for  $C_{32}H_{20}Cl_4^+$ : 544.03136; measured: 544.03056; dev. [ppm]: 1.48, dev. [mmu]: 0.80.

**1,4-Bis(1,8-dichloroanthracen-10-yl)butane (6):** 1,4-Bis(1,8-dichloroanthracen-10-yl)but-2-ene (**5**; 30 mg, 0.06 mmol) was dissolved in boiling *p*-xylene (20 mL). *p*-Toluolsulfonhydrazide (103 mg, 0.55 mmol) was added and the mixture was refluxed for 1 h. Few crystals of the reduced species **6** were isolated and identified by mass spectrometry and X-ray diffraction experiments (see Figure 2). MS (EI, 70 eV): 548.1 [ $M]^+$ ], 512.1 [ $M-Cl]^+$ ], 259.0 [ $C_{15}H_9Cl_2]^+$ ]. HRMS (EI): calculated for  $C_{32}H_{22}Cl_4$ : 546.04756; measured: 546.04570, dev [ppm]: 3.41, dev. [mmu]: 1.86.

**1,4-Bis[1,8-bis(trimethylsilyl)ethynyl]anthracen-10-yl]but-2-ene (8):**

Synthesis according to the general procedure for olefin metathesis reactions using 10-allyl-1,8-bis(trimethylsilyl)ethynylanthracene (**7**; 65 mg, 0.15 mmol) and Grubbs' I catalyst (20mol%). Stirring overnight at 55 °C, filtration and washing with small amounts of cold dichloromethane afforded **8** as a dark yellow solid. Yield: 22 mg (39%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta = 9.33$  (s, 2H,  $H9/H9'$ ), 8.09 (d,  $^3J_{HH} = 9.0$  Hz, 4H,  $H4/H4'/H5/H5'$ ), 7.78 (d,  $^3J_{HH} = 6.5$  Hz, 4H,  $H2/H2'/H7/H7'$ ), 7.37 (dd,  $^3J_{HH} = 8.9, 6.9$  Hz, 4H,  $H3/H3'/H6/H6'$ ), 5.60 (s, 2H,  $CH_2-CH=CH-CH_2$ ), 4.18 (s, 4H,  $CH_2-CH=CH-CH_2$ ), 0.40 [s, 36H,  $Si(CH_3)_3$ ] ppm.  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta = 133.4, 132.0$  ( $C4/C5$ ), 131.2 ( $C3/C6$ ), 131.0 ( $C2/C7$ ), 129.9 ( $CH_2-CH=CH-CH_2$ ), 125.9, 125.2, 123.6, 122.1, 104.0, 100.0, 31.0 ( $CH_2-CH=CH-CH_2$ ), 0.58 [ $Si(CH_3)_3$ ] ppm.  $^{29}Si\{^1H\}$  NMR (99 MHz,  $CDCl_3$ ):  $\delta = -17.5$  ppm. MS (MALDI-TOF, positive ions, DHB):  $m/z$  [assignment] = 792.5 [ $M]^+$ ], 500.4 [ $M-4Si(CH_3)_3]^+$ ]. HRMS (MALDI-TOF): calculated for  $C_{52}H_{56}Si_4^+$ : 792.34536; measured: 792.34595; dev. [ppm]: 0.75, dev. [mmu]: 0.59.

**1,4-Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]but-2-ene (12):**

Synthesis according to the general procedure for olefin metathesis reactions using 10-(allyldimethylsilyl)-1,8-dichloroanthracene (**11**; 41 mg, 0.12 mmol) and Grubbs' I catalyst (20mol%). Reflux for 120 h, column chromatography ( $\varnothing = 3$  cm,  $l = 18$  cm, eluent: *n*-pentane) afforded **12** as a yellow solid.  $R_f = 0.35$  (*n*-pentane). Yield: 28 mg (71%).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 9.41$  (s, 2H,  $H9/H9'$ ), 8.34 (d,  $^3J_{HH} = 9.2$  Hz, 4H,  $H4/H4'/H5/H5'$ ), 7.49 (d,  $^3J_{HH} = 7.1$  Hz, 4H,  $H2/H2'/H7/H7'$ ), 7.05 (dd,  $^3J_{HH} = 9.0, 7.2$  Hz, 4H,  $H3/H3'/H6/H6'$ ), 0.69 [s, 12H,  $Si(CH_3)_2$ ]. Signals of the linking ( $CH_2-CH$ )<sub>2</sub> unit are not observable. MS (ESI, positive ions):  $m/z$  [assignment] = 685.5 [ $M+Na]^+$ ], 437.3 [ $C_{22}H_{25}Si_2Cl_2+Na]^+$ ].

**1,2-Bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (13):**

A solution of *n*-butyllithium (0.77 mL, 1.2 mmol) was added dropwise to a solution of 10-bromo-1,8-dichloroanthracene (**9**; 400 mg, 1.2 mmol) in THF (20 mL) at -78 °C. The dark red mixture was stirred for 1.5 h at this temperature. A solution of 1,2-bis(chlorodimethylsilyl)ethane (134 mg, 0.63 mmol) in THF (5 mL) was slowly added and the mixture was allowed to warm to ambient temperature. After stirring overnight and quenching with water, the aqueous layer was extracted with dichloromethane (3 × 30 mL). The combined organic phases were washed with brine and dried over  $MgSO_4$ . The solvent was evaporated and the crude yellow solid was purified by sublimation (24 h, 50 °C,  $3 \times 10^{-3}$  mbar) and column chromatography on silica gel ( $\varnothing = 3$  cm,  $l = 17$  cm, eluent: *n*-pentane). The desired compound **13** was afforded as bright yellow crystals.  $R_f = 0.4$  (*n*-pentane). Yield: 66 mg (16%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta = 9.34$  (s, 2H,  $H9/H9'$ ), 8.06 (d,  $^3J_{HH} = 9.0$  Hz, 4H,  $H4/H4'/H5/H5'$ ), 7.52 (d,  $^3J_{HH} = 7.0$  Hz, 4H,  $H2/H2'/H7/H7'$ ), 7.11 (dd,  $^3J_{HH} = 8.9, 7.2$  Hz, 4H,  $H3/H3'/H6/H6'$ ), 0.99 (s, 4H,  $SiCH_2$ ), 0.59 [s, 12H,  $Si(CH_3)_2$ ] ppm.  $^{13}C\{^1H\}$  NMR (125 MHz,  $CDCl_3$ ):  $\delta = 138.0, 136.6, 133.1, 128.9, 127.4$  ( $C4/C5$ ), 125.2 ( $C2/C7$ ), 124.6 ( $C3/C6$ ), 123.9 ( $C9$ ), 12.1 ( $SiCH_2$ ), 3.1 [ $Si(CH_3)_2$ ] ppm.  $^{29}Si\{^1H\}$  NMR (99 MHz,  $CDCl_3$ ):  $\delta = -0.8$  ppm. MS (EI, 70 eV):  $m/z$  [assignment] = 636.1 [ $M]^+$ ], 388.1 [ $C_{20}H_{25}Cl_2Si_2]^+$ ], 330.1 [ $C_{18}H_{17}Cl_2Si^+$ ], 303.2 [ $C_{16}H_{13}Cl_2Si^+$ ], 246.0 [ $C_{14}H_7Cl_2]^+$ ]. HRMS (EI): calculated for  $C_{34}H_{30}Cl_4Si_2$ : 634.06347, measured: 634.06644, dev. [ppm]: 4.69, dev. [mmu]: 2.97.

**1,2-Bis[1,8-bis(trimethylsilyl)ethynyl]anthracen-10-yl]dimethylsilyl]ethane (14):**

Synthesis according to the general procedure for Kumada coupling reactions using 1,2-bis[(1,8-dichloroanthracen-10-yl)dimethylsilyl]ethane (**13**; 45 mg, 0.07 mmol),  $PPh_3$  and  $Ni(acac)_2$  (one spatula tip of each compound), reflux for 96 h. Column chromatography ( $\varnothing = 3$  cm,  $l = 18$  cm, eluent: *n*-pentane/dichloromethane (8:1)) afforded **14** as bright yellow crystals.  $R_f = 0.35$  [*n*-pentane/dichloromethane (8:1)]. Yield 16 mg (29%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta = 9.45$  (s, 2H,  $H9/H9'$ ), 8.17 (d,  $^3J_{HH} = 9.0$  Hz, 4H,  $H4/H4'/H5/H5'$ ), 7.71 (d,  $^3J_{HH} = 6.6$  Hz, 4H,  $H2/H2'/H7/H7'$ ), 7.20 (dd,  $^3J_{HH} = 9.0, 6.9$  Hz, 4H,  $H3/H3'/H6/H6'$ ), 0.88 (s, 4H,  $SiCH_2$ ), 0.59

[s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>], 0.39 [s, 36H, C≡C–Si(CH<sub>3</sub>)<sub>3</sub>] ppm. MS (MALDI-TOF, positive ions, DHB): *m/z* [assignment] = 882.3 [M]<sup>+</sup>, 735.4 [M–2Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. HRMS (MALDI-TOF): calculated for C<sub>54</sub>H<sub>66</sub>Si<sub>6</sub><sup>+</sup>: 882.37746; measured: 882.37852, dev. [ppm]: 1.20, dev. [mmu]: 1.06.

**1,8-Dichloro-9-hydroxyanthracen-10(9H)-one (16):** The compound was quantitatively obtained by irradiating a NMR sample of 1,2-bis[(1,8-dichloroanthracene-10-yl)dimethylsilyl]ethane (**13**; 20 mg), dissolved in CDCl<sub>3</sub> (0.45 mL), with UV light (365 nm) for at least 2 h. Analytical data: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.22 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 2H, H4/H5), 7.74 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 2H, H2/H7), 7.52 (t, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 2H, H3/H6), 6.41 (s, 1H CHO), 3.15 (br, 1H, CHO) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 182.6 (C=O), 138.4, 135.1, 135.0 (C2/C7), 132.9, 130.2 (C3/C6), 126.7 (C4/C5), 61.8 (CHO) ppm. MS (EI, 70 eV): *m/z* [assignment] = 277.9 [M]<sup>+</sup>, 260.9 [M–OH]<sup>+</sup>.

**Crystal Structure Determination:** Suitable crystals of the compounds **2**, **3**, **6**, **7**, **10**, **11**, **13**, **14** and **16** were obtained by slow evaporation of saturated solutions of *n*-pentane (**2**, **3**, **10**, **11** and **13**), *p*-xylene (**6**), *n*-pentane/dichloromethane (8:1) mixture (**7** and **14**) and chloroform (**16**). They were selected, coated with *paratone-N* oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a *SuperNova*, *Dual*, *Cu at zero*, *Atlas* diffractometer (**2**, **7**, **10**, **11**, **13**, **14** and **15**) and a *Nonius KappaCCD* diffractometer (**3** and **6**). The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97).<sup>[16]</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table 5. CCDC 1003186 – 1003194 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data\_request/cif.

Table 5: Crystallographic data for **2**, **3**, **6**, **7**, **10**, **11**, **13**, **14** and **16**.

	<b>2</b>	<b>3</b>	<b>6</b>	<b>7</b>	<b>10</b>	<b>11</b>	<b>13</b>	<b>14</b>	<b>16</b>
Empirical formula	C <sub>16</sub> H <sub>10</sub> Cl <sub>2</sub>	C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub>	C <sub>32</sub> H <sub>22</sub> Cl <sub>4</sub> · 1/3 C <sub>8</sub> H <sub>10</sub>	C <sub>27</sub> H <sub>30</sub> Si <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> Cl <sub>2</sub> Si	C <sub>19</sub> H <sub>18</sub> Cl <sub>2</sub> Si	C <sub>34</sub> H <sub>30</sub> Cl <sub>4</sub> Si <sub>2</sub>	C <sub>54</sub> H <sub>66</sub> Si <sub>6</sub>	C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	273.14	287.17	583.68	410.69	331.30	345.32	636.56	883.60	279.10
λ [Å]	1.54178	0.71073	1.54178	0.71073	1.54178	0.71073	0.71073	1.54178	0.71073
<i>T</i> [K]	100.0(1)	100(2)	100(2)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
<i>F</i> (000)	1120	592	2712	440	688	1440	660	1896	568
Crystal system	monoclinic	triclinic	trigonal	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [Å]	7.2894(3)	8.283(1)	39.852(1)	9.6501(1)	11.1944(1)	11.5248(1)	10.0069(1)	22.1694(8)	7.7369(2)
<i>b</i> [Å]	18.8537(6)	8.750(1)	39.852(1)	9.8263(2)	10.8978(1)	12.9907(1)	10.9486(2)	11.8638(4)	7.6348(2)
<i>c</i> [Å]	17.6705(5)	19.030(2)	4.543(1)	13.6139(2)	13.6184(2)	22.7442(3)	13.5126(2)	20.4994(7)	19.2903(6)
α [°]	90	94.12(1)	90	106.665(2)	90	90	90	90	90
β [°]	91.476(4)	91.05(1)	90	101.558(1)	107.690(1)	90	93.467(1)	103.757(3)	93.958(3)
γ [°]	90	100.32(1)	120	91.658(1)	90	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	2427.7(2)	1352.8(2)	6247.9(4)	1206.49(4)	1582.80(3)	3405.14(7)	1477.76(3)	5237.0(3)	1136.8(1)
<i>Z</i>	8	4	9	2	4	8	2	4	4
ρ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.495	1.410	1.396	1.130	1.390	1.347	1.431	1.121	1.631
μ [mm <sup>-1</sup> ]	4.589	0.461	4.047	0.157	4.316	0.445	0.506	1.735	0.558
θ <sub>max</sub> [°]	66.60	25.00	67.49	30.00	72.00	30.00	30.00	66.99	30.00
Index range <i>h</i>	−8 ≤ <i>h</i> ≤ 8	−9 ≤ <i>h</i> ≤ 9	−47 ≤ <i>h</i> ≤ 46	−13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13	−16 ≤ <i>h</i> ≤ 16	−14 ≤ <i>h</i> ≤ 14	−25 ≤ <i>h</i> ≤ 26	−10 ≤ <i>h</i> ≤ 10
Index range <i>k</i>	−22 ≤ <i>k</i> ≤ 22	−10 ≤ <i>k</i> ≤ 10	−44 ≤ <i>k</i> ≤ 47	−13 ≤ <i>k</i> ≤ 13	−13 ≤ <i>k</i> ≤ 12	−18 ≤ <i>k</i> ≤ 18	−15 ≤ <i>k</i> ≤ 15	−14 ≤ <i>k</i> ≤ 14	−10 ≤ <i>k</i> ≤ 10
Index range <i>l</i>	−21 ≤ <i>l</i> ≤ 21	−0 ≤ <i>l</i> ≤ 22	−5 ≤ <i>l</i> ≤ 5	−19 ≤ <i>l</i> ≤ 19	−16 ≤ <i>l</i> ≤ 16	−32 ≤ <i>l</i> ≤ 32	−18 ≤ <i>l</i> ≤ 19	−24 ≤ <i>l</i> ≤ 24	−26 ≤ <i>l</i> ≤ 27
Refl. collect.	41763	7736	17060	71109	16249	189888	84730	23823	19142
Indep. refl.	4291	4618	2498	7022	3113	4957	4302	4677	3305
<i>R</i> <sub>int</sub>	0.0684	–	0.0326	0.0394	0.0270	0.0389	0.0382	0.0386	0.0298
Observed refl., <i>I</i> > 2σ( <i>I</i> )	4020	3894	2218	6401	2961	4656	3972	4045	2894
Parameters	332	344	207	382	243	201	183	293	195
<i>R</i> <sub>1</sub> , <i>I</i> > 2σ( <i>I</i> )	0.0674	0.0702	0.0333	0.0322	0.0256	0.0267	0.0294	0.0763	0.0299
<i>wR</i> <sub>2</sub> , <i>I</i> > 2σ( <i>I</i> )	0.1687	0.1737	0.0917	0.0939	0.0679	0.0736	0.0848	0.2270	0.0768
<i>R</i> <sub>1</sub> (all data)	0.0702	0.0858	0.0372	0.0352	0.0270	0.0285	0.0319	0.0838	0.0360
<i>wR</i> <sub>2</sub> (all data)	0.1704	0.1841	0.0940	0.0963	0.0692	0.0751	0.0869	0.2372	0.0811
<i>GoF</i>	1.109	1.073	1.073	1.064	1.038	1.047	1.053	1.067	1.096
ρ <sub>max/min</sub> [e Å <sup>-3</sup> ]	0.82/−0.81	0.51/−0.49	0.28/−0.17	0.45/−0.21	0.36/−0.24	0.43/−0.25	0.50/−0.26	0.77/−0.68	0.47/−0.22
Remarks	[a]	[b]	[c]	–	–	–	–	[d]	–
CCDC-No.	1003191	1003192	1003193	1003194	1003186	1003187	1003188	1003189	1003190

Remarks: [a] Disorder of C(31) and C(32) on two positions (71.3:28.7); [b] Refined as a two component twin (BASF 0.43153); [c] Disordered *p*-xylol was squeezed. Hydrogen atoms were refined isotropically; [d] Disorder of C(15) – C(19) and Si(1) on two positions (91:9).

**Supporting Information** (see footnote on the first page of this article): NMR spectra of all new compounds and X-ray data in CIF format for compounds **2**, **3**, **6**, **7**, **10**, **11**, **13**, **14** and **16**.

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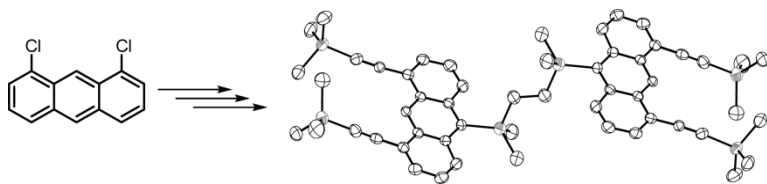
NMR spectra, as well as Dr. Jens Sproß and Heinz-Werner Patruck for measuring mass spectra. We gratefully acknowledge Deutsche Forschungsgemeinschaft (DFG) for financial support.

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1,8-Functionalised anthracenes bearing allyl-containing substituents in position 10 were converted in olefin metathesis reactions and the corresponding linked anthracenes were afforded in good

yields. In addition, flexible 1,2-bis(dimethylsilyl)-ethane-linked anthracene-dimers were synthesised and functionalised with rigid alkyne units.

**J.-H. Lamm, M. Linnemannstöns,  
S. Solyntjes, B. Neumann,  
H.-G. Stammer,  
N. W. Mitzel\*** ..... Page No. – Page No.

Syntheses of Donor-free Linked 1,8-functionalised Anthracene Derivatives

**Keywords:** Anthracenes / Metathesis Reactions / Solid-State Structures



## **Publikation 8**

### **Alkynyl compounds of the rare earth metals**

Anja Nieland, Jan-Hendrik Lamm, Andreas Mix,  
Beate Neumann, Hans-Georg Stammler, Norbert W. Mitzel

*Z. Anorg. Allg. Chem.* **2014**, Manuskript in Begutachtung.



## Alkynyl compounds of the rare-earth metals

Anja Nieland, Jan-Hendrik Lamm, Andreas Mix, Beate Neumann, Hans-Georg Stammer and Norbert W. Mitzel\*

**Keywords:** Rare-earth metals; acetylides; tetramethylaluminates; cations; nitrogen ligands

Conversion of the rare-earth tetramethylaluminates  $[\text{Ln}(\text{AlMe}_4)_3]$  with phenylacetylene afforded the homoleptic alkynyl aluminates  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  ( $\text{Ln} = \text{Ce}$  (**1**),  $\text{Er}$ (**2**)). The reaction of five equivalents of phenylacetylene with the yttrium aluminate  $[\text{Y}(\text{AlMe}_4)_3]$  afforded  $[\text{Y}[(\mu\text{-C}\equiv\text{CPh})\text{AlMe}_3][(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_2]$  (**3**). The cationic yttrium complex  $[(\text{TMTAC})_2\text{YMe}_2][\text{AlMe}_4]$  (**4**), with TMTAC being 1,3,5-trimethyl-1,3,5-triazacyclohexane, was reacted with phenylacetylene to give the product  $[(\text{TMTAC})_2\text{Y}(\text{C}\equiv\text{CPh})_2][\text{Me}_2\text{Al}(\text{C}\equiv\text{CPh})_2]$  (**5**), in which two methyl groups of each, the cation and the anion, were substituted by phenylacetylde

groups. Under the same conditions as for the synthesis of compound **5**, the holmium analogue reveals different reactivity in forming a neutral alkynyl complex  $[(\text{TMTAC})_2\text{Ho}(\text{C}\equiv\text{CPh})_3]$  (**6**). The introduction of 1,8-diethynylanthracene to **4** leads to a structural very similar complex  $[(\text{TMTAC})_2\text{Ho}(\mu\text{-1,8-diethynylanthracene})_3]$  (**7**) and offers the same reactivity as observed for the synthesis of **6**. All compounds were characterized by X-ray diffraction experiments. Compounds **1** – **3** and **5** were also characterized by NMR and elemental analyses.

## Introduction

Since more than 40 years alkynyl complexes of the rare-earth metals are known. Within the last years, the interest in this field is growing because alkynylated rare-earth-metal complexes have shown to be the active catalyst in the dimerization of terminal alkynes to give head-to-head ( $\text{RC}\equiv\text{C}-\text{HC}=\text{CHR}$ ) or head-to-tail ( $\text{RC}\equiv\text{C}-\text{RC}=\text{CH}_2$ ) dimers.<sup>[1]</sup> Several methods for the synthesis of alkynyl complexes of the rare-earth metals are known. One of the first reported alkynyl complexes of SARAN *et al.* in 1970 is the homoleptic scandium compound  $[\text{Sc}(\text{C}\equiv\text{CPh})_3]$ , which was formed by salt metathesis. Amine elimination or alkane elimination are further methods to prepare alkynyl complexes like  $[\text{Ln}(\text{C}\equiv\text{CPh})_3]$  ( $\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{Yb}$ ) and  $[\text{LiLn}(\text{C}\equiv\text{CR})_4(\text{thf})]$  ( $\text{Ln} = \text{Y}, \text{Lu}, \text{Er}, \text{Sm}; \text{R} = \text{tBu}, \text{Ph}$ ).<sup>[2]</sup>

Recently, we reported on a new class of homoleptic rare-earth-metal aluminates  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Y}, \text{Ho}, \text{Tm}$ ) by using the latter mentioned method.<sup>[3]</sup>

Alkynyl ligands have two main coordination modes: terminal or bridging between two metals. In the latter case mostly homonuclear complexes of the type  $[(\text{L})\text{Ln}(\mu\text{-C}\equiv\text{CR})_2]$  are known, where one alkynyl ligand is oriented to one rare-earth metal atom, for instance in  $[\text{Eu}(\mu\text{-C}\equiv\text{CPh})(\text{dig})_2]_2[\text{P}_2\text{C}_3\text{tBu}_3]$  ( $\text{dig} = \text{diglyme}$ ).<sup>[4]</sup> In  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  both alkynyl groups are oriented towards the rare-earth metal atom.<sup>[3]</sup>  $[[\text{Me}_2\text{TACN}(\text{CH}_2)_2\text{N}^t\text{Bu}]\text{La}(\text{CCPh})(\mu\text{-C}\equiv\text{CPh})_2]$  ( $\text{TACN} = 1,4,7\text{-triazacyclononane}$ ) for example shows both modes, one terminal as well as a bridging alkynyl ligand.<sup>[1c]</sup>

## Results and Discussion

Reactions of  $\text{Ln}(\text{AlMe}_4)_3$  with phenylacetylene

First we present two further compounds of the recently reported class  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Sm}, \text{Y}, \text{Ho}, \text{Tm}$ ) namely those of cerium and erbium ( $\text{Ln} = \text{Ce}$  (**1**),  $\text{Er}$  (**2**)). Compounds **1** and **2** were prepared according to the literature with slight modifications and were characterized by NMR spectroscopy, elemental analyses and X-ray diffraction experiments.<sup>[3]</sup> For this class three different crystal structures were observed: The reported two compounds  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  ( $\text{Ln} = \text{La}, \text{Tm}$ ) containing lanthanum, the

\* Fakultät für Chemie  
Universität Bielefeld  
Universitätsstraße 25  
33615. Bielefeld., Germany  
E-mail: mitzel@uni-bielefeld.de  
Fax: +49 (0) 521 106 6026.

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next bigger element to cerium, and thulium, the smaller element next to erbium, show different crystal structures; all other compounds, including **1** and **2** crystallize isostructurally with 2.5 benzene molecules in the unit cell (Figure 1).<sup>[3]</sup>

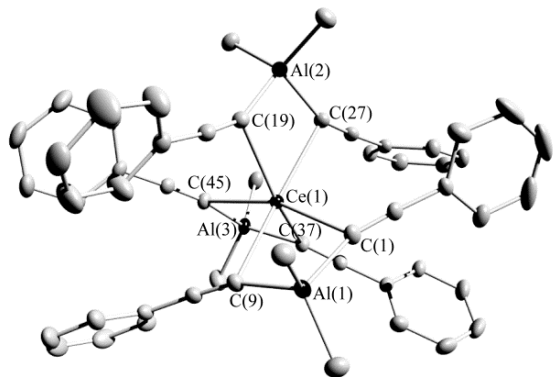


Figure 1. Molecular structure of compound **1** in the crystalline state. Compound **2** is isostructural. Displacement ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

Most of the bridging alkyne compounds of the rare-earth metals are homonuclear complexes with asymmetrical bridging mode, where each alkyne group is oriented to one rare-earth metal (Figure 2, a).<sup>[1b,c,4a,b,4d,5]</sup> The present complexes **1** and **2** show also asymmetrical bonding mode, but both alkyne groups of one  $[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]$ -ligand are oriented to the rare-earth metal.<sup>3</sup>

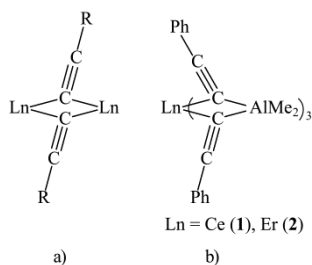


Figure 2. Bonding modes of asymmetric bridging alkyne ligands in rare-earth-metal complexes.

The bond lengths and angles in **1** and **2** are in the expected range and vary slightly according to the lanthanoid ion radius. The Ln–C bonds in **1** are between 2.617(1) (Ce(1)–C(1)) and 2.678(1) Å (Ce(1)–C(9)) and in **2** between 2.471(2) (Er(1)–C(37)) and 2.532(2) Å (Er(1)–C(45)). Due to the decreasing Ln–C bond lengths with decreasing ionic radii, the  $[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]^-$  ligands approach the metal ion more closely, leading to wider C–Ln–C angles: in **1** these angles are between 71.4(1)° (C(1)–Ce(1)–C(9)) and 72.0(1)° (C(19)–Ce(1)–C(27)), in **2** between 75.3(1)° (C(1)–Er(1)–C(9)) and 76.2(1)° (C(19)–Er(1)–C(27)). Detailed structure information of **1** and **2** is given in the supplementary information.

<sup>1</sup>H NMR spectra of **1** and **2** are displayed in Figure 2. Cerium(III) is of paramagnetic nature, but shows small

paramagnetic effects and therefore **1** affords a well resolved spectrum with almost no line broadening.<sup>[6]</sup> The narrow signal at –0.43 ppm refers to the methyl groups and is slightly shifted compared to the diamagnetic yttrium (0.03 ppm) and lanthanum (0.01 ppm) analogous. The protons at the *para* position of the phenyl groups show a triplet at 6.43 ppm, which is slightly overlapping the doublet of the protons in *ortho* position at 6.49 ppm and therefore the signals are not as well-separated as in the paramagnetic analogous samarium and praseodymium compounds. The remaining phenyl-proton shows a separated triplet at 6.69 ppm. For **1** it was possible to record 2D NMR spectra, allowing the signals in <sup>13</sup>C NMR spectrum to be assigned unambiguously, although like for all paramagnetic compounds of the  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  series the signal for the  $\alpha$ -carbon atom of the alkyne group could not be detected. The methyl groups show a signal at –6.4 ppm. At lower field two signals at 116.4 and 126.0 ppm refer to the  $\beta$ -carbon atom of the alkyne group and the *ipso* carbon atom of the phenyl group. The remaining phenyl group carbon atoms show signals at 126.8, 131.7 and 136.1 ppm.

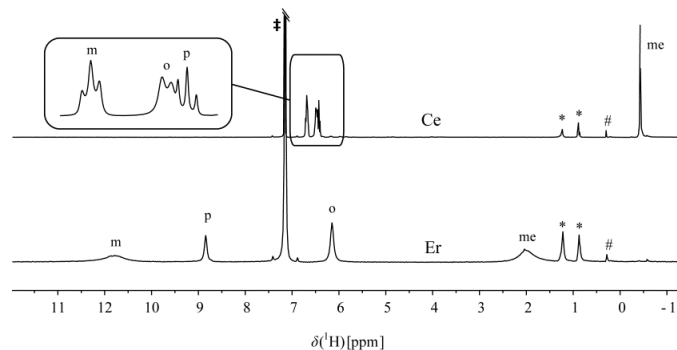


Figure 3. <sup>1</sup>H NMR of  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  (Ln = Ce (**1**), Er (**2**)). The labels o, m, p, and me refer to the *ortho*, *meta*, *para* phenyl protons and the methyl groups, respectively. ‡ denotes solvent signal (C<sub>6</sub>D<sub>6</sub>), \* denotes signals of traces of pentane, # denotes signal of traces of silicon grease.

In contrast to cerium(III), erbium(III) has a pronounced paramagnetic nature, leading to a <sup>1</sup>H NMR spectrum of **2** with broader signals and a wider frequency range (Figure 3).<sup>[3,6b]</sup> As well as for the holmium and thulium compounds with also pronounced paramagnetic nature, **2** shows a spectrum with two broader and two narrower signals. For the methyl groups, as well as for the phenylic protons in *meta* position, two broad signals at 2.02 and 10.78 ppm with a half width of 104 Hz were observed. For comparison, in Er(AlMe<sub>4</sub>)<sub>3</sub> the methyl groups cause a very broad signal at –20 ppm with a half width of 2944 Hz. The protons in *para* and *ortho* position exhibit resonances at 8.85 and 6.17 ppm. In the <sup>13</sup>C NMR spectrum the methyl groups bound to the aluminum atom cause a signal at –16.9 ppm. For the phenylacetylide group just two signals can be assigned by HMBC and HMQC experiments; the signal at 136.1 ppm referred to the protons in *meta* and at 119.8 ppm to the protons in *para* position. The remaining signals cannot be detected by

means of 2D NMR measurements (see the spectra in the Supporting Information).

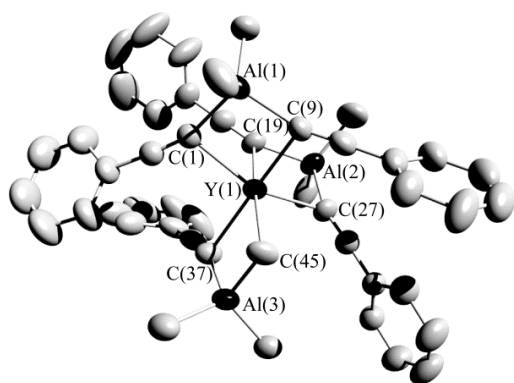


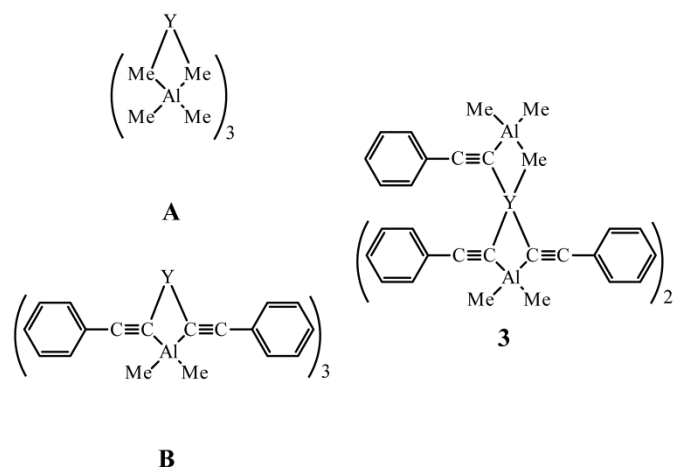
Figure 4. Molecular structure of compound **3** in the crystalline state. Displacement ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] of  $Y(AlMe_4)_3$  (**A**),<sup>[7]</sup>  $[Y[(\mu-C\equiv CPh)_2AlMe_2]_3]$  (**B**)<sup>[3]</sup> and compound **3**.

A		
Y(1)–C(1)	2.505(7)	
Y(1)–C(2)	2.514(8)	
Y(1)–C(5)	2.505(7)	
Y(1)–C(6)	2.505(6)	
Y(1)–C(9)	2.510(6)	
Y(1)–C(10)	2.507(7)	
C(1)–Y(1)–C(2)	84.3(2)	
C(5)–Y(1)–C(6)	84.7(2)	
C(9)–Y(1)–C(10)	84.8(2)	
Y(1)···Al(1)	3.067(3)	
Y(1)···Al(2)	3.068(2)	
Y(1)···Al(3)	3.068(2)	
B		
3		
Y(1)–C(1)	2.527(2)	2.509(3)
Y(1)–C(9)	2.519(2)	2.521(3)
Y(1)–C(19)	2.536(2)	2.500(5)
Y(1)–C(27)	2.495(2)	2.485(4)
Y(1)–C(37)	2.492(2)	2.482(4)
Y(1)–C(45)	2.550(2)	2.542(5)
C(1)–Y(1)–C(9)	74.6(1)	75.1(2)
C(19)–Y(1)–C(27)	75.6(1)	77.1(2)
C(37)–Y(1)–C(45)	75.0(1)	78.4(2)
Y(1)···Al(1)	3.318(1)	3.301(1)
Y(1)···Al(2)	3.301(1)	3.252(2)
Y(1)···Al(3)	3.312(1)	3.226(1)

Incomplete conversion of  $Y(AlMe_4)_3$  (**A**) with five equivalents phenylacetylene instead of six as before led to a new compound  $[Y[(\mu-C\equiv CPh)AlMe_3][(\mu-C\equiv CPh)_2AlMe_2]_2]$  (**3**). The structure in the crystalline state shows two  $[(\mu-C\equiv CPh)_2AlMe_2]^-$  ligands coordinated in the known manner (compare **1** and **2**) and one  $[(\mu-C\equiv CPh)AlMe_3]^-$  ligand in which one methyl- (C(45)) and the alkynyl group coordinates to the yttrium ion, so the coordination number in **3** is also 6

(Figure 4). Selected bond lengths and angles of **A**,  $[Y[(\mu-C\equiv CPh)_2AlMe_2]_3]$  (**B**) and **3** are listed in Table 1, schematic illustrations are depicted in Scheme 1. The Y–C bonds of the alkynyl groups in **3** are slightly shorter than in **B**, whereas the Y–C bond to the methyl group is somewhat longer than those in **A**. Furthermore, considering the Y···Al distances and the C–Y–C angles, the  $[AlMe_4]^-$  ligands in **A** coordinate more closely, so the Y···Al distances are about 0.2 Å shorter and the C–Y–C angles are about 10° wider, than in **B**. Obviously, in **3** both values are better in agreement with the structure of **B**.

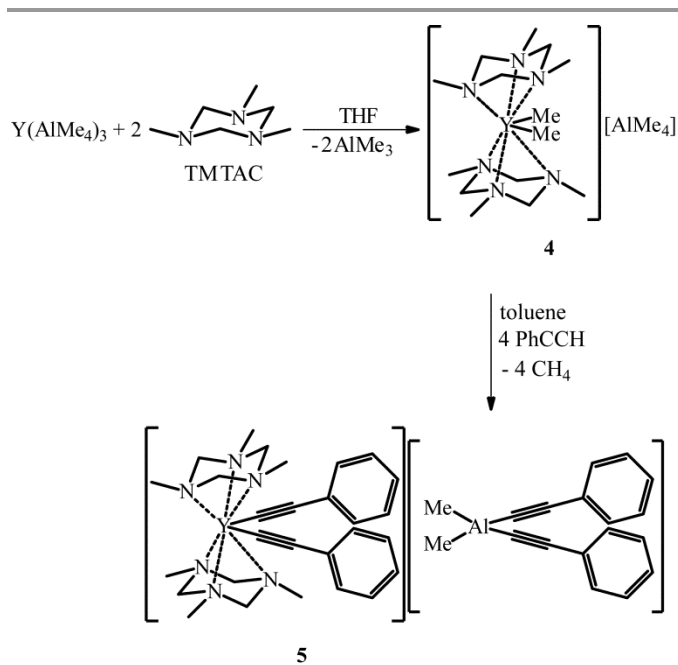


Scheme 1. Schematic illustration of the yttrium compounds  $[Y(AlMe_4)_3]$  (**A**),  $[Y[(\mu-C\equiv CPh)_2AlMe_2]_3]$  (**B**) and **3**.

### Reaction of $[(TMTAC)_2YMe_2][AlMe_4]$ (**4**) with phenylacetylene

In order to compare the reactivity of different types of methyl/yttrium compounds, neutral, as well as cationic complexes towards alkynes, the cationic methyl/yttrium complex  $[(TMTAC)_2YMe_2][AlMe_4]$  (**4**) was reacted with phenylacetylene (Scheme 2). Additional to the earlier reported compound **4** in this working group, here we present its crystal structure and also better elemental analysis data. The reaction of **4** with phenylacetylene showing the same reaction-type as observed for  $Ln(AlMe_4)_3$  in the syntheses of compounds **1** – **3**, **4** also reacts with formation of methane. Interestingly, not only the methyl groups of the cation, coordinating to the yttrium ion, but also two methyl groups of the  $[AlMe_4]^-$  anion were found to react with phenylacetylene leading to the compound  $[(TMTAC)_2Y(C\equiv CPh)_2][Me_2Al(C\equiv CPh)_2]$  (**5**). The formation of complex **5** was also observed, when just a substoichiometric amount (2 eq.) of  $HC\equiv CPh$  was used. We could obtain crystals suitable for X-ray diffraction experiments for both compounds **4** and **5**. The structures in the crystalline state are displayed in Figures 5 and 6, selected bond lengths and angles are listed in Table 2.





Scheme 2. Reaction of 4 with phenylacetylene in toluene.

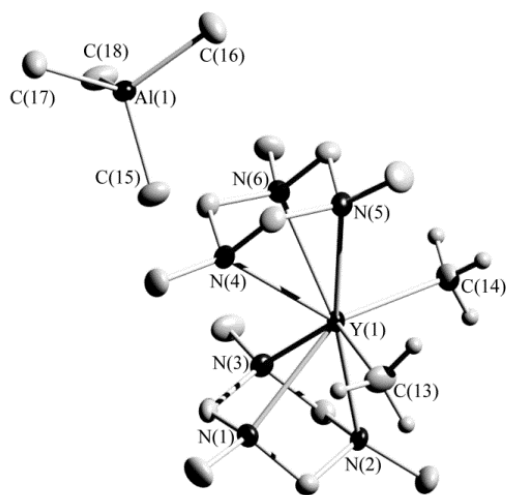


Figure 5. Molecular structure of compound 4 in the crystalline state. Displacement ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

The Y–C bond lengths in 4 are 2.428(4) and 2.432(4) Å, similar to the related compound [(TCyTAC)<sub>2</sub>YMe<sub>2</sub>][AlMe<sub>4</sub>] (Y(1)–C(1): 2.421(2) Å, Y(1)–C(2): 2.415(2) Å), but somewhat longer than in dicationic yttrium complexes [(crown ether)<sub>1–2</sub>YMe(thf)<sub>0–2</sub>][AlMe<sub>4</sub>]<sub>2</sub> (crown ether = [18]crown-6, [15]crown-5, [12]crown-4), where the bond lengths are in the range of 2.405(3) to 2.410(2) Å.<sup>[8]</sup> The C–Y–C angle in 4 is about 6° wider (C(13)–Y(1)–C(14): 103.5(2)°) than in [(TCyTAC)<sub>2</sub>YMe<sub>2</sub>][AlMe<sub>4</sub>] (C(1)–Y(1)–C(2): 96.7(1)°), because the methyl groups are less bulky than the cyclohexyl groups.

Therefore the TMTAC ligands in 4 approach the yttrium atom, so the Y–N bond lengths are shorter than in [(TCyTAC)<sub>2</sub>YMe<sub>2</sub>][AlMe<sub>4</sub>]. The Al–C bonds and C–Al–C angles of the anion in 4 agree well with those of the mentioned complexes.<sup>[8–9]</sup>

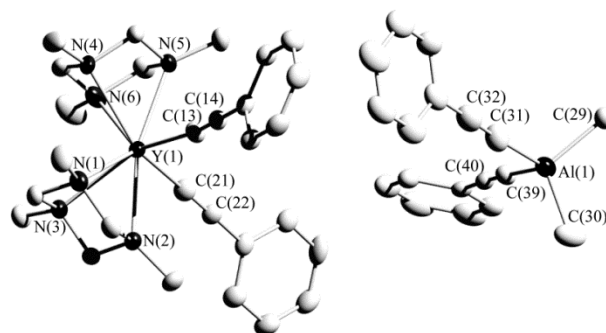


Figure 6. Molecular structure of compound 5 in the crystalline state. Displacement ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] of compound 4 and 5.

4		5	
Y(1)–C(13)	2.428(4)	Y(1)–C(13)	2.405(3)
Y(1)–C(14)	2.432(4)	Y(1)–C(21)	2.398(3)
Al(1)–C(15)	2.018(4)	Al(1)–C(29)	1.995(3)
Al(1)–C(16)	2.015(4)	Al(1)–C(30)	1.979(4)
Al(1)–C(17)	2.028(5)	Al(1)–C(31)	1.980(4)
Al(1)–C(18)	2.005(5)	Al(1)–C(39)	2.004(3)
		C(13)–C(14)	1.218(4)
		C(21)–C(22)	1.219(4)
		C(31)–C(32)	1.233(5)
		C(39)–C(40)	1.204(4)
Y(1)–N(1)	2.635(3)	Y(1)–N(1)	2.580(2)
Y(1)–N(2)	2.553(3)	Y(1)–N(2)	2.518(3)
Y(1)–N(3)	2.617(3)	Y(1)–N(3)	2.546(2)
C(13)–Y(1)–C(14)	103.5(2)	C(13)–Y(1)–C(21)	108.8(1)
		Y(1)–C(13)–C(14)	169.3(2)
		Y(1)–C(21)–C(22)	172.0(3)
C(15)–Al(1)–C(16)	105.6(2)	C(29)–Al(1)–C(30)	112.2(2)
C(15)–Al(1)–C(17)	114.6(2)	C(31)–Al(1)–C(39)	106.6(2)
		Al(1)–C(31)–C(32)	176.4(3)
		Al(1)–C(39)–C(40)	175.5(3)

In 5 four methyl groups are substituted by phenylacetylide ligands. Thus, the Y–C bond lengths of 2.405(3) and 2.398(3) Å are shorter. Furthermore the C–Y–C angle is 5° wider, than in 4. The methyl groups in 4 require more space than the alkynyl groups in 5. This leads the TMTAC ligands to approach the yttrium atom even closer, resulting in shorter Y–N distances. Surprisingly the Y–C≡C angles are much less than 180°; in Y(1)–C(21)–C(22) it is 172.0(3)° and even narrower in Y(1)–C(13)–C(14) (169.3(2)°). In contrast, the Al–C–C angles in the anion approximate 180°. The triple bond lengths in the cation are nearly the same (C(13)–C(14):

1.218(4) Å and C(21)–C(22): 1.219(4) Å), whereas the anion shows different values of 1.233(5) (C(31)–C(32)) and 1.204(4) Å (C(39)–C(40)). Triple bond lengths of the bridged alkynyl groups in  $[Y[(\mu-C\equiv CPh)_2AlMe_2]_3]$  are in the range between 1.216(2) and 1.223(2) Å. The triple bond lengths of terminal acetylide groups are generally shorter than of bridging acetylide groups.<sup>[5a,10]</sup>

Compound **5** is not soluble in non-polar solvent and reacts with thf, therefore NMR analysis of **5** was performed in  $CD_2Cl_2$  within 4 h. The methyl groups show a narrow singlet at –0.94 ppm. Two singlets at 2.43 and 2.48 ppm in an integral ratio of 1:5 and two doublets at 3.23 and 4.43 ppm with coupling constant of 8.5 Hz stem from the coordinating TMTAC ligands. The phenyl protons show resonances in the anticipated regions. In the  $^{13}C$  NMR spectrum the methyl groups, bonded to the aluminum atom result in a broad signal at –6.7 ppm. Methyl and methylene groups of the TMTAC ligands reveal resonances at 40.1 and 77.8 ppm which agrees well with the literature.<sup>[9b,11]</sup> Three signals refer to the  $\alpha$ -carbon atoms of the alkynyl groups. The  $\alpha$ -carbon atoms of the cation were detected as a doublet at 102.0 ppm with a coupling constant of  $^1J_{Y-C} = 10.4$  Hz ( $^1J_{Y-C}$  coupling of  $[Y[(\mu-C\equiv CPh)_2AlMe_2]_3]$  is 11.7 Hz), whereas the anion exhibits two broader resonances at 105.9 and 105.7 ppm. For the phenyl carbon atoms three signals were detected in the anticipated regions at 127, 128, 132 and 139 ppm, respectively.

### Neutral phenylethynyl complexes of holmium and yttrium

Although there are some examples of neutral rare-earth complexes with terminal alkynyl groups,<sup>[12]</sup> the following compounds are the first examples of this type, so far.

In the course of paramagnetic NMR studies we recently synthesized the methyl holmium complex  $[HoMe_2(thf)_5]-[AlMe_4]$ .<sup>[6b]</sup> For further investigations in this field, we attempted the synthesis of  $[(TMTAC)_2Ho(C\equiv CPh)_2]-[Me_2Al(C\equiv CPh)_2]$  in analogy to yttrium compound **5** (Scheme 2).  $Ho(AlMe_4)_3$  was dissolved in cold thf and TMTAC was added. The compound  $[(TMTAC)_2HoMe_2]-[AlMe_4]$  could not be identified by crystal structure determination, but upon layering the yellow colored thf solution with pentane a pink precipitate formed, which was insoluble in non-polar solvents. The dried precipitate was suspended in toluene and upon addition of phenylacetylene gas formation was observed. After 3 d the reaction mixture was filtered and the filtrate was cooled to –30 °C to afford a minor quantity of a few pink crystals after one week. They were suitable for X-ray diffraction experiments, but not for further characterization, so this experiment shows a possible type of reactivity but cannot be used to produce useful quantities of the product. Surprisingly, we observed a different reactivity as expected, because a neutral holmium complex  $[(TMTAC)_2Ho(C\equiv CPh)_3]$  (**6**) with three phenylacetylide ligands was formed. Compound **6** crystallized with half a toluene molecule in the unit cell. The molecular structure of **6** in the crystalline state is displayed in Figure 7 in a side and a top view. Viewed

from the top **6** reveals a wheel-like structure with eclipsed TMTAC ligands and staggered phenylacetylide groups with respect to the TMTAC ligands. The planes (N(4)–N(5)–N(6)) and (N(1)–N(2)–N(3)) are nearly parallel to one another, the dihedral angle being 2.9°. The holmium atom is located in the plane of the  $\alpha$ -carbon atoms of the phenylacetylenide ligands. The Ho–C bond lengths with 2.479(2) (Ho(1)–C(13)), 2.473(2) (Ho(1)–C(21)) and 2.464(2) Å (Ho(1)–C(29)) are much longer than the corresponding bonds in **5**. As the ionic radii of yttrium and holmium are nearly the same, the bond lengths would be expected to be also very similar. Consequently, the elongation can be attributed to the electronic situation: **5** as a cationic complex reveals shorter bonds, while **6** as a neutral complex has longer ones. The wheel-type structure made us expecting C–Ho–C angles to adopt values of about 120°. Indeed, one angle, C(29)–Ho(1)–C(13), is 120.1(1)°, but the remaining alkynyl ligand is slightly displaced so that the C(21)–Ho(1)–C(29) angle is found to be smaller (117.2(1)°), while the C(21)–Ho(1)–C(13) angle is wider (122.7(1)°). The same acetylide group also shows the largest deviation from linearity: the Ho(1)–C(21)–C(22) angle at 169.5(2)° is about 5° smaller than the other Ho–C–C angles in the molecule. Due to the pronounced paramagnetic nature of holmium, the  $^1H$  NMR spectrum of **6** shows very broad signals, which cannot be assigned.

Table 3. Selected bond lengths [Å] and angles [°] of compound **6**.

Ho(1)–C(13)	2.479(2)	Ho(1)–C(13)–C(14)	174.9(2)
Ho(1)–C(21)	2.473(2)	Ho(1)–C(21)–C(22)	169.5(2)
Ho(1)–C(29)	2.464(2)	Ho(1)–C(29)–C(30)	174.1(2)
C(13)–C(14)	1.219(2)	C(13)–Ho(1)–C(21)	122.7(1)
C(21)–C(22)	1.219(2)	C(21)–Ho(1)–C(29)	117.2(1)
C(29)–C(30)	1.220(2)	C(29)–Ho(1)–C(13)	120.1(1)

Remarkably, adding 1,8-diethynylanthracene to the ionic compound **4**, we were able to observe a related reactivity as described above: the formation of a neutral complex by methane and  $AlMe_3$  elimination. However, the conversion of both components in toluene (1:1) led to only very few crystals of  $[(TMTAC)_2Y(\kappa^{-1}-1,8\text{-diethynylanthracene})_3]$  (**7**) (Scheme 3). Like for **6** no useful quantities of **7** could be produced.

The crystal unit cell contains three highly disordered toluene molecules. There is also disorder of one dialkynylanthracene ligand (C(49) – C(66)) over two positions. In Figure 8 just one position is drawn for clarity. The structure in the crystalline state is similar to that of compound **6**: the yttrium atom is sandwich-like coordinated by two TMTAC ligands, which are nearly eclipsed, so the structure looks even more like a wheel. Interestingly, just one of the two alkynyl-units of the anthracene ligand binds to the yttrium atom. The proton of the remaining alkynyl unit does not interact with other atoms in its environment.

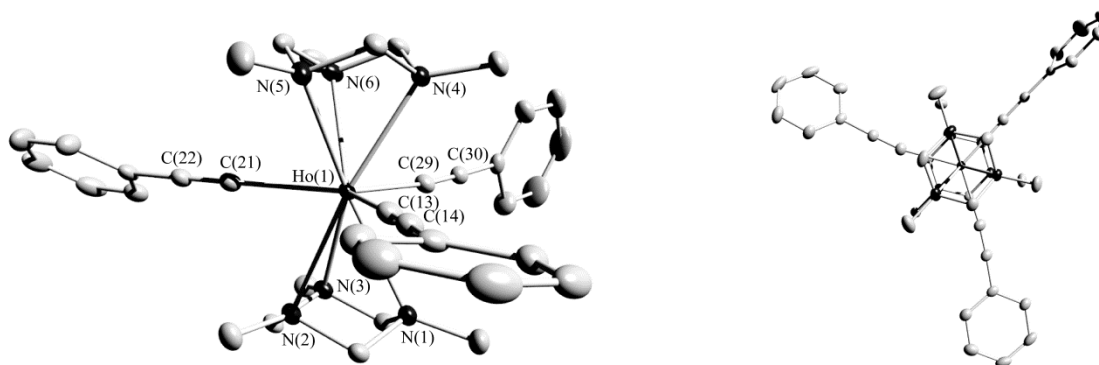


Figure 7. Two views of the molecular structure in the crystalline state of compound **6**. Displacement ellipsoids are set at 50% probability. Hydrogen atoms and the solvent molecule are omitted for clarity.

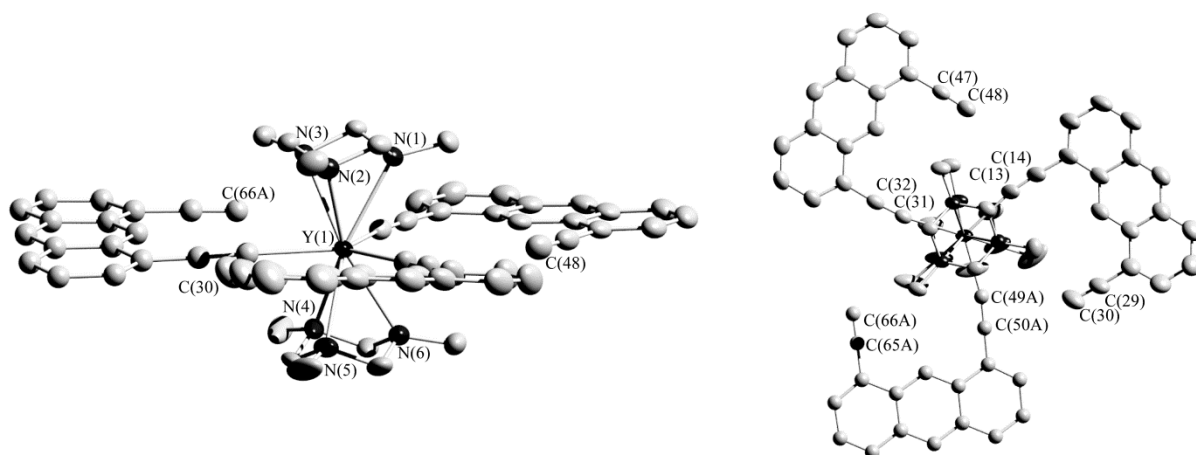
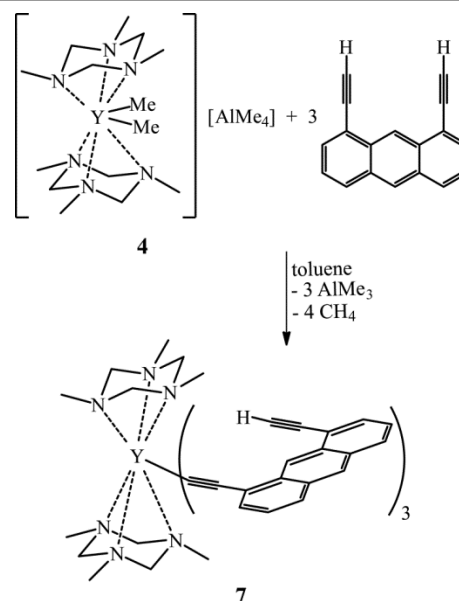


Figure 8. Molecular structure in the crystalline state of compound **7**. Displacement ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

Expectedly, the Ln–C bond lengths in **7** (Table 4) and also the C–Ln–C angles of about 120, 123 and 117° are nearly the same as in **6**. In contrast to **6**, in **7** all three Y–C–C angles show values of about 170°. The triple bond lengths of the coordinated alkynyl units are in the range between 1.215(4) (C(13)–C(14)) and 1.227(7) Å (C(49A)–C(50A)). 1,8-Dialkynylanthracene itself crystallizes with three molecules in the elemental cell and shows triple bond lengths in the range of 1.171(3) to 1.190(4) Å, whereas 1,8-bis(dimethylmetalalkynyl)anthracenes, which can be synthesized by the reaction of 1,8-dialkynylanthracene with MMe<sub>3</sub> (M = Al, Ga, In), show triple bond lengths of 1.219(3), 1.217(3) Å (M = Al), 1.209(3) (M = Ga) and 1.219(3), 1.218(3) Å (M = In).<sup>[13]</sup> Although 1,8-bis(dimethylmetalalkynyl)anthracenes have bridged alkynyl groups, the triple bond lengths of the terminal bonded alkynyl groups in **7** are slightly longer. Despite the very low yields of the reactions yielding **6** or **7**, these structure determinations show that the observed kind of reactivity is possible, even though it may not be the main reaction, and leads to similar arrangements of the ligands at the metal atom.



Scheme 3. Reaction of **4** with 1,8-dialkynylanthracene in toluene

Table 4. Selected bond lengths [Å] and angles [°] of **7**.

Y(1)–C(13)	2.476(3)	Y(1)–C(13)–C(14)	169.9(2)
Y(1)–C(31)	2.487(3)	Y(1)–C(31)–C(32)	169.9(2)
Y(1)–C(49A)	2.476(8)	Y(1)–C(49A)–C(50A)	169.2(10)
Y(1)–C(49B)	2.544(16)	Y(1)–C(49B)–C(50B)	175(3)
C(13)–C(14)	1.215(4)	C(13)–Y(1)–C(49A)	117.7(3)
C(31)–C(32)	1.219(4)	C(13)–Y(1)–C(49B)	125.3(6)
C(49A)– C(50A)	1.227(7)	C(31)–Y(1)–C(49A)	123.0(3)
C(49B)–C(50B)	1.225(12)	C(31)–Y(1)–C(49B)	115.4(6)
C(30)–C(29)	1.156(5)	C(13)–Y(1)–C(31)	119.4(1)
C(47)–C(48)	1.168(4)		
C(65A)– C(66A)	1.150(9)		
C(65B)–C(66B)	1.155(15)		

## Conclusions

In this contribution we could demonstrate that the preparation of alkynyl complexes of the rare-earth elements can be achieved from suitable methyl precursors by methane elimination. In this way neutral complexes as well as cationic and anionic species containing alkynyl groups have been synthesized. The known class of homoleptic alkynyl complexes  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  were complemented by two new representatives (Ln = Ce (**1**), Er(**2**)). Structures in the crystalline state show that at least three different structure types exist: one for  $[\text{La}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  with the biggest rare-earth atom, one for  $[\text{Ln}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  (Ln = Ce – Er) representing the majority of such rare-earth element compounds and one for the smallest atoms (Ln = Tm – Lu).

The closely related compound  $[\text{Y}[(\mu\text{-C}\equiv\text{CPh})\text{AlMe}_3][(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_2]$  (**3**) reveals one ligand with three methyl groups  $[(\text{C}\equiv\text{CPh})\text{AlMe}_3]^-$ . In contrast to  $[\text{Y}[(\mu\text{-C}\equiv\text{CPh})_2\text{AlMe}_2]_3]$  NMR spectroscopic investigations encourage the assumption of methyl group exchange in compound **3**.

Conversion of  $[(\text{TMTAC})_2\text{YMe}_2][\text{AlMe}_4]$  (**4**) with phenylacetylene led to methane elimination within the cation as well as the anion to form  $[(\text{TMTAC})_2\text{Y}(\text{C}\equiv\text{CPh})_2][\text{Me}_2\text{Al}(\text{C}\equiv\text{CPh})_2]$  (**5**). The same conditions applied to obtain compound **5**, were used in an attempt to obtain the holmium analogue, but this afforded a neutral holmium alkynyl complex  $[(\text{TMTAC})_2\text{Ho}(\text{C}\equiv\text{CPh})_3]$  (**6**) in minor quantities. This reactivity type was also observed in a related reaction of **4** with 1,8-dialkynylanthracene to form  $[(\text{TMTAC})_2\text{Y}(\kappa^1\text{-1,8-dialkynylanthracene})_3]$  (**7**).

Compounds **6** and **7** adopt similar structures. In both compounds the metal ions are surrounded by three alkynyl ligands and are sandwich-like coordinated by two TMTAC ligands. The reaction products, especially **5**, **6** and **7** raise the question for the origin of different reaction types. Due to the lack of more substance of **6** or **7**, no further investigations could be undertaken in this field, but nevertheless we again bear witness to Sir William Crookes words, when he addressed the Royal Society in 1887 with this statement on the rare-earth elements: “*These elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us; mocking, mystifying and murmuring strange revelations and possibilities.*”

## Experimental Section

All operations were performed under an inert atmosphere of nitrogen or argon using modified Schlenk-line or glove box techniques. Benzene was distilled from Na, thf was distilled from K and pentane was distilled from  $\text{LiAlH}_4$ . The solvents were degassed three times and stored in a glove box.  $\text{Ln}(\text{AlMe}_4)_3$  were prepared according to the literature.<sup>[6b,14]</sup> Phenylacetylene was distilled, degassed and stored in a glove box before use. NMR spectra were recorded using Bruker Avance III 300, Bruker DRX 500 and Bruker Avance III 500 spectrometers. Elemental analyses were carried out using a EuroEA Elemental Analyser.

**[Ce[( $\mu\text{-C}\equiv\text{CPh}$ )<sub>2</sub>AlMe<sub>2</sub>]<sub>3</sub>] (1).** Ce(AlMe<sub>4</sub>)<sub>3</sub> (40 mg, 0.1 mmol) was dissolved in benzene (1 mL). Phenylacetylene (0.07 mL, 0.06 mmol) was added drop-wise as neat substance to the yellow-green solution. After 1 h the mixture took on a red-orange color. It was left overnight without stirring. In the glove box the solvent was left to evaporate very slowly. Yellow-green crystals were obtained after 1 d. Yield 82 mg (89 %),  $M_r = 918.02$ , found C 70.57, H 5.60 %, C<sub>54</sub>H<sub>48</sub>Al<sub>3</sub>Ce requires C 70.65, H 5.27 %. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 27 °C)  $\delta = -0.43$  (s, 18H, Al-CH<sub>3</sub>), 6.43 (t, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, 6H, Ph<sup>para</sup>), 6.49 (d, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, 12H, Ph<sup>ortho</sup>), 6.69 (t, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, 12H, Ph<sup>meta</sup>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 27 °C)  $\delta = -6.4$  (s, Al-CH<sub>3</sub>), 116.4 (s, CeC≡CC), 126.0 (s, CeC≡CC), 126.8 (s, Ph<sup>meta</sup>), 131.7 (s, Ph<sup>para</sup>), 136.1 (s, Ph<sup>ortho</sup>). No <sup>13</sup>C NMR signal for the  $\alpha$ -carbon atom (CeC≡CC) was detected.

**[Er[( $\mu\text{-C}\equiv\text{CPh}$ )<sub>2</sub>AlMe<sub>2</sub>]<sub>3</sub>] (2).** Er(AlMe<sub>4</sub>)<sub>3</sub> (40 mg, 0.09 mmol) was dissolved in benzene (1.5 mL). Phenylacetylene (0.07 mL, 0.06 mmol) was added drop-wise as neat substance to the pink solution. After 1 h the mixture turned dark brown. It was left overnight without stirring. Pentane (1 mL) was added and the reaction tube was cooled to –30 °C. The solution then was separated from the solid benzene and after 1 d pink crystals were obtained. Yield 73 mg (64 %).  $M_r = 945.16$ , found C 67.36, H 5.22 %, C<sub>54</sub>H<sub>48</sub>Al<sub>3</sub>Er requires C 68.62, H 5.12 %. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 27 °C)  $\delta = 2.02$  (br s,  $\Delta\nu_{1/2} = 104$  Hz, 18H, Al-CH<sub>3</sub>), 6.17 (s, 12H, Ph<sup>ortho</sup>), 8.85 (s, 6H, Ph<sup>para</sup>), 10.78 (br s,  $\Delta\nu_{1/2} = 104$  Hz, 12H, Ph<sup>meta</sup>).

**[Y[( $\mu\text{-C}\equiv\text{CPh}$ )AlMe<sub>3</sub>][( $\mu\text{-C}\equiv\text{CPh}$ )<sub>2</sub>AlMe<sub>2</sub>]<sub>2</sub>] (3).** Y(AlMe<sub>4</sub>)<sub>3</sub> (69 mg, 0.2 mmol) was dissolved in pentane (0.5 mL). The phenylacetylene (101 mg, 0.1 mmol) was added dropwise as neat substance. The mixture was stirred for 18 h and cooled to –30 °C. Colourless crystals were obtained after two weeks. Yield 51 mg (32 %).  $M_r = 780.69$ , found C 70.36, H 6.00 %, C<sub>47</sub>H<sub>46</sub>Al<sub>3</sub>Y requires C 72.31, H 5.94 %. <sup>1</sup>H NMR (300 MHz, toluene-d<sub>8</sub>, 25 °C)  $\delta = 0.01 - 0.07$  (m, 21H, Al-CH<sub>3</sub>), 6.86 (m, 15H, Ph<sup>meta/para</sup>), 7.30 (m, 10H, Ph<sup>ortho</sup>).

**[(TMTAC)<sub>2</sub>YMe<sub>2</sub>][AlMe<sub>4</sub>] (4).** Yield 46%. Found C 45.88, H 10.47, N 18.20 %, C<sub>54</sub>H<sub>48</sub>Al<sub>3</sub>Ce requires C 46.54, H 10.42, N 18.09 %.

**[(TMTAC)<sub>2</sub>Y(C≡CPh)<sub>2</sub>][Me<sub>2</sub>Al(C≡CPh)<sub>2</sub>] (5).** Crystals of  $[(\text{TMTAC})_2\text{YMe}_2][\text{AlMe}_4]$  (90 mg, 0.19 mmol) were suspended in toluene (2 mL). Phenylacetylene (80 mg, 0.78 mmol) was added dropwise as solution in toluene (0.5 mL) affording vigorous gas evolution, which ceased with time. The reaction tube was left without stirring. After 22 h the solution was removed and the precipitate was washed with toluene (2 x 2 mL) and dried *in vacuo*. Yield 72 mg (45 %).  $M_r = 808.86$ , found C 67.63, H 7.10, N 10.34 %, C<sub>46</sub>H<sub>56</sub>N<sub>6</sub>Al<sub>3</sub>Y requires C 68.30, H 6.98, N 10.39 %. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 27 °C)  $\delta = -0.94$  (s, 6H, Al-CH<sub>3</sub>), 2.43 (s, 3H, NCH<sub>3</sub>), 2.48 (s, 15H, NCH<sub>3</sub>), 3.23 (d, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, 6H, NCH<sub>2</sub>N), 4.35 (d, <sup>3</sup>J<sub>H-H</sub> = 8.9 Hz, 2H, NCH<sub>2</sub>N), 4.43 (d, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, 4H, NCH<sub>2</sub>N), 7.31 (m, 20H, Ph). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 27 °C)  $\delta = -6.7$  (s, Al-CH<sub>3</sub>), 40.1 (s, NCH<sub>3</sub>), 77.8 (s, NCH<sub>2</sub>N), 102.0 (d, <sup>3</sup>J<sub>Y-C</sub> = 10.4 Hz, YC≡CC), 105.9 and 105.7 (s, AlC≡CC), 126.8 and 126.1 (s, MC≡CC), 127.1, 127.1 and 127.2 (s, Ph<sup>para</sup>), 128.6, 128.7 and 128.8 (s, Ph<sup>meta</sup>), 132.0, 132.1 and 132.2 (s, Ph<sup>ortho</sup>), 138.5, 139.7 and 140.1 (s, MC≡CC).

**Table 5** Crystal and refinement data for the structure determinations of compounds **1** – **7**.

compound	<b>1</b> -2.5C <sub>6</sub> H <sub>6</sub>	<b>2</b> -2.5C <sub>6</sub> H <sub>6</sub>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b> -0.5C <sub>7</sub> H <sub>8</sub> *	<b>7</b> -3C <sub>7</sub> H <sub>8</sub> **
formula	C <sub>69</sub> H <sub>63</sub> Al <sub>3</sub> Ce	C <sub>69</sub> H <sub>63</sub> Al <sub>3</sub> Er	C <sub>47</sub> H <sub>46</sub> Al <sub>3</sub> Y	C <sub>18</sub> H <sub>48</sub> N <sub>6</sub> AlY	C <sub>46</sub> H <sub>56</sub> N <sub>6</sub> AlY	C <sub>39.5</sub> H <sub>49</sub> N <sub>6</sub> Ho	C <sub>66</sub> H <sub>57</sub> N <sub>6</sub> Y
<i>M<sub>r</sub></i>	1113.25	1140.39	780.69	464.51	808.86	772.77	1023.09
measurement device	SupaNova Atlas	SopaNova Eos	SupaNova Atlas	Nonius Kappa CCD	Nonius Kappa CCD	SupaNova Atlas	Bruker AXS S8 Prospector
$\lambda$ [Å]	0.71073	0.71073	1.54178	0.71073	0.71073	0.71073	1.54178
cryst size [mm]	0.36×0.26×0.21	0.35×0.24×0.18	0.32×0.10×0.04	0.30×0.28×0.23	0.20×0.10×0.10	0.24×0.11×0.03	0.24×0.08×0.03
cryst. syst.	triclinic	triclinic	monoclinic	triclinic	orthorhombic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Cc</i>	<i>P</i> $\bar{1}$	<i>Pca</i> <sub>21</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.68428(12)	11.75475(9)	19.9766(2)	7.741(4)	14.6500(3)	9.89324(11)	12.3323(3)
<i>b</i> [Å]	14.15134(18)	14.07140(12)	11.34951(9)	13.525(5)	13.5330(2)	11.76405(15)	14.3021(3)
<i>c</i> [Å]	19.2334(3)	19.09947(18)	19.0732(2)	14.081(3)	22.6490(4)	17.8474(3)	17.6750(4)
$\alpha$ [°]	109.8356(12)	110.0187(8)	90	66.084(15)	90	70.8320(12)	84.544(1)
$\beta$ [°]	91.4955(10)	91.7994(7)	91.9325(9)	89.47(3)	90	74.4641(11)	78.388(1)
$\gamma$ [°]	90.9909(9)	91.4820(6)	90	88.39(3)	90	80.0512(10)	85.051(1)
<i>V</i> [Å <sup>3</sup> ]	2989.35(6)	2964.57(4)	4321.90(7)	1347.1(8)	4490.4(2)	1882.09(4)	3032.6(1)
<i>Z</i>	2	2	4	2	4	2	2
<i>D</i> <sub>calc</sub> [Mg m <sup>-3</sup> ]	1.237	1.278	1.200	1.145	1.196	1.364	1.120
$\mu$ [mm <sup>-1</sup> ]	0.844	1.499	2.704	2.210	1.355	2.136	1.669
$\theta$ -range [°]	3.06 to 30.00	2.74 to 30.03	4.43 to 76.81	3.02 to 30.00	2.92 to 27.46	2.88 to 27.05	2.56 to 66.91
reflns collected	96994	174048	110303	31651	44171	151040	29195
unique reflns	17411	17333	7818	12178	10185	8637	9980
<i>R</i> <sub>int</sub>	0.0242	0.0619	0.0381	-	0.067	0.0362	0.0422
reflections <i>I</i> > 2 $\sigma$ ( <i>I</i> )	16824	15863	7412	10313	8256	8263	8606
refined param.	910	677	478	248	495	458	719
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0199/0.0487	0.0270/0.0563	0.0348/0.0916	0.0651/0.1594	0.0412/0.0834	0.0145/0.0358	0.0371/0.0926
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [all data]	0.0211/0.0494	0.0322/0.0579	0.0377/0.0947	0.0824/0.1678	0.0602/0.0899	0.0160/0.0365	0.0441/0.0957
$\Delta\rho_{\max/\min}$ [e Å <sup>-3</sup> ]	0.66/−0.39	0.94/−0.85	0.53/−0.40	2.22/−1.34	0.54/−0.46	0.63/−0.32	0.35/−0.57
CCDC no.	965748	965749	965750	965751	965752	965753	965754

\*Disorder of the toluene molecule, C(37) to C(43) over the inversion center.

\*\* The crystal includes three highly disordered toluene molecules. They were treated with the SQUEEZE procedure of the Olex2 program.<sup>[16]</sup> The sum formula and further calculations disregard this electron density. Disorder of C(49) to C(66) over two positions (65:35).

**Crystal structure determination.** Suitable crystals were selected, coated with paratone oil and mounted onto the diffractometer. For structure solution and refinement, SHELX-97 was used.<sup>[15]</sup> Crystal and refinement details, as well as CCDC numbers are provided in Table 5.

**Supporting Information** (see footnote on the first page of this article): Selected bond length and angles of compound **1** and **2**; <sup>13</sup>C and <sup>1</sup>H/<sup>13</sup>C HMQC spectra of **2**.

## Acknowledgement

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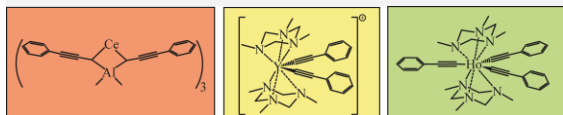
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N. W. Mitzel\* ..... **Page No. – Page No.**

### **Alkynyl compounds of the rare-earth metals**

## **Erklärung**

Hiermit erkläre ich, dass ich die vorliegende Dissertation

**Anthracen-basierte Poly-Lewis-Säuren  
Synthese, Charakterisierung und Wirt-Gast-Chemie**

selbstständig verfasst und dazu keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

Ich erkläre außerdem, dass diese Dissertation weder in gleicher noch in anderer Form bereits in einem anderen Prüfungsverfahren vorgelegen hat.

Bielefeld, im Mai 2014

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Jan-Hendrik Lamm