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Aromaticity

Isolation of a 16π-Electrons 1,4-Diphosphinine-1,4-diide with a Planar C_4P_2 Ring

Dennis Rottschäfer,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Tetiana Sergeieva,[b] Diego M. Andrada,*[b] and Rajendra S. Ghadwal*[a]

Dedicated to Professor F. Ekkehardt Hahn on the occasion to his 65th birthday

Abstract: Herein, we report the first 1,4-diphosphinine-1,4-diide compound $[(\mathrm{ADC^{Ph}})\mathrm{P}]_2$ (**5-Ph**) ($\mathrm{ADC^{Ph}} = \mathrm{PhC\{(NDipp)C\}_2}$; Dipp = 2,6-$i\mathrm{Pr_2C_6H_3}$) derived from an anionic dicarbene ($\mathrm{ADC^{Ph}}$) as a red crystalline solid. Compound **5-Ph** containing a 16π-electron planar fused-tricyclic ring system was obtained by the 4e reduction of $[(\mathrm{ADC^{Ph}})\mathrm{PCl_2}]_2$ (**4-Ph**) with Mg (or KC_8) in a quantitative yield. Experimental and computational results imply that the central 8π-electrons C_4P_2 ring of **5-Ph**, which is fused between two 6π-electrons C_3N_2 aromatic rings, is antiaromatic. Thus, each of the phosphorus atoms of **5-Ph** has two electron-lone-pairs, one in a p-type orbital is in conjugation with the C=C bonds of the C_4P_2 ring, while the second resides in a σ-symmetric orbital. This can be shown with the gold complex $[(\mathrm{ADC^{Ph}})\mathrm{P(AuCl)_2}]_2$ (**6-Ph**) obtained by reacting **5-Ph** with $(\mathrm{Me_2S})\mathrm{AuCl}$. A mixture of **5-Ph** and **4-Ph** undergoes comproportionation in the presence of $MgCl_2$ to form the intermediate oxidation state compound $[(\mathrm{ADC^{Ar}})\mathrm{P}]_2(\mathrm{MgCl_4})$ (**7-Ph**), which is an aromatic species.

The concept of aromaticity, originally proposed by Kekulé[1] in 1865 after Faraday discovered benzene,[2] has undergone a significant transformation (see thematic issues),[3] and continues to drive experimental and theoretical pursuits beyond classical organic chemistry.[4] The early criterion of aromaticity, known as Hückel rules,[5] was attributed to planar cyclic organic molecules with conjugated $4n+2\pi$-electrons. In 1967, Breslow[6] introduced the concept of antiaromaticity to describe the destabilization of cyclic conjugated systems containing $4n$ π-electrons.[7] Benzene (**I**), cyclopentadienyl anion (**II**), cyclobutadiene (**III**), and cyclopentadienyl cation (**IV**) are typical (anti)aromatic examples (Scheme 1).[8] **I**–**IV** have also been intriguing structural motifs in fundamental main-group chemistry.[9] *s*-Indacene (**V**) (E = CH, Scheme 1) is a highly fascinating species that can be regarded as a [12]annulene perturbed by two σ-bonds or a molecule obtained by merging two fulvenes. This formally 12π-electrons antiaromatic system has attracted significant attention in synthetic, theoretical,[10] and materials science.[11] The parent molecule **V** (E = CH, R = H) is, however, unstable but can be kinetically stabilized with bulky substituents (R = *t*Bu).[12] As expected, 2e reduced or oxidized *s*-indacene derivatives formally containing $4n+2\pi$-electrons more stable than *s*-indacene.[13]

Phosphorus is often referred to as a carbon copy[14] in organophosphorus chemistry, thus a "CR" (R = H, alkyl or aryl group) unit of an organic molecule can formally be replaced by a phosphorus atom. While the calculated P=C π-bond strength ($43\ \mathrm{kcal\,mol^{-1}}$) is lower than the C=C π-bond of ethene ($65\ \mathrm{kcal\,mol^{-1}}$)[15] the conjugative properties of both P=C and C=C bonds are comparable.[16] In 1966, Märkl et al. reported the first stable phosphabenzene[17] derivative (2,3,6-$\mathrm{Ph_3C_5P}$).[18] Since then many phosphorus containing aromatic heterocycles,[19] including 1,4-diphosphinines,[20] have been isolated and structurally characterized. Hafner et al. reported two phosphorus compounds in which one (E = P and CH)[21] or both (E = P)[22] of the central CH moieties of *s*-indacene **V** (R = *t*Bu) were formally replaced by a phosphorus atom. In 2017, Streubel et al. reported two 1,4-diphoshinine compounds **VI** based on 1,3-imidazole-2-thione units.[23] These formally 14 π-electrons aromatic systems **VI** have been shown to exhibit interesting reactivity.[24] We recently developed anionic dicarbenes ($\mathrm{ADC^{Ar}}$) (**VII**)[25] (see **2-Ar** in Scheme 2) based on a 1,3-imidazole framework that readily react with white phosphorus to form mesoionic 1,2,3-triphosphol-2-ide compounds (**VIII**).[26]

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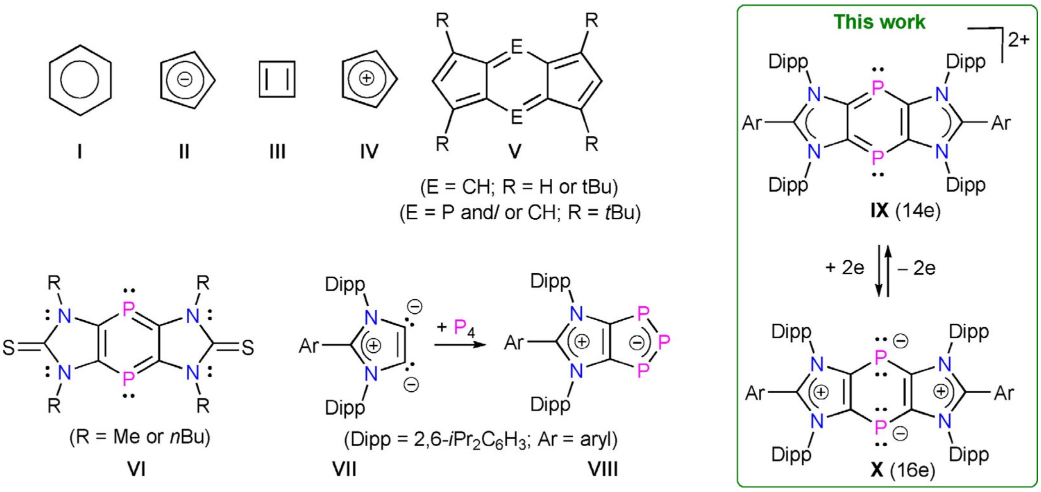
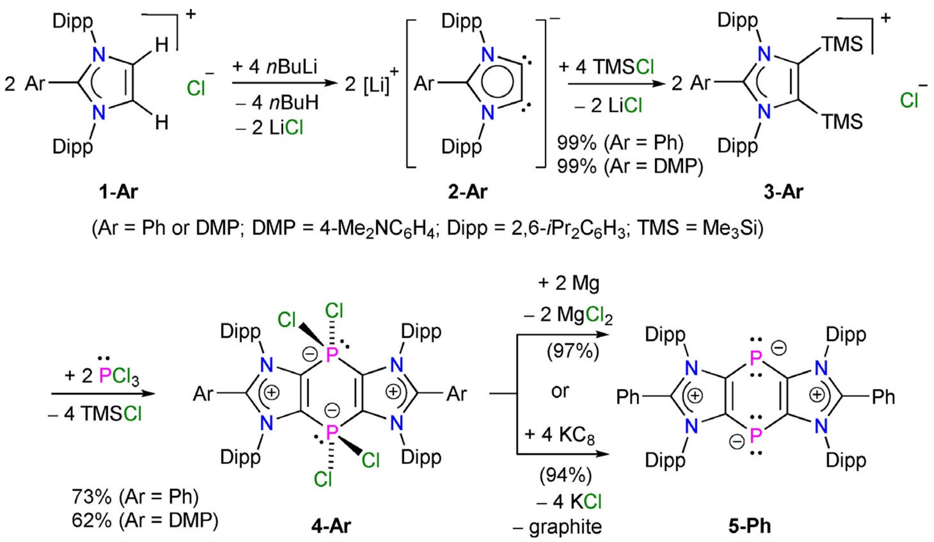
[a] Dr. D. Rottschäfer, B. Neumann, Dr. H.-G. Stammler, Dr. R. S. Ghadwal
Molecular Inorganic Chemistry and Catalysis
Inorganic and Structural Chemistry, Center for Molecular Materials
Faculty of Chemistry, Universität Bielefeld
Universitätsstrasse 25, 33615 Bielefeld (Germany)
E-mail: rghadwal@uni-bielefeld.de
Homepage: http://www.ghadwalgroup.de

[b] Dr. T. Sergeieva, Dr. D. M. Andrada
Inorganic and Computational Chemistry Group
Allgemeine und Anorganische Chemie, Universität des Saarlandes
Campus C4.1, 66123 Saarbrücken (Germany)
E-mail: diego.andrada@uni-saarland.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.202003617.



Scheme 1. Typical examples of aromatic (benzene **I**, cyclopentadienyl anion **II**) and antiaromatic (cyclobutadiene **III**, cyclopentadienyl cation **IV**, *s*-indacene **V-E**) systems. 1,3-Imidazole-2-thione derived 1,4-diphosphinine derivative (**VI**). Anionic dicarbenes (ADCs) (**VII**) and derived 1,2,3-triphosphol-2-ide compounds (**VIII**). The counter cation for **VII** and anions for **IX** are omitted for the sake of clarity.



Scheme 2. Synthesis of C_4P_2 heterocycles **4-Ar**. Reduction of **4-Ph** with Mg (or KC_8) to **5-Ph**.

This promoted us to reason that corresponding C_4P_2 ring compounds with formally 4n (**X**) as well as 4n+2 π-electrons (**IX**) should be synthetically accessible with ADC^{Ar} (**VII**).

Herein, we report the first 1,4-diphosphinine-1,4-diide compound $[(ADC^{Ph})P]_2$ (**5-Ph**) ($ADC^{Ph}=PhC\{(NDipp)C\}_2$; Dipp=2,6-$iPr_2C_6H_3$), a representative of the 16π-e compound **X** (Scheme 1), with a planar C_4P_2 ring as a crystalline solid and explore its structure and reactivity.

Results and Discussion

The desired precursors $Li[ADC^{Ar}]$ (**2-Ar**) were prepared[25] by the double deprotonation of the C2-arylated 1,3-imidazolium salts $(IPr^{Ar})Cl$ (**1-Ar**) ($IPr^{Ar}=ArC\{(NDipp)CH\}_2$; Ar=Ph or DMP=4-$Me_2NC_6H_4$) with *n*BuLi (Scheme 2). Treatment of **2-Ar** with PCl_3 to give **4-Ar** was, however, unsuccessful and led to the formation of an intractable mixture of products. Therefore, we decided to develop an alternative synthetic strategy for **4-Ar**. Interestingly, **2-Ar** readily react with TMSCl to afford the bis-silylated derivatives **3-Ar** in almost quantitative yields. **3-Ar** serve as ADC^{Ar} transfer agents and afford the desired chlorides **4-Ar** on treatment with PCl_3. The only side product TMSCl can be removed under vacuum. **4-Ar** are insoluble in toluene, THF, and fluorobenzene but dissolved freely in DCM and acetonitrile, indicating their zwitterionic properties. Treatment of a THF suspension of **4-Ph** with magnesium turnings (or KC_8) led to the formation of a dark red suspension. Compound **5-Ph** was isolated as a red crystalline solid in 97% yield (Scheme 2). **5-Ph** is extremely air sensitive but stable under an inert (N_2 or Ar) gas atmosphere.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4-Ar** and **5-Ph** exhibit expected resonances for the ADC^{Ar} moieties. The $^{31}P\{^1H\}$ NMR spectra of **4-Ar** (Ar = Ph, −25 ppm; DMP, −17 ppm) show a singlet, which are high-field shifted with respect to those of [(iMIC^{Ar})PPh(Cl)]Br (iMIC^{Ar} = ArC{(NDipp)$_2$CCH}; Ar = Ph 40, DMP 41 ppm).[27] They are also high-field shifted compared to that of the hypercoordinate adduct (IPr)PCl$_3$ (16.9 ppm) (IPr = C{(NDipp)CH}$_2$.[28] This may be due to the stronger σ-donor property of ADC^{Ar} scaffolds than that of IPr.[27] The ^{13}C{^{1}H} NMR spectrum of **5-Ph** shows a doublet of a doublet at 154.1 ppm ($^{1}J_{P,C}$ = 36 Hz, $^{2}J_{P,C}$ = 23 Hz) for the backbone carbon atoms of ADC^{Ph}. The ^{31}P{^{1}H} NMR spectrum of **5-Ph** exhibits a sharp singlet at −48 ppm, which is 23 ppm high-field shifted compared to that of **4-Ph** (−25 ppm). The ^{31}P{^{1}H} NMR signal of **5-Ph** compares well with those of NHC-stabilized arylphosphinidenes (NHC)PAr (−49 to −77 ppm)[29] as well as Robinson's NHC-stabilized diphosphorus compound (IPr)$_2$P$_2$ (−53 ppm).[30] This is, however, considerably high-field shifted than those of Streubel's 1,4-diphosphinine compounds **VI** (ca. 77 ppm).[23]

The solid-state molecular structure of **4-Ph** (Figure 1) reveals the presence of a C$_4$P$_2$ framework. Both phosphorus atoms are four-coordinated, each having two chlorine atoms. One of the chlorine atoms is, however, remotely located from the phosphorus atom as indicated by a considerably large P1–Cl2 distance (3.14 Å). The other P1–Cl1 bond length (2.09(1) Å) is within the range of those of (IPr)PCl$_3$ (2.02–2.49 Å).[28] The P1–C1 bond length of **4-Ph** (1.820(2) Å) is comparable with the P–C single bond length of (IPr)PCl$_3$ (1.87 Å)[28] as well as of cyclic organophosphorus compounds (1.82–1.84 Å) (Table 1).[23,31] The C1–C2 bond length (1.361(3) Å) and N1-C5-N2 bond angle (106.4(2)°) of **4-Ph** are similar to those of **1-Ph** (1.353(2) Å and 106.4(2)°, see the Supporting Information).[32]

The solid-state molecular structure of **5-Ph** (Figure 1) contains 1.5 molecules per asymmetric unit and shows an almost planar six-membered C$_4$P$_2$ ring with two-coordinated phosphorus atoms. The C–P bond lengths of **5-Ph** (1.788(1)-1.796(1) Å)

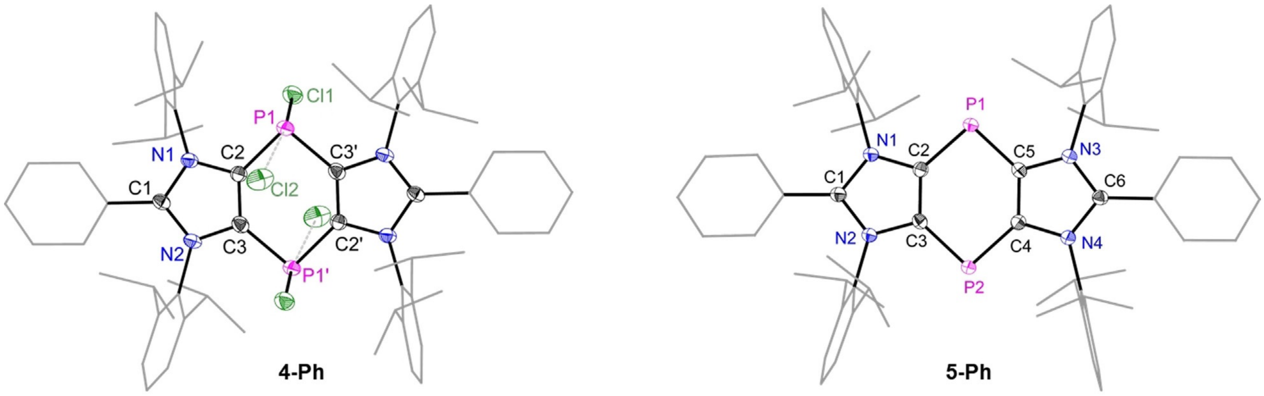
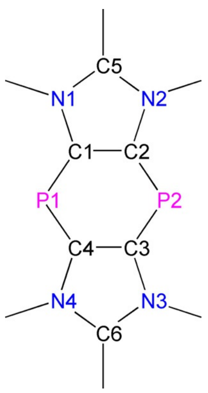


Figure 1. Solid-state molecular structures of **4-Ph** (which has a center of inversion) and **5-Ph**. Hydrogen atoms (and second molecule and toluene solvent molecules for **5-Ph**) are omitted for clarity.

Table 1. Selected experimental and calculated geometries [optimized at the BP86-D3(BJ)/SVP level of theory] bond lengths (Å) and angles (°) of **4-Ph**, **5-Ph**, **6-Ph**, and **7-Ph**.

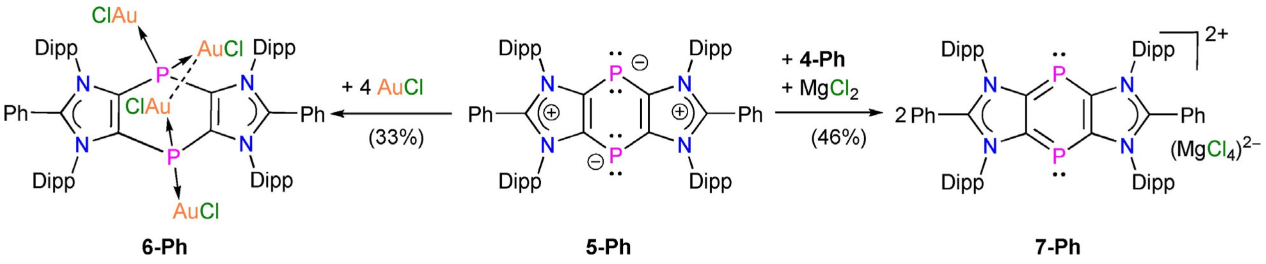
		P1–C1 P1–C4	P2–C2 P2–C3	N1–C1 N1–C5	N2–C2 N2–C5	C1–C2 C3–C4	C1-P1-C4 C2-P2-C3	P1-C1-C2 P2-C2-C1
	**4-Ph**	1.820(2) 1.829(2) [1.835]	1.820(2) 1.829(2) [1.835]	1.395(3) 1.360(3) [1.396]	1.385(3) 1.352(2) [1.396]	1.361(3) 1.361(3) [1.384]	95.5(1) 95.5(1) [94.1]	131.4(2) 131.4(2) [132.0]
	5-Ph	1.788(1) 1.791(1)	1.788(1) 1.794(1)	1.385(2) 1.377(2)	1.388(2) 1.375(2)	1.395(2) 1.393(2)	95.1(1) 94.6(1)	132.3(1) 131.8(1)
	5-Ph[a]	1.796(1) 1.793(1) [1.800]	1.796(1) 1.793(1) [1.800]	1.387(2) 1.388(2) [1.396]	1.388(2) 1.376(2) [1.396]	1.391(2) 1.391(2) [1.414]	94.4(1) – [94.3]	132.4(1) – [132.7]
	6-Ph	1.814(4) 1.825(4)	1.814(4) 1.825(4)	1.386(5) 1.350(5)	1.397(4) 1.356(5)	1.369(5) –	96.0(2)	125.1(3) 125.0(3)
	7-Ph	1.748(2) 1.747(2) [1.769]	1.748(2) 1.747(2) [1.769]	1.408(3) 1.344(3) [1.403]	1.406(3) 1.341(3) [1.403]	1.398(3) [1.422]	96.5(1) – [94.7]	132.7(2) 130.7(2) [132.8]

[a] Second molecule of the asymmetric unit.

are smaller compared to those of **4-Ph** (1.820(2) Å) as well as of phosphinidene adduct (iMIC^{Ph})PPh (1.823 Å),[31,33] indicating that the C_4P_2 ring of **5-Ph** contains a delocalized π-electron system. These bond lengths are nonetheless longer compared to those of 6π-electrons C_4P_2 aromatic species **VI** (av. 1.74 Å),[23] in which the aromaticity augments π-conjugation. Compound **5-Ph** has two additional electrons compared to that of **VI**,[23] which may occupy a π-type (see below) non-bonding or anti-bonding molecular orbital, resulting in a slight elongation of the C–P bonds of **5-Ph**. The C2–C3 1.395(2) and C4–C5 1.392(2) Å bond lengths of **5-Ph** are slightly longer compared to those of **4-Ph** (1.361(3) Å) but comparable with those of **VI** (av. 1.40 Å). The C1-P1-C4 bond angles (Table 1) of **5-Ph** (av. 94.8°) are acute than that of **4-Ph** (95.5°) and **VI** (R = Me, 97.6°; *n*Bu, 97.1°).[23]

Each of the phosphorus atoms of **5-Ph** has two lone-pairs, one resides in a σ-type orbital whereas the other is located in a π-type orbital that is aligned parallel to the π-orbitals of the C=C bonds (see below). Indeed, **5-Ph** readily reacts with $(Me_2S)AuCl$ at room temperature to form the complex **6-Ph** (Scheme 3), in which each phosphorus atom binds to two AuCl entities. Thus, **5-Ph** is an 8π-electron C_4P_2 ring system and may formally be considered as antiaromatic (see below). Consequently, its two-electron oxidation to a 6π-electrons aromatic C_4P_2 ring system should be a thermodynamically favorable process. A related putative $[(ADC^{Ph})PCl]_2$ system can in principle be derived by two-electron reduction of **4-Ph** (Scheme 2). However, all attempts to prepare $[(ADC^{Ph})PCl]_2$ by reducing **4-Ph** with different agents, as evidenced by the formation of an intractable mixture of products in each case, failed. Interestingly, a 1:1 mixture of **5-Ph** and **4-Ph** in the presence of $MgCl_2$ smoothly undergoes comproportionation to form the anticipated product **7-Ph** as an orange crystalline solid (Scheme 3).

Solution ^{1}H, ^{13}C, and ^{31}P NMR data of **6-Ph** and **7-Ph** are fully consistent with their solid-state molecular structures (Figure 2) determined by X-ray diffraction. The ^{31}P{^{1}H} NMR resonance of **7-Ph** (16.5 ppm) is downfield shifted compared to that of **5-Ph** (−48 ppm), which is, however, still at a higher field with respect to those of the aromatic C_4P_2 systems **VI** (ca. 77 ppm).[23] Like **5-Ph**, the C_4P_2 ring of [**7-Ph**]$^{2+}$ (Figure 2) is planar. The C2–P1 (1.748(2) Å) and C2–C3 (1.398(3) Å) bond lengths and C1-P1-C4 (96.5(1)°) internal angle (Table 1) of [**7-Ph**]$^{2+}$ are comparable with those of the related 6π-electron aromatic systems **VI**.[23] The ^{31}P{^{1}H} NMR spectrum of **6-Ph** exhibits one sharp singlet at $\delta = -37.3$ ppm. Unlike **5-Ph** and [**7-Ph**]$^{2+}$, the C_4P_2 ring of **6-Ph** is puckered (Figure 2). In **6-Ph**, the P–C (1.814(4) and 1.825(4) Å) bond lengths are larger compared to those of **5-Ph** and [**7-Ph**]$^{2+}$ (Table 1). Moreover, the C2–C3 bond length of **6-Ph** (1.369(5) Å) is smaller than those of **5-Ph** and [**7-Ph**]$^{2+}$ but comparable to that of **4-Ph**. Interestingly, two of the gold atoms of AuCl units of **6-Ph** show aurophilic behavior as evident by a short Au···Au distance (3.026(1) Å), while the remaining two AuCl fragments point away from each other. The calculated τ_4 parameter ($\tau_4 = 1$ for a perfect tetrahedron) for the P



Scheme 3. Reaction of **5-Ph** with $(Me_2S)AuCl$ to **6-Ph**. Comproportionation of **5-Ph** and **4-Ph** into **7-Ph**.

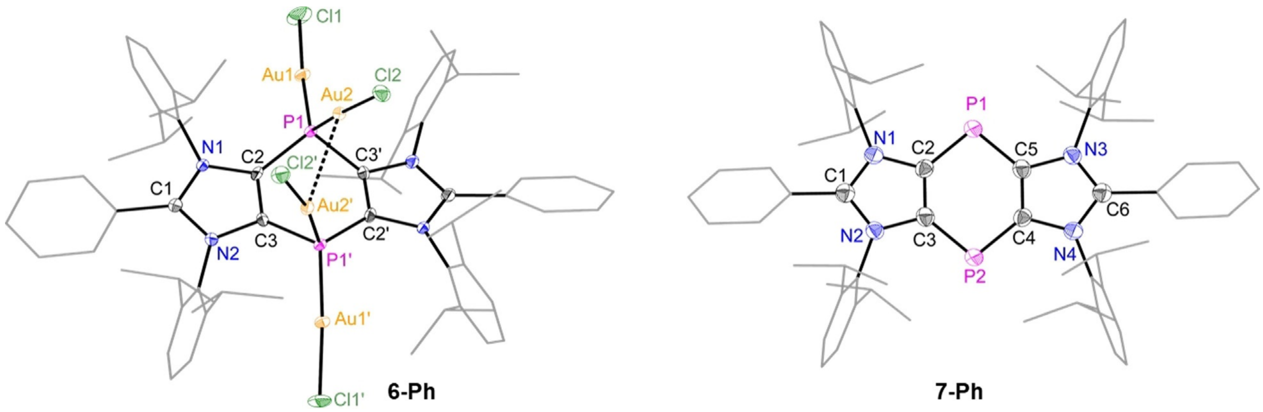


Figure 2. Solid-state structures of **6-Ph** and [**7-Ph**]$^{2+}$. H atoms (and CH_2Cl_2 solvent molecules for **6-Ph**, and $[MgCl_4]^{2-}$ counter anion and PhF solvent molecules for **7-Ph**) are omitted for clarity. The Au2–Au2′ bond length: 3.026(1) Å.

atoms of **6-Ph** ($\tau_4 = 0.88$) suggests a distorted tetrahedral geometry,[34] where the central C_4P_2 ring adopts a boat-like structure. The formation of a boat-like conformation of the six-membered C_4P_4 ring of **6-Ph** is most likely favored by the aurophilic interaction between the two gold atoms (Au2–Au2′ bond length = 3.026(1) Å).[35]

To gain further insight into the electronic structures of **5-Ph** and **7-Ph**, we performed DFT calculations at the BP86-D3(BJ)/def2-SVP level of theory (see the Supporting Information for details). The optimized geometries of **5-Ph** and **7-Ph** (Figure S36) are in good agreement with their solid-state molecular structures determined by X-ray diffraction (Table 1). The singlet-triplet gap ($\Delta E_{S\text{-}T}$) for **5-Ph** (14.7 kcal mol^{-1}) and **7-Ph** (35.3 kcal mol^{-1}) is quite different and suggests an enhanced stability of **7-Ph**. A comparison with different functionals also reveals a similar trend (Tables S4 and S9). The frontier KS (Kohn–Sham) molecular orbitals of **5-Ph** reveal two lone-pairs at each phosphorus atom (Figure 3). The HOMO-3 and HOMO-14 are lone-pair orbitals at the phosphorus atoms with σ-symmetry, whereas HOMO and HOMO-1 are the lone-pair of phosphorus in the π-system. The HOMO-2 and HOMO-15 constitute a constructive and unconstructive combination of the orbitals at the two imidazole π-ring systems and contribute to the central C_4P_2 ring. Consistent with the removal of two electrons from **5-Ph**, the HOMO of **5-Ph** becomes the LUMO of **7-Ph**, leaving only the 6π-electrons on the C_4P_2 moiety (see the Supporting Information). CASSCF(12,12)/cc-pVTZ calculations for a model system **5M**, in which the Dipp substituents of **5-Ph** have been replaced by methyl groups were performed (Figure S55). Our active space includes the three π-orbitals of the two imidazole rings and the lone-pairs at the two phosphorus atoms. The CI vector has a contribution of 0.810 for the (222222000000) configuration and 0.054 for the (222220200000), thus confirming a multiconfiguration nature of **5M** (Table S13). The diradical character calculated with these values according to Bachler et al. was 10.8 % (Table S15).[36]

The localization of the orbitals by NBO analysis for **5-Ph** (Figure S43) shows the presence of one σ-lone-pair on each of the P atoms, four P–C σ-bonding orbitals (with 34.2 % contribution from the P atom and 65.8 % from the C atom), and two P=C bonding π-orbitals (with 64.3 % contribution from the P atom and 35.7 % from the C atom). However, both P=C π-orbitals 0f **5-Ph** are polarized towards the phosphorus atom (Figure S43). Natural population analyses (NPA) for **5-Ph** indicate a positive charge of +0.32e on the P atoms, while for **7-Ph** it is +0.71e (Figure 4). Computed Wiberg bond indices (WBIs) for P–C (1.10 a.u.) and C–C (1.31 a.u.) bonds of **5-Ph** indicate a weaker conjugation in comparison with **7-Ph** (P–C 1.20 a.u.; C–C 1.29 a.u.). Natural resonance theory (NRT) also supports this depiction (Figure 4 and Figure S45). The main resonant structures **A** and **B** (weight 27 % each) of **5-Ph** feature two lone-pairs at one P atom and one lone-pair with a C=P double bond on the other P atom. The resonance structures **C** and **D** (weight 11 % each) also have two lone-pairs on one P and one lone-pair and a double bond C=P on the other. For **7-Ph**, the Kekulé resonance structure (**C**) contributes to 17 %, which is slightly lower than that of **A** and **B** (weight 20 % each) and **D** (weight 25.6 %). Both P atoms in structures **C** and **D** of **7-Ph** feature a C=P double bond and a lone-pair of electrons.

We also analyzed the electron density distribution of the models systems **5M** and **7M** (where Dipp substituents of **5-Ph** and **7-Ph** were replaced by Me groups) with the AIM (atoms in molecules)[37] method and Electron Localization Function (ELF).[38] The Laplacian distribution $\nabla^2\rho(r)$ in the C_4P_2 ring and perpendicular to it are depicted in Figure 5 together with the ELF (see also Figures S46–S49). Dashed red lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid blue lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The Laplacian plot shows an electron accumulation on the phosphorus atoms both in the σ- and π-system for **5M** while for **7M** it is mostly localized on the σ-system. Electron density at the C–P bond critical point (ρ_{BCP}) and the corresponding delocalization index

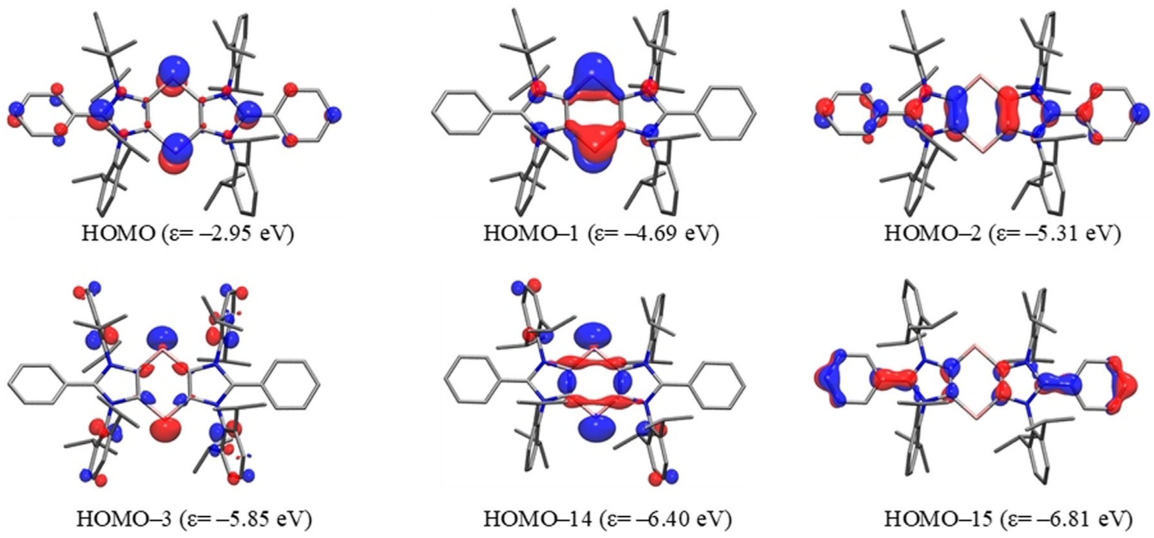

HOMO (ε= −2.95 eV)
HOMO–1 (ε= −4.69 eV)
HOMO–2 (ε= −5.31 eV)
HOMO–3 (ε= −5.85 eV)
HOMO–14 (ε= −6.40 eV)
HOMO–15 (ε= −6.81 eV)

Figure 3. Selected KS molecular orbitals (BP86-D3(BJ)/def2-SVP) of **5-Ph**. Hydrogen atoms are omitted for clarity.

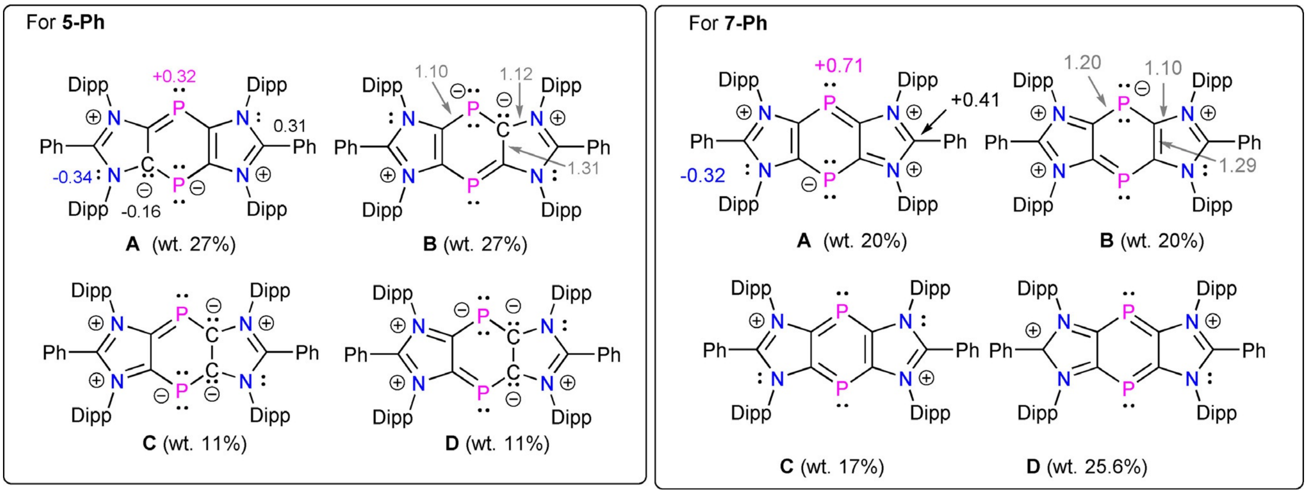


Figure 4. Selected resonance forms, NPA charges, and WBIs for **5-Ph** and **7-Ph** (for the cationic part) calculated at the BP86-D3(BJ)/def2-SVP level of theory. NRT was performed on the central three rings. Structures differing only on the NCN moiety have been taken together. Symmetry equivalent structures have been summed up.

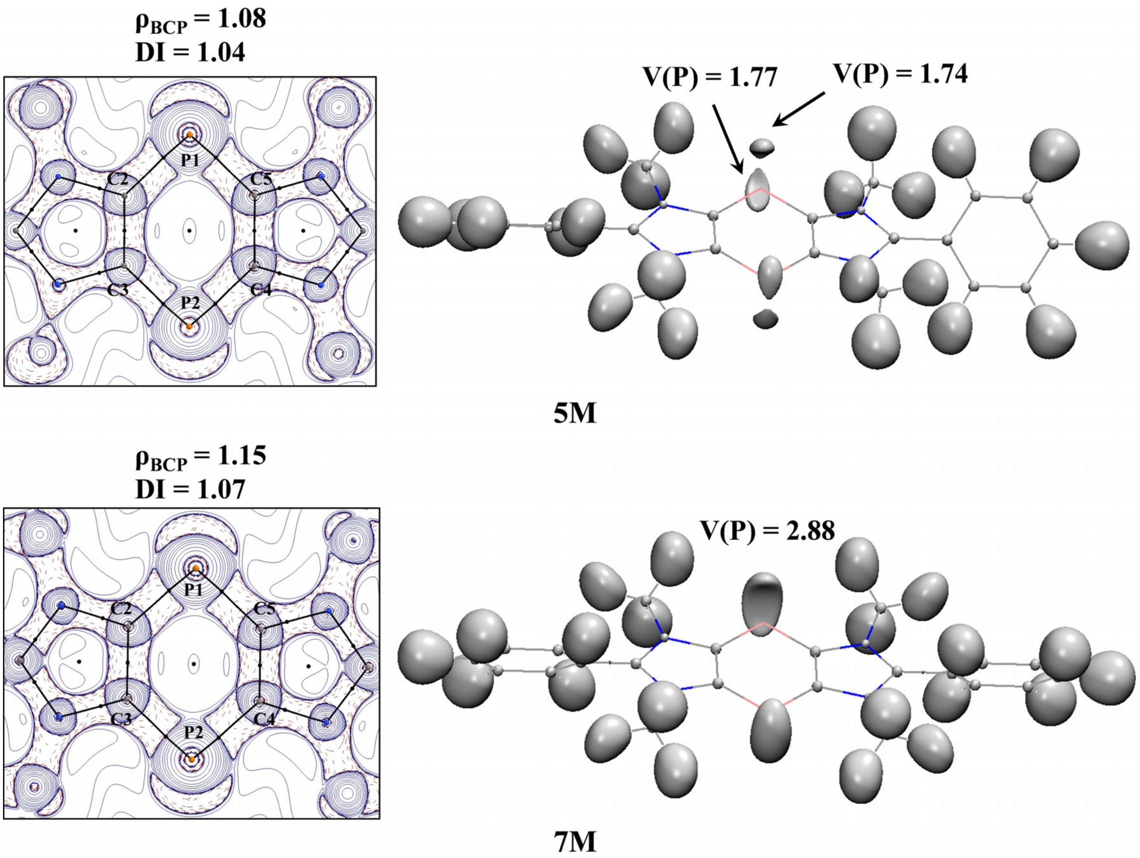


Figure 5. Laplacian distribution of the electron density and ELF (isosurface 0.952) of **5M** and **7M**. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the P1-C2-C3-P2-C4-C5 plane. Dashed red lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid blue lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid lines connecting the atomic nuclei are the bond paths and the small dots are the bond critical points and ring critical point. The electron density on the C–P bond critical point (ρ_{BCP} in e Å^{-3}) and delocalization index (DI). ELF numbers are in electrons.

(DI) are shown in Figure 5. The comparison of the ρ_{BCP} between **5M** (0.16) and **7M** (0.17) exhibits a small difference, while the delocalization index suggest slightly lower delocalization for **5M** (1.04) than for **7M** (1.07), which is in good agreement with the NBO results. ELF for **5M** exhibits the presence of two basins on each of the P atoms with a population of 1.77 e and 1.74 e. In contrast, **7M** has only one basin on each of the P atoms with a population of 2.88 e.

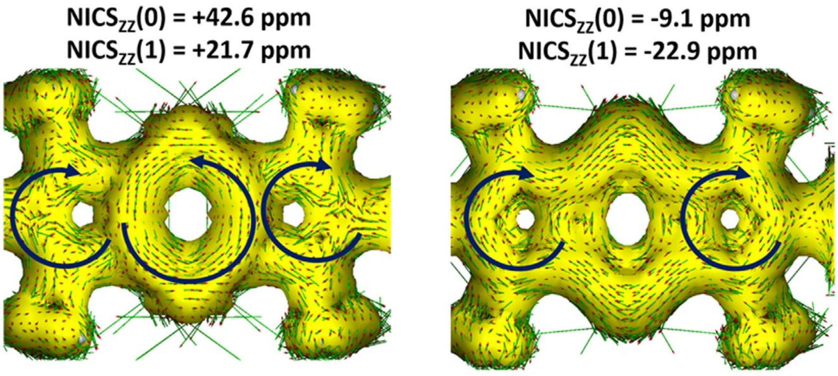
Compounds **5-Ph** and **7-Ph** may also be considered as conjugated fused C_3N_2-C_4P_2-C_3N_2 ring systems comprising 16 or 14 π-electrons, respectively. Therefore, according to the Hückel's rules, **5-Ph** and **7-Ph** may formally be considered as an antiaromatic and an aromatic system, respectively. To probe the π-conjugation and magnetic properties of **5-Ph** and **7-Ph**, we performed AICD (anisotropy of induced current density),[39] NICS (nucleus-independent chemical shift),[7e] and MCI (multicenter bond index)[40] analyses for the model systems **5M** and **7M** (see the Supporting Information for details). The $NICS_{ZZ}(1)$ value (in ppm) for the C_4P_2 ring of **5M** (+21.7) is positive while the same for the neighboring C_3N_2 rings (−3.4) is negative. In contrast, the $NICS_{ZZ}(1)$ values for the central C_4P_2 (−22.9) as well as the peripheral C_3N_2 rings (−20.6) of **7M** are negative. These values are lower than those of *s*-indacene analogues, which is expected because of the lower π-conjugation in cyclic compounds containing heteroatoms such as N or P.[41] The MCI values show weaker delocalization on the central C_4P_2 ring of **5M** (0.007) than **7M** (0.023). The AICD plots of **5M** and **7M** reveal the tropicity (showing the ring current) for each system (Figure 6). While both the peripheral C_3N_2 rings of **5M** show two local diatropic ring currents, but the ring current at the central C_4P_2 ring is paratropic. This indicates that the C_4P_2 ring of **5M** is antiaromatic, which is fused between two aromatic C_3N_2 rings. In contrast, **7M** exhibits a global diatropic current on the periphery of the C_3N_2 and C_4P_2 rings, indicating a fully aromatic system.

Conclusions

In summary, we have reported the first 1,4-diphosphinine-1,4-diide (**5-Ph**) derived from an anionic dicarbene (ADC^{Ph}). The central six-membered C_4P_2 ring of a 16π-electron compound **5-Ph** is planar and has paratropic ring current and hence may be considered as an antiaromatic system. Indeed, **5-Ph** can be readily oxidized to a rather stable molecule **7-Ph** comprising a 14π electron aromatic system. Each of the phosphorus atoms of **5-Ph** has two lone-pairs, one lone-pair remains on the phosphorus atom in a non-bonding orbital, whereas the second lone-pair resides in a π-orbital that is parallel to π-orbitals of the adjacent C=C bonds. This has been shown with the isolation of the gold(I) compound **6-Ph**, in which each of the phosphorus atoms forms two 2c–2e bonds with AuCl moieties. This study reveals that ADCs are well endowed to stabilize unique molecular systems with intriguing electronic structure and thus provide a new platform for the designing of new molecules, which may be useful in developing advanced materials for emerging applications. Further studies are currently underway in this laboratory to access challenging main-group compounds and to explore their structure, reactivity, and physical properties.

Experimental Section

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N_2) using standard Schlenk techniques or a glove-box (MBraun LABMasterPro). Organic solvents were dried over appropriate drying agents, distilled, and stored over 3 Å molecular sieve. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in δ, ppm) are referenced to the residual solvent signal(s): $CDCl_3$ (^1H, 7.26; ^{13}C, 77.16), CD_2Cl_2 (^1H, 5.32; ^{13}C, 53.84), CD_3CN (^1H, 1.94; ^{13}C, 1.32), C_6D_6 (^1H, 7.16; ^{13}C, 128.06), and $[D_8]THF$ (^1H, 3.58; ^{13}C, 67.21 ppm).[42] Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in acetonitrile or THF and introduced by static nano-ESI using in house pulled glass emitters. Nitrogen served both as a nebulizer as well as a dry gas and was generated by a Bruker nitrogen generator NGM 11. Helium served as a cooling gas for the ion trap. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as a calibration standard. UV/Vis spectra were recorded on a ThermoFisher Evolution 300 spectrophotometer. Elemental analyses were performed at the Inorganic and Structural Chemistry Department, Faculty of Chemistry, Universität Bielefeld. Amberlite® IRA-402, Cl Form (Sigma–Aldrich) and *n*BuLi (2.5 M in hexanes, Sigma Aldrich) were used as supplied. TMSCl (TMS = Me_3Si) and PCl_3 were distilled prior to use and stored under N_2. The C2-arylated 1,3-imidazolium bromides ($(IPr^{Ar})Br$ (Ar = Ph or DMP = 4-$Me_2NC_6H_4$) were synthesized according to the reported method.[32,43] The chloride derivatives $(IPr^{Ar})Cl$ (**1-Ar**) (Ar = Ph or DMP) were prepared by the halide-exchange method using $(IPr^{Ar})Br$ and Amberlite® IRA-402 resin (Cl-form).



5-M **7-M**

Figure 6. AICD plots at isosurface values 0.02 a.u for model compounds **5M** and **7M**. In **5M**, the peripheral C_3N_2 rings have a clockwise (diatropic) circulation while the central C_4P_2 ring has a counterclockwise (paratropic) circulation. All three rings of **7M** have clockwise (diatropic) circulation.

Synthesis of [(TMS)$_2$-ADC^{Ph}]Cl (3-Ph): To a 50 mL THF suspension of **1-Ph** (2.0 g, 4.0 mmol) was added *n*BuLi (2.5 M in hexanes, 3.5 mL, 8.8 mmol) at $-50\,^{\circ}$C. The resulting brown solution of in situ generated Li(ADC^{Ph}) (**2-Ph**)[3] was allowed to warm to room temperature (rt). After 1 h stirring, TMSCl (1.3 mL, 9.9 mmol) was added to this solution at $-20\,^{\circ}$C and the reaction mixture was stirred overnight at rt. The volatiles were removed and the residue was suspended in 20 mL dichloromethane (DCM). Filtration through a plug of Celite and then drying the filtrate in vacuo afforded **3-Ph** as a colorless solid in a quantitative yield (2.6 g). Elemental analysis (%), calcd for $C_{39}H_{57}ClN_2Si_2$ (645) (**3-Ph**): C 72.57, H 8.90, N 4.34, found: C 72.29, H 8.78, N 4.31. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 7.66$ (t, $J = 7.9$ Hz, 2 H, *p*-C$_6$*H*$_3$), 7.39 (t, $J = 8.0$ Hz, 1 H, *p*-C$_6$*H*$_5$), 7.34 (d, $J = 7.9$ Hz, 4 H, *m*-C$_6$*H*$_3$), 7.14 (dd, $J = 8.6$, 7.6 Hz, 2 H, *m*-C$_6$*H*$_5$), 6.70 (d, $J = 9.8$ Hz, 2 H, *o*-C$_6$*H*$_5$), 2.39 (sept, $J = 6.8$ Hz, 4 H, C*H*(CH$_3$)$_2$), 1.33 (d, $J = 6.8$ Hz, 12 H, CH(C*H*$_3$)$_2$), 0.79 (d, $J = 6.8$ Hz, 12 H, CH(C*H*$_3$)$_2$), 0.18 ppm (s, 18 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): $\delta = 148.0$ (NCN), 146.5 (NCSi), 144.8, 133.1, 132.9, 131.7, 129.4, 129.2, 126.1, 121.0 (C$_6$H$_3$, C$_6$H$_5$), 29.3 (CH(CH$_3$)$_2$, 24.3, 23.3 (CH(CH$_3$)$_2$), 2.0 ppm (Si(CH$_3$)$_3$). ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 298 K): $\delta = -4.8$ ppm. MS (ESI pos.): $m/z = 609.4$ [(**3-Ph**)-Cl]$^+$, 537.4 [(**3-Ph**)+H$-$TMSCl]$^+$.

Synthesis of [(TMS)$_2$-ADC^{DMP}]Cl (3-DMP): Compound **3-DMP** was synthesized by following a similar protocol as described above for **3-Ph** using **2-DMP** (2.56 g, 4.7 mmol), *n*BuLi (2.5 M, 4.1 mL, 10.2 mmol), and TMSCl (1.5 mL, 11.8 mmol) as a colorless solid. Yield: 99 % (3.2 g). Elemental analysis (%), calcd for $C_{41}H_{62}ClN_3Si_2$ (689) (**3-DMP**): C 71.52, H 9.08, N 6.10, found: C 71.22, H 8.76, N 5.89. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 7.68$ (t, $J = 7.8$ Hz, 2 H, *p*-C$_6$*H*$_3$), 7.38 (d, $J = 7.9$ Hz, 4 H, *m*-C$_6$*H*$_3$), 6.40 (d, $J = 9.4$ Hz, 2 H, C$_6$*H*$_4$), 6.18 (d, $J = 9.4$ Hz, 2 H, C$_6$*H*$_4$), 2.93 (s, 6 H, N(C*H*$_3$)$_2$), 2.45 (sept, $J = 6.8$ Hz, 4 H, C*H*(CH$_3$)$_2$), 1.33 (d, $J = 6.8$ Hz, 12 H, CH(C*H*$_3$)$_2$), 0.84 (d, $J = 6.8$ Hz, 12 H, CH(C*H*$_3$)$_2$), 0.16 ppm (s, 18 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): $\delta = 149.0$ (NCN), 145.0 (NCSi), 132.8, 132.6, 130.6, 126.0, 123.9, 110.8, 105.8 (C$_6$H$_3$, C$_6$H$_4$), 39.9 (N(CH$_3$)$_2$, 29.3 (CH(CH$_3$)$_2$, 24.1, 23.4 (CH(CH$_3$)$_2$), 2.1 ppm (Si(CH$_3$)$_3$). ^{29}Si{^{1}H} NMR (99 MHz, CDCl$_3$, 298 K): $\delta = -5.7$ ppm. MS (ESI pos.): $m/z = 652.5$ [(**3-DMP**)$-$Cl]$^+$, 580.5 [(**3-DMP**)+H$-$TMSCl]$^+$.

Synthesis of [(ADC^{Ph})PCl$_2$]$_2$ (4-Ph): To a precooled ($-30\,^{\circ}$C) fluorobenzene (PhF) solution of **3-Ph** (4.03 g, 6.25 mmol) was added PCl$_3$ (0.55 mL, 6.28 mmol). The resulting suspension was stirred overnight at 65 °C. Insoluble material was isolated by filtration and dried in vacuum to afford **4-Ph** as a colorless solid in 73 % (2.60 g) yield. Single crystals suitable for X-ray diffraction were obtained by storing a saturated DCM solution of **4-Ph** at $-30\,^{\circ}$C for three days. Elemental analysis (%), calcd for $C_{66}H_{78}Cl_4N_4P_2$ (1131) (**4-Ph**): C 70.08, H 6.95, N 4.95, found C 69.96, H 6.95, N 4.91. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 7.67$ (t, $J = 7.8$ Hz, 4 H, *p*-C$_6$*H*$_3$), 7.42 (t, $J = 7.6$ Hz, 2 H, *p*-C$_6$*H*$_5$), 7.39 (d, $J = 7.9$ Hz, 8 H, *m*-C$_6$*H*$_3$), 7.10 (t, $J = 8.1$ Hz, 4 H, *o*-C$_6$*H*$_5$), 6.94 (d, $J = 8.5$ Hz, 4 H, *m*-C$_6$*H*$_5$), 2.92 (sept, $J = 6.4$ Hz, 8 H, C*H*(CH$_3$)$_2$), 1.30 (d, $J = 6.7$ Hz, 24 H, CH(C*H*$_3$)$_2$), 0.73 ppm (d, $J = 6.7$ Hz, 24 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): $\delta = 148.1$, 145.9, (NCN, *i*-C$_6$H$_3$), 139.9 (d, $J_{\text{P-C}} = 31.7$ Hz, NCP), 134.4, 133.7, 130.1, 130.0, 129.2, 126.8, 120.4 (C$_6$H$_3$, C$_6$H$_5$), 29.2 (CH(CH$_3$)$_2$), 24.5, 24.3 ppm (CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (99 MHz, CDCl$_3$, 298 K): $\delta = -25.2$ ppm. MS (ESI pos.): $m/z = 465.4$ [(**1-Ph**)$-$Cl]$^+$, 529.3 [(**4-Ph**)< M-> 2 Cl]$^{2+}$.

Synthesis of [(ADC^{DMP})PCl$_2$]$_2$ (4-DMP): Compound **4-DMP** was synthesized following a similar protocol as described above for **4-Ph** from **3-DMP** (3.83 g, 5.6 mmol) and PCl$_3$ (0.49 mL, 5.6 mmol). Yield: 62 % (2.11 g), pale yellow solid. Elemental analysis (%), calcd for $C_{70}H_{88}Cl_4N_6P_2$ (1217) (**4-DMP**): C 69.07, H 7.29, N 6.90, found: C 69.22, H 7.39, N 6.76. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 7.67$ (t, $J = 7.8$ Hz, 4H *p*-C$_6$*H*$_3$), 7.39 (d, $J = 7.8$ Hz, 8 H, *m*-C$_6$*H*$_3$), 6.54 (d, $J = 9.5$ Hz, 4 H, C$_6$*H*$_4$), 6.18 (d, $J = 9.5$ Hz, 4 H, C$_6$*H*$_4$), 3.07 (br s, 8 H, C*H*(CH$_3$)$_2$), 2.93 (s, 12 H, N(C*H*$_3$)$_2$), 1.30 (d, $J = 6.5$ Hz, 24 H, CH(C*H*$_3$)$_2$), 0.80 ppm (d, $J = 6.7$ Hz, 24 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): $\delta = 152.2$ (*p*-*C*$_6$H$_4$), 148.6, 146.5 (NCN, *i*-C$_6$H$_3$), 137.5 (d, $J_{\text{PC}} = 31.3$ Hz, NCP), 133.3, 131.8, 131.0, 126.6, 110.9 (*C*$_6$H$_3$, *C*$_6$H$_4$), 40.1 (N(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 24.5, 24.2 ppm (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (99 MHz, CDCl$_3$, 298 K): $\delta = -17.3$ ppm.

Synthesis of [(ADC^{Ph})P]$_2$ (5-Ph): A 30 mL THF suspension of **4-Ph** (0.65 g, 0.57 mmol) and Mg turnings (56 mg, 2.30 mmol, 4 equiv.) was stirred at rt. After 16 h, the initially white suspension turned into a dark brown suspension, which was filtered through a plug of Celite. The volatiles from the filtrate were removed under vacuum to obtain **5-Ph** as a red-brown crystalline solid in 97 % (550 mg) yield. Single crystals suitable for X-ray diffraction analysis were obtained by storing a saturated toluene solution of **5-Ph** at $-24\,^{\circ}$C for two weeks. Elemental analysis (%) calcd for $C_{66}H_{78}N_4P_2$ (989) (**5-Ph**): C 80.13; H 7.95; N 5.66; found: C 79.81, H 7.73, N 5.42. ^{1}H NMR (600 MHz, [D$_8$]THF, 298 K): $\delta = 7.32$ (t, $J = 7.7$ Hz, 4 H, *p*-C$_6$*H*$_3$), 7.17 (d, $J = 7.7$ Hz, 8 H, *m*-C$_6$*H*$_3$), 6.43–6.40 (m, 6 H, *p*-/*o*-C$_6$*H*$_5$), 6.04 (br, 4 H, *m*-C$_6$*H*$_5$), 3.32 (sept, $J = 6.8$ Hz, 8 H, C*H*(CH$_3$)$_2$), 1.40 (d, $J = 6.8$ Hz, 24 H, CH(C*H*$_3$)$_2$), 0.94 ppm (d, $J = 6.9$ Hz, 24 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, [D$_8$]THF, 298 K): $\delta = 154.0$ (dd, $^1J_{\text{C-P}} = 35.7$ Hz, $^2J_{\text{C-P}} = 23.1$ Hz, *C*P), 146.5 (N*C*N), 134.7, 131.1, 128.2, 125.9, 124.6, 121.9, 120.4, 118.3, 116.1, 116.0 (*C*$_6$H$_3$, *C*$_6$H$_5$), 29.8 (*C*H(CH$_3$)$_2$), 24.7, 23.9 ppm (CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (202 MHz, [D$_8$]THF, 298 K): $\delta = -47.9$ ppm. UV/Vis (THF, λ (nm) (ε (M^{-1} cm^{-1}))): 262 (101677), 293 (170560), 344 (151370), 361 (149690), 555 (30930).

Alternative synthesis of 5-Ph using 4-Ph and KC$_8$: To a cold ($-95\,^{\circ}$C) THF (15 mL) solution of **4-Ph** (456 mg, 0.40 mmol) was added KC$_8$ (260 mg, 1.80 mmol, 4.5 equiv.). After 1 h, the dark brown suspension was filtered through a plug of Celite. The volatiles were removed under vacuum to obtain **5-Ph** as a red-brown crystalline solid in 94 % (372 mg) yield. The ^{1}H and ^{31}P{^{1}H} NMR spectra recorded in [D$_8$]THF matched those reported above.

Synthesis of [(ADC^{Ph})P(AuCl)$_2$]$_2$ (6-Ph): To a mixture of **5-Ph** (345 mg, 0.25 mmol) and (Me$_2$S)AuCl (150 mg, 0.51 mmol) was added 10 mL THF. The resulting orange suspension was stirred at rt for 16 h. The precipitate formed was isolated by filtration and extracted with DCM (10 mL). The volatiles were removed under vacuum to obtain compound **6-Ph** as a pale yellow solid in 33 % (160 mg) yield. Single crystals suitable for X-ray-diffraction analysis were obtained at rt by a slow diffusion of benzene into a saturated DCM solution of **6-Ph**. Elemental analysis (%) calcd for $C_{66}H_{78}Au_4Cl_4N_4P_2$ (1919) (**6-Ph**): C 41.31, H 4.10, N 2.92, found: C 41.01, H 4.13, N 2.78. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): $\delta = 7.70$ (d, $J = 15.6$ Hz, 4 H, *p*-C$_6$*H*$_3$), 7.41 (d, $J = 7.8$ Hz, 4 H, *m*-C$_6$*H*$_3$), 7.37–7.31 (m, 6 H, *m*-C$_6$*H*$_3$, *p*-C$_6$*H*$_5$), 7.08 (t, $J = 7.9$ Hz, 4 H, *m*-C$_6$*H*$_5$), 6.85 (d, $J = 8.2$ Hz, 4 H, *o*-C$_6$*H*$_5$), 3.03 (sept, $J = 6.7$ Hz, 2 H, C*H*(CH$_3$)$_2$), 2.25 (sept, $J = 6.3$ Hz, 2 H, C*H*(CH$_3$)$_2$), 1.65 (d, $J = 6.4$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.36 (d, $J = 6.5$ Hz, 6 H, CH(C*H*$_3$)$_2$), 0.75 (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$), 0.72 ppm (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): $\delta = 147.8$, 146.5, 143.9, 138.0, 137.6 (d, $J_{\text{P,C}} = 53.4$ Hz, *C*P), 133.6, 133.1, 129.7, 129.6, 129.0, 127.0, 126.3, 121.2, 29.9, 29.7 (*C*H(CH$_3$)$_2$), 26.4, 25.6, 24.1, 23.0 ppm (CH(*C*H$_3$)$_2$). 137.83. ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 298 K): $\delta = -37.32$ ppm.

Synthesis of [(ADC^{Ph})P]$_2$(MgCl$_4$) (7-Ph): To a freshly prepared THF (10 mL) solution of **5-Ph** (100 mg, 0.1 mmol), obtained by stirring a mixture of **4-Ph** and Mg turnings in THF overnight and filtration that also contained MgCl$_2$ side product) was added solid **4-Ph** (119 mg, 0.1 mmol) in one portion. The resulting orange suspension was stirred at rt for 2 h. The volatiles were removed under vacuum and the remaining residue was washed with toluene (10 mL) and PhF (10 mL) to give compound **7-Ph** as an orange solid. Single crystals suitable for X-ray diffraction analysis were obtained at room temperature by storing a saturated PhF solution of **7-Ph** that was layered with *n*-hexane. Yield: 46 % (98 mg). Elemental analysis (%) calcd for $C_{66}H_{78}Cl_4MgN_4P_2$ (1155) (**7-Ph**): C 68.61, H 6.80, N 4.85, found: C 68.33, H 6.72, N 4.69. ^{1}H NMR (500 MHz, CD_3CN, 298 K): $\delta = 7.77–7.71$ (m, 4 H, p-C_6H_3), 7.52 (d, $J = 7.7$ Hz, 8 H, m-C_6H_3), 7.35–7.32 (m, 4 H, m-C_6H_5), 7.27–7.23 (m, 6 H, p-/o-C_6H_5), 2.51 (sept, $J = 6.5$ Hz, 4 H, $CH(CH_3)_2$), 1.18 (d, $J = 6.7$ Hz, 12 H, $CH(CH_3)_2$), 0.94 ppm (d, $J = 6.7$ Hz, 12 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN, 298 K): $\delta = 146.7$ (NCN), 134.1, 131.0, 130.7, 130.4, 130.0, 127.6, 127.6 (C_6H_3, C_6H_5), 30.1 ($CH(CH_3)_2$), 26.2, 25.8, 23.8 ppm ($CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN, 298 K): $\delta = 16.5$ ppm. UV/vis (CH_3CN, λ (nm) (ε (M^{-1} cm^{-1}))): 291 (209929), 301 (267956), 316 (238773), 356 (199467), 452 (85775).

Crystallographic data: Deposition numbers 1992415 (for **1-Ph**), 1992416 (for **4-Ph**), 1992417 (for **5-Ph**), 1992418 (for **7-Ph**) and 1992419 (for **6-Ph**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anionic dicarbenes · antiaromaticity · aromaticity · phosphinidene · phosphorus

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