



Distannabenzene Hot Paper

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 6414–6418

International Edition: doi.org/10.1002/anie.202017078

German Edition: doi.org/10.1002/ange.202017078

An Open-Shell Singlet Sn^I Diradical and H₂ Splitting

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Dedicated to Professor Thomas M. Klapötke on the occasion of his 60th birthday

Abstract: The first Sn^I diradical [(ADC^{Ph})Sn]₂ (**4**) based on an anionic dicarbene (ADC^{Ph} = {CN(Dipp)}₂CPh; Dipp = 2,6-*i*Pr₂C₆H₃) scaffold has been isolated as a green crystalline solid by K_C₈ reduction of the corresponding bis-chlorostannylene [(ADC^{Ph})SnCl]₂ (**3**). The six-membered C₄Sn₂-ring of **4** containing six π-electrons shows a diatropic ring current, thus **4** may also be regarded as the first 1,4-distannabenzene derivative. DFT calculations suggest an open-shell singlet (OS) ground state of **4** with a remarkably small singlet–triplet energy gap (ΔE_{OS-T} = 4.4 kcal mol⁻¹), which is consistent with CASSCF (ΔE_{S-T} = 6.6 kcal mol⁻¹ and diradical character $y = 37\%$) calculations. The diradical **4** splits H₂ at room temperature to yield the bis-hydridostannylene [(ADC^{Ph})SnH]₂ (**5**). Further reactivity of **4** has been studied with PhSeSePh and MeOTf.

Molecules containing two unpaired electrons in two degenerate (or nearly degenerate) orbitals are called diradicals, which may have a singlet or triplet ground state.^[1] Stable diradicals are appealing synthetic targets in fundamental chemistry^[2] and continue to attract interest in materials science and beyond.^[3] This is because of their intriguing electronic structure, reactivity, and physical properties. Four-membered non-Kekulé ring systems (E₂X₂) (E = main-group element, X = N or O), collectively known as Niecek-type diradicaloids,^[4] are classical examples of main-group singlet diradicals.^[5] In 2004, Power et al.^[6] isolated the first germanium diradicaloid, (ArGeNSiMe₃)₂ (Ar = 2,6-(2,6-*i*Pr₂C₆H₃)C₆H₃). At the same time, Lappert et al.^[7] reported

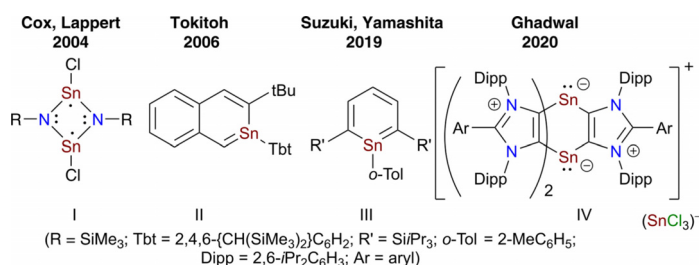


Figure 1. Structurally characterized relevant tin compounds.

the first tin analog (**I**, Figure 1). Interestingly, while Power et al. also reported one more Ge derivative^[8] but **I** remained the only known example of a stable tin diradicaloid. The stability of **I** and other Niecek-type diradicaloids is largely attributed to the presence of a 6π-electron aromatic system like benzene.^[4–9]

Heavier Group 14 benzene derivatives featuring a C_{6-n}E_n ring (E = Si, Ge, or Sn) are intriguing molecules.^[10] The isolation of these species however presents a considerable challenge because of their inherent high reactivity.^[11] While several stable silabenzene and germapenzene derivatives have been isolated,^[11,12] stable monomeric stannabenzene (**II** and **III**)^[11d,j] remained extremely rare.^[13] Also, no stable distannabenzene containing a C₄Sn₂ ring is known to date. The high reactivity of heavy benzene derivatives containing a C_{6-n}E_n ring is most likely due to their open-shell electronic structure arising from an inefficient Cπ–Eπ overlap. Thus, in addition to kinetic stabilization using bulky substituents, the use of new electron-rich ligands seems desirable in accessing stable heavier benzene derivatives.^[14]

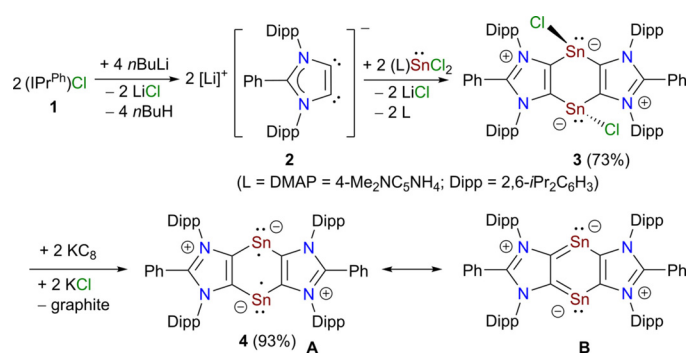
We recently prepared barrelene type Sn^{II} compounds (**IV**)^[15] based on an anionic dicarbene (ADC^{Ar})₂ (ADC^{Ar} = {CN(Dipp)}₂CAr; Ar = aryl; Dipp = 2,6-*i*Pr₂C₆H₃) and subsequently decided to probe the synthetic viability of corresponding 1,4-distannabenzene derivatives. Herein, we report the first example of a Sn^I compound [(ADC^{Ph})Sn]₂ (**4**) containing a C₄Sn₂ ring and describe its electronic structure and reactivity (Scheme 1).

The Li(ADC^{Ph}) (**2**) is accessible by the double deprotonation of the C₂-arylated 1,3-imidazolium salt (IPr^{Ph})Cl (**1**) (IPr^{Ph} = {HCN(Dipp)}₂CPh; Dipp = 2,6-*i*Pr₂C₆H₃) with *n*BuLi (Scheme 1). Treatment of a freshly prepared solution of **2** with (DMAP)SnCl₂ (DMAP = Me₂N₂C₅H₄N) led to the formation of the anticipated bis-chlorostannylene **3** in 73 % yield as a colorless crystalline solid. It should be noted that the use of (DMAP)SnCl₂ is essential to selectively prepare **3** as the

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https://doi.org/10.1002/anie.202017078.

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Scheme 1. Synthesis of **3** and **4**. Diradical (**A**) and benzenoid (**B**) forms of **4**.

reaction of **2** with SnCl₂, irrespective of the ratio, almost exclusively gives [(ADC^{Ph})₃Sn₂]SnCl₃ (**IV**).^[15]

Compound **3** was characterized by NMR and X-ray diffraction (Figure 2). KC₈ reduction of **3** led to the formation of compound **4** (see the Supporting Information), which was isolated as a green crystalline solid in 93% yield. The ¹H NMR spectrum of **3** displays two sets of signals (four doublets and two septets) for the isopropyl groups along with the signals due to the aryl protons. The ¹¹⁹Sn{¹H} NMR spectrum of **3** shows a sharp singlet at –62.8 ppm, which is comparable with those of (NHC)SnCl₂ (–59.4 to –68.7) (NHC = N-heterocyclic carbene).^[17] Unlike **3**, the ¹H NMR spectrum of **4** at 298 K (Figure S4) shows rather broad resonances. The ¹¹⁹Sn{¹H} NMR spectrum of **4** exhibits a high-field signal at –426.0 ppm ($\omega_{1/2}$ = 187 Hz), which is however rather broad compared to that of **3** (–62.8 ppm, $\omega_{1/2}$ = 30 Hz). The broadening of NMR signals of **4** may likely be due to its open-shell electronic structure (see below). Indeed, variable-temperature ¹H NMR studies (Figure S5) show continuous sharpening of signals from 298 to 224 K. At 224 K, the ¹H NMR signals of **4** are resolved and can be reasonably assigned to the ADC^{Ph} units (Figure S6).

The solid-state molecular structures of **3** and **4** (Figure 2) reveal the presence of a six-membered C₄Sn₂ ring with tin atoms at the 1,4-positions. The molecule in each of **3** and **4** resides at a crystallographic center of inversion. The chlorine atoms of **3** are positioned in a *trans*-fashion across the puckered C₄Sn₂ ring. The sum of the bond angles at the Sn1 (Σ Sn1 = 268°) is consistent with the presence of a stereochemically active electron lone pair on the Sn atom. The Sn1–Cl1

bond (2.517(1) Å) of **3** is longer compared with those of (IPr)SnCl₂ (2.439(3) and 2.426(2) Å).^[17a] The Sn1–C2/C3[#] bonds (2.229(1), 2.234(1) Å, respectively) of **3** are, however, shorter than that of (IPr)SnCl₂ (2.341(8) Å).^[17a] This may be because of the greater σ -donor property of ADCs in comparison with classical NHCs.^[18] The transannular Sn–Sn distance in **3** is approx. 4.4 Å, while the C–Sn–C bond angle is 90.9(1)° (see Table S3).

The Sn–C2/C3[#] bonds of **4** (2.202(3) and 2.205(3) Å) are slightly shorter than those of **3** (2.229(1), (2.234(1) Å), **IV** (2.24 to 2.27 Å),^[15] and Jones's Sn⁰ compound (IPr)₂Sn₂ (2.297 Å).^[19] They are, however, longer than the Sn–C bond observed in the stannabenzene derivatives **II** and **III** (2.02–2.08 Å),^[11d,j] each featuring a formally Sn³⁺ center, as well as the Sn=C bonds of stannenes (2.00–2.07 Å).^[20] It should, however, be noted that the bonds in low-valent compounds are always longer than those of related high-valent derivatives because of the lower *s*-character of the bonding orbitals in the former.^[10a,21] The C2–C3 bond length of **4** (1.380(4) Å) is comparable to that of **3** (1.376(1) Å). These structural parameters of **4** indicate that the unpaired electrons on the Sn atoms (see diradical form **A**, Scheme 1) are weakly delocalized over the C₄Sn₂ ring to form a 6 π -electron aromatic system (see benzenoid form **B**). The ¹³C{¹H} NMR signal for the C₄Sn₂ moiety of **4** (186.9 ppm) is downfield shifted compared to that of **3** (171.5 ppm), suggesting a ring-current effect from six π -electrons in the former. The calculated Nucleus Independent Chemical Shift (NICS) values (Table S9) of **4**, (NICS(0) = –7.5 and NICS(1) = –10.2 ppm), indicate the presence of a diatropic ring current derived from the C₄Sn₂ ring.^[22]

The optimized geometries of **3** and **4** (Figure S29) at the B3LYP/6-31G(d) level of theory are fully consistent with their solid-state molecular structures determined by X-ray diffraction (Figure 2). DFT calculations reveal a closed-shell singlet (CS) ground state for **4**, however the triplet state is only 3.3 kcal mol^{–1} higher in energy. Interestingly, unrestricted DFT reveals an open-shell singlet (OS) state of **4**, which is 1.1 kcal mol^{–1} more stable than the CS solution. The frontier Kohn–Sham orbital analysis (Figure S31) of **4**^{CS} exhibits that the HOMO (–2.731 eV) mainly corresponds to a π -type orbital of the Sn–C bonds, while the HOMO–1 (–4.937 eV) and HOMO–2 (–5.257 eV) are the σ -type lone-pair orbitals at the Sn atoms.

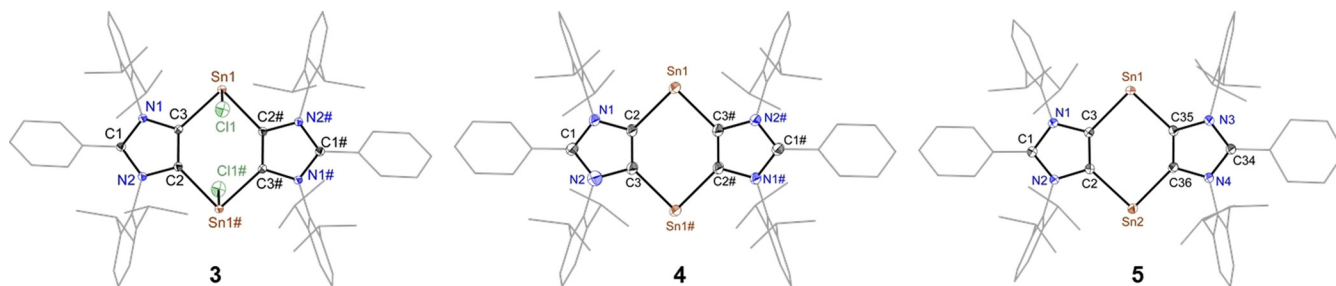


Figure 2. Solid-state molecular structures of **3**, **4** (which have a center of inversion), and **5** (thermal ellipsoids at 50% probability). Selected bond lengths and angles are given in Table S3.

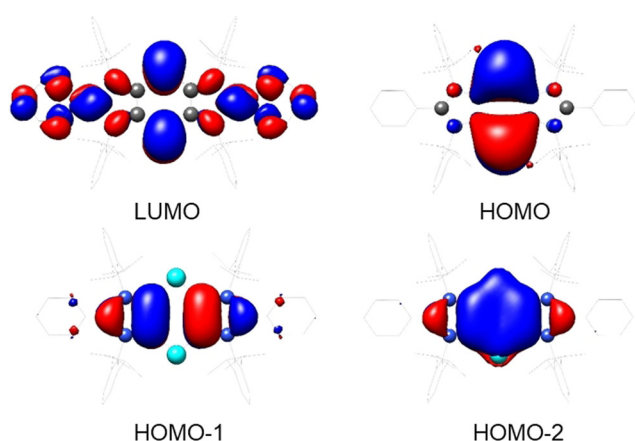


Figure 3. Selected molecular orbitals of **4** calculated at CASSCF-(10,10)/def2TZVPP level of theory. The isovalue was arbitrarily chosen to be 0.02. Hydrogen atoms were omitted for clarity.

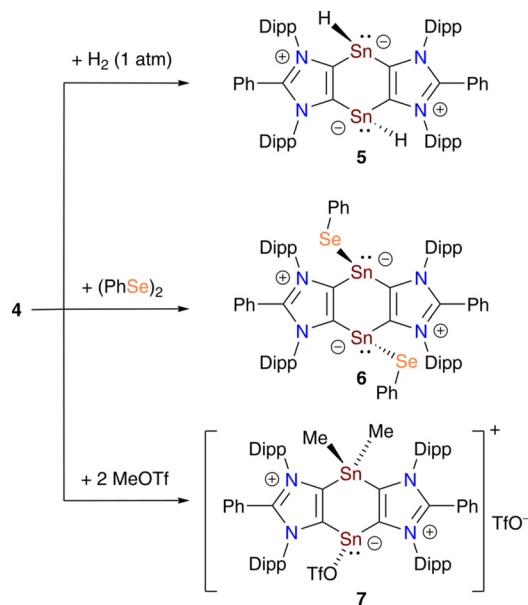
To obtain a clear insight into the electronic structure of **4**, we performed high-level multireference calculations based on the complete active space self-consistent field CASSCF method on the DFT optimized structure. CASSCF(10,10)/def2-TZVPP calculations show that the singlet state (S_0) is energetically more favorable than the triplet state (T_0) by 6.6 kcal mol⁻¹ (Figure S35). The occupation of the HOMO-4 and HOMO-3 (Figure S36), which belong to the lone-pair orbitals of Sn atoms, is 1.99 (Table S12). The next three orbitals (HOMO-2, HOMO-1, HOMO) show occupancies greater than 1.00 (1.09–1.93), consistent with a delocalized electronic structure (Figure 3). The following three orbitals (LUMO, LUMO + 1, LUMO + 2) are partially occupied with an occupation number of 0.39, 0.34, and 0.25, respectively. The spin-density matrix (Table S14) shows a spin density of 0.48 for the HOMO. The LUMO + 1, LUMO + 2, and LUMO + 3 have a spin density of 0.17, 0.16, and 0.17, respectively, which suggests an open-shell singlet diradical structure of **4**. The calculated diradical character ($y=0.37$) clearly supports the singlet diradical structure of **4**. For CAS calculations, three roots for each singlet and triplet states were taken into account (Table S13). Calculations reveal a very small energy gap of 6.6 kcal mol⁻¹ for the vertical $S_0 \rightarrow T_0$ transition. The UV/Vis spectrum of **4** in THF exhibits three main absorptions (Figures S21, S22). Based on CAS calculations, the absorptions at $\lambda_{\max}=656$ and 881 nm may be assigned to the $S_0 \rightarrow S_2$ (673 nm) and $S_0 \rightarrow S_1$ (790 nm) transitions, respectively.

Both DFT and CASSCF calculations suggest a singlet ground state of **4** that has a considerable diradical character (Table S15). The EPR spectrum of **4** at 100 K (Figure S23) shows a featureless doublet, presumably due to the presence of traces of monoradical species. Interestingly, the EPR spectrum of **4** displays a half-field signal at 100 K, a characteristic of triplet diradicals, which is consistent with the calculations and indicates that the triplet state is thermally populated.

The OS diradical property of **4** prompted us to probe its chemical reactivity. The homolytic dihydrogen splitting has been considered as a benchmark reaction of diradicals.^[1c]

Exposure of a [D₈]THF solution of **4** in a J-Young NMR tube with H₂ gas (1 atm) immediately led to a color change from green to red. NMR analyses indicated the complete consumption of **4** and the formation of the Sn^{II} hydride **5** (Scheme 2). Calculations at the B3LYP-D3BJ/6-31G(d) level of theory suggest that $4 + H_2 \rightarrow 5$ ($\Delta G = -8.0$ kcal mol⁻¹) is thermodynamically favored. Compound **5** can also be prepared by an alternative route using **3** and K[sBu₃BH] (see the Supporting Information) as a red crystalline solid. **5** has been characterized by NMR and X-ray diffraction (Figure 2). The structural parameters of **5** are distinct from **4** but compare well with those of **3**, however, hydrogens at the heavy Sn atoms could not be located. The ¹H NMR spectrum of **5** exhibits a singlet at 6.74 ppm, which is consistent with Sn^{II} hydrides.^[23] The ¹¹⁹Sn NMR spectrum of **5** exhibits a doublet at -355.6 ppm (¹J_{Sn,H} = 136 Hz) due to coupling with the hydrogen atom and could be further confirmed by ¹H-¹¹⁹Sn HSQC experiments (Figure S12).

Treatment of **4** with PhSeSePh gave the cyclic bis-stannylene **6** as a yellow crystalline solid in 99% yield (Scheme 2). The ¹¹⁹Sn{¹H} NMR spectrum of **6** shows a singlet at $\delta = -155.3$ ppm, which is upfield shifted with respect to that of **3** ($\delta = -62.8$ ppm). The ⁷⁷Se{¹H} NMR spectrum of **5** exhibits a sharp signal at $\delta = 437$ ppm. The molecular structure of **6** (Figure S27) is comparable with that of **3**. Remarkably, treatment of **4** with MeOTf affords the mixed valent Sn^{IV}/Sn^{II} compound **7** as a colorless crystalline solid in 88% yield (Scheme 2). The ¹¹⁹Sn{¹H} NMR spectrum of **7** displays two signals at $\delta = -93.0$ and -171.3 ppm, which can be assigned to Sn^{II} and Sn^{IV} atoms, respectively. The structural parameters of **7** (Figure S28) are consistent with a mixed-valent Sn^{II}/Sn^{IV} compound. As expected, the Sn-C_{ADC} bond lengths (2.236(2) and 2.238(2) Å) at the Sn^{II} center are similar to those of **3** (2.229(1), 2.234(1) Å) and **6** (2.22–2.25 Å), while the same at the Sn^{IV} atom (2.143(2) and 2.143(3) Å) are smaller.



Scheme 2. Reactions of **4** with H₂, (PhSe)₂, and MeOTf.

In conclusion, we have reported the first Sn^I diradicaloid **4**, which may also be considered as a 1,4-distannabenzene derivative, as a green crystalline solid. Calculations suggest the open-shell singlet ground state for **4** with a considerable diradical character ($y = 37\%$). The appearance of a half-field EPR signal indicates thermal population of the triplet species, which is in line with the calculations. The splitting of H₂ with **4** at room temperature has been shown to give Sn^{II} hydride **5**. Further reactivity studies of **4** have been performed with PhSeSePh and MeOTf to yield **6** and **7**, respectively. All compounds have been characterized in solution by spectroscopic methods, and their structures have been determined by X-ray diffraction.

Deposition numbers 1992953, 1992954, 1992955, 1992956, and 2051225 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.

Acknowledgements

The authors gratefully acknowledge support from the Deutsche Forschungsgemeinschaft (DFG) and thank Professor Norbert W. Mitzel for his continuous encouragement. We thank Dr. Maurice van Gastel (MPI Mülheim) for measuring EPR spectra. The support by computing time provided by the Paderborn Center for Parallel Computing (PC2) is acknowledged. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: aromaticity · diradical · distannabenzene · H₂ splitting · open-shell systems

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Manuscript received: December 23, 2020

Accepted manuscript online: January 18, 2021

Version of record online: February 5, 2021