▌**Tin Chemistry** |*Hot Paper*|

Distannabarrelenes with Three Coordinated Sn[II] Atoms

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Dedicated to Professor Herbert W. Roesky on the occasion of his 85th birthday.

Abstract: Crystalline 1,4-distannabarrelene compounds $[(ADC^{Ar})_3Sn_2]SnCl_3$ (**3-Ar**) ($ADC^{Ar} = \{ArC(NDipp)_2CC\}$; Dipp = $2,6\text{-}i\text{Pr}_2C_6H_3$, Ar = Ph or DMP; DMP = $4\text{-}Me_2NC_6H_4$) derived from anionic dicarbenes $Li(ADC^{Ar})$ (**2-Ar**) (Ar = Ph or DMP) have been reported. The cationic moiety of **3-Ar** features a barrelene framework with three coordinated Sn[II] atoms at the 1,4-positions, whereas the anionic unit $SnCl_3$ is formally derived from $SnCl_2$ and chloride ion. The all carbon substituted bis-stannylenes **3-Ar** have been characterized by NMR spectroscopy and X-ray diffraction. DFT calculations reveal that the HOMO of **3-Ph** ($\varepsilon = -6.40$ eV) is mainly the lone-pair orbital at the Sn[II] atoms of the barrelene unit. **3-Ar** readily react with sulfur and selenium to afford the mixed-valence Sn[II]/Sn[IV] compounds $[(ADC^{Ar})_3SnSn(E)](SnCl_6)_{0.5}$ (E = S **4-Ar**, Ar = Ph or DMP; E = Se **5-Ph**).

Exploration of compounds featuring a low-valent main-group element(s) has been a fascinating research topic in fundamental chemistry because of their intriguing electronic structure[1] and reactivity.[2] Heavier main-group element compounds that are analogues to ubiquitous organic molecules such as alkenes, alkynes, and other unsaturated species have been appealing synthetic targets.[3] Barrelene, bicyclo[2.2.2]octa-2,5,7-triene (**I**) (Figure 1) is the formal Diels–Alder adduct of acetylene **II** and benzene **III**.[4] The name "barrelene" was coined because of its barrel like shape (Figure 1). Barrelene first caught attention in 1955 when Hine et al. noted that this molecule might be aromatic.[5] Since the first synthesis of **I** by Zimmerman and Paufler in 1960,[4] this intriguing molecule has been

in focus of synthetic as well as theoretical chemists.[6] Involvement of barrelene type species have also been predicated in the activation of organic substrates with low-valent main group compounds.[7]

Some barrelene type compounds featuring a Group 13 or 15 element(s) have been isolated over the past years,[8] however, related species featuring Group 14 elements (tetreles), the heavier carbon congeners, remained scarce. The first silabarrelene was reported in 1977 by Barton and Banasiak,[9] which was prepared by the Diels–Alder reaction of an in situ generated silabenzene with an alkyne. Synthesis of barrelene derivatives containing heavier Group 14 elements by classical cycloaddition reactions seems a demanding task because of the synthetic inaccessibility of suitable unsaturated precursors.[10] Breher[11] and Stalke[12] independently reported barrelene type compounds featuring Ge[II] or Sn[II] atoms using pyrazole frameworks, showing an alternative way to access these species, in which the bicyclo[2.2.2] framework is based on nitrogen instead of carbon atoms. Subsequently, several other main-group element systems based pyrazole scaffolds have been also reported.[13]

Robinson et al. reported the C4-H deprotonation of an N-heterocyclic carbene (NHC), the IPr ($IPr = C\{(NDipp)CH\}_2$, Dipp = $2,6\text{-}i\text{Pr}_2C_6H_3$), with nBuLi to access an anionic dicarbene (ADC) **IV** (Figure 1).[14] Over the past years, this and related species have been extensively explored by Goicoechea, Mulvey, Hevia, and other research groups in main-group as well as in transition metal chemistry.[15] The C2/C4-positions of **IV** are remotely located and thus are not suitable for the preparation of cyclic compounds. We recently reported ADCs **V** that feature carbenes at the vicinal C4/C5-positions[16] and hence should be an appropriate choice for constructing heterocyclic rings containing heavier main-group elements.[17] Herein, we report the first distannabarrelenes $[(ADC^{Ar})_3Sn_2]SnCl_3$ ($ADC^{Ar} = ArC(NDipp)_2CC$; Ar = Ph, **3-Ph**; DMP, **3-DMP**; DMP = $4\text{-}Me_2NC_6H_4$) featuring three-coordinated tin(II) atoms as crystalline solids and describe their structure and reactivity (Scheme 1).

The anionic dicarbenes $Li(ADC^{Ar})$ (Ar = Ph, **2-Ph**; DMP, **2-DMP**) are readily accessible by the double deprotonation of C2-arylated 1,3-imidazolium salts ($IPr^{Ar})Cl$ ($IPr^{Ar} = ArC\{(NDipp)CH\}_2$; Ar = Ph, **1-Ph**; DMP, **1-DMP**; Dipp = $2,6\text{-}i\text{Pr}_2C_6H_3$) with nBuLi.[16] Treatment of freshly prepared **2-Ph** and **2-DMP** with $SnCl_2$ affords the compounds $[(ADC^{Ar})_3Sn_2]SnCl_3$ (Ar = Ph, **3-Ph** (76%); DMP, **3-DMP** (95%)) (Scheme 1). **3-Ph** and **3-DMP** are ionic species, each comprising a cationic 1,4-distannabaralene and an anionic $SnCl_3$ moieties. The ADC^{Ar} moiety in **3-Ar**

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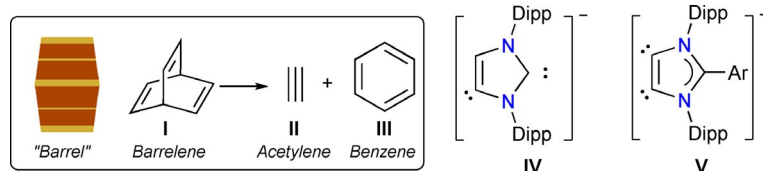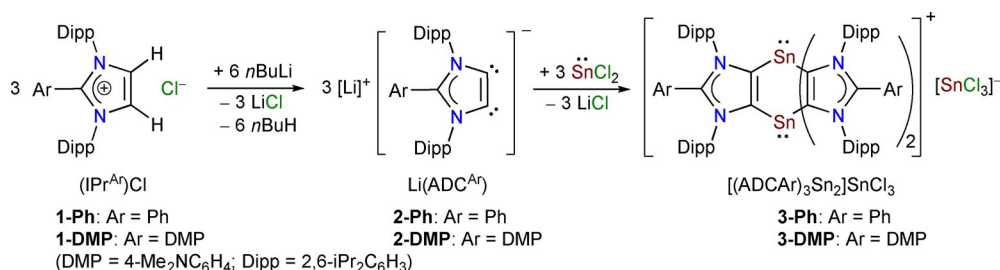**Figure 1.** Barrelene **I**, acetylene **II**, benzene **III**, C2/C4-anionic dicarbene (ADC) **IV**, and C4/C5 ADC **V**.

Scheme 1. Synthesis of distannabarrelene compounds **3-Ph** and **3-DMP**.

serves as a mono-anionic four-electron donor and the remaining chloride combines with an additional $SnCl_2$ to form the $SnCl_3$ counter anion.[18] **3-Ph** and **3-DMP** are colorless crystalline solids and are stable both in solution as well as in the solid state under an inert gas atmosphere.

The ^1H NMR spectra of **3-Ph** and **3-DMP** each shows four doublets and two septets for the isopropyl groups. The $^{13}C\{^1H\}$ NMR spectra of **3-Ph** and **3-DMP** exhibit well resolved resonances for the ADC^{Ar} unit, which are consistent with their ^1H NMR signals. The $^{119}Sn\{^1H\}$ NMR spectrum of **3-Ph** (−298.6 ppm) and **3-DMP** (−297.5 ppm) each shows a singlet, indicating that both the tin atoms of the cationic part are magnetically equivalent. The $^{119}Sn\{^1H\}$ NMR signals of **3-Ar** are high-field shifted compared to those of (NHC)SnX$_2$ (X = Si(SiMe$_3$)$_3$ −196.8 ppm; Ge(SiMe$_3$)$_3$ −115 ppm; 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)C$_6$H$_3$ −150 ppm, Ph −121 ppm)[19] that is consistent with the stronger σ-donor property of ADCs **2-Ar** compared to classical NHCs.[20] They are, however, downfield shifted with respect to that of the poly(pyrazolyl)stannylenes [Sn$_2$(3,5-Me$_2$Pz)$_3$][SnCl$_3$]

(−337 and −498 ppm)[12] and [{Sn(3,5-R$_2$Pz)$_2$}$_2$] (R = CF$_3$, CMe$_3$) (−720 ppm).[11]

The solid-state molecular structures[21] of **3-Ph** and **3-DMP** (Figure 2) show three-fold coordinated tin atoms at the apexes of a cationic bicyclo[2.2.2] framework along with [SnCl$_3^-$] or a mixture of [SnCl$_3^-$] and chloride (in ratio 79:21) as a counter anion, respectively. Each of the tin atoms features a trigonal pyramidal geometry and binds to the backbone carbon atoms of three ADC^{Ar} and comprises one stereoactive electron lone pair. The Sn–C$_{ADC}$ bond lengths (2.24 to 2.27 Å) of **3-Ar** (Table 1) are comparable with the Sn–C bond length of Goicoechea's C4-bound Sn^{II}-NHC compound (2.248(4) Å),[15j] but are slightly smaller than that of Jones's Sn^0 [(IPr)$_2$Sn$_2$ 2.297 Å][22] and Rivard's Sn^{II} [(IPr)SnCl$_2$ 2.341(8) Å][23] compounds. The C$_{ADC}$–Sn–C$_{ADC}$ bond angles in **3-Ar** (86.9 to 90.1°) are in line with those of the N-Sn-N bond angles (85.1 to 92.0°) of the poly(pyrazolyl)stannylenes [Sn$_2$(3,5-Me$_2$Pz)$_3$][SnCl$_3$] consisting six nitrogen atoms on a paddle-wheel with two Sn^{II} atoms on the shaft.[12] The *trans*-annular Sn–Sn distance in **3-Ar** is ca. 4.0 Å.
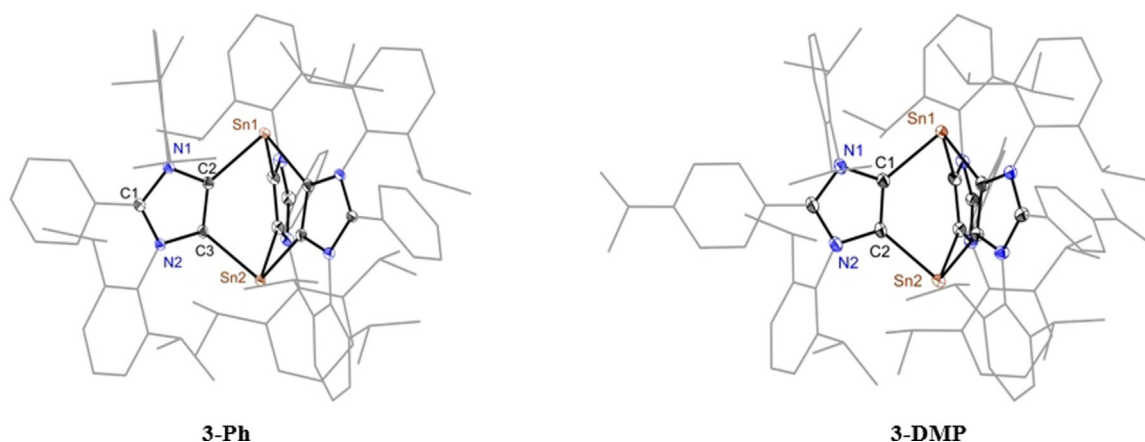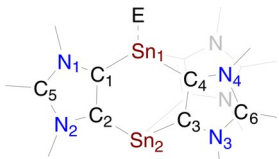

Figure 2. Solid-state molecular structures of **3-Ph** and **3-DMP**. Hydrogen atoms and the counter anion (SnCl$_3^-$) are omitted and aryl groups are shown as wireframe models for clarity.

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Table 1. Selected bond lengths (Å) and angles (°): for **3-Ar**, **4-Ph**, and **5-Ph**.

Compound	Sn1–C1 Sn2–C2	C1–C2 C3–C4	C1–N1 C2–N2	Sn1–E1 (E=S/ Se)	C1-Sn1-C4 C2-Sn2-C3	Sn1-C1-C2 Sn2-C2-C1
3-Ph	2.263(2) 2.266(2)	1.368(3) 1.369(3)	1.411(3) 1.417(3)	–	88.0(1) 88.6(1)	128.5(2) 122.0(2)
3-DMP	2.253(2) 2.259(3)	1.376(4) 1.374(4)	1.414(3) 1.417(3)	–	87.4(1) 88.4(1)	124.3(2) 124.9(2)
4-Ph	2.192(5) 2.261(5)	1.379(8) 1.362(8)	1.395(7) 1.404(7)	2.262(1)	94.3(2) 88.7(2)	117.4(4) 128.9(4)
5-Ph	2.195(4) 2.259(4)	1.357(5) 1.365(5)	1.411(5) 1.418(5)	2.388(1)	94.8(1) 88.4(1)	118.0(3) 129.3(3)

We performed DFT calculations at the B3LYP/6-31G(d) level of theory (LANL2DZ for Sn) for **3-Ph** to gain further insight into the electronic structures of **3-Ar**. The NPA (natural population analyses) atomic partial charges (Table S4) calculated using the NBO (natural bond orbital) method indicate that each tin atom in **3-Ph** (0.94 e) carries a positive charge, whereas each of the carbene carbon atoms bears a negative charge of $-0.30 e$. The calculated WBIs (Wiberg Bond Indices) for the Sn–C_{ADC} bonds

(0.55) are identical and consistent with the experimental Sn–C_{ADC} bond lengths. The HOMO and HOMO−1 of **3-Ph** are mainly the s-type lone-pair orbitals at the Sn^{II} atoms, whereas the LUMO is located at the imidazole moieties (Figure 3). The HOMO–LUMO energy gap of **3-Ph** ($\Delta E_{H-L} = 3.16$ eV) is small, which is also manifested by its reactions with chalcogens.

Treatment **3-Ph** and **3-DMP** each with two equivalents of elemental sulfur led to the formation of mixed valent Sn^{II}/Sn^{IV} compounds **4-Ph** and **4-DMP**, respectively, as yellow solids in an almost quantitative yield. Similarly, reaction of **3-Ph** with selenium also gave the mixed valent Sn^{II}/Sn^{IV} compound **5-Ph** (Scheme 2). Both **4-Ar** and **5-Ph** feature the dianionic counter anion $(SnCl_6)^{2-}$, which is assumed to form through the disproportionation of an in situ generated anion $(ESnCl_3)^-$ as follows: $2\ (ESnCl_3)^- \rightarrow (SnCl_6)^{2-} + (SnE_2)$ or $(ESnCl_3)^- + (SnCl_3)^- \rightarrow (SnCl_6)^{2-} + (SnE)$. Calculations show the transformation $2\ (SSnCl_3)^- \rightarrow (SnCl_6)^{2-} + (SnS_2)$ is thermodynamically favored by $\Delta G = -47.7$ kcal mol^{-1}. **4-Ar** and **5-Ph** do not react further with an excess of chalcogens even at elevated temperature (60–70 °C), indicating that the Sn^{II} moiety of **4-Ar** and **5-Ph** is kinetically inert compared to that of **3-Ar** (see below).

The ^1H NMR spectra of **4-Ph**, **4-DMP**, and **5-Ph** show eight doublets and four septets for the isopropyl groups, which is expected owing to their lower symmetry compared to **3-Ar**. The $^{119}Sn\{^1H\}$ NMR spectrum of **4-Ph** (-290, -376, and -682 ppm), **4-DMP** (-342, -366, and -576 ppm), and **5-Ph** (-290, -376, and -682 ppm) each shows three singlets, which may be assigned to the Sn^{II} and Sn^{IV} nuclei of the cationic part and the Sn^{IV} nucleus of the stannate anion, respectively. The

LUMO ($\varepsilon = -3.24$ eV)   HOMO ($\varepsilon = -6.40$ eV)   HOMO-1 ($\varepsilon = -6.88$ eV)
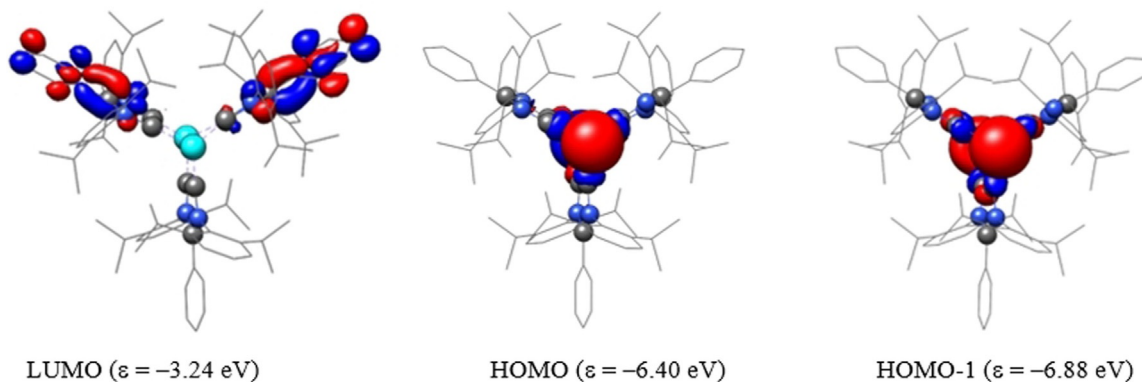
Figure 3. Selected molecular orbitals (isovalue 0.04) of **3-Ph** calculated at B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.

3-Ar (Ar = Ph or DMP)   **4-Ar** (E = S); **5-Ph** (E = Se)

$$2\ Cl_3Sn^- + 2\ E \rightarrow 2\ (ESnCl_3)^- \rightarrow (SnE_2) + (SnCl_6)^{2-}$$
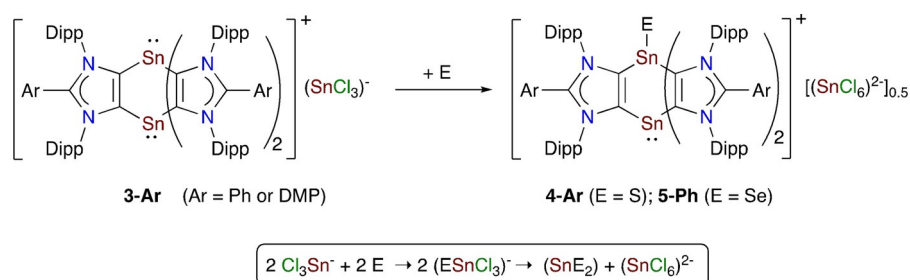
Scheme 2. Reactions of distannabarrelenes **3-Ph** and **3-DMP** with elemental chalcogens to **4-Ar** and **5-Ph**.

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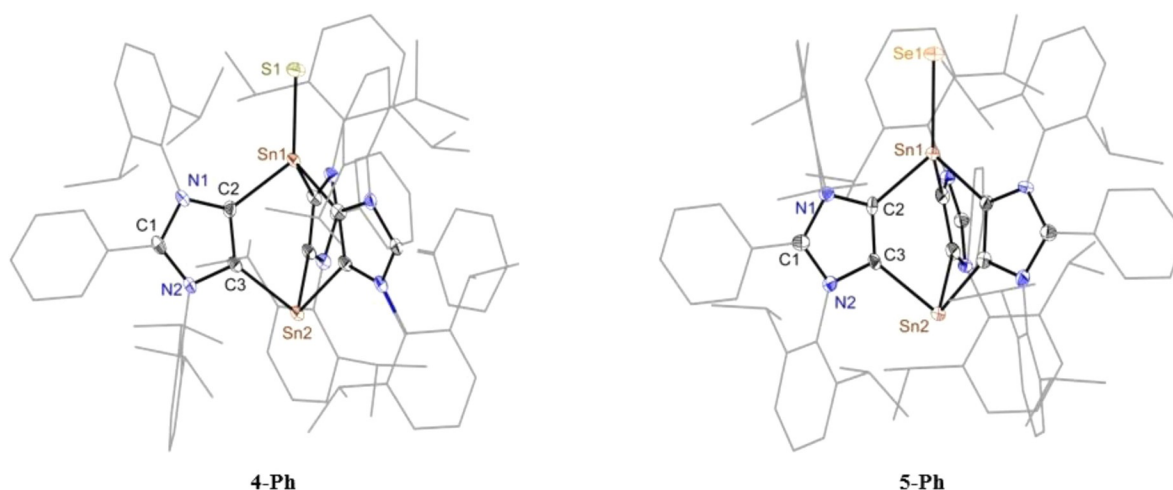European Chemical
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Figure 4. Solid-state molecular structures of **4-Ph** and **5-Ph**. Hydrogen atoms, solvent molecules and the counter anion ($SnCl_6$)$^{2-}$ are omitted and aryl groups are shown as wireframe models for clarity.

$^{119}Sn\{^1H\}$ NMR signals for the SnS moiety of **4-Ph** (-376) and **4-DMP** (-366) are high-field shifted compared to that of Chivers's (-133 ppm)[24] and Parkin's (-301 ppm)[25] terminal sulfido compounds with three or four N-donor substituents at the tin atoms, respectively. The $^{77}Se\{^1H\}$ NMR spectrum of **5-Ph** (-439 ppm) shows a singlet, which is upfield shifted compared to that of Chivers's compound (-174 ppm)[24] with a four-coordinated tin atom, suggesting a large polarized nature of the $Sn^{\delta+}-Se^{\delta-}$ bond of **5-Ph**.[15h]

Compounds **4-Ph**, **4-DMP**, and **5-Ph** belong to a rare family of thiolate/selenolate derivatives with a terminal Sn-E bond (Table 1).[3h, 26] The solid-state molecular structures of **4-Ph** and **5-Ph** (Figure 4) show the expected bond connectivity. The triclinic unit cell of **4-Ph** as well as **5-Ph** contains two cationic fragments, where the counter anion ($SnCl_6$)$^{2-}$ resides at the crystallographic center of inversion. The Sn–S bond length of **4-Ph** (2.262(1) Å) is comparable with that calculated for $H_2Sn=S$ (2.22 Å)[27] as well as those of the literature known compounds containing a terminal Sn=S unit (2.25–2.28 Å) with a four coordinated tin atom.[25, 28] This is, however, considerably smaller with respect to known Sn–S single bond lengths (ca. 2.50 Å).[26, 29] The Sn–Se bond length (2.388(5) Å) in **5-Ph** is in line with the literature known values for Sn=Se double bonds (2.37–2.42 Å) in stannaneselones,[26, 30] but smaller than the Sn–Se single bond length (2.55–2.60 Å).[26, 29] In **4-Ph** and **5-Ph**, the Sn^{II}–C$_{ADC}$ bond lengths (2.26–2.28 Å) are similar to those of **3-Ph** (2.24 to 2.27 Å), whereas the Sn^{IV}–C$_{ADC}$ bond lengths (2.18–2.20 Å) are slightly shorter than those of **3-Ph** (Table 1). This bond length trend for Sn^{II} and Sn^{IV} units is expected, which is also in line with the Jurkschat's Sn^{IV} compounds (2.13–2.15 Å) featuring a C4-bound aNHC.[31] The C$_{ADC}$-Sn-C$_{ADC}$ bond angles of **4-Ph** at the Sn^{II} center (87.8 to 88.8°) are comparable with those of **3-Ph** (86.9 to 90.1°), which are, however, larger at the Sn^{IV} center (94.4 to 95.6°).

The computed NPA (at the B3LYP/6-31G(d) level of theory) show positive charge at the tin atoms of **4-Ph** (1.79 e for Sn^{IV} and 1.55 e for Sn^{II}) and **5-Ph** (1.74 for Sn^{IV} and 1.30 e for Sn^{II}), whereas the sulfur ($-0.56\,e$ for **4-Ph**) and selenium ($-0.27\,e$ for **5-Ph**) atoms have a negative charge. This is consistent with the electronegativity difference between Sn and S/Se atoms and suggests that the Sn=E (E = S, Se) bond in **4-Ph** and **5-Ph** is polarized towards the chalcogen atom. As expected, the carbene carbon atoms in **4-Ph** and **5-Ph** also bear negative charges.[17] The NBO analyses also confirm that the Sn=E bond of **4-Ph** and **5-Ph** is polarized as evidenced by the WBI (Wiberg Bond Indices) of 1.08 and 0.96, respectively. Similar to compound **3-Ph**, the HOMO of **4-Ph** (-12.05 eV) and **5-Ph** (-11.79 eV) each is mainly the lone pair orbital at the Sn^{II} moiety with a small contribution from the p-orbital of sulfur or selenium atom (Figure 5). The HOMO of **4-Ph** and **5-Ph** is, however, considerably stabilized compared to that of **3-Ph** (-6.40 eV), rationalizing their kinetic inertness towards further oxidation with chalcogens. The LUMO of **4-Ph** and **5-Ph** also show contribution from s-orbital of Sn^{II} and p-orbital of sulfur and selenium (see the Supporting Information).

In conclusion, the first distannabarrelenes **3-Ar** featuring two all carbon substituted stannylenes have been reported as crystalline solids. These ionic compounds are derived from ADCs and feature cationic bicyclo[2.2.2]-1,4-bis-stannylene and anionic SnCl$_3$ units. **3-Ar** selectively react with chalcogens (E = S or Se) to form mixed-valence Sn^{II}/Sn^{IV} compounds **4-Ar** and **5-Ph**, in which the barrelene moiety remains intact. The anionic part (SnCl$_3$) of **3-Ar** also reacts with chalcogens to form the (SnCl$_6$)$^{2-}$ anion by the disproportionation of putative (ESnCl$_3$)$^-$ species. This report emphasizes the suitability of ADCs for accessing heterocyclic compounds featuring low-valent maingroup elements with interesting bonding motifs, which may lead to new discoveries in synthesis and materials science.

Acknowledgements

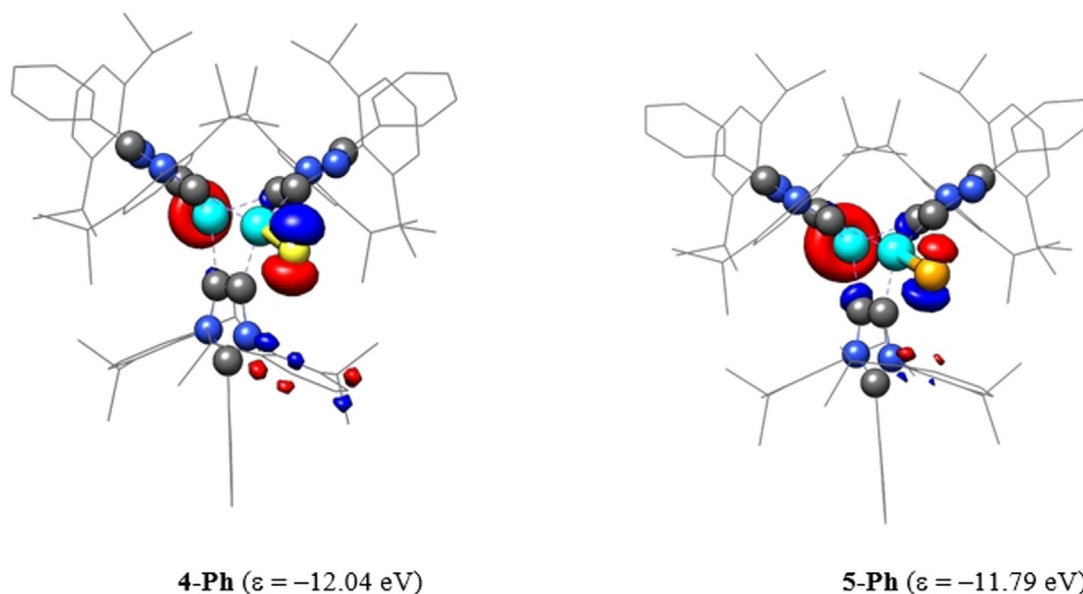**4-Ph** ($\varepsilon = -12.04$ eV)   **5-Ph** ($\varepsilon = -11.79$ eV)

Figure 5. HOMOs (isovalue 0.04) of **4-Ph** and **5-Ph** calculated at B3LYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.

Conflict of interest

The authors declare no conflict of interest.

Keywords: barrelenes · ditopic carbenes · mixed valency · stannylenes · tin

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