

Tin Chemistry | Hot Paper |

Distannabarrelenes with Three Coordinated Sn^{II} AtomsMahendra K. Sharma, Timo Glodde, Beate Neumann, Hans-Georg Stammer, and Rajendra S. Ghadwal^{*[a]}

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

Abstract: Crystalline 1,4-distannabarrelene compounds [(ADC^{Ar})₃Sn₂]SnCl₃ (**3-Ar**) (ADC^{Ar} = {ArC(NDipp)₂CC}; Dipp = 2,6-*i*-Pr₂C₆H₃, Ar = Ph or DMP; DMP = 4-Me₂NC₆H₄) 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 SnCl₃ is formally derived from SnCl₂ 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** ($\epsilon = -6.40$ 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)](SnCl₃)_{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 C–H deprotonation of a N-heterocyclic carbene (NHC), the *i*Pr (IPr = C(NDipp)CH₂, Dipp = 2,6-*i*-Pr₂C₆H₃), with *n*BuLi 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})₃Sn₂]SnCl₃ (ADC^{Ar} = ArC(NDipp)₂CC; Ar = Ph, **3-Ph**; DMP, **3-DMP**; DMP = 4-Me₂NC₆H₄) 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)CH₂; Ar = Ph, **1-Ph**; DMP, **1-DMP**; Dipp = 2,6-*i*-Pr₂C₆H₃) with *n*BuLi.^[16] Treatment of freshly prepared **2-Ph** and **2-DMP** with SnCl₂ affords the compounds [(ADC^{Ar})₃Sn₂]SnCl₃ (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-distannabarrelene and an anionic SnCl₃ moieties. The ADC^{Ar} moiety in **3-Ar**

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