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)3Sn2]SnCl3 (3-Ar) (ADC Ar = (Ar(CN)2)CC; Dipp = 2,6-iPr2C6H3, Ar = Ph or DMP; DMP = 4-Me2NC6H4) derived from anionic dicarbene Li(ADC Ar)2 (2-Ar) (Ar = Ph or DMP) have been reported. The cationic moiety of 3-Ar features a barrelene framework with three coordinated Sn 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 (ε = −6.40 eV) is mainly the lone-pair orbital at the Sn I atoms of the barrelene unit. 3-Ar readily react with sulfur and selenium to afford the mixed-valence Sn III/Sn IV compounds [(ADC Ar)3SnSn(EE)](SnCl6)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 alkynes, allynes, 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). Barrelen 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,[6] this intriguing molecule has been in focus of synthetic as well as theoretical chemists.[6] Interest in barrelene type species has also been predicted 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 IV 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 = (CN)2PhC6H4), 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 carbene 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]SnCl3 (ADC Ar = (Ar(CN)2)CC; 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 dicarbene Li(ADC Ar) (Ar = Ph, 2-Ph; DMP, 2-DMP) are readily accessible by the double deprotonation of C2-arylated 1,3-imidazolium salts (IPrAr)Cl (IPrAr = Ar(CN)(N-Dipp)CH2); Ar = Ph, 1-Ph; DMP, 1-DMP; Dipp = 2,6-iPr2C6H3) with nBuLi.[16] Treatment of freshly prepared 2-Ph and 2-DMP with SnCl4 affords the compounds [(ADC Ar)3Sn]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 SnCl4 moiety. The ADC Ar moiety in 3-Ar

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