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Carbene Complexes of Stannocenes

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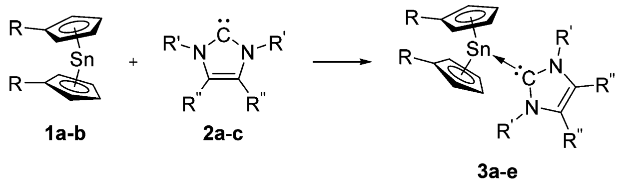
Supporting Information

ABSTRACT: Several stannocene carbene complexes, **3a**−**3g**, were synthesized and examined in solution by NMR spectroscopy and in the solid state by single-crystal X-ray diffraction. In this new class of metallocene carbene complexes, coordination of the carbene to the tin atom was found to be comparably weak and mostly due to attractive dispersion forces, as indicated by density functional theory calculations. Furthermore, coordination of the N-heterocyclic carbenes results in a weakening of the Sn−Cp bonds, making these complexes very reactive and short-lived at room temperature.

Since the first synthesis and isolation of Wanzlick−Arduengo-type N-heterocyclic carbenes (NHCs),[1−3] they have evolved into one of the most important ligands in transition-metal chemistry.[4−7] In addition, numerous examples of main-group metal complexes with NHCs are known.[8] Furthermore, carbenes have played an important role in the isolation of low-valent main-group compounds in recent years.[4,8−11] Among others, several germylene, stannylene, and plumbylene NHC complexes,[12−22] as well as related stannylene isonitrile complexes,[23] have been reported. However, although NHC complexes of group 2 and 4 metallocenes are known[24−26] and Lewis acid−base adducts of stannocene and plumbocene with tetramethylethylenediamine and bipyridine have been reported,[27,28] highlighting the Lewis acidic character of these metallocenes, the reactivity of group 14 metallocenes (tetrelocenes) toward NHCs is unexplored. On this basis, we were intrigued to study the reactivity of stannocenes, one of the longest known group 14 metallocenes, toward NHCs.

When equimolar amounts of stannocene (**1a**) were mixed with NHCs **2a** and **2b** in deuterated benzene at room temperature and the mixture was examined by multinuclear NMR spectroscopy, new sets of signals were detected. Most characteristic, signals in the ^{13}C NMR spectra at 198.3 ppm (in the case of **2a**) and 209.1 ppm (in the case of **2b**), along with signals at −1824 ppm (in the case of **2a**) and −1936 ppm (in the case of **2b**) in the ^{119}Sn NMR spectra, were observed. These spectroscopic findings indicated the formation of stannocene carbene complexes **3a** and **3b**. To verify these findings, an independent synthesis of complexes **3a** and **3b** by the treatment of **2a**·$SnCl_2$ and **2b**·$SnCl_2$ with 2 equiv of cyclopentadienyllithium was carried out, giving **3a** and **3b**, respectively.[29] In order to investigate the dependence of the complexation reaction on steric demand, dimethylstannocene (**1b**) was reacted with NHCs **2a** and **2b** under identical conditions. The analogues products **3c** and **3d** were obtained, indicating little steric effect of the methyl groups on the cyclopentadienyl rings (Scheme 1).

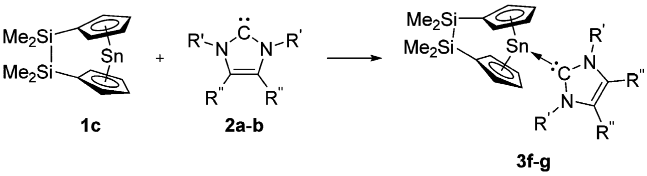
Scheme 1. Reactions of Stannocenes 1a and 1b with NHCs 2a−2c[a]



[a]**1a**: R = H. **1b**: R = Me. **2a**: R′ = *i*Pr and R′′ = Me. **2b**: R′ = Mes and R′′ = H. **2c**: R′ = R′′ = Me. **3a**: R = H, R′ = *i*Pr, and R′′ = Me. **3b**: R = Me, R′ =*i*Pr, and R′′ = Me. **3c**: R = H, R′ = Mes, and R′′ = H. **3d**: R = Me, R′ = Mes, and R′′ = H. **3e**: R = R′ = R′′ = Me.

However, when the steric demand is further increased, coordination of an NHC to the tin atom can be prevented. For example, decamethylstannocene (Cp^*_2Sn) does not react with NHCs, just as there is no reaction between **1a** and *N*,*N*′-bis(2,6-diisopropylphenyl)-substituted NHCs. On the other hand, when the steric demand on the NHC is lowered to a minimum, the stannocene carbene complexes become unstable at room temperature. For example, if **1a** is reacted with *N*,*N*′-dimethyl-substituted carbene **2c**, a complex mixture of products is obtained, along with precipitation of metallic tin. However, when **1b** is reacted with NHC **2c** at 248 K, the corresponding complex **3e** can be obtained. **3e** is stable at temperatures below 253 K for several hours and decomposes rapidly upon warming to room temperature. Similar to the stannocenes **1a** and **1b**, the recently reported stannocenophane (**1c**)[30] gives the corresponding NHC complexes **3e** and **3f** with NHCs **2a** and **2b** (Scheme 2).

Scheme 2. Reactions of 1c with NHCs 2a and 2b[a]



[a]**3f**: R′ = *i*Pr and R′′ = Me. **3g**: R′ = Mes and R′′ = H.

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For all of the carbene complexes **3a**−**3e**, similar NMR spectroscopic parameters are observed (Table S1).[16] The ^{13}C resonances for the carbene carbon atoms experience a high-field shift upon coordination, whereas the ^{119}Sn resonances for **3a**−**3d**, **3f**, and **3g** are downfield-shifted relative to the free stannocenes **1**. To investigate the structure of complexes **3** in more detail, single-crystal X-ray diffraction analysis was performed (Figure 1).

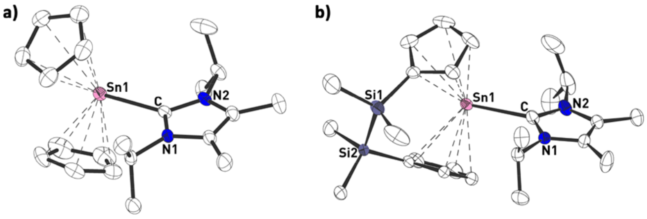


Figure 1. Molecular structures of **3a** (a) and **3f** (b) in the crystal (thermal ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

Complexes **3** all show structural similarities in the solid state, which are very long Sn−C^{NHC} bonds compared to 228.0 pm in $(NHC{\cdot}Sn)_2$,[31] 228.7 pm in a NHC·SnR$^+$ [R = 4-*t*Bu-2,6-$(P(O)(OiPr)_2)_2C_6H_2$],[32] 229.0 pm in **2a**·$SnCl_2$,[33] or 237.9 pm in **2a**·$SnTip_2$ (Tip = 2,4,6-*i*PrC_6H_2),[34] elongated Sn−Cp^{centroid} bonds compared to stannocenes **1a**−**1c**, and an increase in the bending angle α between the cyclopentadienyl ring planes (Table 1 and Figure 2). **3e** exhibits the shortest Sn−C^{NHC} bond of all stannocene carbene complexes **3** as well as the longest Sn−Cp^{centroid} distances. This indicates a relatively strong coordination of the carbene to the tin atom due to little steric bulk in this case, along with weak Sn−Cp bonds. The elongation in the Sn−Cp^{centroid} bonds can be explained by their weakening, due to electron donation from the carbene to the lowest unoccupied molecular orbital (LUMO) of stannocene, which corresponds to an antibonding linear combination of the Sn−Cp bond.[35] This is also the reason for the high reactivity and limited stability of stannocene carbene complexes **3a**−**3g** at room temperature.

In all complexes **3**, unequal Sn−C^{Cp} bond lengths are observed,[38] while there is only one signal in the ^{1}H and ^{13}C NMR spectra for the cyclopentadienyl moieties in **3a** and **3c**.[29] This indicates a fluxional behavior in solution due to rapid [1,5]-Sn sigmatropic rearrangements, as is common for these types of compounds.[39−41] φ angles of 72.2−88.0° between the Cp^{centroid}−Sn−Cp^{centroid} and NHC planes in **3** suggest that there is little to no back-bonding from the lone pair at the tin atom to the NHC. This is in agreement with an energetically low-lying lone pair at the tin atom and an energetically high-lying LUMO of the NHC.[29,35,42] To further investigate the bond strengths in these systems, density functional theory (DFT) calculations at the B3LYP-D3/6-311+G(d,p)(C,H,N,Si);SDD(Sn)/PCM(benzene) level of theory were conducted.[36] The bonding energies of the NHCs **2** to stannocenes **1** in complexes **3** were calculated to be ΔE = 65.9−96.6 kJ·mol^{-1}. When the dispersion force correction terms were omitted [B3LYP/6-311+G(d,p)(C,H,N,Si);SDD(Sn)/PCM(benzene)//B3LYP-D3/6-311+G(d,p)(C,H,N,Si);SDD(Sn)/PCM(benzene)], the calculated BDEs decreased by 70.9−99.8%, indicating that the majority of the complexation energy in complexes **3** can be attributed to attractive dispersion force interactions rather than classical covalent Sn−C^{NHC} bonding.[29] This is in line with recent reports on the importance of dispersion force interactions in many main-group compounds.[43,44] Considering the relatively long Sn−C^{NHC} bonds and the comparably small BDEs, it can be assumed that complexes **3** exist in a dissociative equilibrium with **1** and **2** in solution. This is in agreement with the experimental findings that, upon reaction of **3a** with aluminum chloride, no coordination of $AlCl_3$ to the lone pair at the tin atom is observed, but instead **2a**·$AlCl_3$ along with **1a** is formed, as indicated by ^{27}Al and ^{119}Sn NMR spectroscopy [$\delta(^{27}Al)$ = 107.0; $\delta(^{119}Sn)$ = −2199; Scheme 3].

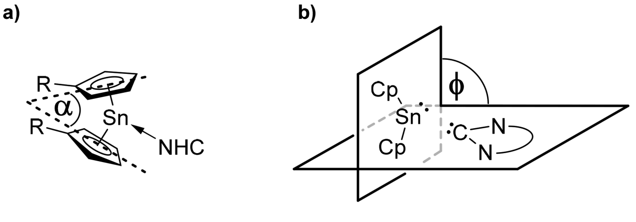


Figure 2. Definition of (a) angle α (angle between cyclopentadienyl planes) and (b) angle φ (angle between the Cp^{centroid}−Sn−Cp^{centroid} and NHC planes) in stannocene NHC complexes **3**.

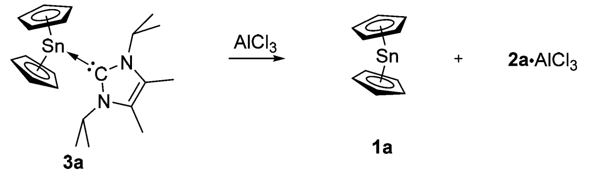
Furthermore, when 2 equiv of **1a** was mixed with 1 equiv of NHC **2a** or 1 equiv of **1a** was mixed with 2 equiv of NHC **2a** in benzene, only one set of signals is observed in the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra, indicating a rapid exchange of coordinated and free carbene in solution at room temperature.

Table 1. Relevant Bond Lengths and Angles and Bond Dissociation Energies (BDEs) for 1a−1c and 3a−3g

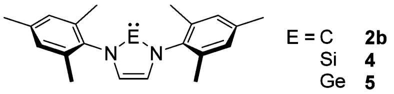
compound	α (deg)[a]	Sn−Cp^{centroid} (pm)	Sn−C^{NHC} (pm)	φ (deg)[a]	BDE (kJ·mol^{-1})[b]
1a	45.9−46.7[c]	237.0−243.7[c]			
1b	50[d]	240[d]			
1c	47.1−47.3[c]	239.4−242.4[c]			
3a	56.4−59.5[c]	256.1−265.3[c]	245.2−246.6[c]	85.6	70.7
3b	55.2	260.5−262.8[c]	245.1	85.6	72.1
3c	65.3	258.7−262.4[c]	246.5	80.5	88.0
3d	57.7−64.9[c]	253.6−259.5[c]	249.8−250.6[c]	72.2	83.6
3e	67.6	264.5−265.5[c]	238.9	79.1	65.9
3f	56.8	260.2−261.9[c]	248.9	84.8	74.9
3g	62.4	263.5−264.7[c]	248.7	88.0	96.6

[a] See Figure 2 for definitions. [b] BDE is calculated as the difference in the absolute energies between **1**, NHC **2**, and the corresponding stannocene NHC complex **3** at the B3LYP-D3/6-311+G(d,p)(C,H,N,Si);SDD(Sn)/SCRF=PCM(benzene) level of theory.[36] [c] Multiple values are given because more than one molecule is found in the asymmetric unit and/or the bond length or angle is found more than once in the molecule. [d] Value determined by gas electron diffraction.[37]

Scheme 3. Reaction of the Stannocene Carbene Complex 3a with Aluminum Chloride



To investigate whether the concept of carbene complexation to stannocenes can be extended to the heavier N-heterocyclic tetrylenes, *N*,*N*′-bis(2,4,6-trimethylphenyl)-substituted N-heterocyclic silylene (**4**)[45,46] and germylene (**5**)[47] were synthesized and reacted with stannocenes **1a** and **1b**.



While the reaction of **1a** with **4** resulted in the formation of a mixture of products along with precipitation of tin metal, no reaction was observed by NMR spectroscopy when **1b** was treated with **4**. Corresponding to this, storage of a toluene solution mixture of **1b** + **4** at 248 K yielded only crystals of the starting materials and not of a stannocene silylene complex. Similarly, no reactions were observed between stannocenes **1a** and **1b** and **5**. These results indicate that, unlike for group 2 metallocenes,[48] the complexation of N-heterocyclic tetrylenes to stannocenes is exclusive to NHCs and cannot be observed for their heavier analogues, like **4** and **5**, because of their decreased σ-donor strengths.

In summary, we were able to show that different stannocenes **1** are capable of forming complexes **3** with NHCs **2**. This is in agreement with the carbene germylene and stannylene complexes reported before.[12−15,34] The heavier analogues of NHC **2b**, silylene **4**, and germylene **5** do not form complexes with stannocenes **1a** and **1b** in the same way. Complexes **3a**−**3g** have been studied in solution by multinuclear NMR spectroscopy and in the solid state by single-crystal X-ray diffraction. In solution, it can be assumed that they exist in a dissociative equilibrium. Their solid-state structures reveal a "side-on coordination" of the carbenes to the stannocene moieties, with no back-bonding from the tin atom to the NHC and therefore long Sn−C$^{\text{NHC}}$ single bonds, rather than a stannene-type structure. Bonding analysis by DFT calculations shows weak coordination of the carbenes to the tin center with calculated complexation energies between 65.9 and 96.6 kJ·mol^{-1}, 70.9−99.8% of which can be attributed to attractive dispersion force interactions rather than classical covalent bond interactions. Complexes **3** present a new class of stannocene complexes, highlighting the Lewis acidic character of the tin atom and the inertness of its lone pair, which opens up this new field of research. Further studies will focus on other related coordination complexes of group 14 metallocenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01432.

Experimental details, NMR spectroscopic data, and computational details (PDF)

Accession Codes

CCDC 1844881−1844887 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(35) See the Supporting Information for a qualitative molecular orbital diagram of group 14 metallocenes (p S22, Figure S23).

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