Main-Group Chemistry

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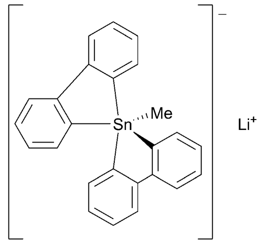
Dilithium Hexaorganostannate(IV) Compounds**

Ireen Schrader, Kornelia Zeckert, and Stefan Zahn**

Abstract: *Hypercoordination of main-group elements such as the heavier Group 14 elements (silicon, germanium, tin, and lead) usually requires strong electron-withdrawing ligands and/or donating groups. Herein, we present the synthesis and characterization of two hexaaryltin(IV) dianions in form of their dilithium salts* $[Li_2(thf)_2\{Sn(2\text{-}py^{Me})_6\}]$ *(*$py^{Me} = C_5H_3N\text{-}5\text{-}Me$*) (**2**) and* $[Li_2\{Sn(2\text{-}py^{OtBu})_6\}]$ *(*$py^{OtBu} = C_5H_3N\text{-}6\text{-}OtBu$*) (**3**). Both complexes are stable in the solid state and solution under inert conditions. Theoretical investigations of compound **2** reveal a significant valence 5s-orbital contribution of the tin atom forming six strongly polarized tin–carbon bonds.*

Hypercoordination is the property of main-group elements in molecular entities to bind more ligands than needed to comply with the Lewis octet rule. Following the expectations, the heavier Group 14 elements silicon, germanium, tin, and lead tend more readily to exceed the normal four-coordination than their lighter congener carbon.[1] Numerous neutral, cationic, or anionic organyl complexes exist, in which tin in particular may exhibit coordination numbers of five, six, or seven if at least one electron-withdrawing (non-carbon) substituent is present or hypercoordination is enforced by intra- or intermolecular donor–acceptor interactions.[2]

Five-coordinate tin(IV) compounds exclusively based on tin–carbon bonds have been proposed as key intermediates in the widely used tin–lithium exchange reactions as evidenced by low-temperature NMR spectroscopy.[3–5] Their observation, however, is far from routine and their isolation appears particular challenging because they are highly unstable, a result of the high liability of such species. Although there are a few examples of the lighter congener silicon,[6] the only isolated pentaorganotin complex is the methylated spirobistannafluorene **1**.[7] Confirmation of a compound containing more than five organic substituents has been elusive to date.



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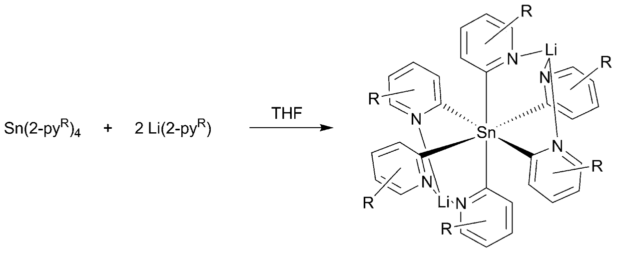
Herein, we show that tin may host six electron-rich aryl ligands to give thermally stable zwitterionic compounds $[Li_2(thf)_n\{Sn(2\text{-}py^R)_6\}]$ ($py^R = C_5H_3N\text{-}5\text{-}Me$, $n = 2$ (**2**); $C_5H_3N\text{-}6\text{-}OtBu$, $n = 0$ (**3**)), in which the counterions are intramolecularly stabilized by a hexaaryltin(IV) dianion.

The complexes **2** and **3** have been prepared from reactions of $Sn(2\text{-}py^R)_4$[8] with two equivalents of (2-pyridyl)lithium at −60 °C and at room temperature, respectively, and isolated in 52 % and 76 % yield, respectively (Scheme 1). Workup and recrystallization from red brownish, saturated tetrahydrofuran (THF) solutions at room temperature afforded **2**[9] and **3** as air- and moisture-sensitive yellow and colorless crystals, respectively, which when sealed in capillaries under nitrogen melt at rather high temperature (137 °C (**2**) and 167 °C (**3**)) with concomitant decomposition.



2, 3

Scheme 1. Synthesis of the hexakis(2-pyridyl)tin(IV) compounds (R = Me (**2**), O*t*Bu (**3**); THF ligand not shown in **2**).

The X-ray diffraction (XRD) structural analyses[10] revealed the core arrangement in both complexes to be similar. The overall structure features a $[Sn(2\text{-}py^R)_6]^{2-}$ ion with the two Li^+ counterions symmetrically coordinated by the N atoms of each of three pyridine rings and, in **2**, one further THF ligand (Figure 1). In **3** the two Li^+ ions are exclusively coordinated by the three pyridine rings without any further contact (see the Supporting Information). This zwitterionic arrangement is close to that found for related (2-pyridyl)tin(II) compounds[11] and differs to **1**[7a] in which the lithium cation is isolated from the anionic core. In **2** the tin

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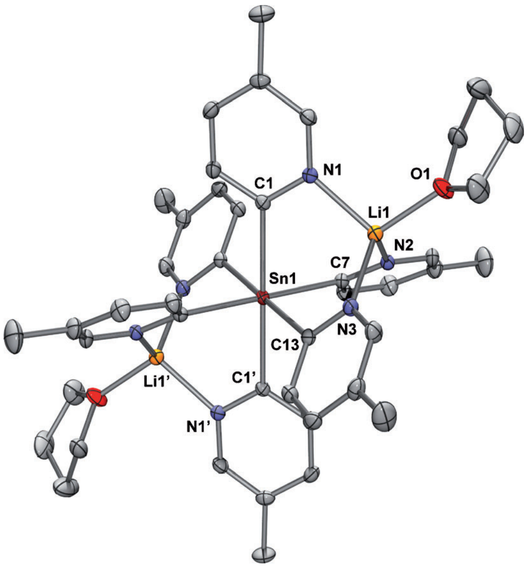

Figure 1. Molecular structure of **2** (thermal ellipsoids set at 40%, hydrogen atoms and the THF solvent molecule have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Sn1–C1 2.293(2), Sn1–C7 2.291(2), Sn1–C13 2.305(2), Sn1⋯Li1 3.368(4), Li1–N1 2.027(4), Li1–N2 2.031(4), Li1–N3 2.015(4), Li1–O1 1.967(4); C1-Sn1-C7 91.88(7), C7-Sn1-C13 92.00(7), C1-Sn1-C13 92.04(7), C1-Sn1-C1′ 180.0, C7-Sn1-C7′ 180.0(1), C13-Sn1-C13′ 180.0(1), N1-Li1-N2 106.8(2), N1-Li1-N3 107.4(2), N2-Li1-N3 107.6(2); symmetry equivalent atoms generated by $-x+2$, $-y$, $-z$.

atom exhibits an almost ideal octahedral geometry with marginally deviating Sn–C_{ipso} bond lengths of 2.291(2)–2.305(2) Å that are considerably longer than typical tin–carbon bonds (2.14 Å).[2] The C_{ipso}-Sn-C_{ipso} angles average 91.97(7)° and 180.0(1)°. The structural parameters of **3** closely resemble those of **2**.

The NMR spectroscopic data of **2** and **3** in solution are consistent with their structure in the solid state. In the ^{119}Sn{^{1}H} NMR spectra, only one resonance at $\delta = -541$ ppm (**2**) and $\delta = -555$ ppm (**3**) is observed, which is significantly shifted upfield compared to those of stannates bearing only five carbon substituents ($\delta = -250$ to -350 ppm)[4,5,7] but contrasts the strong upfield resonance at $\delta = -916$ ppm of in situ generated $[Sn(CN)_6]^{2-}$.[12] The $^{1}J_{\text{Sn-C}}$ coupling of approximately 430 Hz in **2** and **3** is considerably smaller than the $^{1}J_{\text{Sn-C}}$ coupling constant found for the starting material Sn(2-py^{R})$_4$ (ca. 690 Hz). The ^{1}H NMR spectra reveal one set of aromatic protons in accordance with an ideal octahedral molecular symmetry at the tin center on the time scale of the experiment. Complexes **2** and **3** are stable in solution with respect to tin–carbon bond dissociation, even at higher temperature (up to 65 °C in THF). In addition, no formation of the corresponding pentaorganotin derivatives has been observed on either treating Sn(2-py^{R})$_4$ with one equivalent Li(2-py^{R}) or mixing of Sn(2-py^{R})$_4$ with **2** or **3** in appropriate stoichiometry.

Further support for the high stability of the six-coordinate complexes has been obtained from the calculated free reaction enthalpy with -272.9 kJ mol^{-1} (B3LYP-D2/def2-TZVP//BP86-D2(RI)/def2-TZVP) for a formation of compound **2** from Sn(2-py^{Me})$_4$ and (2-pyridyl)lithium in THF solution.

To clarify the nature of bonding in these hexaaryltin(IV) derivatives, the electronic structure of compound **2** was analyzed (see the Supporting Information). The natural population analysis (NPA)[13] revealed a partial charge (q^{NPA}) of $+1.36$ at the Sn atom while the negative charge of the bonded carbon (C_{ipso}) atom is surprisingly small ($q^{\text{NPA}} = -0.09$). Furthermore, quantum chemistry wave-function analysis methods suggest a significant covalent Sn–C_{ipso} bond interaction (Wiberg bond index:[14] 0.54, two-center shared electron number:[15] 0.66).

No indications for three-center-four-electron (3c–4e) bonding were found in agreement with related third-row main-group compounds.[16–18]

Natural bond orbital (NBO) analysis shows that a structure with six very polar covalent Sn–C_{ipso} bonds (Figure 2) is the most suited Lewis structure, in which the valence 5s natural atomic orbital (NAO) makes a strong overall contribution to these Sn–C_{ipso} bonds.[19] Contrary to third-row main-group element compounds, the qualitative influence of the 5d-atomic orbitals of the Sn atom in contracting the metal-to-ligand bonds and hence in stabilizing the hypercoordinate compounds is found to be negligible. The total energy difference between the TZV (without d-atomic orbitals) and TZVPP (with d-atomic orbitals) basis set for **2** is only 14.6 kJ mol^{-1} and a low occupation of 5d NAOs ($n_e = 0.01$) is observed. For comparison, 3d-NAO occupations larger than 0.2 electrons have been reported for related third-row-element compounds and the total energy decreases by more than 400 kJ mol^{-1} if d-orbitals are included in the linear combination atomic orbital (LCAO)ansatz.[20]

Undoubtedly, the intramolecular coordination of the two lithium cations by the hexaaryltin dianion in compounds **2** and

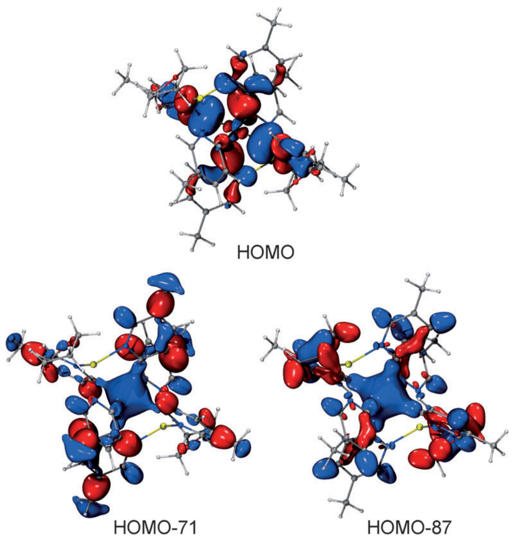

Figure 2. Illustration of selected molecular orbitals for complex **2** (isosurface contours at 0.03 eÅ^{-3}). HOMO−71 and HOMO−87 indicate a covalent interaction of the valence 5s orbital at Sn with 2p orbitals of the C_{ipso} atoms.

3 enables an effective charge separation, and thus contributes to the formation and stabilization of the dianion itself. In a preliminary experiment we found that **3** smoothly reacts with $ZnCl_2$ at ambient temperature to give the stannane Sn(2-py^{OtBu})$_4$ and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) stabilized ZnCl(2-py^{OtBu}) (**4**).[21] Further investigations will be addressed to evaluate the potential use of these compounds as soft aryl transfer agents.

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenk equipment.

2: A suspension of [Sn(2-py^{Me})$_4$LiCl] (0.90 g, 1.7 mmol) in diethyl ether (10 mL) was added to a cooled (−60 °C) solution of Li(2-py^{Me}) (prepared from 2-bromo-5-methylpyridine (0.59 g, 3.4 mmol) and *n*BuLi (2.1 mL, 1.6 M in hexane)) in diethyl ether (20 mL). The reaction mixture was stirred for approximately 3 h during which time it was allowed to warm to room temperature. A pale yellow precipitate formed. After collection by filtration, the residue was dissolved in THF. Concentration of the THF solution and storage at room temperature gave yellow crystals of **2**. Yield: 0.73 g (52 %). Mp: 137 °C (decomposes). C,H,N analysis (%) calcd for $C_{44}H_{52}N_6O_2Li_2Sn$: C 63.71, H 6.32, N 10.13; found C 63.63, H 6.46, N 10.25. ^{1}H NMR (400.1 MHz, [D$_8$]THF, 295 K, TMS): $\delta = 1.69$ (br s, 8 H, thf, CH_2), 2.05 (s, 36 H, Me), 3.54 (br s, 8 H, thf, OCH_2), 6.51 (s, 12 H, py), 8.34 ppm (s, 6 H, py); ^{13}C{^{1}H} NMR (75.49 MHz, [D$_8$]THF, 297 K, TMS): $\delta = 18.7$ (Me), 26.6 (thf), 68.4 (thf), 126.5 (py), 131.7 ($^3J_{\text{C-Sn}} = 31$ Hz, py), 134.6 ($^2J_{\text{C-}^{119}\text{Sn}} = 78$ Hz, $^2J_{\text{C-}^{117}\text{Sn}} = 76$ Hz, py), 147.0 ($^3J_{\text{C-Sn}} = 45$ Hz, py), 204.1 ppm ($^1J_{\text{C-}^{119}\text{Sn}} = 436$ Hz, $^1J_{\text{C-}^{117}\text{Sn}} = 417$ Hz, C_{ipso}); ^{7}Li NMR (155.5 MHz, [D$_8$]THF, 295 K, TMS): $\delta = 3.3$ ppm. ^{119}Sn{^{1}H} NMR (149.2 MHz, [D$_8$]THF, 295 K, TMS): $\delta = -541$ ppm.

3: Li(2-py^{OtBu}) (0.25 g, 1.58 mmol) was added to a solution of Sn(2-py^{OtBu})$_4$ (0.57 g, 0.79 mmol) in THF (15 mL) at room temperature. The dark brownish reaction mixture was stirred for approximately 10 min, then the solution was concentrated and stored at −18 °C overnight to give colorless crystals of **3**. Yield: 0.6 g (72 %). Mp: 163 °C. C,H,N analysis (%) calcd for $C_{55}H_{74}N_6O_6Li_2Sn$: C 62.74, H 7.02, N 8.13; found C 62.42, H 7.02, N 8.09. ^{1}H NMR (400.1 MHz, [D$_8$]THF, 296 K, TMS): $\delta = 1.47$ (s, 54 H, CMe_3), 6.35 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 6 H, py), 6.43 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 6 H, py), 6.80 ppm (t, $^3J_{\text{H-H}} = 7.5$ Hz, 6 H, py); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 297 K, TMS): $\delta = 30.0$ (C*Me*$_3$), 79.3 (*C*Me$_3$), 110.8 (py), 130.6 ($^2J_{\text{C-Sn}} = 73$ Hz, py), 134.0 ($^3J_{\text{C-Sn}} = 33$ Hz, py), 160.9 ($^3J_{\text{C-Sn}} = 45$ Hz, py), 206.2 ppm ($^1J_{\text{C-}^{119}\text{Sn}} = 425$ Hz, $^1J_{\text{C-}^{117}\text{Sn}} = 406$ Hz, C_{ipso}); ^{7}Li NMR (155.5 MHz, [D$_8$]THF, 296 K, TMS): $\delta = 4.4$ ppm; ^{119}Sn{^{1}H} NMR (149.2 MHz, [D$_8$]THF, 297 K, TMS): $\delta = -555$ ppm ($^1J_{\text{Sn-C}} = 434$ Hz).

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[8] In case of py^R = C_5H_3N-5-Me the tetrakis(2-pyridyl)stannane was obtained in form of the LiCl coordinating complex [Sn(2-py^R)$_4$LiCl], which was used without further purification.

[9] Compound **2** crystallized as its solvate **2**·2 THF. The solvating THF molecules were removed in vacuo prior spectroscopic analysis.

[10] For crystallographic data for compounds **2**·2 THF and **3**, see the Supporting Information. CCDC 1002115 (**2**·2 THF) and 1002114 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[21] For crystallographic data for compound **4**, see the Supporting Information. CCDC 1006855 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.