The First Structurally Authenticated Compound Containing a Bond between Divalent Tin and Tetravalent Tin

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*Summary: The reaction of 1 equiv of $[Li(thf)_3{\cdot}Sn(SiMe_3)_3]$ (**1**) with $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)Cl]$ in Et_2O at ambient temperature affords the corresponding divalent Sn−tetravalent Sn compound, $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$ (**2**) in high yield. A single-crystal X-ray diffraction study reveals **2** to be monomeric and the divalent Sn−tetravalent Sn bond to be 2.8689(5) Å; this is the first measurement of such a bond. The $^{119}Sn\{^1H\}$ NMR spectrum exhibits two singlet resonances at δ 897 and −502, each with well-resolved, isotopically shifted, ^{119}Sn and ^{117}Sn satellites (ca. 6700 and ca. 6400 Hz, respectively); this is the first measurement of ^1J coupling between Sn atoms of different valence.*

One aspect of the ongoing research interest in our laboratory (C.J.C, D.J.C., and S.P.C.) is the preparation and characterization of divalent group 14 element derivatives, ER_2 (E = Ge, Sn, or Pb; R = alkyl, aryl, amide, or silyl). In $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)R]$ (R = $C_6H_2\text{-}2,4,6\text{-}Pr^i_3$, $CH(PPh_2)_2$, or $Si(SiMe_3)_3$), we have used the additional intramolecular N-atom coordination provided by the $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$ ligand to stabilize novel heteroleptic derivatives of divalent Sn with respect to ligand redistribution and/or oligomerization.[1] For example, the reaction of 2 equiv of $Li(Et_2O){\cdot}C_6H_2\text{-}2,4,6\text{-}Pr^i_3$ with $SnCl_2$ in Et_2O at −78 °C affords the corresponding Sn(II) species $Sn(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2$, which upon warming to −30 °C, trimerizes to yield the structurally determined $[\{Sn(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2\}_3]$.[1,2] The $CH(PPh_2)_2$ derivative was of interest inter alia as the homoleptic Sn(II) and Pb(II) analogues have been prepared and structurally characterized, and the $CH(PPh_2)_2$ ligands were shown to possess two bonding modes (η^1, C-bound and η^2, P-bound) within the same molecule.[3,4] Furthermore, we were interested in the possible competition between the N atom and two P atoms for lone-pair donation to the Sn center. The $Si(SiMe_3)_3$ derivative was, to the best of our knowledge, the first structurally characterized heteroleptic Sn(II) silyl-containing compound. However, two examples have recently appeared in the literature $[Sn\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}(Si\{(-NCH_2Bu^t)_2\text{-}1,2\text{-}C_6H_4\}R)]$ (R = $C_6H_3\text{-}2,6\text{-}(NMe_2)_2$ or $N(SiMe_3)_2$].[5] These were prepared in good yield by treatment of the Si(II) species $Si\{(-NCH_2Bu^t)_2\text{-}1,2\text{-}C_6H_4\}$[6] with either $[Sn\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}_2]$[7] or $[Sn\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}\{N(SiMe_3)_2\}]$[7] and provide two rare examples in which the central divalent group 14 element is bound to an element more electropositive than carbon. Of particular

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(1) Cardin, C. J.; Cardin, D. J.; Constantine, S. P.; Convery, M. A.; Drew, M. G. B.; Fenske, D.; Rashid, H.; Teixeira, S. Manuscipt in preparation.

(2) Brady, F. J.; Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Devereux, M. M.; Lawless, G. A. *J. Organomet. Chem.* **1991**, *241*, 199−203.

(3) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 2159−2161.

(4) Balch, A. L.; Oram, D. E. *Inorg. Chem.* **1987**, *26*, 1906−1912.

(5) Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1997**, 1845.

(6) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. L.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211.

(7) Drost, C.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J. M. *Chem. Commun.* **1997**, 1141−1142.

(8) Cardin, C. J.; Cardin, D. J.; Convery, M. A.; Dauter, Z.; Fenske, D.; Devereux, M. M.; Power, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 1133−1144.

(9) Synthesis of $[Li(thf)_3{\cdot}Sn(SiMe_3)_3]$ (**1**). To a 500 mL Schlenk tube charged with a large stir bar, Li wire (8.75 g, 1260.81 mmol; cut into 3−4 mm long pieces), and thf (250 mL), cooled to −10 °C using dry ice/acetone, was added $SiMe_3Cl$ (50.8 mL, 43.46 g, 400 mmol) over a 5 min period. After stirring for 45 min, $SnCl_4$ (11.7 mL, 26.05 g, 100 mmol) was added dropwise over a 30 min period. The mixture was stirred for 16 h, solids were allowed to settle, and the yellow thf solution was filtered. Et_2O (100 mL) was added to the solid residue remaining in the reaction tube, the mixture was stirred and allowed to settle, and the solution was filtered and recombined with the thf solution. The solvents were then removed in vacuo to afford a white crystalline material and small amount of a yellow oil. The extremely O_2- and H_2O-sensitive white crystalline **1** was purified by repeated washings with freezing-cold hexane. Yield: 10% (5.40 g, 9.63 mmol). ^1H NMR (C_6D_6, 250.00 MHz): δ 3.68 (thf-α, m, 12H), 1.61 (thf-β, m, 12H), 0.70 (s, 27H, $^3J^{119(117)}Sn-^1H\}$ 8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.86 MHz): δ 68.61 (thf-α), 25.49 (thf-β), 8.12 ($^1J(^{29}Si-^{13}C)$ 35 Hz, $^2J\{^{119(117)}Sn-^{13}C\}$ 23 Hz). $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.662 MHz): δ −13 ($^1J(^{119}Sn-^{29}Si)$ 134 Hz, $^1J(^{117}Sn-^{29}Si)$ 128 Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 93.18 MHZ): δ −878.

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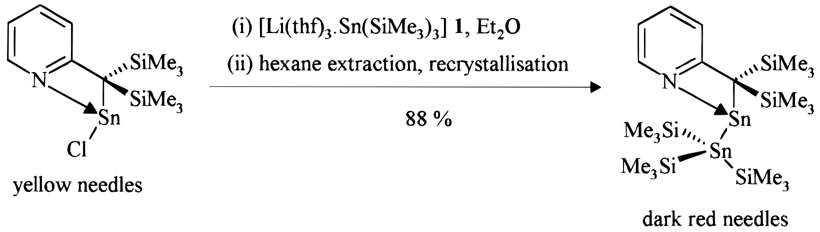
Scheme 1. Synthesis of $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$ (2).



note is that both reactions proceed via the unprecedented insertion of the (unsaturated) silylene into the M−R bond of the group 14 carbene analogue.

As part of our continuing studies into the versatility of group 14 carbene analogues in the preparation of heterometallic (main-group/transition-metal) clusters,[8] we have (i) developed a one-pot synthesis for the preparation of $[Li(thf)_3 \cdot Sn(SiMe_3)_3]$[9,10] and (ii) treated $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)Cl]$[11] with this Li reagent under ambient conditions to afford $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$ (**2**) in high yield.

The slow addition of 1 equiv of **1** to $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)Cl]$ in Et$_2$O at ambient temperature results in the immediate change from yellow-orange to dark red. After the mixture was stirred for 16 h, removal of the Et$_2$O in vacuo, extraction with hexane, and its removal in vacuo afforded **2** as a pyrophoric dark red powder in high yield (88%, Scheme 1).[12] Recrystallization from hexane produced small dark red needle crystals suitable for a single-crystal X-ray diffraction study.[13]

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2**, measured in C$_6$D$_6$ at 298 K, exhibit resonances confirming the proposed formula. The resonance at δ 0.49 in the ^{1}H NMR spectrum (with a ^3J coupling to the Sn(IV) nucleus of 32 Hz) and the resonance at δ 5.99 in the $^{13}C\{^1H\}$ NMR spectrum (with a ^2J coupling to the Sn(IV) nucleus of 38 Hz) correspond to the $Sn(SiMe_3)_3$ ligand. The chemical shifts (and integral values) of the remaining resonances correspond to the $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$ ligand. The formally coordinate Sn(II)−N bond persists in solution and, thus, results in the inequivalence of the two SiMe$_3$ environments.[11] No resonances that might correspond to H ligands on the Sn(II) atom were observed. The $^{119}Sn\{^1H\}$ NMR spectrum of **2** is comprised of two sharp singlet resonances at δ 897 and −502. The high-frequency resonance is to higher frequency compared with the corresponding resonances for other Sn(II) derivatives for which ^{119}Sn NMR chemical shift data have been reported, e.g., $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)R]$, where R = Cl or $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$ and δ = 351 or 140, respectively.[11] Similarly, the other resonance is to much higher frequency than that for the Li precursor **1** (C$_6$D$_6$, δ −878). Both resonances exhibit well-resolved and isotopically shifted $^1J(^{119}Sn-^{119}Sn)$ and $^1J(^{117}Sn-^{119}Sn)$ satellites: the resonance at δ 896.53 has ^{119}Sn satellites with a ^1J coupling of 6746 Hz, "virtually-centered" at δ 897.44 and ^{117}Sn satellites with a ^1J coupling of 6451 Hz, virtually-centered at δ 896.64. The corresponding values for the resonance at δ −501.84 are 6765 Hz and δ −501.68, 6467 Hz and δ −500.71, respectively. Depending on the coordination number and substitution pattern at the Sn centers, values of up to ca. 20 000 Hz for $^1J(^{119/117}Sn-^{119}Sn)$ may be observed.[14] However, more commonly, much lower values are observed, e.g., Ph$_3$Sn−SnPh$_3$ $^1J(^{117}Sn-^{119}Sn)$ = 4470 Hz.[15]

The molecular structure of **2** illustrated in Figure 1 shows it to be monomeric with a distorted trigonal-pyramidal geometry about the three-coordinate Sn(II) atom, typical of heteroleptic $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$ derivatives of Sn(II).[1,11] The Sn(II) atom is bonded to the $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$ ligand via the C atom [C(6)] of the $2\text{-}\{(Me_3Si)_2C\}$ substituent and by a formally coordinate bond with the N atom of the C$_5$H$_4$N ring. The Sn−C(6) bond length of 2.304(2) Å is marginally shorter than that found in the related, covalent $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)R]$ (R = Cl, 2.32(2) Å (both molecules); R = $2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N$, 2.334(6), 2.346(6), and 2.377(7) Å; R = N(SiMe$_3$)$_2$, 2.356(8) Å),[11] a result of the longer Sn(II)−R bond when R = Sn(SiMe$_3$)$_3$, reducing the steric congestion about the Sn(II) center. The Sn(II) and Sn(IV) atoms are bound by a single bond, 2.8689(5) Å in length; this is the first structurally authenticated measurement of such a bond. Two previous reports of compounds containing a divalent Sn−tetravalent Sn

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(10) The preparation and molecular structure of the related Na derivative $[Na(\eta^6\text{-}C_6H_5Me) \cdot Sn\{Si(SiMe_3)_3\}_3]$ has recently been reported. The Li analogue was reported as being similarly accessible, although no experimental details are provided. The reported preparation of both complexes involves the treatment of $Zn\{Si(SiMe_3)_3\}_2$ with the corresponding alkali metal to yield $[(M\{Si(SiMe_3)_3\})_2]$ (82% yield) and its subsequent reaction with $[Sn\{N(SiMe_3)_2\}_2]$ at low temperature in toluene to afford the product (60% yield). Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418−1431.

(11) Jolly, B. S.; Lappert, M. F.; Engelhardt, L. M.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2653−2663.

(12) Synthesis of $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$ (**2**). To a Schlenk tube charged with a solution of $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)Cl]$ (3.99 g, 10.21 mmol) in Et$_2$O (40 mL) was added, over a 5 min period with stirring, **1** (5.73 g, 10.21 mmol) also dissolved in Et$_2$O (40 mL). At the point of addition of each drop, an intense red coloration was observed; after complete addition, the solution had changed from yellow-orange to red. The mixture was stirred for a further 16 h, the Et$_2$O removed in vacuo, and the product extracted from the LiCl byproduct with hexane (3 × 40 ml). The hexane was removed in vacuo, affording **2** as a pyrophoric red microcrystalline material in 88% yield (6.23 g, 8.99 mmol). Crystals suitable for an X-ray diffraction study were grown from a saturated hexane solution. ^{1}H NMR (C$_6$D$_6$, 250.00 MHz): δ 7.75 (dd, 1H), 6.88 (td, 1H), 6.25 (m, 2H), 0.49 (s, 27H, $^3J\{^{119(117)}Sn-^1H\}$ 32 Hz), 0.28 (s, 9H), 0.23 (s, 9H). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 62.86 MHz): δ 173.30, 148.23, 136.81, 127.10, 118.70, 35.60, 5.99 ($^2J\{^{119(117)}Sn-^{13}C\}$ 38 Hz), 3.23 ($^1J(^{29}Si-^{13}C)$ 48 Hz), 1.26 ($^1J(^{29}Si-^{13}C)$ 46 Hz). $^{119}Sn\{^1H\}$ NMR (C$_6$D$_6$, 93.18 MHz): δ 897 ($^1J(^{119}Sn-^{119}Sn)$ 6746 Hz, $^1J(^{117}Sn-^{119}Sn)$ 6448 Hz), −501, ($^1J(^{119}Sn-^{119}Sn)$ 6765 Hz, $^1J(^{117}Sn-^{119}Sn)$ 6467 Hz).

(13) Crystal data for $[Sn(2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)\{Sn(SiMe_3)_3\}]$ ($C_{21}H_{49}NSi_5Sn_2$): Crystallographic measurements were made on station 9.7 at the SRS, Daresbury, using radiation of wavelength 0.6979 Å and a Siemens CCD area detector. The structure was solved by direct methods using SHELX 97 and refined on F^2 by a full-matrix least-squares procedure. T = 160 K. Data for $C_{21}H_{49}NSi_5Sn_2$: 0.1 × 0.1 × 0.1 mm, M_r = 693.47, orthorhombic, space group *Pbca* (No. 61), a = 17.064(3) Å, b = 17.759(5) Å, c = 21.585(3) Å, V = 6541(2) Å^3, D_c = 1.408 g cm^{-3}, Z = 8. For reflections with $1.83° < \theta < 27.13°$, R(F) = 0.0308 for 5403 observed reflections ($I > 4\sigma(I)$) and wR(F^2) = 0.0866 for all 6241 reflections.

(14) Wrackmeyer, B. *Indirect Nuclear ^{119}Sn−X Spin−Spin Coupling*; Wrackmeyer, B., Ed.; John Wiley & Sons, Ltd.: Chichester, 1996.

(15) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73.

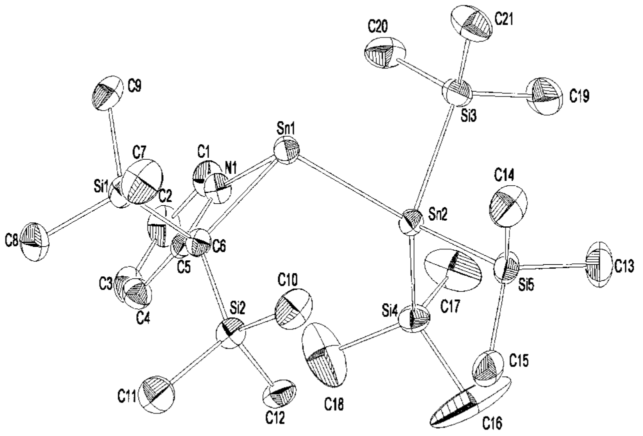

Figure 1. Molecular structure of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)-{$Sn(SiMe_3)_3$}] (**2**) and atom numbering scheme with selected bond lengths (Å) and angles (°): Sn(1)−Sn(2) 2.8689-(5), Sn(1)−C(6) 2.304(2), Sn(1)−N(1) 2.288(2), Sn(2)−Si(3) 2.5770(8), Sn(2)−Si(4) 2.5833(10), Sn(2)−Si(5) 2.5585(10), N(1)−Sn(1)−C(6) 61.36(9), N(1)−Sn(1)−Sn(2) 89.68(6), C(6)−Sn(1)−Sn(2) 108.29(6).

bond, [$Sn(NO_3)(SnPh_3)$] and [{$Sn(NO_3)(AsPh_3)(SnPh_3)$}$_2$], have been made.[16,17] However, in light of inter alia the unusual coordination geometries about the Sn(II) atoms and the short Sn−Sn bond lengths (e.g., for the latter, average 2.53(6) Å), it is not surprising that structural redeterminations of these compounds have revealed that both are in fact Ag/As derivatives, [$Ag(NO_3)(AsPh_3)$] and [$Ag(NO_3)(AsPh_3)_2$]: "...the metal deriving from $AgNO_3$ used as reagent together with $SnPh_2Cl_2$ in the preparation of $SnPh_2(NO_3)_2$".[18] The Sn(IV)−Si(*n*) distances ($n = 3$, 2.5770(8) Å; $n = 4$, 2.5833(10) Å; $n = 5$, 2.5585(10) Å) are in accordance with the covalent radii of the Si(IV) and Sn(IV) nuclei: the Si−Si bond lengths in [$(Me_2Si)_4$], [$Me_3Si-SiPh_3$], and [$(Me_2Si)_6$] are 2.367 and 2.359 Å,[19] 2.355(1) Å,[20] and 2.342(1), 2.339(1), and 2.332(1) Å,[21] respectively. The Sn−Sn bond lengths in [$(Ph_3Sn)_2$] and [$(Ph_2Sn)_6$] are 2.780(4) and 2.759(4) Å (two molecules)[22] for the former and 2.77, 2.78, and 2.77 Å for the latter.[23] On this basis then, we estimate the covalent radius of the Sn(II) nucleus to be ca. 1.483 Å (cf. that of the Sn(IV) nucleus at ca. 1.386 Å).[24] However, the extent to which the steric demand of both of the ligands and the bidentate nature of the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand affect the length of the Sn−Sn bond is very difficult to assess.

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, bond distances and angles, and least-squares planes (6 pages). Ordering information is given on any current masthead page.

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(16) Nardelli, M.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *Z. Anorg. Allg. Chem.* **1977**, *431*, 250.

(17) Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1935−1939.

(18) Nardelli, M.; Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Chem. Soc., Dalton Trans.* **1985**, 321−331.

(19) Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253.

(20) Párkányi, L.; Hengge, E. *J. Organomet. Chem.* **1982**, *235*, 273.

(21) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566.

(22) Preut, H.; Haupt, H.-J.; Huber, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 81.

(23) Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310.

(24) The importance of atom electronegativities with respect to the calculation of covalent radii has been discussed, see: Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37−40. Wells A. F. *J. Chem. Soc.* **1949**, 55.