

Compounds of Germanium, Tin, and Lead Containing the Ligand C(SiMe₃)₂(SiMe₂C₅H₄N-2)

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Reactions between LiC(SiMe₃)₂(SiMe₂C₅H₄N-2), **1**, and the halides GeCl₂·dioxane, SnCl₂, and PbCl₂ gave the isostructural compounds MCl{C(SiMe₃)₂(SiMe₂C₅H₄N-2)} (M = Ge, **2**; Sn, **3**; or Pb, **4**) which contain three-coordinate M. Treatment of the tin derivative **3** with MeI gave the oxidative addition product SnMeClI{C(SiMe₃)₂(SiMe₂C₅H₄N-2)}, **5**, and this reacted with AgOCOCF₃ or AgOSO₂C₆H₄Me-4 to give, respectively, the compounds SnMeX₂{C(SiMe₃)₂(SiMe₂C₅H₄N-2)} with X = OCOCF₃, **6**, or OSO₂C₆H₄Me-4, **7**. Despite the presence of the bulky C(SiMe₃)₂(SiMe₂C₅H₄N-2) ligand, the Sn atom in the solid state structures of **6** and **7** is five-coordinate, and multinuclear NMR studies show that five-coordinate species are present also in THF solutions of **5**, **6**, and **7**.

Introduction

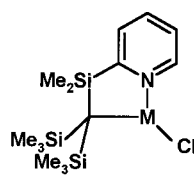
There has been considerable recent interest in the chemistry of organometal(II) chlorides of the type RMCl (M = Ge, Sn, Pb), especially as precursors in the synthesis of compounds containing multiple homo- and heteronuclear M–M bonds.^{1a–d} Compounds containing M–R σ-bonds have been characterized only when the organic group R is bulky, and particular attention has been paid to compounds in which R = {C₆H₃(C₆H₂R'₃-2,4,6)₂-2,6} (R' = Me or ⁱPr),^{1a–d} C₆H₃(NMe₂)₂-2,6,^{1e} CH(SiMe₃)(C₅H₄N-2), or C(SiMe₃)₂(C₅H₄N-2),² and the compounds (RMCl)_n [M = Sn or Pb, R = C(SiMe₂Ph)₃ or C(SiMe₃)₂(SiMe₂OMe)].³ Most of the species characterized in the solid state are halogen-bridged dimers with Cl–Sn–C angles of 90–100°, but Ge{C₆H₂^tBu₃-2,4,6}Cl^{4a} and Ge{C₆H₂^tBu₂-2,4-CH₂NMe₂-6}Cl^{4b} are monomeric, Ge{C₆H₃(C₆H₂Me₃-2,4,6)₂-2,6}Cl is dimeric with Ge–Ge bonds,^{1b} and Pb{C(SiMe₃)₃}Cl is trimeric.^{3b}

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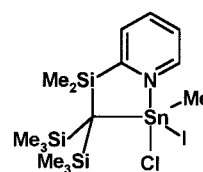
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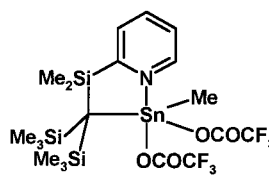
We have recently described the synthesis and structure of an array of organometallic ligand transfer reagents for the attachment of C(SiMe₃)₂(SiMe₂C₅H₄N-2) to a range of metals.⁵ This ligand occupies more space than C(SiMe₃)₃ in the coordination sphere of the metal if the lone pair on nitrogen, like those in the ligands C(SiMe₃)₂(C₅H₄N-2) and C₆H₂^tBu₂-2,4-CH₂NMe₂-6, is able to bind to the metal. We now describe the series of monomeric isostructural compounds MCl{C(SiMe₃)₂(SiMe₂C₅H₄N-2)} (M = Ge, **2**; Sn, **3**; or Pb, **4**), the oxidative addition reaction of **3** with MeI to give the Sn(IV) derivative **5**, and the conversion of **5** into **6** and **7**.



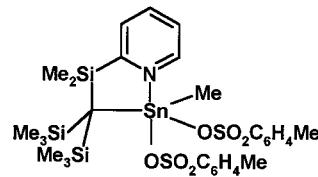
M = Ge **2**; Sn **3**; Pb **4**



5



6



7

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Experimental Section

Air and moisture were excluded as much as possible from all reactions by use of standard Schlenk techniques with Ar as blanket gas. Solvents were dried by the usual procedures and freshly distilled before use. NMR spectra were recorded at 500.1 (^1H), 125.8 (^{13}C), 376.3 (^{19}F), 99.4 (^{29}Si), 186.4 (^{119}Sn), and 104.3 MHz (^{207}Pb) for samples in C_6D_6 , except where indicated. Chemical shifts are relative to SiMe_4 for H, C, and Si, CFCl_3 for F, SnMe_4 for Sn, and PbMe_4 for Pb. EI mass spectra were obtained at 70 eV, and data are given for species with ^{28}Si , ^{35}Cl , ^{74}Ge , ^{120}Sn , and ^{208}Pb ; R refers to the $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)$ fragment. The compound $\text{LiC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)$, **1**, was made as described elsewhere.^{5a}

GeCl $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **2**. A solution of **1** (2.0 mmol) in THF (20 mL) was added to a solution of $\text{GeCl}_2 \cdot$ dioxane (0.46 g, 1.99 mmol) in THF (20 mL) at -78°C . The yellow solution was allowed to warm to room temperature and stirred for a further 2 h, and then volatile material was removed under vacuum. The residue was extracted with toluene (20 mL), the extract was filtered, and the filtrate was reduced to 10 mL and kept at -30°C to give **2** as yellow crystals suitable for an X-ray study (0.58 g, 72%), mp $171-2^\circ\text{C}$ (softens 155°C). Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{ClGeNSi}_3$: C, 41.7; H, 6.95; N, 3.5. Found: C, 41.8; H, 6.95; N, 3.3. ^1H NMR: δ 0.07 and 0.53 (9H, s, SiMe_3), 0.32 and 0.73 (3H, s, SiMe_2), 6.31 (1H, m, 5-H), 6.75 (1H, m, 4-H), 6.82 (1H, d, 3-H), 8.15 (1H, d, 6-H). ^{13}C NMR: δ 4.2 (SiMe_2), 4.4 (SiMe_3), 6.0 ($\text{SiMe}_3 + \text{SiMe}_2$), 22.0 ($^1J_{\text{SiC}} = 35.5$ Hz, CSi_3), 124.6 (5-C), 128.3 (3-C), 137.9 (4-C), 145.6 (6-C), 172.9 (*ipso*-C). ^{29}Si NMR: δ -3.1 (SiMe_3), -2.5 (SiMe_3), 12.9 (SiMe_2). MS: m/z 403 (15, M), 388 (6, M - Me), 368 (20, M - Cl), 294 (5, R), 280 (30, RH - Me), 264 (100, RH - Me - CH_4), 220 (10), 136 (15), 73 (40, SiMe_3).

SnCl $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **3**. A solution of **1** (2.86 mmol) in THF (15 mL) was added to a stirred solution of SnCl_2 (0.54 g, 2.86 mmol) in THF (20 mL) at -78°C , and the red solution was allowed to warm to room temperature during 14 h. The solvent was removed and the sticky residue extracted with toluene (20 mL). The extract was filtered, reduced in volume until crystallization began, and then kept at -30°C to give **3** as red-orange crystals suitable for an X-ray study (0.95 g, 74%), mp $180-181^\circ\text{C}$ (softens 160°C). Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{ClNSi}_3\text{Sn}$: C, 37.4; H, 6.2; N, 3.1. Found: C, 37.4; H, 6.4; N, 3.0. ^1H NMR: δ 0.06 and 0.46 (9H, s, SiMe_3), 0.33 and 0.75 (3H, s, SiMe_2), 6.41 (1H, t, 5-H), 6.84 (1H, t, 4-H), 6.91 (1H, d, 3-H), 7.98 (1H, d, 6-H). ^{13}C NMR: δ 5.4 ($^1J_{\text{SiC}} = 47.0$ Hz) and 6.6 ($^1J_{\text{SiC}} = 50.8$ Hz) (SiMe_3), 5.7 and 5.8 (SiMe_2), 28.6 ($^1J_{^{119}\text{SnC}} = 434$ Hz, CSi_3), 124.5 (5-C), 130.7 (3-C), 137.6 (4-C), 147.0 (6-C), 175.5 (*ipso*-C). ^{29}Si NMR: δ -4.1 (SiMe_3), -3.3 (SiMe_3), 8.6 (SiMe_2). ^{119}Sn NMR: δ 378.0. MS: m/z 449 (25, M), 434 (30, M - Me), 414 (10, M - Cl), 264 (100), 136 (10), 73 (12).

PbCl $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **4**. A solution of **1** (1.69 mmol) in THF (20 mL) was added to a stirred suspension of PbCl_2 (0.47 g, 1.69 mmol) in THF (20 mL) at -78°C . The mixture was protected from light and allowed to warm to room temperature, and then the solvent was removed. The yellow residue was washed with hexane (30 mL) and then extracted with toluene (30 mL). The extract was filtered, reduced to 10 mL, and kept at -30°C to give bright yellow blocks of **4** (0.43 g, 47%), mp $186-7^\circ\text{C}$ (darkens 165°C). Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{ClNPbSi}_3$: C, 31.3; H, 5.2; N, 2.6. Found: C, 31.0; H, 5.1; N, 2.1. ^1H NMR (THF- d_6): δ 0.23 (18H, s, SiMe_3), 0.53 (6H, s, SiMe_2), 6.49 (1H, m, 5-H), 6.84 (2H, m, 3,4-H), 8.00 (1H, d, 6-H). ^{13}C NMR: δ 6.5 (SiMe_3), 8.1 (SiMe_2), 71.8 (CSi_3), 123.8, 132.9, 136.2, (py) 147.9 (6-C), 182.9 (*ipso*-C). ^{29}Si NMR: δ -6.7 (SiMe_3), 4.0 (SiMe_2). ^{207}Pb NMR: (338 K) δ 3812 ($\Delta\nu_{1/2}$ 1.4 kHz). MS: m/z 537 (5, M), 522 (30, M - Me), 502 (55, M - Cl), 294

(20, R), 280 (75, RH - Me), 264 (100, RH - Me - CH_4), 220 (35), 164 (25), 136 (55), 106 (35), 73 (80).

SnMeCl $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **5**. Iodomethane (0.10 g, 0.70 mmol) was added to a stirred solution of **3** (0.10 g, 0.22 mmol) in Et_2O (10 mL) at room temperature, and the mixture was stirred for 14 h and then filtered. The solvent was removed under vacuum and the residue recrystallized from hexane (5 mL) containing 2 or 3 drops of Et_2O at -30°C to give **5** as a colorless solid (0.10 g 76%), mp $210-212^\circ\text{C}$. Anal. Calcd for $\text{C}_{15}\text{H}_{31}\text{ClINSi}_3\text{Sn}$: C, 30.5; H, 5.3; N, 2.4. Found: C, 30.6; H, 5.3; N 2.3. ^1H NMR (THF- d_6): (338 K) δ 0.34 (18H, br s, SiMe_3), 0.6 (6H, br s, SiMe_2), 0.7-2.2 (3H, several peaks, SnMe), 7.51 (1H, t, 5-H), 7.71 (1H, d, 3-H), 7.81 (1h, t, 4-H), 8.79 (1H, d, 6-H); (218 K) -0.48 and 0.28-0.77 (SiMe_2), 0.77-2.28 (SnMe). ^{119}Sn NMR: (338 K) δ -230.5 and -115.1; (218 K) peaks from δ -38 to -307. MS: m/z 576 (50, M - Me), 556 (90, M - Cl), 484 (60, M - Me - $\text{C}_6\text{H}_6\text{N}$), 464 (100, M - I), 414 (40, RSn).

SnMe(OCOCF₃)₂ $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **6**. A mixture of **5** (0.60 g, 1.1 mmol) and AgOCOCF_3 (1.0 g, 4.7 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h and then filtered. The solvent was removed from the filtrate under vacuum, and the residue was extracted with a mixture of toluene (10 mL) and THF (5 mL). The extract was then reduced to 10 mL and kept at room temperature to give colorless blocks of **6** (0.70 g 94%), mp $200-202^\circ\text{C}$. Anal. Calcd for $\text{C}_{19}\text{H}_{31}\text{F}_6\text{NO}_4\text{Si}_3\text{Sn}$: C, 34.9; H, 4.8; N, 2.1. Found: C, 34.9; H, 4.9; N, 2.0. IR: $\nu(\text{CO})$ (cm^{-1}) 1734. ^1H NMR (THF- d_6 , 323 K): δ 0.23 (9H, s, SiMe_3), 0.29 (9H, s, SiMe_3), 0.62 (6H, s, SiMe_2), 1.47 (3H, s, $^2J_{\text{SnH}} = 81.7$ Hz, SnMe), 7.71 (1H, t, 5-H), 7.95 (1H, d, 3-H), 8.11 (1H, t, 4-H), 8.90 (1H, d, 6-H). ^{13}C NMR: (323 K) δ 4.32 and 4.40 (SiMe_3), 2.1 and 2.3 (SiMe_2) (SnMe probably obscured by solvent), 126.7 (5-C), 130.5 (3-C), 140.5 (4-C), 148.2 (6-C), 167.1 (2-C). ^{19}F NMR: δ -76.5. ^{29}Si NMR: (323 K) 0.5 (SiMe_2), 1.9 (SiMe_3); (183 K) -1.67, 1.5 and 2.7 (major component), -1.73, 0.5 and 0.7 (minor component). ^{119}Sn NMR: (323 K) δ -173.7; (195 K) -170.5 (minor component) and -171.7 (major component). MS: m/z 640 (60, M - Me), 542 (20, M - OCOCF_3), 264 (100).

SnMe(OSO₂C₆H₄CH₃-4)₂ $\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}$, **7**. A mixture of **5** (0.60 g, 1.1 mmol) and $\text{AgOSO}_2\text{C}_6\text{H}_4\text{CH}_3-4$ (1.1 g, 4.0 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 15 h and then filtered. The solvent was removed from the filtrate under vacuum, and the residue was extracted with a mixture of toluene (10 mL) and THF (10 mL). The extract was reduced to 10 mL and kept at room temperature to give colorless plates of **7** (0.50 g, 57%), mp $206-208^\circ\text{C}$. Anal. Calcd for $\text{C}_{29}\text{H}_{45}\text{NO}_6\text{S}_2\text{Si}_3\text{Sn}$: C, 45.2; H, 5.9; N, 1.8. Found: C, 45.3; H, 5.9; N, 1.7. ^1H NMR (DMSO- d_6 , 298 K): δ 0.12 (18H, br s, SiMe_3), 0.42 (6H, br s, SiMe_2), 0.77 (3H, s, $^2J_{\text{SnH}} = 76$ Hz, SnMe), 2.22 (3H, s, *p*-Me), 7.14 (4H, d, *o*-H), 7.48 (4H, d, *m*-H), 7.63 (1H, t, 5-H), 7.83 (1H, d, 3-H), 8.02 (1H, t, 4-H), 8.61 (1H, d, 6-H). ^{13}C NMR (298 K): δ 13.7 (SiMe_2), 15.1 (SiMe_3), 18.4 (CSi_3), 18.5 (SnMe), 31.7 (*p*-Me), 136.5 (*o*-C), 137.0 (5-C), 139.8 (*m*-C), 140.7 (3-C), 151.0 (*p*-C), 151.0 (4-C), 153.5 (2-C), 157.2 (6-C), 176.4 (*ipso*-C). ^{29}Si NMR (343 K): δ 0.43 (SiMe_3), 0.98 (SiMe_2). ^{119}Sn NMR (298 K): δ -132.2 (d, $^2J_{\text{SnH}} = 77$ Hz). MS: m/z 756 (30, M - Me), 693 (40, M - $\text{C}_5\text{H}_4\text{N}$), 621 (50, M - Me - $\text{SiMe}_2\text{C}_5\text{H}_4\text{N}$), 600 (100), 264 (30).

Crystallography. Data were collected on a Kappa CCD diffractometer for **2** or a CAD4 diffractometer for **3**, **4**, **6** and **7** and the structures solved by direct methods. Further details are given in Table 1. Refinement was by full matrix least squares (SHELXL-97) with non-H atoms isotropic and H atoms in riding mode. In **6** the high correlation between the parameters of the atoms in the two independent molecules is reflected in the apparently abnormal thermal ellipsoids of some atoms.

Table 1. Summary of Crystallographic Data for **2**, **3**, **4**, **6**, and **7**

	2	3	4	6	7
chem formula	C ₁₄ H ₂₈ ClGeNSi ₃	C ₁₄ H ₂₈ CINSi ₃ Sn	C ₁₄ H ₂₈ CINPbSi ₃	C ₁₉ H ₃₁ F ₆ NO ₄ Si ₃ Sn	C ₂₉ H ₄₅ NO ₆ S ₂ Si ₃ Sn
fw	402.68	448.78	537.28	654.4	770.7
<i>TK</i>	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>C2/c</i> No. 15	<i>C2/c</i> No. 15	<i>C2/c</i> No. 15	<i>P2₁</i> No. 4	<i>P1</i> No. 2
<i>a</i> /Å	17.7983(5)	18.021(8)	19.001(6)	13.387(8)	10.162(4)
<i>b</i> /Å	21.2491(7)	21.555(18)	18.260(4)	11.041(5)	11.755(5)
<i>c</i> /Å	13.3354(4)	14.437(5)	14.474(3)	18.858(7)	15.379(7)
<i>α</i> /deg	90	90	90	90	78.85(4)
<i>β</i> /deg	126.618(1)	132.05(3)	125.38(3)	95.01(4)	76.65(4)
<i>γ</i> /deg	90	90	90	90	86.70(3)
<i>V</i> /Å ³	4048.0(2)	4164(4)	4094(2)	2777(2)	1754(1)
<i>Z</i>	8	8	8	4	2
<i>μ</i> /mm ⁻¹	1.82	1.52	8.54	1.11	0.99
R1, wR2 <i>I</i> > 2σ(<i>I</i>)	0.030, 0.068	0.030, 0.065	0.058, 0.158	0.062, 0.141	0.053, 0.175
all data	0.038, 0.072	0.042, 0.068	0.073, 0.170	0.089, 0.158	0.057, 0.182
no. measured/indep	12 468/4754/0.037	5693/2897/0.0326	3720/3614/0.0373	5371/5160/0.0745	6136/6136
rflns/ <i>R</i> (int)					
rflns with <i>I</i> > 2σ(<i>I</i>)	4116	2381	2930	3913	5563

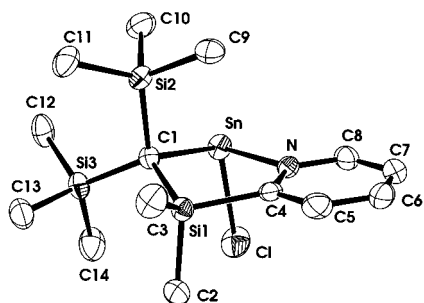


Figure 1. Molecular structure of SnCl{C(SiMe₃)₂-(SiMe₂C₅H₄N-2)}, **3**.

Results and Discussion

The Organometal(II) Chlorides 2–4. The reactions between the lithium derivative **1** and the halides GeCl₂·dioxane, SnCl₂, and PbCl₂ gave good yields of the yellow-orange compounds **2–4**. These were much easier to work with than the previously described thermally unstable, air-, moisture-, and light-sensitive compounds containing C(SiMe₃)₃ and C(SiMe₂Ph)₃ ligands.³ The lead compound **4** appears to be stable indefinitely in the solid state in the absence of light, air, and moisture and seems to melt with little decomposition, but solutions in benzene or THF decompose slowly during several weeks. In contrast, the lead analogue of SnCl{C(SiMe₃)₂(SiMe₂C₅H₄N-2)} could not be isolated.² Since good spectroscopic and structural information was readily obtained, detailed comparisons could be made of data within the series of closely related compounds.

The compounds **2–4** crystallize in the same space group and have similar unit cell dimensions. The structure of the tin compound **3** is shown in Figure 1; those of the germanium and lead compounds are similar. Bond lengths and angles are given in Table 2. In all three molecules the chlorine atom stands sharply out of the nearly planar system defined by the atoms SiCNM and the pyridine ring, and the remaining carbon atom C1 of the metallacycle is bent away slightly on the other side. The bond lengths and angles within the ring are similar in all three compounds. The M–C and M–Cl bonds are normal,^{6,7} and there is little variation in the C–M–Cl angle. The M(II) covalent radii derived from the M–C and M–Cl bonds, viz., Ge 1.30, Sn 1.49,

Pb 1.60 Å, are about 0.06–0.09 Å greater^{8a} than the usually quoted values for M(IV) derivatives⁹ and may be used to calculate the M(II)–N bond lengths for coordinated neutral ligands. The measured value in **2** is close to that calculated, but the value in **4** [2.466(10) Å] is 0.12 Å longer, suggesting that there is a systematic lengthening of the M–N bond in the series from Ge to Pb, beyond that expected from the increase in metal radius. This is accompanied by a systematic increase in the N–C4–Si and C4–Si–C1 angles and implies that there is a weakening of the internal coordination in the derivatives of the heavier metals. For comparison the Pb–N bond lengths are 2.24(2) Å in Pb{N(SiMe₃)₂}₂,^{7c} 2.340(4)–2.597(4) Å in Pb(NSiMe₃PPh₂=NSiMe₃)₂,^{7b} 2.654(6)–2.701(6) Å in Pb{CHSiMe₃PPh₂=NSiMe₃}₂,^{7a} and 2.414(15)–2.806(13) Å in four- and six-coordinate pyrazolyl Pb(II) derivatives.^{7d} There is a little more variation than usual in the lengths of the three bonds from silicon to the central carbon C1 in each of the molecules **2–4**, with bonds to Si2, trans to Cl, slightly longer than the other two, presumably reflecting the way that the Si–Me groups lock the ring into a rigid conformation. The mean Si–C1 bonds (1.88–1.89 Å) are significantly longer than those in the derivatives of the alkali metals (1.82 Å).^{5a} As in all compounds containing the C(SiMe₃)₂(SiMe₂C₅H₄N-2) ligand examined so far (except **6** and **7**; see below), the Si–C1 bonds (to the central carbon) are shorter than the Si–C4 bonds (ca. 1.91 Å) to the pyridine ring.⁵

The ¹H and ¹³C NMR spectra of compounds **2** and **3** at 298 K give separate signals for methyl groups on either side of the metallacycle, and the ²⁹Si NMR spectra show separate signals for the two SiMe₃ groups, as

(6) M–C, M–Cl, and M–N bond lengths in MCl{C(SiMe₃)₂(C₅H₄N-2)} are, respectively, 2.138(5), 2.295(2), and 2.082(4) Å for M = Ge,^{2c} and 2.32(2), 2.440(5), and 2.27(2) Å for M = Sn.^{2b} The Pb(II)–C bond lengths range from 2.27(6) to 2.447(5) Å in the compounds R₂PbCl^{1d,3} or Pb(CHSiMe₃PPh₂=NSiMe₃)₂.^{7a}

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Table 2. Bond Lengths (Å) and Angles (deg) in the Compounds $\overline{\text{MCl}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N-2})\}}$ (M = Ge, **2; Sn, **3**; Pb, **4**)**

	2 ^a	3 ^a	4 ^a
M–C	2.0601(18)	2.262(4)	2.365(11)
M–N	2.0814(16)	2.271(3)	2.466(10)
M–Cl	2.3217(16)	2.466(2)	2.647(3)
Si1–C1	1.870(2)	1.860(4)	1.867(12)
Si2–C1	1.907(2)	1.898(4)	1.903(11)
Si3–C1	1.896(2)	1.887(4)	1.861(11)
av Si–Me	1.877(2)	1.874(5)	1.872(13)
Si–C4	1.905(2)	1.913(4)	1.909(13)
C1–M–N	89.97(7)	85.57(13)	81.5(4)
C1–M–Cl	103.99(5)	102.37(10)	102.3(3)
N–M–Cl	87.92(5)	85.61(9)	85.2(2)
M–N–C4	119.27(12)	119.1(2)	117.3(8)
N–C4–Si	113.88(13)	115.7(3)	116.9(9)
C4–Si–C1	101.10(8)	104.51(17)	106.6(5)
Si1–C1–M	106.30(9)	105.84(17)	106.2(5)
Si2–C1–M	101.28(8)	101.41(17)	113.3(5)
Si3–C1–M	113.96(9)	112.49(17)	101.4(5)
av Si–C1–Si	111.5(1) ^b	112.1(2) ^c	111.8(6)
Me–Si–Me	103.11(11)–107.57(11)	103.1(2)–107.3(2)	103.4(6)–108.4(6)
C1–Si–Me	110.76(10)–117.56(10)	111.53(19)–116.69(19)	110.8(6)–116.3(5)
C4–Si–Me	108.47(10), 106.43(9)	108.16(19), 105.02(18)	104.0(6), 105.9(6)
fold angle at M···Si	32	32	35

^a Where average values are given, esd's of individual measurements are in parentheses. Except where indicated, no individual value differs significantly from the average. ^b Individual values Si1–C–Si2 110.64(10)°, Si1–C–Si3 112.52(10)°, Si2–C–Si3 110.50(9)°. ^c Individual values Si1–C–Si2 110.87(19)°, Si1–C–Si3 113.1(2)°, Si2–C–Si3 112.4(2)°.

expected if the species found in the solid are present in solution. However saturation transfer experiments on the ¹H signals show exchange between the two SiMe₂ and also between the two SiMe₃ resonances. The signals in the germanium compound **2** are still sharp at 345 K; those in the tin compound **3** are broader, but coalescence could not be reached up to the boiling point of the solvent. The spectra of the lead compound **4** at 325 K show single resonances for the SiMe₂ and SiMe₃ groups, but each splits into two below 210 K (ΔG^\ddagger 42 kJ mol⁻¹ at that temperature). These results may be explained by postulating that the ring is opening and re-forming rapidly on the NMR time scale and that the ease with which the M–N bond is broken increases in the series Ge < Sn < Pb, in accord with the X-ray data. For comparison, the compounds $\overline{\text{M}\{\text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N-2})\}\text{Cl}}$ (M = Ge^{2c} or Sn^{2b}) show one signal at 298 K but two at 193 K. The results suggest that the M–N donor bond is more easily broken in the four- than in the five-membered metallacycles. An alternative explanation, that the inversion at tin occurs by dimerization, cannot at present be ruled out.

Although no ²⁰⁷Pb signals could be detected for the compounds RPbCl [R = C(SiMe₃)₃, C(SiMe₂Ph)₃,^{3b} or C₆H₃(C₆H₂Pr-2,4,6)₂-2.6^{1d}], compound **4** gave a broad signal at δ 3812 at 338 K, shifted to 3549 at 198 K. A single peak was obtained at all intermediate temperatures, and a plot of δ vs 1/T was linear. The shifts are similar to that (3583) predicted from the shift of the ¹¹⁹Sn resonance in **3** by the empirical relation derived from M(II) compounds,^{10a} and that (4249) for RPbCl [R = C(SiMe₃)₂(SiMe₂OMe)],^{3b} and indicate that the lead

in **4** is essentially three-coordinate in solution, with the Pb–N bond opened only transiently.

Oxidative Addition. We showed previously that the stannylene $\overline{\text{SnC}(\text{SiMe}_3)_2\text{SiMe}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{C}}$, containing a chelating dicarbanionic ligand, reacted with iodomethane to give the oxidative addition product, which was characterized by its reaction with silver trifluoroacetate.^{8a} We considered that similar oxidative addition to **3** would yield a product, $\overline{\text{SnMeCl}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N-2})\}}$, **5**, which might ionize to give a compound containing a (yet unknown) four-coordinate Sn(IV) cation. (The reluctance of tin in tris(triorganosilyl)methyl derivatives to increase its coordination number from four to five was shown in the case of the compound Sn(ONO₂)Me₂{C(SiMe₂Ph)₃}, in which coordination of the second oxygen atom of the nitrate ligand was weak.^{8b})

The compound **5** was indeed formed and its identity established by analytical data and mass spectrometry. The ¹H NMR signals at 338 K were very broad, suggesting that several species were present in solution. On cooling, the spectra became complex and a full interpretation was impossible (but see brief discussion below). Crystals suitable for an X-ray diffraction study could not be obtained, so we characterized the compound by converting it into the trifluoroacetate $\overline{\text{SnMe}(\text{OCOCF}_3)_2\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N-2})\}}$, **6**, by reaction with AgO-COCF₃. A similar reaction with AgOSO₂C₆H₄CH₃-4 gave the corresponding bis(tosylate), **7**. To our surprise the X-ray diffraction and NMR studies showed unequivocally that despite the size of the organic ligand, five-coordinate species were present both in the solid state and in solution.

The Bis(trifluoroacetate), 6, and the Bis(tosylate), 7. The structure of the bis(trifluoroacetate), **6**,

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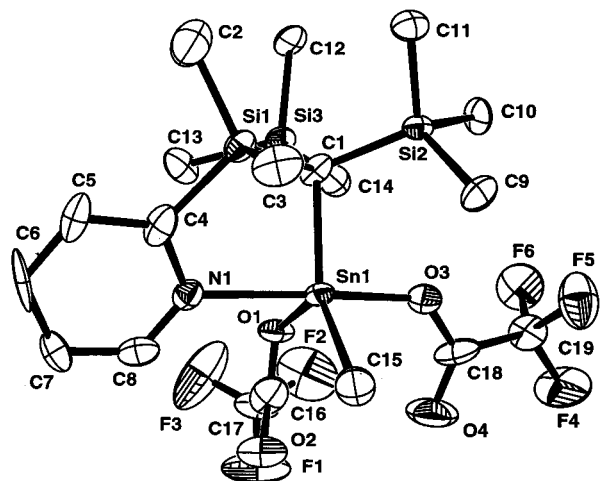


Figure 2. Molecular structure of one of the independent molecules of $SnMe(OCOCF_3)_2\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}$, **6**.

Table 3. Bond Lengths (Å) and Angles (deg) in the Compounds $SnMeX_2\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}$ ($X = OCOCF_3$, **6; $OSO_2C_6H_4Me$, **4**, **7**)**

	6 , molecule A ^a	7 ^a
Sn–Me	2.155(16)	2.131(5)
Sn–C1	2.164(16)	2.165(5)
Sn–N	2.298(15)	2.292(4)
Sn–O _{eq}	2.072(12)	2.050(4)
Sn–O _{ax}	2.141(14)	2.149(4)
Si–C1 ^b	1.900(16)	1.901(5)
Si–Me ^b	1.872(18)	1.869(7)
Si–C4	1.89(2)	1.901(6)
C1–Sn–N	88.5(6)	88.74(17)
C1–Sn–Me	134.0(8)	134.8(2)
N–Sn–Me	94.1(7)	91.8(2)
Sn–N–C4	113.8(12)	115.8(3)
N–C4–Si	116.1(14)	116.0(4)
C4–Si–C1	104.2(8)	105.3(2)
Si1–C1–Sn	101.3(7)	103.7(2)
Si2–C1–Sn	110.3(7)	104.5(2)
Si3–C1–Sn	108.8(8)	113.7(2)
Si–C1–Si	111.5(8) ^b	111.5 ^c
Me–Si–Me ^b	107.0(10)	107.2(3)
C1–Si–Me	110.2(8)–118.1(9)	108.9(2)–116.2(3)
C4–Si–Me	102.5(9), 109.9(9)	104.6(3), 107.0(3)
N–Sn–O _{ax}	165.9(5)	170.50(16)
N–Sn–O _{eq}	83.2(5)	85.45(16)
O _{eq} –Sn–O _{ax}	83.0(5)	85.06(16)
Me–Sn–O _{eq}	115.8(7)	118.6(2)
Me–Sn–O _{ax}	94.0(7)	92.6(2)
C1–Sn–O _{eq}	110.1(5)	106.42(17)
C1–Sn–O _{ax}	94.1(5)	94.15(17)
fold angle at Sn...Si	39	33

^a O_{eq} is O1 in **6** and O4 in **7**; O_{ax} is O3 in **6** and O1 in **7**. In **6** the difference between molecules A and B can be seen from the torsion angles C15–Sn–O–C16 1.2° and C15B–SnB–OB–C16B 40.3°. ^b Average values with esd's of individual measurements in parentheses. None differs significantly from the average. ^c Individual values Si1–C1–Si2 112.0(3)°, Si1–C1–Si3 109.4(3)°, Si2–C1–Si3 113.1(2)°.

shows two independent chiral molecules in the asymmetric unit, related by an approximate inversion center broken only by the conformations of the trifluoroacetate groups in the equatorial positions at the five-coordinate trigonal bipyramidal tin. One of the independent molecules is shown in Figure 2, and bond lengths and angles are given in Table 3. Data for the second molecule are not significantly different. Intraligand

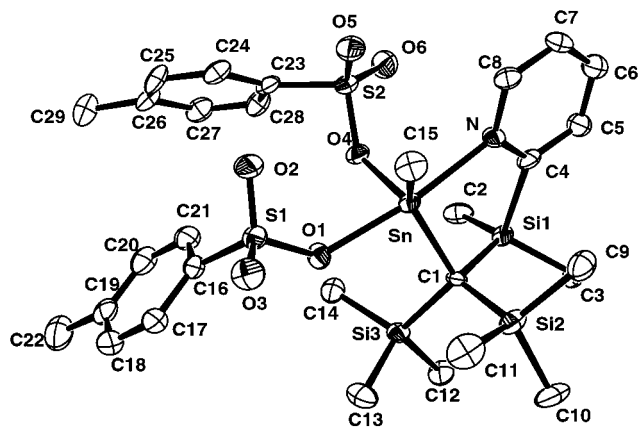


Figure 3. Molecular structure of $SnMe(OSO_2C_6H_4CH_3)_2\{C(SiMe_3)_2(SiMe_2C_5H_4N-2)\}$, **7**.

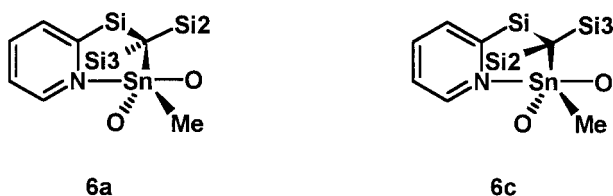
parameters in the Sn(IV) compound **6** differ only slightly from those in the Sn(II) compound **3**, and it is noteworthy that none of the bonds to tin is exceptionally long. The Sn–C1 distance is shorter than that in **3**, the Sn–O bonds are similar to those in other organotin compounds bearing bulky organosilyl groups,⁸ and, as expected, the axial bond in the trigonal bipyramidal coordination sphere is longer than the equatorial bond. The Sn–N bonds are longer than those in **3**, but this is to be expected since the nitrogen occupies an axial position. There is no significant difference between Si–C1 and Si–C4 bond lengths.

The structure of the tosylate **7**, shown in Figure 3, is similar, but in this case there is only one molecule in the asymmetric unit. The Sn(IV)–C, Sn–Cl, and Sn–N bond lengths are all normal and close to the sums of the covalent radii. The Sn–C1 and Sn–C4 bond lengths are again similar, and the axial Sn–O1 [2.149(4) Å] is significantly longer than the equatorial Sn–O4 bond [2.050(4) Å].

The multinuclear NMR spectra of **6** make it possible to give a detailed analysis of the species in THF-*d*₈ solution. The ¹H NMR spectrum at 323 K shows three sharp signals attributed to the SiMe₂, SiMe₃, and SnMe protons and a series of signals assigned to the pyridine ring. There are two peaks in the ²⁹Si spectrum, one in the ¹⁹F spectrum and one in the ¹¹⁹Sn spectrum [²J_{SnH} (81.7 Hz) is larger than usual but not unprecedented].¹⁰ The value of δ_{Sn} (–174) is at much lower frequency than that (1.9) in (CF₃COO)₂MeSnC(SiMe₃)₂SiMe₂CH₂CH₂Me₂Si(Me₃Si)₂CSnMe(OCOCF₃)₂,^{8a} in which the tin has the same C(SiMe₃)₂SiMe₂X, Me, and OCOCF₃ substituents but is four-coordinate. These data strongly suggest that the five-coordinate tin found in solid **6** is present in solution^{10d} but that the axial and equatorial OCOCF₃ groups are exchanging places on the NMR time scale, as are the two methyl groups attached to Si1 and the two SiMe₃ groups attached to C1. The simplest explanation is that the Sn–N bond is transiently broken in solution. A value of ΔG[‡] = ca. 62 kJ mol^{–1} is derived from the coalescence temperatures of the SiMe₃ signal in the ¹H spectrum (316 K) and from that of the CF₃ signal in the ¹⁹F spectrum (315 K).

As the temperature is lowered, complex reversible changes in the NMR spectra provide evidence for a second intramolecular fluxional process. At 183 K there

are two signals in the ^{119}Sn spectrum with relative intensities ca. 3:1 and very similar chemical shifts ($\Delta\delta = 1.2$), and a comparison of the values of δ_{Sn} with those at 295 K suggests that these signals can be assigned to two different species, each with a five-coordinate tin center. There are six signals in the ^{29}Si spectrum with the three stronger about 3 times the intensity of the three weaker peaks. All peaks in the ^1H and the ^{13}C spectra are likewise split, confirming that at this temperature there are two species in solution with different NMR spectra. Exchange between them is slow on the NMR time scale at 183 K. We consider it likely that the two isomers found in the crystal become one enantiomeric pair in solution by free rotation about Sn–O bonds, viz., the species **6a** (molecule A in the solid) and its enantiomer **6b** (molecule B), in which the central carbon atom of the CSi_3 fragment is on the same side of the ring as the trifluoroacetate group. The other species are assumed to be **6c** and its enantiomer **6d**, in which the central carbon atom is on the same side of the ring as the methyl group. This postulate is confirmed by a more detailed examination of the ^1H NMR spectra.



The SiMe_2 signal at δ 0.6 becomes two well-resolved singlets at 273 K. At lower temperatures these broaden, and at 213 K they are almost lost in the baseline. At lower temperatures still they sharpen to give two pairs of widely separated peaks, with relative intensities 3:1. The stronger pair comprises one peak at δ 0.77 and another, identified by saturation transfer, at δ 0.47 among the SiMe_3 peaks. One of the peaks from the weaker pair is at δ 0.82, and saturation transfer shows that the other is also close to δ 0.47. The SiMe_3 signal splits in a more complicated fashion to give six strong signals (only five resolved) at 183 K, as well as a similar weaker set, indicating that in each of the species present in solution all six methyl groups attached to Si2 and Si3 are inequivalent. Two signals, one large and one small, are shifted to very low frequency ($\delta -0.5$) by the pyridine ring current, so the major peak is assigned to the methyl group C13 attached to Si3 in **6a** and the minor peak to a methyl group attached to Si2 in **6c**. Similar effects have been described in the low-temperature spectra of $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{OMe})(\text{SiPh}_2\text{Cl})$ and $(\text{PhMe}_2\text{Si})_3\text{CSiCl}_3$.¹¹ Irradiation at the frequency of the resonance assigned to C13 at 183 K gives no nuclear Overhauser effect (NOE) at the aromatic protons, but there is a large effect at the signals from the other high-frequency SiMe_3 protons, showing that when the isomer **6a** is converted into **6c**, the Si_2Me_3 and Si_3Me_3 groups are exchanged through inversion of the five-membered

CNSnCSi ring at the $\text{Sn}\cdots\text{Si}$ axis. Irradiation at the Sn–Me resonance gives no NOE at the Si–Me resonances, but there is an effect at the signal from the protons at the 6-position (C8) at δ 9.2 and more weakly at the 3-position (C5) at δ 7.84. Irradiation at the high-frequency SiMe_2 signal (C2) gives an NOE at the 3- and 4-positions, C5 and C6. The presence of the stable bicyclic structure is therefore confirmed. The chemical shifts δ_{Si} in the major isomer are more spread out than those in the minor isomer, suggesting that the major isomer is probably **6a**, in which an SiMe_3 fragment is adjacent to a trifluoroacetate group, as found in the crystal, but it is not possible from the NOE measurements to be certain about this point.

Conversion of **6a** into the enantiomer of **6c** could be achieved by a double pseudorotation at the five-coordinate tin center through an intermediate with a linear C1–Sn–C15 axis, but this process does not account for the spectroscopic results since it implies that the methyl groups attached to Si2 and Si3 remain distinct. It seems to be clear therefore that the five-coordinate tin species are stable in THF solution as well as in the crystal and that the bulky ligand is able to lock into two coordination sites in such a way that ready rearrangement at the five-coordinate tin is prevented.

The tosylate **7** was not sufficiently soluble in hydrocarbon and ether solvents for a detailed study of NMR spectra over a range of temperatures. This is puzzling since it is not ionic or polymeric in the solid state. To obtain clear signals, it was necessary to use DMSO as solvent, so the data are not strictly comparable with those from **6** in THF. The peaks in the proton spectrum at 298 K were broad but became sharper at 343 K. There was evidence for two species with a concentration ratio of about 95:5, and chemical exchange between them was shown by saturation transfer experiments. The ^{119}Sn shift ($\delta -132$) indicated that the tin was five- rather than four-coordinate. We assume, therefore, that the species in solutions of **7** are similar to those in solutions of **6**.

The spectra of **6** also throw some indirect light on why it proved to be impossible to make a detailed analysis of the variable-temperature spectra of **5**. The lower symmetry of **5** means that there are more isomers of similar energy; others could be formed by halogen exchange reactions. On cooling, all the signals are split into several components. The 500 MHz signal ascribed to the 6-H protons was split into 14 at 218 K, and saturation transfer by irradiation at one signal demonstrated chemical exchange with all the others. One Si–Me signal was shifted to low frequency (cf. that of C13 in **6**). The ^{119}Sn signals at $\delta -230.5$ and -115.1 at 338 K split into about 20 signals, all within the region expected for five-coordinate tin. These observations strongly suggest that species analogous to **6** are present also in solutions of **5**.

Conclusions

Our NMR and crystallographic studies on the closely related compounds **2–4** show that the balance between C- and N-ligation of the $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)$ fragment is subtly shifted over the series. For **2–4** the

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bonding to nitrogen becomes weaker as M becomes heavier; in contrast for the alkali metals the bonding to nitrogen becomes progressively stronger than that to carbon for the heavier metals. We have made Sn(IV) derivatives containing the $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$ ligand by oxidative addition, but there seems to be no reason they should not be obtained directly from the lithium compound **1** and Sn(IV) precursors, e.g., $SnMeCl_3$; further study of this possibility would be worthwhile. The ligand $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$ has a greater bite angle and thus occupies more space in the metal coordination sphere than the previously used $C(SiMe_3)_2(C_5H_4N-2)$ ligand, so it is remarkable that structures of the five-coordinate species **5**, **6**, and **7** are preserved in solution, with only transient dissociation to four-coordinate species. We are currently examining whether the introduction of more bulky ligands and/or better leaving groups than trifluoroacetate, or more bulky groups attached to tin in place of methyl, will give four-

coordinate Sn(IV) cations similar to the $[GeR_2C_6H_2^tBu_2CH_2NMe_2]^+$ species recently described by Jutzi.¹²

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Supporting Information Available: Molecular structures and numbering schemes for compounds **2**, **4**, and the second molecule of **6**. Details of crystal structure determinations, fractional atomic coordinates, bond lengths and angles, anisotropic displacement factors, hydrogen atom coordinates, torsion angles, and least-squares planes for compounds **2–4**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0009076

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