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Tripodal Triamidostannates and -plumbates[†]

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Reaction of the tripodal trilithium amides $HC\{SiMe_2N(Li)(4\text{-}CH_3C_6H_4)\}_3(THF)_2$ (**1**) and $CH_3Si\{SiMe_2N(Li)(tBu)\}_3(THF)_x$ with $SnCl_2$ or Cp_2Pb gave the corresponding lithium triamidostannates and -plumbates $HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3SnLi(THF)_3$ (**2**), $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Pb][Li(THF)_4]$ **(4),** and $CH_3Si\{SiMe_2N(tBu)\}_3MLi(THF)$ (M = Sn: **7**; Pb: **8**). The X-ray structure analysis of **2** revealed molecular as well as crystallographic 3-fold symmetry and established a short direct Li−Sn contact [d_{av}(Sn−Li) = 2.93(5); two independent molecules in the unit cell]. **2**: hexagonal, $P6_3$ (No. 173), a = 15.664(4) Å, c = 22.421(11) Å, Z = 4, V = 4765(3) Å^3, R = 0.038. An X-ray structure analysis of **8** established direct bonding of the (THF)Li counterion to two N-functions of the triamido metalate unit in a bridging fashion, a situation that, as the NMR spectra show, pertains in solution. **8**: orthorhombic, *Pbca* (No. 61), a = 10.8201(2) Å, b = 20.0825(3) Å, c = 31.5806(3) Å, Z = 8, V = 6862.3(3) Å^3, R = 0.076. If two molar equivalents of $MeN(CH_2CH_2NMe_2)_2$ are added to the *in situ* generated **2** the "solvent separated" ion pair $[\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl][HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn]$ **(5)** is formed, which contains a solvated $[Li_2Cl]^+$ cation. Crystal data of **5** as established in an X-ray structure analysis: triclinic, P-1 (No. 2), a = 12.377(2) Å, b = 15.360(2) Å, c = 17.594(3) Å, α = 77.41(1)°, β = 74.16(2)°, γ = 70.94(3)°, Z = 2, V = 3011.2 Å^3, R = 0.072. While reaction of $H_3CC\{N(Li)SiMe_3\}_3(THF)_3$ with $SnCl_2$ gives the corresponding stannate $H_3CC\{NSiMe_3\}_3SnLi(THF)$ which on the basis of its spectroscopic data is thought to have a similar structure to **7** and **8**, the analogous plumbate could be isolated neither from the reaction with Cp_2Pb nor with $PbCl_2$. The latter showed marked redox reactivity effecting fragmentation of the ligand. From the reaction mixture of this system a crystalline solid was isolated in ca. 25% yield. This was identified by elemental analysis and X-ray structure analysis as $[H_3CC(CH_2NSiMe_3)_2\{CH_2O(Li)\}Pb]_2$ **(11)** which has a fused cage structure. **11**: triclinic, $P\bar{1}$ (No. 2), a = 8.4889(2) Å, b = 11.1832(4) Å, c = 11.7308(3) Å, α = 62.010(5)°, β = 71.163(4)°, γ = 68.528(5)°, Z = 2, V = 899.5(2) Å^3, R = 0.054.

Introduction

Molecular compounds of divalent tin and lead display a rich structural chemistry characterized by a variety of oligomeric arrays or cage structures.[1] Metal−amido and −imido derivatives of the group 14 elements, in particular, have been studied in detail, both in solution (their dynamic behavior) and in the solid state.[2,3] Some of these compounds have found application in organic synthesis[4] or as ligands in transition metal coordination chemistry,[5] but most of all, it has been the fundamental interest in their bonding patterns which has fueled the research efforts in this area.

Whereas the chemistry of compounds of the type $[M(NR_2)_2]_n$ and $[M(NR)]_n$ is thus well developed, far less is known about the corresponding anionic metalates of the type $[M(NR_2)_3]^-$. This is particularly surprising since, for example, metalated tin reagents of the general type R_3SnM (R = alkyl, aryl, alkoxy; M = alkali metal) are well established as versatile tools in organic synthesis.[6] Only recently, a few of these materials have been structurally characterized;[7,8] however, their high reactivity, thermal lability and the difficulties of crystallizing many of them

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[†] We dedicate this paper to Professor F. A. Cotton on the occasion of his 65th birthday.

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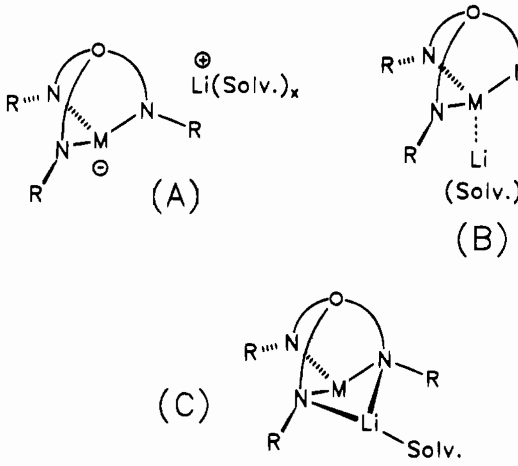

Figure 1. Different modes of cation–anion interaction in triamidostannates defining the principal structural types.

have inhibited further studies. In order to overcome these difficulties, the use of polydentate ligand systems which offer the stabilizing effect of chelation along with the shielding of a large sector in the coordination sphere of the low valent metal was thought to offer a route to systems of greater stability.

We have recently introduced a series of tripodal amido ligands containing neopentane-,[9] trisilylmethane-,[10] and trisilylsilane-backbones[11] to the coordination chemistry of early transition metals.[12] This enabled, for example, the stabilization of unusual coordination geometries or unsupported highly polar metal–metal bonds to late transition metals.[13] Preliminary investigations showed that they indeed effected a similar stabilization of low-coordinate group 14 metal centers in lithium triamido metalate complexes.[14] This opportunity of a more systematic structural investigation of this hitherto barely studied class of compounds led us to investigate the following points of primary interest: (i) Is the lithium counterion directly bound to the metalate anion or separated by a polar solvent acting as a coligand (Type **A**)? (ii) In case of direct bonding of Li^+ to the anion, where is the binding site? The direct bonding to the group 14 metal center (Type **B**) or to the amido-N atoms (Type **C**) are possible structural situations. (iii) Are there differences in the structural topology of the analogous Sn and Pb compounds?

In this paper we report the synthesis of a series of tripodal triamidometalates and discuss the structural patterns in solution and in the solid as established by spectroscopic techniques and X-ray crystallography.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze–pump–thaw" cycles and dried over 4-Å molecular sieves.

The ^1H-, ^{13}C-, ^{29}Si-, and ^7Li-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, 39.76, and 77.78 MHz, respectively) with tetramethylsilane and LiI/H_2O (external) as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. $H_3CC(CH_2NHSiMe_3)_3$,[9] $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$,[12b] and $CH_3Si\{SiMe_2NH(t\text{-}Bu)\}_3$[11] were prepared as reported previously. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. $HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3SnLi(THF)_3$ (2) and $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Pb][Li(THF)_4]$ (4). To a stirred solution of $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$ (1 g =1.98 mmol) in 40 mL of THF which was cooled at −70 °C were added 2.4 mL of BuLi (2.5 M in hexanes), and the reaction mixture was slowly warmed to room temperature. After another 1 h of stirring and renewed cooling to −70 °C, solid $SnCl_2$ (375 mg = 1.98 mmol) or $PbCp_2$ (667 mg = 1.98 mmol) was added and the reaction mixture warmed to room temperature and stirred for another 2 h. The solvent was removed *in vacuo*, the residue extracted with 30 mL of toluene and filtered through Celite to remove the LiCl formed in the reaction. The solution of the crude product was concentrated to ca. 10 mL and stored at −35 °C. The lithium metalates precipitated as colorless crystalline solids which were isolated by filtration.

2. Yield: 1.40 g (83.7%). Anal. Calcd for $C_{40}H_{64}N_3LiO_3SnSi_3$: C, 56.87; H, 7.64; N, 4.97. Found: C, 56.92; H, 7.82; N, 5.01. ^1H-NMR (C_6D_6, 295 K): $\delta = -0.14$ (s, $\mathit{H}C[Si...]_3$), 0.61 [s, $Si(C\mathit{H}_3)_2$], 1.23 (m, $C\mathit{H}_2CH_2O$), 2.24 (s, $4\text{-}C\mathit{H}_3C_6H_4$), 3.14 (m, $CH_2C\mathit{H}_2O$), 6.94 (d, H^2, $^3J_{HH} = 8.2$ Hz), 7.08 (d, H^3). $\{^1H\}^{13}C$-NMR (C_6D_6, 295 K): $\delta = 6.0$ ($[Si(\mathit{C}H_3)_2]$, 11.9 ($H\mathit{C}[Si...]_3$), 20.8 ($4\text{-}\mathit{C}H_3C_6H_4$), 25.3 ($\mathit{C}H_2CH_2O$), 68.2 ($CH_2\mathit{C}H_2O$), 124.6 ($C^3$), 126.0 ($C^2$), 129.3 ($C^4$), 153.5 ($C^1$). $\{^1H\}^{29}Si$-NMR (C_6D_6, 295 K): $\delta = -1.0$. ^7Li-NMR (C_6D_6, 295): $\delta = 2.59$.

4. Yield: 1.55 g (77.9%). Anal. Calcd for $C_{44}H_{72}N_3LiO_4PbSi_3$: C, 52.56; H, 7.22; N, 4.18. Found: C, 52.33; H, 7.54; N, 4.01. ^1H-NMR (C_6D_6, 295 K): $\delta = -0.44$ (s, $\mathit{H}C[Si...]_3$), 0.56 [s, $Si(C\mathit{H}_3)_2$], 1.24 (m, $C\mathit{H}_2CH_2O$), 2.23 (s, $4\text{-}C\mathit{H}_3C_6H_4$), 3.36 (m, $CH_2C\mathit{H}_2O$), 7.01 (m, AB-syst, $H^{2,3}$). $\{^1H\}^{13}C$-NMR (C_6D_6, 295 K): $\delta = 6.9$ ($[Si(\mathit{C}H_3)_2]$, 14.4 ($H\mathit{C}[Si...]_3$), 20.7 ($4\text{-}\mathit{C}H_3C_6H_4$), 25.5 ($\mathit{C}H_2CH_2O$), 68.0 ($CH_2\mathit{C}H_2O$), 125.1 ($C^3$), 126.0 ($C^2$), 129.9 ($C^4$), 152.7 ($C^1$). $\{^1H\}^{29}Si$-NMR (C_6D_6, 295 K): $\delta = 0.3$. ^7Li-NMR (C_6D_6, 295): $\delta = -1.91$.

$[\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl][HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Sn]$ (5). The lithiation of the amine precursor and reaction with $SnCl_2$ were carried out as described in the synthesis of **1** (same scale). To the THF solution of the *in situ* generated stannate which was concentrated to 10 mL, diethyl ether (10 mL) and $Me(CH_2CH_2NMe_2)_2$ (686 mg = 3.96 mmol) were added, and the solution was stored at −35 °C for several days. Compound **3** precipitated as a colorless highly crystalline solid. Yield: 73%. Anal. Calcd for $C_{46}H_{86}N_9Si_3Li_2SnCl$: C, 42.49; H, 8.52; N, 12.39. Found: C, 42.18; H, 8.36; N, 12.24. ^1H-NMR (THF-d_8, 295 K): $\delta = -0.42$ (s, $\mathit{H}C\{Si...\}_3$), 0.24 (s, $Si\{C\mathit{H}_3\}_2$), 2.22 (s, $C\mathit{H}_3C_6H_4$), 2.28 (s, $\{C\mathit{H}_3\}_2N$), 2.33 (s, $NC\mathit{H}_3$), 2.46 (m, $MeN\{C\mathit{H}_2C\mathit{H}_2\}_2$), 6.75 (d, $^3J_{HH} = 8.0$ Hz, Tol-H^2), 6.85 (d, Tol-H^3). $\{^1H\}^{13}C$-NMR (THF-d_8, 295 K): $\delta = 6.4$ ($Si\{\mathit{C}H_3\}_2$), 13.8 ($H\mathit{C}\{Si...\}_3$), 21.2 ($\mathit{C}H_3C_6H_4$), 44.3 ($N\mathit{C}H_3$),46.4 $N\{\mathit{C}H_3\}_2$), 56.0 ($MeN\{CH_2\mathit{C}H_2...\}_2$), 58.5 ($MeN\{\mathit{C}H_2CH_2...\}_2$), 124.3, 129.2, 146.0 155.2 (Tol-$C^{3,5}$, $C^{2,6}$,C^4, C^1). $\{^1H\}^{29}Si$-NMR (THF-d_8, 295 K): $\delta = -0.9$. ^7Li-NMR (THF-d_8): $\delta = 3.37$ (reference LiI/H_2O, 1 M, external; no essential change at 180 K).

$CH_3Si\{SiMe_2N(t\mathrm{Bu})\}_3SnLi(THF)$ (7) and $CH_3Si\{SiMe_2N(t\mathrm{Bu})\}_3PbLi(THF)$ (8). To a stirred solution of $CH_3Si\{SiMe_2NH(t\mathrm{Bu})\}_3$ (1.5 g = 3.32 mmol) in 40 mL of THF which was cooled at −70 °C was added 4.1 mL of BuLi (2.5 M in hexanes), and the reaction mixture was slowly warmed to room temperature. After another 1 h of stirring and renewed cooling to −70 °C, solid $SnCl_2$ (630 mg = 3.32 mmol) or solid Cp_2Pb (1.12 g = 3.32 mmol) was added and the reaction mixture warmed to room temperature and stirred for another 2 h. The

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Table 1. Crystal Data and Experimental Details for **2**, **5**, **8**, and **11**

	2	**5**	**8**	**11**
empirical formula	$C_{40}H_{64}LiN_3O_3Si_3Sn$	$C_{46}H_{86}Cl\ Li_2N_9Si_3Sn$	$C_{23}H_{57}LiN_3OPbSi_4$	$C_{11}H_{27}LiN_2OPbSi_2$
fw	844.83	1017.53	718.21	473.66
cryst syst	hexagonal	triclinic	orthorhombic	triclinic
cell params				
a (Å)	15.664(4)	12.377(2)	10.8201(2)	8.4889(2)
b (Å)		15.360(2)	20.0825(3)	11.1832(4)
c (Å)	22.421(11)	17.594(3)	31.5806(3)	11.7308(3)
α (deg)		77.41(1)		62.010(5)
β (deg)		74.16(2)		71.163(4)
γ (deg)		70.94(3)		68.528(5)
V (Å^3)	4765(3)	3011.2(9)	6862.3(3)	899.5(2)
Z	4	2	8	2
D_{calcd} (g cm^{-1})	1.161	1.08	1.390	1.749
space group	$P6_3$ (No. 173)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
$F(000)$	1728	1604	2920	456
μ(Mo Kα) (cm^{-1})[a]	6.49	5.60	51.10	95.74
2θ(max) (deg)	43.8	48.0	43.9	59.9
no. of observns $I > 3\sigma(I)$[b]	1536 [$I>2\sigma(I)$]	4601	1991	3544
no. of variables[c]	309	559	273	163
residuals R; R_w	0.038; 0.042	0.072; 0.093	0.076; 0.112	0.054; 0.062
goodness of fit	1.08	1.88	4.30	2.27
data/parameter	4.97	8.23	7.29	21.74

[a] An empirical absorption correction, using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158) was applied to all three crystals; the data were corrected for Lorentz and polarization effects. [b] The intensities of three representative reflections were measured every 60 min of X-ray exposure time; they remained constant throughout the data collection indicating in every case crystal and electronic stability (no decay correction was applied). [c] Neutral atom scattering factors were taken from: Cromer, D. T.; Waber, J. T. *International Tables of X-ray Crystallography*, The Kynoch Press: Birmingham, England, 1974. Anomalous dispersion effects were included in the final F_{calc} (Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.)

solvent was removed *in vacuo* and the residue extracted with 30 mL of toluene and filtered through Celite to remove the LiCl (or LiCp) formed in the reaction. The solution of the crude product was concentrated to ca. 10 mL and stored at −35 °C. The lithium metalates precipitated as colorless crystalline solids which were isolated by filtration.

7. Yield: 1.50 g (75.4%). Anal. Calcd for $C_{23}H_{56}N_3OSi_4LiSn$: C, 43.94; H, 8.98; N, 6.68. Found: C, 43.82; H, 8.90; N, 6.61. ^{1}H-NMR (C_6D_6, 295 K): δ = 0.15 (s, H_3CSi{Si...}$_3$), 0.39, 0.73, 0.78 (s, Si-{CH_3}$_2$), 1.19 (m, CH_2CH$_2$O), 1.49, 1.77 (s, {CH_3}$_3$CN), 3.48 (m, CH$_2$CH_2O) {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = −12.8 (CH$_3$Si), 7.2, 9.6, 10.1 (Si{CH$_3$}$_2$), 25.1 (CH$_2$CH$_2$O)), 35.5, 37.0 (C(CH$_3$)$_3$), 57.3, 58.2 (C(CH$_3$)$_3$), 69.2 (CH$_2$CH$_2$O). {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ = −13.8, −8.3. ^{7}Li-NMR (C_6D_6, 295 K): δ = −1.11. IR (Nujol): 1350 (m), 1256 (s), 1238 (m), 1210 (w), 1175 (m), 1120 (m), 1085 (s, br), 1028 (vs), 978 (s), 958 (w), 823 (s), 795 (vs, br), 742 (w), 713 (m), 698 (m) cm^{-1}.

8. Yield: 1.88 g (75.4%). Anal. Calcd for $C_{23}H_{56}N_3OSi_4LiPb$: C, 38.49; H, 7.86; N, 5.85. Found: C, 38.42; H, 7.82; N, 5.82. ^{1}H-NMR (C_6D_6, 295 K): δ = 0.16 (s, H_3CSi{Si...}$_3$), 0.43, 0.74, 0.79 (s, Si-{CH_3}$_2$), 1.16 (m, CH_2CH$_2$O), 1.35, 1.64 (s, {CH_3}$_3$CN), 3.47 (m, CH$_2$CH_2O) {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = −11.9 (CH$_3$Si), 7.1, 10.0, 10.4 (Si{CH$_3$}$_2$), 25.0 (CH$_2$CH$_2$O)), 36.4, 38.2 (C(CH$_3$)$_3$), 56.2, 57.3 (C(CH$_3$)$_3$), 69.2 (CH$_2$CH$_2$O). {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ = −12.2, −8.2. ^{7}Li-NMR (C_6D_6, 295 K): δ = −1.18. IR (Nujol): 1358 (m), 1250 (m), 1225 (m), 1200 (w), 1172 (s), 1112 (w), 1028 (s), 990 (s), 970 (m), 820 (vs), 771 (s), 740 (w), 718 (w), 692 (m) cm^{-1}.

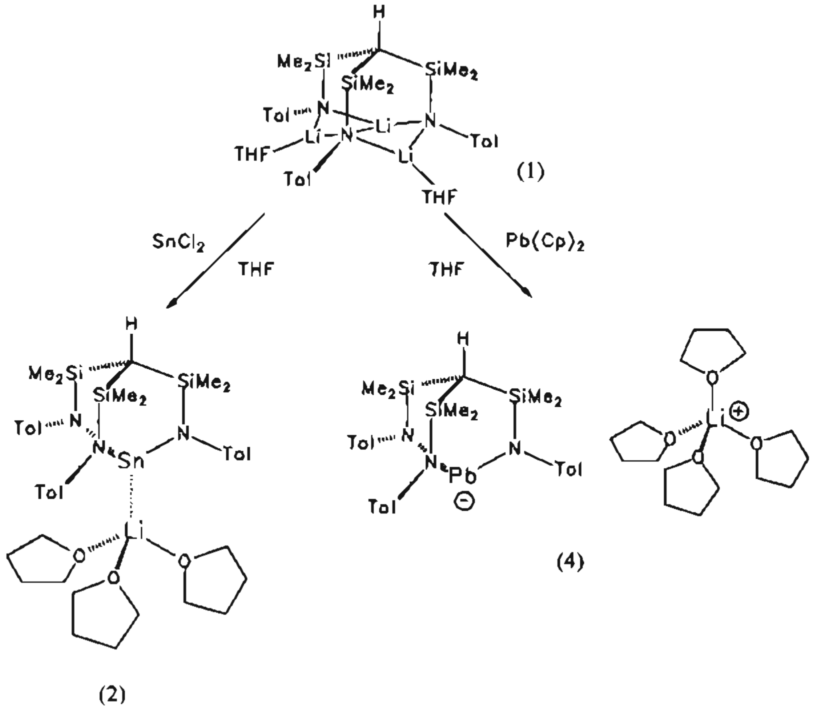
$H_3CC(CH_2NSiMe_3)_3SnLi(OEt_2)$ (10). To a stirred solution of $CH_3C(CH_2NSiMe_3)_3$ (1.0 g = 3.00 mmol) in 30 mL of diethyl ether which was cooled at −70 °C were added 3.60 mL of BuLi (2.5 M in hexanes), and the reaction mixture was slowly warmed to room temperature. After stirring for another 1 h and renewed cooling to −70 °C, solid $SnCl_2$ (568 mg = 3.00 mmol) was added and the reaction mixture warmed to room temperature and stirred for another 2 h. The solvent was removed *in vacuo*, and the residue was extracted with 30 mL of toluene and filtered through Celite to remove the LiCl formed in the reaction. The solvent was again distilled *in vacuo* and the oily residue kept under a vacuum of 10^{-3} Torr for ca. 5 h to remove residual toluene. The reaction product was obtained in an analytically pure form as an oil which did not crystallize even after several weeks of storage. Yield: 1.45 g (91.1%). Anal. Calcd for $C_{18}H_{46}N_3OSi_3LiSn$: C, 40.76; H, 8.74; N, 7.92. Found: C, 40.62; H, 8.86; N, 7.78. ^{1}H-NMR (C_6D_6, 295 K): δ = 0.23, 0.39 (s, Si(CH_3)$_3$), 0.61 (s, CCH_3), 0.86 (t, $^3J_{HH}$ = 6.9, CH_3CH$_2$O), 2.77 (d, $^2J_{HH}$ = 12.4, CH_2N), 3.00 (q, CH$_3$CH_2O), 3.27 (s, CH_2N), 3.29 (d, CH_2N). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = 0.9, 1.2 [(CH$_3$)$_3$Si], 14.8 (CH$_3$CH$_2$O)), 27.3 (CH$_3$C), 41.2 (CCH$_3$), 57.2, 58.5 (CH$_2$N), 66.4 (CH$_3$CH$_2$O). {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ = 0.2, 2.9. ^{7}Li-NMR (C_6D_6, 295 K): δ = −1.37. IR (Nujol): 1291 (vs), 1252 (vs), 1171, 1154 (w), 1111 (m), 1082 (w), 1055 (m), 990 (m), 931 (s), 918 (w), 895 (m), 820 (vs), 695 (w), 655 (w) cm^{-1}.

$[H_3CC(CH_2NSiMe_3)_2\{CH_2O(Li)\}Pb]_2$ (11). To a stirred solution of $CH_3C(CH_2NSiMe_3)_3$ (1.0 g = 3.00 mmol) in 30 mL of THF which was cooled at −70 °C were added 3.60 mL of BuLi (2.5 M in hexanes), and the reaction mixture was slowly warmed to room temperature. After another 1 h of stirring and renewed cooling to −70 °C, solid $PbCl_2$ (833 mg = 3.00 mmol) was added. Almost immediately a black solid material precipitated which slowly disappeared upon warming of the reaction mixture to room temperature. After another 2 h of stirring and filtration through Celite (removal of some of the LiCl) the solution was concentrated to ca. 7 mL and stored at −35 °C. Over a period of several days a colorless highly crystalline solid precipitated from this mixture which was isolated by filtration. Yield: 0.30 g (24.0%). Anal. Calcd for $C_{22}H_{54}N_4O_2Si_4Li_2Pb$: C, 41.65; H, 6.52; N, 6.71. Found: C, 40.99; H, 6.46; N, 6.78. ^{1}H-NMR (thf-d_8, 295): δ = 0.13 (s, Si-(CH_3)$_3$), 0.37 (s, CCH_3), 3.01 (d, $^2J_{HH}$ = 13.4, CH_2N), 3.51 (d, CH_2N), 3.83 (s, CH_2O). {^{1}H}^{13}C-NMR (thf-d_8, 295 K): δ = 1.1 [(CH$_3$)$_3$Si], 30.6 (CH$_3$C), 44.9 (CCH$_3$), 57.8 (CH$_2$N), 76.3 (CH$_2$O). ^{7}Li-NMR (thf-d_8, 295 K): δ = −0.88. IR (Nujol): 1371 (vs), 1299 (w), 1251 (m), 1242 (m), 1154 (w), 1111 (m), 1080 (w), 1051 (m), 995 (w), 905 (w), 860 (m), 840 (m), 831 (w), 735 (w), 720 (m) cm^{-1}.

X-ray Crystallographic Study of 2, 5, 8, and 11. The crystals of all four compounds were colorless (Sn) or light yellow (Pb) and had block-shaped prismatic habits. The crystals (or fragments of appropriate size) were mounted under argon in Lindemann capillaries. The X-ray diffraction data were collected using Enraf Nonius CAD 4A diffractometers with graphite monochromated Mo Kα radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range 20° < 2θ < 30°. Data collection of **2**, **8** and **11** was carried out at 295 K whereas that of **5** was carried out at 223 K. The full details are presented in Table 1.

2: The data analysis and refinement was carried out with SHELX

Scheme 1. Reaction of HC{SiMe$_2$N(Li)(4-CH$_3$C$_6$H$_4$)}$_3$(THF)$_2$ with SnCl$_2$ and Cp$_2$Pb To Give the Corresponding Triamidostannate **2** and -plumbate **4**, Respectively



93. Systematic absences indicated that the space group of **2** is either $P6_3$ or $P6_3/m$. Attempts were made to solve and refine the structure in both space groups; however, only the model of **2** as a racemic twin in $P6_3$ gave a satisfactory solution. The possibility of apparent hexagonal symmetry generated by twinning of crystals of lower symmetry was considered; however, attempts to solve the structure assuming such a model were unsuccessful. The position of the Sn atom was located from a Patterson synthesis using SHELXS 86. All other non-hydrogen atoms were located in subsequent difference Fourier syntheses and refined anisotropically. The asymmetric unit contains one-third of the two independent molecules. Although the C-atoms in one of the coordinated THF molecules are severely disordered, they could be refined anisotropically. Attempts to resolve the disorder were unsuccessful. With the exception of the hydrogen atoms on the disordered THF molecule, all H-atoms were assigned calculated positions and were included in the final full-matrix refinement using the riding model.

5: The data analysis and refinement was carried out with SHELXL 93. The positions of the Sn and Si atoms were located from a Patterson synthesis using SHELX 86. All other non-hydrogen atoms were located in subsequent difference Fourier syntheses and refined anisotropically. All H-atoms were assigned calculated positions and were included in the final full-matrix refinement.

8 and 11: The data analysis and refinement was carried out with the programs of the TEXSAN software package. Both structures were solved by using direct methods and the non-hydrogen atoms were refined anisotropically. All H-atoms were assigned calculated positions and were included in the final full-matrix refinement. The THF molecule as well as the *t*Bu-groups in **8** were found to be severely disordered and did not refine satisfactorily. As a consequence all metric parameters of **8** were determined with high esd's.

Results and Discussion

Synthesis and Structures of Tripodal Triamidometalates Containing the Trisilylmethane-Derived Ligand [HC{SiMe$_2$N-(4-CH$_3$C$_6$H$_4$)}$_3$]$^{3-}$. The starting material for the synthesis of the triamido metalates is the trilithiated triamine precursor HC-{SiMe$_2$N(Li)(4-CH$_3$C$_6$H$_4$)}$_3$(THF)$_2$ (**1**),[12] which is generated *in situ* (Scheme 1). Upon reaction with 1 molar equiv of SnCl$_2$ in THF, the lithium stannate HC{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$SnLi-(THF)$_3$ (**2**) is formed, which may be obtained as a crystalline solid from THF/diethyl ether.

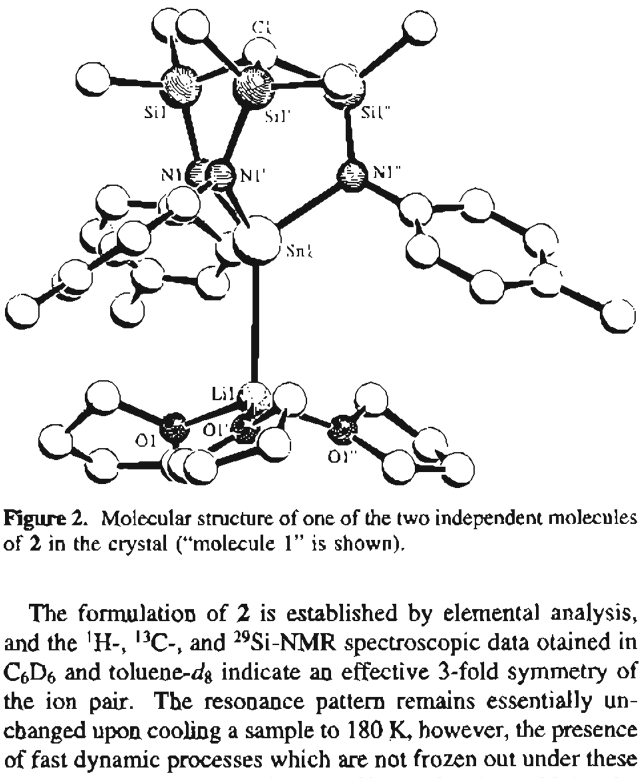


Figure 2. Molecular structure of one of the two independent molecules of **2** in the crystal ("molecule 1" is shown).

The formulation of **2** is established by elemental analysis, and the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectroscopic data otained in C$_6$D$_6$ and toluene-d_8 indicate an effective 3-fold symmetry of the ion pair. The resonance pattern remains essentially unchanged upon cooling a sample to 180 K, however, the presence of fast dynamic processes which are not frozen out under these conditions could not be ruled out. The molecule could thus be either a separate ion pair or a contact ion pair with direct bonding interaction between Sn and Li. The latter structural arrangement recently has been observed by Wright and co-workers in Ph$_3$-SnLi(PMDETA) (**3**) (PMDETA = pentamethyldiethylenetriamine).[7a] Since even at 180 K ^{119}Sn$-^7$Li coupling as found for **3** under these conditions was not observed, the structural elucidation of **2** had to occur by X-ray crystallography.

Compound **2** crystallizes as a racemic twin in the hexagonal space group P6$_3$. Its molecular structure in the crystal is shown in Figure 2, the principal bond parameters are listed in Table 2 while the fractional coordinates are given in Table 3. The unit

Table 2. Selected Bond Lengths (Å) and Interbond Angles (deg) of **2**

Molecule 1			
Sn(1)−N(1)	2.149(10)	Sn(1)−Li(1)	2.89(4)
Sn(1)−C(4)	3.035(13)	Sn(1)−Si(1)	3.314(4)
Si(1)−N(1)	1.715(10)	Si(1)−C(2)	1.87(2)
Si(1)−C(3)	1.88(2)	Si(1)−C(1)	1.884(10)
Li(1)−O(1)	1.91(2)		
N(1′)−Sn(1)−N(1)	92.2(4)	N(1)−Sn(1)−Li(1)	123.7(3)
N(1)−Sn(1)−C(4′)	113.5(4)	N(1)−Sn(1)−Si(1′)	67.2(3)
N(1)−Si(1)−C(1)	104.1(8)	O(1′)−Li(1)−O(1)	112.2(11)
O(1)−Li(1)−Sn(1)	106.6(13)	Si(1)−N(1)−Sn(1)	117.7(6)
Si(1′)−C(1)−Si(1)	110.3(8)		
Molecule 2			
Sn(1A)−N(1A)	2.139(10)	Sn(1A)−Li(1A)	2.97(5)
Sn(1A)−C(4A)	3.05(2)	Sn(1A)−Si(1A)	3.312(4)
Si(1A)−N(1A)	1.724(12)	Si(1A)−C(2A)	1.86(2)
Si(1A)−C(1A)	1.873(9)	Si(1A)−C(3A)	1.90(2)
Li(1A)−O(1A)	1.90(2)		
N(1A′)−Sn(1A)−N(1A)	93.3(4)	N(1A)−Sn(1A)−Li(1A)	122.9(3)
N(1A′)−Sn(1A)−C(4A)	103.1(4)	N(1A)−Sn(1A)−Si(1A′)	68.4(3)
N(1A)−Si(1A)−C(1A)	103.2(8)	O(1A′)−Li(1A)−O(1A)	107(2)
O(1A)−Li(1A)−Sn(1A)	111.5(14)	Si(1A)−N(1A)−Sn(1A)	117.6(6)

Table 3. Fractional Atomic Coordinates ($\times 10^4$) of **2**

atom	*x*	*y*	*z*
Molecule 1			
Sn(1)	0	0	10(1)
Si(1)	−1173(3)	−71(3)	1255(2)
Li(1)	0	0	−1278(19)
N(1)	−905(7)	78(7)	541(4)
O(1)	−1182(7)	−32(8)	−1521(5)
C(1)	0	0	1524(12)
C(2)	−1466(13)	708(13)	1753(8)
C(3)	−2294(10)	−1328(11)	1313(8)
C(4)	−1265(10)	922(10)	268(6)
C(5)	−621(9)	1767(9)	−62(7)
C(6)	−980(10)	2320(10)	−350(7)
C(7)	−1918(12)	2120(12)	−291(7)
C(8)	−2561(11)	1298(11)	29(9)
C(9)	−2253(9)	698(10)	309(6)
C(10)	−2301(14)	2750(13)	−576(11)
C(11)	−2154(12)	−724(15)	−1279(9)
C(12)	−2850(14)	−619(16)	−1640(12)
C(13)	−2310(14)	407(16)	−1836(11)
C(14)	−1245(14)	746(15)	−1821(9)
Molecule 2			
Sn(1A)	6667	3333	3454(1)
Si(1A)	5680(3)	2082(3)	4697(2)
Li(1A)	6667	3333	2129(22)
N(1A)	6008(8)	2010(8)	3972(5)
O(1A)	6552(11)	4397(11)	1820(6)
C(1A)	6667	3333	4943(12)
C(2A)	4414(12)	895(14)	4768(9)
C(3A)	5641(15)	1067(14)	5178(8)
C(4A)	5823(12)	1133(11)	3677(7)
C(5A)	6539(10)	1151(11)	3308(7)
C(6A)	6376(17)	334(18)	2982(9)
C(7A)	5506(19)	−543(17)	3011(9)
C(8A)	4811(13)	−568(11)	3383(12)
C(9A)	4959(12)	251(11)	3726(8)
C(10A)	5291(22)	−1429(15)	2614(13)
C(11A)	6668(68)	4751(51)	1267(22)
C(12A)	6441(29)	5487(28)	1153(19)
C(13A)	6019(33)	5529(28)	1708(16)
C(14A)	6396(30)	5102(24)	2124(12)

cell contains two independent triamidostannate molecules which are aligned along the crystallographic axis and thus possess exact crystallographic 3-fold symmetry. Since their metric parameters do not differ significantly, the discussion of the "average" structure will be given.

The structural center piece is the [2,2,2]bicyclooctane-related cage comprising the trisilylmethane unit and the tris(amido)-stannate unit which are slightly twisted with respect to each other. As in all other previously characterized compounds containing this ligand,[12,13] the twist [average torsion angle 36.4-(7)°] is to be seen as a consequence of the steric repulsion of the methyl groups within the trisilylmethane unit rather than being due to the geometrical requirements of the Sn−N binding in the molecule. The Sn atom is displaced by 1.16(1) Å from the plane defined by the three amido-N atoms which have trigonal planar geometry $[\Sigma\{\angle_N\} = 359.9(8)°]$. The average $\angle$(N−Sn−N′) of 93.3(4)° in the trigonal monopyramidal SnN_3 unit indicates that Sn−N σ-bonding primarily involves the 4p orbitals of the tin atom with the lone pair residing in a molecular orbital of essentially 4s character. However, it should be pointed out that the partially ionic nature of the Sn−N bonds may render orbital overlap and hybridization less important than in alkyl or aryl stannates. The ring planes of the tolyl groups in the ligand periphery are somewhat less twisted with respect to the radial planes defined by C(1), Si, and N [average torsion angle 32.6(6)°] than observed previously in the "lamp shade" structures of transition metal derivatives.[13]

The most remarkable structural feature is certainly the Sn−Li contact [d_{av}(Sn−Li) = 2.93(5) Å] which is significantly longer than the sum of the covalent radii of Sn and Li (ca. 2.74 Å). Due to the fairly high esd a meaningful comparison with the Sn−Li distance found in **3** [*d*(Sn−Li) = 2.871(7) Å][7a] is not possible. The lithium cation is solvated by three THF molecules which is a structural arrangement frequently observed in solvated Li salts.[15] The absence of ionic conductivity of solutions of **2** in THF of diethyl ether indicates that even in a polar environment the situation of a contact ion pair pertains.

The reaction of **1** with $PbCl_2$ did not yield the Pb-analogue of **2** but, as a result of redox reactions leading to the precipitation of metallic lead, produced a complicated mixture of unidentified components. The unspecific nature of this reaction has prohibited the elucidation of the redox processes or even the nature of the products involved. However, if **1** is reacted with 1 molar equiv of Cp_2Pb, substitution of both Cp-ligands takes place and the corresponding triamido plumbate **4** is formed in a clean reaction (Scheme 1). The use of Cp_2M (M = Sn, Pb) as a convenient precursor for the preparation of stannates and plumbates was first reported by Wright and co-workers in the synthesis of the tris(imido)stannate and -plumbate $M[\mu\text{-}N{=}C\text{-}(tBu)(Ph)]_3Li(THF)$ (M = Sn, Pb).[16]

On the basis of its analytical and spectroscopic data compound **4**, a colorles crystalline solid, is formulated as $[HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3Pb][Li(THF)_4]$. While the NMR spectroscopic characteristics of **2** and **4** which involve the metalate unit are almost identical, the different environment of the Li-cation (implied by the presence of the additional molecule of THF) is reflected in the remarkably different chemical shift of the ^{7}Li-NMR resonance (recorded for both compounds under identical conditions: 295 K in C_6D_6; external standard LiI/H_2O, 1.0 M); **4**, $\delta(^7Li) = -1.91$; **2**, +2.59. Although single crystals suitable for an X-ray diffraction study could not be obtained and the definitive structural proof is therefore lacking, it is reasonable to propose a structure containing the plumbate anion and a $[Li(THF)_4]^+$ which, on the basis of lack of appreciable ionic conductivity in THF, form a contact ion pair in solution.

In view of the structure determined for **2**, it was of interest whether the presence of an additional stronger donor ligand

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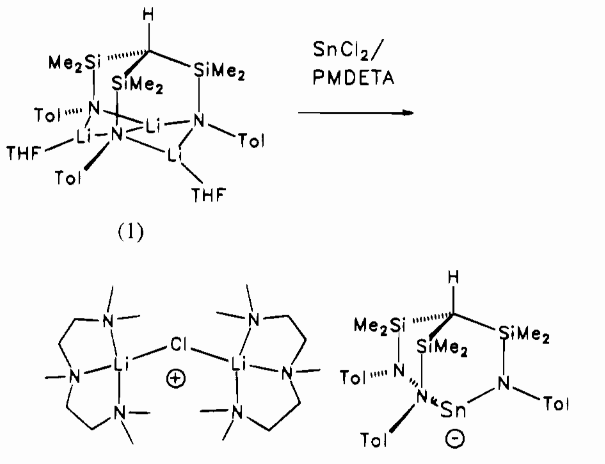
(15) See for example: Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694 and references cited therein.

(16) (a) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1086. (b) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Steiner, A.; Stalke, D.; Wright, D. S. *Inorg. Chem.* **1994**, *33*, 2370.

would effect the disruption of the Sn−Li contact and lead to an ion pair such as observed in the corresponding plumbate **4**. If 2 molar equiv of the chelating triamine PMDETA are added to the solution of *in situ* generated **2** a highly crystalline colorless solid may be isolated (at −35 °C from THF:diethyl ether 1:1) in 73% yield which on the basis of its analytical and NMR spectroscopic data is formulated as $[\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl][HC\{SiMe_2N(p\text{-}Tol)\}_3Sn]$ (**5**) (eq 1).[14] Products with the same analytical and spectroscopic data were obtained on addition of less than 2 equiv of the tridentate amine, albeit in markedly decreased yield.



(1)

(5)

(1)

The seemingly complicated formula was confirmed by a single crystal X-ray structure analysis of **5** (selected bond parameters are given in Table 4, the fractional coordinates are listed in Table 5) which revealed that the Li^+-counterion is indeed separated from the stannate unit $[HC(SiMe_2Np\text{-}Tol)_3Sn]^-$ through coordination by a PMDETA ligand and a ClLi(PMDETA) molecule to generate the complex cation $[\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl]^+$ (Figure 3).

The structure of the anion is very similar to that established in the X-ray crystallographic study of **2** (Table 2) and therefore does not require detailed discussion. However, the twist of the tolyl rings with respect to the radial planes defined by C(1), Si and N [average torsion angle 50.0(4)°] is significantly greater than in **2** and approaches the values observed in transition metal amides containing this tripod ligand.[13] A PMDETA-solvated Li_2Cl^+ cation of the same composition as found in **5** was reported by Eaborn and co-workers in the crystal structure of $[\{MeN(CH_2CH_2NMe_2)_2Li\}_2Cl][Li\{C(SiMe_3)_3\}_2]$.[17] For the latter a linear arrangement [∠(Li−Cl−Li′) = 180°] in which the Cl atom resides upon a crystallographic center of symmetry was reported, and the proposed preference of this geometry was backed up by an *ab initio* study of $[Li_2Cl]^+$ in the gas phase. The nonlinear structure of the cation of **5** [∠(Li−Cl−Li′) = 143.1(6)°], which is not restricted by crystallographic symmetry, clearly shows that the highly ionic nature and therefore low degree of directionality of the Li−Cl bonding allows for considerable Li−Cl−Li′ bending. Due to the spatial separation of the coordinated PMDETA ligands, there are no particular steric constraints imposed, and the actual arrangement may therefore be dictated by crystal packing forces and vary considerably depending on the nature of the respective anion. In the crystal the cation rides in a "pickaback" fashion on the trisilylmethane side of the stannate anion, and there is no significant interaction with the tin atom.

Table 4. Selected Bond Lengths and Interbond Angles of **5**

Sn(1)−N(1)	2.153(5)	N(5)−C(52)	1.41(1)
Sn(1)−N(2)	2.158(5)	N(5)−C(53)	1.50(1)
Sn(1)−N(3)	2.160(5)	N(5)−Li(1)	2.03(2)
Cl−Li(1)	2.23(1)	N(6)−C(61)	1.48(1)
Cl−Li(2)	2.26(1)	N(6)−C(62)	1.52(1)
Si(1)−N(1)	1.723(6)	N(6)−C(63)	1.49(1)
Si(1)−C(1)	1.898(7)	N(6)−Li(1)	2.15(2)
Si(1)−C(6)	1.899(7)	N(7)−C(71)	1.50(1)
Si(1)−C(7)	1.901(7)	N(7)−C(72)	1.48(1)
Si(2)−N(2)	1.725(5)	N(7)−C(73)	1.49(1)
Si(2)−C(1)	1.885(7)	N(7)−Li(2)	2.08(1)
Si(2)−C(4)	1.886(7)	N(8)−C(81)	1.47(1)
Si(2)−C(5)	1.902(8)	N(8)−C(82)	1.50(1)
Si(3)−N(3)	1.710(5)	N(8)−C(83)	1.50(1)
Si(3)−C(1)	1.871(7)	N(8)−Li(2)	2.14(2)
Si(3)−C(2)	1.886(7)	N(9)−C(91)	1.49(1)
Si(3)−C(3)	1.898(8)	N(9)−C(92)	1.45(2)
N(1)−C(11)	1.409(8)	N(9)−C(93)	1.43(1)
N(2)−C(21)	1.381(7)	N(9)−Li(2)	2.10(2)
N(3)−C(31)	1.402(8)	C(11)−C(12)	1.406(8)
N(4)−C(41)	1.45(1)	C(11)−C(16)	1.417(9)
N(4)−C(42)	1.50(1)	C(12)−C(13)	1.395(9)
N(4)−C(43)	1.40(1)	C(13)−C(14)	1.40(1)
N(4)−Li(1)	2.15(2)	C(14)−C(15)	1.39(1)
N(5)−C(51)	1.49(1)	C(14)−C(17)	1.55(1)
N(1)−Sn(1)−N(2)	91.7(2)	Sn(1)−N(2)−Si(2)	117.3(3)
N(1)−Sn(1)−N(3)	91.9(2)	Sn(1)−N(2)−C(21)	116.7(4)
N(2)−Sn(1)−N(3)	92.2(2)	Si(2)−N(2)−C(21)	125.7(4)
Li(1)−Cl−Li(2)	143.1(6)	Sn(1)−N(3)−Si(3)	119.2(3)
N(1)−Si(1)−C(1)	104.4(3)	Sn(1)−N(3)−C(31)	114.9(4)
N(1)−Si(1)−C(6)	112.7(3)	Si(3)−N(3)−C(31)	125.8(5)
N(1)−Si(1)−C(7)	112.3(3)	C(41)−N(4)−C(42)	107(1)
C(1)−Si(1)−C(6)	109.2(3)	C(41)−N(4)−C(43)	107(1)
C(1)−Si(1)−C(7)	114.6(3)	C(41)−N(4)−Li(1)	102.2(8)
C(6)−Si(1)−C(7)	103.8(4)	C(42)−N(4)−C(43)	113(1)
N(2)−Si(2)−C(1)	105.4(3)	C(42)−N(4)−Li(1)	115.9(8)
N(2)−Si(2)−C(4)	111.1(3)	C(43)−N(4)−Li(1)	110.2(8)
N(2)−Si(2)−C(5)	113.2(3)	C(51)−N(5)−C(52)	114(1)
C(1)−Si(2)−C(4)	109.1(4)	C(51)−N(5)−C(53)	109(1)
C(1)−Si(2)−C(5)	114.2(4)	C(51)−N(5)−Li(1)	104.7(8)
C(4)−Si(2)−C(5)	103.8(4)	C(52)−N(5)−C(53)	110(1)
N(3)−Si(3)−C(1)	104.5(2)	C(52)−N(5)−Li(1)	106.9(9)
N(3)−Si(3)−C(2)	112.0(3)	C(53)−N(5)−Li(1)	112.7(8)
N(3)−Si(3)−C(3)	112.3(3)	C(61)−N(6)−C(62)	105.5(9)
C(1)−Si(3)−C(2)	109.9(3)	C(61)−N(6)−C(63)	106(1)
C(1)−Si(3)−C(3)	114.2(3)	C(61)−N(6)−Li(1)	121.5(8)
C(2)−Si(3)−C(3)	104.1(5)	C(62)−N(6)−C(63)	117(1)
Sn(1)−N(1)−Si(1)	117.9(3)	C(62)−N(6)−Li(1)	100.9(7)
Sn(1)−N(1)−C(11)	116.8(4)	C(63)−N(6)−Li(1)	106.2(8)
Si(1)−N(1)−C(11)	125.0(5)	C(71)−N(7)−C(72)	118(1)
N(4)−C(41)−C(51)	116(1)	Cl−Li(1)−N(6)	118.1(8)
N(5)−C(51)−C(41)	117(1)	N(4)−Li(1)−N(5)	87.2(7)
N(5)−C(52)−C(62)	115(1)	N(4)−Li(1)−N(6)	116.6(8)
N(6)−C(62)−C(52)	112.7(9)	N(5)−Li(1)−N(6)	88.9(6)
N(7)−C(71)−C(81)	110(1)	Cl−Li(2)−N(7)	113.2(6)
N(8)−C(81)−C(71)	111.7(9)	Cl−Li(2)−N(8)	136.7(6)
N(8)−C(82)−C(92)	117(1)	Cl−Li(2)−N(9)	111.4(6)
N(9)−C(92)−C(82)	119(1)	N(7)−Li(2)−N(8)	85.7(6)
Cl−Li(1)−N(4)	117.1(7)	N(7)−Li(2)−N(9)	123.7(7)
Cl−Li(1)−N(5)	121.8(8)	N(8)−Li(2)−N(9)	84.7(6)

Synthesis and Structures of Tripodal Triamidometalates Containing the Trisilylsilane-Derived Ligand $[CH_3Si\{SiMe_2N(tBu)\}_3]^{3-}$. Lithiation of $CH_3Si\{SiMe_2NH(tBu)\}_3$ (**6**)[11] in THF and reaction with $SnCl_2$ and Cp_2Pb give the corresponding lithium stannate and plumbate, respectively (eq 2). The compounds isolated after workup in toluene were formulated as $CH_3Si\{SiMe_2N(tBu)\}SnLi(THF)$ (**7**) and $CH_3Si\{SiMe_2N(tBu)\}PbLi(THF)$ (**8**) on the basis of their elemental analyses. The ^1H-, ^{13}C-, and ^{29}Si-NMR spectral patterns of both compounds are entirely analogous and indicate a reduction of the effective symmetry in solution from C_{3v} to C_s. A possible explanation for the reduction in molecular symmetry (as

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(17) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 969.

Table 5. Fractional Atomic Coordinates of 5

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Sn(1)	0.20800(8)	0.23493(6)	0.23785(6)	C(24)	0.293(1)	−0.0838(9)	0.4556(8)
Cl	0.1934(4)	0.0924(3)	0.8628(3)	C(25)	0.383(1)	−0.042(1)	0.4487(9)
Si(1)	0.2484(3)	0.4373(3)	0.2429(2)	C(26)	0.374(1)	0.0529(9)	0.4154(9)
Si(2)	0.2965(3)	0.2805(3)	0.3834(2)	C(27)	0.307(2)	−0.185(1)	0.491(1)
Si(3)	0.0418(3)	0.3841(3)	0.3658(2)	C(31)	−0.043(1)	0.3548(8)	0.2456(7)
N(1)	0.3025(9)	0.3378(7)	0.1981(6)	C(32)	−0.018(1)	0.3693(9)	0.1605(7)
N(2)	0.2603(8)	0.1977(7)	0.3509(6)	C(33)	−0.107(1)	0.3827(9)	0.1174(9)
N(3)	0.0487(8)	0.3364(7)	0.2848(6)	C(34)	−0.222(1)	0.3846(9)	0.1605(9)
N(4)	−0.005(1)	0.1491(8)	0.7219(8)	C(35)	−0.248(1)	0.3726(9)	0.2455(9)
N(5)	0.176(1)	−0.0249(9)	0.7041(8)	C(36)	−0.161(1)	0.3578(9)	0.2879(9)
N(6)	0.025(1)	−0.0698(8)	0.8588(8)	C(37)	−0.316(1)	0.398(1)	0.115(1)
N(7)	0.241(1)	0.2956(9)	0.9062(8)	C(41)	0.059(2)	0.124(1)	0.643(1)
N(8)	0.387(1)	0.2736(9)	0.7495(7)	C(42)	−0.129(2)	0.148(2)	0.731(2)
N(9)	0.490(1)	0.0991(9)	0.8358(9)	C(43)	0.004(3)	0.237(1)	0.724(2)
C(1)	0.192(1)	0.3952(9)	0.3519(8)	C(51)	0.113(2)	0.029(2)	0.640(1)
C(2)	−0.069(1)	0.502(1)	0.3697(9)	C(52)	0.165(2)	−0.116(1)	0.728(1)
C(3)	−0.010(1)	0.313(1)	0.4638(9)	C(53)	0.303(2)	−0.029(2)	0.676(1)
C(4)	0.275(1)	0.261(1)	0.4956(8)	C(61)	−0.101(2)	−0.056(2)	0.894(2)
C(5)	0.457(1)	0.276(1)	0.3464(9)	C(62)	0.052(2)	−0.124(1)	0.790(1)
C(6)	0.365(1)	0.496(1)	0.2349(9)	C(63)	0.086(2)	−0.115(2)	0.926(1)
C(7)	0.135(1)	0.531(1)	0.1931(9)	C(71)	0.312(2)	0.361(1)	0.865(1)
C(11)	0.398(1)	0.3219(8)	0.1324(7)	C(72)	0.114(2)	0.327(2)	0.907(1)
C(12)	0.414(1)	0.3915(8)	0.0671(7)	C(73)	0.259(2)	0.280(2)	0.989(1)
C(13)	0.511(1)	0.370(1)	0.0044(8)	C(81)	0.332(2)	0.366(1)	0.775(1)
C(14)	0.592(1)	0.2818(9)	0.0017(8)	C(82)	0.516(2)	0.234(2)	0.741(1)
C(15)	0.575(1)	0.2123(9)	0.0656(9)	C(83)	0.360(2)	0.277(2)	0.671(1)
C(16)	0.479(1)	0.2318(9)	0.1326(8)	C(91)	0.526(2)	0.103(2)	0.909(2)
C(17)	0.700(1)	0.262(1)	−0.068(1)	C(92)	0.558(2)	0.142(2)	0.766(2)
C(21)	0.273(1)	0.1065(8)	0.3866(7)	C(93)	0.503(2)	0.006(2)	0.827(2)
C(22)	0.179(1)	0.0671(9)	0.3942(8)	Li(1)	0.094(3)	0.045(2)	0.799(2)
C(23)	0.192(1)	−0.027(1)	0.4268(9)	Li(2)	0.315(2)	0.181(2)	0.845(1)

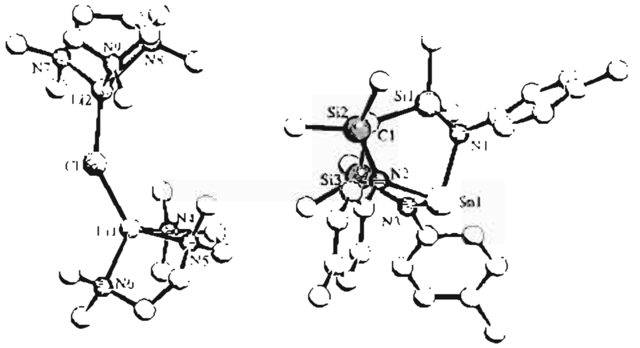


Figure 3. Relative arrangement of the (closest) cation and anion of 5 in the crystal.

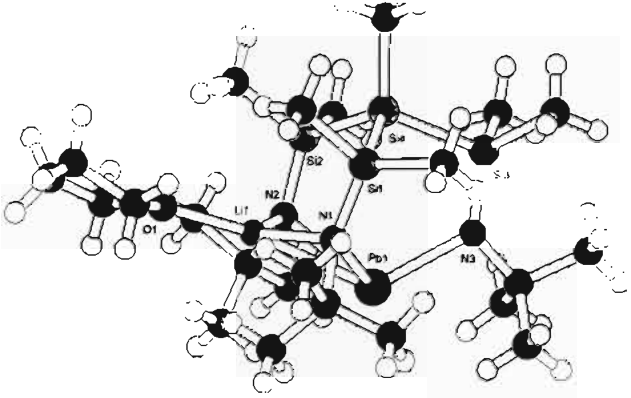
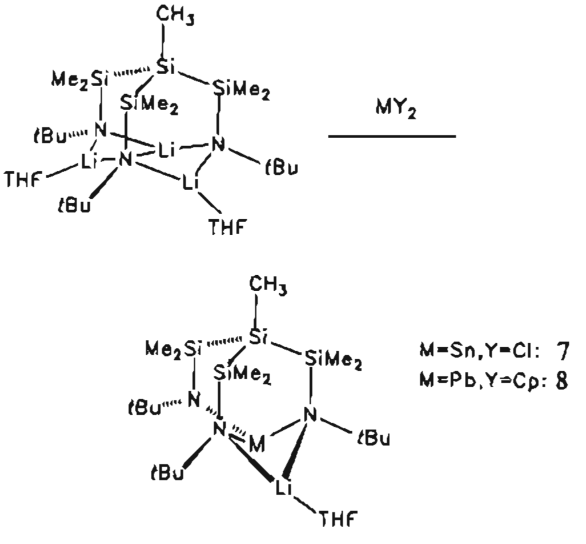


Figure 4. Molecular structure of triamidoplumbate 8 in the crystal.

compared to 2) is the coordination of the mono-THF solvated Li$^+$-cation in a bridging fashion to two amido nitrogen atoms generating a structural arrangement as indicated in eq 2. This proposed molecular geometry was confirmed by a single crystal X-ray structure analysis of **8**. The result of the structure determination of **8** is depicted in Figure 4, the principal bond lengths and interbond angles are given in Table 6, and the fractional coordinates are listed in Table 7.



(2)

The tripod-amidoplumbate cage comprising the four silicon atoms of the trisilylsilane unit and the PbN$_3$-unit is significantly distorted due to the coordination of the (THF)Li$^+$-"counterion" to two of the amido-N atoms. The molecule has idealized C_s-symmetry, the virtual mirror plane being spanned by Si(4), Si(3), N(3), Pb(1), Li(1), and O(1). As a consequence of the binding of the (THF)Li group to the amido framework, the geometry of the two N-functions involved deviates from the trigonal planarity observed for the N(3) atom [$\Sigma\{\angle_{N(1)}\} = 346(2)^\circ$, $\Sigma\{\angle_{N(2)}\} = 350(3)^\circ$, however, $\Sigma\{\angle_{N(3)}\} = 359(3)^\circ$]. Moreover, steric repulsion between the THF ligand and the N(1)- and N(2)-bonded *t*Bu-groups forces the latter appart. On the other hand, the Li atom "ties" the two amido N atoms together generating an N-donor atom arrangement which

Table 6. Selected Bond Lengths (Å) and Interbond Angles (deg) of **8**

Pb(1)−N(1)	2.44(3)	Pb(1)−N(2)	2.47(3)
Pb(1)−N(3)	2.29(3)	Pb(1)−Li(1)	2.83(6)
Si(1)−Si(4)	2.33(2)	Si(1)−N(1)	1.63(3)
Si(1)−C(2)	1.87(4)	Si(1)−C(3)	1.85(4)
Si(2)−Si(4)	2.31(2)	Si(2)−N(2)	1.66(3)
Si(2)−C(8)	1.93(5)	Si(2)−C(9)	1.85(4)
Si(3)−Si(4)	2.31(2)	Si(3)−N(3)	1.66(3)
Si(3)−C(14)	1.92(6)	Si(3)−C(15)	1.95(5)
Si(4)−C(1)	1.88(4)	O(1)−C(20)	1.37(7)
O(1)−C(23)	1.52(8)	O(1)−Li(1)	2.11(7)
N(1)−C(4)	1.58(5)	N(1)−Li(1)	2.10(7)
N(2)−C(10)	1.47(5)	N(2)−Li(1)	1.87(7)
N(3)−C(16)	1.43(5)		

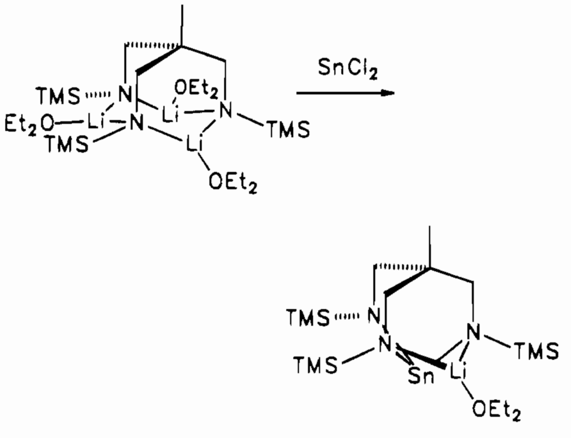
N(1)−Pb(1)−N(2)	82.5(9)	Si(1)−Si(4)−C(1)	110(2)
N(1)−Pb(1)−N(3)	103(1)	Si(2)−Si(4)−Si(3)	109.3(7)
N(1)−Pb(1)−Li(1)	46(1)	Si(2)−Si(4)−C(1)	108(2)
N(2)−Pb(1)−N(3)	109(1)	Si(3)−Si(4)−C(1)	112(2)
N(2)−Pb(1)−Li(1)	41(1)	C(20)−O(1)−C(23)	105(4)
N(3)−Pb(1)−Li(1)	127(1)	C(20)−O(1)−Li(1)	133(4)
Si(4)−Si(1)−N(1)	107(1)	C(23)−O(1)−Li(1)	119(4)
Si(4)−Si(1)−C(2)	110(2)	Pb(1)−N(1)−Si(1)	114(2)
Si(4)−Si(1)−C(3)	105(2)	Pb(1)−N(1)−C(4)	103(2)
N(1)−Si(1)−C(2)	117(2)	Pb(1)−N(1)−Li(1)	77(2)
N(1)−Si(1)−C(3)	110(2)	Si(1)−N(1)−C(4)	129(3)
C(2)−Si(1)−C(3)	108(2)	Si(1)−N(1)−Li(1)	109(2)
Si(4)−Si(2)−N(2)	107(1)	C(4)−N(1)−Li(1)	113(3)
Si(4)−Si(2)−C(8)	110(2)	Pb(1)−N(2)−Si(2)	115(2)
Si(4)−Si(2)−C(9)	109(1)	Pb(1)−N(2)−C(10)	106(3)
N(2)−Si(2)−C(8)	115(2)	Pb(1)−N(2)−Li(1)	80(2)
N(2)−Si(2)−C(9)	112(2)	Si(2)−N(2)−C(10)	129(3)
C(8)−Si(2)−C(9)	104(2)	Si(2)−N(2)−Li(1)	107(3)
Si(4)−Si(3)−N(3)	102(1)	C(10)−N(2)−Li(1)	110(3)
Si(4)−Si(3)−C(14)	107(2)	Pb(1)−N(3)−Si(3)	126(2)
Si(4)−Si(3)−C(15)	107(2)	Pb(1)−N(3)−C(16)	109(3)
N(3)−Si(3)−C(14)	118(2)	Si(3)−N(3)−C(16)	124(3)
N(3)−Si(3)−C(15)	116(2)	C(14)−Si(3)−C(15)	106(3)
Si(1)−Si(4)−Si(2)	111.8(6)	Si(1)−Si(4)−Si(3)	105.5(7)

Table 7. Fractional Atomic Coordinates ($\times 10^4$) of **8**

atom	x	y	z
Pb(1)	0.3713(2)	0.13656(7)	0.67013(4)
Si(1)	0.409(1)	0.1346(6)	0.5618(3)
Si(2)	0.670(1)	0.1839(6)	0.6382(4)
Si(3)	0.557(1)	0.0068(6)	0.6291(4)
Si(4)	0.597(1)	0.1038(6)	0.5921(4)
O(1)	0.447(3)	0.342(1)	0.590(1)
N(1)	0.331(3)	0.174(1)	0.598(1)
N(2)	0.548(3)	0.214(1)	0.664(1)
N(3)	0.442(3)	0.030(1)	0.6606(9)
C(1)	0.717(5)	0.091(2)	0.550(2)
C(2)	0.333(4)	0.060(2)	0.538(1)
C(3)	0.451(5)	0.192(2)	0.518(1)
C(4)	0.189(4)	0.191(2)	0.599(1)
C(5)	0.112(4)	0.133(3)	0.605(1)
C(6)	0.160(5)	0.250(3)	0.625(2)
C(7)	0.159(4)	0.212(2)	0.551(1)
C(8)	0.798(5)	0.147(2)	0.674(2)
C(9)	0.750(3)	0.249(2)	0.608(1)
C(10)	0.545(4)	0.255(2)	0.702(2)
C(11)	0.575(5)	0.211(3)	0.749(2)
C(12)	0.427(4)	0.292(2)	0.710(1)
C(13)	0.664(5)	0.302(2)	0.701(1)
C(14)	0.526(6)	-0.062(3)	0.588(2
C(15)	0.711(5)	-0.018(3)	0.657(1)
C(16)	0.387(5)	-0.012(2)	0.692(2)
C(17)	0.440(7)	0.003(3)	0.738(3)
C(18)	0.411(6)	-0.086(3)	0.683(2)
C(19)	0.257(8)	-0.011(3)	0.698(2)
C(20)	0.375(7)	0.369(3)	0.559(2)
C(21)	0.449(9)	0.417(4)	0.533(3)
C(22)	0.511(6)	0.439(3)	0.567(2)
C(23)	0.514(7)	0.400(4)	0.610(2)
Li(1)	0.442(6)	0.250(3)	0.623(2)

deviates from the otherwise more or less undistorted trigonal monopyramidal arrangement of the N_3Pb-unit [∠(N(1)−Pb(1)−N(2)) = 82.5(9)°, but ∠((N)−Pb(1)−N(3)) = 103(1)° and ∠(N(2)−Pb(1)−N(3)) = 109(1)°]. As a consequence of both structural changes imposed by the coordinated cation, the two $SiMe_2$ groups at Si(1) and Si(2) adopt an ecliptic conformation (i.e. are twisted toward each other) not observed in any of the trisilylmethane-derived tripodal amido complexes. The longer Si−Si distance [d_{av}(Si−Si) = 2.32(2) Å] in the trisilylsilanes in comparison to the Si−C distance [d_{av}(Si−C) = 1.87 Å] in the trisilylmethanes reduces the steric interaction between the methyl groups and therefore makes an arrangement as found in **8** more favorable. In view of the high esd's of the metric parameters determined for **8**, which are a consequence of inresolved disorder of the coordinated THF molecule along with some disorder in the N-bonded *t*Bu groups, a detailed discussion of the bond parameters of the N_3Pb unit is not possible. In particular, it has to remain undecided whether there is any direct bonding interaction between Pb and Li [d(Pb(1)−Li(1)) = 2.83(6) Å]. The results of MNDO calculations on Li(μ-NCH_2)$_3$Pb reported by Wright et al.,[16] indicating the absence of Pb−Li bonding in this trigonal bipyramidal cage, are probably not significant for **8** in view of its markedly different (and so far unprecedented) geometry.

Reactions of $H_3CC\{CH_2N(Li)SiMe_3\}_3(THF)_3$ with Sn(II) and Pb(II) Substrates. Crystal Structure of the Pb/Li-Cage [$H_3CC(CH_2NSiMe_3)_2\{CH_2O(Li)\}Pb]_2$ (11). The reaction of $H_3CC\{CH_2N(Li)SiMe_3\}_3(Et_2O)_3$ (**9**)[9b] with $SnCl_2$ gives the triamido stannate $H_3CC\{CH_2NSiMe_3\}_3SnLi(Et_2O)$ (**10**) while the corresponding plumbate could neither be obtained from the reactions with $PbCl_2$ nor with Cp_2Pb. Compound **10** is obtained analytically pure as a light yellow oil upon work up of the reaction mixture (eq 3). Its formulation as a mono-Et_2O adduct



(10)

(3)

is based on the analytical data as well as the integration of the signals in the ^{1}H-NMR spectrum. The NMR data (^{1}H, ^{13}C, ^{29}Si) are again consistent with an overall C_s-symmetry of the molecule, indicating a molecular arrangement closely related to that established for **7** and **8**.

In contrast to the reactions of the **1** and the lithiated derivative of **6** with $PbCl_2$ which gave no isolable products, a colorless crystalline solid **11** could be reproducibly otained in yields between 15 and 30% directly from the reaction mixture generated upon reacting **9** with $PbCl_2$ at −70 °C in THF and slow warming to ambient temperature. The material isolated is almost insoluble in aliphatic and aromatic hydrocarbons, sparingly soluble in diethyl ether, but sufficiently soluble in THF for spectroscopic investigations. The C,H,N-analysis of the

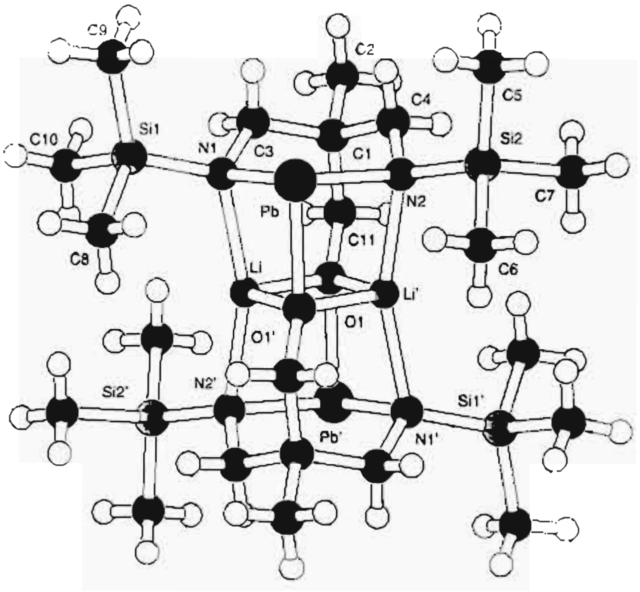


Figure 5. Molecular structure of **11** in the crystal.

Table 8. Selected Bond Lengths (Å) and Interbond Angles (deg) of **11**

Pb−O(1)	2.246(7)	Pb−N(1)	2.268(8)
Pb−N(2)	2.237(9)	Pb−Li	3.06(2)
Si(1)−N(1)	1.714(9)	Si(1)−C(8)	1.86(1)
Si(1)−C(9)	1.88(2)	Si(1)−C(10)	1.86(1)
Si(2)−N(2)	1.705(9)	Si(2)−C(5)	1.88(2)
Si(2)−C(6)	1.87(2)	Si(2)−C(7)	1.85(1)
O(1)−C(11)	1.40(1)	O(1)−Li	1.92(2)
N(1)−C(3)	1.48(1)	N(1)−Li	2.11(2)
N(2)−C(4)	1.49(1)	N(2)−Li	2.12(2)
O(1)−Pb−N(1)	81.3(3)	C(11)−O(1)−Li	121.8(8)
O(1)−Pb−N(2)	82.4(3)	Li−O(1)−Li	81.5(8)
O(1)−Pb−Li	38.0(4)	Pb−N(1)−Si(1)	109.8(4)
O(1)−Pb−Li	38.7(4)	Pb−N(1)−C(3)	113.8(6)
N(1)−Pb−N(2)	90.2(3)	Pb−N(1)−Li	88.6(5)
N(1)−Pb−Li	43.5(4)	Si(1)−N(1)−C(3)	114.7(6)
N(1)−Pb−Li	81.2(4)	Si(1)−N(1)−Li	113.4(7)
N(2)−Pb−Li	81.9(4)	C(3)−N(1)−Li	113.7(8)
N(2)−Pb−Li	43.9(4)	Pb−N(2)−Si(2)	111.3(4)
Li−Pb−Li	47.9(6)	Pb−N(2)−C(4)	114.0(6)
N(1)−Si(1)−C(8)	106.5(5)	Pb−N(2)−Li	89.1(6)
N(1)−Si(1)−C(9)	114.0(6)	Si(2)−N(2)−C(4)	116.5(7)
N(1)−Si(1)−C(10)	111.9(6)	Si(2)−N(2)−Li	110.0(6)
C(8)−Si(1)−C(9)	107.4(8)	C(4)−N(2)−Li	112.8(8)
C(8)−Si(1)−C(10)	109.6(7)	C(2)−C(1)−C(3)	105.2(9)
C(9)−Si(1)−C(10)	107.3(8)	C(2)−C(1)−C(4)	107.4(9)
N(2)−Si(2)−C(5)	113.1(6)	C(2)−C(1)−C(11)	104.8(9)
N(2)−Si(2)−C(6)	106.6(5)	C(3)−C(1)−C(4)	112.6(9)
N(2)−Si(2)−C(7)	113.0(6)	C(3)−C(1)−C(11)	113.1(9)
C(5)−Si(2)−C(6)	108.8(8)	C(4)−C(1)−C(11)	112.9(9)
C(5)−Si(2)−C(7)	105.7(7)	Pb−O(1)−Li	94.3(6)
C(6)−Si(2)−C(7)	109.7(7)	Pb−O(1)−Li	95.0(6)
Pb−O(1)−C(11)	128.7(6)	C(11)−O(1)−Li	123.2(8)

material obtained indicated the loss of one Me_3SiN-group per ligand unit, and the remarkably simple spectral patterns observed in the NMR spectra were consistent with a C_s-symmetrical structure. Since on the basis of the data obtained a formulation of **11** was not possible, a single-crystal X-ray structure analysis was carried out. It revealed a dimeric cage structure of **11** which is formulated as $[H_3CC(CH_2NSiMe_3)_2\{CH_2O(Li)\}Pb]_2$ (**11**). Its molecular structure in the crystal is shown in Figure 5, and the principal bond parameters are given in Table 8 while the fractional coordinates are listed in Table 9.

The structure confirms the notion derived from the analysis that the tripod ligand has "lost" a (trimethylsilyl)amido function, the third donor position is now occupied by an alkoxy group which is part of the tripod ligand system. Together with the lithium counterion it forms the central Li_2O_2 square which constitutes the interface between the two fused tripod-amido plumbate cages. Significantly, the alkoxy group in the ligand unit is not bonded to the lead atom to which the two remaining Me_3SiN-functions are coordinated but to the respective other lead center. The two halves of the cage are related by a crystallographic center of symmetry which is located in the Li_2O_2 plane [$\angle(Li{-}O1{-}Li') = 81.5(8)°$, $\angle((O){-}Li{-}O(1')) = 98.5(8)°$]. The six-membered ligand−framework−diamido−lead ring adopts a chair conformation normally not observed whenever the tripod ligand binds to a single metal atom. The donor−lead−donor angles are more acute than observed in the other structurally characterized tripodal triamidometalates [$\angle(O(1){-}Pb{-}N(1)) = 81.3(3)°$, $\angle(O(1){-}Pb{-}N(2)) = 82.4(3)°$, $\angle(N(1){-}Pb{-}N(2)) = 90.2°$] and approach the values determined in the trigonal bipyramidal cage of $Pb[\mu\text{-}N{=}C(tBu)(Ph)]_3Li(THF)$ [$\angle_{av}(N{-}Pb{-}N) = 76.7(5)°$][16] and the cubane-related structure of $[Pb\{N(2,6\text{-}i\text{-}Pr_2C_6H_3)\}]_4$ [$\angle_{av}(N{-}Pb{-}N) = 82.2(8)°$].[18] As a consequence of their coordination to the Li atoms, the amido-N atoms deviate from a trigonal planar geometry to give a distorted tetrahedral environment at the nitrogen.

The Pb−N, Pb−O, Si−N, and Li−O distances [$d_{av}(Pb{-}N) = 2.253(9)$ Å, $d(Pb{-}O) = 2.246(7)$ Å, $d_{av}(Si{-}N) = 1.71(1)$ Å, $d_{av}(Li{-}O) = 1.91(2)$ Å] are within the expected range;[19-21] however, the Li−N distances of $d_{av}(Li{-}N) = 2.12(2)$ Å are significantly longer than those observed in most lithium amides.[21] Due to the overall cage structure of **11** the coordination geometry imposed at the lithium atoms may be described as either highly distorted tetrahedral or derived from a distorted trigonal bypyramid by formally removing a ligand in the equatorial plane. The $\angle(N(1){-}Li{-}N(2'))$ of 160.7(9)° contrasts with the $\angle(O(1){-}Li{-}O(1'))$ of 98.5(8)° and the O−Li−N angles lying in the range 93.8(7)−98.7(8)°.

The question of how the $\{CH_2NSiMe_3\}^-$ function is converted to a ligand-integrated $\{CH_2O\}^-$ group could not be

Table 9. Fractional Atomic Coordinates (×10^4) of **11**

atom	*x*	*y*	*z*
Pb	−0.18558(5)	−0.18205(5)	0.54035(4)
Si(1)	0.0855(4)	−0.2168(4)	0.2797(3)
Si(2)	−0.2374(4)	−0.2359(4)	0.8475(3)
O(1)	0.1695(8)	−0.0380(7)	0.5275(7)
N(1)	0.084(1)	−0.200(1)	0.4182(8)
N(2)	−0.083(1)	−0.216(1)	0.7093(8)
C(1)	0.240(1)	−0.297(1)	0.613(1)
C(2)	0.395(2)	−0.417(1)	0.661(1)
C(3)	0.220(1)	−0.307(1)	0.494(1)
C(4)	0.088(1)	−0.320(1)	0.725(1)
C(5)	−0.306(2)	−0.401(2)	0.914(1)
C(6)	−0.428(2)	−0.082(2)	0.801(1)
C(7)	−0.167(2)	−0.241(2)	0.984(1)
C(8)	−0.091(2)	−0.071(2)	0.201(1)
C(9)	0.043(3)	−0.386(2)	0.313(2)
C(10)	0.294(2)	−0.205(2)	0.163(1)
C(11)	0.291(1)	−0.164(1)	0.579(1)
Li	0.063(2)	0.006(2)	0.387(2)

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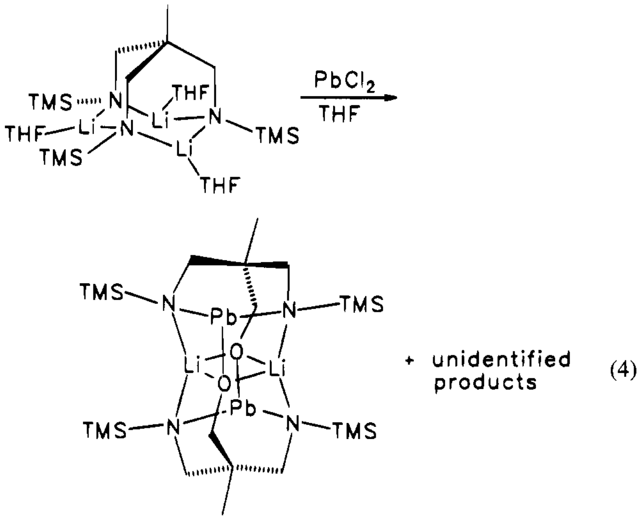
answered (eq 4). In view of the observed redox chemistry (precipitation and re-dissolution of metallic lead) radical species are probably involved in the process. It should be pointed out that THF was found to be the only reaction medium from which the material could be isolated. In view of the careful exclusion of air and moisture in all the reactions reported in this paper as well as the yields of **11** up to 30%, air (dioxygen) and water may be discarded as sources of the alkoxy oxygen. It may well be that the solvent itself, which has been previously found to be activated by radical intermediates, acts as the source of the oxygen found in the crystal structure of **11** and confirmed by the elemental analysis.



(11)

(4)

Conclusions

This study has established the three types of anion–cation interaction in tripodal triamidostannates and -plumbates discussed in the introduction. The direct Sn–Li contact of Type **A** was found in **2**, compounds **4** and **5** are representatives of Type **B** while **7**, **8** and **10** contain the Li cation in an amido-N bonded fashion (Type **C**). The considerable thermal stability of all the systems investigated allows their use in substance for further transformations. The question of how the different kinds of ion pair aggregation may influence the reactivity of the compounds is the focus of current and future work in this area.

The metalates are powerful nucleophiles and some have already been employed in the synthesis of tin–transition metal heterobimetallics[22] as well as in the preparation of novel organotin reagents.[23] In particular with regard to the latter, the use of the recently established chiral tripodal amido ligands[12b] opens up new applications in organic transformations.

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Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, the positional and thermal parameters, interatomic distances, angles and torsion angles for **2**, **5**, **8**, and **11** (49 pages). Ordering information is given on any masthead page.

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