$[\{\mathrm{MeN(CH_2CH_2NMe_2)_2Li}\}_2\mathrm{Cl}][\mathrm{HC}\{\mathrm{SiMe_2N(4\text{-}CH_3C_6H_4)}\}_3\mathrm{Sn}]$, a "Solvent-Separated" Tripodal Tris(amido)stannate and a $[\mathrm{Li_2Cl}]^+$ Cation Revisited†

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Metalated tin reagents of the general type R_3SnM (R = alkyl, aryl, alkoxy, imide; M = alkali metal) are well established as versatile synthetic tools in organic synthesis.[1] However, it is only recently that the solid state structures of a few of these compounds have been determined.[2] This is partly due to their high reactivity and in many cases thermal lability in their isolated crystalline form. 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 tin was thought to offer a route to systems of greater stability which lend themselves to a more detailed investigation of their structures and reactivity.

Multifunctional amides have recently been employed in the generation and stabilization of new types of transition metal coordination compounds with novel structural and reactive patterns.[3] It was therefore of interest whether they would effect a similar stabilization of low-coordinate group 14 metal centers. Here we report the synthesis and structural characterization of a tris(amido)stannate, $[\mathrm{HC}\{\mathrm{SiMe_2N(4\text{-}CH_3C_6H_4)}\}_3\mathrm{Sn}]^-$, which contains a trisilylmethane-derived tripodal amido ligand.

The reaction of the trilithium triamide $\mathrm{HC}\{\mathrm{SiMe_2N(Li)(4\text{-}CH_3C_6H_4)}\}_3\cdot\mathrm{2THF}$ [3e,4] with 1 molar equiv of $SnCl_2$ in THF at −50 °C, with subsequent warming to ambient temperature and removal of the solvent, yielded a yellow oily material. On addition of $\mathrm{CpM(CO)_2Cl}$ (M = Fe, Ru) this reagent yielded the respective M—Sn-bonded species $\mathrm{HC}\{\mathrm{SiMe_2N(4\text{-}CH_3C_6H_4)}\}_3\mathrm{SnM(CO)_2Cp}$ (M = Fe (**1**), Ru (**2**)) which indicated the initial generation of the (amido)stannate.[5] Upon addition of 2 equiv of $\mathrm{MeN(CH_2CH_2NMe_2)_2}$ as a coligand to the $\mathrm{THF/Et_2O}$ solution of the in situ generated stannate and cooling to −30 °C a clear colorless highly crystalline solid (**3**) of remarkable thermal and chemical stability precipitated.[6]

A single-crystal X-ray structure analysis of **3** has established the molecular structure of the lithium stannate which was found to crystallize as a "solvent-separated" ion pair (the "solvent" in this case being the triamine coligand) consisting of a $[\{\mathrm{MeN(CH_2CH_2NMe_2)_2Li}\}_2\mathrm{Cl}]^+$ cation and the tripodal (amido)stannate $[\mathrm{HC}\{\mathrm{SiMe_2N(4\text{-}CH_3C_6H_4)}\}_3\mathrm{Sn}]^-$, which has idealized C_3 point symmetry (Figure 1).[7] Its structural center piece is the [2.2.2]bicyclooctane-related cage comprising the trisilylmethane unit and the tris(amido)stannate unit (Figure 2), which are slightly twisted with respect to each other [average torsion angle 37.2(7)°]. Similar to the Ti(IV) complexes containing this ligand[3c] [in which the coordinated metal has a much smaller ionic radius than Sn(II)] this twist 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 1.197(1) Å from the plane defined by the three amido N atoms all three of which display trigonal planar geometry $[\Sigma_{av}\{\angle_N\} = 359.8(4)°]$ similar to that previously observed in structures of silyl- and/or stannyl-substituted amines[1,8] as well as that normally observed in transition metal amide chemistry in which amido ligands act as 4-electron σ- and π-donors.[9] The average $\angle$(N—Sn—N) of 91.9(2)° 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 electron pair residing in a molecular orbital of essentially 4s-character. The ring planes of

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† Dedicated to Professor R. Schmutzler on the occasion of his 60th birthday.

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(5) Data for **1** are as follows. Anal. Calcd for $\mathrm{C_{35}H_{45}FeN_3O_2Si_3Sn}$: C, 52.64; H, 5.68; N, 5.26. Found: C, 53.01; H, 6.10; N, 5.63. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = -0.30$ (s, $\mathrm{HC\{Si...\}_3}$), 0.32 (s, $\mathrm{Si\{CH_3\}_2}$), 2.16 (s, $\mathrm{C\mathit{H}_3C_6H_4}$), 3.53(s, $\mathrm{C_5\mathit{H}_5}$), 6.89 (d, $^3J_{\mathrm{HH}}$ = 7.7 Hz, Tol-$\mathrm{H^2}$), 7.02 (d, Tol-$\mathrm{H^3}$). ^{13}C-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = 5.5$ ($\mathrm{Si\{\mathit{C}H_3\}_2}$), 9.4 ($\mathrm{H\mathit{C}\{Si...\}_3}$), 20.8 ($\mathrm{\mathit{C}H_3C_6H_4}$), 81.8 ($\mathrm{\mathit{C}_5H_5}$), 127.7, 129.8, 130.6 149.5 (Tol-$\mathrm{C^{3,5}}$, $\mathrm{C^{2,6}}$, $\mathrm{C^4}$, $\mathrm{C^1}$), 212.3 (CO). ^{29}Si-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = 3.8$. IR ν(CO) (toluene) 2000, 1962 cm^{-1}. Data for **2** are as follows. Anal. Calcd for $\mathrm{C_{35}H_{45}RuN_3O_2Si_3Sn}$: C, 49.82; H, 5.38; N, 4.98. Found: C, 49.80; H, 5.32; N, 5.07. ^{1}H-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = -0.29$ (s, $\mathrm{HC\{Si...\}_3}$), 0.59 (s, $\mathrm{Si\{C\mathit{H})_3\}_2}$), 2.21 (s, $\mathrm{C\mathit{H}_3C_6H_4}$), 4.00 (s, $\mathrm{C_5\mathit{H}_5}$), 7.05 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, Tol-$\mathrm{H^2}$), 7.17 (d, Tol-$\mathrm{H^3}$). ^{13}C-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = 5.5$ ($\mathrm{Si\{\mathit{C}H_3\}_2}$), 9.2 ($\mathrm{H\mathit{C}\{Si...\}_3}$), 20.8 ($\mathrm{\mathit{C}H_3C_6H_4}$), 84.5 ($\mathrm{\mathit{C}_5H_5}$), 127.8, 129.8, 130.2 149.9 (Tol-$\mathrm{C^{3,5}}$, $\mathrm{C^{2,6}}$, $\mathrm{C^4}$, $\mathrm{C^1}$), 198.8 (CO). ^{29}Si-NMR ($\mathrm{C_6D_6}$, 295 K): $\delta = 3.7$. IR ν(CO) (toluene) 2021, 1975 cm^{-1}.

(6) Yield: 73%. Anal. Calcd for $\mathrm{C_{46}H_{86}N_9Si_3Li_2SnCl}$: C, 54.30; H, 8.52; N, 12.39. Found: C, 54.18; H, 8.36; N, 12.24. Selected spectroscopic data: ^{1}H-NMR (d_8-thf, 295 K): $\delta = -0.42$ (s, $\mathrm{HC\{Si...\}_3}$), 0.24 (s, $\mathrm{Si\{CH_3\}_2}$), 2.22 (s, $\mathrm{C\mathit{H}_3C_6H_4}$), 2.28 (s, $\mathrm{\{C\mathit{H}_3\}_2N}$), 2.33 (s, $\mathrm{NC\mathit{H}_3}$), 2.46 (m, $\mathrm{MeN\{C\mathit{H}_2C\mathit{H}_2\}_2}$), 6.75 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, Tol-$\mathrm{H^2}$), 6.85 (d, Tol-$\mathrm{H^3}$). ^{13}C-NMR (d_8-thf, 295 K): $\delta = 6.4$ ($\mathrm{Si\{\mathit{C}H_3\}_2}$), 13.8 ($\mathrm{H\mathit{C}\{Si...\}_3}$), 21.2 ($\mathrm{\mathit{C}H_3C_6H_4}$), 44.3 ($\mathrm{N\mathit{C}H_3}$), 46.4 $\mathrm{N\{\mathit{C}H_3\}_2}$), 56.0 ($\mathrm{MeN\{CH_2\mathit{C}H_2...\}_2}$), 58.5 ($\mathrm{MeN\{\mathit{C}H_2CH_2...\}_2}$), 124.3, 129.2, 146.0 155.2 (Tol-$\mathrm{C^{3,5}}$, $\mathrm{C^{2,6}}$,$\mathrm{C^4}$, $\mathrm{C^1}$). ^{7}Li-NMR (d_8-thf): $\delta = 3.37$ (reference $\mathrm{LiI/H_2O}$, 1 M, external; no essential change at 180 K). ^{29}Si-NMR (d_8-thf, 295 K): $\delta = -0.9$.

(7) Data collection was carried out at 223 K. A total of 4601 observed reflections were collected $[F/\sigma(F) > 3.0]$. Crystal data for **3**: $\mathrm{C_{46}H_{86}N_9Si_3Li_2SnCl}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.377(2)$ Å, $b = 15.360(2)$ Å, $c = 17.594(3)$ Å, $\alpha = 77.41(1)°$, $\beta = 74.16(2)°$, $\gamma = 70.94(3)°$, $M = 1017.53$, $V = 3011.2$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.08$ g cm^{-1}, $\mu(\mathrm{Mo\text{-}K_\alpha}) = 5.6$ cm^{-1}, $R = 0.072/R_w = 0.093$. Three peaks of electron density in the final difference Fourier map (1.304, 1.153, 1.008 e Å^3) which neither belonged to the cation nor anion and which did not refine as potential solvent atoms (with occupancy of approximately 0.3) were not included in the final refinement cycles.

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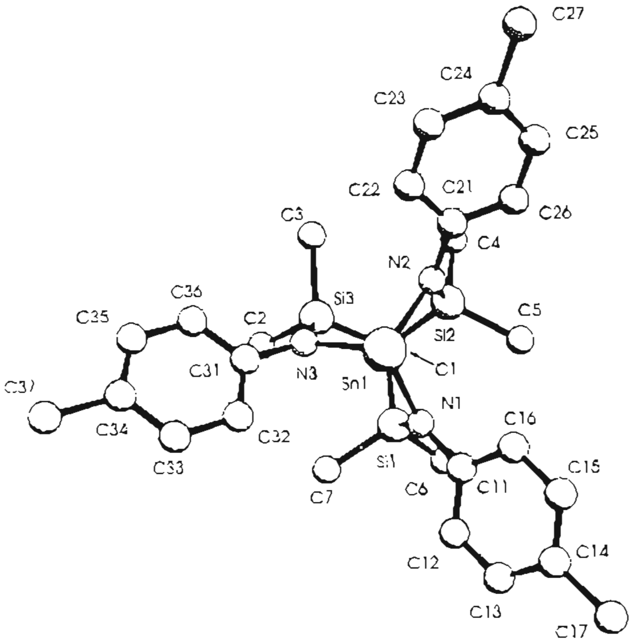

Figure 1. Molecular structure of the stannate anion in 3 viewed along the idealized molecular 3-fold axis. Selected bond lengths (Å) and interbond angles (deg): Sn1—N1 2.153(5), Sn1—N2 2.158(5), Sn1—N3 2.160(5), average Si—N 1.719(5), N1—Sn1—N2 91.7(2), N1—Sn1—N3 91.9(2), N2—Sn1—N3 92.2(2).

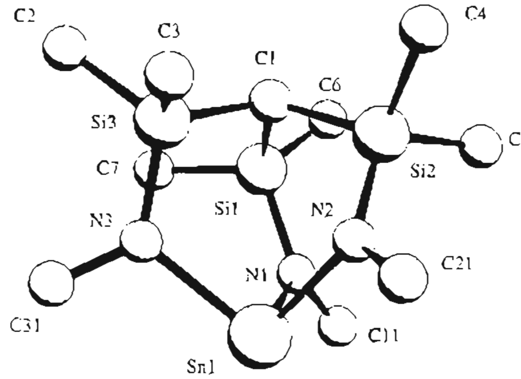

Figure 2. Structural arrangement of the central cage in the stannate anion, showing the exposed situation of the tin atom and the twisted arrangement of the trisilylmethane and tris(amido)stannate units.

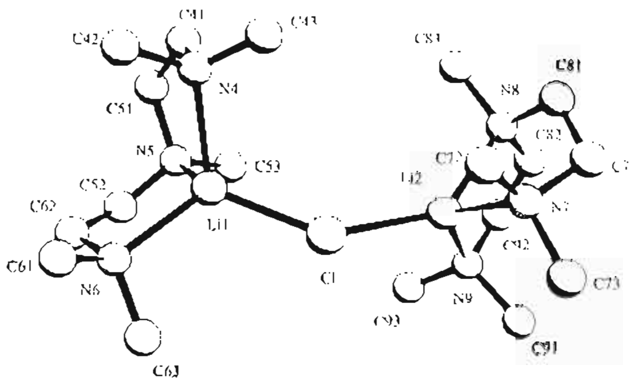

Figure 3. Structure of the [{MeN(CH$_2$CH$_2$NMe$_2$)$_2$Li}$_2$Cl]$^+$ cation in 3. Selected bond lengths (Å) and interbond angles (deg): Li1—Cl 2.23(1), Li2—Cl 2.26(1), average Li—N 2.11(2), Li1—Cl—Li2 143.1(6), N4—Li1—N5 87.2(7), N4—Li1—N6 116.6(8), N5—Li1—N6 88.9(6), N7—Li2—N8 85.7(6), N7—Li2—N9 123.7(7), N8—Li2—N9 84.7(6).

the tolyl groups in the ligand periphery are twisted with respect to the radial planes defined by C1, Si, and N [average dihedral angle 50.0(4)°], generating an overall "lamp shade" arrangement of the molecule.

The most notable feature of the counterion [{MeN(CH$_2$CH$_2$NMe$_2$)$_2$Li}$_2$Cl]$^+$ (Figure 3) is the Li1—Cl—Li2 angle of 143.1(6)°, which is in stark contrast to the arrangement observed in the only known structure of a salt containing this entity, [{MeN(CH$_2$CH$_2$NMe$_2$)$_2$Li}$_2$Cl][Li{C(SiMe$_3$)$_3$}$_2$].[10] For the latter, Eaborn and co-workers reported a linear arrangement [∠(Li—Cl—Li′) = 180°] in which the Cl atom resides upon a crystallographic center of symmetry. The preference of the linearity was backed up by an *ab initio* study of [Li$_2$Cl]$^+$ in the gas phase. While this situation may be rationalized even by simple electrostatic considerations, the primary ionic nature and thus low degree of directionality of the Li—Cl bonding, along with the spatial separation of the coordinated amine coligand, is expected to allow for a considerable degree of Li—Cl—Li′ bending. The actual arrangement of the cation may therefore be by no means necessarily linear but dictated by crystal packing forces and vary considerably depending on the nature of the respective anion. Such a case is observed in the crystal structure of 3.

There is no appreciable cation–anion interaction (Li···Sn, Cl···Sn > 6.78 Å) on the Sn side of the stannate molecule but closer (van der Waals) association of the coligand-methyl groups with those of the trisilylmethane unit (C···C = 3.5–4.5 Å). The ion pair in the crystal may therefore be viewed as cation riding in a "pickaback" fashion on the stannate anion, a situation not involving the tin atom itself.

Since 3 is almost insoluble in hydrocarbon solvents and slowly decomposes in halogenated hydrocarbons, studies in solution were confined to ether solvents. Conductivity measurements performed in THF showed the absence of ionic conductivity and indicated that dissolution occurred without dissociation, i.e., that 3 probably forms a contact ion pair in this type of solvent. Cross relaxation between the ^{1}H-nuclei of the methyl groups in the trisilylmethane units of the stannate and the terminal methyl groups in the amine ligand of the cation observed in ^{1}H-NOESY experiments performed at 250 and 310 K support the notion of a contact ion pair in solution.

Products with the same analytical and spectroscopic data were obtained on addition of less than 2 molar equiv of the tridentate amine MeN(CH$_2$CH$_2$NMe$_2$)$_2$, albeit in markedly decreased yield. The coligand-free system has thus far defied a satisfactory spectroscopic and structural characterization.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and complete bond distances and interbond angles and a figure showing the ^{1}H-NOESY spectrum of 3 (13 pages). Ordering information is given on any current masthead page.

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(11) Mixing times chosen in the NOESY experiments: t_{mix} = 0.5, 1.5, and 3 s. Cross relaxation between ^{1}H nuclei in the stannate unit, which are at close proximity to each other, was also observed (see also ref 3e).