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First structural characterization of a mixed valent thallium(I/III) amide bearing an *n*-butylthallium(III) unit stabilized by a tripodal amido ligand

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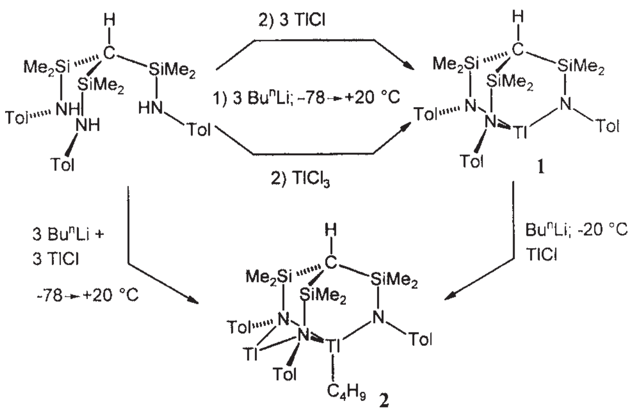
Lithiation of the tripodal amine $HC\{SiMe_2NH(p\text{-}Tol)\}_3$ with Bu^nLi in the presence of TlCl yielded the Tl(I/III) mixed valent complex $[HC\{SiMe_2N(p\text{-}Tol)\}_3(TlBu^n)(Tl)]$ 2; an X-ray diffraction study established the central *n*-butyl–thallium(III) unit coordinated by the amido tripod in which two of the amido functions are additionally bridged by the Tl(I) atom.

The chemistry of formally closed shell low valent heavy p-block metals is characterized by unusual patterns of aggregation in the solid state through attractive metal–metal interactions.[1,2] We have recently begun to systematically investigate the structural chemistry of amidothallium(I) compounds in which the metal atoms occupy exposed positions thus making the molecules potential building blocks for larger aggregates.[3,4] The tripodal amido ligands developed by us were found to provide the platform for a whole series of polynuclear thallium(I) amides.[5,6] These are generally obtained by metal exchange reaction of the *in situ* generated or isolated lithium amides with TlCl in an ether or hydrocarbon solvent. In all cases the complete lithiation of the amine precursor was achieved before the metal exchange step. A simultaneous reaction of the alkyllithium reagent and thallium(I) chloride was expected to yield products which differ significantly from the compounds studied to date, and provide an entry into new types of mixed amido/alkylthallium complexes. Here, we report the remarkable first results of these variable metallation strategies.

Complete lithiation of the tripodal amine $HC\{SiMe_2NH(p\text{-}Tol)\}_3$ with Bu^nLi and subsequent reaction with either 3 molar equivalents of TlCl or 1 equivalent of $TlCl_3$ gave the Tl^{III} amide $[HC\{SiMe_2NH(p\text{-}Tol)\}_3Tl]$ **1** which was characterized by elemental analysis as well as ^1H and ^{13}C NMR spectroscopy (Scheme 1).† However, upon carrying out the lithiation and transmetallation in one step by addition of 3 molar equivalents of *n*-butyllithium and thallium(I) chloride to the amine at −78 °C in *n*-pentane and subsequent slow warming to ambient temperature over a period of 15 h a different type of compound was obtained as a yellow–orange crystalline solid **2**. The yield of the compound isolated in several preparations varied between 15 and 35% based on the amine starting material. The same material was isolated in higher yield (*ca.* 50%) upon reaction of **1** with 1 equivalent of *n*-butyllithium and transmetallation with TlCl. Its elemental analysis was consistent with two thallium atoms per ligand unit, and ^1H and ^{13}C NMR spectroscopy indicated that the product contained one residual *n*-butyl group.† A single crystal X-ray structure analysis confirmed the molecular structure of the Tl(III)/Tl(I) mixed metal complex **2** in which an *n*-butylthallium(III) unit is coordinated by the tripodal amido ligand while two of the donor atoms are bridged by a thallium(I) atom (Fig. 1).‡ The observation that the reaction of the lithium amide with TlCl exclusively leads to the Tl^{III} amide **1** which may be rationally converted to **2** by addition of Bu^nLi across a Tl^{III}–N bond and subsequent metal exchange (Scheme 1) suggests a formation of the *n*-butylthallium species along a similar route in the reaction of a mixture of Bu^nLi and TlCl with the amine.



Scheme 1 Preparative routes leading to compounds **1** and **2**. In the conversion of **1** → **2** Bu^nLi probably first adds across one Tl^{III}–N bond alkylating the Tl^{III} centre. Subsequent $Li–Tl^I$ exchange then gives **2**.

Compound **2** is the first example of a structurally characterized long chain alkylthallium complex in contrast to the considerable number of methylthallium derivatives reported in the literature.[7] Such nonfunctionalized long chain alkylthallium species are thought to be thermally labile,[8] and it seems to be this particular coordination environment which renders **2** sufficiently stable to allow its isolation and characterization. The central thallium atom is not symmetrically coordinated by the ligand tripod due to the external bonding of the Tl(1) atom which not only draws the donor functions N(2) and N(3) together [N(2)–Tl(1)–N(3) 83.5(3)° in comparison to N(1)–Tl(1)–N(2) 99.3(3) and N(1)–Tl(1)–N(3) 104.7(3)°] but also induces an lengthening of the two Tl(1)–N bonds involved [Tl(1)–N(2) 2.321(7) Tl(1)–N(3) 2.326(7) Å in comparison to Tl(1)–N(1) 2.155(7) Å]. In contrast, the Tl–N bonds to monovalent Tl(2) are, as expected, significantly longer [Tl(2)–N(2) 2.694(7) and Tl(2)–N(3) 2.721(8)], in fact longer than those found in all thallium(I) amides hitherto investigated.[3–6,9] This may be a consequence of the extreme steric congestion in this part of the molecule in which the two heavy metal atoms are forced into close proximity by the bridging donor atoms; this leads to a remarkably short Tl(1)···Tl(2) contact of 3.3620(9) Å. The Tl(1)–C(40) bond length of 2.188(9) lies in the usual range of alkyl–Tl bonds in $TlMe_2$-complexes.[7]

The ^1H and ^{13}C NMR spectra of **2** recorded at 295 K in d_8-toluene are consistent with an effective threefold symmetry. The signals are broadened and coalesce upon cooling to 200 K, however, the rapid precipitation of the complex prohibited the detection of the low temperature limit. These observations suggest that the compound is fluxional with the 'external' Tl(I) atom exchanging between the different bridging positions. Such a 'rotation' of a monovalent metal atom coordinated to an amido tripod is reminiscent of the dynamic behaviour of the tripodal lithium triamidostannates investigated previously by us[10] and a similar dynamic behaviour has also been observed by Veith

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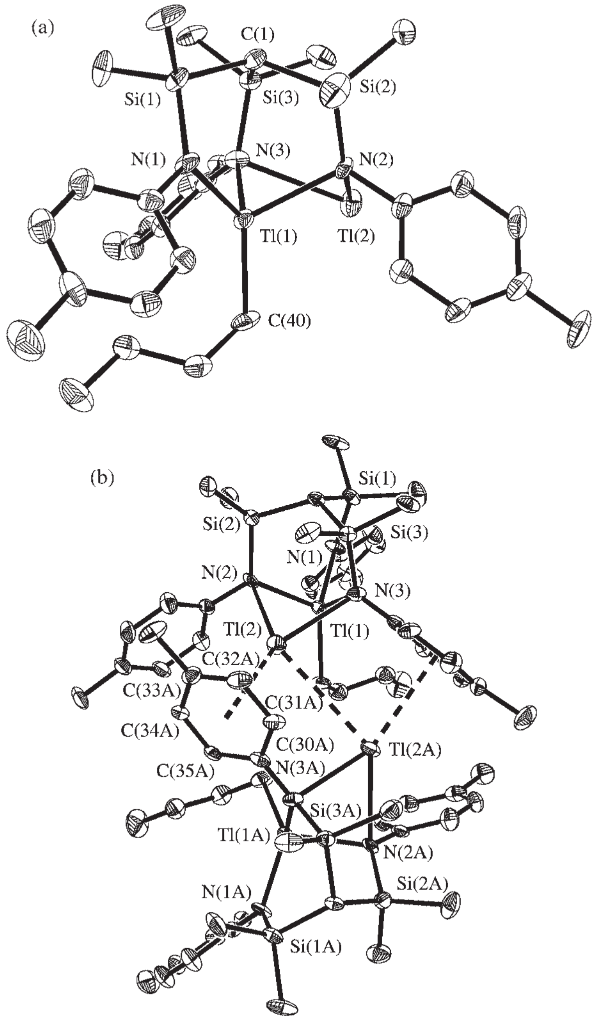

Fig. 1 (a) Molecular structure of [HC{SiMe$_2$N(*p*-Tol)}$_3$(TlBu^n)(Tl)] **2**. Selected bond lengths (Å) and interbond angles (°): C(1)–Si(1) 1.888(9), Si(1)–N(1) 1.733(8), Tl(1)–N(1) 2.155(7), Tl(1)–N(2) 2.321(7), Tl(1)–N(3) 2.326(7), Tl(2)–N(2) 2.694(7), Tl(2)–N(3) 2.721(8), Tl(1)–C(40) 2.188(9); Si(1)–C(1)–Si(2) 113.2(5), N(1)–Si(1)–C(1) 105.1(4), N(1)–Tl(1)–N(2) 99.3(3), N(1)–Tl(1)–N(3) 104.7(3), N(2)–Tl(1)–N(3) 83.5(3), N(2)–Tl(2)–N(3) 69.7(2), Tl(1)–N(2)–Tl(2) 83.8(2), Tl(1)–N(3)–Tl(2) 83.1(2), N(1)–Tl(1)–C(40) 131.9(3). (b) Dimeric aggregate of **2** in the solid state through π-arene–thallium contacts [Tl(2)–Tl(2A) 3.7615(13) Å].

et al. for a range of mixed Li–group 13 metal amido complexes.[11]

A closer inspection of the crystal structure of **2** revealed that the complex is aggregated in the form of weakly associated dimers [Fig. 1(b)]. This type of association occurs through weak π-arene–Tl(I) contacts[12] with, respectively one tolyl group of the neighbouring molecule: Tl(2)–C(Ar′) 3.26–3.51 Å; Tl(2)–centroid: 3.093 Å. This arrangement is supplemented by a relatively short intermetallic distance of Tl(2)–Tl(2′) 3.7615(13). While being significantly shorter than the sum of the van der Waals radii (4.0 Å) this Tl–Tl contact is nevertheless at the long end of the range found for such metal–metal contacts and therefore thought to play a secondary role.

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Notes and references

† *Selected spectroscopic and analytical data*: for **1**: ^{1}H NMR (200.13 MHz, C$_6$D$_6$, 295 K) δ −0.78 (s, 1 H, CH), 0.51 [br s, 18 H, Si(CH$_3$)$_2$], 2.18 (s, 9 H, C$_6$H$_4$C*H*$_3$), 6.74 (d, 6 H, $^3J_{\mathrm{H2H3}}$ 7.5 Hz, H^2, C$_6$H$_4$), 6.97 (d, 6 H, H^3, C$_6$H$_4$); {^{1}H} ^{13}C NMR (50.32 MHz, C$_6$D$_6$, 295 K) δ 8.4 [Si(CH$_3$)$_2$], 13.8 (CH), 20.6 (C$_6$H$_4$*C*H$_3$), 123.7 (C, C^4, C$_6$H$_4$), 129.3 (CH, C^2, C$_6$H$_4$), 131.3 (CH, C^3, C$_6$H$_4$), 153.8 (CN, C^1, C$_6$H$_4$); ^{29}Si {^{1}H} NMR (39.76 MHz, C$_6$D$_6$, 295 K) δ −4.1; C$_{28}$H$_{40}$N$_3$Si$_3$Tl (707.29). Calc. C 47.55, H 5.70, N 5.94, Tl 28.90. Found: C 47.04, H 5.53, N 6.10, Tl 27.85%.

For **2**: ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 295 K) δ −0.76 (br s, 1 H, CH), 0.44 [vbr s, 20 H, Si(CH$_3$)$_2$ + Tl(CH$_2$)], 0.49 [br s, 2 H, Tl(CH$_2$C*H*$_2$)], 0.57 [t, 2 H, $^3J_{\mathrm{H^aH^b}}$ 7.1 Hz, H^a, Tl((CH$_2$)$_2$C*H*$_2$)], 0.97 [q, 3 H, H^b, Tl((CH$_2$)$_3$C*H*$_3$)], 2.16 (br s, 9 H, C$_6$H$_4$C*H*$_3$), 6.68–6.87 (br m, 6 H, H^2, C$_6$H$_4$), 6.93–7.06 (br m, 6 H, H^3, C$_6$H$_4$); {^{1}H} ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 295 K) δ 6.7 [br d, $^3J_{\mathrm{TlC}}$ 66 Hz, Si(CH$_3$)$_2$], 11.0 (CH), 11.6 [Tl((CH$_2$)$_3$*C*H$_3$)], 13.4 [br, Tl(CH$_2$)], 20.6 [C$_6$H$_4$(*C*H$_3$)], 30.2 [Tl((CH$_2$)$_2$*C*H$_2$)], 33.7 [br, Tl(CH$_2$*C*H$_2$)], 125.0 (br, C, C^4, C$_6$H$_4$), 128.3 (CH, C^2, C$_6$H$_4$), 130.2 (CH, C^3, C$_6$H$_4$), 150.4 (vbr, CN, C^1, C^{6}H$_4$; C$_{32}$ H$_{49}$N$_3$Si$_3$Tl$_2$·0.5C$_5$H$_{12}$ (1004.83). Calc. C 41.24, H 5.52, N 4.18, Tl 40.68. Found: C 41.14, H 5.33, N 3.99, Tl 41.12%.

‡ *Crystal data* for [HC{SiMe$_2$N(*p*-Tol)}$_3$(TlC$_4$H$_9$)(Tl)·0.5C$_5$H$_{12}$] **2**: C$_{32}$H$_{49}$N$_3$Si$_3$Tl$_2$·0.5C$_5$H$_{12}$, orange blocks, crystal dimensions 0.6 × 0.4 × 0.3 mm, M = 1004.83, monoclinic, space group $C2/c$, a = 21.346(6), b = 14.4015(13), c = 26.384(10) Å, β = 107.869(14)°, U = 7719(4) Å^3, Z = 8, D_c = 1.729 g cm^{-3}, μ = 8.459 mm^{-1}, F(000) = 3896, 7684 reflections collected (2.00 < θ < 24.99°) at 193(2) K, 6781 independent (R_{int} = 0.0423), 5138 observed [$I > 2\sigma(I)$] 6781 used in the structure refinement; R_1 = 0.0471 [$I > 2\sigma(I)$], wR_2 = 0.1287 (all data), GOF = 1.069 for 382 parameters and 0 restraints, largest difference peak, hole = 2.214, −2.920 e Å^{-3}. The comparatively high residual electron density in **1** was in the vicinity of the thallium atoms.[13,14]

CCDC 157350. See http://www.rsc.org.suppdata/cc/b1/b100760m/ for crystallographic data in .cif or other electronic format

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