Aggregation of tripodal thallium(I) amides through weak TlI⋯TlI interactions

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Metal exchange between the lithium amide MeSi[SiMe₂N-(Li)Buᵗ]₃ and TlCl yields the corresponding thallium amide MeSi[SiMe₂N(Tl)Buᵗ]₃ **1** which aggregates in the solid through weak attractive Tl⋯Tl interactions to form infinite molecular chains; competing redox chemistry leads to the dimetallated species HC[SiMe₂N(Tl)Buᵗ]₂[SiMe₂NHBuᵗ] **2** in the analogous metal-exchange process involving the trisilylmethane derivative.

In contrast to the structural patterns found in molecular alkali-metal compounds in which electrostatic ligand–metal interactions dominate the forms of aggregation,[1] the analogous derivatives of the heavy monovalent group 13 metals are expected to display markedly different intra- and inter-molecular interactions mainly based on weak dispersive attraction between the metal centres.[2] These weak attractive forces between closed shell $d^{10}s^2$ metal centres have been the focus of several systematic studies[3] and their nature the subject of some debate during the past five years.[4]

The availability of formally trianionic tripodal amido ligands containing trisilylmethane or trisilylsilane frameworks[5] having a well established structural chemistry with lithium,[5–7] which may serve as starting materials and structural points of reference, has allowed us to investigate the role of closed shell $d^{10}s^2$ metal⋯metal interactions in their Tl analogues. Our preliminary results, presented here, reveal unprecedented structural types in complexes of the tripodal amides; in particular, we show that the course of the metal-exchange reaction employed in the synthesis of the thallium amides depends upon very subtle structural features in the ligand (Scheme 1).

Stirring a solution of MeSi[SiMe₂N(Li)Buᵗ]₃(dioxane)₂[6,8] with TlCl in dioxane at room temperature led to a complete metal exchange and the work up of the deep red solution afforded a red highly crystalline solid, the analytical data of which were consistent with its formulation as MeSi-[SiMe₂N(Tl)Buᵗ]₃ **1**. The resonance patterns in the ¹H and ¹³C NMR spectra recorded in [²H₈]toluene at 295 and 185 K indicated threefold molecular symmetry on the timescale of the experiments in solution, as indicated in Scheme 1. This would be expected for an adamantoid cage which has been observed previously for the non-solvated lithium amide MeSi[SiMe₂N-(Li)Buᵗ]₃.[7] A single-crystal X-ray structure analysis,† however, revealed an unexpected molecular structure and mode of packing in the solid state (Fig. 1).

In contrast to the structure of the corresponding lithium amide, the tripodal amido ligand in **1** experiences considerable distortion and has little resemblance to the adamantoid
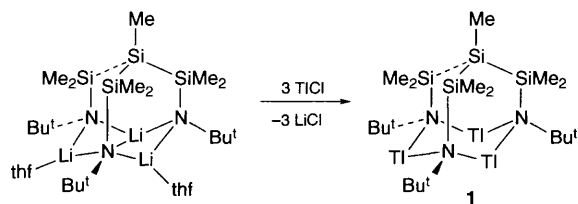
arrangement of the former. The structure is polymeric [Fig. 1(b)] and in the monomer two Tl atoms and two amido N atoms form a four-membered ring Tl(1)–N(2)–Tl(2)–N(3), while the remaining amido-Tl group appears to be 'pendant' on the ligand framework.

The Tl atoms in the monomeric unit are in close proximity, Tl(1)–Tl(2) 3.653(1), Tl(1)–Tl(3) 3.521(2) Å. In this context it is worth noting that the closest metal–metal distances in α-thallium are 3.408 and 3.457 Å.[8] Theoretical studies of other ligated TlI systems[4,9] indicate that there is no bonding interaction between the N-bridged Tl₂ centres in **1** but that the short intramolecular Tl(1)⋯Tl(3) interaction should be weakly attractive. The unusual structural arrangement of the molecular unit arises from a combination of the latter and its mode of polymerization in the crystal. In the solid, molecular units related by a glide plane are connected via short intermolecular Tl⋯Tl contacts [Tl(2)⋯Tl(3′) 3.673(2) Å] to form infinite chains of amidothallium molecules. While the solid state structure of the thallium amide {CH₃Si[N(Tl)Buᵗ]₃}₂ reported by Veith et al. consists of isolated dimeric units with Tl⋯Tl contacts,[10] aggregation in **1** occurs in the form of an infinite chain. The weak attraction of the TlI centres appears to drive the distortion of the molecular unit and hence determines this structure.

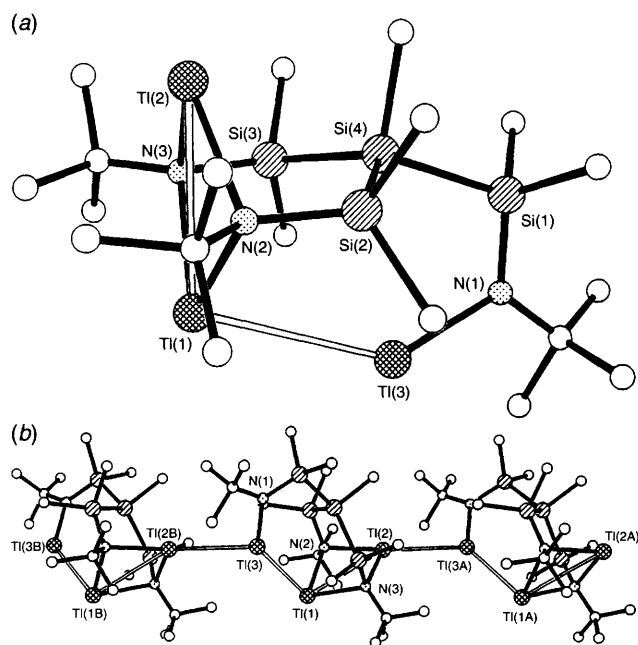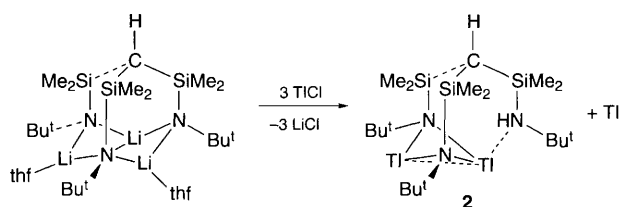That the metal-exchange reactions performed with the tripodal lithium amides depend upon very subtle features of the

(a)

(b)

Fig. 1 Crystal structure of **1**; (a) the molecular unit and (b) the polymeric chain viewed onto the ac plane. Principal bond lengths (Å) and angles (°): Tl(1)–N(2) 2.53(2), Tl(1)–N(3) 2.54(2), Tl(2)–N(2) 2.47(2), Tl(2)–N(3) 2.48(2), Tl(3)–N(1) 2.23(2), Tl(1)–Tl(3) 3.521(2), Tl(1)–Tl(2) 3.6537(14), Tl(2)–Tl(3B) 3.673(2); N(2)–Tl(1)–N(3) 83.3(5), N(2)–Tl(2)–N(3) 85.6(5), Tl(2)–N(2)–Tl(1) 94.0(6), Tl(2)–N(3)–Tl(1) 93.2(6), Tl(3)–Tl(1)–Tl(2) 108.74(3), Tl(1)–Tl(2)–Tl(3B) 151.67(4), Tl(1)–Tl(3)–Tl(2A) 108.76(4).

Scheme 1

ligand structures is evident from the result of the analogous reaction involving the trisilylmethane instead of the trisilylsilane derivative. In contrast to the clean transmetallation yielding 1, competing redox processes lead to the precipitation of 1 equiv. of thallium metal in the course of the reaction and the corresponding dimetallated species 2 is isolated in 71% yield (Scheme 2).

The formulation of 2 was initially based on the analytical data and the observation of a ν(N–H) band in the IR spectrum of the compound. This was substantiated by a single-crystal X-ray structure analysis which established a molecular structure which is closely related to the structure of the monomer of 1 in the crystal (Fig. 2).† The two thallium atoms [Tl(1), Tl(2)] and the amido-N atoms N(2) and N(3) form an analogous four-membered ring with the two Tl atoms being 3.515(1) Å apart. As for 1, no significant intermetallic bonding is expected in the Tl_2N_2 ring. The remaining nitrogen donor function in 2 has been converted to an NH-amino function and weakly coordinates to Tl(1) [Tl(1)–N(1) 2.898(11) Å].

In contrast to the aggregation of the monomeric units in 1 there are no close (< 4 Å) intermolecular Tl···Tl contacts in the partially metallated species 2. As to the conversion of one amido function to an amino donor ligand, we suggest that the redox reaction leading to the precipitation of the thallium metal in the course of the metal exchange generates an unstable (and as yet undetected) radical intermediate which readily abstracts a hydrogen atom from the solvent (dioxane) to form the formally 'protonated' species. Direct protonation (through traces of moisture) may be ruled out under the reaction conditions chosen and in view of the high yield as well as the precipitation of Tl.

These first results have established a reactivity and structural chemistry which is significantly determined by attractive metal–metal interactions and which sets these thallium amides well apart from the established patterns found for their alkali-metal analogues.

Footnote

† Crystal data: 1; $C_{19}H_{48}N_3Si_4Tl_3$, M_r = 1044.07, monoclinic, space group $C2/c$, a = 33.737(7), b = 11.475(3), c = 16.971(4) Å, β = 101.09(2)°, U = 6447(3) A^3, Z = 8, $F(000)$ = 3856, D_c = 2.151 g cm^{-3}, μ(Mo-Kα) = 15.12 mm^{-1}, λ(Mo-Kα) = 0.71073 Å. Data were collected from a red crystal (0.28 × 0.30 × 0.40 mm) mounted in a Lindemann tube under argon in the range θ 1.23–25.00° using a Siemens P4 four-circle diffractometer. The structure was solved by direct methods and refined on F^2 for 5676 unique, semi-empirical (from Ψ-scans) absorption-corrected data (R_{int} = 0.0712, T_{max} = 0.7028, T_{min} = 0.5002). Refinement converged at R_1 = 0.1866, wR_2 = 0.1589 (all data), R_1 = 0.0672, wR_2 = 0.1069 [I > $2\sigma(I)$], GOF = 1.009 for 269 parameters and 1 restraint. The highest peak in the final difference map was 1.4 e Å^{-3} situated 1.03 Å from Tl(2).

2; $C_{19}H_{47}N_3Si_3Tl_2$, M_r = 810.61, monoclinic, space group $P2_1/c$, a = 9.5439(13), b = 17.680(3), c = 16.904(3) Å, β = 95.827(11)°, U = 2837.6(8) A^3, Z = 4, $F(000)$ = 1544, D_c = 1.897 g cm^{-3}, μ(Mo-Kα) = 11.48 mm^{-1}, λ(Mo-Kα) = 0.71073 Å. Data were collected from a yellow crystal (0.28 × 0.35 × 0.42 mm) mounted in a Lindemann tube under argon in the range θ 1.67–25.03° as above. The structure was solved by the Patterson superposition method and refined on F^2 for 4991 unique, semi-empirical (from Ψ-scans) absorption-corrected data (R_{int} = 0.0634, T_{max} = 0.4467, T_{min} = 0.2125). Refinement converged at R_1 = 0.1404, wR_2 = 0.1202 (all data), R_1 = 0.0596, wR_2 = 0.0937 [I > $2\sigma(I)$], GOF = 1.010 for 245 parameters. The highest peak in the final difference map was 1.05 e Å^{-3} situated 1.62 Å from Tl(2). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/266.
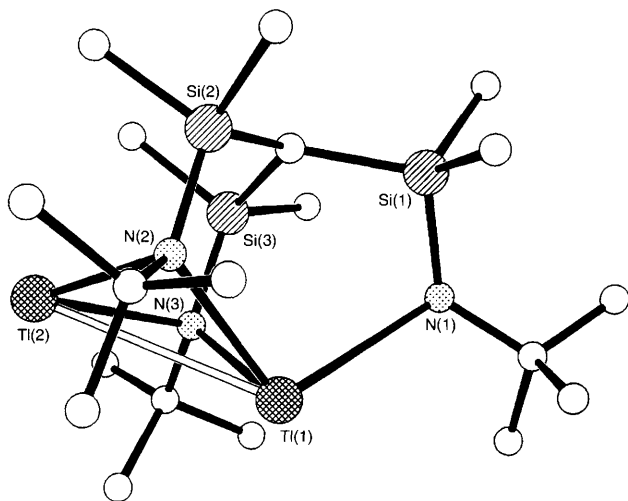

Scheme 2

Fig. 2 Molecular structure of 2. Principal bond lengths (Å) and angles (°): Tl(1)–N(2) 2.545(11), Tl(1)–N(1) 2.868(11), Tl(1)–N(3) 2.544(12), Tl(2)–N(2) 2.499(11), Tl(2)–N(3) 2.543(11), Tl(1)–Tl(2) 3.5154(10); N(2)–Tl(1)–N(3) 79.6(4), N(1)–Tl(1)–N(2) 106.1(3), N(3)–Tl(1)–N(1) 81.4(3), N(2)–Tl(1)–Tl(2) 45.3(3), N(3)–Tl(1)–Tl(2) 46.3(3), N(1)–Tl(1)–Tl(2) 118.2(2), N(2)–Tl(2)–N(3) 80.5(4), N(2)–Tl(2)–Tl(1) 46.4(3), N(3)–Tl(2)–Tl(1) 46.3(3).

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