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Metal−Metal versus Metal−Arene Interactions in Polyfunctional Thallium(I) Amides[†]

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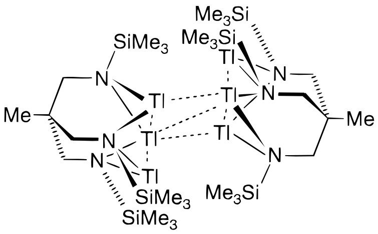
The structural chemistry of formally closed shell low-valent heavy p-block metals is characterized by attractive metal−metal interactions which determine the patterns of aggregation in the solid state.[1,2] We have recently begun to systematically investigate the structural chemistry of amidothallium(I) compounds in which the metal atoms occupy exposed positions, thus making the molecules potential building blocks for larger aggregates.[3,4] In fact, thallium(I) amides have been found to be particularly prone to aggregate via metal−metal contacts in the absence of stronger interactions between other functional groups present in the molecules. Thus a large variety of hitherto unknown patterns of aggregation could be characterized.[5]



Aggregation in discrete dimeric units in the solid has been observed for the tripodal thallium amide $[H_3CC\{CH_2N(Tl)SiMe_3\}_3]_2$, the intermolecular Tl···Tl contacts lying in the range 3.6−3.7 Å.[5] In view of the known interaction of heavy p-block elements and in particular thallium(I) with arene rings,[6] we were interested in finding out how the introduction of an arene group in the ligand backbone of such a tripodal thallium amide would affect its solid state structure. It was conceivable that a combination of Tl···Tl and Tl···arene interactions would lead to a structural arrangement which is significantly different from the previously studied system. To this end we employed the tripodal amido ligand $[(C_6H_5)C(CH_2NSiMe_3)_3]^{3-}$ which we developed previously[7] and which is entirely analogous to the neopentane-derived tripod mentioned above.

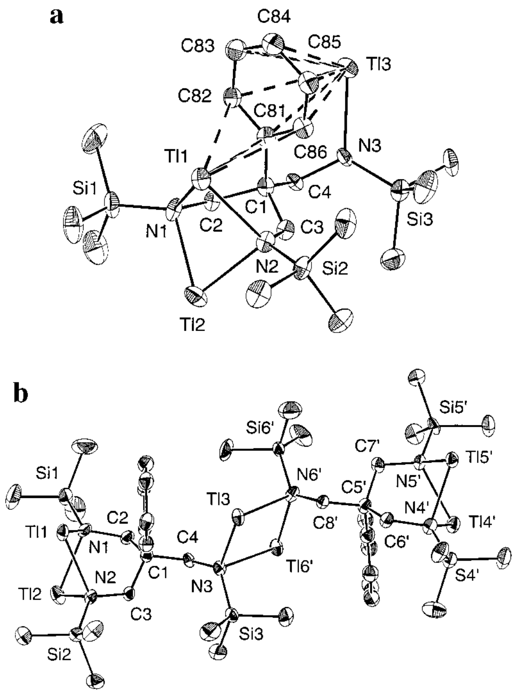


Figure 1. (a) Molecular structure of the monomeric unit showing the thallium···arene interaction. (b) Structure of the amido dimer, in which the two halves of the molecule are related by a center of symmetry. Principal bond lengths (Å) and angles (deg): Tl(1)−N(1) 2.43(2), Tl(1)−N(2) 2.502(19), Tl(3)−N(3) 2.406(18), Tl(3)−N(6′) 2.75(2), Tl(1)−C(81) 2.87(3), Tl(1)···Tl(5) 3.7471(15); Tl(2)−N(2)−Tl(1) 88.1(6), Tl(1)−N(1)−Tl(2) 89.9(7), N(1)−Tl(1)−N(2) 72.9(6), Tl(3)−N(3)−Tl(6′) 90.8(6), N(3)−Tl(3)−N(6′) 89.3(6), C(4)−N(3)−Tl(3) 116.9(14), C(1)−C(81)−Tl(1) 91.5(14).

Stirring the lithium amide $[(C_6H_5)C\{CH_2N(Li)SiMe_3\}_3]_2$[7] and an equimolar amount of solid TlCl in pentane for 88 h yielded an orange solution from which, after workup, the thallium amide $[(C_6H_5)C\{CH_2N(Tl)SiMe_3\}_3]$ (**1**) could be isolated as an orange, highly crystalline solid (yield 56%).[8] While the ^1H- and ^{13}C-NMR spectroscopic data confirmed the integrity of the ligand, the nature of the reaction product was unambiguously established by complete elemental analysis. Single crystals obtained from the reaction mixture were suitable for an X-ray structure analysis of the compound.[9]

The single molecular units adopt the remarkable structural arrangement shown in Figure 1a. Instead of the claw-like conformation normally observed for the tripodal amides, the metalated amido claws bend upward, bringing two of the three

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[†] Dedicated to Prof. M. F. Lappert on the occasion of his 70th birthday.

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(1) Krebs, B., Ed. *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente*; VCH: Weinheim, 1992.

(2) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(3) (a) Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Stalke, D. *Chem. Commun.* **1997**, 527. (b) Hellmann, K. W.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *Chem. Commun.* **1996**, 2515.

(4) Hellmann, K. W.; Gade, L. H.; Steiner, A.; Stalke, D.; Möller, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 160.

(5) Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Kottke, T. *Chem.−Eur. J.* **1997**, *3*, 1801.

(6) Examples: (a) Waezsada, S. D.; Belgardt, T.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1351. (b) Frank, W.; Kuhn, D.; Müller-Becker, S.; Ravazi, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 90. (c) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216. (d) Schmidbaur, H.; Bublak, W.; Huber, B.; Hofmann, J.; Müller, G. *Chem. Ber.* **1989**, *122*, 102. (e) Beck, J.; Strähle, J. *Z. Naturforsch., Sect. B* **1986**, *41*, 1381. (f) Frank, W.; Korrell, G.; Reiss, G. J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 765. (g) Frank, W.; Korrell, G.; Reiss, G. J. *J. Organomet. Chem.* **1996**, *506*, 293. (h) Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414. (i) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3851. (j) Hellmann, K. W.; Galka, C.; Gade, L. H.; Steiner, A.; Wright, D. S.; Kottke, T.; Stalke, D. *Chem. Commun.* **1998**, 549. Review: (k) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107.

(7) Hellmann, K. W.; Friedrich, S.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Chem. Ber.* **1995**, *128*, 29.

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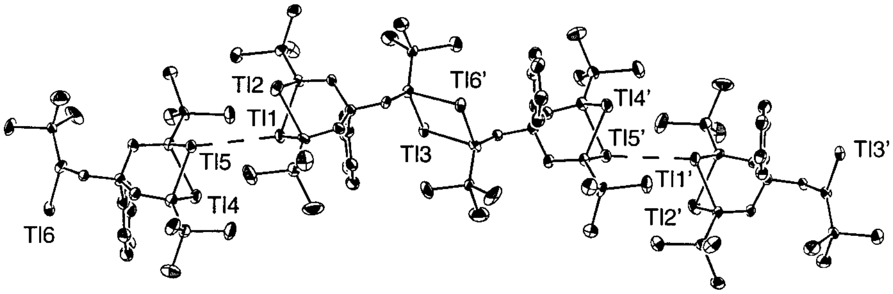

Figure 2. Aggregation of **1** in infinite chains in the crystal through weak Tl···Tl interactions.

thallium atoms into close contact with the apical phenyl group. Whereas Tl(3) adopts a slightly slipped η^6-coordination of the aryl ring with Tl···C distances lying in the range 3.34−3.74 Å, which is typical of weakly attractive arene···metal contacts in heavy p-block element chemistry,[6,10] Tl(1), which is part of an intramolecular Tl_2N_2 four-membered ring, is located very close to the *ipso* phenyl carbon atom C(81). In fact, the distance Tl−C(81) of 2.87 Å is far shorter than usually observed for heavy metal π-bonding in heavy main group element chemistry and approaches the regime found in Tl−C interactions in CpTl derivatives.[6k] Only the ipso C atom and the two ortho carbons C(82) and C(86) lie within a range of potential bonding interactions with respect to Tl(1) [d{Tl(1)−C(82)} = 3.24 Å, *d*{Tl(1)−C(86)} = 3.22 Å], formally making this arrangement an η^3-coordination.

In the solid the amidothallium units are dimeric, and the apparently pendant amido−Tl(3) unit in Figure 1a is in fact part of a Tl_2N_2 four-membered-ring structure the center of which coincides with a crystallographic center of symmetry (Figure 1b). In the crystal structure these dimers form infinite chains which are defined by intermolecular thallium−thallium contacts (Figure 2). The intermolecular metal−metal distance of *d*{Tl(1)−Tl(5)} = 3.75 Å, while being shorter than the sum of the van der Waals radii (4.00 Å), lies at the extreme end of such metal−metal contacts, and the attractive interaction therefore is thought to be rather weak.

In conclusion, these first results of our investigation into the relative importance of metal−metal and metal−arene interactions in thallium(I) amide chemistry have shown that a comparatively minor change in the ligand backbone, such as the introduction of a phenyl group at the apex of a tripodal ligand, may completely alter the solid state structure of a polyfunctional thallium(I) amide. Due to the weakness of the attractive metal−metal interaction responsible for the pattern of aggregation found for most thallium amides to date, such structural arrangements are readily perturbed by the introduction of "functional groups", and the interpretation of an observed structural pattern therefore requires some care.

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Supporting Information Available: Tables containing crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for **1**. An X-ray crystallographic file, in CIF format, for compound **1** is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Solid TlCl (1.74 g, 7.25 mmol) was added to a stirred solution of $[(C_6H_5)C\{CH_2N(Li)SiMe_3\}_3]_2$[7] (1.00 g, 1.21 mmol) in *n*-pentane (40 mL) which was cooled at −35 °C. After the mixture was stirred for 88 h at room temperature, the LiCl formed in the reaction was removed by centrifugation and the orange solution was concentrated to ca. 25 mL. Upon storage of the solution at −35 °C for several days, compound **1** was obtained as an orange, highly crystalline solid (yield: 1.35 g, 56%). Anal. Calcd for $C_{38}H_{76}N_6Si_6Tl_6 \cdot C_5H_{12}$: C, 24.78; H, 4.26; N, 4.03; Tl, 58.84. Found: C, 24.56; H, 4.13; N, 4.10; Tl, 58.08. ^1H NMR (C_6D_6, 295 K): δ 0.24 (s, 27 H, $Si(CH_3)_3$), 4.4 (br s, 6 H, CH_2), 6.79 (tt, 1 H, $^3J_{HbHc} = 7.3$ Hz, $^4J_{HaHc} = 1.8$ Hz, H_c, C_6H_5), 7.18 (td, 2 H, H_b, C_6H_5), 7.35 (d, 2 H, H_a, C_6H_5). $\{^1H\}^{13}C$ NMR (C_6D_6, 295 K): δ 2.1 (br, $Si(CH_3)_3$), 58.0 (br, $C[\mathit{C}H_2NSi(CH_3)_3]_2$), 59.3 (br, $\mathit{C}[CH_2NSi(CH_3)_3]_2$), 127.5 (CH, C_6H_5), 129.8 (br, CH, C_6H_5), 130.8 (br, CH, C_6H_5), 148.1 (C, C_6H_5).

(9) Crystal data for **1**: $C_{38}H_{76}N_6Si_6Tl_6 \cdot C_5H_{12}$, $M = 2083.95$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.656(3)$ Å, $b = 34.522(5)$ Å, $c = 16.359(4)$ Å, $\beta = 104.384(10)°$, $V = 6376(2)$ Å^3, $Z = 4$, $F(000) = 3832$, $D_c = 2.171$ g cm^{-3}, μ(Mo Kα) = 15.252 mm^{-1}, $T = 193(2)$ K, $\lambda = 0.710\,73$ Å. The structure was solved by direct methods[11] and refined[12] on F^2 for 8297 unique, semiempirical (from ψ-scans) absorption-corrected data ($R_{int} = 0.0662$, $T_{max} = 0.9980$, $T_{min} = 0.5225$) out of a total of 9469 reflections collected. Refinement converged at R1 = 0.1241, wR2 = 0.1589 (all data), R1 = 0.0658, wR2 = 0.1289 [$I > 2\sigma(I)$]. GOF (F^2) = 1.030 for 569 parameters and 745 restraints, largest difference peak, hole = 1.382, −2.628 e Å^{-3}. One *n*-pentane molecule was refined with restraints.

(10) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893.

(11) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(12) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.