Aggregation of lithium and mixed thallium(ɪ)–lithium amides through η³- and η⁶-π-arene interactions in the solid

Konrad W. Hellmann,[a] **Christian Galka,**[a] **Lutz H. Gade,**[*a] **Alexander Steiner,**[b] **Dominic S. Wright,**[b] **Thomas Kottke**[a] **and Dietmar Stalke**[a]

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*

The mixed Li–Tl amide [C₁₀H₆{N[Li(thf)₂]SiMe₃}{N(Tl)SiMe₃}] has been synthesized and shown to aggregate *via* η⁶-arene–thallium coordination in the solid; a related pattern of aggregation is found for the partially solvated homometallic Li amide [C₁₀H₆{N[Li(thf)]SiMe₃}{N(Li)SiMe₃}] which displays an unusual η³-arene–lithium interaction.

A comparison of the structural patterns observed in the solid state structures of lithium and thallium(ɪ) amides reveals marked differences in the bonding patterns. Mainly ionic forms of aggregation controlled by electrostatic interactions and the steric demand of the organic periphery occur in the case of lithium amides (and other alkali metal amides).[1] However, the few structurally characterized thallium(ɪ) amides known to date are not well described by the electrostatic model but rather display attractive intermolecular contacts between the heavy metal atoms which appear to arise from weak dispersion forces.[2,3] Another significant difference is the tendency for solvation of the metal atoms, with lithium being most readily coordinated by donor solvents while monovalent thallium appears to be more resistant to increasing its coordination number by donor solvation.

Here, we give a first account of our systematic attempts to break-up the hitherto established structural patterns in Tlᴸ–amide chemistry by incorporating potentially coordinating molecular units into the ligands employed, and to obtain mixed alkali metal–thallium amides which combine the characteristics of the two structural regimes mentioned above. As the ligand precursor we chose the known 1,8-bis(trimethylsilylamino)naphthalene **1** containing an aryl backbone[4] which may potentially interact with the metal centres and thus generate novel forms of aggregation. In this context it should be noted that MO calculations reported for the related dilithiated α-naphthylamine already suggested metal–C-8 interactions in the gas phase which were, however, not found in the decameric solid state structure [(C₁₀H₇NLi₂)₁₀(Et₂O)₆].[5] With this in mind, we assumed that the formal addition of a donor functionality in or close to the C-8 position of the naphthyl unit would generate a significantly different structural pattern.

Lithiation of **1** in thf cleanly yielded the solvated Li–amide [C₁₀H₆{N[Li(thf)₂]SiMe₃}₂] **2** which was isolated and employed as a starting material. Stirring **2** with 1 equiv. of TlCl in thf for 5 h followed by work-up by removal of the solvent, extraction with toluene and crystallization at −35 °C gave an orange crystalline solid in moderate yield. The analytical data and the ¹H and ¹³C NMR spectra were consistent with its formulation as [C₁₀H₆{N[Li(thf)₂]SiMe₃}{N(Tl)SiMe₃}] **3**, *i.e.* the first example of a mixed Tlᴸ–Li amide.† While cryoscopy in benzene indicated the presence of monomeric units in solution, its crystal structure revealed an intriguing dimeric aggregation in the solid (Fig. 1).‡

The two halves of the dimer, in which a Tlᴵ atom and a (thf)₂Li⁺ cation bridge the amido-N atoms, are related by a crystallographic centre of symmetry. The Tl···Tl distance of

3.982(2) Å does not indicate a significant metal–metal interaction. Instead, the interaction between the Tl centres and one of the naphthalene arene rings appears to provide the driving force for the dimeric aggregation in the solid. The distance between the Tl atom and the centroid of the η⁶-coordinated arene ring of 3.5106 Å is somewhat greater than some of the previously reported Tl–arene contacts, in particular that found in [{2,6-Prᵢ₂C₆H₃N(Tl)SiMe₃}₄] (3.11 Å),[6a] but clearly within the range expected for a heavy metal arene coordination.[6b–d] The crystal structure of **3** nicely illustrates the structural principles outlined above, the solvation of the 'peripheral' Li atoms and aggregation involving the arene unit in the ligand backbone.

When the Li–Tl exchange is carried out with 2 molar equiv. of TlCl the completely transmetallated amide [C₁₀H₆{N(Tl)SiMe₃}₂] **4** is formed which has a much decreased solubility in hydrocarbon solvents. It is therefore thought to be polymeric in the solid possibly as a result of metal···arene interactions similar to those established for **3**.

That the 1,8-naphthadiyl backbone of the bidentate amido ligand may strongly influence the aggregation of its metallated derivatives became apparent upon stirring the Li–amide **2** for
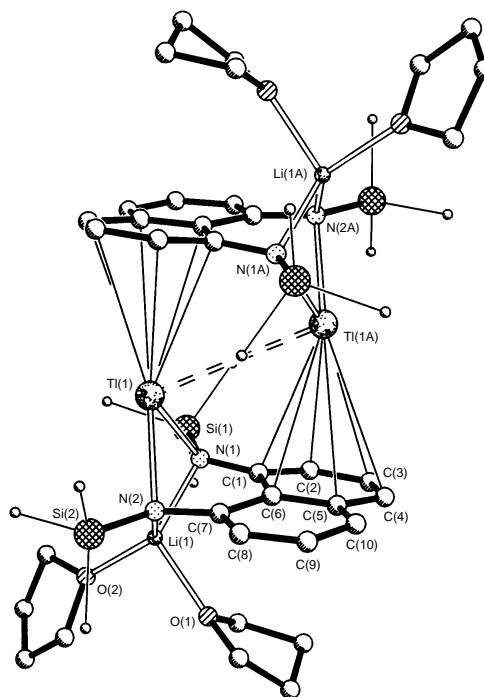
Fig. 1 Molecular structure of **3**. Selected atomic distances (Å) and interbond angles (°): Tl(1)–N(1) 2.467(11), Tl(1)–N(2) 2.497(10), Tl(1)–Li(1) 3.24(3), Tl(1)–C(2A) 3.628(14), Tl(1)–C(6A) 3.810(13), Tl(1)–C(3A) 3.82(2), Tl(1)–C(4A) 3.90(2), Tl(1)–C(5A) 3.91(2), Tl(1)–Tl(1A) 3.982(2), Li(1)–N(2) 1.97(3), Li(1)–N(1) 2.02(3), Li(1)–O(2) 2.06(3), Li(1)–O(1) 2.06(3); N(1)–Tl(1)–N(2) 69.8(3), N(1)–Li(1)–N(2) 90.4(11), Li(1)–N(1)–Tl(1) 91.8(9), Li(1)–N(2)–Tl(1) 92.3(9).
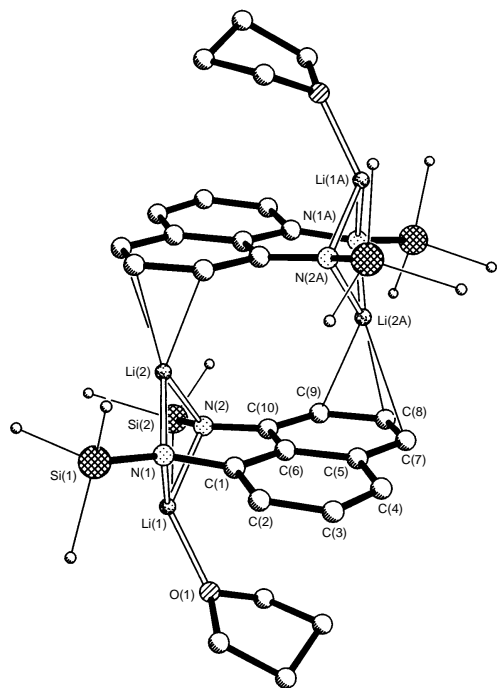
Fig. 2 Molecular structure of **5**. Selected atomic distances (Å) and interbond angles (°): N(1)–Li(1) 1.989(6), N(2)–Li(1) 1.995(6), N(1)–Li(2) 1.987(6), N(2)–Li(2) 1.861(4), Li(1)–O(1) 1.917(5), Li(2)–Li(2A) 4.117(6), Li(2)–C(9A) 2.596(6), Li(2)–C(8A) 2.399(6), Li(2)–C(7A) 2.577(6); Li(1)–N(1)–Li(2) 86.3(2), Li(1)–N(2)–Li(2) 86.3(2), N(1)–Li(1)–N(2) 89.2(2), N(1)–Li(2)–N(2) 89.6(2).

ca. 15 h in dioxane or toluene in the absence of TlCl. Instead of the disolvated Li–amide **2** large single crystals of a monosolvate $[C_{10}H_6\{N[Li(thf)]SiMe_3\}\{N(Li)SiMe_3\}]$ **5** were obtained.† The displacement of three of the thf ligands under these conditions was unexpected and indicated the formation of an unusual amide structure. This was confirmed by the single crystal X-ray structure analysis of the compound which revealed a dimeric structure closely related to that of **3** (Fig. 2).‡

The two molecular units are again related by a centre of inversion which generates a structural array which closely parallels that of the mixed metal amide **3**. The Li cation which has lost all of its donor ligands is coordinated by one of the naphthalene arene rings in an η^3-fashion [Li(2)–C(9A) 2.596(6), Li(2)–C(8A) 2.399(6), Li(2)–C(7A) 2.577(6) Å; nearest non-bonding Li–arene distances: Li(2)–C(5A) 2.956(6), Li(2)–C(10A) 2.992(6) Å]. The second Li atom which is located at the periphery is coordinated by only one thf molecule. At the vacant coordination site, which is occupied by a second thf molecule in **3**, a methyl group of the neighbouring dimeric unit is located [Li(1)–C(14′) 3.656(6) Å]. Although π-interactions of lithium cations with arene rings are known,[7] the η^3-mode of π-coordination observed in **5** is unprecedented in lithium amide chemistry.

Since lithium has a smaller ionic radius than thallium(I) and, consequently, forms shorter metal–arene distances, the two naphthalene ring systems are considerably closer in **5** than in **3** (lengths of the normal vectors between the arene planes in **3**: 5.41, **5**: 3.60 Å).

In conclusion, these first results indicate that the use of polydentate amido ligands containing potentially ligating backbone units generates structural arrays which differ markedly from those previously obtained with amido ligands containing an 'inactive' alkyl or silyl periphery.[3]

Notes and References

* E-mail: lutz.gade@mail.uni-wuerzburg.de

† *Selected spectroscopic and analytical data*: **3**: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K) δ 0.38 [s, 18 H, Si(CH$_3$)$_3$], 0.85 (m, 8 H, CH_2CH$_2$O), 3.05 (m, 8 H, CH$_2$CH_2O), 6.74–7.30 (m, 6 H, C$_{10}$H$_6$); $\{^1$H$\}^7$Li NMR (77.78 MHz, C_6D_6, 295 K) δ 3.98; $\{^1$H$\}^{29}$Si NMR (39.76 MHz, C_6D_6, 295 K) δ −6.0; $C_{24}H_{40}LiN_2O_2Si_2Tl$ (656.09). Calc: C 43.94, H 6.14, N 4.27. Found: C 43.46, H 5.95, N 4.01%. **5**: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K). δ 0.39 [s, 18 H, Si(CH$_3$)$_3$], 0.88 (m, 4 H, CH_2CH$_2$O), 3.08 (m, 4 H, CH$_2$CH_2O), 6.77 (dd, 2 H, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1,1 Hz, C$_{10}$H$_6$), 7.13–7.32 (m, 4 H, C$_{10}$H$_6$); $\{^1$H$\}^7$Li NMR (77.78 MHz, C_6D_6, 295 K) δ −0.68; $\{^1$H$\}^{29}$Si NMR (39.76 MHz, C_6D_6, 295 K) δ −12.6; $C_{20}H_{32}Li_2N_2OSi_2$ (386.54). Calc. C 62.15, H 8.34, N 7.25. Found: C 61.88, H 8.05, N 7.19%.

‡ *Crystal data*: **3**: $C_{24}H_{40}LiN_2O_2Si_2Tl$, red blocks, crystal dimensions 0.2 × 0.2 × 0.2 mm, M = 656.07, triclinic, space group $P\bar{1}$, a = 10.912(4), b = 11.162(4), c = 12.662(5) Å, α = 92.43(5), β = 101.47(5), γ = 110.90(4)°, U = 1401.1(9) Å^3, Z = 2, D_c = 1.555 g cm^{-3}, μ = 5.871 mm^{-1}, $F(000)$ = 652, 4504 reflections collected (4.03 < θ < 22.50°) at 153(2) K, 3640 independent (R_{int} = 0.090), 3625 used in the structure refinement; R_1 = 0.058 [$I > 2\sigma(I)$], wR_2 = 0.189 (all data), GOF = 1.104 for 328 parameters and 297 restraints, largest difference peak, hole = 1.624, −1.787 e Å^{-3}. The comparatively high residual electron density is due to absorption by Tl and to a third component of disorder of a thf molecule which could not be refined.

5: $C_{20}H_{32}Li_2N_2OSi_2$, yellow blocks, crystal dimensions 0.3 × 0.3 × 0.2 mm, M = 386.54, monoclinic, space group $P2_1/n$, a = 10.646(2), b = 11.918(1), c = 17.687(3) Å, β = 93.40(1)°, U = 2240.2(6) Å^3, Z = 4, D_c = 1.146 g cm^{-3}, μ = 0.169 mm^{-1}, $F(000)$ = 832, 3918 reflections collected (3.42 < θ < 24.99°) at 173(2) K, 3325 independent (R_{int} = 0.027), 3325 used in the structure refinement; R_1 = 0.052 [$I > \sigma(I)$], wR_2 = 0.113 (all data), GOF = 1.015 for 269 parameters and 37 restraints, largest difference peak, hole = 0.222, −0.191 e Å^{-3}.[8–10] CCDC 182/751.

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