Structural Patterns and Forms of Aggregation of Metallated Diamido Donor Ligands upon Going from Lithium to Thallium(I)

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Dedicated to Professor Max Schmidt on the occasion of his 75th birthday

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Two polyfunctional lithium amides, $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_2R\}_2]_2$ [R = Me (**3**), *t*Bu (**4**)], have been synthesized and structurally characterized by X-ray crystallography. They were found to have dimeric structures containing ladder-type Li–N arrangements in which the form of aggregation and thus folding of the ladder appears to be influenced by the steric demand of the *N*-bonded silyl groups. Substitution of the lithium ions by thallium(I) was achieved in two steps, yielding the mixed metal amide $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}\{CH_2N(Tl)SiMe_3\}]_2$ (**5**) and the thallium(I) diamide $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Tl)SiMe_3\}_2]_2$ (**6**). X-ray diffraction studies of both compounds revealed a dimeric ring structure through Li–N links for the former, while the latter is monomeric and only weakly aggregated in the crystal structure through a short, unsupported thallium(I)–thallium(I) contact of 3.500(2) Å.

Introduction

Alkali metal amides derived from polyfunctional amines display molecular structures and forms of aggregation which are largely dictated by the relative orientation of the functional groups joined by the ligand framework.[1,2] This reduction of the structural degrees of freedom may lead to patterns of aggregation which are different from those of simple monofunctional amides.[3,4] More significantly, the integration of several functional groups within a ligand system enables systematic control of their role in the assembly of metallated derivatives. This provides an alternative to the well-established co-aggregation of alkali metal amides and neutral ligands or donor solvents.[1,2]

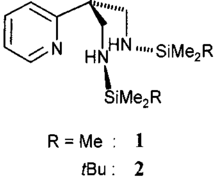
We recently reported the synthesis of a novel dianionic tripodal ligand in which two amido functions are combined with a neutral pyridyl unit.[5,6] This ligand system provides the key to stabilizing a whole range of early transition metal complexes, among these a series of imido complexes.[7,8] Whereas the role of this polydentate ligand in transition metal chemistry is clearly the protection of a large part of the coordination sphere around the metal centre and the masking of potentially accessible coordination sites by the displaceable neutral pyridyl function, the latter may play the part of a "capping" functionality in aggregates of its main group derivatives. While the structures of the group-1 metal amides may be viewed as resulting from primarily ionic interactions between the N-functions and the metal cations,[1] we and others have previously shown that monovalent thallium amides display structures which are markedly different.[9−12]

In this paper we present a systematic study of the forms of aggregation adopted by the lithium amides containing the ligand $[(2\text{-}C_5H_4N)C(CH_3)(CH_2NR)_2]^{2-}$, their thallium analogues and the mixed lithium−thallium species. It will be shown that stepwise replacement of the alkali metal ions by thallium(I) is feasible under appropriate reaction conditions, thus enabling the synthesis of a mixed metal species. The aim will be not only to demonstrate how the ligand enforces the relative arrangement of the metal atoms but also to elucidate the way interactions between the monovalent metal ions themselves determine the structural patterns.

Results and Discussion

Synthesis and Structural Characterization of $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_2R\}_2]_2$ [R = Me (3), *t*Bu (4)]

Reaction of the pyridyl diamines $(2\text{-}C_5H_4N)C(CH_3)(CH_2NHSiMe_2R)_2$ [R = Me (**1**), *t*Bu (**2**)] with two



R = Me : **1**
*t*Bu : **2**

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molar equivalents of *n*-butyllithium and subsequent workup yields the corresponding lithium amides. Whereas the ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectra of **4** in C_6D_6 display structural patterns consistent with a C_s-symmetric monomeric structure, the NMR spectra of **3** indicate aggregation of the lithium amide. The inequivalence of the signals assigned to the methyl groups of the $SiMe_3$ substituents and the patterns of the signals from the protons and carbon nuclei in the ligand framework indicate dimerization of the lithium amide and thus reduction of the local symmetry of the diamidopyridine ligand. This postulated dimerization is supported by a cryoscopic study of **3** in benzene, which also indicated a degree of aggregation lower than two for the analogous compound **4** containing the bulkier ligand periphery. It is assumed that the solution NMR data of the latter are those of the monomeric species. In order to obtain more specific information of the structures of the aggregates, an X-ray crystallographic study of both complexes was clearly essential.

Large colourless single crystals of **3** and **4** were obtained by cooling solutions of the lithiated amines in toluene and pentane, respectively. X-ray structure analyses of both compounds established their dimeric structures in the solid state, which are depicted in Figure 1 and 2 along with selected lengths and inter-bond angles.

The only available crystals of **4** diffracted poorly, leading to relatively high ESDs for all parameters in this structure, but although bond lengths have to be treated with caution, the overall structure is well established and it is interesting to compare the ladder arrangement in the two dimeric molecules. The dilithium diamide units are aggregated in both structures forming four-rung ladders which are terminated by coordination of the neutral pyridyl functions. In compound **3** this lithium amide ladder adopts a boat-type arrangement which is derived from the $(LiN)_4$ cube previously observed in difunctional lithium amides such as $[CH_2\{CH_2N(Li)SiMe_3\}_2]_2$,[13] $[\{t\text{BuN(Li)}\}_2SiMe_2]_2$ [14] and $[\{rac\text{-N}(t\text{Bu})CH(Me)CH(Me)Nt\text{Bu}\}Li]_2$.[15] Coordination of the neutral donor function has led to opening of one face of the cubic structure to generate the ladder arrangement with crystallographic C_2 symmetry. In **3**, the three Li_2N_2 parallelograms are each planar to within 0.006 Å, and the two symmetry-related outer Li_2N_2 units are folded by 62.3° towards cubic from a possible co-planar arrangement with the central unit. In contrast, in the dimeric ag-

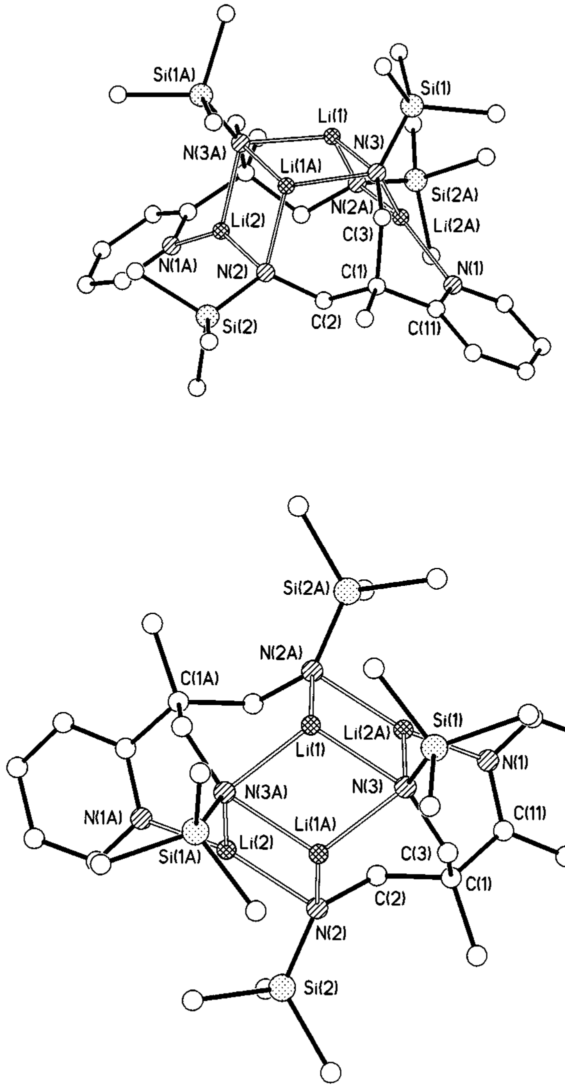

Figure 1. a) (top) Molecular structure of **3** showing the boat-type arrangement of the lithium amide ladder; b) (bottom) the same molecule viewed along the twofold crystallographic axis; selected bond lengths [Å] and angles [°]: Li(1)−N(3) 2.111(8), Li(1)−N(3A) 2.038(8), Li(1)−N(2A) 1.964(8), Li(2)−N(1A) 1.985(8), Li(2)−N(2) 2.023(7), Li(2)−N(3A) 1.984(7); Li(1)−N(3)−Li(1A) 70.9(3), Li(1)−N(3)−Li(2A) 69.9(3), N(3A)−Li(1)−N(3) 109.0(3), N(2A)−Li(1)−N(3A) 111.0(4), N(2A)−Li(1)−N(3) 107.6(4), Li(1A)−N(2)−Li(2) 72.1(3), Li(2A)−N(3)−Li(1A) 106.3(3)

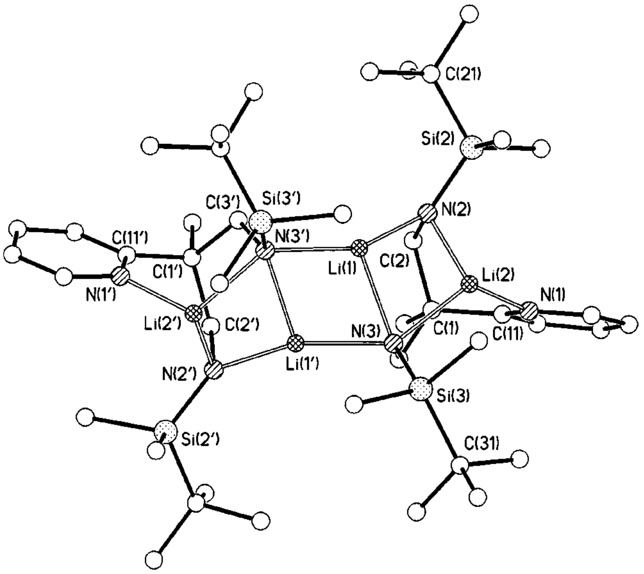

Figure 2. Molecular structure of **4**, which has virtual C_2 symmetry, showing the almost linear arrangement of the lithium amide ladder; mean values of selected bond lengths [Å] and angles [°]: Li(1)−N(2) 1.93(1), Li(1)−N(3) 2.11(1), Li(1)−N(3′) 2.11(2), Li(2)−N(1) 1.85(1), Li(2)−N(2) 1.97(1); N(1′)−Li(1)−N(2) 151(1), N(2)−Li(1)−N(3) 94(1), N(3)−Li(1)−N(3′) 109(1), N(2)−Li(2)−N(3) 105(1), N(3)−Li(2)−N(1) 109(1), N(3)−Li(2)−N(2) 97(1), Li(1)−N(2)−Li(2) 79(1), Li(2)−N(3)−Li(1) 71(1), Li(2)−N(3)−Li(1′) 140 (1)

gregate of compound **4**, unlike the arrangement in **3**, the lithium amide ladder is stepped in the normal way (Figure 2). Six atoms of the Li_4N_4 ladder in **4** show only a small "bowing" from planarity [maximum deviations: Li(1), Li(1′): 0.19 Å and Li(2), Li(2′): −0.19 Å], but the two outer amido nitrogen atoms, N(2) and N(2′), each lie out of this plane by 1.0 Å in the same direction. The mean dihedral angle between the best planes of the inner and each of the outer Li_2N_2 unit, which fold towards each other, is only 20.5° in **4**.

Compound **3** has exact C_2 symmetry, and although compound **4** has only virtual C_2 symmetry, all chemically equivalent bond lengths and angles are equal within experimental error, so the mean values are used (with the atomic symbols for one half of the molecule) in the caption to Figure 2 and in the following discussion. The two lithium atoms in each half of the molecules of **3** and **4** are three-coordinate with Li(1) connected to three amido functions, and Li(2) to two amide groups and one pyridyl group. The amido−N−Li distances of 1.964(8)−2.111(8) Å in **3**, and 1.93(1)−2.11(1) Å in **4**, lie in the expected range for lithium amides.[16] The structure of **4** is readily envisaged as two similar dinuclear monomeric units in which Li(1) and Li(2) are bridged by both amido groups N(2) and N(3) of one ligand, with a third bond from N(3) to a lithium atom, Li(1′), of the second dinuclear unit forming the only bridge between the virtually identical monomer units. In contrast the structure of **3** is intrinsically tetranuclear with the two amido groups of each ligand spanning all four lithium atoms, so that N(2) bridges Li(2) and Li(1A) and N(3) bridges Li(1) and Li(2A) and also forms a bridge to Li(1A) to complete the ladder arrangement. These solid-state structural features are consistent with the observed differences in the NMR spectra of these two compounds, **4** giving a C_s spectrum characteristic of the dinuclear monomer, and **3** giving the less symmetric spectrum characteristic of the Li_4 aggregate. The more linear arrangement in **4** leads to a greater spatial separation of the silyl groups, which are considerably bulkier than those in **3**. It is probable that steric interaction of the peripheral *N*-bound substituents in **4** favours the more open form of aggregation.

Synthesis and Structural Characterization of $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}\{CH_2N(Tl)SiMe_3\}]_2$ (5) and $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Tl)SiMe_3\}_2]_2$ (6)

We have recently established the crystal structures of several polyfunctional thallium(I) amides and found patterns of aggregation which differ markedly from those of the alkali metal derivatives.[11,12] A polyfunctional system containing both neutral and anionic donor atoms has not been studied to date. In view of the results described above, it was of interest to find out how the analogous thallium(I) amides aggregate in the solid.

Reaction of $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}_2]_2$ (**3**) with two molar equivalents of TlCl (per monomeric unit) in pentane over a period of four days led to the exchange of the lithium ions by Tl^+. After workup, two types of crystalline solid, **5** and **6**, were obtained by cooling the pentane solution of the reaction product(s). Colourless crystals (**5**) were collected along with a deep orange crystalline solid (**6**) and were separated by hand. Whereas the orange product did not contain any lithium and was analyzed as the dithallium(I) diamide $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Tl)SiMe_3\}_2]_2$ (**6**) the colourless product was found to be a mixed lithium−thallium amide and was formulated as $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}\{CH_2N(Tl)SiMe_3\}]_2$ (**5**). Repeated runs of this metal exchange under the same reaction conditions gave both compounds in every case as described above whereas use of 1,4-dioxane as solvent exclusively led to formation of the dithallium(I) diamide **6**.

In order to establish their patterns of aggregation in the solid single-crystal X-ray structure analyses of both compounds were carried out. Their molecular structures are displayed in Figure 3 and 4 along with selected bond lengths and angles.

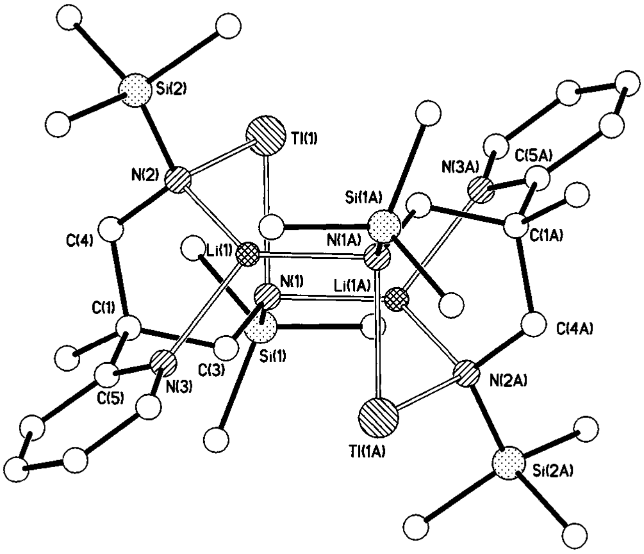

Figure 3. Molecular structure of **5**; selected bond lengths [Å] and angles [°]: Li(1)−N(1A) 2.044(12), Li(1)−N(2) 1.998(12), Li(1)−N(3) 2.102(12), Tl(1)−N(1) 2.483(5), Tl(1)−N(2) 2.455(5); N(2)−Li(1)−N(1A) 135.0(6), N(2)−Li(1)−N(3) 99.3(5), Tl(1)−N(2)−Li(1) 111.4(4), Li(1A)−N(1)−Tl(1) 88.9(3), N(1)−Tl(1)−N(2) 83.29(17), N(3)−Li(1)−N(1A) 123.1(6)

The structural centrepiece of **5** is a $Li_2Tl_2N_4$ macrocycle in which the thallium atoms occupy intramolecular bridging positions and the lithium atoms link the two metallated diamidopyridine ligands. The centre of this cyclic structure coincides with a crystallographic centre of inversion which relates the two halves of the molecule. Whereas the dicoordinate thallium centres adopt the typically exposed positions, the lithium atoms are three-coordinate due to additional bonding of the pyridyl units. The Tl−N distances of Tl(1)−N(2) [2.455(5) Å] and Tl(1)−N(1) [2.483(5) Å] lie in the usual range observed for thallium(I) amides.[10−12,17] The amido-N−Li bond lengths of Li(1)−N(2) [1.998(12) Å] and Li(1)−N(1A) [2.044(12) Å] are significantly shorter than the corresponding value for the pyridyl-N−Li bond of 2.102(12) Å.

In contrast to the dimeric mixed metal amide **5**, the homometallic species $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Tl)\text{-}$

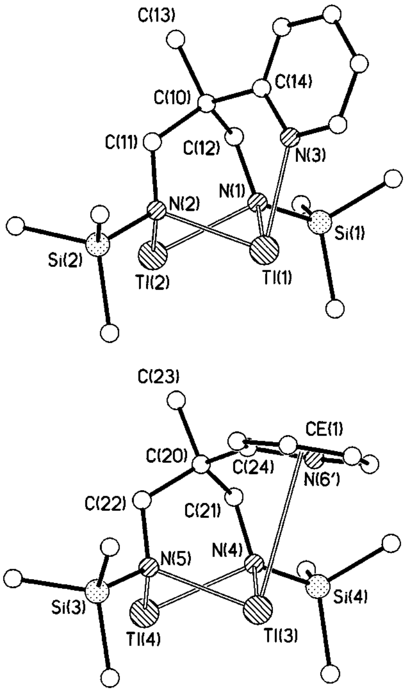

Figure 4. Molecular structure of the monomeric dithallium compound **6**: a) (top) fully ordered monomer unit of **6**, which is one half of the asymmetric unit in the crystal; b) (bottom) second isomer **6′**, present as a 30% component disordered in the second "molecule" of the asymmetric unit of **6**; selected bond lengths [Å] and angles [°]: Tl(1)−N(1) 2.470(14), Tl(1)−N(2) 2.406(15), Tl(1)−N(3) 2.468(15), Tl(2)−N(1) 2.445(13), Tl(2)−N(2) 2.434(14); N(2)−Tl(1)−N(1) 72.4(5), N(3)−Tl(1)−N(1) 80.0(5), N(3)−Tl(1)−N(2) 84.1(5), Tl(1)−N(3)−C(18) 119.2(14), Tl(1)−N(3)−C(14) 121.8(11), Tl(1)−N(2)−Tl(2) 90.4(5), Tl(1)−N(1)−Tl(2) 88.6(4)

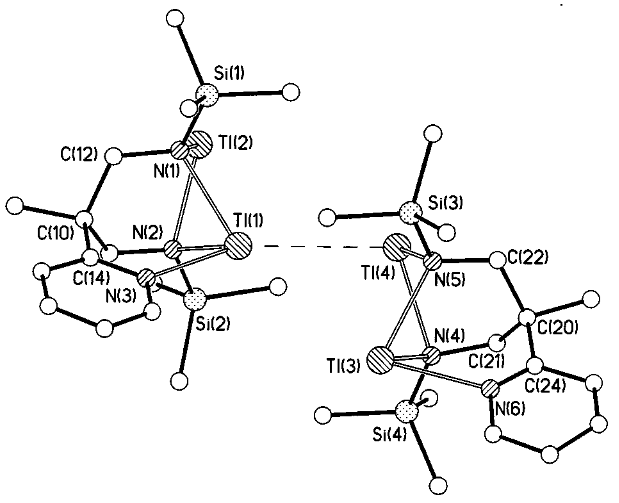

Figure 5. The asymmetric unit of **6** showing the aggregation of the two monomers via weak Tl−Tl interactions [Tl(1)Tl(4) 3.500(2) Å]

$\mathrm{SiMe_3\}_2]_2}$ (**6**) is monomeric in the solid state with two independent molecules in the asymmetric unit. The structure of the first molecule, which is fully ordered, is shown in Figure 4 (a); disorder present in the second molecular unit involves two orientations of the pyridyl ring which corresponds to 30% occupancy by a second isomer [Figure 4 (b)], in which rotation of the pyridyl ring gives a π-interaction of this ring with a thallium atom [Tl(3)−centroid: 3.524 Å]. The ordered monomer unit of **6** has one three-coordinate [Tl(1)] and one two-coordinate thallium centre [Tl(2)] and possesses almost exact molecular mirror symmetry, the virtual mirror plane containing the pyridyl ring, the ligand backbone atoms C(10) and C(13) as well as the two thallium atoms Tl(1) and Tl(2). With respect to Tl(1), the ligand adopts the typical tripod arrangement previously established for the early transition metal derivatives of this system.[6−8] Remarkably, the Tl−N distances to Tl(1) of the two anionic amido functions [Tl(1)−N(1) 2.470(14) Å and Tl(1)−N(2) 2.406(15) Å] and the neutral pyridyl function [Tl(1)−N(3) 2.468(15) Å] lie in the same range and thus do not allow for differentiation between the two types of metal−ligand interactions.

The orientation of the two monomeric units in the crystal corresponds to a weak association to dimeric aggregates (Figure 5) of the type previously established for several other thallium amides, with an unsupported Tl−Tl contact.[9−12] This involves the three-coordinate thallium centre of one monomer and the two-coordinate metal atom of a neighbouring molecule ("head-to-tail" arrangement). The intermetallic distance of Tl(1)−Tl(4) [3.500(2) Å] is significantly shorter than the sum of the van der Waals radii (ca. 4.0 Å) and is thought to reflect a weakly attractive dispersive interaction between the metal centres.

Comparison of the Crystal Structures of 3−6: Variation of the Patterns of Aggregation upon Replacement of Lithium by Thallium(I)

The progression from the lithium amides via the mixed metal amide **5** to the homometallic thallium species **6** may be viewed as a gradual opening of a molecular cage. This is best represented if the cubic dimeric structure of the simple dilithium diamide $[\mathrm{CH_2\{CH_2N(Li)SiMe_3\}_2}]$, which we reported recently,[13] is added to the series (Figure 6). If we begin with the cube, addition of the neutral pyridyl units first leads to an opening to form a ladder structure, either of the boat-type arrangement found in **3** or the stepped arrangement found for **4**. Replacement of lithium by thallium leads to a reduction in the nitrogen−metal interaction and breakdown of the dimer to give the weakly associated structure found for the thallium complex **6**.

Conclusions

In this study we have presented the first systematic structural investigation of lithium and thallium(I) derivatives of a polydentate amido donor ligand. The combination of these two different metal monocations leads to disparate forms of aggregation in the solid, ranging from the principally electrostatic amido−metal interaction in the alkali metal derivatives to the weakly dispersive metal attraction found for the thallium complex. Current work is aimed at extending the structural chemistry of mixed alkali

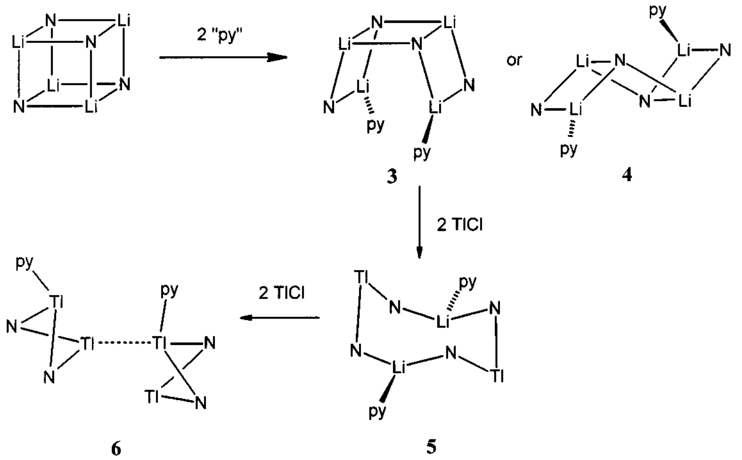

Figure 6. Opening of the heterocubane structure of bidentate lithium amides upon integration of neutral donors and substitution of lithium by thallium(I)

metal–thallium amides in order to gain further insight into the interactions defining their aggregation in the solid state.

Experimental Section

All manipulations were performed under dried argon in standard (Schlenk) glassware, which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR-spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4-Å molecular sieves. – The ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectra were recorded with a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable-temperature unit (at 200.13, 50.32, 39.76, and 77.77 MHz, respectively) with tetramethylsilane or LiI/H_2O (1 M) as reference. – The IR spectra were recorded with a Bruker IFS 25 FT-IR spectrometer. – Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. – The compounds $(2\text{-}C_5H_4N)C(CH_3)(CH_2NH_2)_2$ and $(2\text{-}C_5H_4N)C(CH_3)(CH_2NHSiMe_3)_2$ (**1**) were prepared as reported previously.[6] All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of $(2\text{-}C_5H_4N)C(CH_3)(CH_2NHSiMe_2tBu)_2$ (2): To a stirred solution of of $(2\text{-}C_5H_4N)C(CH_3)(CH_2NH_2)_2$ (9.01 g, 54.5 mmol) in thf (250 mL), NEt_3 (16.0 mL, 114.8 mmol), and then $tBuMe_2SiCl$ (16.4 g, 109.0 mmol) in thf (50 mL) was added in small portions at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. After filtration, the solvent was removed under reduced pressure. Compound **2** was obtained as a colourless liquid after distillation under reduced pressure (yield: 20.6 g, 96%). – B.p.: 150 °C/3 mbar. – ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = −0.3, −0.1 [s, 12 H, $Si(CH_3)_2$], 0.73 (m, 2 H, NH), 0.91 [s, 18 H, $SiC(CH_3)_3$], 1.33 [s, 3 H, $C(CH_3)$], 3.09 {dd, 2 H, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 8.5 Hz, $C[C\mathit{H}HNHSi(CH_3)_2]_2$}, 3.31 {dd, 2 H, $^3J_{HH}$ = 8.1 Hz, $C[CH\mathit{H}NHSi(CH_3)_2]_2$}, 6.58 (m, 1 H, H^5, C_5H_4N), 7.06 (m, 1 H, H^3, C_5H_4N), 7.10 (m, 1 H, H^4, C_5H_4N), 8.46 (m, 1 H, H^6, C_5H_4N). – {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = −4.8, −4.7 [$Si(CH_3)_3$], 18.7 [$SiC(\mathit{C}H_3)_3$], 21.2 [$C(\mathit{C}H_3)$], 26.8 [$Si\mathit{C}(CH_3)_3$], 48.6 [$\mathit{C}(CH_3)$], 51.2 {$C[\mathit{C}H_2NHSi(CH_3)_2]_2$}, 120.9 (CH, C^5, C_5H_4N), 121.9 (CH, C^4, C_5H_4N), 135.7 (CH, C^3, C_5H_4N), 149.2 (CH, C^6, C_5H_4N), 166.4 (C, C^2, C_5H_4N). – {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): δ = 8.3. – IR (film): $\tilde{\nu}$ = 3396 w, 2952 vs, 2927 vs, 2982 s, 2854 vs, 1588 s, 1569 w, 1471 vs, 1431 s, 1401 vs, 1360 s, 1254 vs, 1110 vs, 1084 vs, 1006 s, 829 vs, 811 s, 777 s, 746 s, 662 s cm^{-1}. – $C_{21}H_{43}N_3Si_2$ (393.8): calcd. C 64.06, H 11.01, N 10.67; found C 63.73, H 10.79, N 10.78.

Preparation of $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}_2]_2$ (3) and $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_2tBu\}_2]_2$ (4): To a stirred solution of **1** (1.01 g, 3.26 mmol) or **2** (1.28 g, 3.26 mmol) in *n*-pentane (20 mL), a 2.5 M solution of *n*BuLi in *n*-hexane (2.61 mL = 6.52 mmol) was added at −30 °C. The mixture was warmed to room temperature and stirred for 16 h. After concentration to 5 mL, the solution was stored at −35 °C. Compounds **3** and **4** were obtained as colourless, highly crystalline solids (yields: **3**: 880 mg, 84%; **4**: 1.01 g, 77%).

3: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = 0.24, 0.46 [s, 18 H, $Si(CH_3)_3$], 1.40 [s, 3 H, $C(CH_3)$], 3.10, 3.17 {d, 2 H, $^2J_{HH}$ = 13.8 Hz, $C[C\mathit{H}HNSi(CH_3)_3]$}, 3.48, 3.72 {d, 2 H, $C[CH\mathit{H}NSi(CH_3)_3]$}, 6.47 (ddd, 1 H, $^3J_{H5H4}$ = 6.9 Hz, $^3J_{H5H6}$ = 5.1 Hz, $^4J_{H5H3}$ = 1.7 Hz, H^5, C_5H_4N), 6.95–7.11 (m, 2 H, H^3/H^4, C_5H_4N), 8.34 (ddd, 1 H, $^4J_{H4H6}$ = 1.8 Hz, $^5J_{H3H6}$ = 1.1 Hz, H^6, C_5H_4N). – {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = 0.2, 4.4 [$Si(CH_3)_3$], 24.4 [$C(CH_3)$], 50.7 {$\mathit{C}[CH_2NSi(CH_3)_3]_2$}, 55.4, 58.6 {$C[\mathit{C}H_2NSi(CH_3)_3]_2$}, 120.9, 121.7 (CH, C^3/C^5, C_5H_4N), 137.7 (CH, C^4, C_5H_4N), 147.3 (CH, C^6, C_5H_4N), 169.6 (C, C^2, C_5H_4N). – {^{1}H}^{7}Li NMR (77.77 MHz, C_6D_6, 295 K): δ = 0.16, 0.88. – {^{1}H}^{29}Si NMR (39.76 MHz, C_6D_6, 295 K): δ = −7.6, −4.4. – $C_{30}H_{58}Li_4N_6Si_4$ (642.9): calcd. C 56.04, H 9.09, N 13.07; found C 55.69, H 9.38, N 12.82.

4: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = −0.04, 0.03 [s, 12 H, $Si(CH_3)_2$], 1.01 [s, 18 H, $SiC(CH_3)_3$], 1.22 [s, 3 H, $C(CH_3)$], 3.60 {d, 2 H, $^2J_{HH}$ = 12.0 Hz, $C[C\mathit{H}HNSi(CH_3)_2]_2$}, 3.80 {d, 2 H, $C[CH\mathit{H}NSi(CH_3)_2]_2$}, 6.59 (m, 1 H, H^5, C_5H_4N), 6.91 (m, 1 H, H^3, C_5H_4N), 7.10 (m, 1 H, H^4, C_5H_4N), 8.02 (m, 1 H, H^6, C_5H_4N). – {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = −2.3, −2.4 [$Si(CH_3)_3$], 20.1 [$SiC(\mathit{C}H_3)_3$], 25.8 [$C(\mathit{C}H_3)$], 28.4 [$Si\mathit{C}(CH_3)_3$], 47.7 [$\mathit{C}(CH_3)$], 62.5 {$C[\mathit{C}H_2NSi(CH_3)_2]_2$}, 120.7 (CH, C^5, C_5H_4N), 121.2 (CH, C^4, C_5H_4N), 137.4 (CH, C^3, C_5H_4N), 146.1 (CH, C^6, C_5H_4N), 168.6 (C, C^2, C_5H_4N). – {^{1}H}^{7}Li NMR (77.77 MHz, C_6D_6, 295 K): δ = 0.08, 0.79. – $C_{42}H_{82}Li_4N_6Si_4$ (811.3): calcd. C 62.18, H 10.19, N 10.36; found C 61.97, H 10.21, N 10.25.

Preparation of $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Li)SiMe_3\}\{CH_2N(Tl)SiMe_3\}]_2$ (5) and $[(2\text{-}C_5H_4N)C(CH_3)\{CH_2N(Tl)SiMe_3\}_2]_2$ (6): Solid TlCl (720 mg, 3.00 mmol) was added to a stirred solution of

482 mg (1.50 mmol) **3** in *n*-pentane (25 mL) at −55 °C. After the mixture was warmed to room temperature and stirred for 94 h, the LiCl formed in the reaction was removed by centrifugation and the yellow solution was stored at −35 °C. Compound **5** was obtained as a colourless, and compound **6** as an orange, highly crystalline solid (yield: **5**: 83 mg, 10%; **6**: 579 mg, 54%).

5: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = 0.02 [s, 18 H, Si(CH$_3$)$_3$], 1.34 [s, 3 H, C(CH$_3$)], 2.96, 3.02 {d, 2 H, $^2J_{HH}$ = 8.4 Hz, C[C*H*HNSi(CH$_3$)$_3$]$_2$}, 3.27, 3.33 {d, 2 H, C[CH*H*NSi(CH$_3$)$_3$]$_2$}, 6.59 (ddd, 1 H, $^3J_{H4H5}$ = 6.6 Hz, $^3J_{H5H6}$ = 4.8 Hz, $^4J_{H3H5}$ = 1.8 Hz, H^5, C$_5$H$_4$N), 7.02−7.10 (m, 2 H, H$^{3/4}$, C$_5$H$_4$N), 8.50 (ddd, 1 H, $^3J_{H5H6}$ = 4.8 Hz, $^4J_{H4H6}$ = 1.8 Hz, $^5J_{H3H6}$ = 1.1 Hz, H^6, C$_5$H$_4$N). − {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = 0.3 [Si(CH$_3$)$_3$], 21.0 [C(CH$_3$)], 48.4, 50.7 {C[*C*H$_2$NSi(CH$_3$)$_3$]$_2$}, 65.1 {*C*[CH$_2$NSi(CH$_3$)$_3$]$_2$}, 120.8, 122.0 (CH, C$^{3/5}$, C$_5$H$_4$N), 135.6 (CH, C^4, C$_5$H$_4$N), 149.2 (CH, C^6, C$_5$H$_4$N), 166.5 (C, C^2, C$_5$H$_4$N). − $C_{15}H_{29}LiN_3Si_2Tl \cdot 0.5\,C_5H_{12}$ (555.0): calcd. C 37.87, H 6.36, N 7.57, Tl 36.83; found C 37.38, H 6.11, N 7.28, Tl 36.72.

6: ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = 0.17 [br s, 18 H, Si(CH$_3$)$_3$], 1.08 [s, 3 H, C(CH$_3$)], 3.70 {br m, 1 H, C[C*H$_2$*NSi(CH$_3$)$_3$]$_2$}, 4.30 {br m, 3 H, C[C*H$_2$*NSi(CH$_3$)$_3$]$_2$}, 6.48 (ddd, 1 H, $^3J_{H4H5}$ = 7.8 Hz, $^3J_{H5H6}$ = 4.9 Hz, $^4J_{H3H5}$ = 1.0 Hz, H^5, C$_5$H$_4$N), 7.05 (td, 1 H, $^3J_{H3H4}$ = 7.8 Hz, $^4J_{H4H6}$ = 2.1 Hz, H^4, C$_5$H$_4$N), 7.27 (dt, 1 H, $^3J_{H3H4}$ = 7.8 Hz, $^4J_{H3H5}$ = 1.0 Hz, H^3, C$_5$H$_4$N), 8.25 (ddd, 1 H, $^3J_{H5H6}$ = 4.9 Hz, $^4J_{H4H6}$ = 2.1 Hz, $^5J_{H3H6}$ = 1.0 Hz, H^6, C$_5$H$_4$N). − {^{1}H}^{13}C NMR (50.32 MHz, C_6D_6, 295 K): δ = 1.0 [dd, $^3J_{TlC}$ = 56 Hz, $^3J_{TlC}$ = 106 Hz, Si(CH$_3$)$_3$], 27.8 [br, C(*C*H$_3$)], 55.6 [d, $^3J_{TlC}$ = 143 Hz, *C*(CH$_3$)], 60.2 {dd, $^2J_{TlC}$ = 60 Hz, $^2J_{TlC}$ = 115 Hz, C[*C*H$_2$NSi(CH$_3$)$_3$]$_2$}, 121.3 (CH, C$^{3/5}$, C$_5$H$_4$N), 121.6 (d, $^3J_{TlC}$ = 27 Hz, CH, C$^{3/5}$, C$_5$H$_4$N), 137.6 (d, $^4J_{TlC}$ = 28 Hz, CH, C^4, C$_5$H$_4$N), 149.4 (d, $^2J_{TlC}$ = 91 Hz, CH, C^6, C$_5$H$_4$N), 169.4 (d, $^2J_{TlC}$ = 15 Hz, C, C^2, C$_5$H$_4$N). − $C_{15}H_{29}N_3Si_2Tl_2$ (716.4): calcd. C 25.15, H 4.08, N 5.87, Tl 57.06; found C 24.66, H 3.98, N 5.53, Tl 56.31.

X-ray Crystallographic Study of 3−6: Data of **3** and **4** were collected using a Siemens P4 diffractometer at a temperature of 198(2) K (**3**) and 305(2) K (**4**), respectively, with oil-coated crystals mounted in Lindemann tubes. Data of **5** and **6** were collected using an Enraf−Nonius CAD4 diffractometer at a temperature of 133(2) K (**5**) and 193(2) K (**6**), respectively, with oil-coated shock-cooled crystals[18] mounted on the top of a glass pin under nitrogen. Crystal data and experimental details for the crystals of **3−6** are given in Table 1. All data for the structures **5** and **6** were corrected for absorption using Ψ-scans. No absorption correction was applied for structure **3** and **4**. Structure **5** was solved by Patterson methods, structures **3**, **4**, and **6** by direct methods (SHELXS-86: **3**, **5**, **6**; SHELXS-97: **4**) and refined on F^2 (SHELXL-93: **3**; SHELXL-97: **4−6**).[19] The comparatively high residual electron density in **5** and **6** was in the vicinity of the thallium atoms. Due to extremely poor diffraction by the only crystals of **4** available, data was collected in a very limited θ range (θ < 18°) and the chemically equivalent bond lengths in the two halves of the molecule were constrained in the refinement to be equal within an esd of 0.03 Å, because of the shortage of data. In the case of **5** a solvent molecule (*n*-pentane) was disordered across the inversion centre. In the case of **6**, disorder of the pyridine ring in one molecule in the asymmetric unit corre-

Table 1. Crystal data and structure refinement for **3−6**

	3	**4**	**5**	**6**
Empirical formula	$C_{30}H_{58}Li_4N_6Si_4$	$C_{42}H_{82}Li_4N_6Si_4$	$C_{30}H_{58}Li_2N_6Si_4Tl_2 \cdot C_5H_{12}$	$C_{15}H_{29}N_3Si_2Tl_2$
*M*r	642.94	811.26	1109.94	716.33
Temperature	198(2) K	305(2) K	133(2) K	193(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Z	4	2	1	4
Unit cell dimensions	*a* = 22.366(2) Å *b* = 9.3954(8) Å *c* = 19.404(3) Å β = 104.874(10)°	*a* = 10.369(3) Å *b* = 13.142(4) Å *c* = 20.092(12) Å α = 94.72(3)° β = 102.09(3)° γ = 91.03(2)°	*a* = 9.7249(19) Å *b* = 12.065(2) Å *c* = 12.181(2) Å α = 119.59(3)° β = 95.59(3)° γ = 106.03(3)°	*a* = 11.755(5) Å *b* = 13.480(6) Å *c* = 15.149(6) Å α = 99.51(2)° β = 97.41(3)° γ = 109.34(2)°
Volume	3940.9(7) Å^3	2666.4(19) Å^3	1146.8(4) Å^3	2190.1(16) Å^3
$D_{calcd.}$	1.084 g cm^{-3}	1.010 g cm^{-3}	1.607 g cm^{-3}	2.173 g cm^{-3}
Absorption coefficient	0.177 mm^{-1}	0.143 mm^{-1}	7.151 mm^{-1}	0.202 mm^{-1}
F(000)	1392	888	546	1320
Crystal size	0.2 × 0.36 × 0.42 mm	0.35 × 0.38 × 0.4 mm	0.2 × 0.2 × 0.2 mm	0.2 × 0.2 × 0.2 mm
Scan method	ω/2θ scan	θ/2θ scan	ω scan	ω/θ scan
θ range for data collection	1.88−25.00°	1.95−18.00°	2.00−24.99°	2.10−22.46°
Limiting indices	$-26 \le h \le 26$, $-11 \le k \le 11$, $-23 \le l \le 23$	$-9 \le h \le 1$, $-11 \le k \le 11$, $17 \le l \le 17$	$-11 \le h \le 1$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-12 \le h \le 0$, $-13 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	7110	4193	4394	9655
Independent reflections	3472	3420	4051	5708
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	3472/0/206	3420/349/505	4051/0/243	5708/245/457
$T_{max/min}$	−/−	−/−	0.9993/0.7767	0.9981/0.7297
Goodness-of-fit on F^2	1.003	0.839	1.056	1.055
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$, $wR_2 = 0.1036$	$R_1 = 0.0962$, $wR_2 = 0.2346$	$R_1 = 0.0342$, $wR_2 = 0.0777$	$R_1 = 0.0524$, $WR_2 = 0.0907$
R indices (all data)	$R_1 = 0.1609$, $wR_2 = 0.1335$	$R_1 = 0.2563$, $wR_2 = 0.3347$	$R_1 = 0.0407$, $wR_2 = 0.0813$	$R_1 = 0.0877$, $wR_2 = 0.1076$
Largest diff. peak/hole	0.292/−0.287 e Å^{-3}	0.252/−0.321 e Å^{-3}	2.656/−1.795 e Å^{-3}	1.285/−1.073 e Å^{-3}

sponds to a random distribution at this site, throughout the crystal, of two isomers **6** and **6′** (differing only in the orientation of this pyridine ring) in a 70:30% ratio. In the final cycles of refinement all non-hydrogen atoms of **3−6** were assigned anisotropic displacement parameters. Hydrogen atoms were included in idealized positions riding on the parent atoms and were assigned isotropic displacement parameters of 1.2 U_{eq} (=CH, CH_2) and 1.5 U_{eq} (CH_3) of the parent atom. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142874 (**3**), -142875 (**4**), -142876 (**5**), -142877 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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