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Metal–Ligand versus Metal–Metal Redox Chemistry: Thallium(I)-Induced Synthesis of 4,9-Diaminoperylenequinone-3,10-diimine Derivatives[**]

Konrad W. Hellmann, Christian H. Galka, Ina Rüdenauer, Lutz H. Gade,[*] Ian J. Scowen, and Mary McPartlin

While the structural chemistry of thallium(I) amides and related molecular compounds in the solid state is characterized by supramolecular forms of aggregation defined by weakly attractive metal–metal contacts,[1–3] redox disproportionations of the monovalent metal complexes of thallium and indium dominate their reactivity in solution.[4] These may either lead to the mixed-valent M^IM^{II} and M^IM^{III} compounds (M = In, Tl) or, alternatively, generate the products of partial or complete thermal demetalation. In the latter case the corresponding amines are formed probably via nitrogen radical intermediates.

It was our aim to study the demetalation more closely and use it preparatively for the specific coupling of the transient intermediates generated by the demetalation. We thus set out to investigate the thallium(I) and indium(I) amide chemistry of such ligands which upon thermal demetalation would give intermediates of greater stability and lifetime. Instead of immediately abstracting hydrogen atoms from the solvent, they could undergo C–C coupling and related reactions. To this end we chose a bidentate amido ligand derived from 1,8-diaminonaphthalene which, given the known redoxchemistry of arylamines,[5] offered the opportunity of directing the chemically induced redox conversions into pathways other than simple demetalations.

As starting material we selected 1,8-bis(trimethylsilylamino)naphthalene (**1**), which was readily converted into the lithium amide $[Li_2\{C_{10}H_6(NSiMe_3)_2\}(thf)_4]$ (**2**).[6] The attempted metal exchange of **2** with InCl in THF led to an immediate redox disproportionation of the monovalent In^I compound and the generation of the dinuclear In^{II}–In^{II} complex $[In\{C_{10}H_6(NSiMe_3)_2\}(thf)]_2$ (**3**; Scheme 1, Table 1). Its formulation was established by elemental analysis and the NMR spectra, while a single-crystal X-ray structure analysis[7] of the bright yellow compound confirmed the presence of a metal–metal bond (Figure 1). The In–In distance of 2.7237(6) Å is the shortest established for a diindane to date.[4c, 8] The midpoint of the In–In vector lies on a crystallographic center

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[*] Priv.-Doz. Dr. L. H. Gade, Dr. K. W. Hellmann, C. H. Galka, I. Rüdenauer
Institut für Anorganische Chemie der Universität
Am Hubland, D-97074 Würzburg (Germany)
Fax: (+49) 931-888-4605
E-mail: lutz.gade@mail.uni-wuerzburg.de

Dr. I. J. Scowen, Prof. M. McPartlin
School of Applied Chemistry, University of North London
Holloway Road, London N7 8DB (UK)

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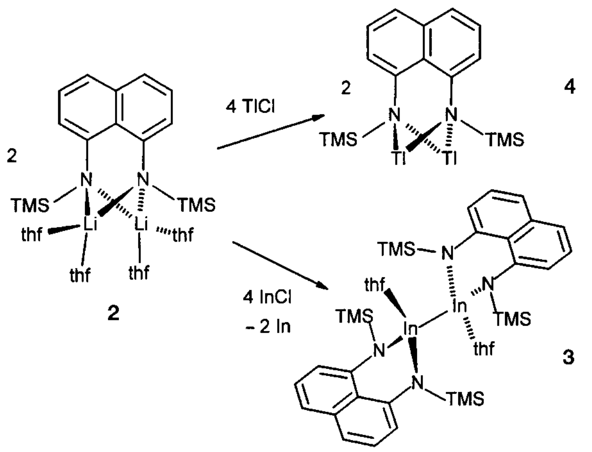


Scheme 1. Synthesis of the indium(II) amide **3** (In–In) and thallium(I) amide **4**.

Table 1. Selected spectroscopic data for compounds **3**–**7**.[a]

3: ^{1}H NMR (C_6D_6): $\delta = 0.44$ (s, 36H, Si(CH_3)$_3$), 0.88 (m, 8H, CH_2CH_2O), 3.39 (m, 8H, CH_2CH_2O), 6.95 (dd, 4H, $^3J_{H,H} = 7.1$ Hz, $^4J_{H,H} = 1.2$ Hz, $C_{10}H_6$), 7.16–7.27 (m, 8H, $C_{10}H_6$); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 4.4$ (Si(CH_3)$_3$), 24.5 (CH_2CH_2O), 69.7 (CH_2CH_2O), 118.6 (CH, $C_{10}H_6$), 120.2 (CH, $C_{10}H_6$), 125.8 (CH, $C_{10}H_6$), 126.3 (C, $C_{10}H_6$), 139.3 (C, $C_{10}H_6$), 153.7 (CN, $C_{10}H_6$); $^{29}Si\{^1H\}$ NMR ([D$_8$]THF): $\delta = -0.8$.

4: ^{1}H NMR (C_6D_6): $\delta = 0.28$ (s, 18H, Si(CH_3)$_3$), 6.74 (dd, 2H, $^3J_{H,H} = 6.4$ Hz, $^4J_{HH} = 2.8$ Hz, $C_{10}H_6$), 7.33–7.38 (m, 4H, $C_{10}H_6$); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 0.6$ (br, Si(CH_3)$_3$), 116.1 (br, CH, $C_{10}H_6$), 119.4 (CH, $C_{10}H_6$), 122.2 (br, C, $C_{10}H_6$), 126.9 (CH, $C_{10}H_6$), 140.1 (C, $C_{10}H_6$), 151.0 (br, CN, $C_{10}H_6$); $^{29}Si\{^1H\}$ NMR ([D$_8$]THF): $\delta = -7.9$.

5a: ^{1}H NMR (C_6D_6): $\delta = 0.48$ (s, 36H, Si(CH_3)$_3$), 7.19 (d, 4H, $^3J_{H,H} = 9.7$ Hz, $C_{20}H_8$), 8.13 (d, 4H, $C_{20}H_8$), 14.13 (s, 2H, NH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 1.4$ (Si(CH_3)$_3$), 112.2 (C, $C_{20}H_8$), 124.3 (C, $C_{20}H_8$), 125.4 (CH, $C_{20}H_8$), 126.4 (C, $C_{20}H_8$), 128.0 (CH, $C_{20}H_8$), 161.9 (CN, $C_{20}H_8$); $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = -0.9$.

5b: ^{1}H NMR ($CDCl_3$): $\delta = 0.41$ (s, 24H, Si(CH_3)$_2$), 1.00 (s, 36H, SiC(CH_3)$_3$), 7.21 (d, 4H, $^3J_{H,H} = 9.8$ Hz, $C_{20}H_8$), 8.38 (d, 4H, $C_{20}H_8$), 13.42 (s, 2H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -2.1$ (Si(CH_3)$_2$), 19.2 (SiC(CH_3)$_3$), 26.9 (SiC(CH_3)$_3$), 111.6 (C, $C_{20}H_8$), 123.7 (C, $C_{20}H_8$), 125.7 (C, $C_{20}H_8$), 126.0 (CH, $C_{20}H_8$), 127.1 (CH, $C_{20}H_8$), 161.8 (CN, $C_{20}H_8$); $^{29}Si\{^1H\}$ NMR (C_6D_6): $\delta = 4.9$.

6: ^{1}H NMR ([D$_6$]DMSO[b]): $\delta = 7.16$ (d, 4H, $^3J_{H,H} = 9.8$ Hz, $C_{20}H_8$), 8.47 (d, 4H, $C_{20}H_8$), 8.65 (brs, 6H, NH/NH$_2$); $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): $\delta = 105.7$ (C, $C_{20}H_8$), 123.0 (C, $C_{20}H_8$), 125.0 (C, $C_{20}H_8$), 125.4 (CH, $C_{20}H_8$), 127.3 (CH, $C_{20}H_8$), 159.6 (CN, $C_{20}H_8$).

7: ^{1}H NMR (C_6D_6): $\delta = 0.22$ (s, 36H, Si(CH_3)$_3$), 5.43 (brs, 4H, NH), 6.72 (d, 4H, $^3J_{H,H} = 9.2$ Hz, $C_{20}H_8$), 7.88 (d, 4H, $C_{20}H_8$).

[a] NMR spectra recorded at 200.13 (^{1}H), 50.32 (^{13}C), and 39.76 MHz (^{29}Si). Correct elemental analyses obtained for all compounds. [b] DMSO = Dimethyl sulfoxide.

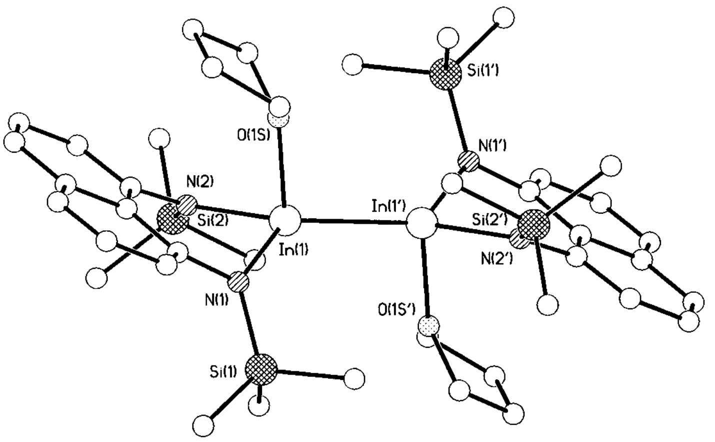
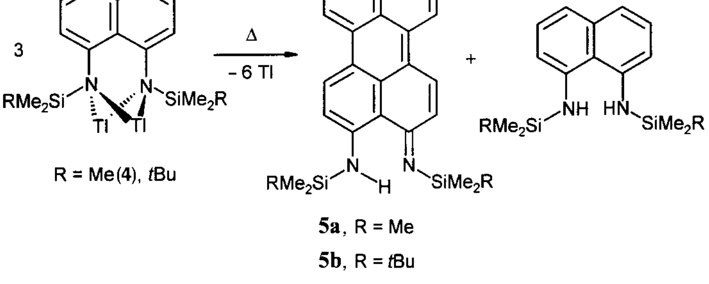


Figure 1. Molecular structure of **3** in the solid state; selected bond lengths [Å] and angles [°]: In(1)–In(1') 2.7237(6), In(1)–N(1) 2.085(3), In(1)–N(2) 2.089(3), In(1)–O(1S) 2.283(3), Si(1)–N(1) 1.722(4), Si(2)–N(2) 1.725(3); N(1)-In(1)-N(2) 90.91(13), N(1)-In(1)-O(1S) 96.75(13), N(2)-In(1)-O(1S) 93.17(12), N(1)-In(1)-In(1') 127.96(10), N(2)-In(1)-In(1') 134.45(9), C(1)-N(1)-Si(1) 125.5(3), C(1)-N(1)-In(1) 114.1(3), Si(1)-N(1)-In(1) 117.9, C(7)-N(2)-Si(2) 122.2(3), C(7)-N(2)-In(1) 114.6(3), Si(2)-N(2)-In(1) 123.1(2).

of symmetry, and the metal atoms are located significantly outside the planes of the aromatic ligand backbones (0.984 Å) with the SiMe$_3$ groups pointing in the opposite direction to generate the almost planar geometry at the amido N atoms. The coordination geometry of the indium centers may be viewed as being between the two extremes of a trigonal-planar arrangement to be expected for a non-THF-solvated complex and the distortion towards a tetrahedral geometry induced by the coordination of the THF ligands.

In contrast with the immediate disproportionation of the In^I species during the course of the metal exchange, the corresponding reaction of **2** with TlCl exclusively led to the monovalent synthetic target [$Tl_2\{C_{10}H_6(NSiMe_3)_2\}$] (**4**) which was isolated as a microcrystalline, orange solid and characterized by elemental analysis and NMR spectroscopy. When **4** was stirred in 1,4-dioxane at 90 °C, thallium metal precipitated and the initially orange solution turned deep green. Monitoring the reaction by ^{1}H NMR spectroscopy revealed a very selective conversion of **4** into the amine **1** and a hitherto unknown product **5a** in a 1:1 molar ratio. After completion of the reaction and workup **5a** was isolated in 50% yield (based on **4**) as a black-green highly crystalline solid with a purple luster.[9] The elemental analysis of **5a** indicated the absence of thallium, and X-ray diffraction studies of the SiMe$_3$-substituted compound, as well as its Si*t*BuMe$_2$-substituted analogue **5b,** established their identity as perylene derivatives (Scheme 2).[10]

Both **5a** and **5b** are formulated as derivatives of 4,9-diaminoperylenequinone-3,10-dimine **6** which may be obtained by desilylation with fluoride. Compound **6** was first reported by Zinke and co-workers.[11] However, it has received little attention since then, probably due to its



5a, R = Me

5b, R = *t*Bu

Scheme 2. Thermolytic conversion of **4** into the perylene derivative **5a** and the amine **1**.

extremely cumbersome synthesis by exhaustive nitration of unsubstituted perylene and reduction of the tetranitro derivative formed. This lack of attention is surprising in view of the close structural relationship to 4,9-dihydroxyperylene-3,10-quinones (the oxygen analogues), such as the natural product hypocrelline A; some of these compounds are employed in photodynamic therapy and display cancerostatic and antiviral activity.[12]

The patterns of bond lengths in the molecular structures of **5a** and **5b** are similar but due to poor diffraction by the crystals of **5a**, caused by considerable rotational disorder of the trimethylsilyl groups, the estimated standard deviations in the former are relatively high and preclude detailed discussion. The structure of **5b** is well established, and the corresponding bond lengths on the two sides of the virtually planar ring system are equal within experimental error (Figure 2).

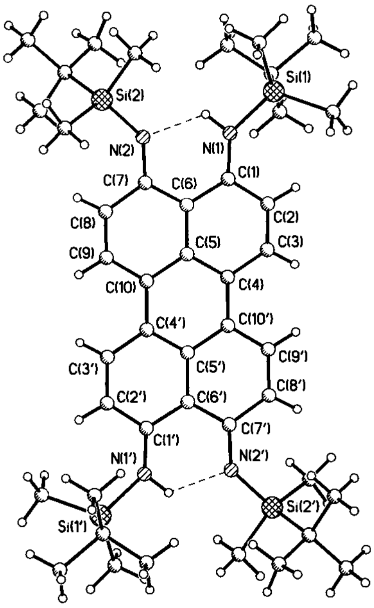


Figure 2. The structure observed for the two independent centrosymmetric molecules in the crystal of **5b**. Selected bond lengths [Å] with those for the second molecule in brackets: Si(1)–N(1) 1.748(3) [1.740(3)], Si(2)–N(2) 1.734(3) [1.738(3)], N(2)–C(7) 1.330(4) [1.326(4)], N(1)–C(1) 1.334(5) [1.332(4)], C(1)–C(2) 1.428(5) [1.430(5)], C(7)–C(8) 1.435(5) [1.436(5)], C(1)–C(6) 1.436(5) [1.439(5)], C(6)–C(7) 1.436(5) [1.433(5)], C(2)–C(3) 1.342(5) [1.337(5)], C(8)–C(9) 1.343(5) [1.339(5)], C(3)–C(4) 1.415(5) [1.420(5)], C(9)–C(10) 1.421(5) [1.426(5)], C(5)–C(10) 1.420(5) [1.426(5)], C(4)–C(5) 1.418(5) [1.410(5)], C(5)–C(6) 1.440(5) [1.441(5)], mean N–H 0.98, N···H 1.86.

The overall solid-state structure of the molecules is the result of a random 50:50 disorder of two tautomers throughout the crystal. There are significant differences in the bond lengths relative to the reported values of the parent compound perylene.[13] In particular, the mean lengths of C(2)–C(3) and C(8)–C(9) of 1.341 and C(4)–C(10′) of 1.421 Å are considerably shorter than the analogous values in perylene of 1.40 and 1.48 Å, respectively. A similar shortening of these bonds has been observed previously for the perylene dianion, where the respective mean values are 1.37 and 1.43 Å,[14] as well as in the hydroxyperylenequinones mentioned above.[15]

The solid state structures of a large number of perylenebis(carboximide) derivatives have been studied in order to investigate the correlation between molecular packing and color in pigments.[16] In most cases stacked face-to-face arrangements (separation between the parallel oriented ring systems between 3.345 and 3.476 Å) of perylenes are found provided that no bulky substituent prevent this.[17] The crystal structures in the present study are markedly different with no face-to-face interactions. Instead, in the butyldimethylsilylated derivative **5b** there are close contacts between alkyl groups and the aromatic ring, with neighboring molecules being oriented almost perpendicular to each other, whereas in **5a** the aromatic ring systems of adjacent molecules exhibit edge-to-face interactions resulting in an overall "herring-bone" arrangement in the crystal (Figure 3).

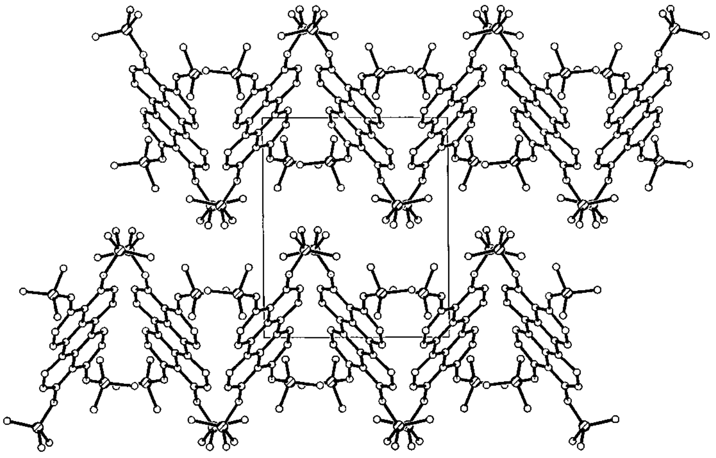
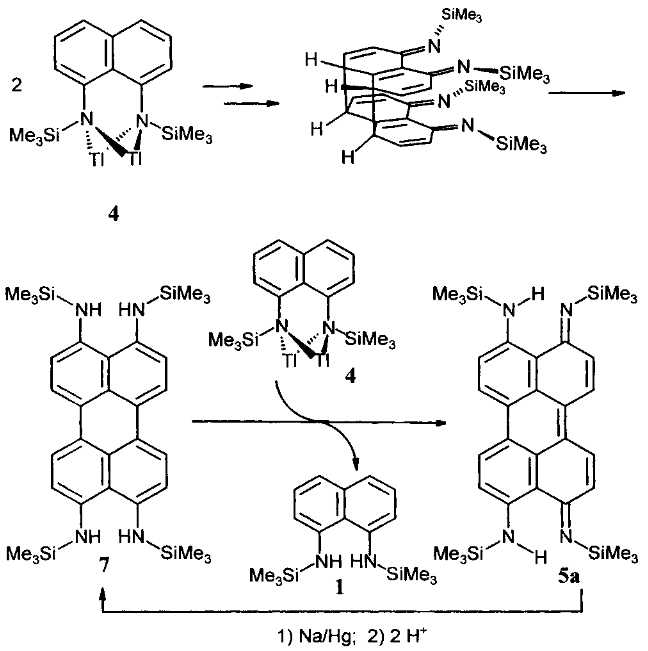


Figure 3. Packing of the perylene derivative **5a** in a "herring bone" arrangement in the crystal.

The high selectivity in the formation of **5a** from **4** and the exact 1:1 ratio in which the perylene and the diaminonaphthalene are formed raises the question of the possible mechanism of this coupling reaction (Scheme 3). ^{1}H NMR studies of the reaction in solution revealed the absence of any detectable intermediates, and a preliminary kinetic study suggests a rate law which is first order with respect to **4**. The demetalation of **4** may either lead to diradicals[18] or proceed by a disproportionation step similar to the reaction observed with InCl to generate **3.** This would be followed by subsequent demetalation and coupling (possibly in a concerted step) of the two naphthalene units. A hydrogen shift and flattening of the ring system, with concomitant aromatization, produces the tetraaminoperylene **7**. This strong reducing agent, which also may be generated specifically by Na/Hg reduction and subsequent protonation of **5a**, reacts with the third equivalent of the thallium amide **4** to form **5a** and the amine **1**, as required by the observed stoichiometry. The latter step could be studied independently by allowing **7** to react with **4**.

On the basis of the generation of **5a** and **5b** described above, a convenient one-pot synthesis of these perylene derivatives has been developed starting with silylated amines such as **1**. Subsequent in situ lithiation, metal exchange, and thermolysis gives the dyes in good yields (50–52% with respect to the diaminonaphthalene starting material, the theoretical maximum being 66%) with no detectable amounts of thallium remaining in solution, as established at the ppb



Scheme 3. Proposed mechanism for the formation of the perylenes from the thallium amides generated in situ.

level by atomic emission spectroscopy. Both the diaminonaphthalenes produced and the thallium metal may be retrieved and reused in subsequent conversions.

In conclusion, we have shown that the redoxchemistry in solution of amides of the heavy monovalent Group 13 metals may vary between predominantly metal–metal disproportionation, observed for indium, and oxidation of the ligand, observed for thallium. Given the appropriate type of "ligand system", this type of reaction can be developed into a powerful organic synthetic tool.

Experimental Section

3: Solid InCl (853 mg, 5.68 mmol) was added to a stirred solution of **2** (1.71 g, 2.83 mmol) in THF (30 mL) which was cooled to −60 °C. After the mixture was warmed to room temperature and stirred for 18 h the solvent was removed under reduced pressure, and the residue extracted with toluene (30 mL). The LiCl and indium metal formed in the reaction were removed by centrifugation,[20] and the centrifugate was evaporated to dryness. The residue was redissolved in THF (30 mL) and stored at 0 °C. Compound **3** precipitated as a yellow, highly crystalline solid (yield: 1.24 g, 90 %, m.p. 83 °C (decomp)).

4: Solid TlCl (959 mg, 4.00 mmol) was added to a stirred solution of **2** (1.21 g, 2.00 mmol) in THF (40 mL) which was cooled at −30 °C. After the mixture was stirred for 16 h at room temperature the solvent was removed in vacuo, and the residue extracted with toluene (40 mL). The LiCl formed in the reaction was separated by centrifugation, and the deep orange solution concentrated to 20 mL. Upon storing the solution at −35 °C for several days, compound **4** precipitated as a microcrystalline, orange solid (yield: 380 mg, 27 %).

5a, **b**: Solid TlCl (1.19 g, 4.98 mmol) was added at room temperature to a stirred solution of $[Li_2\{C_{10}H_6(NSiRMe_2)_2\})thf)_4]$ (R = Me, *t*Bu; 2.49 mmol) in 1,4-dioxane (40 mL), and the mixture was heated at 90 °C for 17 h. After removal of the solvent the residue was extracted with toluene (75 mL), and the LiCl and thallium metal formed in the reaction were removed by centrifugation. The dark green solution was concentrated to 40 mL and stored at −35 °C for 24 h. Compounds **5a** and **5b** precipitated as black-green needles with a purple luster (yield: **5a**: 373 mg, 50 %, m.p. 212 °C; **5b**: 497 mg, 52 %, m.p. 252 °C).

7: A solution of **5a** (300 mg, 0.50 mmol) in THF (35 mL) was added at room temperature to Na/Hg (Na: 1.00 mmol). After the mixture was stirred for 24 h the Hg metal was removed by filtration, and solid NEt_3HCl (138 mg, 1.00 mmol) in THF (15 mL) was added to the deep blue reaction mixture at −55 °C. After the reaction mixture was stirred for another 18 h at room temperature the solvent was removed under reduced pressure, the residue extracted with toluene (75 mL), and the NaCl generated in the reaction removed by centrifugation. The deep red solution was concentrated to 15 mL and stored at −35 °C for 24 h. Compound **7** was obtained as a vermillion solid (yield: 123 mg, 41 %).

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[7] Crystal data for **3**: $C_{40}H_{64}In_2N_4O_2Si_4$, $M_r = 974.95$, monoclinic, space group $P2_1/n$, $a = 10.3086(14)$, $b = 18.402(2)$, $c = 12.7880(14)$ Å, $\beta = 105.661(10)^\circ$, $V = 2335.8(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.386$ g cm^{-3}, $F(000) = 1004$, $\mu(Mo_{K\alpha}) = 1.125$ mm^{-1}, $T = 298(2)$ K. A yellow crystal ($0.20 \times 0.24 \times 0.36$ mm^3) was mounted in a Lindemann tube for data collection on a Siemens P4 diffractometer. The structure was determined by direct methods and refined on F^2 for 4109 independent reflections corrected for absorbance (T_{max} 0.883, T_{min} 0.691) of 5171 collected ($1.99 \leq \theta \leq 24.99^\circ$), $R(int) = 0.0264$. Anisotropic thermal parameters were assigned for all non-hydrogen atoms. The asymmetric unit consists of the half the centrosymmetric molecule. The hydrogen atoms were included in idealized positions and assigned the isotropic thermal parameters $U_{iso} = 1.2\ U_{eq}$ of the parent carbon atom for methylene groups and aromatic hydrogen atoms, and $U_{iso} = 1.5\ U_{eq}$ for methyl hydrogen atoms. At final convergence $R_1 = 0.0384$, $wR_2 = 0.0587$ ($I > 2\sigma(I)$), $R_1 = 0.0737$, $wR_2 = 0.0680$ (all data), GOF(F^2) = 0.995 for 490 parameters.[10b] For programs, see reference [19].

[8] Shorter covalent In–In bonds in a molecular compound have been reported for $[In\{In(2,4,6\text{-}iPr_3C_6H_2)_2\}_3]$: P. J. Brothers, K. Hübler, U. Hübler, B. C. Noll, M. Olmstead, P. P. Power, *Angew. Chem.* **1996**, *108*, 2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2355. Shorter In–In distances have also been established in the ternary oxide $In_{11}Mo_{40}O_{62}$ which contains linear In_5^{7+} and In_6^{8+} ions with In–In distances ranging between 2.624 and 2.689 Å.

[9] The identical UV/Vis spectra of **5a** and **5b** (recorded in pentane) are characterized by two intense bands in the visible region corresponding

to the π–π* transition ($\lambda_{max} = 635$ nm, $\lg\varepsilon = 4.3$, vibrational progression towards lower wavelengths: 1310 cm^{-1}) and the n–π* transition ($\lambda_{max} = 444$ nm, $\lg\varepsilon = 4.7$) involving the N substituents.

[10] Crystal data for **5a**: "$[Me_3SiN]_4$–perylene": $C_{32}H_{46}N_4Si_4$, $M_r = 599.09$, monoclinic, space group $P2_1/c$, $a = 13.727(17)$, $b = 10.587(10)$, $c = 12.885(10)$ Å, $\beta = 111.32(7)^\circ$, $V = 1744(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.141$ g cm^{-3}, $F(000) = 644$, $\mu(Mo_{K\alpha}) = 0.197$ mm^{-1}, $T = 293(2)$ K. All samples inspected diffracted extremely poorly. A dark green block ($0.72 \times 0.44 \times 0.32$ mm^3) was mounted in a Lindemann tube for data collection with a Siemens P4 diffractometer. The structure was determined by direct methods and refined on F^2 for 1198 independent reflections of 2189 collected ($1.59 \leq \theta \leq 18.00^\circ$), $R(\text{int}) = 0.1955$. Anisotropic thermal parameters were assigned for all non-hydrogen atoms, and chemically equivalent bonds in the structure were constrained to common values. Hydrogen atoms were included in idealized positions and assigned $U_{iso} = 1.5\,U_{eq}$ or $U_{iso} = 1.2\,U_{eq}$ of the parent carbon atom for methyl groups and aromatic carbon atoms, respectively. The amino hydrogen was disordered over two sites of equal occupancy and assigned a fixed isotropic thermal parameter of 0.10 Å^2. At final convergence $R_1 = 0.1063$, $wR_2 = 0.2020$ ($I > 2\sigma(I)$), $R_1 = 0.2421$, $wR_2 = 0.3195$ (all data), GOF (F^2) = 1.053 for 181 parameters. For programs, see reference [19]. Crystal data for **5b**: "$[t\text{BuMe}_2SiN]_4$-perylene": $C_{44}H_{70}N_4Si_4$, $M_r = 767.40$, triclinic, space group $P\bar{1}$, $a = 11.034(2)$, $b = 13.852(2)$, $c = 15.485(2)$ Å, $\alpha = 84.411(8)$, $\beta = 79.200(10)$, $\gamma = 80.047(9)^\circ$, $V = 2284.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.116$ g cm^{-3}, $F(000) = 836$, $\mu(Mo_{K\alpha}) = 0.164$ mm^{-1}, $T = 198(2)$ K. A dark green block ($0.60 \times 0.50 \times 0.34$ mm^3) was mounted in a Lindemann tube for data collection on a Siemens P4 diffractometer. The structure was determined by direct methods and refined on F^2 for 8055 independent reflections corrected for absorption (T_{max} 0.954, T_{min} 0.532) of 16109 collected ($1.34 \leq \theta \leq 25.00^\circ$), $R(\text{int}) = 0.0591$. Anisotropic thermal parameters were assigned for all non-hydrogen atoms. The asymmetric unit consists of the halves of two independent molecules each of which is exactly centrosymmetric. The two amino hydrogen atoms in the asymmetric unit were disordered over the four independent nitrogen atoms and were assigned half occupancy and a common isotropic thermal parameter which refined to 0.04 Å^2. The remaining hydrogen atoms were included in idealized positions and assigned $U_{iso} = 1.2\,U_{eq}$ of the parent carbon atom for methylene groups and aromatic hydrogen atoms, and $U_{iso} = 1.5\,U_{eq}$ for methyl hydrogen atoms. At final convergence $R_1 = 0.0674$, $wR_2 = 0.1525$ ($I > 2\sigma(I)$), $R_1 = 0.1228$, $wR_2 = 0.1858$ (all data), GOF(F^2) = 0.981 for 490 parameters. For programs, see reference [19]. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101183. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+49)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] All attempts to observe diradical intermediates by performing the thermolysis in an ESR tube and subsequent quenching the reaction in liquid N_2 were unsuccessful. The use of spin-trapping reagents was precluded by the extremely high reactivity of **4**, which thermally and unspecifically reacted with the trapping agents prior to its thermolysis. Attempts to detect radical intermediates by NMR spectroscopy at different field strengths and temperatures through observation of a CIDNP effect were equally unsuccessful. These results either indicate the absence of a free radical species in the coupling reaction or, alternatively, their short-lived nature.

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The Behavior of $[RAlX_2 \cdot THF]$ Compounds under Reductive Conditions: Tetrakis[tris(trimethylsilyl)methylaluminum(I)]—A Neutral Aluminum(I) Compound with σ-Bound Alkyl Groups and a Tetrahedral Structure[**]

Christoph Schnitter, Herbert W. Roesky,[*] Cord Röpken, Regine Herbst-Irmer, Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

The great interest in low-valent compounds of the higher homologues of Group 13 is reflected in several recent reviews on this class of compounds.[1] The first univalent aluminum compound that is stable at room temperature—$[\{AlCp^*\}_4]$, $Cp^* = \eta^5\text{-}C_5Me_5$, which contains π-bound C_5Me_5 groups—was synthesized and structurally characterized in 1991 by Schnöckel et al. It was prepared by the treatment of $(AlCl)_x$ with $[MgCp^*_2]$.[2] Somewhat later we reported a more facile synthesis of this compound: the reductive dehalogenation of $[\{Cp^*AlCl(\mu\text{-}Cl)\}_2]$ with potassium.[3] Despite many attempts, only two further neutral organoaluminum(I) compounds of type $[\{AlR\}_n]$ ($[\{AlCH_2CMe_3\}_4]$[4a] and $[\{AlSit\text{Bu}_3\}_4]$)[4b,c,e] have been reported; this is due to the tendency of this type of compound to disproportionate into elemental aluminum and AlR_3. The disproportionation reaction can be largely inhibited by the use of very bulky substituents. However, it has not as yet been possible to characterize these two compounds by diffraction methods.[4c,e]

The tris(trimethylsilyl)methyl group (trisyl group) is regarded as a particularly bulky group with electronically stabilizing properties.[5] The use of this substituent permitted the synthesis of the tetrameric compounds $[\{MC(SiMe_3)_3\}_4]$ of gallium,[6] indium,[7] and thallium.[8] We recently reported the synthesis of the trisylaluminum dihalides $[\{(Me_3Si)_3CAlF_2\}_3]$ and $[(Me_3Si)_3CAlX_2 \cdot THF]$ (X = F, Cl, Br, I),[9] which should be suitable precursors for the synthesis of low-valent trisylaluminum compounds.

We began our reduction experiments with the THF-free difluoride $[\{(Me_3Si)_3CAlF_2\}_3]$; however, it could not be dehalogenated, even with Na/K alloy in refluxing toluene. In contrast, the reaction of the THF-containing dichloride compound $[(Me_3Si)_3CAlCl_2 \cdot THF]$ with the appropriate reducing agent in toluene did not lead to the expected $[\{AlC(SiMe_3)_3\}_n]$, but to the tricyclic chiral compound **1** in high yields [Eq. (1)]. During the reductive dehalogenation the ring of the coordinated THF molecule had opened, which resulted in dimerization. Compound **1** is a colorless solid (m.p. 246 °C) that was completely characterized by ^{1}H NMR, ^{29}Si NMR, and IR spectroscopy as well as by mass spectrom-

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[*] Prof. Dr. H. W. Roesky, Dipl.-Chem. C. Schnitter, Dipl.-Chem. C. Röpken, Dr. R. Herbst-Irmer, H.-G. Schmidt, Dr. M. Noltemeyer
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-37077 Göttingen (Germany)
Fax: (+49)551-39-3373
E-mail: hroesky@gwdg.de

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