$[Ln^{II}Al^{III}_2(alkyl)_8]_x$: donor addition instead of donor-induced cleavage†

Marcus G. Schrems, H. Martin Dietrich, Karl W. Törnroos and Reiner Anwander*

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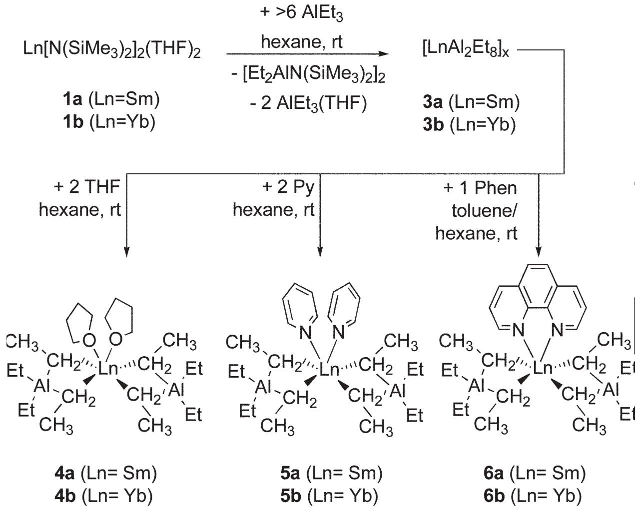
$(SmAl_2Me_8)_x$ and $(SmAl_2Et_8)_x$ are obtained *via* a silylamide elimination reaction from $Sm[N(SiMe_3)_2]_2(THF)_2$ and excess AlR_3 (R = Me, Et); $(LnAl_2Et_8)_x$ (Ln = Sm, Yb) react with THF, pyridine, and 1,10-phenanthroline to form the first donor adducts of homoleptic peralkylated Ln–Al heterobimetallic complexes.

Potential applications of rare-earth metal tetraalkylaluminate complexes in olefin polymerization, be it as initiator or model compounds,[1–3] or as molecular precursors for mixed metal semiconductor materials,[4] have motivated substantial research in this area. Moreover, our recent work has shown that application of Lappert's concept of Lewis base-induced aluminate cleavage[5] can be utilized for the generation of novel organolanthanide species. Accordingly, such donor-induced cleavage of homoleptic $Ln(AlMe_4)_3$ (Ln = Y, Lu) led to previously elusive alkyl compounds $[YMe_3]_n$ and $[LuMe_3]_n$.[6,7] While these investigations have focused on Ln^{III} derivatives, the chemistry of corresponding Ln^{II}–Al^{III} heterobimetallic species remained largely unexplored and to date, only the synthesis and solid state structure of homoleptic $(YbAl_2Et_8)_x$ have been reported.[8] It is anticipated that such Ln^{II}–Al^{III} heterobimetallic species can display multifunctional reagents in organic synthesis and precursors for novel organolanthanide(II) chemistry.

Heterobimetallic peralkylated complexes $(SmAl_2Me_8)_x$ **2a** and $(SmAl_2Et_8)_x$ **3a** formed by treatment of $Sm^{II}[N(SiMe_3)_2]_2(THF)_2$ **1a** with excess AlR_3 (R = Me, Et) (Scheme 1).‡[9] Isolation of light purple **2a** was facilitated by its quantitative precipitation from hexane solution, while **3a** could be obtained by fractional crystallization as a purple black solid in 80% isolated yield. Complex **2a** is insoluble in aliphatic or aromatic solvents, however, readily dissolves in THF. The ^1H NMR spectrum of hexane-soluble paramagnetic **3a** exhibits only two resonances at −38.3 (CH_2) and −1.4 ppm (CH_3) for the ethyl ligands indicating a highly fluxional alkyl bonding.[10] In order to examine the feasibility of donor (Do)-induced cleavage reactions *via* formation of $AlEt_3Do$ complexes $LnAl_2Et_8$ **3a** (Ln = Sm) and **3b** (Ln = Yb) were reacted with Do molecules of varying bonding strength and bonding mode.‡ However, instead of putative "aluminate" cleavage, donor adducts $LnAl_2Et_8(THF)_2$ [**4a**: Ln = Sm, **4b**: Ln = Yb (light-yellow)], $LnAl_2Et_8(Py)_2$ [**5a**: Ln = Sm, **5b**: Ln = Yb (red)] and $LnAl_2Et_8(Phen)$ [**6a**: Ln = Sm, **6b**: Ln = Yb (dark green)] formed in good yields. The ^1H NMR spectra of the Yb^{II} compounds show a triplet and a quartet resonance for the ethyl groups, whereas the black paramagnetic Sm^{II} congeners each display broad singlets. For **4a**, the proton resonances appear at −28.0 (CH_2) and 1.9 ppm (CH_3) in C_6D_6; surprisingly, in THF-d_8 a strong paramagnetic shift was absent and signals of $SmAl_2Et_8(THF\text{-}d_8)_2$ were detected at −2.3 (CH_2) and −0.6 ppm (CH_3). For both the methylene and methyl protons of the diamagnetic Yb^{II} adducts, a marked shift to lower field compared to the donor-free compound was found, depending on the donor strength. For example, the ^1H resonances of **4b** appeared at 0.20 (CH_2) and 1.54 ppm (CH_3), in comparison to the 0.11 (CH_2) and 1.30 ppm (CH_3) of homoleptic **3b**. This is also in agreement with the different colours of compounds **4b–6b**indicating significant metal-to-ligand charge transfer. For comparison, enhanced metal-to-ligand charge transfer and formation of paramagnetic $Yb^{III}Do^{\bullet -}$ species occurred in ytterbocene Do adduct complexes, depending on the substituents of the cyclopentadienyl rings and the reduction potential of the Do ligands.[11] Accordingly, an electron exchange coupling was discussed in the presence of the electron-donating pentamethylcyclopentadienyl ligand affording paramagnetic complexes $(C_5Me_5)_2Yb(BiPy)$ [red-brown] and $(C_5Me_5)_2Yb(Phen)$ [dark blue] (note that dark green $(C_5Me_5)_2Yb(Py)_2$ is diamagnetic). In contrast, electron-withdrawing $SiMe_3$ substituents gave diamagnetic complexes $[1,3\text{-}(Me_3Si)_2\text{-}C_5H_3]_2Yb(BiPy)$ [green] and $[1,3\text{-}(Me_3Si)_2C_5H_3]_2Yb(Phen)$ [red].

Single crystals of **4a** and **4b** were grown from a hexane–toluene mixture and subjected to X-ray diffraction analysis.§ The molecular structure of **4a/b** is shown in Fig. 1 together with selected bond lengths and angles. THF adduct complex **4a** is a rare example of a σ-bonded Sm^{II} alkyl compound.[12,13] Complexes **4a**



Scheme 1 Synthesis of homoleptic $LnAl_2Et_8$ according to the silylamide route and their conversion into donor adduct complexes.

Department of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway. E-mail: reiner.anwander@kj.uib.no.

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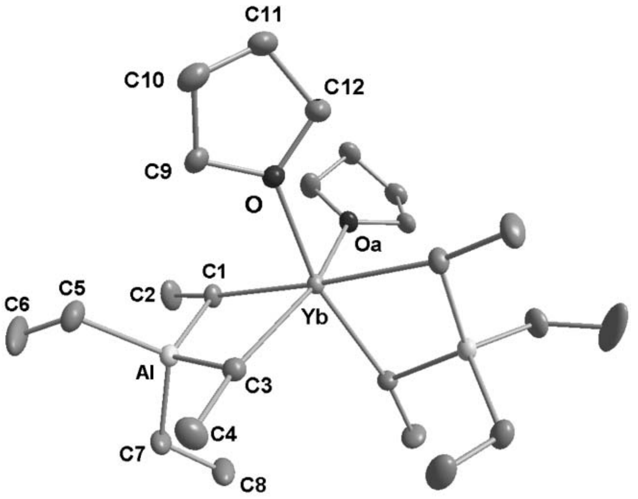

Fig. 1 Molecular structure of **4b**. Selected bond lengths (Å) and angles (°) for **4b**: Yb–Al 3.2139(5), Yb–C1 2.652(2), Yb–C3 2.673(2), Yb–O 2.395(1), Al–C1 2.059(2), Al–C3 2.066(2); O–Yb–Oa 87.23(6), O–Yb–C1 92.39(5), O–Yb–C3 91.31(5), C1–Yb–C3 79.42(5), Yb–C1–C2 166.7(1), Yb–C3–C4 169.8(1), Al–C1–Yb 85.06(6), Al–C3–Yb 84.35(5), C1–Al–C3 111.15(7); for **4a**: Sm–Al 3.3240(8), Sm–C1 2.765(3), Sm–C3 2.783(2), Sm–O 2.498(2), Al–C1 2.059(3), Al–C3 2.067(2); O–Sm–Oa 88.6(9), O–Sm–C1 91.0(7), O–Sm–C3 90.6(7), C1–Sm–C3 76.4(7), Sm–C1–C2 166.1(2), Sm–C3–C4 169.1(2), Al–C1–Sm 85.8(8), Al–C3–Sm 85.2(8), C1–Al–C3 112.6(1).

and **4b** are isostructural featuring the commonly observed η^2-coordination mode of the *homobridging* tetraethylaluminate ligands. The overall alkyl bonding and molecule geometry is similar to that found for the "anionic unit" of precursor compound **3b**, which was described formally as a polymeric network of $[Yb(AlEt_4)]^+$ and $[Yb(AlEt_4)_3]^-$ units.[8] Displacement of one of the $AlEt_4^-$ units of the network structure of **3b** by two THF molecules gives the monolanthanide species **4b**. The average Yb–C(CH_2) bond length of 2.663 Å in 6-coordinate **4b** agrees with that in 6-coordinate $Yb^{II}(C_6F_5)_2(THF)_4$ [2.649(3) Å],[14] however, it is significantly longer than the Yb–C σ-bond distances in homoleptic formally 2-coordinate, yet agostically saturated $Yb^{II}[C(SiMe_3)_3]_2$ (av. 2.495 Å)[15] and heteroleptic 5-coordinate $Yb^{II}(C_6H_3Ph_2\text{-}2,6)I(THF)_3$ [2.529(4) Å].[16] Similar Yb–C(CH_2) bond lengths were found in $YbAl_2Et_8$ **3b** (av. 2.675 Å) while *heterobridged* complex η^6-(Me_3Si-fluorene-$AlMe_3$)- η^5-(Me_3Si-fluorenyl)Yb^{II} exhibits two longer Yb–C($AlMe_3$) distances (2.70 and 2.80 Å) in the "agostic" range.[13] The average Yb–O bond distance of 2.394 Å is similar to that found in $[Yb^{II}(C_6H_3Ph_2\text{-}2,6)_2(THF)_2]$ (2.412 Å).[17] Complexes $[Yb^{II}\{C(SiMe_3)_3\}I(OEt_2)]_2$ [2.348(1)] and $Yb^{II}(C_6F_5)_2(THF)_4$ [av. 2.434 Å] show considerably shorter and longer Yb–O bond distances, respectively.[14,15] Due to its larger radius, the Sm^{II} derivative **4a** reveals longer average Ln–C(CH_2) and Ln–O bond distances of 2.774 Å and 2.499 Å, respectively. $[Sm^{II}\{C(SiMe_3)_2(SiMe_2OMe)\}_2(THF)]$ featuring a donor-functionalized alkyl ligand shows similar Sm–C and Sm–O(THF) bond distances of 2.787(5)/2.845(5) and 2.545(4) Å, respectively.[12] The considerably longer Sm–C distances of 2.87 ($AlMe_3$) and 2.92 Å ($AlEt_3$) in *heterobridged* complexes $[\eta^6$-(Me_3Si-fluorene-AlR_3)$]_2Sm^{II}$ (R = Me, Et) were discussed as agostic interactions.[13]

In conclusion, the different reactivity of heterobimetallic homoleptic $Ln^{III}Al^{III}{}_3Me_{12}$ and $Ln^{II}Al^{III}{}_2R_8$ (R = Me, Et) toward Lewis base molecules clearly reflects a different Ln–C bonding. While the former display true aluminate complexes $Ln[AlMe_4]_3$ like $Li[AlEt_4]$ and $Mg[AlMe_4]_2$,[18,19] divalent derivatives such as complexes **4–6** are better described as lanthanidate complexes $[AlEt_2]_2[LnEt_4(Do)_x]$ similar to $[Li(Do)_x]_3[Ln^{III}Me_6]$.[20] This implicates that the Ln–C bonding nature cannot be rationalized on the basis of an electronegativity scale E_N of the metal centres involved (E_N scale according to Pauling: Li = 1.0, Ln^{III} = 1.1–1.3, Al^{III} = 1.6).[21] Due the dependency of E_N on the oxidation state of the metal centre the E_N value for Ln^{II} centers should be <1.1 and therefore favour aluminate bonding. Also, the Lewis acidity criterion ($Al^{III} > Ln^{III} >> Ln^{II}$) commonly considered as the driving force for AlR_3Do separation seems to be not applicable. Rather it has to be the increased covalent Ln^{II}–ligand bonding which controls such easily performed Lewis base addition reactions. We are currently investigating the potential of "$Ln^{II}AlR_4$" moieties as synthetic precursors or ancillary ligand sets in organolanthanide chemistry.

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Notes and references

‡ All operations were performed with rigorous exclusion of air and water, using high-vacuum and glovebox techniques. $Sm^{II}[N(SiMe_3)_2]_2(THF)_2$ **1a** was synthesized according to a slightly modified literature procedure[9] by reacting $SmI_2(THF)_2$ with 1.9 eq. $KN(SiMe_3)_2$ in THF and crystallizing from hexane. Representative synthesis for **2a**, **4b**, **5b**, and **6b**: Addition of a solution of $AlMe_3$ (3.99 mmol, 288 mg) in 10 ml of hexane to a stirred solution of **1a** (0.50 mmol, 308 mg) in 10 ml of hexane caused precipitation of light purple **2a**. After 2 hours stirring the reaction mixture was centrifuged and washed several times with hexane to give **2a** in almost quantitative yield (154 mg, 95%). IR (Nujol, cm^{-1}): 1195 w, 1171 w, 1039 m, 795 w, 778 w, 705 m, 627 w, 602 w, 573 m, 554 m, 512 w, 476 w, 459 w, 424 w. Elemental analysis: calculated C (29.60), H (7.45); found C (30.53), H (7.54). **3b** (0.30 mmol, 138 mg) was dissolved in 8 ml of hexane and a mixture of THF (0.64 mmol, 46 mg) and 8 ml of hexane was added. After 2 hours stirring the solution was concentrated to 5 ml. **4b** crystallized at −35 °C (148 mg, 82%): ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 3.33 (m, 8H, THF-I), 1.54 [t, $^3J_{H,H}$ = 7.8 Hz, 24H, CH_2CH_3], 1.17 (m, 8H, THF-II), 0.20 (q, $^3J_{H,H}$ = 7.8 Hz, 16H, CH_2CH_3). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ = 70.3 (–CH_2CH_2O–), 25.2 (–CH_2O–), 12.0 (–CH_3), 7.0 (Al–CH_2). IR (Nujol, cm^{-1}): 1154 w, 1020 m, 975 m, 925 w, 863 m, 634 m, 527 w. Elemental analysis: calculated C (47.75), H (9.35); found C (47.43), H (9.24). To a stirred solution of **3b** (0.26 mmol, 120 mg) in 8 ml of hexane were added 2 eq. of pyridine (Py, 0.53 mmol, 42 mg) diluted with 8 ml of hexane. The colour of the solution changed from yellow to red. After 2 hours stirring, half of the solvent was evaporated. The remaining solution was filtered and cooled to −35 °C overnight yielding **5b** as red crystals (135 mg, 84%). ^1H NMR (C_6D_6, 25 °C): δ = 8.16 (br s, 4H, Py), 6.77 (br t, 2H, Py), 6.45 (br t, 4H, Py), 1.55 (t, $^3J_{H,H}$ = 7.8 Hz, 24 H, CH_2CH_3), 0.43 (q, $^3J_{H,H}$ = 7.8 Hz, 16H, CH_2CH_3). ^{13}C NMR (C_6D_6, 25 °C): 149.0 (Py), 139.2 (Py), 121.9 (Py), 12.2 (–CH_3), 7.8 (Al–CH_2). IR (Nujol, cm^{-1}): 1598 w, 1216 w, 1186 w, 1157 w, 1070 w, 1037 w, 981 m, 952 m, 753 m, 698 m, 645 m, 630 m. Elemental analysis: calculated C (50.56), H (8.16), N (4.54); found C (49.65), H (7.90), N (4.51). To a stirred solution of **3b** (0.30 mmol, 138 mg) in 8 ml of hexane was added 1 eq. of phenanthroline (Phen, 59 mg, 0.30 mmol) dissolved in 10 ml of toluene. The colour of the solution changed from yellow to dark green. After 2 hours stirring, half of the solvent was evaporated. The remaining solution was filtered and cooled to −35 °C overnight yielding **6b** as dark green crystals (171 mg, 89%). ^1H NMR (C_6D_6, 25 °C): δ = 8.72 (d, $^3J_{H,H}$ = 4.3 Hz, 2H, Phen), 7.24 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, Phen), 6.80 (s, $^3J_{H,H}$ = 4.3 Hz, 2H, Phen), 6.73 (dd,

${}^3J_{H,H}$ = 4.3 Hz, ${}^3J_{H,H}$ = 8.1 Hz, 2H, Phen), 1.52 (t, ${}^3J_{H,H}$ = 7.6 Hz, 24H, CH_2CH_3), 0.46 (q, ${}^3J_{H,H}$ = 7.6 Hz, 16H, CH_2CH_3). ${}^{13}C$ NMR (C_6D_6, 25 °C): 150.1 (Phen), 144.1 (Phen), 138.9 (Phen), 129.7 (Phen), 127.1 (Phen), 124.5 (Phen), 12.0 (–CH_3), 7.2 (Al–CH_2). IR (Nujol, cm^{-1}): 1517 w, 1146 w, 1098 w, 980 m, 944 m, 841 m, 766 w, 649 m. Elemental analysis: calculated C (52.57), H (7.56), N (4.38); found C (53.17), H (7.52), N (4.45).

§ Crystallographic data for **4a** and **4b**: $C_{24}H_{56}Al_2O_2Sm$, M = 581.00, monoclinic, space group $C2/c$ (no. 15), a = 15.139(1) Å, b = 14.626 (1) Å, c = 14.325(1) Å, β = 99.302(1)°, V = 3130.2(5) Å^3, Z = 4, ρ_{calc} = 1.233 g cm^{-3}, $F(000)$ = 1216, μ(Mo-K$_\alpha$) = 1.947 mm^{-1}, λ = 0.71073 Å, T = 153 K. The 25778 reflections measured on a Bruker SMART 2K CCD area detector yielded 4600 unique data (θ_{max} = 30.0°, R_{int} = 0.054) [4309 observed reflections ($I > 2\sigma(I)$]. $R1$ = 0.0300, w$R2$ = 0.0775. CCDC reference number 282719. $C_{24}H_{56}Al_2O_2Yb$, M = 603.69, monoclinic, space group $C2/c$ (no. 15), a = 14.8252(5) Å, b = 14.5838(5) Å, c = 14.3734(5) Å, β = 98.311(1)°, V = 3075.0(2) Å^3, Z = 4, ρ_{calc} = 1.304 g cm^{-3}, $F(000)$ = 1248, μ(Mo-K$_\alpha$) = 3.113 mm^{-1}, λ = 0.71073 Å, T = 153 K. The 24331 reflections measured on a Bruker SMART 2K CCD area detector yielded 4695 unique data (θ_{max} = 30.5°, R_{int} = 0.020) [4502 observed reflections ($I > 2\sigma(I)$]. $R1$ = 0.0169, w$R2$ = 0.0444. CCDC 282720. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512047k

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