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High tetraalkylaluminate fluxionality in half-sandwich complexes of the trivalent rare-earth metals†

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Steric factors govern the formation of half-sandwich complexes $(C_5Me_4R)Ln[N(SiHMe_2)_2]_2$ according to acid–base reactions utilising $Ln[N(SiHMe_2)_2]_3(thf)_2$ and substituted cyclopentadienes. Subsequent trimethylaluminium-promoted silylamide elimination produces the first half-sandwich bis(tetramethylaluminate) complexes $(C_5Me_4R)Ln(AlMe_4)_2$.

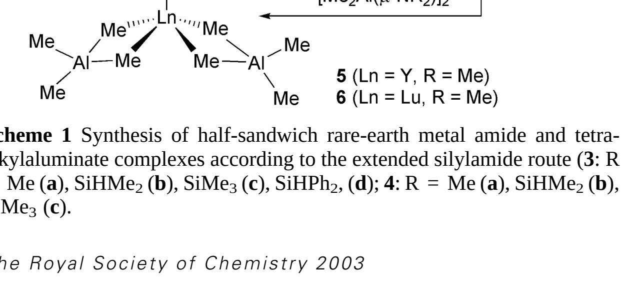
New synthetic pathways toward bis(amido) and bis(hydrocarbyl) half-sandwich complexes are a prominent target in organolanthanide(III) chemistry.[1] Such mono(cyclopentadienyl) derivatives is ascribed a high potential in homogeneously catalyzed reactions, e.g. in the polymerization of styrene or acrylonitrile.[2] This potential applicability was probably rationalised on the basis of the superb performance of structurally related $CpTiX_3$-type compounds in syndiotactic styrene polymerization when combined with MAO.[3–5] However, compared to the ubiquitous "$Cp_2Ln(III)X$" lanthanidocene complexes, derivatives $CpLn(III)X_2$ display enhanced electronic and steric unsaturation, and hence, are more difficult to handle.[6–9] As a consequence, extensive Lewis base complexation and ligand redistribution reactions due to high Cp and X ligand mobility are commonly observed. Noteworthy, Cp^*LnR_2 (Ln = La, Ce, R = $CH(SiMe_3)_2$; Ln = Ce, R = $N(SiMe_3)_2$)[6] and $Cp^*Gd(CH_2Ph)_2(thf)$[7] and ate complexes $[Li(thf)_4][(C_5H_4t\text{-}Bu)Yb(NPh_2)_3]$ and $[Li(dme)_3][(C_5H_4Me)La(NPh_2)_3]$[9] represent the only structurally characterized mononuclear mono(cyclopentadienyl) complexes featuring one type of additional hydrocarbyl and amide ligand, respectively.

Depending on the size of the metal centre and the steric bulk of the cyclopentadienyl ligand, complexes $(C_5Me_4R)Ln[N(SiHMe_2)_2]_2$ (**3**: Ln = Y, **4**: Ln = Lu; R = H, Me, $SiHMe_2$, $SiMe_3$, $SiHPh_2$) can be selectively obtained by the extended silylamide route (Scheme 1).[10]†‡ The silyl-substituted tetramethylcyclopentadienes were synthesized by standard methods.[11]

For example, the combination of small rare-earth metal centres and Cp* (R = Me) affords such half-sandwich complexes in moderate crystallised yields (**3a**: Y/Cp*, 73%;[12] **4a**: Lu/Cp*, 40%). Interestingly, the THF donor molecules are completely displaced during the acid–base ligand exchange. The corresponding La/Cp*-reaction gave a mixture of complexes $Cp^*La[N(SiHMe_2)_2]_2$ and $Cp^*_2La[N(SiHMe_2)_2]$.[13]§ The IR spectra (Nujol mull) of complexes $Cp^*Ln[N(SiHMe_2)_2]_2$ (**3a**, Ln = Y; **4a**, Ln = Lu) reveal the presence of asymmetrically coordinated silylamide ligands as evidenced by two strong, well-resolved ν(SiH) bands at 2066 (2069) and 1833 (1820) cm^{-1}, respectively. The lower-energy frequencies indicate strong Ln–H–Si β-agostic interactions in the solid state. A variable temperature NMR study in the range of 25 to −90 °C showed only a single Si*H* signal at 4.49 (**3a**) and 4.59 (**4a**) ppm, which is in agreement with highly fluxional silyl groups in solution. The use of silyl-substituted tetramethylcyclopentadienes $HC_5Me_4(SiR_3)$ gave the half-sandwich complexes in excellent yields which can be attributed to the lower p*K*a values of the ligand precursor (**3b**: Y/$SiHMe_2$, 93%; **3c**: Y/$SiMe_3$, 93%; **3d**: $SiHPh_2$, 83%; **4b**: Lu/$SiHMe_2$, 90%; **4c**: Lu/$SiMe_3$, 87%; yields determined by NMR only).†,‡

We found that a trimethylaluminium-promoted alkylation of complexes **3a** and **4a** is a viable route for the synthesis of mono-Cp Ln(III) hydrocarbyl complexes (Scheme 1).†,‡ Remarkably, complete silylamide elimination occurred without ligand redistribution as evidenced by spectroscopic and microanalytical data. The bis(aluminate) complexes $Cp^*Ln(AlMe_4)_2$ (**5a**, Ln = Y; **6a**, Ln = Lu) could be efficiently separated from the co-product $\{Me_2Al[\mu\text{-}N(SiHMe_2)_2]\}_2$ by fractional crystallization from hexane solution. Enhanced steric unsaturation in these half-sandwich complexes was clearly revealed by ^1H NMR spectroscopy. Even at −90 °C only a single proton resonance appeared for the tetramethylaluminate ligands which is consistent with rapid exchange of the bridging and terminal methyl groups.

Complex **6a** was also characterized by an X-ray structure analysis (Fig. 1).¶ The most striking feature of the solid state structure is the differently bonded tetramethylaluminate moieties. One $AlMe_4^-$ ligand coordinates in the routinely observed η^2-fashion forming an almost planar heterobimetallic $Lu(\mu\text{-}CH_3)_2Al(CH_3)_2$ moiety with a torsion angle ∠C–Lu–C–Al1 of 6°.[14] However, the second $AlMe_4^-$ ligand features an unusual η^2-coordination, which is seen by (*i*) an atypically bent heterobimetallic $Lu(\mu\text{-}CH_3)_2Al(CH_3)_2$ moiety (∠C–Lu–C–Al2 28°), (*ii*) elongated Lu–(μ-CH_3) bond lengths (Δ_{Lu-C} = ca. 0.08 Å), (*iii*) a shortened Lu–Al distance (Δ_{Lu-Al} = ca. 0.15 Å), and (*iv*) an additional Lu–(μ-CH_3) contact of 3.447 Å. For comparison, the Lu–C(μ) bond lengths in homometallic asymmetrically bridged $Cp^*_2Lu(\mu\text{-}Me)LuCp^*_2Me$ with 7- or 8-coordinate lutetium centres are 2.440(9) and 2.756(9) Å,



Scheme 1 Synthesis of half-sandwich rare-earth metal amide and tetraalkylaluminate complexes according to the extended silylamide route (**3**: R = Me (**a**), $SiHMe_2$ (**b**), $SiMe_3$ (**c**), $SiHPh_2$, (**d**); **4**: R = Me (**a**), $SiHMe_2$ (**b**), $SiMe_3$ (**c**).

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† Electronic supplementary information (ESI) available: complete synthesis and characterization data. See http://www.rsc.org/suppdata/cc/b2/b212754g/

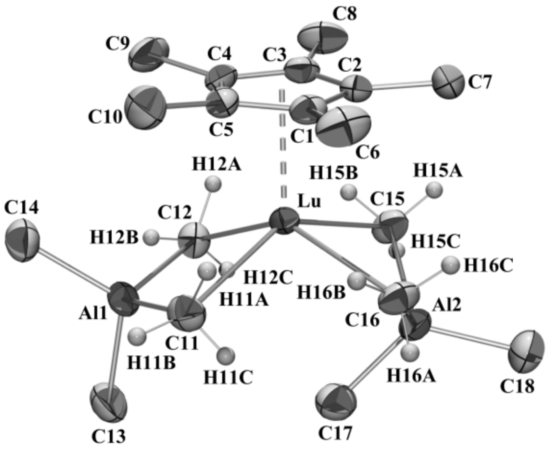
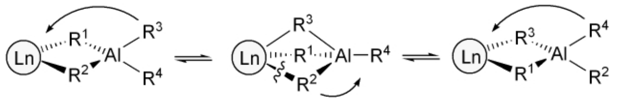


Fig. 1 Molecular structure of **6a**. Selected bond lengths (Å) and angles (°): Lu–Al1 3.0612(9), Lu–Al2 2.9138(9), Lu–C(Cp*) 2.566(3)–2.603(3), Lu–C11 2.501(3), Lu–C12 2.509(3), Lu–C15 2.597(3), Lu–C16 2.572(3), Lu–H11A 2.41(3), Lu–H12A 2.44(3), Lu–H15B 2.46(4), Lu–H16B 2.41(3), Al1–C11 2.082(3), Al1–C12 2.072(3), Al1–C13 1.962(3), Al1–C14 1.972(3), Al2–C15 2.065(3), Al2–C16 2.067(4), Al2–C17 1.959(3), Al2–C18 1.963(3); Al1–Lu–Al2 112.01(2), C11–Lu–C12 84.4(1), C15–Lu–C16 80.0(1), C11–Lu–C16 84.5(1), C12–Lu–C15 85.0(1), Lu–C11–Al1 83.3(1), Lu–C12–Al1 83.3(1), Lu–C15–Al2 76.4(1), Lu–C16–Al2 77.0(1), Lu–C11–H11A 73(2), Lu–C11–H11B 162(2), Lu–C11–H11C 90(2), Lu–C12–H12A 74(2), Lu–C12–H12B 161(2), Lu–C12–H12C 93(2), Lu–C15–H15A 118(2), Lu–C15–H15B 71(2), Lu–C15–H15C 139(3), Lu–C16–H16A 137(2), Lu–C16–H16B 69(2), Lu–C16–H16C 116(2).

respectively.[15] A considerably smaller deviation of the four-membered metallacycle from planarity was also reported for complex $Cp_2Y(\mu\text{-}CH_3)_2Al(CH_3)_2$ (∠C–Y–C–Al1 10–13°).[16] In complex **6a**, the hydrogen atoms of the bridging methyl groups were located and refined. The bridging 5-coordinate carbon atoms display severely distorted trigonal bipyramidal geometries with one hydrogen atom and the lutetium metal in the apical positions (∠Lu–C11–H11B 162(2)°). Moreover, one of the equatorial hydrogen atoms each forms a close contact to the lutetium centre (2.41(3)–2.46(4) Å) involving angles ∠Lu–C–H as acute as 69(2)°. These solid-state structural features can be interpreted in terms of Lu–H–C interactions, which, however, cannot be observed by any spectroscopic method.

We have recently detected truly η³-coordinating $AlEt_4^-$ ligands in the solid state structure of homoleptic $[Yb(AlEt_4)_2]_n$ involving the *large* Yb(II) centre.[17] This previous structural evidence combined with the highly fluxional behaviour of **6a** in solution, implicating transient η²/η³-coordinating $AlMe_4^-$ moieties, gives striking evidence for an associative methyl group exchange at sterically unsaturated rare-earth metal centres (Scheme 2).‖[18] Note that intramolecular methyl group exchange in trimethylaluminium, Al_2Me_6, occurs via a dissociative mechanism.[19]



Scheme 2 Proposed associative methyl group exchange in rare-earth tetraalkylaluminate complexes.

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Notes and references

‡ All operations were performed with rigorous exclusion of air and water, using high-vacuum and glovebox techniques. Representative synthesis for **4a** and **6a**: A solution of Cp*H (21.00 mmol, 2.861 g) in 10 mL of toluene was added to a solution of **1b** (7.00 mmol, 5.013 g) in toluene and refluxed for 70 h. After removal of solvent and released silylamine, the residue was extracted with hexane and the hexane fraction crystallized at −45 °C. **4a** was isolated as colourless plates (2.80 mmol, 1.60 g, 40%): IR (Nujol, ν/cm^{-1}): 2069vs, 1820s, 1732m, 1460vs, 1377s, 1246s, 1044vs, 900vs, 841s, 790s, 765s, 721m, 646w, 623w, 603w, 409w. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 4.59 (sp, $^3J_{H,H}$ = 3.0 Hz, 4H, SiH); 2.15 (s, 15H, Cp–Me); 0.26 (d, $^3J_{H,H}$ = 3.0 Hz, 24H, NSiMe). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 119.3 (Cp–C), 11.4 (Cp-Me), 3.0 (NSiMe). **4a** (0.87 mmol, 500 mg) was dissolved in 10 mL of hexane and an excess of $AlMe_3$ (6.9 mmol, 501 mg) added. After stirring for 2 h at ambient temperature, the slightly cloudy reaction mixture was centrifuged. The clear solution yielded colourless crystals of **6a** at −45 °C (0.62 mmol, 300 mg, 71%): IR (Nujol, ν/cm^{-1}): 1462vs, 1377vs, 1258w, 1237m, 1213m, 1193m, 1023w, 913w, 855m, 721s, 579m, 499w, 458w. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.75 (s, 15H, Cp–Me); −0.18 (s, 24H, AlMe). ^{13}C NMR (100.6 MHz, C_6D_6, 25°C): δ 120.9 (Cp-C), 11.8 (Cp-Me), 1.49 (br s, AlMe). Satisfactory elemental analyses were obtained for **4a** and **6a** (C, H, N).

§ Similar observations were made by Teuben et al. when studying corresponding acid–base reactions of homoleptic complexes $Ln[N(SiMe_3)_2]_3$ and $Ln[CH(SiMe_3)_2]_3$ with Cp*H. However, due to an increased thermal lability of the hydrocarbyl ligand and a higher kinetic barrier for Cp* introduction [steric bulk: $CH(SiMe_3)_2 \approx N(SiMe_3)_2 > N(SiHMe_2)_2$], well-defined half-sandwich complexes of the smaller rare-earth elements could not be obtained.[13] Also for steric reasons, putative $Cp^*Lu[CH(SiMe_3)_2]_2$ could not be obtained by a salt metathesis reaction starting from $Cp^*Lu[CH(SiMe_3)_2]_2Cl_2Li(thf)_2$ and $LiCH(SiMe_3)_2]_2$.[6b]

¶ *Crystallographic data for* **6a**: $C_{18}H_{39}Al_2Lu$, M = 484.42, orthorhombic, space group *P*bca, a = 17.2295(1), b = 14.3690(1), c = 17.9638(1) Å, V = 4447.31(5) Å³, Z = 8, ρ_{calc} = 1.447 gcm^{-3}, $F(000)$ = 1952, $\mu(\text{Mo–K}_\alpha)$ = 4.513 mm^{-1}, λ = 0.71073 Å, T = 173 K. The 48726 reflections measured on a Nonius Kappa CCD system yielded 4063 unique data (Θ_{max} = 25.4°, R_{int} = 0.033) [3617 observed reflections ($I > 2\sigma(I)$]. $R1$ = 0.0208, $wR2$ = 0.0499. CCDC reference number 200967. See http://www.rsc.org/suppdata/cc/b2/b212754g/ for crystallographic data in cif or other electronic format.

‖ An associative mechanism is also found by a variable temperature NMR investigation of *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y(AlMe_4)$ in the temperature range of 25 to 100 °C. Line shape treatment led to an entropy barrier ΔS‡ of −130(8) J K^{-1}mol^{-1} which is in agreement with a highly ordered transition state favouring an η³-bonded tetramethylaluminate moiety (cf., ΔS‡ = +123.1 J K^{-1}mol^{-1} for Al_2Me_6).[15]

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