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 CpTiX₃-type compounds in syndiotactic styrene polymerization when combined with MAO.3-5 However, compared to the ubiquitous "Cp₂Ln(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 $[Li(thf)_4][(C_5H_4t-$ Bu)Yb(NPh₂)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(SiHMe₂)₂]₂ and Cp*₂La[N(SiHMe₂)₂].¹³§ (Nujol mull) IŔ of The spectra 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 v(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 SiH signal at 4.49 (3a) and 4.59 (4a) ppm, which is in agreement with highly fluxional

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

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 pK_a values of the ligand precursor (**3b**: Y/SiHMe₂, 93%; **3c**: Y/SiMe₃, 93%; **3d**: SiHPh₂, 83%; **4b**: Lu/SiHMe₂, 90%; **4c**: Lu/SiMe₃, 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(AlMe₄)₂ (**5a**, Ln = Y; **6a**, Ln = Lu) could be efficiently separated from the coproduct {Me₂Al[μ -N(SiHMe₂)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 AlMe₄⁻ ligand coordinates in the routinely observed η^2 -fashion forming an almost planar heterobimetallic Lu(μ -CH₃)₂Al(CH₃)₂ moiety with a torsion angle \angle C–Lu–C–Al1 of 6°.¹⁴ However, the second AlMe₄⁻ ligand features an unusual η^2 -coordination, which is seen by (*i*) an atypically bent heterobimetallic Lu(μ -CH₃)₂Al(CH₃)₂ moiety (\angle C–Lu–C–Al2 28°), (*ii*) elongated Lu–(μ -CH₃) bond lengths (Δ_{Lu-C} = ca. 0.08 Å), (*iii*) a shortened Lu–Al distance (Δ_{Lu-A1} = ca. 0.15 Å), and (*iv*) an additional Lu–(μ -CH₃) contact of 3.447 Å. For comparison, the Lu–C(μ) bond lengths in homometallic asymmetrically bridged Cp*₂Lu(μ -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), SiHMe₂ (b), SiMe₃ (c), SiHPh₂, (d); 4: R = Me (a), SiHMe₂ (b), SiMe₃ (c).



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 1.995(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–C11–Al1 83.3(1), 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 fourmembered metallacycle from planarity was also reported for complex Cp₂Y(μ -CH₃)₂Al(CH₃)₂ (\angle 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 (\angle 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 \angle 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 η^3 -coordinating AlEt₄– ligands in the solid state structure of homoleptic [Yb(AlEt₄)_{2]n} involving the *large* Yb(π) centre.¹⁷ This previous structural evidence combined with the highly fluxional behaviour of **6a** in solution, implicating transient η^2/η^3 -coordinating AlMe₄– 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, Al₂Me₆, occurs via a dissociative mechanism.¹⁹

$$(n) \xrightarrow{R^{1}}_{R^{2}} AI \xrightarrow{R^{3}}_{R^{4}} \longrightarrow (n) \xrightarrow{R^{3}}_{R^{2}} AI \xrightarrow{R^{4}}_{R^{2}} AI \xrightarrow{R^{4}}_{R^{4}} AI \xrightarrow{R^{4}}_{R^{4}}$$

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, $\nu/$ cm-1): 2069vs, 1820s, 1732m, 1460vs, 1377s, 1246s, 1044vs, 900vs, 841s, 790s, 765s, 721m, 646w, 623w, 603w, 409w. 1H NMR (400 MHz, C6D6, 25 °C): $\delta 4.59$ (sp, ${}^{3}J_{H,H} = 3.0$ Hz, 4H, SiH); 2.15 (s, 15H, Cp–Me); 0.26 (d, ${}^{3}J_{\text{H,H}} = 3.0 \text{ Hz}, 24\text{H}, \text{NSiMe}$). ${}^{13}\text{C} \text{ NMR} (100.6 \text{ MHz}, C_6D_6, 25 °C)$: 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 AlMe₃ (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, v/cm⁻¹): 1462vs, 1377vs, 1258w, 1237m, 1213m, 1193m, 1023w, 913w, 855m, 721s, 579m, 499w, 458w. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ1.75 (s, 15H, Cp-Me); -0.18 (s, 24H, AlMe). ¹³C NMR (100.6 MHz, C₆D₆, 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} $\approx N(SiHMe_{2})_{2}$], well-defined half-sandwich complexes of the smaller rareearth 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}]_{2}Cl_{2}Li(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, $\rho_{calc} = 1.447$ gcm⁻³, F(000) = 1952, μ (Mo-K_{α}) = 4.513 mm⁻¹, $\lambda = 0.71073$ Å, T = 173 K. The 48726 reflections measured on a Nonius Kappa CCD system yielded 4063 unique data ($\Theta_{max} = 25.4^{\circ}$, $R_{int} = 0.033$) [3617 observed reflections ($I > 2\sigma(I)$]. R1 = 0.0208, wR2 = 0.0499. CCDC reference number 200967. See http://www.rsc.org/suppdata/cc/b/2/12754g/ for crystallographic data in cif or other electronic format.

|| An associative mechanism is also found by a variable temperature NMR investigation of *rac*-[Me₂Si(2-Me-C₉H₃)₂]Y(AlMe₄) in the temperature range of 25 to 100 °C. Line shape treatment led to an entropy barrier ΔS^{+}_{+} of -130(8) J K⁻¹mol⁻¹ which is in agreement with a highly ordered transition state favouring an η^{3} -bonded tetramethylaluminate moiety (cf., $\Delta S^{+}_{+} = +123.1$ J K⁻¹mol⁻¹ for Al₂Me₆).¹⁵

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