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Ln(AlMe$_4$)$_3$ as New Synthetic Precursors in Organolanthanide Chemistry: Efficient Access to Half-Sandwich Hydrocarbyl Complexes

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The homoleptic complexes Ln(AlMe$_4$)$_3$ (Ln = Y, La, Nd, Lu) were reacted with pentamethylcyclopentadiene to yield the corresponding half-sandwich complexes (C$_5$Me$_5$)Ln(AlMe$_4$)$_2$ in high yield and purity. NMR spectroscopic investigations revealed a highly dynamic nature of the bridging and terminal alkyl groups, even at −85 °C. In the solid state, the tetramethylaluminato ligands coordinate differently to the metal center, as shown by an X-ray structure analysis of the lanthanum derivative. Due to the steric unsaturation of the large lanthanum metal center, one of the aluminate ligands adopts an unusual distorted μ:η^3 coordination mode, while the second ligand bonds in a routine μ:η^2 fashion. An alcoholysis reaction of (C$_5$Me$_5$)Y(AlMe$_4$)$_2$ with HOCH*t*Bu$_2$ gave the heteroleptic complex (C$_5$Me$_5$)Y(OCH*t*Bu$_2$)(AlMe$_4$). (C$_5$Me$_5$)Nd(AlMe$_4$)$_2$ was reacted with dehydrated periodic mesoporous silica MCM-41, affording surface-grafted (C$_5$Me$_5$)Nd(AlMe$_4$)$_2$@MCM-41. The half-metallocene bis(aluminate) complexes were converted into donor-free [(C$_5$Me$_5$)LnMe$_2$]$_3$ (Ln = Y, Lu) via stoichiometric THF-induced cleavage and reversibly regenerated by addition of trimethylaluminum. The organolanthanide complexes were fully characterized by NMR and FTIR spectroscopy and elemental analysis. The organometallic−inorganic hybrid materials were characterized by FTIR spectroscopy, elemental analysis, and nitrogen physisorption.

Introduction

Organolanthanide complexes supported by only one cyclopentadienyl-type ancillary ligand are ascribed a high potential in homogeneously catalyzed reactions such as the polymerization of styrene or acrylonitrile.[1,2] Moreover, an intrinsic stereoelectronic unsaturation is anticipated to impart unprecedented structural chemistry.[3,4] A very limited number of catalytically relevant bis(amide) and bis(hydrocarbyl) half-sandwich complexes has been structurally examined, disclosing undesirable features such as (i) Lewis base (solvent) complexation, (ii) *ate* complexation, and (iii) metal-size-dependent ligand redistribution reactions.[2,4−10] Recently, we described the synthesis of mono(tetramethylcyclopentadienyl) bis(silylamide) complexes according to our previously established *extended silylamide route*. A trialkylaluminum-mediated silylamide → alkyl transformation afforded donor-free half-sandwich complexes of the type CpLn[(μ-R)$_2$AlR$_2$]$_2$ of the smaller rare-earth metals yttrium and lutetium.[11] Herein we describe a highly efficient synthetic route to mono(cyclopentadienyl) complexes of both smaller and larger lanthanide(III) centers. Note that the synthetic approaches toward half-lanthanidocene bis(hydocarbyl) complexes reported so far were applicable only for either smaller or larger Ln metal centers using Ln(CH$_2$SiMe$_3$)$_3$(THF)$_x$ (x = 2, 3) and Ln[CH(SiMe$_3$)$_2$]$_3$ as synthetic precursors, respectively.[2,7,12,13]

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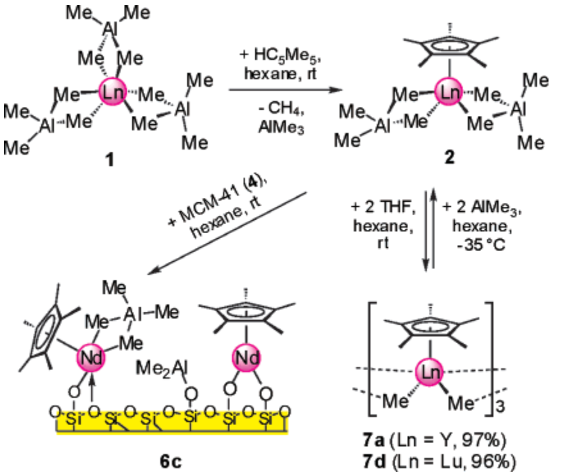
Scheme 1. Synthesis of Half-Sandwich Rare-Earth Metal Tetraalkylaluminate Complexes 2 (Ln = Y (a), La (b), Nd (c), Lu (d)) According to an Alkane Elimination and Secondary Tetraalkylaluminate Ligand Exchange



Results and Discussion

Synthesis and Characterization of Half-Lanthanidocene Bis(tetramethylaluminato) Complexes. Homoleptic tetramethylaluminates $Ln[(\mu\text{-}Me)_2AlMe_2]_3$ (**1**: Ln = Y(**a**), La (**b**), Nd (**c**), Lu (**d**)) were synthesized according to the literature method and are readily available on a 10 g scale by the reaction of $LnCl_3(THF)_x$ (x = 3.5 (Y), 1.25 (La), 1.75 (Nd), 3 (Lu)) with 3 equiv of freshly prepared $LiNMe_2$ and a subsequent $AlMe_3$-mediated $[NMe_2] \rightarrow [AlMe_4]$ transformation.[14-17] We found that such peralkylated rare-earth metal complexes **1** are ideal precursors for mono(C_5Me_5)−bis(alkyl) complexes via a protonolysis reaction. Accordingly, $(C_5Me_5)Ln[(\mu\text{-}Me)_2AlMe_2]_2$ (**2**: Ln = Y(**a**), La (**b**), Nd (**c**), Lu (**d**)) were obtained from **1** and 1,2,3,4,5-pentamethylcyclopentadiene (Scheme 1).[18] The volatile byproducts trimethylaluminum and methane can easily be removed under vacuum to afford the pure compounds in high yield (Y (86%), La (93%), Nd (91%), Lu (91%)). *Caution!* The evaporated hexane fractions containing $AlMe_3$ react violently when exposed to air; deactivation by addition of anhydrous 2-propanol is recommended.

^1H NMR spectroscopic investigations of complexes **2** at 25 °C showed one signal in the metal alkyl region. In comparison to the homoleptic precursors **1** the methyl resonances of the diamagnetic derivatives **2a** (−0.33 vs −0.27), **2b** (−0.29 vs −0.20), and **2d** (−0.18 vs 0.35) are shifted slightly to higher field. The corresponding broad signal of the paramagnetic neodymium complex **2c** appeared at 4.2 ppm compared to the 10.7 ppm in **1c**. As evidenced for the yttrium derivative **2a** by variable-temperature NMR spectroscopy, the aluminate moieties are highly fluxional, even at −85 °C. This clearly revealed a rapid exchange of bridging and terminal aluminate methyl groups.[11] The spectrum of complex **2a** also showed the characteristic doublet ($^2J_{Y,H}$ = 2.0 Hz) for the $AlMe_4^-$ ligands.[19,20]

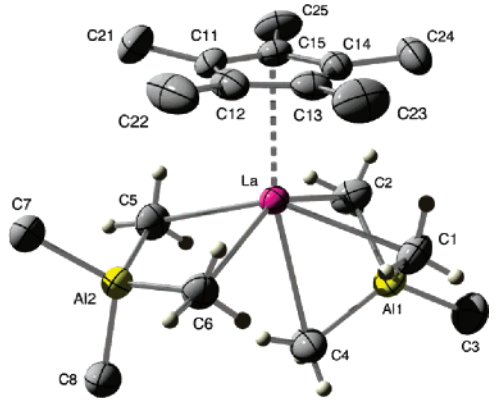


Figure 1. Molecular structure of **2b** (ORTEP drawing). Atoms are represented by atomic displacement ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): La- - -Al1 = 3.0141(9), La- - -Al2 = 3.2687(9), La−C(C_5Me_5) = 2.753(2)−2.801(3), La−C1 = 2.794(3), La−C2 = 2.802(4), La- - -C4 = 3.140(3), La−C5 = 2.694(3), La−C6 = 2.707(3), La−H12 = 2.88(4), La−H13 = 2.75(4), La−H21 = 2.51(5), La−H22 = 3.06(5), La−H41 = 2.83(4), La−H51 = 2.60(3), La−H52 = 2.68(3), La−H61 = 2.70(3), La−H62 = 2.62(3), Al1−C1 = 2.058(3), Al1−C2 = 2.058(3), Al1−C3 = 1.960(4), Al1−C4 = 1.994(3), Al2−C5 = 2.077(3), Al2−C6 = 2.074(3), Al2−C7 = 1.969(4), Al2−C8 = 1.968(4); Al1−La−Al2 = 117.23(2), C1−La−C2 = 73.0(1), C5−La−C6 = 78.5(1), C1−La−C6 = 94.3(1), C2−La−C5 = 94.4(1), La−C1−Al1 = 75.1(1), La−C2−Al1 = 74.9(1), La−C5−Al2 = 85.5(1), La−C6−Al2 = 85.2(1), La−C1−H11 = 169(3), La−C1−H12 = 85(2), La−C1−H13 = 77(2), La−C2−H21 = 62(3), La−C2−H22 = 98(4), La−C2−H23 = 150(3), La−C5−H51 = 74(2), La−C5−H52 = 79(2), La−C5−H53 = 174(2), La−C6−H61 = 80(2), La−C6−H62 = 74(2), La−C6−H63 = 174(2), La−C4−H41 = 62(3), La−C4−H42 = 129(2), La−C4−H43 = 134(3). Bond lengths and angles involving hydrogen atoms should be discussed carefully, due to their location close to heavy atoms.

Decisively, the formation of lanthanidocene complexes $(C_5Me_5)_2Ln(AlMe_4)$ via ligand redistribution was not observed. We have recently reported the solid-state structure of lutetium derivative **2d** obtained according to a different synthetic route.[11] The present X-ray structure analysis of lanthanum complex **2b** featuring the largest Ln(III) metal center gives further evidence of differently coordinated tetramethylaluminate ligands (Figure 1).[11] One $AlMe_4^-$ ligand coordinates in an η^2 fashion with an almost planar heterobimetallic $[La(\mu\text{-}CH_3)_2Al]$ moiety (torsion angle ∠C5−La−C6−Al2 = −2.2(1)°). The second $AlMe_4^-$ ligand shows structural features similar to those previously found for the lutetium complex **2d**, including (i) an atypically bent heterobimetallic $[La(\mu\text{-}CH_3)_2Al]$ moiety (∠C1−La−C2−Al1 = 32.5(1)°, interplanar angle LaC1C2−Al1C1C2 =

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Table 1. Analytical Data, Pore Volume, Surface Area, and Effective Mean Pore Diameter of Supported Neodymium Tetraalkylaluminate Complexes

material[a]	C/ wt %	Nd loading/ mmol g^{-1}	a_s[b]/ m^2 g^{-1}	V_p[c]/ cm^3 g^{-1}	d_p[d]/ nm
MCM-41 (**4**)[e]			1040	1.06	3.3
Nd[(μ-Me)$_2$AlMe$_2$]$_3$@MCM-41 (**5c**)	10.84	1.73	650	0.54	2.8
Cp*Nd[(μ-Me)$_2$AlMe$_2$]$_2$@MCM-41 (**6c**)	16.71	1.49	570	0.42	2.5

[a] Pretreatment temperature: 280 °C, 4 h, 10^{-3} Torr for **4**; 25 °C, 5 h, 10^{-3} Torr for **5c** and **6c**. Cp* = C_5Me_5. [b] Specific BET surface area. [c] BJH desorption cumulative pore volume of pores between 1.5 and 6.5 nm diameter. [d] Pore diameter according to the maximum of the BJH pore size distribution. [e] A pore-expanded sample of **4** was synthesized by using the *divalent* surfactant C_{16-3-1} and hydrothermal restructuring; the silanol population was derived as 3.45 mmol g^{-1} from the functionalized material HN(SiHMe$_2$)$_2$@MCM-41.[23b]

118.0(2)°), (ii) elongated La$-$(μ-CH$_3$) bond lengths (Δ_{La-C} = ca. 0.10 Å), and (iii) a shortened La- - -Al distance ($\Delta_{La---Al}$ = ca. 0.255 Å). However, due to an enhanced steric unsaturation of the larger lanthanum center, an even shorter additional La$-$(μ-CH$_3$) contact of 3.140(3) Å is observed (cf. **2d**, Lu- - -(μ-CH$_3$) = 3.447 Å). This pronounced La- - -C4 contact is also evidenced by different bond angles ∠La$-$Al$-$C$_{terminal}$ of the bent (∠La$-$Al1$-$C3/4 = 168.8(2), 74.6(1)) compared to the η^2-bonded aluminate ligands (∠La$-$Al2$-$C7/8 = 120.9(1), 122.5(1)°). Hence, the bent AlMe$_4^-$ ligand accomplishes a distorted η^3 coordination mode comparable to that of the [Yb(μ-Et)$_3$AlEt]$^+$ moiety in the homoleptic complex [Yb(AlEt$_4$)$_2$]$_n$, involving the even *larger* Yb(II) center.[21] For comparison, the La$-$C(μ) bond lengths in six-coordinate La(NMe$_2$)$_2$(GaMe$_3$)$_2$(GaMe$_4$) and seven-coordinate Ln[OSi(O*t*Bu)$_3$](AlMe$_4$)$_2$(AlMe$_3$) are in the ranges of 2.742(2)$-$2.992(5) and 2.668(5)$-$2.798(3) Å, respectively.[16,22] The bridging five-coordinate carbon atoms of the η^2-coordinating AlMe$_4^-$ ligand display distorted-trigonal-bipyramidal geometries with one hydrogen atom and the lanthanum metal in the apical positions (∠La$-$C5$-$H53, ∠La$-$C6$-$H63 = 174(2)°). Two of the equatorial hydrogen atoms each form a close contact to the lanthanum center (2.60(3)$-$2.70(3) Å) involving ∠La$-$C$-$H angles as acute as 74(2)°. It is worth noting that the η^3-coordinating AlMe$_4^-$ ligand features the shortest La- - -H contact (2.51(5) Å) and the most acute angles ∠La$-$C$-$H (62(3)°).

Ligand Exchange at Half-Lanthanidocene Bis(tetramethylaluminato) Complexes. The feasibility of secondary ligand exchange reactions for complexes **2** was initially examined for a simple alcoholysis reaction. A tetramethylaluminate → alkoxide transformation could be achieved by reacting **2a** with di-*tert*-butylcarbinol. The heteroleptic complex (C$_5$Me$_5$)Y(OCH*t*Bu$_2$)(AlMe$_4$) (**3a**), featuring three different monoanionic ligands, was formed as the main product after crystallization from hexane solution. This tetramethylaluminate/alkoxide exchange implicates a stronger bonding of the remaining [La(μ-CH$_3$)$_2$Al(CH$_3$)$_2$] moiety, as evidenced by an increased coupling constant $^2J_{Y,H}$ of 3.2 Hz. In another preliminary study, Nd(AlMe$_4$)$_3$ (**1c**) and (C$_5$Me$_5$)Nd(AlMe$_4$)$_2$ (**2c**) were grafted onto a high-surface-area periodic mesoporous silica material, i.e., MCM-41 (**4**) of hexagonal topology with a two-dimensional mesopore system.[23-25] The resulting organometallic$-$inorganic hybrid materials were characterized by FTIR spectroscopy, elemental analysis, and nitrogen physisorption (Table 1).

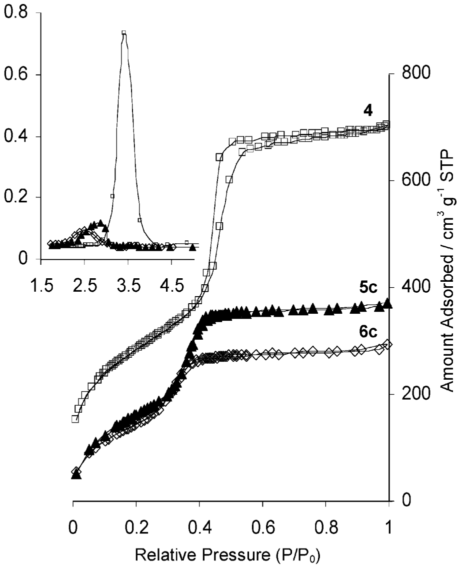

Figure 2. Nitrogen adsorption/desorption isotherms at 77.4 K and the corresponding BJH pore size distributions of the parent and modified MCM-41 materials **4**, **5c**, and **6c** (cf. Table 1).

A dehydrated sample of pore-enlarged MCM-41 (**4**) was treated with an excess of each of the tetraalkylaluminate complexes to give a blue reaction mixture, from which after several hexane washings blue-green materials **5c** and **6c** were isolated. The enhanced steric bulk of the C$_5$Me$_5$ ligand implies a significantly lower Nd loading of **6c**, while the high carbon content of **6c** suggests the presence of surface-confined half-metallocene species (proposed surface species for material **6c** are shown in Scheme 1).[25,26] Also, the nitrogen adsorption/desorption isotherms of the materials **4**, **5c**, and **6c** (Figure 2) clearly indicate a distinct filling of the mesopores depending on the ligand environment of the neodymium surface centers. The mesoporosity of the hybrid materials was retained; however, analysis of the Barret$-$Joyner$-$Halenda (BJH) pore size distributions shows drastically reduced pore diameters.[27]

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Lappert's Donor-Induced Aluminate Cleavage at Half-Lanthanidocene Bis(tetramethylaluminato) Complexes. The applicability of Lappert's concept of a donor (THF)-induced aluminate cleavage revealed complexes **2** to exhibit true *masked* bis(hydrocarbyl) complexes. Lappert and co-workers showed that lanthanidocene deriviatives $(C_5H_5)_2Ln(AlMe_4)$ (Ln = Y, Dy, Ho, Er, Tm, Yb) can be converted into alkyl-bridged complexes $[(C_5H_5)_2Ln(\mu\text{-}Me)]_2$ by addition of equimolar amounts of pyridine and separation of $AlMe_3(Py)$.[28] Correspondingly, addition of 2 equiv of THF as a Lewis base to a solution of complexes **2a** and **2d** in hexane instantly formed $[(C_5Me_5)LnMe_2]_3$ (**7a**, Ln = Y; **7d**, Ln = Lu) as a white precipitate (Scheme 1). Microanalytical and ^{1}H NMR spectroscopic data are consistent with the molecular compositions of **7a** and **7d**. The ^{1}H NMR spectrum of complex **2a** revealed a quartet for the Y-bonded methyl groups with a small $^2J_{Y,H}$ coupling of 1.2 Hz.[29] Interestingly, as previously found for lanthanidocene complexes *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]YR$ (R = Me, $AlMe_4$) and $[(C_5H_5)_2Ln(\mu\text{-}Me)]_2$ this donor-induced aluminate cleavage is a reversible process.[18,28] Treatment of complexes **7** suspended in hexane with 2 equiv of $AlMe_3$ quantitatively redissolved **7** as **2a** and **2d** (Scheme 1).

Conclusions

Homoleptic $Ln(AlMe_4)_3$ complexes are efficient synthetic precursors for highly soluble, mononuclear bis(tetraalkylaluminate) half-sandwich complexes of large (La, Nd), medium (Y), and small (Lu) Ln(III) centers. Given the accessibility of $(C_5Me_5)Ln(AlMe_4)_2$ to various ligand exchange reactions, including a Lewis base-mediated "reversible" $[AlMe_4] \rightarrow [Me]$ transformation and a silanolysis-driven [Cp*Ln] surface attachment, applications in polymerization catalysis can be anticipated.

Experimental Details

General Procedures. All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum, and glovebox techniques (MB Braun MB150B-G-II; <1 ppm O_2, <1 ppm H_2O). Hexane was purified by using Grubbs columns. Toluene and THF were predried and distilled from Na/K alloy (benzophenone ketyl) under argon. C_6D_6 was obtained from Deutero GmbH, degassed, dried over Na/K alloy for 24 h, and filtered. Trimethylaluminum and 1,2,3,4,5-pentamethylcyclopentadiene were purchased from Aldrich and used as received. Lithium dimethylamide was synthesized via deprotonation of dimethylamine with ^{n}BuLi. Homoleptic $Ln(AlMe_4)_3$ (Ln = Lu, Y, Nd, La) were synthesized according to the literature method.[14] Hexadecyldimethylamine ($C_{16}NMe_2$) and (3-bromopropyl)trimethylammonium bromide were purchased from Aldrich. Pore-expanded MCM-41 (**4**) was prepared according to slightly changed literature procedures using the divalent surfactant (3-(trimethylammonio)propyl)hexadecyldimethylammonium dibromide, $[CH_3(CH_2)_{15}N(CH_3)_2(CH_2)_3N(CH_3)_3]^{2+}Br^-{}_2$ (C_{16-3-1}), as a structure-directing agent (SDA), and hydrothermal posttreatment methods.[23c] C_{16-3-1} was synthesized according to the literature by reacting $C_{16}NMe_2$ with (3-bromopropyl)trimethylammonium bromide.[23c,30] The tetramethyldisilazane-mediated surface silylation was performed according to the literature method.[23b] ^{1}H and ^{13}C NMR data were obtained in C_6D_6 solution at 25 °C on FT-JEOL-JNM-GX-400 (^{1}H, 399.80 MHz; ^{13}C, 100.51 MHz) and FT-JEOL-JNM-GX-270 instruments (^{1}H, 270 MHz; ^{13}C, 67.5 MHz). ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin-Elmer 1650-FTIR spectrometer as Nujol mulls. Elemental analyses were performed in the microanalytical laboratory at TUM. Nitrogen adsorption–desorption isotherms were measured with an ASAP 2010 volumetric adsorption apparatus (Micromeritics) at 77.4 K for relative pressures from 10^{-2} to 0.99 ($a_m(N_2, 77\ K) = 0.162\ nm^2$). The samples were outgassed in the degas port of the adsorption analyzer, as indicated in Table 1. The BET specific surface area was obtained from the nitrogen adsorption data in the relative pressure range from 0.04 to 0.2. The pore size distributions were derived from the desorption branches using the BJH method.

General Procedure for the Preparation of Half-Sandwich Bis(aluminato) Complexes 2a–d. In a glovebox, $Ln(AlMe_4)_3$ was dissolved in hexane. 1,2,3,4,5-Pentamethylcyclopentadiene (1 equiv) in 5 mL of hexane was added under vigorous stirring to the alkylaluminate solution. Instant gas formation was observed. After the reaction mixture was stirred for 5 min, the solvent was removed in vacuo. After they were dried for 1 h, the products were obtained in pure crystalline form and in high yields.

(1,2,3,4,5-Pentamethylcyclopentadienyl)bis(tetramethylaluminato)yttrium(III) (2a). Following the procedure described above, $Y(AlMe_4)_3$ (350 mg, 1.00 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (136 mg, 1.00 mmol) yielded **2a** (343 mg, 86%) as a colorless crystalline solid. IR (Nujol, cm^{-1}): 1462 vs, 1377 vs, 1258 w, 1233 w, 1193 m, 1022 w, 916 m, 857 m, 720 s, 580 m, 506 m, 469 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.72 (s, 15H, CpCH_3); −0.33 (s, 24H, AlCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 122.3 (*C*pC), 11.8 (Cp*C*H$_3$), 0.13 (br s, Al*C*H$_3$) ppm. Anal. Calcd for $C_{18}H_{39}Al_2Y$ (398.376): C, 54.27; H, 9.87. Found: C, 53.96; H, 9.66.

(1,2,3,4,5-Pentamethylcyclopentadiene)bis(tetramethylaluminato)lanthanum(III) (2b). Following the procedure described above, $La(AlMe_4)_3$ (400 mg, 1.00 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (136 mg, 1.00 mmol) yielded **2b** (417 mg, 93%) as a colorless crystalline solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.81 (s, 15H, CpCH_3); −0.29 (s, 24H, AlCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 125.0 (*C*pC), 11.6 (Cp*C*H$_3$), 2.4 (br s, Al*C*H$_3$) ppm. Anal. Calcd for $C_{18}H_{39}Al_2La$ (448.36): C, 48.22; H, 8.77. Found: C, 47.94; H, 8.53.

(1,2,3,4,5-Pentamethylcyclopentadienyl)bis(tetramethylaluminato)neodymium(III) (2c). Following the procedure described above, $Nd(AlMe_4)_3$ (406 mg, 1.00 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (136 mg, 1.00 mmol) yielded **2c** (413 mg, 91%) as a blue-green crystalline solid. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 12.08 (s, 15H, CpCH_3); 4.21 (s, 24H, AlCH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 258.1 (*C*pC), 229.3 (br s, Al*C*H$_3$), −21.0 (Cp*C*H$_3$) ppm. Anal. Calcd for $C_{18}H_{39}Al_2Nd$ (453.711): C, 47.65; H, 8.66. Found: C, 47.43; H, 8.35.

(1,2,3,4,5-Pentamethylcyclopentadienyl)bis(tetramethylaluminato)lutetium(III) (2d). Following the procedure described above, $Lu(AlMe_4)_3$ (436 mg, 1.00 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (136 mg, 1.00 mmol) yielded **2d** (441 mg, 91%) as a colorless crystalline solid. IR (Nujol, cm^{-1}):

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(29) Complex **7a** was previously obtained by reacting $(C_5Me_5)Y(OC_6H_3tBu_2\text{-}2,6)_2$ with 1.6 equiv of MeLi in hexane/ether. The hexane-insoluble products $[(C_5Me_5)Y(\mu\text{-}Me)_2]_3$ and $Li(OC_6H_3tBu_2\text{-}2,6)$ were separated by benzene washings and the trinuclear structure proposed from the quartet ^{1}H resonance of fluxional methyl groups, which experience coupling to a Y_3 framework: Schaverien, C. J. *Organometallics* **1994**, *13*, 69.

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1462 vs, 1377 vs, 1258 w, 1237 w, 1193 m, 1023 w, 913 m, 855 m, 721 s, 579 m, 499 m, 458 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.75 (s, 15H, CpCH_3), −0.18 (s, 24H, AlCH_3) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 120.9 (*C*pC), 11.8 (CpCH_3), 1.5 (br s, AlCH_3) ppm. Anal. Calcd for $C_{18}H_{39}Al_2Lu$ (484.440): C, 42.36; H, 6.22. Found: C, 41.29; H, 6.12.

(Di-*tert*-butylmethoxy)(1,2,3,4,5-pentamethylcyclopentadienyl)(tetramethylaluminato)yttrium(III) (3a). In a glovebox, $(C_5Me_5)Y(AlMe_4)_2$ (199 mg, 0.50 mmol) was dissolved in hexane and cooled to −35 °C. A solution of di-*tert*-butylmethanol (144 mg, 1.00 mmol) was added under vigorous stirring at −35 °C. After the mixture was stirred for 1 h at ambient temperature, the solvent was removed in vacuo. The product was crystallized from the crude reaction mixture at −35 °C, which yielded 93 mg (41%) of colorless crystals. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.32 (s, 1H, OC*Ht*Bu_2), 1.92 (s, 15H, CpCH_3), 0.97 (s, 18H, *t*BuCH_3), −0.26 (d, 12H, AlCH_3) ppm. Anal. Calcd for $C_{23}H_{46}AlOY$ (454.504): C, 60.78; H, 10.20. Found: C, 60.54; H, 10.03.

$Nd[(\mu-Me)_2AlMe_2]_3$@MCM-41 (5c). Dehydrated MCM-41 (**4**; 250 mg) was suspended in hexane, and a solution of **1c** (512 mg, 1.26 mmol) in hexane was added. The blue mixture was stirred for 3 h at ambient temperature. After centrifugation and several hexane washings **5c** was dried to constant weight, yielding 360 mg of a light green material. Anal. Found: C, 10.84; H, 2.98. The amount of recovered **1c** was determined to be 340 mg (0.84 mmol, 66%). IR (Nujol, cm^{-1}): the sharp signal at 3695 cm^{-1} attributed to isolated SiO−H completely disappeared.

$(C_5Me_5)Nd[(\mu-Me)_2AlMe_2]_2$@MCM-41 (6c). Dehydrated MCM-41 (**4**; 125 mg) was suspended in hexane, and a solution of **2c** (297 mg, 0.65 mmol) in hexane was added. The blue mixture was stirred for 3 h at ambient temperature. After centrifugation and several hexane washings, separated light blue-green material **6c** was dried to constant weight. Yield: 280 mg. Anal. Found: C, 16.71; H, 3.07. The amount of recovered **2c** was determined as 211 mg (0.46 mmol, 71%). Note that ligand redistribution via formation of homoleptic **1c** and metallocene $(C_5Me_5)_2Nd(AlMe_4)$ did not occur during the solution grafting reaction. IR (Nujol, cm^{-1}): the sharp signal at 3695 cm^{-1} attributed to isolated SiO−H completely disappeared and a weak broad band centered at 3650 cm^{-1} appeared.

General Procedure for the Preparation of Half-Sandwich Dimethyl Complexes 7a,b. In a glovebox, $(C_5Me_5)Ln(AlMe_4)_2$ was dissolved in hexane. Tetrahydrofurane (2 equiv) in 5 mL of hexane was added with vigorous stirring to the aluminate solution. Instantly, the formation of a white precipitate was observed. After the reaction mixture was stirred for 5 min, the product had precipitated completely and was separated by centrifugation and washed three times with hexane. Drying in vacuo produced analytically pure complexes **7** as white powders in almost quantitative yields. Due to the low solubility of complexes **7** in benzene, useful solution ^{13}C NMR spectra could not be obtained. For a solid-state ^{13}C NMR spectrum of **7a**, see ref 17.

(1,2,3,4,5-Pentamethylcyclopentadienyl)dimethylyttrium(III) (7a). Following the procedure described above, $(C_5Me_5)Y(AlMe_4)_2$ (199 mg, 0.50 mmol) and tetrahydrofurane (72 mg, 1.00 mmol) yielded **7a** (123 mg, 97%) as a white powder. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 2.00 (s, 15H, Cp CH_3), −0.41 (q, 6H, YCH_3) ppm. Anal. Calcd for $C_{12}H_{21}Y$ (484.440): C, 56.70; H, 8.33. Found: C, 57.03; H, 8.45.

(1,2,3,4,5-Pentamethylcyclopentadienyl)dimethyllutetium(III) (7b). Following the procedure described above, $(C_5Me_5)Lu(AlMe_4)_2$ (242 mg, 0.50 mmol) and tetrahydrofurane (72 mg, 1.00 mmol) yielded **7b** (164 mg, 96%) as a white powder. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 2.00 (s, 15H, CpCH_3), 0.04 (s, 6H, LuCH_3) ppm. Anal. Calcd for $C_{12}H_{21}Lu$ (340.269): C, 42.36; H, 6.22. Found: C, 42.81; H, 6.57.

Table 2. Crystal Data and Data Collection Parameters of Complex 2b

chem formula	$C_{18}H_{39}Al_2La$
fw	448.36
color/shape	colorless/fragment
cryst size (mm)	0.64 × 0.43 × 0.38
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a (Å)	14.6850(1)
b (Å)	18.1332(1)
c (Å)	17.2624(1
V (Å^3)	4596.74(5)
Z	8
T (K)	143(1)
ρ_{calcd} (g cm^{-3})	1.296
μ (mm^{-1})	1.930
F_{000}	1840
θ range (deg)	2.14−25.38
data collected (h,k,l)	±17, ±21, ±20
no. of rflns collected	88226
no. of indep rflns/R_{int}	4219 (all)/0.057
no. of obsd rflns ($I > 2\sigma(I)$)	3487 (obsd)
no. of params refined	347
R1 (obsd/all)	0.0222/0.0317
wR2 (obsd/all)	0.0504/0.0537
GOF (obsd/all)	1.059/1.059
max/min $\Delta\rho$ (e Å^{-3})	+0.855/−0.399

X-ray Crystallography and Crystal Structure Determination of 2b. Crystals suitable for diffraction experiments were selected in a glovebox, coated with perfluorinated ether, and fixed in a capillary. Preliminary examination of the crystal quality and data collection were carried out on a Nonius KappaCCD diffractometer in combination with a rotating anode X-ray generator and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) employing the COLLECT software package.[31] A total of 1092 collected images were processed using Denzo.[32] Absorption and/or decay effects were corrected during the scaling procedure.[32] The structures were solved by direct methods[33] and refined with standard difference Fourier techniques.[34] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the difference Fourier maps and refined freely with individual isotropic thermal displacement. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ employing the SHELXL-97 weighting scheme and stopped at maximum shift/error of <0.002. In the final model, 347 parameters were refined to wR2 = 0.0537 based on all 4219 data. For details see Table 2.

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Supporting Information Available: A CIF file giving crystallographic data for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0506163

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