Synthesis and Structures of Scandium and Lutetium Benzyl Complexes

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Scandium and lutetium benzyl complexes were prepared. Reaction of [$ScCl_3(THF)_3$] with potassium benzyl afforded [$Sc(CH_2Ph)_3(THF)_3$] (**1**). In the solid state the coordination polyhedron is a distorted octahedron, in which the benzyl groups are located in a facial arrangement on one side of the molecule. One of the coordinated THF molecules could be removed by trituration with toluene and recrystallization of **1** from toluene to give [$Sc(CH_2Ph)_3(THF)_2$] (**2**). A significantly different compound is obtained by starting the transmetalation reaction at −196 °C. Under these conditions the reaction of $ScCl_3$ with KCH_2Ph led to a two-dimensional coordination polymer of composition [$Sc(CH_2Ph)_5K_2(THF)_3$]$_n$ (**3**), in which the scandium atom is surrounded by five benzyl groups in a trigonal bipyramidal fashion. Under the same reaction conditions, but using $LuCl_3$ as the starting material, the analogue of **1**, [$Lu(CH_2Ph)_3(THF)_3$] (**4**), is obtained, which can also be induced to lose a coordinated THF ligand to give [$Lu(CH_2Ph)_3(THF)_2$] (**5**).

Introduction

An attractive alternative to the usual salt metathesis reaction involving lanthanide halides for the synthesis of organometallic compounds of group 3 metals and the lanthanides is the use of an amine or alkane elimination route starting from homolepetic lanthanide amides or alkyls. Thus, in amido chemistry the so-called "silyl amide route" or "extended silyl amide route" starting from [$Ln\{N(SiMe_3)_2\}_3$] and [$Ln\{N(SiHMe_2)_2\}_3(THF)_x$], respectively, was established about a decade ago.[1,2] To obtain the more reactive alkyl complexes the homoleptic trialkyl complexes of the type [$Ln(CH_2SiMe_3)_3(THF)_n$] ($n = 2, 3$)[3–6] and [$Ln\{CH(SiMe_3)_2\}_3$][7] are proving to be valuable starting materials. Since homoleptic benzyl complexes are well established as starting material in zirconium chemistry[8] we and others were attracted by homoleptic tribenzyl complexes of the lanthanides as starting materials for the synthesis of alkyl complexes.[9–11] In this context Manzer[12] and Harder[10] reported the synthesis of rare-earth tribenzyl complexes bearing intramolecularly coordinating groups on the aryl moiety, whereas some of us prepared the salt-free lanthanum tribenzyl complexes of composition [$La(CH_2Ph)_3(THF)_3$] and [$La(CH_2$-Ph-4-$Me)_3(THF)_3$].[9] Now, we report here on benzyl complexes of the smallest rare-earth elements. To our surprise, small differences in the preparation result in significantly different scandium and lutetium benzyl complexes.

Results and Discussion

Scandium Complexes. Transmetalation of [$ScCl_3(THF)_3$] with 3 equiv of potassium benzyl in THF at room temperature,

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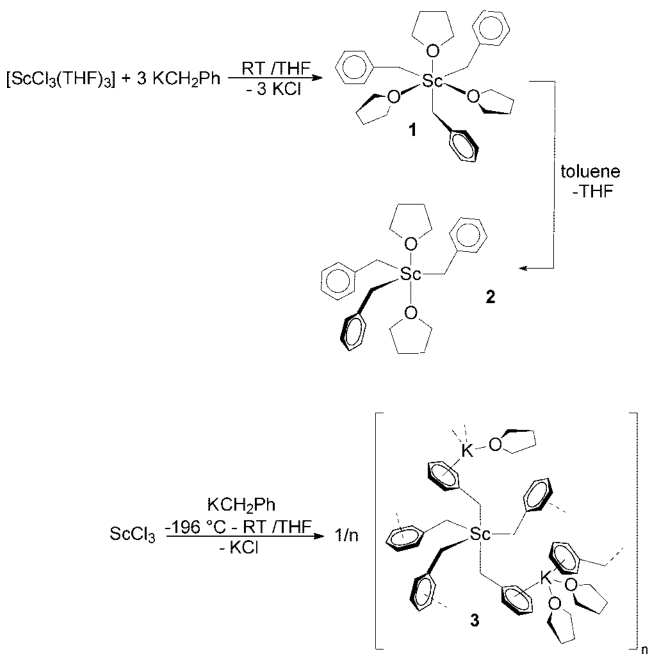
10.1021/om701171y CCC: $40.75

Scheme 1



followed by centrifugation and decantation (to remove the KCl) and subsequent crystallization from THF/hexane, afforded [$Sc(CH_2Ph)_3(THF)_3$] (**1**) as analytically pure light-orange crystals in 75% yield (Scheme 1). Trituration of **1** with toluene results in ready loss of one THF ligand. Subsequent crystallization from toluene allows isolation of [$Sc(CH_2Ph)_3(THF)_2$] (**2**) as orange blocks in high yield (Scheme 1). The difference between compounds **1** and **2** is obviously the number of THF molecules that are attached to the metal center. Similar observations were made previously for [$Y(CH_2SiMe_3)_3(THF)_2$] and [$Y(CH_2SiMe_3)_3(THF)_3$].[4f,13] A significantly different compound is obtained by using anhydrous scandium trichloride in THF and starting the reaction at −196 °C. Under these conditions the reaction with 3 equiv of KCH_2Ph leads to a two-dimensional coordination polymer of composition [$Sc(CH_2Ph)_5K_2(THF)_3$]$_n$ (**3**), in which the scandium atom is surrounded by five benzyl groups in a trigonal bipyramidal fashion. Surprisingly, attempts to generate and isolate **3** in higher yield, by using the appropriate 5:1 KCH_2Ph to $ScCl_3$ stoichiometry, were not successful. In these attempts, apparently not all KCH_2Ph was consumed, and an intractable mixture of products was formed.

The new complexes have been characterized by standard spectroscopic techniques and the structures were confirmed by single-crystal X-ray diffraction in the solid state. Data collection parameters and selected bond lengths and angles are given in Table 1 and the corresponding figure captions.

Complexes **1** and **2** are soluble in hydrocarbon solvents, whereas compound **3** is rather poorly soluble. NMR spectra of the latter compound could be recorded in THF-d_8. All complexes show one singlet in the ^1H NMR spectrum for the benzyl methylene protons. This is in accord with the symmetrical solid state structures of compounds **1** and **2** (vide infra), but shows that the polymeric structure of **3** is disrupted in THF solution. For compound **1** the NMR spectra were recorded in C_6D_6 and THF-d_8 to study the influence of the solvent on the spectra. Most significant is a downfield shift of the benzyl methylene signal by changing the solvents ($\delta(C_6D_6)$ 1.83 ppm vs δ(THF-d_8) 2.11 ppm). However, the shape of the signals is not influenced. The benzyl methylene $^{13}C\{^1H\}$ NMR resonances are found at $\delta(C_6D_6)$ 57.2 ppm and δ(THF-d_8) 60.0 ppm (**1**), $\delta(C_6D_6)$ 57.8 ppm (**2**), and δ(THF-d_8) 56.6 ppm (**3**).

Compound **1** crystallizes in the monoclinic space group *Cc* having four molecules in the unit cell. The structure reveals a metal center bound to three benzyl groups and three THF molecules, with Sc−O bond distances of Sc−O1 2.290(2) Å, Sc−O2 2.267(2) Å, and Sc−O3 2.268(2) Å (Figure 1). The latter are located in a facial arrangement on one side of the molecule, with O−Sc−O angles of 79.64(6)−81.74(6)°. Thus, the coordination polyhedron is a distorted octahedron. In contrast to the previously reported lanthanum tribenzyl complex [$La(CH_2Ph)_3(THF)_3$],[9] in which the benzyl groups are η^2 bound to the metal center, an η^1 coordination is observed in compound **1**, with an average Sc−CH_2−C angle of 119.58 (17)°. This is obviously a result of the smaller ionic radius of scandium.[14] The observed Sc−C bond distances of Sc−C13 2.308(3) Å, Sc−C20 2.309(3) Å, and Sc−C27 2.317(3) Å are slightly longer than those observed in the only other structurally characterized neutral scandium benzyl compound, [{(Ar)NC(*t*Bu)CHC(*t*Bu)-N(Ar)}$Sc(CH_2Ph)_2$] (Ar = 2,6-*i*Pr-C_6H_3) (2.263 and 2.203 Å).[15,16]

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The coordination polyhedron, which is formed by two THF molecules and three benzyl groups, is a slightly distorted trigonal bipyramid with THF molecules occupying the axial positions (Figure 2). The O1−Sc−O2 angle of 173.04(4)° is almost linear and the C−Sc−C angles of the benzyl group in the plane are close to the expected value of 120° (C9−Sc−C16 120.91(6)°, C9−Sc−C23 123.33(6)°, and C16−Sc−C23 115.76(6)°). As a result of the lower coordination number of the scandium center atom the Sc−C bond distances are shorter (av 2.290(5) Å) and the Sc−CH_2−C angles (av 113.64 (11)°) are smaller than those observed in **1**.

In contrast to compounds **1** and **2**, compound **3** is a two-dimensional coordination polymer, in which the scandium center is surrounded by five η^1-benzyl groups in a trigonal bipyramidal fashion (Figure 3). Formally the $\{Sc(CH_2Ph)_5\}^{2-}$ subunit can be considered as an analogue to compound **2**, in which the two axial THF ligands are substituted by benzyl groups. The two benzyl groups, which are located in the apex of the trigonal bipyramid, are coordinated in an ideal linear fashion (C1−Sc−C15 179.38(14)°). As usual for a trigonal bipyramidal geometry, the Sc−C bond distances (av 2.396(4) Å) to these ligands are longer than the corresponding equatorial bond lengths (av 2.32(1) Å). The latter distances are somewhat longer than the values in **1** and **2**, a reflection of the dianionic nature of **3**. The distances between potassium ions and carbon atoms of the aromatic benzyl rings are all less than 3.50 Å, a conservative limit for K−C interactions.[17] By using these criteria, the phenyl rings of all benzyl groups are η^6 coordinated to the potassium atoms. Thus, K1 is surrounded by two η^6-coordinated phenyl rings and two molecules of THF, whereas K2 is coordinated by three η^6-

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Table 1. Crystallographic Details of [$Sc(CH_2Ph)_3(THF)_3$] (1), [$Sc(CH_2Ph)_3(THF)_2$] (2), [$Sc(CH_2Ph)_5K_2(THF)_3$]$_n$ (3), and [$Lu(CH_2Ph)_3(THF)_3$] (4)[a]

	1	2	3	4
formula	$C_{33}H_{45}O_3Sc$	$C_{29}H_{37}O_2Sc$	$C_{47}H_{59}K_2O_3Sc$	$C_{33}H_{45}O_3Lu$
formula weight	534.67	462.57	795.10	664.66
space group	*Cc* (no. 9)	$P\bar{1}$ (no. 2)	$Pna2_1$ (no. 33)	*Cc* (no. 9)
a, Å	17.202(4)	7.6779(6)	25.471(5)	17.3716(9)
b, Å	20.759(5)	11.3723(9)	9.295(2)	20.9550(14)
c, Å	8.267(2)	14.824(1)	18.336(4)	8.3958(4)
α, deg		86.423(1)		
β, deg	93.695(4)	82.664(1)		93.571(4)
γ, deg		78.332(1)		
V, Å ^{3}	2946.0(12)	1256.4(2)	4341(2)	3050.3(3)
Z	4	2	4	4
density (g/cm^3)	1.205	1.223	1.216	1.447
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	0.280	0.315	0.399	3.266
abs corr	SADABS	SADABS	none	integration (X-shape)
no. of reflns collected	12243	11481	19529	13424
no. of unique reflns	5994 [R_{int} = 0.0387]	5968 [R_{int} = 0.0164]	10588 [R_{int} = 0.0493]	5033 [R_{int} = 0.0381]
no. of obsd reflns	5392	5105	6643	4745
abs structure parameter (Flack)	0.03(2)		0.01(4)	−0.001(8)
data; parameters	5994; 514	5968; 437	10588; 446	5033; 334
R1[b]); *w*R2[c])	0.0399; 0.0852	0.0418; 0.1105	0.0568; 0.1427	0.0203; 0.0454

[a] All data collected at 100 (**1** and **2**) or at 200 K (**3** and **4**). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

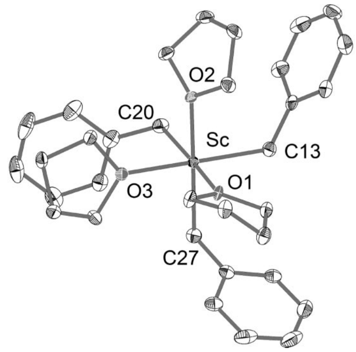


Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] or angles [deg] (also given for isostructural **4**): **1**, Sc−O1 2.290(2), Sc−O2 2.267(2), Sc−O3 2.268(2), Sc−C13 2.308(3), Sc−C20 2.309(3), Sc−C27 2.317(3) and O1−Sc−O2 79.64(6), O1−Sc−O3 81.43(6), O1−Sc−C13 92.72(8), O1−Sc−C20 172.63(8), O1−Sc−C27 91.43(8), O2−Sc−O3 81.74(6), O2−Sc−C13 94.24(8), O2−Sc−C20 94.95(8), O2−Sc−C27 170.35(8), O3−Sc−C13 173.39(8), O3−Sc−C20 92.91(7), O3−Sc−C27 93.40(8), C13−Sc−C20 92.67(9), C13−Sc−C27 89.79(9), C20−Sc−C27 93.61(9); **4**, Lu−O1 2.356(3), Lu−O2 2.387(4), Lu−O3 2.361(3), Lu−C13 2.404(7), Lu−C20 2.408(4), Lu−C27 2.413(5) and O1−Lu−O2 78.75(13), O1−Lu−O3 80.82(11), O1−Lu−C13 94.2(2), O1−Lu−C20 168.99(15), O1−Lu−C27 94.8(2), O2−Lu−O3 80.82(13), O2−Lu−C13 92.63(14), O2−Lu−C20 90.98(15), O2−Lu−C27 171.6(2), O3−Lu−C13 172.4(2), O3−Lu−C20 93.74(15), O3−Lu−C27 92.8(2), C13−Lu−C20 90.2(2), C13−Lu−C27 93.3(2), C20−Lu−C27 95.0(2).

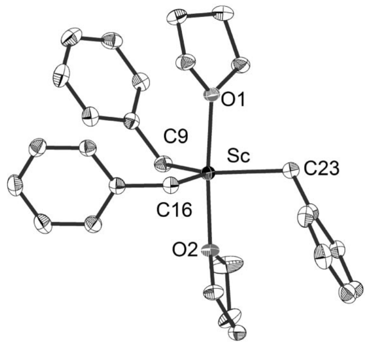


Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] or angles [deg]: Sc−O1 2.1870(11), Sc−O2 2.1868(11), Sc−C9 2.299(2), Sc−C16 2.281(2), Sc−C23 2.289(2) and O1−Sc−O2 173.04(4), O1−Sc−C9 90.75(5), O1−Sc−C16 93.81(5), O1−Sc−C23 85.31(5), O2−Sc−C9 87.16(5), O2−Sc−C16 92.96(5), O2−Sc−C23 90.30(5), C9−Sc−C16 120.91(6), C9−Sc−C23 123.33(6), C16−Sc−C23 115.76(6).

bonded phenyl rings and one molecule of THF. As a result of these coordination modes the potassium ions are acting as a knot between [$K(THF)Sc(CH_2Ph)_5K(THF)_2$] units.

Lutetium Complexes. In contrast to Sc, Lu behaves more simply. Transmetalation of $LuCl_3$ with 3 equiv of the potassium benzyl in THF under the reaction conditions used for the preparation of the polymeric compound **3** resulted in [$Lu(CH_2Ph)_3(THF)_3$] (**4**) (Scheme 2). Compound **4**, which is also obtained when a slurry of $LuCl_3(THF)_x$ is treated with a THF solution of potassium benzyl at low temperature (see the Experimental Section), is the lutetium analogue of compound **1**. As observed with [$Sc(CH_2Ph)_3(THF)_3$] (**1**), trituration of compound **4** elicits the removal of one THF molecule and gives [$Lu(CH_2Ph)_3(THF)_2$] (**5**).

The structure of **4** in the solid state was confirmed by single-crystal X-ray diffraction (Figure 1). Unfortunately attempts to obtain suitable single crystals of **5** for structural work have, so far, been unsuccessful. Data collection parameters and selected bond lengths and angles for **4** are given in Table 1 and the caption of Figure 1. In the solid state compound **4** is isostructural to the Sc analogue. Thus, the structure reveals a metal center bound to three molecules of THF and three benzyl groups with Lu−C bond distances of Lu−C13 2.404(7) Å, Lu−C20 2.408(4) Å, and Lu−C27 2.413(5) Å and an average Lu−CH_2−C angle of 118.57°. Thus, despite the increased metal size relative to Sc, the benzyl groups are η^1-coordinated. Since, to the best of our knowledge, this is the first structurally characterized lutetium benzyl complex the Lu−C bond distances cannot be compared with other data. The THF molecules of compound **4** are located in a facial arrangement on one side of the complex, with O−Lu−O angles of 78.75(13)−80.82(11)°. Thus, the coordination polyhedron is again a distorted octahedron.

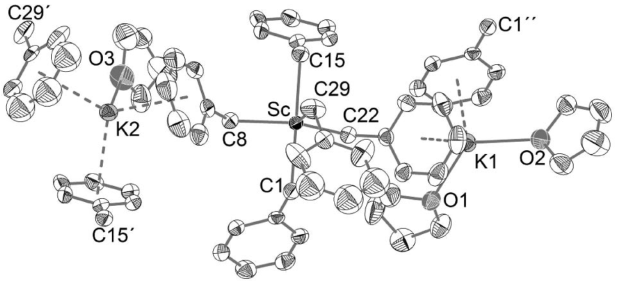
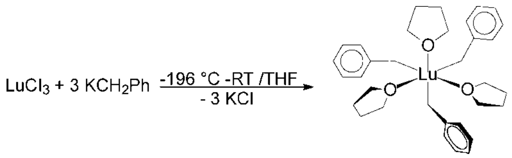


Figure 3. Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 50% probability. Shown is one unit out of the polymeric structure and the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [deg]: Sc−C1 2.387(4), Sc−C8 2.327(4), Sc−C15 2.404(4), Sc−C22 2.331(4), Sc−C29 2.288(4), K1−O1 2.776(3), K1−O2 2.664(3), K2−O3 2.726(3) and C1−Sc−C29 92.91(15), C1−Sc−C15 179.38(14), C1−Sc−C22 89.30(13), C1−Sc−C8 90.62(13), C8−Sc−C15 89.07(13), C8−Sc−C22 127.37(13), C8−Sc−C29 117.63(2), C15−Sc−C22 90.46(13), C15−Sc−C29 87.71(15), C22−Sc−C29 114.93(2).

Scheme 2



4

The ^{1}H NMR spectra of compounds **4** in C_6D_6 and **5** in toluene-d_8 showed one set of resonances for the three benzyl ligands, with well-resolved H−H coupling, and one for the THF ligands, consistent with symmetrical *fac*-octahedral and trigonal bipyramidal coordination geometries of complexes **4** and **5**, respectively. Contrary to the scandium complex **1**, the room temperature ^{1}H NMR spectrum of the lutetium complex **4** in THF-d_8 showed broad signals for the benzyl protons, an indication of dynamic solution behavior. In an effort to slow down the process and to obtain a well-resolved ^{1}H NMR spectrum, a VT NMR study in THF-d_8 was carried out. To our surprise, instead of sharpening the peaks broadened and, already at 0 °C, the benzyl *p*-H signal resolved into two broad signals. Lowering the temperature resulted in sharpening of the resonances and, at −80 °C, two sets of well-resolved benzyl aryl-H and Lu-CH_2 signals were observed, with an intensity ratio greater than 2:1. Two sets of signals were also seen in the ^{13}C NMR spectrum at low temperature. Curiously, this seems to indicate the presence of a mixture of **4** and **5** in solution at low temperature instead of a potential solvent-induced *fac*-to-*mer* isomerization.

Conclusions

We have prepared the first tribenzyl complexes of the smallest rare-earth elements, scandium and lutetium. It turned out that small differences in the preparation resulted in significantly different scandium complexes. Thus, a transmetalation of [$ScCl_3(THF)_3$] with potassium benzyl afforded [$Sc(CH_2Ph)_3(THF)_3$]. One of the coordinated THF molecules could be removed by recrystallization of **1** from toluene to give [$Sc(CH_2Ph)_3(THF)_2$]. A significantly different compound is obtained by starting the transmetalation reaction at −196 °C. Under these conditions the reaction of $ScCl_3$ with KCH_2Ph led to a two-dimensional coordination polymer of composition [$Sc(CH_2Ph)_5K_2(THF)_3$]$_n$. Under the same reaction conditions, but using $LuCl_3$ as starting material, [$Lu(CH_2Ph)_3(THF)_3$] is obtained, which is the analogue of the corresponding Sc compound **1**. In the solid state both scandium (**1**) and lutetium (**4**) complexes exhibit a six-coordinate octahedral geometry with *facial* disposition of the like ligands.

Experimental Section

General. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum (10^{-4} torr) line, or in an argon-filled MBraun or nitrogen/helium-filled Vacuum Atmospheres Company glovebox. Ether solvents (tetrahydrofurane and diethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (diethyl ether) benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH or Cambridge Isotope Laboratories (all ≥99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a JNM-LA 400 FT-NMR or a Varian Unity 500 spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses were carried out with an Elementar vario EL at the FU Berlin or at the Microanalytical Department of H. Kolbe (Mülheim an der Ruhr), or at the Analytical and Instrumentation Laboratory, University of Alberta. $ScCl_3$,[18] $LuCl_3$,[18] and KCH_2Ph[19] were prepared according to literature procedures.

[$Sc(CH_2Ph)_3(THF)_3$] (1). To a mixture of solid $K(CH_2Ph)$ (0.87 g, 6.0 mmol) and $ScCl_3(THF)_3$ (0.73 g, 2.0 mmol) in a Centrifuge Schlenk Vessel (CSV-100 mL) was added 100 mL of THF. The dark red mixture was sonicated (due to the large crystal size of $ScCl_3(THF_3)$) and hand shaken for 15 min (by then the mixture features an orange color), centrifuged, and then decanted from the KCl precipitate. The solution was concentrated under reduced pressure to about 10 mL, during which crystalline solid formed. Hexane was layered onto the mixture, and cooling to −30 °C afforded the title compound as light-orange crystals (0.81 g, 1.5 mmol, 75%).

^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.14 (t, $^3J_{HH}$ = 7.6 Hz, 6H, *m*-H), 6.84 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *o*-H), 6.80 (t, $^3J_{HH}$ = 7.2 Hz, 3H, *p*-H), 3.57 (m, 12H, α-THF), 1.83 (s, 6H, $ScCH_2$), 1.17 (m, 12H, β-THF). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ 151.6 (Ar C_{ipso}), 128.8 (Ar CH), 125.0 (Ar CH), 119.1 (Ar CH), 70.6 (α-THF), 57.2 (br, $ScCH_2$), 25.3 (β-THF).

^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 6.80 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *m*-H), 6.70 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *o*-H), 6.37 (t, $^3J_{HH}$ = 6.7 Hz, 3H, *p*-H), 2.11 (s, 6H, $ScCH_2$). $^{13}C\{^1H\}$ NMR (75.4 MHz, THF-d_8, 20 °C): δ 156.8 (Ar C_{ipso}), 129.1 (Ar CH), 125.6 (Ar CH), 118.2 (Ar CH), 60.0 (br, $ScCH_2$). Anal. Calcd for $C_{33}H_{45}O_3Sc$ [534.29]: C, 74.13; H, 8.48. Found: C, 73.70; 8.46.

[$Sc(CH_2Ph)_3(THF)_2$] (2). A solution of [$Sc(CH_2Ph)_3(THF)_3$] (0.25 g, 0.47 mmol) in toluene (5 mL) was evaporated to dryness, leaving a somewhat sticky crystalline orange residue. Recrystallization from toluene (3 mL) provides the title compound as orange blocks (0.15 g, 0.3 mmol, 69%).

^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ 7.16 (t, $^3J_{HH}$ = 7.1 Hz, 6H, *m*-H), 6.87 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *o*-H), 6.83 (t, $^3J_{HH}$ = 7.0 Hz, 3H, *p*-H), 3.55 (m, 8H, α-THF), 1.88 (s, 6H, $ScCH_2$), 1.07 (m, 8H, β-THF). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 20 °C): δ 151.6 (Ar C_{ipso}), 128.7 (Ar CH), 125.0 (Ar CH), 119.0 (Ar CH), 71.4

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(α-THF), 57.8 (br, ScCH$_2$), 25.2 (β-THF). Anal. Calcd for $C_{29}H_{37}O_2Sc$ [462.23]: C, 75.30; H, 8.06. Found: C, 74.80; H, 7.90.

[Sc(CH$_2$Ph)$_5$K$_2$(THF)$_3$]$_n$ (3). THF (20 mL) was condensed at −196 °C onto a mixture of ScCl$_3$ (0.45 g, 3 mmol) and potassium benzyl (1.17 g, 9 mmol) and the mixture was stirred for 16 h at ambient temperature. The dark red solution was then filtered off, concentrated, and layered with pentane. X-ray quality colorless crystals were grown overnight. The crystals were isolated and washed with pentane to give the analytically pure product (0.56 g, 0.7 mmol, 24%).

^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 6.62 (t, 10 H, $^3J_{H,H}$ = 7.3 Hz, *m*-H), 6.45 (d, 10 H, $^3J_{H,H}$ = 7.3, *o*-H), 6.06 (t, 5 H, $^3J_{H,H}$ = 7.0 Hz, *p*-H), 1.82 (s, 10 H, ScCH$_2$). ^{13}C{^{1}H} NMR (100.4 MHz, THF-d_8, 25 °C): δ 156.1 (Ar CH), 128.2 (Ar CH), 123.1 (Ar CH), 113.1 (Ar CH), 56.6 (ScCH$_2$). Anal. Calcd for $C_{47}H_{59}K_2O_3Sc$ [795.14]: C, 71.00; H, 7.48. Found: C, 69.89, H, 7.57.

[Lu(CH$_2$Ph)$_3$(THF)$_3$] (4). Method A. THF (10 mL) was condensed at −196 °C onto a mixture of LuCl$_3$ (0.28 g, 1 mmol) and potassium benzyl (0.39 g, 3 mmol) and the mixture was stirred for 16 h at ambient temperature, resulting in a color change from dark red to yellow. Ten milliliters of toluene was condensed onto the mixture and the solution was then filtered of, concentrated, and layered with pentane. X-ray quality light yellow crystals were grown overnight. The crystals were isolated and washed with pentane to give the analytically pure product. Yield: 0.57 g (0.8 mmol, 80%). Anal. Calcd for $C_{33}H_{45}O_3Lu$ [664.68]: C, 59.63; H, 6.83. Found: C, 60.04; 7.15.

Method B. A suspension of anhydrous LuCl$_3$ (1.07 g, 3.80 mmol) was stirred overnight in THF (14 h). The suspension was then cooled to −10 °C with stirring for another 1 h. A cold THF solution of KCH$_2$Ph (1.48 g, 11.4 mmol) was slowly added to the suspension over about 10 min. During addition, the bright orange-red color of the KCH$_2$Ph disappeared immediately and LuCl$_3$ suspension dissolved giving a very pale yellow emulsion-like mixture, which was stirred at this temperature for a further 2 h.

The mixture was centrifuged to remove KCl and the pale yellow supernatant was concentrated to about 10 mL, layered with Et$_2$O, and kept at −30 °C overnight to obtain a pale yellow microcrystalline solid, which was dried under vacuum to obtain the title compound in 60% yield (1.523 g, 2.3 mmol). The compound is sufficiently pure for spectroscopic characterization and further reactions. X-ray quality crystals were grown from THF/OEt$_2$ mixture. An analytically pure sample was obtained by careful, repeated crystallization. Anal. Calcd for $C_{33}H_{45}O_3Lu$ [664.68]: C, 59.63; H, 6.83. Found: C, 59.40; H, 6.78.

^{1}H NMR (400 MHz, 27 °C, C$_6$D$_6$): δ 7.17 (t, $^3J_{HH}$ = 7.6 Hz, 6H, Ph *m*-H), 6.85 (d, $^3J_{HH}$ = 7.6 Hz, 6H, Ph *o*-H), 6.78 (t, $^3J_{HH}$ = 7.6 Hz, 3H, Ph *p*-H), 3.48 (s br, 12H, α-THF), 1.62 (s, 6H, LuCH$_2$), 1.20 (s br, 12H, β-THF). ^{13}C{^{1}H} NMR (100.58 MHz, 27 °C, C$_6$D$_6$): δ 152.3 (Ph C$_{ipso}$), 129.0 (Ph *o*/*m*-CH), 124.3 (Ph *o*/*m*-CH), 118.3 (Ph *p*-CH), 69.7 (α-THF), 59.3 (Lu-CH$_2$), 25.3 (β-THF).

^{1}H NMR (400 MHz, THF-d_8, 27 °C): δ 6.78 (s br, 6H, Ph *m*-H), 6.67 (d, $^3J_{HH}$ = 7.2 Hz, 6H, Ph *o*-H), 6.25 (s br, 3H, Ph *p*-H), 3.62 (m, 12H, α-THF), 1.77 (m, 12H, β-THF), 1.64 (s, 6H, Lu-C*H$_2$*). ^{1}H NMR (400 MHz, THF-d_8, −80 °C): δ 6.84 (t, $^3J_{HH}$ = 7.6 Hz, Ph *m*-H), 6.73 (d, $^3J_{HH}$ = 7.6 Hz, Ph′ *o*-H), 6.67–6.62 ((doublet overlapping with a triplet and other minor peaks) d, $^3J_{HH}$ = 7.6 Hz, Ph *o*-H; t, $^3J_{HH}$ = 7.2 Hz, Ph′ *m*-H), 6.32 (t, $^3J_{HH}$ =7.4 Hz, Ph *p*-H), 5.98 (t, $^3J_{HH}$ = 7.0 Hz, Ph′ *p*-H), 3.62 (m, 12H, α-THF), 1.78 (m, 12H, β-THF), 1.73 (s, (partially buried under THF-d_8 solvent peak) Lu-C*H$_2$*), 1.52 (s br, Lu′-C*H$_2$*).

The two sets of resonances at LT are in a 2.7:1 ratio, minor peaks marked with prime. Other minor peaks were also seen. The intensity ratio of these signals was difficult to ascertain.

^{13}C{^{1}H} NMR (100.58 MHz, 27 °C, THF-d_8): δ 156.9 (Ph C$_{ipso}$ v br.), 128.0 (Ph *o*/*m*-*C*H), 124.0 (Ph *o*/*m*-*C*H), 115.9 (Ph *p*-*C*H v br), 68.3 (THF), 59.0 (Lu-*C*H$_2$ v br), 26.3 (THF). ^{13}C{^{1}H} NMR (100.58 MHz, −80 °C, THF-d_8): δ 159.2 (Ph′ C$_{ipso}$), 156.3 (Ph C$_{ipso}$), 128.4 (Ph *o*/*m*-*C*H), 127.8 (Ph′ *o*/*m*-*C*H), 123.9 (Ph *o*/*m*-*C*H), 122.6 (Ph′ *o*/*m*-*C*H), 116.0 (Ph *p*-*C*H), 112.3 (Ph′ *p*-*C*H), 70.7 (br, THF), 68.4 (α-THF), 59.3 (Lu-*C*H$_2$), 53.5 (Lu′-*C*H$_2$), 26.5 (β-THF).

[Lu(CH$_2$Ph)$_3$(THF)$_2$] (5). A suspension of 0.3 g (0.45 mmol) of Lu(CH$_2$Ph)$_3$(THF)$_3$ in 15 mL of toluene was stirred at room temperature for 1.5 h. During stirring, the color became slightly deeper than the original. After 1.5 h, the solvent was stripped under vacuum to obtain a yellow solid. The above procedure was repeated once more to obtain a yellow-orange solid after stripping the solvent in vacuum. The solid was further dried in vacuum for another 2 h to obtain 0.23 g (0.39 mmol, 85%) of yellow-orange solid. An attempt to crystallize the compound from a saturated toluene solution (−30 °C, for several days) gave only powdery solid.

^{1}H NMR (400 MHz, C$_7$D$_8$, 25 °C): δ 7.10 (“t”, $^3J_{HH}$ = 7.6 Hz, 6H, Ph *m*-H), 6.74 (d, $^3J_{HH}$ = 7.6 Hz, 6H, Ph *o*-H), 6.71 (t, $^3J_{HH}$ = 7.2 Hz, 3H, Ph *p*-H), 3.43 (m, 8H, α-THF), 1.50 (s, 6H, Lu-CH$_2$), 1.15 (m, 8H, β-THF). ^{13}C{^{1}H} NMR (100.58 MHz, C$_7$D$_8$, 25 °C): δ 152.1 (Ph C$_{ipso}$), 129.0 (Ph *o*/*m*-CH), 124.3 (Ph *o*/*m*-CH), 118.3 (Ph *p*-CH), 71.0 (α-THF), 59.5 (br, Lu-CH$_2$), 25.1 (β-THF). Anal. Calcd for $C_{29}H_{37}O_2Lu$ (592.58): C, 58.78; H, 6.29. Found: C, 58.85; H, 6.26.

X-ray Crystallographic Studies of 1–4. All structures were solved by the Patterson method (SHELXS-97[20]). The remaining non-hydrogen atoms were located from successive difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, using the program SHELXL-97.[21] Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances, and angles have been deposited as Supporting Information.

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Supporting Information Available: NMR spectra and tables of crystallographic data in CIF file format, including bond lengths and angles of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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