Synthesis, Characterization, and Reactivity of Mono(phospholyl)lanthanoid(III) Bis(dimethylaminobenzyl) Complexes

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Reaction of 2,5-di-*tert*-butyl-3,4-dimethylphospholide potassium [K(Dtp)] with YCl_3 or $SmI_3(THF)_{3.5}$ in THF followed by reaction with *o*-dimethylaminobenzylpotassium [$K(CH_2C_6H_4NMe_2$-*o*)] afforded the solvent-free mono(phospholyl)lanthanoid bis(benzyl) complexes [(Dtp)Ln($CH_2C_6H_4NMe_2$-*o*)] (Ln = Y (**3-Y**), Sm (**3-Sm**)). The Sc analogue could not be obtained under these conditions, as the reaction between K(Dtp) and $ScCl_3$ in THF led to the THF-ring-opened product [{Sc[μ-O$(CH_2)_4$(Dtp)]$Cl_2(THF)_2$}$_2$] (**5**). Replacing THF by a mixture of toluene/pyridine gave [(Dtp)$ScCl_2$(pyridine)] (**6**), which on further reaction with [$K(CH_2C_6H_4NMe_2$-*o*)] in toluene afforded [(Dtp)Sc$(CH_2C_6H_4NMe_2$-*o*$)_2$] (**3-Sc**). Protonation of [K(Dtp)] with *p*-toluenesulfonic acid gave the 1*H* phosphole Dtp-H (**7**), which could not be isolated pure but is stable in solution at room temperature. **3-Sc** could also be obtained from the reaction between the in-situ-prepared **7** and [Sc$(CH_2C_6H_4NMe_2$-*o*$)_3$] in toluene. Complexes **3-Ln** were activated with [Ph_3C]-[$B(C_6F_5)_4$] and tested in the syndiospecific polymerization of styrene. Whereas **3-Sm** did not show any activity, **3-Y** and **3-Sc** gave good to excellent results.

Introduction

Monocyclopentadienyl lanthanoid complexes have recently attracted growing interest due to their high potential in organic transformations and polymerization catalysis (the lanthanoid elements being defined as Sc, Y, and La−Lu).[1] Whereas the neutral complexes often lack reactivity toward alkenes,[2] cationic complexes based on the smaller elements, Sc, Y, and Lu, have shown very high activity in a number of homo- and copolymerization reactions.[3] The ligands employed to stabilize the half-sandwich complexes are either bulky anionic cyclopentadienyl derivatives, in some cases carrying further donor groups, or dianionic cyclopentadienyl derivatives bearing linked amide or phosphide groups, thus generating the so-called constrained geometry complexes (CGC).[4] So far, no study has been reported on the influence of heteroatom-containing cyclopentadienyl ligands on the olefin polymerization activity of half-sandwich lanthanoid complexes.

Bulky phospholyl ligands have recently been introduced into lanthanoid chemistry, allowing for the isolation of a number of divalent complexes that exhibited higher stability than their cyclopentadienyl analogues.[5] This observation was attributed to the good π-accepting and poor π-donating properties of the phospholyl ligands.[6] In addition, a recent study on the synthesis of phospholyl scandium complexes showed that the phospholyl ligand was a weaker ligand than the cyclopentadienyl derivative, as it was easily replaced by alkyl groups.[7] In the case of monophospholyl lanthanoid complexes the electronic properties of the phospholyl ligand should lead to a more electrophilic lanthanoid center with higher reactivity toward alkenes.

Different benzyl ligands have been introduced into organolanthanoid complexes;[8] however, they are still much less often used than alkyl or allyl ligands. The chelating *o*-dimethylaminobenzyl ($CH_2C_6H_4NMe_2$-*o*) ligand has recently been reinvestigated in lanthanoid chemistry as a readily available alternative to alkyl and allyl ligands.[9] The homoleptic complexes [Ln-($CH_2C_6H_4NMe_2$-*o*)l)$_3$] (Ln = Y, La) were stabilized by σ-bond-

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ing and intramolecular NMe_2 coordination. The unstabilized benzylic CH_2 functionality revealed its high basicity in the double deprotonation of 9-t-BuN(H)$SiMe_2$-fluorene.[9b]

The majority of monocyclopentadienyl complexes used in polymerization catalysis were obtained by in situ deprotonation of cyclopentadiene ligands by lanthanoid tris(alkyl) or tris(amide) precursors.[1,3] Salt metathesis reactions often led to mixtures of mono- and biscyclopentadienyl complexes due to ligand rearrangement to afford the more stable biscyclopentadienyl complexes. Hence, additional separation steps were required that reduced the yield of the desired products.[1] In the case of the phospholyl ligands, no example has been reported using the acid−base approach to access metal complexes. This is mainly due to the instability of most 1*H*-phospholes, which can be detected at low temperatures, but readily undergo [1,5]-*H* shift at room temperature. The resulting 2*H*-phospholes form immediately Diels−Alder or other coupling products.[10] Bulky substituents on the phosphole ring may inhibit follow-up reactions and allow for the stabilization of 2*H*-phospholes and, hence, due to the reversibility of [1,5]-*H* shifts, give access to 1*H* phospholes. One potential candidate is the 2,5-di-*tert*-butyl-3,4-dimethylphospholyl ligand (Dtp), in which both the bulky t-Bu groups in the α-positions and the additional steric bulk induced by the two methyl groups in the *β*-positions should disfavor following Diels−Alder reactions.

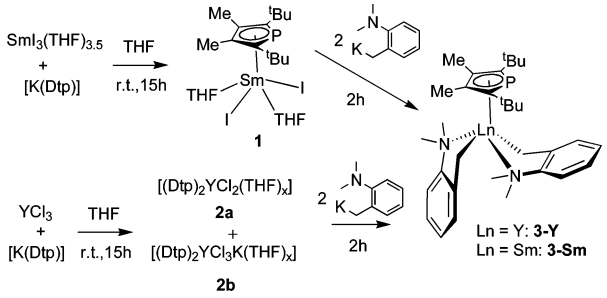
It should be noted that previously the only 1*H* phospholes known to be stable were those with annelated benzo rings that prevented the [1,5]-*H* shift: a 1*H*-dibenzophosphole was already successfully used for the synthesis of a new ligand,[11] and recently the first crystallographically characterized 1*H*-phosphoindole was reported.[12]

We herein report on the synthesis of new mono(phospholyl)-lanthanoid bis(benzyl) complexes bearing the bulky 2,5-di-*tert*-butyl-3,4-dimethylphospholide ligand (Dtp) using both salt metathesis reactions and for the first time the acid−base approach. We selected samarium, yttrium, and scandium as representative lanthanoids according to their respective large, medium, and small size of the corresponding tripositive cations. The resulting complexes were tested in the polymerization of styrene.

Results and Discussion

Synthesis of Monophospholyl Complexes of Sm and Y. The reaction between equimolar amounts of $SmI_3(THF)_{3.5}$ and [K(Dtp)] in THF at room temperature yielded the corresponding monophospholyl samarium diiodide complex [(Dtp)$SmI_2(THF)_2$] (**1**), which was isolated in good yield and fully characterized by multinuclear NMR studies, X-ray diffraction, and elemental analysis (Scheme 1). The reaction between YCl_3 and [K(Dtp)] in the same conditions had a different outcome. The ^{31}P NMR spectrum showed complete disappearance of [K(Dtp)] and the appearance of two signals at 92 and 99 ppm, in the typical region of an η^5-bound phospholyl ligand,[5] with relative intensities depending on the concentration. These signals thus clearly belong to species in which the Dtp ligand is η^5-bonded to yttrium. A tentative explanation for this could be that both a

Scheme 1



neutral and an anionic species, such as respectively [(Dtp)YCl_2-$(THF)_x$] (**2a**) and [(Dtp)$YCl_3K(THF)_x$] (**2b**), are present in solution. This hypothesis is supported by the fact that by switching to a less polar reaction medium such as THF/toluene the reaction led mostly to the product at 92 ppm, which could then correspond to the neutral, less polar compound **2a**. Surprisingly, no Y−P coupling was observed, in contrast to the previously reported [$(PC_4Me_4)_2YCl_2Li(DME)_2$].[13] In the case of the samarium complex **1**, some minor amounts of bisphospholyl complex formed, as indicated by ^{31}P NMR (28 ppm), in addition to the monosubstituted product (80 ppm).

Further addition of 2 equiv of *o*-dimethylaminobenzyl potassium [K($CH_2C_6H_4NMe_2$-*o*)] to the in-situ-generated compounds **1** and **2** resulted in an immediate color change, and ^{31}P NMR indicated quantitative transformation of the starting materials. After workup the monophospholylbis(benzyl) complexes [(Dtp)-$Ln(CH_2C_6H_4NMe_2$-*o*$)_2$] (Ln = Y (**3-Y**), Sm (**3-Sm**)) were isolated in good yields and fully characterized by multinuclear NMR, X-ray studies, and elemental analysis (Scheme 1). In the ^{31}P NMR spectra single peaks were observed at 92 and 63 ppm for **3-Y** and **3-Sm**, respectively. Again, no Y−P coupling was observed for **3-Y**.

Synthesis of Mono(phospholyl)scandium Complexes. (a) Salt Metathesis. In the case of Sc, the reaction between $ScCl_3$ and 1 equiv of [K(Dtp)] in THF at room temperature probably resulted initially in the formation of the corresponding monophospholyl dichloride complex **4**, which was detected by a resonance at 100 ppm in the ^{31}P NMR spectrum; however, **4** was not stable in the reaction conditions because this resonance disappeared completely within 72 h with the concomitant appearance of a signal at 6 ppm, in the typical region of P-substituted phospholes.[10] Compound **5**, a product resulting from a ring-opening reaction with THF, could be isolated in nearly quantitative yield and characterized by NMR and X-ray studies (Scheme 2).

In order to prevent this unwanted ring-opening reaction, the reaction between $ScCl_3$ and [K(Dtp)] was performed in a 5:1 toluene/pyridine mixture instead of THF. This time the monophospholyl dichloride complex **6** (^{31}P NMR: 120 ppm) was obtained in very good yield (Scheme 2). X-ray studies confirmed the η^5-coordination of the phospholyl ligand to scandium. Addition of 2 equiv of [K($CH_2C_6H_4NMe_2$-*o*)] to the in-situ-formed complex **6** resulted in a mixture of products. In contrast, the reaction of the isolated compound **6** with 2 equiv of [K($CH_2C_6H_4NMe_2$-*o*)] in toluene afforded the monophospholyl bis(benzyl) scandium complex **3-Sc** as major product, as shown by NMR studies.

(b) Acid−Base Approach. Since the synthesis of **3-Sc** using the salt metathesis approach had proven to be less efficient than the one-pot syntheses of **3-Y** and **3-Sm**, the acid−base approach was investigated to access **3-Sc**.

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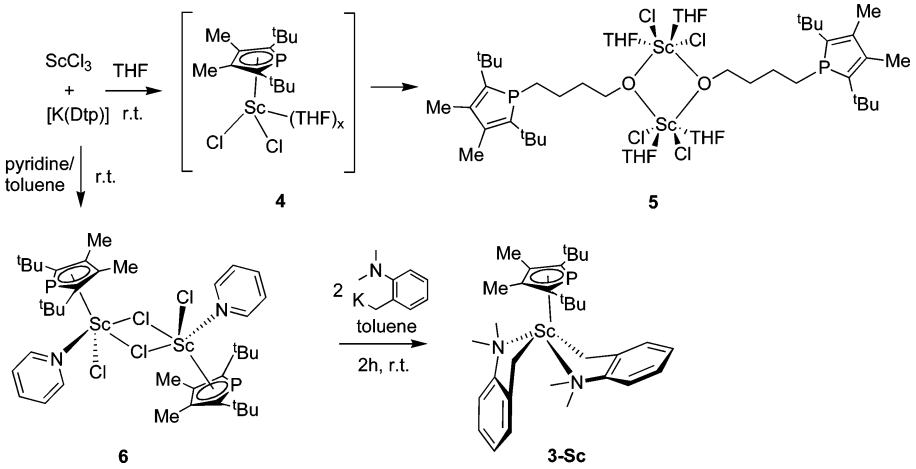
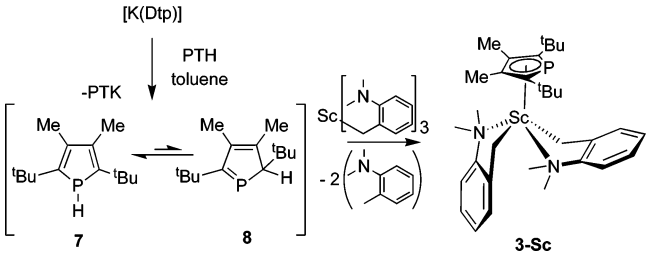
Scheme 2



Scheme 3



Protonation of [K(Dtp)] with 1 equiv of *p*-toluenesulfonic acid (PTH) in toluene resulted in the formation of 1*H*-phosphole **7** as the major compound, as indicated by the shift in the ^{31}P NMR from 58 to −53 ppm, a doublet with a typical P−H coupling of 211 Hz.[10] A small peak at 220 ppm, in the typical range of dicoordinated phosphorus compounds,[14] was attributed to 2*H*-phosphole **8**. The ratio between these two peaks remains constant over time, suggesting that an equilibrium between **7** and **8** is present, strongly shifted to the side of the 1*H*-phosphole **7**. No trace of a phosphole dimer could be detected in the reaction mixture. It thus seems that the substitution pattern on the Dtp ring kinetically stabilizes the Dtp-H phosphole in both the 1*H* and the 2*H* forms; however, all attempts to isolate **7** were unsuccessful.

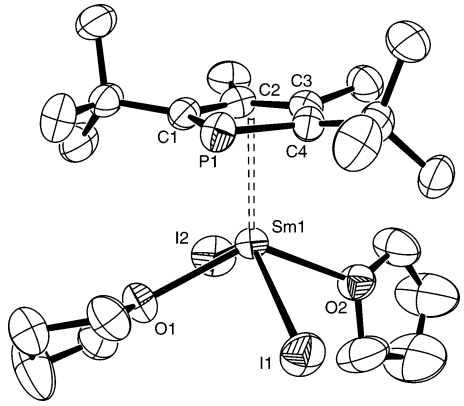


Figure 1. ORTEP plot (50% ellipsoids) of [(Dtp)$SmI_2(THF)_2$] (**1**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Sm(1)−O(2) = 2.443(4), Sm(1)−O(1) = 2.442(4), Sm(1)−P(1) = 2.9112(14), Sm(1)−I(2) = 3.0575(5), Sm(1)−I(1) = 3.0663(6), O(2)−Sm(1)−O(1) = 131.37(13), O(2)−Sm(1)−I(2) = 77.97(9), O(1)−Sm(1)−I(2) = 83.41(9), O(2)−Sm(1)−I(1) = 79.92(1), O(1)−Sm(1)−I(1) = 81.27(9), I(2)−Sm(1)−I(1) = 133.363(16).

Nonetheless, addition of 1 equiv of [$Sc(CH_2C_6H_4NMe_2$-*o*)$_3$] to the in-situ-generated **7** and heating the reaction mixture at 60 °C for one night led to the quantitative formation of complex **3-Sc**, as indicated by ^{31}P NMR (Scheme 3). **3-Sc** was characterized by multinuclear NMR and X-ray studies. To the best of our knowledge, this is the first example of the successful synthesis of a phospholyl-metal complex using the deprotonation of a 1*H* phosphole.

Structures of Monophospholyl Dihalide Complexes. An X-ray study was carried out for [(Dtp)$SmI_2(THF)_2$] (**2**), which crystallized in the conformation of a four-legged piano-stool complex with the two iodide ligands and the two THF molecules trans to each other. Whereas all the reported monocyclopentadienyl samarium diiodide complexes crystallize with three solvent molecules,[15] the bulky Dtp ligand allowed for the coordination of only two solvent molecules.

In contrast to the monomeric structure of the samarium diiodide **1** (Figure 1), the scandium dichloride complex [(Dtp)Sc(μ-Cl)Cl(NC_5H_5)]$_2$ (**6**) (Figure 2) formed a dimer in the solid state with two bridging chlorides and one pyridine coordinated to the metal center. The Sc−$(Dtp)_{centroid}$ distance (2.252 Å) lies between the ones observed for [$(Me_4C_4P)_2ScCl_2Li$(tmeda)] (2.29(1) Å) and for [$(Me_4C_4P)Sc[CH(SiMe_3)_2]Cl_2Li$(tmeda)] (2.220(3) Å).[7] This is in agreement with the different coordination numbers observed in these complexes. The bridging chlorides in **6** show Sc−Cl bond distances of 2.623 and 2.502 Å, which are significantly longer than in [$(Me_4C_4P)Sc[CH(SiMe_3)_2]Cl_2Li$(tmeda)] (2.445 and 2.444 Å), due to the presence of the strong donating pyridine and the terminal chloride ligand. In contrast the Sc−Cl nonbridging bond distances in **6** are comparable to those observed in **5** or in other mono(cyclopentadienyl)scandium complexes.[16]

Structure of the Ring-Opened Scandium Complex. THF ring opening with phosphide complexes was observed by Evans[17] in [$Cp^*_2SmPPh_2$(THF)] and Schumann[18] in [Cp_2-

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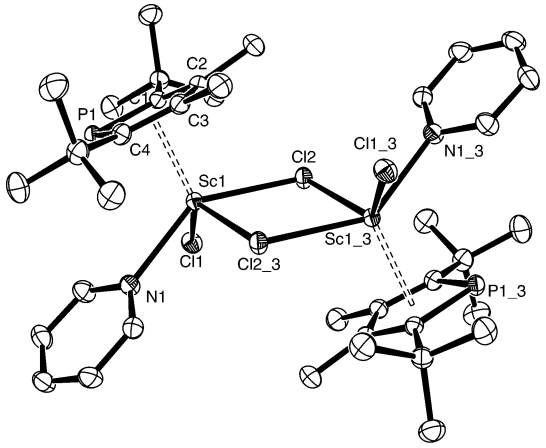

Figure 2. ORTEP plot (50% ellipsoids) of $[(Dtp)Sc(\mu\text{-}Cl)Cl(NC_5H_5)]_2$ (**6**). Hydrogen atoms and one molecule of co-crystallized toluene have been omitted for clarity. Selected bond distances (Å) and angles (deg): Sc(1)−N(1) = 2.383(1), Sc(1)−Cl(1) = 2.4090(5), Sc(1)−Cl(2) = 2.6231(5), Sc(1)−Cl(2_3) = 2.5022(5), Sc(1)−P(1) = 2.6960(5), N(1)−Sc(1)−Cl(1) = 82.42(3), N(1)−Sc(1)−Cl(2_3) = 83.38(3), Cl(1)−Sc(1)−Cl(2_3) = 124.71(2), N(1)−Sc(1)−Cl(2) = 140.83(4), Sc(1_3)−Cl(2)−Sc(1) = 103.84(2), Cl(1)−Sc(1)−Cl(2) = 82.40(2), Cl(2_3)−Sc(1)−Cl(2) = 76.16(2).

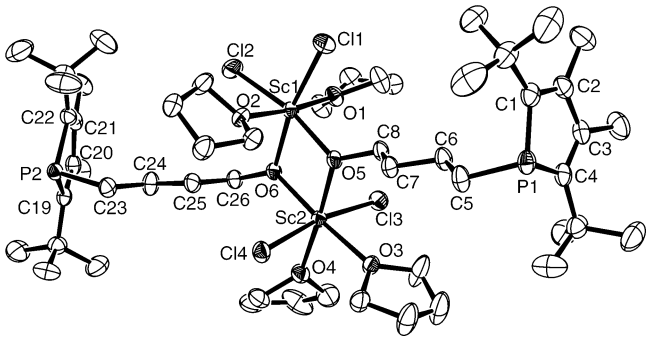

Figure 3. ORTEP plot (50% ellipsoids) of $[\{Sc[\mu\text{-}O(CH_2)_4(Dtp]Cl_2(THF)_2\}_2]$ (**5**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): P(1)−C(5) = 1.862(2), P(2)−C(23) = 1.862(2), Sc(1)−O(5) = 2.092(1), Sc(1)−O(6) = 2.093(1), Sc(1)−O(1) = 2.173(1), Sc(1)−O(2) = 2.199(1), Sc(1)−Cl(2) = 2.4383(5), Sc(1)−Cl(1) = 2.4425(5), Sc(1)−Sc(2) = 3.2848(5), Sc(2)−O(6) = 2.051(1), Sc(2)−O(5) = 2.072(1), Sc(2)−O(4) = 2.227(1), Sc(2)−O(3) = 2.251(1), Sc(2)−Cl(3) = 2.4545(5), Sc(2)−Cl(4) = 2.4385(5), O(6)−Sc(2)−O(5) = 76.04(4), O(5)−Sc(1)−O(6) = 74.73(4), Sc(2)−O(5)−Sc(1) = 104.16(4), Sc(2)−O(6)−Sc(1) = 104.86(5), Cl(2)−Sc(1)−Cl(1) = 97.87(2), Cl(4)−Sc(2)−Cl(3) = 169.94(2), O(1)−Sc(1)−O(2) = 174.26(4), O(4)−Sc(2)−O(3) = 91.20(4).

$LuPPh_2(THF)]$, leading to $[Cp^*_2Sm[O(CH_2)_4PPh_2](THF)]$ and $[\{Cp_2Lu(\mu\text{-}O(CH_2)_4PPh_2\}_2]$, respectively. In both cases, nucleophilic attack of the phosphide on the activated metal-bound THF can be presumed. With the η^5-bound phospholyl ligand, a similar transformation seems less likely. However, from group 4 chemistry it is known that an equilibrium between the η^5- and η^1-coordination of the phospholyl ligand to the metal center can occur.[19] On this basis the following mechanism for the formation of **5** is proposed: the reaction of $ScCl_3$ and [K(Dtp)] leads first to the formation of $[(\eta^5\text{-}Dtp)ScCl_2(THF)_x]$, which can be observed for a short time in ^{31}P NMR. This compound is in equilibrium with $[(\eta^1\text{-}Dtp)ScCl_2(THF)_x]$ (not detectable in ^{31}P NMR), which can undergo THF ring opening by nucleophilic attack of the phosphide on the ether group of THF, which is highly activated by the Lewis acidic Sc center. The resulting low-coordinated Sc complex further dimerizes immediately to **5**.

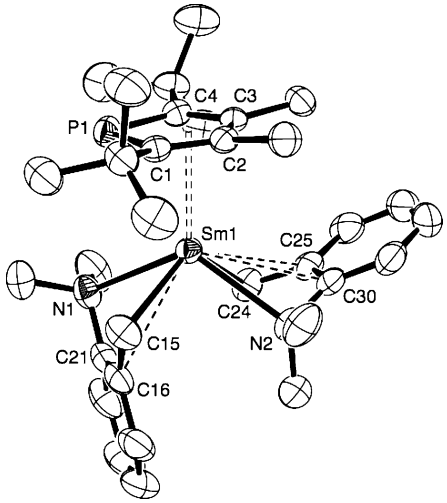

Figure 4. ORTEP plot (50% ellipsoids) of $[(Dtp)Sm(CH_2C_6H_4\text{-}NMe_2\text{-}o)_2]$ (**3-Sm**). Hydrogen atoms have been omitted for clarity. Only one molecule of the two independent molecules in the unit cell is shown. The additional bonding interactions (Sm1−C16, Sm1−C25, and Sm1−C30) are shown with dashed lines.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 3-Ln

	3-Sc	3-Y	3-Sm
Ln1−P1	2.769(1)	2.928(1)	3.009(1)
Ln1−C1	2.631(3)	2.793(4)	2.862(3)
Ln1−C2	2.673(3)	2.814(4)	2.834(3)
Ln1−C3	2.717(3)	2.820(4)	2.866(3)
Ln1−C4	2.724(3)	2.862(4)	2.926(4)
Ln1−C15	2.289(3)	2.443(3)	2.505(3)
Ln1−C24	2.283(3)	2.447(4)	2.519(4)
Ln1−N1	2.529(2)	2.595(4)	2.630(3)
Ln1−N2	2.453(2)	2.576(3)	2.620(3)
Ln1−C16	3.043(4)	3.025(5)	3.022(4)
Ln1−C25	2.995(4)	3.013(5)	2.981(4)
Ln1−C30	3.071(4)	3.084(5)	3.029(3)
N1−Ln−C15	69.9(1)	67.4(1)	66.4(1)
N2−Ln−C24	71.1(1)	68.6(1)	67.6(1)
N1−Ln−C24	84.6(1)	87.8(2)	86.8(1)
N2−Ln−C15	83.8(1)	84.2(1)	84.5(1)
C15−Ln−C24	121.9(1)	116.9(2)	120.6(1)
N1−Ln−N2	126.93(8)	129.6(1)	123.8(1)

The X-ray structure of **5** (Figure 3) reveals many similarities to the above-mentioned Lu compound. The Sc_2O_2 center is quasi planar (dihedral angle 3.5°) with a Sc−Sc distance (3.285 Å) that is shorter than the corresponding Lu−Lu distance (3.475 Å) due to the differences in metal size and coordination numbers. The chloride ligands and the THF molecules are trans to each other, as already observed for **2**. In the phosphole ring the double bonds (1.355−1.360 Å) can be clearly distinguished from the single bond (1.475 Å) and the $P-CH_2$ bond (1.862 Å) is close to that observed in the Lu compound (1.847 Å).[18]

Structures of Monophospholyl Bis(benzyl) Complexes 3-Ln. 3-Sm and **3-Y** were obtained as monoclinic crystals in the space group $P2_1$ with two molecules of a single enantiomer in the unit cell. On the other hand, **3-Sc** crystallized as monoclinic crystals in the space group $P2_1/n$ with one molecule of each enantiomer in the unit cell. Some selected bond distances and angles are summarized in Table 1 (Figure 4).

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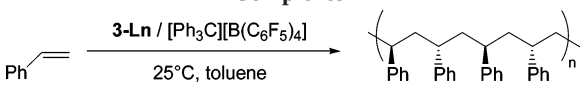
Table 2. Crystal Data and Data Collection Parameters for Compounds 1, 5, 6, 3-Sc, 3-Y, and 3-Sm

	1	5	6	3-Sc	3-Y	3-Sm
molecular formula	$C_{22}H_{40}I_2O_2PSm$	$C_{52}H_{96}Cl_4O_6P_2Sc_2$	$C_{38}H_{58}Cl_4N_2P_2Sc_2$, C_7H_8	$C_{32}H_{48}N_2PSc$	$C_{32}H_{48}N_2PY$	$C_{32}H_{48}N_2PSm$
molecular weight	771.66	1110.95	928.66	536.65	580.60	642.04
cryst habit	dark red block	colorless needle	colorless block	pale yellow plate	yellow plate	black block
cryst dimens (mm)	0.40 × 0.30 × 0.10	0.23 × 0.10 × 0.08	0.22 × 0.20 × 0.16	0.22 × 0.16 × 0.03	0.60 × 0.30 × 0.05	0.50 × 0.20 × 0.10
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1$	$P2_1$
a (Å)	17.435(2)	10.698(1)	13.808(1)	21.860(1)	15.253(1)	15.379(1)
b (Å)	8.688(1)	26.473(1)	15.315(1)	11.952(1)	12.080(1)	12.077(1)
c (Å)	18.590(3)	21.439(1)	11.507(1)	23.239(1)	16.770(1)	16.759(1)
β (deg)	96.765(2)	91.163(1)	107.981(1)	96.430(1)	92.676(1)	92.095(1)
V (Å^3)	2796.5(7)	6070.4(7)	2314.5(3)	6033.5(6)	3086.6(4)	3110.6(4)
Z	4	4	2	8	4	4
d (g cm^{-3})	1.833	1.216	1.333	1.182	1.249	1.371
F(000)	1484	2384	980	2320	1232	1324
μ (cm^{-1})	4.379	0.495	0.626	0.319	1.963	1.961
$\theta_{max.}$	27.54	30.03	30.01	24.71	26.37	27.55
no. of reflns measd	16 574	51 982	15 958	30 171	17 813	19 491
no. of unique data	6243	17 677	6720	10 134	11 505	12 494
R_{int}	0.0359	0.0266	0.0189	0.0598	0.0434	0.0199
no. of reflns used	4707	13139	5510	6011	6813	11773
wR2	0.0928	0.1255	0.1273	0.1239	0.0545	0.0534
R1	0.0409	0.0418	0.0385	0.0470	0.0415	0.0259
GoF	1.009	1.065	1.104	0.945	0.740	0.984

Table 3. Syndiospecific Polymerization of Styrene by 3-Ln Complexes[a]



run	Ln	[M]/[Ln]	t (min)	yield[b] (%)	activity[c]	M_n[d] (10^3)	M_w/M_n[d]
1	Sc	500	<1	100	>3125	300.0	2.07
2	Y	500	30	84	87	77.7	1.55
3	Y	100	1	50	308	8.8	1.67
4	Sm	100	30	0	0		

[a] Conditions: Ln, 21 μmol; [Ln]/[B] = 1/1 (mol/mol); solvent/monomer = 5:1 (v/v). [b]Weight of polymer obtained/weight of monomer used. [c]Given in (kg of sPS) × (mol Ln)$^{-1}$ × h^{-1}. [d]Determined by GPC in trichlorobenzene at 145 °C against polystyrene standard.

The average Ln−(Dtp)$_{centroid}$ distances increase consistent with the metal size going from **3-Sc** (2.36 Å) over **3-Y** (2.52 Å) to **3-Sm** (2.59 Å). These values also show the elongation of the metal−(Dtp)$_{centroid}$ distance when the two halide ligands in **2** and **6**, with Ln−(Dtp)$_{centroid}$ distances of 2.51 and 2.25 Å, respectively, are replaced by the dimethylaminobenzyl ligand. These observations were attributed to the higher steric demand of the benzyl ligand. The average Y−CH_2 (2.44 Å) and Y−NMe_2 (2.58 Å) distances of **3-Y** are similar to the distances observed in [Y($CH_2C_6H_4NMe_2$-*o*)$_3$], 2.47 and 2.56 Å, respectively.[8b] A multihapto binding mode was reported for the benzyl ligand in [Ln($CH_2C_6H_4NMe_2$-*o*)$_3$] (Ln = Y, La).[8b] This observation was confirmed by **3-Y** and **3-Sm**, although less pronounced, in which some interactions between Y and C_{ipso} and between Sm and C_{ipso} and C_{ortho} could be considered. In contrast, **3-Sc** did not show any interaction between the metal and the C_{ipso} or C_{ortho} atoms of the benzyl ligand.

Styrene Polymerization. The use of cationic lanthanoid alkyl complexes bearing monocyclopentadienyl ligands for the syndiospecific polymerization of styrene was recently reported.[3] Complexes **3-Ln** were therefore tested in this reaction to see the influence of the phospholyl ligand on the reaction outcome (Table 3).

Addition of styrene to a 1:1 reaction mixture of **3-Sc** or **3-Y** and [Ph_3C][(C_6F_5)$_4$B] in toluene at room temperature led to the immediate formation of syndiotactic polystyrene. **3-Sc** gave excellent results that could be well compared with those reported for the $C_5Me_4SiMe_3$-ligated Sc bis(alkyl) complex [($C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$(THF)].[20] The phospholyl ligand did not negatively influence the polymerization as it was observed for some group 4 catalysts.[21] Surprisingly, the activity observed for **3-Y** was much higher than that for [($C_5Me_4SiMe_3$)Y(CH_2SiMe_3)$_2$(THF)].[20] However, the activated **3-Sm** complex did not show any activity under the same conditions, in accordance with a previous observation on the reactivity of monocyclopentadienyl complexes of the larger lanthanoids in styrene polymerization.[20] Overall, the polymerization results can be compared with the most active titanium catalysts reported for syndiospecific styrene polymerization.[22]

Conclusion

Solvent-free mono(phospholyl)lanthanoid bis(aminobenzyl) complexes [(Dtp)Ln($CH_2C_6H_4NMe_2$-*o*)$_2$] (Ln = Sm, Y) can be obtained from the one-pot reactions of lanthanoid trihalides $LnCl_3$ with 1 equiv of [K(Dtp)] and 2 equiv of [K($CH_2C_6H_4NMe_2$-*o*)]. The analogous Sc complex can be prepared either from the reaction between the isolated monophospholyl dichloride compound and 2 equiv of [K($CH_2C_6H_4NMe_2$-*o*)] or from the reaction between the protonated Dtp-H ligand and [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$]. These complexes constitute the first examples of catalytically active mono(phospholyl)-ligated lanthanoid metal bis(hydrocarbyl) complexes. The Sc and Y complexes showed high activity for the syndiospecific polymerization of styrene when treated with 1 equiv of [Ph_3C][(C_6F_5)$_4$B]. Further polymerization studies are under investigation.

Experimental Section

General Procedures. All reactions were performed under an inert atmosphere with purified, dry, deoxygenated solvents by using vacuum line and drybox techniques. The following compounds were prepared according to literature procedures: [K(Dtp)],[23] [K($CH_2C_6H_4NMe_2$-*o*)],[9b] [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$].[9a] All other materials were

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commercially available and used without further purification. NMR measurements were carried out at 25 °C, unless mentioned otherwise. Elemental analyses were performed at the Organometallic Chemistry Laboratory, RIKEN, Japan, and at the "Service de Microanalyse de l'Université de Dijon", Dijon (Bourgogne), France.

Synthesis of [(Dtp)SmI$_2$(THF)$_2$] (1). $SmI_3(THF)_{3.5}$ (0.400 g, 0.510 mmol) and [K(Dtp)] (0.134 g, 0.510 mmol) were stirred in THF (10 mL) for 15 h. The reaction was checked by ^{31}P NMR, which indicated that no starting material was left. The red solution was filtered and the solvent evaporated. The residue was taken up in toluene and filtered again. After evaporation the product was washed with diethyl ether to give a red powder of **1** in 62% yield (0.244 g, 0.316 mmol). Crystals suitable for X-ray analysis were grown from a diethyl ether solution at −30 °C.

^{1}H NMR (300 MHz, THF-d_8): δ 3.73 (m, 8H, THF), 2.57 (s, 6H, CCH_3), 1.88 (m, 8H, THF), 0.58 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, THF-d_8): δ 18.4 (s, C*C*H$_3$), 27.7 (d, $^3J_{P-C}$ = 7.1 Hz, C(*C*H$_3$)$_3$), 33.9 (d, $^2J_{P-C}$ = 8.3 Hz, *C*(CH$_3$)$_3$), 135.5 (s, PC*C*), 157.7 (d, $^1J_{P-C}$ = 10.3 Hz, P*C*). ^{31}P NMR (120 MHz, THF-d_8): δ 77.5 (s). Anal. Calcd for $C_{22}H_{40}I_2O_2PSm$ (771.70): C, 34.24, H, 5.22. Found: C, 35.06, H, 4.99.

Synthesis of [(Dtp)Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$] (3-Y). Anhydrous YCl_3 (0.125 g, 0.641 mmol) and [K(Dtp)] (0.168 g, 0.641 mmol) were stirred in THF (10 mL) for 15 h. The reaction was checked by ^{31}P NMR, which indicated that no starting material was left. To the reaction mixture was added a solution of [K(CH$_2$C$_6$H$_4$NMe$_2$-*o*)] (0.222 g, 1.282mmol) in THF (4 mL), and a color change to yellow-green occurred immediately. After 2 h a ^{31}P NMR spectrum showed that the reaction was finished. The solvent was evaporated, and diethyl ether was added onto the residue. After filtration and evaporation a yellow foam was obtained, which was washed with hexane to give the title compound in 68% yield (0.253 g, 0.436 mmol). Crystals suitable for X-ray analysis were grown from a diethyl ether solution at −30 °C.

^{1}H NMR (300 MHz, C_6D_6, 50 °C): δ 6.85 (s, 4H, CH_{arom}) 6.66 (s, 4H, CH_{arom}), 2.41 (br s, 12H, N(CH_3)$_2$), 1.74 (br s, 6H, CCH_3), 1.51 (s, 18H, C(CH_3)$_3$), 1.43 (br s, 4H, YCH_2). ^{13}C NMR (75 MHz, C_6D_{12}): δ 17.8 (C*C*H$_3$), 32.5 (d, $^3J_{P-C}$ = 10.5 Hz, C(*C*H$_3$)$_3$,), 36.1 (d, $^2J_{P-C}$ = 16.6 Hz, *C*(CH$_3$)$_3$), 44.0 (s, N(*C*H$_3$)$_2$), 45.7 (d, $^1J_{C-Y}$ = 31.7 Hz, Y*C*H$_2$), 117.3, 120.0, 127.3, 130.6 (aromatics), 135.2 (s, PC*C*), 142.2, 143.4 (aromatics), 152.9 (s, P*C*). ^{31}P NMR (120 MHz, C_6D_{12}): δ 88.9 (s). Anal. Calcd for $C_{32}H_{48}N_2PY$ (580.62): C, 66.20, H, 8.33, N, 4.82. Found: C, 66.54, H, 8.40, N, 5.19.

Synthesis of [(Dtp)Sm(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$] (3-Sm). (a) To a solution of **1** (0.150 g, 0.239 mmol) in THF (6 mL) was added a solution of *o*-Me$_2$N-benzylpotassium (0.082 g, 0.478 mmol) in THF (4 mL), and a color change to red-violet occurred immediately. After stirring the reaction mixture for 2 h ^{31}P NMR indicated that no starting material was left. The solvent was evaporated, and the residue was taken up in diethyl ether. After filtration and evaporation **3-Sm** was obtained as dark red powder in 80% yield (0.123 g, 0.191 mmol). Crystals suitable for X-ray analysis were grown from a diethyl ether solution at −30 °C.

(b) $SmI_3(THF)_{3.5}$ (0.400 g, 0.510 mmol) and [K(Dtp)] (0.134 g, 0.510 mmol) were stirred in THF (10 mL) for 15 h. The reaction was checked by ^{31}P NMR, which indicated that no starting material was left. To the reaction mixture was added a solution of [K(CH$_2$C$_6$H$_4$NMe$_2$-*o*)] (0.176 g, 1.020 mmol) in THF (4 mL), and a color change to red-violet occurred immediately. After 2 h a ^{31}P NMR spectrum showed that the reaction was finished. The solvent was evaporated, and diethyl ether was added onto the residue. After filtration and evaporation the product was washed with cold diethyl ether to give pure **3-Sm** in 64% yield (0.209 g, 0.326 mmol).

^{1}H NMR (300 MHz, tol-d_8, 80 °C): δ 14.44 (v br s, 4H, SmCH_2), 9.79 (s, 2H, aromatics), 7.56−7.70 (m, 4H, aromatics), 4.68 (s, 2H, aromatics), 2.03 (s, 18H, C(CH_3)$_3$), 0.59 (br s, 6H, CCH_3), −2.29 (br s, 12H, N(CH_3)$_2$). ^{31}P NMR (125 MHz, tol-d_8): δ 62.2 (s). Anal. Calcd for $C_{32}H_{48}N_2PSm$ (642.08): C, 59.86, H, 7.54, N, 4.36. Found: C, 59.79, H, 7.36, N, 4.63.

Synthesis of [{Sc[μ-O(CH$_2$)$_4$(Dtp)]Cl$_2$(THF)$_2$}$_2$] (5). Anhydrous $ScCl_3$ (0.097 g, 0.641mmol) and [K(Dtp)] (0.168 g, 0.641 mmol) were stirred in THF (10 mL) for 72 h. The reaction was checked by ^{31}P NMR, which indicated that no starting material was left. After centrifugation the solvent was evaporated and **5** was obtained as white powder in 95% yield (0.338 g, 0.304 mmol). Crystals suitable for X-ray analysis were obtained from slow diffusion of hexanes into a THF solution of **5**.

^{1}H NMR (300 MHz, THF-d_8): δ 0.98 (br s, 4H, CH_2CH$_2$P), 1.33 (s, 36H, C(CH_3)$_3$), 1.80 (br s, 20H, THF + OCH$_2$CH_2), 2.06 (s, 16H, CH_3 + PCH_2), 3.65 (br s, 16H, THF), 4.09 (m, 4H, OCH_2). ^{13}C NMR (75 MHz, THF-d_8): d 14.6 (d, $^1J_{P-C}$ = 3.8 Hz, C*C*H$_3$), 19.1 (d, $^3J_{P-C}$ = 10.9 Hz, P(CH$_2$)$_2$*C*H$_2$), 23.5 (d, $^2J_{P-C}$ = 32.9 Hz, PCH$_2$*C*H$_2$), 23.8 (s, THF), 29.1 (d, $^3J_{P-C}$ =10.4 Hz, C(*C*H$_3$)$_3$), 32.3 (d, $^2J_{P-C}$ = 25.7 Hz, *C*(CH$_3$)$_3$), 32.5 (d, $^1J_{P-C}$ = 6.0 Hz, P*C*H$_2$), 65.6 (s, THF), 67.6 (s, P(CH$_2$)$_3$*C*H$_2$), 141.1 (d, $^2J_{P-C}$ = 10.0 Hz, PC*C*), 143.9 (d, $^1J_{P-C}$ = 6.5 Hz, P*C*). ^{31}P NMR (125 MHz, thf-d_8): δ 6.0 (s). No correct elemental analysis could be obtained for this compound.

Synthesis of [{(Dtp)Sc(μ-Cl)Cl(NC$_5$H$_5$)}$_2$] (6). Anhydrous $ScCl_3$ (0.097 g, 0.641mmol) and [K(Dtp)] (0.168 g, 0.641 mmol) were stirred in a toluene/pyridine mixture (5:1) (6 mL) for 15 h. The reaction was checked by ^{31}P NMR, which indicated that no starting material was left. After centrifugation the solvent was evaporated and a white powder of **6** was obtained in 90% yield (0.242 g, 0.288 mmol). Crystals suitable for X-ray analysis were obtained from slow diffusion of hexanes into a THF solution of **6**.

^{1}H NMR (300 MHz, C_6D_6): δ 1.52 (s, 36H, C(CH_3)$_3$), 2.56 (s, 12H, CCH_3), 6.31 (m, 4H, pyridine), 6.65 (m, 2H, pyridine), 8.78 (d, 4H, ^3J = 4.8 Hz, pyridine). ^{13}C NMR (75 MHz, C_6D_6): d 18.2 (C*C*H$_3$), 32.8 (d, $^3J_{P-C}$ = 9.8 Hz, C(*C*H$_3$)$_3$), 37.3 (d, *C*(CH$_3$)$_3$), $^2J_{P-C}$ = 15.8 Hz), 124.8, 140.2 (pyridine), 142.5 (d, $^2J_{P-C}$ = 3.8 Hz, PC*C*), 150.6 (pyridine), 168.1 (d, $^1J_{P-C}$ = 55.5 Hz, P*C*). ^{31}P NMR (125 MHz, C_6D_6): δ 123.0 (s). Anal. Calcd for $C_{38}H_{58}Cl_4N_2P_2Sc_2$ (836.56): C, 54.56, H, 6.99, N, 3.35. Found: C, 55.95, H, 7.11, N, 2.97.

Synthesis of [(Dtp)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$] (3-Sc). (a) To a solution of **6** (0.100 g, 0.240 mmol) in toluene (5 mL) was slowly added under vigorous stirring a suspension of [K(CH$_2$C$_6$H$_4$NMe$_2$-*o*)] (0.083 g, 0.480 mmol) in toluene (5 mL), resulting in an orange solution. The reaction was left with stirring for 2 h, after which ^{31}P NMR indicated that all the starting material had been consumed. After centrifugation the solvent was evaporated at 40 °C for 5 h and the residue was recrystallized from hexanes to afford pure **3-Sc** as a yellow solid in 40% yield (0.052 g, 0.096 mmol). Crystals suitable for X-ray analysis were obtained from a saturated benzene solution.

(b) Addition of *p*-toluenesulfonic acid (0.047 g, 0.250 mmol) to a solution of [K(Dtp)] (0.066 g, 0.252 mmol) in toluene (4 mL) resulted in the protonation of Dtp, as indicated by ^{31}P NMR. After addition of [Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.112 g, 0.251 mmol) the reaction was heated to 50 °C and left to stir for 15 h. After this period ^{31}P NMR indicated that no starting material was left. Evaporation of the solvent at 40 °C for 5 h and recrystallization from hexanes gave **3-Sc** as yellow powder in 70% yield (0.094 g, 0.175 mmol).

^{1}H NMR (300 MHz, C_6D_{12}): δ 1.38 (s, 18H, C(CH_3)$_3$), 1.44 (s, 4H, ScCH_2), 1.60 (s, 6H, CCH_3), 2.63 (s, 12H, N(CH_3)$_2$), 6.55−6.73 (m, 8H, aromatics). ^{13}C NMR (75 MHz, C_6D_{12}): δ 16.8 (C*C*H$_3$), 32.4 (d, $^3J_{P-C}$ = 10.5 Hz, C(*C*H$_3$)$_3$), 36.7 (d, $^2J_{P-C}$ = 17.3 Hz, *C*(CH$_3$)$_3$), 48.5 (N(*C*H$_3$)$_2$), 50.3 (Sc*C*H$_2$), 115.8, 121.1, 126.3, 130.5 (aromatics), 135.4 (d, $^2J_{P-C}$ = 3.8 Hz, PC*C*), 144.3, 147.4 (aromatics), 163.7 (d, $^1J_{P-C}$ = 54 Hz, P*C*). ^{31}P NMR (120 MHz, C_6D_{12}): δ 99.0 (s). Anal. Calcd for $C_{32}H_{48}N_2PSc$ (536.68): C, 71.62, H, 9.01, N, 5.22. Found: C, 69.55, H, 8.99, N, 4.70.

Synthesis of Dtp-H (7) (NMR experiment). To a mixture of [K(Dtp)] (0.010 g, 0.038 mmol) and *p*-toluene sulfonic acid (0.007 g, 0.038 mmol) in an NMR tube was added THF-d_8, leading to the immediate protonation of Dtp.

^{1}H NMR (300 MHz, THF-d_8): δ 1.32 (s, 18H, C(CH_3)$_3$), 2.08 (s, 6H, CCH_3), 4.91 (d, 1H, $^1J_{P-H}$ = 219 Hz, P*H*). ^{13}C NMR (75 MHz, THF-d_8): δ 16.3 (d, $^3J_{P-C}$ = 3 Hz, C*C*H$_3$), 30.8 (d, $^3J_{P-C}$ = 7.3 Hz, C(*C*H$_3$)$_3$), 34.1 (d, $^2J_{P-C}$ = 14.9 Hz, *C*(CH$_3$)$_3$), 143.7 (d, $^1J_{P-C}$ = 18.7 Hz, P*C*), 145.4 (d, $^2J_{P-C}$ = 2.5 Hz, PC*C*). ^{31}P NMR (120 MHz, THF-d_8): δ −53.3 (d, 211.2 Hz).

Typical Polymerization Procedure for Styrene. In the glovebox, a toluene solution (7 mL) of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.019 g, 0.021 mmol) was added to a toluene solution (5 mL) of [Sc(Dtp)(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$] (0.011 g, 0.021 mmol) in a 100 mL flask. The mixture was stirred at room temperature for a few minutes, and styrene (1.074 g, 10.5 mmol) was added under vigorous stirring. After a few seconds the stirring ceased due to the viscosity. The flask was then taken outside the glovebox, and after ca. 1 min, methanol (2 mL) was added to stop the polymerization. The mixture was poured into methanol (200 mL) to precipitate the polymer product. The white polymer was collected by filtration and dried under vacuum at 60 °C to a constant weight (1.074 g, 10.5 mmol).

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in the drybox and sealed in thin-walled glass capillaries or mounted on a fiberglass needle using Paratone-N oil. Data collection was performed at 150−160 K on a Bruker SMART APEX diffractrometer or a Nonius KappaCCD diffractometer with CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71069 A). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[24] The raw frame data were processed using SAINT[25] and SADABS[26] to yield the reflection data file. The structures were solved by using the SHELXTL program.[27] Refinement for all compounds was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares methods. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydride atoms in all compounds were located by difference Fourier synthesis, and their coordinates and isotropic parameters were refined. (Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.) The residual electron densities were of no chemical significance. Crystal data and processing parameters for **1**, **5**, **6**, **3-Sc**, **3-Y**, and **3-Sm** are summarized in Table 2.

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Supporting Information Available: ORTEP plots for **1**, **5**, **6**, **3-Sc**, **3-Y**, and **3-Sm** and crystallographic CIF files for all structurally described compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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