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Article

Ytterbium and Samarium Bis(diphosphanylamides): Syntheses and Structures of Lanthanide Complexes Having Two $\{(Ph_2P)_2N\}^-$ Ligands in the Coordination Sphere

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Bis(diphosphanylamide) complexes of the lanthanides have been sythesized. Two approaches to obtain these compounds are shown. Reaction of $YbCl_3$ with a slight excess of $[K(THF)_n][N(PPh_2)_2]$ gives $[\{(Ph_2P)_2N\}_2YbCl(THF)_2]$, which can be further reacted with $K(C_5Me_5)$ to give the corresponding pentamethylcyclopentadienyl complex $[\{(Ph_2P)_2N\}_2Yb(C_5Me_5)]$. In a second approach to bis(diphosphanylamide) complexes of the lanthanides, $Na(C_5H_5)$ was treated with $SmCl_3$ to generate $[(C_5H_5)SmCl_2(THF)_3]$ in situ. Further reaction with 2 equiv of $[K(THF)_n][N(PPh_2)_2]$ gave the desired complex $[\{(Ph_2P)_2N\}_2Sm(C_5H_5)(THF)]$.

Introduction

Recently, there has been a significant research effort in d- and f-block transition metal chemistry to find, in addition to the well-established cyclopentadienyl ligand,[1] new ancillary ligands for stabilizing highly reactive metal centers. In this regard, one approach among others is the use of phosphines with P–N bonds.[2] Recently, we have introduced the well-known monophosphanylamide, $(Ph_2PNPh)^-$,[3] and diphosphanylamide, $\{(Ph_2P)_2N\}^-$,[4–6] as ligands in lanthanide chemistry. Depending on the steric demand of the ligand, either metalate complexes of composition $[Li(THF)_4][(Ph_2PNPh)_4Ln]$ (Ln = Y, Yb, Lu)[3] or the homoleptic compounds $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, La, Nd, Er)[4] can be obtained. The latter complexes were used as catalysts for the polymerization of ϵ-caprolactone. Significant differences in terms of correlations of theoretical and experimental molecular weights as well as polydispersities were observed depending on the nature of Ln. Furthermore, monosubstituted diphosphanylamide complexes, $[\{(Ph_2P)_2N\}LnCl_2(THF)_3]$, of yttrium and the lanthanides were obtained by reacting $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$) with anhydrous yttrium or lanthanide trichlorides.[6] The single-crystal X-ray structures of these complexes always show an η^2-coordination of the ligand via the nitrogen and one phosphorus atom. In solution, a dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorus atoms. The mono- and trisubstituted complexes $[\{(Ph_2P)_2N\}LnCl_2(THF)_3]$ and $[Ln\{N(PPh_2)_2\}_3]$, respectively, were easily obtained in high yields by reacting $[K(THF)_n][N(PPh_2)_2]$ and $LnCl_3$ in the appropriate ratio. However, the missing links between these complexes, i.e., obtaining the bis(diphosphanylamide) complexes of the lanthanides of general composition $[\{(Ph_2P)_2N\}_2LnCl(THF)_x]$, turned out to be more difficult to obtain. In this article, we report the first results in this area.

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 M. Braun glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from Na/K benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from

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$LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥99 atom % D) and were dried, degassed, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR). Mass spectra were recorded at 70 eV on a Varian MAT 711 instrument. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at University of Karlsruhe, Germany. $YbCl_3$,[7] $K(C_5Me_5)$,[8] $Na(C_5H_5)$,[9] and $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$)[4] were prepared according to literature procedures.

$[\{(Ph_2P)_2N\}_2YbCl(THF)_2]$ (1). THF (20 mL) was condensed at −196 °C onto a mixture of 0.909 g (1.83 mmol) of $[K(THF)_n][N(PPh_2)_2]$ and 0.250 g (0.89 mmol) of $YbCl_3$, and the mixture was stirred for 18 h at room temperature. The mixture was filtered, and the solvent removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2). Yield: 0.473 g (47%), orange-red crystals. IR [KBr (cm^{-1})]: 3050 (w, νC═C−*H*), 2997 (m, νC−H), 2980 (m, νC−H), 1583 (w, νC═C), 1478 (m), 1432 (s), 1093 (m), 1015 (m, νPC), 917 (m), 898 (m), 696 (m). $C_{56}H_{56}ClN_2O_2P_4Yb$ (1121.40): calcd. C 59.98, H 5.03, N 2.50; found C 59.91, H 4.89, N 2.31.

$[\{(Ph_2P)_2N\}_2Yb(C_5Me_5)]$ (2). THF (20 mL) was condensed at −196 °C onto a mixture of 0.241 g (0.21 mmol) of **1** and 0.041 g (0.24 mmol) of $K(C_5Me_5)$. The mixture was refluxed for 6 h at room temperature, filtered, and the solvent removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2). Yield: 0.096 g (42%), dark red crystals. $C_{58}H_{55}N_2P_4Yb$ (1076.96): calcd. C 64.68, H 5.15, N 2.60; found C 64.28, H 4.87, N 2.25.

$[\{(Ph_2P)_2N\}_2Sm(C_5H_5)(THF)]$ (3). THF (20 mL) was condensed at −196 °C onto a mixture of 0.041 g (0.47 mmol) of $Na(C_5H_5)$ and 0.120 g (0.47 mmol) of $SmCl_3$. The mixture was stirred for 6 h at room temperature, and the solvent was removed in vacuo. $[K(THF)_n][N(PPh_2)_2]$ (0.466 g, 0.94 mmol) was added to the remaining residue, and the mixture was stirred for 18 h at room temperature. The suspension was filtered, and the solvent was removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2). Yield: 0.165 g (33%), red crystals. IR [KBr (cm^{-1})]: 3061 (w, νC═C−*H*), 3051 (m), 1582 (w, νC═C), 1477 (m), 1431 (s), 1091 (m), 1015 (m, νPC), 920 (s), 781 (m), 739 (m), 700 (m), 666 (m). ^1H NMR (d_8-THF, 400 MHz, 25 °C): δ 1.74−1.79 (m, 4H, THF), 3.58−3.63 (m, 4H, THF), 7.00−7.10 (m, 16H, Ph), 7.12−7.23 (m, 8H, Ph), 7.70 (br, 16H, Ph), 7.88 (br, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (d_8-THF, 100.4 MHz, 25 °C): δ 26.4 (THF), 68.2 (THF), 107.8 (C_5H_5), 128.4−128.7 (m, Ph), 133.3−133.5 (m, Ph), 141.7 (Ph). $^{31}P\{^1H\}$ NMR (d_8-THF, 161.7 MHz, 25 °C): δ −58.0 (br). $C_{57}H_{53}N_2OP_4Sm$ (1056.24): calcd. C 64.81, H 5.06, N 2.65; found C 65.03, H 5.29, N 2.33.

X-ray Crystallographic Studies of 1−3. Crystals of **1**−**3** were grown from hot THF. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

Table 1. Crystallographic Details of $[\{(Ph_2P)_2N\}_2Yb(C_5Me_5)]$ (**2**)[a]

	2·(2THF)
formula	$C_{58}H_{55}N_2P_4Yb$
formula weight	2153.92
space group	$P2_1/c$ (no. 14)
a, Å	10.916(2)
b, Å	21.288(4)
c, Å	21.608(4)
β, deg	93.33(3)
V, Å^3	5013(2)
Z	4
density (g/cm^3)	1.427
radiation	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	2.033
absorption correction	none
reflections collected	36499
unique reflections	9994 (R_{int} = 0.0510)
observed reflections	9262
data, parameters	9994, 591
GOF on F^2	1.175
R1,[b] wR2[c]	0.0226, 0.0708

[a] All data collected at 203 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

All structures were solved by the Patterson method (SHELXS-97[10]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out with the program SHELXL-97[11] by using the 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, respectively.

Because of twinning problems, only the structure of compound **2** was fully refined. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated, and the hydrogen atoms were allowed to ride on the carbons 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. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-237447. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, +(44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

Reaction of $[K(THF)_n][N(PPh_2)_2]$ with anhydrous ytterbium trichloride in THF in a 2:1 molar ratio does not lead selectively to a product of composition $[\{(Ph_2P)_2N\}_2YbCl(THF)_2]$ (**1**). Usually, traces of the homoleptic complex $[Yb\{N(PPh_2)_2\}_3]$ and $[\{(Ph_2P)_2N\}YbCl_2(THF)_3]$ are also formed during the course of the reaction. Recrystallization of the crude product does not yield pure **1** but instead increases the ratio of the less-soluble compound $[\{(Ph_2P)_2N\}YbCl_2$-

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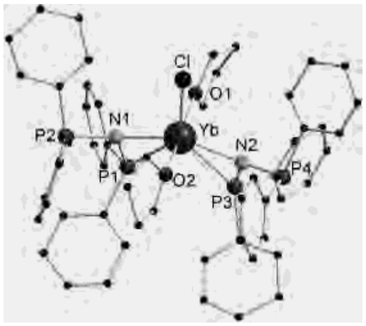
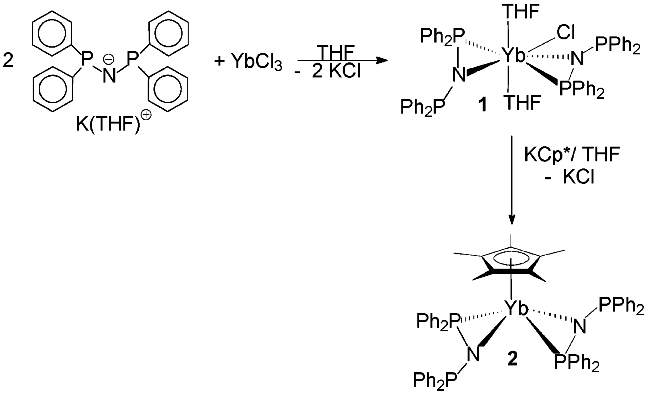


Figure 1. Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms.

Scheme 1



(THF)$_3$]. In contrast, by running the reaction with a slight excess of [K(THF)$_n$][N(PPh$_2$)$_2$], only **1** and [Yb{N(PPh$_2$)$_2$}$_3$] are formed. In this case, **1** can be obtained after recrystallization as the analytically pure product (Scheme 1). The new complex has been characterized by IR spectroscopy and elemental analysis. The structure of **1** in the solid state was confirmed by single-crystal X-ray diffraction (Figure 1). Compound **1** crystallizes in the monoclinic space group $P2_1$ having two molecules of **1** in the unit cell. The metal atoms are surrounded by seven ligands in a distorted pentagonal biypramidal arrangement in which two THF molecules are located in the apex. As observed in the homoleptic complexes [Ln{N(PPh$_2$)$_2$}$_3$][4] and the monosubstituted complexes [{(Ph$_2$P)$_2$N}LnCl$_2$(THF)$_3$],[5,6] the diphosphanylamide ligand in **1** is η^2-coordinated via the nitrogen and one phosphorus atom. Thus, one of the phosphorus atoms of the ligand binds to the ytterbium center, whereas the other phosphorus atom is bent away. The structure of compound **1** was solved as a racemic twin but could not be fully refined. Because the quality of the refinement is low, only the lattice constants but no detailed discussion is presented, although the overall structure of the molecule was clearly established.[12]

Treatment of complex **1** with an excess of K(C$_5$Me$_5$) in THF, followed by crystallization from THF/*n*-pentane (1:2), afforded the corresponding pentamethylcyclopentadienyl complex [{(Ph$_2$P)$_2$N}$_2$Yb(C$_5$Me$_5$)] (**2**) as dark red crystals (Scheme 1). Compound **2** was characterized by elemental analysis, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are reported in Tables 1 and 2, respectively. Compound **2** adopts a distorted square pyramidal conformation in the solid state. This geometry is formed by the η^5-coordinated pentamethylcyclopentadienyl ring, which is located on top of the pyramid, and two η^2-{(Ph$_2$P)$_2$N}$^-$ ligands, which are on the base. Thus, the ytterbium atom is 9-fold-coordinated if η^5-C$_5$Me$_5$ is considered as a pentadentate ligand. The Cg−Yb distance [Cg−Yb 2.300(8) Å] and the C−Yb bond lengths [avg 2.598(2) Å] are in the expected range (Cg = C$_5$Me$_5$-ring centroid).[13] In the {(Ph$_2$P)$_2$N}$_2$Yb core structure, which is roughly C_2 symmetric, the N−Yb and P−Yb bond distances are N1−Yb 2.254(2) Å, N2−Yb 2.251(2) Å, P1−Yb 2.7844(9) Å, and P3−Yb 2.7146(7) Å. These distances are shorter than those observed in [{(Ph$_2$P)$_2$N}LnCl$_2$(THF)$_3$] [N−Yb 2.295(2) Å and P−Yb 2.8280(8) Å].[6] The free

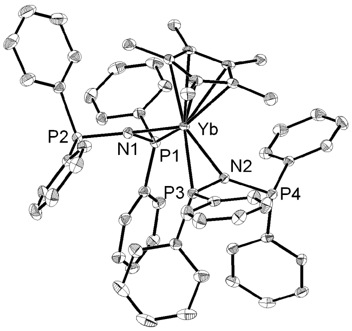


Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [{(Ph$_2$P)$_2$N}$_2$Yb(C$_5$Me$_5$)] (**2**)[a]

Bond Lengths (Å)	
N1−P1	1.671(2)
N2−Yb	2.251(2)
P1−Yb	2.7844(9)
P3−Yb	2.7146(7)
N1−Yb	2.254(2)
Cg−Yb	2.300(8)
N1−P2	1.724(2)
N2−P3	1.664(2)
N2−P4	1.722(2)
Bond Angles (deg)	
N1−Yb−N2	119.34(7)
N1−Yb−P1	36.86(6)
N1−Yb−P3	106.32(6)
N2−Yb−P1	99.49(5)
N2−Yb−P3	37.71(6)
Cg−Yb−N1	122.82(1)
Cg−Yb−N2	117.38(1)
Cg−Yb−P1	130.72(1)
Cg−Yb−P3	118.55(1)
P1−N1−Yb	89.09(10)
P2−N1−Yb	149.24(12)
P1−N1−P2	120.92(12)
P3−N2−Yb	86.44(9)
P4−N2−Yb	142.76(11)
P3−N2−P4	127.62(12)

[a] Cg = C$_5$Me$_5$-ring centroid.

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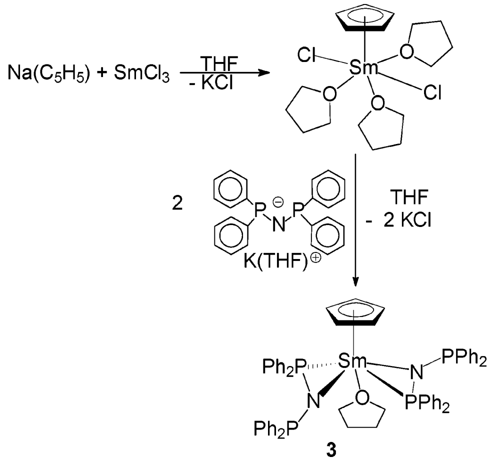
[12] Crystallographic data for [{(Ph$_2$P)$_2$N}$_2$YbCl(THF)$_2$] (**1**): C$_{56}$H$_{56}$ClN$_2$O$_2$P$_4$Yb, fw = 1121.40, monoclinic, space group $P2_1$, a = 15.064(3) Å, b = 12.672(3) Å, c = 15.069(3) Å, β = 95.42(3)°, V = 2863.8(10) Å^3, Z = 2, ρ = 1.300 g cm^{-3}, μ = 0.983 mm^{-1}.

[13] Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986.

Scheme 2



electron pair of the nonbonded phosphorus atoms points away from the ytterbium center. The P−N−P angles within the η^2-$\{(Ph_2P)_2N\}^-$ ligand are P1−N1−P2 120.92(12)° and P3−N2−P4 127.62(12)°. Within the ligand, the P−N bond distance varies. The phosphorus atom that binds to the lanthanide atom is significantly closer located to the nitrogen atom [N1−P1 1.671(2) Å, N1−P2 1.724(2) Å, N2−P3 1.664(2) Å, N2−P4 1.722(2) Å].

A different approach to obtain bis(diphosphanylamide) complexes of the lanthanides is the reaction of $LnCl_3$ with 1 equiv of an ancillary ligand, which leads to complexes of general composition $[RLnCl_2]$. In a second step, the remaining two chlorine atoms can be replaced by two η^2-$\{(Ph_2P)_2N\}^-$ ligands. This reaction sequence can be performed in a one-pot reaction (see Scheme 2). Thus, $Na(C_5H_5)$ was treated with $SmCl_3$ to generate $[(C_5H_5)SmCl_2(THF)_3]$ in situ.[14] Further reaction of $[(C_5H_5)SmCl_2(THF)_3]$ with 2 equiv of $[K(THF)_n][N(PPh_2)_2]$ gave the desired complex $[\{(Ph_2P)_2N\}_2Sm(C_5H_5)(THF)]$ (**3**) as small red crystals. The solid-state structure of **3** was investigated by single-crystal X-ray diffraction. The structure was solved in the monoclinic space group *Cc*, but as a result of a twinning problem, no satifactory refinement could be obtained.[15]

Compound **3** was characterized by elemental analysis, and IR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopies. As a result of the paramagnetic influence of the samarium atom, the ^1H NMR resonances are broad and shifted over a wide range. Thus, the signals of the five-membered ring are low-field-shifted (δ 7.88 ppm) compared to those of the starting material $Na(C_5H_5)$ (δ 5.60 ppm).[9] A similar downfield shift has been observed in other cyclopentadienyl Sm complexes such as $[Li(THF)_4][(C_5H_5)_2Sm(NPh_2)_2]$ (δ 8.25 ppm).[16] The signals of the phenyl rings are split into three multiplets in the range of δ 7.00−7.10 ppm, δ 7.12−7.23 ppm, and δ 7.70 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of the $(C_5H_5)^-$ ring is observed at δ 107.8 ppm. One broad signal is seen at δ 58.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum, showing that the phosphorus atoms are chemically equivalent in solution at room temperature. A similar dynamic behavior is observed for all other $\{(Ph_2P)_2N\}^-$ lanthanide compounds. As shown earlier,[4] the $\{(Ph_2P)_2N\}^-$ ligand acts as hemilabile ligand.[17,18] Thus, the hard nitrogen atom always binds to the lanthanide atom, whereas the phosphorus atoms, which are weak Lewis bases, form only poor Lewis acid−base adducts with the lanthanides and thus might easily be replaced by a hard donor atom such as oxygen in a catalytic cycle.[19]

In contrast to compound **2**, in **3**, one additional equivalent of THF is coordinated to the center metal, showing that the metal center is not completely shielded by two η^2-$\{(Ph_2P)_2N\}^-$ ligands and the smaller $(C_5H_5)^-$ ligand. A similar coordination of one molecule of THF was observed in $[(C_5H_5)_3Sm(THF)]$,[20] indicating that the steric demand of the η^2-$\{(Ph_2P)_2N\}^-$ ligand is somewhat similar to that of the well-known cyclopentadienyl group.

Summary

In summary, we have prepared bis(diphosphanylamide) complexes of the lanthanides. Two approaches to obtain these compounds were shown. In the first approach, $YbCl_3$ was reacted with a slight excess of $[K(THF)_n][N(PPh_2)_2]$ to give the desired bis(diphosphanylamide) complex $[\{(Ph_2P)_2N\}_2YbCl(THF)_2]$. In the second approach, a complex of general composition $[RLnCl_2]$ was obtained with the use of an ancillary ligand. The remaining two chlorine atoms can be selectively substituted in a second reaction step. By following the second approach, the samarium complex $[\{(Ph_2P)_2N\}_2Sm(C_5H_5)(THF)]$ was prepared.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (DFG Schwerpunktprogramm 1166: Lanthanoidspezifische Funktionalitäten in Molekül und Material) and the Fonds der Chemischen Industrie. Additionally, much generous support from Prof. Dr. D. Fenske (Universität Karlsruhe) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystallographic data for $[\{(Ph_2P)_2N\}_2Sm(C_5H_5)(THF)]$ (**3**): $C_{57}H_{53}N_2OP_4Sm$, fw = 1056.24, monoclinic, space group *Cc*, $a = 10.844(2)$ Å, $b = 43.838(9)$ Å, $c = 10.863(2)$ Å, $\beta = 104.74(3)°$, $V = 4994(2)$ Å^3, $Z = 4$, $\rho = 1.405$ g cm^{-3}, $\mu = 0.721$ mm^{-1}. The structure was solved by the Patterson and Fourier methods.

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