Inorg. Chem. **1995,** *34,* 5378−5379

Phosphido Complexes of the Lanthanides. Synthesis and X-ray Crystal Structure Determination of a Tris(phosphido) Species of Neodymium: $Nd[P(SiMe_3)_2]_3(thf)_2$

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Received March 22, 1995

The lanthanide ions, including the group 3 elements scandium, yttrium, and lanthanum, are generally considered to be “hard” Lewis acids. Therefore, a rich coordination chemistry with oxygen- and nitrogen-containing ligands has been developed. On the other hand, there are only a few reports in the literature on lanthanide metal complexes involving ligand systems based on second-row donor ligands containing elements such as sulfur or phosphorus.[1−6]

Tris[bis(trimethylsilyl)amido] species of both divalent[7] and trivalent lanthanide elements as well as scandium[8−10] and the actinide element uranium[11] have been reported in the literature. Bradley and co-workers presented “mixed” amido−phosphido complexes of the general formulas $Ln[N(SiMe_3)_2]_2(PPh_2)$ (Ln = La, Eu) and $Ln[N(SiMe_3)_2]_2(PPh_2)(Ph_3PO)$ (Ln = La, Eu, Y).[4] However, due to the fact that these complexes were found to be exceedingly air- and moisture-sensitive, all reactions were carried out in sealed NMR tubes and characterization was based solely on ^{31}P and ^{1}H NMR spectroscopy. Recently, Aspinall et al. were able to structurally characterize the first “mixed” amido−phosphido complex $Ln[N(SiMe_3)_2]_2(PPh_2)(Ph_3PO)_2$[5] using 2 equiv of the strong donor ligand Ph_3PO. Also, reaction of $Li[La(N^iPr_2)_4]$ with 2 equiv of bis(*o*-methoxyphenyl)phosphine yielded $[(^iPr_2N)_2La\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(thf)]$,[6] which was characterized by X-ray diffraction as its toluene solvate. However, to our knowledge no homoleptic lanthanide complexes with heavier congeners of group 15 of the general formula $Ln[ER_2]_3(L)_x$ (E = P, As, Sb, Bi; L = donor ligand) have been structurally characterized so far.

As part of our continuing effort to investigate the coordination chemistry of the lanthanides with phosphido ligand systems as well as the corresponding bonding aspects, we systematically studied the reactivity of lanthanide halide[12,13] and triflate[14] complexes of the general formula $LnX_x(thf)_y$ (Ln = lanthanide element; X = I, OSO_2CF_3) with alkali metal phosphides MPR_2 (M = Li, K; R = Ph, $SiMe_3$, ^tBu). Recently, we reported the synthesis and structural characterization of the first lanthanide tris(phosphido) complex, $Tm[P(SiMe_3)_2]_3(thf)_2$.[15] Further studies in this area of chemistry lead to the synthesis and structural characterization of a series of divalent lanthanide phosphido species $Ln[PPh_2]_2(L)_4$ (Ln = Sm, Yb; L = thf, *N*-methylimidazole).[16] Other investigations produced two novel four-coordinate lanthanide phosphido complexes surrounded by only phosphorus donor ligands, trivalent $(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ and divalent $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$.[17] Here we report the synthesis and structural characterization of the first tris(phosphido) complex of the lanthanide element neodymium.

Neodymium metal reacts with 1.5 equiv of 1,2-diiodoethane in tetrahydrofuran to give a tetrahydrofuran-insoluble brownish powder which analyzes as $NdI_3(thf)_x$ (x = 3.5; satisfactory elemental analyses obtained for C, H, and I). Reaction of the neodymium halide complex with 3 equiv of potassium bis(trimethylsilyl) phosphide[18] gives a greenish-brownish slurry from which $Nd[P(SiMe_3)_2]_3(thf)_2$, **1**, can be isolated as a green material in 50% yield (eq 1).

$$NdI_3(thf)_x + 3KP(SiMe_3)_2 \rightarrow \underset{\mathbf{1}}{Nd[P(SiMe_3)_2]_3(thf)_2} + 3KI$$

X-ray-quality crystals of **1** were obtained from a saturated toluene solution at −30 °C.[19] The molecular structure of **1** (Figure 1) features the neodymium atom in a distorted trigonal-bipyramidal environment with the phosphido ligands in equatorial and the tetrahydrofuran ligands in axial positions. The arrangement of the $-P(SiMe_3)_2$ ligands can best be described as “propeller shaped” relative to the P_3 plane. Two independent molecules were found to be present in the asymmetric unit of **1** (**1a** and **1b**). Although the crystal structure of **1** and the molecular structure determined for $Tm[P(SiMe_3)]_3(thf)_2$ are related, the unit cell dimensions and space groups for both systems were found to be clearly different.[15,19]

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(19) Crystal data for **1** ($C_{26}H_{70}NdO_2P_3Si_6$): M_r = 820.52, monoclinic, space group $P2_1/c$ with a = 17.449(3) Å, b = 13.486(2) Å, c = 38.867(5) Å, β = 100.803(7)°, V = 8984(2) Å^3, ϱ = 1.213 g cm^{-3}, Z = 8, $F(000)$ = 3448; Siemens P4 diffractometer. The structure was solved by direct methods. Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, T_{min} = 0.5234, T_{max} = 0.5675, μ(Mo Kα) = 1.44 mm^{-1}]. Data were collected at 158 K with Mo Kα (λ = 0.710 73 Å). From 12 829 collected and 11 744 independent reflections, 5926 were considered “observed” [$F_o > 6\sigma(F_o)$] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were calculated and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions (d(C−H) = 0.96 Å; $U_{iso(fix)}$ = 0.08 Å^2). The structure converged for 315 refined parameters to R_F (R_{wF}) value of 0.090 (0.091). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F) + 0.0001F^2$. Residual electron densities: +1.79/−1.75 e Å^{-3}.

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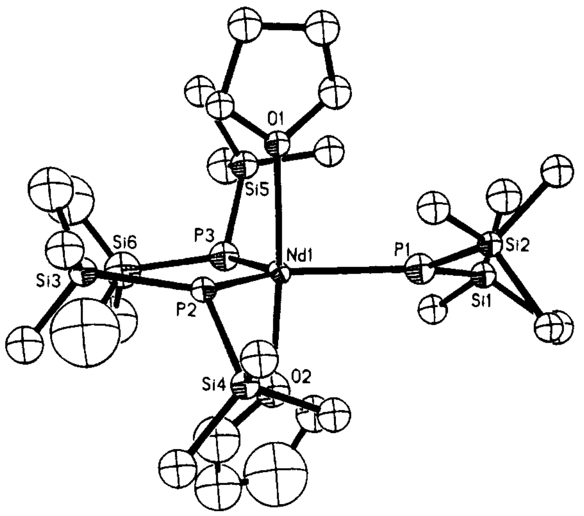

Figure 1. Thermal ellipsoid plot of Nd[P(SiMe$_3$)$_2$]$_3$(thf)$_2$, **1**, drawn at the 30% probability level (only one independent molecule (**1a**) shown). Hydrogen atoms are omitted for clarity.

The 2.80(4) and 2.83(3) Å average Nd–P distances for **1a** and **1b**, respectively, are equivalent within the error limits of the determinations. Consistent with Shannon's radii,[20] these distances are longer than the Tm–P distances (2.709(1) and 2.701(2) Å) in pentacoordinated Tm[P(SiMe$_3$)$_2$]$_3$(thf)$_2$,[15] but significantly shorter than the coordinative 3.154(2) Å Nd···P distances in the hexacoordinated tertiary phosphine complex Nd(OC^{t}Bu$_2$CH$_2$PMe$_2$)$_3$.[21] Furthermore, the Nd–P distances for **1a** and **1b** can be compared with the Nd–N distances reported by Andersen et al. for Nd[N(SiMe$_3$)$_2$]$_3$ (2.29(2) Å).[9] The difference between Nd–P and Nd–N distances is expected to be approximately 0.41 Å.[22] Therefore, the observed Nd-P distances in **1** can be considered as somewhat long, which can be explained by the presence and steric need of two additionally coordinated solvent molecules. Direct comparison of these data in terms of coordination number using Shannon's radii[20] is difficult due to the facts that coordination numbers below 6 are not given in these tables and that different coordination numbers are present in **1** and Nd[N(SiMe$_3$)$_2$]$_3$. The Nd–O distances are 2.521(13)/2.353(16) Å (**1a**) and 2.365(14)/2.500(10) Å (**1b**), respectively. As expected, these distances are longer than the corresponding Tm–O distances (2.314(3) Å) found for Tm[P(SiMe$_3$)$_2$]$_3$(thf)$_2$.[15] The deviation from trigonal-bipyramidal geometry is most readily seen by examining the interligand angles. The six P–Nd–P angles are 119.3(2), 113.5(3), and 127.2(2)° (**1a**) and 118.3(2), 110.2 (2), and 130.4(2)° (**1b**), respectively, with O–Nd–O angles of 175.0(6)° (**1a**) and 175.5(5)° (**1b**). The central neodymium atom deviates 0.013 Å (**1a**) and 0.171 Å (**1b**) from the plane which is described by the three phosphorus atoms. The P–Nd–O angles range from 85.8(4) to 94.7(5)° (**1a**) and from 80.8(3) to 96.9(4)° (**1b**), respectively. The dihedral angles between the PSi$_2$ planes and the P$_3$ plane are 18.2, 43.4, and 55.6° for **1a** (17.9, 45.7, and 60.8° for **1b**). The P–Si distances range from 2.162(13) to 2.232(10) Å (average: 2.20(3) for **1a** and 2.22(4) for **1b**) with sums of the angles around phosphorus ranging from 324.6° (P(6)) to 359.5° (P(1)) and Si–P–Si angles from 104.0(5) to 110.7(4)°. The molecular structures of **1a** and **1b** can furthermore be compared with the gas phase structure[23] as well as the solid state structure[24] of tris(trimethylsilyl)phosphine, both of which show a distinctly pyramidal environment around phosphorus (gas phase sum of angles around phosphorus = 315.6°, average P–Si distances of 2.259(1) Å and average Si–P–Si angles of 105.1(2)°; solid state sum of angles around phosphorus = 318.1°, average P–Si distances of 2.245(3) Å and average Si–P–Si angles of 106.0(3)°).

NMR spectroscopic investigations were found to be difficult due to the strong paramagnetism of **1**. The proton NMR spectrum of **1** in deuterated benzene at room temperature shows only a singlet at −2.33 ppm. We were unable to observe signals for the coordinated tetrahydrofuran molecules. Furthermore, we failed to detect any signals in the ^{13}C as well as in the ^{31}P NMR spectrum of **1**. No molecular peaks could be found by mass spectral analysis using EI, FI, and FD techniques.

The synthesis of **1** introduces a new hexane-soluble homoleptic lanthanide tris(phosphido) complex. The formation of **1** demonstrates that, with careful control of stoichiometry, a class of novel lanthanide complexes is accessible using the −P(SiMe$_3$)$_2$ ligand. We were able to show that this ligand system meets the electrostatic and steric requirements necessary to form thermally stable, isolable complexes of the lanthanides. Furthermore, we could prove that the −P(SiMe$_3$)$_2$ ligand provides the steric bulk needed to sterically saturate the coordination environment of the relatively large lanthanide ion Nd(III). The utility of the neodymium complex **1** derivable in one step from NdI$_3$(thf)$_x$ remains to be determined by its chemistry in a variety of systems.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk double-manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained by following typical laboratory procedures. NdI$_3$(thf)$_x$ (x = 3.5) was prepared from neodymium metal (Strem) and 1,2-diiodoethane (Aldrich). KP(SiMe$_3$)$_2$ was prepared according to the literature.[18]

Nd[P(SiMe$_3$)$_2$]$_3$(thf)$_2$, 1. In the glovebox, KP(SiMe$_3$)$_2$ (167 mg, 0.77 mmol) dissolved in 5 mL of tetrahydrofuran was added to a slurry of NdI$_3$(thf)$_x$ (x = 3.5) (200 mg, 0.26 mmol) in 7 mL of tetrahydrofuran to give a greenish-brownish suspension. After 20 min, the reaction mixture was centrifuged. Removal of solvent and subsequent crystallization from hexanes at −30 °C gave **1** as green crystals (106 mg, 50%). ^{1}H NMR {270 MHZ, C$_6$D$_6$, SiMe$_4$ (external)}: δ −2.33 (s, $\nu_{1/2}$ = 8 Hz). IR (Nujol): 1396 m, 1306 w,, 1240 s, 1014 s, 828 vs, 745 s, 679 s, 625 s cm^{-1}. Raman (647.1 nm): 680 m, 632 vs, 440 m, 429 m, 147 s cm^{-1}. UV–vis (hexane, λ_{max}, nm (ϵ)): 232 (18 850), 237 (19 500), 242 (19 850), 248 (21 900), 254 (22 550), 260 (19 850), 271 (14 650), 326 (11 950). Anal. Calcd for C$_{26}$H$_{70}$O$_2$P$_3$Si$_6$Nd: C, 38.06; H, 8.60; P, 11.32. Found: C, 37.48; H, 8.84; P, 11.06. Elemental analysis was performed using single-crystalline material of **1**. Due to Si–carbide formation the C value was found to be somewhat low. Addition of V$_2$O$_5$ and WO$_3$ helped to suppress formation of SiC. However, this formation could not be excluded completely. Magnetic susceptibility: χ_M^{293K} = 5.08 × 10^{-3} cgsu; μ_{eff} = 3.5 μ_B. Mp: 156 °C dec.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, and the National Science Foundation for financial support for this research. G.W.R. thanks the Deutsche Forschungsgemeinschaft for the award of a fellowship.

Supporting Information Available: Thermal ellipsoid plots, X-ray experimental details, and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (21 pages). Ordering information is given on any current masthead page.

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