Synthesis and Structural Characterization of the First Lanthanide Tris(phosphido) Complex: $Tm[P(SiMe_3)_2]_3(thf)_2$

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$TmI_3(thf)_x$ (x = 3.5) reacts with 3 equiv. of $KP(SiMe_3)_2$ in thf at room temperature to form an orange suspension from which trivalent $Tm[P(SiMe_3)_2]_3(thf)_2$, **1**, can be isolated in 60% yield (monoclinic, space group *C2/c*, four molecules in the unit cell); the structure of **1** features the five-coordinate thulium atom in a distorted trigonal bipyramidal environment with two thf molecules in the axial and the bis(trimethylsilyl)phosphido ligands in the equatorial positions.

Tris[bis(trimethylsilyl)amido] species of Group 13 elements,[1–3] first row transition metals,[3–5] lanthanides[3,6] and uranium[7] have been reported in the literature. Furthermore, there have been reports about bis(trimethylsilyl)amido complexes of the divalent lanthanide elements samarium, europium and ytterbium.[8] Group 13 elements and Ti–Co show trigonal planar arrangements of the three ligands. In contrast, the corresponding derivatives of Sc, Nd, Eu and U exhibit trigonal pyramidal arrangements of the amido ligands in the solid state. All of the tris(amido) species of main group elements, first row transition metals, lanthanides and uranium are propellor-shaped molecules with the planes of the NSi_2 fragments inclined perpendicular to the N_3 plane.

Bonding in lanthanide chemistry has generally been considered as predominantly ionic. Due to the limited radial extension of 4f orbitals, backbonding is somewhat unlikely. If covalency in lanthanide complexes is possible, the most likely ligand systems should be the ones containing 'soft' donor systems, such as phosphido or arsenido ligands. We have now focused our interest on the synthesis and properties of f-element complexes with Ln–E bonds to the heavier Group 15 elements. There is considerable interest in molecules of the general formula $Ln(PR_2)_3(L)_x$ (L = coordinated solvent) because of their potential application as precursors for chemical vapour deposition processes.

Recent publications include reports from Buhro *et al.* about neutral homoleptic complexes $\{M[P(SiMe_3)_2]_2\}_2$ (M = Zn, Cd, Hg, Sn, Pb, Mn)[9] and $M[P(SiPh_3)_2]_2$ (M = Zn, Cd, Hg, Sn),[10] as well as reports from Westerhausen and coworkers about $M[P(SiMe_3)_2]_2(thf)_4$ (M = Sr, Ba),[11,12] $Ca[P(SiMe_3)_2]_2(tmta)_2$ (tmta = 1,3,5-trimethyl-1,3,5-triazinane)[11] and $[(Me_3Si)_2P]Sr[\mu\text{-}P(SiMe_3)_2]_2Sr(thf)_3$.[12] Additionally, 'mixed' complexes of transition metal bis(trimethylsilyl)amides with secondary phosphanes and arsanes of the general formula $\{M[N(SiMe_3)_2][\mu\text{-}E(mes)_2]\}_2$ (M = Mn, Fe; E = P, As; mes = $C_6H_2Me_3$-2,4,6) have been reported by Power *et al.*[13] Bradley and coworkers have shown that lanthanide complexes $Ln[N(SiMe_3)_2]_3$ react with 1 equiv. of $HPPh_2$ to give the partial substitution product $Ln[N(SiMe_3)_2]_2(PPh_2)$ (Ln = La, Eu).[14] Due to the extreme air sensitivity of these complexes, all reactions were carried out in sealed NMR tubes. Characterization was based on ^{31}P and ^1H NMR spectroscopy.

Here we report the first representative of a new class of lanthanide complexes with the general formula $Ln(PR_2)_3(L)_x$. Thulium metal reacts with a 20% excess of 1,2-diiodoethane in tetrahydrofuran to give a thf-insoluble beige powder which analyses as $TmI_3(thf)_x$ (x = 3.5; satisfactory elemental analysis for C, H and I obtained). Reaction of 3 equiv. of $KP(SiMe_3)_2$[15] with 1 equiv. of $TmI_3(thf)_x$ (x = 3.5) in thf produces $Tm[P(SiMe_3)_2]_3(thf)_2$, **1**,† which can be isolated in 60% yield as an orange solid.

Suitable crystals‡ of **1** were obtained from a toluene solution at −30 °C. They are composed of monomeric molecules of **1** (Fig. 1) with a crystallographic twofold axis passing through Tm and P(2). The thulium atom is located in the centre of a distorted trigonal bipyramid, with the $P(SiMe_3)_2$ groups in the equatorial and the tetrahydrofuran molecules in the axial positions (Fig. 2). Tm–P distances are expected to be around 41 pm[16] longer than corresponding Tm–N distances. Due to this difference in metal–ligand distances the coordination sphere around thulium in **1** is not as sterically saturated as in the case of the corresponding tris[bis(trimethylsilyl)amido] species. This additional space around the metal centre allows for the coordination of two solvent molecules in axial positions. As in the case of the tris(amido) species, the $P(SiMe_3)_2$ fragments are inclined in a propellor-shaped way to the P_3 plane with angles between the PSi_2 planes and the P_3 plane of 43.4° [Si(11)–P(1)–Si(12)] and 46.9° [Si(2)–P(2)–Si(2a)]. The Tm–P bond distances are 270.9(1) and 270.1(2) pm and the Tm–O bond distance is 231.5(3) pm with P–Tm–P angles of 127.0(1) and

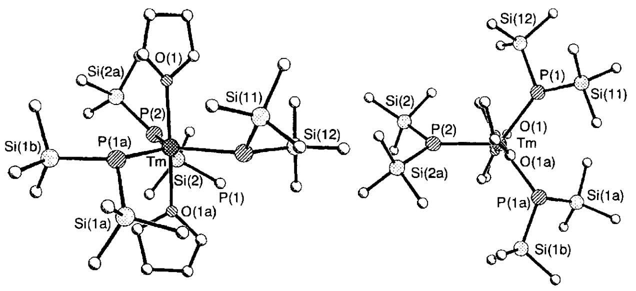

Fig. 1 Two views of the molecular structure of **1** [SCHAKAL, H atoms omitted for clarity, only one orientation of the disordered $Si(2)Me_3$ group is shown]. Selected bond distances (pm) and angles (°): Tm–P(1) 270.9(1), Tm–P(2) 270.1(2), Tm–O(1) 231.5(3), P(1)–Si(11) 222.6(2), P(1)–Si(12) 222.1(2), P(2)–Si(2) 218.9(2); P(1)–Tm–P(2) 127.0(1), P(1a)–Tm–P(1) 105.9(1), O(1)–Tm–P(1) 94.3(1), O(1)–Tm–P(2) 86.0(1), O(1)–Tm–O(1a) 172.1(1).

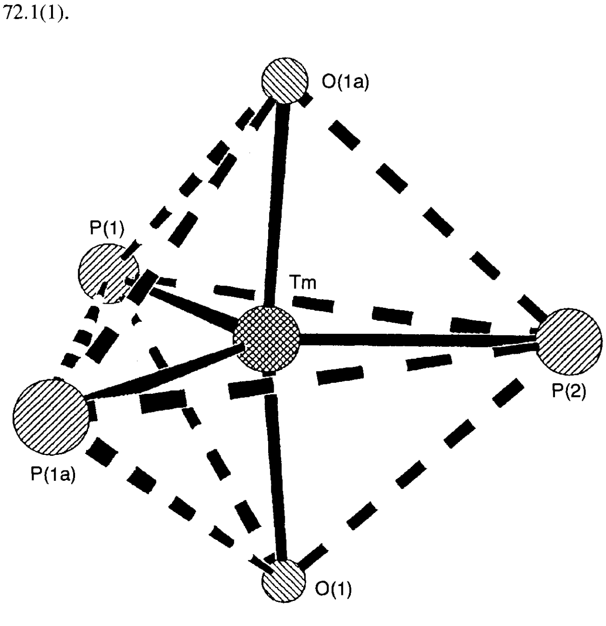

Fig. 2 Trigonal bipyramidal arrangement of the two axial oxygen and three equatorial phosphorus atoms around thulium in $Tm[P(SiMe_3)_2]_3(thf)_2$, **1**

105.9(1)° and an O–Tm–O angle of 172.1(1)°. The O–Tm–P angles range from 86.0(1) to 94.3(1)°.

The proton NMR spectrum of **1** shows one broad signal with $\nu_{1/2}$ = 300 Hz, which can be assigned to the Me_3Si groups. However, the coordinated thf molecules could not be found in the ^1H NMR spectrum. Due to the strong paramagnetism of **1**, no signals were observed in the ^{13}C and ^{31}P NMR spectra. In contrast to the corresponding tris(amido) species, no molecular peak was observed in the CI or FI mass spectra.

Complex **1** represents the first example of a new type of lanthanide complex containing three bis(trimethylsilyl)phosphido ligands. It may be interesting to study the influence of the size of the lanthanide cation on the structure and coordination environments of complexes of the type $Ln(PR_2)_3(thf)_x$ as well as the structural changes which might result from using different ligand systems PR_2. As in the area of transition metal and main group chemistry, the $P(SiMe_3)_2$ ligand appears to offer special opportunities for the lanthanide metals. This 'soft' monodentate ligand provides new opportunities to develop the coordination environments of the lanthanides. Further investigation of the $P(SiMe_3)_2$ ligand in lanthanide chemistry is clearly warranted. This area of lanthanide chemistry is presently under investigation.

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Footnotes

† *Selected data* for **1**: ^1H NMR [270 MHz, C_6D_6, $SiMe_4$ (ext.)]: δ 15.0–18.0 ($\nu_{1/2}$ = 300 Hz). IR ν/cm^{-1} (Nujol) 1300w, 1240s, 1038w, 1004m, 917w, 828vs, 746m, 679m, 625s. Satisfactory elemental analysis for C, H and P were obtained. Magnetic susceptibility: $\chi_M^{293\,K} = 2.46 \times 10^{-7}$ m^3 mol^{-1}; $\mu_{eff} = 6.8\ \mu_B$.

‡ *Crystal data*: $C_{26}H_{70}O_2P_3Si_6Tm$, M_r = 845.22, monoclinic, a = 18.908(4), b = 13.617(2), c = 17.734(3) Å, β = 101.69(1)°, space group $C2/c$, Z = 4, V = 4471.3 Å^3, D_c = 1.255 g cm^{-3}, $F(000)$ = 1760; Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71069 Å), T = −59 °C. Data were corrected for Lorentz and polarization effects as well as for decay (−46%) and absorption [empirical, T_{min} = 0.815, T_{max} = 1.000, μ(Mo-Kα) = 22.9 cm^{-1}]. The structure was solved by Patterson methods. From 10112 measured [$(\sin\theta/\lambda)_{max}$ = 0.64 Å^{-1}] and 4756 unique reflections, 4257 were considered as observed [$F_o > 4\sigma(F_o)$] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters, with the exception of the methyl C-atoms attached to Si(2), which were disordered in split positions. Hydrogen atoms of the disordered $Si(2)Me_3$ group were neglected, all other H-atoms were calculated, allowed to ride on their corresponding carbon atom, and included with isotropic contributions [$U_{iso(fix)}$ = 0.08 Å^2]. The structure converged for 170 refined parameters to an R (R_w) value of 0.0335 (0.0365). The function minimized was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. Residual electron densities: +0.74/−0.77 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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