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Note

Synthesis and crystal structure of a homoleptic, alkali metal-free lanthanide(II) phosphide complex

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Abstract

Thermal treatment of [Sm{P(CH[SiMe$_3$]$_2$)(C$_6$H$_4$-2-CH$_2$NMe$_2$)}$_2$(THF)] (**2**) under reduced pressure for several hours leads to complete de-solvation and isolation of the homoleptic phosphide complex [Sm{P(CH[SiMe$_3$]$_2$)(C$_6$H$_4$-2-CH$_2$NMe$_2$)}$_2$] (**3**). X-ray crystallography shows complex **3** to be monomeric, with a four-coordinate, distorted tetrahedral Sm(II) center. The close contacts between Sm and the *ipso*-carbon atoms of the ligands observed in **2** are absent in **3**. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Samarium(II); P-ligands; Crystal structure; Homoleptic

1. Introduction

Until recently the chemistry of the three lanthanide elements which may be isolated in the +2 oxidation state (Sm, Eu, Yb) was largely confined to complexes with hard donor ligands such as alkoxides, amides and (substituted) cyclopentadienyls [1–6]. However, over the last 5 years the chemistry of the lanthanide elements with softer (di)organophosphide ligands has seen a remarkable expansion; a range of such complexes with ligands including ^{t}Bu$_2$P, Ph$_2$P, (mes)$_2$P and (Me$_3$Si)$_2$P has been isolated and crystallographically characterized [mes = 2,4,6-Me$_3$-C$_6$H$_2$] [7–19]. These complexes adopt a variety of structures, including solvated monomers [(R$_2$P)$_2$LnL$_n$], ate complexes [L$_n$Li(μ-PR$_2$)$_2$Ln(μ-PR$_2$)$_2$LiL$_n$] and unsymmetrical dimers [L$_n$Ln(μ-PR$_2$)$_3$Ln(PR$_2$)]. We recently reported that incorporation of additional donor functionality into the periphery of a sterically demanding phosphide ligand allowed the synthesis of the first homoleptic, solvent- and alkali metal-free lanthanide(II) phosphide complex [{([Me$_3$Si]$_2$CH)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)}$_2$Yb] (**1**), although efforts to characterize this complex thoroughly by X-ray crystallography were unsuccessful [20]. We now report the synthesis and structural characterization of the solvent-free samarium(II) analogue of **1**, [{([Me$_3$Si]$_2$CH)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)}$_2$Sm] (**3**), the first such complex to be crystallographically characterized.

2. Results and discussion

In our recent report of the synthesis of the samarium(II) phosphide complex [{([Me$_3$Si]$_2$CH)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)}$_2$Sm(THF)] (**2**) [20] we observed that there was a strong signal in the EI mass spectrum of this complex for the fragment [**2**-THF]$^+$ (THF = tetrahydrofuran). This suggested to us that de-solvation of **2** on a bulk scale might be achieved by sublimation or thermal treatment. We find that complete de-solvation of **2** is readily attained by heating a solid sample at ~120°C under vacuum (10^{-2} mm Hg), according to Eq. (1). Slight decomposition occurs under these conditions to give a small quantity of the secondary phosphine {(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-CH$_2$NMe$_2$)PH, which may be removed by distillation.

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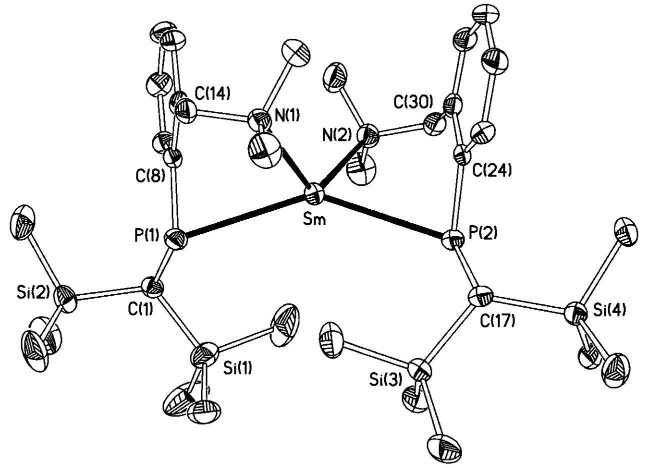

Fig. 1. Molecular structure of **3** with 40% probability ellipsoids and with H atoms omitted for clarity.

$$[\{([Me_3Si]_2CH)P(C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2Sm(THF)] \xrightarrow{\Delta} [\{([Me_3Si]_2CH)P(C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2Sm] + THF \quad (1)$$

Like **2**, complex **3** is very soluble in hydrocarbon solvents and may be obtained as dark green rectangular blocks by recrystallization from cold methylcyclohexane. The ^{1}H-NMR spectrum of **3** in benzene-d_6 is similar to that of the solvated precursor **2**, with signals lying in the range -29.9 to $+19.4$ ppm. This is a much wider chemical shift range than is normally associated with complexes of Sm(II), a phenomenon which can reasonably be ascribed to the extremely close proximity of several of the ligand protons to the paramagnetic Sm(II) center [5,21]. Assignment of the ^{1}H-NMR spectrum is tentative at this stage and was achieved with the aid of a 2-D proton COSY experiment.

X-ray crystallography shows that **3** crystallizes as discrete monomers containing a four-coordinate Sm center with a distorted tetrahedral geometry (Fig. 1). Selected bond lengths and angles for **3** are given in Table 1. The samarium atom is bound by the N and P atoms of the two aminophosphide ligands to give two puckered six-membered chelate rings. The chelate bite angles of 77.03(7) and 79.12(7)° in **3** are slightly larger than the bite angle of 75.01(6)° in the C_2-symmetric complex **2**, consistent with the lower coordination number samarium in the former complex [20].

The Sm–P(1) and Sm–P(2) distances of 2.993(1) and 2.990(1) Å, respectively, are significantly shorter than the same distance in **2** [3.0873(8) Å]. These distances compare with Sm–P distances of 2.953(3) and 2.955(3) Å in $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Sm(THF)(DME)]$ and 2.988(6) and 3.049(5) Å in $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Sm(DME)]$ [20], and are at the lower end of the range of Sm(II)–P distances reported to date (DME = 1,2-dimethoxyethane). For example, a Sm(II)–P distance of 3.139(3) Å has been reported for the octahedral complex $[(Ph_2P)_2Sm(N\text{-}MeIm)_4]$ (*N*-MeIm = *N*-methylimidazole) [11] and distances of 3.019(3)–3.178(3) Å have been reported for the binuclear, phosphido-bridged complex $[(THF)_3Sm\text{-}\{\mu\text{-}P(SiMe_3)_2\}_3Sm\{P(SiMe_3)_2\}]$ [14]. Similarly, the Sm–N(1) and Sm–N(2) distances of 2.662(2) and 2.626(3) Å in **3** are somewhat shorter than the same distance in **2** [2.682(3) Å], reflecting the lower coordination number in the former complex. However, these distances fall within the range typical for Sm(II)–N bonds. For example, the Sm–N distances in $[(Ph_2P)_2Sm(N\text{-}MeIm)_4]$ are 2.633(7) and 2.609(7) Å [11].

We had previously observed that in **2** the two *ipso*-carbons adjacent to phosphorus exhibit weak but significant contacts with samarium [Sm–C_{ipso} = 3.030(3) Å] [20]. Somewhat surprisingly, given the extremely low coordination number of the samarium center, the Sm–C_{ipso} distances in **3** of 3.152 and 3.156 Å are substantially longer, suggesting a significantly weaker interaction in **3** than in **2**. This hypothesis is supported by the Sm–P–C_{ipso} angles, which are significantly wider in **3** [Sm–P(1)–C(8) and Sm–P(2)–C(24) = 77.65(12) and 77.81(11)°, respectively] than in **2** [Sm–P(1)–C(8) = 70.89(9)°], clearly indicating a weaker interaction in the former complex.

Table 1
Selected bond lengths (Å) and angles (°) for **3**

Sm–P(1)	2.9930(11)	Sm–P(2)	2.9897(11)	Sm–N(1)	2.622(3)
Sm–N(2)	2.626(3)	P(1)–C(1)	1.894(4)	P(1)–C(8)	1.818(4)
P(2)–C(17)	1.890(4)	P(2)–C(24)	1.822(4)	C(1)–Si(1)	1.862(4)
C(1)–Si(2)	1.877(4)	C(17)–Si(3)	1.873(4)	C(17)–Si(4)	1.877(4)
N(1)–Sm–P(1)	79.12(7)	N(2)–Sm–P(2)	77.03(7)		
N(1)–Sm–N(2)	118.28(10)	P(1)–Sm–P(2)	143.47(3)		
N(1)–Sm–P(2)	120.42(7)	N(2)–Sm–P(1)	123.32(7)		
C(8)–P(1)–Sm	77.65(12)	C(8)–P(1)–C(1)	104.15(17)		
C(1)–P(1)–Sm	121.21(12)	C(24)–P(2)–Sm	77.81(11)		
C(24)–P(2)–C(17)	105.75(17)	C(17)–P(2)–Sm	115.52(12)		
P(1)–C(1)–Si(1)	108.9(2)	P(1)–C(1)–Si(2)	108.91(19)		
Si(1)–C(1)–Si(2)	119.5(2)	P(2)–C(17)–Si(3)	105.41(19)		
P(2)–C(17)–Si(4)	110.13(19)	Si(3)–C(17)–Si(4)	119.0(2)		

The P(1)–Sm–P(2) angle [143.47(3)°] is highly distorted from the usual tetrahedral value because of the need to accommodate the two sterically demanding $CH(SiMe_3)_2$ groups; the P(1)–Sm–N(2) and P(2)–Sm–N(1) angles are 123.32(7) and 120.42(7)°, respectively.

The P atoms in **3** are distinctly pyramidal; the sums of the angles about phosphorus are 303.01 and 299.08° for P(1) and P(2), respectively. This compares with a value of 305.82° for the sum of angles about phosphorus in **2**.

3. Conclusions

The steric properties of the phosphide ligands in **2** are sufficient to enable its facile de-solvation by heating at moderate temperatures under vacuum. The complex obtained (**3**) is a rare example of a solvent- and alkali metal-free lanthanide(II) phosphide complex and is the first such complex to be crystallographically characterized.

The chemistry of this and related coordinately unsaturated lanthanide phosphide complexes is expected to prove extremely interesting and is currently under investigation.

4. Experimental

4.1. General comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Light petroleum (b.p. 40–60°C) and methylcyclohexane were distilled from sodium–potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film. Deuterated benzene was distilled from potassium and was deoxygenated by three freeze–pump–thaw cycles and stored over activated 4 Å molecular sieves. $[Sm\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2(THF)]$ was prepared according to a previously published procedure [20].

^{1}H-NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500 MHz and chemical shifts are quoted in ppm relative to tetramethylsilane. Elemental analyses were obtained by Elemental Microanalysis Ltd., Okehampton, UK.

4.2. Preparation of $[Sm\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2]$ (**3**)

A solid sample of $[Sm\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2(THF)]$ (0.57 g, 0.65 mmol) was heated to 120°C at 10^{-2} mm Hg for 3 h. The dark green solid remaining after this time was dissolved in methylcyclohexane (5 ml) and cooled to −30°C for 12 h. The dark green crystals of **3** were isolated, washed with a little cold (−40°C) light petroleum and residual solvent was removed in vacuo. Yield 0.41 g, 78%. Anal. Found: C, 48.31; H, 7.94; N, 3.43. Calc. for $C_{32}H_{62}N_2P_2Si_4Sm$: C, 48.07; H, 7.82; N, 3.50%. (H) (THF-d_8; tentative assignment only): −29.86 (*s*, 1H, CH_2N), −12.36 (*s*, 1H, CH_2N), −2.18 (*s*, 15H, $SiMe_3$), −0.82 (*s*, 1H, $CHSi_2$), 4.68 (*s*, 1H, ArH), 6.31 (*s*, 6H, NMe_2), 9.26 (*s*, 1H, ArH), 10.77 (*s*, 1H, ArH), 12.60 (*s*, 1H, ArH), 19.39 (*s*, 3H, $SiMe_3$).

4.3. Crystal structure determination of **3**

Data were collected at 160 K on a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{32}H_{62}N_2P_2Si_4Sm$, $M = 799.5$, dark green rectangular blocks, crystal size 0.32 × 0.12 × 0.06 mm, monoclinic, space group $P2_1/c$, $a = 12.6844(8)$, $b = 18.2621(12)$, $c = 17.8281(11)$ Å, $\beta = 95.385(2)°$, $V = 4111.5(5)$ Å^3, $Z = 4$, $\mu = 1.65$ mm^{-1}, R (F; $F^2 > 2\theta$) = 0.0414, R_w (F^2; all data) = 0.0816, $S = 0.949$ for 9655 unique, absorption-corrected data and 387 refined parameters; final difference map extremes +0.50 and −0.72 e Å^{-3}. Programs: Bruker AXS SMART (diffractometer control), SAINT (data integration), and SHELXTL (structure solution and refinement).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 145942 for compound **3**. Copies of this information are available free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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