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Notes

Synthesis and X-ray Crystal Structure Determination of the First Homoleptic Four-Coordinate Phosphido Complex of Samarium: $Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$

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As part of an effort to develop the coordination environments of the lanthanides using phosphido ligands, as well as to investigate the corresponding bonding aspects, we have been examining the reaction behavior of lanthanide triflates[1] with lithium bis(*tert*-butyl)phosphide.[2]

Recently, we described the synthesis and structural characterization of a novel four-coordinate homoleptic phosphido complex of divalent ytterbium: $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$.[3] A question of considerable interest is how the size of the lanthanide cation influences the observed structure. To probe this issue we decided to determine whether the structure of the above-mentioned ytterbium species in the solid state would change employing the larger samarium(II) cation in place of ytterbium(II). Additionally, $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ was found to exhibit strongly photoluminescent properties.[3] We wanted to find out whether this behavior is determined by the ligand system or the metal center. Here we report the synthesis and X-ray crystal structure determination of a tetrakis(phosphido) species of divalent samarium.

Reaction of $Sm(OSO_2CF_3)_3$[1] with 5 equiv of LiP^tBu_2[2] proceeds under immediate reduction of trivalent samarium to give the dark purple monomeric bis "ate" complex $Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, **1**, and $^1/_2$ equiv of $^tBu_2P\text{-}P^tBu_2$ (eq 1). Complex **1** was the only samarium containing species being formed both for a 1:3 and a 1:5 ratio of reagents. Formation of $^tBu_2P\text{-}P^tBu_2$ was demonstrated by ^{31}P NMR spectroscopy of the hexanes fraction ($\delta = 40.0$ ppm in C_6D_6) and comparison with a standard sample.

$$Sm(OSO_2CF_3)_3 + 5LiP^tBu_2 \rightarrow \underset{\mathbf{1}}{Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2} + 3LiOSO_2CF_3 + {}^1/_2{}^tBu_2P\text{-}P^tBu_2 \quad (1)$$

Formation of the tetrakis(phosphido) species **1** is surprising in light of earlier reports on the formation of the hexa-coordinate bis(phosphido) complex $Sm[PPh_2]_2(thf)_4$, which does form using three different synthetic routes.[4] Reduction of Sm(III) was reported as well in other systems.[5−7]

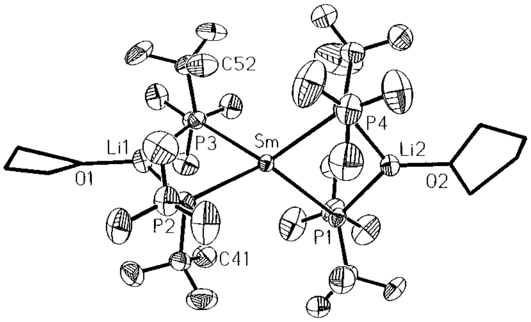

Figure 1. Thermal ellipsoid plot of $Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, **1**, drawn at the 50% probability level. Hydrogen atoms were omitted for clarity, and only one orientation of the heavily disordered tetrahydrofuran molecules is shown.

Contrary to the ytterbium(II) species $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, **2** ($f^{14}$), the samarium(II) analogue **1** (f^6) was not found to exhibit photoluminescent properties, indicating that the nature of the lanthanide(II) cation is probably responsible for this behavior rather than the properties of the ligand system.

The molecular structure of complex **1** (Figure 1)[8] features the four-coordinate samarium cation surrounded by phosphido ligands only, arranged in a distorted tetrahedral fashion. The molecular structures of complexes **1** and **2** are isostructural. The samarium(II)−P distances in complex **1** range from 3.036(1) to 3.070(2) Å (average: 3.048(13) Å). These distances are approximately 0.09 Å longer than the corresponding values found for $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, **2** [2.948(1)−2.985(1) Å; average 2.959(15) Å]. According to Shannon,[9] samarium(II) can be expected to be approximately 0.14 Å larger than ytterbium(II) for a given coordination number. Therefore, the observed Sm(II)−P distances in **1** are shorter than one would expect. As a matter of fact, these distances are significantly shorter than the Sm(II)−P distance of 3.1908(6) Å reported for hexa-coordinate $(\eta^1\text{-}C_{12}H_8P)_2Sm(thf)_4$[10] as well as the 3.139(3) Å distance in hexa-coordinated $Sm[PPh_2]_2(N\text{-MeIm})_4$[4] (*N*-MeIm = *N*-methylimidazole). Also, they are slightly shorter than the corresponding distance of 3.0775(1) Å in π-bonded $(\eta^5\text{-}2,3\text{-}(CH_3)_2(C_9H_6P)_2Sm(thf)_2$.[10] However, they can be compared with the shortest Sm(II)−P distances (3.019(3)−3.066(3) Å) found in $(Me_3Si)_2PSm[\mu\text{-}P(SiMe_3)_2]_3Sm(thf)_3$.[11]

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(1) Hamidi, M. E. M.; Pascal, J.-L. *Polyhedron* **1994**, *13*, 1787.

(2) Issleib, K.; Krech, F. *J. Organomet. Chem.* **1968**, *13*, 283.

(3) Rabe, G. W.; Riede, J.; Schier, A. *Inorg. Chem.* **1996**, *35*, 40.

(4) Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1995**, *34*, 4521.

(5) Berardini, M.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1995**, *34*, 5327.

(6) Song, J.-I.; Gambarotta, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2141.

(7) Cary, D. R.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 1791.

(8) Crystal data for **1** ($C_{40}H_{88}Li_2O_2P_4Sm$) at 231 K: $M_r = 889.27$, monoclinic, space group $P2_1/c$, with $a = 21.651(2)$ Å, $b = 12.252(1)$ Å, $c = 20.556(2)$ Å, $\beta = 108.86(1)°$, $V = 5160.1$ Å^3, $D_{calcd} = 1.145$ g cm^{-3}, $Z = 4$, and $F(000) = 1888$; Enraf Nonius CAD4 diffractometer. The structure was solved by direct methods. Data collected at 211 K with Mo Kα ($\lambda = 0.710\,69$ Å). Data were corrected for Lorentz and polarization effects as well as for absorption [empirical, $T_{min} = 0.7820$, $T_{max} = 0.9999$, μ(Mo Kα) = 12.89 cm^{-1}]. From 9720 measured [$(\sin \Theta)/\lambda_{max} = 0.59$ Å^{-1}] and 8018 unique reflections, 6700 were considered "observed" [$F_o > 4\sigma(F_o)$] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters, except for those of the two tetrahydrofuran molecules, which were heavily disordered in split positions. Accordingly, the corresponding H-atoms were neglected. All other H-atoms were calculated and allowed to ride on their corresponding carbon atom with fixed isotropic contributions ($U_{iso(fix)} = 0.08$ Å^2). The structure converged for 456 refined parameters to an R (R_w) value of 0.0375 (0.0417). The function minimized was $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. Residual electron densities: +1.13/−0.64 eÅ^{-3}, located at the samarium atom.

(9) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(10) Nief, F.; Ricard, L. *J. Organomet. Chem.* **1994**, *464*, 149.

(11) Rabe, G. W.; Riede, J.; Schier, A. *Organometallics* **1996**, *15*, 439.

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The two bridging P−Sm−P angles of **1** are 82.6(1) [P(3)−Sm−P(2)] and 83.0(1)° [P(4)−Sm−P(1)], respectively, and can be compared with the corresponding angles found for complex **2** [83.3(1) and 84.1(1)°]. All other P−Sm−P angles range from 120.3(1) to 127.4(1)°. These values match the numbers we reported for complex **2** [120.3(1)−126.2(1)°] within the error limits. The P−C distances range from 1.880(7) to 1.896(6) Å and are in excellent agreement with our reports on the P−C distances in the moleculear structure of **2**. Two three-coordinate lithium atoms are present, each one of these surrounded by two phosphido ligands and one tetrahydrofuran molecule with Li−P distances from 2.50(1) to 2.54(1) Å [2.481(6) to 2.512(7) Å for the ytterbium analogue **2**]. The P−Li−P angles in complex **1** [P(3)−Li(1)−P(2): 105.8(4)°; P(4)−Li(2)−P(1): 106.3(3)°] are only slightly larger than the corresponding values reported for complex **2** [103.6(3) and 104.8(3)°].

The molecular structure of **1** shows a formally four-coordinate samarium center. However, an accurate determination of the coordination number in this particular molecule is difficult given the fact that agostic interactions between certain ^{t}Bu groups and the lanthanide center are present, thus leading to a higher effective coordination number than four (as was observed in the case of complex **2**). The closest non-bonding Sm···C distances are 3.482(6) Å [Sm···C(41)] and 3.578(7) Å [Sm···C(52)] (Figure 1). All other nonbonding Sm···C distances were found to be longer than 4.0 Å. These numbers can be compared with reports from Evans and co-workers on agostic Sm···C distances in the formally four-coordinate divalent samarium bis(amido) complex $Sm[N(SiMe_3)_2]_2(thf)_2$ (3.32(1)−3.46(1) Å).[12] To the best of our knowledge, there are only two other reports in the literature on low-coordinate Sm(II) complexes, namely $(4\text{-Me-}2,6\text{-}^tBu_2C_6H_2O)_2Sm(thf)_3$[13] and $(4\text{-Me-}2,6\text{-}^tBu_2C_6H_2O)_3SmK$.[14] Another example of a four-coordinate lanthanide complex is the $[Lu(CMe_3)_4]^-$ anion.[15]

No signals could be detected in the ^{31}P NMR spectrum of **1**, which is probably a result of the strongly paramagnetic properties of divalent samarium. The ^{7}Li NMR spectrum of complex **1** in deuterated benzene shows a rather peculiar chemical shift of −60.8 ppm. Again, this observation is probably due to the strong paramagnetism of divalent samarium. Interestingly, two signals were found in the ^{7}Li NMR spectrum of **1** in deuterated tetrahydrofuran. This observation contrasts with our reports on the corresponding spectrum of the ytterbium analogue **2**, which exhibits only one ^{7}Li signal in both tetrahydrofuran and benzene solution.[3] In an attempt to clarify the cause of this unusual spectrum a VT ^{7}Li NMR study of $Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ in tetrahydrofuran solution between +55 and −80 °C was performed: At +55 °C, a very broad signal is observed at −7 ppm ($\nu_{1/2} = 1700$ Hz) along with a broad signal at −51 ppm ($\nu_{1/2} = 1000$ Hz). The ratio of intensities of these signals is approximately 2:3. Upon cooling, the half-widths of both signals decrease. Concomitantly, the signal at lower field shifts gradually downfield, while the signal at higher field shifts gradually upfield, accompanied by a continuous decrease of intensity. At −80 °C, only the signal at lower field could be detected ($\delta = -0.3$ ppm, $\nu_{1/2} = 85$ Hz).

The synthesis of the formally four-coordinate lanthanide complex $Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, **1**, introduces a novel phosphido species of divalent samarium. The utility of this complex remains to be determined by examination of its chemistry in a variety of systems.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk double manifold, high-vacuum, and glove-box (M. Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. $Sm(OSO_2CF_3)_3$[1] and LiP^tBu_2[2] were prepared according to the literature. The UV-vis spectrum was recorded on a Shimadzu UV 240 instrument. NMR spectra were recorded on a Jeol JMN-GX 400 instrument.

$Sm[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$, 1. In the glovebox, LiP^tBu_2 (255 mg, 1.67 mmol) dissolved in 7 mL of tetrahydrofuran was added to a slurry of $Sm(OSO_2CF_3)_3$ (200 mg, 0.33 mmol) in 7 mL of tetrahydrofuran to immediately give a dark greenish-purplish solution. After 20 min, the solvent was removed. Subsequent extraction using hexane/toluene (1:1) followed by crystallization at −30 °C gave **1** as dark purple crystals (205 mg, 70%). Anal. Calcd for $C_{40}H_{88}Li_2O_2P_4Sm$: C, 54.02; H, 9.97; Li, 1.56; P, 13.93. Found: C, 53.90; H, 10.16; Li, 1.52; P, 14.07. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.18 (br, $\nu_{1/2} = 30$ Hz, 8H), 1.3 (s, $\nu_{1/2} = 10$ Hz, 72H), 1.7 (br, $\nu_{1/2} = 50$ Hz, 8H). ^{1}H NMR (400 MHz, C_4D_8O, 20 °C): δ 1.06 (s, $\nu_{1/2} = 17$ Hz). ^{13}C NMR (100.4 MHz, C_6D_6, 20 °C): δ 9.6 (br, $\nu_{1/2} = 10$ Hz, thf), 23.7 (s, $\nu_{1/2} = 4$ Hz), 68.4 (vbr, thf). No signals could be detected in the ^{13}C NMR spectrum of complex **1** in tetrahydrofuran-d_8 at room temperature. ^{7}Li NMR (C_6D_6, 155.5 MHz, 20 °C): δ −60.8 (s, $\nu_{1/2} = 86$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, 55 °C): δ −7 (vbr, $\nu_{1/2} = 1700$ Hz), −51 (br, $\nu_{1/2} = 1000$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, 20 °C): δ −5 (vbr, $\nu_{1/2} = 1700$ Hz), −58 (br, $\nu_{1/2} = 625$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, 0 °C): δ −1 (vbr, $\nu_{1/2} = 1200$ Hz), −63 (br, $\nu_{1/2} = 400$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, −20 °C): δ − 0.6 (br, $\nu_{1/2} = 530$ Hz), −67.6 (br, $\nu_{1/2} = 300$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, −40 °C): δ −0.5 (br, $\nu_{1/2} = 250$ Hz), −72.1 (br, $\nu_{1/2} = 210$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, −60 °C): δ −0.3 (br, $\nu_{1/2} = 85$ Hz), −78.2 (br, $\nu_{1/2} = 110$ Hz). ^{7}Li NMR (C_4D_8O, 155.5 MHz, −80 °C): δ −0.3 (br, $\nu_{1/2} = 85$ Hz). IR (Nujol): 1353 s, 1293 w, 1160 m, 1043 vs, 916 w, 889 m, 814 m, 722 w, 675 w, 520 w, 468 m, 432 s cm^{-1}. UV−vis (hexane; λ_{max}, nm (ϵ)): 237 (sh, 6630), 242 (7970), 248 (9830), 254 (10730), 260 (9470), 281 (sh, 6530), 314 (8170). Magnetic susceptibility: $\chi_M^{293K} = 4.61 \times 10^{-3}$ cgs; $\mu_{eff} = 3.3\ \mu_B$. BM. Mp: 212 °C dec.

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Supporting Information Available: Thermal ellipsoid plots and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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(12) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575.

(13) Qi, G.-Z.; Shen, Q.; Lin, Y.-H. *Acta Crystallogr.* **1994**, *C50*, 1456.

(14) Evans, W. J.; Anwander, R.; Ansari, M. A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5.

(15) Schumann, H.; Genthe, W.; Hahn, E.; Pickardt, J.; Schwarz, H.; Eckart, K. *J. Organomet. Chem.* **1986**, *306*, 215.