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Divalent Lanthanide Chemistry: Three Synthetic Routes to Samarium(II) and Ytterbium(II) Bis(phosphido) Species Including the Structural Characterization of $\mathrm{Yb[PPh_2]_2(thf)_4}$ and $\mathrm{Sm[PPh_2]_2(\mathit{N}\text{-}MeIm)_4}$[1]

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The 4f-block elements, "hard" Lewis acids, have a rich coordination chemistry with "hard" bases such as nitrogen and oxygen ligands. Bonding in lanthanide chemistry has generally been considered as predominantly ionic because of the limited radial extension of 4f orbitals. However, if covalent bonding in lanthanide chemistry is possible, the most likely complexes are those containing "soft" P or S donors due to the availability of suitable orbitals for accepting metal electrons.

We were interested in the chemistry of the lanthanide elements with heavier congeners of group 15. The corresponding bis(amido) or tris(amido) species of both divalent and trivalent lanthanide metals have been known in the literature for many years.[2−6]

Our studies have centered on the preparation of lanthanide complexes with ligand systems of the general formula $-[\mathrm{PR_2}]^-$. We are interested in finding out whether "soft" phosphido ligands meet the electrostatic and steric requirements necessary to form thermally stable, isolable complexes of the lanthanides.

Recently we reported the synthesis and structural characterization of the first lanthanide tris(phosphido) complexes, $\mathrm{Ln[P(SiMe_3)_2]_3(thf)_2}$ (Ln = Tm, Nd).[7] Here we report on three different synthetic routes to divalent lanthanide bis(phosphido) complexes of the general formula $\mathrm{Ln[PPh_2]_2(L)}_x$ (Ln = Sm, Yb; L = thf, *N*-methylimidazole).[8,9]

1. Dark blue $\mathrm{SmI_2(thf)_2}$[10] reacts with 2 equiv of $\mathrm{KPPh_2}$ in tetrahydrofuran immediately to form a dark green suspension from which $\mathrm{Sm[PPh_2]_2(thf)_4}$, **1a**, can be isolated in 90% yield as a dark green powder. Similarly, orange $\mathrm{Yb[PPh_2]_2(thf)_4}$, **1b**, can be prepared in almost quantitative yield (eq 1). Both tetrasolvated adducts **1a,b** tend to become partially desolvated when exposed to vacuum for long periods of time. The remaining material analyzes as $\mathrm{Ln[PPh_2]_2(thf)}_x$.[8]

$$\mathrm{LnI_2(thf)_2 + 2KPPh_2 \rightarrow Ln[PPh_2]_2(thf)_4 + 2KI} \tag{1}$$

$$\mathrm{Ln = Sm,\ Yb}$$

2. A suspension of $\mathrm{LnI_3(thf)_3}$ (Ln = Sm, Yb)[11] in tetrahydrofuran reacts with 3 equiv of strongly reducing $\mathrm{KPPh_2}$ immediately to give a dark green (**1a**) or an orange (**1b**) suspension, respectively. Removal of solvent and subsequent washing of the crude product with toluene gives toluene-insoluble **1** in 70% yield (eq 2). Formation of $\mathrm{Ph_2P{-}PPh_2}$ was shown by ^{31}P NMR spectroscopy of the toluene fraction ($\delta = -14.6$ ppm in $\mathrm{C_6D_6}$) and comparison with a standard sample. The reaction mixture of elemental samarium or ytterbium with

$$\mathrm{LnI_3(thf)_3 + 3KPPh_2 \rightarrow Ln[PPh_2]_2(thf)_4 + 3KI + {}^1\!/_2 Ph_2P{-}PPh_2} \tag{2}$$

$$\mathrm{Ln = Sm,\ Yb}$$

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(8) Characterization data of $\mathrm{Ln[PPh_2]_2(thf)_4}$, **1**, are as follows. **1a**: ^{1}H NMR (THF-d_8, 400 MHz, 20 °C) δ 6.76 (s, $\nu_{1/2} = 20$ Hz, 8H), 8.42 (s, $\nu_{1/2} = 35$ Hz, 4H), 9.44 (s, $\nu_{1/2} = 40$ Hz, 8H); ^{13}C NMR (THF-d_8, 100.8 MHz, 20 °C) δ 25.8 (thf), 68.2 (thf), 114.1 ($\nu_{1/2} = 40$ Hz), 119.3 ($\nu_{1/2} = 50$ Hz), 133.2 ($\nu_{1/2} = 50$ Hz), 173.0 (br). **1a** becomes partially desolvated upon drying over longer time periods. The remaining residue analyzes as $\mathrm{Sm[PPh_2]_2(thf)}_x$ ($x = 1.75$). Anal. Calcd for $\mathrm{C_{31}H_{34}O_{1.75}P_2Sm}$: C, 57.52; H, 5.29; P, 9.57. Found: C, 57.38; H, 5.22; P, 9.57. IR (Nujol): 1572 m, 1428 m, 1262 w, 1180 w, 1072 w, 1023 s, 988 w, 887 w, 728 vs, 693 vs, 502 w, 468 s cm^{-1}. **1b**: ^{1}H NMR (THF-d_8, 400 MHz, 20 °C) δ 6.57 (t, $J = 7.3$ Hz, 4H), 6.82 (t, $J = 7.3$ Hz, 8H), 7.33 (m, $\nu_{1/2} = 40$ Hz, 8H); ^{13}C NMR (THF-d_8, 100.4 MHz, 20 °C) δ 26.3 (thf), 68.2 (thf), 121.1 ($\nu_{1/2} = 20$ Hz), 127.8 ($\nu_{1/2} = 30$ Hz), 131.3 (d, $^2J_{\mathrm{C-P}} = 15$ Hz), 153.3 (d, $^1J_{\mathrm{C-P}} = 34$ Hz); ^{31}P NMR (THF-d_8, 161.7 MHz, 20 °C) δ −3.0 (s, $\nu_{1/2} = 53$ Hz, $^1J_{\mathrm{P-Yb}} = 840$ Hz). **1b** also becomes partially desolvated as well upon drying over longer time periods. The remaining residue analyzes as $\mathrm{Yb[PPh_2]_2(thf)}_x$ ($x = 0.5$). Anal. Calcd for $\mathrm{C_{26}H_{24}O_{0.5}P_2Yb}$: C, 53.90; H, 4.17; P, 10.69. Found: C, 53.62; H, 4.27; P, 10.95. IR (Nujol): 3039 w, 1574 m, 1295 w, 1261 m, 1180 m, 1072 m, 1024 s, 988 w, 913 w, 870 m, 729 s, 693 s cm^{-1}.

(9) Characterization data of $\mathrm{Ln[PPh_2]_2(N\text{-}MeIm)_4}$, **2**, are as follows. **2a**: ^{1}H NMR (THF-d_8, 400 MHz, 20 °C) δ 2.83 (s, 12H), 3.53 (s, 4H), 4.42 (s, $\nu_{1/2} = 20$ Hz, 4H), 4.54 (s, $\nu_{1/2} = 20$ Hz, 4H), 7.27 (s, $\nu_{1/2} = 25$ Hz, 8H), 8.82 (s, $\nu_{1/2} = 25$ Hz, 4H), 12.28 (s, $\nu_{1/2} = 35$ Hz, 8H); ^{13}C NMR (THF-d_8, 100.4 MHz, 20 °C) δ 29.4 ($\mathrm{CH_3}$), 105.9 ($\nu_{1/2} = 40$ Hz), 114.3 ($\nu_{1/2} = 30$ Hz), 123.5 ($\nu_{1/2} = 40$ Hz), 135.0 ($\nu_{1/2} = 25$ Hz), 161.9 ($\nu_{1/2} = 100$ Hz), 179.5 ($\nu_{1/2} = 150$ Hz), 186.8 (br). Anal. Calcd for $\mathrm{C_{40}H_{44}N_4P_2Sm}$: C, 56.58; H, 5.22; N, 13.20; P, 7.29. Found: C, 56.68; H, 5.35; N, 13.02; P, 7.22. IR (Nujol): 3097 w, 1568 m, 1525 w, 1510 w, 1284 m, 1263 w, 1230 m, 1178 w, 1109 s, 1069 s, 1029 m, 1020 m, 988 m, 923 s, 888 w, 839 m, 819 m, 746 s, 733 vs, 697 s, 673 w, 666 s, 615 m cm^{-1}. **2b**: ^{1}H NMR (THF-d_8, 400 MHz, 20 °C) δ 3.50 (s, $\nu_{1/2} = 15$ Hz, 12H), 6.51 (t, $J = 7.4$ Hz, 4H), 6.73 (t, $J = 7.4$ Hz, 8H), 6.84 (s, $\nu_{1/2} = 15$ Hz, 4H), 7.05 (s, $\nu_{1/2} = 20$ Hz, 4H), 7.31 (t, $J = 6.1$ Hz, 8H), 7.42 (s, $\nu_{1/2} = 25$ Hz, 4H). ^{13}C NMR (THF-d_8, 100.4 MHz, 20 °C) δ 33.3 ($\mathrm{CH_3}$), 120.3 ($\nu_{1/2} = 15$ Hz), 120.6 ($\nu_{1/2} = 15$ Hz), 127.5 (d, $^3J_{\mathrm{C-P}} = 6$ Hz), 130.2 ($\nu_{1/2} = 20$ Hz), 131.1 (d, $^2J_{\mathrm{C-P}} = 17$ Hz), 140.2 ($\nu_{1/2} = 50$ Hz), 154.6 (d, $^1J_{\mathrm{C-P}} = 37$ Hz); ^{31}P NMR (THF-d_8, 109.4 MHz, 55 °C) δ −0.9 (s, $\nu_{1/2} = 35$ Hz); ^{31}P NMR (THF-d_8, 109.4 MHz, 20 °C): δ −2.1 (s, $\nu_{1/2} = 40$ Hz); ^{31}P NMR (THF-d_8, 109.4 MHz, −30 °C) δ −3.8 (s, $\nu_{1/2} = 50$ Hz); ^{31}P NMR (THF-d_8, 109.4 MHz, −60 °C) δ −4.8 (s, $\nu_{1/2} = 65$ Hz); ^{31}P NMR (THF-d_8, 109.4 MHz, −90 °C) δ −6.8 (s, $\nu_{1/2} = 65$ Hz). Anal. Calcd for $\mathrm{C_{40}H_{44}N_4P_2Yb}$: C, 55.11; H, 5.09; N, 12.85; P, 7.11. Found: C, 54.85; H, 5.14; N, 12.69; P, 6.73. IR (Nujol): 3095 w, 1568 m, 1525 w, 1277 m, 1228 m, 1172 w, 1108 m, 1069 s, 1020 m, 988 w, 925 m, 842 m, 821 m, 747 s, 733 vs, 697 s, 673 m, 660 vs, 615 vs cm^{-1}.

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Ph_2P-PPh_2 in tetrahydrofuran in the presence of mercury dichloride does not react to form **1**.

3. $Ln[N(SiMe_3)_2]_2(thf)_2$ (Ln = Sm, Yb)[3] reacts with 2 equiv of Ph_2PH in tetrahydrofuran to give **1** in 80% yield (eq 3). However, no reaction was observed using the divalent bis(amido) species and 2 equiv of $(^tBu)_2PH$ or $(Mesityl)_2PH$.

$$Ln[N(SiMe_3)_2]_2(thf)_2 + 2Ph_2PH \rightarrow Ln[PPh_2]_2(thf)_4 + 2HN(SiMe_3)_2 \quad (3)$$

$$Ln = Sm, Yb$$

Complex **1** can be converted to $Ln(PPh_2)_2(N\text{-}MeIm)_4$ (Ln = Sm, Yb), **2**, in tetrahydrofuran using 4 equiv of the strong donor ligand *N*-methylimidazole (*N*-MeIm) in almost quantitative yield (eq 4).[9]

$$Ln[PPh_2]_2(thf)_4 + 4N\text{-}MeIm \rightarrow Ln[PPh_2]_2(N\text{-}MeIm)_4 + 4thf \quad (4)$$

$$Ln = Sm, Yb$$

Figure 1 shows the molecular structure of **1b**, and an ORTEP of **2a** is found in the supporting information.[12] The structures display slightly distorted octahedral environments around the lanthanide atom, situated at an inversion center, with the two phosphido ligands in *trans* positions. The Yb–P distance in the molecular structure of **1b** is 2.991(2) Å and can be compared with the Yb–P distances in bis(η^5-2,5-diphenylphospholyl)Yb-$(thf)_2$ (2.959(1) Å).[13] Further Yb–P distances have been reported for divalent $\{(thf)Li[C(PMe_2)_2(SiMe_3)]\}_2 \cdot YbI_2(thf)$ (2.96(1)–3.08(1) Å)[14] as well as for divalent $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$ (3.012 (4) Å)[2] and trivalent $Yb(C_5Me_5)_2Cl[Me_2PCH_2PMe_2]$ (2.941 (3) Å).[15]

According to Shannon,[16] divalent samarium is expected to be approximately 0.14 Å larger than divalent ytterbium. The Sm–P distance of 3.139(3) Å found for **2a** matches therefore the expectations. This Sm–P distance is significantly shorter than the Sm–P distance of 3.1908(6) Å reported for the divalent samarium bis(η^1-dibenzophospholyl) species, $(\eta^1\text{-}C_{12}H_8P)_2Sm(thf)_4$.[17] Ytterbium(II)/samarium(II)–P distances are expected to be around 0.41 Å longer than the corresponding ytterbium(II)/samarium(II)–N distances.[18] Taking this information and the expected difference in radii between divalent ytterbium and samarium into account, the Yb–P distance of 2.991(2) Å in **1b** and the Sm–P distance of 3.139(3) Å found for **2a** are relatively long compared with the average Yb/Sm–N distances reported on divalent *cis*-$(C_{12}H_8N)_2Yb(1,2\text{-dimethoxyethane})$-*cis*-$(thf)_2$ (2.44(1) Å),[19] on *cis*-$(C_{12}H_8N)_2Sm(thf)_4$ (2.565 (13) Å), and on *trans*-$(C_{12}H_8N)_2Sm(N\text{-}MeIm)_4$ (2.591(3) Å).[20] They are definitely very long compared with the 2.331(13) Å divalent Yb–N distances in $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$[2] as well as the 2.424(9)–2.445(7) Å divalent samarium amide distances in $[(Me_3Si)_2N]_2Sm(thf)_2$ and $\{[(Me^3Si)_2N]Sm(\mu\text{-}I)(dme)(thf)\}_2$.[3] However, comparison of these data in terms of bond distances using Shannon's radii[16] is difficult given the fact that the exact coordination number in some of the above mentioned complexes is hard to define due to agostic interactions.

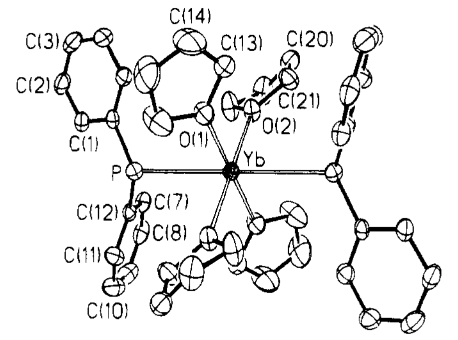

Figure 1. ORTEP diagram and numbering scheme of $Yb[PPh_2]_2(thf)_4$, **1b**, drawn at the 35% probability level. Hydrogen atoms omitted for clarity.

The deviation from octahedral geometry is most readily seen by examining the interligand angles. The L–Yb–(*cis* L) angles in **1b** range from 85.1(1) to 94.9(1)° (84.5(1) to 94.6(2)° for the L–Sm–(*cis* L) angles in **2a**). The Yb–O distances in **1b** are 2.437(4) and 2.430(4) Å and match the corresponding Yb–O(thf) distances reported for *cis*-$(C_{12}H_8N)_2Yb(1,2\text{-dimethoxyethane})$-*cis*-$(thf)_2$ (2.41(2) and 2.48(2) Å).[19] The Sm–N distances in **2a** are 2.633(7) and 2.609(7) Å and are not too different from the average Sm–N(*N*-MeIm) distance of 2.685 (14) Å found for *trans*-$(C_{12}H_8N)_2Sm(N\text{-}MeIm)_4$.[20]

The geometry around the phosphorus atoms in both cases is pyramidal; the sum of the bond angles around P is 332.7° (**1b**) and 343.1° (**2a**), respectively. These data can be compared with the numbers reported on the molecular structure of triphenylphosphine ($\Sigma CPC = 308.3°$).[21] The Yb–P–C angles of 110.2(1) and 119.4(1)° and the Sm–P–C angles of 112.8(2) and 124.0(3)° can be compared with the corresponding angles of 95.78(6) and 105.83(6)° reported by Nief.[17]

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters and an ORTEP diagram (17 pages). Ordering information is given on any current masthead page.

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(12) Crystal data for **1b**, $C_{40}H_{52}O_4P_2Yb$ at 234 K: monoclinic, $P2_1/n$, a = 10.090(3) Å, b = 17.647(3) Å, c = 11.050(3) Å, β = 102.24(2)°, V = 1922.8(9) Å^3, Z = 2, D_{calcd} = 1.437 g cm^{-3}, μ(Mo Kα) = 25.53 cm^{-1}. Crystal data for **2a**, $C_{40}H_{44}N_8P_2Sm$ at 250 K: monoclinic, $P2_1/n$, a = 10.042(4) Å, b = 17.743(4) Å, c = 11.299(4) Å, β = 95.23 (3)°; V = 2004.9(11) Å^3; Z = 2, D_{calcd} = 1.405 g cm^{-3}, μ(Mo Kα) = 15.81 cm^{-1}. Data were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation (0.710 73 Å) in the Wyckoff scan mode. Totals of 3532 reflections for **1b** and 2768 reflections for **2a** were collected in the scan ranges $4.0 < 2\theta < 50.0$ and $4.0 < 2\theta < 45.0$, respectively. Refinement converged for **1b** at $R_F = 2.75\%$ ($R_{wF} = 3.44\%$) for 2198 observed independent reflections $[F_o \geq 5\sigma(F_o)]$ with $N_o/N_v = 11.5$; refinement converged for **2a** at $R_F = 3.42\%$ ($R_{wF} = 4.84\%$) for 1821 observed independent reflections $[F_o \geq 4\sigma(F_o)]$ with $N_o/N_v = 7.8$.

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