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Synthesis, X-ray Crystal Structure Determination, and NMR Spectroscopic Investigation of Two Homoleptic Four-Coordinate Lanthanide Complexes: Trivalent $({}^{t}Bu_2P)_2La[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]$ and Divalent $Yb[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]_2$[†,1]

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$La(OSO_2CF_3)_3$ reacts with 4 equiv of $LiP^{t}Bu_2$ in tetrahydrofuran to give dark red $({}^{t}Bu_2P)_2La[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]$ (**1**). $Yb(OSO_2CF_3)_3$ reacts with $LiP^{t}Bu_2$ in tetrahydrofuran in a 1:5 ratio to produce $Yb[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]_2$ (**2**) and 1/2 an equiv of ${}^{t}Bu_2P-P^{t}Bu_2$. Both **1** and **2** crystallize in the monoclinic space group $P2_1/c$. Crystal data for **1** at 214 K: $a = 11.562$ (1) Å, $b = 15.914$ (1) Å, $c = 25.373$ (3) Å, $\beta = 92.40$ (1)°; $V = 4664.5$ Å^3; $Z = 4$; $D_{calcd} = 1.137$ g cm^{-3}; $R_F = 2.61\%$. Crystal data for **2** at 217 K: $a = 21.641$ (2) Å , $b = 12.189$ (1) Å, $c = 20.485$ (2) Å, $\beta = 109.01$ (1)°; $V = 5108.9$ Å^3; $Z = 4$; $D_{calcd} = 1.185$ g cm^{-3}; $R_F = 2.80\%$. The molecular structures of **1** and **2** show the four-coordinate lanthanide atoms in distorted tetrahedral environments. These complexes are the first representatives of the lanthanide elements surrounded by four only-phosphorus-containing substituents. The main features of the crystal structure of **1** are the shortest La−P distances (2.857(1) and 2.861(1) Å) reported so far and a three-coordinate lithium cation. The molecular structure of **2** represents a divalent bis "ate" complex with two three-coordinate lithium cations. Complex **2** shows photoluminescent properties. VT NMR spectra (^{7}Li and ^{31}P) are reported for **1** and **2**.

Introduction

Lanthanide ions are generally considered to be hard Lewis acids, and consequently the coordination chemistry of the 4f-block metals with nitrogen and oxygen based ligands is very well developed. As part of our continuing effort to investigate the coordination environments of the lanthanides and group 3 elements with phosphido ligands, as well as the corresponding bonding aspects, we were interested in the reaction behavior of lanthanide triflates[2] with lithium bis(*tert*-butyl)phosphide.[3] Phosphides are of interest as ligands because of the way they differ electrostatically from amides. The differing behaviors of these two classes of ligands can be ascribed to normal periodic trends that distinguish the properties of N and P, e.g. lower electronegativity, larger size, and lower hybridization tendency of P. The focus of this effort was to determine the structural changes which result by employing different ligand systems of the type$-PR_2$. The influence of the size of the lanthanide or group three element cation on the structure and coordination environment of complexes which contain structural fragments of the general formula $Ln[PR_2]_x$ is another center of interest.

We recently described the synthesis and structural characterization of the first lanthanide tris(phosphido) complexes, $Ln[P(SiMe_3)_2]_3(thf)_2$ (Ln = Tm, Nd),[4] as well as three different synthetic routes to divalent lanthanide bis(phosphido) species.[5] A limited number of reports on cyclopentadienyl-based lanthanide phosphido species has appeared in the literature.[6−8] Here we report on the preparation and structure determination of the two novel low-coordinate lanthanide phosphido "ate" complexes $({}^{t}Bu_2P)_2La[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]$ (**1**) and $Yb[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]_2$ (**2**) starting from the corresponding triflate complexes[2] of trivalent lanthanum and ytterbium. Complexes **1** and **2** represent the first reports on trivalent and divalent lanthanide complexes containing four only-phosphorus ligands.

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 following typical laboratory procedures. $Ln(OSO_2CF_3)_3$ (Ln = La, Yb)[2] and $LiP^{t}Bu_2$[3] were prepared according to the literature. UV−vis spectra were recorded on a Shimadzu UV 240 instrument. The fluorescence spectrum was recorded on a Perkin Elmer LS 50B luminescence spectrometer. NMR spectra were recorded on Jeol JMN-GX 270 and JMN-GX 400 instruments.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for 1 and 2. Small crystals were mounted in glass capillaries. Graphite-monochromated Mo Kα radiation was used ($\lambda = 0.710\,69$ Å). Data were collected on an Enraf Nonius CAD4 diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares calculations (SHELXTL PLUS).[9]

$({}^{t}Bu_2P)_2La[(\mu\text{-}P^{t}Bu_2)_2Li(thf)]$ (1). In the glovebox, addition of a solution of $LiP^{t}Bu_2$ (208 mg, 1.36 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of $La(OSO_2CF_3)_3$ (200 mg, 0.34 mmol) in 7 mL of tetrahydrofuran resulted in a slow color change to dark red. After 14 h, the solvent was removed. Subsequent extraction of the residues using hexanes and crystallization at −30 °C gave **1** as dark red crystals (218 mg, 80%). Complex **1** is soluble in hexanes. Anal. Calcd for $C_{36}H_{80}LiOP_4La$: C, 54.13; H, 10.09; Li, 0.87; P, 15.51.

[†] Dedicated to Professor Dr. Dr.$_{h.c.}$ Herbert W. Roesky on the occasion of his 60th birthday.

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Table 1. Crystallographic Data for the Lanthanide Phosphido Complexes $(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ (**1**) and $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (**2**)

complex	**1**	**2**
formula	$C_{36}H_{80}LaLiOP_4$	$C_{40}H_{88}Li_2O_2P_4Yb$
fw	798.78	911.96
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.562(1)	21.641(2)
b (Å)	15.914(1)	12.189(1)
c (Å)	25.373(3)	20.485(2)
β (deg)	92.40(1)	109.01(1)
cell vol (Å^3)	4664.5	5108.9
Z	4	4
D_{calcd} (g cm^{-3})	1.137	1.185
temp (K)	214	217
μ_{calcd} (cm^{-1})	10.76	19.90
transm coeff (min−max)		0.905−0.999
R (%)	2.63	2.80
R_w (%)	2.83	3.10
ρ_{max}/ρ_{min} (e Å^{-3})	+0.49/−0.72	+0.65/−0.59

Found: C, 54.05; H, 10.16; Li, 0.85; P; 15.73. ^1H NMR (C_6D_6, 270 MHz, 20 °C): δ 1.18 (m, 4H), 1.71 (d, $^3J_{H-P} = 11$ Hz, 72H), 3.48 (m, 4H). ^{13}C NMR (C_6D_6, 100.4 MHz, 20 °C): δ 25.2 (thf), 35.5 (d, $^2J_{C-P} = 9$ Hz, CH_3-*C*), 36.4 (d, $^1J_{C-P} = 18$ Hz, CH_3-*C*), 69.5 (thf). ^7Li NMR (C_6D_6, 155.5 MHz, 20 °C): δ 2.6 (quintett, $^1J_{Li-P} = 28$ Hz). ^7Li NMR (C_4D_8O, 155.5 MHz, 20 °C): δ −0.7 (s, $\nu_{1/2} = 15$ Hz). ^7Li NMR (C_4D_8O, 155.5 MHz, −105 °C): δ −1.2 (s, $\nu_{1/2} = 8$ Hz). ^{31}P NMR (C_6D_6, 109.4 MHz, 20 °C): δ 135−180 (br, $\nu_{1/2} = 2000$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, 20 °C): δ 170−225 (br, $\nu_{1/2} = 3000$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, −90 °C): δ 165−210 (br, $\nu_{1/2} = 3000$ Hz). IR (Nujol): 2698 w, 1355 s, 1166 s, 1035 m, 1016 m, 918 w, 886 m, 815 m, 722 w, 678 w, 574 w, 473 w, 449 m cm^{-1}. UV−vis (hexane, λ_{max}, nm (ϵ)): 223 (26 560), 264 (18 520), 268 (18 360), 331 (18 560). Mp: 147 °C (dec.).

X-ray Crystal Structure Determination for $(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ (1). Data were corrected for Lorentz and polarization effects and decay (−5%), but not for absorption. From 10 728 measured $[((\sin\theta)/\lambda)_{max} = 0.64$ Å$^{-1}]$ and 9350 unique reflections, 8286 were considered "observed" $[F_o > 4\sigma(F_o)]$ and used for refinement. All non-H atoms were refined with anisotropic displacement parameters. H atoms at C113 and C421 were found and refined isotropically. All the 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 412 refined parameters to an R (R_w) value of 0.0261 (0.0280). The function minimized was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. Further details are given in Table 1.

$Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (2). In the glovebox, addition of a solution of LiP^tBu_2 (245 mg, 1.61 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of $Yb(OSO_2CF_3)_3$ (200 mg, 0.32 mmol) in 7 mL of tetrahydrofuran caused an immediate color change to orange. Removal of solvent, extraction of the residues with toluene, and crystallization at −30 °C gave **2** as orange crystals (220 mg, 75%). Complex **2** is slightly soluble in hexanes. Anal. Calcd for $C_{40}H_{88}Li_2O_2P_4Yb$: C, 52.68; H, 9.73; Li, 1.52; P, 13.59. Found: C, 52.56; H, 9.61; Li, 1.50; P; 13.34. ^1H NMR (C_6D_6, 270 MHz, 20 °C): δ 1.22 (m, 8H), 1.72 (t, $^3J_{H-P} = 5.6$ Hz, 72H), 3.58 (m, 4H). ^1H NMR (C_4D_8O, 270 MHz, 20 °C): δ 1.30 (s). ^{13}C NMR (C_6D_6, 100.4 MHz, 20 °C): δ 25.2 (thf), 34.1 (t, $^1J_{C-P} = 6.9$ Hz, CH_3-*C*), 36.7 (t, $^2J_{C-P} = 5.5$ Hz, *C*H_3-C), 69.0 (thf). ^{13}C NMR (C_4D_8O, 100.4 MHz, 20 °C): δ 25.8 (thf), 33.9 (CH_3-*C*), 36.5 (*C*H_3-C), 67.8 (thf). ^7Li NMR (C_6D_6, 155.5 MHz, 20 °C): δ 3.0 (t, $^1J_{Li-P} = 58$ Hz). ^7Li NMR (C_4D_8O, 155.5 MHz, 20 °C): δ 0.6 (s, $\nu_{1/2} = 68$ Hz). ^7Li NMR (C_4D_8O, 155.5 MHz, −60 °C): δ −0.1 (s, $\nu_{1/2} = 25$ Hz). ^7Li NMR (C_4D_8O, 155.5 MHz, −90 °C): δ −0.1 (d, $^1J_{Li-P} = 73$ Hz). ^{31}P NMR (C_6D_6, 109.4 MHz, 20 °C): δ 62.5 (quartet, $^1J_{P-Li} = 58$ Hz; $^1J_{P-Yb} = 873$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, 20 °C): δ 48 (br, $\nu_{1/2} = 250$ Hz), 61 (br, $\nu_{1/2} = 230$ Hz), 79 (v br), 87 (br, $\nu_{1/2} = 350$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, −30 °C): δ 47.4 (s, $\nu_{1/2} = 40$ Hz), 58 (br), 83.7 (s, $^1J_{P-Yb} = 1260$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, −60 °C): δ 45.9 (br, $\nu_{1/2} = 125$ Hz), 79.7 (s, $^1J_{P-Yb} = 1225$ Hz). ^{31}P NMR (C_4D_8O, 109.4 MHz, −90 °C): δ 44.1 (quartet, $^1J_{P-Li} = 73$ Hz), 71.8 (s, $^1J_{P-Yb} = 1175$ Hz), 74.6 (br). IR (Nujol): 2692 w, 1353 vs, 1167 s, 1042 vs, 1015 m, 916 m, 890 s, 815 m, 723 w, 675 w, 471 m, 438 m cm^{-1}. UV−vis (hexane, λ_{max}, nm (ϵ)): 222 (21 350), 270 (17 850), 300 (16 950), 363 (sh, 4500). Mp: 215 °C (dec.).

X-ray Crystal Structure Determination for $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (2). Data were corrected for Lorentz and polarization effects as well as for decay (−6.5%) and absorption. From 11912 measured $[((\sin\theta)/\lambda)_{max} = 0.64$ Å$^{-1}]$ and 10 052 unique reflections, 8420 were considered "observed" $[F_o > 4\sigma(F_o)]$ and used for refinement. All non-H atoms were refined with anisotropic displacement parameters. H atoms at C121 and C212 were found and refined isotropically. All the 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 466 refined parameters to an R (R_w) value of 0.028 (0.031). The function minimized was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. Further details are given in Table 1.

Results and Discussion

A Trivalent Lanthanide Phosphido Complex. Treatment of $La(OSO_2CF_3)_3$[2] with 4 equiv of LiP^tBu_2[3] in tetrahydrofuran results in a slow color change from pale yellow to dark red (eq 1).

$$\mathrm{La(OSO_2CF_3)_3 + 4LiP^tBu_2 \rightarrow \underset{\mathbf{1}}{(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]} + 3LiOSO_2CF_3} \quad (1)$$

Complex **1** can be isolated from this reaction mixture as a dark red material by evaporation of the solvent, extraction of the residues using hexanes, and crystallization. Interestingly, compound **1** is formed whether a 1:3 or a 1:4 stoichiometry is applied in this system.

A Divalent Ytterbium Phosphido Complex. The reaction of $Yb(OSO_2CF_3)_3$[2] with 5 equiv of LiP^tBu_2 proceeds under immediate reduction of trivalent ytterbium to give the orange-red monometallic four-coordinate bis "ate" complex $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (**2**) and half an equivalent of $^tBu_2P-P^tBu_2$ (eq 2). Again, as in the reaction leading to compound **1**, the stoichiometry initially applied in this system was 1:3. However, we observed that **2** was the only ytterbium containing species being formed both for a 1:3 and for a 1:5 ratio of reagents. Formation of $^tBu_2P-P^tBu_2$ was shown by ^{31}P NMR spectroscopy of the hexanes fraction (δ = 40.0 ppm in C_6D_6) and comparison with a standard sample.

$$\mathrm{Yb(OSO_2CF_3)_3 + 5LiP^tBu_2 \rightarrow \underset{\mathbf{2}}{Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2} + 3LiOSO_2CF_3 + {}^1/_2\,{}^tBu_2P-P^tBu_2} \quad (2)$$

Equation 2 requires an extra separation step (a hexanes wash) to remove the $^tBu_2P-P^tBu_2$ byproduct. Compound **2** was isolated by extraction and subsequent crystallization using toluene. Isolated yields of analytically pure **1** and **2** were >70%, and no lanthanide-containing byproducts were detected. As observed in the reaction of $LnI_3(thf)_3$ (Ln = Sm, Yb) with 3 equiv of potassium diphenylphosphide,[5] reduction of the lanthanide triflate complex occurs with a diphosphine species being formed as the corresponding oxidation product. Interestingly, in the case of **2** a bis "ate" complex is the resulting product vs a tetrasolvated diphosphido species with a linear P−Ln−P arrangement reported for the above mentioned reaction.[5] Reduction of Yb(III) was also observed in the reaction of $YbCl_3$ with 3 equiv of NaTePh[10] as well as in cyclopentadienyl-based Yb(III) systems.[11]

Structures. The molecular structure of **1** (Figure 1) features a four-coordinate lanthanum ion with a distorted tetrahedral arrangement of the phosphido ligands and a three-coordinate

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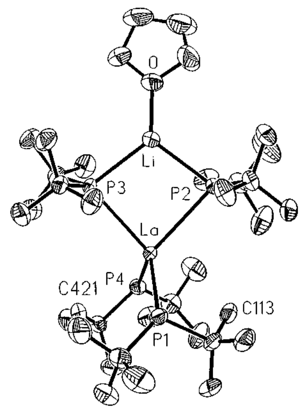

Figure 1. Thermal ellipsoid plot of $(^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ (**1**) drawn at the 50% probability level.

lithium cation surrounded by two phosphido ligands and one coordinated tetrahydrofuran molecule. The coordination of one rather than two tetrahydrofuran molecules is probably due to steric constraints. Coordinatively unsaturated, monomeric lithium salts are rare and so far only a few examples have been structurally characterized.[12−16] Coordination number four in lanthanide chemistry is also not very common.[17] Especially in the case of the relatively large trivalent cation of lanthanum, to our knowledge structural reports have so far been limited to $La[N(SiMe_3)_2]_3(OPPh_3)$,[18] $[La\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)Li(pmdeta)]$,[19] and $[La(OCPh_3)_2(\mu\text{-}OCPh_3)]_2$.[20] Anionic perphosphido complexes in the area of group 13 chemistry have been reported for gallium and indium.[21] However, the structures determined for $[M(PPh_2)_4][Li(thf)_4]$ (M = Ga, In) feature solvent separated anion-cation pairs and no direct Li···P interaction is present as found for **1**.

The lanthanum metal in **1** shows a preference for the phosphido ligands and no tetrahydrofuran molecule is coordinated to the metal center. The terminal La−P distances in **1** are 2.857(1) and 2.861(1) Å and represent by far the shortest La−P distances reported until today. They are not much longer than the sum of covalent radii reported for La (1.69 Å) and P (1.10 Å).[21] These short terminal as well as the longer bridging La−P bond distances (3.007(1) and 2.982(1) Å) can be compared with the corresponding distances found for the phosphinomethanide complexes $La[(Ph_2P)_2CH]_3$ (2.940(1) − 3.035 (1)Å)[23] and $\{La[(Me_2P)_2CSiMe_3]_4\}Li$ (3.039(2) − 3.234(2) Å),[24] the "mixed" amido−phosphido complexes $\{La[N(SiMe_3)_2]_2(PPh_2)(Ph_3PO)_2\}$ (3.165(6) Å)[25] and $\{(N^iPr_2)_2La[\mu\text{-}(C_6H_4OMe\text{-}o)_2P]_2Li(thf)$ (3.141(4) Å),[26] as well as the lanthanum tertiary phosphine complex $La[TeSi(SiMe_3)_3]_3(dmpe)_2$ (3.127(2) - 3.216(2) Å).[27] The P−La−P angles in **1** range from 106.8(1) to 119.7(1)° with the exception of P2−La−P3, which is only 84.9 (1)°. This deviation from ideal tetrahedral values is easily explained by the constraints placed on the system by the bridging lithium cation. The P−C distances are normal, ranging from 1.886(3) to 1.892(3) Å. The sum of angles around phosphorus in the terminal phosphido ligands is 350.8° (P1) and 346.8° (P4), respectively, thus showing an only slightly pyramidal environment around these phosphorus atoms. Both P atoms deviate from the plane which is described by the lanthanum metal and C11 and C12 (for P1) 0.37 and 0.45 Å (La, C42 and C42 for P4), respectively. This trend towards planarity around phosphorus is probably due to a change of hybridization at phosphorus on binding to an electropositive metal center.

The structure of **1** can be compared regarding the terminal phosphido groups with the molecular structures of $1,2\text{-}M(P^tBu_2)_2(NMe_2)_4$ (M = Mo, W),[28] which exhibit similar geometries around P as found for **1**. The sum of angles around the phosphorus atoms were reported to be 348.5° (Mo) and 355.6° (W), respectively. On the other hand, the molecular structure of $Hg(P^tBu_2)_2$[29] shows a clearly pyramidal environment around P (313.3 and 320.8°), much more similar to that of tertiary phosphines. Further comparison can be made with the homoleptic transition metal phosphido complexes $Mo_2(\mu\text{-}^tBu_2P)_2(^tBu_2P)_2$,[30] $Mo(PCy_2)_4$,[31] and $[Li(DME)(\mu\text{-}PCy_2)_2Hf(PCy_2)_3]$,[31] all of which show virtually planar geometries around the terminal phosphorus atoms. The Li−P distances of 2.537(5) and 2.545(5) Å can be compared with the corresponding distances found for the three-coordinate lithium cations in $\{Li[C(PMe_2)_2(SiMe_2Ph)]\}_3$ (2.564(8) and 2.619(8) Å)[14] and $[Li_2(\mu_3\text{-}^tBu_2P)(\mu_2\text{-}^tBu_2P)(C_4H_8O)]_2$[32] (2.654(7) and 2.470(7) Å) as well as the Li−P distances reported for $[Li(thf)\{Sn(P^tBu_2)_3\}]$ (2.49(3) and 2.48(3) Å) and $Li(thf)\{Pb(P^tBu_2)_3\}]$ (2.57(6) and 2.46(4) Å).[15] The P−Li−P angle in **1** of 105.4(2)° is much larger than the corresponding angle reported for the three-coordinate lithium atom in $\{Li[C(PMe_2)_2(SiMe_2Ph)]\}_3$ (65.5(2)°), but is very close to the angle of 108.1(2)° found for $[Li_2(\mu_3\text{-}^tBu_2P)(\mu_2\text{-}^tBu_2P)(C_4H_8O)]_2$. The Li-O distance of 1.890(5) Å in **1** matches the 1.919(7) Å distance in $[Li_2(\mu_3\text{-}^tBu_2P)(\mu_2\text{-}^tBu_2P)(C_4H_8O)]_2$ within the error limits.

The molecular structure of **2** shows the ytterbium metal surrounded by four phosphido ligands (Figure 2). The arrangement of ligands can best be described as distorted tetrahedral. Again, no solvent molecule is found to be coordinated to the lanthanide element. Two three-coordinate lithium atoms are present surrounded by two phosphido ligands and one tetrahydrofuran molecule. The Yb−P distances in **2** range from 2.948(1) to 2.985(1) Å (average 2.959(15) Å) and match the corresponding distances reported for $Yb[PPh_2]_2(thf)_4$ (2.991(2) Å),[5] $Yb[PMes_2]_2(thf)_4$ (2.925(2) Å),[33] and bis(η^5-2,5-diphe-

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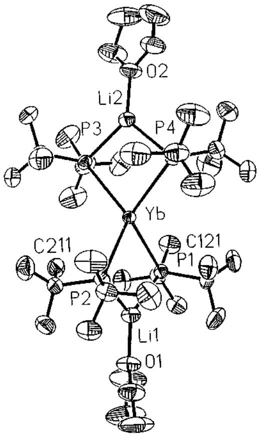

Figure 2. Thermal ellipsoid plot of Yb[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**) drawn at the 50% probability level.

Table 2. Significant Bond distances (Å) and Angles (deg) of Complexes **1** and **2**

1		**2**	
La−P1	2.857(1)	Yb−P1	2.951(1)
La−P2	3.007(1)	Yb−P2	2.953(1)
La−P3	2.982(1)	Yb−P3	2.985(1)
La−P4	2.861(1)	Yb−P4	2.948(1)
Li−P2	2.537(5)	Li1−P1	2.481(6)
Li−P3	2.545(5)	Li1−P2	2.512(7)
		Li2−P3	2.511(8)
		Li2−P4	2.504(8)
P1−La−P2	111.2(1)	P1−Yb−P2	83.3(1)
P1−La−P3	119.7(1)	P1−Yb−P3	124.9(1)
P1−La−P4	112.7(1)	P1−Yb−P4	120.3(1)
P2−La−P3	84.9(1)	P2−Yb−P3	123.5(1)
P2−La−P4	119.2(1)	P2−Yb−P4	126.2(1)
P3−La−P4	106.8(1)	P3−Yb−P4	84.1(1)
P2−Li−P3	105.4(2)	P1−Li1−P2	103.6(3)
		P3−Li2−P4	104.8(3)

nylphospholyl)Yb(thf)$_2$ (2.959(1) Å).[34] Further Yb−P distances have been reported for the divalent ytterbium phosphinomethanide complex {(thf)Li[C(PMe$_2$)$_2$(SiMe$_3$)]}$_2$·YbI$_2$(thf) (2.96(1)−3.08(1) Å)[24] as well as the tertiary phosphine complexes of divalent Yb[N(SiMe$_3$)$_2$]$_2$[Me$_2$PCH$_2$CH$_2$PMe$_2$] (3.012(4) Å)[35] and trivalent Yb(C$_5$Me$_5$)$_2$Cl[Me$_2$PCH$_2$PMe$_2$] (2.941(3) Å).[36] Besides the two bridging P−Yb−P angles (P1−Yb−P2, 83.3(1)°; P3-Yb−P4, 84.1(1)°), the P−Yb−P angles in **2** range from 120.3(1) to 126.2(1)° with P−C distances from 1.884(5) to 1.896(5) Å. The Li−P distances in **2** range from 2.481(6) to 2.512(7) Å and are slightly shorter than the corresponding distances observed for **1** (2.537(5) and 2.545(5) Å). The P−Li−P angles (P2−Li1−P1, 103.6(3)°; P4−Li2−P3, 104.8(3)°) in **2** are in good agreement with the P3−Li−P2 angle in **1** (105.4(2)°). The Li−O distances of 1.911(8) and 1.913(8) Å match the Li−O distance in **1** (1.890(5) Å) within the error limits. Selected bond distances and angles of **1** and **2** (Table 2) show the similarity of these two molecular structures.

According to Shannon,[37] the ionic radii for trivalent lanthanum (1.03 Å) and divalent ytterbium (1.02 Å) are reported to be very similar for the formal coordination number 6. However, both structures of **1** and **2** show formally four-coordinate lanthanide metals. An accurate determination of the coordination number in **1** and **2** is difficult due to a certain amount of agostic interactions between the metal center and certain *tert*-butyl groups. Therefore, direct comparison of data in terms of oxidation state and coordination number using Shannon's radii is complicated by the fact that some methyl groups are oriented toward the metal centers in these complexes. In **1**, the closest La···C distances are 3.232(3) Å (La−C113) and 3.254(3) Å (La−C421) and belong to the terminal phosphido groups (Figure 1). The closest Yb···C distances for **2** (Figure 2), namely 3.459(6) Å (Yb···C211) and 3.558(6) Å (Yb···C121), are considerably longer than the ones found for **1**. These clearly nonbonding Yb···C interactions are definitely weaker than the ytterbium−γ-carbon interaction with an Yb···C distance of 3.04 Å reported by Andersen for Yb[N(SiMe$_3$)$_2$]$_2$[Me$_2$PCH$_2$CH$_2$PMe$_2$][35] as well as the Yb···C distance of 2.852(13) Å in Yb[C(SiMe$_3$)$_3$]$_2$.[38]

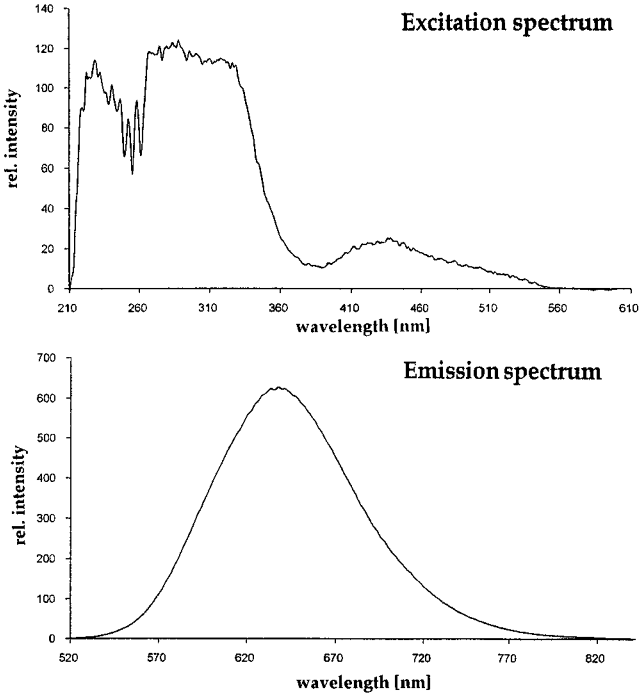

Figure 3. Photoluminescence spectrum of Yb[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**) in hexanes solution ($c = 5 \times 10^{-5}$ mol L^{-1}, 293 K; excitation = 304 nm for the emission spectrum).

The three hydrogen atoms bonded to C113 and C421 (**1**) and C211 and C121 (**2**), respectively, were located and refined isotropically to reasonable tetrahedral positions around the C atoms. The closest La···H distances in **1** refined to 2.83(3) and 2.92(3) Å for C113 and 2.84(3) and 3.02(3) Å for C421. The corresponding Yb···H distances in **2** were found to be 2.92(4) and 3.30(4) Å (C211) as well as 3.03(6) and 3.45(7) Å (C121). All of these nonbonding Ln···H distances are clearly longer than the shortest Yb···H agostic interaction in Yb[N(SiMe$_3$)$_2$]$_2$[Me$_2$PCH$_2$CH$_2$PMe$_2$][35] (2.76(8) Å).

Photoluminescence of Yb[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (2). Compound **2** exhibits strongly photoluminescent properties in the solid state as well as in hexanes, toluene or benzene solution when exposed to UV light (253 and 366 nm). It is interesting to note that only very weak photoluminescence could be detected in tetrahydrofuran solution. Figure 3 shows the excitation and emission spectrum of **2** in hexanes solution. A strong emission was observed with a maximum at 639 nm. This observation can be compared with reports from Ellis and co-workers on luminescent properties of adducts of bis(η^5-pentamethylcyclopentadienyl)ytterbium(II) in the near-IR region.[39−41] Reaction of samples of **2** with air yields chemiluminescence (CL). The

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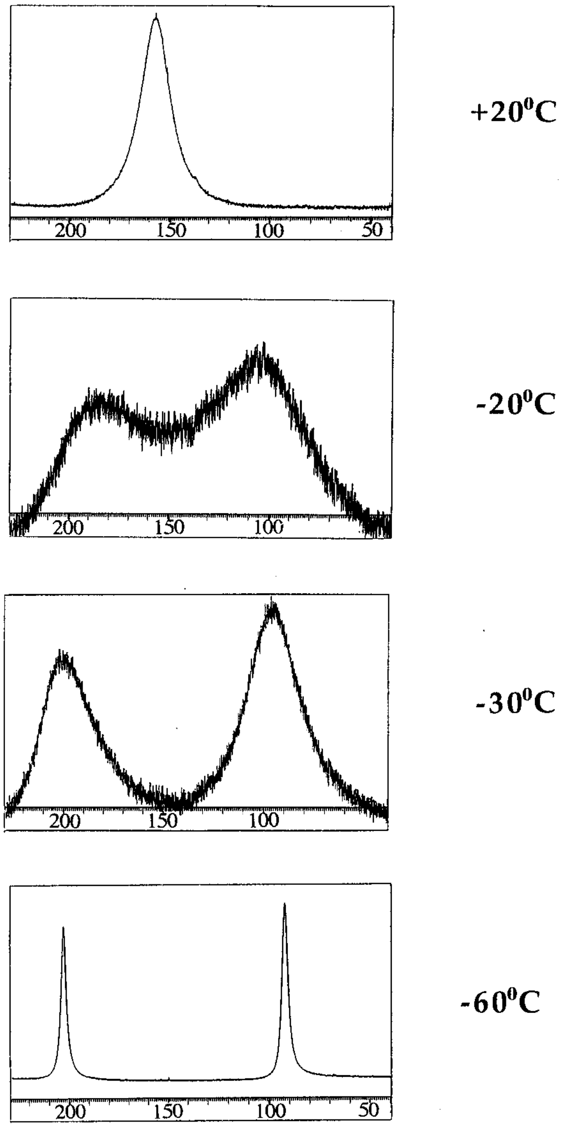

Figure 4. ^{31}P-VT NMR spectra of (^{t}Bu$_2$P)$_2$La[(μ-P^{t}Bu$_2$)$_2$Li(thf)] (**1**) in toluene-d_8 (δ /ppm).

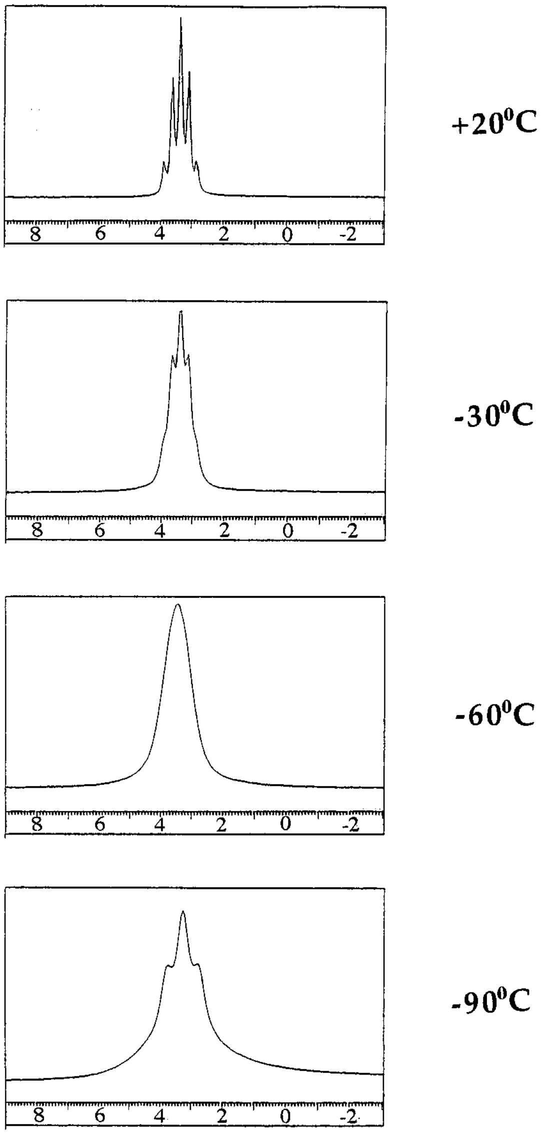

Figure 5. ^{7}Li-VT NMR spectra at low temperatures of (^{t}Bu$_2$P)$_2$La-[(μ-P^{t}Bu$_2$)$_2$Li(thf)] (**1**) in toluene-d_8 (δ/ppm).

duration of CL (an orange glowing) in air is approximately 1−2 min.

NMR Spectroscopic Studies. (^{t}Bu$_2$P)$_2$La[(μ-P^{t}Bu$_2$)$_2$Li(thf)] (1). At room temperature, the ^{31}P NMR spectrum of **1** in deuterated toluene (Figure 4) shows a broad signal with a center at 155 ppm ($\nu_{1/2} = 2000$ Hz). The line broadening is probably due to fluxionality and the direct presence of two quadrupolar nuclei (^{139}La, $I = {}^{7}/_{2}$; ^{7}Li, $I = {}^{3}/_{2}$). On cooling to −30 °C, two broad resonances with approximate intensities 1:1 are observed (200 ppm, $\nu_{1/2} = 3000$ Hz; 95 ppm, $\nu_{1/2} = 3000$ Hz). Further cooling to −60 °C gave two well-resolved signals at 200 ppm ($\nu_{1/2} = 350$ Hz) and 90 ppm ($\nu_{1/2} = 375$ Hz), indicating a structure in solution similar to that observed in the solid state. Heating of the toluene solution of **1** resulted in a decrease of the line widths for the ^{31}P NMR signal (160 ppm, $\nu_{1/2} = 500$ Hz at 100 °C). No $J_{\text{P−Li}}$ coupling could be detected. In tetrahydrofuran solution a very broad signal was observed in the ^{31}P NMR spectrum of **1** at room temperature (195 ppm, $\nu_{1/2} = 3000$ Hz). This signal was found to be unchanged at −90 °C.

The ^{7}Li NMR spectrum of **1** in deuterated toluene (Figure 5) at room temperature exhibits a quintet due to ^{31}P to ^{7}Li nuclear spin coupling (an A_2B_2X spin system with A, B = P and X = Li) with an average coupling constant of 28 Hz, therefore indicating a fluxional process in which some degree of P−Li bonding is maintained. Typically, $^{1}J_{\text{Li−P}}$ coupling constants can be expected to be in the range between 50 and 60 Hz.[42] At −30 °C, the ^{7}Li signal converts into a signal which can be described better as a triplet than a quintet. Further cooling to −90 °C resulted in a signal with the approximate shape of a broad triplet. A ^{7}Li NMR investigation of the toluene solution behavior of **1** at high temperatures is presented in Figure 6, resulting in a stepwise transition from a quintet to a broad singlet at temperatures above 60 °C (2.6 ppm and $\nu_{1/2} = 30$ Hz at 100 °C). The ^{7}Li signal for **1** was found to be converted into a singlet at room temperature using tetrahydrofuran instead of benzene as a solvent for the NMR spectroscopic investigation. This ^{7}Li NMR signal could not be resolved by cooling to −105 °C. These solvent effects could be indicative for the formation of solvent separated ion pairs vs contact ion pairs in non-coordinating solvents.

Yb[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (2). The ^{31}P NMR spectrum of **2** in deuterated benzene shows a well-resolved four line pattern due to coupling with the quadrupolar lithium-7 nucleus (Figure 7). Furthermore, the ^{171}Yb satellites ($I = {}^{1}/_{2}$; 14.3% abundance)

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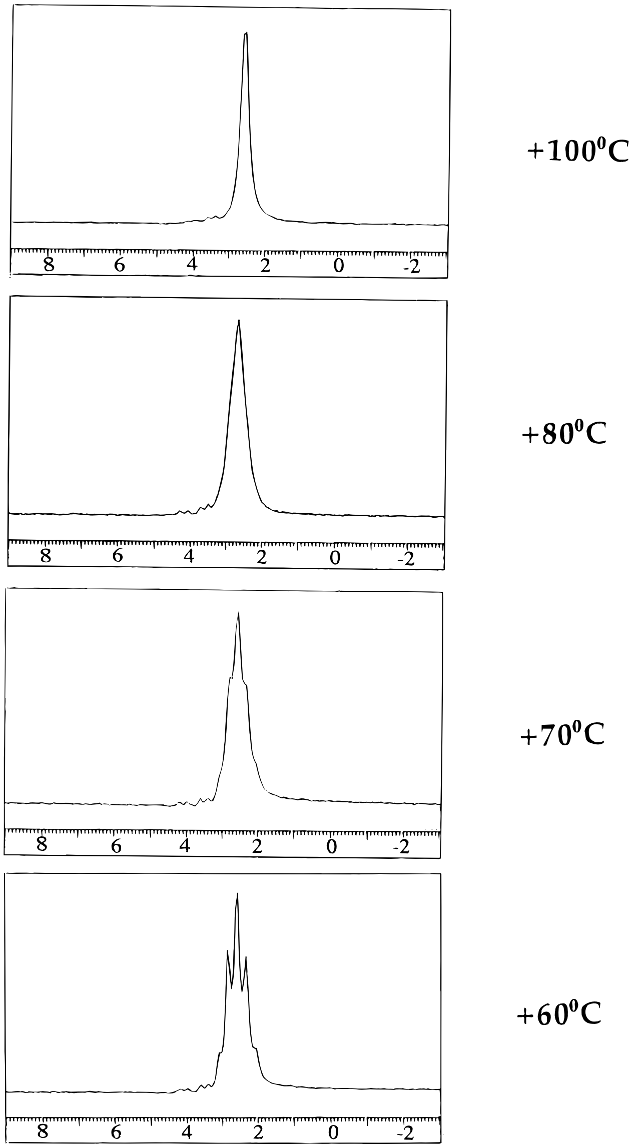

Figure 6. ^{7}Li-VT NMR spectra at high temperatures of $(^t\mathrm{Bu_2P})_2\mathrm{La}[(\mu\text{-}\mathrm{P}^t\mathrm{Bu_2})_2\mathrm{Li(thf)}]$ (**1**) in toluene-d_8 (δ/ppm).

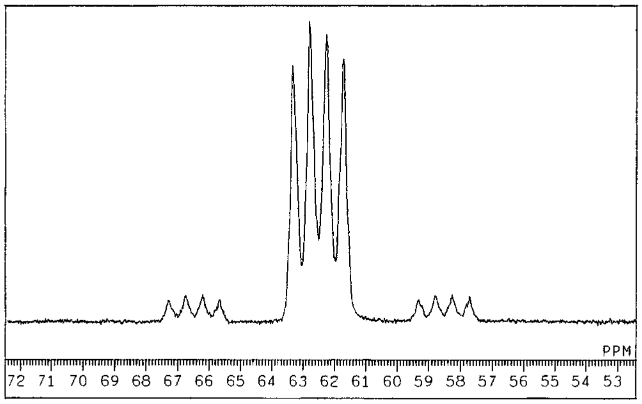

Figure 7. ^{31}P NMR spectrum of $\mathrm{Yb}[(\mu\text{-}\mathrm{P}^t\mathrm{Bu_2})_2\mathrm{Li(thf)}]_2$ (**2**) in C_6D_6 at 293 K (δ/ppm).

with a $^1J_{\mathrm{P-Yb}}$ coupling constant of 873 Hz are observed. This separation was found to be the same at different field strength, indicating the satellites are indeed due to coupling. The value of 873 Hz represents by far the largest coupling constant between these two nuclei reported so far and can be compared with reports from Karsch et al.[43] on $\{(\mathrm{thf})\mathrm{Yb}[\mathrm{C}(\mu\text{-}\mathrm{PMe_2})_2(\mathrm{SiMe_3})\mathrm{Li(thf)}]_2\mathrm{I_2}\}$ ($^1J_{\mathrm{Yb-P}}$ = 497.3 Hz) and $\{(\mathrm{thf})\mathrm{Yb}[\mathrm{C}(\mu\text{-}\mathrm{PMe_2})_2(\mathrm{PMe_2})\mathrm{Li(thf)}]_2\mathrm{I_2}\}$ ($^1J_{\mathrm{Yb-P}}$ = 511.5 Hz) as well as reports from Fryzuk et al. for $\mathrm{Yb[N(SiMe_2CH_2PR_2)_2]_2}$[44] (R = Me, $^1J_{\mathrm{Yb-P}}$ = 665 Hz; R = Ph, $^1J_{\mathrm{Yb-P}}$ = 522 Hz). As complex **2** contains anionic phosphido ligands, the larger coupling constant is consistent with a stronger bond compared to the tertiary phosphine adducts or phosphinomethanide complexes cited above, which only possess formally dative bonds. Interestingly, the ^{31}P NMR spectrum of **2** in deuterated tetrahydrofuran solution is significantly different, showing four broad lines with different line widths. No ^{171}Yb satellites could be detected. Stepwise cooling gave better resolved signals. For example, the ^{31}P NMR spectrum at −90 °C shows a singlet at 71.8 ppm ($^1J_{\mathrm{P-Yb}}$ = 1175 Hz), a broad signal at 74.6 ppm, and quartet at 44.1 ppm ($^1J_{\mathrm{P-Li}}$ = 73 Hz).

The ^{7}Li NMR spectrum of **2** in deuterated benzene shows a triplet with a $^1J_{\mathrm{Li-P}}$ coupling constant of 58 Hz and matches the corresponding value reported by Aspinall et al.[26] for $\{(\mathrm{N}^i\mathrm{Pr_2})_2\mathrm{La}[\mu\text{-}(\mathrm{C_6H_4OMe}\text{-}o)_2\mathrm{P}]_2\mathrm{Li(thf)}\}$. As observed for complex **1**, the ^{7}Li NMR signal of **2** is found to be converted as well into a singlet at room temperature using tetrahydrofuran instead of benzene as a solvent for the NMR spectroscopic investigation. In the case of **2** we were able to demonstrate that this broad singlet can be resolved by cooling to −90 °C into a doublet with a $^1J_{\mathrm{P-Li}}$ coupling constant of 73 Hz.

The nature of complex **2** in tetrahydrofuran solution at low temperatures is not clear. However, it can be concluded from the ^{31}P and ^{7}Li NMR spectra at −90 °C that a species is present which contains a $\mathrm{Li-P}^t\mathrm{Bu_2}$ fragment with no ytterbium attached to phosphorus as well as an $\mathrm{Yb-P}^t\mathrm{Bu_2}$ fragment with no lithium coordinated to the phosphorus. For comparison, we examined the ^{7}Li and ^{31}P NMR spectra of a tetrahydrofuran solution of $\mathrm{Li}^t\mathrm{Bu_2}$ at room temperature and at −90 °C and observed similar chemical shifts, but significantly different line widths (^{7}Li NMR: $\nu_{1/2}$ = 22 Hz vs 68 Hz for **2**; ^{31}P NMR: $\nu_{1/2}$ = 25 Hz vs 250 Hz for **2**) at room temperature as well as a lower coupling constant ($^1J_{\mathrm{P-Li}}$ = 61 Hz vs 73 Hz for **2**) at −90 °C.

Conclusion. The synthesis of **1** and **2** introduces two novel homoleptic lanthanide phosphido complexes with somewhat related, but still significantly different, structural features. Further studies are presently undertaken in order to investigate, whether more structural diversity can be achieved using different types of ligand systems $-\mathrm{ER_2}$ (E = P, As, Sb; R = bulky substituent) on one hand and varying the lanthanide component on the other. More structural data are clearly needed for a systematic study on effects determining these structural changes as well as the nature of the Ln−E bond. Further investigations are necessary here as well as on the nature of the photoluminescent and chemiluminescent properties of the lanthanide phosphido complex **2**. The potential application of the presented complexes as precursors to new materials is presently under investigation.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (23 pages). Ordering information is given on any current masthead page.

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