Articles

Lanthanide Phosphido Complexes: A Comparison of the Divalent Homoleptic Species $Ln[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (Ln = Yb, Eu, Sm) Including the Structural Characterization and a Europium-151 Mössbauer Spectrum of $Eu[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$[1]

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A comparison of the three isostructural homoleptic lanthanide phosphide species $Ln[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ [Ln = Yb (**1**), Eu (**2**), Sm (**3**)] is reported. $Eu(OSO_2CF_3)_3$ reacts with 5 equiv of LiP^tBu_2 in tetrahydrofuran to give the europium complex $Eu[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (**2**) in 50% yield plus 0.5 equiv of $^tBu_2P-P^tBu_2$. **2** crystallizes in space group $P2_1/c$. Crystal data for **2** at 248 K: $a = 21.740(3)$ Å, $b = 12.345(1)$ Å, $c = 20.633(2)$ Å, $\beta = 109.13(1)°$; $V = 5231.5(10)$ Å^3; $Z = 4$; $D_{calcd} = 1.131$ g cm^{-3}; $R_F = 3.29\%$. The molecular structure shows the four-coordinate europium atom in a distorted tetrahedral environment. A main feature of the crystal structure of **2** is the shortest Eu−P distance [3.034(1) Å] of divalent europium reported so far. A ^{151}Eu Mössbauer spectrum at 4.2 K is reported exhibiting an isomer shift of −11.7 mm/s.

Introduction

In the past years there has been an increasing interest in the preparation and structural characterization of lanthanide complexes with sterically demanding phosphides[2−7] and chalcogenolates[8−12] as the only anions. This work has demonstrated that stable complexes with Ln−phosphide or Ln−chalcogenolate bonds can be isolated without using sterically demanding supporting ligands such as highly electronegative pentamethylcyclopentadienyl (Cp*)[13,14] or heteroallylic ligand systems.[15,16] This area of research focuses predominantly on the fundamental nature of the lanthanide−pnicogen or lanthanide−chalcogen bond but also on applied motivations.[9]

Phosphido complexes are of interest because of the way they differ electrostatically from the corresponding amido species. Also, in light of an increasing recent interest in the synthesis of lanthanide chalcogenolate complexes[17−19] for use as precursors to materials which are dilute magnetic semiconductors, our results provide new opportunities for the formation of novel mixed lanthanide/main group element species.

Here we report the preparation and structure determination of the formally four-coordinate homoleptic lanthanide phosphido bis "ate" complex $Eu[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (**2**). Also, a ^{151}Eu Mössbauer spectrum of complex **2** is reported.

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 by following typical laboratory procedures. $Eu(OSO_2CF_3)_3$[20] and LiP^tBu_2[21] were prepared according to the literature. The UV−vis spectrum was recorded on a Perkin-Elmer Lambda 2 instrument. The ^{151}Eu Mössbauer spectrum was obtained using samarium-151 in Sm_2O_3 as a source.

$Eu[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (2). In the glovebox, addition of a solution of LiP^tBu_2 (254 mg, 1.67 mmol) in 5 mL of tetrahydrofuran to a colorless suspension of $Eu(OSO_2CF_3)_3$ (200 mg, 0.33 mmol) in 7 mL of tetrahydrofuran caused an immediate color change to orange-yellow. Removal of solvent, extraction of the residues with hexane, and crystallization at −30 °C gave **2** as orange-yellow crystals (149 mg, 50%). Complex **2** is slightly soluble in hexanes. Anal. Calcd for

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Table 1. Crystallographic Data for Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**)[a]

formula	$C_{40}H_{88}EuLi_2O_2P_4$	V (Å^3)	5231.5(8)
fw	890.82	Z	4
temp (K)	248	ρ_{calc} (g/cm^{-3})	1.131
space group	$P2_1/c$	λ(Mo Kα)	0.710 73
a (Å)	21.740(3)	μ (cm^{-1})	13.48
b (Å)	12.345(1)	$R(F)$ (%)	3.29
c (Å)	20.633(2)	$R(wF^2)$ (%)	7.46
β (deg)	109.136(6)		

[a] The quantity minimized was $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$, $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

$C_{40}H_{88}EuLi_2O_2P_4$: C, 53.93; H, 9.96; Li, 1.56; P, 13.91. Found: C, 53.94; H, 10.08; Li, 1.50; P; 14.25. IR (Nujol): 1353 s, 1164 m, 1042 s, 1014 m, 916 w, 890 m, 815 w, 727 m, 673 w, 664 w, 468 w, 429 m cm^{-1}. UV−vis (hexane, λ_{max}, nm (ϵ)): 225 (25 700), 240 (22 500), 245 (21 300), 251 (20 000), 258 (19 100), 263 (18 600), 313 (22 450). Magnetic susceptibility: $\chi_M^{293K} = 2.7 \times 10^{-2}$ cgs; $\mu_{eff} = 8.0\ \mu_B$. Mp: 214 °C (dec).

X-ray Data Collection, Structure Determination, and Refinement for Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (2). A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed glass capillary. Graphite-monochromated Mo Kα radiation was used (λ = 0.710 73 Å). Data were collected on an Siemens P4 diffractometer. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° < 2θ < 24°). The systematic absences in the diffraction data are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). Crystal, data collection, and refinement parameters are given in Table 1. Further details of the crystal structure determination can be ordered from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, under the depository number CSD-404301.

Results and Discussion

A Divalent Europium Phosphido Complex. The reaction of Eu(OSO$_2$CF$_3$)$_3$[20] with 5 equiv of LiP^{t}Bu$_2$[21] proceeds under immediate reduction of trivalent europium to give the orange-yellow four-coordinate bis "ate" complex Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**) and 0.5 equiv of ^{t}Bu$_2$P−P^{t}Bu$_2$ (eq 1). Complex **2** was found to be extremely air sensitive. The stoichiometry initially applied in this system was 1:3. However, we observed that **2** was the only europium-containing species being formed both for a 1:3 and a 1:5 ratio of reagents giving yields of 50%. Formation of ^{t}Bu$_2$P−P^{t}Bu$_2$ was shown by ^{31}P NMR spectroscopy of the hexane fraction (δ = 40.0 ppm in C$_6$D$_6$) and comparison with a standard sample. We were unable to obtain preliminary information on the nature of complex **2** from multinuclear NMR spectroscopy since the room-temperature magnetic moment of **2** (μ = 8.0 μ_B) prevents the use of NMR spectroscopy in its characterization.

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

Reduction of europium(III) was observed before in the reaction of Eu[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of HTeSi(SiMe$_3$)$_3$ in the presence of excess DMPE[11] as well as in the reaction of EuCl$_3$ with 3 equiv of NaEPh (E = Se,[19] Te[20]).

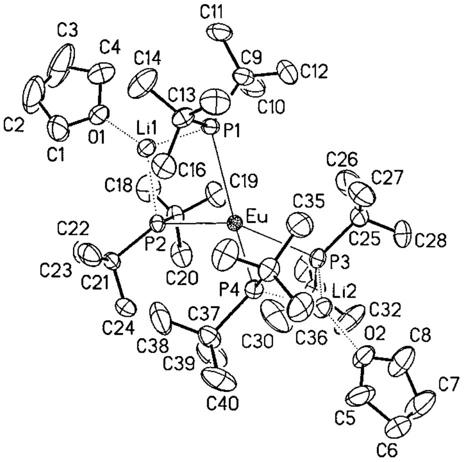

Figure 1. ORTEP diagram and numbering scheme of Eu[(μ-P^{t}Bu$_2$)$_2$-Li(thf)]$_2$ (**2**) drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Significant Interatomic Separations (Å) and Angles (deg) of Complexes **1**−**3**

	1 (Ln = Yb)	**2** (Ln = Eu)	**3** (Ln = Sm)
Ln−P	2.948(1)	3.034(1)	3.036(1)
	2.951(1)	3.040(1)	3.041(1)
	2.953(1)	3.042(1)	3.044(2)
	2.985(1)	3.068(1)	3.070(2)
Li−P	2.481(6)	2.495(8)	2.504(9)
	2.504(8)	2.528(9)	2.52(1)
	2.511(8)	2.530(8)	2.52(1)
	2.512(7)	2.530(8)	2.54(1)
P−Ln−P	83.3(1)	82.47(3)	82.6(1)
	84.1(1)	83.20(3)	83.0(1)
	120.3(1)	120.50(3)	120.3(1)
	123.5(1)	123.75(4)	123.8(1)
	124.9(1)	125.44(3)	125.6(1)
	126.2(1)	127.21(4)	127.4(1)
P−Li−P	103.6(3)	105.7(3)	105.8(4)
	104.8(3)	106.6(3)	106.3(3)

We reported earlier formation of the corresponding tetrakis(phosphido) complexes of divalent ytterbium (**1**)[4a] and samarium (**3**).[4b] All three systems were found to be isomorphous in the solid state, thus allowing a detailed comparison of lanthanide−phosphorus bonding parameters for all three related systems (Table 2) which have not been obtainable before with other systems.

Complexes **1**−**3** were found to melt under decomposition at similar temperatures (within the error limit of the determinations), thus indicating a similar stability of these three systems with respect to their physical properties.

Molecular Structure of Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (2). Definitive identification of **2** was derived from a low-temperature single-crystal X-ray diffraction study. The molecular structure of **2** (Figure 1) features a four-coordinate europium cation with a heavily distorted tetrahedral (or disphenoidic) arrangement of the phosphide ligands. Two three-coordinate lithium cations—each surrounded by two phosphide ligands and one coordinated tetrahydrofuran molecule—are another interesting feature of this molecular structure that merits comment. The coordination of one rather than two tetrahydrofuran molecules is probably due to steric constraints. Significant interatomic separations and angles are listed in Table 2. The Eu−P distances in **2** range from 3.034(1) to 3.068(1) Å [average: 3.046(7) Å] and can be compared with reports from Arnold and co-workers on {Eu[TeSi(SiMe$_3$)$_3$]$_2$(DMPE)$_2$}$_2$(μ-DMPE), a europium phosphane complex [3.165(2)−3.249(2) Å, average: 3.20(1) Å].[11] Further comparison of these Eu−P inter-

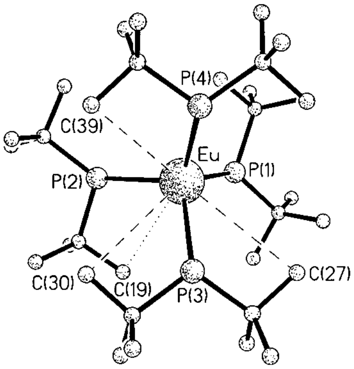

Figure 2. Central Eu(P^{t}Bu$_2$)$_4$ core of complex **2** showing the closest nonbonding Eu···C distances.

atomic separations is hampered by the lack of structural data of other europium phosphanes or phosphides.[22]

Agostic Interactions. An accurate determination of the coordination number in complexes **1**−**3** 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[23] is complicated by the fact that some methyl groups are oriented toward the metal centers in these complexes.

Examination of the agostic interactions in **2** gave the following results: The closest Eu···C distance for the formally four-coordinate complex **2** (Figure 2) is 3.630(8) Å [Eu···C(19)]. This clearly nonbonding Eu···C interaction is definitely weaker than the shortest europium−γ-carbon interaction with an Eu···C distance of 2.971(7) Å reported for NaEu[N(SiMe$_3$)$_2$]$_3$.[24] All other nonbonding Eu···C distances in **2** were found to be much longer [the next closest distances are 4.035(8) Å (C(27)), 4.094(8) Å (C(39)), and 4.106(8) Å (C(30))].

The agostic interactions in complex **2** can be compared with our observations in the molecular structures of complexes **1** and **3**. In the case of the ytterbium analogue **1**, we found that *two* methyl groups from different *tert*-butyl groups [at the same (thf)Li(P^{t}Bu$_2$)$_2$ fragment, attached to different phosphorus atoms] are oriented toward the metal center with Yb···C distances of 3.459(6) and 3.558(6) Å. These interactions are definitely weaker than the Yb(II)···C distances observed in Cp*$_2$Yb(μ-Me)Be(Cp*) [2.766(4) Å][25] as well as in (dippe)Pt(μ-CH$_3$)$_2$-YbCp*$_2$ [2.908(8) and 2.88(1) Å].[26] Other reports on Yb···C distances are found for Yb[N(SiMe$_3$)$_2$]$_2$[Me$_2$PCH$_2$CH$_2$PMe$_2$] (3.04 Å)[27] and in Yb[C(SiMe$_3$)$_3$]$_2$ [2.852(13) Å].[28] In the case of the samarium species **3** again *two* methyl groups [also at the same (thf)Li(P^{t}Bu$_2$)$_2$ fragment and attached to different phosphorus atoms] point toward the metal center with nonbonding Sm···C distances of 3.482(6) and 3.578(7) Å. The observation of different agostic interactions in **2** (Ln = Eu) and **3** (Ln = Sm) but similar ones in **1** (Ln = Yb) and **3** (Ln = Sm) is rather peculiar since samarium and europium are almost identical with respect to the size of their ionic radii. According to Shannon,[23] samarium(II) and europium (II) can be expected to be approximately 0.14 and 0.12 Å, respectively, larger than ytterbium(II) for a given coordination number.

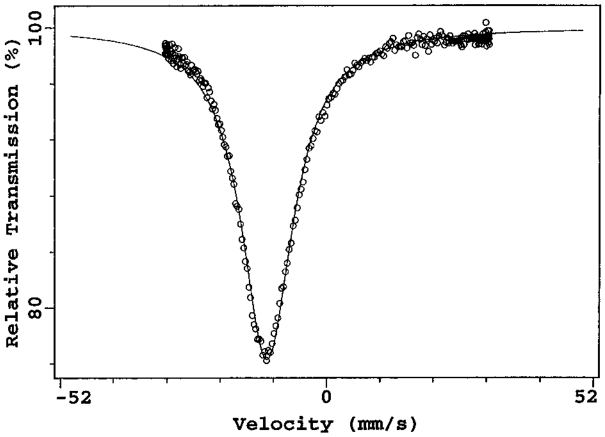

Figure 3. ^{151}Eu Mössbauer spectrum of Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**) at 4.2 K.

These agostic interactions in complexes **1**−**3** can be described as an electrostatic interaction Ln(δ+)···C(δ−). The reason for the occurence of the agostic interactions in complexes **1**−**3** is not clear. It is likely that the presence of a large, electropositive lanthanide cation in a coordinatively unsaturated environment is the main cause of the occurence of this interaction, thus relieving itself of the coordinative unsaturation by interacting with ligands that are in its direct neighborhood. However, the observed clearly nonbonding interactions might also be a result of crystal-packing forces. Different amounts of agostic interactions observed for complex **2** (Ln = Eu) on one hand and **1** (Ln = Yb) and **3** (Ln = Sm) on the other [but similar interactions for **1** (Ln = Yb) and **3** (Ln = Sm)] indicate that the origin of this phenomenon is probably fortuitously, presumably mostly determined by crystal-packing forces.

We failed to detect these interactions in the case of the diamagnetic species **1** using variable-temperature solution-state NMR spectroscopy (^{1}H, ^{13}C, ^{171}Yb) in different solvent systems. No long-range $^4J_{\mathrm{Yb-H}}$ coupling[29] of the ^{171}Yb nucleus to the methyl protons of the phosphide ligand could be resolved at variable temperatures. This result confirms that the energy of the interactions must be very small thus not allowing characterization *via* NMR spectroscopy.

^{151}Eu Mössbauer Spectroscopy. Among the lanthanides, europium is one of the definitely more interesting elements, first, because there are two different formal oxidation states accessible, magnetic Eu(II) (^{8}S$_{7/2}$) and nonmagnetic Eu(III) (^{7}F$_0$) and, second, because the ^{151}Eu isotopomer can be used for Mössbauer spectroscopy. ^{151}Eu Mössbauer spectroscopy is a useful tool for investigating the nature of bonding in both divalent and trivalent europium complexes. Both valence states can easily be distinguished through their different isomer shifts. Europium(II) compounds are typically found to show isomer shifts of ca. −12 mm/s. Contrarily, europium(III) complexes have isomer shifts of 0−1 mm/s. So far, only a very limited number of reports have appeared on Mössbauer spectroscopic investigations of molecular europium species.[30−34] To the best of our

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knowledge, there are only two reports[30,31] on Mössbauer studies of molecular complexes of formally *divalent* europium.

Here we report the ^{151}Eu Mössbauer spectrum of complex **2** at 4.2 K. We were motivated to undertake this Mössbauer study in light of the very much distorted tetrahedral (or disphenoidic) environment of the formally four-coordinate europium(II) cation in complex **2**. The Mössbauer spectrum (Figure 3) exhibits a single line with a line width of 12.3 mm/s. The isomer shifts of −11.7 mm/s confirms the divalent nature of the europium cation in complex **2**.

Conclusion. This study allows for a detailed comparison of a series of isomorphous tetrakis(phosphido) complexes of divalent samarium, europium, and ytterbium with respect to structural trends and does also provide a comparative listing of bonding parameters. Also, this study demonstrates that ^{151}Eu Mössbauer spectroscopy can be used effectively for studying the electronic environment of this particular lanthanide nucleus in its phosphide derivatives.

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Supporting Information Available: Text describing X-ray procedures and of crystal data, positional parameters, bond distances and angles, and thermal parameters (10 pages). Ordering information is given on any current masthead page.

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