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Note

Phosphide complexes of divalent europium: synthesis and structural characterization of $Eu[PPh_2]_2(N\text{-}MeIm)_4$

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Abstract

The synthesis and X-ray crystal structure determination of a bis(phosphido) complex of divalent europium, $Eu[PPh_2]_2(N\text{-}MeIm)_4$ (**1**), is reported. Complex **1** crystallizes in the monoclinic space group $P2_1/n$. Crystal data for **1** at 298 K: $a = 10.016(5)$, $b = 18.018(8)$, $c = 11.218(5)$ Å, $\beta = 95.45(3)°$; $V = 2015(2)$ Å^3; $Z = 2$; $D_{calc} = 1.402$ g cm^{-3}; $R_F = 4.59\%$. The molecular structure of **1** shows the hexa-coordinate lanthanide atom (on an inversion center) in a distorted octahedral environment with the phosphide ligands in *trans* positions. © 1998 Elsevier Science S.A.

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1. Introduction

The number of structurally characterized organometallic complexes of divalent europium is limited to only relatively few examples [1]. Presumably, this can be seen partially as a consequence of the fact that the element europium is one of the rarest and therefore quite costly lanthanide elements. Also, the chemistry of divalent lanthanide species is relatively undeveloped as compared to numerous reports in the literature on complexes of formally trivalent lanthanide elements.

Among all the different types of lanthanide complexes only relatively little information is available for phosphide derivatives. We have focussed our interest to this class of lanthanide species since phosphide complexes differ electrostatically from the corresponding amides. Therefore, one would expect different structural types in the solid-state structures of phosphide complexes as opposed to amide derivatives. We [2–6] and others [7,8] have shown in earlier reports that different structural types can be isolated and structurally characterized for both trivalent and divalent species of the lanthanides.

We report here the synthesis and structural characterization of a bis(phosphido) species of divalent europium thereby providing rare bonding parameters for an Eu–P system.

2. Experimental

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. The UV–Vis spectrum was recorded on a Shimadzu UV 240 instrument. $EuI_2(THF)_2$ [9] was prepared from the metal and 1,2-diiodoethane. $KPPh_2$ was purchased from Aldrich as a 0.5 M solution in tetrahydrofuran. Redistilled *N*-methylimidazole (*N*-MeIm) was obtained from Aldrich (water content 0.013% by Analytische Laboratorien GmbH, D-51789 Lindlar, Germany).

2.1. $Eu[PPh_2]_2(N\text{-}MeIm)_4$ (1)

In a glovebox, addition of 1.5 ml of a 0.5 M solution of $KPPh_2$ (0.73 mmol) in tetrahydrofuran to a pale yellow solution of $EuI_2(thf)_2$ (200 mg, 0.36 mmol) in 7 ml tetrahydrofuran caused an immediate color change to orange. Subsequent addition of 0.12 ml *N*-MeIm (4 equiv.) to the obtained orange slurry resulted in a more intensely orange colored suspension. Centrifugation of the reaction mixture followed by removal of solvent, extraction of the residues with hexane/tetrahydrofuran (1:1) and crystallization at −30°C gave **1** as orange crystals (216 mg, 70%). Complex **1** is soluble in tetrahydrofuran, but insoluble in hexanes, toluene and benzene. *Anal.* Calc. for $C_{40}H_{44}EuN_8P_2$: C,

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Table 1
Crystallographic data for Eu[PPh$_2$]$_2$(*N*-MeIm)$_4$ (**1**) [a]

Formula	$C_{40}H_{44}EuN_8P_2$	V (Å^3)	2015(2)
FW	850.73	Z	2
Temperature (K)	298	ρ_{calc} (g cm^{-3})	1.402
Space group	$P2_1/n$	λ(Mo Kα) (Å)	0.71073
a (Å)	10.016(5)	μ (cm^{-1})	16.74
b (Å)	18.018(8)	$R(F)$ (%)	4.59
c (Å)	11.218(5)	$R(wF^2)$ (%)	7.72
β (°)	95.45(3)		

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

56.47; H, 5.21; N, 13.17; P, 7.28. Found: C, 56.26; H, 5.32; N, 12.93; P; 7.02%. IR (Nujol): 1568 m, 1535 m, 1518 m, 1284 m, 1230 m, 1179 w, 1109 m, 1070 s, 1020 m, 988 w, 923 m, 831 m, 820 m, 746 m, 732 s, 697 m, 673 w, 660 s, 616 m, 502 w, 468 m, 424 w cm^{-1}. UV–Vis (tetrahydrofuran, λ_{max}, nm (ε)): 214 (18 000), 245 (6200), 267 (sh, 3000). Magnetic susceptibility: χ_M(293 K) = 2.6 × 10^{-2} cgs; μ_{eff} = 7.8 BM. M.p.: 130°C.

2.2. *X-ray data collection, structure determination and refinement for Eu[PPh$_2$]$_2$(N-MeIm)$_4$ (1)*

A suitable crystal was selected and mounted in a thin-walled, nitrogen-flushed, glass capillary. Graphite-monochromated Mo Kα radiation was used (λ = 0.71073 Å). Data were collected on a Siemens P4 diffractometer. The systematic absences in the diffraction data are uniquely consistent for the reported space group. The atomic coordinates of the isomorphous samarium analogue [5a] were used as a trial structure which was 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.

3. Results and discussion

3.1. *Synthesis of Eu[PPh$_2$]$_2$(N-MeIm)$_4$ (1)*

Reaction of EuI$_2$(thf)$_2$ with 2 equiv. of KPPh$_2$ in tetrahydrofuran solution at room temperature gives Eu[PPh$_2$]$_2$(thf)$_4$, which can be converted easily and almost quantitatively in a one-pot-synthesis to Eu[PPh$_2$]$_2$(*N*-MeIm)$_4$ (**1**) by treatment of the former product with 4 equiv. of the strong donor ligand *N*-methylimidazole (*N*-MeIm) in tetrahydrofuran solution (Eq. (2)).

$$\mathrm{EuI_2(thf)_2 + 2KPPh_2 \rightarrow Eu[PPh_2]_2(thf)_4 + 2KI} \qquad (1)$$

$$\mathrm{Eu[PPh_2]_2(thf)_4} + 4N\text{-}\mathrm{MeIm} \rightarrow \underset{\mathbf{1}}{\mathrm{Eu[PPh_2]_2}(N\text{-}\mathrm{MeIm})_4} + 4\mathrm{thf} \qquad (2)$$

We were able to demonstrate that complex **1** can also be obtained by reduction of EuI$_3$(thf)$_3$ with 3 equiv. of potassium diphenylphosphide in tetrahydrofuran solution, followed by addition of 4 equiv. of *N*-methylimidazole. The corresponding oxidation product was identified by ^{1}H and ^{31}P NMR spectrometry as well as by mass spectrometry as the diphosphane Ph$_2$P–PPh$_2$. 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 [10], also in the reaction of EuCl$_3$ with 3 equiv. of NaEPh (E = Se [11], Te [12]), as well as in the case of our report on the reaction of Eu(OSO$_2$CF$_3$)$_3$ with LiP^{t}Bu$_2$ yielding the tetrakis(phosphido) species Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ [6].

3.2. *Molecular structure of Eu[PPh$_2$]$_2$(N-MeIm)$_4$ (1)*

X-ray quality crystals of **1** were obtained by slow diffusion of hexanes into a tetrahydrofuran solution at room temperature. The molecular structure of the bis(phosphido) species **1** shows the hexa-coordinate lanthanide atom (on an inversion center) in a slightly distorted octahedral environment with the phosphide ligands in *trans* positions, and a configuration at phosphorus approaching planarity (sum of angles around P: 343.3°). A selection of significant interatomic separations and angles as well as a comparison with the isomorphous samarium [5a] and the ytterbium [5b] analogue is given in Table 2. An ORTEP drawing of **1** is given in Fig. 1.

The Eu–P distance in **1** of 3.034(1) Å is roughly the same as the corresponding distances in Eu[(μ-P^{t}Bu$_2$)$_2$Li(thf)]$_2$ (**2**) [6] ranging from 3.034(1) to 3.068(1) Å (av. 3.046(7) Å), even though different coordination numbers are present in the complexes. One might expect the Eu–P distance in the tetrakis(phosphido) complex **2** to be shorter than the corresponding value found for complex **1**. A likely explanation for the observed relatively long interatomic separations in **2** is the fact that the phosphide ligands are bridging versus terminal phosphide ligands in **1**. The Eu–P distance in **1** is significantly shorter than the corresponding numbers reported on the seven-coordinated europium phosphane adduct {Eu[TeSi(SiMe$_3$)$_3$]$_2$(DMPE)$_2$}$_2$(μ-DMPE) (3.165(2)–3.249(2) Å, av. 3.20(1) Å) [10]. To the best of our knowledge [13] these are the two only reports on other Eu–P systems that have been structurally characterized before.

4. Conclusions

The data presented above demonstrate that a bis(phosphido) species of divalent europium is easily accessible in good yield in a one-pot synthesis starting from europium

Table 2
Significant interatomic separations (Å) and angles (°) of the bis(phosphido) complexes Ln[PPh$_2$]$_2$(*N*-MeIm)$_4$ (Ln = Yb [5b], Eu, Sm [5a])

	Ln = Yb	Ln = Eu	Ln = Sm
Ln–P (Å)	3.028(1)	3.127(3)	3.139(3)
P–C (Å)	1.813(2)	1.809(9)	1.805(7)
	1.814(3)	1.820(8)	1.812(8)
Ln–N (Å)	2.437(2)	2.605(7)	2.609(7)
	2.495(2)	2.611(7)	2.633(7)
Ln–P–C (°)	114.6(1)	113.7(3)	112.8(2)
	123.0(1)	123.0(3)	124.0(3)
C–P–C (°)	106.4(1)	106.6(4)	106.3(3)
ΣP (°)	344.0	343.3	343.1
Deviation of P from the Ln···C···C plane (Å)	0.492	0.508	0.510
Dihedral angle of the phenyl rings (°)	48.3	48.9	49.4

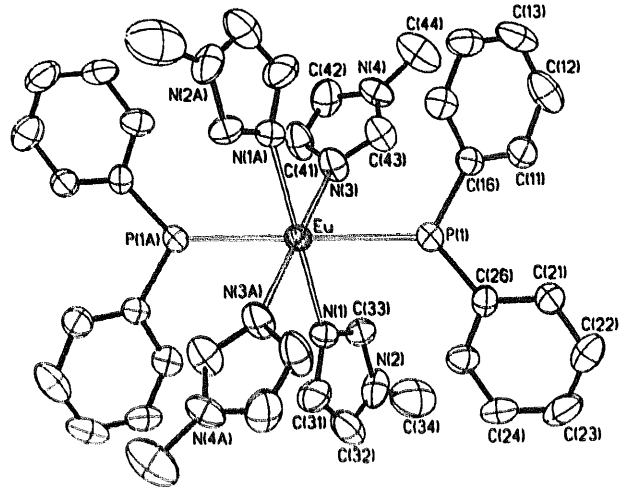

Fig. 1. ORTEP diagram and numbering scheme of Eu[PPh$_2$]$_2$(*N*-MeIm)$_4$ (1), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

diiodide, potassium diphenylphosphide and *N*-methylimidazole using careful control of stoichiometry. This study allows a detailed comparison of a series of isomorphous bis(phosphido) complexes of divalent samarium, europium and ytterbium with respect to structural trends, and also provides a comparative listing of bonding parameters.

5. Supplementary material

Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (9 pages) are available from the authors on request.

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