Synthesis and X-ray Crystal Structure Determination of the First Lanthanide Complexes Containing Primary Phosphide Ligands: Ln[P(H)Mes*]₂(thf)₄ (Ln = Yb, Eu)

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As part of an effort to investigate the coordination chemistry of the lanthanides with phosphide ligand systems as well as the corresponding bonding aspects, we now extended our systematic studies toward the reactivity of divalent lanthanide iodide[1] complexes of the general formula $LnI_2(thf)_2$ (Ln = Yb, Eu) with the potassium salt of a *primary* phosphane, namely KP(H)Mes* (Mes* = 2,4,6-$^tBu_3C_6H_2$).[2] Earlier work has demonstrated that different structural types of *secondary* phosphide derivatives of the lanthanides[3,4] can be prepared and structurally characterized.

We now report the synthesis and crystal structure determination of two novel phosphide derivatives of the lanthanides of the general formula Ln[P(H)Mes*]₂(thf)₄ (Ln = Yb (**1**), Eu (**2**)). $LnI_2(thf)_2$ (Ln = Yb, Eu) reacts immediately with 2 equiv of KP(H)Mes* in tetrahydrofuran at room temperature to give complexes **1** and **2**, respectively, in 60% yield. Interestingly, **1** and **2** are formed using both a 1:1 and a 1:2 ratio of reagents. Crystals of both orange-yellow **1** and bright yellow **2** were obtained from toluene/thf/pyridine at −30 °C.

The molecular structures of **1** and **2** were determined crystallographically[5] as formally hexacoordinated Ln[P(H)-Mes*]₂(thf)₄ (Figure 1, Ln = Yb). Additionally, two tetrahydrofuran solvent molecules are present in both crystal lattices. It is interesting to note that the presence of pyridine is essential for a successful induction of crystal growth of **1** and **2**. However, pyridine molecules are neither coordinated to the metal center nor incorporated in the crystal lattice. This observation is certainly surprising in light of the fact that pyridine is a stronger base than tetrahydrofuran. Additional confirmation for the absence of pyridine was obtained from both the ¹H NMR and the ¹³C NMR spectra of crystals of **1** in tetrahydrofuran-d_8.

The isomorphous molecular structures of **1** and **2** display distorted octahedral environments around the lanthanide cation, situated at an inversion center, with the two −[P(H)Mes*] ligands in *trans* positions (with a P−Yb−P angle of 162.54(6)° and a P−Eu−P angle of 160.5(1)°, respectively). The deviation from ideal octahedral geometry can best be seen by examing the interligand angles. The L−Yb−(*cis* L) angles

in **1** range from 76.3(2) to 108.5(1)° (76.0(3) to 111.2(2)° for the corresponding angles in **2**). The molecular structures of complexes **1** and **2** resemble the structural motif that we observed earlier in lanthanide bis(phosphido) complexes of the general formula Ln[PR₂]₂(L)₄ (L = thf, N-methylimidazole).[3g−i]

The Yb−P distance in the molecular structure of **1** is 3.025 (2) Å. It can be compared, e.g., with the Yb−P distances in Yb[PPh₂]₂(thf)₄ (2.991(2) Å)[3g] and in bis(η^5-2,5-diphenylphospholyl)Yb(thf)₂ (2.959(1) Å)[4b] and also with the corresponding distances reported for the divalent ytterbium phosphinomethanide complex {(thf)Li[C(PMe₂)₂(SiMe₃)]}₂·YbI₂(thf) (2.96(1)− 3.08(1) Å)[6] and the tertiary phosphane adducts of divalent Yb[N(SiMe₃)₂]₂[Me₂PCH₂CH₂PMe₂] (3.012(4) Å)[7] and trivalent Yb(C₅Me₅)₂Cl[Me₂PCH₂PMe₂] (2.941(3) Å).[8]

(5) Crystal data for **1**·2thf: $C_{60}H_{108}O_6P_2Yb$, M_r = 1160.44, monoclinic, C2/c, a = 22.4646(3) Å, b = 19.2702(1) Å, c = 18.7672(3) Å, β = 126.325(1)°, V = 6545.5(1) Å³, Z = 4, ρ_{calc} = 1.178 g cm⁻³, F(000) = 2464, Mo Kα radiation (λ = 0.710 73 Å), T = 222(2) K, μ(Mo Kα) = 1.520 mm⁻¹. A total of 11 459 reflections were collected on a Siemens P4/CCD diffractometer for a yellow crystal with approximate dimensions 0.55 × 0.10 × 0.10 mm³ in the range 3.1° ≤ 2θ ≤ 56.3°; 6920 reflections were independent, and 5927 reflections were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares calculations based on F^2 to final residuals of R_1 = 0.0447 and wR_2 = 0.1308 for 5927 observed data (I > 2σ(I)) and GOF = 1.036. Minimal/maximal residual electron density: 0.888/ −0.692 e Å⁻³. Crystal data for **2**·2thf: $C_{60}H_{108}EuO_6P_2$, M_r = 1139.36, monoclinic, C2/c, a = 22.2985(3) Å, b = 19.2553(4) Å, c = 18.7396(4) Å, β = 126.290(1)°, V = 6485.4(2) Å³, Z = 4, ρ_{calc} = 1.169 g cm⁻³, F(000) = 2436, Mo Kα radiation (λ = 0.710 73 Å), T = 222(2) K, μ(Mo Kα) = 1.061 mm⁻¹. A total of 10 619 reflections were collected on a Siemens P4/CCD diffractometer for a yellow crystal with approximate dimensions 0.55 × 0.40 × 0.40 mm³ in the range 3.1° ≤ 2θ ≤ 56.6°; 5966 reflections were independent, and 3648 reflections were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares calculations based on F^2 to final residuals of R_1 = 0.0816 and wR_2 = 0.2002 for 3648 observed data (I > 2σ(I)) and GOF = 1.024. Minimal/maximal residual electron density: 1.308/−1.453 e Å⁻³. The function minimized was $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$, $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. The systematic absences in the diffraction data were consistent for space groups C2/c and Cc. E statistics suggested the centrosymmetric space group, C2/c, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Structures **1** and **2** are isomorphous. The complex molecules are each located on a 2-fold axis. The asymmetric unit also contains a solvent molecule of tetrahydrofuran. In order to model disorder in the free molecule of THF, it was constrained to the same geometry as one of the coordinated tetrahydrofuran ligands. One peak from the final difference map of **2** that remained, 1.22 e Å⁻³, was 0.63 Å from the metal and was considered noise. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on phosphorus was located, and its thermal parameter was refined while the P−H distance was constrained to 1.400(2) Å. All other hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens, XRD, Madison, WI). Atomic coordinates, bond distances and angles, and thermal parameters of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (Depository No. CSD-100132).
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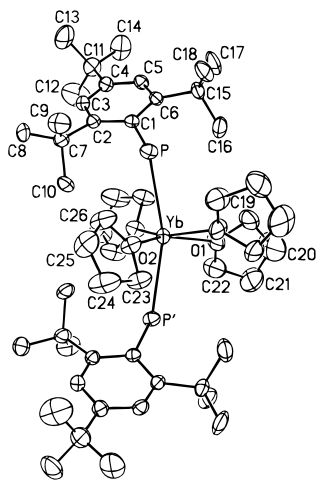
Figure 1. Molecular structure of Yb[P(H)Mes*]₂(thf)₄ (**1**) showing a distorted octahedral coordination environment around the lanthanide center. Selected interatomic separations (Å) and angles (deg): Yb–P = 3.025(2), Yb–O(1) = 2.480(4), Yb–O(2) = 2.506(3), P–C(1) = 1.859(4), P–H = 1.400(2); P–Yb–P = 162.54(6), Yb–P–C(1) = 121.4(1), O(1)–Yb–O(1A) = 79.6(3), O(1)–Yb–O(2) = 152.4(2), O(1A)–Yb–O(2) = 76.3(2), O(2)–Yb–O(2A) = 130.0(2), O(1)–Yb–P = 108.5(1), O(1A)–Yb–P = 85.1(1), O(2)–Yb–P = 82.8(1), O(2A)–Yb–P = 89.4(1)°.

The Eu–P distance in complex **2** (3.143(3) Å) is quite long compared with the terminal Eu–P distance of 3.034(1) Å[3i] in hexacoordinated Eu[PPh₂]₂(L)₄ (L = *N*-methylimidazole) and with the bridging Eu–P distances in four-coordinated Eu[(μ-P^tBu₂)₂Li(thf)]₂ (**2**)[3f] ranging from 3.034(1) to 3.068(1) Å (average: 3.046 (7) Å). Interestingly, the Eu–P distance in complex **2** is not much shorter than the values ranging from 3.165(2) to 3.249(2) Å reported for the europium phosphane adduct {Eu[TeSi(SiMe₃)₃]₂(DMPE)₂}₂(μ-DMPE) (average: 3.20(1) Å), which exhibits the coordination number 7 at the lanthanide center.[9] To the best of our knowlege,[10] these are the only reports on other Eu–P systems that have been structurally characterized.

The Yb–O distances in **1** are 2.480(4) and 2.506(3) Å (2.551(7) and 2.587(6) Å for **2**, respectively). They are slightly longer than the corresponding distances which we reported earlier for Yb[PPh₂]₂(thf)₄ (2.430(4) and 2.437(4) Å).[3g] The closest nonbonding Yb⋯C distances in **1** are 3.96(1) Å [C(10)] and 4.72(1) Å [C(16)]. These distances seem too large even for very weak agostic interactions in our Ln[P(H)Mes*]₂(thf)₄ complexes.

The geometry around the phosphorus atom in the Ln[P(H)-Mes*]₂(thf)₄ species is distinctly pyramidal; e.g., the sum of bond angles around the phosphorus atom in **1** is 313°. This value can be compared with that reported for the molecular structure of Yb[PPh₂]₂(thf)₄ (∑P = 332.7°),[3g] which was found to exhibit a less pronounced pyramidal environment around the phosphorus atom. The Yb–P–C angle of 121.4(1)° (**1**) and the corresponding angle of 117.1(3)° in **2** can be compared, e.g., with the corresponding angles of 110.2(1) and 119.4(1)° reported for Yb[PPh₂]₂(thf)₄.[3g]

Both **1** and **2** desolvate rapidly upon exposure to vacuum, thus precluding a reliable characterization by elemental analysis. Analytical data (C, H, P) for both **1** and **2** are consistent with the formulation Ln[P(H)Mes*]₂(thf)ₓ ($x < 4$), with differing numbers of tetrahydrofuran molecules, depending on the time the samples were exposed to vacuum.[11]

NMR spectroscopic investigations of the europium species **2** were found to be difficult because of the strong paramagnetism of europium(II).[11] However, the diamagnetic ytterbium derivative **1** could be studied in solution using mulitnuclear NMR spectroscopy (¹H, ¹³C, ³¹P, ¹⁷¹Yb).[11] The proton-decoupled ³¹P NMR spectrum of crystals of **1**·2thf in tetrahydrofuran-d_8 at room temperature shows a singlet at −90.1 ppm. Very broad ¹⁷¹Yb satellites were detected with a P–Yb coupling constant of approximately 650 Hz. The corresponding signal in the proton-coupled ³¹P NMR spectrum shows splitting into doublets with a P–H coupling constant of 179 Hz, thereby documenting the presence of the P–H proton. The ³¹P NMR spectrum of **1** at −60 °C consists of a singlet at −88.9 ppm with much better resolved ytterbium satellites (J_{P-Yb} = 647 Hz). The ¹⁷¹Yb NMR spectrum at −60 °C exhibits a triplet at 406.9 ppm (J_{Yb-P} = 647 Hz). Were were unable to detect any signals in the ¹⁷¹Yb NMR spectrum of complex **1** at room temperature. This observation might be attributed to a fast interligand exchange.

The synthesis of **1** and **2** introduces a novel class of lanthanide bis(phosphido) complexes, based on primary phosphides. Formation of **1** and **2** demonstrates that, with careful control of stoichiometry, stable lanthanide complexes are accessible using primary phosphides (e.g. the −P(H)Mes* ligand) as the only anionic ligands. We were able to show that this ligand system meets the electrostatic and steric requirements necessary to form thermally stable, isolable complexes of the lanthanides, without using sterically demanding supporting ligands such as, e.g., pentamethylcyclopentadienyl (Cp*) or cyclooctatetraenyl (COT). Furthermore, we could prove that the −P(H)Mes* ligand provides the steric bulk needed to saturate the coordination environment of the relatively large[12] divalent lanthanide cations. The utility of complexes **1** and **2** as suitable precursors for the generation of lanthanide phosphinidene species of the type [(thf)ₓLn=P–R] or related species remains to be determined.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, bond lengths and angles, and thermal parameters and an ORTEP diagram of complex **2** (16 pages). Ordering information is given on any current masthead page.

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(11) Complexes **1** and **2** are soluble in tetrahydrofuran but insoluble in toluene. Characterization data for **1** are as follows. ¹H NMR (C₄D₈O, 400 MHz, 25 °C): δ 1.19 (s, 18H), 1.61 (s, 36H), 3.00 (d, J_{P-H} = 179 Hz, 2H), 7.03 (s, 4H). ³¹P NMR (C₄D₈O, 161.9 MHz, 25 °C): δ −90.1 (d, J_{P-H} = 179 Hz; J_{P-Yb} = 650 Hz). ³¹P NMR (C₄D₈O, 161.9 MHz, −60 °C): δ −88.9 (d, J_{P-H} = 184 Hz; J_{P-Yb} = 647 Hz). ¹³C NMR (C₄D₈O, 100.4 MHz, 25 °C): δ 32.2, 32.3, 32.4, 34.8 (CH₃–C), 38.6 (CH₃–C), 120.6 (*meta*-C), 140.1 (*para*-C), 148.4 (*ortho*-C), 149.6 (d, J_{C-P} = 60 Hz, *ipso*-C). ¹⁷¹Yb NMR (C₄D₈O, 70.0 MHz, −60 °C): δ 406.9 (t, J_{Yb-P} = 647 Hz). IR (Nujol): 2364 s, 1755 w, 1596 m, 1282 m, 1238 m, 1170 m, 1074 s, 1026 s, 918 s, 872 s, 749 m, 723 m, 667 w, 636 w, 593 w, 487 w cm⁻¹. **1** becomes partially desolvated upon drying. As an example, the remaining residue was found to analyze as Yb[P(H)Mes*]₂(thf)ₓ (x = 1.3). Anal. Calcd for C₄₁.₂H₇₀.₄O₁.₃P₂Yb: C, 60.23; H, 8.64; P, 7.54. Found: C, 60.54; H, 8.98; P, 7.25. Characterization data for **2** are as follows. IR (Nujol): 2360 s, 1596 w, 1283 m, 1167 m, 1074 s, 1031 s, 916 m, 727 m, 668 w, 635 w cm⁻¹. Magnetic susceptibility: χ_M^{293K} = 2.85 × 10⁻² cgsu; μ_{eff} = 8.2 μ_B. **2** also becomes partially desolvated upon drying. As an example, the remaining residue was found to analyze as Eu[P(H)-Mes*]₂(thf)ₓ (x = 0.9). Anal. Calcd for C₃₉.₆H₆₇.₂EuO₀.₉P₂: C, 61.64; H, 8.78; P, 8.03. Found: C, 61.93; H, 8.99; P, 7.88.

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