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Syntheses and structures of calcium and ytterbium bis(diphosphanylamido) complexes

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Dedicated to Professor Dr. Dr. h.c. Mult. Wolfgang A. Herrmann.

Abstract

Bis(diphosphanylamido) complexes of calcium and ytterbium, $[\{(Ph_2P)_2N\}_2M(THF)_3]$ (M = Ca (**1**), Yb (**2**)), have been prepared by reaction of $[K(THF)_nN(PPh_2)_2]$ ($n = 1.25, 1.5$) and MI_2. The single crystal X-ray structures of compounds **1** and **2** always show a η^2-coordination of the ligand via the nitrogen and one phosphorus atom. In solution a dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorus atoms.

Keywords: Calcium; Chelates; Coordination chemistry; Ytterbium; N,P ligands

1. Introduction

Recently, there has been a significant research effort in d- and f-transition metal chemistry to find an alternative to the well established cyclopentadienyl ligand [1] for stabilizing high reactive metal centers. In these regards, one approach among others is the use of phosphines with P–N bonds [2]. In this context, we have introduced the well known monophosphanylamide, $(Ph_2PNPh)^-$ [3], and diphosphanylamide, $\{(Ph_2P)_2N\}^-$ [4–6], as ligands in trivalent lanthanide chemistry. In dependence of the steric demand of the ligand, either metallate complexes of composition $[Li(THF)_4][(Ph_2PNPh)_4Ln]$ (Ln = Y, Yb, Lu) [3] or the homoleptic compounds $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, La, Nd, Er) [4] can be obtained. The later complexes were used as catalysts for the polymerization of ε-caprolactone. Significant differences in terms of correlation of theoretical and experimental molecular weights, as well as polydispersities, were observed depending on the nature of Ln. The single crystal X-ray structures of these complexes solely show a η^2-coordination of the ligand via the nitrogen and one phosphorus atom. In solution a dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorus atoms. Thus, the coordination of phosphorus atom to the metal center is weak and the corresponding bond length is rather long.

Recently, we also introduced the $\{(Ph_2P)_2N\}^-$ ligand into divalent lanthanide and heavy alkaline earth metal chemistry [7,8]. Whereas to the best of our knowledge, the $\{(Ph_2P)_2N\}^-$ ligand was not previously used in group 2 chemistry, the oxidized version, $\{(Ph_2PO)_2N\}^-$, was taken very recently to synthesize complexes of composition $[M\{(OPPh_2)_2N]_2$ (M = Sr, Ba) [9]. It is well established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals are somewhat related [10]. This similarity in coordination chemistry originates from the similar ion radii (for CN 6 (pm): Ca^{2+} 100, Yb^{2+} 102, Sr^{2+} 118, Eu^{2+} 117, Ba^{2+} 135) [11]. Bis(diphosphanylamido) complexes of strontium and europium, $[\{(Ph_2P)_2N\}_2M(THF)_3]$ (M = Sr, Eu), were obtained by reaction of $[K(THF)_nN(PPh_2)_2]$ ($n = 1.25, 1.5$) and MI_2. The single crystal X-ray structures of these compounds again show a η^2-coordination of the ligand

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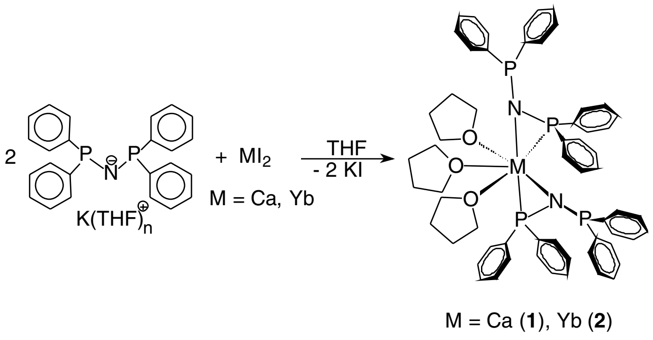
via the nitrogen and one phosphorus atom. As a result of the larger ion radius treatment of $[K(THF)_nN(PPh_2)_2]$ with BaI_2 leads to the coordination polymer $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]_n$. In the solid state, the infinite chain is formally held together by π-coordination of the phenyl rings to the potassium atoms.

Besides the strontium, barium, and europium complexes, now we are interested in synthesizing bis(diphosphanylamido) derivatives of the remaining two metals in the series of divalent lanthanide metals and the heavier alkaline earth metals, such as calcium and ytterbium.

2. Results and discussion

Reaction of the previously described potassium compound $[K(THF)_nN(PPh_2)_2]$ [4] with anhydrous calcium diiodide and $YbI_2(THF)_2$, respectively, in THF in a 2:1 molar ratio, followed by crystallization from THF/*n*-pentane (1:2), led selectively to products of composition $[\{(Ph_2P)_2N\}_2M(THF)_3]$ (M = Ca (**1**), Yb (**2**)) in good yields (Scheme 1). The new complexes have been characterized by standard analytical/spectroscopic techniques and the solid-state structures were established by single crystal X-ray diffraction. The ^1H and $^{31}P\{H\}$ NMR spectra of both complexes were investigated. The ^1H NMR spectra are not very characteristic. Besides the THF signals, two multiplets are observed in the aromatic region. In contrast, the $^{31}P\{^1H\}$ NMR spectra are very characteristic. Only one signal for all phosphorus atoms of each compound is observed at room temperature (δ 43.2 ppm (**1**) and δ 44.9 ppm (**2**)), showing that the phosphorus atoms in each case are chemically equivalent in solution. A similar dynamic behavior and chemical shift is seen in $[\{(Ph_2P)_2N\}_2Sr(THF)_3]$ (δ 48.0 ppm). Since the solid state structures of **1** and **2** (see below) show two non equivalent phosphorus atoms of each ligand, a dynamic behavior in solution is anticipated.

Even Ca(II) and Yb(II) have almost the same ionic radii, and the solid state structures of compounds **1** and **2** look alike; they crystallize in different unit cells and thus the respective bond distances and bond angles between **1** and **2** vary a bit. Selected bond lengths and bond angles are given in Table 1. As a representative example the solid structure of compound **1** is shown in Fig. 1. Compound **1** crystallizes in the space group $P2_1/n$ having four molecules of **1** in the unit cell, whereas compound **2** crystallizes in the space group $C2/c$ having eight molecules of **2** and 12 molecules of THF in the unit cell. Even more surprising to us is the fact that the structure of compound **1** is isostructural to the previously reported europium compound $[\{(Ph_2P)_2N\}_2Eu(THF)_3]$ [7].



Scheme 1.

In both compounds **1** and **2**, two chelating η^2-$\{(Ph_2P)_2N\}^-$ ligands and three molecules of THF are coordinated to the metal atom, resulting in a sevenfold coordinated metal atom. The $\{(Ph_2P)_2N\}^-$ ligands coordinate via the nitrogen and one phosphorus atom. In the coordination polyhedron, the $\{(Ph_2P)_2N\}^-$ ligands are bend to each other, thus P1 is opposite to N2. As observed for the analogous strontium and europium compounds [4], the bond distances between these two atoms and the metal atom are longer than the corresponding bond distances of

Table 1
Selected bond lengths (pm) and bond angles (°) of $[\{(Ph_2P)_2N\}_2Ca(THF)_3]$ (**1**) and $[\{(Ph_2P)_2N\}_2Yb(THF)_3]$ (**2**)

1		**2**	
Bond lengths (Å)			
Ca–N1	245.5(3)	Yb–N1	242.9(3)
Ca–N2	249.1(3)	Yb–N2	247.8(3)
Ca–P1	294.43(12)	Yb–P1	302.29(10)
Ca–P3	288.09(13)	Yb–P3	295.62(10)
Ca–O1	239.0(3)	Yb–O1	246.7(3)
Ca–O2	241.7(8)[a]	Yb–O2	242.0(3)
Ca–O3	245.2(3)	Yb–O3	249.3(3)
P1–N1	166.3(3)	P1–N1	166.8(3)
P2–N1	169.5(3)	P2–N1	169.8(3)
P3–N2	163.7(4)	P3–N2	166.4(3)
P4–N2	170.2(3)	P4–N2	169.3(3)
Bond angles (°)			
N1–Ca–N2	134.78(11)	N1–Yb–N2	133.81(10)
N1–Ca–P1	34.38(7)	N1–Yb–P1	33.44(8)
N1–Ca–P3	101.01(8)	N1–Yb–P3	100.37(8)
N1–Ca–O1	96.46(10)	N1–Yb–O1	94.36(11)
N1–Ca–O2	90.1(3)[a]	N1–Yb–O2	95.11(11)
N1–Ca–O3	125.15(10)	N1–Yb–O3	117.65(10)
N2–Ca–P1	168.01(9)	N2–Yb–P1	166.17(7)
N2–Ca–P3	34.52(8)	N2–Yb–P3	34.25(7)
N2–Ca–O1	94.91(11)	N2–Yb–O1	94.26(10)
N2–Ca–O2	88.2(2)	N2–Yb–O2	91.04(10)
N2–Ca–O3	99.66(11)	N2–Yb–O3	108.53(10)
O1–Ca–O2	167.0(2)[a]	O1–Yb–O2	160.96(10)
O1–Ca–O3	82.50(10)	O1–Yb–O3	80.04(11)
O2–Ca–O3	84.8(2)	O2–Yb–O3	80.93(11)
O1–Ca–P1	90.77(8)	O1–Yb–P1	83.58(7)
O2–Ca–P1	87.0(2)[a]	O2–Yb–P1	95.40(8)
O3–Ca–P1	90.77(8)	O3–Yb–P1	95.40(8)
O1–Ca–P3	93.79(8)	O1–Yb–P3	90.79(7)
O2–Ca–P3	95.7(2)[a]	O2–Yb–P3	103.67(7)
O3–Ca–P3	133.83(8)	O3–Yb–P3	141.31(8)
P1–Ca–P3	135.40(4)	P1–Yb–P3	131.96(3)
P1–N1–P2	118.8(2)	P1–N1–P2	120.89(18)
P3–N2–P4	123.0(2)	P3–N2–P4	121.88(18)

[a] Average value of two disordered positions.

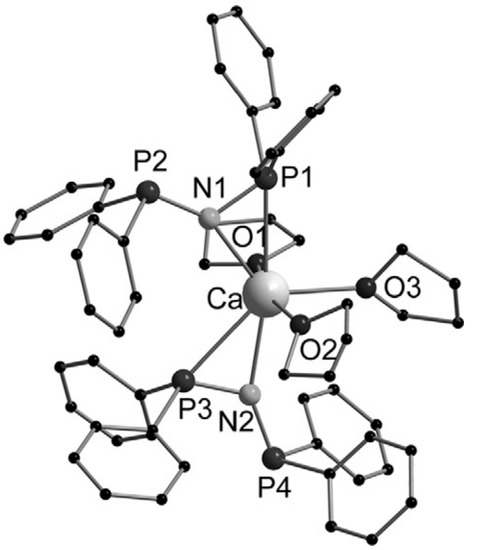


Fig. 1. Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms.

P3 and N1 (M–N1 245.5(3) pm (**1**), 242.9(3) pm (**2**), and M–N2 249.1(3) pm (**1**), 247.8(3) pm (**2**) and M–P1 294.43(12) pm (**1**), 302.29(10) pm (**2**), and M–P3 288.09(13) pm (**1**), 295.62(10) pm (**2**)). In compounds **1** and **2**, the THF molecules which are located in one plane are not symmetrically arranged, resulting in a significantly different O–M–O bond angles; e.g., in **2** O1–Yb–O2 160.96(10)°, O1–Yb–O3 80.04(11)°, O2–Yb–O3 80.93(11)°. The M–O bond distances are also non-equivalent. It is obvious that O3, which is located in the most crowded environment, is also most remote from the metal center; e.g., the Yb–O distances in complex **2** are Yb–O1 246.7(3) pm, Yb–O2 242.0(3) pm, and Yb–O3 249.3(3) pm. The Ca–N bond distances (Ca–N1 245.5(3) pm, Ca–N2 249.1(3) pm) of compound **1** are rather long (e.g., 233.1(6) pm in $[\{CH(PPh_2N\text{-}Mes)_2\}CaN(SiMe_3)_2]$ [12] and 228.1(9) pm in $[(Me_3Si)_2NCa\{\mu\text{-}P(H)Si\mathit{i}Pr_3\}_3Ca(thp)_3]$ (thp = tetrahydropyran) [13]), whereas the Ca–P bond lengths are in the expected range [13]. The Yb–N and Yb–P bond distances of compound **2** (Yb–N1 242.9(3) pm, Yb–N2 247.8(3) pm, Yb–P1 302.29(10) pm, Yb–P3 295.62(10) pm) are in the range of the mono(diphosphanylamido) $[\{CH(PPh_2NSiMe_3)_2\}Yb\{N(PPh_2)_2\}Cl]$ (Yb–N 241.2(3) pm and Yb–P 294.96(11) pm), which were recently published by us [8].

Values for the N–M–P bite angles (N1–M–P1 34.38(7)° (**1**), 33.44(8)° (**2**), and N2–M–P3 34.52(8)° (**1**) and N2–Yb–P3 34.25(7)° (**2**)) show that the angles are rather small. Whereas one of the phosphorus atoms of each ligand binds to the metal center, the other phosphorus atom is bent away. The P–N–P angles within the ligand are P1–N1–P2 118.8(2)° (**1**), 120.89(18)° (**2**) and P3–N2–P4 123.0(2)° (**1**), 121.88(18)° (**2**). Within the ligand the P–N bond distance varies slightly. The phosphorus atom which binds to the metal atom is always a bit closer located to the nitrogen atom.

3. Summary

In summary, we have synthesized bis(diphosphanylamide) complexes of calcium and ytterbium of the general composition $[\{(Ph_2P)_2N\}_2M(THF)_3]$. The single crystal X-ray structures of these complexes solely show a η^2-coordination of the ligand, in which only one of the phosphorus atoms coordinates to the metal center. In solution a dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorus atoms.

4. Experimental

4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in a flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glove box. THF was predried over Na wire and distilled under nitrogen from K and benzophenone ketyl prior to use. *N*-pentane was distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ⩾99 at.% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. The NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively. Elemental analyses were carried out with an Elementar vario EL. $YbI_2(THF)_2$ [14], and $[K(THF)_n\text{-}N(PPh_2)_2]$ ($n = 1.25, 1.5$) [4] were prepared according to the literature procedures. CaI_2 was purchased from Aldrich Inc.

4.1.1. *[{(Ph₂P)₂N}₂Ca(THF)₃] (**1**)*

20 mL of THF was condensed at −196 °C onto a mixture of 147 mg (0.5 mmol) of CaI_2 and 500 mg (1 mmol) of $[K(THF)_nN(PPh_2)_2]$, and the mixture was stirred for 20 h at room temperature. The mixture was filtered and the filtrate was concentrated (5 mL). Pentane (10 mL) was layered on the top of the THF solution. Colorless crystals were obtained after one day.

Yield: 280 mg (54%). ^1H NMR (C_6D_6, 400 MHz, 20 °C): δ 1.37 (br, 12H, THF), 3.61 (br, 12H, THF), 7.01–7.11 (m, 24H, Ph), 7.32–7.35 (m, 16H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): δ 43.2. *Anal.* Calc. for $C_{60}H_{64}CaN_2O_3P_4$ (1025.16): C, 70.30; H, 6.29; N, 2.73. Found: C, 69.72; H, 6.09; N, 2.02%.

4.1.2. *[{(Ph₂P)₂N}₂Yb(THF)₃] (**2**)*

20 mL of THF was condensed at −196 °C onto a mixture of 286 mg (0.5 mmol) of $[YbI_2(THF)_2]$, and 500 mg

(1 mmol) of $[K(THF)_nN(PPh_2)_2]$ and the mixture was stirred for 20 h at room temperature. The mixture was filtered and the filtrate was concentrated (5 mL). Pentane (10 mL) was layered on the top of the THF solution. Red crystals were obtained after one day.

Yield: 310 mg (53%). ^1H NMR (C_6D_6, 400 MHz, 20 °C): δ 1.24 (br, 12H, THF), 3.45 (br, 12H, THF), 6.94–7.11 (m, 24H, Ph), 7.84 (br, 16H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): δ 44.9. *Anal.* Calc. for $C_{60}H_{64}N_2O_3P_4Yb$ (1158.1): C, 62.23; H, 5.57; N, 2.42. Found: C, 61.92; H, 5.26; N, 2.27%.

4.2. X-ray crystallographic studies of ***1*** *and* ***2***

Crystals of **1** and **2** were grown from THF/*n*-pentane (1:2). A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C cold stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV Personal Computer.

1. (Mo Kα radiation); data collection and refinement: SHELXS-97 [15], SHELXL-97 [16]; monoclinic, space group $P2_1/n$ (no. 14); lattice constants $a = 1091.26(6)$ pm, $b = 1234.98(5)$ pm, $c = 3979.4(2)$ pm, $\beta = 89.970(4)°$, $V = 5363.0(5)\ 10^6\ pm^3$, $Z = 4$; $\mu(\text{Mo K}\alpha) = 0.283\ mm^{-1}$; $\theta_{max.} = 25.00$; 9442 ($R_{int} = 0.0773$) unique reflections measured, of which 6960 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.486 and −0.801 e $Å^{-3}$; 624 parameters (all non-hydrogen atoms, except C50, C51, C53–C56, and O2, were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0681$; $wR_2 = 0.2208$.

(2 · ***2****) · 3*. THF: (Mo Kα radiation); data collection and refinement: SHELXS-97 [15], SHELXL-97 [16]; monoclinic, space group $C2/c$ (no. 15); lattice constants $a = 3178.8(2)$ pm, $b = 1986.04(8)$ pm, $c = 2109.38(13)$ pm, $\beta = 115.169(4)°$, $V = 12052.8(11)\ 10^6\ pm^3$, $Z = 4$; $\mu(\text{Mo K}\alpha) = 1.708\ mm^{-1}$; $\theta_{max.} = 25.00$; 10574 ($R_{int} = 0.0409$) unique reflections measured, of which 6960 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.726 and −0.461 e $Å^{-3}$; 656 parameters (all non-hydrogen atoms, except C55, C57–C60, and the non-coordinated THF molecules, were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0315$; $wR_2 = 0.0730$.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-294422–294423. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.03.016.

References

[1] Reviews: (a) F.T. Edelmann, Angew. Chem. 107 (1995) 2647;
(b) F.T. Edelmann, Angew. Chem. Int. Ed. 34 (1995) 2466;
(c) F.T. Edelmann, D.M.M. Freckmann, H. Schumann, Chem. Rev. 102 (2002) 1851.

[2] M.S. Balakrishna, V. Sreenivasa Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett, St. Laurent, Coord. Chem. Rev. 129 (1994) 1.

[3] (a) T.G. Wetzel, S. Dehnen, P.W. Roesky, Angew. Chem. 111 (1999) 1155;
(b) T.G. Wetzel, S. Dehnen, P.W. Roesky, Angew. Chem. Int. Ed. 38 (1999) 1086;
(c) S. Wingerter, M. Pfeiffer, F. Baier, T. Stey, D. Stalke, Z. Anorg. Allg. Chem. 626 (2000) 1121.

[4] P.W. Roesky, M.T. Gamer, M. Puchner, A. Greiner, Chem. Eur. J. 8 (2002) 5265.

[5] M.T. Gamer, G. Canseco-Melchor, P.W. Roesky, Z. Anorg. Allg. Chem. 629 (2003) 2113.

[6] P.W. Roesky, M.T. Gamer, N. Marinos, Chem. Eur. J. 10 (2004) 3537.

[7] P.W. Roesky, Inorg. Chem. 45 (2006) 798.

[8] T.K. Panda, A. Zulys, M.T. Gamer, P.W. Roesky, J. Organomet. Chem. 690 (2005) 5078.

[9] J. Morales-Juarez, R. Cea-Olivares, M.M. Moya-Cabrera, V. Jancik, V. Garcia-Montalvo, R.A. Toscano, Inorg. Chem. 44 (2005) 6924.

[10] (a) C. Eaborn, P.B. Hitchcock, K. Izod, Z.-R. Lu, J.D. Smith, Organometallics 15 (1996) 4783;
(b) F. Weber, H. Sitzmann, M. Schultz, C.D. Sofield, R.A. Andersen, Organometallics 21 (2002) 3139;
(c) H. Schumann, S. Schutte, H.-J. Kroth, D. Lentz, Angew. Chem. 116 (2004) 6335;
(d) H. Schumann, S. Schutte, H.-J. Kroth, D. Lentz, Angew. Chem. Int. Ed. 43 (2004) 6208;
(e) S. Harder, Angew. Chem. 116 (2004) 2768;
(f) S. Harder, Angew. Chem. Int. Ed. 43 (2004) 2714.

[11] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.

[12] M.S. Hill, P.B. Hitchcock, Chem. Commun. (2003) 1758.

[13] M. Westerhausen, M.H. Digeser, M. Krofta, N. Wiberg, H. Nöth, J. Knizek, W. Ponikwar, T. Seifert, Eur. J. Inorg. Chem. (1999) 743.

[14] J.L. Namy, P. Girand, H.B. Kagan, P.E. Caro, in: W.A. Herrmann, G. Brauer (Eds.), Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 6, Thieme, Stuttgart, 1997, pp. 26–27.

[15] G.M. Sheldrick, SHELXS-97, Program of Crystal Structure Solution, University of Göttingen, Germany, 1997.

[16] G.M. Sheldrick, SHELXL-97, Program of Crystal Structure Refinement, University of Göttingen, Germany, 1997.