Inorg. Chem. **2006**, *45*, 798–802

Inorganic Chemistry
Article

Syntheses and Structures of Strontium, Barium, and Europium Bis(diphosphanylamido) Complexes

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Received October 7, 2005

Bis(diphosphanylamido) complexes of strontium and europium, $[\{(Ph_2P)_2N\}_2M(THF)_3]$ (M = Sr (**1**), Eu (**2**)), have been prepared by reaction of $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$) 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. As a result of the radius of the larger ion, treatment of $[K(THF)_n][N(PPh_2)_2]$ with BaI_2 gives the coordination polymer $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]_n$ (**3**). Two of the three $\{(Ph_2P)_2N\}^-$ ligands of compound **3** bind to the metal in η^2 (N, P) while the third shows a heteroallylic (P, P) coordination mode. In the solid state, the infinite chain is formally held together by π coordination of the phenyl rings to the potassium atoms.

Introduction

Recently there has been a significant research effort in d and f transition metal chemistry to find, in addition to the well-established cyclopentadienyl ligand,[1] new ancillary ligands for stabilizing highly reactive metal centers. In this regard, one approach is the use of phosphines with P−N bonds.[2] Recently we introduced the well-known monophosphanylamide, $(Ph_2PNPh)^-$,[3] and diphosphanylamide, $\{(Ph_2P)_2N\}^-$,[4,5,6,7] as ligands in lanthanide chemistry. Dependent on the steric demand of the ligand, either metalate complexes of composition $[Li(THF)_4][(Ph_2PNPh)_4Ln]$ (Ln = Y, Yb, Lu)[3] or homoleptic compounds $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, La, Nd, Er)[4] can be obtained. The latter complexes were used as catalysts for the polymerization of ϵ-caprolactone. Significant differences in terms of the correlation of the theoretical and experimental molecular weights, as well as polydispersities, were observed depending on the nature of Ln. Furthermore, mono- and di-substituted diphosphanylamide complexes of composition $[\{(Ph_2P)_2N\}LnCl_2(THF)_3]$ and $[\{(Ph_2P)_2N\}_2LnCl(THF)_2]$, respectively, were obtained by reacting $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$) with anhydrous yttrium or lanthanide trichlorides.[6,7] Both kinds of complexes were further reacted to give various organometallic compounds. The single-crystal X-ray structures of these complexes always show a η^2 coordination of the ligand via the nitrogen and one phosphorus atom, whereas the other phosphorus atom is bent away.

Now we are interested in introducing the $\{(Ph_2P)_2N\}^-$ ligand into divalent lanthanide and heavy alkaline earth metal chemistry. It is well established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals is somewhat similar.[8] 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).[9] Whereas, to the best of our

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10.1021/ic051738q CCC: $33.50

knowledge, the $\{(Ph_2P)_2N\}^-$ ligand was not previously used in group 2 chemistry, the oxidized version, $\{(Ph_2PO)_2N\}^-$, was used very recently to synthesize complexes of composition $[M\{(OPPh_2)_2N]_2$ (M = Sr, Ba).[10] Upon exposure to atmospheric oxygen, the latter compounds were transformed to the dinuclear species $[Sr_2\{(OPPh_2)_2N\}]_4$•(methoxyacetic acid) and $[Ba_2\{(OPPh_2)_2N\}]_4$•(*γ*-hydroxybutyric acid), respectively, in which the coordinated carboxylic acids were obtained from the oxidative degradation of DME and THF.

Experimental Section

General. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in 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 glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from Na/K benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were 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 atom % D) and were dried, degassed, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a 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). Raman spectra were performed on a Bruker RFS 100. Elemental analyses were carried out with an Elementar vario EL. SrI_2 and BaI_2 were purchased from Aldrich Inc. $EuI_2(THF)_2$[11] and $[K(THF)_n][N(PPh_2)_2]$ (n = 1.25, 1.5)[4] were prepared according to literature procedures.

[{(Ph$_2$P)$_2$N}$_2$Sr(THF)$_3$] (1). THF (20 mL) was added to a mixture of 500 mg (1.0 mmol) of $[K(THF)_n][N(PPh_2)_2]$ and 170 mg (0.5 mmol) of SrI_2 at −196 °C, and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and toluene was added to the mixture. The mixture was filtered, and the solvent removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2). Yield: 420 mg (78%). Colorless crystals. mp: 120−122 °C. Raman (solid, cm^{-1}): 3045 (m, *ν*C=C−*H*), 2985 (w, *ν*C−H), 2940 (w, *ν*C−H), 1581 (s, *ν*C=C), 1089 (m), 1026 (m, *ν*PC), 997 (vs), 669 (m), 617 (m). ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): *δ* 1.74 (m, 12H, THF), 3.60 (m, 12H, THF), 7.07 (m, 24H, Ph), 7.45 (m, 16H, Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 161.7 MHz, 25 °C): *δ* 48.0. Anal. Calcd for $C_{60}H_{64}N_2O_3P_4Sr$ (1073.69): C, 67.12; H, 6.01; N, 2.61. Found: C, 67.49; H, 6.31; N, 2.61.

[{(Ph$_2$P)$_2$N}$_2$Eu(THF)$_3$] (2). THF (20 mL) was added to a mixture of 500 mg (1.0 mmol) of $[K(THF)_n][N(PPh_2)_2]$ and 275 mg (0.5 mmol) of $EuI_2(THF)_2$ at −196 °C, and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and toluene was added to the mixture. The mixture was filtered, and the solvent removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2). Yield: 390 mg (72%). Yellow crystals. mp: 127−128 °C. Raman (solid, cm^{-1}): 3045 (m, *ν*C=C−*H*), 2985 (w, *ν*C−H), 2947 (w, *ν*C−H), 1581 (s, *ν*C=C), 1089 (m), 1026 (m, *ν*PC), 997 (vs), 669 (m), 617 (m). Anal. Calcd for $C_{52}H_{48}EuN_2OP_4$ (992.82) (**3** − 2THF): C, 62.91; H, 4.87; N, 2.82. Found: C, 62.22; H, 5.00; N, 2.43.

[{(Ph$_2$P)$_2$N}$_2$Ba(THF){(Ph$_2$P)$_2$N}K]$_n$ (3). THF (20 mL) was addedto a mixture of 750 mg (1.0 mmol) of $[K(THF)_n][N(PPh_2)_2]$ and 195 mg (0.5 mmol) of BaI_2 at −196 °C, and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and toluene was added to the mixture. The mixture was filtered, and the solvent was reduced in vacuo. The product was recrystallized from hot toluene. An oil is formed which slowly crystallizes. Yield: 372 mg (66%). Colorless crystals. mp: 75−78 °C. Raman (solid, cm^{-1}): 3049 (m, *ν*C=C−*H*), 1582 (s, *ν*C=C), 1091 (m), 1025 (m, *ν*PC), 998 (vs), 670 (m), 617 (m), 521 (m). ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): *δ* 1.27 (m, 4H, THF), 2.09 (s, toluene), 3.39 (m, 4H, THF), 6.97 (m, 36H, Ph), 7.27 (m, toluene), 7.32 (m, toluene), 7.49 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR (THF-d_8, 161.7 MHz, 50 °C): *δ* 51.6. Anal. Calcd $C_{173}H_{160}Ba_2K_2N_6O_2P_{12}$ (3079.58) (2 × **2** + 3toluene = single crystals): C, 67.47; H, 5.24; N, 2.54. Found: C, 67.80; H, 5.10; N, 2.57.

X-ray Crystallographic Studies of 1−3. Crystals of **1** and **2** were grown from THF/*n*-pentane (1:2); crystals of **3** were obtained from toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C N_2 stream of a Stoe IPDS or a Bruker Smart 1000 CCD diffractometer. Subsequent computations were carried out on an Intel Pentium III PC or Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97).[12] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[13] Compound **3** crystallizes as a racemic twin. As a result of the low quality of the data set of **3**, it is possible that not all noncoordinating solvent molecules in the unit cell were localized. In the final cycles of each refinement, all non-hydrogen atoms except the solvent molecules in **2** and **3** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated but not refined. The final values of the refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances, and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

Results and Discussion

The reaction of $[K(THF)_n][N(PPh_2)_2]$ with anhydrous strontium diiodide in THF in a 2:1 molar ratio followed by crystallization from THF/*n*-pentane (1:2) lead selectively to a product of composition $[\{(Ph_2P)_2N\}_2Sr(THF)_3]$ (**1**) in good yields (Scheme 1). The new complex has been characterized

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Table 1. Crystallographic Details of [$\{(Ph_2P)_2N\}_2Sr(THF)_3$] (**1**), [$\{(Ph_2P)_2N\}_2Eu(THF)_3$] (**2**), and [$\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]_n$ (**3**)[a]

	1	**2**	2(**3**) × (3toluene)
formula	$C_{60}H_{64}N_2O_3P_4Sr$	$C_{60}H_{64}EuN_2O_3P_4$	$C_{173}H_{160}Ba_2K_2N_6O_2P_{12}$
fw	1072.63	1136.97	3079.58
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P3_121$ (No. 152)
a (Å)	12.669(3)	10.9566(7)	25.164(4)
b (Å)	26.179(5)	12.5657(11)	
c (Å)	16.239(3)	39.541(3)	29.389(6)
β (deg)	90.108(5)	90.521(5)	
V (Å^3)	5386(2)	5443.6(7)	16117(5)
Z	4	4	3
density (g/cm^3)	1.323	1.387	0.952
radiation	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
μ (mm^{-1})	1.166	1.316	0.532
abs correction	empirical	empirical	numerical
reflns collected	66843	65343	95979
unique reflns	16414 [$R_{int} = 0.0419$]	16535 [$R_{int} = 0.0296$]	22854 [$R_{int} = 0.1382$]
observed reflns	12098	15064	15389
data, params	16414, 626	16535, 624	22854, 808
GOF on F^2	1.013	1.311	1.142
absolute structure parameter (Flack)			0.45(2)
R_1[b], wR_2[c]	0.0373, 0.0870	0.0613, 0.1202	0.0921, 0.2393

[a] All data collected at 200 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 1

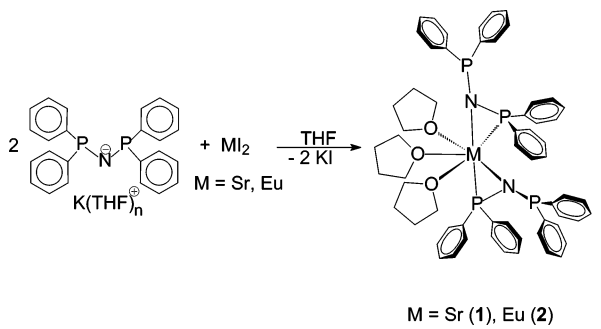

Table 2. Selected Bond Lengths (Å) and Angles (deg) of [$\{(Ph_2P)_2N\}_2Sr(THF)_3$] (**1**) and [$\{(Ph_2P)_2N\}_2Eu(THF)_3$] (**2**)

1		**2**	
Sr−N1	2.5817(15)	Eu−N1	2.565(3)
Sr−N2	2.6322(14)	Eu−N2	2.603(3)
Sr−P1	3.1146(7)	Eu−P1	3.0531(10)
Sr−P3	3.0079(6)	Eu−P3	2.9829(10)
Sr−O1	2.5530(14)	Eu−O1	2.549(3)
Sr−O2	2.5447(14)	Eu−O2	2.552(7)[a]
Sr−O3	2.5515(12)	Eu−O3	2.590(3)
P1−N1	1.6748(14)	P1−N1	1.659(3)
P2−N1	1.6971(14)	P2−N1	1.691(3)
P3−N2	1.6628(14)	P3−N2	1.637(4)
P4−N2	1.6970(14)	P4−N2	1.700(4)
N1−Sr−N2	139.55(4)	N1−Eu−N2	133.79(11)
N1−Sr−P1	32.51(3)	N1−Eu−P1	32.91(7)
N1−Sr−P3	106.16(3)	N1−Eu−P3	101.67(7)
N1−Sr−O1	98.56(5)	N1−Eu−O1	98.83(11)
N1−Sr−O2	88.85(5)	N1−Eu−O2	90.6(2)[a]
N1−Sr−O3	120.96(4)	N1−Eu−O3	124.81(10)
N2−Sr−P1	166.68(3)	N2−Eu−P1	165.10(9)
N2−Sr−P3	33.46(3)	N2−Eu−P3	33.21(8)
N2−Sr−O1	90.63(5)	N2−Eu−O1	94.54(11)
N2−Sr−O2	89.47(5)	N2−Eu−O2	86.5(2)[a]
N2−Sr−O3	99.26(4)	N2−Eu−O3	100.99(11)
O1−Sr−O2	168.38(4)	O1−Eu−O2	165.5(2)[a]
O1−Sr−O3	81.86(5)	O1−Eu−O3	79.89(10)
O2−Sr−O3	86.66(5)	O2−Eu−O3	85.9(2)[a]
O1−Sr−P1	100.95(3)	O1−Eu−P1	95.06(8)
O2−Sr−P1	80.51(3)	O2−Eu−P1	87.1(2)[a]
O3−Sr−P1	88.97(3)	O3−Eu−P1	91.91(8)
O1−Sr−P3	95.66(4)	O1−Eu−P3	93.34(8)
O2−Sr−P3	90.81(4)	O2−Eu−P3	95.3(2)[a]
O3−Sr−P3	132.71(3)	O3−Eu−P3	133.51(8)
P1−Sr−P3	137.085(13)	P1−Eu−P3	134.58(3)
P1−N1−P2	116.80(8)	P1−N1−P2	120.6(2)
P3−N2−P4	121.63(8)	P3−N2−P4	124.3(2)

[a] Average value of two disordered positions.

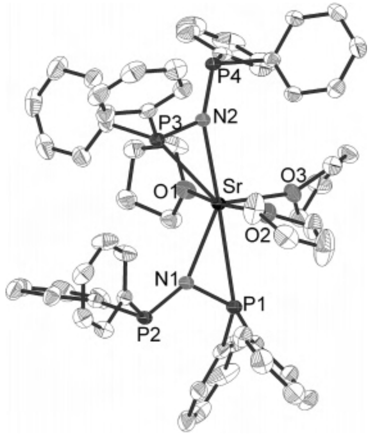

Figure 1. Perspective ORTEP view of the molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 1). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ having four molecules of **1** in the unit cell. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Two chelating η^2-$\{(Ph_2P)_2N\}^-$ ligands and three molecules of THF are coordinated to the strontium atom resulting in a 7-fold 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 bent toward each other; thus, P1 is opposite to N2. Interestingly, the bond distances between these two atoms and Sr is longer than the corresponding bond distance of P3 and N1 (Sr−N1 = 2.5817(15) Å, Sr−N2 = 2.6322(14) Å, and Sr−P1 = 3.1146(7) Å, Sr−P3 = 3.0079(6) Å). Because of the bending in **1**, the THF molecules which are located in one plane are not symmetrically arranged resulting in significantly different O−Sr−O bond angles of O1−Sr−O2 = 168.38(4)°, O1−Sr−O3 = 81.86(5)°, and O2−Sr−O3 = 86.66(5)°. The Sr−O (Sr−O1 = 2.5530(14) Å, Sr−O2 = 2.5447(14) Å, and Sr−O3 = 2.5515(12) Å), the Sr−N, and the Sr−P bond lengths are in the expected range: Sr−O = 2.596(7), 2.609(9), and 2.617(6) Å, Sr−N = 2.631(7) and 2.663(8) Å, and Sr−P = 3.062(4) and 3.088(3) Å in [$Sr(THF)_3\{Me_3SiNC(Ph)PSiMe_3\}_2$].[14] Values for the N−Sr−P bite angles (N1−Sr−P1 = 32.51(3)° and N2−Sr−P3 = 33.46(3)°) show that the angle is 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 116.80(8) and 121.63(8)° for P1−N1−P2 and P3−N2−P4, respectively. Within the ligand, the P−N bond distance varies slightly. The phosphorus atom which binds

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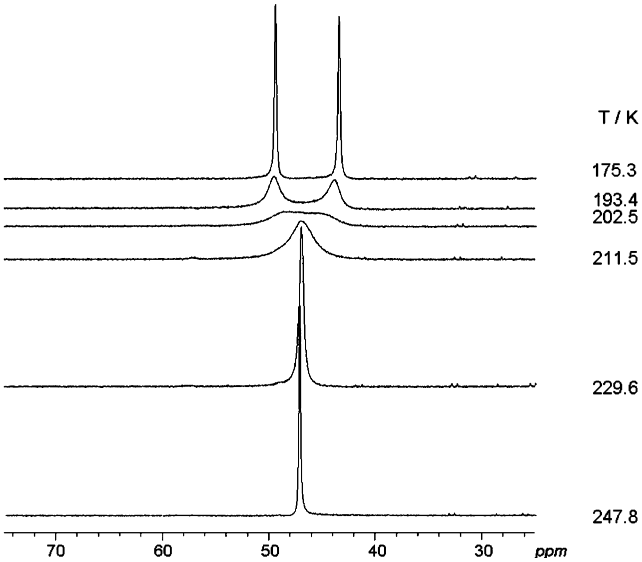
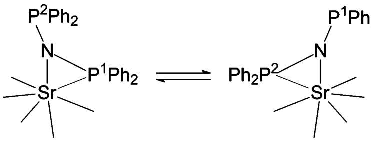


Figure 2. VT ^{31}P NMR spectra of **1**: $T_c = 202.5$ K, $\Delta\nu = 1205$ s^{-1}, 202.45 MHz NMR, $\Delta G_{Tc}^{\ddagger} = 35.65$ kJ/mol.

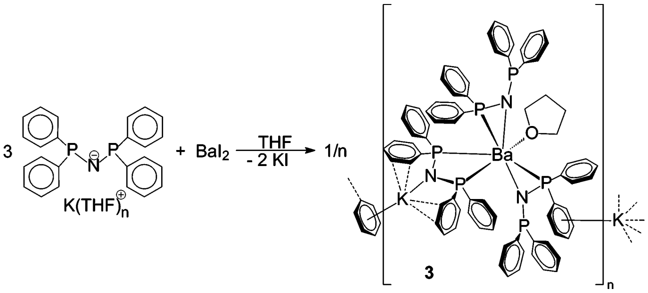
Scheme 2



to the metal atom is always a bit closer located to the nitrogen atom.

The ^{1}H and ^{31}P{H} NMR spectra of complex **1** were investigated. The ^{1}H NMR spectrum is not very characteristic. In addition to the THF signals, two mulitplets are observed at 7.07 and 7.45 ppm. At room temperature, one sharp signal in the ^{31}P{^{1}H} NMR spectrum (48.0 ppm) is observed showing that the phosphorus atoms are chemically equivalent in solution. A similar dynamic behavior is seen in trivalent lanthanide complexes such as [Ln{N(PPh$_2$)$_2$}$_3$] (Ln = Y, La).[4] Since the solid-state structure of **1** shows two nonequivalent phosphorus atoms for each ligand, a dynamic behavior in solution is anticipated (Scheme 2). Therefore VT ^{31}P{H} NMR spectra of **1** were recorded (Figure 2). In accordance with the solid-state structure at low temperature (173 K), two sets of signals for the phosphorus atoms are observed. Because of the low solubility of **1** at these temperatures, only broad signals without a hyperfine structure are observed. These signals start to coalesce with increasing temperature having a coalescence temperature of about $T_c = 202.5$ K. At higher temperatures (up from 229 K), the signals appear as one sharp singlet. From the coalescence temperature ($T_c = 202.5$ K) and the separation ($\Delta\nu = 1205$ s^{-1}, 202.45 MHz NMR) of the two coalescing signals, the free energy for the exchange of the two phosphorus atoms was calculated: $\Delta G_{Tc}^{\ddagger} = 35.65$ kJ/mol.[15]

Scheme 3



As already mentioned in the Introduction, the reactivities and coordination behaviors of the divalent lanthanide metals and the heavier alkaline earth metals are somewhat similar.[8] Therefore, a certain relationship between **1** and an analogous europium(II) compound was expected. To prove this expectation, [K(THF)$_n$][N(PPh$_2$)$_2$] was reacted with EuI$_2$(THF)$_2$ in THF at room temperature to give the corresponding europium complex [{(Ph$_2$P)$_2$N}$_2$Eu(THF)$_3$] (**2**) in a good yield (Scheme 1). Compound **2** was characterized by Raman spectroscopy and elemental analysis, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Even Sr(II) and Eu(II) have almost the same ionic radii, and the structures of compounds **1** and **2** look alike, they crystallize in different unit cells, and thus the bond distances and angles within **1** and **2** vary a bit. Nevertheless, the coordination polyhedron of **1** and **2** is similar; therefore, as observed in compound **1**, the europium atom of **2** is surrounded by two chelating η^2-{(Ph$_2$P)$_2$N}$^-$ ligands and three molecules of THF of which one is disordered. The Eu−O (av Eu−O = 2.563 Å), the Eu−N (Eu−N1 = 2.565(3) Å, Eu−N2 = 2.603(3) Å), and the Eu−P bond lengths (Eu−P1 = 3.0531(10) Å, Eu−P3 = 2.9829(10) Å) are in the expected range: Eu−O = 2.638(4) and 2.756(4) Å, Eu−N = 2.530(4) Å in [Eu(DME)$_2${N(SiMe$_3$)$_2$}],[16] and av Eu−P = 3.046 Å in [Eu(μ-P*t*Bu$_2$)$_2$Li(thf)]$_2$.[17]

Compared to strontium(II) and europium(II), barium(II) has a significantly larger ion radius. Therefore, it forms unique structures in some cases. Treatment of BaI$_2$ with [K(THF)$_n$][N(PPh$_2$)$_2$] in a 1:3 molar ratio followed by crystallization from toluene produced the metalate complex [{(Ph$_2$P)$_2$N}$_2$Ba(THF){(Ph$_2$P)$_2$N}K]$_n$ (**3**) as an oil, which slowly crystallizes (Scheme 3). Compound **3** was characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Figure 4). Data collection parameters are given in Table 1. Compound **3**, which crystallizes in the trigonal space group $P3_121$ as a racemic twin consisting of an infinite chain. The barium atoms are surrounded by three {(Ph$_2$P)$_2$N}$^-$ ligands and one molecule of THF resulting in a metalate substructure of composition [{(Ph$_2$P)$_2$N}$_3$Ba(THF)]$^-$. As observed in **1** and **2**, two out of the three {(Ph$_2$P)$_2$N}$^-$ ligands are η^2 coordinated via the nitrogen (N1, N2) and one phosphorus atom (P1, P3), whereas the third {(Ph$_2$P)$_2$N}$^-$

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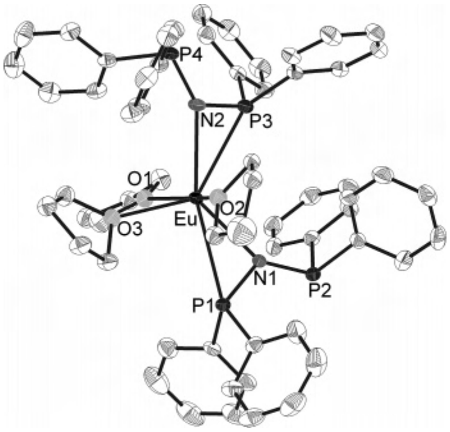

Figure 3. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

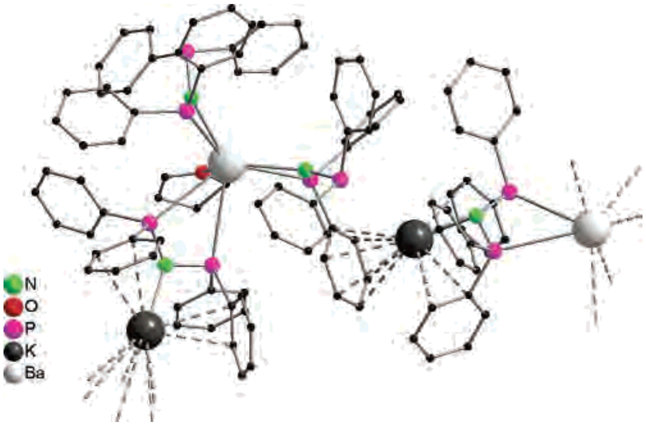

Figure 4. Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms.

ligand coordinates in a heteroallylic fashion via the two phosphorus atoms (P5, P6). The potassium atom is coordinated by the nitrogen atom (N3) of the latter $\{(Ph_2P)_2N\}^-$ ligand. Furthermore, two $\eta^2-\pi$ coordinations of the phenyl rings are observed. In the solid state, the chain is formally held together by π coordination of one phenyl ring of one $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]$ subunit to the potassium atom of a neighboring subunit. In Figure 4, all C−K interactions up to a value of 3.50 Å, a conservative limit for C−K interactions, are marked as dotted lines.[18] With these criteria, the potassium atom is η^6 coordinated to one phenyl ring of a neighboring $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]$ subunit. The structure of compound **3** was solved as a racemic twin. Since the quality of the refinement is low, no detailed discussion on bond length and angles is presented.

The ^1H and $^{31}P\{H\}$ NMR spectra of complex **3** were investigated. The ^1H NMR spectrum shows, in addition to the signals of coordinated THF, only uncharacteristic signals in the phenyl regions. The $^{31}P\{H\}$ NMR spectrum shows one signal (51.6 ppm) in THF-d_8 at 50 °C. Lowering the temperature to −80 °C leads to line broadening first, followed by the appearance of two signals (56.9 and 44.8 ppm), but no sharp point of coalescence could be determined.

Summary

In summary, bis(diphosphanylamide) complexes with strontium, europium, $[\{(Ph_2P)_2N\}_2M(THF)_3]$ (M = Sr (**1**), Eu (**2**)), and barium, $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]_n$ (**3**), were prepared. To the best of my knowledge, these are the first complexes of these elements having the $\{(Ph_2P)_2N\}^-$ ligand in the coordination sphere. The single-crystal X-ray structures of compounds **1** and **2** always show η^2 coordination of the ligand via the nitrogen and one phosphorus atom. In solution, a dynamic behavior of the ligand caused by the rapid exchange of the two different phosphorus atoms is observed. As a result of its larger ion radius, barium compound **3** shows a polymeric setup in the solid state, which consists of $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]$ subunits. Two of the three $\{(Ph_2P)_2N\}^-$ ligands of compound **3** bind to the metal in η^2 (N, P), while the third shows a heteroallylic (P, P) coordination mode. In the solid state, the infinite chain is formally held together by π coordination of one phenyl ring of one $[\{(Ph_2P)_2N\}_2Ba(THF)\{(Ph_2P)_2N\}K]$ subunit to the potassium atom of a neighboring subunit.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. Dr. Andreas Schäfer and Dr. Michael Gamer (FU Berlin) are acknowledged for recording the VT $^{31}P\{H\}$ NMR spectra.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org. 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 CCDC-289541-289543. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223−336−033; email: deposit@ccdc.cam.ac.uk).

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