Homoleptic Lanthanide Complexes of Chelating Phosphanamides—An Experimental and Theoretical Study**

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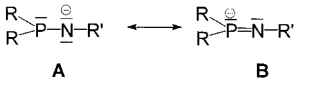
Phosphanamides (phosphazanes), phosphanimides (phosphazenes), and their cyclic analogues have long been known and have attracted the attention of experimentalists and theorists alike because of their comparatively short P–N bonds.[1] If a phosphanamine of the general formula $R_2PN(H)R'$ or a phosphanimine of the general formula $R_2(H)P{=}NR'$ is deprotonated, the resulting anion could in principle be described as phosphanamide **A** or iminophosphide **B** [Eq. (1)].[2] Theoretical studies showed that the anion



(1)

has a shortened P–N bond, but nevertheless basically corresponds to a phosphanamide with the negative charge mainly located on the nitrogen atom.[1b] Phosphanamides are known to act as both bridging and terminal ligands for middle and late transition metals.[3, 4]

Herein we report on the first phosphanamide complexes of Group 3 metals and the lanthanides. We were mainly interested in the coordination of phosphanamides (chelating ligands which feature a hard and a soft donor atom close together) to the hard lanthanide(III) ions. Transmetalation of **1** with anhydrous $LnCl_3$ (Ln = Y, Yb, Lu) in THF leads to products **2** (Ln = Y (**2a**), Yb (**2b**), and Lu (**2c**)) [Eq. (2)].

$$\underset{\mathbf{1}}{2[(Et_2O)Li(Ph_2PNPh)]_2 + LnCl_3} \xrightarrow[-3\,LiCl,\;-4\,Et_2O]{thf} \underset{\mathbf{2}}{[Li(thf)_4][(Ph_2PNPh)_4Ln]} \quad (2)$$

Even with an excess of $LnCl_3$ **2** was the only product which could be isolated. The new complexes have been characterized by standard analytical and spectroscopic techniques, and the solid-state structures of **2b** and **2c** (Figure 1) as well as of the neutral ligand $Ph_2PN(H)Ph$ (**3**)[5] were established by single-crystal X-ray diffraction.[6] Crystals of **2b** and **2c** that consist of an ion pair composed of a $[Li(thf)_4]^+$ cation and a $[(Ph_2PNPh)_4Ln]^-$ anion are isomorphous. The ligands of the anions show η^2 coordination, thus forming four three-membered rings (azaphosphametallacyclopropanes). Whereas a large number of homoleptic eight-coordinated compounds with four-, five-, and six-membered rings are known, homoleptic three-membered rings are extremely rare and to the best of our knowledge unknown for the lanthanides.[4, 7]

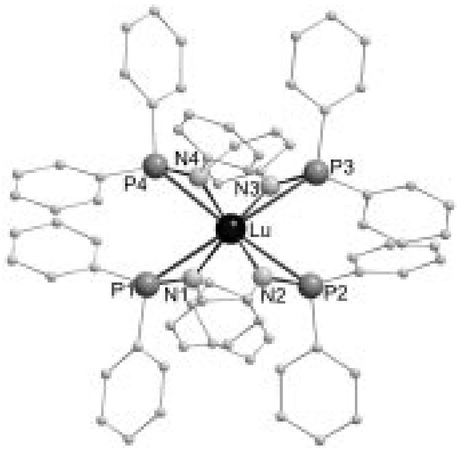


Figure 1. Solid-state structure of $[(Ph_2PNPh)_4Lu]^-$ (without hydrogen atoms, SCHAKAL drawing). Selected bond lengths [pm] and angles [°] (also given for the isostructural $[(Ph_2PNPh)_4Yb]^-$): Lu–N 225.2(7)–227.2(8), Yb–N 226.2(7)–227.9(7), Lu–P 288.6(3)–304.0(3), Yb–P 288.5(2)–303.1(2); N-Lu-N 100.7(3)–125.0(3), N-Yb-N 100.3(3)–126.4(3).

At a first glance the N_4P_4 coordination polyhedron of the anions looks highly symmetric, and D_2 symmetry is expected. A closer look shows that the polyhedron has no symmetry at all and may be best described as an extremely distorted cube. In fact none of the classical polyhedra known for coordination number eight gives a correct description.[8] Nevertheless, the anions are chiral, with both enantiomers cocrystallizing in the unit cell.

Not only the positions of the phenyl rings, which disturb the nearly realized C_2 symmetry, but also the strong differences of the Ln–P distances are the reasons for the unsymmetry. Whereas the Ln–N bond lengths are equal within the limits of error (**2b**: 226.2(7)–227.9(7) pm; **2c**: 225.2(7)–227.2(8) pm), the Ln–P bond lengths differ by about 15 pm (**2b**: 288.5(2)–303.1(2) pm; **2c**: 288.6(3)–304.0(3) pm). The geometry of the LnN_4 subunit is a distorted tetrahedron having N-Ln-N angles in the range 100.3(3)–126.4(3)° (**2b**) or 100.7(3)–125.0(3)° (**2c**), whereas the LnP_4 subunit is best described as a twisted rectangle with the metal atom in the center. The two P_2N_2 planes of the coordination polyhedron are distorted to give elongated parallelograms. The P-N-P angles amount to 109.7(7)–112.7(9)° (**2b**) or 109.9(9)–113.(9)° (**2c**). The N-P-N angles range between 62.3(2)° and 67.5(5)° (**2b**) or between 61.46(2)° and 67.31(6)° (**2c**). The two P_2N_2 parallelograms are staggered, being rotated by about 120° with respect to one another. Comparable Ln–P contacts are reported for the few known Ln–PR_3 compounds (e.g. 294.1(3) pm for $[(Me_5C_5)_2YbCl(Me_2PCH_2PMe_2)]$[9] and 288.1(1)–294.7(1) pm for $[(Me_3SiO)Lu\{C(PMe_2)_2(SiMe_3)\}_3]^-$[10]). In terms of bond lengths and angles, the neutral ligand **3** and the coordinated $[Ph_2PNPh]^-$ anion do not differ significantly. Thus the P–N bond lengths of **2b** (av 167.2(8) pm), **2c** (av 167.3(8) pm), and **3** (169.6(3) pm) all lie in a narrow range.

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To probe further the coordination of the $[Ph_2PNPh]^-$ anion to the lanthanides, ^1H and ^{31}P NMR spectra of **2a** and **2c** were recorded in solution. As expected the ^{31}P NMR spectra show only one signal. For **2a** $^2J(P,Y)$ coupling of 5.4 Hz could be observed,[11] whereas $^1J(P,Y)$ and $^2J(P,P)$ coupling were not detected, even at low temperature (203 K). This may be the result of a rapid isomerization (dissociation/association) of the phosphorus atoms in solution. Therefore, the Ln–P interaction can only be weak.

To better understand the nature of the Ln–P contacts, as well as the reason for the unsymmetry of **2**, theoretical investigations with DFT methods[12] (DFT = density functional theory) and the MP2 method[13] (MP2 = Møller–Plesset second-order perturbation theory) of a series of $[(R_2PNR)_4Y]^-$ complexes were carried out. The calculations were undertaken with the program system TURBOMOLE.[14] To study the steric as well as the electronic influence of the substituent R of the R_2PNR^- ligand, three compounds with R = H, Me, or Ph were computed. For minimization of the computational effort, an idealized C_2 symmetry was assumed for all calculated complexes. The structure optimizations with the DFT method were in all cases followed by a population analysis based on occupation numbers by Erhardt and Ahlrichs.[15]

It can be seen from the calculations that increasing steric demand of R causes both significant shortening of the Y–P contacts (on average) besides slightly elongated Y–N bonds. Additionally, there is increasing disparity in the two types of Y–P distances, even though all structure optimizations were started with equal Y–P or Y–N bond lengths.[16] The calculated Y–P distances are larger than the distances in known $Y{-}PR_3$ complexes (281.7–304.5 pm)[17] in all cases, except for one extrapolated value. Since all the other interatomic distances of the computed $[(Ph_2PNPh)_4Y]^-$ anion correspond well with the experimental data, the discrepancy concerning the Y–P contacts might indicate a very weak interaction. This would allow packing constraints in the crystal to play a superior role. A comparison of the DFT and the MP2 structural parameters for the Me- or Ph-substituted complexes indicates the mainly dispersive nature of the Y–P contacts.[18] Whereas the Y–N bonds are shortened by a typical value of only about 3 pm with respect to the DFT bond length, the Y–P distances are more strongly affected (up to 24.5 pm shorter) for the MP2 method. The population analyses[19] show a significant but unsymmetric tightening of the Y–P interactions when going from R = H to R = Ph. We assume that electronic effects are not very important for the discussed observation, as the tendency of decreasing Y–P distances is independent of the electron-pushing (Me) or electron-pulling nature (Ph) of the substituents.

We suggest that the unsymmetric coordination pattern of the P atoms can be explained by the following effect of the large Ph substituents: On the one hand, the steric demand of the Ph groups in η^1-coordinated N-bound R_2PNR^- ligands at the periphery of the complex forces the phosphorus atoms to approach the metal center, tending towards η^2 coordination (no Y–P contact is formed in the case of the sterically less demanding H_2PNH^- ligand). On the other hand, the formation of four equally spaced chelating rings is hindered by the newly arising steric interactions of the hypothetical η^2 coordination.

The single-crystal X-ray and the computed structure of **2** feature the following results. The first phosphanamide complexes of Group 3 metals and the lanthanides were isolated. These are also the first complexes of Group 3 metals and the lanthanides having four ligands showing near-η^2 coordination, which leads to a distorted structure. According to theoretical investigations the differences in Ln–P bond lengths, which cause the unsymmetric shape of the coordination polyhedron, is best explained by steric effects. Nevertheless, based on the very weak calculated Ln–P binding interactions, packing constraints are suggested to have a further influence on the geometry.

Experimental Section

2a: THF (50 mL) was added at room temperature to YCl_3 (195 mg, 1.0 mmol) and $[(Et_2O)Li(Ph_2PNPh)]_2$ (1.428 g, 2.0 mmol), and the mixture was stirred for 18 h at room temperature. Then the suspension was filtered, and pentane (100 mL) was layered on top of the filtrate. After 2 d colorless crystals were obtained. Yield 260 mg (15%). ^1H NMR ($[D_8]THF$, 250 MHz, 25 °C): $\delta = 1.71-1.79$ (m, thf), 3.59–3.66 (m, thf), 6.17–6.25 (m, 4H, Ph), 6.59–6.65 (m, 4H, Ph), 6.72–6.78 (m, 8H, Ph), 6.87–6.93 (m, 4H, Ph), 7.21–7.28 (m, 16H, Ph), 7.44–7.50 (m, 4H, Ph); $^{31}P\{^1H\}$ NMR ($[D_8]THF$, 101.3 MHz, 25 °C): $\delta = 9.20$ (d, $^2J(Y,P) = 5.4$ Hz); ^{89}Y NMR ($[D_8]THF$, 14.7 MHz, 25 °C): $\delta = 296$.

2b: Yield 190 mg (11%). IR (KBr): $\tilde{\nu} = 3296$ (m), 1595 (vs), 1495 (vs), 1433 (s), 1290 (s), 892 (vs), 756 (s), 739 (vs), 695 (vs) cm^{-1}.

2c: Yield 170 mg (10%). IR (KBr): $\tilde{\nu} = 3296$ (m), 1593 (vs), 1482 (vs), 1432 (s), 1287 (s), 892 (vs), 740 (s), 739 (vs), 695 (vs) cm^{-1}; ^1H NMR ($[D_8]THF$, 250 MHz, 25 °C): $\delta = 1.72-1.77$ (m, 16H, thf), 3.57–3.61 (m, 16H, thf), 6.70–6.77 (m, 4H, Ph), 6.97–7.12 (m, 16H, Ph), 7.33–7.47 (m, 24H,Ph), 7.86–7.95 (m, 16H, Ph); $^{31}P\{^1H\}$ NMR ($[D_8]THF$, 101.3 MHz, 25 °C): $\delta = 16.69$.

Methods of the theoretical investigations: The efficient RIDFT program[20] was used for all the calculations with employment of the Becke–Perdew (B-P) functional[21] and the grid size m3. Basis sets were of SV(P) quality.[22] For Y, a relativistically corrected effective core potential with 28 core electrons (ECP-28) was used.[23] The large Y–P distances for the calculated $[(Ph_2PNPh)_4Y]^-$ anion were computed as being about 18 or 19 pm longer than the experimentally observed Lu–P or Yb–P bond lengths in $[(Ph_2PNPh)_4Yb]^-$ or $[(Ph_2PNPh)_4Lu]^-$. Therefore, MP2 calculations were carried out employing the efficient RIMP2 program.[24] Basis sets were of SV(P) quality for C and H, TZVP quality for P and N, and TZVPP quality for Y.[25] For the latter, the ECP-28 was again used. Owing to the huge computational effort of the MP2 calculation, the method was employed only for the two smaller systems $[(H_2PNH)_4Y]^-$ and $[(Me_2PNMe)_4]^-$. The differences in interatomic distances between the DFT and MP2 structures were used to extrapolate to a hypothetically computed Ph-substituted MP2 structure $[(Ph_2PNPh)_4Y]^-$ (see the supporting information). The extrapolated values represent an improvement over the DFT results when compared to the X-ray structural parameters. The largest differences again arose at the weak Y–P contacts. The extrapolation provided values that were as much as 6.5 pm too short.

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[6] Single-crystal X-ray diffraction data: **2b** ($C_{100}H_{116}LiN_4O_7P_4Yb$, M_r = 1785.82): STOE-STADI IV, space group $P2_1/c$ (no. 14), a = 1487.97(13), b = 2454.0(2), c = 2606.90(3) pm, β = 103.897(7)°, T = 203 K, Z = 4, V = 9240(1) × 10^6 pm^3, ρ_{calcd} = 1.287 g cm^{-3}, θ_{max} = 45°, 11554 reflections collected, 11554 independent reflections. The structure was solved by Patterson methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 8262 reflections with $I > 2\sigma(I)$, R_1 = 0.0610 and wR_2 = 0.1369. **2c** ($C_{100}H_{116}LiLuN_4O_7P_4$, M_r = 1791.76): STOE-STADI IV, space group $P2_1/c$ (no. 14), a = 1487.1(5), b = 2450.9(5), c = 2607.4(4) pm, β = 104.032(8)°, T = 203 K, Z = 4, V = 9220(4) × 10^6 pm^3, ρ_{calcd} = 1.291 g cm^{-3}, θ_{max} = 45°, 12007 reflections collected, 12007 independent reflections. The structure was solved by Patterson methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 8241 reflections with $I > 2\sigma(I)$, R_1 = 0.0607 and wR_2 = 0.1300. **3** ($C_{18}H_{16}NP$, M_r = 277.29): STOE-STADI IV, space group $Pca2_1$ (no. 29), a = 930.8(3), b = 1709.2(5), c = 951.5(3) pm, T = 200 K, Z = 4, V = 1513.8(8) × 10^6 pm^3, ρ_{calcd} = 1.217 g cm^{-3}, θ_{max} = 48°, 1274 reflections collected, 1274 independent reflections. The structure was solved by direct methods (SHELXS-86 and SHELXL-93) and refined by full-matrix least-square techniques using 1131 reflections with $I > 2\sigma(I)$, R_1 = 0.0299 and wR_2 = 0.0659. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410439 (**3**), CSD-410440 (**2b**), and CSD-410441 (**2c**).

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[16] Selected atomic distances [pm] and angles [°] of the calculated anions: $[(H_2PNH)_4Y]^-$: a) DFT: Y–N 226.0 and 226.1, Y–P 351.1 and 351.6, N-Y-N 101.9–113.4; b) MP2: Y–N 224.4, Y–P 348.1, N-Y-N 102.5–113.1; $[(Me_2PNMe)_4Y]^-$: a) DFT: Y–N 228.0 and 228.7, Y–P 321.8 and 325.7, N-Y-N 106.6–117.6; b) MP2: Y–N 225.8 and 225.9, Y–P 310.3 and 311.5, N-Y-N 101.2–122.5; $[(Ph_2PNPh)_4Y]^-$: a) DFT: Y–N 232.4 and 234.5, Y–P 306.7 and 321.9, N-Y-N 102.5–113.0; b) MP2 (extrapolated): Y–N 229.6 and 230.5, Y–P 287.6 and 297.4, N-Y-N 91.8–122.9.

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Solvothermal Synthesis of the Canted Antiferromagnet $\{K_2[CoO_3PCH_2N(CH_2CO_2)_2]\}_6 \cdot x H_2O$**

Siegfried O. H. Gutschke, Daniel J. Price, Annie K. Powell, and Paul T. Wood*

Derivatives of phosphonic acid have recently been shown to introduce structural diversity into metal oxide based materials produced both solvothermally and by conventional means.[1] We are currently investigating the use of solvothermal reactions to construct metal–ligand frameworks and have found that rigid aromatic carboxylic acid derivatives are excellent structural members around which to form infinite lattices.[2] However, the number of molecular clusters synthesized by using solvothermal techniques is still relatively small[3] and the factors which promote formation of molecular rather than infinite structures are poorly understood. We report herein the results of the extension of our efforts to the synthesis of large molecular species based on flexible chelating ligands.

When Co^{II} nitrate is treated with the potassium salt of the ligand (phosphonomethyl)iminodiacetic acid under hydrothermal conditions only blue-purple solutions are obtained. When the solvent is changed to methanol, the purple crystalline product **1** is formed in good yield. X-ray structure

$\{K_2[CoO_3PCH_2N(CH_2CO_2)_2]\}_6 \cdot x H_2O$ **1**

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