Yttrium and Lanthanide Diphosphanylamides: Syntheses and Structures of Complexes with one $\{(Ph_2P)_2N\}^-$ ligand in the Coordination Sphere

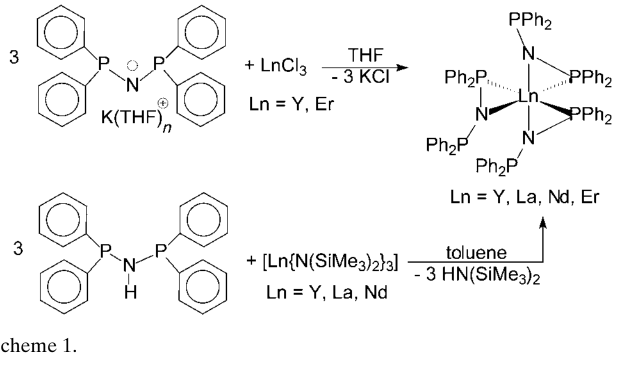
Peter W. Roesky,* Michael T. Gamer, and Nicolas Marinos[a]

Abstract: Treatment of the recently reported potassium salt $[K(thf)_n][N(PPh_2)_2]$ ($n = 1.25$, 1.5) with anhydrous yttrium or lanthanide trichlorides in THF leads after crystallization from THF/*n*-pentane (1:2) to the monosubstituted diphosphanylamide complexes $[LnCl_2\{(Ph_2P)_2N\}(thf)_3]$ (Ln = Y, Sm, Er, Yb). The single-crystal X-ray structures of these complexes show that the metal atoms are surrounded by seven ligands in a distorted pentagonal bipyramidal arrangement, in which the chlorine atoms are located in the apical positions. The diphosphanylamide ligand is always η^2-coordinated through the nitrogen atom and one phosphorus atom. Further reaction of $[SmCl_2\{(Ph_2P)_2N\}(thf)_3]$ with $K_2C_8H_8$ or reaction of $[LnI(\eta^8\text{-}C_8H_8)(thf)_3]$ with $[K(thf)_n][N(PPh_2)_2]$ in THF gives the corresponding cyclooctatetraene complexes $[Ln\{(Ph_2P)_2N\}(\eta^8\text{-}C_8H_8)(thf)_2]$ (Ln = La, Sm). The single crystals of these compounds contain enantiomerically pure complexes. Both compounds adopt a four-legged piano-stool conformation in the solid state. The structures of the *A* and the *C* enantiomers were established by single-crystal X-ray diffraction. The more soluble bistrimethylsilyl cyclooctatetraene complex $[Y\{(Ph_2P)_2N\}(\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6)(thf)_2]$ was obtained by transmetallation of $Li_2[1,4\text{-}(Me_3Si)_2C_8H_6]$ with anhydrous yttrium trichloride in THF followed by the addition of one equivalent of $[K(thf)_n][N(PPh_2)_2]$. The ^{89}Y NMR signal of the complex is split up into a triplet, supporting other observations that the phosphorus atoms are chemically equivalent in solution and, thus, dynamic behavior of the ligand in solution can be anticipated.

Keywords: chelates • cyclooctatetraene • lanthanides • N,P ligands • structure elucidation • yttrium

Introduction

Recently there has been a significant research effort in d- and f-transition-metal chemistry to substitute the well-established cyclopentadienyl ligand[1] by anionic nitrogen-based ligand systems.[2] In lanthanide chemistry one approach, among others, is the use of inorganic amides. In particular P–N systems such as phosphinimides (R_2PNR'),[3] phosphoraneiminato (R_3PN),[4] phosphiniminomethanides ($(RNPR'_2)CH$),[5] phosphiniminomethandiides ($(RNPR'_2)C$),[6] and diiminophosphinates ($(R_2P(NR'))$)[7] have been used as ligands. These investigations have shown that some lanthanide complexes which have P–N ligands in the coordination sphere[4] may not only exhibit unusual coordination modes, but they also can be used as catalysts for ε-caprolactone polymerization.[8] We have recently introduced the monophosphanylamide, $(Ph_2PNPh)^-$, and the diphosphanylamide, $\{(Ph_2P)_2N\}^-$, as ligands in lanthanide chemistry. Due to the steric demand of the ligand, either metallate complexes of composition $[Li(thf)_4][Ln(Ph_2PNPh)_4]$ (Ln = Y, Yb, Lu)[3a] or the homoleptic compounds $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, La, Nd, Er) have been obtained. These last complexes were obtained by reacting $[K(thf)_n][N(PPh_2)_2]$ with anhydrous yttrium or lanthanide trichlorides or by treatment of the homoleptic bis(trimethylsilyl)amides of yttrium and lanthanides ($[Ln\{N(SiMe_3)_2\}_3]$) with three equivalents of $(Ph_2P)_2NH$ in boiling toluene (Scheme 1).[9] The single-crystal X-ray structures of these complexes always show a η^2-coordination of



Scheme 1.

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[a] Prof. Dr. P. W. Roesky, Dr. M. T. Gamer, N. Marinos
Institut für Chemie, Freie Universität Berlin
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49) 30-838-52440
E-mail: roesky@chemie.fu-berlin.de

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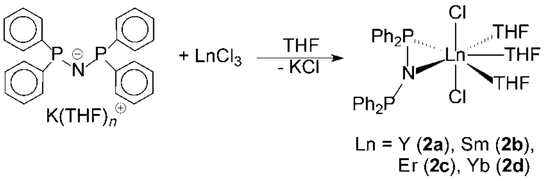
the ligand through the nitrogen atom and one phosphorus atom. In solution dynamic behavior of the ligand is observed; this is caused by the rapid exchange of the two different phosphorus atoms. [Ln{N(PPh$_2$)$_2$}$_3$] was also used as catalyst for the polymerization of ε-caprolactone. Significant differences in terms of correlation of theoretical and experimental molecular weights as well as polydispersities were observed depending on the nature of Ln.

Based on these results, we were interested to learn more about the coordination behavior and the reactivity of the {(Ph$_2$P)$_2$N}$^-$ ligand in lanthanide chemistry. In this article we focus on monosubstituted diphosphanylamide complexes, [LnCl$_2${(Ph$_2$P)$_2$N}(thf)$_3$], of yttrium and the lanthanides. Beside the syntheses and solid-state structures of these complexes, further reactions with substituted and nonsubstituted cyclooctatetraenes are reported.

Results and Discussion

Chloride complexes: The recently reported potassium salt [K(thf)$_n$][N(PPh$_2$)$_2$] (**1**; $n = 1.25$, 1.5), which can be obtained from (Ph$_2$P)$_2$NH and KH in THF, was treated with anhydrous yttrium or lanthanide trichlorides in a 1:1.1 molar ratio in THF. This reaction leads to the mono substituted diphosphanylamide complexes [LnCl$_2${(Ph$_2$P)$_2$N}(thf)$_3$] (Ln = Y (**2a**), Sm (**2b**), Er (**2c**), Yb (**2d**)) after crystallization from THF/n-pentane (1:2) (Scheme 2). The new complexes have been characterized by standard analytical/spectroscopic techniques and the solid-state structures of all four compounds were established by single-crystal X-ray diffraction.



Scheme 2.

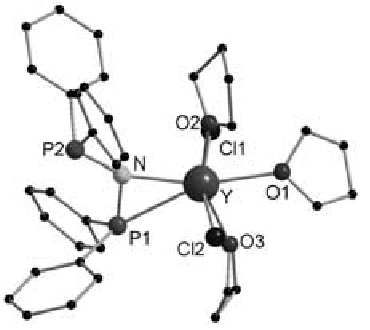
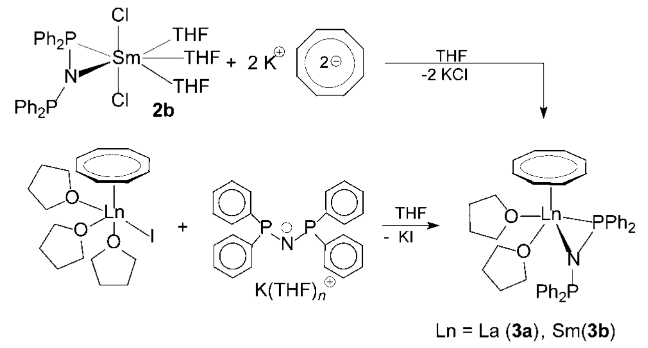


Figure 1. Solid-state structure of **2a** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°] (also given for isostructural **2b–d**): **2a**: N–P1 168.8(6), N–P2 168.9(6), N–Y 234.5(6), O1–Y 241.8(5), O2–Y 236.2(6), O3–Y 239.1(5), P1–Y 285.6(2), Cl1–Y 260.3(2), Cl2–Y 258.8(2); P1-N-P2 119.0(4), N-Y-O1 164.2(2), N-Y-O2 90.1(2), N-Y-O3 116.6(2), O1-Y-O2 75.0(2), O1-Y-O3 78.6(2), O2-Y-O3 153.1(2), N-Y-Cl1 93.55(13), N-Y-Cl2 102.10(13), O1-Y-Cl1 82.46(13), O2-Y-Cl1 93.39(12), O3-Y-Cl1 87.73(12), O1-Y-Cl2 82.29(13), O2-Y-Cl2 86.10(13), O3-Y-Cl2 85.77(12), Cl1-Y-Cl2 164.34(7); **2b**: N–P1 168.02(15), N–P2 170.03(15), N–Sm 238.94(15), O1–Sm 249.60(14), O2–Sm 243.02(13), O3–Sm 245.44(14), P1–Sm 290.17(6), Cl1–Sm 267.34(6), Cl2–Sm 265.79(6); P1-N-P2 120.07(8), N-Sm-O1 164.85(5), N-Sm-O2 90.92(5), N-Sm-O3 116.24(5), O1-Sm-O2 74.52(5), O1-Sm-O3 78.58(5), O2-Sm-O3 152.68(5), N-Sm-Cl2 102.47(4), N-Sm-Cl1 94.85(4), O1-Sm-Cl1 81.98(4), O2-Sm-Cl1 92.83(4), O3-Sm-Cl1 88.03(4), O1-Sm-Cl2 81.04(4), O2-Sm-Cl2 86.08(4), O3-Sm-Cl2 85.14(4), Cl1-Sm-Cl2 162.651(15); **2c**: N–P1 168.8(7), N–P2 170.7(6), N–Er 232.2(6), O1–Er 242.3(7), O2–Er 236.0(7), O3–Er 238.1(6), P1–Er 282.7(2), Cl1–Er 258.3(3), Cl2–Er 257.2(2); P1-N-P2 118.9(4), N-Er-O1 164.3(3), N-Er-O2 89.6(2), N-Er-O3 117.5(3), O1-Er-O2 75.8(2), O1-Er-O3 77.5(2), O2-Er-O3 152.6(2), N-Er-Cl1 92.9(2), N-Er-Cl2 102.6(2), O1-Er-Cl1 82.3(2), O2-Er-Cl1 93.6(2), O3-Er-Cl1 88.8(2), O1-Er-Cl2 82.6(2), O2-Er-Cl2 86.3(2), O3-Er-Cl2 84.4(2),Cl1-Er-Cl2 164.50(8); **2d**: N–P1 168.1(2), N–P2 170.5(3), N–Yb 229.5(2), O1–Yb 239.6(2), O2–Yb 233.0(2), O3–Yb 236.4(2), P1–Yb 282.80(8), Cl1–Yb 256.95(8), Cl2–Yb 255.61(7); P1-N-P2 118.82(14), N-Yb-O2 89.99(8), N-Yb-O3 117.01(8), N-Yb-O1 164.73(8), O1-Yb-O2 75.56(8), O1-Yb-O3 77.75(8), O2-Yb-O3 152.84(8), N-Yb-Cl1 93.66(6), N-Yb-Cl2 101.61(6), O1-Yb-Cl1 82.52(6), O2-Yb-Cl1 93.62(6), O3-Yb-Cl1 87.82(6), O1-Yb-Cl2 82.71(6), O2-Yb-Cl2 86.45(5), O3-Yb-Cl2 85.27(6), Cl1-Yb-Cl2 164.72(3).

Due to the similar ionic radii of the lanthanides, the single-crystal X-ray structures of **2a–d** are isostructural. As a representative example, the structure of **2a** is shown in Figure 1. Compounds **2a–d** crystallize in the monclinic space group $P2_1/c$, with four molecules of **2** in the unit cell. The metal atoms are surrounded by seven ligands in a distorted pentagonal biypramidal arrangement, in which the chlorine atoms are located in the apical positions (Ln–Cl1: 260.3(2) (**2a**), 267.34(6) (**2b**), 258.3(3) (**2c**), 256.95(8) pm (**2d**); Ln–Cl2: 258.8(2) (**2a**), 265.79(6) (**2b**), 257.2(2) (**2c**), 255.61(7) pm (**2d**)). The two chlorine atoms are bend away from the diphosphanylamide group (Cl1-Ln-Cl2: 164.34(7)° (**2a**), 162.651(15)° (**2b**), 164.50(8)° (**2c**), 164.72(3)° (**2d**)); this is most likely due to steric reasons. The pentagonal plane is occupied by the chelating η^2-{(Ph$_2$P)$_2$N}$^-$ ligand and three THF molecules. Two of the THF molecules, which are located in *cis* position to the {(Ph$_2$P)$_2$N}$^-$ ligand, are bent towards the third THF molecule, which is in the *trans* position relative to the diphosphanylamide (O2-Ln-O3: 153.1(2)° (**2a**), 152.68(5)° (**2b**), 152.6(2)° (**2c**), 152.84(8)° (**2d**)). The O-Ln-O angles of two neighboring THF molecules are close to the expected one of 72° in an ideal pentagon (O1-Ln-O2: 74.52(5) (**2a**), 74.52(5) (**2b**), 75.8(2) (**2c**), 75.56(8)° (**2d**); O1-Ln-O3: 78.58(5) (**2a**), 78.58(5) (**2b**), 77.5(2) (**2c**), 77.75(8)° (**2d**)). As observed in the homoleptic complexes [Ln{N(PPh$_2$)$_2$}$_3$], the diphosphanylamide ligand in **2a–d** is η^2-coordinated through the nitrogen atom and one phosphorus atom. Thus, one of the phosphorus atoms of the ligand binds to the lanthanide center, whereas the other phosphorus atom is bent away. The Ln–N1 and Ln–P1 bond lengths are 234.5(6) and 285.6(2) pm (**2a**), 238.94(15) and 290.17(6) pm (**2b**), 229.5(2) and 282.80(8) pm (**2c**), and 229.5(2) and 282.80(8) pm (**2d**), respectively. The free electron pair of the non-bonded phosphorus atom points away from the lanthanide center. The P-N-P angles within the η^2-{(Ph$_2$P)$_2$N}$^-$ ligand are 119.0(4) (**2a**), 120.07(8) (**2b**), 118.9(4) (**2c**), and 118.82(14)° (**2d**). Within the ligand the P–N bond length varies. The phosphorus atom that binds to the lanthanide atom is located slightly closer to the nitrogen atom (N–P1 168.8(6) (**2a**), 168.02(15) (**2b**), 168.8(7) (**2c**), 168.1(2) pm (**2d**), and N–P2 168.9(6) (**2a**), 170.03(15) (**2b**), 170.7(6) (**2c**), 170.5(3) pm (**2d**)). The arrangement of the $\{(Ph_2P)_2N\}^-$ ligand around the lanthanide atoms is in contrast to the isoelectronic phosphinomethanide ligand $\{(R_2P)_2CH\}^-$, which was pioneered by Karsch et al.[10] The phosphinomethanide ligand usually has η^3-coordination in a heteroallylic fashion. Depending on the nature of the substituents, homoleptic complexes with this ligand are obtained either as monomeric (e.g., $[La\{CH(PPh_2)_2\}_3]$)[10a] or as dimeric species (e.g., $[\mu\text{-}\eta^3\text{-}\{CH(PPh_2)_2\}_2\text{-}(Sm\{CH(PPh_2)_2\}_2)]$).[10c]

The NMR spectra of the diamagnetic yttrium compound **2a** and the paramagnetic samarium complex **2b** were investigated. The ^1H spectra of these compounds are not very characteristic. In the ^1H NMR spectrum of **2a** two mulitplets in the range of $\delta = 7.06$–7.15 and 7.61–7.68 ppm are observed. For compound **2b** only one muliplet in the region $\delta = 7.24$–7.34 ppm is seen. More characteristic are the $^{31}P\{^1H\}$ NMR spectra. For complex **2a** a characteristic doublet at $\delta = 39.5$ ppm is seen with a $^2J(P,Y)$ coupling of 5.3 Hz. A similar chemical shift is observed for **2b** ($\delta = 38.04$ ppm). Both signals are shifted upfield relative to **1** ($\delta = 58.6$ ppm), showing that the phosphorus atoms in each case are chemically equivalent in solution at room temperature.



Scheme 3.

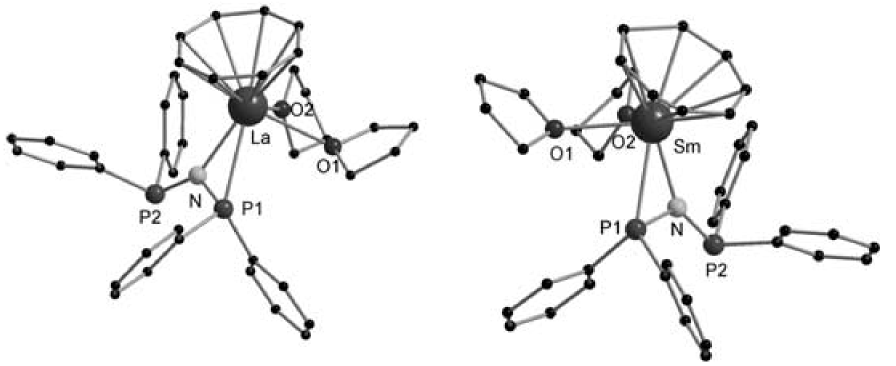
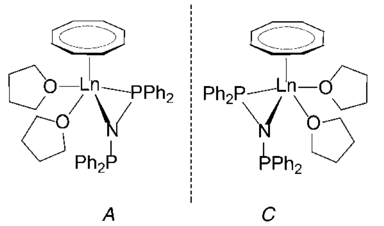


Figure 2. Solid-state structure of **3a** (left) and **3b** (right) showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [pm] or angles [°]: **3a**: C_g–La 204.7(0), N–P1 166.2(2), N–P2 169.3(3), N–La 250.1(2), O1–La 265.7(2), O2–La 253.9(2), P1–La 300.53(7); C_g-La-O1 117.02(10), C_g-La-O2 123.88(10), C_g-La-N 137.09(10), C_g-La-P1 134.59(10), P1-N-P2 125.17(13), N-La-O1 100.63(8), N-La-O2 86.13(8), O2-La-O1 71.04(8) (C_g = ring centroid); **3b**: C_g–Sm 192.5(10), N–P1 165.3(5), N–P2 169.7(5), N–Sm 242.1(5), O1–Sm 258.7(4), O2–Sm 246.1(4), P1–Sm 290.6(2); C_g-Sm-O1 119.44(10), C_g-Sm-O2 129.92(10), C_g-Sm-N 131.42(10), C_g-Sm-P1 127.98(10), P1-N-P2 124.2(3), N-Sm-O2 84.94(15), N-Sm-O1 101.4(2), O2-Sm-O1 72.40(15), P1-N-P2 125.17(13), N-Sm-O1 100.63(8), N-Sm-O2 86.13(8), O2-Sm-O1 71.04(8) (C_g = ring centroid)

Cyclooctatetraene complexes: To learn more about the reactivity of complexes **2a–d** we were interested in synthesizing some cyclooctatetraene derivatives. Cyclooctatetraene is, after cyclopentadiene, the most important π-perimeter ligand in f-element chemistry. Today it is well accepted that the large flat cyclooctatetraene ligand represents an especially valuable alternative to the popular cyclopentadienyl ligands. Among non-cyclopentadienyl organolanthanide complexes, cyclooctatetraene derivatives form a large and well investigated group of compounds.[1b]

Reaction of $[LnI(\eta^8\text{-}C_8H_8)(thf)_3]$ with **1** in a 1:1 molar ratio in THF at room temperature afford the corresponding diphosphanylamide complexes $[Ln\{(Ph_2P)_2N\}(\eta^8\text{-}C_8H_8)(thf)_2]$ (Ln = La (**3a**), Sm (**3b**)) (Scheme 3). Compound **3b** was also obtained by reaction of $K_2C_8H_8$ with **2b** prepared in situ. The complexes were characterized by standard analytical/spectroscopic techniques. By recrystallizing from THF/*n*-pentane (1:2) single crystals were obtained. The solid-state structures of both **3a** and **3b** were established by single-crystal X-ray diffraction (Figure 2). Compounds **3a** and **3b** crystallize in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. Since **3a** and **3b** are chiral molecules, which crystallize in a chiral space group, the single crystals of **3a** and **3b** contain enantiomerically pure complexes. Both compounds adopt a four-legged piano-stool conformation in the solid state. For compound **3a** the structure of the *A* enantiomer was established, whereas for **3b** the structure of the *C* enantiomer (for an explanation of the *A* and *C* nomenclature see reference [11]) was determined by single-crystal X-ray diffraction (Scheme 4).

The four-legged piano stool of **3a** and **3b** is formed by the η^8-coordinate cyclooctatetraene ring, which is located on top of the coordination polyhedron, two THF molecules, and

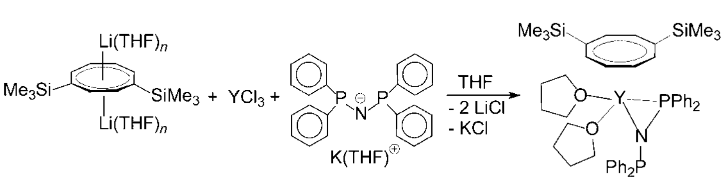


Scheme 4.

the η^2-$\{(Ph_2P)_2N\}^-$ ligand. Thus the lanthanide atom is twelve fold coordinated if η^8-cyclooctatetraene is considered as an octadentate ligand. The Ln–C bond lengths are in the expected range of 272.8(4)–275.3(5) pm (av. 274.1(5) pm)) for **3a** and 264.6(11)–269.8(10) pm (av. 267.3(11) pm) for **3b**. As observed in **2a–d** and in $[Ln\{N(PPh_2)_2\}_3]$, the diphosphanylamide ligand is again η^2-coordinated through the nitrogen atom and one phosphorus atom.[9] The Ln–N1 and Ln–P1 bond lengths are 250.1(2) and 300.53(7) pm in **3a** and 242.1(5) and 290.6(2) pm in **3b**, respectively. Thus, for **3b** the Sm–N bond length is shorter than for **2b** (Sm–N 238.94(15) pm), whereas the Sm–P bond length is in the same range (Sm–P 290.17(6) pm).

The observed signals in the NMR spectra of **3a** and **3b** are in good agreement with the observed solid-state structure. Due to the dynamic behavior of the $\{(Ph_2P)_2N\}^-$ ligand, which shows only signal for both phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectra ($\delta = 42.5$ (**3a**), 43.0 ppm (**3b**)), a racemization of **3a** and **3b** takes place in solution. Relative to the signals found for **2b** ($\delta = 38.04$ ppm), a slight downfield shift of the $^{31}P\{^1H\}$ NMR signal in **3b** is observed. The ^1H NMR spectra of **3a** and **3b** show a characteristic singlet for the $C_8H_8^{2-}$ ring at $\delta = 6.35$ (**3a**) and 10.55 ppm (**3b**). Due to the paramagnetic metal center the signal of the cyclooctatetraene ring in known samarium compounds is shifted over a wide range, for example, $\delta = 9.33$ ppm in $[Sm(\eta^8\text{-}C_8H_8)\{(i\text{-}Pr)_2ATI\}(thf)]$[12] ($(i\mathrm{Pr})_2\mathrm{ATI} = N$-isopropyl-2-(isopropylamino)troponiminate), $\delta = 13.2$ ppm in $[Li(thf)_3\{\mu\text{-}(\eta^2{:}\eta^8\text{-}C_8H_8)\}Sm(\eta^8\text{-}C_8H_8)]$,[13] and $\delta = 13.5$ ppm in $[Sm(\eta^8\text{-}C_8H_8)(hmpa)_3][Sm(\eta^8\text{-}C_8H_8)_2]$.[14] The $C_8H_8^{2-}$ ring also shows a characteristic signal in the $^{13}C\{^1H\}$ NMR spectra ($\delta = 97.7$ (**3a**) and 82.0 ppm (**3b**)). The EI mass spectrum of **3b** shows the molecular ion without coordinated THF, as well as its characteristic fragmentation pattern.

To get a better insight into the behavior of the cyclooctatetraene complexes in solution we were interested in synthesizing more soluble complexes. Therefore, we wanted to obtain 1,4-bis(trimethylsilyl)cyclooctatetraene diphosphanylamide lanthanide complexes. Transmetallation of dilithium-1,4-bis(trimethylsilyl)cyclooctatetraene, $Li_2[1,4\text{-}(Me_3Si)_2\text{-}C_8H_6]$, with anhydrous yttrium in a 1:1 molar ratio in THF at room temperature followed by the addition of one equivalent of **1** to the reaction mixture afforded the corresponding mono cyclooctatetraene complexes $[Y\{(Ph_2P)_2N\}(\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6)(thf)_2]$ (**4**) as yellow crystals in good yields (Scheme 5). The reagent $Li_2[1,4\text{-}(Me_3Si)_2C_8H_6]$ was prepared by in situ lithiation of 1,4-bis(trimethylsilyl)cycloocta-2,5,7-triene in THF.[15,16] Complex **4** was characterized by ^1H, ^{13}C, ^{29}Si, and ^{89}Y NMR spectroscopy and elemental analysis. The observed ^{89}Y NMR chemical shift for **4** ($\delta(C_6D_6) = 52.3$ ppm) is in the range found for monocyclooctatetraene benzamidinate ($\delta([D_8]THF) = 62.4$ ppm $[Y(\eta^8\text{-}C_8H_8)\{p\text{-}MeOC_6H_4C(NSiMe_3)_2\}(thf)]$[17], $\delta([D_8]THF) = 61.8$ ppm $[Y(\eta^8\text{-}C_8H_8)\{p\text{-}CF_3C_6H_4C(NSiMe_3)_2\}(thf)]$[17]) and aminotroponiminate complexes ($\delta(C_6D_6) = 59.7$ ppm $[Ln\{\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6\}\{(i\mathrm{Pr})_2ATI\}(thf)]$).[12] The ^{89}Y NMR signal of **4** is split into a triplet. This splitting is a result of the $^2J(P,Y)$ coupling from both phosphorus atoms; this indicates that the phosphorus atoms are chemically equivalent in solution (Figure 3). Thus, dynamic behavior of the ligand in solution is anticipated. The $^2J(P,Y)$ coupling constant of 10.1 Hz is in the expected range.[3a,18] Consequently, in the $^{31}P\{^1H\}$ NMR spectrum of **4** a doublet is observed at $\delta = 38.1$ ppm, which is comparable to those signals found for **3a** and **3b**. The ^1H NMR spectrum of **4** shows the typical signals of the η^8-$1,4\text{-}(Me_3Si)_2C_8H_6$ ring, which consist of a sharp singlet of the Me_3Si group ($\delta = 0.56$ ppm), and a singlet ($\delta = 6.85$ ppm) and a multiplet for the ring protons ($\delta = 6.77$–6.84 ppm).[15,19] In accordance with these results four signals are observed for the eight membered ring in the $^{13}C\{^1H\}$ NMR spectrum ($\delta = 100.0$, 100.8, 101.4, 102.0 ppm).



Scheme 5.

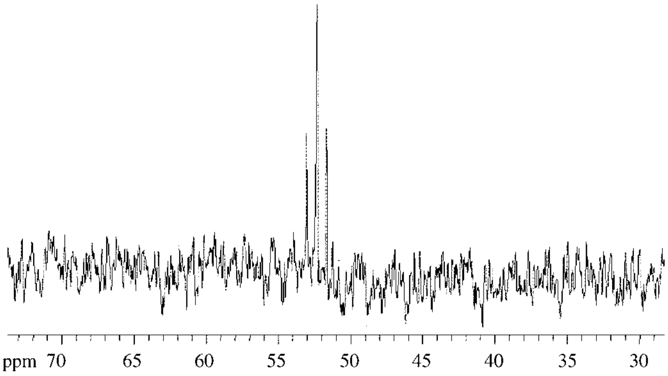


Figure 3. ^{89}Y NMR spectrum of **4**.

Conclusion

In summary, it can be emphasized that a series of monosubstituted diphosphanylamide complexes $[LnCl_2\{(Ph_2P)_2N\}(thf)_3]$ were prepared. The single-crystal X-ray structures of these complexes always show that the ligand is in a η^2-coordination mode. In solution, dynamic behavior of the ligand is observed; this is caused by the rapid exchange of the two different phosphorus atoms. Further reaction of $[\{(Ph_2P)_2N\}LnCl_2(thf)_3]$, prepared in situ, with $K_2C_8H_8$ or reaction of $[(\eta^8\text{-}C_8H_8)LnI(thf)_3]$ with $[K(thf)_n][N(PPh_2)_2]$ in THF gives the corresponding cyclooctatetraene complexes $[Ln\{(Ph_2P)_2N\}(\eta^8\text{-}C_8H_8)(thf)_2]$ (Ln = La, Sm). The single crystals of these compounds contain enantiomerically pure complexes. Both compounds adopt a four-legged piano-stool conformation in the solid state. For the lanthanum compound **3a** the structure of the *A* enantiomer was established, whereas for the samarium compound **3b** the structure of the *C* enantiomer was determined by single-crystal X-ray diffraction. The more soluble bistrimethylsilyl cyclooctatetraene complex $[Y\{(Ph_2P)_2N\}(\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6)(thf)_2]$ was obtained by transmetallation of $Li_2[1,4\text{-}(Me_3Si)_2C_8H_6]$ with anhydrous yttrium trichloride in THF followed by the addition of one equivalent of $[K(thf)_n][N(PPh_2)_2]$. The ^{89}Y NMR signal of the complex is split into a triplet, indicating that the phosphorus atoms are chemically equivalent in solution.

Experimental Section

General: All manipulations of air-sensitive materials were performed under 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 glove box. Ether solvents (tetrahydrofuran and diethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy 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 Aldrich (all 99 atom% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on Bruker AC250 or or JNM-LA400 FT-NMR spectrometers. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (^1H and ^{13}C NMR) and 85% phosphoric acid (^{31}P NMR). Mass spectra were recorded at 70 eV on Varian MAT 711. Raman spectra were performed on a Bruker RFS100 instrument. IR spectra were obtained on a Shimadzu FTIR-8400 s spectrometer. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at Karlsruhe. $LnCl_3$,[20] $(Ph_2P)_2NH$,[21] $1,4\text{-}(Me_3Si)_2C_8H_8$,[19] $[SmI(C_8H_8)(thf)_3]$,[22] $[LaI(C_8H_8)(thf)_3]$,[22] and $[K(thf)_n][N(PPh_2)_2]$ (n = 1.25, 1.5)[9] were prepared according to literature procedures.

$[\{(Ph_2P)_2N\}LnCl_2(thf)_3]$ (Ln = Y (2a), Sm (2b), Er (2c), Yb (2d)): THF (20 mL) was condensed at −196 °C onto a mixture of **1** (500 mg, 1.0 mmol) and $LnCl_3$ (1.1 mmol); then the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo and toluene condensed onto the mixture. The mixture was filtered, and the solvent was removed in vacuo. The product was recrystallized from THF/*n*-pentane (1:2).

Compound 2a (Ln = Y): Yield 528 mg (69%), colorless crystals; ^1H NMR ($[D_8]$THF, 250 MHz, 25 °C): $\delta = 1.74\text{–}1.80$ (m, 12H; THF), 3.59–3.64 (m, 12H; THF), 7.06–7.15 (m, 12H; Ph), 7.61–7.68 ppm (m, 8H; Ph); $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 101.3 MHz, 25 °C): $\delta = 39.5$ ppm (d, $^2J(Y,P) = 5.3$ Hz); elemental analysis calcd (%) for $C_{36}H_{44}Cl_2NO_3P_2Y$ (760.47): C 56.86, H 5.83, N 1.84; found: C 56.44, H 5.77, N 1.62.

Compound 2b (Ln = Sm): Yield 440 mg (54%), yellow crystals; ^1H NMR ($[D_8]$THF, 250 MHz, 25 °C): $\delta = 1.72\text{–}1.76$ (m, 12H; THF), 3.57–3.61 (m, 12H; THF), 7.24–7.34 ppm (m, 20H; Ph); $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 101.3 MHz, 25 °C): $\delta = 38.0$ ppm.

Compound 2c (Ln = Er): Yield 467 mg (56%), pink crystals; Raman (solid): $\tilde{\nu} = 3137$ (w, C=C–*H*), 2982 (m, C–H), 1584 (m, C=C), 1026 (m), 998 (s, PC), 616 cm^{-1} (m); IR (KBr): $\tilde{\nu} = 3049$ (w, C=C–*H*), 2967 (m, C–H), 2900 (m), 1583 (w, C=C), 1479 (m), 1432 (s), 1030 (m), 1016 (m), 931 (vs, PC), 747 (s), 719 cm^{-1} (s); elemental analysis calcd (%) for $C_{36}H_{44}Cl_2ErNO_3P_2$ (838.82): C 51.55, H 5.29, N 1.67; found: C 51.23, H 5.02, N 1.39.

Compound 2d (Ln = Yb): Yield 707 mg (84%), red crystals; IR (KBr): $\tilde{\nu} = 3049$ (w, C=C–*H*), 2967 (m, C–H), 2900 (m), 1583 (w, C=C), 1480 (m), 1432 (s), 1016 (m), 1009 (m), 977 (vs, PC), 736 (m), 721 cm^{-1} (m); elemental analysis calcd (%) for $C_{36}H_{44}Cl_2NO_3P_2Yb$ (844.60): C 51.19, H 5.25, N 1.66; found: C 50.74, H 5.31, N 1.51.

$[\{(Ph_2P)_2N\}Ln(\eta^8\text{-}C_8H_8)(thf)_2]$ (Ln = La (3a), Sm (3b))

Route A: THF (20 mL) was condensed at −196 °C onto a mixture of **1** (245 mg, 0.49 mmol) and $LnCl_3$ (0.55 mmol). This mixture was stirred for 18 h at room temperature and filtered. At −78 °C a freshly prepared solution of $K_2C_8H_8$ (0.49 mmol) was added to the filtrate, and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuum, and toluene (10 mL) was condensed onto the mixture. Then, the solution was filtered, and the solvent was removed. The product was recrystallized from THF/*n*-pentane (1:2).

Route B: Toluene (20 mL) was condensed at −196 °C onto a mixture of **1** (250 mg, 0.50 mmol) and $[LnI(\eta^8\text{-}C_8H_8)(thf)_3]$ (0.50 mmol). The mixture was refluxed for 6 h at room temperature and filtered. The product was recrystallized from THF/*n*-pentane (1:2).

Compound 3a (Ln = La, route B): Yield 264 mg (70%), orange crystals; ^1H NMR ($[D_8]$THF, 400 MHz, 25 °C): $\delta = 1.73\text{–}1.78$ (m, 8H; THF), 3.58–3.63 (m, 8H; THF), 6.35 (s, 8H; C_8H_8), 7.06–7.15 (m, 12H; Ph), 7.33–7.41 ppm (m, 8H; Ph); $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 100.4 MHz, 25 °C): $\delta =$ 26.3 (THF), 68.2 (THF), 97.7 (C_8H_8), 128.1 (m, Ph), 132.9 (m, Ph), 145.6 ppm (m, Ph); $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 161.7 MHz, 25 °C): $\delta =$ 42.5 ppm; elemental analysis calcd (%) for $C_{40}H_{44}LaNO_2P_2$ (771.61): C 62.26, H 5.75, N 1.82; found: C 62.03, H 6.11, N 1.48.

Compound 3b (Ln = Sm, routes A and B): Yield 304 mg (78%, *Route B*), dark red crystals; ^1H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 1.42$ (br, 8H; THF), 3.43 (br, 8H; THF), 6.80–7.10 (m, 12H; Ph), 7.66 (br, 8H; Ph), 10.55 ppm (br, 8H; C_8H_8); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): $\delta =$ 26.6 (THF), 72.7 (THF), 82.0 (C_8H_8), 129.0 (m, Ph), 129.1 (m, Ph), 132.8 (Ph), 139.4 ppm (Ph); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz, 25 °C): $\delta =$ 43.0 ppm; EI-MS (70 eV): *m*/*z* (%): 640 (12) $[M-2THF]^+$, 536 (71) $[M-2THF-C_8H_8]^+$, 385 (100) $[C_{24}H_{21}NP_2]^+$, 200 (70) $[C_{12}H_{11}NP]^+$; elemental analysis calcd (%) for $C_{40}H_{44}NO_2P_2Sm$ (783.05): C 61.35, H 5.66, N 1.79; found: C 61.14, H 5.76, N 1.63.

$[\{(Ph_2P)_2N\}Y(\eta^8\text{-}1,4\text{-}(Me_3Si)_2C_8H_6)(thf)_2]$ (4): A solution of *n*BuLi in hexane (1.6 M, 2.50 mL, 4.0 mmol) was slowly added to a stirred solution of $1,4\text{-}(Me_3Si)_2C_8H_8$ (500 mg, 2.0 mmol) in THF (40 mL) at −78 °C. The solution was allowed to warm to room temperature with stirring for another 16 h; during this time the color of the solution changed from yellow to green-brown. The solvent was removed in vacuum and the oily residue was dissolved in pentane (10 mL). The pentane was also removed in vacuum and solid YCl_3 (390 mg, 2 mmol) was added to the remaining residue. Then, THF (10 mL) was condensed at −196 °C onto the mixture, and the suspension was stirred for 2 h at room temperature. The solvent was then evaporated in vacuum and solid **1** (1.00 g, 2 mmol) was added to the remaining solid. Again, THF (10 mL) was condensed at −196 °C onto the mixture, and the suspension was stirred for 18 h at room temperature. The solvent was then evaporated in vacuum, and toluene (10 mL) was condensed onto the mixture. Then, the solution was filtered and the solvent was removed. The remaining solid was washed with pentane (10 mL) and dried in vacuum. Yield: 1.25 g (69%); ^1H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 0.56$ (s, 18H; Me_3Si), 1.02 (br, 8H; THF), 3.20 (br, 8H; THF), 6.77–6.84 (m, 4H; C_8H_6), 6.85 (s, 2H; C_8H_6), 7.04–7.11 (m, 8H; Ph), 7.52–7.60 ppm (m, 12H; Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): $\delta = 2.2$ ($SiMe_3$), 26.1 (THF), 71.0 (THF), 100.0 (C_8H_6), 100.8 (C_8H_6), 101.4 (C_8H_6), 102.0 (C_8H_6), 129.6 (Ph), 132.4 (m, Ph), 133.3 (m, Ph), 144.7 ppm (Ph); ^{29}Si NMR (C_6D_6, 49.7 MHz, 25 °C): $\delta = 4.3$ ppm; $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz, 25 °C): $\delta = 38.1$ ppm (d, $^2J(P,Y) =$ 10.1 Hz); ^{89}Y NMR (C_6D_6, 14.7 MHz, 25 °C): δ ppm 52.3 (t, $^2J(Y,P) =$ 10.1 Hz); elemental analysis calcd (%) for $C_{46}H_{60}NO_2P_2Si_2Y$ (866.01): C 63.80, H 6.98, N 1.62; found C 63.39, H 6.81, N 1.44.

X-ray crystallographic studies of 2a–d, 3a, and 3b: Crystals of **2a–d**, **3a** and **3b** were grown from THF/*n*-pentane (1:2). A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS or a Brucker Smart 1000 CCD diffractometer. Subsequent computations were carried out on a Intel Pentium III PC.

All structures were solved by the Patterson method (SHELXS-97[23]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o-F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[24] In the final cycles of each refinement, all non-hydrogen atoms, except C1–C8, in **3b** 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 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, and bond lengths and angles have been deposited as supporting information. CCDC-224746–2247751 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Compound 2a: $C_{36}H_{44}Cl_2NO_3P_2Y$, monoclinic, $P2_1/c$ (No. 14), lattice constants $a = 1204.72(6)$, $b = 1555.36(13)$, $c = 1958.54(11)$ pm, $\beta = 103.821(6)°$, $V = 3563.6(4) \times 10^6$ pm^3, $Z = 4$, $\mu(Ag_{K\alpha}) = 1.039$ mm^{-1}, $\theta_{max} = 23.12$; 8420 [$R_{int} = 0.1814$] independent reflections measured, of which 4176 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.885 and -0.962 e A^{-3}, 406 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0796, w$R2$ (all data) = 0.1930.

Compound 2b: $C_{36}H_{44}Cl_2NO_3P_2Sm$, monoclinic, $P2_1/c$ (No. 14), lattice constants $a = 1206.0(3)$, $b = 1563.3(3)$, $c = 1961.5(4)$ pm, $\beta = 104.201(5)°$, $V = 3585.1(14) \times 10^6$ pm^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 1.912$ mm^{-1}, $\theta_{max} = 30.52$; 10918 [$R_{int} = 0.0236$] independent reflections measured, of which 9815 were considered observed with $I > 2\sigma(I)$; max residual electron density 2.091 and -0.966 e A^{-3}, 788 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0231, w$R2$ (all data) = 0.0586.

Compound 2c: $C_{36}H_{44}Cl_2ErNO_3P_2$, monoclinic, $P2_1/c$ (No. 14), lattice constants $a = 1212.3(2)$, $b = 1556.4(3)$, $c = 1968.8(4)$ pm, $\beta = 103.99(3)$, $V = 3604.8(12) \times 10^6$ pm^3, $Z = 4$, $\mu(Ag_{K\alpha}) = 1.393$ mm^{-1}, $\theta_{max} = 22.30$; 8646 [$R_{int} = 0.1565$] independent reflections measured, of which 5627 were considered observed with $I > 2\sigma(I)$; max residual electron density 2.695 and -4.132 e A^{-3}, 406 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0745, w$R2$ (all data) = 0.2075.

Compound 2d: $C_{36}H_{44}Cl_2NO_3P_2Yb$, monoclinic, $P2_1/c$ (No. 14), lattice constants $a = 1207.42(8)$, $b = 1554.16(7)$, $c = 1962.81(14)$ pm, $\beta = 103.541(8)°$, $V = 3580.9(4) \times 10^6$ pm^3, $Z = 4$, $\mu(Ag_{K\alpha}) = 1.548$ mm^{-1}, $\theta_{max} = 22.36$; 9181 [$R_{int} = 0.0390$] independent reflections measured, of which 7302 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.947 and -0.791 e A^{-3}, 406 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0285, w$R2$ (all data) = 0.0693.

Compound 3a: $C_{40}H_{44}LaNO_2P_2$, orthorhombic, $P2_12_12_1$ (No. 19), lattice constants $a = 1055.22(5)$, $b = 1124.32(7)$, $c = 3040.46(14)$ pm, $V = 3607.2(3) \times 10^6$ pm^3, $Z = 4$, $\mu(Ag_{K\alpha}) = 0.696$ mm^{-1}, $\theta_{max} = 24.00$; 9510 [$R_{int} = 0.0349$] independent reflections measured, of which 8790 were considered observed with $I > 2\sigma(I)$; max residual electron density 0.814 and -0.474 e A^{-3}, 415 parameters, Flack parameter $-0.04(2)$, $R1$ [$I > 2\sigma(I)$] = 0.0305, w$R2$ (all data) = 0.0775.

Compound 3b: $C_{40}H_{44}NO_2P_2Sm$, orthorhombic, $P2_12_12_1$ (No. 19), lattice constants $a = 1052.02(7)$, $b = 1119.34(7)$, $c = 3015.6(3)$ pm, $V = 3551.1(5) \times 10^6$ pm^3, $Z = 4$, $\mu(Ag_{K\alpha}) = 0.954$ mm^{-1}, $\theta_{max} = 20.77$; 5570 [$R_{int} = 0.0500$] independent reflections measured, of which 5274 were considered observed with $I > 2\sigma(I)$; max residual electron density 1.080 and -1.100 e A^{-3}, 407 parameters, Flack parameter $-0.02(2)$, $R1$ [$I > 2\sigma(I)$] = 0.0346, w$R2$ (all data) = 0.0993.

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