Homoleptic Lanthanide Complexes of Chelating Bis(phosphanyl)amides: Synthesis, Structure, and Ring-Opening Polymerization of Lactones

Peter W. Roesky,*[a] Michael T. Gamer,[a] Mario Puchner,[b] and Andreas Greiner*[b]

Abstract: Treatment of the bis(phosphanyl)amide $(Ph_2P)_2NH$ with KH in boiling THF followed by crystallization from THF/*n*-pentane leads to $[K(thf)_n][N(PPh_2)_2]$ ($n = 1.25$, 1.5). Reaction of $[K(thf)_n][N(PPh_2)_2]$ with anhydrous yttrium or lanthanide trichlorides in a 3:1 molar ratio afforded homoleptic bis(phosphanyl)amide complexes $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, Er) as large crystals in good yields. $[Ln\{N(PPh_2)_2\}_3]$ can also be obtained by reaction of the homoleptic bis(trimethylsilyl)amides of Group 3 metals and lanthanides $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = Y, La, Nd) with three equivalents of $(Ph_2P)_2NH$ in boiling toluene. The single-crystal X-ray structures of these complexes always show η^2 coordination of the ligand. Dynamic behavior of the ligand is observed in solution and is caused by rapid exchange of the two different phosphorus atoms. $[Ln\{N(PPh_2)_2\}_3]$ was 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. On the basis of the crystal structure of the heteroleptic complex $[Lu\{N(PPh_2)_2\}_3(thf)]$, we suggest that in the initiation step of ε-caprolactone polymerization the lactone adds to the lanthanide atom to form a sevenfold coordination sphere around the central atom.

Keywords: chelates • lanthanides • lactones • N,P ligands • ring-opening polymerization

Introduction

Recently there has been a significant research effort in d- and f-block transition metal chemistry to substitute the well-established cyclopentadienyl ligand[1] by anionic nitrogen-based ligands.[2] In lanthanide chemistry one approach is the use of inorganic amides. In particular, P,N systems such as phosphinimides R_2PNR',[3] phosphoraneiminates R_3PN,[4] phosphiniminomethanides $(RNPR'_2)_2CH$,[5] phosphiniminomethanediides $(RNPR'_2)_2C$[6] and diiminophoshinates $R_2P(NR')_2$[7] were used as ligands. These studies showed that some lanthanide complexes having a P,N ligand in the coordination sphere[4] may not only exhibit unusual coordination modes, but also can be used as catalysts for ε-caprolactone polymerization.[8] Formerly, cyclic esters such as ε-caprolactone and δ-valerolactone could only be polymerized by lanthanide compounds such as cyclopentadienyl[9] and alkoxide complexes.[10] Today lanthanide amides are used successfully as catalysts for lactone polymerization and the formation of block copolymers.[11]

We recently showed that reaction of $[Li(Et_2O)(Ph_2PNPh)]_2$ with anhydrous yttrium, ytterbium, and lutetium trichloride always gives ate complexes $[Li(thf)_4][Ln(Ph_2PNPh)_4]$ (Ln = Y, Yb, Lu; Eq. (1)).[3a] Even with an excess of lanthanide trichloride, no other products were observed. The anions $[(Ph_2PNPh)_4Ln]^-$ were the first complexes of Group 3 metals and lanthanides having four η^2-coordinated ligands, which are arranged in a somewhat distorted fashion around the metal atom. These results drew our attention to the bis(phosphanyl)amide $(Ph_2P)_2N^-$ as a potential precursor to stable lanthanide complexes. We expected this ligand to have a greater steric demand than the monophosphanylamide $\{Ph_2PNPh\}^-$ and thus lead to neutral, homoleptic lanthanide complexes. The Ph_2P moieties may allow $\{(Ph_2P)_2N\}^-$ to act as dangling ligand in a catalytic transformation. As a weak Lewis base, phosphorus forms only weak Lewis acid–base adducts with the lanthanides and thus can easily be replaced by a hard donor atom such as oxygen.

Here we report the synthesis of potassium bis(diphenylphosphanyl)amide and its reactions with yttrium and lanthanide halides to give a series of homoleptic bis(phosphanyl)-

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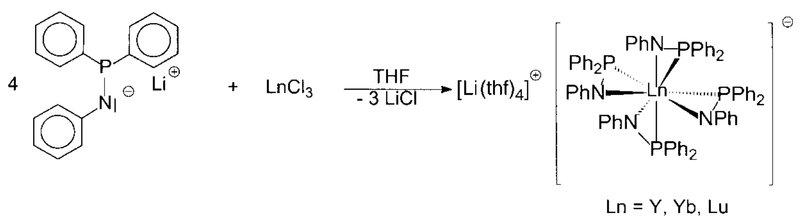

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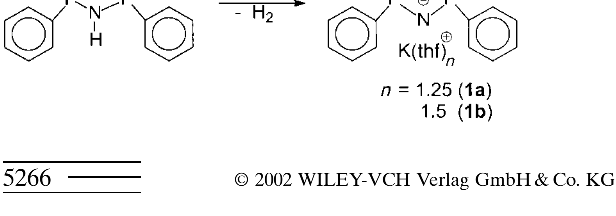
amide complexes $[Ln\{N(PPh_2)_2\}_3]$. Moreover, the same complexes were also obtained from reaction of the neutral ligand $(Ph_2P)_2NH$ with the homoleptic bis(trimethylsilyl)amides $[Ln\{N(SiMe_3)_2\}_3]$. The utility of the bis(phosphanyl)amide ligand in the design of new catalysts for ring-opening polymerization of lactones was assessed.

Results and Discussion

The ligand: The neutral disphosphane ligand $(Ph_2P)_2NH$[12] is well known in late transition metal chemistry for assembling metal atoms in bi- and polynuclear metal complexes.[13] Alkali metal derivatives were obtained by deprotonation of $(Ph_2P)_2NH$ with *n*BuLi, NaH, and *t*BuOK to give $[Li(thf)N(PPh_2)_2]_2$,[14] $[Na(pmdta)N(PPh_2)_2]$,[15] $[K(pmdta)N(PPh_2)_2]$,[16] respectively (PMDTA = pentamethyldiethylenetriamine). The lithium salt was used for further reactions such as the synthesis of the titanium complex $[TiCl_2\{N(PPh_2)_2\}_2]$.[17]

To avoid the well-known problems[18] of incorperation of lithium chloride and undesired coligands such as PMDTA into the coordination sphere of the lanthanide metal, we were initially interested in the synthesis of potassium bis(diphenylphosphanyl)amide in the absence of PMDTA. Treatment of $(Ph_2P)_2NH$ with KH in boiling THF followed by crystallization from THF/*n*-pentane (1/2) led to the desired reagent $[K(thf)_n][N(PPh_2)_2]$ ($n = 1.25$ (**1a**), 1.5 (**1b**)) in high yield [Eq. (2)]. Under these conditions **1a** and **1b** co-crystallize as white blocks (**1a**) and white needles (**1b**).



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The structures of **1a** and **1b** were confirmed by single-crystal X-ray diffraction (Figure 1). Compound **1a** crystallizes in the space group $C2/c$, and **1b** in $P2_1/c$. The compounds both consist of infinite chains but differ in the coordination of the potassium atoms (Scheme 1). Compound **1b** has a uniform arrangement in which all potassium atoms are fourfold coordinated by one THF molecule, the N atom of one $\{(Ph_2P)_2N\}^-$ ligand and the P atoms of another $\{(Ph_2P)_2N\}^-$ unit. In **1a** every other K atom has the same coordination sphere. One group of K atoms is only coordinated by the nitrogen atoms of two neighboring $\{(Ph_2P)_2N\}^-$ ligands. Furthermore, some π coordination of the phenyl rings is observed. In contrast the other group of K atoms is sixfold coordinated by four P atoms of two $\{(Ph_2P)_2N\}^-$ ligands and two molecules of THF. In contrast to $[K(pmdta)N(PPh_2)_2]$,[16] in which the K atom is only coordinated by N atoms, in **1a** and **1b** coordination of all P atoms is observed. The bond lengths in **1a** and **1b** are in the expected range (av P−K 340.7(1) (**1a**), 342.8(2) (**1b**); av N−K 275.15(2) (**1a**), 274.9(5) pm (**1b**)). Due to the η^2 coordination of only one phenyl ring of each $\{(Ph_2P)_2N\}^-$ unit to K2 in **1a**, asymmetric coordination of the ligands to K2 but not to K1 is observed. Therefore, the angle P4-N2-K1 (111.71(11)°) is significantly smaller than the corresponding angle P3-N2-K1 (132.58(13)°). In compound **1b** η^2-coordination of several phenyl rings to K1 and K2 is observed and results in asymmetric coordination of the ligands around the potassium atoms. The N-P-K angles differ by up to 7° (e.g., N2-P3-K1 101.62(12), N2-P4-K1 94.47(12)°).

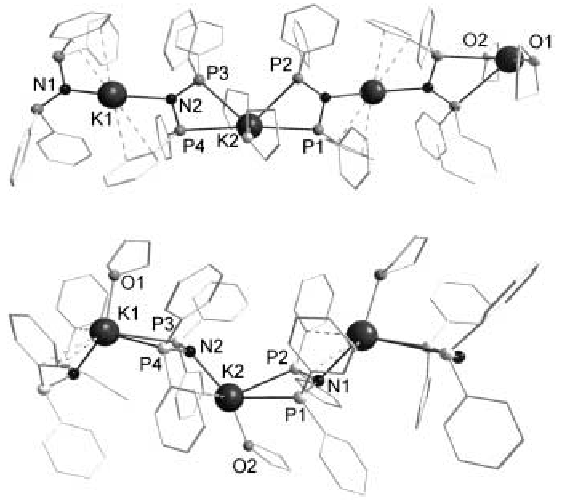
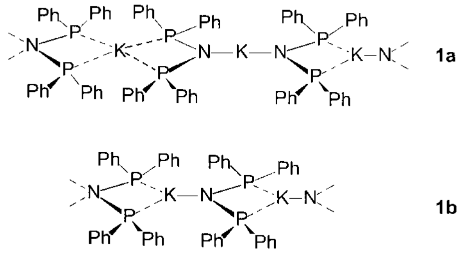


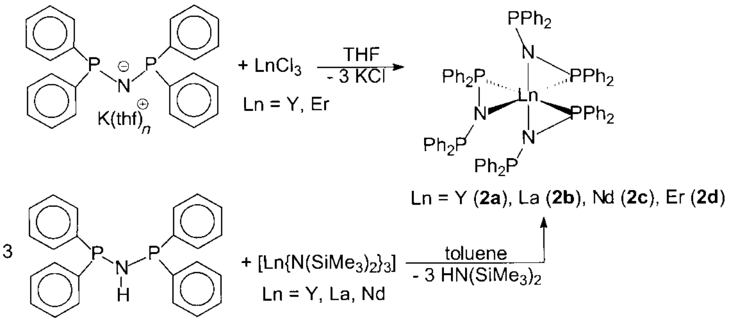
Figure 1. Solid-state structures of **1a** (top) and **1b** (bottom) (hydrogen atoms omitted for clarity). One unit out of an infinite chain is shown. Selected bond lengths [pm] and angles [°]: **1a**: N1−K1 275.5(2), N2−K1 274.8(2), O1−K2 286.9(3), O2−K2 273.4(4), P1−K2 341.35(10), P2−K2 340.23(11), P3−K2 339.41(10), P4−K2 342.04(10); P1-N1-P2 112.57(14), P3-N2-P4 111.82(14); P1-N1-K1 109.02(11), P2-N1-K1 134.86(12), P3-N2-K1 132.58(13), P4-N2-K1 111.71(11), N1-P1-K2 99.48(9), N1-P2-K2 99.95(9), N2-P3-K2 100.87(9), N2-P4-K2 99.70(9). **1b**: N1−K1 276.4(4), N2−K2 273.3(3), O1−K1 265.1(4), O2−K2 268.8(4), P1−K2 348.2(2), P2−K2 338.2(2), P3−K1 332.7(2), P4−K1 352.0(2); P1-N1-P2 113.98(19), P3-N2-P4 115.1(2), N1-P1-K2 96.45(12), N1-P2-K2 100.39(11), N2-P3-K1 101.62(12), N2-P4-K1 94.47(12).



Scheme 1. Schematic view of the different coordination modes of the $\{(Ph_2P)_2N\}^-$ ligand around the potassium atoms. THF molecules and π interactions are omitted for clarity.

As expected, in solution **1a** and **1b** form the same species, which is further referred to as compound **1**. The ^{1}H and ^{13}C{^{1}H} NMR spectra show only uncharacteristic signals in the phenyl region. In contrast, one sharp signal ($\delta = 58.6$) is observed in the ^{31}P{^{1}H} NMR spectrum.

Metal complexes: Reaction of **1** with anhydrous yttrium or lanthanide trichlorides in a 3:1 molar ratio in THF followed by crystallization from hot toluene afforded homoleptic bis(phosphanyl)amide complexes [Ln{N(PPh$_2$)$_2$}$_3$] (**2**; Ln = Y, Er) as large crystals in good yields (Scheme 2). Complexes **2** can also be obtained by reaction of the homoleptic bis(trimethylsilyl)amides of Group 3 metals and lanthanides [Ln{N(SiMe$_3$)$_2$}$_3$][19] (Ln = Y, La, Nd) with three equivalents of (Ph$_2$P)$_2$NH in boiling toluene (Scheme 2). The new complexes were 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.

Due to the similar ionic radii of the lanthanides, **2a–d** are isostructural. As a representative example, the structure of **2a** is shown in Figure 2. Compounds **2a–d** crystallize in the trigonal space group $P\bar{1}$ with two molecules of **2** and two molecules of toluene in the unit cell. Three symmetrically chelating (η^2) (Ph$_2$P)$_2$N$^-$ ligands are coordinated to the lanthanide atom, and the six-coordinate LnN$_3$P$_3$ geometry is close to trigonal-prismatic. The three P atoms which are bound to the lanthanide atom are located on one triangular plane of the trigonal prism, and the N atoms on the opposite plane. As expected, the Ln−N and Ln−P distances increase with increasing ionic radius of the central metal atom in the series **2a–d** (av Ln−N 227.4(3) (**2a**), 242.4(4) (**2b**), 236.5(2) (**2c**), 225.7(2) pm (**2d**); av Ln−P 278.3(3) (**2a**), 295.1(2) (**2b**), 288.0(9) (**2c**), 276.2(8) pm (**2d**)). The Ln−N and L−P bond lengths are in the expected ranges.[20, 21] In contrast to the [(Ph$_2$PNPh)$_4$Ln]$^-$ ions,[3] in which the Ln−P distances differ by about 15 pm, the Ln−P bond lengths of **2a–d** lie in a narrow range. The N-Ln-P bite angles (av 37.0(8) (**2a**), 34.27(12) (**2b**), 35.55(7) (**2c**), 37.3(7)° (**2d**)) are rather small.

Whereas one of the P atoms of each ligand binds to the lanthanide atom, the other is bent away. The average P-N-P angles within the ligand are 120.0(2) (**2a**), 122.6(3) (**2b**), 121.9(2) (**2c**), and 119.9 (2)° (**2d**). Within the ligand the P−N distance varies significantly. The P atom bound to the lanthanide atom is always closer to the N atom. The arrangement of the (Ph$_2$P)$_2$N$^-$ ligand around the lanthanide atoms differs from that of the isoelectronic phosphanylmethanide ligand (R$_2$P)$_2$CH$^-$, which was pioneered by Karsch et al.[21] This ligand always exhibits heteroallylic η^3 coordination. Depending on the nature of the substituents homoleptic complexes of this ligand are monomeric (e.g., [La{CH(PPh$_2$)$_2$}$_3$])[21a] or dimeric (e.g., [μ-η^3-{CH(PPh$_2$)$_2$}$_2$-(Sm{CH(PPh$_2$)$_2$}$_2$)]).[21c]

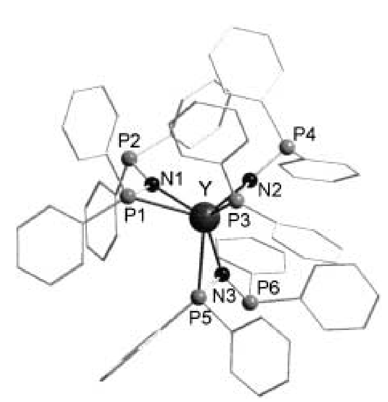


Figure 2. Solid-state structure of **2a** (hydrogen atoms omitted for clarity). Selected bond lengths [pm] and angles [°] (also given for isostructural **2b–d**): **2a:** N1−P1 167.7(3), N1−P2 171.2(3), N2−P3 167.2(3), N2−P4 171.3(3), N3−P5 167.9(3), N3−P 171.9(3), N1−Y 227.7(4), N2−Y 226.0(3), N3−Y 228.6(3), P1−Y 278.2(4), P3−Y 278.1(2), P5−Y 278.7(3); P1-N1-P2 120.1(2), P3-N2-P4 123.5(2), P5-N3-P6 116.4(2), P1-N1-Y 88.1(2), P2-N1-Y 151.8(2), P3-N2-Y 88.7(2), P4-N2-Y 147.7(2), P5-N3-Y 87.9(2), P6-N3-Y 154.1(2), N1-Y-P1 37.06(8), N2-Y-P3 36.93(8), N3-Y-P5 37.01(9). **2b:** N1−P1 165.9(5), N1−P2 170.9(5), N2−P3 165.6(5), N2−P4 170.7(5), N3−P5 166.9(5), N3−P6 170.6(5), N1−La 241.9(5), N2−La 240.9(4), N3−La 244.5(4), P1−La 295.6(2), P3−La 294.94(15), P5−La 294.65(15); P1-N1-P2 122.6(3), P3-N2-P4 125.8(3), P5-N3-P6 119.5(3), P1-N1-La 90.9(2), P2-N1-La 146.3(3), P3-N2-La 91.1(2), P4-N2-La 143.0(3), P5-N3-La 89.4(2), P6-N3-La 149.0(3), N1-La-P1 34.15(12), N2-La-P3 34.15(12), N3-La-P5 34.51(12). **2c:** N1−P1 168.0(3), N1−P2 171.1(3), N2−P3 166.6(3), N2−P4 171.0(3), N3−P5 167.8(3), N3−P6 171.7(3), N1−Nd 236.3(3), N2−Nd 235.3(3), N3−Nd 238.0(3), P1−Nd 288.03(10), P3−Nd 288.52(9), P5−Nd 287.44(9); P1-N1-P2 121.6(2), P3-N2-P4 125.7(2), P5-N3-P6 118.5(2), P1-N1-Nd 89.22(11), P2-N1-Nd 148.99(15), P3-N2-Nd 90.08(11), P4-N2-Nd 144.16(15), P5-N3-Nd 88.42(11), P6-N3-Nd 151.23(15), N1-Nd-P1 35.67(7), N2-Nd-P3 35.28(7), N3-Nd-P5 35.70(7). **2d:** N1−P1 167.9(3), N1−P2 171.1(3), N2−P3 166.5(3), N2−P4 171.2(3), N3−P5 167.9(3), N3−P6 172.0(3), N1−Er 225.5(3), N2−Er 224.8(2), N3−Er 226.8(2), P1−Er 276.31(9), P3−Er 276.43(8), P5−Er 275.83(8); P1-N1-P2 119.8(2), P3-N2-P4 123.49(15), P5-N3-P6 116.35(15), P1-N1-Er 87.95(11), P2-N1-Er 152.16(15), P3-N2-Er 88.57(11), P4-N2-Er 147.84(15), P5-N3-Er 87.32(10), P6-N3-Er 154.74(15), N1-Er-P1 37.40(6), N2-Er-P3 37.03(7), N3-Er-P5 37.46(7).

The NMR spectra of the diamagnetic compounds **2a** and **2b** and the paramagnetic neodymium complex **2c** were investigated. The ^{1}H and ^{13}C{^{1}H} NMR spectra of these compounds are not very characteristic. The ^{1}H NMR spectra of **2a,b** show broad signals in the range of $\delta = 6.94-7.40$ ppm (**2a**) and $\delta = 6.93-7.28$ ppm (**2b**). Due to the paramagnetic metal center in **2c** these signals are observed in the broader range of $\delta = 6.60-9.13$ ppm. The ^{31}P{^{1}H} NMR spectra are more characteristic. At room temperature complexes **2a–c** each show one sharp signal in the ^{31}P{^{1}H} NMR spectrum ($\delta = 42.0$ (**2a**), 44.6 (**2b**), 44.6 ppm (**2c**)) shifted upfield relative to **1** ($\delta = 58.6$ ppm), that is, the phosphorus atoms are chemically equivalent in solution. Furthermore, in the ^{31}P{^{1}H} NMR spectrum of **2a** a ^2J(P,Y) coupling constant of 6.9 Hz is observed.

Since the solid-state structures of **2a**–**d** show two non-equivalent P atoms for each ligand, dynamic behavior in solution is expected. Therefore, variable-temperature $^{31}P\{^1H\}$ NMR spectra of **2b** were recorded (Figure 3). In accordance with the solid-state structure, at low temperature (173 K) two sets of signals for the P atoms are observed. Due to the low solubility of **2a** at these temperatures, only broad signals without hyperfine structure were observed. These signals start to coalesce on warming, with a coalescence temperature of $T_c \approx 200$ K. Above 233 K the signals appear as a sharp singlet. From the coalescence temperature ($T_c = 200$ K) and the separation ($\Delta\nu = 2295.2\ s^{-1}$, 101.25 MHz NMR) of the two coalescing signals, the free energy for the exchange of the two P atoms was calculated to be $\Delta G^{\ddagger}_{T_c} = 34.04\ kJ\,mol^{-1}$.[22]

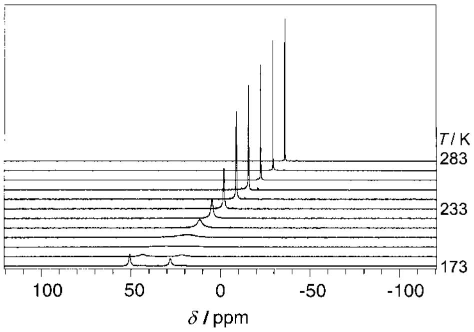


Figure 3. Variable-temperature ^{31}P NMR spectra of **2b**. $T_c = 200$ K, $\Delta\nu = 2295.2\ s^{-1}$, 101.25 MHz NMR, $\Delta G^{\ddagger}_{T_c} = 34.04\ kJ\,mol^{-1}$.

Catalysis: The efficacy of the homoleptic complexes **2** as precatalysts for polymerization reactions was assayed with ε-caprolactone (CL). Complexes **2a**–**d** showed high activity in the polymerization of CL at room temperature. Molar monomer/initiator ratios of 150/1 afforded corresponding polycaprolactone (PCL) with excellent yields (95–99%) within 1 min. The obtained molecular weights ($M_n = 17200$–26200) were slightly higher than the theoretical molecular weights (based on molar monomer/initiator ratio and monomer conversion; Table 1). Moderate M_w/M_n (1.58–1.83) was observed with catalysts **2a**, **b**, **d**, but a narrow distribution with catalyst **2c** (1.12). No significant correlation was found for molecular weight and polydispersity with the size of the metal atoms of catalysts **2**.

To better understand the initiation step of the catalytic cycle we tried to crystallize **2a**–**d** in the presence of various oxygen-donor solvents, which are comparable to CL. We were interested to see if one of the Ln–P bonds is broken in the presence of these solvents. We only obtained crystals when lutetium was used as the central metal. Similar to the preparation of **2a**–**d**, the heteroleptic bis(phosphanyl)amide complex $[Lu\{N(PPh_2)_2\}_3(thf)]$ (**3**) can be obtained by treating **1** with anhydrous lutetium trichloride in a 3:1 molar ratio in THF followed by crystallization from THF/*n*-pentane. Attempts to obtain a homolepetic lutetium complex by crystallizing the reaction product from toluene failed. The new complex **3** was characterized by standard analytical/spectroscopic techniques. The data are comparable to those of **2a**–**d**. The solid-state structure of **3** was established by single-crystal X-ray diffraction (Figure 4). Compound **3** crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell. The structure reveals a sevenfold coordination sphere around the Lu atom. Six coordination sites are occupied by three chelating $(Ph_2P)_2N^-$ ligands, and the other by THF. The $(Ph_2P)_2N^-$ ligand geometry of **3** is comparable to those of **2a**–**d**. The Lu–N and Lu–P bond lengths are in the expected ranges (av Lu–N 227.9(6), av Lu–P 275.8(2) pm), and the average N-Lu-P bite angle is 37.38(13)°. The average O-Lu-N angle is 93.1(2)°.

Table 1. Polymerization of CL with **2**.

Initiator	Yield [%]	M_n	M_w/M_n	M_n[a]
2a	99	26200	1.58	16900
2b	99	21600	1.83	16900
2c	95	17200	1.12	16300
2d	99	20700	1.61	16900

[a] Theoretical molecular weight based on monomer/initiator molar ratio and monomer conversion.

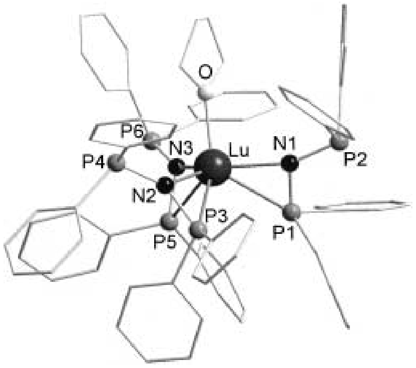


Figure 4. Solid-state structure of **3** showing the atom labeling scheme and omitting hydrogen atoms. Selected bond lengths [pm] and angles [°]: N1–P1 168.4(5), N1–P2 172.0(6), N2–P3 168.3(5), N2–P4 169.9(5), N3–P5 167.9(5), N3–P6 171.5(6), N1–Lu 229.5(6), N2–Lu 227.2(5), N3–Lu 227.0(6), P1–Lu 277.9(2), P3–Lu 273.8(2), P5–Lu 275.7(2), O–Lu 228.3(5); P1-N1-P2 118.9(3), P3-N2-P4 139.8(3), P5-N3-P6 118.7(4), P1-N1-Lu 87.2(2), P2-N1-Lu 153.0(3), P3-N2-Lu 86.3(2), P4-N2-Lu 133.8(3), P5-N3-Lu 87.2(2), P6-N3-Lu 153.5(3), N1-Lu-P1 37.24(13), N3-Lu-P5 37.46(13), N2-Lu-P3 37.84(13), N1-Lu-O1 91.8(2), N2-Lu-O1 94.6(2), N3-Lu-O1 93.0(2).

Both **2a**–**d** and **3** were prepared by the same reaction pathway in THF. The only difference is the method of recrystallization. Single crystals of **2a**–**d** were obtained from toluene, whereas crystals of **3** were grown from THF/*n*-pentane. From these results we suggest that the $(Ph_2P)_2N^-$ ligand shows a certain flexibility in its coordination behavior. In the absence of a suitable donor ligand three equivalents of the $\{(Ph_2P)_2N\}^-$ ligand are sufficient to shield large metal atoms such as lanthanum, but in the presence of a donor ligand a heteroleptic complex can be formed even with the smallest lanthanide (Lu). Therefore, we suggest, that from the steric point of view, in the initiation step of CL polymerization the lactone adds to the lanthanide atom to form a sevenfold coordination sphere around the central atom. Thus, no Ln–P bond is broken at that time. We anticipate that initially CL coordinates to the metal atom through the carbonyl group.

Conclusion

A series of homoleptic complexes and one heteroleptic lanthanide complex of the $\{(Ph_2P)_2N\}^-$ ligand were reported. These are the first lanthanide complexes of this ligand. The single-crystal X-ray structures of these complexes always show η^2 coordination of the ligand. This is in contrast to the isoelectronic phosphinomethanide ligand, which always undergoes heteroallylic η^3 coordination. In solution dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorus atoms. The homoleptic complexes **2a–d** are catalysts for the polymerization of CL. Remarkably narrow polydispersity was observed with catalyst **2c**, as well as good agreement of theoretical and experimental molecular weights, and this justifies further investigations on **2c** as a catalyst for ring-opening polymerization of lactones. On the basis of the crystal structure of **3** we suggest that in the initiation step of ε-caprolactone polymerization the lactone adds to the lanthanide atom by forming a seven-coordinate complex.

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 glove box. Tetrahydrofuran and diethyl ether were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. 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 Inc. (all 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks.

NMR spectra were recorded on a Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane or 85% phosphoric acid (^{31}P NMR). Mass spectra were recorded at 70 eV on a Varian MAT 711. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at Karlsruhe. $LnCl_3$,[23] $(Ph_2P)_2NH$,[24] and $[Ln\{N(SiMe_3)_2\}_3]$[25] were prepared according to literature procedures.

CL (Acros) was dried over calcium hydride for six days, distilled under reduced pressure, stored over 4 Å molecular sieves for one day, distilled under reduced pressure, and degassed before use.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC). A Knauer GPC apparatus equipped with two 10 μm polymer mixed gel columns (600 × 8 mm, PSS) and a Knauer differential refractometer/viscometer K200 was used. Molecular weights were corrected by universal calibration relative to polystyrene standards. Polymers were dissolved in THF, and elution was performed at a flow rate of 0.63 mL min^{-1}.

[K(thf)$_n$][N(PPh$_2$)$_2$] (*n* = 1.25 (1a), 1.5 (1b)): THF (50 mL) was added to a mixture of KH (0.60 g, 15.0 mmol) and $(Ph_2P)_2NH$ (3.85 g, 10 mmol) at 0 °C. The yellow mixture was then stirred for 18 h at room temperature The remaining KH was then filtered off, and the solvent evaporated in vacuo. The remaining solid was washed with *n*-pentane (25 mL) and dried in vacuo. Finally, the product was crystallized from THF/*n*-pentane (1/2). **1a** and **1b** cocrystallize as white blocks (**1a**) and needles (**1b**). Yield 5.1 g. ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 1.76$ (m; THF), 3.60 (m; THF), 6.93–7.00 (m, 4H; PhP), 7.04–7.29 (m, 8H; PhP), 7.57–7.61 ppm (m, 8H; PhP); ^{13}C{^{1}H} NMR ([D$_8$]THF, 62.9 MHz, 25 °C): $\delta = 126.0$, 127.4, 131.3 (t, ^3J(C,P) = 9.5 Hz), 154.5 ppm; ^{31}P{^{1}H} NMR ([D$_8$]THF, 101.3 MHz, 25 °C): $\delta = 58.6$ ppm.

[Ln{N(PPh$_2$)$_2$}$_3$] (Ln = Y (2a), La (2b), Nd (2c), Er (2d)): Route A: THF (20 mL) was condensed at −196 °C onto a mixture of **1** (750 mg, 1.5 mmol) and $LnCl_3$ (0.5 mmol), and the mixture was stirred for 24 h at room temperature. The solvent was then evaporated in vacuo, and toluene condensed onto the mixture. The mixture was filtered, and the solvent removed in vacuo. The product was recrystallized from toluene.

Route B: Toluene (20 mL) was condensed at −196 °C onto a mixture of $[Ln\{N(SiMe_3)_2\}_3]$ (0.5 mmol) and $(Ph_2P)_2NH$ (650 mg, 1.5 mmol). The mixture was refluxed for 6 h, filtered, and the solvent removed in vacuo. The product was recrystallized from toluene.

2a (routes A and B): Yield 460 mg (74%); ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 6.94$–7.40 ppm (m, 60H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 62.9 MHz, 25 °C): $\delta = 128.4$ (m), 128.8–129.7 (m), 132.4 (d, J(C,P) = 20.5 Hz), 144.0 ppm (dd, J(C,P) = 11.2 Hz); ^{31}P{^{1}H} NMR ([D$_8$]THF, 101.3 MHz, 25 °C): $\delta = 42.0$ ppm (d, ^2J(P,Y) = 6.9 Hz); elemental analysis (%) calcd for $C_{72}H_{60}N_3P_6Y$ (1242.04): C 69.63, H 4.87, N 3.38; found: C 69.80, H 4.94, N 3.25.

2b (route B): Yield 530 mg (77%); ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 6.93$–7.28 ppm (m, 60H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 62.9 MHz, 25 °C): $\delta = 128.4$, 128.8–129.6 (m), 133.2 (m), 144.4 ppm (br, J(C,P) = 11.2 Hz); ^{31}P{^{1}H} NMR ([D$_8$]THF, 101.3 MHz, 25 °C): $\delta = 44.6$ ppm; elemental analysis (%) calcd for $C_{72}H_{60}N_3P_6La$ (1384.18): C 68.55, H 4.95, N 3.04; found: C 68.67, H 5.15, N 3.01.

2c (route B): Yield 450 mg (65%); ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 6.60$–6.66 (m, 8H), 6.96–7.37 (m, 36H), 9.13 ppm (br, 16H); ^{31}P{^{1}H} NMR ([D$_8$]THF, 101.3 MHz, 25 °C): $\delta = 44.6$ ppm; elemental analysis (%) calcd for $C_{79}H_{68}NNd_3P_6$ (**2c** · toluene, 1389.51): C 68.29, H 4.93, N 3.02; found: C 68.36, H 5.10, N 3.01.

2d (route A): Yield 420 mg (64%); elemental analysis (%) calcd for $C_{79}H_{68}ErN_3P_6$ (**2d** · toluene, 1412.53): C 67.18, H 4.85, N 2.97; found: C 67.92, H 5.01, N 2.98.

[Lu{N(PPh$_2$)$_2$}$_3$(thf)] (3): THF (20 mL) was condensed at −196 °C onto a mixture of **1** (750 mg, 1.5 mmol) and $LuCl_3$ (140 mg, 0.5 mmol), and the mixture stirred for 24 h at room temperature. The solvent was then evaporated in vacuo, and toluene condensed onto the mixture. The mixture was filtered, and the solvent removed in vacuo. The product was recrystallized from toluene. A microcrystalline material was obtained. Single crystals were grown from THF/*n*-pentane (1/2). Yield 350 mg (48%); ^{1}H NMR ([D$_8$]THF, 250 MHz, 25 °C): $\delta = 1.74$–1.80 (m, 4H, THF), 3.60–3.66 (m, 4H, THF), 6.96–7.35 ppm (m, 60H); ^{13}C{^{1}H} NMR ([D$_8$]THF, 62.9 MHz, 25 °C): $\delta = 26.3$ (THF), 68.2 (THF), 128.1 (m), 128.4 (m), 132.5 (m), 143.8 ppm (m); ^{31}P{^{1}H} NMR ([D$_8$]THF, 101.3 MHz, 25 °C): $\delta = 43.8$ ppm; elemental analysis (%) calcd for $C_{76}H_{68}LuN_3OP_6$ (**3** · 0.5 toluene, 1446.19): C 66.02, H 5.02, N 2.91; found C 59.88, H 4.98, N 2.76.

X-ray crystallographic studies on 1a,b, 2a–d, and 3: Crystals of **2a–d** were grown from hot toluene. Crystals of **1a,b** and **3** were obtained 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 N_2 stream of a Stoe IPDS or a Stoe STADI 4 diffractometer. Subsequent computations were carried out on an Intel Pentium III PC.

All structures were solved by the Patterson method (SHELXS-97[26]). The remaining non-hydrogen atoms were located from successive difference Fourier maps. 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 $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, by using the program SHELXL-97.[27] In the final cycles of each refinement, all non-hydrogen atoms except C53–C58 and O3 in **1a**, C49–C60 and O3 in **1b**, C79 in **2a,b** and **2d**, as well as C9–C11, C15–C17, C21–C23, C27–C29, C33–C35, C39–C41, C45–C47, C51–C53, C57–C59, C63–C65, C69–C71, and C77–C80 in **3** were assigned anisotropic temperature factors. The positions of carbon-bound hydrogen atoms were calculated and allowed to ride on the carbon atom to which they were bonded with 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 and the magnitude of the residual electron densities were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited CCDC-186707–186713 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).

1a: $C_{116}H_{120}K_4N_4O_5P_8$, monoclinic, *C*2/*c* (no. 15); $a = 2180.13(12)$, $b = 2515.56(12)$, $c = 2061.94(12)$ pm, $\beta = 105.676(7)^\circ$; $V = 10887.6(10) \times 10^6$ pm^3, $Z = 4$; $\mu(\mathrm{Ag}_{K\alpha}) = 0.178$ mm^{-1}; $\theta_{\max} = 22.3$; 14031 ($R_{\mathrm{int}} = 0.0641$) independent reflections measured, of which 4320 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.014/–0.523 e Å^{-3}; 788 parameters, $R1 = 0.0661$ ($I > 2\sigma(I)$), w$R2 = 0.1982$ (all data).

1b: $C_{60}H_{64}K_2N_2O_3P_4$, monoclinic, $P2_1/c$ (no. 14); $a = 1145.0(2)$, $b = 2511.9(4)$, $c = 2039.5(7)$ pm, $\beta = 94.45(3)^\circ$; $V = 5848(2) \times 10^6$ pm^3, $Z = 4$; $\mu(\mathrm{Mo}_{K\alpha}) = 0.315$ mm^{-1}; $\theta_{\max} = 25.0$; 9573 ($R_{\mathrm{int}} = 0.0770$) independent reflections measured, of which 5945 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 0.839/–0.520 e Å^{-3}; 788 parameters, $R1 = 0.0639$ ($I > 2\sigma(I)$), w$R2 = 0.1730$ (all data).

2a: $C_{79}H_{68}N_3P_6Y$ (**2a** · toluene), triclinic, $P\bar{1}$ (no. 2); $a = 1364.5(7)$, $b = 1371.5(9)$, $c = 2082(2)$ pm, $\alpha = 91.19(11)$, $\beta = 97.83(10)$, $\gamma = 118.15(6)^\circ$; $V = 3387(5) \times 10^6$ pm^3, $Z = 2$; $\mu(\mathrm{Ag}_{K\alpha}) = 0.573$ mm^{-1}; $\theta_{\max} = 20.7$; 13517 ($R_{\mathrm{int}} = 0.0632$) independent reflections measured, of which 10625 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.490/–0.917 e Å^{-3}; 788 parameters, $R1 = 0.0496$ ($I > 2\sigma(I)$); w$R2 = 0.1393$ (all data).

2b: $C_{79}H_{68}N_3LaP_6$ (**2b** · toluene), triclinic, $P\bar{1}$ (no. 2); $a = 1377.56(12)$, $b = 1384.58(12)$, $c = 2071.53(12)$ pm, $\alpha = 91.307(10)$, $\beta = 97.806(10)$, $\gamma = 118.356(10)^\circ$; $V = 3427.5 \times 10^6$ pm^3, $Z = 2$; $\mu(\mathrm{Ag}_{K\alpha}) = 0.431$ mm^{-1}; $\theta_{\max} = 20.8$; 13900 ($R_{\mathrm{int}} = 0.0738$) independent reflections measured, of which 9374 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.801/–0.713 e Å^{-3}; 783 parameters, $R1 = 0.0598$ ($I > 2\sigma(I)$); w$R2 = 0.1317$ (all data).

2c: $C_{79}H_{68}N_3NdP_6$ (**2c** · toluene), triclinic, $P\bar{1}$ (no. 2); $a = 1371.75(2)$, $b = 1380.9(3)$, $c = 2082.5(3)$ pm, $\alpha = 90.9581(2)$, $\beta = 98.076(2)$, $\gamma = 118.338(2)^\circ$; $V = 3421.8(9) \times 10^6$ pm^3, $Z = 2$; $\mu(\mathrm{Mo}_{K\alpha}) = 0.945$ mm^{-1}; $\theta_{\max} = 25.0$; 12055 ($R_{\mathrm{int}} = 0.0447$) independent reflections measured, of which 10502 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.356/–0.757 e Å^{-3}; 793 parameters, $R1 = 0.0364$ ($I > 2\sigma(I)$); w$R2 = 0.0922$ (all data).

2d: $C_{79}H_{68}ErN_3P_6$ (**2d** · toluene), triclinic, $P\bar{1}$ (no. 2); $a = 1362.66(12)$, $b = 1367.55(12)$, $c = 2078.1(2)$ pm, $\alpha = 90.905(11)$, $\beta = 97.950(11)$, $\gamma = 118.181(9)^\circ$; $V = 3366.1(5) \times 10^6$ pm^3, $Z = 2$; $\mu(\mathrm{Ag}_{K\alpha}) = 0.772$ mm^{-1}; $\theta_{\max} = 20.7$; 13460 ($R_{\mathrm{int}} = 0.0393$) independent reflections measured, of which 12289 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 2.277/–1.316 e Å^{-3}; 783 parameters, $R1 = 0.0327$ ($I > 2\sigma(I)$); w$R2 = 0.0981$ (all data).

3: $C_{76}H_{68}LuN_3OP_6$ (**3** · 0.5 toluene), orthorhombic, *Pbca* (no. 61); $a = 1503.8(3)$, $b = 2088.2(4)$, $c = 4518.7(9)$ pm; $V = 14190(5) \times 10^6$ pm^3, $Z = 8$; $\mu(\mathrm{Ag}_{K\alpha}) = 0.847$ mm^{-1}; $\theta_{\max} = 19.00$; 11295 ($R_{\mathrm{int}} = 0.0852$) independent reflections measured, of which 7710 were considered observed with $I > 2\sigma(I)$; max./min. residual electron density 1.163/–0.943 e Å^{-3}; 624 parameters, $R1 = 0.0553$ ($I > 2\sigma(I)$); w$R2$ (all data) $= 0.1471$.

Polymerization of CL: The required amount of **2** (**a**: 38.8 mg, 0.031 mmol; **b**: 42.2 mg, 0.031 mmol; **c**: 51.0 mg, 0.039 mmol; **d**: 45.5 mg, 0.031 mmol) was placed under an atmosphere of argon in a Schlenk tube and dissolved in toluene (5 mL). CL (0.54 g, 4.7 mmol) was introduced into the toluene solution by syringe with vigorous stirring. The reaction mixture became highly viscous within 1 min. After completion of the polymerization the reaction mixture was precipitated in excess methanol containing few drops of HCl. For purification the polymer was reprecipitatad twice from dichloromethane/methanol and finally dried under vacuum at room temperature for 24 h.

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[1] Review: F. T. Edelmann, *Angew. Chem.* **1995**, *107*, 2647–2669; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2466–2488.

[2] Review: a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) R. Kempe, *Angew. Chem.* **2000**, *112*, 478–504; *Angew. Chem. Int. Ed.* **2000**, *39*, 468–49.

[3] a) T. G. Wetzel, S. Dehnen, P. W. Roesky, *Angew. Chem.* **1999**, *111*, 1155–1158; *Angew. Chem. Int. Ed.* **1999**, *38*, 1086–1088; b) S. Wingerter, M. Pfeiffer, F. Baier, T. Stey, D. Stalke, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1121–1130.

[4] a) S. Anfang, K. Harms, F. Weller, O. Borgmeier, H. Lueken, H. Schilder, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 159–166; b) S. Anfang, T. Gröb, K. Harms, G. Seybert, W. Massa, A. Greiner, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1853–1859; c) T. Gröb, G. Seybert, W. Massa, F. Weller, R. Palaniswami, A. Greiner, K. Dehnicke, *Angew. Chem.* **2000**, *112*, 4542–4544; *Angew. Chem. Int. Ed.* **2000**, *39*, 4373–4375; d) T. Gröb, G. Seybert, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* **2001**, *627*, 304–306.

[5] M. T. Gamer, S. Dehnen, P. W. Roesky, *Organometallics* **2001**, *20*, 4230–4236.

[6] K. Aparna, M. Furguson, R. G. Cavell, *J. Am. Chem. Soc.* **2000**, *122*, 726–727.

[7] a) F. T. Edelmann, *Top. Curr. Chem.* **1996**, *179*, 113–148; b) U. Reissmann, P. Poremba, M. Noltemeyer, H.-G. Schmidt, F. T. Edelmann, *Inorg. Chim. Acta* **2000**, *303*, 156–162; c) A. Recknagel, A. Steiner, M. Noltemeyer, S. Brooker, D. Stalke, F. T. Edelmann, *J. Organomet. Chem.* **1991**, *414*, 327–35; d) A. Recknagel, M. Witt, F. T. Edelmann *J. Organomet. Chem.* **1989**, *371*, C40–C44.

[8] a) S. Agarwal, C. Mast, K. Dehnicke, A. Greiner, *Macromol. Rapid Commun.* **2000**, *21*, 195–212; b) P. Ravi, T. Groeb, K. Dehnicke, A. Greiner, *Macromolecules* **2001**, *34*, 8649–8653.

[9] a) M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, *Macromolecules* **1996**, *29*, 1798–1806; b) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845–4856.

[10] a) S. J. McLain, N. E. Drysdale, *Polym. Prepr.* **1992**, *33*, 174–175; b) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra, J. Feijen, *Macromolecules* **1996**, *29*, 3332–3333; c) Y. Shen, Z. Shen, Y. Zhang, K. Yao, *Macromolecules* **1996**, *29*, 8289–8295; d) K. Tortosa, T. Hamaide, C. Boisson, R. Spitz, *Macromol. Chem. Phys.* **2001**, *202*, 1156–1160.

[11] a) S. Agarwal, M. Karl, S. Anfang, K. Dehnicke, A. Greiner, *Polym. Prepr.* **1998**, *39*, 361–362; b) H. Noss, M. Oberthür, C. Fischer, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **1999**, 2283–2288; c) D. Barbier-Baudry, A. Bouazza, C. H. Brachais, A. Dormond, M. Visseaux, *Macromol. Rapid Commun.* **2000**, *21*, 213–217.

[12] P. Bhattacharyya, J. D. Woollins, *Polyhedron* **1995**, *14*, 3367–3388.

[13] a) P. Braunstein, J. Durand, G. Kickelbick, M. Knorr, X. Morise, R. Pugin, A. Tiripicchio, F. Ugozzoli, *J. Chem. Soc. Dalton Trans.* **1999**, 4175–4186; b) M. Knorr, C. Strohmann, *Organometallics* **1999**, *18*, 248–257; c) P. Braunstein, J. Cossy, M. Knorr, C. Strohmann, P. Vogel, *New J. Chem.* **1999**, *23*, 1215–1222; d) I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, *J. Organomet. Chem.* **1999**, *588*, 143–151; e) J. Blin, P. Braunstein, J. Fischer, G. Kickelbick, M. Knorr, X. Morise, T. Wirth, *J. Chem. Soc. Dalton Trans.* **1999**, 2159–2170.

[14] a) J. Ellermann, M. Lietz, *Z. Naturforsch., B.* **1980**, *35*, 64–67; b) H. Schmidbaur, S. Lautenschläger, F. H. Köhler, *J. Organomet. Chem.* **1984**, *271*, 173–180.

[15] J. Ellermann, M. Schütz, F. W. Heinemann, M. Moll, *Z. Anorg. Allg. Chem.* **1998**, *624*, 257–262.

[16] J. Ellermann, M. Schütz, F. W. Heinemann, M. Moll, *Chem. Ber./Recl.* **1997**, *130*, 141–143.

[17] O. Kühl, T. Koch, F. B. Somoza, P. C. Junk, E. Hey-Hawkins, D. Plat, M. S. Eisen, *J. Organomet. Chem.* **2000**, *604*, 116–125.

[18] F. T. Edelmann in *Comprehensive Organometallic Chemisty II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**.

[19] D. C. Bradley, J. S. Ghorta, F. A. Hart, *J. Chem. Soc. Dalton. Trans.* **1973**, 1021–1023.

[20] R. Anwander, *Top. Curr. Chem.* **1996**, *179*, 33–112.

[21] a) H. H. Karsch, A. Appelt, G. Miller, *Angew. Chem.* **1986**, *98*, 832–834; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 823–825; b) H. H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman, W. Hiller, *Angew. Chem.*

1993, *105*, 1814–1817; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1739–1742; c) H. H. Karsch, G. Ferazin, H. Kooijman, O. Steigelmann, A. Schier, P. Bissinger, W. Hiller, *J. Organomet. Chem.* **1994**, *482*, 151–167; d) H. H. Karsch, G. Feruzin, P. Bissinger, *Chem. Commun.* **1994**, 505–506; e) S. Hao, J. I. Song, H. Aghabozorg, S. Gambarotta, *Chem. Commun.* **1994**, 157–158.

[22] H. Kessler *Angew. Chem.* **1970**, *82*, 237–253; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 219–235.

[23] M. D. Taylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–391.

[24] H. Noeth, L. Meinel, *Z. Anorg. Allg. Chem.* **1967**, *349*, 225–240.

[25] D. C. Bradley, J. S. Ghorta, F. A. Hart *J. Chem. Soc. Dalton. Trans.* **1973**, 1021–1023.

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

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

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