Kinetic analysis of the 12 clones: The clones were labeled at the 5′-end with γ-^{32}P-ATP and incubated at 1.0 nM in SB+8 mM $MgCl_2$ at 37 °C. Aliquots were taken at different times, quenched with urea and EDTA on ice, and loaded onto a denaturating PA gel. Bands corresponding to the uncleaved and cleaved fractions were quantified by phosphorImaging (Molecular Dynamics). The k_{obs} values were then determined by using an exponential curve fitting of the measured values of the uncleaved ribozyme fraction during the first 3 min.

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Homoleptic Phosphoraneiminato Complexes of Rare Earth Elements as Initiators for Ring-Opening Polymerization of Lactones**

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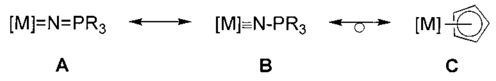
Kurt Dehnicke*

Phosphoraneiminato complexes of transition metals containing the NPR_3^- group are known in many coordination-chemical variations[1] as a result of varying bonding modes. In complexes with metal ions in low oxidation states (+I, +II) the NPR_3^- group acts as μ_3-N bridging ligand, in medium oxidation states (+III, +IV) preferably as μ_2-N bridging ligand, and in high oxidation states (+V to +VIII) exclusively as terminal ligand. In the latter mode short metal–nitrogen distances and linear or almost stretched M-N-P axes are observed, which can be described with the resonance structures **A** and **B**. As first deduced for imido complexes (NR^{2-})[2] style **B** requires a σ, 2π orbital set for the M≡N bond that proves the NPR_3^- ligand to be ψ-isolobal to the η^5-cyclopentadienide(Cp) ligand **C** [3] with respect to equal charge. Recent ab initio calculations confirm this interpretation.[4]



Since we surprisingly found the bonding mode **A**/**B** also in the mixed-ligand complexes $[Ln_2Cp_3(NPPh_3)_3]$ (Ln = Y, Dy, Er, Yb) containing Ln^{3+} ions,[5] we examined the opportunity to synthesize homoleptic compounds $[Ln(NPPh_3)_3]$, too, and to compare them with the ψ-isolobal complexes $[LnCp^*_3]$ ($Cp^* = C_5Me_5$) that are known as initiators for ring-opening polymerization (ROP) of lactones.[6–8]

Compounds **1** are formed in almost quantitative yields by reacting the alkaline phosphoraneiminates $MNPPh_3$ (M = Na, K, Rb, Cs)[9] with the anhydrous metal trichlorides or anhydrous metal triflates in THF [Eq. (1)]. Interestingly, only the lanthanum compound crystallizes as a THF-solvate, that is **1a**·2THF, whereas the ytterbium compound **1b** forms a solvate-free complex due to the ionic radius of the Yb^{3+} ion which is 16 pm smaller than that of the La^{3+} ion.[10]

$$2\,LnCl_3 + 6\,NaNPPh_3 \xrightarrow[-\,NaCl]{} [\{Ln(NPPh_3)_3\}_2] \quad (1)$$

Ln = La (**1a**), Yb (**1b**)

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The X-ray crystal structure analysis of **1a** · 2 THF (Figure 1) reveals that both the lanthanum atoms are linked through N atoms of two $NPPh_3^-$ groups to give a nonplanar La_2N_2 four-membered butterfly arrangement. This is a result of the additional μ-O function of the lanthanum-bridging THF molecule that leads to a trigonal-bipyramidal coordination around the lanthanum atoms with N1 (and N1A, respectively) and O1 at the axial positions. The μ-O-bridging function of THF is not unusual, it has occasionally been observed in organolithium compounds[12] and in transition metal complexes.[13] The La–N distances of the La_2N_2 ring (246.0 and 252.4 pm) are much longer than the La–N distances of the two terminally bound $NPPh_3^-$ groups which are among the shortest known La–N bonds (228.4 and 231.6 pm). Together with the large bonding angles at N1 (163.9°) and N3 (168.1°), this corresponds to mode **A**/**B**.[14]

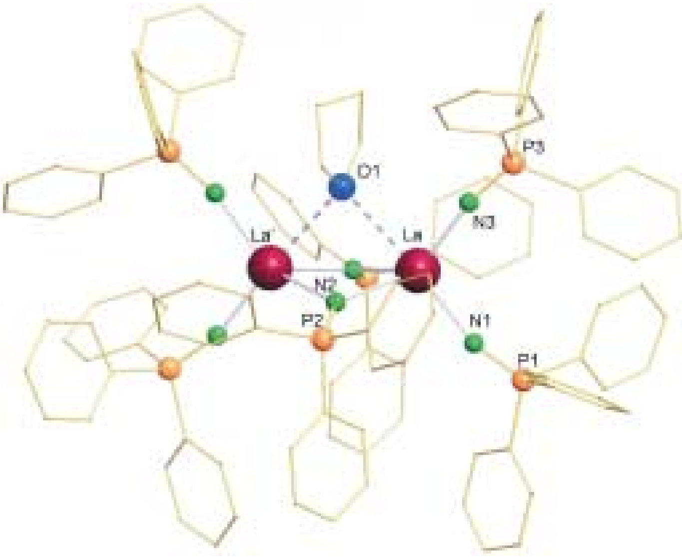

Figure 1. Structure of $[\{La(NPPh_3)_3\}_2] \cdot 2THF$ (**1a** · 2THF). Selected bond lengths [pm] and angles [°]: La-N1 228.3(6), La-N3 231.9(6), La-N2 245.4(7), La-N2A 252.3(7), La-O1 282.5(6), N1-La-O1 174.9(2), N1-La-N3 105.0(3), N1-La-N2 105.7(2), N2-La-N2A 79.9(3), N2-La-N3 120.5(3), N2A-La-N3 130.7(2), La-N1-P1 163.9(4), La-N3-P3 168.1(5).

According to the X-ray crystal structure analysis[11] the ytterbium complex **1b**, which crystallizes solvate-free from THF/toluene, has a centrosymmetric dimeric molecular structure with tetrahedrally coordinated Yb atoms (Figure 2). The Yb–N distances in the Yb_2N_2 planar four-membered ring differ only slightly (225.0 and 226.2 pm) and, as expected, are significantly longer than the Yb–N distances to the terminal $NPPh_3^-$ groups (210.7 and 213.7 pm). In relation to the La–N bonds in **1a** · 2THF both kinds of Yb–N bonds are still a little shorter than expected by ionic radii contraction according to Shannon,[10] which is probably associated with the lower coordination number in **1b**.

If excess alkaline phosphoraneiminate is used in the reaction shown in Equation (1) homoleptic "ate-complexes" $[Ln(NPPh_3)_4]^-$ are obtained that are catalytically inactive although some other "ate-complexes" of rare earth elements with lower steric shielding of the metal atoms are effective initiators for the ring-opening polymerization of lactones.[15]

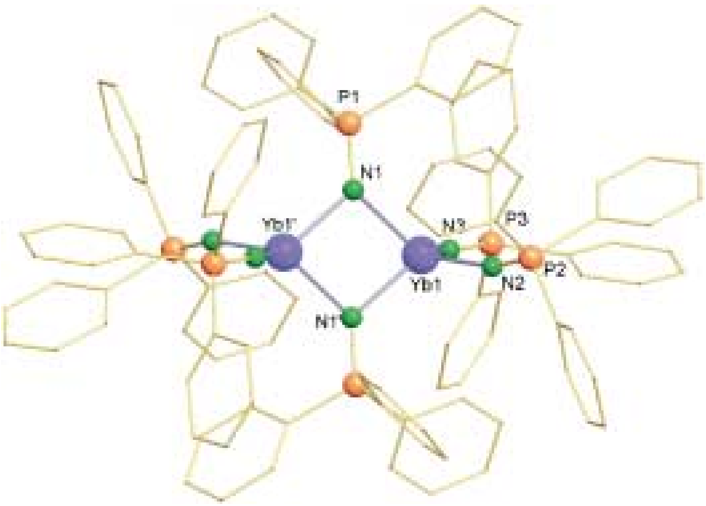

Figure 2. Structure of $[\{Yb(NPPh_3)_3\}_2]$ (**1b**). Selected bond lengths [pm] and angles [°]: Yb1-N1 225.0(4), Yb1-N1A 226.2(4), Yb1-N2 210.7(4), Yb1-N3 213.7(4), Yb1-N1-Yb1A 97.7(2), N1-Yb1-N1A 82.3(2), N1-Yb1-N2 108.4(2), N1-Yb1-N3 120.8(2), N2-Yb1-N1A 117.7(2), N2-Yb1-N3 110.2(2), N1A-Yb1-N3 115.3(2), Yb1-N2-P2 158.0(3), Yb1-N3-P3 158.5(3).

Despite the much smaller shape of phosphoraneiminato ligands compared to η^5-Cp^- ligands, the rare-earth metal atoms in **1a** and **1b** preserve noticeably low coordination numbers (4 and 4+1, respectively). The special bonding modes of $NPPh_3^-$ groups in these structures show promise for use as initiators in polymerization reactions.

Indeed, **1a** and **1b** initiate the ring-opening polymerization of ε-caprolactone (CL) to poly-ε-caprolactone (PCL) within very short reaction times and in yields of >90%. The molecular weights of PCLs obtained from ratios of **1a**:CL = 1:150 at 20°C in toluene are a little lower than those theoretically expected with reference to the dimeric complex **1a** (Table 1). Apparently, only the dimeric complex initiates the polymerization of CL at one active position, while the possible dissociation of **1a** plays a minor role.

Table 1. Ring-opening polymerization of ε-caprolactone (CL), initiated by **1a**, **1b**, **2**, and **3** at 20°C.

	CL:**1** (molar)	t [min]	Yield PCL [%]	$M_n \times 10^{-4}$ (exp.)	M_w/M_n[a]
1a	150	<1	91	1.303	1.77
1a	250	<1	90	3.507	1.47
1b	150	3	98	1.266	1.32
1b	250	3	91	2.612	1.38
2	150	80	98	3.265	1.70
2	250	120	80	2.358	1.53
3	150	120	80	0.969	1.14
3	250	200	54	0.751	1.47

[a] M_n = Number-average molecular weight. M_w = Weight-average molecular weight. M_w/M_n = Polydispersity index.

By decreasing the ratio of **1b**:CL use of the ytterbium complex **1b** as catalyst leads to an increasingly better correlation between theoretical and experimental molecular weight, again related to the dimeric complex.

As a contribution to the study of the ψ-isolobal relationship between the Cp^- and the $NPPh_3^-$ ligand we have also

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investigated the polymerization activities of [LaCp$_3$] (**2**) and [YbCp$_3$] (**3**) under analogous conditions. Overall we found far worse and more nonuniform results with regard to yield, molecular weight, and polydispersity index of the polymers. However, the polymerizations with the initiators **1a** and **1b** did not produce the quality of polymers prepared by heteroleptic pentamethylcyclopentadienyl complexes [LnCp$^*_2$X] of rare-earth elements.[6, 16]

The future importance of catalysts based on phosphoraneiminato complexes lies in the almost unlimited possibilities to vary the phosphorus-bound residues R, including the introduction of chiral groups. This should provide fascinating new possibilities for controlling polymerizations of functionalized monomers.

Experimental Section

General: Standard Schlenk techniques; degassed and dried solvents under argon; IR: Bruker FT-IR IFS 88, nujol, CsI/PE plates; ^{31}P NMR: Bruker AM-400, 161.975 MHz, 85% H_3PO_4; polymer analysis: Knauer GPC (polystyrene standard (PSS), 600 × 8 mm, 10 µm), Knauer differential refracto-/ viscometer K 200, polystyrene standard, THF solution.

1a: A solution of NaNPPh$_3$ (1.75 g, 5.60 mmol) in THF (15 mL) was added dropwise to LaCl$_3$ · 1.5 THF (0.66 g, 1.87 mmol) in THF (5 mL) and stirred for 24 h. After removal of THF in vacuo the solid was extracted by filtration with hot toluene. The filtrate was concentrated to about 5 mL and **1a** was precipitated as a beige solid (0.55 g, 31%) by adding diethyl ether (20 mL). Single crystals of **1a** · 2 THF were obtained by cooling a saturated solution (hot) of toluene/THF (10/1). THF was removed under vacuum. Elemental analysis (%): calcd for $C_{108}H_{90}La_2N_6P_6$ ($M = 1935.60\ \text{g mol}^{-1}$): C 67.02, H 4.69, N 4.34; found: C 62.49, H 4.57, N 4.36; IR: $\tilde{\nu} = 1195$ (vs), 1163 (vs), 1141 (vs), 1101 (s), 1089 (m), 1067 (w), 1042 (vw), 1025 (w), 998 (w), 919 (vw), 875 (w), 748 (m), 706 (vs), 695 (vs), 552 (s), 534 (vs), 465 (m), 447 (m), 428 (w), 412 (w), 378 (m), 351 (vw), 321 (vw), 308 (m), 288 (m), 254 (m), 212 (m), 194 (m), 177 (m), 146 (m), 122 cm^{-1} (vw); ^{31}P NMR (THF, 25 °C): $\delta = -17.3$ (s).

1b: A solution of NaNPPh$_3$ (1.79 g, 6.00 mmol) in THF (5 mL) was added to [Yb(O$_3$SCF$_3$)$_3$] (1.24 g, 2.00 mmol) in THF (35 mL). By stirring for 24 h **1b** (1.10 g, 55%) was precipitated as a colorless powder of low solubility, whereas NaO$_3$SCF$_3$ remains dissolved. The resulting solution was reduced to a volume of 5 mL and extracted with toluene with accompanying precipitation of NaO$_3$SCF$_3$. After filtration colorless diamond-shaped crystals were formed within 12 h. The compounds are only sparingly soluble in toluene and THF both at room temperature as well as under higher temperatures. Elemental analysis (%): calcd for $C_{108}H_{90}N_6P_6Yb_2$ ($M = 2003.87\ \text{g mol}^{-1}$): C 64.73, H 4.53, N 4.19; found: C 62.57, H 4.21, N 4.24; IR: $\tilde{\nu} = 1308$ (w), 1221 (s), 1200 (vs), 1178 (s), 1155 (m), 1134 (s), 1103 (s), 1084 (s), 1069 (m), 1026 (m), 997 (m), 746 (m), 712 (s), 694 (vs), 568 (m), 542 (s), 534 (vs), 472 (m), 447 (m), 424 (m), 317 (w), 294 (w), 253 (vw), 215 (vw), 191 (vw), 156 (vw), 131 cm^{-1} (vw); ^{31}P NMR (THF, 25 °C): $\delta = 17.0$ (s), -256.8 (s).

Polymerizations: Lactone was added to a suspension of the catalyst in toluene. This led to a spontaneous rise of solution viscosity. The product was precipitated with methanol/HCl, recrystallized twice from THF, and dried in vacuum for 24 h.

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[11] X-ray crystal structure analysis: **1a** · 2 THF: four-circle diffractometer Siemens P4, Mo$_{K\alpha}$ radiation, graphite monochromator, ω scans, direct methods, refinement to F^2, absorption correction DIFABS, $\mu(\text{Mo}_{K\alpha}) = 9.61\ \text{cm}^{-1}$, H atoms in calculated positions. SHELXS-97, SHELXL-97, SHELXTL. Space group *P*bcn, $Z = 4$, $a = 1761.3(5)$, $b = 2046.7(6)$, $c = 2870.2(8)$ pm, $V = 10347(5)$ Å^3, $\rho_{\text{calcd}} = 1.345\ \text{g cm}^{-3}$, 223(2) K, 10507 reflections collected, 7334 independent reflections ($R_{\text{int.}} = 0.0368$), 3819 reflections with $I > 2\sigma(I)$, 490 parameters, $R = 0.0592$, wR_2 (all data) $= 0.1879$. **1b**: Four-circle diffractometer Siemens P4, Mo$_{K\alpha}$ radiation, graphite monochromator, ω scans, Patterson method, refinement to F^2, empirical absorption correction, $\mu(\text{Mo}_{K\alpha}) = 21.74\ \text{cm}^{-1}$, H atoms in calculated positions. SHELXS-97, SHELXL-97, SHELXTL-5.03. Space group $P\bar{1}$, $Z = 1$, $a = 1355.8(4)$, $b = 1410.2(2)$, $c = 1413.4(3)$ pm, $\alpha = 74.298(14)$, $\beta = 62.337(14)$, $\gamma = 81.37(2)°$, $V = 2303.1(9)$ Å^3, $\rho_{\text{calcd}} = 1.445\ \text{g cm}^{-3}$, 223(2) K, 7596 reflections collected, 7231 symmetry independent ($R_{int.} = 0.0562$), 6595 reflections with $I > 2\sigma(I)$, 550 parameters, $R = 0.0397$, wR_2 (all data) $= 0.1093$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143722 (**1a**),and CCDC-142589(**1b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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