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Peter Roesky, Jelena Jenter, Tianshu Li. New Development in Rare Earth Metal Complexes Containing Anionic Bis(imino)pyrrolyl and Bis(phosphanyl)amide Ligands. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (12), pp.2148. 10.1002/zaac.201000169 . hal-00568239

HAL Id: hal-00568239

<https://hal.science/hal-00568239>

Submitted on 23 Feb 2011

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**New Development in Rare Earth Metal Complexes
Containing Anionic Bis(imino)pyrrolyl and
Bis(phosphanyl)amide Ligands**

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000169.R1
Wiley - Manuscript type:	Research Report
Date Submitted by the Author:	18-May-2010
Complete List of Authors:	Roesky, Peter; Karlsruher Institut für Technologie (KIT), Institut für Anorganische Chemie Jenter, Jelena; Karlsruher Institut für Technologie (KIT), Institut für Anorganische Chemie Li, Tianshu; Karlsruher Institut für Technologie (KIT), Institut für Anorganische Chemie
Keywords:	Rare Earth Elements, N-ligand, Coordination Compounds, Catalysis, Chelates
<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p>	
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RESEARCH REPORT

New Development in Rare Earth Metal Complexes Containing Anionic Bis(imino)pyrrolyl and Bis(phosphanil)amide Ligands

Tianshu Li,^[a] Jelena Jenter^[a] and Peter W. Roesky^{[a]*}

Keywords: Rare Earth Elements; N-ligand; Coordination Compounds; Catalysis;
Chelates

Abstract Rare earth element complexes having the very bulky 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl, and the sterically less demanding bis(phosphanil)amide ligand, (PPh₂)₂N⁻, in the coordination sphere are reviewed in this research report. The coordination chemistry, the reactivity, and the catalytic application of the corresponding complexes are discussed.

* Prof. Dr. Peter W. Roesky

Fax: +49-721-608-4854

E-Mail: roesky@kit.edu

[a] Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT),

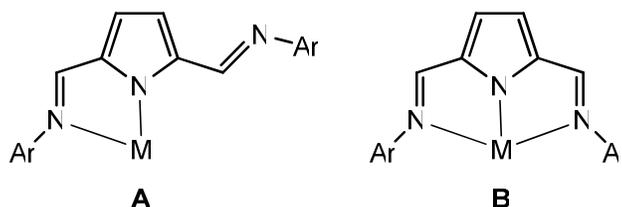
Geb. 30.45, Engesserstr. 15, D-76131 Karlsruhe, Germany

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3 Recently there has been tremendous research progress in the non-cyclopentadienyl
4 chemistry [1, 2]. In this research report, we emphasize on two different anionic amido
5 ligands, an NNN tridentate bis(imino)pyrrolyl ligand and a PN bidentate
6 bis(phosphanil)amide ligand, and present our results in the synthesis and catalytic
7 applications of the rare earth metal complexes containing these two ligands.
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18 **1. Bis(imino)pyrrolyl Ligands**

19 **1.1 Introduction**

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22 2,5-Bis(*N*-aryliminomethyl)pyrrolyl ligands are monoanionic ligands, which can be
23 easily accessed by deprotonation of the corresponding bis(imino)pyrroles [3].
24 Bis(imino)pyrroles are prepared by condensation of 2,5-diformylpyrrole with the
25 analogous anilines [4]. 2,5-Bis(*N*-aryliminomethyl)pyrrolyl ligands contain a pyrrolyl
26 unit and two imino groups, which create three possible coordination sites. As shown in
27 Scheme 1, bis(imino)pyrrolyl derivatives can act as bi- or tridentate chelating ligands to
28 form either **A** or **B** coordination mode with a metal center [5].
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47 **Scheme 1**

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52 The coordination mode of the resulting complexes depends on the nature of the aryl-
53 substituents of the ligand, the number of ligands coordinated, the ionic radius of the metal
54 center and the bulkiness of additional ligands coordinated to the metal atom. 2,5-Bis(*N*-
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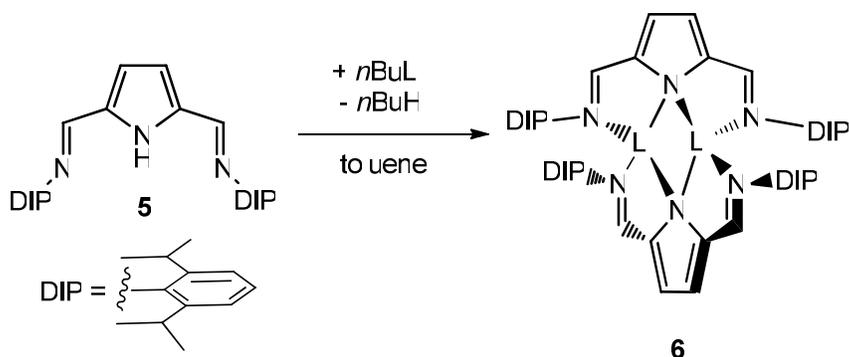
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3 The reaction of the 2,6-dimethylphenyl substituted ligand with $[Y\{N(SiMe_3)_2\}_3]$ led to
4 the mono-substituted complex **1** in which the ligand is coordinated by all three nitrogen
5 atoms to the metal center. By using the bulkier 2,6-diisopropylphenyl substituted ligand,
6 the bis(pyrrolyl) complex **2** was formed, in which both pyrrolyl ligands coordinate to the
7 metal center in a bidentate fashion. The reaction of $[Y\{N(SiMe_3)_2\}_3]$ with the 2-
8 methylphenyl substituted ligand gave a 4:1 mixture of mono(pyrrolyl) complex **3a** and
9 bis(pyrrolyl) complex **3b**. The reaction of 4-methoxyphenyl or 4-methylphenyl
10 substituted ligand with $[Y\{N(SiMe_3)_2\}_3]$ afforded the homoleptic tris(pyrrolyl)
11 complexes **4a** and **4b** in which the pyrrolyl ligands are bound in a tridentate fashion to the
12 metal center. The catalytic activities of yttrium complexes **1**, **2**, **4a** and **4b** were
13 investigated for the polymerization of ϵ -caprolactone (CL) [4]. The homoleptic pyrrolyl
14 complexes **4a** and **4b** showed no activity, while complexes **1** and **2** were active catalysts
15 for the polymerization of CL. The polymers obtained with **2** exhibited narrower
16 polydispersities compared with the polymers produced by **1**. The early investigation
17 showed that **2** containing the steric demanding 2,6-diisopropylphenyl substituted ligand
18 afforded the best catalytic activity. Our new development of the rare earth metal
19 bis(imino)pyrrole complexes has been focused on this ligand system [5].
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46 1.2 Alkali Metal Compounds

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48 The rare earth metal complexes are generally synthesized by two methods: salt
49 metathesis and amine or alkane elimination. The preparation of the corresponding alkali
50 metal salts of the ligand is required for salt metathesis reactions. The lithium salt
51 $[(DIP_2pyr)Li]_2$ (**6**) was first synthesized by Bochmann and coworkers in 2000 *via* the
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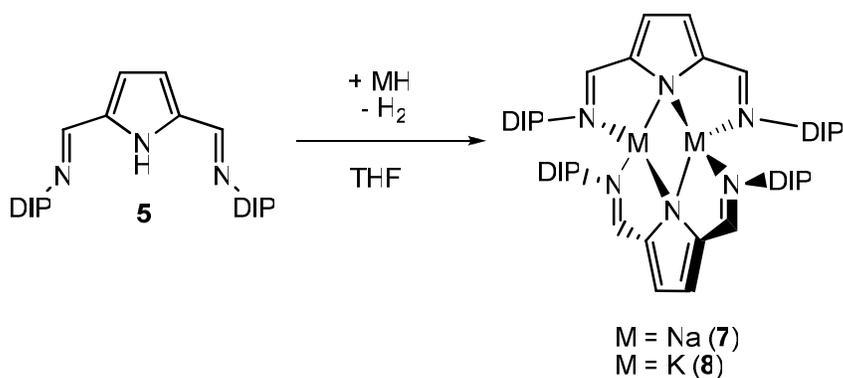
reaction of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole (**5**) with *n*BuLi in toluene (Scheme 3) [9].



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Scheme 3

Treatment of **5** with NaH or KH in hot THF afforded [(DIP₂pyr)₂M] (M = Na (**7**), K (**8**)) (Scheme 4) [10].



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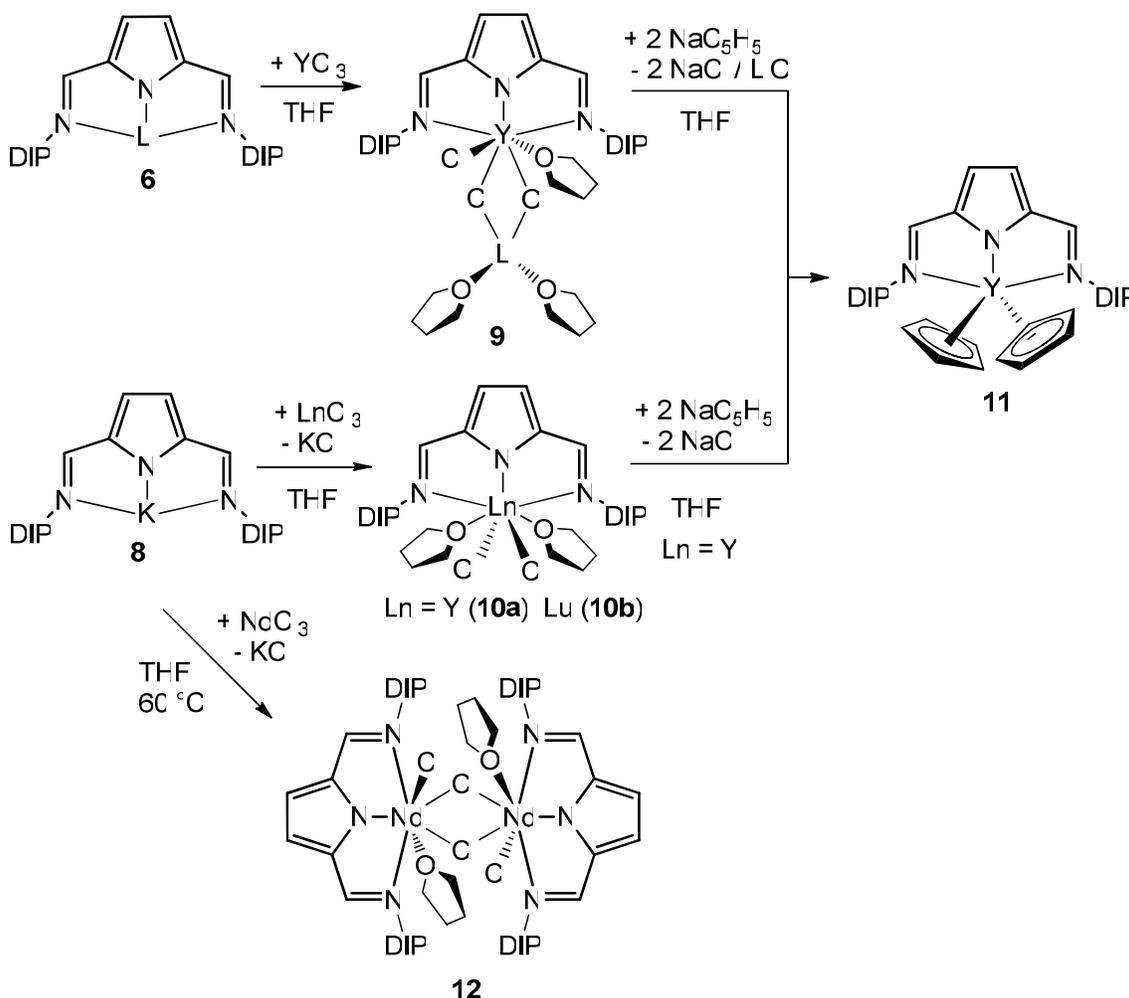
Scheme 4

The solid state structures of complexes **6** and **7** were established by single crystal X-ray diffraction and showed a dimeric structure, in which two (DIP₂pyr)⁻ ligands are

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3 bridged by two metal atoms, forming a diamond-shaped M_2N_2 core [11]. This structural
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5 motif is very rare in lithium chemistry and unknown for sodium compounds [5, 12-14].
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10 **1.3 Rare Earth Metal Complexes**

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12 Whereas the transmetallation of the lithium salt **6** with anhydrous yttrium trichloride
13 afforded the “ate”-complex **9**, the salt metathesis reaction of the potassium salt **8** with
14 anhydrous $LnCl_3$ led to the neutral complexes $[(DIP_2pyr)LnCl_2(THF)_2]$ ($Ln = Y$ (**10a**), Lu
15 (**10b**)) [10] and $[(DIP_2pyr)NdCl_2(THF)]_2$ (**12**) [15] instead (Scheme 5). The solid state
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17 structure of neodymium complex **12** is dimeric, while the chloride complexes of the
18
19 smaller rare earth metal ions yttrium and lutetium are monomeric. The same product
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21 $[(DIP_2pyr)Y(C_5H_5)_2]$ (**11**) was produced by the reaction of 2 equiv $Na(C_5H_5)$ with either
22
23 yttrium complex **9** or **10a** in THF at room temperature. This seems to indicate that
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25 yttrium complexes **9** and **10a** have a similar reactivity, regardless of their structural
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27 difference. The crystal structures of the complexes **9**, **10a**, **11** and **12** showed that the
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29 $(DIP_2pyr)^-$ ligand coordinates to the yttrium center in a tridentate fashion [5].
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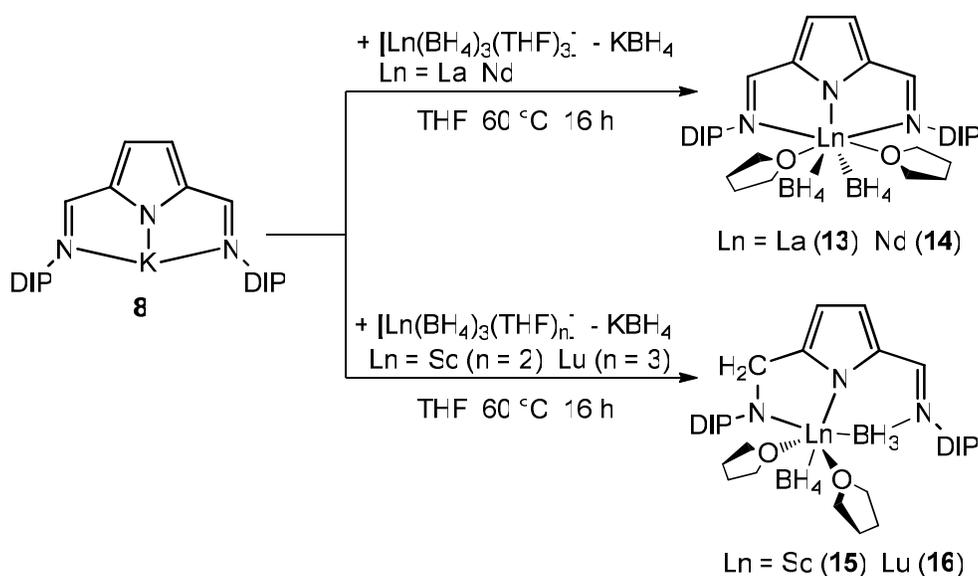


Scheme 5

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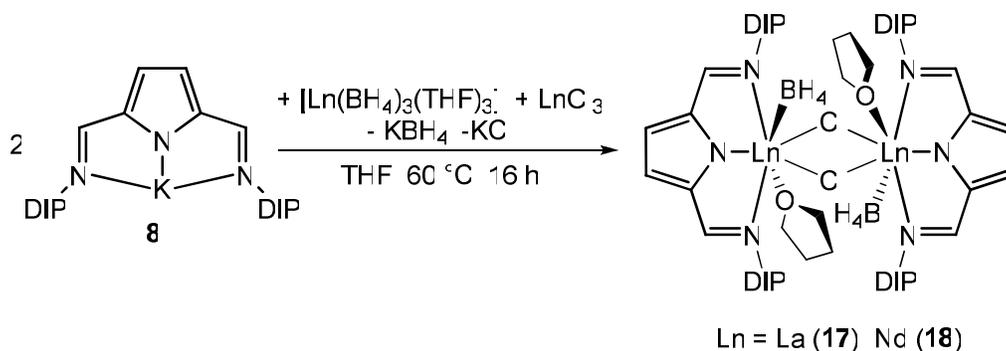
Many rare earth metal borohydrides and their derivatives were reported as efficient catalysts for the polymerization and copolymerization of styrene [16-18], isoprene [16, 19-22] and ethylene [21, 23]. $[\text{Ln}(\text{BH}_4)_3(\text{THF})_n]$ is a valuable precursor for preparing rare earth metal borohydride derivatives via salt metathesis reactions with the alkali salt of the corresponding ligand [5]. After the first rare earth metal borohydride complexes of the $(\text{DIP}_2\text{pyr})^-$ ligand were prepared in our group in 2009 [24], we have widely developed this catalogue of complexes [15, 25]. The borohydride complexes **13-**

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3 **16** were synthesized by reacting **8** with $[\text{Ln}(\text{BH}_4)_3(\text{THF})_n]$ ($\text{Ln} = \text{Sc}$, $n = 2$; $\text{Ln} = \text{La}$, Nd ,
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5 Lu , $n = 3$) in THF at 60 °C. The reaction of **8** with the larger rare earth metal
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7 trisborohydrides $[\text{Ln}(\text{BH}_4)_3(\text{THF})_3]$ ($\text{Ln} = \text{La}$, Nd) led to $[(\text{DIP}_2\text{pyr})\text{Ln}(\text{BH}_4)_2(\text{THF})_2]$ (Ln
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9 = La (**13**), Nd (**14**)). One borohydride ligand was eliminated to form KBH_4 as a
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11 byproduct (Scheme 6). The single crystal X-ray crystallography of **13** also confirmed that
12
13 the BH_4^- groups are η^3 -coordinated. On the contrary, the smaller rare earth metal
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15 trisborohydrides $[\text{Ln}(\text{BH}_4)_3(\text{THF})_n]$ ($\text{Ln} = \text{Sc}$ ($n = 2$), Lu ($n = 3$)) underwent a redox
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17 reaction between one BH_4 -group and one of the Schiff-base functions of the ligand. As a
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19 result, a dianionic ligand containing a N-BH_3 unit was formed and coordinates *via* the
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21 amido and the pyrrolyl unit to the metal center. The N-BH_3 unit coordinates in a η^2 -
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23 fasion *via* two hydrogen atoms to the metal center. The resulting products $[(\text{DIP})(\text{DIP-}$
24
25 $\text{BH}_3)\text{pyr}\}\text{Ln}(\text{BH}_4)(\text{THF})_2]$ ($\text{Ln} = \text{Sc}$ (**15**), Lu (**16**)) are shown in Scheme 6. During the
26
27 ligand reduction process, the symmetry of the ligand in **15** and **16** was broken. The η^2 -
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29 coordination mode of the $=\text{N-BH}_3$ moiety and the η^3 -coordination mode of the BH_4^-
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31 ligand in complexes **15** and **16** were confirmed in the solid state by single crystal X-ray
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33 diffraction as well. To the best of our knowledge, this coordination mode and a
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35 comparable reactivity of the BH_4^- group have not been observed before. We believe that
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37 the steric strain resulted from smaller metal center such as scandium and lutetium may
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39 cause this unusual redox reactivity [5, 24].
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Scheme 6

28 Mixed borohydride-chloride complexes are unusual in rare earth metal chemistry and
 29 were only observed in clusters [26]. Recently, we have prepared two mixed borohydride-
 30 chloride complexes containing the $(\text{DIP}_2\text{pyr})^-$ ligand [15]. The dimeric compounds
 31 $[(\text{DIP}_2\text{pyr})\text{LnCl}(\text{BH}_4)(\text{THF})_2]$ ($\text{Ln} = \text{La (17), Nd (18)}$) were synthesized by the reaction of
 32 **8** with a 1:1 mixture of the corresponding trisborohydrides $[\text{Ln}(\text{BH}_4)_3(\text{THF})_3]$ and
 33 anhydrous lanthanide trichlorides in THF at 60°C (Scheme 7).
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Scheme 7

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3 The single crystal X-ray diffraction study revealed that both metal complexes are
4 bridged almost symmetrically by two chlorine atoms and the BH_4^- anions are terminally
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6 η^3 -coordinated [15].
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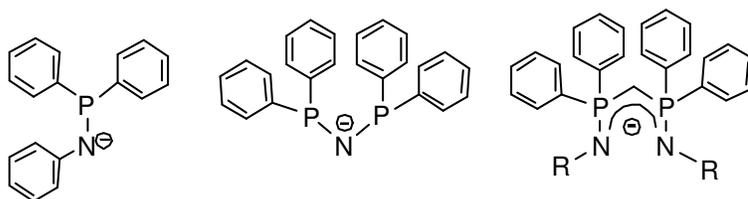
9
10 Neodymium-based Ziegler-Natta systems play a major role in the industrial
11 polymerization of 1,3-butadiene to poly-*cis*-1,4-butadiene [26-29]. The $(\text{DIP}_2\text{pyr})^-$
12 complexes of neodymium, $[(\text{DIP}_2\text{pyr})\text{NdCl}_2(\text{THF})_2]$ (**12**) and
13 $[(\text{DIP}_2\text{pyr})\text{Nd}(\text{BH}_4)_2(\text{THF})_2]$ (**14**) were investigated for the polymerization of 1,3-
14 butadiene. The polymerization studies were performed in the presence of $\text{AlEt}_3/\text{B}(\text{C}_6\text{F}_5)_3$,
15 $\text{AlEt}_3/[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ or MMAO-3A (trimethylaluminum and
16 triisobutylaluminum) as cocatalysts and cyclohexane as solvent at 65 °C. In all reactions,
17 molar ratio of 1,3-butadiene to the catalyst was in the range of 20000 to 22600. Both
18 complexes exhibited very high activity and good *cis*-selectivity. By using MMAO-3A as
19 cocatalyst, the chloro compound **12** showed a five times higher activity than those of the
20 borohydride complex **14**. The highest turnover frequency of approximately 19000 (mol of
21 $\text{Nd}^{-1} \text{h}^{-1}$) was observed for compound **12** by using $\text{AlEt}_3 / \text{B}(\text{C}_6\text{F}_5)_3$ (7.2 mmol: 100.98
22 μmol) as cocatalyst mixture [25].
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43 **2. Bis(phosphanyl)amide Ligand**

44 **2.1 Introduction**

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46 An alternative approach for stabilizing highly reactive metal centers is the use of
47 phosphines with P-N bonds [30]. The monoanionic ligands that contain P-N units such
48 as mono(phosphanyl)amide $(\text{PPh}_2\text{NPh})^-$, bis(phosphanyl)amide $(\text{PPh}_2)_2\text{N}^-$ and
49 bis(phosphinimino)methanides have become more and more popular in rare earth metal
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chemistry (Scheme 8) [31-35]. In 1999, we prepared the first rare earth metal ate complexes of mono(phosphanyl)amide $[(PPh_2NPh)_4Ln]^-$ ($Ln = Y, Yb, Lu$). The anionic bidentate P-N ligands are coordinated to the metal center in a η^2 fashion. They are also the first homoleptic rare earth metal complexes containing only three-member ring system [36]. $(PPh_2)_2N^-$ has a greater steric demanding than $(PPh_2NPh)^-$, thus leads to neutral homoleptic complexes. Additionally, the two PPh_2 units may allow $(PPh_2)_2N^-$ to act as a dangling ligand in a catalytic transformation [37]. In this report, we only include the results related to $(PPh_2)_2N^-$ ligand.



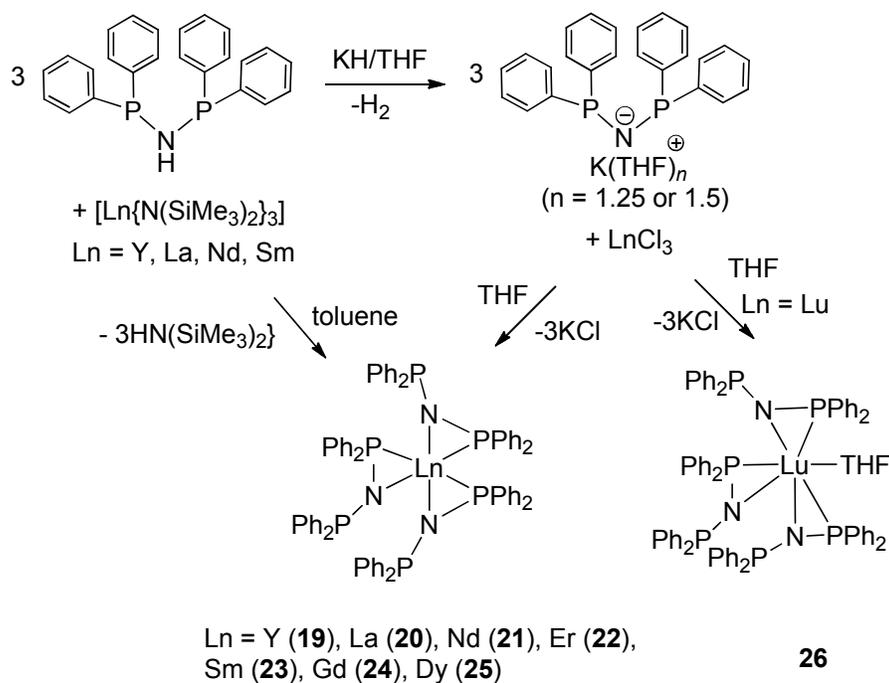
Scheme 8

2.2 Rare Earth Metal Complexes

It is well known that the neutral diphosphine amine $NH(PPh_2)_2$ [38] can be used as a bridging ligand to assemble bi- or polynuclear late transition metal complexes [39-43]. Since we reported the first rare earth metal complexes of $(PPh_2)_2N^-$ in 2002 [30, 37], we have prepared various complexes containing $(PPh_2)_2N^-$.

As shown in Scheme 9, a series of homoleptic complexes $[(PPh_2)_2N]_3Ln$ ($Ln = Y$ (**19**), La (**20**), Nd (**21**), Er (**22**), Sm (**23**), Gd (**24**), Dy (**25**)) were obtained via salt or amine elimination followed by crystallization from toluene [37, 44]. The precursor $[K(THF)_n][N(PPh_2)_2]$ ($n = 1.25, 1.5$) was prepared by treating $NH(PPh_2)_2$ with KH in THF. The salt elimination reaction of anhydrous $LnCl_3$ and $[K(THF)_n][N(PPh_2)_2]$ in 3:1

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3 molar ratio in THF led to the complexes **19**, **22-25**. The amine elimination reaction of
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6 $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and 3 equiv of $\text{NH}(\text{PPh}_2)_2$ afforded the complexes **19-21**, **23**. The
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8 single X-ray structure showed that the complexes **19-25** are iso-structural. Three η^2
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10 $(\text{PPh}_2)_2\text{N}^-$ ligands are coordinated to a metal center in a trigonal prismatic geometry.
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12 Within the ligand the P-N bond distance varies significantly. The ^{31}P NMR data shows a
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14 dynamic behavior of the ligand in solution. This is caused by rapid exchange of the two
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16 different phosphorus atoms [37, 44]. The lutetium complex **26** was prepared by the salt
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18 elimination in THF followed by crystallization in THF/pentane (Scheme 9). The solid
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20 state structure of **26** reveals a seven coordination sites around the lutetium center. Other
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22 than six coordination sites are occupied by three ligands, the seventh is by a THF
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24 molecule. This result suggests the $(\text{PPh}_2)_2\text{N}^-$ ligand is flexible in its coordination
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26 behavior [37].
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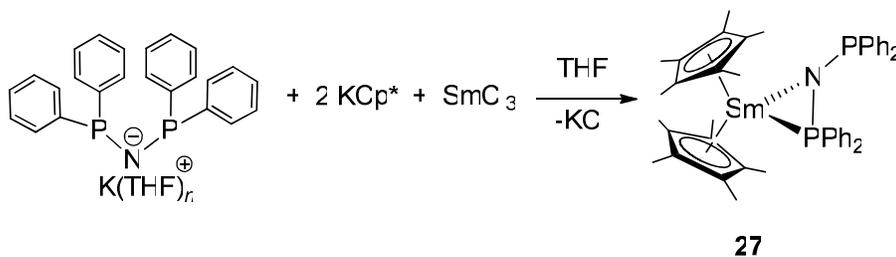
Scheme 9

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The homoleptic $(PPh_2)_2N^-$ ligand rare earth metal complexes **19-22** have been investigated for the polymerization of CL. All the complexes are highly active catalysts for the polymerization of CL at room temperature. With molar monomer/initiator ration of 150/1, **19-22** afforded corresponding polycaprolactone (PCL, $M_n = 17200-26200$) in 95-99 % yields within 1 min. Moderate polydispersity M_w/M_n (1.58-1.83) was observed with catalysts **19**, **20** and **22**. The neodymium complex **21** showed remarkable narrow polydispersity ($M_w/M_n = 1.12$). Based on the crystal structure of seven coordination complex **26**, we propose the initial step of CL polymerization is the lactone insertion to the lanthanide atom to form a seven coordination sphere around the central atom [37].

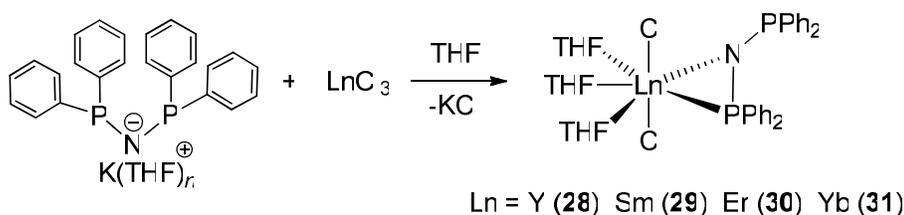
In order to further study the coordination behavior and the steric demanding of the $(PPh_2)_2N^-$ ligand, we prepared different categories of complexes, which contained one or two $(PPh_2)_2N^-$ groups.

The first heteroleptic $(PPh_2)_2N^-$ ligand lanthanide complex $[Cp^*_2Sm\{(PPh_2)_2N\}]$ ($Cp^* = \eta^5-C_5Me_5$) (**27**) was prepared via the salt elimination reaction of anhydrous $SmCl_3$ and $[K(THF)_n][N(PPh_2)_2]$ followed by an addition of KCp^* (Scheme 10) [45].



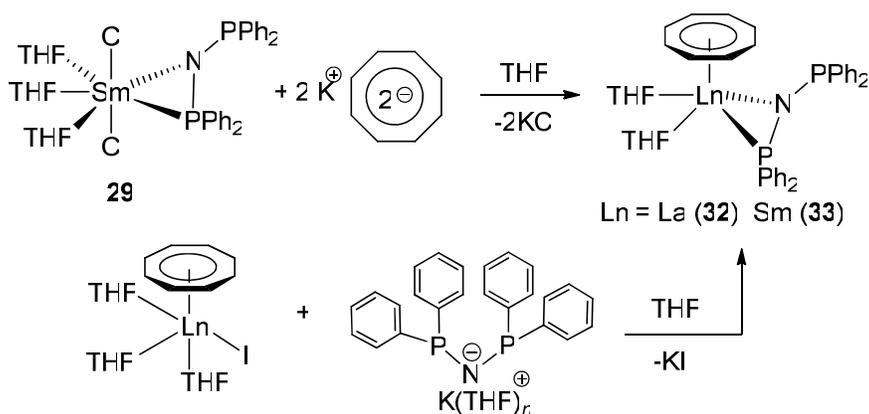
Scheme 10

The chloride complexes **28-31** containing mono substitute ligand were prepared by the salt elimination reaction of anhydrous LnCl_3 and $[\text{K}(\text{THF})_n][\text{N}(\text{PPh}_2)_2]$ (Scheme 11). The solid state structures of these complexes show a distorted pentagonal bipyramidal geometry, in which chlorine atoms are located in the apical positions [46].



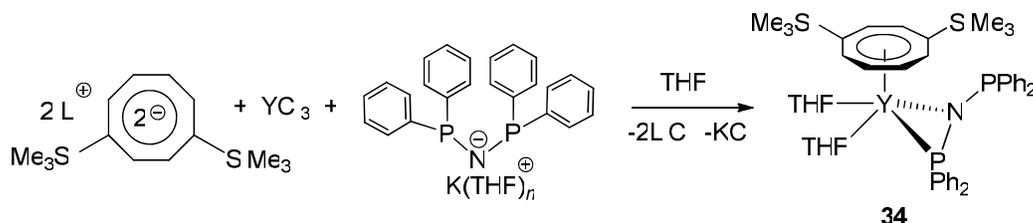
Scheme 11

The cyclooctatetraene complexes **32** and **33** can be obtained either by the reaction of the samarium mono ligand chloride complex **29** and $\text{K}_2\text{C}_8\text{H}_8$ or by the reaction of $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)(\text{THF})_3\text{I}]$ and $[\text{K}(\text{THF})_n][\text{N}(\text{PPh}_2)_2]$ (Scheme 12). The single crystal X-ray structure revealed that both complexes **32** and **33** adopt a four-legged piano-stool conformation [46].



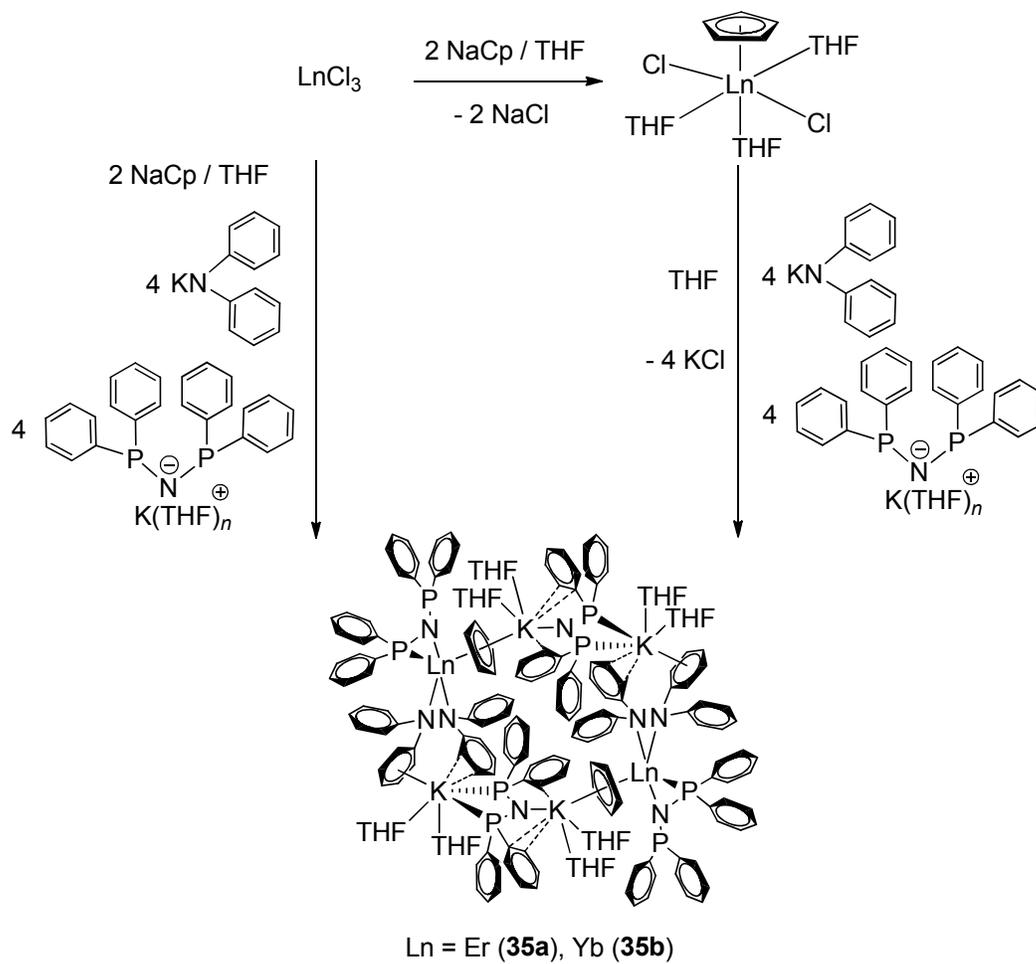
Scheme 12

The more soluble bistrimethylsilyl cyclooctatetrene complex **34** was prepared by the reaction of $\text{Li}_2[1,4-(\text{Me}_3\text{Si})_2\text{C}_8\text{H}_6]$ with anhydrous YCl_3 in THF followed by an addition of $[\text{K}(\text{THF})_n][\text{N}(\text{PPh}_2)_2]$ (Scheme 13). A triplet in the ^{89}Y NMR suggests the phosphorus atoms are chemically equivalent in solution [46].

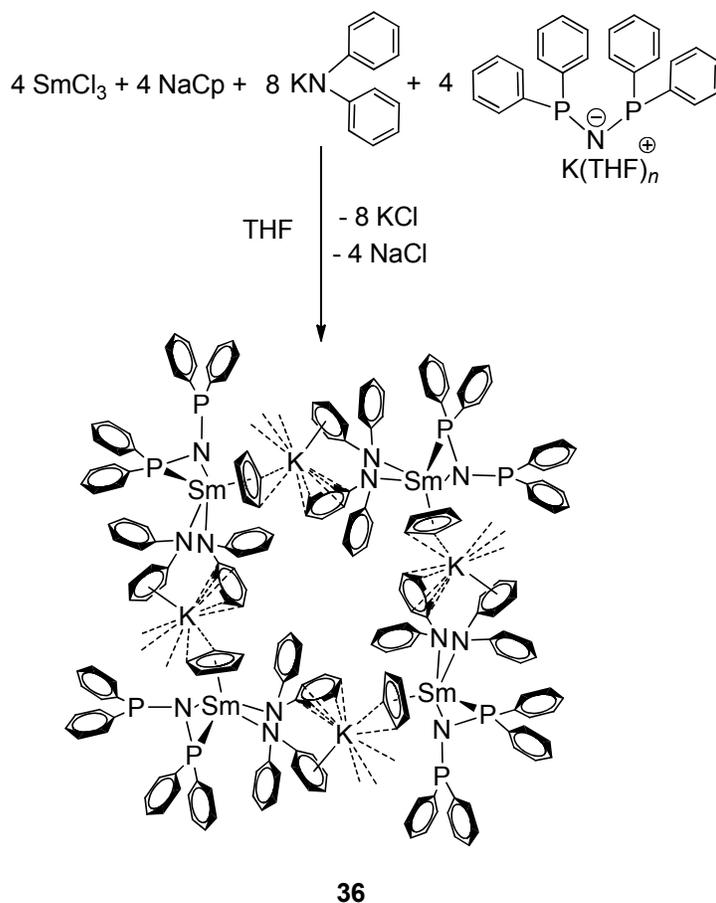


Scheme 13

Several mixed potassium-lanthanide complexes with an interesting wheel-shaped structure were obtained from the one pot reaction of anhydrous LnCl_3 , $[\text{K}(\text{THF})_n][\text{N}(\text{PPh}_2)_2]$, NaC_5H_5 and KNPh_2 in THF. $[\text{CpLn}(\text{NPh}_2)_2\{\text{N}(\text{PPh}_2)_2\}_2\text{K}_2(\text{THF})_4]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) ($\text{Ln} = \text{Er}$ (**35a**), Yb (**35b**)) are hexanuclear coordination oligomers (Scheme 14), while $[\text{CpSm}(\text{NPh}_2)_2\{\text{N}(\text{PPh}_2)_2\}_2\text{K}]_m$ (**36**) is an octanuclear coordination polymer (Scheme 15). These unusual complexes were formed as a result of the insufficient shielding of the lanthanide atom by the small ligands. These metallate complexes are connected to each other via the potassium ions. The potassium cations bridge the metallate units via π -coordination to the aromatic rings from the ligands, thus forming wheel-shaped oligomers and polymers. The shape of the “wheel” appears to depend on the lanthanide ionic radius [47].



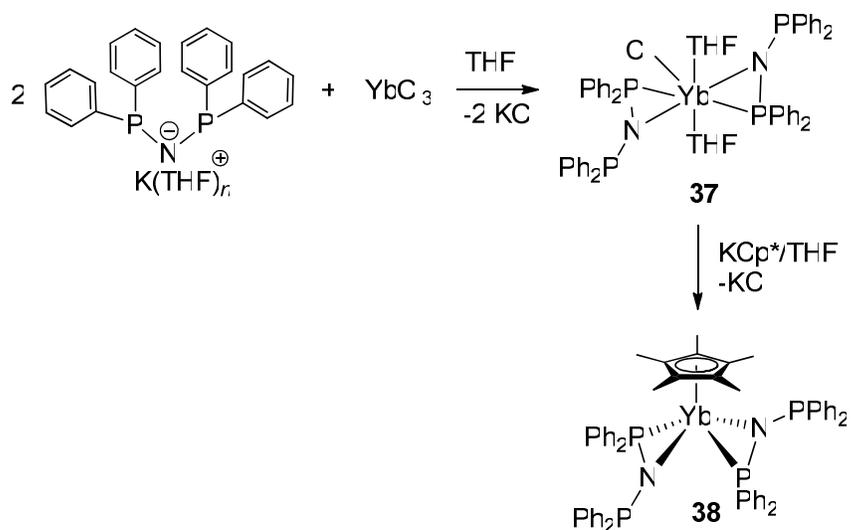
Scheme 14



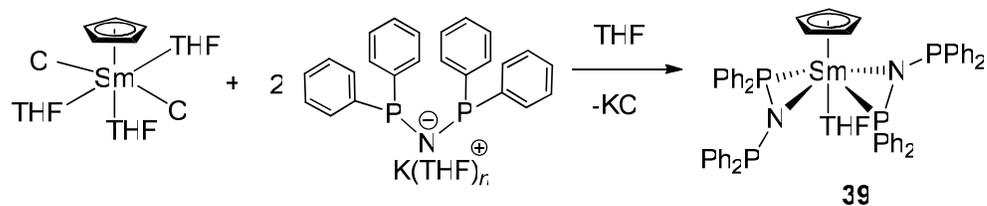
Scheme 15

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In 2004, we reported several bis (PPh₂)₂N⁻ ligand substitute rare earth metal complexes. [{(PPh₂)₂N}₂Yb(THF)₂Cl] (**37**) was synthesized by the reaction of YbCl₃ and a slightly excess of [K(THF)_n][N(PPh₂)₂] in THF. Further reacting **37** with KCp* afforded [{(PPh₂)₂N}₂YbCp*] (**38**) (Scheme 16). [{(PPh₂)₂N}₂SmCp(THF)] (**39**) was obtained by treating [CpSmCl₂(THF)₂] with 2 equiv of [K(THF)_n][N(PPh₂)₂] in THF (Scheme 17). A similar coordination of one THF molecule in [Cp₃Sm(THF)] indicates that the steric demand of (PPh₂)₂N⁻ ligand is similar to Cp ring [48].

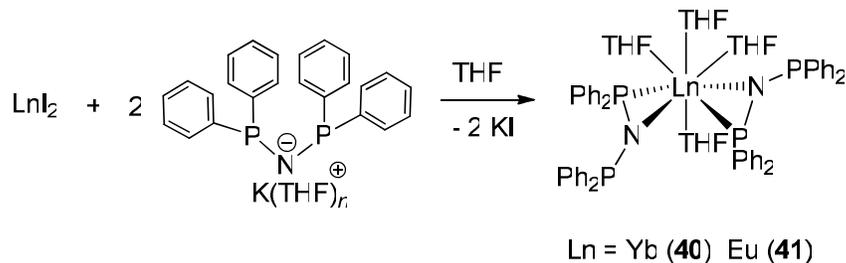


Scheme 16



Scheme 17

Recently we have applied the $(PPh_2)_2N^-$ ligand to divalent lanthanide complexes. $[(PPh_2)_2N]_2Ln(THF)_3$ ($Ln = Yb$ (**40**), Eu (**41**)) were prepared by the salt elimination reaction of LnI_2 and 2 equiv of $[K(THF)_n][N(PPh_2)_2]$ in THF (Scheme 18) [49, 50].



Scheme 18

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3 The solid state structure of the rare earth metal complexes containing the $(\text{PPh}_2)_2\text{N}^-$
4 group shows that the bidentate P-N ligand always coordinates to the metal center in a η^2
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6 fashion.
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10 11 12 13 **3. Conclusion**

14
15 Three types of $(\text{DIP}_2\text{pyr})^-$ ligand rare earth metal complexes including chlorides,
16 borohydrides, and mixed borohydride chloride were successfully prepared and fully
17 characterized. The borohydride complexes are the first examples of rare earth metals
18 borohydride complexes containing the $(\text{DIP}_2\text{pyr})^-$ ligand. An unusual redox reaction of a
19 BH_4^- anion with the Schiff-base function of the ligand was observed for the smaller rare
20 earth metal complexes. As product $[\{(\text{DIP})(\text{DIP-BH}_3)\text{pyr}\}\text{Ln}(\text{BH}_4)(\text{THF})_2]$ ($\text{Ln} = \text{Sc}, \text{Lu}$)
21 with a new coordination mode was isolated. In addition, the two neodymium complexes
22 **12** and **14** were investigated as Ziegler-Natta catalysts for the polymerization of 1,3-
23 butadiene to form poly-*cis*-1,4-butadiene with various cocatalysts. High activity and good
24 selectivity were achieved by using the chloride complex **12**.
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39 Mono-, bis- and tris- $(\text{PPh}_2)_2\text{N}^-$ ligand rare earth metal complexes were successfully
40 prepared and characterized. The bidentate P-N ligand coordinates to the metal center in a
41 η^2 fashion in all the cases. The homoleptic tris- $(\text{PPh}_2)_2\text{N}^-$ ligand complexes **19-22** are
42 highly active catalysts for the polymerization of CL. The neodymium complex **21**
43 showed remarkable narrow polydispersity.
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4. Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) Schwerpunktprogramm (SPP 1166): Lanthanoidspezifische Funktionalitäten in Molekül und Material.

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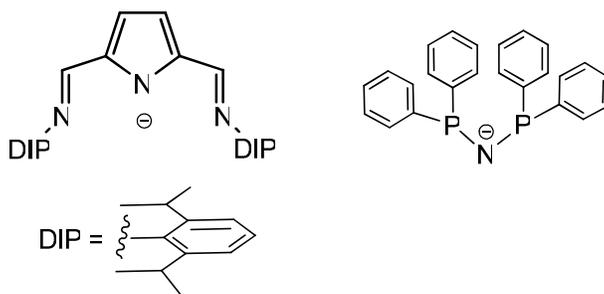
Biographical Sketch

Peter W. Roesky was born in Göttingen, Germany, in 1967. He obtained his diploma in 1992 from the University of Würzburg and his doctoral degree from the Technical University of Munich (with Prof. W. A. Herrmann) in 1994. He was as a postdoc with Prof. T. J. Marks at Northwestern University (1995-1996). In 1999 he completed his Habilitation at the University of Karlsruhe under the guidance of Prof. D. Fenske. As a full professor he joined the faculty of the Freie Universität Berlin in 2001. Since 2008 he holds the chair for inorganic functional material at the University of Karlsruhe. He received in 1996 a Liebig-Stipendium of the Fonds der Chemischen Industrie, in 1999 a Heisenberg-Stipendium, and in 2000 a Karl-Winnacker-Stipendium. His current research interest is focused on the synthesis of inorganic and organometallic compounds of the lanthanides, gold, zinc, and the alkaline earth elements for catalytic applications and for material science.



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Rare earth element complexes having the very bulky 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl, and the sterically less demanding bis(phosphanyl)amide ligand, (PPh₂)₂N⁻, in the coordination sphere are reviewed.



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