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Living Polymerization

Cationic Alkyl Rare-Earth Metal Complexes Bearing an Ancillary Bis(phosphinophenyl)amido Ligand: A Catalytic System for Living *cis*-1,4-Polymerization and Copolymerization of Isoprene and Butadiene**

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The creation of new polymer materials with well-controlled microstructures and desired properties relies on the development of new generations of polymerization catalysts. *cis*-1,4-Regulated polyisoprene (PIP) and polybutadiene (PBD) are among the most important elastomers used for tires and other elastic materials. As the demand for high-performance synthetic rubbers has increased, the development of high-quality elastomers by polymerization of isoprene and butadiene has grown in importance. In addition, the limited supply of natural rubber has promoted the need for improved synthetic polyisoprene.[1]

To date a variety of catalyst systems have been reported for the polymerization of butadiene and isoprene, among which catalysts based on rare-earth metals have attracted special attention because of their high activity and high *cis*-1,4 selectivity.[2] The catalysts utilized industrially for the *cis*-1,4 polymerization of butadiene and isoprene are heterogeneous Ziegler–Natta-type multicomponent systems that consist typically of a rare-earth metal (e.g., Nd) carboxylate, ethylaluminum chloride, and isobutylaluminum hydride.[2a–c]

To mimic and improve the industry catalyst systems, and to gain a better understanding of the mechanistic aspects of these heterogeneous catalysts, various discrete rare-earth metal carboxylate and alkoxide complexes as well as rare-earth metal/aluminum heterometallic alkyl complexes have been investigated.[3] Some of these molecular systems show very high *cis*-1,4 selectivity (up to 99 %) when combined with a chloride additive, such as Et_2AlCl. However, similar to the heterogeneous industrial catalysts, such binary or ternary catalyst systems generally lack "livingness" and yield polymers with rather broad molecular-weight distributions. On the other hand, lanthanide metallocene-based catalyst systems, such as $[(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2]/Al(i\mathrm{Bu})_3/[Ph_3C][B(C_6F_5)_4]$,[4b] have been found to afford polymers with both high *cis*-1,4 selectivity (up to 99 %) and a narrow molecular-weight distribution, or "livingness" ($M_w/M_n = 1.20$–1.23), in the polymerization of butadiene under appropriate conditions,[4] however, the polymerization of isoprene has not been achieved in a "living" fashion with such catalyst systems.[4f] Very recently, the combination of a Nd/Mg heterotrimetallic allyl complex with methylaluminoxane (MAO) was reported to show both high *cis*-1,4 selectivity (95–99 %) and a relatively narrow molecular-weight distribution ($M_w/M_n = 1.3$–1.7) for the polymerization of isoprene.[5,6]

A common feature in the reported catalyst systems is that they all require an aluminum additive, such as AlR_2Cl, AlR_3, or MAO, to show high activity and high *cis*-1,4 selectivity, which makes it difficult to identify the true catalytic species and to understand the mechanistic aspects of the polymerization process.[2–8] Recently, cationic methylyttrium species, such as $[YMe_{2-n}(\mathrm{solv})_x]^{n+1}$ ($n = 0, 1$; solv = solvent), have been reported to show activity for the polymerization of butadiene and isoprene in the absence of an aluminum additive, but the use of a bulky alkyl aluminum additive, such as $Al(i\mathrm{Bu})_3$, was again essential to achieve significant *cis*-1,4 selectivity (67 % vs. 90 % for isoprene polymerization with and without $Al(i\mathrm{Bu})_3$, respectively).[9] A related aluminum-free cationic alkyl yttrium species bearing silylene-linked cyclopentadienylphosphido ligands shows exclusive 3,4-selectivity for the polymerization of isoprene, while a cationic alkyl yttrium species bearing the $C_5Me_4SiMe_3$ ligand yields a mixture of 3,4- and 1,4-polyisoprenes under similar conditions.[10] The search for more selective, simpler, and better-controlled catalyst systems for the *cis*-1,4 polymerization and copolymerization of isoprene and butadiene is therefore of interest and importance.

Herein we report a new catalyst system based on a cationic alkyl rare-earth metal species bearing an ancillary bis(phosphinophenyl)amido (PNP) ligand. This catalyst system provides extremely high *cis*-1,4 selectivity (99 %) and excellent livingness ($M_w/M_n = 1.05$–1.13) with no need for an aluminum additive to show high activity and high selectivity for the polymerization of isoprene and butadiene, and can also be applied to the copolymerization of isoprene and butadiene in a living *cis*-1,4 fashion. The isolation and structural characterization of a related cationic alkyl lutetium complex $[(PNP^{Ph})Lu(CH_2SiMe_3)(thf)_2][B(C_6F_5)_4]$ ($PNP^{Ph} = \{2\text{-}(Ph_2P)C_6H_4\}_2N$) is also described as this is a suitable structural model complex for the true active species and for the mechanistic understanding of the polymerization process.

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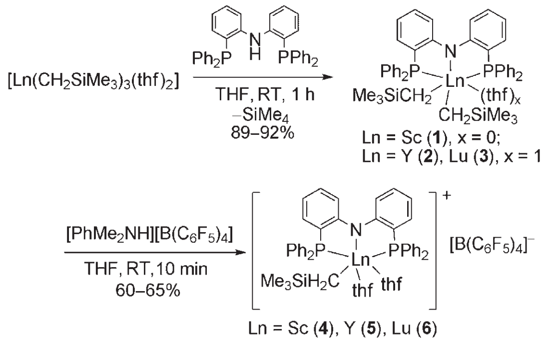
Our interest in the PNP-ligated cationic alkyl rare-earth metal species stems from our recent studies on the use of cationic half-sandwich (mono-cyclopentadienyl) rare-earth metal complexes in olefin polymerization.[10,11] Although late transition-metal complexes containing PNP ligands have received much interest recently,[12] studies on PNP-ligated rare-earth metal complexes remain very limited.[13] Analogous to the synthesis of half-sandwich rare-earth metal bis(alkyl) complexes,[10,11] the acid/base reaction of the tris(alkyl) complexes [Ln(CH$_2$SiMe$_3$)$_3$(thf)$_2$] with one equivalent of (2-(Ph$_2$P)C$_6$H$_4$)$_2$NH[12a] gave the corresponding bis(alkyl) complexes [(PNP$^{\text{Ph}}$)Ln(CH$_2$SiMe$_3$)$_2$(thf)$_x$] (**1**: Ln = Sc, $x=0$; **2**: Ln = Y, $x=1$; **3**: Ln = Lu, $x=1$) in a straightforward manner in high yields (Scheme 1). The Y and Lu complexes **2** and **3** contain a thf ligand, while the smaller Sc complex **1** is thf-free, as confirmed by ^{1}H NMR spectroscopy and elemental analysis. The structure of the Lu complex **3** was further confirmed by an X-ray crystallographic analysis, which revealed that **3** adopts a distorted octahedral structure in which the tridentate PNP$^{\text{Ph}}$ ligand is arranged in a facial fashion (Figure 1).[14] This structural feature is in contrast to the situation observed in related late transition-metal complexes, where the PNP$^{\text{Ph}}$ ligand usually adopts a meridional form.[12b,c,e,j] The ^{31}P{^{1}H} NMR spectrum of complex **2** in C$_6$D$_6$ and [D$_8$]THF shows a doublet at $\delta = -11.60$ ($J_{\text{Y,P}} = 38$ Hz) and -11.63 ppm ($J_{\text{Y,P}} = 31$ Hz), respectively, which suggests that the Y–P bonds in **2** are retained in both solvents.



Scheme 1. Synthesis of neutral and cationic rare-earth-metal alkyl complexes bearing a bis(2-diphenylphosphinophenyl)amido (PNP$^{\text{Ph}}$) ligand.

Monitoring the reactions of **1**–**3** with one equivalent of [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Cl at 25 °C by ^{1}H NMR spectroscopy showed the instant disappearance of the signals for **1**–**3**, quantitative formation of SiMe$_4$ and PhMe$_2$N, and the appearance of new signals assignable to [(PNP$^{\text{Ph}}$)Ln(CH$_2$SiMe$_3$)(thf)$_x$]$^+$ ($x = 0$, 1). However, such cationic alkyl species are unstable and decompose rapidly in C$_6$D$_5$Cl. When the reactions were carried out in THF, however, the corresponding bis(thf)-coordinated cationic alkyl complexes [(PNP$^{\text{Ph}}$)Ln(CH$_2$SiMe$_3$)(thf)$_2$][B(C$_6$F$_5$)$_4$] (Ln = Sc (**4**), Y (**5**), Lu (**6**)) could be isolated (Scheme 1). These cationic alkyl species are more stable, and single crystals of the Lu complex **6** could be grown from chlorobenzene/hexane at −30 °C. An X-ray diffraction study revealed that **6** is a separated ion pair in which the [(PNP$^{\text{Ph}}$)Lu(CH$_2$SiMe$_3$)(thf)$_2$]$^+$ ion adopts a distorted octahedral structure similar to that of its neutral precursor **3** (Figure 2).[14] The Lu–P (av. 2.888(2) Å) and Lu–N bond lengths (2.258(7) Å) in **6** are significantly shorter than those in **3** (2.9431(9) and 2.342(3) Å, respectively), thus indicating that the interactions between the PNP$^{\text{Ph}}$ ligand and the metal center in the cationic species **6** are stronger than those in the neutral precursor **3**.

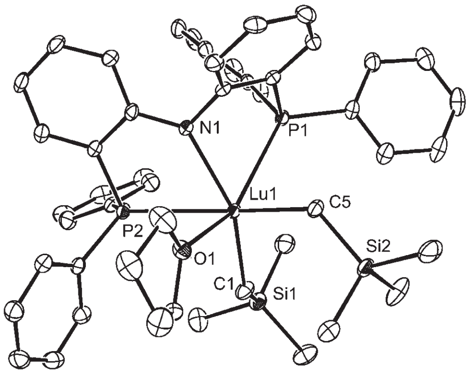


Figure 1. ORTEP structure of **3** with thermal ellipsoids set at 30% probability. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1–N1 2.342(3), Lu1–P1 2.9096(9), Lu1–P2 2.9765(9), Lu1–C1 2.354(3), Lu1–C5 2.385(3), Lu1–O1 2.278(2); C1-Lu1-C5 103.50(12), N1-Lu1-P1 65.42(7), N1-Lu1-P2 66.23(7), P1-Lu1-P2 102.76(2).

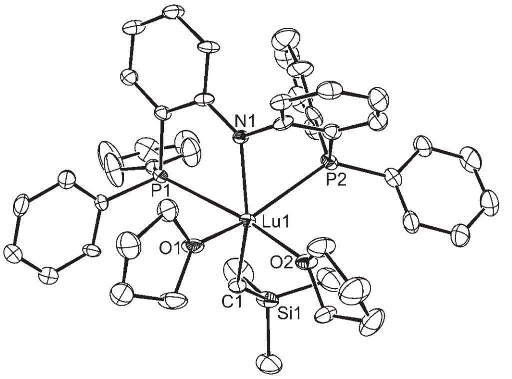
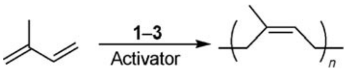


Figure 2. ORTEP structure of **6** with thermal ellipsoids set at 30% probability. Hydrogen atoms, the [B(C$_6$F$_5$)$_4$] anion, and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1–N1 2.258(7), Lu1–P1 2.871(2), Lu1–P2 2.904(2), Lu1–C1 2.336(8), Lu1–O1 2.294(6), Lu1–O2 2.255(6); C1-Lu1-O1 95.4(3), O1-Lu1-N1 111.0(2), N1-Lu1-P2 68.03(18), P2-Lu1-C1 109.0(2), P2-Lu1-P1 106.67(7).

The cationic alkyl species generated in situ upon treatment of **1**–**3** with one equivalent of [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Cl show excellent activity for the polymerization of isoprene, although they are not stable enough to be isolated. Addition of 600 equivalents of isoprene to a mixture of **2** and [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] in C$_6$H$_5$Cl at room temperature afforded polyisoprene quantitatively in one hour (Table 1, run 3). More remarkably, the resultant polymer showed a very

Table 1: Living *cis*-1,4-polymerization of isoprene (IP).[a]



Run	Cat.	T_p [°C]	t [min]	Yield [%]	M_n[b] ($\times 10^5$)	M_w/M_n[b]	Structure[c] *cis*-1,4-	Structure[c] 3,4-	T_g[d] [°C]	Eff.[e] [%]
1	**1**–**3**	RT	60	0						
2	**1**/**A**[f]	RT	60	100	1.6	1.10	96.5	3.5	−66	26
3	**2**/**A**[f]	RT	60	100	2.3	1.10	99.3	0.7	−69	18
4	**3**/**A**[f]	RT	60	100	1.9	1.09	97.1	2.9	−67	22
5	**2**/**B**[f]	RT	60	79	3.2	1.11	99.3	0.7	−69	10
6	**2**/**C**[f]	RT	60	0						
7	**2**/**A**[g]	RT	10	40	0.5	1.05	99.3	0.7	−69	33
8	**2**/**A**[g]	RT	15	90	1.0	1.05	99.3	0.7	−69	37
9	**2**/**A**[g]	RT	20	100	1.2	1.07	99.3	0.7	−69	34
10	**2**/**A**[g,h]	RT	40	150	1.8	1.08	99.3	0.7	−69	34
11	**2**/**A**[g,h]	RT	60	200	2.3	1.08	99.3	0.7	−69	36
12	**2**/**A**[g]	0	180	100	1.3	1.06	99.6	0.4	−69	31
13	**2**/**A**[i]	50	10	90	0.7	1.05	98.7	1.3	−68	53
14	**2**/**A**[i,j]	50	20	188	1.4	1.05	98.7	1.3	−68	55
15	**2**/**A**[i]	80	2	66	0.6	1.05	98.5	1.5	−68	45
16	**2**/**A**[i]	80	5	100	0.8	1.05	98.5	1.5	−68	51

[a] Conditions: C_6H_5Cl (10 mL); Ln (25 μmol); $[IP]_0/[Ln]_0 = 600$; $[Ln]_0/[activator]_0 = 1{:}1$ (activator = $[PhMe_2NH][B(C_6F_5)_4]$ (**A**), $[Ph_3C][B(C_6F_5)_4]$ (**B**), $B(C_6F_5)_3$ (**C**)), unless otherwise noted. [b] Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard. [c] Determined by ^{1}H and ^{13}C NMR spectroscopy. [d] Measured by differential scanning calorimetry (DSC). [e] Catalyst efficiency = M_n(calculated)/M_n(measured). [f] In runs 2–6, IP was added to a mixture of **2** and the activator. [g] In runs 7–12, a C_6H_5Cl solution of activator **A** was added to a solution of the neutral complex and IP. [h] After polymerization of 1.022 g (600 equiv) of IP for 30 min, another 1.022 g of IP was added and the mixture was stirred for a further 10 (run 10) or 30 min (run 11). [i] In runs 13–16, a mixture of **2** and IP in C_6H_5Cl (3 mL) was added to a preheated C_6H_5Cl solution (7 mL) of **A**. [j] $[IP]_0/[\mathbf{2}]_0 = 1200$.

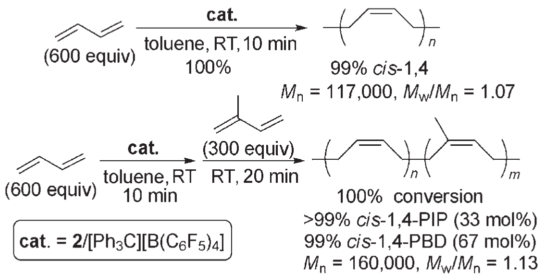
high *cis*-1,4 content (99.3%) and very narrow molecular-weight distribution ($M_w/M_n = 1.10$). No evidence for *trans*-1,4 polyisoprene was observed. Similarly, the Sc and Lu complexes **1** and **3** also show high activity and excellent livingness for the polymerization of isoprene, albeit with slightly lower *cis*-1,4 selectivity (96.5–97.1%; Table 1, runs 2 and 4). In contrast, complexes **1**–**3** in the absence of activator and the bis(thf)-coordinated cationic complexes **4**–**6** are not active under the same conditions. These results suggest that the true active species in the present catalyst systems should be a cationic alkyl species similar to $[(PNP^{Ph})Ln(CH_2SiMe_3)(thf)_x]^+$ ($x \leq 1$) with one or fewer thf ligands per metal center.

Complex **2** was then examined further as a catalyst precursor for the polymerization of isoprene under various conditions. When the polymerization was carried out by adding the activator $[PhMe_2NH][B(C_6F_5)_4]$ to a mixture of the neutral complex **2** and isoprene, the catalyst efficiency and activity were found to be almost twice as high as with the polymerization reaction that involves addition of isoprene to a pre-generated cationic species, while the molecular-weight distribution of the resultant polymers became even narrower ($M_w/M_n = 1.05$–1.07; Table 1, runs 7–9). As the isoprene conversion increased, the molecular weight of the resulting polymers also increased linearly (Table 1, runs 7–11). Addition of another 600 equivalents of isoprene to a completed polymerization mixture yielded a polymer with almost double the molecular weight and sustained high *cis*-1,4 selectivity (99.3%) and narrow molecular-weight distribution ($M_w/M_n = 1.07$–1.08; Table 1, runs 9 and 11). More remarkably, the excellent "livingness" and the high *cis*-1,4 selectivity of the present polymerization system are maintained even at high temperatures ($M_w/M_n = 1.05$–1.08, *cis*-1,4 selectivity > 98.5%, at 50–80°C; Table 1, runs 13–16). As far as we are aware, this is the first example of well-defined, living *cis*-1,4 polymerization of isoprene, and also a rare example of a stereospecific, living polymerization of any olefin monomer at high temperature. These results suggest that although the PNP^{Ph}-supported cationic alkyl species generated by the reaction of **2** with $[PhMe_2NH][B(C_6F_5)_4]$ in C_6H_5Cl is not stable and might decompose rapidly in the absence of isoprene, the corresponding PNP^{Ph}-supported cationic η^3-π-butenyl species formed by the reaction of the alkyl species with isoprene is thermally stable.

The present catalyst system was also used for the living *cis*-1,4 polymerization of butadiene and living *cis*-1,4 copolymerization of butadiene and isoprene to give the corresponding polymers with extremely high *cis*-1,4 content (99%) and very narrow molecular weight distribution ($M_w/M_n \leq 1.13$), as shown in Scheme 2.[15]

To gain insight into the origin of the exclusive *cis*-1,4 selectivity exhibited by the present polymerization system,[9,10] the cationic alkyl scandium species $[(PNP^{Ph})Sc(CH_2SiMe_3)]^+$ was chosen as a model for a computational study, which showed that coordination of isoprene to the Sc center in a *cis*-1,4 fashion is around 5–7 kcal mol^{-1} more favored than that in a 3,4-fashion; *trans*-1,4 coordination is not accessible. The geometry (or sterics) of the PNP^{Ph} ancillary ligand therefore seems to play an important role in determining the regio- and stereoselectivity.[16]

In summary, we have demonstrated that a cationic rare-earth metal alkyl species bearing a PNP ancillary ligand, generated by treatment of the corresponding dialkyl com-



Scheme 2. Living *cis*-1,4-polymerization of butadiene (BD) and its block copolymerization with isoprene (IP).

plexes, such as **2**, with one equivalent of a borate compound, such as $[PhMe_2NH][B(C_6F_5)_4]$, can serve as an excellent catalyst for the living *cis*-1,4 polymerization of both isoprene and butadiene as well as for the living *cis*-1,4 copolymerization of isoprene and butadiene. This system affords, for the first time, polyisoprene, polybutadiene, and poly(isoprene-*b*-butadiene) with both an extremely high *cis*-1,4 content (ca. 99%) and an extremely narrow molecular-weight distribution ($M_w/M_n = 1.13$). Such excellent selectivity and livingness can be maintained even at elevated temperatures (up to 80 °C), which is a rare, although not the first, example of stereospecific, living polymerization at high temperature. The isolation and structural characterization of the cationic alkyl lutetium complex **6** have provided a suitable structural model for the active species and for understanding the mechanistic aspects of the polymerization process. The present catalyst system is thus the best defined system for the exclusive *cis*-1,4 polymerization and copolymerization of isoprene and butadiene, as far as we are aware. Studies on the polymerization and copolymerization of dienes and other olefin monomers by this, and related, catalyst systems are in progress.

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[14] CCDC-616257 (**3**) and CCDC-616258 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] To obtain reproducible results in butadiene polymerization, the commercial butadiene should be purified very carefully. Typically, butadiene was first stirred with a small amount (0.5–1 mol %) of $\mathrm{Al}(i\mathrm{Bu})_3$ in toluene for 10 min, and then the neutral complex **2** and a borate compound, such as $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$, were added.

[16] The absence of *trans*-1,4-polyisoprene in the present polymerization may suggest that the *anti-syn* isomerization of an η^3-π-butenyl species, which has been observed in other catalyst systems, does not occur here. For a theoretical study of Ni-catalyzed butadiene polymerization, see: S. Tobisch, *Acc. Chem. Res.* **2002**, *35*, 96–104.