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Between Enamide and Azaallyl Structures: Novel Flexible N-Chelate Ligands in the Lanthanide Chemistry

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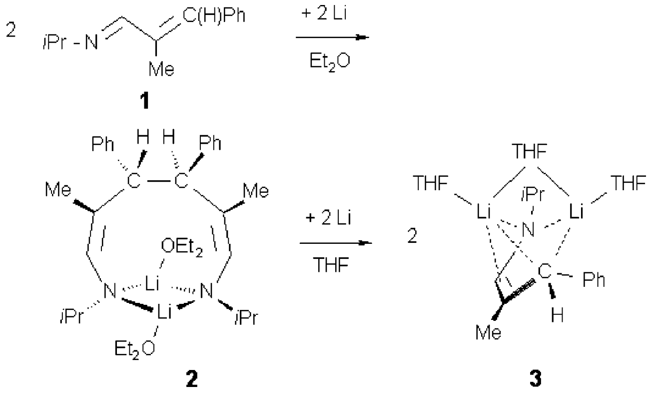
Summary: Novel types of hexa-1,5-diene-1,6-diamide neodymium complexes were prepared from the corresponding neodymium bromide $NdBr_3(THF)_{3.5}$ with the appropriate dilithium hexa-1,5-diene-1,6-diamide reagent. The molecular structures of the new complexes revealed that the chelating hexa-1,5-diene-1,6-diamide can be bound either as an enamide or as an azaallyl-type ligand.

Several lanthanide compounds are known to catalyze the polymerization of olefins.[1] These are mainly metallocene complexes, as so far the development of the lanthanide chemistry has been associated with the use of stabilizing Cp and Cp* ligands.[2] Inspired by work on the very high polymerization activity of titanium and other transition-metal complexes with dianionic bis(amide) ligands,[3] recently a growing interest has also been directed toward lanthanide complexes with polydentate amide ligands.[4] In comparison with the well-established metallocene-based catalysts, those based on amide complexes have advantages, because their complex centers are often coordinatively unsaturated and therefore are exposed to lower steric strain and have a higher Lewis acidity.[5] Moreover, the steric and electronic situation at the metal center can be selectively influenced by variation of the ligand substituents, even though the coordination geometry is mostly predetermined by the limited flexibility of the polydentate diamide ligands.

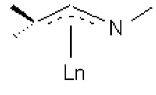
Scheme 1. Course of the Reaction of the 1-Aza-1,3-diene 1 with Lithium



Recently we reported on the reduction of the 1-aza-1,3-diene **1** to the 1-azabut-2-ene-1,4-diyl dianion **3**, where—initially unexpected but nearly quantitatively—the dilithium hexa-1,5-diene-1,6-diamide **2** was generated as an intermediate during the course of the reaction (Scheme 1).[6]

However, it is the 2-fold enamide structure rather than the exceptional preparative approach that makes **2** such an interesting novel ligand system for the chemistry of lanthanides: different from alkyl-bridged diamide ligands, **2** also offers, in addition to the amide functions, π-electron systems for the ligand metal bonding. Thus, depending on the steric and electronic situation at the complex center, the hexa-1,5-diene-1,6-diamide **2** with both ligand termini can be bound either as an enamide ligand (**a**, η^1- or σ-azaallyl) or as an azaallyl ligand (**b**, η^3- or π-azaallyl).[7]

a



b

In the following we will demonstrate that in novel neodymium complexes this flexible bonding behavior is actually realized. Here we report for the first time on the syntheses and structures of these complexes and also on their suitability as catalysts for the polymerization of buta-1,3-diene.

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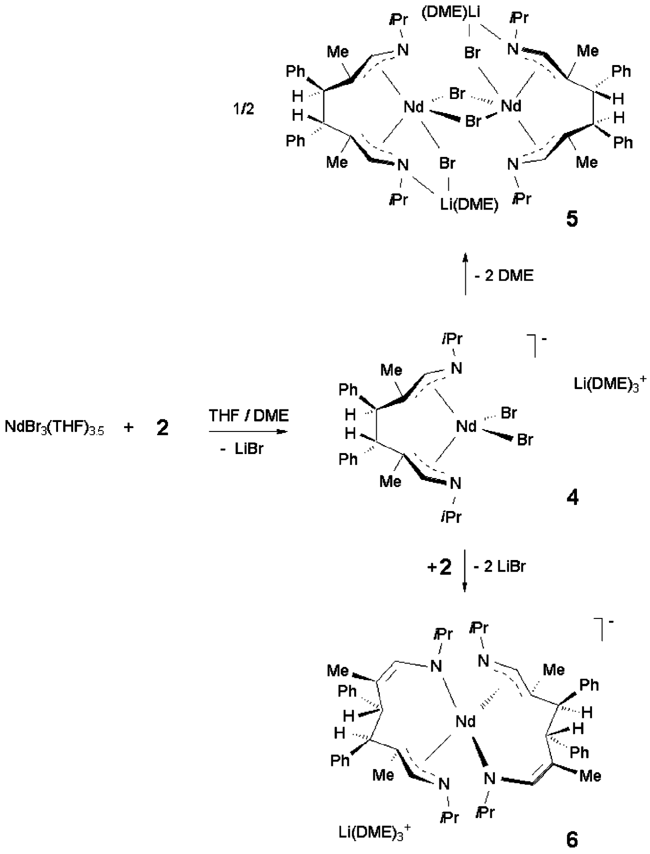
Scheme 2. Synthesis of the Hexa-1,5-diene-1,6-diamide Neodymium Complexes 4−6



Treatment of $NdBr_3(THF)_{3.5}$ with 1 equiv of the dilithium hexa-1,5-diene-1,6-diamide compound **2** in THF as solvent led to the formation of the very air- and moisture-sensitive (hexa-1,5-diene-1,6-diamide)neodymium complex **4** in 65% yield (Scheme 2). Corresponding to its ionic constitution, **4** is very soluble in THF and DME but only moderately soluble in diethyl ether. Nearly colorless crystals of a monoclinic as well as of a triclinic modification were obtained by recrystallization from THF.[8] Unfortunately, in both cases the crystals were not of high quality, but the main features of their structures, which are very similar, could be clearly identified.

As expected, the hexa-1,5-diene-1,6-diamide (Figure 1) is coordinated as an ethylene-bridged bis(π-azaallyl) chelate ligand using the two amide functions N1 and N2 as well as the adjacent π-systems C1=C2 and C5=C6, respectively, for bonding to the neodymium. The charge centers of the π-azaallyl units and the two bromide ligands define the tetrahedral coordination geometry around the neodymium, which meets the common structural pattern known from most of the lanthanide metallocene complexes.[2] Unfortunately, the ^{1}H NMR spectra of **4** and the other neodymium complexes reported here are uninformative, due to their very broad low-intensity resonances combined with a strong paramagnetic shift.

Surprisingly, as a result of our efforts to improve the crystal quality of the neodymium complex **4** by repeated recrystallization from DME, the solubility of the complex increased significantly. After prolonged standing at −10 °C colorless crystals precipitated again. The X-ray structure analysis now reveals the dimeric neodymium complex **5** bridged by two bromide ligands (Figure 2).[8]

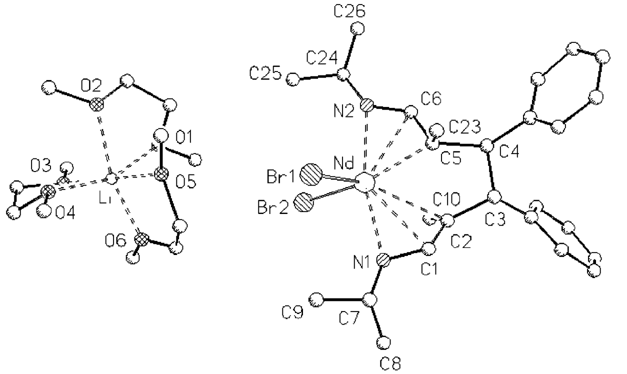


Figure 1. Molecular structure and numbering scheme of **4**. The hydrogen atoms have been omitted for clarity. Due to the poor crystal quality, a listing of bond lengths and angles was abandoned.

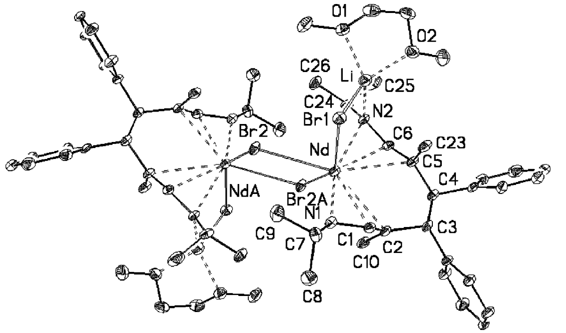


Figure 2. Molecular structure of **5**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd−Br1 = 2.9186(5), Nd−Br2 = 3.0021(5), Nd−N1 = 2.352(4), Nd−N2 = 2.553(4), Li−Br1 = 2.597(9), Li−N2 = 2.043(9), Nd−C1 = 2.698(4), Nd−C2 = 2.864(4), Nd−C5 = 2.938(5), Nd−C6 = 2.704(5), N1−C1 = 1.374(6), N2−C6 = 1.383(5), C1−C2 = 1.360(6), C2−C3 = 1.526(6), C3−C4 = 1.541(6), C4−C5 = 1.546(5), C5−C6 = 1.360(6); Br1−Nd−Br2 = 79.47(1), Br1−Nd−Br2A = 145.29(1), Br2−Nd−Br2A = 73.18(1), Nd−Br1−NdA = 106.82(1), N1−Nd−N2 = 157.2(1), N1−C1−C2 = 124.0(4), N2−C6−C5 = 125.7(4), C2−C3−C4−C5 = 52.8(4).

Probably the dimerization of **4** can be ascribed to the high Lewis acidity of the neodymium additionally promoted by its low coordination number. However, the loss of DME in the course of the crystallization of **5** results in a situation different from that in **4**, since the Li^+ ions are no longer completely surrounded by solvent molecules. Instead, the Li^+ ions are closely bound to the terminal bromide ligands Br2 and Br2A, respectively (Li−Br = 2.597(9) Å), as well as to the amide functions N2 and N2A, respectively (Li−N2 = 2.043(9) Å).

These contacts lead to elongated Nd−N2 and NdA−N2A bonds, respectively (Nd−N2 = 2.553(4) Å), in contrast to Nd−N1 (2.352(4) Å), but the η^3 coordination of the two π-azaallyl units of the hexa-1,5-diene-1,6-diamide ligand is maintained. In any event, the differences between the Nd−C bonds (Nd−C1 = 2.698(4) Å and the Nd−C2 = 2.864(4) Å or Nd−C6 = 2.704(5) Å and Nd−C5 = 2.938(5) Å, respectively) are striking. They indicate that the η^3-azaallyl coordination in **5**

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differs markedly from that of a symmetrical π-coordination as is found, for example, in the (η^3-allyl)neodymium complexes (η^3-C_3H_5)$_3$Nd(DME)[9a] and [(η^3-C_3H_5)$_2$Nd(μ-Cl)(THF)]$_2$.[9b] On the other hand, the bond distances and angles largely agree with those of the, to our knowledge, only structurally characterized (η^3-azaallyl)lanthanide complexes, [$Me_3SiCHC(t$Bu)N(SiMe$_3$)]$_2$SmI(THF) and [$Me_3SiCHC(t$Bu)N(SiMe$_3$)]$_2$Yb,[10] whose π-azaallyl ligands, however, are not connected by an alkyl bridge.

When the mole ratio of the two reactants **2** and NdBr$_3$(THF)$_{3.5}$ was increased to 2:1, then the nearly colorless, air- and moisture sensitive neodymium complex **6** was obtained in 75% yield (Scheme 2). Complex **6** can be formally considered as a derivative of the ionic compound **4**, in which the two bromine ligands are substituted by a second hexa-1,5-diene-1,6-diamide ligand. Therefore, it is not much of a surprise that, at least in the crystalline state, the [(hexa-1,5-diene-1,6-diamide)$_2$Nd]$^-$ anion and the [Li(DME)$_3$]$^+$ cation exist—much like in the case of **4**—as a solvent-separated ion pair (Figure 3).[8]

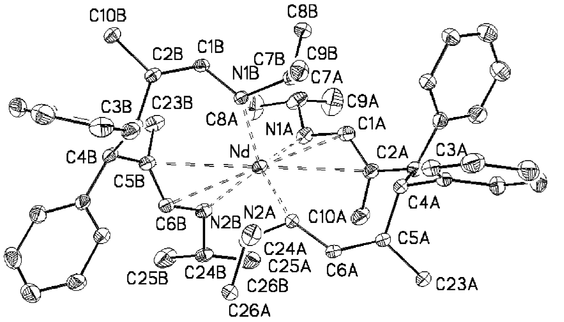

Figure 3. Molecular structure of the anion of **6**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd−N1A = 2.393(3), Nd−N2A = 2.364(3), Nd−N1B = 2.380(3), Nd−N2B = 2.397(3), Nd−C1A = 2.842(4), Nd−C2A = 3.170(4), Nd−C5B = 3.101(4), Nd−C6 = 2.834(4), N1A−C1A = 1.370(5), N2A−C6A = 1.374(5), C1A−C2A = 1.358(6), C2A−C3A = 1.519(6), C3A−C4A = 1.558(6), C4A−C5A = 1.523(5), C5A−C6A = 1.337(5), N1B−C1B = 1.382(4), N2B−C6B = 1.368(5), C1B−C2B = 1.335(5), C2B−C3B = 1.520(5), C3B−C4B = 1.560(5), C4B−C5B = 1.525(5), C5B−C6B = 1.356(5); N1A−Nd−N2A = 124.4(1), N1B−Nd−N2B = 125.8(1), N1A−C1A−C2A = 124.3(4), N2A−C6A−C5A = 129.1(4), N1B−C1B−C2B = 128.5(3), N2B−C6B−C5B = 124.1(4).

Due to the limited space in the coordination sphere of the metal center, the two hexa-1,5-diene-1,6-diamide ligands are forced into the more space-saving enamide function (η^1- and σ-azaallyl, respectively), each at the expense of one η^3-azaallyl function. As a consequence thereof, the configuration of the double bonds C5A═C6A and C1B═C2B changes from *E* to *Z* and thus prevents an increase of the ring tension. The result of the crystal structure analysis furthermore indicates that the Nd−C distances of the other two η^3-azaallyl units are slightly longer than those of **5** (Nd−C1A = 2.842(4) Å, Nd−C2A = 3.170(4) Å, Nd−C6 = 2.834(4) Å, Nd−C5B = 3.101(4) Å). However, the bonding mode of the hexa-1,5-diene-1,6-diamide ligands in **6** is still best described as η^3-azaally η^1-enamide bonding.

Ziegler−Natta catalysts containing neodymium have been used in the industrial production of poly-*cis*-1,4-butadiene for some time now.[11] The above-mentioned (η^3-allyl)neodymium complexes (η^3-C_3H_5)$_3$Nd(dioxane)[9a] and [(η^3-C_3H_5)$_2$Nd(μ-Cl)(THF)]$_2$ [9b] as well as (η^3-C_3H_5)NdCl$_2$(THF)$_2$ [9b] have actually been shown to be extremely active and highly selective complex catalysts for the 1,4-cis polymerization of buta-1,3-diene. To obtain preliminary information about the catalytic activity of the novel azaallyl neodymium complexes **4** and **6**, polymerization of buta-1,3-diene was conducted with them using MMAO as cocatalyst (molar ratio of about 0.1:30) and cyclohexane as the solvent at 80 °C. For comparison we also studied the hexa-1,5-diene-1,6-diamide lanthanum complex **7**, whose structure was established by ^{1}H NMR and resembles that of **5** (see Experimental Section). The results of the polymerization experiments are listed in Table 1. As expected, the coordinatively less saturated

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[8] (a) *Crystal data for* **4**. *Modification I*: [$C_{12}H_{30}O_6Li$]$^+$[$C_{26}H_{34}Br_2N_2Nd$]$^-$, $M_r = 955.91$, colorless prism, size $0.10 \times 0.08 \times 0.06$ mm^3, monoclinic, space group $P2_1$, $a = 12.1509(3)$ Å, $b = 28.9797(8)$ Å, $c = 12.8885(3)$ Å, $\beta = 96.685(2)°$, $V = 4507.6(2)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.409$ g cm^{-3}, μ(Mo Kα) = 29.65 cm^{-1}, ψ-scan, minimum transmission 0.7559, maximum transmission 0.8422, $F(000) = 1948$, 17 486 reflections in h (−14 to +15), k (−37 to +24), l (−16 to +12), measured in the range $1.59° \leq \theta \leq 27.11°$, completeness $\theta_{max} = 92.7\%$, 12 240 independent reflections, $R_{int} = 0.063$, 10 476 reflections with $F_o > 4\sigma(F_o)$, 896 parameters, 1 restraint, $R1_{obsd} = 0.083$, $wR2_{obsd} = 0.201$, $R1_{all} = 0.097$, $wR2_{all} = 0.219$, GOF = 1.085, Flack parameter 0.07(2), largest difference peak/hole 7.089/−1.453 e Å^{-3}. *Modification II*: triclinic, space group $P\bar{1}$, $a = 12.1499(7)$ Å, $b = 12.8905(7)$ Å, $c = 29.0650(10)$ Å, $\alpha = 86.015(3)°$, $\beta = 88.674(3)°$, $\gamma = 83.328(3)°$, $V = 4509.8(4)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.787$ g cm^{-3}, μ(Mo Kα) = 65 cm^{-1}, ψ-scan, minimum transmission 0.5626, maximum transmission 0.6244, $F(000) = 2388$, 18 964 reflections in h (−12 to +15), k (−16 to +16), l (−27 to +37), measured in the range $1.59° \leq \theta \leq 27.45°$, completeness $\theta_{max} = 98.6\%$. The X-ray data of both of the two modifications of compound **4** are of minor quality. Therefore, only their crystallographic data and the conformation of **4** are published. Bond lengths and angles are not listed. *Crystal data for* **5**: $C_{60}H_{88}Br_4Li_2N_4Nd_2O_4\cdot 2C_4H_{10}O$, $M_r = 1699.58$, colorless prism, size $0.10 \times 0.09 \times 0.06$ mm^3, triclinic, space group $P\bar{1}$, $a = 12.3196(5)$ Å, $b = 13.2774(5)$ Å, $c = 13.5081(6)$ Å, $\alpha = 94.649(3)°$, $\beta = 112.393(2)°$, $\gamma = 105.774(2)°$, $V = 1923.22(14)$ Å^3, $T = -90$ °C, $Z = 1$, $\rho_{calcd} = 1.467$ g cm^{-3}, μ(Mo Kα) = 34.59 cm^{-1}, semiempirical, minimum transmission 0.623, maximum transmission 0.834, $F(000) = 858$, 22 302 reflections in h (−15 to +15), k (−16 to +17), l (−17 to +13), measured in the range $1.89° \leq \theta \leq 27.44°$, completeness $\theta_{max} = 99.6\%$, 8743 independent reflections, $R_{int} = 0.084$, 6529 reflections with $F_o > 4\sigma(F_o)$, 371 parameters, 0 restraints, $R1_{obsd} = 0.046$, $wR2_{obsd} = 0.097$, $R1_{all} = 0.075$, $wR2_{all} = 0.110$, GOF = 1.024, largest difference peak/hole 0.716/−1.414 e Å^{-3}. *Crystal data for* **6**: [$C_{12}H_{30}LiO_6$]$^+$[$C_{52}H_{68}N_4Nd$]$^-$, $M_r = 1170.64$, colorless prism, size $0.10 \times 0.10 \times 0.09$ mm^3, monoclinic, space group $P2_1/c$, $a = 10.8383(3)$ Å, $b = 37.8916(9)$ Å, $c = 15.8874(4)$ Å, $\beta = 94.797(1)°$, $V = 6501.8(3)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.196$ g cm^{-3}, μ(Mo Kα) = 8.47 cm^{-1}, $F(000) = 2484$, 40 749 reflections in h (−14 to +13), k (−49 to +35), l (−20 to +20), measured in the range $1.96° \leq \theta \leq 27.44°$, completeness $\theta_{max} = 97.6\%$, 14 472 independent reflections, $R_{int} = 0.055$, 9932 reflections with $F_o > 4\sigma(F_o)$, 717 parameters, 0 restraints, $R1_{obsd} = 0.049$, $wR2_{obsd} = 0.108$, $R1_{all} = 0.088$, $wR2_{all} = 0.125$, GOF = 1.007, largest difference peak and hole: 0.875/−0.635 e Å^{-3}. (b) The detailed crystallographic data of this publication are available as Supplementary Publications CCDC-215583 (**5**) and CCDC-215584 (**6**) from the Cambridge Crystallographic Data Centre. The data can be ordered without charge via www.cam.ac.uk/conts/retrieving.html (or by postal mail in Great Britain: Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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Table 1. Selected Results of the Buta-1,3-diene Polymerization with the Hexa-1,5-diene-1,6-diamide Complexes 4 and 6 and also with the Lanthanum Complex 7[a]

complex	activity[b]	yield[c]	microstructure of the polybutadiene[d]
4	116.4	82.1 (2 h 15 min)	93.5/5.5/1.0
6	23.3	5.1 (1 h 39 min)	not defined
7	529.1	84.5 (1 h 34 min)	93.7/4.7/1.7

[a] The polymerization experiments were performed at Dow BSL Olefinverbund GmbH. [b] Activity in g of polymer (mmol of complex)$^{-1}$ h^{-1}. [c] Yield of polybutadiene in percent. [d] Content of isomers of 1,4-*cis*-/1,4-*trans*-/1,2-polybutadiene in percent.

bromide-containing neodymium complex **4** displays a markedly higher activity than the bis(hexa-1,5-diene-1,6-diamide)neodymium complex **6**. In any event, the high activity and selectivity of the lanthanum complex **7** is consistent with that of comparable Ziegler−Natta systems, as for example Nd(versatat)$_3$/MAO (1:264) with a turnover frequency of approximately 12 000 mol of buta-1,3-diene (mol of Nd)$^{-1}$ h^{-1} and a cis selectivity of 91%.[11b]

The results at hand show that with the easily available hexa-1,5-diene-1,6-diamide a ligand system with a truly unexpected versatility is available to the chemistry of lanthanides: a combination of the amide and the alkene functions within the hexa-1,5-diene-1,6-diamide results in the formation of azaallyl units. Thus, the bonding mode may vary in the range between a bis-enamide structure on the one hand and a bis-azaallyl structure on the other, depending on the electronic and steric situation at the complex center. The consequent structural variety of size and geometry of the chelate ring and the catalytic activity of the novel neodymium complexes offer enough reasons for more extended investigations in this field.

Experimental Section. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (THF, diethyl ether) or LiAlH$_4$ (pentane) under argon and stored over activated 4 Å molecular sieves. The lanthanide bromide complexes LaBr$_3$(THF)$_{3.5}$ and NdBr$_3$(THF)$_{3.5}$ [12] as well as the dilithium hexa-1,5-diene-1,6-diamide **2**[6] were prepared according to literature procedures. The ^{1}H NMR spectrum of **7** was recorded in THF-d_8 on a Varian 300 BB spectrometer (^{1}H NMR at 300.075 MHz). Elemental analyses were carried out by the analysis laboratory at the Martin-Luther-University of Halle-Wittenberg.

4. To a solution of 6.78 g (12.64 mmol) of **2** in 200 mL of DME was added 8.04 g (12.64 mmol) of NdBr$_3$(THF)$_{3.5}$ at −20 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. Then, the mixture was evaporated to dryness, and the product was dissolved in diethyl ether (200 mL). After the mixture stood for 12 h at −20 °C crystalline LiBr(DME)$_2$ precipitated at first and was separated by filtration. The filtrate was concentrated to 100 mL and stored for another 48 h at −20 °C. A yield of 7.68 g (8.22 mmol, 65% referenced to the starting NdBr$_3$(THF)$_{3.5}$) of colorless crystals of **4** was obtained. Mp: 132−135 °C dec. Anal. Calcd for $C_{38}H_{64}Br_2N_2O_6LiNd$: C, 47.74; H, 6.75; N, 2.93. Found: C, 47.70; H, 6.81; N, 2.99.

5. A 2.50 g portion (2.62 mmol) of **4** was dissolved in 50 mL of DME with mild heating. Subsequently, the solution was filtered and stored at −20 °C for 24 h. Colorless crystals of the dimeric neodymium complex **5** precipitated. This procedure was repeated several times. Mp: 158−160 °C dec. Anal. Calcd for $C_{68}H_{108}Br_4N_4O_6Li_2Nd_2$: C, 48.05; H, 6.40; N, 3.30. Found: C, 48.09; H, 6.42; N, 3.38.

6. A 3.14 g portion (4.94 mmol) of NdBr$_3$(THF)$_{3.5}$ was added to a solution of 5.30 g (9.88 mmol) of **2** in 200 mL of DME at −20 °C. The reaction mixture was warmed to room temperature and stirred for 48 h. Then, the solvent was distilled off under vacuum and the remaining solid was dissolved in 200 mL of Et$_2$O. Initially, at −20 °C, crystalline LiBr(DME)$_2$ precipitated from the solution and was separated by filtration. The volume of the filtrate was reduced to 100 mL. After the mixture stood for another 48 h at −20 °C, 4.33 g of colorless crystals of **6** (3.70 mmol, 75% referenced to the starting NdBr$_3$(THF)$_{3.5}$) was obtained. Mp: 124 °C. Anal. Calcd for $C_{64}H_{98}N_4O_6LiNd$: C, 65.66; H, 8.44; N, 4.79. Found: C, 65.53; H, 8.50; N, 4.83.

7. To a solution of 4.20 g (7.83 mmol) of **2** in 100 mL of DME was added 4.94 g (7.83 mmol) of LaBr$_3$(THF)$_{3.5}$ at −20 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. The mixture was then evaporated to dryness, and the product was dissolved in diethyl ether (200 mL). Crystalline LiBr(DME)$_2$, which precipitated first, was separated by filtration. After the mixture stood for 48 h at −20 °C, a yield of 4.10 g (2.66 mmol, 68% referenced to the starting LaBr$_3$(THF)$_{3.5}$) of colorless needlelike crystals of the dimeric lanthanum complex **7** was obtained. Mp: 143−145 °C dec. ^{1}H NMR (THF-d_8, 300 MHz, 20 °C): δ 7.53 (br d, 8H, *o*-Ph), 6.92−6.68 (m, 12H, *m*-Ph, *p*-Ph), 6.22 (s, 4H, C*H*=CMe), 3.98 (br s, 4 H, C*H*Ph), 3.53 (s, 8H, OC*H*$_2$, DME), 3.35 (s, 12H, OCH$_3$, DME), 2.91 (sept, ^3J(H,H) = 6.4 Hz, 4H, NC*H*Me$_2$), 1.60 (s, 12H, CH=C*Me*), 1.06 (br d, ^3J(H,H) = 6.4 Hz, 24H, NCH*Me*$_2$). Anal. Calcd for $C_{60}H_{88}Br_4Li_2N_4La_2O_4$: C, 46.77; H, 5.76; N, 3.64. Found: C, 46.59; H, 5.79; N, 3.71.

Butadiene Polymerization. The polymerization experiments were carried out in a double-walled steel reactor at +80 °C in cyclohexane. The polymerization was started by addition of the lanthanide complex to the cyclohexane solution of buta-1,3-diene and the activator MMAO (300−600 equiv per lanthanide complex). For the termination of the polymerization process, the polymer solution was transferred into methanol which contained Irganox 1520 as polymer stabilizer. The microstructure of the polybutadiene was analyzed spectroscopically.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for complexes **4**−**6**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pups.acs.org.

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(12) LaBr$_3$(THF)$_{3.5}$ and NdBr$_3$(THF)$_{3.5}$ were prepared by reaction of chippings of the lanthanide metals with CH$_2$Br$_2$ in THF. See also: Taube, R.; Maiwald, S.; Sieler, J. *J. Organomet. Chem.* **2001**, *621*, 327−336.