# (Cyclopentadienyl)neodymium borohydrides with auxiliary N₃-heterocyclic ligands

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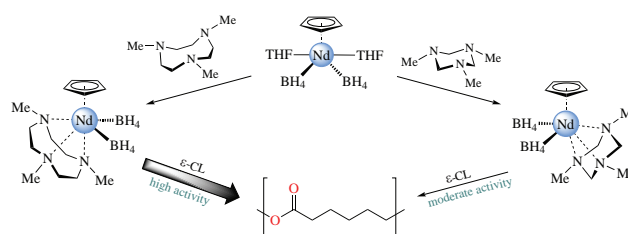[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
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Mononuclear [CpNd(BH₄)₂L] borohydrides comprising L = 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me₃tach) and L = 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃tacn) were obtained and structurally characterized. Their catalytic activity in coordination–insertion ring-opening polymerization of ε-caprolactone was studied.
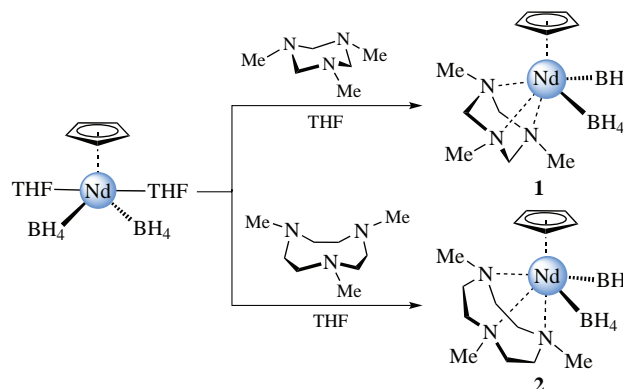
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Cyclopentadienyl borohydride lanthanide complexes have great potential in the rare-earth chemistry due to the higher covalency of the metal (Ln)–ligand (BH₄) bond, compared with the lanthanide halide analogs, since the borohydride ligand is more electron-donating.[1–4] Another attractive feature of borohydride complexes is their structural diversity due to different types of coordination of the borohydride ligand with the Ln³⁺ cation, namely, tri-hapto (η³), di-hapto (η²), and even mono-hapto (η¹) mode.[5–10] The latter easily becomes a drawback resulting in a mixture of products in the synthesis of borohydride complexes. We recently reported on the synthesis of a series of La, Nd, and Tb borohydride complexes.[11] A wide variety of structural types of cyclopentadienyl borohydride complexes of neodymium and lanthanum was observed, including five different structural types of Cp-lanthanide borohydrides. Three of them showed satisfactory activity in the polymerization reaction of ε-caprolactone. We assumed that in order to control the formation of a certain structural type in the Cp–Ln–BH₄ series, it is necessary to use an auxiliary ligand that effectively blocks the lanthanide ion coordination sphere. We have previously shown, using rare-earth arylcyclopentadienyl halide complexes, that saturated N-heterocyclic compounds such as 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me₃tach) and 1,4,7-tri-methyl-1,4,7-triazacyclononane (Me₃tacn) were highly effective in blocking the Ln³⁺ coordination sphere.[12] Therefore, the goal of this work is the synthesis and characterization of cyclopentadienyl neodymium borohydrides containing Me₃tach or Me₃tacn ligands, and the study of their catalytic activity in the coordination–insertion ring-opening polymerization of ε-caprolactone.

Complexes [CpNd(BH₄)₂(Me₃tach)] **1** and [CpNd(BH₄)₂(Me₃tacn)] **2** were obtained by the reaction of

[CpNd(BH₄)₂(THF)₂] with an excess of Me₃tach or Me₃tacn in THF (Scheme 1). Crystallization from THF/hexane solutions gave single crystals of **1** and **2**, respectively, suitable for X-ray diffraction. Both complexes are insoluble in nonpolar solvents and moderately soluble in THF, although markedly worse than their synthetic precursor [CpNd(BH₄)₂(THF)₂]. Complex **2** is less soluble in THF than complex **1**; a similar trend in solubility was observed for the (triphenylcyclopentadienyl)neodymium chloride complexes.[12]

The structures of complexes **1** and **2** were established by X-ray diffraction analysis.† In both crystal structures under
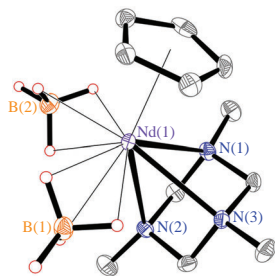


**Scheme 1**

**Figure 1** General view of complex **1**. The atoms are shown as thermal ellipsoids (*p* = 50%). Except for B*H₄*, all hydrogen atoms are omitted for clarity.
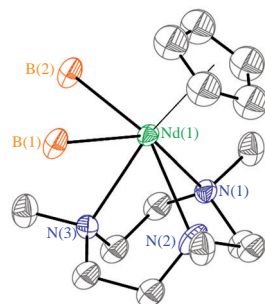


**Figure 2** General view of complex **2**. The atoms are shown as thermal ellipsoids (*p* = 50%), hydrogen atoms are omitted for clarity.

study, the $Nd^{3+}$ cations are coordinated by a cyclopentadienyl ligand, three nitrogen atoms of the triaza ligand, and two borohydride ligands giving the neodymium cations a coordination number of eight (Figures 1, 2). The main geometrical parameters of complexes **1** and **2** are similar, despite significant differences in the size of the triaza ligands they contain. The $Nd–Cp_{cent}$ distances are 2.489(13) Å (**1**) and 2.452(7) Å (**2**). The Nd–N distances are in the range of 2.642(2)–2.698(2) Å for complex **1** and 2.637(9)–2.655(12) Å for complex **2**. The major structural difference between **1** and **2** is the mutual arrangement of the cyclopentadienyl and the triaza ligands. Thus, the angle between the plane of the cyclopentadienyl ligand and the plane defined by the three nitrogen atoms is 60.2° for **1** and 46.0° for **2**. Apparently, such a noticeable difference is due to the fact that the bulkier $Me_3tacn$ ligand in complex **2** experiences stronger repulsion from the cyclopentadienyl ligand than the $Me_3tach$ ligand in complex **1**, which leads to a decrease in the angle between the corresponding planes. The consequence of this is a decrease in the coordination gap aperture.

The behavior of complexes **1** and **2** in solution is significantly different, despite their structural and chemical similarity. Thus, the $^1H$ and $^{11}B$ NMR spectra of complex **1** in THF-$d_8$ indicate that the structure of **1** in solution is retained. At the same time, the $^1H$ NMR spectrum of the analytically pure sample **2**, along with the signals of **2**, contains the signals for the free $Me_3tacn$

ligand and other neodymium borohydride and triazacyclononane complexes (for the NMR spectra images, see Online Supplementary Materials, Figures S1–S5). Apparently, complex **2** is kinetically labile and undergoes redistribution reactions.

It is known that lanthanide borohydride complexes exhibit catalytic activity in the coordination–insertion ring-opening polymerization of ε-caprolactone. The catalytic activity of such complexes depends significantly on the ligand environment of the lanthanide ion.[13–19] We have previously reported that mono- and bis(cyclopentadienyl)neodymium borohydrides could be used as such catalysts.[11] It was of undoubted interest to compare the catalytic activity of complexes **1** and **2** with the activity of those cyclopentadienyl neodymium borohydrides, especially knowing that in the polymerization of ethylene, the catalytic activity of triphenylcyclopentadienyl neodymium dichloride complexes would increase with the introduction of the $Me_3tach$ ligand.[12]

To estimate the catalytic performance of **1** and **2** in comparison with the cyclopentadienyl neodymium borohydride complexes of a similar structure, but not containing N-donor ligands, namely $[CpNd(BH_4)_2(THF)_2]$ **3** and $[Cp_2Nd(BH_4)(THF)]$ **4**, polymerization was carried out under conditions similar to those described earlier (Table 1).[11] Both complexes exhibit higher activity in the polymerization of caprolactone compared with the activity of **3** and **4**, but only in the range of relatively high catalyst loadings, significantly decreasing at a catalyst/substrate molar ratio of 1 : 1000. Both complexes provide polymers with rather narrow polydispersity indices.

Interestingly, complex **2** shows higher activity than **1** despite the greater steric loading of **2** (containing the $Me_3tacn$ ligand) compared to **1** (containing the $Me_3tach$ ligand). There are at least two reasons for this. The first reason is that the initiation of the polymerization process begins with the interaction of the monomer molecules with the borohydride ligand, the availability of which depends only slightly on the coordination gap aperture. The second reason is the higher lability of $Me_3tacn$ compared with that of $Me_3tach$ in neodymium complexes. However, more research is needed to explain the advantage in using triazacyclononane ligand in the design of catalytic systems for caprolactone ring-opening polymerization, compared with triazacyclohexane.

In summary, auxiliary triaza heterocyclic ligands were used in the preparation of new cyclopentadienyl borohydride neodymium complexes possessing well-defined structures, in contrast to their precursors. The obtained complexes can effectively initiate ε-caprolactone polymerization, surpassing their synthetic precursors in catalytic activity.

**Table 1** Polymerization of ε-caprolactone (CL) initiated by complexes **1** and **2**.[a]

| Entry | Initiator | CL/Nd ratio | 1 min conversion[b] (%) | *t*/min | Yield[c]/ g (%) | $M_{n,exp}$[d]/ ×10⁻³ g mol⁻¹ | *Đ*[d] |
|---|---|---|---|---|---|---|---|
| 1 | **1** | 250 | 16 | 2.5 | 1.78 (89) | 33.7 | 1.39 |
| 2 | **1** | 500 | 1 | 4.5 | 1.68 (84) | 51.4 | 1.41 |
| 3 | **1** | 750 | n.d. | 6 | 1.15 (58) | 61.7 | 1.17 |
| 4 | **1** | 1000 | n.d. | >60 | 0.75 (38) | 33.0 | 1.51 |
| 5 | **2** | 250 | 93 | 0.66 | 1.85 (93) | 29.9 | 1.34 |
| 6 | **2** | 500 | 37 | 1 | 1.89 (94) | 41.9 | 1.59 |
| 7 | **2** | 750 | 14 | 1.33 | 1.84 (92) | 54.4 | 1.55 |
| 8 | **2** | 1000 | 5 | >60 | 0.58 (29) | 43.3 | 1.35 |

[a] General polymerization conditions: 1 M CL in THF and 25 °C. [b] Monomer conversion in 1 min determined gravimetrically by the polymer yield in a separate series of experiments. [c] Yield: weight of the polymer obtained/ weight of monomer, used after the reaction stopped. [d] Measured by GPC relative to polystyrene standards, $Đ = M_w/M_n$.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.019.

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