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One-pot synthesis of an ionic half-sandwich complex of neodymium. Application to isoprene polymerisation catalysis

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Abstract

The reaction of one equivalent of $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ with an half equivalent of dialkylmagnesium in the presence of a stoichiometric amount of pentamethylcyclopentadiene cleanly affords a new kind of half-sandwich of neodymium that is stable toward comproportionation. This strategy can be advantageously applied to generate in situ catalysts allowing the controlled polymerisation of isoprene. **To cite this article:** *M. Visseaux et al., C. R. Chimie 10 (2007).*

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Résumé

La réaction d'un équivalent de $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ avec un demi-équivalent de dialkylmagnésium en présence d'une quantité stœchiométrique de pentaméthylcyclopentadiène conduit de façon univoque à un hémimétallocène de néodyme d'un nouveau type, stable vis-à-vis de la comproportionation. Cette stratégie peut être appliquée de façon avantageuse pour générer in situ des catalyseurs permettant la polymérisation contrôlée de l'isoprène. **Pour citer cet article :** *M. Visseaux et al., C. R. Chimie 10 (2007).*

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Mots-clés : Néodyme ; Héli-lanthanidocène ; Catalyse de polymérisation ; *Trans*-polyisoprène

1. Introduction

Lanthanides-based molecular catalysis has been steadily increasing in the last few years (e.g. see the 2002 special issue of *Chemical Reviews*, vol. 102, no. 6), and particularly in the field of polymerisation

reactions [1]. Between the classical metallocenes and the more recent post-metallocenes developed for this specific area, the hemi-metallocene — also called “half-sandwich” — framework has attracted much less attention, despite spectacular catalytic abilities [2–4]. The major reason is that the hemi-lanthanidocenes have been until now rather difficult to prepare [5], undergoing comproportionation reactions, especially with the larger elements of the series [2,6], and even in the presence of a bulky cyclopentadienyl ligand [7,8].

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Two general strategies have been employed until now to prepare half-sandwich lanthanide complexes: ionic or σ -bond metathesis [2]. Using the former method, we have shown earlier that half-sandwich lanthanide compounds of formula $(C_5Me_4nPr)Ln(BH_4)_2(THF)_n$ ($Ln = Nd, n = 2$; $Ln = Sm, n = 1$) could be isolated in the borohydride series, taking advantage of the bridging ability of the BH_4 group. However, desolvation and clustering were observed, leading to the formation of hexamers $[(C_5Me_4nPr)Ln(BH_4)_2]_6$ as the crystalline form [9]. On the other hand, the σ -bond metathesis method allows the straightforward formation of the expected product, but it requires highly sensitive homoleptic LnR_3 precursors ($R = \text{alkyl}$ [2], allyl [10], phenyl [11], or amido group [12]) [13]. Moreover, owing to the basicity of the R group, heating is often necessary to achieve the metathesis reaction, and ligand scrambling may be not completely excluded [5,11]. $Ln(BH_4)_3(THF)_3$ are common lanthanide compounds, they are nowadays recognized as efficient precursors for organolanthanides syntheses [14], and we expected that they could be involved for σ -bond metathesis to produce C_5Me_5 -supported compounds.

In this paper we describe the synthesis and characterization, including X-ray structure, of a new ionic half-sandwich of neodymium, prepared according to a direct *in situ* σ -bond metathesis involving $Nd(BH_4)_3(THF)_3$ /BEM (butylethylmagnesium) and C_5Me_5H as starting materials. The isolated complex has the same efficiency as its neutral homologue — whose synthesis requires by contrast the previous preparation of KC_5Me_5 — for the controlled polymerisation of isoprene. Varying the nature of the cyclopentadiene allows us to evaluate very easily the impact of the Cp ligand upon the catalytic ability, without necessarily needing to isolate the related monocyclopentadienyl complex.

2. Results and discussion

2.1. Synthesis of complex 2

First attempts of a direct reaction between $Nd(BH_4)_3(THF)_3$ (**1**) and C_5Me_5H were made, but failed, even after a prolonged reaction time (1H NMR monitoring). On the other hand, we recently established that Ln –alkyl bonds are readily obtained from the reaction of a $[Ln]-(BH_4)$ moiety with an alkylating agent, enabling the preparation of highly efficient catalytic systems for the polymerisation of non-polar monomers [3b,14–17]. Following this idea, a solution of BEM (*n*BuEtMg) was added to a 1:1 toluene mixture of C_5Me_5H and **1** at room temperature. A clean reaction took place within

a few minutes, affording a compound consisting of one C_5Me_5 ligand for three BH_4 groups whereas no precipitation of the expected $Mg(BH_4)_2$ occurred (Scheme 1).¹

After slow concentration of the toluene solution, light blue single crystals could be isolated from gentle evaporation of the toluene solution. X-ray structure determination allowed us to establish $[(C_5Me_5)Nd(BH_4)_3]_2[Mg(THF)_6]$ (**2**) as molecular formula for the isolated complex.² It must be emphasized that this unprecedented synthetic method, that we call the “borohydride/alkyl route”, requires very mild experimental conditions and ordinary lanthanides precursors.

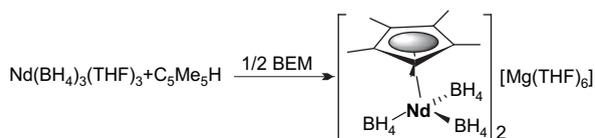
2.2. X-ray structure

of $[(C_5Me_5)Nd(BH_4)_3]_2[Mg(THF)_6]$ (**2**)

Complex **2** is a trinuclear ionic compound comprising two anionic half-neodymocene trisborohydride $[(C_5Me_5)Nd(BH_4)_3]^-$ moieties and one cationic hexa-THF magnesium $[Mg(THF)_6]^{2+}$ adduct (Fig. 1) that

¹ Preliminary 1H NMR experiments: 10.0 mg of **1** (25 μ mol) and 1 equiv of C_5Me_5H (3.4 mg) were weighed in an NMR tube and 0.4 mL of C_6D_6 was added. No reaction took place as shown by the presence of both unreacted starting materials in the 1H NMR spectrum, even after warming for a prolonged time. A solution of BEM (0.5 equiv, 7 mg) was added. Immediately, the solution turned pale blue and no precipitation (especially of any uncoloured inorganic salt) was observed. δ (ppm) = 61.5 (br, 12H, BH_4 , $\nu^{1/2} = 800$ Hz), 8.22 (s, 15H). The paramagnetic THF signals could be depicted (2.45 and 1.02 ppm) but the presence of hexanes (BEM solvent) prevented an accurate integration. The spectrum remained unchanged after 20 h at 75 °C. Bulk synthesis: $[(C_5Me_5)Nd(BH_4)_3]_2[Mg(THF)_6]$ (**2**): 291 mg (0.53 mmol) of a solution of BEM diluted in 5 mL of toluene were added dropwise, at room temperature, to a solution of **1** (430.0 mg, 1.06 mmol) and C_5Me_5H (195 mg, 1.43 mmol) in toluene (30 mL). The mixture turned from light purple to blue immediately. After 12 h stirring at room temperature, the resulting blue solution was filtrated to eliminate the insoluble residues present in very small quantities (ca. 20 mg). The solution was concentrated of one third and after 12 h, a crop of well-formed crystals (60 mg) could be collected. The mother liquor was then concentrated to ca. 2 mL, providing a blue crystalline powder which was rinsed twice with pentane and finally dried under vacuum ($m = 402$ mg). Complex **2** was found quite soluble in aromatic solvents. Total yield: 83.3%. Anal. Calc. $C_{44}H_{102}B_6O_6Nd_2Mg$: C, 47.80; H, 9.20. Found: C, 46.84; H, 9.88. 1H NMR (C_6D_6) δ : 63.8 (ν br, 12H, BH_4 , $\nu^{1/2} = 600$ Hz), 8.28 (s, MeCp, 15H), 1.57 (s, THF, 12H), 0.54 (s, THF, 12H).

² Compound **2** ($C_{44}H_{102}B_6MgNd_2O_6$) crystallizes in the monoclinic space group $P2_1$ with $a = 11.064(2)$, $b = 30.027(4)$, $c = 17.525(3)$ Å, $\beta = 106.586(2)^\circ$, $V = 5580(2)$ Å³, and $\rho = 1.315$ g cm⁻³ for $Z = 4$. CCDC-606630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033 or deposit@ccdc.cam.ac.uk).

Scheme 1. Synthesis of the half-sandwich complex **2**.

alternate in the unit cell without direct cation–anion interaction. The asymmetric unit contains two slightly different trimetallic Nd/Mg/Nd entities. The Nd anions have a pseudotetrahedral tri-legged piano-stool geometry. It is noteworthy that the Nd–B distances (six coordination) fall in a narrow range of 2.582(5)–2.586(5) Å, typical of monomeric borohydride complexes bearing a tridentate Nd–(η^3 -H)₃B–H terminal group [14,18]. All hydrogens belonging to borohydride groups could be located; geometric parameters (B–H, Nd–H distances and B–H–Nd angles) confirm the η^3 -mode, likely distorted, however [16,19]. The Mg cation exhibits the octahedral geometry with oxygen atoms of THF molecules. The absence of coordinated THF to the neodymium atom points out the higher affinity of the lanthanide toward ionic ligands.

Though structurally characterized molecular Cp^RLnX₃[−] (Cp^R is a substituted cyclopentadienyl ligand) species have been observed occasionally [10,20], the borohydride anionic [(C₅Me₅)Nd(BH₄)₃][−] is singular. Moreover, we checked (¹H NMR, C₆D₆) that a solution

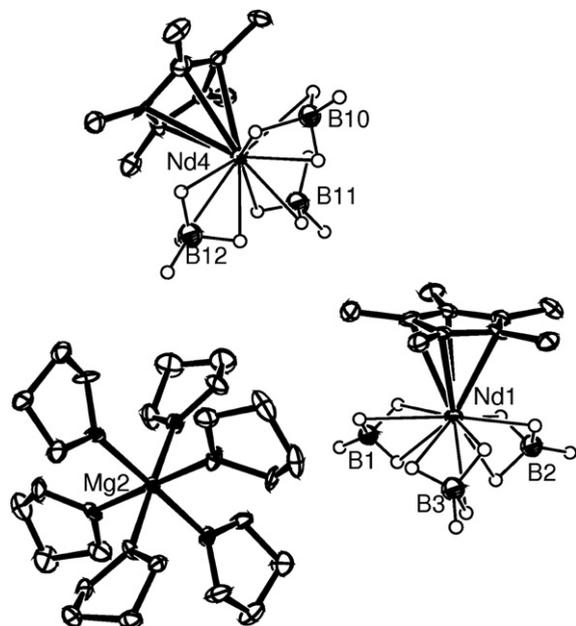


Fig. 1. ORTEP structure of one of the two entities of the asymmetric unit showing the molecular structure of **2** (thermal ellipsoids at the 30% level; non-BH₄ hydrogen atoms omitted for clarity).

Table 1
Isoprene polymerisation with (borohydrido half-neodymocene/BEM) catalysts

Catalytic system ^a	Yield [%]	Rate of <i>trans</i> -PI [%] ^c	<i>M</i> _n ^d	<i>M</i> _w / <i>M</i> _n	<i>M</i> _{n(calc.)} ^e
2/1 BEM	84	98.2	58 200	1.16	56 000
2 ^b /1 BEM	68	98.0	46 500	1.16	48 800
3/1 BEM	80	97.4	52 300	1.18	53 700
4 ^b /1 BEM	57	96.7	31 200	1.41	37 300
5 ^b /1 BEM	60 ^f	91.4	25 300	1.90	40 100
1/1 BEM ^g	87	95.5	58 200	1.35	52 100

^a Conditions: 10 μmol Nd, 1 mL toluene, [monomer]/[Nd] = 1000, *T* = 50 °C, *t* = 2 h.

^b In situ prepared precatalyst Nd(BH₄)₃(THF)₃/HCp^R/0.5 BEM, 2': Cp^R = C₅Me₅, 4': Cp^R = 1,2,4-Ph₃C₅H₂, 5': Cp^R = C₅H₅.

^c Determined by both ¹H and ¹³C NMR integrations.

^d Determined by Steric Exclusion Chromatography calibrated with PS standards.

^e ([monomer]/[Nd]) × 68 × (yield%).

^f *t* = 24 h.

^g See Ref. [25].

of **2** prepared in our one-pot procedure remained unchanged after 20 h at 75 °C¹. Thus, (C₅Me₅)LnX₃[−] appears as a stable molecular entity in the borohydride series, with respect to comproportionation or clustering. The ionic trinuclear structure of compound **2** is comparable to that of [Mg(THF)₆][Nd(allyl)₄]₂(2THF), obtained by ionic metathesis, with discrete [Mg(THF)₆]²⁺ cation and allyl neodymate anions [21].

2.3. Isoprene polymerisation

Precatalyst **2** combined with 1 equiv of BEM afforded a very efficient initiator toward isoprene polymerisation (Table 1), whose catalytic behaviour was fully comparable

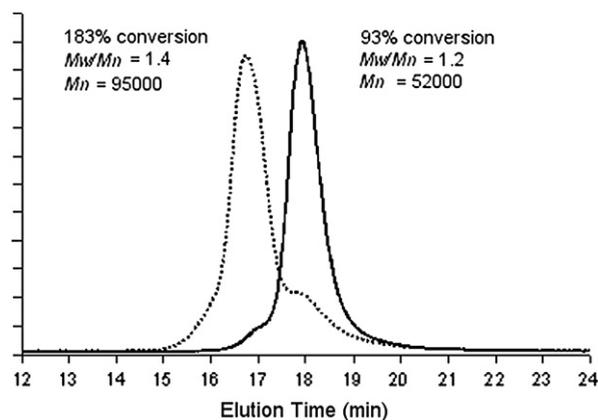
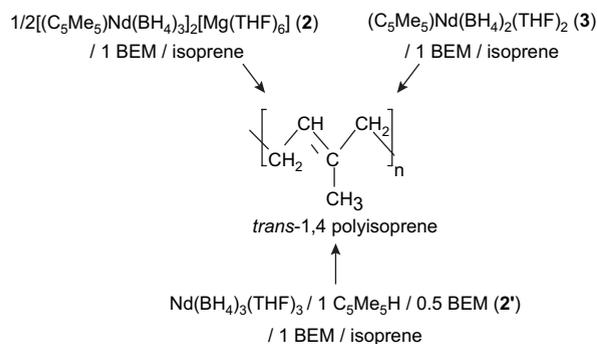


Fig. 2. GPC profiles before (plain line) and after (dot line) the second feed of isoprene obtained with 3/1 BEM catalytic system.



Scheme 2. Synthesis of *trans*-polyisoprene from **2**, **2'** and **3**, in combination with BEM.

to the one obtained from neutral (C₅Me₅)Nd(BH₄)₂(THF)₂ (**3**) with 1 equiv of BEM using a procedure that we previously described [3b]. As can be seen from the *M_n* values, such polymerisation process was found to be “living” with one growing chain per Nd.

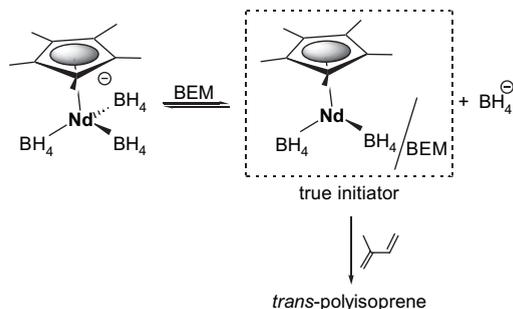
The “living” character of the latter catalyst is confirmed by a double-feed monomer experiment, showing the typical GPC profiles (Fig. 2) [22].

Ultimately, we found that a mixture made of **1**, C₅Me₅H, and BEM in the 1/1/1.5 ratio shows a very similar reactivity toward isoprene. In that latter case, it is likely that (i) a half-sandwich compound forms in solution (precatalyst **2'**, Table 1) from the reaction between **1**, C₅Me₅H, and 0.5 equiv of BEM, (ii) the subsequent combination of this precatalyst with the residual equivalent of BEM affords the catalytic species (Scheme 2). The somewhat lower activity of this catalytic system is tentatively ascribed to the number of THF molecules initially coordinated to the neodymium atom.

According to the high and very close levels of *trans*-selectivity, along with the controlled macromolecular data – fitting well with one growing chain – the three different pathways most probably involve the same half-sandwich catalytic species. One can thus propose that **2** dissociates in solution in the presence of 1 equiv of BEM [23] (Scheme 3) to afford a Nd/Mg bimetallic compound bearing one Nd–alkyl active bond, as already observed from **3**.³

To generalize the above procedure, additional in situ experiments were carried out with 1,2,4-Ph₃C₅H₂ and C₅H₅ as ligands (precatalysts **4'** and **5'**, respectively) [24]: in both cases, the process was much less controlled and the activity was lower (Table 1), showing

³ According to an NMR study, the active species involved in the catalytic process from **3** is probably a [(C₅Me₅)Nd]–(μ-BH₄)–Mg bimetallic one, see Ref. [3b].



Scheme 3. Formation of the active species from anionic half-sandwich moiety of complex **2**.

the specific role played by the presence of a C₅Me₅ ligand in the coordination sphere of the neodymium atom for such catalysis.

3. Conclusion

To conclude, we report herein that the “borohydride/alkyl route” is an elegant alternative for the preparation of half-sandwiches of early lanthanides, enabling a one-pot and high yield synthesis and starting with simple precursors. By using this method, it is possible to prepare in situ and very easily sophisticated lanthanide-based catalysts, but also to simply evaluate the impact of a Cp^R ligand upon a catalytic process in a high throughput screening context.

Further results related to the extension of this “borohydride/alkyl route” to the preparation of lanthanidocenes are in progress and will be published in a forthcoming paper.

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