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(*t*-BuC₅H₄)₃Nd: A triscyclopentadienyl rare earth compound as non-classical isoprene polymerization pre-catalyst



Ines Rodrigues, Tan Yong Xue, Pascal Roussel, Marc Visseaux*

Unité de Catalyse et Chimie du Solide (UCCS), UMR CNRS 8181, Université de Lille Nord de France, USTL-ENSCL, Bat C7, BP 90108, 59652 Villeneuve d'Ascq, France

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Dedicated to Professor André Mortreux at the occasion of his 70th birthday.

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1. Introduction

Tris(cyclopentadienyl) derivatives of the rare earths represent a model of thermodynamically stable compounds, since the set of three cyclopentadienyl ligands is known as particularly well suited to complete the steric/electronic features of a rare earth metal [1]. De facto, tris(cyclopentadienyl) complexes have often been observed as the main – unexpected, but yet – isolated products of syntheses that were intended to yield metallocene-like organolanthanides [2]. The simplest representative in this frame is the Cp_3Ln ($Cp = C_5H_5$, Ln = rare earth metal), which was synthesized in the early times of organometallic chemistry [3]. With the lightest "early" rare earths, which are also the biggest ones, it was frequent to isolate adducts, even with substituted cyclopentadienyls [4]. Due to their ability to easily sublimate and their stability, such compounds were mainly investigated as potential precursors for OMCVD [5]. Actually, because of an apparent steric saturation, tris(cyclopentadienyl) derivatives may be seen as compounds that are relatively inert toward the activation of small molecules, which is generally considered as the first stage of a catalytic process. However, after the pioneering

ABSTRACT

Homoleptic tris(cyclopentadienyl) Cp'_3Nd ($Cp' = C_5H_4t$ -Bu) complex has been unprecedentedly considered as potential pre-catalyst for isoprene polymerization. The X-ray structural analysis establishes a monomeric non-solvated nature for this compound. Upon activation with appropriate borate/aluminium co-catalyst combinations, Cp'_3Nd affords in good yields polyisoprene more than 95% *cis*-regular. © 2013 Elsevier B.V. All rights reserved.

investigations of Wilkinson dedicated to the reactivity of the Cp₃Ln derivatives [6], it was shown that Bronsted acids react with tris(cvclopentadienyl) complexes to afford the corresponding bis(cyclopentadienyl) derivatives and cyclopentadiene [7]. Later. combinations of Cp₃Ln compounds with NaH were described as efficient for a number of organic reactions [8]. Putative [Cp₂LnH] active species, arising from the displacement of one Cp ring by NaH, were postulated by the authors, on the basis of previous studies by Schumann, who initially proposed the cleavage of tris(cyclopentadienyl)lanthanide complexes with alkylating reagents to afford alkylbis(cyclopentadienyl)lanthanides. This method was useful in the early series since the latter complexes, prone to act as potential catalysts, are not accessible via the classical alkylation reaction from bis(cyclopentadienyl)lanthanide halides [9]. To our knowledge, Evans has reported a few examples of polymerization induced with tris(cyclopentadienyl) f-element complexes in the (C₅Me₅)₃M series with Nd, Sm, and U. But such compounds act as single component initiators to promote, via $\eta^5 - \eta^1$ shift, the polymerization of ethylene, and this peculiar reactivity is attributed to overcrowding of the complexes [10]. The same author showed that $(C_5Me_5)_3$ Sm could also react for similar reasons with Lewis acids like borane or alkylaluminium, generally used to activate pre-catalysts in polymerization reactions, to displace one pentamethylcyclopentadienyl ligand [11].



^{*} Corresponding author. Tel.: +33 3 20 33 64 83; fax: +33 3 20 43 65 86. *E-mail address:* marc.visseaux@ensc-lille.fr (M. Visseaux).

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Since in general numerous lanthanides-based polymerization catalysts are made of lanthanidocenes and half-lanthanidocenes [12], and considering that the synthesis of such derivatives may eventually be hard to achieve because of frequently observed ligands scrambling [13], an alternative can thus consist in the use of the tris(cyclopentadienyl) compounds as potential source of active species.

In this study, we proposed to investigate the ability of tris(cyclopentadienyl) derivatives as pre-catalysts for isoprene polymerization, in combination with an aluminum co-catalyst, and in the presence of a boron based molecule, which is known to act as an activator by alkyl abstraction. Two complexes of neodymium, an element known to give rise to efficient catalysts *vs.* dienes polymerization [14], were chosen in this frame: Cp'₃Nd (1), and Cp₃Nd (2) (Cp' = C₅H₄t-Bu, Cp = C₅H₅). The X-ray structure of 1, until now not described in the literature, is briefly presented in a preliminary section. The results in polymerization are then discussed in details, including some mechanistic considerations.

2. Material and methods

All operations were performed under dry argon by using Schlenk techniques. The solvents were dried over sodium/benzophenone ketyl, deoxygenated by distillation, and stored over molecular sieves (3A) in a glove box. Styrene (99% from Aldrich) and isoprene (99% from Aldrich) were dried over calcium hydride, distilled twice, and stored over molecular sieves (3A) in a glove box. Triisobutylaluminum (Ali-Bu₃), tris(pentafluorophenyl)borane $B(C_6)$ F_5)₃ and trityl tetra(pentafluorophenyl)borate [CPh₃][B(C₆F₅)₄] were purchased from Aldrich and used as received. Dimethylphenylanilinium tetra(pentafluorophenyl)borate $[HNMe_2Ph][B(C_6F_5)_4]$ was purchased from Strem and used as received. Cp₃Nd was synthesized and purified by sublimation according to the published procedure [3]. NMR scale experiments were conducted in a glove box in tubes equipped with a Teflon valve (YoungTM). ¹H and ¹³C NMR spectra of organometallic complexes and of polyisoprenes were recorded on a Bruker Avance 300 instrument at 300 K in C₆D₆ (7.16 ppm) and in CDCl₃ (7.26 ppm, 77.16 ppm), respectively, with reference to residual proton or carbon signal in brackets. When necessary, deuterated THF (1.72 ppm) or toluene (2.09 ppm), were used as NMR solvents for mechanistic studies. Size exclusion chromatography of samples was performed in THF as an eluent at 40 °C (1 mL min⁻¹) with a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards.

2.1. Synthesis of Cp'₃Nd, 1

Complex **1** (2 g, 5.1 mmol) was synthesized according to the published procedure [5], with the following modification: the mixture of reactants was refluxed in THF for 48 h followed with toluene extraction, evaporation of the toluene and addition of pentane (30 mL). After filtration, the pentane solution was concentrated to one third and let to crystallize at room temperature, yielding finally 1.90 g (73%) of deep blue–red crystals. ¹H NMR (C₆D₆): $\delta = -17.7$ (18H, *t*-Bu); -2.9 (4H, C₅H₄); 27.6 (4H, C₅H₄) [15]. Elemental analysis found (calc.) for C₂₇H₃₉Nd: C% 63.79 (63.88); H% 7.73 (7.69).

2.2. Synthesis of $Cp'_{3}Y$

The same procedure carried out with yttrium (YCl₃, 0.5 g, 2.55 mmol; KCp' [2d], 1.3 g, 8.1 mmol) led to a brownish oily compound (0.78 g, 67.6% yield) which solidified after a week at room temperature. This solid was unfortunately not suitable for X-

ray analysis. The ¹H NMR spectrum was compatible with the formula of a non-solvated Cp'₃Y complex since only signals attributed to the ligand were present. ¹H NMR (C₆D₆): $\delta = 6.13$ (4H, C₅H₄), 6.01 (4H, C₅H₄), 1.17 (18H, *t*-Bu). This compound was authenticated by a bulk synthesis carried out from different precursors: Y(BH₄)₃(THF)₃ (0.5 g, 1.43 mmol) and a three-fold excess of KCp' (0.7 g, 4.37 mmol) and in toluene (20 mL) at room temperature followed by extraction with pentane. No crystals could be obtained but the compound obtained after evaporation of the solvents had a honey-like aspect, and it finally solidified in 24 h at room temperature in the glove box (0.51 g, 79% yield). Its ¹H NMR spectrum was the exact replication of the previous one received from the synthesis carried out from YCl₃. Elemental analysis found (calc.) for C₂₇H₃₉Y: C% 69.79 (71.68); H% 8.56 (8.63).

2.3. X-ray structure determination of 1

Purple single crystals suitable for X-ray diffraction of 1 were grown from pentane. The crystals were carefully chosen using a stereo zoom microscope supported by a rotatable polarizing stage. The data were collected at room temperature on Bruker's KAPPA APEX II CCD X8 with graphite monochromated Mo-Ka radiation (0.71073 Å). The crystals were glued to a thin glass fiber using inert oil and afterward placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat with a nominal stability of 0.1 K. The intensity data were processed using Bruker's suite of data processing programs [16], and absorption corrections were applied using SADABS [17]. The crystal structure was solved by charge flipping method using SUPERFLIP [18] and the data was refined by full matrix least-squares refinement on F with anisotropic displacement parameters for non-H atoms, using CRYSTALS [19]. Crystal data of 1: Molecular formula = $C_{27}H_{39}Nd_1$, Formula weight = 507.85, Crystal system = orthorhombic, space group = $P2_12_12_1$, a = 8.3916 (2) Å, b = 16.4447 (4) Å, c = 17.1450(5) Å, V = 2365.96 (11) Å³, T = 100 K, Z = 4, Dc = 1.426 g cm⁻³, 39,722 reflections measured, 5774 independent reflections, 5558 observed reflections $[I > 3.0\sigma(I)]$, R1_obs = 0.0138, Goodness of fit = 1.11.

2.4. Isoprene polymerization

In a typical polymerization (run 9 in Table 1 is given here as an example), a flask was charged, in a glove box, with the pre-catalyst (Cp'₃Nd, 5.1 mg, 10 µmol Nd). The solvent (toluene, 1 mL) was added, followed by the co-catalyst (Al(*i*-Bu)₃, 38 µL, 150 µmol), and the boron activator ($[CPh_3][B(C_6F_5)_4]$, 27.6 mg, 30 µmol). At last, the monomer (isoprene, 3 mL, 30 mmol) was added with a syringe. The polymerization was conducted outside the glove box, under an inert atmosphere, at given monitored temperature and running time. After that time, the viscous mixture was guenched with a few drops of toluene/HCl and treated with methanol containing 2,6-ditert-butyl-4-methylphenol (ca 1.0 wt%) as a stabilizer. The resulting isolated polymeric material was dried under vacuum at room temperature to a constant weight. The yield was determined by gravimetry (m = 1.87 g, yield 91.8%). Stereoselectivities were determined with ¹H and ¹³C NMR when overlapping of signals as previously described [20].

2.5. NMR monitoring

Reaction of **1** with trityl perfluorophenylborate then triisobutylaluminum in C_6D_6 : 3 mg (5.9 µmol) of **1** and 11 mg (11.9 µmol) of [CPh₃][B(C_6F_5)₄] were weighed in the glove box in an NMR tube equipped with a Teflon valve. At the addition of C_6D_6 (0.4 mL) the formation of an oily brown insoluble compound was observed

Table 1		
Selected results of the isoprene polymerization with	h Cp ⁷ ₂ Nd (1) as pre-catalyst using different sys	stems

Run ^a	Activator ^b	Co-cat ^c (Al equiv)	[I]/[Ln]	$T(^{\circ}C)^{d}$	<i>t</i> (h)	Yield (%)	3,4/1,4trans/1,4cis ^e	Mn (PDI) ^f
1	1 TB	5	1000	50	20	11.0	18.2/81.8	_
2	2 TB	10	1000	50	20	90.9	15.8/8.0/76.2	19,800 (2.1)
3	2 TB	10	1000	RT	96	9.0	16.5/83.5	_
4	2 TB	10	2000	50	5	40.4	20.3/2.2/77.5	32,000 (2.1)
5	2 TB	10	2000	50	20	62.6	19.9/80.1	27,000 (2.3)
6	3 TB	15	1000	RT	72	36.0	16.8/6.7/76.5	-
7	3 TB	15	3000	RT	60	30.0	17.9/14.6/67.5	-
8	3 TB	15	3000	50	12	64.3	19.3/80.7	-
9 ^g	3 TB	15	3000	RT	72	91.8	14.5/5.5/80.0	28,200 (4.4)
10 ^g	3 TB	15	3000	50	12	94.8	16.8/2.4/81.9	-
11 ^g	5 TB	15	1000	50	20	14.7	3.9/8.4/87.7	_
12	5 TB	15	1000	50	20	16.8	9.7/35.5/54.8	-
13 ^g	5 TB	25	1000	50	5 h 30	88.5	6.8/3.3/89.9	14,200 (2.4)
14 ^g	5 TB	25	1000	RT	60	75.2	3.3/1.2/95.5	59,100 (2.4)
15 ^g	5 TB	25	3000	RT	44	60.9	6.1/1.5/92.4	30,000 (3.5)
16 ^g	5 TB	25	3000	50	17	85.6	3.6/1.3/95.1	_
17 ^{g,h}	5 TB	25	1000	50	17	64.9	8.9/91.1	17,000 (2.1)
18	5 TB	_	1000	_	1 min	Ins ⁱ	_	-
19	3 B	15	1000	50	20	78.2	5.1/10.1/84.9	24,200 (2.7)
20 ^g	3 B	15	1000	50	20	87.3	4.9/7.7/87.4	18,700 (2.8)
21	3 B	15	1000	RT	36	26.8	4.0/6.0/90.0	30,600 (3.5)
22 ^j	2 TB	10	1000	50	20	0	_	_
23 ^k	2 TB	10	3000	50	72	2.1	_	-
24 ^{g,k}	2 TB	10	3000	RT	10 min	71.2	24.2/17.3/58.5	47,700 (3.8)

^a Toluene 1 mL; addition order: pre-cat/solvent/activator/co-cat/monomer.

^b TB = trityl borate ([CPh₃][B(C₆F₅)₄]); B = tri(perfluoro)phenylborane (B(C₆F₅)₃).

^c Ali-Bu₃ equivalents.

^d RT = room temperature.

^e The 3,4/1,4 ratio was determined from ¹H NMR integration. The *cis/trans* relative intensities were determined when low overlapping by ¹H NMR. In case of overlap of the Me signals, an average with data obtained from ¹³C NMR quantitative analysis was considered.

^f Determined from SEC with reference to PS standards.

^g Addition order: pre-cat/solvent/co-cat/activator/monomer.

^h Solvent = pentane.

ⁱ Insoluble.

^j Pre-catalyst Cp₃Nd (2).

^k Pre-catalyst Cp'₃Y synthesized according to Scheme 1.

along with discoloration of the initial light blue tint of **1**. ¹H NMR showed the complete consumption of 1, paramagnetic signals attributed to a Cp' ligand attached to Nd: δ ppm = 11.8 (5.5H, br, m), -18.9 (3.5H, s), -23.3 (9H, s), and diamagnetic signals compatible with possible isomers of *tert*-BuC₅H₄CPh₃: δ ppm = 7.40 (o-Ph), 7.05 (m, p-Ph), 6.45 (C₅H₄), 6.16 (C₅H₄), 6.09 (C₅H₄), 4.6 (allylic C₅H₄), 0.9 (tert-Bu). These diamagnetic signals were also found present in the ¹H NMR spectrum of Cp'₃Y with [CPh₃] $[B(C_6F_5)_4]$ (see further). After recording of the ¹H NMR spectrum of **1** with trityl perfluorophenylborate, a 10 equiv amount of $Al(i-Bu)_3$ (15 μ L, 59 μ mol) was added in the NMR tube in the glove box. The dark oil immediately dissolved, to give according to ¹H NMR a new neodymium compound as evidenced by the paramagnetic signals: δ ppm = 11.9 (minor), -12.7 (major), -23.2 (major). Signals corresponding to Al(*i*-Bu)₃ were observed as well: δ ppm = 1.95 (1H, m), 1.02 (6H, d), 0.31 (2H, d).

Reaction of **1** with triisobutylaluminum then trityl perfluorophenylborate in C_7D_8 : 4.5 mg (8.8 µmol) of **1** was weighed in an NMR tube equipped with a Teflon valve. C_6D_6 (0.4 mL) and then 22 µL (88 µmol) of Al(*i*-Bu)₃ were added in the glove box. ¹H NMR analysis showed a little change of signals of **1** (by comparison with the above experiment, though in C_6D_6), whereas the signals relative to Al(*i*-Bu)₃ were found shifted and broadened: δ ppm = 27.4 (Cp, Nd), -2.7 (Cp, Nd), -17.4 (*tert*-Bu, Nd), 2.12 (CH, Al), 1.14 (Me₂, Al), 0.45 (CH₂, Al). After subsequent addition of [CPh₃][B(C_6F_5)₄] (16 mg, 17.4 µmol) all was soluble, no formation of an oily compound was this time observed. Signals of **1** had totally disappeared, and they were replaced by other paramagnetic signals, slightlydifferent from the ones observed in the experiment described above, with no possibility of clear interpretation: δ ppm = 12.5–13.7 (minor), –17.1 (major), –23.2 (major). Signals corresponding to Al(*i*-Bu)₃ were observed as well as same as before.

Reaction of **1** with trityl perfluorophenylborate in THF-*d*₈: 2.5 mg (4.9 µmol) of **1** and 10 mg (10.8 µmol) of [CPh₃][B(C₆F₅)₄] were weighed in the glove box in an NMR tube equipped with a Teflon valve. At the addition of THF-*d*₈ (0.4 mL), a brown solution formed, which was become solid within minutes, likely due to the polymerization of THF. A second try was done but the tube was immersed in an acetone/carbonic ice mixture allowing to wait before NMR analysis. The ¹H NMR spectrum showed paramagnetic resonances: δ ppm = 23.3, 12.8, 10.3, -0.3, -1.1, -8.7, and signals compatible with the presence of *tert*-BuC₅H₄CPh₃ isomers: δ ppm = 7.1–7.3 (Ph), 5.9–6.6 (C₅H₄), 2.7–3.1 (allylic C₅H₄), 1.05–1.2 (*tert*-Bu).

Reaction of **1** with dimethylphenylanilinium tetra(pentafluorophenyl)borate in C_6D_6 : 5.1 mg (10 µmol) of **1** and 15.8 mg (20 µmol) of [HNMe₂Ph][B(C_6F_5)₄] were weighed in the glove box in an NMR tube equipped with a Teflon valve. As same as with [CPh₃] [B(C_6F_5)₄], as soon as C_6D_6 (0.4 mL) was added, the formation of an oily brown insoluble compound was observed along with discoloration of the initial light blue tint of **1**. ¹H NMR spectrum showed some residual **1** accompanied with diamagnetic resonances that could be attributed to HCp': δ ppm = 6–6.5, 2.8, 1.10–1.15, and to NMe₂Ph: δ ppm = 6.5–6.8, 2.45. The latter signals were quite broad, likely due to coordination of the amine molecule to paramagnetic Nd atom. Further extraction with THF-*d*₈ showed signals typical of NMe₂Ph in this solvent: 6.67, 6.99, 2.91 [21], and a new compound was detected which paramagnetic signals were close to what observed in the reaction of **1** with trityl borate: δ ppm = 22.1, 14.9, -7.8.

Reaction of Cp'₃Y with successive amounts of trityl perfluorophenylborate in C_6D_6 : to a light orange solution of Cp'_3Y (4.5 mg, 10 μ mol) in C₆D₆ in an NMR tube equipped with a Teflon valve, was added 1 equiv. $[CPh_3][B(C_6F_5)_4]$ (9.2 mg, 10 µmol). The solution immediately changed to light yellow along with formation of an oily phase at the bottom of the tube. ¹H NMR showed the complete consumption of initial Cp'₃Y, and signals attributed to $Cp'CPh_3$: δ ppm = 7.40 (o-Ph, 6H), 7.05 (*m*,*p*-Ph, 9H), 6.44 (C₅H₄, vinyl 1H), 6.17 (C₅H₄, vinyl 1H), 6.09 (C₅H₄, vinyl 1H), 4.62 (C₅H₄, allyl 1H), 0.9 (tert-Bu, 9H), and to a set of signals compatible with the formula of a cationic yttrium derivative $[Cp'_2Y][B(C_6F_5)_4]$: δ ppm = 5.97 (C₅H₄, 4H), 5.74 (C₅H₄, 4H), 0.82 (*tert*-Bu, 18H). After addition of a second crop of $[CPh_3][B(C_6F_5)_4]$ (9.2 mg, 10 µmol), the same compounds were present in solution, but the inferior oily phase had increased. Addition of a third equiv $[CPh_3][B(C_6F_5)_4]$ $(9.2 \text{ mg}, 10 \mu \text{mol})$ afforded a mixture in which the signals of the putative cationic [Cp'₂Y][B(C₆F₅)₄] were still observed, in company with those of Cp'CPh₃, but the resolution was seriously altered due to large quantity of brown oil in the bottom of the tube.

3. Results and discussion

3.1. Synthesis of tris(cyclopentadienyl) complex Cp'₃Nd (1)

The title complex was synthesized according to metathetical reaction between $NdCl_3(THF)_2$ and KCp' (Scheme 1) as already described [5], but in refluxing THF and followed by extraction with toluene and evaporation to get the THF-free complex [4].

The crude neodymium product was recrystallized from pentane, affording large dichroic reddish crystals of Cp'_3Nd free of solvent molecule, according to ¹H NMR [15] and elemental analysis. As far as we are aware, it is the first time that this compound, already known as THF-solvated lithium halide (bromide [2a] or chloride [22]) is isolated without any additional ligand in its coordination sphere.

3.2. X-ray structure of $Cp'_3Nd(1)$

Crystals of **1** are orthorhombic, space group P2₁2₁2₁, with cell dimensions of a = 8.3916 (2) Å, b = 16.4447 (4) Å and c = 17.1450 (5) Å (Fig. 1). In contrast to previously described unsolvated tris [(monosubstituted)cyclopentadienyl] derivatives of neodymium, the basic structural unit in this crystal is the discrete (C₅H₄t-Bu)₃Nd, without (η^{1} : η^{5}) bridging cyclopentadienyl with an external Nd, like in (C₅H₄Me)₃Nd [23]. In the *i*-Bu series, the tri-substituted neodymium derivative is isolated as a mono-THF adduct [24].

Nd–CP distances are 2.493, 2.498, 2.520 Å (CP is the centroid of a cyclopentadienyl ligand). This is slightly smaller to what observed in Cp'₃NdBrLi(THF)₃ [2a] and Cp'₃NdClLi(THF)₃ [22] (average value 2.568 Å and 2.584 Å, respectively), and reflects the absence of a fourth coordinated ligand. CP–Nd–CP are 119.24, 119.45, and 120.94°, which is superior to the values found for Cp'₃NdBrLi(THF)₃ (116–117°) and Cp'₃NdClLi(THF)₃ (115.7–118°) for the same reasons. One can note that the CP–Nd–CP in **1** are close to 120°, as expected for a homoleptic complex having only three ligands and no extra external Cp interaction. Surprisingly, among the early lanthanides family and with the same Cp' ligand, no other molecular structure was determined [25]. However to our knowledge, in the monosubstituted cyclopentadienyl series, two other scarce examples of triscyclopentadienides of neodymium having like **1** a

$$NdCl_3(THF)_2 + 3 KCp' \xrightarrow{1. THF} Cp'_3Nd + 3 KCl$$

Scheme 1. Synthesis of
$$Cp'_3Nd(1)(Cp' = C_5H_4t-Bu)$$
.



Fig. 1. Asymmetric unit showing the molecular structure of complex **1**. Selected distances [Å] and angles $[^{\circ}]$: Nd–CP (average) 2.50, CP–Nd–CP (average) 119.88.

formal CN number of nine have been structurally characterized: $(C_5H_4CHTMS_2)_3Nd$ [26] and the recently described $(C_5H_4TMS)_3Nd$ [27] (TMS = SiMe₃). Both complexes compare very well with **1** in terms of structural features, particularly Nd–CP distances and CP–Nd–CP angles (ca 2.50 Å and 120°, respectively).

3.3. Isoprene polymerization using tris(cyclopentadienyl) derivatives as pre-catalysts

The homoleptic Cp'₃Nd **1** was assessed as pre-catalyst for isoprene polymerization. Due to the lack of coordinated THF, one could expect some reactivity if at least one Cp' ligand could be displaced. The pre-catalyst was combined with a boron activator – chosen among $[\text{HNMe}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (dimethylanilinium perfluorophenylborate designed here as HNB), $[\text{CPh}_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (trityl perfluorophenylborate, TB), or $[\text{B}(\text{C}_6\text{F}_5)_3]$ (perfluorophenylborane, B) – which is well-known to afford efficient isoprene polymerization catalysts with rare earth alkyls [28] or borohydrides [29], and an aluminum co-catalyst (MMAO or Al*i*-Bu₃). Selected results are gathered in Table 1.

No polymerization reaction took place with HNB (1, 2 or 3 equiv), whereas this boron-based molecule in particular has been successfully used as activator for polymerization reactions [30]. We observed in turn the production of polymer with 1 equiv $[CPh_3]^+[B(C_6F_5)_4]^-$ and in the presence of 5 equiv Ali-Bu₃ (run 1). The choice of such catalytic conditions was guided from the literature and our previous experience in the field [31]. The yield was low but the regio-selectivity observed (ca 82% 1,4-) was encouraging. With 2 equiv trityl borate and 10 equiv Ali-Bu₃, quite quantitative yield was obtained at 50 °C (run 2) and the selectivity was 84% 1,4- with 95/5 cis-/trans-ratio. At room temperature, very low conversion was received (run 3) with similar selectivity. Enhancing the monomer/catalyst ratio had weak effect upon the result (runs 4, 5). It is, however, noteworthy that SEC traces of the polymers for these runs displayed a shape that was nearly monomodal, indicative of the likely formation of one single active species. An additional equivalent of (trityl borate/5 Ali-Bu₃) was necessary to obtain significant conversion at room temperature (run 6), but the 1,4-*cis* rate was found that time less than 80%. The same was obtained by increasing the monomer to catalyst ratio (run 7). By raising the temperature to 50 °C, some polymer was received with good conversion (run 8). Interestingly, complete conversion was received in 12 h at 50 °C (run 9) and also at room temperature upon 72 h reaction time (run 10) when inversing the addition order of trityl borate/Ali-Bu₃. This better activity may be correlated with the initial solubility of the active species (see Section 2.5). In all experiments carried out with this (1/3 borate/15 Al) combination, at least ca 15% 3,4-defects were still present in the polymer.

Basically, we observed that five equivalents of trityl borate were mandatory in order to get high *cis*-rates, but at the condition to change the addition order (*ie* first Al, second borate): when maintaining the quantity of 15 equiv Al, 87% cis-rate (with less than 4% 3,4-polyisoprene, run 11) was received, whereas when adding first trityl borate and then Al-co-catalyst, a polymer containing a high amount of trans-motives (ca 35%, run 12) was formed. This result could be connected to steric hindrance in the coordination sphere of the neodymium atom [32]. With 25 equiv Ali-Bu₃, ie with the previous Al/borate ratio of 5, and upon reverse addition (first Al, second borate), high conversion along with ca 90% cis-rate was observed (run 13) at 50 °C. In the presence of 25 equiv Al but this time at room temperature, highly cis-stereoregular polyisoprene (95.5%, and cis/trans ratio close to 99%), of relatively high molecular weight, was obtained (run 14). At high monomer to catalyst ratio (3000, run 15), however, no improvement in terms of molecular weights but broadening of the polymolecularity was noticed. At 50 °C, the activity was higher than at room temperature, together with high cis-selectivity that was maintained at a level superior to 95% (run 16). When toluene was replaced by pentane with the same co-catalyst conditions, the catalyst was less efficient, with higher amounts of 3,4-polymer (run 17).

In terms of comparison with the literature for other neodymium catalysts [14,29a], the catalytic systems presented herein are only reasonably active (up to ca 16,000 g PI/mol Nd/h, run 10); this is likely related to the presence of the sterically demanding three Cp' ligands set surrounding the neodymium atom in the pre-catalyst. An experiment carried out with just trityl borate in the absence of co-catalyst yielded, within minutes, an intractable material typical of cationic polymerization affording cross-linked material (run 18). With pentafluorophenylborane $B(C_6F_5)_3$ as activator, and with the same Al/B ratio of 5, good conversion was obtained at 50 °C (runs 19-21). The reverse addition of co-catalyst/activator had this time no impact upon the final result. Good cis-selectivities were received (85-90%) but the SEC traces showed broader polymolecularities. Reactions conducted with Cp'₃Nd and MMAO (100 and 500 equiv) failed to produce polyisoprene and they are not included in Table 1. The "simple" Cp₃Nd (2) was also assessed as pre-catalyst, in the presence of trityl borate $([CPh_3]^+[B(C_6F_5)_4]^-)$ as boron activator, and Al(*i*-Bu)₃ as co-catalyst, but the experiments were not successful (run 22). This may be attributed to the low solubility of complex 2 in the solvent of polymerization. Additional preliminary polymerization experiments were also undertaken with the yttrium analog of **1**, $Cp'_{3}Y$, which was synthesized as described in Scheme 1 and characterized by ¹H NMR and elemental analysis.¹ We were able to obtain polyisoprene with high activity, but with addition of Al-cocatalyst and then borate activator in this order (runs 23, 24). The high amount of 3,4-defects (ca 25%) in the isolated polymer may be connected to the smaller size of the rare earth element, by comparison with neodymium, which favors single diene coordination.

3.4. Mechanistic investigations

As reminded above in the text, the reaction of a Bronsted acid with a tris(cyclopentadienyl)lanthanide compound was published in the early 1960's [7]. Just recently, this strategy was utilized to elaborate phenoxide complexes as initiators for lactide polymerization [33]. However, to our knowledge, such reactivity involving tris(cyclopentadienyl) derivatives of the rare earths, had not been exploited until now to promote the polymerization of conjugated dienes [34]. Kaita et al. largely explored the potentialities in this frame of Ln/Al bimetallics, in the bisCp* series, through borate activation of alkyl precursors [35]. Our approach strongly differs from Kaita's one, since in our case the general idea was based on the possibility to eliminate (at least) one η^5 Cp-type ligand (here a Cp' one) by direct protonation with an acidic borate activator. This type of reactivity had already been reported by Ephritikhine ten years ago in the case of a phospholyl abstraction (Scheme 2) [36].

We thus envisaged the three boron-based molecules – HNB, TB, or B (see above) – as possible activators in our catalytic combinations as described in Table 1. It is worth to be noted that the abstraction of an η^5 Cp-type ligand (rather than an alkyl one in the present case) by trityl borate was reported recently by Chen: a mono(indenyl)bis(alkyl) scandium complex lost its indenyl ligand by the reaction with TB to afford the corresponding Ph₃C-indene and a dialkylscandium cation [37]. Tardif described on his side both reactivity pathways, i.e. alkyl and ring abstraction, starting from bisindenylsilylamido rare earths complexes with either anilinium or trityl borate, giving rise to the elimination of an indenyl group [38]. Finally, trityl borate was found capable to extract one C₅Me₄H ligand from (C₅Me₄H)₃Al [39]. We thus expected that Cp^R₃Ln $(Cp^{R} = Cp' \text{ or } Cp; Ln = Nd \text{ or } Y)$ would behave comparably (Scheme 3, boron activator = HNB, TB, or B), to *in fine* generate an active species by subsequent reaction with an alkylating reagent such as AlR₃.

The question of the displacement of a Cp-type ligand (noted here as Cp^R) by an alkylating reagent could also be considered, having in mind the above-mentioned article of Schumann [9]. Thus, activation of a $(Cp^R)_3Ln$ pre-catalyst by an alkylaluminum reagent, as depicted in Scheme 4, had to be taken into account in this regard, despite the *a priori* steric saturation of a tris(cyclopentadienyl) derivative, and as also confirmed by the weak Nd–Al interaction reported by Arnold when (C_5Me_5)Al is added to (C_5H_4TMS)₃Nd [27].

On the other hand, comproportionation reactions that have been observed in the Cp' series, and which proceed through bimolecular processes, account for a possible Cp' "mobility" in Cp'₃Ln compounds (Scheme 5) [2d].

We undertook a series of reactions at the NMR scale aiming at identifying possible active species involved in the polymerization process. When **1** was reacted with trityl borate (2 equiv) in C_6D_6 , we observed by ¹H NMR the complete consumption of starting compound **1** along with diamagnetic signals that could be compatible with *tert*-BuC₅H₄CPh₃ (see Experimental). Some paramagnetic signals typical of a Cp'-supported Nd compound [15] were present, but of low intensity due to poor solubility of the compound formed. At the addition of Al(*i*-Bu)₃ (10 equiv), all was soluble again,

 $^{^1}$ To confirm this chemical formula, a synthesis of Cp'_3Y was carried out by ionic metathesis from Y(BH_4)_3(THF)_3. The isolated complex displayed the same 1H NMR spectrum that the one isolated from YCl_3.



Scheme 2. Activation of a Nd compound by protonation of a phospholyl ligand induced by a borate activator (COT = aromatic C_8H_8 , P^* = aromatic tetramethylphospholyl C_4Me_4P).

$$(Cp^R)_3Nd \xrightarrow{boron activator} [(Cp^R)_2Nd(solvent)_n]^+[borate]^- \xrightarrow{AIR_3} "(Cp^R)_2Nd-R'$$

Scheme 3. Reaction of a Cp^R₃Nd compound with a boron activator to generate an active species and the subsequent reaction with an alkylaluminum to generate the catalyst.

 $Cp'_{3}Nd + AIR_{3} \longrightarrow [Cp'_{2}Nd(\mu-Cp')(\mu-R)AIR_{2}] \longrightarrow Cp'_{2}NdR + AICp'R_{2}$

Scheme 4. Possible displacement of a Cp' ring by AlR₃ in 1.

2 (Cp')₃Sm + Sm(BH₄)₃(THF)₃ \longrightarrow 3/2 [(Cp')₂Sm(BH₄)]₂

 $\mbox{Scheme 5.}$ Comproportionation reaction from $\mbox{Cp'}_3\mbox{Sm}$ affording mixed $\mbox{Cp'/BH}_4$ complex.

showing among others the signals of free Al(*i*-Bu)₃ and of a paramagnetic species. When the reaction of **1** with trityl borate (2 equiv) was carried out in deuterated THF at room temperature, polymerization of THF took place within minutes, as already observed by others [30c,31d,40]. This was clearly indicative of the likely formation of a cationic species, which is known to rapidly promote such polymerization. Another experiment was done again but with immediate storage of the mixture at low temperature until the ¹H NMR spectrum was recorded. One could observe signals that could be attributed to *tert*-BuC₅H₄CPh₃ isomers and paramagnetic resonances compatible (one big signal at high fields and several others of less importance) with Cp'[Nd] species. The reaction of **1** with [HNMe₂Ph][B(C₆F₅)₄] (2 equiv) in C₆D₆ gave rise to the consumption of most part of **1** and formation of HCp' and free amine [41], as depicted in Scheme 6. Extraction with THF-d₈ confirmed the presence of $PhNMe_2$ [21], whereas a new compound was detected, which paramagnetic signals were close to what observed in the reaction of **1** with trityl borate.

Finally, the reaction of **1** with $Al(i-Bu)_3$ (10 equiv) showed no reaction at all, but signals of both reactants were slightly modified in terms of chemical shifts, and Al signals were found broadened. This accounts for a mechanism in which the Al-cocatalyst by itself is not able to displace a Cp' ligand, but a [Nd]···Al(*i*-Bu)₃ interaction is here clearly evidenced. The subsequent addition of trityl borate (2 equiv) showed on the ¹H NMR spectrum the disappearance of **1** with residual Al(*i*-Bu)₃ (initially present in large excess), along with apparition of paramagnetic signals, but their assignation to a possible active species was not possible.

To summarize these NMR experiments, a pattern emerges regarding paramagnetic data: one can observe in general two types of resonances, one or two bigger signals in the range [-10; -25 ppm] and smaller ones in the range [11-14 ppm]. These data support the presence of a Cp' ligand still attached to neo-dymium. Similar reactions at the NMR scale conducted with diamagnetic Cp'₃Y showed the complete consumption of the latter when reacted with 1 equiv [CPh₃][B(C₆F₅)₄]. The signals of Cp'CPh₃

 $(Cp')_3Nd + [HNMe_2Ph][B(C_6F_5)_4] \longrightarrow [(Cp')_2Nd]^+[B(C_6F_5)_4]^- + Cp'H + Me_2NPh$

Scheme 6. Reaction of Cp'₃Nd (1) with [HNMe₂Ph][B(C₆F₅)₄] to generate an active species.



Fig. 2. ¹H NMR reaction of Cp'₃Y with one equiv. [CPh₃][B(C₆F₅)₄] showing the complete disappearance of the starting material (C₆D₆).



Fig. 3. ¹H NMR reaction of Cp'₃Y with successive amounts of [CPh₃][B(C₆F₅)₄].

were clearly observed, along with those which could correspond to a cationic yttrium derivative $[Cp'_2Y][B(C_6F_5)_4]$ (Fig. 2). Interestingly, this compound was still present in solution in the presence of additional amounts of $[CPh_3][B(C_6F_5)_4]$ (Fig. 3). On the other hand, the poorly soluble oily phase observed in the NMR tube, which increased with the amount of trityl reagent added, was the probable indication of the formation of cationic active species in our polymerization mixtures.

Up to now and despite our efforts, syntheses devoted to the isolation of a cationic-like derivative that could arise from the reaction of a trisCp'Ln complex with a borate activator have not been successful yet, due to the too high reactivity in THF or low stability in other solvents [41.42]. However, it seems established that, at least, one Cp' ligand is abstracted from the coordination sphere of the rare earth in our catalytic combinations. The selectivity of the polymerization may be related to the number of Cp' ligands that could be displaced from the coordination sphere of the metal upon activation with the boron compound. Indeed, a [Cp'₂Ln⁺] active species would probably lead to a polymer with significant amount of 3,4-motives, which is generally accepted as arising from a single η^2 coordination of the isoprene monomer [29a]. In general from Table 1, it appears that quite high amounts of 3,4-defects are present in the polyisoprene prepared with 1–3 equiv borate activator. Considering the high cis-selectivity and the much lower 3,4-defects quantity observed in the presence of 5 equiv borate, one can postulate a possible displacement of a second Cp' ligand. Consequently, the formation of a cationic half-sandwich [Cp'LnR⁺] active species could also be proposed in such conditions, in line with the well-known high cis-selectivity of catalysts bearing such half-sandwich framework [43]. This also resembles the dicationic active species proposed by Okuda in the presence of excess borate activator [31c]. Further experiments aiming at completing this preliminary study for a better understanding of the mechanism involved are in progress.

4. Conclusion

The homoleptic Cp'_3Nd complex (Cp' = t-Bu C_5H_4) has been considered as potential polymerization pre-catalyst on the basis of its solvent-free molecular structure, despite the steric set of three cyclopentadienyl ligands surrounding the metal. The X-ray structure of this compound is presented for the first time. When combined with appropriate amounts of borate activators and aluminum co-catalyst, Cp'_3Nd successfully afforded a highly selective catalyst for the polymerization of isoprene. Up to 95.5% *cis*-regular polymer was produced with good activity. This reactivity is tentatively ascribed to the displacement of one or more Cp' ligand, on the basis of NMR experiments. Studies aiming at unequivocally establishing the formation of active bisCp' and monoCp' active species in such catalytic processes are in due course.

In summary, we have demonstrated in this work that the activation of an *a priori* saturated and easily available compound can be considered as a valuable approach to afford a catalyst for conjugated dienes polymerization.

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Appendix A. Supplementary material

CCDC 908388 contains 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.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.06.035.

References

- H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
 Selected examples: (a) S. Song, Q. Shen, S. Jin, Polyhedron 11 (1992) 2863;
- [2] Selected examples. (a) S. Song, Q. Shen, S. Jin, Polyhedron 11 (1992) 2803,
 (b) Z. Wu, Z. Xu, X. You, X. Zhou, X. Wang, J. Chen, Polyhedron 13 (1994) 379;
 (c) S. Wang, Y. Yu, Z. Ye, C. Qian, J. Organomet. Chem. 464 (1994) 55;
 (d) D. Baudry, A. Dormond, B. Lachot, M. Visseaux, G. Zucchi, J. Organomet.
- Chem. 547 (1997) 157.
- [3] J.M. Birmingham, G. Wilkinson, J. Am. Chem. Soc. 76 (1954) 6210.
- [4] S.D. Stults, R.A. Andersen, A. Zalkin, Organometallics 9 (1990) 115.
- [5] W.A. Herrmann, R. Anwander, M. Kleine, K. Ofele, J. Riede, W. Scherer, Chem. Ber. 125 (1992) 2391.
- [6] J.M. Birmingham, G. Wilkinson, J. Am. Chem. Soc. 78 (1956) 42.
- [7] R.E. Maginn, S. Manastyrskyj, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 672.
 [8] (a) C. Qian, D. Zhu, Y. Gu, J. Organomet. Chem. 401 (1991) 23;
- (b) C. Qian, D. Zhu, D. Li, J. Organomet. Chem. 430 (1992) 175.
- [9] H. Schumann, G. Jeske, Angew. Chem. Int. Ed. Engl. 24 (1985) 226.
- [10] (a) W.J. Evans, K.J. Forrestal, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 36 (1997) 774;
 - (b) W.J. Evans, J.M. Perotti, S.A. Kozimor, T.M. Champagne, B.L. Davis, G.W. Nyce, C.H. Fujimoto, R.D. Clark, M.A. Johnston, J.W. Ziller, Organometallics 24 (2005) 3916.
- [11] W.J. Evans, K.J. Forrestal, M.A. Ansari, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 2180.
- [12] Selected references: (a) J. Gromada, J.F. Carpentier, A. Mortreux, Coord. Chem. Rev. 248 (2004) 397;
 - (b) Z. Hou, Bull. Chem. Soc. Jpn. 76 (2003) 2253;
 - (c) Y. Nakayama, H. Yasuda, J. Organomet. Chem. 689 (2004) 4489;
- (d) P.M. Zeimentz, S. Arndt, B.R. Elvidge, J. Okuda, Chem. Rev. 106 (2006) 2404. [13] See for example: (a) R. Anwander, M.G. Klimpel, H.M. Dietrich, D.J. Shorokhov,
 - W. Scherer, Chem. Commun. (2003) 1008;
 - (b) S. Arndt, J. Okuda, Chem. Rev. 102 (2002) 1953;
 - (c) H.J. Heeres, A. Meetsma, J.H. Teuben, R.D. Rogers, Organometallics 8 (1989) 2637.
- [14] L. Friebe, O. Nuyken, W. Obrecht, Adv. Polym. Sci. 204 (2006) 1.
- [15] The complex had previously been synthesized in situ for the sake of NMR characterization but it was not isolated: M. Visseaux, A. Dormond, D. Baudry Bull. Soc. Chim. Fr. 130 (1993) 173.

- [16] Bruker Analytical X-ray Systems, Inc., Apex2, Version 2 User Manual (2006). M86-E01078, Madison, WI.
- [17] Siemens Industrial Automation, Inc., SADABS: Area-detector Absorption Correction. Madison, WI (1996).
- [18] L. Palatinus, G. Chapuis, J. Appl. Crystallogr. 40 (2007) 786.
- [19] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr. 36 (2003) 1487.
- [20] M.J. Vitorino, P. Zinck, M. Visseaux, Eur. Polym. J. 48 (2012) 1289.
- [21] S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J.H. Teuben, Chem. Commun. (2003) 522.
- [22] J. Guan, Q. Shen, S. Jin, Y. Lin, Acta Crystallogr. C50 (1994) 891.
- [23] J.H. Burns, W.H. Baldwin, F.H. Fink, Inorg. Chem. 13 (1974) 1916.
- [24] W.A. Herrmann, R. Anwander, F.C. Munck, W. Scherer, Chem. Ber. 126 (1993) 331.
- [25] The physical properties of (C₅H₄t-Bu)₃Ce were claimed as nearly identical with those of (Me₃SiC₅H₄)₃Ce, which was isolated as a base-free compound isostructural with (C₅H₄SiMe₃)₃U as shown by X-ray powder diffraction studies: A. Zalkin, J.G. Brennan, R.A. Andersen Acta Crystallogr. C44 (1988) 2104.
- [26] S. Al-Juaid, Y.K. Gun'ko, P.B. Hitchcock, M.F. Lappert, S.J. Tian, Organomet. Chem. 582 (1999) 143.
- [27] S.G. Minasian, J.L. Krinsky, J.D. Rinehart, R. Copping, T. Tyliszczak, M. Janousch, D.K. Shuh, J. Arnold, J. Am. Chem. Soc. 131 (2009) 13767.
- [28] S. Kaita, Z. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 9078. and refs cited therein.
- [29] (a) Z. Zhang, D. Cui, B. Wang, B. Liu, Y. Yang, Struct. Bond. 137 (2010) 49;
 (b) M. Visseaux, F. Bonnet, Coord. Chem. Rev. 255 (2011) 374.
- [30] (a) S. Li, W. Miao, T. Tang, W. Dong, X. Zhang, D. Cui, Organometallics 27 (2008) 718;
 - (b) R. Litlabø, M. Enders, K.W. Tornroos, R. Anwander, Organometallics 29 (2010) 2588:
 - (c) L. Zhang, Y. Luo, Z. Hou, J. Am. Chem. Soc. 127 (2005) 14562;
 - (d) M. Visseaux, M. Mainil, M. Terrier, A. Mortreux, P. Roussel, T. Mathivet, M. Destarac, Dalton Trans. (2008) 4558.
- [31] (a) Y. Luo, S. Fan, J. Yang, J. Fang, P. Xu, Dalton Trans. 40 (2011) 3053;
 (b) Z. Jian, D. Cui, Z. Hou, X. Li, Chem. Commun. 46 (2010) 3022;
 (c) S. Arndt, K. Beckerle, P.M. Zeimentz, T.P. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 44 (2005) 7473;
 (d) F. Bonnet, C. Da Costa Violante, P. Roussel, A. Mortreux, M. Visseaux, Chem. Commun. (2009) 3380.
- [32] G. Du, Y. Wei, L. Ai, Y. Chen, Q. Xu, X. Liu, S. Zhang, Z. Hou, X. Li, Organometallics 30 (2011) 160.
- [33] K. Nie, X. Gu, Y. Yao, Y. Zhang, S. Qi, Dalton Trans. 39 (2010) 6832.
- [34] Evans showed that $(C_5Me_5)_3Nd$ can be protonated by HNEt₃BPh₄ to yield the corresponding cation. This reactivity is attributed to the " η^1 -C₅Me₅ alkyl-like reactivity of the $(C_5Me_5)_3Ln$ complex", see Ref. [10].
- [35] (a) S. Kaita, Z. Hou, M. Nishiura, Y. Doi, J. Kurazumi, A.C. Horiuchi, Y. Wakatsuki, Macromol. Rapid Commun. 24 (2003) 179; (b) S. Kaita, M. Yamanaka, A.C. Horiuchi, Y. Wakatsuki, Macromolecules 39 (4) (2006) 1359.
- [36] S.M. Cendrowski-Guillaume, G. Le Gland, M. Lance, M. Nierlich, M. Ephritikhine, C. R. Chim. 5 (2002) 73.
- [37] X. Xu, Y. Chen, J. Sun, Chem. Eur. J. 15 (2009) 846.
- [38] O. Tardif, S. Kaita, Dalton Trans. (2008) 2531.
- [39] S.J. Lee, P.J. Shapiro, B. Twamley, Organometallics 25 (2006) 5582.
- [40] Y. Luo, J. Baldamus, Z. Hou, J. Am. Chem. Soc. 126 (2004) 13910.
- [41] M. Zimmermann, K.W. Tornroos, R. Anwander, Angew. Chem. Int. Ed. 47 (2008) 775.
- [42] L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, Angew. Chem. Int. Ed. 47 (2008) 2642.
- [43] Z. Hou, Y. Luo, X. Li, J. Organomet. Chem. 691 (2006) 3114.