ELSEVIER

Journal of Organometallic Chemistry 574 (1999) 213–218

Journal of Organo metallic Chemistry

Co-ordinatively unsaturated neodymium hydrides, stability in solution

Marc Visseaux [a,*], Denise Baudry [a], Alain Dormond [a], Changtao Qian [b]

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométallique, UMR 5632 CNRS, Faculté des Sciences Gabriel, 6, Boulevard Gabriel, 21000 Dijon, France*

[b] *Department of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Fenglin Lu, Shanghai, People's Republic of China*

Received 5 January 1998

Abstract

The tris-alkylborohydride $Cp^Q_2NdHBEt_3$ ($Cp^Q = C_5H_4CH_2CH_2OCH_3$) obtained by reaction of $NaHBEt_3$ with Cp^Q_2NdCl is fairly stable in solution whereas the hydride Cp^Q_2NdH formed from Cp^Q_2NdCl and NaH or by hydrogenolysis of Cp^Q_2NdR ($R = CH_2SiMe_3$ or $CH(SiMe_3)_2$) is a species of very short life, undergoing rearrangement to Cp^Q_3Nd. This transient hydride is not observed but can be trapped with ketones—propanone or pivalone, leading to the alkoxides $Cp^Q_2NdOCHR'_2$ ($R' = Me$ or CMe_3). The same alkoxides are obtained from $Cp^Q_2NdHBEt_3$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkylborohydride; Hydride; Lanthanides; Neodymium

1. Introduction

There is now a growing interest in the use of metallocenes for the stereospecific polymerisation of olefins [1,2]. Hydrides of the early lanthanides could be versatile catalysts for the α-olefins or dienes polymerization [3]. To be active as catalysts, organometallic hydrides ought to offer an accessible metal site and if possible a non-bridged, terminal hydride. Sterically unsaturated compounds of the lanthanides are not easily obtained—in the absence of ancillary ligands, auto-association leading to insoluble and untractable material occurs. It was then of interest to determine what are the limits of stability of non-hindered lanthanide metallocene hydrides and what are the best ways of synthesis.

A promising way to obtain stable although reactive hydride functionalities could be to synthesise, instead of a dimer of general formula $[L_2LnH]_2$ (L = cyclopentadienyl type ligand) bearing a μ-H bridge [4], the corresponding monomeric tris-alkylborohydride $L_2LnHBEt_3$ [5] (in some cases with a supplementary ancillary ligand, in compensation for the opening of the bridge). Aliphatic ethers are less co-ordinating than the ubiquitous THF, which is a poison for the polymerization reactions because of its strong co-ordination, it is not displaced by olefins. The use of a chelating cyclopentadienyl–ether ligand could provide a good compromise between stability and accessibility. Recently, Qian et al. described the preparation, by a simple nucleophilic displacement of a chloride ligand using NaH as a reagent, of some lanthanide hydrides of general formula Cp^Q_2LnH ($Cp^Q = C_5H_4CH_2CH_2OCH_3$) [6]. The X-ray crystal structure established the dimeric structure of the yttrium derivative—this element of small ionic radius has the same behaviour as the late small lanthanides. The nature of the early corresponding lanthanum and praseodymium compounds was inferred from IR data and elemental analyses.

We here describe the formation and the characterisation of both hydride and alkylborohydride from the same precursor Cp^Q_2NdCl, with the hydridic NaH and $NaHBEt_3$ reagents or by hydrogenolysis [7,8] of the corresponding alkyl compounds Cp^Q_2NdR and we discuss the mechanisms of the hydride formation.

---

* Corresponding author. Tel.: + 33 0380396084; fax: + 33 03806007.

PII S0022-328X(98)00549-X

Table 1
^{1}H-NMR data of complexes **1** to **8** in C_6D_6 (297 K; δ (ppm) versus TMS)

Compound	O–CH$_3$	–O–CH$_2$	–CH$_2$	Cp	Alkyl or H
Cp$^{Q}_{2}$NdCl (**1**)	−15.2	−9.5	0.5	14.5; 32.1	
Cp$^{Q}_{3}$Nd (**2**)	−16.1	−9.6	3.2	0.6; 13.1	
Cp$^{Q}_{3}$Nd^{a} (**2**)	−15.6	−9.3	3.1	Not depicted; 13.1	
Cp$^{Q}_{2}$NdCH$_2$SiMe$_3$ (**3**)	−17.8	−10.4	11.9	−9.7; 18.9	2.8 ($C\underline{H}_2$–Si); 4.9 (SiMe_3)
Cp$^{Q}_{2}$NdHBEt$_3$ (**4**)	−16.3	−11.6	6.4	−3.7; 11.4	198.0 (Nd–$\underline{H}$–B)
Cp$^{Q}_{2}$NdBH$_4$ (**5**)	−18.4	−10.2	4.9	−3.0^{b}; 15^{b}; −2.72^{c}; 12.32^{c}	74.0 ($B\underline{H}_4$)
Cp$^{Q}_{2}$NdOCHMe$_2$ (**6**)	−23.2	−21.1	−5.5	Not depicted	64.3 (O–$C\underline{H}$); 26.4 (CMe_2)
Cp$^{Q}_{2}$NdOCH(CMe$_3$)$_2$ (**7**)	−25.7	−21.2	−3.9	−11.5^{d}; 18^{d}	61.8 (O–$C\underline{H}$); 14.5 (CMe_3)
Cp$^{Q}_{2}$NdCH(SiMe$_3$)$_2$ (**8**)	−15.0	−5.3	8.3	−9.2; 10.3	27.6 ($C\underline{H}$–Si); −2.7 (SiMe_3)

[a] In THFD$_8$.
[b] $\nu_{1/2} > 400$ Hz.
[c] Recorded at 323 K; $\nu_{1/2} = 100$ Hz.
[d] $\nu_{1/2} > 800$ Hz.

2. Results and discussion

2.1. Reaction of NaH

We first tried to use NaH to get the neodymium hydride from the bis-cyclopentadienylchloro derivative **1**, as described for yttrium [6]. The reaction of NaH on **1** was performed in toluene or THF at room temperature (r.t.) or at −50°C. All attempts afforded the same new compound, **2**, which did not react with dimethylketone as a hydride would [5]. Compound **2** was found identical to a sample obtained [9] from the reaction of $NdCl_3$ with three equivalents of Cp^{Q}Na and identified as the tris-cyclopentadienyl Cp$^{Q}_{3}$Nd by comparison with an authentic sample characterised by X-ray analysis (see below).

$$\underset{\mathbf{1}}{Cp^{Q}{}_2NdCl} + NaH \xrightarrow[50\ ^{\circ}C]{THF,\ 7\ days} \mathbf{2} \xrightarrow[CH_3C(O)CH_3]{} \text{no reaction}$$

2.2. Hydrogenolysis experiments

In a first step, the convenient alkyl complex **3** (R = CH_2SiMe_3) was synthesised in situ in an NMR-tube. After degassing and pressurisation with dihydrogen, ^{1}H-NMR monitoring showed the progressive disappearance of the starting alkyl **3** and the concomitant formation of **2**. The hydrogenolysis was complete after 12 h at r.t. and the solution only exhibited the signals of **2** (Table 1).

$$\underset{\mathbf{1}}{Cp^{Q}{}_2NdCl} + LiCH_2SiMe_3 \xrightarrow[RT,\ 12\ h]{H_2} \mathbf{2}$$

Crystals of **2**, suitable for X-ray analysis, were isolated in an attempted synthesis of the trimethylsilylmethyl derivative **3** at a preparative scale, by the reaction of **1** with one equivalent of $LiCH_2SiMe_3$ in toluene. After removal of the solvent at r.t., addition of pentane, filtration of the blue solution and concentration, the NMR analysis showed the presence of **3** as the major product, contaminated with a small amount of **2** (ca. 10%). After standing for 2 weeks at r.t., blue–violet needles of **2** were obtained, and NMR analysis of the mother liquor revealed the presence of **2** alone. The structure of these crystals was found to be identical to that of a sample, already elucidated, but obtained by a classical method—addition of three equivalents of the cyclopentadienide reagent onto the neodymium chloride [9].

$$\underset{\mathbf{1}}{Cp^{Q}{}_2NdCl} + LiCH_2SiMe_3 \xrightarrow[RT]{40\ min}$$

$$\underset{\mathbf{3}}{Cp^{Q}{}_2NdCH_2SiMe_3} \xrightarrow[RT]{2\ weeks} \underset{\mathbf{2}}{Cp^{Q}{}_3Nd}$$

Because the hydrogenolytic way did not allow the obtention of a hydride, no further attempts for the synthesis of **3** were made.

2.3. Supported hydrides

The hydridic reagent $NaHBEt_3$ reacted on the monomeric chloride Cp$^{Q}_{2}$NdCl to give a new product, **4**. The presence of a very broad signal at 198 ppm in the ^{1}H-NMR spectrum led us to think that **4** was a neodymium hydride [5,10]. The absence of the ^{11}B-signal of free BEt_3 (δ = 86.9 ppm) implied that the new compound was an alkylborane supported hydride [11].

$$\underset{\mathbf{1}}{Cp^{Q}{}_2NdCl} + NaHBEt_3 \longrightarrow \underset{\mathbf{4}}{Cp^{Q}{}_2NdHBEt_3}$$

The formation of a tris-alkylborohydride had been previously observed for an analogous samarium compound, $(C_5H_4^tBu)_2SmHBEt_3(THF)_2$ [12] but also for pyrazolylboratoYb(II) [13] and Yb(III) [14] derivatives. Then it appears that the formation of a supported hydride occurs readily for the 4f-elements, which are hard Lewis acids whereas for the softer 5f-elements and especially uranium the formation of a hydride and the elimination of BEt_3 is invariably observed [15,16]:

$$(C_5H_4PPh_2)_3UCl + NaHBEt_3 \longrightarrow (C_5H_4PPh_2)_3UH + BEt_3$$

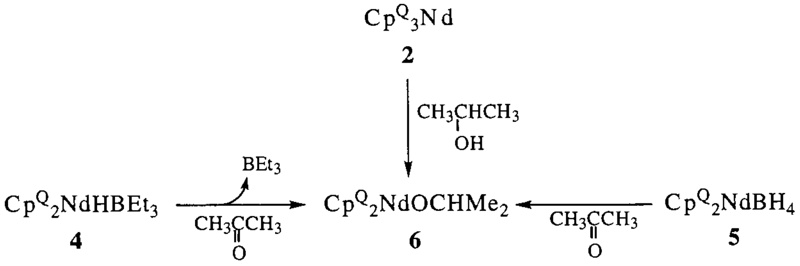
The hydride **4** was fairly stable in solution. After 12 h, 90% of the product was still present but 10% of **2** was also detected. The disproportionation affording **2** was complete within 1 week at r.t. Nevertheless it was found that after removal of the solvents of a crude solution, the percentage of **2** increased dramatically—from 5% in the initially freshly prepared solution to 30% (^{1}H-NMR). This fact was not really surprising—bimolecular reactions leading to rearranged products [17] are greatly favoured by concentration. It was then estimated that the synthesis of **4** in bulk would also lead to considerable rearrangements.

To prove the hydridic nature of **4**, the following reactions (more convenient for the f-elements than the usual methods involving treatment with halide derivatives [18]) were conducted:

(a) reaction with borane (from its dimethylsulfide adduct in toluene solution) led to the known borohydride **5**, which was identified by comparison with an authentic sample obtained by the published procedure [19];

$$\underset{\mathbf{4}}{Cp^{Q}_{2}NdHBEt_3} + BH_3{,}SMe_2 \longrightarrow \underset{\mathbf{5}}{Cp^{Q}_{2}NdBH_4} \longleftarrow \underset{\mathbf{1}}{Cp^{Q}_{2}NdCl} + TlBH_4$$

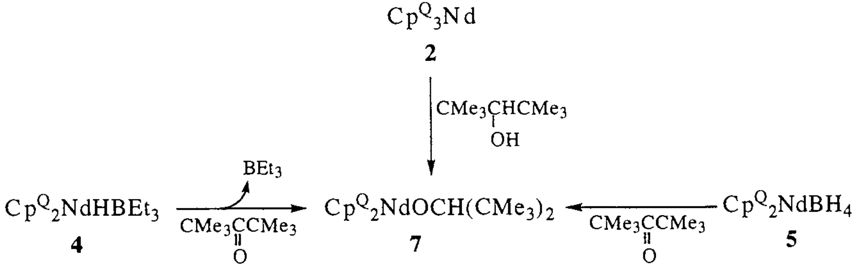
(b) reaction with dimethylketone afforded the alkoxy derivative **6** and free BEt_3, as established by ^{11}B-NMR of the crude reaction mixture. The alkoxide **6** has been also obtained by two other ways—insertion of dimethylketone in the Nd–H bond of the borohydride derivative **5** or alcoholysis of **2** with isopropanol.



$$\begin{tikzcd} & \mathrm{Cp^{Q}_{3}Nd}\ \mathbf{2} \arrow[d, "\mathrm{CH_3\underset{\underset{OH}{|}}{C}HCH_3}"] & \\ \mathrm{Cp^{Q}_{2}NdHBEt_3}\ \mathbf{4} \arrow[r, "\mathrm{BEt_3}", "\mathrm{CH_3\underset{\underset{O}{\|}}{C}CH_3}"'] & \mathrm{Cp^{Q}_{2}NdOCHMe_2}\ \mathbf{6} & \mathrm{Cp^{Q}_{2}NdBH_4}\ \mathbf{5} \arrow[l, "\mathrm{CH_3\underset{\underset{O}{\|}}{C}CH_3}"'] \end{tikzcd}$$

All attempts to isolate **6** have failed. After evaporation of the solvents, no solid material could be isolated—a slightly soluble blue oil was obtained. The NMR spectrum was no more interpretable, just revealing the presence of the tris-derivative **2** (20–30%). It is noteworthy that non-hindered lanthanide alkoxides are associated, the formation of dimers or oligomers invariably occurs [20,21]. Moreover, it was already published that bis-CpLn alkoxides easily undergo rearrangements leading to the corresponding tris-derivatives [22].

In contrast, the same reaction of **4** with a hindered ketone, the pivalone, afforded the pure alkoxide **7**. Analytically pure purple crystals of **7** were obtained in a one-pot reaction from the starting compound **1** and $NaHBEt_3$, in the presence of pivalone. **7** was also formed in the alcoholysis of **2** with pivalic alcohol and by reaction of pivalone with **5**.



$$\begin{tikzcd} & \mathrm{Cp^{Q}_{3}Nd}\ \mathbf{2} \arrow[d, "\mathrm{CMe_3\underset{\underset{OH}{|}}{C}HCMe_3}"] & \\ \mathrm{Cp^{Q}_{2}NdHBEt_3}\ \mathbf{4} \arrow[r, "\mathrm{BEt_3}", "\mathrm{CMe_3\underset{\underset{O}{\|}}{C}CMe_3}"'] & \mathrm{Cp^{Q}_{2}NdOCH(CMe_3)_2}\ \mathbf{7} & \mathrm{Cp^{Q}_{2}NdBH_4}\ \mathbf{5} \arrow[l, "\mathrm{CMe_3\underset{\underset{O}{\|}}{C}CMe_3}"'] \end{tikzcd}$$

2.4. The transient formation of $Cp^{Q}_{2}NdH$

The easy formation of the supported hydride **4** led us to reconsider the failure of the obtention of $Cp^{Q}_{2}NdH$ by NaH or by the hydrogenolytic method. In a previous study [12], we established that in order to get in good yield solution of the hydride $(Cp'_2SmH)_2$, it was necessary to use experimental conditions precluding the opening of the dimeric structure of the starting material $(Cp'_2SmCl)_2$, because the co-ordinatively unsaturated monomeric hydride Cp'_2SmH was unstable and rearranged very rapidly into the tris-derivative Cp'_3Sm. The unstability of the monomeric species could also be invoked in the neodymium series. The precursors $Cp^{Q}_{2}NdCl$ and $Cp^{Q}_{2}NdR$ are monomeric (only the lanthanum chloride was found to be dimeric [23]), and the displacement of the chloride by the smaller hydride ligand provided from NaH, or the hydrogenolysis of the Nd–C bond, would lead to a transient, unstable monomeric $Cp^{Q}_{2}NdH$ species.

Therefore, if the monomeric hydride $Cp^{Q}_{2}NdH$ was really formed, it should be trapped by a convenient reagent. Such a reagent could be a hindered ketone, unable to react with the starting alkyl material in the hydrogenolytic way. We investigated the hydrogenolysis of a hindered alkyl derivative, the bis-trimethylsilyl $Cp^{Q}_{2}NdCH(SiMe_3)_2$ **8**, in the presence of pivalone (**8** was made in situ and used immediately because of its tendency to disproportionation observed in a bulk synthesis). The NMR spectrum of the mixture **8** + pivalone was recorded to be sure that no insertion of the ketone occurred and the hydrogenolysis was carried out at 70°C. NMR monitoring showed the formation of the alkoxide **7** as the major product after 3 h. The obtention of this compound is the irrefutable proof of the intermediate formation of the monomeric hydride $Cp^{Q}_{2}NdH$.

$$\underset{\mathbf{8}}{Cp^{Q}{}_2NdCH(SiMe_3)_2} \xrightarrow[2)\ H_2]{1)\ CMe_3COCMe_3} \underset{\mathbf{7}\ (80\ \%)}{Cp^{Q}{}_2NdOCH(CMe_3)_2}$$

It was in this way established that the hydrogenolysis of the monomeric alkyl compound **8** afforded the expected monomeric hydride. To avoid the disproportionation leading to **2**, it was attempted to stabilise this unstable species by using an ancillary ligand such as PMe_3. Towards this goal, the trimethylsilyl derivative **3** was synthesised in situ in the presence of one equivalent of PMe_3 (in the starting material **1**, the phosphine was weakly co-ordinated to the metallic cation: ^{31}P-NMR: $\delta = -38$ ppm (very broad), $\nu_{1/2} = 120$ Hz; ^{1}H-NMR: $\delta = 0.68$ ppm). After addition of the alkylating reagent, a solution containing only **3** and apparently free trimethylphosphine (^{31}P-NMR: $\delta = -64$ ppm, $\nu_{1/2} = 2$ Hz; ^{1}H-NMR: $\delta = 0.79$ ppm) was obtained. No traces of the trisubstituted product **2** were detected unlike previously observed in an attempted synthesis of **3**, suggesting that PMe_3 might be weakly co-ordinated to **3**. The hydrogenolysis reaction performed on the mixture **3** + PMe_3 required 48 h to complete at r.t. (instead of 12 h in the absence of phosphine) proving that even weakly co-ordinated, the phosphine efficiently compete with the hydrogen to occupy a co-ordination site on the metal and thus decreasing the hydrogenolysis rate.

Nevertheless, the co-ordinating ability of the phosphine was too weak to offer a protecting effect towards the disproportionation leading to **2** which was again, after concentration of the freshly prepared solution, the sole product finally obtained.

3. Conclusion

In the neodymium series, the transient formation of the monomeric hydrides is established, but these co-ordinatively unsaturated compounds cannot be isolated even as the more stable dimeric species due to rapid rearrangement to give the stable tris-cyclopentadienyls and other unidentified neodymium species. The supported hydrides seem to be more stable, at least in solution, but all attempts to isolate these compounds in a solid state have failed. The reactivity of the supported hydride has been studied and the chemical evidence for its hydridic nature was established.

4. Experimental

4.1. General procedures

All manipulations were carried out under an atmosphere of purified nitrogen in a Jacomex glove-box or under argon using standard vacuum line techniques. Solvents were distilled from appropriate drying agent, stored over Na/benzophenone and vacuum transferred to reaction vessels immediately before use. ^{1}H- and ^{31}P-NMR spectra and ^{11}B-NMR spectra were recorded on AC 200 and DRX 500 Bruker spectrometers, respectively, at 297 K. The ^{31}P and ^{11}B-chemical shifts were measured versus H_3PO_4 in D_2O and BF_3,Et_2O in $CDCl_3$ as external reference, respectively. Elemental analyses were performed on a Fisons EA 1108 apparatus or by the Service Central d'Analyse du CNRS.

The compounds $Li(CHTMS)_2$ [24] and $LiCH_2TMS$ [25] were synthesised following published methods. $NaCp^{Q}$ was made by reaction of NaH over $Cp^{Q}H$ [23].

The syntheses in NMR-tubes were performed on about 10 mg of the compound dissolved in 0.4 ml of C_6D_6 or $THFD_8$ and monitored by ^{1}H-NMR. Yields were generally estimated by integration of the cyclopentadienyl or Me protons signals.

*4.2. Reaction of $Cp^{Q}_{2}NdCl$, **1** with NaH*

A large excess of NaH (27.7 mg, 1.15 mmol) was added to a solution of **1** (50 mg, 0.115 mmol) in 3 ml of $THFD_8$. After stirring for 24 h at 50°C, the mixture was analysed by NMR. It contained ca. 20% of unreacted **1** and 80% of $Cp^{Q}_{3}Nd$, **2**. After 2 days, the consumption of **1** was complete and a small amount of the anion Cp^{Q-} was identified nearby **2** as the major product. The same experiment from two equivalents of NaH gave the same results.

*4.3. Synthesis of $Cp^{Q}_{3}Nd$, **2***

This compound has been prepared using the published method [9] and two other procedures:

(a) The storage at r.t. of a concentrated solution of $\mathrm{Cp_2^{Q}NdCH_2SiMe_3}$, **3**, prepared in situ (see below) led after two weeks to blue crystals of **2** (62 mg, 0.012 mmol). One crystal was suitable for X-ray analysis.

(b) **1** (92 mg, 0.21 mmol) was dissolved in toluene (20 ml) and 0.21 ml of a molar solution of $\mathrm{NaHBEt_3}$ (0.21 mmol) in toluene was added dropwise. A white precipitate deposited immediately and after 30 min stirring, the mixture was filtered and concentrated to ca. 5 ml. After 24 h at r.t., as no crystals had appeared, the resulting solution was evaporated to dryness. The crude product contained ca. 90% of **2** as soluble materials, nearby unidentified products.

4.4. *Synthesis of* $\mathrm{Cp_2^{Q}NdCH_2SiMe_3}$, ***3***

Toluene (20 ml) was condensed at −80°C onto $\mathrm{LiCH_2SiMe_3}$ (26 mg, 0.27 mmol) and **1** (115 mg, 0.27 mmol). The mixture was allowed to increase back to r.t. After 40 min stirring, the solvent was removed and the crude product was extracted with 30 ml pentane. The blue solution was filtered and concentrated to ca. 5 ml leading to a blue oil containing (^{1}H-NMR) 90% of **3** and 10% of **2**. The decomposition of **3** into **2** was complete within 2 weeks at r.t.

4.5. *Hydrogenolysis of* ***3***

(a) Without ancillary ligand: an NMR-tube containing **3** synthesised in situ from 7 mg (0.016 mmol) of **1** and 1.5 mg (0.016 mmol) of $\mathrm{LiCH_2SiMe_3}$ in $\mathrm{C_6D_6}$ was filled with $\mathrm{H_2}$ (1 atm.). The reaction was monitored by NMR—the signals of **2** appeared immediately and, after 12 h, only **2** was present in the solution.

(b) In the presence of $\mathrm{PMe_3}$: in a NMR-tube, $\mathrm{PMe_3}$ (2 μl, 0.019 mmol) was added to a solution of **1** (8 mg, 0.019 mmol) in $\mathrm{C_6D_6}$ and NMR analysis showed $\mathrm{PMe_3}$ weakly co-ordinated to the metal (^{31}P-NMR: $\delta = -38$ ppm, $\nu_{1/2} = 120$ Hz; ^{1}H-NMR: $\delta = 0.68$ ppm). Addition of $\mathrm{LiCH_2SiMe_3}$ (2 mg, 0.020 mmol) led to the immediate and quantitative formation of **3** in the presence of free $\mathrm{PMe_3}$. The tube was filled with $\mathrm{H_2}$. **2** began to appear only after 1 h. After 48 h, the solution contained only **2** as identified product.

4.6. $\mathrm{Cp_2^{Q}NdHBEt_3}$, ***4***

A toluene solution of $\mathrm{NaHBEt_3}$ (15 μl, 0.015 mmol) was added to a solution of **1** (6.5 mg, 0.015 mmol) in $\mathrm{C_6D_6}$. ^{1}H- and ^{11}B($\delta = 10.5$ ppm)-NMR studies showed the formation of **4** with ca. 5% of **2**.The solvents were removed and the ^{1}H-NMR spectrum recorded after addition of $\mathrm{C_6D_6}$ revealed 70% of **4** and 30% of **2**.

4.7. $\mathrm{Cp_2^{Q}NdBH_4}$, ***5***

(a) The published method [19] was modified, $\mathrm{TlBH_4}$ in toluene was used instead of $\mathrm{NaBH_4}$ in THF: **1** (11 mg, 0.026 mmol) and $\mathrm{TlBH_4}$ (5 mg, 0.024 mmol) were stirred by ultrasound in $\mathrm{C_6D_6}$. After 4 h at 65°C, the solution contained only **5**. The same experiment was also conducted with one equivalent of $\mathrm{KBH_4}$ (16.5 mg, 0.305 mmol) in toluene for 130 mg (0.305 mmol) of **1**. After refluxing for 3 days, the reaction was not complete: **5**, **2** and **1** could be found in the mixture (75%, 5% and 20%, respectively).

(b) A solution of $\mathrm{BH_3{,}SMe_2}$ (7.5 μl, 0.015 mmol) was added to a solution of freshly prepared **4** in $\mathrm{C_6D_6}$. **5** was formed as the unique product.

4.8. $\mathrm{Cp_2^{Q}NdOCHMe_2}$, ***6***

(a) To a solution of **4** formed in situ from **1** (20 mg, 0.047 mmol) and $\mathrm{NaHBEt_3}$ (0.047 mmol, 47 μl of a 1M toluene solution) in $\mathrm{C_6D_6}$, dimethylketone (5 μl, 0.063 mmol) was added. The ^{1}H-NMR spectrum, recorded immediately after the addition, showed the immediate formation of **6**.

(b) **2** (8 mg, 0.016 mmol) was dissolved in $\mathrm{C_6D_6}$ and 2-propanol (0.75 ml, 0.016 mmol) was added. NMR analysis showed the slow formation of **6**—30% after 1 h, 60% after 24h.

(c) Dimethylketone (1.5 μl, 0.021 mmol) was added to a freshly prepared solution of **5** (0.023 mmol) in $\mathrm{C_6D_6}$. The almost quantitative formation of **6** was immediately evidenced by NMR.

4.9. $\mathrm{Cp_2^{Q}NdOCH(CMe_3)_2}$, ***7***

(a) **1** (304 mg, 0.713 mmol) was dissolved in 10 ml toluene and pivalone (122.8 μl, 0.713 mmol) was added—no reaction occurred. $\mathrm{NaHBEt_3}$ (0.713 mmol) in toluene was added. The colour turned immediately blue–green and a white precipitate of NaCl deposited. After filtration and concentration of the solvent to 4 ml, the solution was allowed to stand for 24 h at 0°C. The blue–violet crystals were washed with cold pentane and dried for 12 h under reduced pressure at r.t. Yield: 270 mg (71%). Anal. Found: C, 56.14; H, 7.80. $\mathrm{C_{25}H_{41}O_3Nd}$. Calc.: C, 56.25; H, 7.74%.

(b) A solution of pivalone (3.4 μl, 0.02 mmol) in $\mathrm{C_6D_6}$ was reduced by $\mathrm{NaHBEt_3}$ (20 μl of a 1 M solution, 0.02 mmol), followed by protonolyse with one equivalent of water (0.36 μl, 0.02 mmol). NMR monitoring confirmed the disappearance of the ^{t}Bu proton's signal of the pivalone ($\delta = 1.09$ ppm), replaced by the ^{t}Bu protons signal of the pivalic alcohol ($\delta = 0.92$ ppm). **2** (10.4 mg, 0.02 mmol) was added. After 1 h at r.t., the solution contained **7**, free

$C_5H_5CH_2CH_2OCH_3$, and small amounts of unreacted **2** and pivalic alcohol.

(c) Pivalone (52 μl, 0.305 mmol) was added to a solution of **5** (yield evaluated by NMR 80%) prepared by refluxing for 3 days a mixture containing **1** (130 mg, 0.305 mmol) and an equimolar amount of KBH_4 in toluene (20 ml). The quantitative transformation of **5** into **7** was immediately evidenced by NMR. No crystallisation occurred after concentration (ca. 5 ml) and addition of pentane (2 ml), followed by a 12 h standing at −10°C. The solution was then evaporated to dryness and an NMR of the crude product revealed the presence of **2** (50%) and **7** (40%). All attempts to separate **7** from **2** failed.

4.10. Synthesis of $Cp^{Q}_{2}NdCH(SiMe_3)_2$, 8

In a NMR-tube, $LiCH(SiMe_3)_2$ and **1** (10 mg, 0.023 mmol) were dissolved in C_6D_6. The formation of **8** was quite quantitative with a very small amount of **2** (< 5%).

4.11. Synthesis of 7 from $Cp^{Q}_{2}NdCH(SiMe_3)_2$, 8

Pivalone (3.5 μl, 0.02 mmol) was added to a C_6D_6 solution of **8** (10 mg, 0.018 mmol) in a NMR-tube. The tube was filled with hydrogen to atmospheric pressure and stored at r.t. No reaction occurred. After 3 h heating at 70°C, the tube contained **7** (80%), **2** (10%) and unidentified by-products.

References

[1] W.A. Herrmann, B. Cornils, Angew. Chem. Int. Ed. Engl. 36 (1997) 1048–1067.

[2] L. Jia, X.M. Yang, A.M. Seyam, et al., J. Am. Chem. Soc. 118 (1996) 7900–7913.

[3] E. Ihara, M. Nodono, H. Yasuda, N. Kanehisa, Y. Kai, Macromol. Chem. Phys. 197 (1996) 1909–1917.

[4] G.L. Soloveichik, New J. Chem. 19 (1995) 597–618.

[5] M. Visseaux, D. Baudry, A. Dormond, C.T. Qian, C.R. Acad. Sc. Sér. IIb 323 (1996) 415–419.

[6] D.L. Deng, Y.Q. Jiang, C.T. Qian, G. Wu, P.J. Zheng, J. Organomet. Chem. 470 (1994) 99–107.

[7] G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091–8103.

[8] H. Schumann, G. Jeske, Angew. Chem. Int. Ed. Engl. 24 (1985) 225–226.

[9] C.T. Qian, B. Wang, D.L. Deng, et al., J. Chem. Soc. Dalton Trans. (1996) 955–960.

[10] M. Visseaux, A. Dormond, D. Baudry, Bull. Soc. Chim. Fr. 130 (1993) 173–184.

[11] H. Noth, B. Wrackmeyer, Nuclear Magnetic Properties of Boron, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR Basic Principles and Progress, vol. 14, Berlin, 1978, pp. 5–9.

[12] D. Baudry, A. Dormond, B. Lachot, M. Visseaux, G. Zucchi, J. Organomet. Chem. 547 (1997) 157–165.

[13] L. Hasinoff, J. Takats, X.W. Zhang, A.H. Bond, R.D. Rogers, J. Am. Chem. Soc. 116 (1994) 8833–8834.

[14] J. Takats, personal communication.

[15] M. Ephritikhine, New J. Chem. 16 (1992) 451–469.

[16] D. Baudry, A. Dormond, A. Hafid, New J. Chem. 17 (1993) 465–470.

[17] S.W. Wang, Y.F. Yu, Z.W. Ye, C.T. Qian, X.Y. Huang, J. Organomet. Chem. 464 (1994) 55–58.

[18] Z. Xie, C. Qian, H. Y, J. Organomet. Chem. 412 (1991) 61–69.

[19] D.L. Deng, X.F. Zheng, C.T. Qian, J. Sun, L. Zhang, J. Organomet. Chem. 466 (1994) 95–100.

[20] L.G. Hubertpfalzgraf, New J. Chem. 19 (1995) 727–750.

[21] W.J. Evans, New J. Chem. 19 (1995) 525–533.

[22] Z.Z. Wu, Z. Xu, X.Z. You, X.G. Zhou, X.Y. Huang, J.T. Chen, Polyhedron 13 (1994) 379–384.

[23] C.T. Qian, B. Wang, D.L. Deng, J.Q. Hu, J. Chen, G. Wu, P.J. Zheng, Inorg. Chem. 33 (1994) 3382–3388.

[24] P.J. Davidson, D.H. Harris, M.F. Lappert, J. Chem. Soc. Dalton Trans. (1976) 2268.

[25] R.R. Schrock, J.D. Fellman, J. Am. Chem. Soc. 95 (1973) 5529.