ELSEVIER

Journal of Organometallic Chemistry 562 (1998) 71–78

Journal of Organo metallic Chemistry

Half-sandwich and *ansa*-niobiocenes: synthesis and reactivity[1]

Laurent Djakovitch [2], Wolfgang A. Herrmann *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching b. München, Germany

Received 15 July 1997

Abstract

The reaction of [Nb(NMe$_2$)$_3$(=N-2,6-iPr$_2$C$_6$H$_3$)] **1** with the cyclopentadienyl-indenyl isopropylidene ligand **2** gave the new half-sandwich niobium complex [Nb(η^5- C$_5$H$_4$R)(NMe$_2$)$_2$(=N-2,6-iPr$_2$C$_6$H$_3$)] (R = CMe$_2$C$_9$H$_7$) **3** in high yield. The new *ansa*-type niobiocene [Nb(NMe$_2$)(=N-2,6-i-Pr$_2$C$_6$H$_3$)(η^5:η^1-{C$_5$H$_4$}C(CH$_3$)$_2${C$_9$H$_6$}] **4** was obtained at higher temperatures by an intramolecular deprotonation with concomitant coordination of the indenyl group. The reactivity of the new *ansa*-niobiocene **4** towards electrophilic reagents, giving chloro- and cationic *ansa*-type niobium complexes is described. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Niobium; Amido complexes; Imido complexes; Cationic complexes

1. Introduction

Ansa-metallocene complexes have been extensively developed due to their large application as homogeneous Ziegler–Natta polymerization catalyst precursors for α-olefins using methylaluminoxane (MAO) as co-catalysts [1,2]. Most of these derivatives are known for the group 4 transition metals (group of Zr and Ti) [3]. The development of new systems, in order to control both the stereospecificity and the molecular mass of the final polymer is a goal of many research groups. Only recently, *ansa*-metallocenes of the group 5-elements (Nb, Ta) attracted increasing interest; niobium and tantalum complexes have become known as catalyst precursors for the 'living polymerization' of ethylene [4].

In previous work, we have reported a series of half-sandwich imido complexes and *ansa*-metallocenes of niobium and tantalum that were investigated as catalyst precursors for the ethylene polymerization [5]. In our continuing research on these systems, we now report the preparation and the reactions of a niobium *ansa*-metallocene based on the cyclopentadienyl-indenyl isopropylidene ligand.

2. Results and discussion

The imido-tris-amido-niobium (V) complex [Nb(NMe$_2$)$_3$(=N-2,6-iPr$_2$C$_6$H$_3$)] **1** was treated with an equimolar amount of the protic ligand C$_5$H$_5$C(CH$_3$)$_2$C$_9$H$_7$ **2**. Deprotonation by an amido ligand of **1** of the cyclopentadiene ring, resulting in its η^5-coordination to the metal centre, occurs smoothly at 100°C in toluene [5]. Monitoring the reaction by ^{1}H NMR showed that the reaction is completed within 2 h without noticeable thermal decomposition of the complex **3**. The new half-sandwich niobium complex **3** is formed quantitatively, and is isolated in good yield (88%) as a yellow-brown oil (Scheme 1). The complex **3** showed characteristic ^{1}H NMR resonances for the cyclopentadienyl ligand which gave as expected two *pseudo*-triplets at $\delta = 5.77$ and 6.05 ppm with a charac-

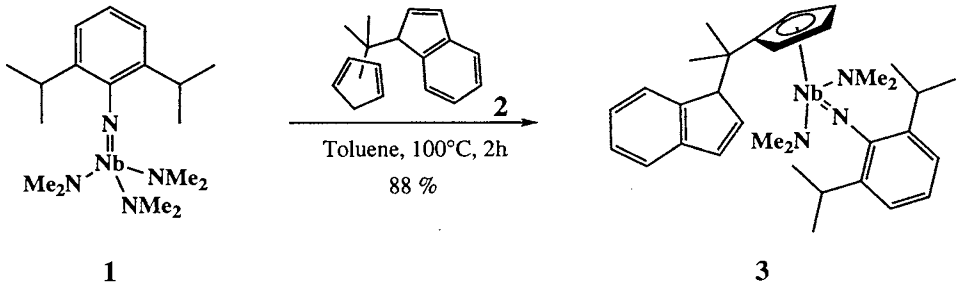
---

* Corresponding author. Fax: +49 89 28913473.

[1] Dedicated to Professor Bruce King on the occasion of his 60th birthday.

[2] Research Fellow of the Alexander von Humboldt Foundation (1995–1997).

PII S0022-328X(97)00720-1



Scheme 1.

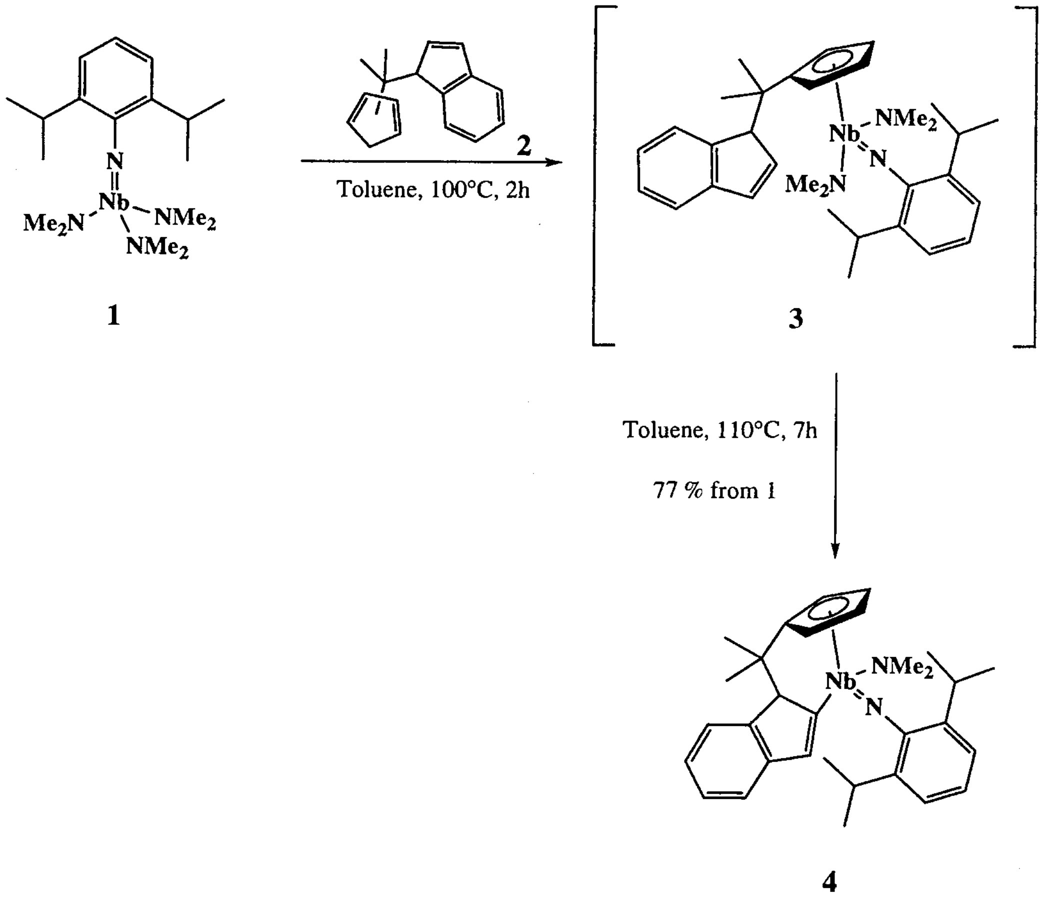
teristic coupling constant ^3J(H,H) ≈ 2.5 Hz. ^{1}H NMR data do not indicate interactions between the metal centre and the indenyl ligand, i.e. no detectable π-interactions with the vinylic part of the indenyl group.

Investigating the thermal stability of the complex **3** by ^{1}H NMR in toluene-D_8, it was found that it was quite stable below 100°C even for long reaction times of several hours. Further reactions were observed at 110°C in toluene-D_8 giving the new *ansa*-niobiocene **4** in high yield, characterised by a strong modification in the ^{1}H NMR of the cyclopentadienyl region which showed two *pseudo*-quartets at $\delta = 5.70$ and 5.80 ppm plus one *pseudo*-triplet at $\delta = 5.94$ ppm (Scheme 2).

While the coordination of the indenyl group could directly be studied from the precursor complex **3**, we studied this reaction in a one-pot synthesis. After a reaction time of 2 h between the niobium (V) complex **1** and the ligand **2** at 100°C in toluene, the mixture was then refluxed at 110°C for different reaction times. Monitoring the reaction by ^{1}H NMR, we found that the indenyl coordination was completed after 7 h without noticeable decomposition of the *ansa*-niobiocene **4**. The longer reaction time observed for the coordination of the indenyl ligand versus the cyclopentadienyl ligand is only due to the difference in pK_a between the cyclopentadienyl and the indenyl group (respectively 16 and 20) [6]. The new *ansa*-metallocene **4** was synthesised quantitatively and isolated as a yellow amorphous powder from heptane in good yield (77%) (Scheme 2). It is characterised in ^{1}H NMR by two *pseudo*-quartet at $\delta = 5.70$ and 5.80 ppm with a coupling constant ^3J(H, H) ≈ 3.0 Hz plus one *pseudo*-triplet at $\delta = 5.94$ ppm with a characteristic coupling constant ^3J(H, H) ≈ 3.0 Hz for the cyclopentadienyl region, two broad singulets at $\delta = 3.94$ ppm for the *ipso*-CH of the indenyl function and $\delta = 6.94$ ppm for the vinylic-CH of the indenyl group. In the ^{13}C NMR, the cyclopentadienyl ligand gives four signals in the range of $\delta \approx 98$–108 ppm for the resonance of the CH group plus one signal at $\delta \approx 136$ ppm for the *ipso*-C. In addition, the complex **4** is characterised by the resonance of the η^1-coordinated indenyl ligand at $\delta \approx 178$ ppm for the carbon coordinated to the metal centre, attribution confirmed by ^{13}C[^{1}H] coupled NMR experiment (this signal appears as a singulet, i.e. no H atom is attached to this carbon) and one signal at $\delta \approx 40$ ppm for the *ipso*-CH of the indenyl group. All the values obtained in ^{1}H and ^{13}C NMR are in agreement with the η^1-coordination attributed to the indenyl ligand in the complex **4**.

Finally the complex **4** was monitored by temperature programmed ^{1}H NMR from 20 to 100°C in toluene-D_8. The records showed that from 50°C the broad singulet observed for the amido ligand becomes sharper to give at 80°C sharp signal at $\delta = 3.34$ ppm resulting from a free rotation of this group. At the same time, the cyclopentadienyl region is modified. The *pseudo*-triplet observed at room temperature at $\delta = 5.94$ ppm splits into two *pseudo*-quartets to give finally at 80°C two well separated signals at $\delta = 5.96$ and 6.01 ppm with a coupling constant ^3J(H, H) ≈ 2.7 Hz. This modification of the cyclopentadienyl region results probably from the free rotation of the amido ligand, which does not contribute further to the stabilisation of the complex through donation of nitrogen lone pair.

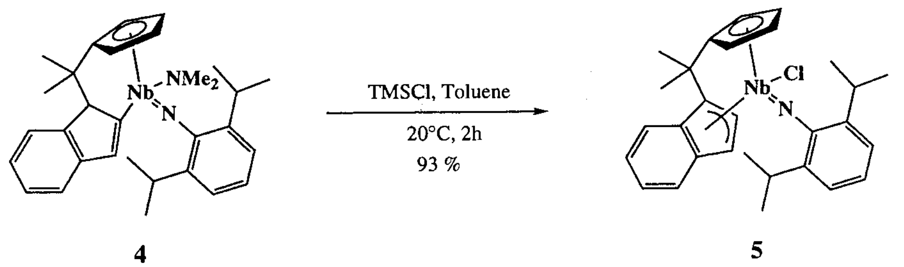
Treatment of the complex **4** with trimethylsilylchloride in excess at − 78°C in toluene gave after a reaction time of 2 h at room temperature quantitatively the new *ansa*-niobiocene **5** (Scheme 3). The initial yellow solution of **4** in toluene turned quickly dark red at room temperature, resulting from the formation of the new chloro complex **5**. The complex **5** was isolated in high yield (93%) as a micro-crystalline material from a heptane solution. It is characterised in ^{1}H NMR by four *pseudo*-quartets in the range from $\delta \approx 5.5$ to $\delta = 6.3$ ppm with a coupling constant ^3J(H, H) ≈ 2.5 Hz for the cyclopentadienyl ligand. In addition, the ^{1}H NMR showed two signals at $\delta = 5.84$ and 6.18 ppm for the resonance of the vinylic CH of indenyl ligand. In the ^{13}C NMR, the cyclopentadienyl ligand gives four signals in the range from $\delta \approx 98$ to 110 ppm for the resonance of the CH group plus one signal at $\delta \approx 133$ ppm for the *ipso*-C. In addition, the complex **5** is characterised by resonances from the η^3-coordinated indenyl ligand at $\delta \approx 112$–113 ppm as two signals for the two vinylic CH group plus one signal at $\delta \approx 121$ ppm for the *ipso*-C of the indenyl ligand. All these values are in agreement with the commonly accepted values for the η^3-coordination of an indenyl ligand [7].



Scheme 2.

Treatment of the complex **4** with an equimolar amount of $[HNMe_3][B(C_6H_5)_4]$ at −40°C in THF gave quantitatively, after a reaction time of 12 h at room temperature, the new cationic *ansa*-niobiocene **6a** (Scheme 4). The initial yellow-brown solution of **4** in THF turned slowly red at room temperature, resulting from the formation of the new cationic complex **6a**. The niobiocene **6a** was isolated in good yield (60%) as a red amorphous material from a pentane-THF solution. It is characterised in ^1H NMR by four *pseudo*-quartets in the range from $\delta \approx 6.4$ to $\delta = 6.8$ ppm with a coupling constant $^3J(H, H) \approx 2.5$ Hz for the cyclopentadienyl ligand. In addition, the ^1H NMR showed two septets at $\delta = 3.37$ and 4.13 ppm with a coupling constant $^3J(H, H) \approx 6.5$ Hz for the resonance of the CH of the isopropyl group of the imido ligand, one doublet at $\delta = 1.51$ ppm with a coupling constant $^3J(H, H) \approx 7.1$ Hz for the resonance of the methyl group of the coordinated amino ligand. Two signals are observed for the resonance of vinylic CH groups of the indenyl ligand, one *pseudo*-triplet at $\delta = 7.03$ ppm with a coupling constant $^3J(H, H) \approx 8.1$ Hz and one signal at $\delta = 7.55$ ppm (overlapping with another aromatic signal). In the ^{13}C NMR, the cyclopentadienyl ligand gives four signals in the range of $\delta \approx 98$ to 108 ppm for the resonance of the CH groups plus one signal at $\delta \approx 136$ ppm for the *ipso*-C and the coordinated amino ligand a signal at $\delta \approx 41$ ppm for the resonance of the methyl groups. In addition, the complex **6a** is characterised by the resonance of the η^3-coordinated indenyl ligand at $\delta \approx 126$ and 133 ppm for the vinylic CH group plus one signal at $\delta \approx 118$ ppm for the *ipso*-C of the indenyl ligand. All these values are in agreement with the η^3-coordination of an indenyl ligand [7].

Treatment of the complex **4** with equimolar amount of $[HNMe_3][Cl]$ at −40°C in THF gave quantitatively, after a reaction time of 2 h at room temperature, the new cationic *ansa*-niobiocene **6b** (Scheme 4). The initial yellow-brown solution of **4** in THF turned quickly dark red at room temperature, resulting from the formation of the new cationic complex **6b** isolated in good yield (73%) as a dark red material from a pentane-THF solution. It is characterised in ^1H NMR by four broad *pseudo*-quartets in the range from $\delta \approx 6.2$ to 6.8 ppm for the cyclopentadienyl ligand. In addition, the ^1H NMR showed two septets at $\delta = 3.08$ and 3.97 ppm with a coupling constant $^3J(H, H) \approx 7.0$ Hz for the resonance of the CH groups of the isopropyl group of the imido ligand and one doublet at $\delta = 1.28$ ppm with a coupling constant $^3J(H, H) \approx 6.5$ Hz for the reso-



Scheme 3.

nance of the methyl group of the coordinated amino ligand. One *pseudo*-triplet at $\delta = 6.67$ ppm with a coupling constant $^3J(H, H) \approx 8.3$ Hz and one doublet at $\delta = 6.99$ ppm with a coupling constant $^3J(H, H) \approx 8.3$ Hz are observed for the resonance of vinylic CH of the indenyl ligand. In the ^{13}C NMR, the cyclopentadienyl ligand gives four signals in the range from $\delta \approx 98$ to 113 ppm for the resonance of the CH group plus one signal at $\delta \approx 131$ ppm for the *ipso*-C and the coordinated amino ligand a signal at $\delta \approx 40$ ppm. In addition, the complex **6b** is characterised by the resonance of the η^3-coordinated indenyl ligand at $\delta \approx 121$ and 124 ppm for the vinylic CH plus one signal at $\delta \approx 120$ ppm for the *ipso*-C of the indenyl ligand. All these values are in agreement with the η^3-coordination of an indenyl ligand [7].

Both isolated cationic complexes **6a** and **6b** are quite stable under argon, but at room temperature in THF solution a slow ligand exchange between the amino group and THF takes place (Scheme 5) giving less stable complexes **7a–b**, which decomposed affording new unassignable products. Monitoring this reaction by ^{1}H NMR in THF-D_8 we showed that after 10 h at r.t. 22% of the amino ligand was exchanged by THF-D_8, characterised by the apparition of a doublet for the free dimethylamine at $\delta = 2.28$ ppm with a coupling constant $^3J(H, H) \approx 6.3$ Hz. The low stability of the new complexes is probably due to a lower contribution of the coordinated THF to the stabilisation of the cationic complexes. The rapid decomposition of both **7a** and **7b** in solution prevented us from obtaining well defined data of these compounds.

The new niobium complexes **3–6** are very sensitive to air, rapidly leading to the formation of white solid resulting from hydrolysis. They can be stored at room temperature under argon for several weeks without any noticeable decomposition.

The catalytic activity of the new *ansa*-metallocenes of niobium **3–6** as catalyst precusors for the α-olefin polymerisation as well as the ethylene/CO copolymerisation using MAO as co-catalysts has to be subject of further investigations [4]. Their reactivity towards the insertion reactions by activation of small molecules (e.g. CO, C_2H_4,...) [8], and for the selective C–H activation of hydrocarbons is a promising topic, too [9].

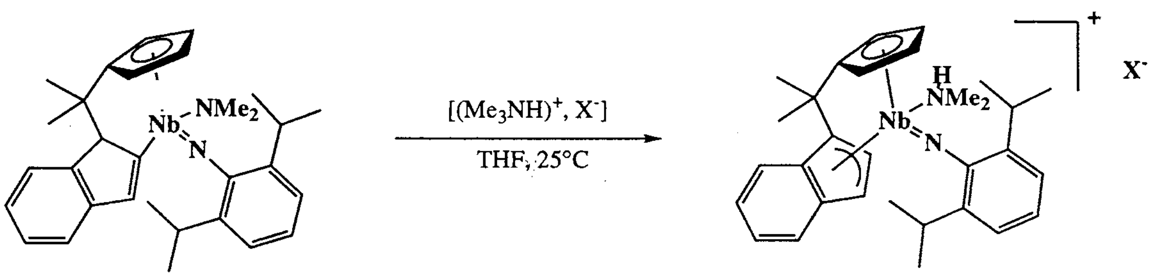
All preparations, manipulations and reactions were carried out under Argon using standard techniques for handling air-sensitive materials, such as Schlenk Techniques and Glove-box. Pentane, heptane, THF and Toluene were freshly distilled over Na/K amalgam under argon from purple benzophenone ketyl before use (Caution: Solvent should not be distilled to dryness). Deuterated solvents were dried over Na/K amalgam and then vacuum transfered and stored under an argon atmosphere. All glassware were base- and acid-washed, oven dried and additionally dried under high vaccum. The cyclopentadienyl-indenyl isopropylidene ligand and the niobium-trisamido-imido compound [Nb(NMe$_2$)$_3$(=N-2,6-*i*Pr$_2$C$_6$H$_3$)] **3** were prepared as reported in the literature [10,5]. Dimethylfulvene and indene were distilled before use, and all other chemicals were used as received.

NMR spectra were recorded with either a JEOL-LMN-GX 400 or a Bruker AM 400 spectrometer (^{1}H NMR were referenced to the residual protio-solvent: C_6D_6, $\delta = 7.15$ ppm and D_8-THF, $\delta = 1.72$ and 3.57 ppm; ^{13}C NMR were referenced to the C-signal of the deutero solvent: C_6D_6, $\delta = 128$ ppm and D_8-THF, $\delta =$ 25.3 and 67.4 ppm), Mass spectra (CI) were measured with a Varian MAT 90 spectrometer, and elemental analyses were performed in our analytical laboratory.

3. Experimental section

1 Preparation of the niobium compound [Nb(η^5-C_5H_4R)(NMe$_2$)$_2$(=N-2,6-*i*Pr$_2$C$_6$H$_3$)] (R = CMe$_2$C$_9$H$_7$) **3** from [Nb(NMe$_2$)$_3$(=N-2,6-*i*Pr$_2$C$_6$H$_3$)] **1** and the ligand **2**.

A solution of the niobium precursor **1** (100 mg, 0.25 mmol) in toluene (10 ml) was treated with a solution of the ligand **2** (56 mg, 0.25 mmol) in toluene (5 ml) at −40°C. The mixture was allowed to warm-up to room temperature, then it was slowly warmed-up to 100°C. The stirring was continued for 2 h and the solvent was evaporated. The product of the reaction was dried under vaccum (10^{-2} mmHg) for 12 h. Then pentane (5 ml) was added to the residue, the solution filtered through a glass plug and evaporated under high vac-



4

6a: $X^- = BPh_4^-$; 60 % yield

6b: $X^- = Cl^-$; 73 % yield

Scheme 4.

cum to give 127 mg of **3** as a yellow-brown oil. Yield: 88%.

^{1}H NMR, C_6D_6, 400.13 MHz: 1.26 (d, 12H, ^3J(H, H) = 7.0 Hz, $CH(C\underline{H}_3)_2$); 1.54 (s, 6H, $C(C\underline{H}_3)_2$); 3.15 (s, 12H, $N(C\underline{H}_3)_2$); 3.48 (br. s, 1H, *ipso*$C\underline{H}$-C_9H_7); 4.02 (sept., 2H, ^3J(H, H) = 7.0 Hz, $C\underline{H}(CH_3)_2$); 5.77 (*pseudo*-t, 2H, ^3J(H, H) = 3.0 Hz, $C_5\underline{H}_4$); 6.05 (*pseudo*-t, 2H, ^3J(H, H) = 2.5 Hz, $C_5\underline{H}_4$); 6.58 (m, 1H, vinyl$C\underline{H}$-C_9H_7); 6.86 (m, 1H, vinyl$C\underline{H}$-C_9H_7); 6.92 (t, 1H, ^3J(H, H) = 7.5 Hz, p-$C_6\underline{H}_3$); 7.07 (d, 2H, ^3J(H, H) = 7.5 Hz, m-$C_6\underline{H}_3$); 7.02–7.18 (m, 2H, arom$C\underline{H}$-C_9H_7); 7.23 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_7); 7.28 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_7). $^{13}C\{^1H\}$ NMR, C_6D_6, 100.62 MHz: 23.68 ($CH(\underline{C}H_3)_2$); 26.26 ($C(\underline{C}H_3)_2$); 27.72 ($\underline{C}H(CH_3)_2$); 35.77 ($\underline{C}(CH_3)_2$); 37.87 (*ipso*$\underline{C}$-C_9H_7); 57.88 ($N(\underline{C}H_3)_2$); 105.88 and 107.32 ($\underline{C}_5H_4$); 121.13, 123.47, 124.63 and 126.01 (arom$\underline{C}H$-C_9H_7); 122.74 (m-$\underline{C}_6H_3$); 123.09 (p-$\underline{C}_6H_3$); 130.86 and 132.84 (vinyl$\underline{C}H$-C_9H_7); 133.41 (*ipso*$\underline{C}$-C_5H_4); 142.00 (o-$\underline{C}_6H_3$); 142.62 and 144.25 ($\underline{C}$-C_9H_7); 152.06 (*ipso*$\underline{C}$-C_6H_3).

$C_{33}H_{46}N_3Nb$ - Mass: 577.2748 — Mass Spectra: *m/z* (%): [M^+] 577.4 (33); [M^+ –NMe_2] 533.3 (100); [M^+ – $HNMe_2$] 532.3 (58); [M^+ –2 × NMe_2] 489.3 (24). Elemental Analysis [Found (Calc.)]: C: 69.02 (68.60), H: 8.12 (8.03), N: 7.16 (7.28).

2 Preparation of the Niobium compound [$Nb(NMe_2)$(=N-2,6-*i*-$Pr_2C_6H_3$)(η^5:η^1-$\{C_5H_4\}C(CH_3)_2\{C_9H_6\}$] **4** from [$Nb(NMe_2)_3$(=N-2,6-*i*$Pr_2C_6H_3$)] **1** and the ligand **2**.

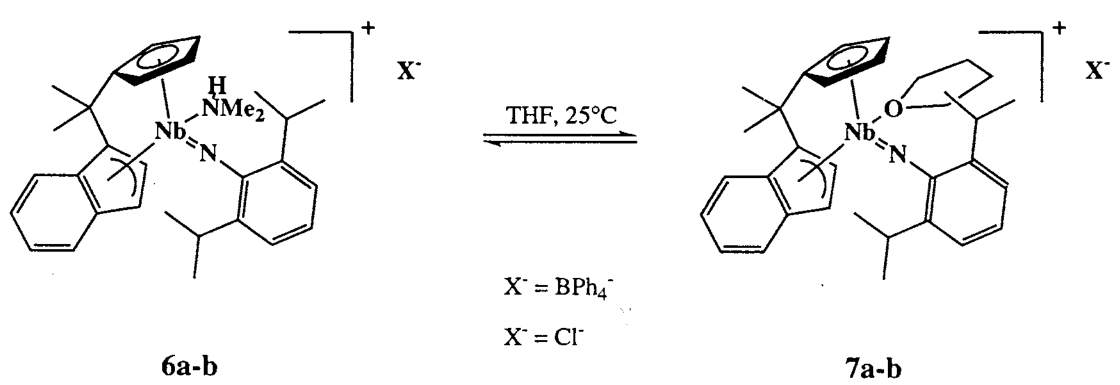
A solution of the niobium precursor **1** (200 mg, 0.50 mmol) in toluene (10 ml) was treated with a solution of the ligand **2** (112 mg, 0.50 mmol) in toluene (5 ml) at – 40°C. The mixture was allowed to warm-up to room temperature, then it was slowly warmed-up to 100°C. The stirring was continued for 2 h and then the temperature increased up to 110°C. The stirring was maintained for 7 h and the solvent was evaporated. The product of the reaction was dried at r.t. under vacuum (10^{-2} mmHg) for 12h. Then pentane (7 ml) was added to the residue, the solution filtered through a glass plug, and evaporated. The residue was added of heptane (5 ml) and the solution left under argon at – 78°C to give slowly 205 mg of **4** as an amorphous yellow material. Yield: 77%.

^{1}H NMR, C_6D_6, 400.13 MHz: 1.16 (d, 6H, ^3J(H, H) = 7.1 Hz, $CH(C\underline{H}_3)_2$); 1.18 (d, 6H, ^{3}J(H, H) = 7.1 Hz, $CH(C\underline{H}_3)_2$); 1.68 (s, 3H, $C(C\underline{H}_3)_2$); 1.76 (s, 3H, $C(C\underline{H}_3)_2$); 3.15 (br.s, 6H, $N(C\underline{H}_3)_2$); 3.94 (br.s, 1H, *ipso*$C\underline{H}$-C_9H_6); 4.01 (br. sept., 2H, ^3J(H, H) = 7.1 Hz, $C\underline{H}(CH_3)_2$); 5.70 (*pseudo*-q, 1H, ^3J(H, H) = 3.1 Hz, $C_5\underline{H}_4$); 5.80 (*pseudo*-q, 1H, ^3J(H, H) = 3.0 Hz, $C_5\underline{H}_4$); 5. 94 (*pseudo*-t, 2H, ^3J(H, H) = 3.1 Hz, $C_5\underline{H}_4$); 6.92 (t, 1H, ^3J(H, H) = 7.5 Hz, p-$C_6\underline{H}_3$); 6.94 (br.s, 1H, vinyl$C\underline{H}$-C_9H_6); 7.05 (d, 2H, ^3J(H, H) = 7.5 Hz, m-$C_6\underline{H}_3$); 7.11 (t, 1H, ^3J(H, H) = 7.3 Hz, arom$C\underline{H}$-C_9H_6); 7.23 (t, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_6); 7.37 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_6); 7.48 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_6). $^{13}C\{^1H\}$ NMR, C_6D_6, 100.62 MHz: 24.16 and 24.57 ($CH(\underline{C}H_3)_2$); 25.99 and 26.54 ($C(\underline{C}H_3)_2$); 27.74 ($\underline{C}H(CH_3)_2$); 35.08 ($\underline{C}(CH_3)_2$); 40.88 (*ipso*$\underline{C}$-C_9H_6); 47.85 ($N(\underline{C}H_3)_2$); 98.99, 105.21, 106.13 and 108.93 ($\underline{C}_5H_4$); 119.81, 123.59, 124.33 and 125.96 (arom$\underline{C}H$-C_9H_6); 122.71 (m-$\underline{C}_6H_3$); 123.37 (p-$\underline{C}_6H_3$); 127.42 (vinyl$\underline{C}H$-C_9H_6); 136.54 (*ipso*$\underline{C}$-C_5H_4); 143.36 (o-C_6H_3); 145.36 and 148.80 ($\underline{C}$-C_9H_6); 150.53 (*ipso*$\underline{C}$-C_6H_3); 178.36 (*ipso*$\underline{C}$-vinylC_9H_6).

$C_{31}H_{39}N_2Nb$ — Mass: 532.2173 — Mass Spectra: *m/z* (%): [M +] 532.7 (100) no fragments. Elemental Analysis [Found (Calc.)]: C: 69.53 (69.91), H: 7.32 (7.39), N: 5.19 (5.26).

3 Preparation of the Niobium compound [Nb(Cl)(=N-2,6-*i*-$Pr_2C_6H_3$)(η^5:η^3-$\{C_5H_4\}$ $C(CH_3)_2\{C_9H_6\}$] **5** from [$Nb(NMe_2)$(=N-2,6-*i*-$Pr_2C_6H_3$)(η^5:η^1-$\{C_5H_4\}C$ $(CH_3)_2\{C_9H_6\}$] **4**.

A solution of the niobium complex **4** (266 mg, 0.50 mmol) in toluene (10 ml) was treated with a solution of the Me_3SiCl (82 mg, 0.75 mmol) in toluene (5 ml) at – 78°C. The mixture was allowed to warm-up to room temperature. The stirring was continued for 2 h and the



Scheme 5.

solvent was evaporated. The product of the reaction was dried at r.t. under vaccum (10^{-2} mmHg) for 12 h. Then pentane (7 ml) was added to the residue, the solution filtered through a glass plug, and evaporated. The residue was added of heptane (5 ml) and the solution left under argon at −78°C to give slowly 243 mg of **5** as a red micro-crystaline material. Yield: 93%.

^{1}H NMR, C_6D_6, 400.13 MHz: 1.15 (d, 6H, ^3J(H, H) = 6.6 Hz, $CH(C\underline{H}_3)_2$); 1.31 (d, 6H, ^3J(H, H) = 6.4 Hz, $CH(C\underline{H}_3)_2$); 1.56 (s, 3H, $C(C\underline{H}_3)_2$); 1.58 (s, 3H, $C(C\underline{H}_3)_2$); 4.01 (br. sept., 2H, ^3J(H, H) = 6.6 Hz, $C\underline{H}(CH_3)_2$); 5.48 (*pseudo*-q, 1H, ^3J(H, H) = 2.6 Hz, $C_5\underline{H}_4$); 5.84 (dq, 1H, ^3J(H, H) = 12 Hz and ^5J(H, H) = 2.7 Hz, vinyl$C\underline{H}$-C_9H_6); 5.92 (*pseudo*-q, 1H, ^3J(H, H) = 2.6 Hz, $C_5\underline{H}_4$); 6. 01 (*pseudo*-q, 1H, ^3J(H, H) = 2.5 Hz, $C_5\underline{H}_4$); 6.18 (m, 1H, vinyl$C\underline{H}$-C_9H_6); 6.29 (*pseudo*-q, 1H, ^3J(H, H) = 2.6 Hz, $C_5\underline{H}_4$); 6.94 (t, 1H, ^3J(H, H) = 7.5 Hz, p-$C_6\underline{H}_3$); 7.02–7.33 (m, 5H, m-$C_6\underline{H}_3$ and arom$C\underline{H}$-C_9H_6); 7.38 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_6). $^{13}C\{^1H\}$ NMR, C_6D_6, 100.62 MHz: 24.01, 24.08, 24.24 and 24.96 ($CH(\underline{C}H_3)_2$); 26.18 ($C(\underline{C}H_3)_2$); 28.02 and 28.25 ($\underline{C}H(CH_3)_2$); 32.03 ($\underline{C}(CH_3)_2$); 98.74, 107.11, 109.38 and 110.01 ($\underline{C}_5H_4$); 112.08 and 112.97 (vinyl$\underline{C}H$-C_9H_6); 121.03 (*ipso*$\underline{C}$-C_9H_6); 122.72 (m-$\underline{C}_6H_3$); 123.32 (p-$\underline{C}_6H_3$); 124.40, 125.67, 126.49 and 128.67 (arom$\underline{C}H$-C_9H_6); 132.74 (*ipso*$\underline{C}$-C_5H_4); 142.51 (o-$\underline{C}_6H_3$); 145.05 and 145.66 ($\underline{C}$-C_9H_6); 152.08 (*ipso*$\underline{C}$-C_6H_3).

$C_{29}H_{33}NNbCl$ — Mass: 523.1358 — Mass Spectra: *m*/*z* (%): [M +] 523.4 (100) no fragments. Elemental Analysis [Found (Calc.)]: C: 65.91 (66.48), H: 6.29 (6.35), N: 2.67 (2.67).

4 Preparation of the Niobium compound $[Nb(NHMe_2)(=N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(\eta^5:\eta^3\text{-}\{C_5H_4\}C(CH_3)_2\{C_9H_6\}]^+$, $[B(C_6H_5)_4]^-$ **6a** from $[Nb(NMe_2)(=N\text{-}2,6\text{-}i\text{-}Pr_2)C_6H_3)(\eta^5:\eta^1\text{-}\{C_5H_4\}C(CH_3)_2\{C_9H_6\}]$ **4**.

A solution of the niobium complex **4** (266 mg, 0.50 mmol) in THF (10 ml) was treated with a suspension of $[NHMe_3][B(C_6H_5)_4]$ (190 mg, 0.50 mmol) in THF (5 ml) at −40°C. The mixture was allowed to warm-up to room temperature. The stirring was continued for 12 h, and the solution filtered through a glass plug, then the solvent was evaporated. The product of the reaction was dried at r.t. under vacuum (10^{-2} mmHg) for 12 h. Then THF (4 ml) was added to the residue to give a dark red solution, to which pentane (1.5 ml) was added. The solution was left under argon at −78°C to give 247 mg of **6a** as an amorphous red material. Yield: 60%.

^{1}H NMR, D_8-THF, 400.13 MHz: 1.43 (d, 6H, ^3J(H, H) = 6.5 Hz, $CH(C\underline{H}_3)_2$); 1.51 (d, 6H, ^3J(H, H) = 7.1 Hz, $HN(C\underline{H}_3)_2$); 1.65 (d, 6H, ^3J(H, H) = 6.5 Hz, $CH(C\underline{H}_3)_2$); 2.40 (s, 3H, $C(C\underline{H}_3)_2$); 2.50 (s, 3H, $C(C\underline{H}_3)_2$); 3.37 (sept., 1H, ^3J(H, H) = 6.5 Hz, $C\underline{H}(CH_3)_2$); 4.03 (br. s, 1H, $\underline{H}N(CH_3)_2$); 4.13 (sept., 1H, ^3J(H, H) = 6.5 Hz, $C\underline{H}(CH_3)_2$); 6.45 (*pseudo*-q, 1H, ^3J(H, H) = 2.5 Hz, $C_5\underline{H}_4$); 6.54 (*pseudo*-q, 1H, ^3J(H, H) = 3.0 Hz, $C_5\underline{H}_4$); 6.66 (*pseudo*-q, 1H, ^3J(H, H) = 2.1 Hz, $C_5\underline{H}_4$); 6.85 (*pseudo*-q, 1H, ^3J(H, H) = 2.5 Hz, $C_5\underline{H}_4$); 7.03 (*pseudo*-t, 1H, ^3J(H, H) = 8.1 Hz, vinyl$C\underline{H}$-C_9H_6); 7.22 (t, 1H, ^3J(H, H) = 7.5 Hz, p-$C_6\underline{H}_3$); 7.25 (*pseudo*-t, 4H, ^3J(H, H) = 7.5 Hz, p-$C_6\underline{H}_5B$); 7.33 (d, 2H, ^3J(H, H) = 7.5 Hz, m-$C_6\underline{H}_3$); 7.39 (*pseudo*-t, 8H, ^3J(H, H) = 7.5 Hz, o-$C_6\underline{H}_5B$); 7.43 (t, 1H, ^3J(H, H) = 7.1 Hz, arom$C\underline{H}$-C_9H_6); 7.55 (m, 2H, arom$C\underline{H}$-C_9H_6 and vinyl$C\underline{H}$-C_9H_6); 7.71 (d, 1H, ^3J(H, H) = 6.5 Hz, arom$C\underline{H}$-C_9H_6); 7.82 (br. m, 8H, m-$C_6\underline{H}_5B$); 7.88 (d, 1H, ^3J(H, H) = 7.5 Hz, arom$C\underline{H}$-C_9H_6). $^{13}C\{^1H\}$ NMR, D_8-THF, 100.62 MHz: 23.91 and 24.30 ($CH(\underline{C}H_3)_2$); 26.41 ($C(\underline{C}H_3)_2$); 27.72 ($\underline{C}H(CH_3)_2$); 34.13 ($\underline{C}(CH_3)_2$); 41.10 ($HN(\underline{C}H_3)_2$); 98.35, 104.27, 105.86 and 108.60 ($\underline{C}_5H_4$); 118.68 (*ipso*$\underline{C}$-C_9H_6); 120.86 (p-$\underline{C}_6H_5B$); 121.34 (p-$\underline{C}_6H_3$); 121.84 (m-$\underline{C}_6H_3$); 122.32, 122.94, 123.76 and 127.62 (arom$\underline{C}H$-C_9H_6); 124.72 (m-$\underline{C}_6H_5B$); 126.02 and 133.52 (vinyl$\underline{C}H$-C_9H_6); 135.66 (*ipso*$\underline{C}$-C_5H_4); 142.34 (o-$\underline{C}_6H_3$); 143.76 (o-$\underline{C}_6H_5B$); 147.89 and 149.78 ($\underline{C}$-C_9H_6); 151.04 (*ipso*$\underline{C}$-C_6H_3); 163.95 (q, ^1J(B, C) = 49.6 Hz, *ipso*$\underline{C}$-C_6H_5B).

$C_{55}H_{60}N_2NbB$ — Mass: 852.3905 — Elemental Analysis [Found (Calc.)]: C: 76.83 (77.43), H: 6.92 (7.09), N: 3.02 (3.29).

5 Preparation of the Niobium compound $[Nb(NHMe_2)(=N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(\eta^5{:}\eta^3\text{-}\{C_5H_4\}\ C(CH_3)_2\{C_9H_6\}]^+$, $[Cl]^-$ **6b** from $[Nb(NMe_2)(=N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(\eta^5{:}\eta^1\text{-}\{C_5H_4\}\ C(CH_3)_2\{C_9H_6\}]$ **4**.

A solution of the niobium complex **4** (266 mg, 0.50 mmol) in THF (10 ml) was treated with a solution of $[NHMe_3][Cl]$ (48 mg, 0.50 mmol) in THF (5 ml) at −40°C. The mixture was allowed to warm-up to room temperature. The stirring was continued for 2 h, and the solution filtered through a glass plug, then the solvent was evaporated. The product of the reaction was dried at r.t. under high vacuum (10^{-2} mmHg) for 12 h. Then THF (4 ml) was added to the residue to give a dark red solution, to which pentane (2 ml) was added. The solution was left under argon at −78°C to give 207 mg of **6b** as an amorphous dark red material. Yield: 73%.

^1H NMR, D_8-THF, 400.13 MHz: 1.18 (d, 6H, $^3J(H, H) = 7.0$ Hz, $CH(C\underline{H}_3)_2$); 1.28 (d, 6H, $^3J(H, H) = 6.5$ Hz, $HN(C\underline{H}_3)_2$); 1.33 (d, 6H, $^3J(H, H) = 7.0$ Hz, $CH(C\underline{H}_3)_2$); 1.85 (s, 3H, $C(C\underline{H}_3)_2$); 1.98 (s, 3H, $C(C\underline{H}_3)_2$); 3.05 (sept., 1H, $^3J(H, H) = 7.0$ Hz, $C\underline{H}(CH_3)_2$); 3.97 (sept., 1H, $^3J(H, H) = 7.0$ Hz, $C\underline{H}(CH_3)_2$); 4.22 (br. s, 1H, $\underline{H}N(CH_3)_2$); 6.18 (br. *pseudo*-q, 1H, $C_5\underline{H}_4$); 6.28 (br. *pseudo*-q, 1H, $C_5\underline{H}_4$); 6.51 (br. *pseudo*-q, 1H, $C_5\underline{H}_4$); 6.67 (*pseudo*-t, 1H, $^3J(H, H) = 8.3$ Hz, vinyl$C\underline{H}$-C_9H_6); 6.80 (br. *pseudo*-q, 1H, $C_5\underline{H}_4$); 6.92 (t, 1H, $^3J(H, H) = 7.5$ Hz, p-$C_6\underline{H}_3$); 6.99 (d, 1H, $^3J(H, H) = 8.3$ Hz, vinyl$C\underline{H}$-C_9H_6); 7.06 (d, 2H, $^3J(H, H) = 7.5$ Hz, m-$C_6\underline{H}_3$); 7.15 (t, 1H, $^3J(H, H) = 7.0$ Hz, arom$C\underline{H}$-C_9H_6); 7.23 (t, 1H, $^3J(H, H) = 7.5$ Hz, arom$C\underline{H}$-C_9H_6); 7.33 (d, 1H, $^3J(H, H) = 6.9$ Hz, arom$C\underline{H}$-C_9H_6); 7.59 (d, 1H, $^3J(H, H) = 7.5$ Hz, arom$C\underline{H}$-C_9H_6). $^{13}C\{^1H\}$ NMR, D_8-THF, 100.62 MHz: 21.57 and 22.86 ($CH(\underline{C}H_3)_2$); 25.29 ($C(\underline{C}H_3)_2$); 27.05 ($\underline{C}H(CH_3)_2$); 29.25 ($\underline{C}(CH_3)_2$); 40.38 ($HN(\underline{C}H_3)_2$); 98.28, 106.10, 111.78 and 113.25 ($\underline{C}_5H_4$); 119.88 (*ipso*$\underline{C}$-C_9H_6); 121.55 (m-$\underline{C}_6H_3$); 121.63 (p-$\underline{C}_6H_3$); 116.77, 122.79, 123.52 and 125.18 (arom$\underline{C}H$-C_9H_6); 121.70 and 124.56 (vinyl$\underline{C}H$-C_9H_6); 131.11 (*ipso*$\underline{C}$-C_5H_4); 142.58 (o-$\underline{C}_6H_3$); 143.94 and 146.42 ($\underline{C}$-C_9H_6); 153.58 (*ipso*$\underline{C}$-C_6H_3).

$C_{31}H_{40}N_2NbCl$ — Mass: 568.1936 — Elemental Analysis [Found (Calc.)]: C: 64.91 (65.47), H: 6.95 (7.09), N: 4.63 (4.93).

Acknowledgements

We are grateful to Professor Dr R. Taube (Technische Universität München) and Dr W. Baratta (Post-Doc) for useful discussions, to the Alexander Humboldt Foundation for a research grant to L.D. and the Technische Universität of München for support.

References

[1] W.A. Herrmann, B. Cornils, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH-Wiley, Weinheim, 1996, p. 9.

[2] (a) J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 100 (1988) 100. (b) J.A. Ewen, M.J. Elder, R.L. Jones, I. Haspeslagh, J.L. Atwood, S.G. Bott, K. Robinson, Makromol. Chem. 48/49 (1989) 253. (c) W. Kaminsy, A. Ahlers, N. Möller-Lindenhof, Angew. Chem. 101 (1989) 1304. (d) ibid, Angew. Chem. Int. Ed. Engl. 28 (1989) 1216. (e) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometall. 9 (1990) 867. (f) J. Okuda, Chem. Ber. 123 (1990) 1649. (g) W. Kaminsky, R. Engehausen, K. Zoumis, W. Spalek, J. Rohrmann, Makromol. Chem. 193 (1992) 1643. (h) W. Mengele, J. Diebold, C. Troll, W. Röll, H.H. Brintzinger, Organometall. 12 (1993) 1931. (i) J. Okuda, Nachr. Chem. Tech. Lab. (Weinheim/Germany) 41 (1993) 8. (j) A.K. Hughes, A. Meetsma, J.H. Teuben, Organometall. 12 (1993) 1936. (k) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (l) W.A. Herrmann, M.J. Morawietz, J. Organomet. Chem. 482 (1994) 169. (m) M. Aulbach, F. Küber, Chemie uns. Zeit 28 (1994) 197. (n) T.N. Doman, T.K. Hollis, B. Bonisch, J. Am. Chem. Soc. 117 (1995) 1352. (o) J. Okuda, F.J. Schattenmann, S. Wocallo, W. Massa, Organometall. 14 (1995) 789. (p) G. Fink, R. Mülhaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Berlin, 1995.

[3] (a) J.A. Smith, J. von Seyerl, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 173 (1979) 175. (b) J.A. Smith, H.H. Brintzinger, J. Organomet. Chem. 218 (1981) 159. (c) P. Burger, H.H. Brintzinger, J. Organomet. Chem 407 (1991) 208. (d) R.L. Halterman, Chem. Rev. 92 (1992) 965.

[4] (a) K. Mashima, S. Fujikawa, A. Nakamura, J. Am. Chem. Soc. 115 (1993) 10990. (b) K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, Chem. Commun. (1994) 1623. (c) K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, Organometall. 14 (1995) 2633. (d) K. Mashima, Y. Tanaka, A. Nakamura, J. Organomet. Chem. 502 (1995) 19.

[5] (a) W.A. Herrmann, W. Baratta, J. Organomet. Chem. 506 (1996) 357. (b) W.A. Herrmann, W. Baratta, Angew. Chem. 108 (1996) 2098. (c) ibid, Angew. Chem. Int. Ed. Engl. 35 (1996) 1951. (d) L. Djakovitch, W.A. Herrmann, J. Organomet. Chem. (1997) in press.

[6] J. March, Advanced Organic Chemistry, 4th ed., Wiley, New York, 1992, p. 251.

[7] A.N. Chernega, M.L.H. Green, A.G. Suárez, Can. J. Chem. 73 (1995) 1157.

[8] (a) K. Mashima, Y. Yamanaka, S. Fujikawa, H. Yasuda, A. Nakamura, J. Organomet. Chem. 428 (1992) C5. (b) A. Nakamura, K. Mashima, J. Organomet. Chem. 500 (1995) 261 and references cited therein.

[9] (a) A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, Riedel, Boston, MA, 1984. (b) P.J. Walsh, F.J. Hollander, R.G. Bergamn, J. Am. Chem. Soc. 110 (1988) 8729. (c) C.C. Cummins, S.M. Baxter, P.T. Wolcanski, J. Am. Chem. Soc. 110 (1988) 8731. (d) C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989. (e) P.L. Watson (Ed.), Selective Hydrocarbon Activation, VCH, Toledo, OH, 1989. (f) N.D. Parkyns, Chem. Ber. 9 (1990) 841. (g) C.P. Schaller, P.T. Wolcanski, Inorg. Chem. 32 (1993) 131. (h) C.P. Schaller, J.B. Bonnanno, P.T. Wolcanski, J. Am. Chem. Soc. 116 (1994) 4133. (i) J.L. Bennett, P.T. Wolcanski, J. Am.

Chem. Soc. 116 (1994) 2179. (j) M.T. Benson, T.R. Cundari, E.W. Moody, J. Organomet. Chem. 504 (1995) 1. (k) R. Burch, M.J. Hayes, J. Mol. Cat. A Chem. 100 (1995) 13. (l) S. Yeoul, R.G. Bergman, J. Am. Chem. Soc. 117 (1995) 5877. (m) D.J. Duncalf, R.J. Harrison, A. McCamley, B.W. Royan, J. Chem. Soc. Chem. Commun. (1995) 2421. (n) C.P. Schaller, C.C. Cummins, P.T. Wolcanski, J. Am. Chem. Soc. 118 (1996) 591. (o) T. Lian, S.E. Bromberg, H. Yang, G. Proulx, R.G. Bergman, C.Y. Harris, J. Am. Chem. Soc. 118 (1996) 3769.

[10] W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, New J. Chem. 14 (1990) 499.