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Bridged half-sandwich niobiocenes by intramolecular CH activation

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Abstract

The reaction of $[Nb(NMe_2)_3(=N-2,6-iPr_2C_6H_3)]$ **3** with the cyclopentadienes C_5H_5R ($R = C_3H_5$, C_6H_5, $CH_2C_6H_5$) **2a–c** gave the new half-sandwich niobium complexes $[Nb(\eta^5-C_5H_4R)(NMe_2)_2(=N-2,6-iPr_2C_6H_3)]$ **4a–c** in high yields. The new *ansa*-type half-sandwich complexes $[Nb(NMe_2)(=N(2,6)i-PrC_6H_3)(\eta^5:\eta^3-\{C_5H_4\}C(CH_3)_2\{C_3H_4\}]$ **5a**, $[Nb(NMe_2)(=N(2,6)i-PrC_6H_3)(\eta^5:\eta^1-\{C_5H_4\}C(CH_3)_2\{C_6H_4\}]$ **5b**, $[Nb(NMe_2)(=N(2,6)i-PrC_6H_3)(\eta^5:\eta^3-\{C_5H_4\}C(CH_3)_2\{CHC_6H_5\}]$ **5c** were thus obtained at higher temperatures by an intramolecular C–H activation resulting in the coordination of the R group. © 1997 Elsevier Science S.A.

Keywords: Niobium; CH activation; Amido complexes; Imido complexes
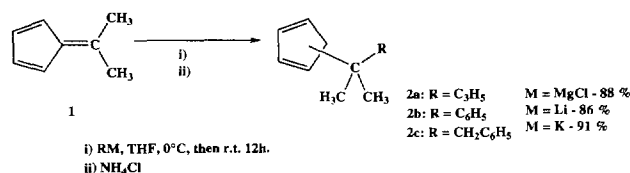
1. Introduction

We previously described a series of half-sandwich imido complexes of niobium and tantalum [1] which have been investigated as catalysts for the ethylene polymerization, analogously to the group IV ansa-metal-locenes (group of Zr and Ti). While many metal-imido complexes are known, only a few have attracted interest since, in most of them, the M=N bond is inert [2]. A few years ago a renaissance of metal-imido complex chemistry has emerged because of their catalytic activity in C–H activation. Selective C–H activation is the first and probably the most important process in the catalytic conversion of light alkanes and other petrochemical feedstocks into functionalized products [3–14]. C–H activation at niobium has been seen with a benzylidene ligand [15].

In previous work we have used niobium imido amido complexes of the general formulae $[Nb(NR_2)_3(=NAr)]$ for the synthesis of both ansa-metallocenes and bridged niobiocenes [1,16]. In these cases, the imido ligand was mostly a "spectator", i.e. it was not involved in the reactions. We report here the first example of the bifunctional reactivity of the niobium imido amido complexes.

2. Results and discussion

The ligands **2a–c** were synthesized in good yields (**2a** 88%, **2b** 86%, **2c** 91%) using a procedure reported by Spaleck et al. [17]. The reaction of dimethylfulvene with RM (**2a** C_3H_5MgCl, **2b** PhLi, **2c** $PhCH_2K$) proceeds smoothly at room temperature in THF (Scheme 1). The ligands were easily purified by distillation under high vacuum without noticeable polymerization (a quick distillation through a short Vigreux column was in this case possible also at low temperature, i.e. below 100°C, thus preventing the risk of polymerization). From ^1H NMR and ^{13}C NMR, a mixture of isomers for the ligands is observed. Two major isomers were found to be stable under argon when stored at low temperature (i.e. −35°C) but led to slow polymerization at room temperature.

The precursor niobium(V) complex $[Nb(NMe_2)_3(=N-2,6-iPr_2C_6H_3)]$ **3** was treated with equimolar amounts of the protic ligands **2a–c**. Deprotonation of the cyclopentadiene ring, resulting in its coordination to the metal centre, occurs smoothly. Monitor-

i) RM, THF, 0°C, then r.t. 12h.
ii) NH₄Cl

2a: R = C₃H₅   M = MgCl - 88 %
2b: R = C₆H₅   M = Li - 86 %
2c: R = CH₂C₆H₅ M = K - 91 %

Scheme 1.

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i) n-Bu₂O, 100 °C, 2 h.
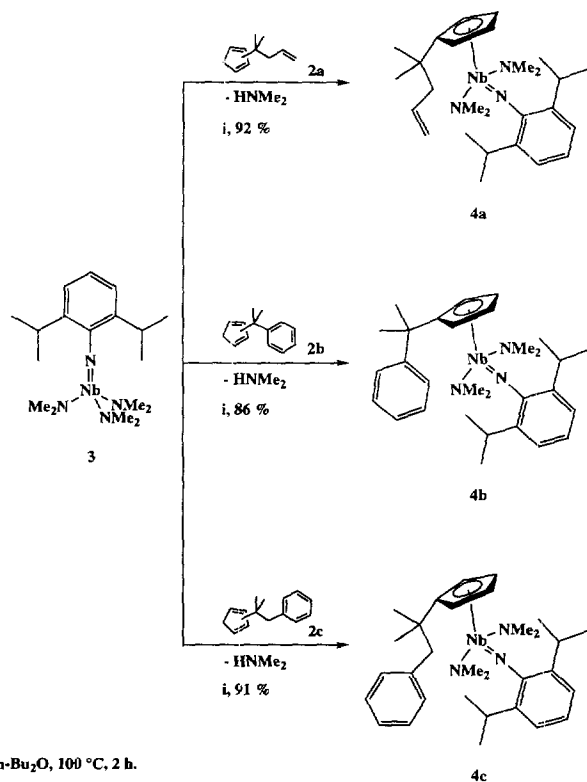
Scheme 2.

ing the reaction by ^{1}H NMR showed that it was completed within 2 h at 100°C in n-Bu$_2$O. The new half-sandwich niobium complexes 4a–c are formed quantitatively, and were isolated in high yields as yellow oils (4a 92%, 4b 86%, 4c 91%, Scheme 2). The reaction of 3 with 2a–c was monitored by ^{1}H NMR in toluene-D$_8$ at 100°C, showing that the reactions proceed without any decomposition of the half-sandwich complexes. These complexes showed characteristic ^{1}H NMR resonances for the cyclopentadienyl ligand which gave as expected two pseudo-triplets at $\delta \approx 5.8$ and $\delta \approx 5.9$–6.0 ppm (this region is very similar for the three complexes, while the corresponding signals are closer to each other in the case of 4c) with a characteristic coupling constant $^3J(\text{H,H}) \approx 2.5$–3 Hz. ^{1}H NMR data do not indicate interactions between the metal centre and the rest of the ligand, i.e. no detectable interactions with the allyl, phenyl or benzyl function of the ligand. These compounds were found to be extremely sensitive to air, giving immediately a white, insoluble product resulting from hydrolysis and concomitant oxide formation. They were found thermally stable and can be stored for a long time at room temperature under an argon atmosphere without noticeable decomposition or secondary reactions from the ligands (i.e. no polymerization products resulting from ligand self-condensation).
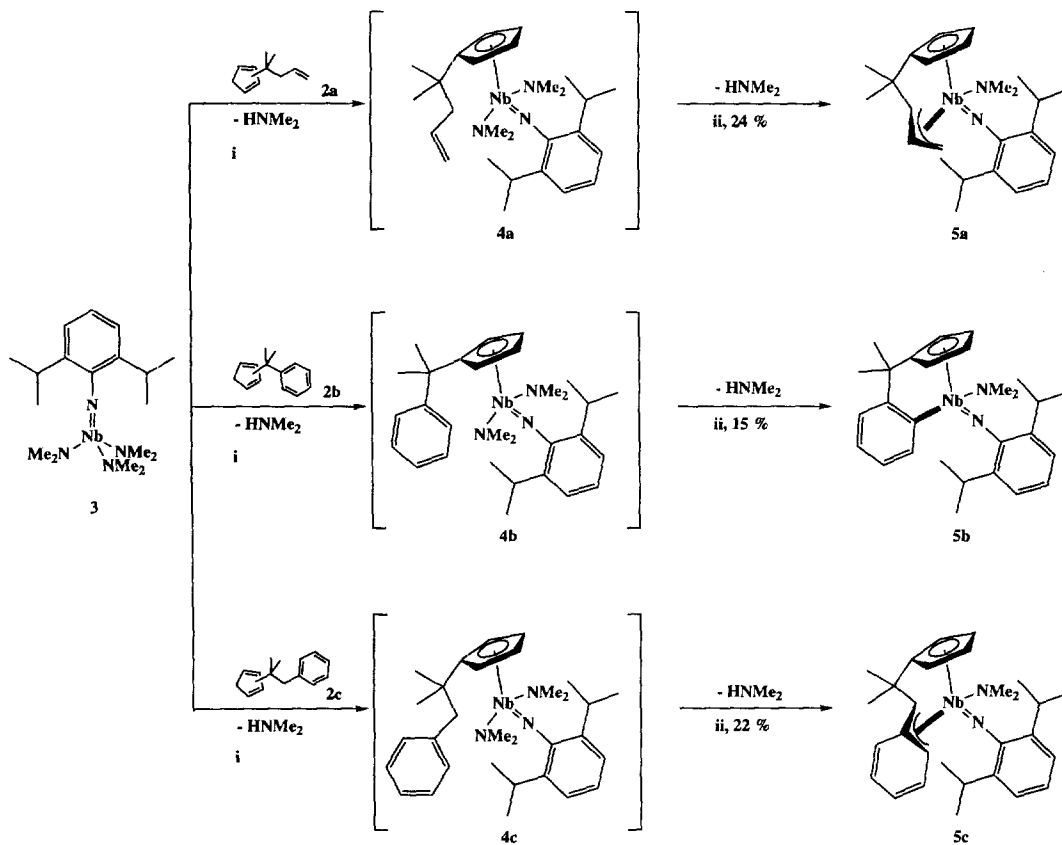
i) n-Bu₂O, 100 °C, 2 h, then ii) n-Bu₂O, 160 °C, 4 d (except for 5a: 7 days.)
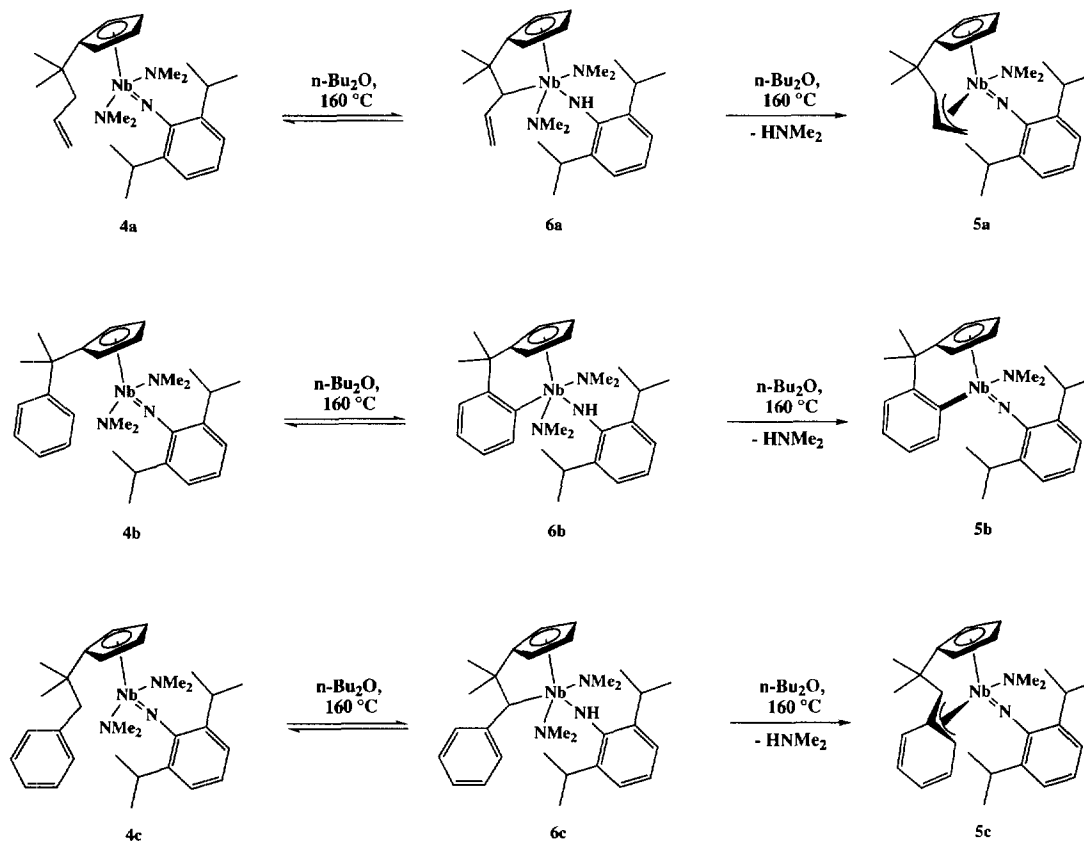
Scheme 3.

Monitoring the reactions of the complexes **4a–c** by ^{1}H NMR in toluene-D$_8$, it was found that these complexes were quite stable below 100°C even for longer reaction times of several days. Further reactions were observed only at 150°C in toluene-D$_8$ (using a special pressure-resistant NMR tube) giving the new niobium complexes **5a–c**, but only in very low yields (typically 5–7%) after 3 d. Characteristic signals were detectable by ^{1}H NMR, which indicated the coordination of ligand functions (i.e. coordination of allyl, phenyl or benzyl), as well as a strong modification of the ^{1}H NMR cyclopentadienyl region which showed expected four pseudo-quartets at $\delta \approx 5.7$–6.0 ppm with a characteristic coupling constant $^3J(H,H) \approx 2.0$–2.5 Hz (Scheme 2). The use of n-Bu$_2$O as solvent was found to be important, since it allows higher temperatures.

While the coordination of the allyl, phenyl, or benzyl functions could directly be studied from the precursor complexes **4a–c**, we studied these reactions in a one-pot synthesis. It was shown previously that the reactions between the niobium(V) complex **3** and the ligands **2a–c** were completed after 2 h at 100°C in n-Bu$_2$O. The mixtures were then refluxed in n-Bu$_2$O at 160°C for different reactions times. Monitoring these reactions by ^{1}H NMR, we found that contrary to the deprotonation reactions of the cyclopentadiene, the kinetics of the

reactions resulting to the coordination of the allyl, phenyl, or benzyl functions were very slow, particularly for intramolecular reactions. In general, conversion rates of ca. 10% after 18 h and 55–60% after 4 d were reached (Scheme 3). Longer reaction times allow complete coordination of the ligand functions, but result also in an extensive decomposition of the complexes **5a–c** which reduce dramatically the final yields.

The complex **5a** could not be isolated from the mixture of **4a** and **5a**, since it is, as its precursor, an oil. The best way for its purification was to pursue the reaction for 7 days at 160°C in n-Bu$_2$O. Complete coordination of the allylic group to the metal centre was then observed but strong decomposition of the final complex **5a** occurs, too. **4a** was isolated in 24% yield as a brown oil, after evaporation of the n-Bu$_2$O under high vacuum and filtration of the decomposition products from n-heptane. It is characterized in ^{1}H NMR by the resonance signals of the cyclopentadienyl ligand, as four pseudo-quartet being in the range from $\delta \approx 5.7$ to $\delta \approx 6.1$ ppm with a characteristic coupling constant of $^3J(H,H) \approx 2.0$ Hz, and by the resonance of the π-allyl ligand at $\delta \approx 3.2$ ppm, $\delta \approx 4.8$ ppm and $\delta \approx 5.4$ ppm which are in the range of the commonly accepted values for a η^3-coordination of the allylic group [18,19]. In the ^{13}C NMR spectra, the cyclopentadienyl ligand gives

Scheme 4.

four signals for the resonance of the CH group in the range from $\delta \approx 102$ to $\delta \approx 107$ ppm plus one signal for the ipso-C at $\delta \approx 134$ ppm and the allyl ligand gives three C resonance at $\delta \approx 72$ ppm, $\delta \approx 117$ ppm and $\delta \approx 139$ ppm values which are consistent with the η^3-coordination of the allyl group.

Complex 5b, isolated as beige amorphous powder in 15% yield, shows in the ^{1}H NMR spectra characteristic signals for the cyclopentadienyl ligand, as four pseudo-quartet in the range from $\delta \approx 5.7$ ppm to $\delta \approx 6.1$ ppm with a coupling constant ^3J(H,H) ≈ 2.0 Hz. In the ^{13}C NMR spectra 5b is characterized by four signals due to the CH resonance of the cyclopentadienyl ligand in the range of $\delta \approx 98$ ppm to $\delta \approx 110$ ppm, plus one signal for the ipso-C of the cyclopentadienyl ligand at $\delta \approx 137$ ppm. In addition the complex 5b is characterized by the resonance of the η^1-phenyl ring at $\delta \approx 172$ ppm, a value which is consistent with the reported values for η^1-phenyl complexes of niobium [20].

Complex 5c, isolated as beige amorphous powder in 22% yield, shows in the ^{1}H NMR spectra characteristic signals for the cyclopentadienyl ligand, as four pseudo-quartet in the range from $\delta \approx 5.5$ ppm to $\delta \approx 6.0$ ppm with a coupling constant ^3J(H,H) ≈ 2.5 Hz and in addition 5c is characterized by the resonance of the η^3-benzylic-CH at $\delta \approx 3.4$ ppm, value being consistant with the η^3-coordination of the benzylic group. Four signals due to the CH resonance of the cyclopentadienyl ligand in the range of $\delta \approx 100$ ppm to $\delta \approx 110$ ppm, plus one signal for the ipso-C of the cyclopentadienyl ligand at $\delta \approx 137$ ppm are seen in the ^{13}C NMR spectra; in addition a resonance of the benzylic-CH at $\delta \approx 127$ ppm occurs.

The new niobium complexes 5a–c are very sensitive to air, rapidly leading to the formation of white solid resulting from hydrolysis. They can be stored for a relatively long time (i.e. several weeks) at room temperature under argon without noticeable decomposition.

Based on the kinetic observations and according to the high temperature required to observe metal coordination of the ligand functions, we propose that this last step of the reactions proceed via C-H activation of the ligand (i.e. the allylic, the o-phenylic, and the benzylic positions) by the imido ligand of the complexes 4a–c (Scheme 4). This proposed mechanism is in agreement with observations made by Wolczanski et al. for the C–H activation with tantalum complexes [8,11], which requires high temperatures (i.e. 182°C), and the results separately reported by Bergman et al. [2,14] and by Wolczanski et al. [12] who described the C–H activation of benzene with zirconium complexes. This step should be rate-limiting for two reasons: i) Its reversibility, the complexes 6a–c being able to give the complexes 4a–c or the observed compounds 5a–c via irreversible elimination of dimethylamine. ii) The formation of the transition state required for the C–H

activation with the correct orientation of the C–H bond to be activated. The driving force for the success of the reaction is the irreversible elimination of dimethylamine, and the stability of the complexes 5a–c under the reaction conditions. Finally, in none of our experiments, did we ever observe the activation of the methyl groups of the bridging ligands. This observation is consistant with the increased ability of the ligand functions (i.e. allyl, phenyl and benzyl) to stabilize the complexes 5a–c by π-donation to the electrophilic metal centre bearing an imido ligand and also in terms of additional resonance stabilisation [11]. In the absence of more detailed physical data, the explanation of this reaction step remains incomplete. We cannot actually exclude another possibility for the formation of the complexes 5a–c from 4a–c, e.g. direct deprotonation of the ligand functions by the amido ligand.

The new half-sandwich complexes 5a–c are to our knowledge the first isolated complexes resulting from an intramolecular CH activation of a ligand function by an imido ligand at niobium. Their reactivity towards insertion reactions of small molecule (e.g. CO, C_2H_4) has to be subject of further investigations. They can also be interesting candidates as ethylene and propylene polymerization catalysts, particularly 5a, as well as for ethylene/CO co-polymerization.

3. Experimental section

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 n-Bu_2O were freshly distilled over Na/K amalgam under argon from purple benzophenone ketyl before use (caution: solvent should not be distilled to dryness). Deuterates solvent were dried over Na/K amalgam and then vacuum transfered and stored under argon atmosphere. All glassware were base- and acid-washed, oven dried and additionally dried under high vaccum. The benzyl potassium and the niobium-trisamidoimido compound $Nb[N(CH_3)_2]_3[=N-2,6-iPr_2C_6H_3)]$ 3 are prepared as reported in the literature [16,21,22]. Dimethylfulvene was 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 HDPX 400 spectrometer (^{1}H NMR were referenced to the residual protio-solvent: C_6D_6, $\delta = 7.15$ ppm and $CDCl_3$, $\delta = 7.24$ ppm; ^{13}C NMR were referenced to the C-signal of the deutero solvent: C_6D_6, $\delta = 128$ ppm and $CDCl_3$, $\delta = 77$ ppm), mass spectra (CI) were measured with a Varian MAT 90 spectrometer, the GC-MS were performed on a gas-chromatograph HP5970 connected to a selective mass spectrometer detector HP 5970, using helium as

carrier gas, a column model BGB-1 (25m, $d = 0.32$ mm, film thickness $= 0.52$ μm, material, 95% methyl-α-polysiloxan, 5% phenylpolysiloxan) from SCP-Seitz GmBH with a constant pressure of 200 kPa, the methods AS 60 and AS 100 refering to rate programs, and elemental analyses were performed by the Analytical Laboratory of the Inorganic Chemical Department, Technische Universität München.

GC-rate programms: AS 60: 4 min at 60°C, heating 15°C/min up to 120°C, 2 min at 120°C, heating 35°C/min up to 240°C and 6.5 min at 240°C. AS 100: 2 min at 100°C, heating 15°C/min up to 170°C, 2 min at 170°C, heating 35°C/min upto 240°C, 13.8 min at 240°C, heating 50°C/min up to 265°C and 2 min at 265°C.

4. Procedures

1. General method for the preparations of the ligands **2a**, **2b** and **2c** from dimethylfulvene **1** and RM. (The synthesis gave as expected a mixture of isomeres. Only the major signals are given for the NMR data.)

A solution of RM (70 mmol) in THF (100 ml) was treated with a solution of dimethylfulvene **1** (7.5 g, 70 mmol) in THF (50 ml) at 0°C. The mixture was allowed to warm-up to room temperature, stirred for 12 h, then quenched by addition of saturated ammonium chloride (100 ml), and extracted with ether (3 × 40 ml). The organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was then distilled under vacuum (5 × 10^{-2} mmHg) to give a slightly yellow oil.

a. Preparation of $C_5H_5C(CH_3)_2C_3H_5$ **2a** from C_3H_5MgCl (solution 2M in THF; 35 ml). Yield: 88%-Eb:57°C.

^{1}H NMR, CDCl$_3$, 400.13 MHz: 1.15 and 1.16 (s, 6H, C(CH$_3$)$_2$); 2.21 and 2.23 (d, 2H, ^3J(H,H) = 7.5 Hz, CH$_2$–CH=CH$_2$); 2.90 and 2.92 (d, 2H, ^3J(H,H) = 1.5 Hz, CH$_2$-allyl–C$_5$H$_5$); 4.97 (m, 2H, CH$_2$=CH–CH$_2$); 5.68 (m, 1H, CH$_2$=CH–CH$_2$); 5.95, 6.15, 6.40 and 6.57 (m, 3H, CH–vinyl–C$_5$H$_5$); ^{13}C{^{1}H} NMR, CDCl$_3$, 100.62 MHz: 27.14 and 28.28 (C(CH$_3$)2); 35.04 and 36.12 (C(CH$_3$)$_2$); 40.09 and 40.79 (CH$_2$–allyl–C$_5$H$_5$); 46.71 and 48.05 (CH$_2$–CH=CH$_2$); 116.45 (CH$_2$=CH–CH$_2$); 123.74, 130.46, 131.91, 132.50, 133.42, 135.61 (CH–vinyl–C$_5$H$_5$); 135.62 (CH$_2$=CH–CH$_2$); 155.07 and 157.42 (ipsoC-C$_5$H$_5$). CG: method AS 60. $t_R = 8.70$ min.

$C_{11}H_{16}$-mass: 148.25017-mass spectra: m/z (%): [M$^+$] 148 (11); 107 (100); 91 (74). Elemental Analysis [Found (Calc.)]: C: 88.56 (89.12), H: 10.74 (10.88).

b. Preparation of $C_5H_5C(CH_3)_2C_6H_5$ **2b** from C_6H_5Li (solution 1.8M in cyclohexane/ether; 39 ml). Yield: 86%-Eb: 78°C.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.22 and 1.28 (s, 6H, C(CH$_3$)$_2$); 2.39 and 2.58 (d, 2H, ^3J(H,H) = 1.5 Hz, CH$_2$–Allyl–C$_5$H$_5$); 5.80, 6.03, 6.08 and 6.19 (m, 3H,

CH–vinyl–C$_5$H$_5$); 6.84–7.08 (m, 5H, C$_6$H$_5$). ^{13}C{^{1}H} NMR, CDCl$_3$, 100.62 MHz: 29.35 and 30.11 (C(CH$_3$)$_2$); 39.87 (C(CH$_3$)$_2$); 40.88 and 40.97 (CH$_2$–allyl–C$_5$H$_5$); 124.27, 128.00, 133.55 and 134.04 (CH–vinyl–C$_5$H$_5$); 126.64 (p-C$_6$H$_5$); 127.44 and 127.75 (o-C$_6$H$_5$); 128.23 and 128.37 (m-C$_6$H$_5$); 149.05 and 150.10 (ipsoC-C$_6$H$_5$); 155.92 and 158.00 (ipsoC-C$_5$H$_5$).

CG: Method AS 100. $t_R = 8.73$ min.

$C_{14}H_{16}$-Mass: 184.12-mass spectra: m/z (%): [M$^+$] 184 (50); 169 (100); 154 (44); 91 (47). Elemental Analysis [Found (Calc.)]: C: 90.63 (91.24), H: 8.67 (8.76).

c. Preparation of $C_5H_5C(CH_3)_2CH_2C_6H_5$ **2c** from $C_6H_5CH_2K$ (9.2 g).

Yield: 91%-Eb:84°C.

^{1}H NMR, CDCl$_3$, 400.13 MHz: 1.26 (s, 6H, C(CH$_3$)$_2$); 2.83 and 2.85 (br.s, 2H, CH$_2$–allyl–C$_5$H$_5$); 2.99 (br.s, 2H, CH$_2$-benzylic); 5.91, 6.17, 6.55 and 6.75 (m, 3H CH–vinyl–C$_5$H$_5$); 7.07 (m, 2H, o-C$_6$H$_5$); 7.25 (m, 3H, p-C$_6$H$_5$ and m-C$_6$H$_5$). ^{13}C{^{1}H} NMR, CDCl$_3$, 100.62 MHz: 27.05 and 28.05 (C(CH$_3$)$_2$); 36.31 and 37.28 (C(CH$_3$)$_2$); 40.59 and 40.83 (CH$_2$–allyl–C$_5$H$_5$); 48.51 and 50.38 (CH$_2$-benzylic); 124.52, 131.92, 132.86 and 133.42 (CH–vinyl–C$_5$H$_5$); 125.72 (p-C$_6$H$_5$); 127.33 and 127.44 (o-C$_6$H$_5$); 130.25 and 130.32 (m-C$_6$H$_5$); 138.94 (ipsoC-C$_6$H$_5$); 154.68 and 157.32 (ipsoC-C$_5$H$_5$).

CG: Method AS 100. $t_R = 9.75$ min.

$C_{15}H_{18}$-Mass: 198.1408-mass spectra: m/z (%): [M$^+$] 198 (10); 107 (100); 154 (44); 91 (47); 65 (19). Elemental Analysis [Found (Calc.)]: C: 90.37 (90.84), H: 9.29 (9.16).

2. General method for the preparation of the niobium compounds **4a**, **4b** and **4c** from Nb[N(CH$_3$)$_2$]$_3$[=N-2,6-iPr$_2$C$_6$H$_3$)] **3** and respectively the ligands **2a**, **2b** and **2c**.

A solution of the niobium precursor **3** (100 mg, 0.25 mmol) in n-Bu$_2$O (10 ml) was treated with a solution of the appropriate ligand (0.25 mmol) in n-Bu$_2$O (5 ml) at −78°C. The mixture was allowed to warm-up to room temperature, then 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 at 80°C under high vaccum (10^{-2} mmHg) for 8 h. Then pentane (5 ml) was added to the residue, the solution filtered through a glass plug and evaporated under high vaccum to give a yellow oil.

a. Preparation of Nb[N(CH$_3$)$_2$][=N-2,6-iPr$_2$C$_6$H$_3$)][η^5-C$_5$H$_4$C(CH$_3$)$_2$C$_3$H$_5$] **4a** from **2a** (38 mg).

Yield: 92%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.12 (s, 6H, C(CH$_3$)$_2$); 1.31 (d, 12H, ^3J(H,H) = 7.1 Hz, CH(CH$_3$)$_2$); 2.18 (d, 2H, ^3J(H,H) = 6.0 Hz, CH$_2$–CH=CH$_2$); 3.26 (s, 12H, N(CH$_3$)$_2$); 4.05 (sept., 2H, ^3J(H,H) = 7.1 Hz,

CH(CH$_3$)$_2$); 4.85 (m, 2H, CH$_2$=CH–CH$_2$); 5.57 (m, 1H, CH$_2$=CH–CH$_2$); 5.89 (pseudo-t, 2H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.01 (pseudo-t, 2H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.93 (t, 1H, ^3J(H,H) = 7.5 Hz, p-C$_6$H$_3$); 7.07 (d, 2H, ^3J(H,H) = 7.5 Hz, m-C$_6$H$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 23.36 (CH(CH$_3$)$_2$); 27.63 (C(CH$_3$)$_2$); 27.89 (CH(CH$_3$)$_2$); 34.46 (C(CH$_3$)$_2$); 48.92 (CH$_2$–CH=CH$_2$); 50.92 (N(CH$_3$)$_2$); 105.50 and 106.35 (C$_5$H$_4$); 116.24 (CH$_2$=CH–CH$_2$); 122.98 (m-C$_6$H$_3$); 123.06 (p-C$_6$H$_3$); 134.11 (CH$_2$=CH–CH$_2$); 134.33 (ipsoC–C$_5$H$_4$); 141.77 (o-C$_6$H$_3$); 151.23 (ipsoC-C$_6$H$_3$).

C$_{27}$H$_{44}$N$_3$Nb-mass: 503.5782-mass spectra: m/z (%): [M$^+$] 503.4 (70); [M + -NMe$_2$] 459.2 (100); [M$^+$-2 × HNMe$_2$] 413.2 (21). Elemental Analysis [Found (Calc.)]: C: 63.92 (64.38), H: 8.72 (8.81), N: 8.19 (8.35), Nb (18.46).

b. Preparation of Nb[N(CH$_3$)$_2$]$_2$[=N-2,6-iPr$_2$C$_6$H$_3$)][η^5-C$_5$H$_4$C(CH$_3$)$_2$C$_6$H$_5$] **4b** from **2b** (48 mg).

Yield: 86%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.32 (d, 12H, ^3J(H,H) = 6.5 Hz, CH(CH$_3$)$_2$); 1.54 (s, 6H, C(CH$_3$)$_2$); 3.26 (s, 12H, N(CH$_3$)$_2$); 4.09 (sept., 2H, ^3J(H,H) = 6.5 Hz, CH(CH$_3$)$_2$); 5.90 (pseudo-t, 2H, ^3J(H,H) = 3.0 Hz, C$_5$H$_4$); 6.09 (pseudo-t, 2H, ^3J(H,H) = 3.0 Hz, C$_5$H$_4$); 7.09 (m, 8H, C$_6$H$_3$ and C$_6$H$_5$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 23.62 (CH(CH$_3$)$_2$); 26.29 (C(CH$_3$)$_2$); 28.75 (CH(CH$_3$)$_2$); 38.75 (C(CH$_3$)$_2$); 50.96 (N(CH$_3$)$_2$); 106.39 and 106.81 (C$_5$H$_4$); 121.62 (p-C$_6$H$_3$); 121.77 (m-C$_6$H$_3$); 124.57 (p-C$_6$H$_5$); 124.77 (m-C$_6$H$_5$); 127.14 (o-C$_6$H$_5$); 134.38 (ipsoC-C$_5$H$_4$); 140.86 (ipsoC-C$_6$H$_5$); 141.98 (o-C$_6$H$_3$); 149.68 (ipsoC-C$_6$H$_3$).

C$_{30}$H$_{44}$N$_3$Nb-mass: 539.2591-mass spectra: m/z (%): [M$^+$ + H] 540.4 (100); [M$^+$-NMe$_2$] 495.4 (44); [M$^+$-(HNMe$_2$ + CH$_2$=NMe)] 462.0 (8). Elemental Analysis [Found (Calc.)]: C: 66.12 (66.76), H: 8.16 (8.22), N: 7.59 (7.79), Nb: (17.23).

c. Preparation of Nb [N(CH$_3$)$_2$]$_2$[=N-2,6-iPr$_2$C$_6$H$_3$)][η^5-C$_5$H$_4$C(CH$_3$)$_2$CH$_2$C$_6$H$_5$] **4c** from **2c** (51 mg).

Yield: 91%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.12 (s, 6H, C(CH$_3$)$_2$); 1.28 (d, 12H, ^3J(H,H) = 6.5 Hz, CH(CH$_3$)$_2$); 2.58 (s, 2H, CH$_2$-benzylic); 3.26 (s, 12H, N(CH$_3$)$_2$); 4.01 (sept., 2H, ^3J(H,H) = 6.5 Hz, CH(CH$_3$ _)); 5.85 (pseudo-t, 2H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 5.87 (pseudo-t, 2H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.72 (m, 2H, o-C$_6$H$_5$); 6.92 (t, 1H, ^3J(H,H) = 7.5 Hz, p-C$_6$H$_3$); 7.07 (m, 5H, m-C$_6$H$_3$ and m-C$_6$H$_5$ and p-C$_6$H$_5$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 25.03 (CH(CH$_3$)$_2$); 27.61 (C(CH$_3$)$_2$); 27.83 (CH(CH$_3$)$_2$); 37.14 (C(CH$_3$)$_2$); 52.25 (N(CH$_3$)$_2$); 52.76 (CH$_2$-benzylic); 107.28 and 107.69 (C$_5$H$_4$); 122.94 (p-C$_6$H$_3$); 123.03 (m-C$_6$H$_3$); 126.18 (p-C$_6$H$_5$); 126.34 (o-C$_6$H$_5$); 130.81 (m-C$_6$H$_5$); 135.16 (ipsoC-C$_5$H$_4$); 138.82 (ipsoC-C$_6$H$_5$); 143.14 (o-C$_6$H$_3$); 152.72 (ipsoC-C$_6$H$_3$).

C$_{31}$H$_{46}$N$_3$Nb-mass: 553.2748-Mass Spectra: m/z (%): [M$^+$] 553.4 (100) no fragments. Elemental Analysis [Found (Calc.)]: C: 66.97 (67.24), H: 8.34 (8.38), N: 7.36 (7.59), Nb: (16.79).

3. General method for the preparation of the niobium compounds **5a**, **5b** and **5c** from Nb[N(CH$_3$)$_2$]$_3$[=N-2,6-iPr$_2$C$_6$H$_3$)] **3** and respectively the ligands **2a**, **2b** and **2c**.

A solution of the niobium precursor **3** (200 mg, 0.50 mmol) in n-Bu$_2$O (10 ml) was treated with a solution of the appropriate ligand (0.50 mmol) in n-Bu$_2$O (5 ml) at −78°C. The mixture was allowed to warm-up to room temperature, then slowly warmed-up to 100°C. The stirring was continued for 2 h and then the temperature was warmed-up to 160°C. The stirring was maintained for 4 days and the solvent was evaporated. The product of the reaction was dried at 80°C under high vaccum (10 − 2 mmHg) for 8 h. Then pentane (7 ml) was added to the residue, the solution filtered through a glass plug, and evaporated. The residue was added to heptane (5 ml) and the solution left under argon to give slowly an amorphous beige material (for **5b** and **5c**) or evaporated to give a brown oil (for **5a**).

a. Preparation of Nb[N(CH$_3$)$_2$]$_2$[=N-2,6-iPr$_2$C$_6$H$_3$)][η^5:η^3-{C$_5$H$_4$}C(CH$_3$)$_2${C$_3$H$_4$}] **5a** from **2a** (74 mg).

Yield: 24%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.16 (s, 3H, C(CH$_3$)$_2$); 1.18 (s, 3H, C(CH$_3$)$_2$); 1.22 (d, 6H, ^3J(H,H) = 7.3 Hz, CH(CH$_3$)$_2$); 1.32 (d, 6H, ^3J(H,H) = 7.3 Hz, CH(CH$_3$)$_2$); 3.05 (s, 6H, N(CH$_3$)$_2$); 3.23 (m, 1H, CH–CH=CH$_2$); 3.94 (br. sept., 2H, ^3J(H,H) = 7.3 Hz, CH(CH$_3$)$_2$); 4.79 (m, 2H, CH$_2$=CH–CH); 5.42 (m, 1H, CH$_2$=CH–CH); 5.76 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 5.85 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 5.92 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.01 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.94 (t, 1H, ^3J(H,H) = 7.5 Hz, p-C$_6$H$_3$); 7.05 (d, 2H, ^3J(H,H) = 7.5 Hz, m-C$_6$H$_3$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 23.11 and 23.59 (C(CH$_3$)$_2$); 26.32, 26.45, 26.59 and 26.76 (CH(CH$_3$)$_2$); 28.82 and 31.03 (CH(CH$_3$)$_2$); 34.46 (C(CH$_3$)$_2$); 51.81 (N(CH$_3$)$_2$); 72.61 (CH–CH=CH$_2$); 102.02, 103.36, 106.31 and 107.66 (C$_5$H$_4$); 117.51 (CH$_2$=CH–CH); 121.68 (m-C$_6$H$_3$); 122.39 (p-C$_6$H$_3$); 134.34 (ipsoC-C$_5$H$_4$); 138.93 (CH$_2$=CH–CH); 142.08 (o-C$_6$H$_3$); 151.36 (ipsoC-C$_6$H$_3$).

C$_{25}$H$_{37}$N$_2$Nb-mass: 458.4934-mass spectra: m/z (%): [M$^+$] 459.0 (40); [M$^+$-NMe2] 415.2 (12). Elementarl Analysis [Found (Calc.)]: C: 65.97 (65.47), H: 8.06 (8.14), N: 6.49 (6.11), Nb: (20.28).

b. Preparation of Nb[N(CH$_3$)$_2$][=N-2,6-iPr$_2$C$_6$H$_3$)][η^5:η^1-{C$_5$H$_4$}C(CH$_3$)$_2${C$_6$H$_4$}] **5b** from **2b** (92 mg).

Yield: 15%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.15 (d, 6H, ^3J(H,H) = 7.1 Hz, CH(CH$_3$)$_2$); 1.22 (d, 6H, ^3J(H,H) = 7.1 Hz,

CH(CH$_3$)$_2$); 1.31 (s, 3H, C(CH$_3$)$_2$); 1.54 (s, 3H, C(CH$_3$)$_2$); 3.26 (s, 6H, N(CH$_3$)$_2$); 3.94 (br. sept., 2H, ^3J(H,H) = 7.1 Hz, CH(CH$_3$)$_2$); 5.72 (pseudo-q, 1H, ^3J(H,H) = 2.0 Hz, C$_5$H$_4$); 5.82 (pseudo-q, 1H, ^3J(H,H) = 2.0 Hz, C$_5$H$_4$); 5.97 (pseudo-q, 1H, ^3J(H,H) = 2.0 Hz, C$_5$H$_4$); 6.04 (pseudo-q, 1H, ^3J(H,H) = 2.0 Hz, C$_5$H$_4$); 6.94–7.08 (m, 7H, C$_6$H$_3$ and C$_6$H$_5$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 24.80 and 25.06 (CH(CH$_3$)$_2$); 27.88 (C(CH$_3$)$_2$); 30.45 (CH(CH$_3$)$_2$); 32.38 (C(CH$_3$)$_2$); 52.33 (N(CH$_3$)$_2$); 98.61, 106.64, 109.56, and 109.86 (C$_5$H$_4$); 124.04 (p-C$_6$H$_3$); 121.61 and 122.14 (m-C$_6$H$_3$); 124.84 (p-C$_6$H$_5$); 126.14 and 126.77 (m-C$_6$H$_5$); 128.99 (o-C$_6$H$_5$); 137.26 (ipsoC-C$_5$H$_4$); 143.34 (ipsoC-C$_6$H$_5$); 143.73 (o-C$_6$H$_3$); 148.08 (ipsoC-C$_6$H$_3$); 173.96 (o-metallated-C$_6$H$_5$).

C$_{28}$H$_{37}$N$_2$Nb-mass: 494.2013-mass spectra: m/z (%): [M$^+$] 493.9 (100); [M$^+$-NMe2] 450.8 (72). Elemental Analysis [Found (Calc.)]: C: 67.17 (67.99), H: 7.46 (7.55), N: 5.59 (5.67), Nb: (18.80).

c. Preparation of Nb[N(CH$_3$)$_2$][=N-2,6-iPr$_2$C$_6$H$_3$)][η^5:η^3-{C$_5$H$_4$}C(CH$_3$)$_2${CHC$_6$H$_5$}] 5c from 2c (99 mg)

Yield: 22%.

^{1}H NMR, C$_6$D$_6$, 400.13 MHz: 1.14 (d, 6H, ^3J(H,H) = 7.0 Hz, CH(CH$_3$)$_2$); 1.15 (d, 6H, ^3J(H,H) = 7.0 Hz, CH(CH$_3$)$_2$); 1.16 (s, 3H, C(CH$_3$)$_2$); 1.20 (s, 3H, C(CH$_3$)$_2$); 2.61 (br. s, 6H, N(CH$_3$)$_2$); 3.42 (br. s, 1H, CH-benzylic); 3.84 (sept., 2H, ^3J(H,H) = 7.0 Hz, CH(CH$_3$)$_2$); 5.50 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 5.66 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 5.69 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.04 (pseudo-q, 1H, ^3J(H,H) = 2.5 Hz, C$_5$H$_4$); 6.85–7.24 (m, 8H, C$_6$H$_3$ and C$_6$H$_5$). ^{13}C{^{1}H} NMR, C$_6$D$_6$, 100.62 MHz: 21.29, 22.56, 23.51 and 24.75 (CH(CH$_3$)$_2$); 27.82 and 28.14 (C(CH$_3$)$_2$); 31.91 and 28.58 (CH(CH$_3$)$_2$); 34.73 (C(CH$_3$)$_2$); 59.05 (N(CH$_3$)$_2$); 100.68, 102.15, 108.90, and 109.09 (C$_5$H$_4$); 122.59 (p-C$_6$H$_3$); 123.09 (m-C$_6$H$_3$); 123.42 and 124.72 (o-C$_6$H$_5$); 124.81 (p-C$_6$H$_5$); 126.94 (CH-benzylic); 129.65 and 130.83 (m-C$_6$H$_5$); 137.58 (ipsoC-C$_5$H$_4$); 139.71 (ipsoC-C$_6$H$_5$); 144.11 (o-C$_6$H$_3$); 146.08 (ipsoC-C$_6$H$_3$).

C$_{29}$H$_{39}$N$_2$Nb-mass: 508.2169-mass spectra: m/z (%): [M$^+$] 508.5 (100); [M$^+$-CH$_2$=NMe] 465.5 (60); [M$^+$-HNMe$_2$] 463.5 (18). Elemental Analysis [Found (Calc.)]: C: 67.98 (68.47), H: 7.66 (7.73), N: 5.39 (5.51), Nb: (18.28)

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