Ansa-bridged η-cyclopentadienyl imido and amido derivatives of titanium, zirconium, niobium and molybdenum [1]

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Abstract

An improved synthesis of the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ is described. It has been used to prepare the *ansa* compounds $\{Ti[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$, $\{Ti[\eta\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)]Cl)\}_2$, $\{Zr[\eta:\sigma C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$, $\{Zr[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](SMe_2)Cl_2\}$ and $\{Mo[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)](PMe_3)Cl_3\}$. Treatment of $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N]Cl_2\}$ with MeMgBr gives the dimer $\{MeNb[\eta\text{-}C_5H_4(CH_2)_3(\mu\text{-}N)(\mu\text{-}\sigma(N):\eta^2\text{-}(N,C)\text{-}NCH(CH_2)_2\text{-}\eta\text{-}C_5H_4)]NbMe_2\}$ whose crystal structure has been determined. The new compounds $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N](\eta\text{-}C_5H_5)(\sigma\text{-}C_5H_5)\}$, $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N](CH_2C_6H_5)_2\}$ and $Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N][CH_2C(CH_3)CH_2]_2\}$ have also been prepared. The zirconium compounds together with methylaluminoxane act as catalysts for ethylene and propylene polymerisation. © 1997 Elsevier Science S.A.

Keywords: Titanium; Niobium; Zirconium; Molybdenum

Recently we reported the synthesis of the compound $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ and showed that it reacted readily with niobium pentachloride to give the *ansa*-bridged η-cyclopentadienylimido derivative $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N]Cl_2\}$ [1]. In view of the current interest in *ansa*-bridged η-cyclopentadienyl-amido compounds of the Group IV metals as homogeneous catalysts for α-olefin polymerisation [2–4] we have explored further the synthetic potential of the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$, as described below.

We have identified an improved route to the ligand precursor $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ shown in Scheme 1. Treatment of $[Br(CH_2)_3NH_3]Br$ with three equivalents of $(Me_3Si)SO_3CF_3$ and NEt_3 gave $Br(CH_2)_3N(SiMe_3)_2$ **1** which was then reacted with

sodium cyclopentadienide giving an isomeric mixture of $[(C_5H_5)(CH_2)_3N(SiMe_3)_2]$ **2**. Addition of t-butyl lithium to **2** followed by Me_3SiCl gives the desired compound $\{[C_5H_4(SiMe_3)](CH_2)_3N(SiMe_3)_2\}$ **3** as a mixture of isomers. The overall yield of **3** from $[Br(CH_2)_3NH_3]Br$ was reproducibly 50–55%, on a 20 g scale.

Treatment of $TiCl_4$ in toluene with **3** gave orange crystals of $\{Ti[\eta:\sigma\text{-}C_5H_4(CH_2)_3N(SiMe_3)]Cl_2\}$ **4**. The analytical and spectroscopic data characterising **4**, and all the other new compounds described below, are given

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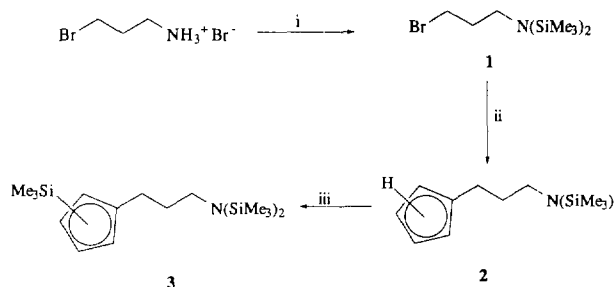
Scheme 1. Synthesis of the ligand precursor **3**. (i) $(Me_3Si)SO_3CF_3$ (3 equiv.) and NEt_3 (3 equiv.) in Et_2O, 0 °C to r.t., 4 h. (ii) $Na(C_5H_5)$ (1.1 equiv.) in THF, −10 °C to r.t., 12 h. (iii) $LiBu^t$ (1 equiv.) in hexane, −78 °C to r.t., 12 h, then Me_3SiCl (1.5 equiv.) 5 h.

in the footnotes. [5] The elimination of $SiMe_3Cl$ from **4** occurs readily in toluene at 60 °C to give {Ti[η-$C_5H_4(CH_2)_3(\mu$-N)]Cl}$_2$ **5**. The dimeric structure of **5** is confirmed by the ^1H NMR spectrum [6] which shows diastereotopic signals for the aliphatic chain protons.

Treatment of [$ZrCl_4(SMe_2)_2$] with **3** gave white crystals of the amido derivative {Zr[η:σ-$C_5H_4(CH_2)_3N(SiMe_3)$](SMe_2)Cl_2} **6**. The ^1H NMR spectrum of this compound shows a fluxional behaviour that can be attributed to the sulphur inversion in the SMe_2 group. The reaction of **3** with $ZrCl_4$ in dichloromethane gives (Zr[η:σ-$C_5H_4(CH_2)_3N(SiMe_3)$]Cl_2} **7**. Attempts to induce thermal elimination of $SiMe_3Cl$ from **6** and **7** were unsuccessful.

Treatment of molybdenum pentachloride with **3** gave red-brown microcrystals of {Mo[η:σ-$C_5H_4(CH_2)_3N(SiMe_3)$](C_4H_8O)Cl_3} **8**. Treatment of **8** with trimethylphosphine causes substitution of the tetra-

hydrofuran ligand giving orange-brown {Mo[η:σ-$C_5H_4(CH_2)_3N(SiMe_3)$](PMe_3)Cl_3] **9**.

We have explored the alkylation of the compound {Nb[η:σ-$C_5H_4(CH_2)_3N$]Cl_2} **10**. Treatment of **10** with an excess of MeMgBr in diethyl ether gave orange crystals of the binuclear compound {MeNb[η-$C_5H_4(CH_2)_3(\mu$-N)(μ-σ(N):η^2(N,C)–NCH(CH_2)_2-η-C_5H_4)]NbMe_2} **11**. The crystal structure of **11** has been determined [7] and the molecular structure is shown in Fig. 1 together with selected bond lengths and angles. The molecule has only three methyl groups and one hydrogen has been lost from a CH_2 group adjacent to an imido nitrogen. A GC/MS analysis showed that methane was the only volatile product evolved from the reaction mixture.

The Nb–Nb distance of 2.929(1) Å is consistent with a single bond [5]. The almost linear C(21)–N(2)–Nb(1) (168.0(7)°) suggests that the lone pair of the sp-hybridised nitrogen is donating to the Nb(1). Whilst the –C(H)=N double bond is η^2-coordinated to the Nb(2) atom. The (C=N) bond length is slightly greater than in related systems [6]. The deprotonated chain bond is the second structurally characterised example of a bridging μ-(σ:π-C(H)=N) azaalkenylidene system [7]. The methyl groups bonded to Nb(2) (containing the atoms C(2) and C(3)) lie either side of the plane containing the two Nb atoms and the centroids of the η-C_5 rings.

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[5] Satisfactory microanalysis has been obtained for all the new compounds. Selected NMR data (J/Hz, δ/ppm) Cp* = η-C_5H_4, ^1H NMR at 300MHz and 18 °C. For **4**; (^1H in CD_2Cl_2, δ): 6.57 (t, 2H, Cp*); 6.19 (t, 2H, Cp*); 3.52 (c, 2H, CH_2N); 2.67 (t, 2H, Cp*CH_2); 2.08 (m, 2H, Cp*CH$_2$CH_2); 0.46 (s, 9H, Si(CH_3)$_3$). For **5**; (^1H in CD_2Cl_2, δ): 6.85 (q, 2H, Cp*); 6.38 (q, 2H, Cp*); 6.08 (q, 2H, Cp*); 5.62 (q, 2H, Cp*); 3.71 (m, 2H, H$_g$); 3.44 (m, 2H, H$_g$); 2.97 (m, 2H, H$_e$); 2.70 (m, 2H, H$_e$); 2.55 (m, 2H, H$_f$); 1.72 (m, 2H, H$_f$). For **6**; (^1H in CD_2Cl_2, δ): 6.66 (t, 2H, Cp*); 6.43 (t, 2H, Cp*); 2.83 (m, 2H, CH_2N); 2.71 (t, 2H, Cp*CH_2); 2.59 (s, br, S(CH_3)$_2$); 1.69(m, 2H, Cp*CH_2CH_2); 0.90 (s, 9H, Si(CH_3)$_3$). For **7**; (^1H in C_6D_6, δ): 6.18 (t, 2H, Cp*); 5.58 (t, 2H, Cp*); 2.78 (m, 2H, CH_2N); 2.08 (m, 2H, Cp*CH_2); 1.41 (m, 2H, Cp*CH$_2$CH_2); 0.43 (m, 9H, Si(CH_3)$_3$). For **8** and **9**; paramagnetic. For **11**; (^1H in ([$^2H_8$] toluene, 20 °C, δ): 6.05 (q, 1H, H$_a$); 5.99 (q+q, 2H, J_{HH} = 2.4Hz, H$_b$ +H$_b'$); 5.52 (q, 1H, J_{HH} = 2.4Hz, H$_a'$); 5.19 (q, 1H, H$_c$); 5.10 (s, 1H, H$_{g'}$); 4.90 (q, 1H, J_{HH} = 2.4Hz, H$_{c'}$); 4.15 (m, 1H, H$_{g1}$); 4.02 (q, 1H, J_{HH} = 2.4Hz, H$_d$); 3.90 (m, 1H, H$_{g2}$); 3.86 (q, 1H, J_{HH} = 2.4Hz, H$_{d'}$); 3.12 (m, 1H, H$_{f'2}$); 2.61 (m, 1H, H$_{f'1}$); 2.47 (m, 1H, H$_e$); 2.22 (m, 1H, H$_{e'}$); 1.96 (m, 1H, H$_f$); 1.72–1.58 (m, 3H, H$_{e'}$ +H$_f$ +H$_e$); 0.65 (br s, 6H, Me$_b$ +Me$_c$); −0.54 (s, 3H, Me$_a$). For **12**; (^1H in [$^2H_8$] THF, 20 °C δ) r.t. spectrum with very broad features; (at −40 °C δ): 6.24 (v br, σ-C_5H_5); 5.99 (q, 1H, J_{HH} = 2.4Hz, Cp*H$_{d(a)}$); 5.95 (s, 5H, η-C_5H_5); 5.58 (q, 1H, J_{HH} = 2.4Hz, Cp*H$_{c(b)}$); 4.92 (q, 1H, J_{HH} = 2.4Hz, Cp*H$_{b(c)}$); 3.71 (m, 1H, CHH–N); 3.62 (q, 1H, J_{HH} = 2.4Hz, Cp*H$_{a(d)}$); 3.42 (m, 1H, CHH–N); 2.53 (m, 1H, Cp*CHH); 2.22 (m, 1H, Cp*CHH); 1.80 (m, 2H, Cp*CH$_2$CH_2). For **13**; (^1H in [$^2H_8$] toluene δ): 7.00 (m, 2H, H$_{para}$); 6.98 (m, 4H, H$_{meta}$); 6.67 (m, 4H, H$_{ortho}$); 5.19 (t, 2H, J_{HH} = 2.5Hz, Cp*); 4.90 (t, 2H, J_{HH} = 2.5Hz, Cp*); 2.96 (t, 2H, J_{HH} = 5.5Hz, CH_2–N); 2.00 (m, 2H, Cp*CH_2); 1.69 (d, 2H, $^2J_{HH}$ = 7.8Hz, Nb–CHPh); 1.44 (m, 2H, Cp*CH$_2$CH_2); 1.41 (d, 2H, $^2J_{HH}$ = 7.8Hz, Nb–CHHPh). For **14**; (^1H in [$^2H_8$] toluene, δ): (CH_2C(Me)CH_2 absent) 5.34 (br t, 2H, J_{HH} = 2.3Hz, Cp*), 4.77 (br s, 2H, Cp*), 2.79 (t, 2H, J_{HH} = 5.5Hz, CH_2–N), 2.24 (m, 2H, CpCH_2), 1.76 (br s, CH$_2$C(Me)CH$_2$), 1.60 (m, 2H, CpCH$_2$CH_2).

[6] See footnote 5.

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[7] X-ray crystal data for {MeNb[η-$C_5H_4(CH_2)_3(\mu$-N)(μ-σ(N):η^2(N,C)–NCH(CH$_2$)$_2$-η-C_5H_4)]NbMe_2} **11** C$_{19}$H$_{28}$N$_2$Nb$_2$, M = 470.26, crystal size ca. $0.25 \times 0.40 \times 0.60$ mm^3, orthorhombic, space group $Pn2_1a$ (non-standard setting of $Pna2_1$, N° 33), a = 18.935(5), b = 7.354(8), c = 13.374(5)Å, V = 1862.2 Å^3, Z = 4, D_c = 1.68 g cm^{-3}, μ(MoKα) = 11.79 cm^{-1}, $F(000)$ = 952, scan type ω−2θ, T = 293K, 2 < 2θ < 50°, total unique data 1773, no. of observations [I > 3σ(I)] 1572, observations/variables 7.5, R_{merge} = 0.025, R = 0.032, R_w = 0.037, maximum peak in final Fourier difference synthesis 0.48e$^-$ Å^{-3}. Data were collected on an Enraf–Nonius CAD4 diffractometer. An empirical absorption correction based on azimuthal scan data was applied and the data were corrected for Lp effects. Systematically absent reflections were rejected and equivalent reflections were merged. The heavy atom positions were determined from a Patterson synthesis. Subsequent difference syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms could not be located from difference syntheses and were placed in estimated positions (C–H = 0.96 Å) with isotropic thermal parameters 1.3 times that of the U_{eq} of the attached carbon atom. The non-hydrogen atoms were refined using full-matrix least squares procedures with the hydrogen atoms 'riding' on their supporting carbon atoms. The data were corrected for the effects of anomalous dispersion and isotropic extinction in the final stages of refinement. Crystallographic calculations were carried out using the CRYSTALS program on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
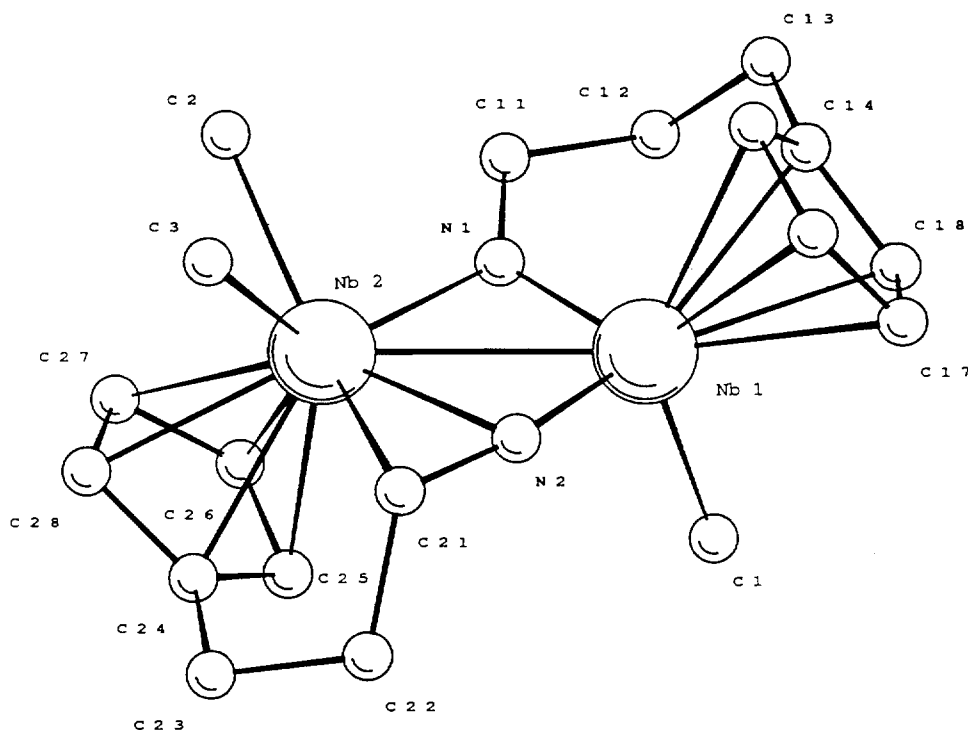
Fig. 1. Molecular structure of {MeNb[η-C$_5$H$_4$(CH$_2$)$_3$(μ-N)(μ-σ(N):η^2(N,C)–NCH(CH$_2$)$_2$-η-C$_5$H$_4$)]NbMe$_2$} **11**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) as follows: Nb(1)–C(1) 2.21(1), Nb(1)–N(1) 1.901(8), Nb(1)–N(2) 1.847(8), Nb(1)–Nb(2) 2.929(1), Nb(2)–C(2) 2.26(1), Nb(2)–C(3) 2.28(1), Nb(2)–N(1) 2.134(7), Nb(2)–N(2) 2.225(7), Nb(2)–C(21) 2.32(1), N(2)–C(21) 1.34(1), C(21)–C(22) 1.55(2); Nb(1)–N(1)–Nb(2) 92.9(3), Nb(1)–N(2)–Nb(2) 91.5(3), C(21)–N(2)–Nb(1) 168.0(7), C(21)–N(2)–Nb(2) 76.6(5), C(11)–N(1)–Nb(2) 133.0(6), C(11)–N(1)–Nb(1) 133.7(6), C(14)–C(13)–C(12) 114.9(9), C(12)–C(11)–N(1) 114.6(9), N(2)–C(21)–Nb(2) 69.1(5), C(22)–C(21)–N(2) 118.0(9), C(22)–C(21)–Nb(2) 116.0(8), C(23)–C(22)–C(21) 107.9(9), C(24)–C(23)–C(22) 107.9(8).

8   **9**
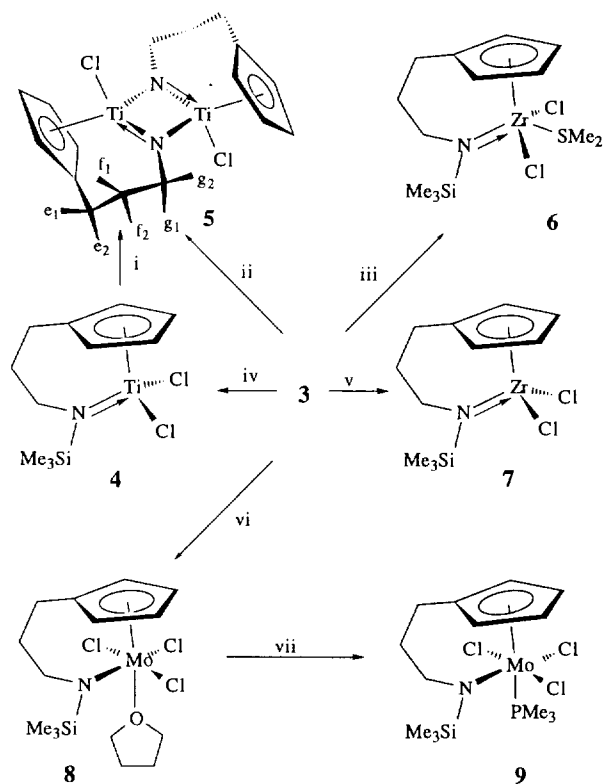
According to the solid state structure these groups should be chemically inequivalent in the NMR spectra of **11**. However, variable-temperature ^{1}H and ^{13}C NMR studies of **11** show that rapid exchange occurs above 293 K when the two methyl groups Me$_b$ and Me$_c$ become equivalent. Detailed NMR studies including a phase-sensitive ^{1}H–^{1}H dipolar-correlated 2D (PSEXSY) NMR study are consistent with the methyl exchange mechanism shown in the Scheme 3.

Addition of sodium cyclopentadienide to **10** gives the yellow tris-cyclopentadienyl derivative {Nb[η:σ-C$_5$H$_4$(CH$_2$)$_3$N)](η-C$_5$H$_5$)(σ-C$_5$H$_5$)} **12** in 80% yield. This compound undergoes a complex fluxional behaviour similar to that for the non-*ansa* analogue [Nb(η-C$_5$H$_5$)$_2$(σ-C$_5$H$_5$)(NBu^t)] [8], namely: rotation of the

Scheme 2. Reactions of the ligand precursor **3**. (i) In toluene at 60 °C for 12 h or in CH$_2$Cl$_2$ at r.t. for 12 h. (ii) TiCl$_4$ (1 equiv.) in toluene, at −78 °C then warm to 60 °C for 12 h. (iii) ZrCl$_4$(SMe$_2$)$_2$ (1 equiv.) in CH$_2$Cl$_2$, at −10 °C, warm to r.t. for 10 h. (iv) TiCl$_4$ (1 equiv.) in toluene, at −78 °C, warm to r.t. for 12 h. (v) ZrCl$_4$ (1 equiv.) in toluene at r.t. for 2 days. (vi) MoCl$_5$ (1 equiv.) in CH$_2$Cl$_2$ at −78 °C, warm to r.t. for 12 h, then THF. (vii) PMe$_3$ (1.5 equiv.) in THF, at r.t.
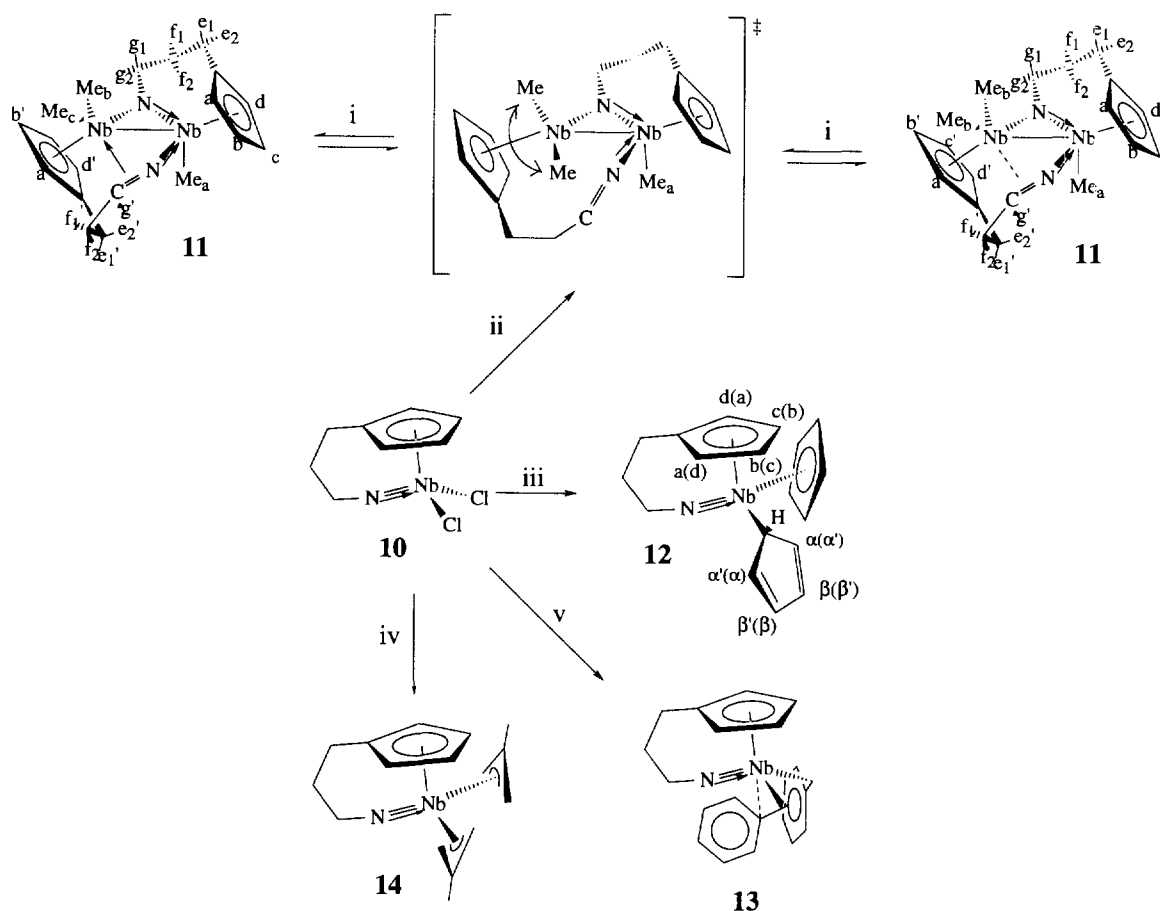
Scheme 3. Reactions of compound **10**. (i) Proposed mechanism for interchange of Me_a and Me_b. (ii) MgBrMe (excess) in Et_2O at r.t. for 12 h; (iii) $Na(C_5H_5)$ (2 equiv.) in Et_2O–THF (1:1) at r.t. for 12 h. (iv) $MgCl(2$-methylallyl) (2 equiv.) in Et_2O, $-78\,°C$, warm to r.t. for 12 h. (v) $PhCH_2MgCl$ (2 equiv.) in Et_2O, $-40\,°C$ warm to r.t. for 4 h.

σ-C_5H_5 ligand about the Nb–C_i bond; 1,2-migration of the niobium centre between the carbon atoms of the σ-C_5H_5 ligand; interchange between the η- and σ-C_5H_5 ligands.

Treatment of **10** with $PhCH_2MgCl$ gave the pale yellow dibenzyl derivative $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N)](CH_2Ph)_2\}$ **13**, in 92% yield. The NMR data show the ^1H ortho (δ 6.67) and ^{13}C CH_2Ph (δ 40.7; $J_{CH} = 135\,Hz$) resonances are shifted upfield and exhibit a small geminal coupling constant indicative of a diastereotopic CH_2Ph ($\delta_{HH} = 7.8\,Hz$) and the data suggest that either one or both benzyl ligands are η^2-bonded [3,9]. In contrast, the NMR data of the non-ansa analogue $\{Nb[\eta\text{-}C_5Me_5)(N\text{-}2,6\text{-}iPr_2C_6H_3)(CH_2Ph)_2\}$ indicate that both benzyl ligands coordinate in an η^1 fashion [10]. Addition of (2-methylallyl)MgCl to **10** gave $\{Nb[\eta:\sigma\text{-}C_5H_4(CH_2)_3N][CH_2C(CH_3)CH_2]_2\}$ **14** in which the two allylic ligands are undergoing a slow exchange process at room temperature and, at 100 °C, near the fast-exchange-limit region, only one resonance is observed for the anti- and syn-CH_2 protons (δ 3.13) and one resonance for the methyl group (δ 1.71).

The reactions and structures proposed for the new compounds are shown in Schemes 2 and 3. A preliminary study shows that the zirconium amido compound **6** in the presence of methylaluminoxane (with the Al/Zr ratio ca. 1000) polymerises ethylene (9×10^4 g of polyethylene $(mol\,of\,Zr)^{-1}\,h^{-1}\,atm^{-1}$; $N_t \approx 1.8\,s^{-1}$) and oligomerises propylene (660 g of polypropylene $(mol\,of\,Zr)^{-1}\,h^{-1}\,atm^{-1}$; $N_t \approx 0.5\,min^{-1}$).

In conclusion, the ansa-η-$C_5H_4(CH_2)_3$–N moiety is a versatile ligand system likely to lead to an extensive chemistry of compounds with the potential for catalytic activity.

References

[1] D.M. Antonelli, M.L.H. Green, P. Mountford, J. Organomet. Chem. 438 (1992) C4.

[2] J.C. Stevens, F.J. Timmers, R.D. Wilson, G.F. Schmidt, P.N. Nicklas, R.K. Rosen, G.W. Knight, S.-Y. Lai, European Patent 0416815A2, 1991. J.M. Canich, G.G. Hlatky, H.W. Turner, Int. Patent WO 92/00333, 1992.

[3] A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936.

[4] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623. W.A. Herrmann, M.J.A. Moraweitz, J. Organomet. Chem. 482 (1994) 1. W.A. Herrmann, W. Baratta, M.J.A. Moraweitz, J. Organomet. Chem. 497 (1995) C4. W.A. Herrmann, M.J.A. Morawietz, W. Baratta, J. Organomet. Chem. 506 (1996) 357.

[5] D.A. Lemenovskii, V.P. Fedin, Yu.L. Slovohotov, Yu.T. Struchkov, J. Organomet. Chem. 228 (1982) 153.

[6] A. Antiñolo, M. Fajardo, R. Gil-Sainz, C. López-Mardomingo, P. Martín-Villa, A. Otero, M.M. Kubicki, Y. Mugnier, S. Elkrami, Y. Mourad, Organometallics 12 (1993) 381. A. Antiñolo, M. Fajardo, C. López-Mardomingo, A. Otero, Y. Mugnier, Y. Mourad, Organometallics, 9 (1990) 2919.

[7] M.T. Churchill, H.J. Wasserman, P.A. Belmonte, R.R. Schrock, Organometallics 1 (1982) 559. J.E. Bercaw, D.L. Davies, P. Wolczanski, Organometallics 5 (1986) 443. M. Bochmann, L.M. Wilson, M.B. Hursthouse, M. Motevalli, Organometallics 7 (1988) 1148 and references cited therein. Y.W. Alelyunas, R.F. Jordan, S.F. Echols, S.L. Borowsky, P.K. Bradley, Organometallics 10 (1991) 1406. G.A. Luinstra, J. Vogelzang, J.H. Teuben, Organometallics 11 (1992) 2273.

[8] M.L.H. Green, D.M. Michaelidou, P. Mountford, A.G. Suárez, L.-L. Wong, J. Chem. Soc. Dalton Trans., (1993) 1593.

[9] S.L. Latesky, A.K. McMullen, G.P. Niccolai, I.P. Rothwell, J.C. Huffman, Organometallics 4 (1985) 902. P. Legzdins, R.H. Jones, E.C. Phillips, V.C. Yee, J. Trotter, F.W.B. Einstein, Organometallics 9 (1990) 882.

[10] J.K. Cockcroft, V.C. Gibson, J.A.K. Howard, A.D. Poole, U. Siemeling, C. Wilson, J. Chem. Soc. Chem. Commun. (1992) 1668.