ansa-η-Cyclopentadienylimide derivatives of niobium*

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Treatment of the *ansa*-bridged η-cyclopentadienylimide compound [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Cl_2] **1** with MgMeBr gave the binuclear *ansa*-bridged η-cyclopentadienylimide derivative [MeNb{μ-$C_5H_4(CH_2)_3N$}{μ-$NCH(CH_2)_2C_5H_4$}$NbMe_2$] **2**. The crystal structure of **2** has been determined. Detailed ^{1}H and ^{13}C NMR studies showed that **2** undergoes an interesting fluxional process involving interchange of two methyl groups under an *ansa* arch. Reaction of **1** with Na(C_5H_5) gave [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η^5-C_5H_5)(η^1-C_5H_5)] **3**, which is also fluxional and undergoes diverse dynamic processes including exchange between η^1- and η^5-cyclopentadienyl rings. The compounds [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}$(CH_2Ph)_2$] and [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}{$CH_2C(Me)CH_2$}$_2$] have also been prepared.

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-cyclopentadienylimide derivative [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Cl_2] **1**.[1,2] We have also reported the synthesis of a series of cyclopentadienyl-imide and -amide derivatives of early transition metals[2] having in view the current interest in such Group 4 compounds as homogeneous catalysts for α-olefin polymerisation.[3–6] We have explored further the synthetic potential of the ligand precursor $C_5H_4(SiMe_3)(CH_2)_3N(SiMe_3)_2$, and here describe the preparation of alkyl derivatives of **1**. It was envisaged that the dialkyl derivatives [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}R_2], where R = methyl or benzyl, would be precursors for the monoalkyl cations [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}R]$^+$ and that these cations might have catalytic activity. A preliminary account of part of this work has been published.[2]

Results and Discussion

Synthesis

Treatment of [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Cl_2] **1** with an excess of MgMeBr (3–6 equivalents) in diethyl ether affords orange crystals of the binuclear compound [MeNb{μ-$C_5H_4(CH_2)_3N$}{μ-$NCH(CH_2)_2C_5H_4$}$NbMe_2$] **2** (*ca.* 60% yield). This compound decomposes when in contact with chlorinated solvents. It could not be isolated from the reaction between **1** and 2 equivalents of MgMeBr.

The crystal structure of compound **2** has been determined and the molecular structure is shown in Fig. 1. Selected distances and angles are given in Table 1. The structure contains only three methyl groups and interestingly a hydrogen has been lost from a CH_2 group adjacent to an imide nitrogen. There is a virtually linear alkenylideneamide ligand[8–12] bridging the two niobium atoms. This is the second structurally characterised example of a bridging η^2,κ*N*-C(H)=N alkenylideneamide system.[12] It is bound through a Nb(1)–N(2) double bond the length [1.847(8) Å] of which is typical of co-ordinated linear alkenylideneamides (1.85–2.01 Å),[9,12,13] lying in-between the normal ranges observed for Nb–N single (2.16–2.33 Å)[14] and triple bonds (1.73–1.79 Å).[1,15,16] The almost linear C(21)–N(2)–Nb(1) geometry [168.0(7)°] indicates a sp-hybridised nitrogen which is bonding to Nb(1). The C(H)=N double bond is clearly η^2-co-ordinated to the Nb(2) centre. However, the distances Nb(2)–C(21) [2.32(1) Å] and Nb(2)–N(2) [2.225(7) Å] are somewhat longer than those observed in [(η^5-C_5Me_4Et)Cl_2Ta(μ-NCHMe)(μ-Cl)(μ-H)TaCl(η^5-C_5Me_4Et)] (2.195 and 2.059 Å, respectively),[12] in niobium–η^2-iminoacyl systems (≈2.18 and 2.16 Å, respectively)[17] or in niobium–η^2(C,N)-ketenimine fragments (≈2.16 and 2,14 Å, respectively).[18] This increase reflects geometrical constraints arising from strain in the bridging *ansa* system. The C(21)–N(2) distance [1.34(1) Å] is also larger than for other co-ordinated alkenylideneamides (1.26–1.28 Å),[9,13] is close to those found in niobium–η^2-iminoacyl and niobium–η^2(C,N)-ketenimine compounds (1.23–1.33 Å)[17,18] but is shorter than in the bridging alkenylideneamide tantalum compound (1.435 Å).[12] The imide nitrogen atom N(1) attached to the non-deprotonated chain is sp^2 hybridised and bridges the two metal centres. The corresponding bond lengths Nb(2)–N(1) [2.134(7) Å] and Nb(1)–N(1) [1.901(8) Å] point to a double-bond character in the latter, as a consequence of the nitrogen lone-pair donation to the Nb(1) centre. The Nb(2)–Nb(1) distance [2.929(1) Å] is similar to the values found for other imide-bridged niobium dimers,[19] it is slightly larger than in niobium metal (2.85 Å) and substantially larger than for Nb–Nb double (2.70–2.74 Å) and triple bonds (2.61–2.63 Å).[20] The two niobium, two nitrogen, and two carbon atoms C(11) and C(21) are nearly coplanar; the maximum deviation from the best fit Nb(1), Nb(2), N(1), N(2), C(11), C(21) least-squares plane is 0.06 Å. The saturated $(CH_2)_3$ chain linking the bridging imide group to the η^5-C_5H_4 ring co-ordinated to Nb(1) appears

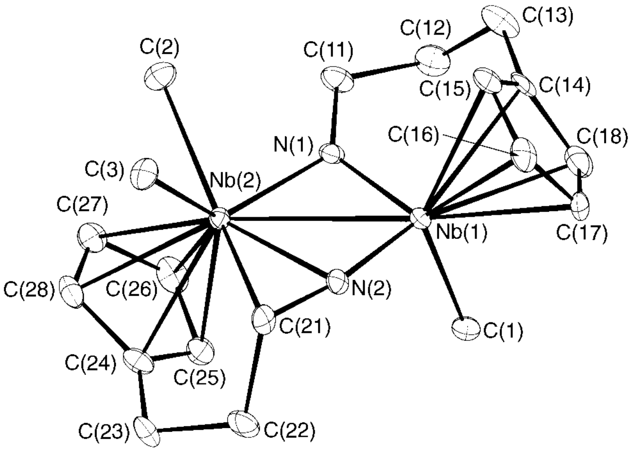

Fig. 1 A CAMERON[7] plot of [MeNb{μ-$C_5H_4(CH_2)_3N$}{μ-$NCH(CH_2)_2C_5H_4$}$NbMe_2$] **2**. Thermal ellipsoids are drawn at the 20% probability level and H atoms are omitted for clarity

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* *Non-SI unit employed:* bar = 10^5 Pa.

Table 1 Selected bond lengths (Å) and angles (°) for [MeNb{μ-C_5H_4-$(CH_2)_3N$}{μ-$NCH(CH_2)_2C_5H_4$}$NbMe_2$] **2** with estimated standard deviations (e.s.d.s) in parentheses

Nb(1)–N(1)	1.901(8)	Nb(2)–C(2)	2.26(1)
Nb(1)–Nb(2)	2.929(1)	Nb(2)–C(3)	2.28(1)
Nb(1)–N(2)	1.847(8)	Nb(2)–C(21)	2.32(1)
Nb(1)–C(1)	2.21(1)	N(1)–C(11)	1.46(1)
Nb(2)–N(1)	2.134(7)	N(2)–C(21)	1.34(1)
Nb(2)–N(2)	2.225(7)		
Nb(2)–N(1)–Nb(1)	92.9(3)	C(14)–C(13)–C(12)	114.9(9)
Nb(2)–N(2)–Nb(1)	91.5(3)	C(12)–C(11)–N(1)	114.6(9)
C(11)–N(1)–Nb(2)	133.0(6)	N(2)–C(21)–Nb(2)	69.1(5)
C(11)–N(1)–Nb(1)	133.7(6)	C(22)–C(21)–N(2)	118.0(9)
C(21)–N(2)–Nb(1)	168.0(7)	C(22)–C(21)–Nb(2)	116.0(8)
C(21)–N(2)–Nb(2)	76.6(5)	C(23)–C(22)–C(21)	107.9(9)
C(12)–C(11)–N(1)	114.6(9)	C(24)–C(23)–C(22)	107.9(8)
C(13)–C(12)–C(11)	115.1(10)		

to be strained as suggested by the angles subtended at the three formally sp^3 carbons of the $(CH_2)_3$ linkage (average 114.9°). The bonding in **2** indicated by the molecular structure suggests Nb(1) and Nb(2) are 18- and 16-electron centres, respectively.

The mechanism of formation of compound **2** is unknown but two observations are pertinent. First, a gas chromatographic-mass spectrometric analysis of the gas-phase products of the reaction between **1** and MgMeBr found CH_4 as the only volatile product and secondly, the formation of **2** in good yields requires a minimum stoichiometric ratio Nb : MgMeBr of 1 : 3. It is possible there is an initial extraction of a proton from the relatively acidic CH_2N hydrogens in compound **1** by CH_3^- of the Grignard reagent giving methane. The resulting compound would be a chloromagnesium ketimide niobium derivative, [Nb{$C_5H_4(CH_2)_2C(H){=}N(MgBr)$}$Cl_2$], which upon reaction with a second molecule of **1** would substitute one chlorine giving rise to the chlorinated precursor of **2**, namely [ClNb{μ-$C_5H_4(CH_2)_3N$}{μ-$NCH(CH_2)_2C_5H_4$}$NbCl_2$], and elimination of $MgCl_2$. A similar reaction occurs[21] when lithium ketimides ($LiNCR_2$) react with [M(η-$C_5H_5)_2Cl_2$], where M = Ti or Zr. Further reaction of the chloro analogue of **2** with MgMeBr would lead to **2**.

Attempts to synthesize [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Me_2] or the analogous [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}$(CH_2SiMe_3)_2$], by the addition of either stoichiometric amounts or an excess of LiMe or the less reducing $ZnMe_2$ or $LiCH_2SiMe_3$ to [Nb{η^5,κ*N*-C_5H_4-$(CH_2)_3N$}Cl_2] **1**, were unsuccessful and gave complex decomposition products.

Dynamic NMR studies on compound 2

The ^1H and ^{13}C NMR spectra of compound **2** have been studied in detail. There are 22 inequivalent hydrogens groups and all the 19 carbon nuclei of the asymmetric compound (C_1 symmetry) are inequivalent. Using the NMR experiments[22] ^{13}C-{^1H} distortionless enhancement by polarisation transfer (DEPT), ^1H–^1H shift-correlated two-dimensional spectroscopy (COSY) and ^{13}C–^1H shift correlation, the spectra may be fully assigned as shown in Table 2. Variable-temperature NMR studies show **2** is fluxional involving the interchange of the two methyl groups Me_b and Me_c. A phase-sensitive ^1H–^1H dipolar-correlated two-dimensional (PSEXSY) NMR spectrum[23] at 233 K and using a mixing time $\tau_m = 0.5$ s provided some spatial assignments for **2** (Fig. 2). The observation of negative cross-peaks confirmed that at 233 K Me_b and Me_c were slowly exchanging, and further that these groups were the only ones undergoing exchange. The positive NOE cross-peak correlating the alkenylideneamide proton $H_{g'}$ (δ 5.12) with Me_c (δ 1.14) allows its spatial distinction from Me_b (δ 0.52). The strong cross-peak obtained for $H_{f'_1}$ (δ 2.59) with $H_{a'}$ (δ 5.48) does not conform to the solid-state structure shown in Fig. 1. The data suggest that at 233 K the structure of **2** in solution adopts a different conformation whereby there has been a clockwise rotation about the $C_{f'}$–$C_{e'}$ bond (see Scheme 1).

The chemical shift data for compound **2** are unexceptional, except those for the alkenylideneamide group. The ^1H and ^{13}C resonances of the CH=N group occur at δ 5.10 and 109.1, respectively, and they are strongly shifted upfield compared to the values for linear alkenylideneamide transition-metal compounds, for example, δ 8.39 and 164.9 for [Sc(η-$C_5Me_5)_2$-{N=C(H)CMe_3}],[8] δ 9.38 and 154.4 ($J_{CH} = 161$ Hz) for [Sc(η-$C_5Me_5)_2$N=C(H)C_6H_4OMe}],[8] δ 7.61 and 166.2 ($J_{CH} = 160$ Hz) for [Ti(η-$C_5Me_5)_2${N=C(H)CMe_3}Cl][11] and δ 170–186 for the compounds [M(η-$C_5H_5)_2${N=C(Me)R}L]BPh_4, where M=Ti[9] or Zr, R = alkyl or Ph, L = NCR or tetrahydrofuran,[10] but less than in the μ-C(H)=N alkenylideneamide tentalum compound (δ 3.89).[12] The NMR features of this group in **2** are consistent with its strained η^2-C=N co-ordination to Nb(2), as observed in the molecular structure.

A typical temperature dependence of the ^1H NMR spectra of compound **2** is shown in Fig. 3. The interchange of the methyl groups Me_b and Me_c reaches the slow-exchange-limit spectrum at 193 K and shows two singlets at δ 0.70 and 1.27. These resonances broaden as the temperature approaches 225 K and coalesce at $T_c = 259$ K. At 333 K a single narrow resonance shows the fast-exchange-limit region has been attained. All other ^1H resonance lines remain largely unaffected by the exchange process and remain sharp throughout the range of temperatures studied. Below 233 K the Me_b ^1H resonance sharpens to about the same value of the Me_a linewidth ($\Delta\nu_{\frac{1}{2}} = 3.5$ Hz, at 213 K), whilst the Me_c line sharpening is not so pronounced ($\Delta\nu_{\frac{1}{2}} = 6$ Hz, at 213 K). This broadening can be attributed to a faster relaxation due to a stronger interaction with the quadrupolar moment of the ^{93}Nb nucleus ($I = \frac{9}{2}$). At 193 K the whole spectrum broadens due to increasing solvent viscosity. Identical features are present in a similar variable-temperature ^1H NMR study performed at 500 MHz, in which the coalescence temperature is now $T_c = 277$ K. At this temperature the rate constant $k = 2^{\frac{1}{2}}\pi(\Delta\nu)$[24] and the free energy of activation ($\Delta G^{\ddagger}$) of the exchange process can be estimated as 1391 s^{-1} and 51.0 kJ mol^{-1}, respectively.

The variable-temperature ^{13}C-{^1H} NMR spectra of compound **2** in the range 193–293 K are shown in Fig. 4. No ^{13}C resonance assignable to Me_a could be observed; this absence may be attributed to a strong scalar coupling interaction with the quadrupolar ^{93}Nb nucleus.[25] We note the Nb(1)–C(1) bond distance is approximately 0.06 Å shorter than the other two Nb–Me distances. The ^{13}C-{^1H} spectra clearly show a methyl exchange process. At 193 K the somewhat broad resonance observed at δ 41.5 corresponds to Me_c and the sharp one at δ 38.6 to Me_b. At higher temperatures these lines coalesce and finally merge into a single peak (δ 39.3) at 293 K. All the other resonances remain sharp with increasing temperature except that of the $C_{g'}$ alkenylidene carbon (δ 108.2 at 193 K and 109.1 at 293 K), which broadens considerably and almost disappears at 293 K. This broadening is occurring in the same temperature range as for the methyl exchange and, although no corresponding broadening is observed for the $H_{g'}$ resonance (even at higher temperatures, see Fig. 3), it seems reasonable to assume there is a common underlying cause for the two observations.

A possible mechanism for the fluxional process is shown in Scheme 2(*a*). A stereochemically non-rigid niobium site could be envisaged undergoing some geometrical isomerisation process[26,27] possibly induced by dissociation of the strained alkenylideneamide ligand from the niobium atom bearing Me_b and Me_c. During this rearrangement, the two methyl ligands would be able to exchange co-ordination positions by rotation, under the *ansa* arch. In this equally populated A_3B_3 mutual exchange process[28] the planar inversion of the sp nitrogen in the alkenylideneamide ligand may also occur [Scheme 2(*b*)].[29,30]

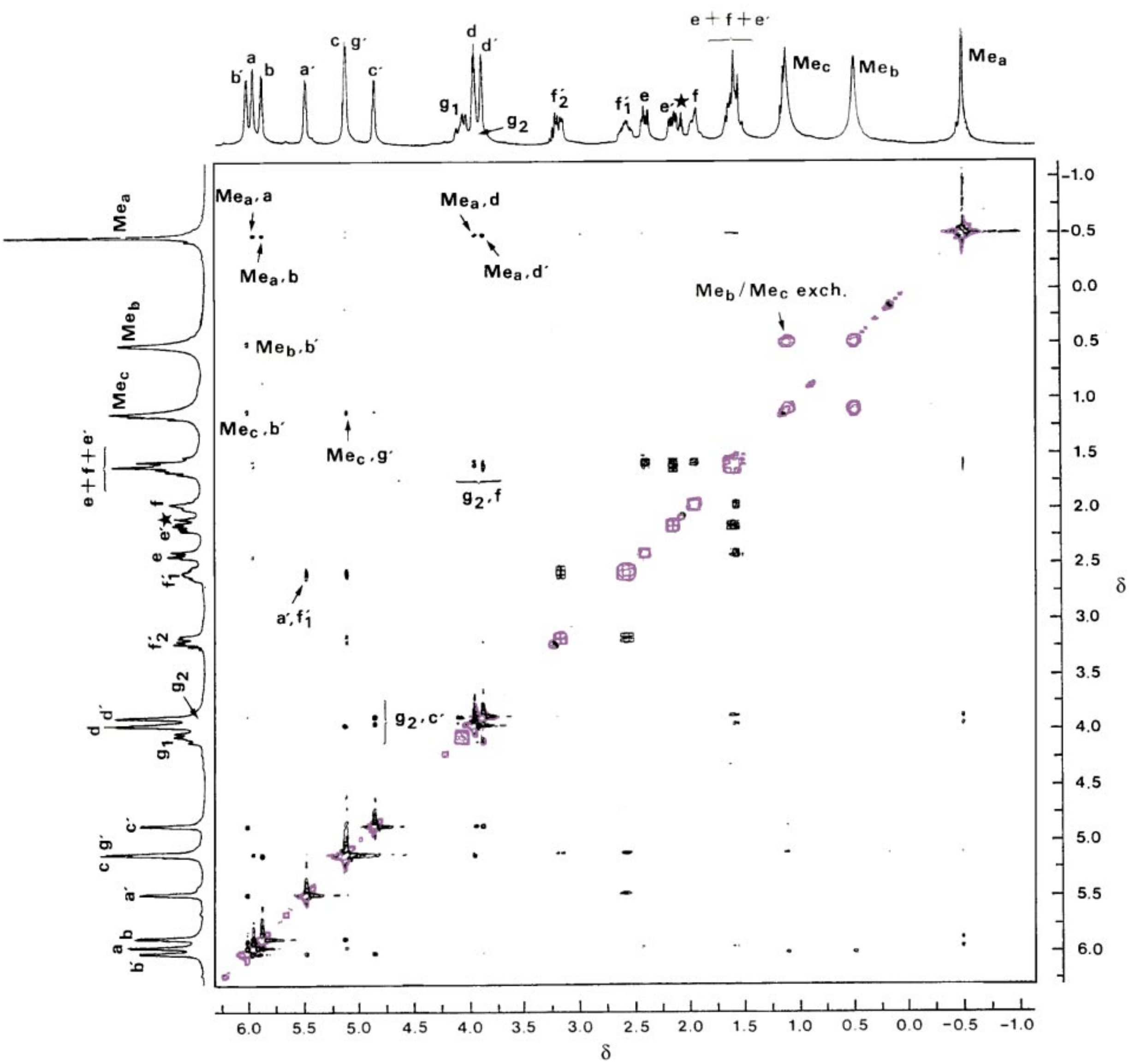
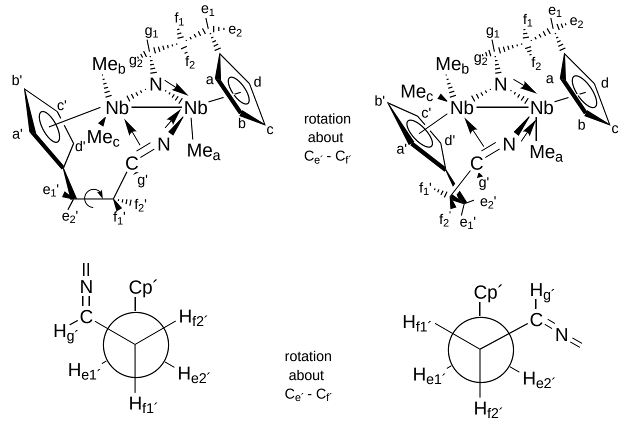


Fig. 2 Two-dimensional ^1H–^1H PSEXSY NMR spectrum for compound **2** acquired at 233 K. Some of the most important nuclear Overhauser effect (NOE) correlations (the heavier black lines indicate positive peaks) and the Me_b/Me_c chemical exchange process are indicated (the negative peaks are magenta)



Scheme 1 Solid-state structure (left) and solution conformation at −40 °C (right) of compound **2**

Synthesis of compound 3 and dynamic NMR study

Treatment of [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Cl_2] **1** with sodium cyclopentadienide gives the yellow tris(cyclopentadienyl) compound [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η^5-C_5H_5)(η^1-C_5H_5)] **3** in 80% yield. This formally 20-valence-electron compound is analogous to the non-*ansa* bridged [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)(NBu^t)].[31] The NMR data show compound **3** is fluxional in a manner similar to that observed for [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)(NBu^t)].[31] There are three fluxional processes, namely rotation of the η^1-C_5H_5 ligand about the Nb–C_i bond, migration of the niobium centre amongst the carbon atoms of a η^1-C_5H_5 ligand, and chemical exchange between the η^5- and η^1-C_5H_5 ligands.

Variable-temperature ^1H and ^{13}C-{^1H} NMR spectra of compound **3** are shown in Figs. 5 and 6, respectively. The techniques[22] DEPT, ^{13}C–^1H shift correlation and selective ^1H-decoupled ^{13}C, were used to assign the majority of the resonances. At 193 K the ^1H NMR spectrum shows a single resonance for the η^5-C_5H_5 ring at δ 6.02 and five resonances for a ‘static’ η^1-C_5H_5 ligand, as found for [Nb(η^5-C_5H_5)$_2$(η^1-C_5H_5)(NBu^t)]. The full assignments are given in Table 2. The band assigned to $H_{a(d)}$ is a broad signal which may be attributed to a faster relaxation due to the quadrupolar moment of the ^{93}Nb nucleus. Similarly, this $H_{a(d)}$ line broadening is observed in the ^{13}C-{^1H} spectrum. The lowest-temperature (first) fluxional process, namely, rotation of the η^1-C_5H_5 ligand about the Nb–C_i bond, is better observed in the 500 MHz ^1H and 125.7 MHz ^{13}C-{^1H} NMR spectra (in the range 183–223 K). The olefinic protons of the η^1-C_5H_5 ligand show pairwise coalescence while H_i remains at the same chemical shift. Above 223 K

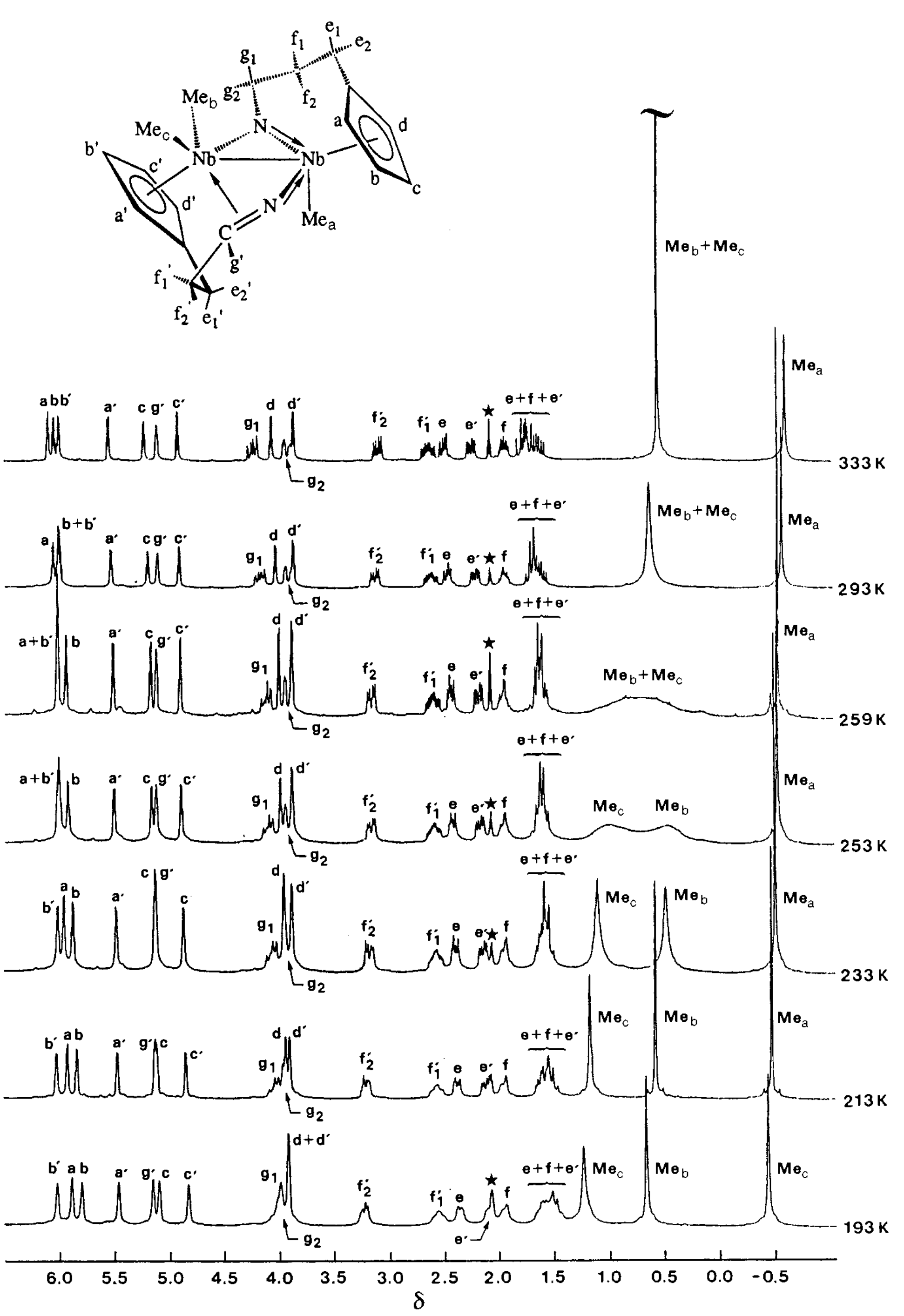


Fig. 3 Variable-temperature 300 MHz ^1H NMR spectra of compound **2** in [$^2H_8$]toluene. Asterisk denotes the residual CHD_2 solvent resonance

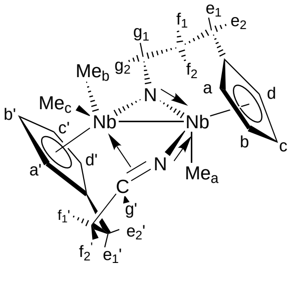
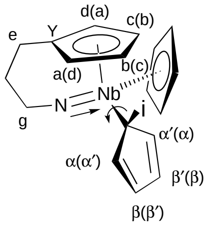
the three η^1-C_5H_5 resonances broaden and coalesce, and a broad resonance emerges from the baseline and sharpens progressively. Such behaviour is attributed to migration of the niobium metal centre amongst the carbon atoms of the η^1-C_5H_5 ligand, through a 1,2-shift mechanism. Above 263 K, broadening and coalescence (around 293 K) of the bands due to the η^1- and η^5-C_5H_5 groups indicate that the two groups are slowly exchanging. At the same time a similar process occurs for the diastereotopic H_e and H_g chain protons since the four resonances of the $(CH_2)_3$ chain broaden then collapse. It is interesting that the H_f have near identical chemical shifts at all temperatures.

At 328 K a resonance at δ 6.00 may be assigned to coalescence of the signals of the two C_5H_5 rings; there is one resonance at δ 5.18 for H_b and H_c, and one resonance for H_a and H_d, the latter being hidden under the C_5H_5 peak. This spectrum confirms there is a fast η^5-$C_5H_5 \longleftrightarrow \eta^1$-$C_5H_5$ exchange which, in consequence, causes a shift in the apparent molecular symmetry from C_1 to C_s, since there is an apparent mirror plane formed by the nitrogen atom, the chain carbon atoms, the substituted cyclopentadienyl ring centroid and the Nb atom. At this temperature the process has not attained the fast-exchange limit since the peaks are still broadened. The ^{13}C-{^1H} resonance of the *ipso*-carbon (C_Y) of the C_5H_4 group at δ 124.7 remains sharp with increasing temperature, while the other four carbon resonances are fully collapsed at 298 K. These features reflect the averaging effect of the two fast exchanging C_5H_5 groups, and the static nature of the *ansa*-bridged C_5H_4 ring. The exchange between the two C_5H_5 rings may involve η^3–η^5 equilibria.[31] A summary of the fluxional processes observed for **3** is presented in Scheme 3.

Synthesis and characterisation of compounds 4 and 5

Treatment of compound **1** with 2, or more, equivalents of

Table 2 Analytical and spectroscopic data

Compound[a]	NMR data[b]
1 $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}Cl_2]$ C, 34.9 (33.8); H, 3.8 (3.6); N, 4.6 (4.9) Mass spectrum: *m/z* 283 (M^+)	^1H (r.t.):[c] 6.57 (t, 2 H, $J_{HH} = 2.5$, C_5H_4), 5.79 (t, 2 H, $J_{HH} = 2.5$, C_5H_4), 3.50 (t, 2 H, $J_{HH} = 5.5$, CH_2N), 2.68 (m, 2 H, $C_5H_4CH_2$), 2.27 (m, 2 H, $C_5H_4CH_2CH_2$) ^1H (r.t.):[d] 5.93 (t, 2 H, $J_{HH} = 2.4$, C_5H_4), 5.04 (t, 2 H, $J_{HH} = 2.4$ C_5H_4), 2.67 (t, 2 H, $J_{HH} = 5.4$, CH_2N), 1.69 (m, 2 H, $C_5H_4CH_2$), 1.33 (m, 2 H, $C_5H_4CH_2CH_2$) ^{13}C-{^1H} (r.t.):[c] 124.0 (*ipso*-C of C_5H_4), 117.5 (CH of C_5H_4), 107.4 (CH of C_5H_4), 58.1 (CH_2N), 32.3 ($C_5H_4CH_2CH_2$), 24.9 ($C_5H_4CH_2$)
2 $[MeNb\{\mu\text{-}C_5H_4(CH_2)_3N\}\{\mu\text{-}NCH\text{-}(CH_2)_2C_5H_4\}NbMe_2]$ C, 48.3 (48.5); H, 6.1 (6.0); N, 5.9 (6.0)  	^1H (r.t.):[e] 6.05 (q + q, 2 H, H_a), 5.99 (q + q, 2 H, $J_{HH} = 2.4$, $H_b + H_{b'}$), 5.52 (q, 1 H, $J_{HH} = 2.4$, $H_{a'}$), 5.19 (q, 1 H, H_c), 5.10 (s, 1 H, $H_{g'}$), 4.90 (q, 1 H, $J_{HH} = 2.4$, $H_{c'}$), 4.15 (m, 1 H, H_{g1}), 4.02 (q, 1 H, $J_{HH} = 2.4$, H_d), 3.90 (m, 1 H, H_{g2}), 3.86 (q, 1 H, $J_{HH} = 2.4$, $H_{d'}$), 3.12 (m, 1 H, $H_{f'2}$), 2.61 (m, 1 H, $H_{f'1}$), 2.47 (m, 1 H, H_e), 2.22 (m, 1 H, $H_{e'}$), 1.96 (m, 1 H, H_f), 1.72–1.58 (m, 3 H, $H_e + H_f + H_{e'}$), 0.65 (br s, 6 H, $Me_b + Me_c$), −0.54 (s, 3 H, Me_a) ^1H (r.t.):[d] 6.05 (q + q, 2 H, $H_a + H_{b'}$), 5.99 (q, 1 H, $J_{HH} = 2.4$, H_b), 5.55 (q, 1 H, $J_{HH} = 2.4$, $H_{a'}$), 5.18 (q + s, 2 H, $H_c + H_{g'}$), 4.93 (q, 1 H, $J_{HH} = 2.4$, $H_{c'}$), 4.18 (m, 1 H, H_{g1}), 4.03 (q, 1 H, $J_{HH} = 2.4$, H_d), 3.92 (m, 1 H, H_{g2}), 3.90 (q, 1 H, $J_{HH} = 2.4$, $H_{d'}$), 3.14 (m, 1 H, $H_{f'2}$), 2.62 (m, 1 H, $H_{f'1}$), 2.43 (m, 1 H, H_e), 2.20 (m, 1 H, $H_{e'}$), 1.94 (m, 1 H, H_f), 173–1.55 (m, 3 H, $H_e + H_f + H_{e'}$), 0.80 (br s, 6 H, $Me_b + Me_c$), −0.47 (s, 3 H, Me_a) ^{13}C (r.t.):[e] 124.7[f] (*ipso*-C of C_5H_4), 121.3 (*ipso*-C of C_5H_4) 113.5 ($J_{CH} = 181$, C_a or $C_{b'}$), 112.9 ($J_{CH} = 171$, C_a or $C_{b'}$), 109.1 ($J_{CH} = 161$, br, $C_{g'}$), 107.4 ($J_{CH} = 174$, C_b), 105.5 ($J_{CH} = 179$, $C_{d'}$), 102.1 ($J_{CH} = 174$, C_c), 101.6 ($J_{CH} = 175$, C_d), 101.2 ($J_{CH} = 173$, $C_{a'}$), 97.1 ($J_{CH} = 171$, $C_{c'}$), 61.3 ($J_{CH} = 135$. C_g), 39.3 (br, $Me_b + Me_c$, $J_{CH} = 131$) (Me_a missing), 38.3 ($J_{CH} = 130$, C_f), 37.5 ($J_{CH} = 129$, $C_{f'}$), 27.3 ($J_{CH} = 130$, C_e), 24.4 ($J_{CH} = 129$, $C_{e'}$) ^{13}C-{^1H} (r.t.):[d] 124.7 (*ipso*-C of C_5H_4), 121.3 (*ipso*-C of C_5H_4), 113.6 (C_a or $C_{b'}$), 112.6 (C_a or $C_{b'}$), 109.0 (br, $C_{g'}$), 107.4 (C_b), 105.4 ($C_{d'}$), 102.2 ($_c$), 101.6 (C_d), 101.2 ($C_{a'}$), 97.1 ($C_{c'}$), 61.3 (C_g), 39.2 (br, $Me_b + Me_c$) (Me_a missing), 38.3 (C_f), 37.6 ($C_{f'}$), 27.2 (C_e), 24.6 ($C_{e'}$)
3 $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}(\eta^5\text{-}C_5H_5)\text{-}(\eta^1\text{-}C_5H_5)]$ C, 62.7 (63.0); H, 5.8 (5.9); N, 4.1 (4.1) Mass spectrum: *m/z* 343 (M^+)  	^1H (20 °C):[g] vbr peaks ^1H (−40 °C):[g] 6.24 (vbr, 5 H, η^1-C_5H_5), 5.99 (q, 1 H, $J_{HH} = 2.4$, $H_{d(a)}$), 5.95 (s, 5 H, η^5-C_5H_5), 5.58 (q, 1 H, $J_{HH} = 2.4$, $H_{c(b)}$), 4.92 (q, 1 H, $J_{HH} = 2.4$, $H_{b(c)}$), 3.71 (m, 1 H, CHHN), 3.62 (q, 1 H, $J_{HH} = 2.4$, $H_{a(d)}$), 3.42 (m, 1 H, CHHN), 2.53 (m, 1 H, C_5H_4CHH), 2.22 (m, 1 H, C_5H_4CHH), 1.80 (m, 2 H, $C_5H_4CH_2CH_2$) ^1H (−80 °C):[g] 6.65 (br s, 1 H, $H_{\alpha(\alpha')}$), 6.35 (br s, 1 H, $H_{\alpha'(\alpha)}$), 6.26 (br s, 1 H, $H_{\beta(\beta')}$), 6.19 (br s, 1 H, $H_{\beta''(\beta)}$), 6.02 (br s, 6 H, η^5-C_5H_5 and $H_{d(a)}$), 5.71 (br s, 1 H, $H_{c(b)}$), 5.22 (br s, 1 H, H_i), 4.90 (br s, 1 H, $H_{b(c)}$), 3.73 (br m, 1 H, CHHN), 3.43 (br m, 1 H, CHHN), 3.28 (vbr, 1 H, $H_{a(d)}$), 2.56 (br m, 1 H, C_5H_4CHH), 2.12 (br m, 1 H, C_5H_4CHH), 1.79 (br m, 2 H, $C_5H_4CH_2CH_2$) ^{13}C-{^1H} −40 °C:[g] δ 124.7 (C_Y), 116.2 ($C_{a(d)}$), 114.5 ($C_{c(b)}$), 110.4 (η^5-C_5H_5), 107.8 ($C_{n(c)}$), 92.8 ($C_{d(a)}$), 59.2 (C_g), 28.5 (C_f), 25.8 (C_e). ^{13}C-{^1H}(−80 °C):[g] 139.1 ($C_{\alpha'(\alpha)}$), 137.8 ($C_{\alpha(\alpha')}$), 124.7 (C_Y), 120.2 ($C_{\beta'(\beta)}$), 120.0 ($C_{\beta(\beta')}$), 117.9 (vbr, $C_{a(d)}$), 114.5 ($C_{c(b)}$), 110.4 (η^5-C_5H_5), 106.8 ($C_{b(c)}$), 92.4 ($C_{d(a)}$), 59.2 (C_g), 57.1 (C_i), 27.7 (C_f), 25.8 (C_e)
4 $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}(CH_2Ph)_2]$ C, 67.2 (66.8); H, 6.3 (6.1); N, 3.5 (3.7)	^1H (r.t.):[e] 7.00 (m, 2 H, *p*-H of Ph), 6.98 (m, 4 H, *m*-H of Ph), 6.67 (m, 4 H, *o*-H of Ph), 5.19 (t, 2 H, $J_{HH} = 2.5$, C_5H_4), 4.90 (t, 2 H, $J_{HH} = 2.5$, C_5H_4), 2.96 (t, 2 H, $J_{HH} = 5.5$, CH_2N), 2.00 (m, 2 H, $C_5H_4CH_2$), 1.69 (d, 2 H, $^2J_{HH} = 7.8$, NbCHHPh), 1.44 (m, 2 H, $C_5H_4CH_2CH_2$), 1.41 (d, 2 H, $^2J_{HH} = 7.8$, NbCHHPh) ^{13}C (r.t.):[e] 140.5 (*ipso*-C of Ph), 129.0 ($J_{CH} = 162$, *o*- and *m*-H of Ph), 124.2 ($J_{CH} = 151$, *p*-H of Ph), 117.3 (*ipso*-C of C_5H_4), 107.9 ($J_{CH} = 178$, CH of C_5H_4), 101.9 ($J_{CH} = 175$, CH of C_5H_4), 55.8 ($J_{CH} = 136$, CH_2N), 40.7 ($J_{CH} = 135$, $NbCH_2Ph$), 32.9 ($J_{CH} = 128$, $C_5H_4CH_2CH_2$), 25.3 ($J_{CH} = 127$, $C_5H_4CH_2$)
5 $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}\{\eta\text{-}CH_2C\text{-}(Me)CH_2\}_2]$[h]	^1H (18 °C):[e] [$CH_2C(CH_3)CH_2$ absent], 5.34 (br t, 2 H, $J_{HH} = 2.3$, C_5H_4), 4.77 (br s, 2 H, C_5H_4), 2.79 (t, 2 H, $J_{HH} = 5.5$, CH_2N), 2.24 (m, 2 H, $C_5H_4CH_2$), 1.76 [br s, $CH_2C(CH_3)CH_2$], 1.60 (m, 2 H, $C_5H_4CH_2CH_2$) ^1H (100 °C):[e] 5.38 (t, 2 H, $J_{HH} = 2.3$, C_5H_4), 4.65 (t, 2 H, $J_{HH} = 2.3$, C_5H_4), 3.13 [vbr, 8 H, $CH_2C(CH_3)CH_2$], 2.80 (t, 2 H, $J_{HH} = 5.5$, CH_2N), 2.29 (m, 2 H, $C_5H_4CH_2$), 1.71 [s, 6 H, $CH_2C(CH_3)CH_2$], 1.58 (m, 2 H, $C_5H_4CH_2CH_2$)

[a] Analytical data given as: found (calculated) %. [b] ^1H NMR at 300 MHz, ^{13}C at 75 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet; br = broad, v = very), relative intensity, coupling constant (in Hz) and assignment. [c] In CD_2Cl_2. [d] In [$^2H_6$]benzene. [e] In [$^2H_8$]toluene. [f] Hidden under the solvent peak. [g] In [$^2H_8$]thf. [h] Characterised by NMR spectra only.

$Mg(CH_2Ph)Cl$ gives pale yellow $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}\text{-}(CH_2Ph)_2]$ **4** in 92% yield. Compound **4** is an analogue of the non-*ansa*-bridged $[Nb(\eta^5\text{-}C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)(CH_2Ph)_2]$[32] and apparently has isostructural relationships with the *ansa*-bridged zirconocene derivative $[Zr(ebthi)(CH_2Ph)_2]$ [ebthi = *rac*-ethylenebis(tetrahydroindenyl)]. This 16-electron zirconium compound has two η^1-benzyl ligands.[33] However, it is well known that, depending on the degree of participation of the phenyl π system in the metal–ligand bonding, benzyl groups are capable of adopting a variety of co-ordination modes ranging from η^1 to η^7.[34,35] Among the π-benzyl d^0 early-transition-metal complexes the η^2 co-ordination mode is the most common.[35] It has been noted that η^2-benzyl ligands (three-electron donor) can be differentiated from the η^1-benzyls by their NMR features.[4,34,36] The η^2-benzyl ligands show higher-field shifts of the *ortho* ^1H resonances (δ < 6.8), a higher-field shift of the CH_2 ^{13}C resonance (δ < 75) together with large methylene $^1J_{CH}$ coupling constants (>130 Hz) and smaller CH_2 geminal coupling constants ($4 < {}^2J_{HH} < 7$ Hz), compared with those for η^1-benzyl groups ($8 < {}^2J_{HH} < 2$ Hz).

The ^1H NMR spectrum of compound **4** shows three resonances for the methylene chain protons (δ 1.44, 2.00 and 2.96) and an A_2B_2 pattern for the C_5H_4 ring protons (δ 4.90 and 5.19) indicating a C_s symmetry, with a mirror plane containing the nitrogen, the chain carbons, the η-C_5H_4 ring centroid and the Nb atom. Two equivalent benzyl ligands are present, each

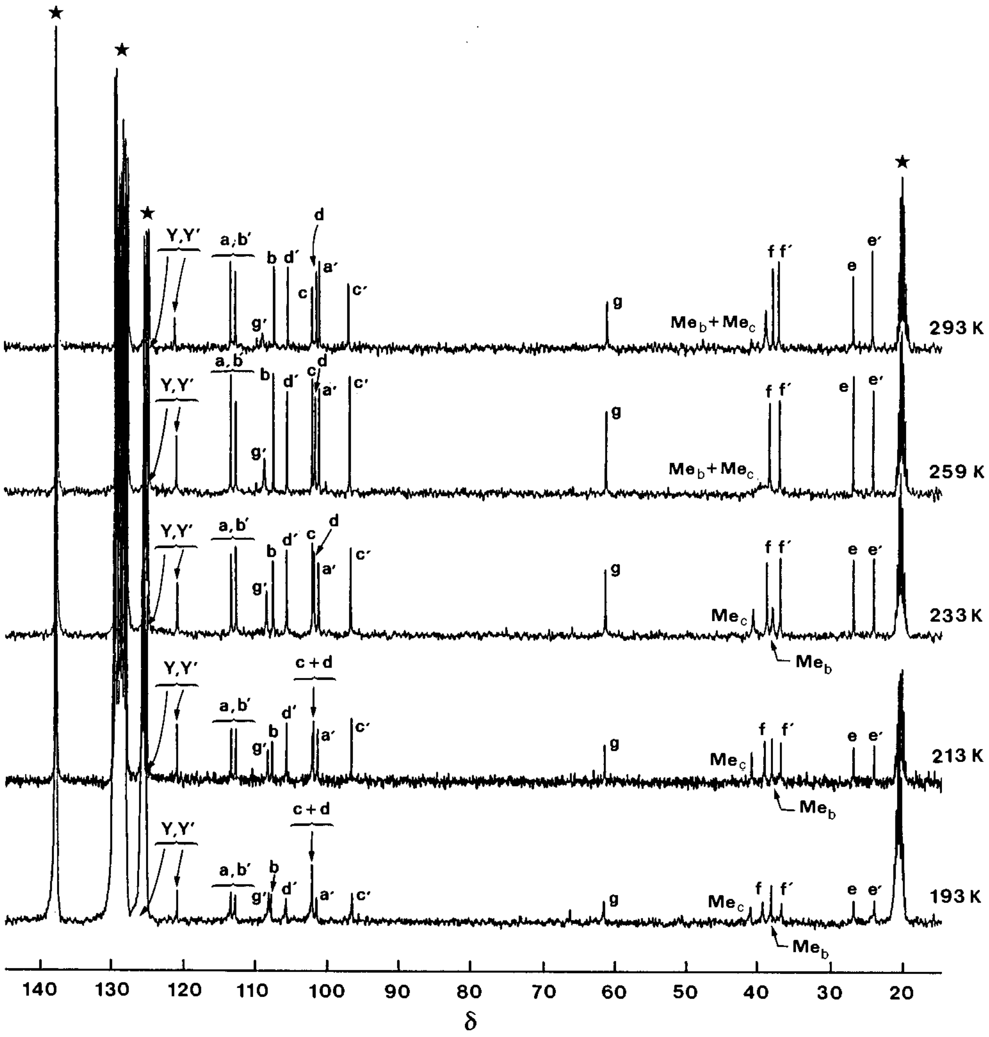
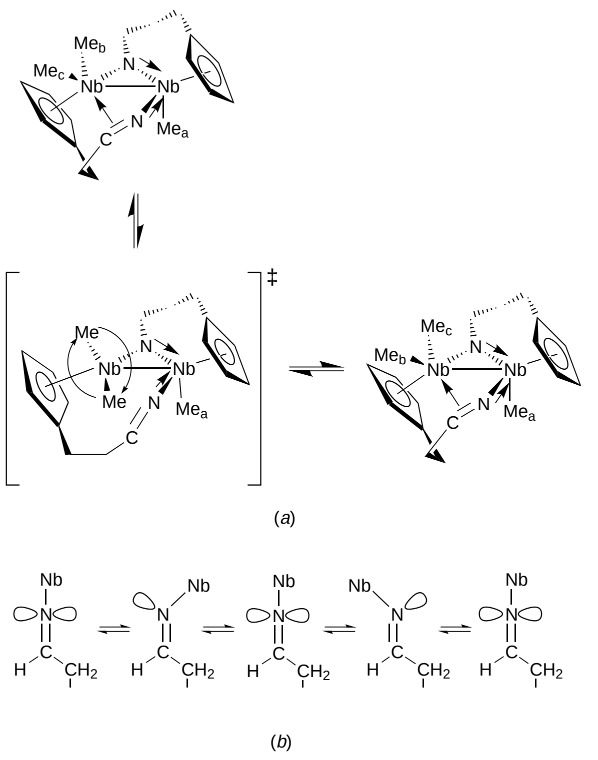


Fig. 4 Variable-temperature 75.43 MHz ^{13}C NMR spectra of compound **2** in [$^2H_8$]toluene. Asterisks denote the solvent residual resonances



Scheme 2 (*a*) Proposed mechanism for the interconversion of the methyl groups Me$_b$ and Me$_c$ of compound **2**. (*b*) The proposed inversion about the planar nitrogen in the alkenylidene ligand

possessing two diastereotopic CH_2Ph protons. These appear as an AB pattern at δ 1.69 and 1.41 with geminal $J_{HH} = 7.8$ Hz. A multiplet at δ 6.67 can be assigned to the shielded *o*-protons. In the ^{13}C NMR spectrum the CH_2Ph resonance appears at a relatively high field (δ 40.7) with a C–H coupling ($J_{CH} = 135$ Hz) indicating some sp^2 character. According to these NMR data, which are similar to those found for the isoelectronic zirconium cyclopentadienylamide analogue [Zr{η^5,κ*N*-C_5H_4-$(CH_2)_3$NMe}$(CH_2Ph)_2$],[4] two situations are possible. Either both benzyl ligands are co-ordinated in a η^2 fashion or there is one η^2- and one η^1-co-ordinated benzyl undergoing rapid exchange. Variable-temperature NMR experiments [room temperature (r.t.) to −80 °C] were inconclusive since niobium quadrupolar broadening effects operate at low temperatures. However, no loss of symmetry was observed for **4** down to −60 °C. If two η^2-benzyl groups were bound to Nb then this would give a formally 20-electron compound. As noted for [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3$N}(η^5-C_5H_5)(η^1-C_5H_5)] **3** and its non-*ansa*-bridged analogue[31] this is not an unprecedented situation for cyclopentadienylimide niobium compounds.

The NMR data for [Nb(η-C_5Me_5)($NC_6H_3Pr^i_2$-2,6)$(CH_2Ph)_2$][32] which is a close analogue of **4** suggest that in this compound both the benzyl ligands are η^1-co-ordinated. Thus, the ^{13}C resonance of the CH_2 group appears at δ 57.68 with a geminal coupling $J_{HH} = 10.8$ Hz and this is too large for an η^2 co-ordination. The absence of η^2 co-ordination by the benzyl groups of [Nb(η-C_5Me_5)($NC_6H_3Pr^i_2$-2,6)$(CH_2Ph)_2$] may reflect the more sterically demanding η-C_5Me_5 group and/or the lack of strain introduced by the *ansa*-bridging propyl chain. The latter effect could facilitate the interaction of the benzyl Ph

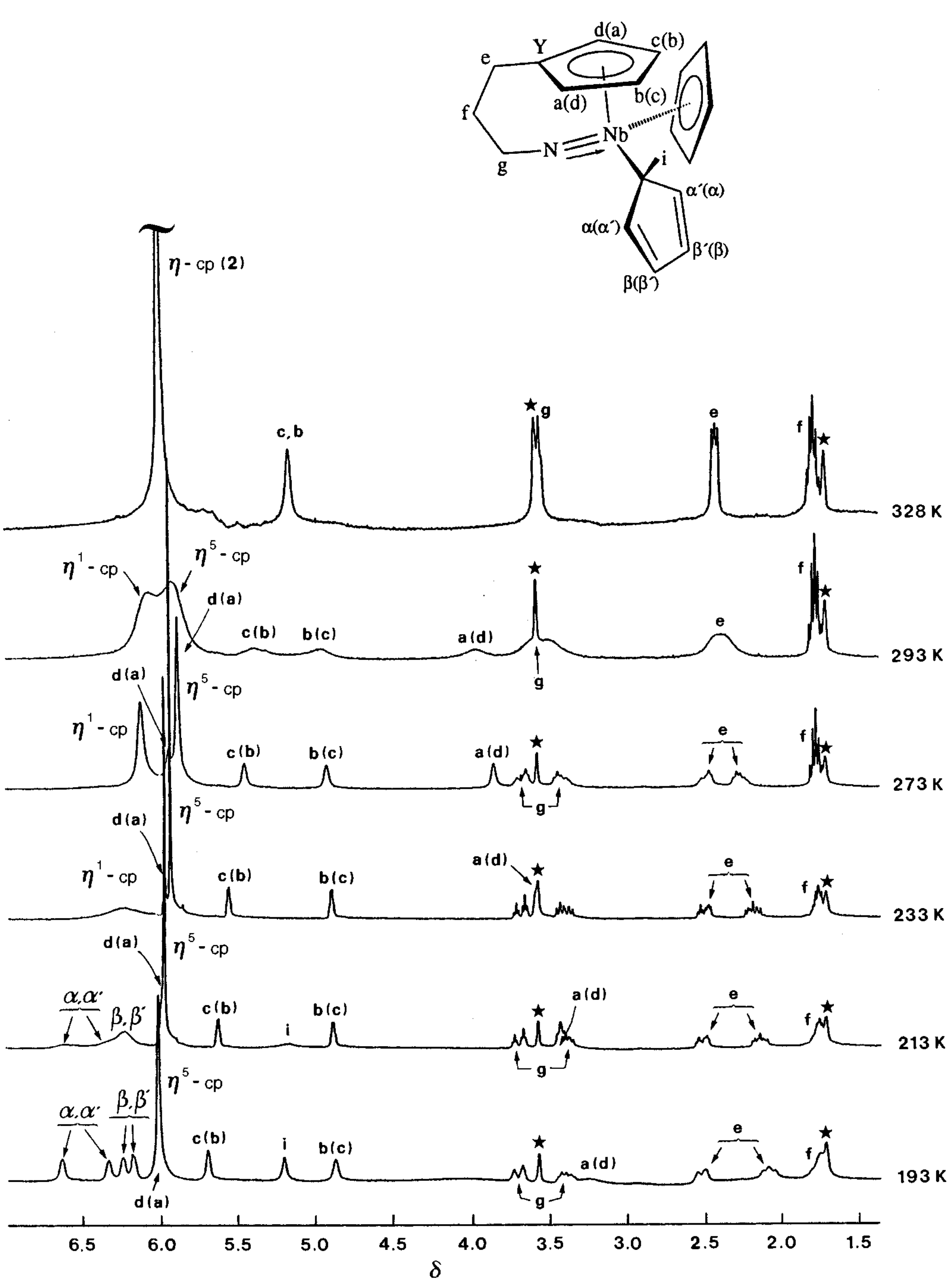


Fig. 5 Variable-temperature 300 MHz ^1H NMR spectra of compound **3** in $[^2H_8]$thf. Asterisks denote the solvent resonances; cp = C_5H_5

rings with the laterally projecting lowest unoccupied molecular orbital (LUMO) in compound **4**.[16]

Attempts to polymerise ethylene with compound **4** were unfruitful. The addition of $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$, or an excess of mao (mao = methylaluminoxane) to a toluene solution of **4** in the presence of ethylene gave no polyethylene. We note that the compound $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}Cl_2]$ **1** is isoelectronic and an isolobal analogue of the compound $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ which is a well known precursor to a homogeneous Ziegler–Natta catalyst. However, all the attempts to polymerise ethylene using **1** in the presence of mao (1:1000) under the conditions[37] used for $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ were unsuccessful.

Compound **1** was treated with 2 equivalents of $Mg(C_3H_4\text{-}Me\text{-}2)Cl$ giving $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}\{CH_2C(Me)CH_2\}_2]$ **5** as a colourless oil in 76% yield. The room-temperature ^1H NMR spectrum of **5** showed bands at δ 2.80, 2.29 and 1.58 assignable to the three methylene protons of the *ansa* chain and there were two somewhat broad resonances for the C_5H_4 ring. The data confirm a C_s symmetry for this compound. A broad signal at δ 1.76 is assigned to methyl groups of the allylic ligands, whereas all the CH_2 allyl protons are collapsed into the baseline. This is a situation similar to that observed for **3**, and corresponds to chemical exchange between the two allyl ligands at an intermediate rate. As the temperature is raised to 100 °C there is a marked sharpening of the methyl and C_5H_4 resonances, the latter acquiring the typical multiplicities of an A_2B_2 pattern. Simultaneously, it is observed that a broad resonance emerges from the baseline at δ 3.13 and sharpens out progressively while approaching the fast-exchange limit. At this temperature this resonance integrates for eight protons, being assigned to all the *anti-* and *syn-*protons in both of the now fast-exchanging 2-methylallyl groups. Correspondingly, the Me peak integrates for six protons. However, at lower temperatures (*e.g.* −40 °C) very complex spectra are obtained due to gradual slowing of allyl fluxionality.[27,38] This complexity arises from the several possible

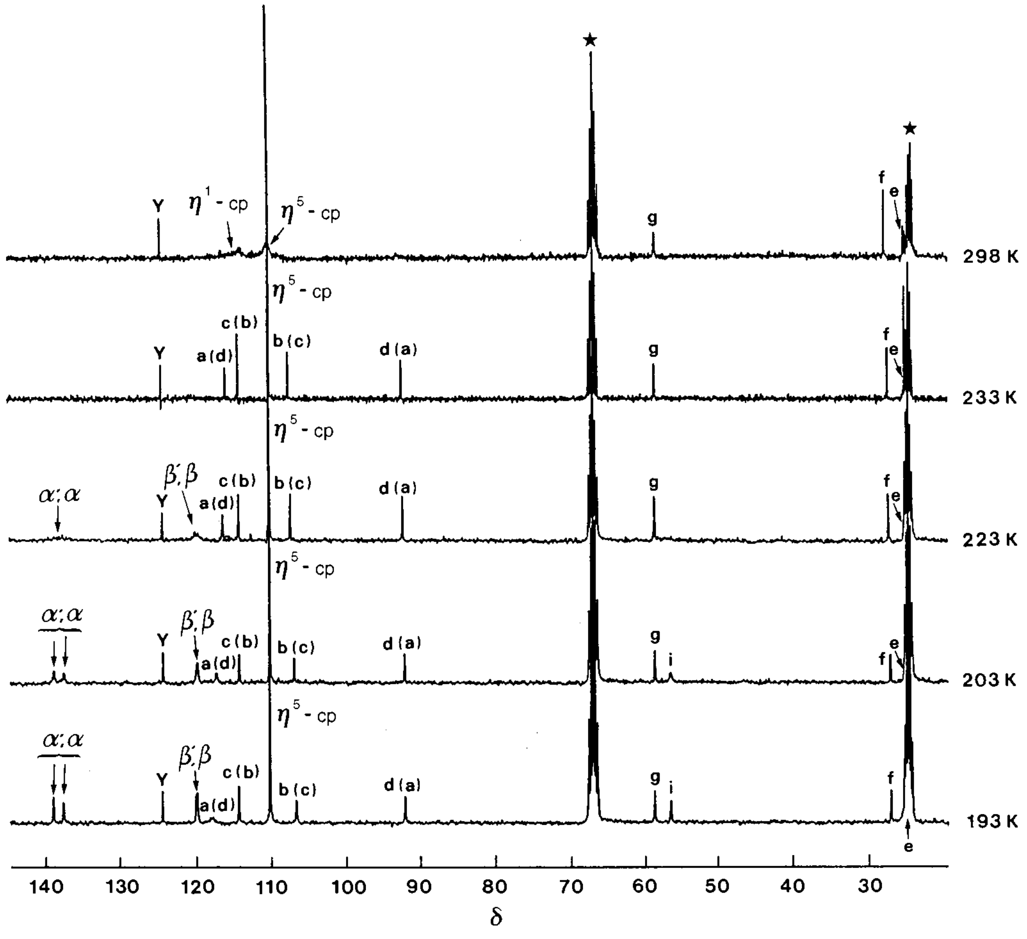
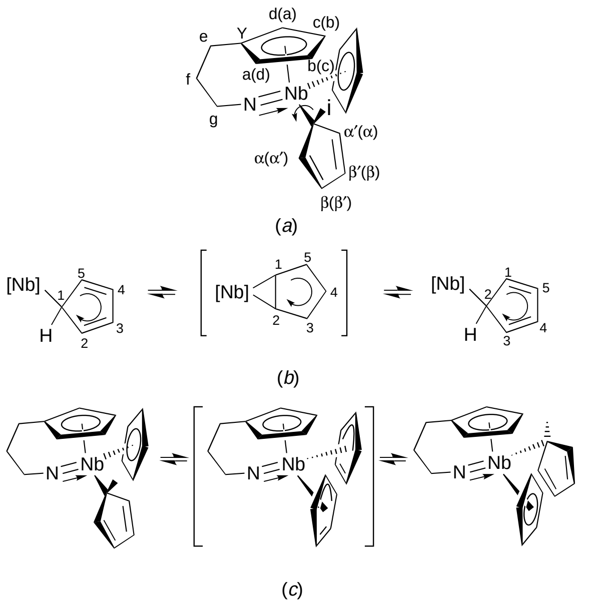


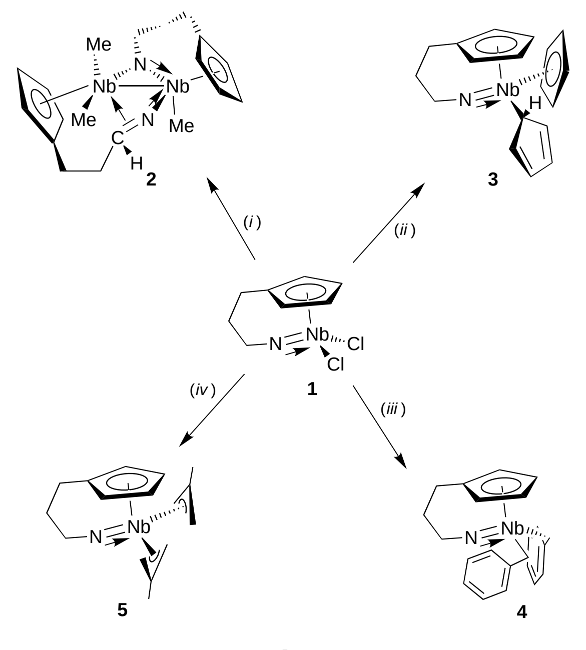
Fig. 6 Variable-temperature 75.43 MHz ^{13}C NMR spectra of compound **3** in [$^2H_8$]thf. Asterisk denotes the solvent resonance; cp = C_5H_5



Scheme 3 Fluxional processes proposed for compound **3**: (*a*) rotation of the η^1-C_5H_5 ligand about the Nb–C_{ipso} bond; (*b*) a 1,2 shift mechanism for migration of the niobium centre around the η^1-C_5H_5 ring, [Nb] = Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η-C_5H_5); and (*c*) η^5-$C_5H_5 \longleftrightarrow \eta^1$-$C_5H_5$ ring exchange

combinations of η^3 and η^1 co-ordination of the two 2-methylallyl groups in **5**, namely as in [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η^1-C_3H_4Me-2)$_2$], [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η^3-C_3H_4Me-2)(η^1-C_3H_4Me-2)] or [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}(η^3-C_3H_4Me-2)$_2$], and/or from the possible existence of several allyl rotational isomers (*endo* or *exo*).

In conclusion, the new reactions and structures proposed for the compounds **2**–**5** are shown in Scheme 4. No catalytic activity towards olefin polymerisation was found using these *ansa*-η-cyclopentadienylimide compounds. It seems probable that the lack of catalytic activity is due to the relevant frontier orbitals



Scheme 4 Reactions of [Nb{η^5,κ*N*-$C_5H_4(CH_2)_3N$}Cl_2] with some alkylating agents. (*i*) MgMeBr (excess) in diethyl ether, room temperature, 12 h; (*ii*) Na(C_5H_5) (2 equivalents) in diethyl ether–thf (1 : 1), room temperature, 12 h; (*iii*) Mg(CH_2Ph)Cl (2 equivalents) in diethyl ether, −40 °C to room temperature, 4 h; (*iv*) Mg(C_3H_4Me-2)Cl (2 equivalents) in diethyl ether, −80 °C to room temperature, 12 h

being too dissimilar to those of the bent bis(η-cyclopentadienyl) analogues. We note, however, that other mono- and bis(imido) complexes have been shown to be precursors to ethene polymerisation catalysts.[39–41]

Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen (<10 ppm oxygen or water) using standard Schlenk vessels and vacuum-line techniques or in an inert-atmosphere box. Solvents were predried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from potassium (tetrahydrofuran), sodium (toluene), sodium–potassium alloy [light petroleum (b.p. 40–60 °C) and diethyl ether] and stored under dinitrogen. Deuteriated NMR solvents were stored in ampoules over activated molecular sieves (C_6D_6, $[^2H_8]$toluene and CD_2Cl_2) or dried using Na/K alloy ($[^2H_8]$tetrahydrofuran) and transferred by vacuum distillation.

The NMR spectra were recorded on a Brüker AM-300 [^{1}H, 300 MHz; ^{13}C, 75.43 MHz] or AM-500 [^{1}H, 500 MHz; ^{13}C, 125.72 MHz] and referenced internally using residual ^{1}H and ^{13}C solvent resonances relative to tetramethylsilane (δ 0). Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services Ltd. Elemental analyses were performed by the Analytical Laboratory in this Department.

Syntheses

$[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}Cl_2]$ 1. A solution of $C_5H_4(SiMe_3)(CH_2)_3N(SiMe_3)_2$[1,2] (3.60 g, 10.60 mmol) in CH_2Cl_2 (100 cm^3) was added dropwise to a suspension of $NbCl_5$ (2.863 g, 10.60 mmol) in CH_2Cl_2 (500 cm^3) at −80 °C. The mixture was allowed to warm to r.t. and was stirred for 3 d. The solvent was removed under vacuum and the residue extracted with toluene (3 × 60 cm^3) at 80 °C. The resulting dark brown extract was concentrated until a powdery precipitate separated. The mixture was then cooled to −80 °C. After 3 d a yellow powder was obtained. Yield 1.58 g, 53%.

$[MeNb\{\mu\text{-}C_5H_4(CH_2)_3N\}\{\mu\text{-}NCH(CH_2)_2C_5H_4\}NbMe_2]$ 2. A suspension of compound **1** (0.38 g, 1.35 mmol) in Et_2O (30 cm^3) was treated dropwise at r.t. with an excess of MgMeBr in Et_2O (2.20 cm^3 of 1.87 mol dm^{-3} solution, 4.11 mmol). An initial yellow-orange oily precipitate gradually transformed into an orange solution and a pale $MgBrCl{\cdot}Et_2O$ precipitate. This mixture was stirred for 12 h at r.t. The volatiles were removed under reduced pressure and the residue was extracted with pentane (60 cm^3). The solvent was removed from the filtrate under reduced pressure and the residue redissolved in Et_2O (30 cm^3). The resulting orange extract was filtered, concentrated to about 10 cm^3 and cooled to −80 °C giving orange crystals. Yield 0.19 g, 60%.

$[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)]$ 3. To a suspension of compound **1** (0.31 g, 1.09 mmol) in Et_2O (40 cm^3) was added dropwise a solution of $Na(C_5H_5)$ (0.21 g, 2.38 mmol) in thf (40 cm^3) at r.t. The mixture changed from yellow to orange in the first minutes and was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with Et_2O (70 cm^3). Concentration and cooling of the extracts to −80 °C gave two crops of yellow microcrystals of **3**. Yield 0.3 g, 80%.

$[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}(CH_2Ph)_2]$ 4. A suspension of compound **1** (0.24 g, 0.85 mmol) in Et_2O (30 cm^3) was cooled to −40 °C and a solution of $Mg(CH_2Ph)Cl$ in Et_2O (1.42 cm^3 of a 1.2 mol dm^{-3} solution, 1.70 mmol) added dropwise. The mixture was allowed to warm to r.t. and stirred for 4 h. The solvent was removed under reduced pressure and the residue extracted with pentane (50 cm^3). The resulting yellow extract was filtered from the off-white $MgCl_2{\cdot}Et_2O$ residue and the volatiles were removed under reduced pressure. After extraction of the residue with Et_2O (60 cm^3) and filtration, the filtrate was concentrated and cooled to −80 °C giving pale yellow crystals of **4**. A second crop of crystals was isolated by concentration of the mother-liquor. Combined yield 0.31 g, 92%.

$[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}\{CH_2C(Me)CH_2\}_2]$ 5. A suspension of compound **1** (0.287 g, 1.01 mmol) in Et_2O (30 cm^3) was cooled to −80 °C and a solution of $Mg(C_3H_4Me\text{-}2)Cl$ in Et_2O (4.9 cm^3 of a 0.42 mol dm^{-3} solution, 2.06 mmol) was added dropwise. The mixture was allowed to warm to r.t. and stirred overnight. The solvent was removed under reduced pressure and the residue extracted with pentane (50 cm^3). The resulting colourless solution was filtered from the off-white $MgCl_2{\cdot}Et_2O$ residue and the volatiles were removed under reduced pressure. After extraction with Et_2O (60 cm^3) and filtration, the solvent was removed under reduced pressure to give **5** as an off-white oil. Yield 0.230 g, 76%.

Attempted polymerisation of ethylene

Using the $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}Cl_2]$–mao system. A solution of mao (2.311 g, 39.8 mmol) in toluene (15 cm^3) at 25 °C was equilibrated with ethylene at 2 bar relative pressure. A yellow toluene solution (5 cm^3) of compound **1** (0.011 g, 0.039 mmol) was added to the mao solution and the pressure was maintained at 2 bar. Initially the solution turned to pale orange. After 26 h no polyethylene was observed and the deep orange reaction mixture contained a small amount of a deep red precipitate. Work-up of the reaction mixture showed the absence of polyethylene fractions.

Using the $[Nb\{\eta^5,\kappa N\text{-}C_5H_4(CH_2)_3N\}(CH_2Ph)_2]$–$[CPh_3][B(C_6F_5)_4]$ system. A pale yellow solution of compound **4** (0.018 g, 0.046 mmol) in toluene (25 cm^3) was transferred to a Fischer-Porter pressure vessel. This solution at 25 °C was equilibrated with ethylene at 2 bar relative pressure. Addition of an orange solution of $[CPh_3][B(C_6F_5)_4]$ (0.041 g, 0.046 mmol) in toluene (25 cm^3) and re-establishment of the ethylene pressure gave, after 2 h, a deep red solution with a trace of a dark precipitate. After 7 h the solution was greenish and a dark precipitate could be observed. After 17 h the excess of ethylene was vented and some drops of methanol were added which immediately recovered a red colour. Subsequent addition of methanol caused decomposition of the system. No polyethylene fractions could be recovered after the mixture work-up.

Crystallography

Data collection and processing parameters for compound **2** are given in Table 3. Data were collected on an Enraf-Nonius CAD4 diffractometer, an empirical absorption correction based on azimuthal ψ-scan data was applied and the data were corrected for Lorentz-polarisation effects. Systematically absent reflections were rejected and equivalent reflections were merged. The heavy-atom positions were determined from a Patterson synthesis. Subsequent Fourier-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_{equiv} of the supporting carbon atom. The non-hydrogen atoms were refined against F_o 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[42] program on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford.

Table 3 Data collection and processing parameters for compound **2**

Formula	$C_{19}H_{28}N_2Nb_2$
M	470.26
Crystal size/mm	0.25 × 0.40 × 0.60
Crystal system	Orthorhombic
Space group	$Pn2_1a$
a/Å	18.935(5)
b/Å	7.354(8)
c/Å	13.374(5)
U/Å^3	1862.2
Z	4
D_c/g cm^{-3}	1.677
Radiation (λ/Å)	Mo-Kα (0.710 69)
μ/cm^{-1}	11.79
F(000)	952
2θ Limits /°	2–50
Scan mode	ω–2θ
Total unique data collected	1773
No. observations [$I > 3\sigma(I)$]	1572
No. variables	209
Obs./variables	7.5
Weighting scheme	Unit weights
Maximum, minimum peaks in final difference map/e Å^{-3}	0.48, −0.03
r.m.s. shift/e.s.d. in final least-squares cycle	0.022
R^a	0.032
R'^b	0.037

$^a\ R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/526.

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