Studies on Bis(η-indenyl)niobium Complexes *

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The reaction between $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) and $Li[C_9H_7]$ or $Na[C_9H_7]$·thf gives $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ **1**, which reacts with $NaBH_4$ to give $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ **2**. The bridging and terminal tetrahydroborate protons in **2** exchange on the NMR time-scale ($\Delta G^{\ddagger} = 55.2 \pm 1.6$ kJ mol^{-1}). Compound **2** reacts with PMe_2Ph or pyridine *via* BH_3 extraction to give $[NbH(\eta\text{-}C_9H_7)_2(PMe_2Ph)]$ **3** and $[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$ **4** respectively. The pyridine ligand in **4** undergoes restricted rotation about the Nb–N bond ($\Delta G^{\ddagger} = 52 \pm 1$ kJ mol^{-1}). The reaction of **2** with NMe_3 in the presence of CO, $H_2C{=}C{=}CH_2$, *trans,trans*-hexa-2,4-diene or styrene gives the new complexes $[Nb(\eta\text{-}C_9H_7)(CO)_4]$ **5**, $[Nb(\eta\text{-}C_9H_7)_2(\eta\text{-}CH_2CHCH_2)]$ **6**, $[Nb(\eta\text{-}C_9H_7)_2(\eta\text{-}MeCHCHCHCH_2Me)]$ **7** and *endo*-$[NbH(\eta\text{-}C_9H_7)_2(\eta\text{-}H_2C{=}CHPh)]$ **9** respectively. The styrene hydride (complex **9**) is fluxional and this process has been studied using both one- and two-dimensional NMR techniques. The activation barrier to olefin hydride exchange has been determined by coalescence methods to be $\Delta G^{\ddagger} = 70.0 \pm 2$ kJ mol^{-1} at 50 °C, this is significantly lower than that for the analogous $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$ complexes. A mechanism that involves a ring slipped intermediate is proposed.

A range of $\eta\text{-}C_9H_7$ complexes have been described for a variety of transition metals, and the replacement of $\eta\text{-}C_5R_5$ (R = H or Me) by $\eta\text{-}C_9H_7$ has been demonstrated to have a significant effect on the chemistry of such complexes. The most notable of these effects is the enhancement of many reactions which involve ring-slip to an η^3 bonding mode; this indenyl effect has been reviewed.[1,2] Although Multani, Rastogi and co-workers[3–15] have described a number of bis(indenyl)niobium complexes, these are limited to compounds containing OR, SR or carboxylate as co-ligands. The same workers have also described a number of tris(indenyl)niobium complexes.

We set out to prepare and compare the properties of bis(η-indenyl)niobium analogues of several bis(η-cyclopentadienyl)-niobium derivatives for the reasons outlined below.

Results and Discussion

Addition of $Li[C_9H_7]$ to a tetrahydrofuran (thf) suspension of $[NbCl_4(thf)_2]$ rapidly produces a dark green solution which becomes red over 1 h and precipitates a green solid over 12 h. The green product, $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ **1**, can be isolated in typical yields of 30–35%, Scheme 1. This complex had been previously described by Multani, Rastogi and co-workers using a synthesis analogous to an early preparative method for $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$.[16] The green colour contrasts with that of $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ (dark red in solid and solution)[16] and $[Nb(\eta\text{-}C_5Me_5)_2Cl_2]$ (brown).[17] The characterising data for **1** and all other compounds described in this work appear in Table 1, and will not be further discussed except where interpretation is not straightforward.

The reaction between $Na[C_9H_7]$·thf and $[NbCl_4(thf)_2]$ was also performed in thf but no precipitate appeared, a dark red solid was obtained when the solvent was removed under reduced pressure. This crude solid was found to be suitable for further reaction with $NaBH_4$ (see below), but it was found to be impossible to obtain pure $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ by the use of the sodium salt $Na[C_9H_7]$·thf.

Addition of 1,2-dimethoxyethane (dme) to a mixture of solid $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ **1** and an excess of $NaBH_4$ gave an intense purple solution, from which $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ **2** was isolated as a dark red-purple amorphous solid. The IR spectrum of **2** shows bands at 2448, 2412 and 2311 cm^{-1} associated with the BH_4 ligand.[18,19] The 300 MHz ^{1}H NMR spectrum at 25 °C shows four resonances for the indenyl protons with integrals in the ratio 2:2:2:1. This multiplicity indicates that the molecule has C_{2v} symmetry.

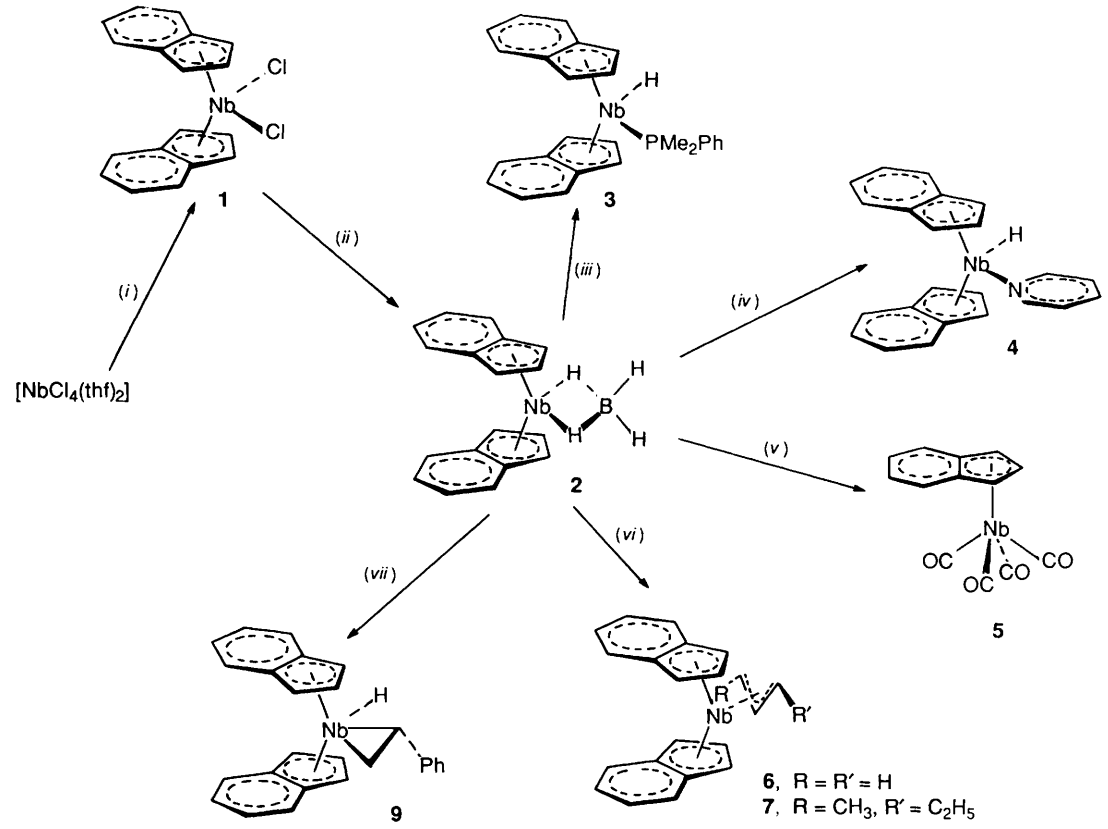
The ^{1}H NMR resonances of the BH_4 moiety in **2** are broad. Two mechanisms are responsible for this. First the interaction with the quadrupolar ^{11}B ($I = \frac{3}{2}$, 80.4%), ^{10}B ($I = 3$, 19.6%) and ^{93}Nb ($I = \frac{9}{2}$, 100%) nuclei causes broadening. The BH_4 protons are also broadened by a bridge–terminal exchange process. This process has been studied previously for $[Nb(\eta\text{-}C_5H_5)_2(\mu\text{-}H_2BH_2)]$ and $[Nb(\eta\text{-}C_5Me_5)_2(\mu\text{-}H_2BH_2)]$.[17] The 200 MHz ^{1}H-{^{11}B}–^{1}H difference spectrum reveals the BH_4 resonances; the terminal BH_2 appears at δ 5.7, and the bridging BH_2 at δ −14.2. The ^{11}B-{^{1}H} spectrum is a singlet at δ 33.8 and the ^{11}B NMR spectrum reveals a quintet [J(H–B) = 82 Hz]. The bridge–terminal exchange rate at room temperature is fast compared with the ^{1}H–^{11}B coupling constants. Hence, the observed coupling constant is an average of the typical bridging (30–60 Hz) and terminal (120–160 Hz) coupling constants.

The $\Delta G^{\ddagger}$ value for the bridge–terminal exchange process was determined from the coalescence temperature of the bridge and terminal ^{1}H NMR resonances.[20] The value obtained is 55.2 ± 1.6 kJ mol^{-1} at 331 ± 5 K, which compares with the values for $[Nb(\eta\text{-}C_5H_5)_2(\mu\text{-}H_2BH_2)]$ (61.0 ± 0.8 kJ mol^{-1} at 346 ± 3 K) and $[Nb(\eta\text{-}C_5Me_5)_2(\mu\text{-}H_2BH_2)]$ (68.5 ± 1.6 kJ mol^{-1} at 388 ± 8 K).[17]

A mechanism for this exchange process has been proposed following a study of the related complex $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)(\mu\text{-}H_2BH_2)]$.[21] The observed kinetics was interpreted in terms of an η^3-BH_4 intermediate with a concomitant ring slip to retain an 18-electron configuration. The $\Delta G^{\ddagger}$ value reported here for the $\eta\text{-}C_9H_7$ complex is lower than for the $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$ complexes. The relative order of these values is consistent with an exchange process that involves an associative mechanism and an intermediate with an η^3-co-ordination of one of the rings.

Addition of PMe_2Ph to a toluene solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ gave a deep blue solution from which $[NbH(\eta\text{-}C_9H_7)_2(PMe_2Ph)]$ **3** was isolated. The ^{1}H NMR spectrum of **3** shows seven indenyl resonances of equal integrals; the molecule thus has C_s symmetry with the mirror plane containing the Nb, P and H atoms. The ^{13}C NMR spectrum of **3** confirms the symmetry of the molecule as deduced from the

* *Non-SI units employed:* atm = 101 325 Pa, mmHg ≈ 133 Pa.



Scheme 1 The preparation and reactions of $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ and $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$. Reagents and conditions: (*i*) Li$[C_9H_7]$, thf, 15 h, 34%; (*ii*) $NaBH_4$, dme, 4 h, 80%; (*iii*) PMe_2Ph, toluene, 80 h, 36%; (*iv*) C_5H_5N, toluene, 5 h, 41%; (*v*) CO and NMe_3, toluene, 15 h, 33%; (*vi*) allene and NMe_3, toluene, 36 h, 40%, R = R′ = H, **6**; *trans,trans*-hexa-2,4-diene and NMe_3, toluene, 36 h, 51%, R = CH_3, R′ = CH_2CH_3, **7**; (*vii*) styrene and NMe_3, toluene, 15 h, 46%

^{1}H NMR data; the assignment of this spectrum was confirmed by a ^{13}C–^{1}H shift-correlation experiment. The ^{31}P-{^{1}H} NMR spectrum at room temperature shows a broad singlet ($\Delta\nu_{\frac{1}{2}}$ = 430 Hz) at δ 24.1, the broadness of this signal is due to interaction with the ^{93}Nb ($I = \frac{9}{2}$, 100%) nucleus.

The reaction of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ with pyridine under hydrogen was investigated. This reaction was prompted by the observation of Bercaw and co-workers[17] that $[Nb(\eta\text{-}C_5Me_5)_2(\mu\text{-}H_2BH_2)]$ reacts with pyridine in the presence of hydrogen to give $[NbH_3(\eta\text{-}C_5Me_5)_2]$,[17] the preparation of $[NbH_3(\eta\text{-}C_9H_7)_2]$ being one of the initial targets of our work. Addition of an excess of pyridine to a toluene solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ gave an identical deep green solution under both hydrogen (either at 1 or at 40 atm) and nitrogen atmospheres. The green product was identified as $[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$ **4**, and was found to display fluxional ^{1}H and ^{13}C NMR spectra.

The ^{1}H NMR spectrum of **4** at room temperature shows seven sharp resonances, of equal integral, assigned to a diastereotopic indenyl ligand; there is also a slightly broad triplet at δ 5.8 and a number of other broad low-field resonances. A broad resonance at δ −4.4 is assigned to a Nb–H hydride, broadened due to the quadrupolar ^{93}Nb nucleus. The broad peak at δ 5.8 suggested some fluxional process involving the pyridine ligand; this was investigated by variable-temperature ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of **4** in the low-temperature limit at 210 K shows the seven indenyl resonances which are unchanged. The broad low-field resonance at δ 5.8 had decoalesced to give two triplet resonances, and a number of doublets have sharpened out of the baseline. A COSY-45 spectrum was recorded at 203 K and identified the presence of one diastereotopic pyridine ligand (integrals in the ratio 1:1:1:1:1) and one non-diastereotopic pyridine ligand (integrals in the ratio 2:2:1). The ratio of the integrals of the indenyl ligands and the diastereotopic pyridine ligand is always *ca.* 14:5. The two sets of pyridine resonances are in the approximate ratio 1:1 (this ratio is sample dependent). On the basis of reference spectra the non-diastereotopic pyridine was assigned to free pyridine which co-crystallises with complex **4**. Attempts to remove this pyridine by either sublimation *in vacuo* or further crystallisations from toluene were only partially successful, and samples were found always to contain at least 20% free pyridine. In the ^{1}H NMR spectrum at 210 K the resonances at δ 9.65 (d, *ortho*), 5.80 (t, *meta*), 6.30 (t, *para*), 5.55 (t, *meta'*) and 4.20 (d, *ortho'*) are assigned to the diastereotopic pyridine ligand. The very large chemical shift difference between the *ortho* and *ortho'* resonances is noteworthy.

The fluxionality of **4** is interpreted in terms of restricted rotation of the pyridine ligand about the Nb–N bond; this is believed to arise as a consequence of steric effects. The coalescence of the *meta* protons allows the activation barrier to the rotation to be calculated as $\Delta G^{\ddagger} = 52 \pm 1$ kJ mol^{-1}.[20] Alternative processes involving dissociation of the pyridine or exchange with the free pyridine can be discounted, since these would raise the symmetry to C_{2v} by inversion at Nb and reduce the multiplicity of the $\eta\text{-}C_9H_7$ resonances. Furthermore, there is no exchange between the free pyridine and the co-ordinated pyridine ligand on the chemical time-scale; thus, the C_5H_5N ligand in $[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$ does not exchange with $[^2H_5]$pyridine.

The ^{13}C NMR spectrum of $[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$ at room temperature reveals seven indenyl C–H resonances, the ring-junction quaternary resonances are coincident. The resonances due to the pyridine ligand are broad at room temperature due to the exchange process discussed above. Since the complex readily crystallises from toluene at −25 °C variable-temperature ^{13}C NMR experiments using direct observation were not

attempted. Instead the low-temperature ^{13}C NMR spectrum was obtained using a ^{1}H-detected ^{1}H-^{13}C shift correlation experiment at 210 K using the pulse sequence of Bax and Subramanian.[22] Although this technique has been used to determine the chemical shifts of low-abundance and low-γ nuclei such as ^{183}W and ^{187}Os,[23] it has rarely been used for ^{13}C NMR. In suitable cases (^{1}H T_1 values of 1–2 s and molecular weights of less than a few thousand) this experiment is a powerful technique for obtaining ^{13}C spectra when sensitivity is limited by the amount of sample available or, as here, solubility. The spectrum (Fig. 1) was recorded in less than 4 h and allows the unambiguous extraction of the ^{13}C NMR chemical shifts for the indenyl ligand and the co-ordinated pyridine ligand. The concentration of free pyridine in this sample was too low for the

Table 1 Analytical and spectroscopic data

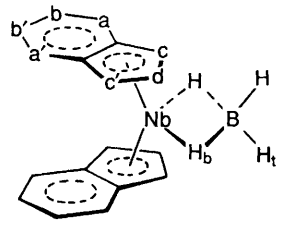
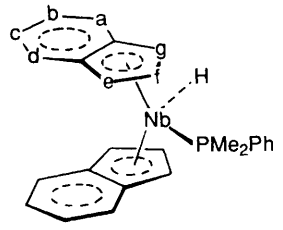
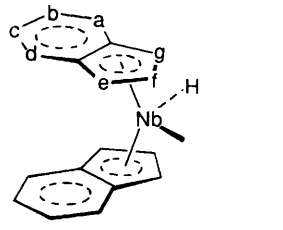
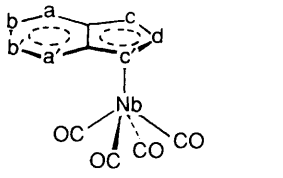
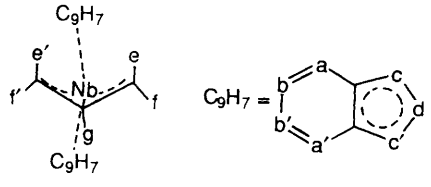
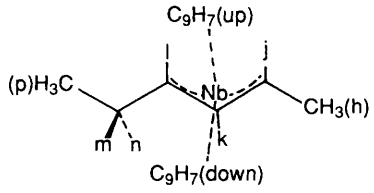
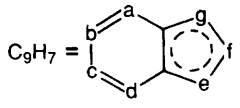
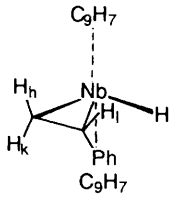
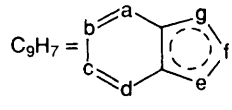
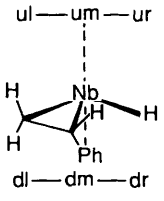
Compound Colour and analysis[a] (%)	NMR data[b]
1 $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$[c] Green C, 54.1 (54.8); H, 3.8 (3.6)	
2 $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$[d] Purple–mauve C, 60.7 (63.9); H, 5.2 (5.4) 	^{1}H: 6.80 [dd, 4 H, J(HH) 6, 3, $H_{a,a'}$ or $H_{b,b'}$], 6.53 [dd, 4 H, J(HH) 6, 3, $H_{b,b'}$ or $H_{a,a'}$], 5.94 [t, 2 H, J(HH) 3, H_d], 4.58 [d, 4 H, J(HH) 3, $H_{c,c'}$] ^{13}C: 128.3 (partially obsc., $C_{a,a'}$ or $C_{b,b'}$), 125.2 [d, J(CH) 156, $C_{b,b'}$ or $C_{a,a'}$], 115.1 (s, C_{quat}), 93.75 [d, J(CH) 176, $C_{c,c'}$], 90.5 [d, J(CH) 182, C_d]
3 $[NbH(\eta\text{-}C_9H_7)_2(PMe_2Ph)]$[e] Blue C, 67.3 (67.5); H, 5.6 (5.7) 	^{1}H: 7.1–6.5 (overlapping m, 13 H, phenyl and $H_{a,b,c,d}$), 5.30 [t, 2 H, J(HH) 3, H_f], 4.24 [d, 2 H, J(HH) 3, H_g or H_e], 4.07 [d, 2 H, J(HH) 3, H_e or H_g], 1.30 [d, 6 H, J(HP) 6.6, PMe], −4.55 [d, 1 H, J(HP) 40.5, Nb–H] ^{13}C: 131.8, 131.6, 128.6, 128.0, 127.9, 126.0, 125.2, 123.7, 122.1 (aromatic), 111.5 (2 overlapping s, C_{quat}), 80.4 [d, J(CH) 179, C_f], 79.8 [d, J(CH) 174, C_g or C_e], 79.5 [d, J(CH) 175, C_e or C_g], 20.2 [dq, J(CH) 131, J(CP) 21, PMe_2]
4 $[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$[f] Dark green C, 68.2 (68.5); H, 4.9 (5.0) 	^{1}H (at 293 K): 7.00 [d, 2 H, J(HH) 8, H_a or H_d], 6.55 [t, 2 H, J(HH) 8, H_b or H_c], 6.51 [partially obsc. t, J(HH) 8, H_{para}], 6.47 [t, 2 H, J(HH) 8, H_c or H_b], 5.80 (br t, 2 H, H_{meta}), 5.60 [d, 2 H, J(HH) 8, H_d or H_a], 5.14 (virt. t, 2 H, J_{app} 2, H_g or H_e), 4.58 (virt. q, 2 H, J_{app} 2, H_f), 3.91 (virt. t, 2 H, J_{app} 2, H_e or H_g), −4.40 (br s, 1 H, $\Delta\nu_{\frac{1}{2}} \approx 30$, Nb–H) ^{13}C (at 210 K, [$^{2}H_8$]toluene): 161.1 [d, J(CH) 195, C_{ortho}], 152.9 [d, J(CH) 186, C_{ortho}], 136.9 [d, J(CH) 166, C_{para}], 125.9 (C_c or C_b), 125.2 (C_a or C_d), 123.1 (C_d or C_a), 122.9 (C_{meta}), ≈120.2 (C_{meta}), 119.6 [d, J(CH) 161, C_b or C_c], 80.3 [d, J(CH) 185, C_g or C_e], 79.2 [d, J(CH) 180, C_f], 76.6 [d, J(CH) 174, C_e or C_g]
5 $[Nb(\eta\text{-}C_9H_7)(CO)_4]$[g] Light brown C, 47.8 (48.7); H, 2.9 (2.2) 	^{1}H: 6.99 [dd, 2 H, J(HH) 3, 6, $H_{aa'}$ or $H_{bb'}$], 6.59 [dd, 2 H, J(HH) 3, 6, $H_{bb'}$ or $H_{aa'}$], 5.35 [d, 2 H, J(HH) 3, $H_{cc'}$], 4.97 [t, 1 H, J(HH) 3, H_d] ^{13}C: 124.7 [d, J(CH) 161, $C_{aa'}$ or $C_{bb'}$], 124.2 [d, J(CH) 160, $C_{bb'}$ or $C_{aa'}$], 114.2 (s, C_{quat}), 97.1 [d, J(CH) 174, C_d], 83.8 [d, J(CH) 177, $C_{cc'}$]
6 $[Nb(\eta\text{-}C_9H_7)_2(\eta^3\text{-}CH_2CHCH_2)]$ Dark purple C, 68.8 (69.2); H, 5.6 (5.3) 	^{1}H: 7.10 [partially obsc., 2 H, $H_{a,a'}$ ring 1], 6.92 [dd, 2 H, J(HH) 6, 3, $H_{b,b'}$ ring 1], 6.70 [dd, 2 H, J(HH) 6, 3, $H_{b,b'}$ ring 2], 6.57 [dd, 2 H, J(HH) 6, 3, $H_{a,a'}$ ring 2], 5.61 [t, 1 H, J(HH) 4, H_d ring 1], 4.82 [t, 1 H, J(HH) 4, H_d ring 2], 3.97 [d, 2 H, J(HH) 4, $H_{c,c'}$ ring 1], 3.86 [d, 2 H, J(HH) 4, $H_{c,c'}$ ring 2], 2.10 (m, 3 H, H_g and $H_{f,f'}$ or $H_{c,c'}$), 1.10 (m, 2 H, $H_{c,c'}$ or $H_{f,f'}$) ^{13}C-{^{1}H}: 126.6 ($C_{bb'}$ ring 1), 125.3 ($C_{aa'}$ ring 2), 124.0 ($C_{bb'}$ ring 2), 123.6 ($C_{aa'}$ ring 1), 91.0 (C_d ring 1), 88.8 ($C_{cc'}$ ring 1), 86.7 (C_g), 86.2 ($C_{cc'}$ ring 2), 82.5 (C_d ring 2), 46.0 (CH_2, $C_{ff'}$ and $C_{cc'}$)

Table 1 (*continued*)

Compound Colour and analysis[a] (%)	NMR data[b]
7 [Nb(η-C_9H_7)$_2$(η^3-MeCHCHCHCH$_2$Me)] Dark purple C, 70.9 (70.9); H, 6.0 (6.2)  	^{1}H: 7.08 (m, 1 H, H_a or H_d up), 7.02 (m, 1 H, H_d or H_a up), 6.90 (m, 2 H, H_b and H_c up), 6.80 (m, 2 H, H_c and H_d down), 6.75 (m, 1 H, H_a down), 6.64 (m, 1 H, H_b down), 5.47 [t, 1 H, *J*(HH) 3, H_f up], 4.28 (m, 1 H, H_g or H_e up), 4.20 [t, 1 H, *J*(HH) 3, H_f down], 4.07 (m, 1 H, H_e or H_g down), 3.92 (m, 1 H, H_g or H_e down), 3.73 (m, 1 H, H_e or H_g up), 3.16 [t, 1 H, *J*(HH) 13, H_k], 2.00 (m, 1 H, H_n or H_m), 1.46 [d, 3 H, *J*(HH) 5.5, H_h], 1.40–1.22 (overlapping m, 3 H, H_m or H_n, H_j and H_i), 0.88 [apparent t, 3 H, *J*(HH) 7, H_p] ^{13}C: 127.2 [d, *J*(CH) 160, C_d or C_a up], 126.6 [d, *J*(CH) 159, C_c or C_d down], 126.0 [d, *J*(CH) 157, C_a or C_d up], 125.8 [d, *J*(CH) 158, C_b or C_c down], 123.9 [d, *J*(CH) 159, C_a or C_d down], 123.8 [d, *J*(CH) 160, C_a or C_b or C_c or C_d down], 123.7 [d, *J*(CH) 159, C_b or C_c up], 123.1 [d, *J*(CH) 160, C_c or C_b up], 111.5 (s, C_{quat}), 110.8 (two overlapping s, C_{quat}), 110.1 (s, C_{quat}), 92.2 [d, *J*(CH) 175, C_k], 88.7 [d, *J*(CH) 177, C_e or C_g up], 88.2 [d, *J*(CH) 179, C_f up], 87.4 [d, *J*(CH) 178, C_e or C_g up], 84.6 [d, *J*(CH) 178, C_g or C_e down], 84.4 [d, *J*(CH) 178, C_e or C_g down], 79.7 [d, *J*(CH) 180, C_f down], 66.7 [d, *J*(CH) 145, CH_j], 54.4 [d, *J*(CH) 148, CH_i], 29.1 [t, *J*(CH) 130, $CH_{m,n}$], 20.25 [q, *J*(CH) 131, CH_h], 18.3 [q, *J*(CH) 127, CH_p]
 	
9 [NbH(η-C_9H_7)$_2$(*endo*-η-H_2C=CHPh)] Red-brown C, 72.9 (72.8); H, 5.4 (5.4)   	^{1}H: 7.47 [d, 2 H, *J*(HH) 7.5, H_{ortho}], 7.24 [t, 2 H, *J*(HH) 7.5, H_{meta}], 7.08 (br, 1 H, $H_{a,b,c\text{ or }d}$ ring a or b), 6.95 (br, 1 H, $H_{a,b,c\text{ or }d}$ ring a or b), 6.93 [t, 1 H, *J*(HH) 7.5, H_{para}], 6.79 (br q, 2 H, $H_{a,b,c,\text{ or }d}$ ring a or b), 6.67 (br app. d, 3 H, $H_{a,b,c\text{ or }d}$ ring b or a), 6.55 (br app. d, 1 H, $H_{a,b,c\text{ or }d}$ ring b or a), 5.07 [t, 1 H, *J*(HH) ≈3, H_f ring a or b], 5.04 (sl br, 1 H, $H_{g\text{ or }e}$ ring b or a), 4.64 (sl br, 1 H, $H_{e\text{ or }g}$ ring b or a), 4.40 [t, 1 H, *J*(HH) ≈3, H_f ring b or a], 4.37 (sl br, 1 H, $H_{e\text{ or }g}$ ring a or b), 4.04 (sl br, 1 H, $H_{g\text{ or }e}$ ring a or b), 1.29 (m, 2 H, $H_{h\text{ or }k}$ and H_i), −0.97 (s, 1 H, Nb–H), −1.33 [dd, 1 H, *J*(HH) 4.2, 8.6, $H_{k\text{ or }h}$] ^{13}C (at 283 K): 153.1 (s, C_{ipso}), 127.6 [d, *J*(CH) 160, C_{ortho}], 126.6 [d, *J*(CH) 160, C_{meta}], 125.8 [d, *J*(CH) 161, ring a or b], 125.5 [d, *J*(CH) 161, ring b or a], 125.2 [d, *J*(CH) 161, ring b or a], 124.7 [d, *J*(CH) 162, ring a or b], 124.5 [d, *J*(CH) 161, ring a or b], 124.0 [d, *J*(CH) 163, ring b or a], 123.9 [d, *J*(CH) 160, ring a or b], 122.7 [d, *J*(CH) 160, C_{para}], 122.0 [d, *J*(CH) 163, ring b or a], 115.7 (C_{quat}), 114.6 (C_{quat}), 112.0 (C_{quat}), 110.7 (C_{quat}), 99.3 [d, *J*(CH) 177, C_f ring a or b], 94.5 [d, *J*(CH) 174, C_f ring b or a], 92.5 [d, *J*(CH) 179, $C_{g\text{ or }e}$ ring a or b], 85.9 [d, *J*(CH) 177, $C_{e\text{ or }g}$ ring a or b], 83.8 [d, *J*(CH) 177, $C_{e\text{ or }g}$ ring b or a], 82.8 [d, *J*(CH) 178, $C_{g\text{ or }e}$ ring b or a], 51.5 [d, *J*(CH) 154, CH_2], 30.7 [d, *J*(CH) 150, CH]
 	

[a] Required values are given in parentheses. [b] Unless otherwise stated, all ^{1}H and ^{13}C NMR data were recorded at 300 MHz (^{1}H) or 75.43 MHz (^{13}C) at 293 K for ^{1}H and 298 K for ^{13}C in [$^2H_6$]benzene. The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), qnt (quintet), m (multiplet), sl (slight), br (broad), obsc. (obscured), virt. (virtual), J_{app} (apparent coupling constant) and C_{quat} (quaternary carbon). [c] Cl 17.6 (18.0)%. Electron impact (EI) mass spectrum *m/z* 278 [*P* − Cl]$^+$, 208 [*P* − 2Cl]$^+$. [d] ^{1}H-{^{11}B}-^{1}H (200 MHz, 282 K, [$^2H_6$]benzene) δ 5.7 (br s, Nb–H_t), −14.2 (br s, B–H_b–B); ^{11}B (64.17 MHz, 283 K, [$^2H_6$]benzene) δ 33.79 [qnt, *J*(HB) 82]. Selected IR data (CsI pellet) 2448m, 2412m and 2311m cm^{-1} ν(B–H). [e] ^{31}P-{^{1}H} (121.49 MHz, 298 K, [$^2H_6$]benzene) δ 24.1 (br s, $\Delta\nu_{\frac{1}{2}}$ 430 Hz). Selected IR data (Nujol mull, KBr plates) 1633m cm^{-1} Nb–H. [f] H_{ortho} not observed at 293 K; only selected *J*(CH) data available. Additional ^{1}H NMR data (300 MHz, 203 K, [$^2H_8$]toluene), δ 9.65 [d, 2 H, *J*(HH) 4, H_{ortho}], 7.10 (obsc., H_a or H_d), 6.65 [t, 2 H, *J*(HH) 8, H_b or H_c], 6.52 [t, 2 H, *J*(HH) 8, H_c or H_b], 6.30 [t, 1 H, *J*(HH) 4, H_{para}], 5.80 [t, 1 H, *J*(HH) 4, H_{meta}], 5.70 [d, 2 H, *J*(HH) 8, H_d or H_a], 5.64 [virt. t, 2 H, J_{app} ≈2, H_g or H_e], 5.55 [t, 1 H, *J*(HH) 4, $H_{meta'}$], 5.21 (virt. q, 2 H, J_{app} ≈2, H_f), 4.20 [d, 1 H, *J*(HH) 4, $H_{ortho'}$], 3.80 (virt. t, 1 H, J_{app} ≈2 Hz, H_e or H_g), −4.40 (br s, $\Delta\nu_{\frac{1}{2}}$ ≈20 Hz, Nb–H]. [g] Additional ^{13}C NMR data (75.43 MHz, 191 K, [$^2H_8$]toluene); δ 252.0 (br s, $\Delta\nu_{\frac{1}{2}}$ 30 Hz, CO). Selected IR data [light petroleum (b.p. 100–120 °C) solution, KBr cell] 2034m, 1947(sh) and 1931s ν(C≡O) cm^{-1}.

correlations due to this to be observed. Free pyridine was observed on another occasion in a distortionless enhancement by polarisation transfer (DEPT) ^{13}C NMR experiment. The most notable feature is that the separation of the resonances due to the *ortho* and *ortho'* sites of the pyridine ligand is considerably smaller in the ^{13}C spectrum (7.1 ppm or 536 Hz) than in the ^{1}H spectrum (5.45 ppm or 1635 Hz). The ^{1}H-coupled ^{13}C DEPT spectrum at 210 K provides access to some of the ^1J(C–H) coupling constants, those for the *ortho* resonances are 195 and 186 Hz. These data mitigate against a structure with an *ortho* agostic interaction, *i.e.* [NbH(η-C_9H_7)$_2$(η^2-NC_5H_5)], where the indenyl ligands are undergoing rapid η^5–η^3 ring shifts. The reaction of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with Lewis bases, L (L = PMe_2Ph or pyridine) results in the formation of [NbH(η-C_9H_7)$_2$L], this is presumed to occur *via* a [NbH(η-C_9H_7)$_2$] intermediate; the adduct BH_3L is believed to be the other product. With the aim of trapping the [NbH(η-C_9H_7)$_2$] fragment with alternative reagents a number of reactions were performed using NMe_3 in the presence of potential ligands.

The reaction of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with excess CO in the presence of an excess of NMe_3 gave a brown-yellow solution from which polycrystalline needles of [Nb(η-C_9H_7)(CO)$_4$] **5**, were isolated. The ^{1}H NMR spectrum of **5** indicates the presence of a non-diastereotopic indenyl ring, *i.e.* there are four resonances in the ratio 2:2:2:1. The ^{13}C NMR spectrum of **5** shows two CH resonances for the C_6 ring, one quaternary ring resonance and two CH resonances for the C_5 ring in the approximate ratio 2:1. Additionally, on cooling the sample to −82 °C, a broad carbonyl resonance at δ 252 is observed. The solution IR spectrum shows two strong bands at 2034 and 1931 cm^{-1} and a weak shoulder at 1947 cm^{-1}. These are consistent with the complex [Nb(η-C_9H_7)(CO)$_4$] having approximately

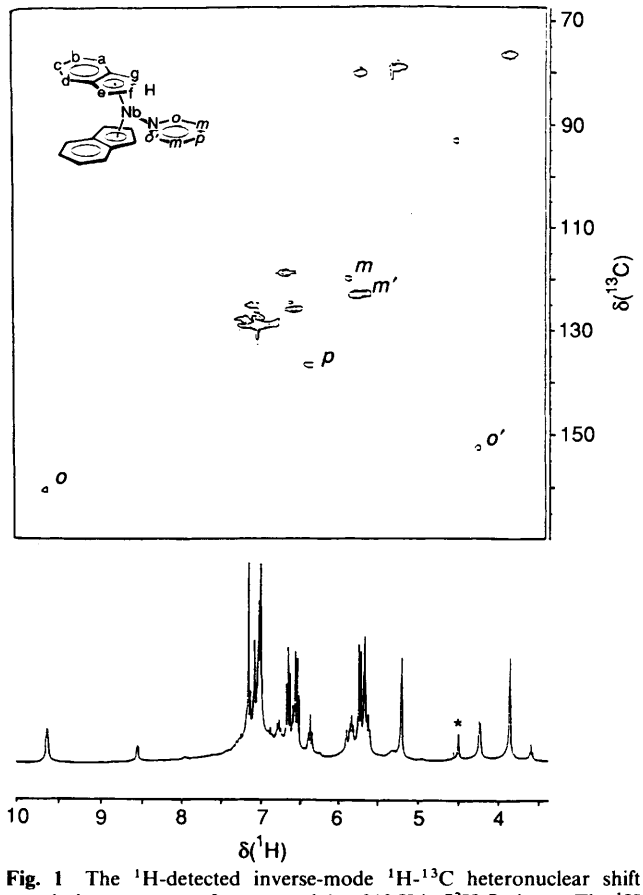


Fig. 1 The ^{1}H-detected inverse-mode ^{1}H-^{13}C heteronuclear shift correlation spectrum of compound **4** at 210 K in [$^2H_8$]toluene. The ^{1}H projection is shown at the bottom of the figure, the resonances assigned to the pyridine ligand are labelled, the peak marked with an asterisk is due to an impurity

C_{4v} local symmetry, the E and A_1 symmetry stretches are symmetry allowed, and the weak shoulder is assigned to the symmetry-forbidden (under true C_{4v}) B_1 band.

As further confirmation of the identity of the product, the reaction of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with NMe_3 in the presence of excess CO was carried out in a NMR tube. After 12 h, the ^{1}H NMR spectrum showed signals assigned to free indene by comparison with a genuine sample. The ratio of free indene to complexed indenyl was *ca.* 1:1 by integration.

Trogler and co-workers[24] have reported that the reaction of [V(η-C_9H_7)$_2$] with CO forms the dicarbonyl complex [V(η-C_9H_7)(η^3-C_9H_7)(CO)$_2$]; this represents one of a growing number of η^3-C_9H_7 complexes that have been structurally characterised. On warming this complex under excess CO, an indenyl ligand is lost to give [V(η-C_9H_7)(CO)$_4$], which had been previously prepared *via* another route.[25] This suggests that the reaction of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with CO may proceed *via* mono- and di-carbonyl intermediates, but no such intermediates were observed.

The reaction of a toluene solution of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with a mixture of allene (H_2C=C=CH_2) and trimethylamine gave a very deep purple solution from which amorphous [Nb(η-C_9H_7)$_2$(η-C_3H_5)] **6** was obtained by crystallisation from light petroleum. The ^{1}H NMR spectrum shows four indenyl resonances with integrals in the ratio 4:4:4:2 as well as two complex multiplets centred at δ 2.10 and 1.10 with integrals in the ratio 3:2. The multiplicity of the indenyl resonances indicates that the molecule has C_s symmetry with the mirror plane perpendicular to the indenyl ligands and containing the Nb and allyl C–H atoms. The ^{13}C NMR spectrum of **6** confirms the symmetry of the molecule as deduced from the ^{1}H NMR data.

Addition of trimethylamine to a toluene solution of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] containing *trans,trans*-hexa-2,4-diene gave a deep purple solution from which [Nb(η-C_9H_7)$_2$(η^3-MeCH-CHCHCH_2Me)] **7** was obtained by crystallisation from pentane. The substitution of the allyl ligand in this complex results in C_1 symmetry. As a consequence, compound **7** contains 17 separate CH groups, one diastereotopic CH_2 group, two CH_3 groups and four indenyl quaternary carbons. The ^{1}H NMR spectrum of **7** shows a number of complex multiplets in the aromatic region (δ 6.6–7.1), these are assigned to the eight inequivalent aromatic C_6-ring indenyl protons. The resonances are heavily overlapped, but the phase-sensitive double-quantum-filtered ^{1}H–^{1}H COSY (COSY–DQF) allowed a tentative assignment to be made. The C_5-ring resonances for the two inequivalent rings are clearly distinguished. A COSY optimised for long-range coupling (COSYLR) was also run, and this shows weak correlations between the C_5- and C_6-indenyl rings which allow the connections between the rings to be elucidated. The remaining ^{1}H resonances were assigned to the substituted allyl ligand on the basis of the COSY-DQF experiment. The heavily overlapped region around δ 1.30 contains resonances assigned to H_m (or H_n) and H_j and H_l. Due to the overlap of these resonances, the full assignment of the ^{1}H spectrum was only obtained with the assistance of the ^{13}C-DEPT and ^{13}C–^{1}H correlation experiments.

A phase-sensitive ^{1}H–^{1}H nuclear Overhauser effect (NOESY) experiment showed weak correlations between the allyl resonances $H_{j/l}$ and $H_{e/g}$ for one indenyl ring and also between the allyl resonance H_k and $H_{e/g}$ for the other indenyl ring. This result was used to assign the indenyl rings as 'up' and 'down' relative to the allyl ligand.

The reaction of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] with isoprene and a mixture of pyridine and triethylamine gave a red-brown solution from which no crystalline material could be isolated. The ^{1}H NMR spectrum of the crude oil **8** showed a multitude of resonances spanning the region from δ 8.2 to −2.2 and clearly indicates that more than one isomer is present; no conclusions have been reached about the molecular structure of any of these isomers. We note that, although the related complex [Ta(η-C_5H_5)$_2$(η^3-CH_2CHCHMe)] was prepared by the reaction of [Ta(η-C_5H_5)$_2$$Cl_2$] with Mg($CH_2$CHCHC$H_2$), attempts to perform the corresponding reaction with Mg(CH_2CHC-MeCH_2) gave more than one isomer.[26]

Addition of NMe_3 to a toluene solution of [Nb(η-C_9H_7)$_2$(μ-H_2BH_2)] containing an excess of styrene slowly produced a deep red solution from which the styrene hydride complex *endo*-[NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)] **9** was obtained as an amorphous red solid by crystallisation from pentane. Compound **9** was found to be thermally stable to 100 °C in solution, and to display fluxional ^{1}H and ^{13}C NMR spectra.

The ^{1}H NMR spectrum of **9** shows resonances assigned to the styrene phenyl ring and the indenyl C_6 ring in the region δ 6.5–7.1; the six C_5 resonances are clearly resolved between δ 4.0 and 5.1. There is a complex multiplet at δ 1.29, which is assigned to the olefin CH overlapping with one of the diastereotopic CH_2 protons, the other CH_2 proton appears at δ −1.33 as a doublet of doublets. The hydride resonance appears as a slightly broadened singlet at δ −0.97. This assignment was assisted by a ^{1}H–^{1}H COSY–DQF spectrum. The connection between the C_5 and C_6 rings was successfully determined from a COSYLR experiment.

The ^{13}C NMR spectrum of **9** was assigned on the basis of a ^{13}C–^{1}H shift-correlation spectrum. The ^{13}C–^{1}H correlation experiment was run on a very strong sample (350 mg of compound) and shows minor peaks due to a second compound. These are very tentatively assigned to the *exo* isomer of the styrene complex, although no data will be presented to characterise this minor isomer.

At ambient probe temperature (294 K) the C_5-ring and C_6-ring resonances in the 300 MHz ^{1}H NMR spectrum of **9** are broadened, and on slight warming the CH_2 and CH resonances

Table 2 Activation parameters for some styrene hydride complexes of niobium[a]

Complex	$\Delta G^{\ddagger}$ (at 50 °C)	Ref.
endo-[NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)]	70.0 ± 2[b]	This work
endo-[NbH(η-C_5H_5)$_2$(η-H_2C=CHPh)]	85.7(4)[c]	28
endo-[NbH(η-C_5Me_5)$_2$(η-H_2C=CHPh)]	76.5(4)[d]	27

[a] All values are in kJ mol^{-1} corrected to 50 °C assuming that $\Delta S^{\ddagger}$ = +28 (± 20) J K^{-1} mol^{-1}. [b] From coalescence of the olefin resonances. [c] By magnetisation transfer. [d] From coalescence of the C_5Me_5 (^{1}H) resonances.

also become broadened. The process which causes this broadening is well understood from the analogous η-C_5H_5 and η-C_5Me_5 complexes,[27,28] and involves insertion of the olefin into the Nb–H bond followed by rotations in the resulting 'alkyl' and regeneration of the olefin hydride. We, and others, have recently re-investigated the mechanism of this process for the η-C_5H_5 complexes.[29,30] Complex **9** provided an opportunity further to investigate these dynamic processes.

The most simple approach to studying the fluxionality in **9** involved the use of the coalescence method for the ^{1}H NMR spectra. The variable-temperature ^{1}H NMR spectra were recorded at 300 MHz in [$^2H_{10}$]*o*-xylene. The resonances assigned to the CH_2, CH and Nb–N protons were observed to coalesce at 364 ± 10 K, the exact position of the coalescence is not clear since there are two sets of overlapping resonances in exchange (*i.e.*, Nb–H ⟷ C–H and CH_2 ⟷ CH_2). Since both CH_2 and CH olefin resonances are observed to be involved in the coalescence, it is clear that the isomer involved is the *endo* isomer. For the *exo* isomer, we would observe exchange between the Nb–H and both CH_2 resonances, but no exchange with the CH. The olefin–hydride exchange process also results in exchange of the indenyl ligand resonances. In the ^{1}H NMR spectrum, the six resonances assigned to the C_5 ring at low temperature coalesce to give two resonances (at δ 4.61 and 4.49) in the ratio 1:2 at 374 K. Above 375 K the complex decomposes to give ethylbenzene (identified by reference spectra); thus, the high temperature limiting spectrum for the olefin resonances was not observed.

From the approximate coalescence temperature of the olefin resonances the activation energy can be estimated to be $\Delta G^{\ddagger}$ = 67.5 ± 2 kJ mol^{-1} at 364 K. In order to make comparisons with the data for the η-C_5H_5 and η-C_5Me_5 analogues this value is corrected to 70.0 ± 2 kJ mol^{-1} at 50 °C ($\Delta S^{\ddagger}$ = +28 J K^{-1} mol^{-1}).[28] The $\Delta G^{\ddagger}$ values at 50 °C for the η-C_5H_5, η-C_5Me_5 and η-C_9H_7 *endo*-styrene hydride complexes are presented in Table 2. The rate of insertion of these complexes is in the order η-C_9H_7 > η-C_5Me_5 > η-C_5H_5.

Bercaw and co-workers[28] have interpreted the relative order of the olefin insertion rates of the η-C_5H_5 and η-C_5Me_5 styrene hydride complexes as being due to steric influences. Thus, the activated state in the exchange process involves a linear Nb–CH_2CH_2Ph fragment (this gives the C_{2v} symmetry observed for the ^{1}H NMR spectra of [NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)] in the fast-exchange limit) which is less sterically demanding than the olefin hydride ground state.[28] In contrast, in the case of the four ethylene hydride complexes [MH(η-C_5R_5)$_2$(η-H_2C=CH_2)] (M = Nb or Ta; R = H or Me) the insertion rates are determined by the enhanced donor ability of η-C_5Me_5 relative to η-C_5H_5, this stabilises the formally M^V metallacyclopropane ground state more for the η-C_5Me_5 complex. Thus, the order of insertion rates is η-C_5H_5 > η-C_5Me_5 for both Nb and Ta. In the case of the propene hydride complexes and the styrene hydride complexes (as discussed above) the influence of steric factors is dominant.

The enhanced rate of olefin insertion for the indenyl complex might be attributed to steric factors, although this implies that the η-C_9H_7 is larger than the η-C_5Me_5 ligand by approximately the same proportion as the η-C_5Me_5 ligand is larger than the η-C_5H_5 ligand. This assertion appears unlikely. There is no evidence that the rate of olefin insertion in the styrene hydride complexes is controlled by electronic factors. Furthermore, photoelectron spectroscopic data have demonstrated that the η-C_9H_7 ligand is intermediate between the η-C_5H_5 and η-C_5Me_5 ligands in donor ability.[31]

We suggest an explanation based on the mechanism we have proposed to account for the observed kinetics in the *exo*-[MH(η-C_5H_5)$_2$(η-H_2C=CHMe)] (M = Nb of Ta) complexes.[29,30] The mechanism as applied to the *endo* isomer of a styrene hydride is depicted in Fig. 2. The initial step involves olefin insertion into the Nb–H bond to give an agostic alkyl **A**, the reverse of this insertion step creates no net exchange of hydrogen nuclei. In order to exchange Nb–H with C–H, it is necessary to perform an in-place rotation to give species **C**. The reverse of the olefin insertion step from this species will result in an olefin hydride where Nb–H and C–H have exchanged, also the CH_2 sites have exchanged. The 'transition state' to the in-place rotation is proposed to be the 'doubly agostic' species **B**, which might be formally considered as a 20-electron intermediate. In order to maintain an 18-electron count for this intermediate we propose a ring slip to give an η^3-ligand. We have previously observed that this in-place rotation is the rate limiting step for *exo*-[NbH(η-C_5H_5)$_2$(η-H_2C=CHMe)] whilst the olefin insertion step is rate limiting for the Ta analogue.[30] Thus, the substitution of η-C_5R_5 (R = H or Me) by the η-C_9H_7 ligand is likely to result in a faster rate for *this* exchange process as a consequence of the 'indenyl effect'.

As a further complicating factor we note that the exchange process described above is only one of the two possible processes which result in the observed NMR exchange. Thus this process results in time-averaged C_s symmetry. That is, the 'up' and 'down' η-C_9H_7 ligands are exchanged, but the 'left' and 'right' sides of the ligands are not exchanged. A second process is required to account for the observed C_{2v} symmetry of the system in the high-temperature limiting ^{1}H NMR spectrum. This second process is depicted in Fig. 3 and involves dissociation of the agostic alkyl **A** to give a 16-electron alkyl intermediate **B**. This alkyl group may then swing through the wedge defined by the η-C_9H_7 ligands before reassociating to give the agostic alkyl (**C** or **D**). This process may achieve no exchange of Nb–H with C–H (or of the CH_2 groups) as seen for species **C**, or may exchange these sites (species **D**). Both of these exchange events also achieve some combination of exchange of 'up' with 'down' and of 'left' with 'right' within the Nb(η-C_9H_7)$_2$ fragment. This process would not be expected to be significantly affected by the substitution of η-C_9H_7 for η-C_5R_5 (R = H or Me). Clearly, the presence of exchange involving the diastereotopic indenyl ligands potentially provides further kinetic data on this process. Thus, we attempted to obtain further quantitative data.

Two-dimensional exchange experiments were attempted using the ^{1}H–^{1}H nuclear Overhauser enhancement spectroscopy (NOESY) [or phase-sensitive exchange correlation spectroscopy (PSEXSY)] technique. Although these clearly show which C_5-ring resonances are undergoing exchange it was not possible quantitatively to analyse the data from these experiments, due to peak overlap. However, the existence of a cross-peak (indicating exchange) between the Nb–H resonance and the CH resonance and between the CH_2 resonances provides further evidence that the complex is the *endo* isomer. The coincidence of resonances also frustrated attempts to measure exchange rates using saturation transfer in the ^{1}H NMR spectrum.[32]

The exchange between the indenyl ligand resonances was studied in the ^{13}C NMR spectrum using magnetisation transfer (using the DANTE sequence[33]), the greater dispersion of the ^{13}C resonances eliminates overlap. The data from these

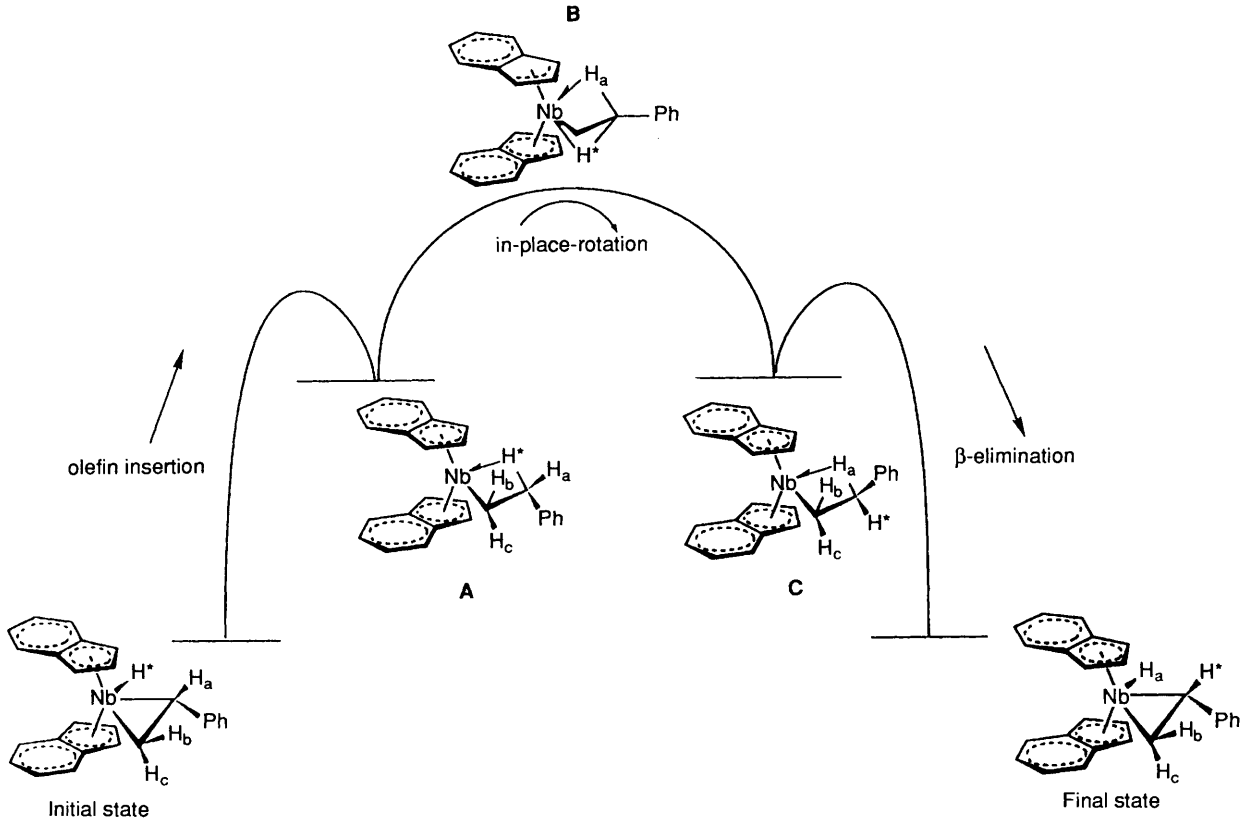


Fig. 2 The non-dissociative mechanism, involving in-place rotation of an agostic alkyl, proposed to account for part of the exchange processes in compound **9**

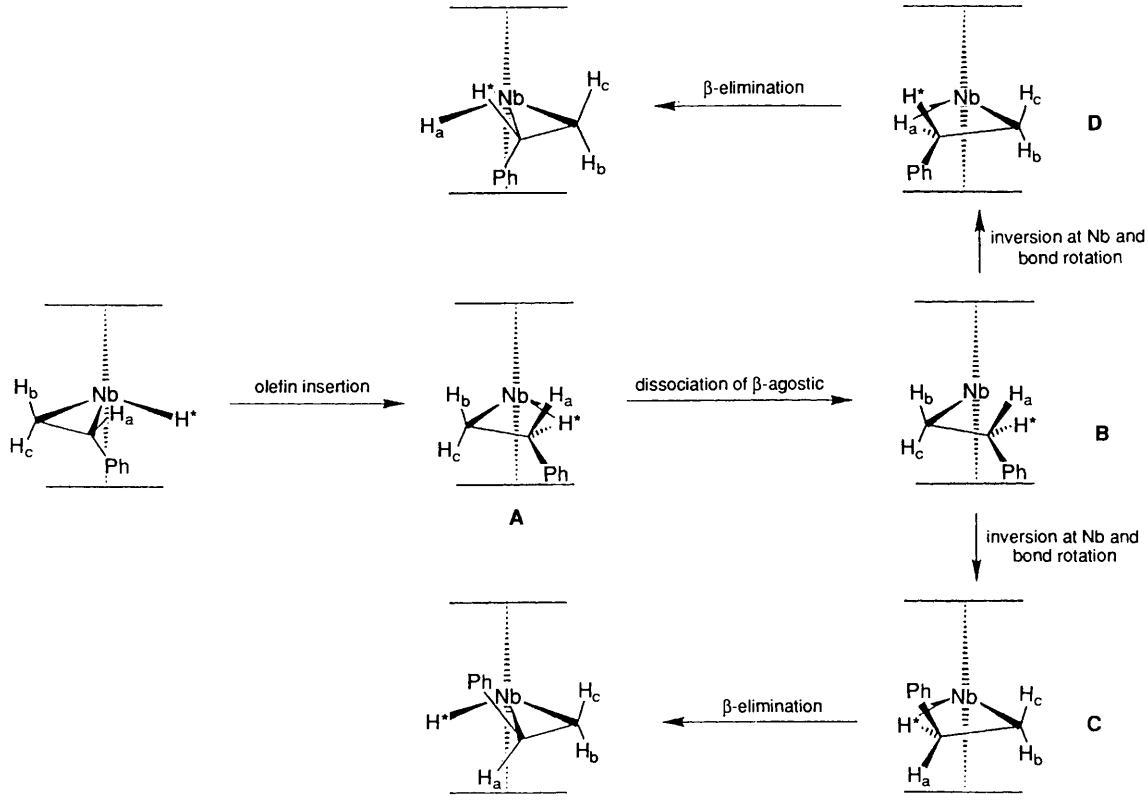


Fig. 3 The dissociative mechanism, involving rotation of a non-agostic alkyl, proposed to account for part of the exchange processes in compound **9**. The figures use a modified Newman-type projection for clarity, the η-C_9H_7 rings are represented as horizontal lines

experiments were found to display large error bars, and the T_1 values determined by this technique differed greatly from those determined by an inversion-recovery experiment. These data were thus disregarded as suspect.

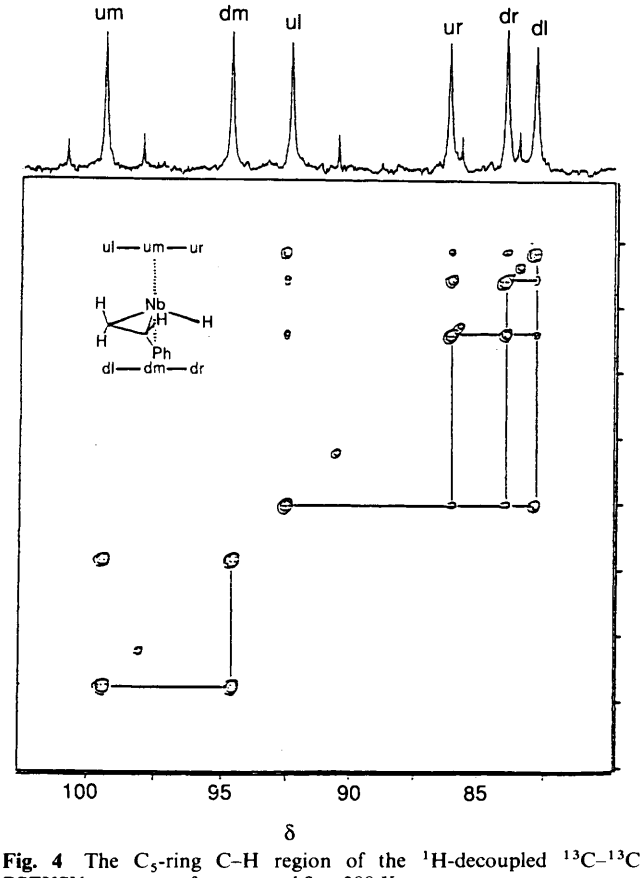


Fig. 4 The C_5-ring C–H region of the ^{1}H-decoupled ^{13}C–^{13}C PSEXSY spectrum of compound **9** at 288 K

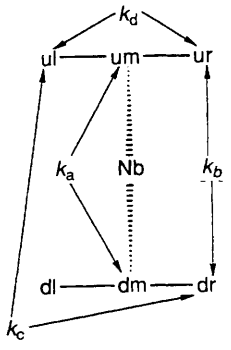


Fig. 5 The four distinct exchange rates that are observed in the exchange of the C_5-ring C–H resonances of compound **9**

Table 3 Magnetisation transfer (k_{MT}) rates for *endo*-[NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)] **9** obtained using ^{13}C PSEXSY experiments[a,b]

	Rates[c]/s^{-1}			
T/K	k_a	k_b	k_c	k_d
283	2.15(11)	1.49(11)	0.44(13)	0.41(28)
288	4.29(2)	2.98(6)	1.05(6)	0.41(18)
298	10.23(10)	7.66(72)	1.71(23)	0.90(66)
308	26.67(21)	18.51(99)	3.50(32)	4.45(85)

[a] All data at 75.43 MHz, [$^2H_6$]benzene. [b] Analysis was performed using the D2DNMR program. [c] Rates are labelled as discussed in the text.

The PSEXSY experiment and the D2DNMR program were developed to study exchange in heteronuclear NMR;[34] this experiment is well suited to ^{13}C since ^{13}C is a dilute spin and there are no complications due to ^{13}C–^{13}C nuclear Overhauser enhancement (NOE) or scalar coupling. The most serious disadvantage is that a very strong sample is required so that a two-dimensional data set can be obtained in reasonable time. Fig. 4 shows the region of the ^{13}C–^{13}C PSEXSY containing the C_5-ring C–H resonances of *endo*-[NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)] at 288 K.

Analysis of the data shows that there are four distinct rates (Fig. 5), this is consistent with four possible exchange events (u = up, d = down, r = right, l = left, m = middle): (*i*) the simple up-down exchange (um ⟷ dm) labelled k_a, (*ii*) the up-down exchange of the diastereotopic carbons (ul ⟷ dl) and (ur ⟷ dr) labelled k_b, (*iii*) the cross-exchange (ul ⟷ dr) and (ur ⟷ dl) labelled k_c, and (*iv*) the left-right exchange within one ring (ur ⟷ ul) and (dr ⟷ dl) labelled k_d.

The ^{13}C PSEXSY experiment was performed for **9** at four temperatures and the magnetisation transfer rates (k_{MT}) thus obtained are presented in Table 3.

The rates can be placed in order, it is clearly the case that k_a is the fastest exchange rate followed by k_b, and that k_c and k_d are slower than either k_a or k_b. However, the order of k_c and k_d is not clear, indeed at all temperatures except 288 K these rates are the same within experimental error (3 e.s.d.s). Attempts were made to investigate the relationship between the experimentally measured rates k_a, k_b, k_c, k_d and the mechanistic rates by considering certain limiting cases. These investigations did not give satisfactory results and it did not prove possible to analyse the data in this way. Thus, we have not been able to investigate the relative activation barriers to the in-place rotation and dissociative exchange processes in *endo*-[NbH(η-C_9H_7)$_2$(η-H_2C=CHPh)].

Experimental

All preparations, manipulations and reactions were carried out under an inert atmosphere of dinitrogen (< 10 ppm oxygen, < 20 ppm water) using standard Schlenk-tube and vacuum-line techniques, or in a dry-box. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

Solvents were pre-dried over activated molecular sieves and then distilled from potassium [tetrahydrofuran (thf), 1,2-dimethoxyethane (dme)], sodium [toluene, light petroleum (b.p. 100–120 °C)], sodium–potassium alloy [light petroleum (b.p. 40–60 °C unless otherwise stated), diethyl ether, pentane], or phosphorus pentaoxide (dichloromethane), under an inert atmosphere of dinitrogen before use. Deuteriated solvents for NMR samples were used as received (Aldrich), or after drying over Na–K alloy, samples being prepared in the dry-box. Celite 545 filtration aid (Koch–Light) was pre-dried in an oven at 80 °C before use.

NMR spectra were recorded on either a Brüker AM-200 [^{1}H (200 MHz), ^{11}B (64.17 MHz)] or a Brüker AM-300 [^{1}H (300 MHz), ^{13}C (75.43 MHz), ^{31}P (121.44 MHz)] spectrometer. Spectra were referenced internally using the residual solvent (^{1}H and ^{13}C) resonances relative to tetramethylsilane (δ = 0), or externally using either trimethyl phosphate [P(O)(OMe)$_3$] in D_2O (^{31}P) or BF_3·Et_2O (^{11}B). All chemical shifts are quoted in δ, high-field shifts being taken as negative, and coupling constants are in Hertz (Hz). NMR samples were either prepared under nitrogen in screw-capped tubes (Wilmad), or under vacuum in sealed soda-glass NMR tubes. Two-dimensional NMR experiments were acquired using standard Brüker software, and processed using an ASPECT 3000 computer.

Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data handling system supplied by Mass Spectrometry Services Ltd. Elemental analyses were performed by the Analysis Department in this laboratory or, in the cases of very air-sensitive compounds, by Analytische Laboratorien, Elbach. Infrared spectra were recorded as CsI or KBr pellets on a Masston Polaris FT-IR interferometer.

The compound [$NbCl_4(thf)_2$] was prepared by a literature method.[35] Indene and styrene (Aldrich) were distilled prior to use, all other reagents were used as received.

The salt $Li[C_9H_7]$ was prepared by the addition of LiBu (100 cm^3 of 1.6 mol dm^{-3} solution in hexanes, 0.16 mol) to a solution of indene (20 g, 0.17 mol) in light petroleum (600 cm^3). After stirring for 48 h the product was collected on a frit, washed with light petroleum (2 × 50 cm^3) and dried *in vacuo*. Yield 17.8 g, 91%.

The salt $Na[C_9H_7]$·thf was prepared by slowly (1 h) adding a thf (200 cm^3) solution of indene (30 g, 0.25 mol) to a suspension of washed NaH (10 g, 0.4 mol) in thf (100 cm^3). After stirring for 15 h the solution was filtered and the solvent removed under reduced pressure to give a light brown solid which was washed with a little light petroleum (50 cm^3). The stoichiometry was confirmed by ^1H NMR spectroscopy in CD_3CN before use. Yield 90%.

Preparations.—$[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ **1**. A vigorously stirred suspension of $[NbCl_4(thf)_2]$ (14.47 g, 38.2 mmol) in thf (80 cm^3) was treated with a solution of $Li[C_9H_7]$ (9.325 g, 76.4 mmol) in thf (120 cm^3). During the addition the yellow solid turned green and then gave a red solution. The mixture was stirred overnight. The green solid was isolated on a bed of Celite, then extracted into warm CH_2Cl_2 (250 cm^3), filtered and cooled to −80 °C giving green crystals which became red on drying *in vacuo*. A second crop was obtained by reducing the volume of the mother-liquors to 60 cm^3 and cooling to −80 °C. Yield 5.15 g, 34%.

$[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ **2**. A stirred mixture of $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ (1.8 g, 4.6 mmol) and $NaBH_4$ (1.0 g, 26 mmol) was treated with dme (80 cm^3). After 30 s gas was evolved and the solution became purple. After 4 h the solution was filtered and the solvent removed under reduced pressure. The mauve residue was extracted into toluene (40 cm^3), filtered and the volume of the filtrate was reduced to 30 cm^3 and pentane (15 cm^3) added. Cooling the solution to −80 °C gave purple crystals which were washed with cold pentane. Yield 1.23 g, 80%. An analytically pure sample was obtained after two further recrystallisations from toluene–pentane.

One-pot preparation of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ **2**. A stirred suspension of $[NbCl_4(thf)_2]$ (21.1 g, 55.8 mmol) in thf (200 cm^3) was treated with a solution of $Na[C_9H_7]$·thf (23.5 g, 101.6 mmol) in thf (300 cm^3), instantly giving a dark red–brown suspension which was stirred overnight. The solvent was removed under reduced pressure to give an oily solid. Sodium tetrahydroborate (4 g, 105 mmol) was added, followed by dme (600 cm^3), slight effervescence being observed. After stirring overnight, the solvent was removed under reduced pressure from the purple solution and the product recrystallised from either toluene–light petroleum (1:1), hot light petroleum (b.p. 100–120 °C), or used without further purification. Typical yield 4.8 g, 14.2 mmol, 25% based on $[NbCl_4(thf)_2]$.

$[NbH(\eta\text{-}C_9H_7)_2(PMe_2Ph)]$ **3**. A solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ (500 mg, 1.5 mmol) in toluene (40 cm^3) was treated with PMe_2Ph (0.5 cm^3, ≈2 equivalents) giving a dark blue solution which was left to stand for 80 h. Volatiles were removed under reduced pressure, and any borane products sublimed onto a −196 °C probe at 10^{-2} mmHg. The residue was extracted into diethyl ether (60 cm^3) giving a blue-green solution. Filtration and cooling to −80 °C gave green crystals. Yield 250 mg, 36%.

$[NbH(\eta\text{-}C_9H_7)_2(NC_5H_5)]$ **4**. A frozen (−196 °C) solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ (1.23 g, 3.64 mmol) in toluene (100 cm^3) was treated with an excess of pyridine (7 cm^3). The vessel was evacuated and back-filled with hydrogen, and allowed to warm to room temperature. A dark green solution resulted, which was stirred for 5 h. The solvent was removed under reduced pressure, and C_5H_5N·BH_3 removed by vacuum sublimation (2 h, 40 °C, 10^{-2} mmHg) to a probe at −196 °C. The residue was extracted into toluene (100 cm^3), filtered and the volume reduced to 20 cm^3. Dark green needles were produced on cooling to −25 °C. Despite repeated attempts at purification, these needles were shown by NMR always to contain at least 20% pyridine. Yield 0.6 g, 41%.

$[Nb(\eta\text{-}C_9H_7)(CO)_4]$ **5**. A solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ (600 mg, 1.8 mmol) in toluene (60 cm^3) was evacuated and NMe_3 (≈10 mmol) distilled into the vessel and CO (1 atm) was admitted. Over 1 h the solution became orange and was stirred overnight. The solvent was removed under reduced pressure and the residue was extracted into pentane (50 cm^3) and filtered. The filtrate was cooled to −80 °C to give the yellow–brown microcrystalline product. Yield 190 mg, 33%.

$[Nb(\eta\text{-}C_9H_7)_2(\eta^3\text{-}CH_2CHCH_2)]$ **6**. Allene (≈6 mmol) and NMe_3 (≈4 mmol) were vacuum transferred using a calibrated vacuum manifold into a 200 cm^3 Young's ampoule containing a solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ (500 mg, 1.5 mmol) in toluene (40 cm^3) cooled to −196 °C. The solution was warmed to room temperature and stirred at 20 °C for 36 h, producing very little colour change. The solvent was removed under reduced pressure, and the residue extracted with light petroleum (50 cm^3), filtered and cooled to −80 °C to give a dark powder. Yield 40%.

$[Nb(\eta\text{-}C_9H_7)_2(\eta^3\text{-}MeCHCHCHCH_2Me)]$ **7**. A solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2]$ (1.15 g, 3.4 mmol) in toluene (80 cm^3) in a Young's ampoule was treated with *trans,trans*-hexa-2,4-diene (0.6 cm^3, 6 mmol). The solution was cooled to −196 °C and NMe_3 (≈12 mmol) added by vacuum transfer. The solution was warmed to room temperature and stirred for 36 h giving a very deep mauve solution. The solvent was removed under reduced pressure and the residue extracted into light petroleum (3 × 70 cm^3), filtered through Celite and cooled to −80 °C giving purple polycrystallites. Yield 0.7 g, 51%.

endo-$[NbH(\eta\text{-}C_9H_7)_2(\eta\text{-}H_2C{=}CHPh)]$ **9**. A solution of $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ (1.5 g, 4.5 mmol) in toluene (90 cm^3) was treated with an excess of styrene (3–4 cm^3) and NMe_3 (≈ 1 cm^3) added by vacuum transfer. The solution soon became orange and was stirred overnight. The solvent was removed under reduced pressure and the residue was extracted into diethyl ether–pentane (1:1, 300 cm^3) and filtered. The volume of the filtrate was reduced to 60 cm^3 under reduced pressure. Cooling to −80 °C gave the dark orange polycrystalline product. Yield 900 mg, 46%.

Analysis of the ^{13}C–^{13}C *PSEXSY Data for* **9**.—The Brüker PSEXSY.AUR microprogram[36] was modified to give heteronuclear spectra using composite pulse decoupled ^1H decoupling. The spectral width was made as narrow as possible by folding. The mixing times were selected carefully to provide satisfactory cross-peak intensities for both the slow- and fast-exchange rates. The recycle delay was set to 5 × T_1, the ^{13}C NMR T_1 values were determined by inversion-recovery and are in the range 1–1.3 s. Prior to Fourier transformation the data were treated with suitable window functions, typically Lorentzian (LB = 6 Hz) in t2 with shifted sine-bell squared in t1. The unsymmetrised matrix was examined before the data were symmetrised, no appreciable artifacts were found; the positive levels were found to be insignificant.

Standard Brüker software was used to measure volume integrals for the diagonal- and cross-peaks in the C_5 region of the ^{13}C-$\{^1H\}$ PSEXSY spectrum of **9** at four different temperatures. When these integrals were measured more than once the errors were found to be relatively small. Hence, it was decided not to record such integrals more than once or to apply statistical methods to these data. The volume integrals were used as inputs to the D2DNMR program. The rates in Table 3 are the mean values for those rates which are equivalent by symmetry together with standard deviations. No attempts were made to produce more rigorous estimated errors by recording each data set more than once.

Conclusion

We have presented a facile synthesis of the indenyl complexes $[Nb(\eta\text{-}C_9H_7)_2Cl_2]$ and $[Nb(\eta\text{-}C_9H_7)_2(\mu\text{-}H_2BH_2)]$ and demonstrated that the tetrahydroborate complex is a useful

precursor to a range of $Nb(\eta\text{-}C_9H_7)_2$ complexes. The chemistry of these complexes reflects the chemistry of their $Nb(\eta\text{-}C_5R_5)_2$ (R = H or Me) analogues, although significant differences are observed. The reasons for these differences have been investigated together with a number of fluxional processes in these complexes. These investigations have provided further evidence for enhancement of exchange processes which are associated with ring-slipped η^3-indenyl intermediates or transition states.

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