Synthesis, Structure and Dynamic Behaviour of the Compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\sigma\text{-C}_5\text{H}_5)(\text{NBu}^t)]$ *

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The new compound $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\sigma\text{-C}_5\text{H}_5)(\text{NBu}^t)]$ has been prepared and its crystal structure determined. Variable-temperature NMR studies reveal diverse dynamic processes including exchange between the σ- and η^5-cyclopentadienyl rings.

Organometallic imido complexes[1] are important since they are implicated in industrial processes and synthetic methodologies. Although bis(η-cyclopentadienyl) derivatives of the transition metals have been a focus of considerable interest for many years,[2] bis(η-cyclopentadienyl)imido derivatives have been elusive. Following our recent synthesis of such derivatives of molybdenum and tungsten[3] we now report the synthesis and properties of the bis(η-cyclopentadienyl)imido-niobium derivative $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\sigma\text{-C}_5\text{H}_5)(\text{NBu}^t)]$.

Results and Discussion

Treatment of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2(\text{NBu}^t)]$[4] with $\text{Na}(\text{C}_5\text{H}_5)$ in tetrahydrofuran (thf) at room temperature affords blue slightly air-sensitive crystals of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\sigma\text{-C}_5\text{H}_5)(\text{NBu}^t)]$ **1** in *ca.* 63% yield. The crystal structure of **1** has been determined by X-ray diffraction (Fig. 1) and selected bond distances and angles are given in Table 1, atomic coordinates in Table 2. The compound is a monomer in the solid state. The metal–nitrogen bond length (Nb–N 1.756 Å) is comparable to the values found for other Nb=NR groups where NR acts as a four-electron donor ligand.[5] The Nb–N–C linkage is nearly linear [Nb–N–C(16) 176.8°] which further implies that there is a metal–nitrogen triple bond.[1] Supporting spectroscopic evidence comes from the large chemical shift difference ($\Delta\delta = 38.0$ ppm) between the quaternary and the methyl carbons of the NBu^t group in the $^{13}\text{C-}\{^1\text{H}\}$ NMR spectrum of **1**. This large value lies at the high end of the range previously recorded for *tert*-butylimido species,[4,6] and indicates a low electron density on the imido nitrogen due to the high degree of $\text{N}\rightarrow\text{M}$ π donation.[1,7]

The (ring centroid)–metal–(ring centroid) angle $[\text{Cp}_{\text{cent}(1)}\text{–Nb–Cp}_{\text{cent}(2)}$ 124.51°] of complex **1** is smaller than for the niobium metallocene derivatives $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2]^-$ (141.2°),[8] $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ (141.6°),[9] $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\eta\text{-C}_2\text{H}_4)\text{Et}]$ (132.4°),[10] and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (130.9°).[11] Also, the niobium-ring centroid distances $[\text{Nb–Cp}_{\text{cent}(1)}$ 2.217 Å and $\text{Nb–Cp}_{\text{cent}(2)}$ 2.208 Å] are slightly longer than the 2.03–2.10 Å normally found in bis(η-cyclopentadienyl)niobium compounds. Finally, the $\sigma\text{-C}_5\text{H}_5$ ligand is bent away from the NBu^t group (see Fig. 1 and Scheme 1); this presumably reflects a degree of steric congestion at the metal centre.

These structural data for complex **1** are closely reminiscent of those for the bis(η-cyclopentadienyl)molybdenum compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$ and for the cation $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)\text{Me}]^+$.[3] It was proposed for these molybdenum compounds that the lone pair on the imido ligand was destabilising the metal–η-cyclopentadienyl bonding. Photoelectron spectral data supported this suggestion. Therefore, it seems likely that there is also a degree of destabilisation of the bonding of the bis(η-cyclopentadienyl)niobium system. Further, the substitutional lability of the η-cyclopentadienyl rings in the bis(η-cyclopentadienyl)molybdenum compounds was associated with the structural features and bonding.[3]

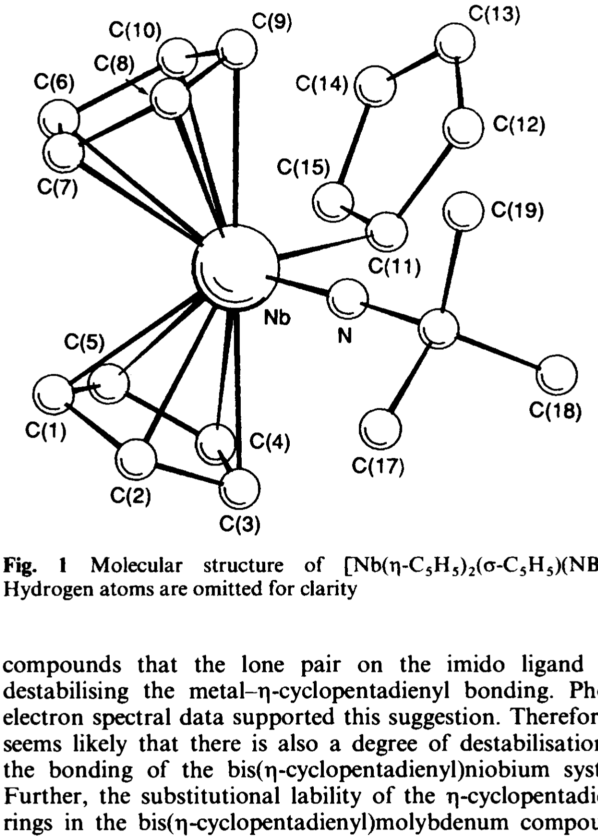

Fig. 1 Molecular structure of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\sigma\text{-C}_5\text{H}_5)(\text{NBu}^t)]$. Hydrogen atoms are omitted for clarity

The variable-temperature NMR spectra of complex **1** in CD_2Cl_2 show three fluxional processes, namely rotation of the $\sigma\text{-C}_5\text{H}_5$ ligand about the Nb–C_{ipso} bond, migration of the niobium centre between the carbon atoms of the $\sigma\text{-C}_5\text{H}_5$ ligand, and exchange between the η- and $\sigma\text{-C}_5\text{H}_5$ ligands. The slow-exchange-limit ^1H NMR spectrum at 173 K (Fig. 2) shows two resonances for the two $\eta\text{-C}_5\text{H}_5$ ligands, at δ 5.96 and 5.09. The inequivalence of the two rings arises from the asymmetric disposition of the $\sigma\text{-C}_5\text{H}_5$ ligand in the static structure (see Scheme 1). Accordingly, the $\sigma\text{-C}_5\text{H}_5$ ligand shows five resonances, at δ 6.79, 6.56, 6.27, and 6.22 for the olefinic hydrogens H_α, $\text{H}_{\alpha'}$, H_β, $\text{H}_{\beta'}$, and at 4.97 for the hydrogen on the niobium-bound *ipso*-carbon. The hydrogens of the NBu^t group are observed as a singlet at δ 1.03.

As the temperature is raised, the resonances due to the olefinic hydrogens of the $\sigma\text{-C}_5\text{H}_5$ ligand broaden and show pairwise coalescence while that due to the hydrogen on the *ipso*-carbon is

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Selected bond lengths (Å) and angles (°) for [Nb(η-C_5H_5)$_2$-(σ-C_5H_5)(NBu^t)]

Nb–N	1.756(3)	Nb–C(1)	2.516(4)
Nb–C(2)	2.425(4)	Nb–C(3)	2.480(4)
Nb–C(4)	2.531(4)	Nb–C(5)	2.586(4)
Nb–C(6)	2.580(4)	Nb–C(7)	2.486(4)
Nb–C(8)	2.453(4)	Nb–C(9)	2.466(4)
Nb–C(10)	2.517(4)	Nb–C(11)	2.330(3)
N–C(16)	1.449(5)	C(11)–C(12)	1.458(5)
C(11)–C(15)	1.454(5)	C(12)–C(13)	1.355(5)
C(13)–C(14)	1.421(6)	C(14)–C(15)	1.357(5)
C(16)–C(17)	1.526(6)	C(16)–C(18)	1.523(6)
C(16)–C(19)	1.517(6)	Nb–Cp$_{cent(1)}$	2.217
Nb–Cp$_{cent(2)}$	2.208		
Nb–N–C(16)	176.8(3)	N–Nb–C(11)	91.8(1)
Nb–C(11)–C(12)	112.0(2)	Nb–C(11)–C(15)	114.3(2)
C(12)–C(11)–C(15)	104.0(3)	N–Nb–Cp$_{cent(1)}$	112.01
N–Nb–Cp$_{cent(2)}$	113.03	C(11)–Nb–Cp$_{cent(1)}$	102.43
C(11)–Nb–Cp$_{cent(2)}$	106.82	Cp$_{cent(1)}$–Nb–Cp$_{cent(2)}$	124.51

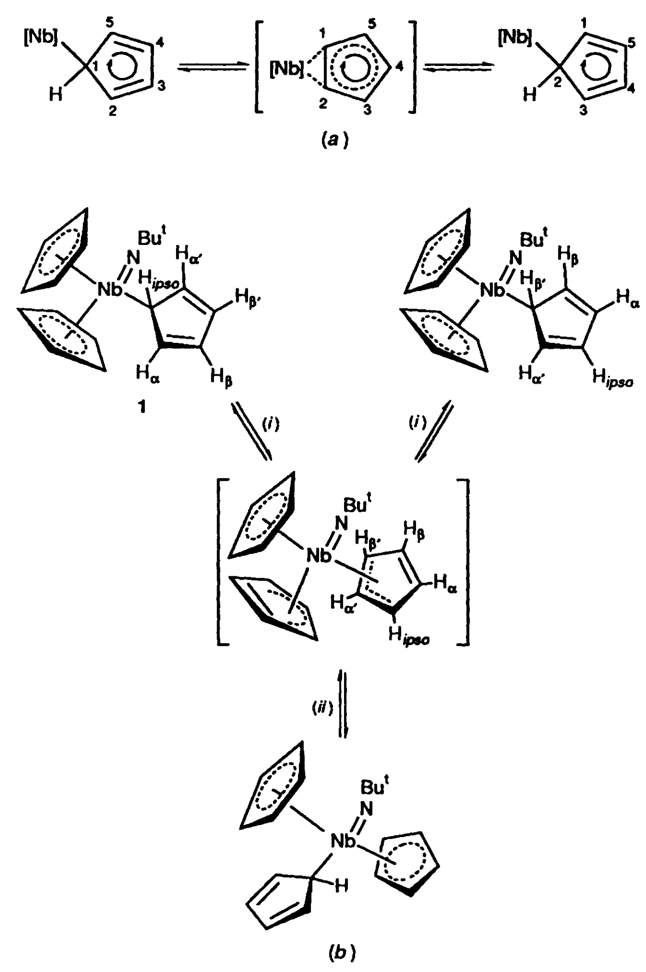
Cp$_{cent(1)}$ and Cp$_{cent(2)}$ refer to the computed η-C_5H_5 centroids for atoms C(1)–C(5) and C(6)–C(10) respectively.

Table 2 Atomic coordinates for complex **1**

Atom	X/a	Y/b	Z/c
Nb	0.041 35(1)	0.319 73(1)	0.020 93(3)
N	−0.035 3(1)	0.305 2(1)	0.115 0(3)
C(1)	0.155 1(3)	0.318 4(3)	0.147 0(7)
C(2)	0.105 2(3)	0.318 6(3)	0.256 4(6)
C(3)	0.074 3(3)	0.380 2(2)	0.256 6(5)
C(4)	0.103 4(3)	0.417 3(2)	0.142 4(5)
C(5)	0.154 5(2)	0.379 9(3)	0.073 7(6)
C(6)	0.118 6(2)	0.264 1(2)	−0.178 9(6)
C(7)	0.096 9(3)	0.215 2(2)	−0.071 4(6)
C(8)	0.027 7(3)	0.207 8(2)	−0.093 1(6)
C(9)	0.006 8(2)	0.251 7(2)	−0.200 6(6)
C(10)	0.061 9(3)	0.286 7(2)	−0.251 8(5)
C(11)	−0.001 5(2)	0.415 1(2)	−0.099 4(4)
C(12)	−0.057 9(2)	0.399 0(2)	−0.199 1(4)
C(13)	−0.042 8(2)	0.418 4(2)	−0.342 9(4)
C(14)	0.021 7(2)	0.449 4(2)	−0.343 2(4)
C(15)	0.046 2(2)	0.449 0(2)	−0.198 9(4)
C(16)	−0.096 5(2)	0.292 8(2)	0.200 6(4)
C(17)	−0.077 5(3)	0.263 1(3)	0.355 1(5)
C(18)	−0.133 2(2)	0.359 5(2)	0.221 5(6)
C(19)	−0.140 3(2)	0.243 4(3)	0.113 7(7)

unchanged (Fig. 2). This is consistent with the onset of rotation of the σ-C_5H_5 ligand about the Nb–C$_{ipso}$ bond. The coalescence temperature T_c for the resonances at δ 6.79 and 6.56 is T_c = 199 K, for those at 6.27 and 6.22, 188 K. The ligand-rotation process will also necessarily result in exchange between the two η-C_5H_5 ligands and hence coalescence of their resonances at δ 5.96 and 5.09 (T_c = 209 K, see Fig. 2).

At 223 K the σ-C_5H_5 ligand shows three resonances of relative intensities 2:2:1 indicating that the rate constant of rotation is large compared to the chemical shift difference between H_α and $H_{\alpha'}$, and between H_β and $H_{\beta'}$. When the temperature is raised above 223 K these three resonances broaden and coalesce, with a broad, exchange-averaged, resonance emerging from the baseline at 263 K. This behaviour is characteristic of the metal centre in a metal–cyclopentadienide system migrating between the carbon atoms of the σ-C_5H_5 ligand, first observed in [Hg(σ-C_5H_5)$_2$].[12] At temperatures above 283 K (Fig. 3) the singlet resonance at δ 5.60 assigned to the two η-C_5H_5 ligands (now equivalent on the NMR time-scale) begins to broaden due to exchange between the η-C_5H_5 and σ-C_5H_5 ligands ($\eta^5 \longleftrightarrow \sigma$ ring shift). At 353 K a single resonance is observed for all the C_5H_5 ligands in **1**. Almost identical, albeit less well resolved, fluxional behaviour has been observed in the molybdenum compound [Mo(η-C_5H_5)$_2$(σ-C_5H_5)(NO)],[13] which is isoelectronic with **1** if NO is acting as a three-electron donor.



Scheme 1 (*a*) A 1,2-shift mechanism for migration of the niobium centre around the σ-C_5H_5 ring, [Nb] = Nb(η-C_5H_5)$_2$(NBu^t). (*b*) Ring-slip (concerted or otherwise) steps (*i*) lead to a 1,3-shift mechanism for migration of the niobium centre around the σ-C_5H_5 ring; steps (*i*) and (ii) lead to η-$C_5H_5 \longleftrightarrow \sigma$-$C_5H_5$ ring exchange

The same analysis is applicable to the variable-temperature ^{13}C-{^1H} NMR spectra. The spectrum at 180 K (Fig. 4) shows different resonances for the carbons of the σ-C_5H_5 ligand and two for the η-C_5H_5 ligands. Upon warming, rotation about the Nb–C$_{ipso}$ bond results in pairwise coalescence of the olefinic carbon resonances of the σ-C_5H_5 ring, and the two η-C_5H_5 rings also become equivalent. At temperatures above 233 K (Fig. 5) the resonances due to the σ-C_5H_5 ligand (at δ 138.7, 120.0 and 57.2) broaden and coalesce as the niobium centre migrates between the ring carbons. Finally, reversible $\eta^5 \longleftrightarrow \sigma$ ring shifts result in a single resonance for all C_5H_5 ligands (data not shown).

Of the three exchange processes described above, it is possible only to extract the activation energy of the rotation process (see below). Rotation results in the pairwise coalescences observed in the ^1H and ^{13}C-{^1H} NMR spectra in Figs. 2 and 4. The rate constant of rotation at the coalescence temperatures can be estimated using $k = \pi(\Delta v)2^{\frac{1}{2}}$.[14] Three such rate constants can be calculated in either the ^1H or ^{13}C-{^1H} NMR spectra (Table 3) and the activation free energy of rotation is determined to be 43.4 kJ mol^{-1}.

Mechanistic Considerations.—The mechanisms of the two higher-temperature processes are of interest. The η^5-$C_5H_5 \longleftrightarrow \sigma$-$C_5H_5$ exchange process likely proceeds *via* a η^3-C_5H_5/η^3-C_5H_5 intermediate formed by stepwise or concerted hapticity

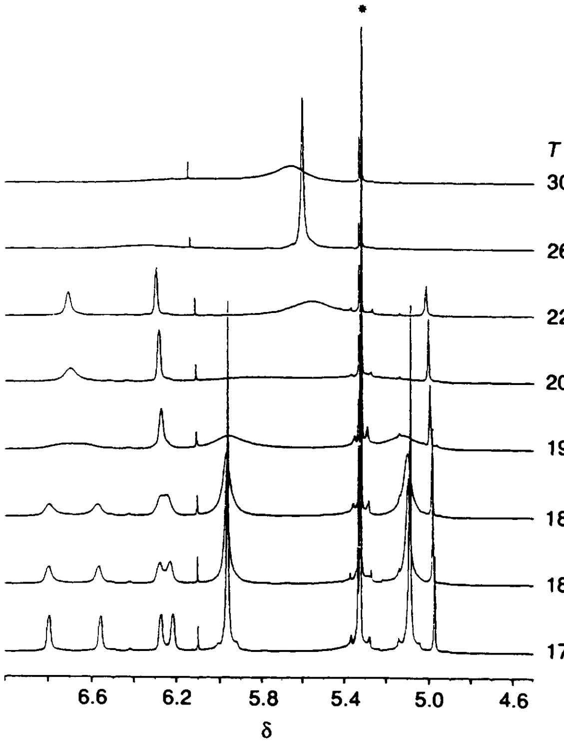


Fig. 2 Low-temperature 500 MHz ^1H NMR spectra of $[Nb(\eta-C_5H_5)_2(\sigma-C_5H_5)(NBu^t)]$ in CD_2Cl_2, showing the dynamic behaviour of the C_5H_5 ligands. At 173 K the five inequivalent hydrogens of the $\sigma-C_5H_5$ ligand are at δ 6.79, 6.56, 6.27, 6.22 and 4.97, and the inequivalent $\eta-C_5H_5$ rings are at 5.96 and 5.09. The NBu^t hydrogens are at δ 1.03 (not shown). The asterisk denotes the solvent resonance

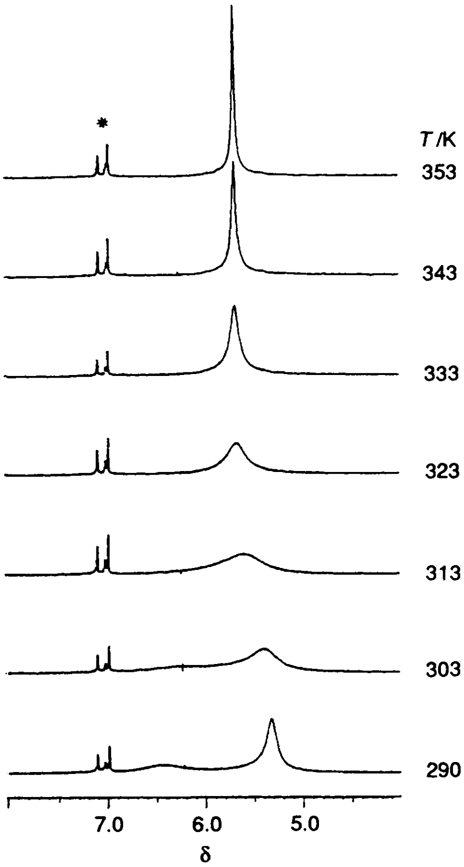


Fig. 3 Variable-temperature 300 MHz ^1H NMR spectra of $[Nb(\eta-C_5H_5)_2(\sigma-C_5H_5)(NBu^t)]$ in $[^2H_8]$toluene, showing the equivalence of all three C_5H_5 ligands at high temperatures. The asterisk denotes the solvent resonance

changes of the two C_5H_5 rings concerned. Migration of the niobium centre in complex **1** between the carbons of the $\sigma-C_5H_5$ ligand could occur by a 1,2- or 1,3-shift mechanism. In cases where the mechanisms of such migrations have been investigated, a 1,2-shift mechanism is favoured.[15] A 1,3-shift mechanism can be envisaged to proceed *via* an allyl-type metal–$\eta^3-C_5H_5$ intermediate. In 18-electron $L_nM(\sigma-C_5H_5)$ compounds, where L is a *simple* two-electron donor ligand, this intermediate would be a 20-electron species, and the mechanism is disfavoured. In **1**, which has formally a 20-electron niobium centre, the destabilising effect of the imido lone-pair electrons could facilitate an $\eta^5 \longrightarrow \eta^3$ ring-slippage shift of one of the $\eta-C_5H_5$ ligands. The 1,3-shift mechanism would therefore have the same intermediate as for the $\eta^5 \longleftrightarrow \sigma$ ring-exchange process and possibly become the dominant mechanism in **1** because its activation energy has been lowered by the special bonding between the imido lone pairs and the niobium centre. Experimentally, if the rate constants of the two higher-temperature fluxional processes in **1** are identical, the 1,3-shift mechanism would be operating.

We examined the possibility of determining the rate constants of the two processes but the exchange system proved to be intractable by the methods available. We therefore turned to more qualitative methods. We noted that, in the ^1H NMR spectrum at 283 K (Fig. 6) and the $^{13}C-\{^1H\}$ spectrum at 301 K (Fig. 5), the $\sigma-C_5H_5$ resonances are almost at the regime of fast exchange while the $\eta-C_5H_5$ resonance remains relatively sharp. This observation alone argues strongly against a common mechanism for the two exchange processes. Further, as Cotton and co-workers[15] pointed out in their classic paper on the fluxionality in $[Fe(\eta-C_5H_5)(CO)_2(\sigma-C_5H_5)]$, a 1,2-shift mechanism for the migration of the metal centre will lead to faster *initial* broadening of the resonances assigned to the two hydrogens (and carbons) in α positions relative to the *ipso* carbon. Similarly, a 1,3-shift mechanism will result in preferential initial broadening of the resonances assigned to the two β-carbons and two β-hydrogens.[16,17] The assignment of the mechanism then depends on these NMR spectroscopic assignments.

On the basis that the carbon and hydrogen nuclei in the α positions are closer to the niobium centre and therefore more affected by the asymmetry at the metal centre, we predict that the chemical shift difference between the α and α′ nuclei will be larger than that between the β and β′ nuclei.[16] We therefore propose that H_α and $H_{\alpha'}$ be assigned to the resonances at δ 6.79 and 6.56, and H_β and $H_{\beta'}$ to those at δ 6.27 and 6.22, in the ^1H NMR spectrum at 173 K. Using selective heteronuclear double-resonance methods, we then assigned C_α and $C_{\alpha'}$ to the resonances at δ 139.38 and 136.63 and C_β and $C_{\beta'}$ to those at δ 119.64 and 118.53, in the $^{13}C-\{^1H\}$ NMR spectrum at 183 K. Hence the chemical shift difference prediction is self-consistent in that what we assigned as the α-hydrogens are attached to the two carbons with the larger chemical shift difference. We also attempted a direct assignment by measuring the $^{13}C-^{13}C$ coupling pattern of the $\sigma-C_5H_5$ ligand using INADEQUATE (incredible natural abundance double quantum transfer experiment), but the compound is insufficiently soluble in common solvents for this experiment.

Close inspection of the ^1H and $^{13}C-\{^1H\}$ NMR spectra in the temperature range where initial broadening of the $\sigma-C_5H_5$ resonance occurs (Figs. 5 and 6) clearly shows that the greatest initial broadening occurs for the *ipso* and α,α′ resonances. This is particularly significant because the chemical shift difference between these resonances is greater than that between the *ipso* and β,β′ resonances. The mechanism for metal migration is clearly non-random, and the qualitative arguments presented

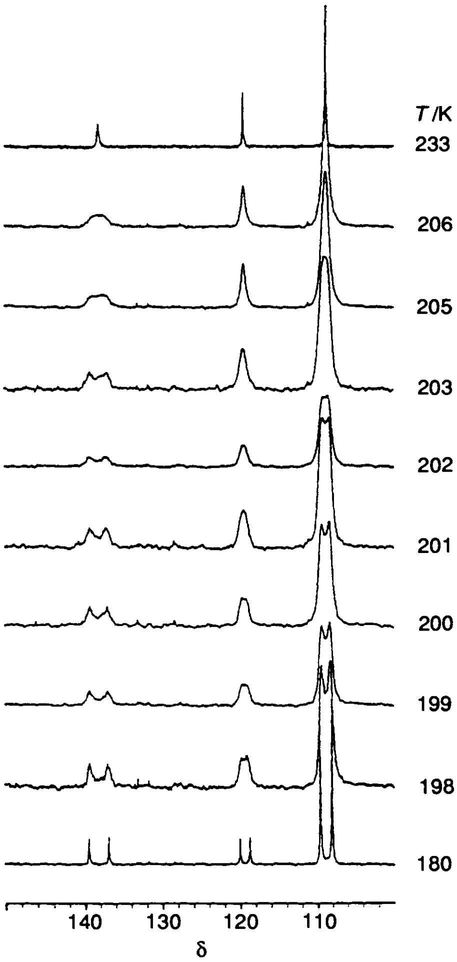


Fig. 4 Low-temperature 125.7 MHz ^{13}C-{^1H} NMR spectra of [$Nb(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NBu^t)$] in CD_2Cl_2, showing the dynamic behaviour of resonances due to the η-C_5H_5 rings (at δ 109.8 and 108.3) and the olefinic carbons of the σ-C_5H_5 ligand (at δ 139.5, 136.9, 120.0 and 118.7)

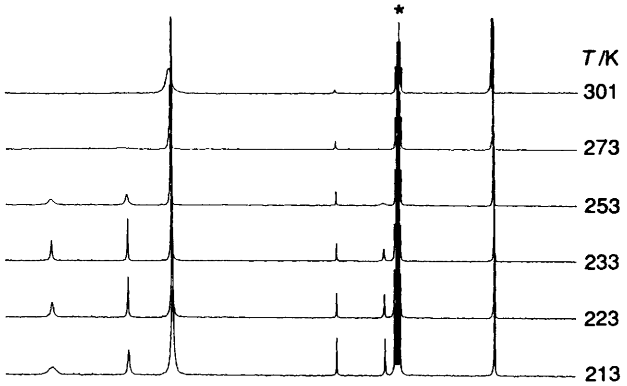


Fig. 5 Variable-temperature 125.7 MHz ^{13}C-{^1H} NMR spectra of [$Nb(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NBu^t)$] in CD_2Cl_2, showing preferential broadening of resonances due to the σ-C_5H_5 ligand above 233 K. The asterisk denotes the solvent resonance

above lead us to conclude that a 1,2-shift mechanism is operating for the σ-cyclopentadienyl ring in complex **1**.

It is important to note that, in cases where exchange between the η- and σ-C_5H_5 ligands in the same molecule is observed in the NMR spectrum, *i.e.* in [$Ti(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)_2$],[18] [$Mo(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NO)$],[13] and **1**, there are relatively facile pathways for the formation of the proposed η^3-C_5H_5/η^3-C_5H_5 intermediate. In [$Ti(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)_2$], as noted by Cotton and co-workers,[18] the metal centre has 16 electrons, and the ring-exchange process could proceed *via* the relatively accessible 18-electron intermediate [$Ti(\eta$-$C_5H_5)_2(\eta^3$-$C_5H_5)$-$(\sigma$-$C_5H_5)$]. In both [$Mo(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NO)$] and **1** the metal centres are formally 20-electron but, by analogy with [$Mo(\eta$-$C_5H_5)_2(NBu^t)$],[3] the extra electron pair resides in an orbital which is localised on the ligands. Nevertheless, the metal–ring bonding is weakened and the initial $\eta^5 \longrightarrow \eta^3$ ring slip could be described as an (18 + 2 electron)-⟶ 18-electron step; witness the ring-substitution lability in [$Mo(\eta$-$C_5H_5)_2(NBu^t)$]. In other 18-electron organotransition-metal compounds containing both η- and σ-C_5H_5 rings and where no such pathways for ring slip are available there is no $\eta^5 \longleftrightarrow \sigma$ ring exchange.

Table 3 Coalescence temperatures T_c and rate constants *k* for the Nb–C_{ipso} bond-rotation process in [$Nb(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NBu^t)$]

Δv/Hz	T_c/K	k/s^{-1}	Exchanging nuclei
27.5	188	122.2	H_β, $H_{\beta'}$ [a]
116.9	199	519.4	H_α, $H_{\alpha'}$ [a]
436.8	209	1940.7	η-C_5H_5, η-C_5H_5 [a]
162.3	200	721.1	C_β, $C_{\beta'}$ [b]
194.2	203	862.8	η-C_5H_5, η-C_5H_5 [b]
324.6	206	1442.2	C_α, $C_{\alpha'}$ [b]

[a] Data from the ^1H NMR spectra. [b] Data from the ^{13}C-{^1H} NMR spectra.

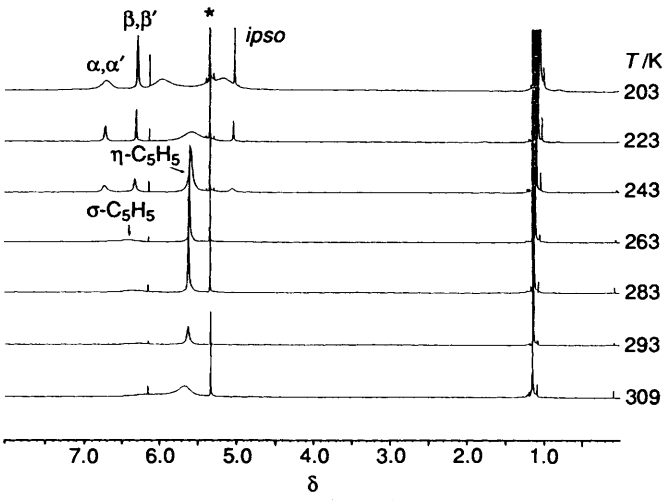


Fig. 6 Variable-temperature 500 MHz ^1H NMR spectra of [$Nb(\eta$-$C_5H_5)_2(\sigma$-$C_5H_5)(NBu^t)$] in CD_2Cl_2, showing preferential broadenings of resonances due to the C_5H_5 ligands. The asterisk denotes the solvent resonance

Conclusion

We have shown that σ-C_5H_5 rotation, metal migration around the σ-C_5H_5 ligand by a 1,2-shift, and η^5-C_5H_5/σ-C_5H_5 exchange occurs in complex **1**. Although the 1,3-shift mechanism is a possibility because it should share the same intermediate as the η^5-$C_5H_5 \longleftrightarrow \sigma$-$C_5H_5$ exchange process, the activation energy is still too high for it to become the dominant mechanism for metal migration. The η^5-$C_5H_5 \longleftrightarrow \sigma$-$C_5H_5$ exchange is facilitated by weakening of the metal–η^5-C_5H_5 bonding due to the extra lone pair on the imido nitrogen. It is tempting to suggest that such weakening of the bond(s) to other ligand(s) in the metal complex by an imido group could have interesting and important implications in catalysis.

Experimental

All manipulations and reactions were carried out under an atmosphere of dinitrogen (< 10 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a dry-box.

Solvents were pre-dried over activated 5 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] or phosphorus pentaoxide (dichloromethane). Deuteriated solvents for NMR samples were stored in ampoules over activated molecular sieves (C_6D_6) or with sodium ([$^2H_8$]-toluene) or dried using calcium hydride (CD_2Cl_2) and transferred by vacuum distillation.

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

Synthesis of $[Nb(\eta\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)(NBu^t)]$ **1**.—A solution of $[Nb(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$[4] (5.3 g, 17.7 mmol) in thf (350 cm^3) was treated dropwise (30 min) with sodium cyclopentadienide (3.58 g, 40.7 mmol) in thf (minimum volume) at room temperature and then the mixture was stirred for 12 h. The volatiles were removed under reduced pressure and the solid was extracted with toluene and filtered. The filtrate was evaporated to dryness. The bright dark green solid obtained was dissolved in the minimum amount of toluene, light petroleum (b.p. 40–60 °C, 100 cm^3) was added and the mixture placed at −25 °C. After 24 h the dark blue crystals were separated from the solvent and dried *in vacuo*. Yield 4.0 g, 63% (Found: C, 63.9; H, 3.8; N, 6.7. Calc.: C, 63.5; H, 3.9; N, 6.7%). Mass spectrum: *m*/*z* 359, $[M]^+$; 294, $[M - C_5H_5]^+$; 279, $[M - C_5H_5 - CH_3]^+$; and 223, $[M - C_5H_5 - NBu^t]^+$.

Crystallography.—$C_{19}H_{24}NNb$, $M = 359.31$, tetragonal, space group $P4_2/n$, $a = 19.887(12)$, $c = 8.783(7)$ Å, $F(000) = 1488$, scan mode ω–2θ, $\theta_{max} = 25°$, $U = 3473.2$ Å^3, $Z = 8$, $D_c = 1.374$ g cm^{-3}, μ(Mo-Kα) = 0.710 69 cm^{-1}, crystal size *ca.* 0.25 × 0.40 × 0.70 mm, total unique data 3054, number of observations $[I > 3\sigma(I)]$ 2027, observations/variables 10.6, $R_{merge} = 0.045$, $R = 0.029$, $R' = 0.030$ (Chebyshev parameters 7.28, −10.2, 6.09, −3.13, 0.158), maximum peak in final Fourier difference synthesis 0.4 e Å^{-3}.

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. Empirical absorption corrections were applied and the structure was solved using direct methods and Fourier difference synthesis, and refined using full-matrix least-squares, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located from the difference map, assigned a U_{iso} of 0.1 Å^2 and refined riding on the C atoms. Crystallographic calculations[19] were carried out using CRYSTALS on a Micro VAX 3800 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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