Synthesis, Spectroscopic Characterization and Dynamic Behaviour of Niobium Complexes with Poly(pyrazol-1-yl)methane Ligands†

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The complex $[\{NbCl_3(dme)\}_n]$ **1** (dme = 1,2-dimethoxyethane) reacted with an excess of bis(pyrazol-1-yl)methane (bzpm), bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) or bis(5-trimethylsilylpyrazol-1-yl)methane (btpzm) to give the binuclear complexes $[\{NbCl_3(bpzm)\}_2]$ **2**, $[\{NbCl_3(bdmpzm)\}_2]$ **3** and $[\{NbCl_3(btpzm)\}_2]$ **4**, respectively. Mononuclear acetylene complexes $[NbCl_3(L\text{–}L)(RC{\equiv}CR')]$ (R = R' = Ph, L–L = bpzm **5**, bdmpzm **6** or btpzm **7**; R = R' = CO_2Me, L–L = btpzm **8**; R = R' = Me, L–L = bpzm **9**, bdmpzm **10** or btpzm **11**) have been prepared from either the reaction of **2**–**4** with acetylenes or the interaction of acetylene complexes $[NbCl_3(dme)(RC{\equiv}CR')]$ with the appropriate L–L. This last reaction with tris(pyrazol-1-yl)methane (tpzm) or tris(3,5-dimethylpyrazol-1-yl)methane (tdmpzm) in the presence of 1 equivalent of $AgBF_4$ afforded the cationic complexes $[NbCl_2(L\text{–}L\text{–}L)(RC{\equiv}CR')]BF_4$ (R = R' = Ph, L–L–L = tpzm **12** or tdmpzm **13**; R = R' = Me, L–L–L = tpzm **14** or tdmpzm **15**). The structures of these complexes have been determined by spectroscopic methods. Variable-temperature NMR studies of some of the complexes were carried out in order to establish their fluxional behaviour in solution and free activation energy values were calculated at the coalescence temperature.

In recent years poly(pyrazol-1-yl)borates have been widely used in the preparation of a large number of metal complexes,[1] while the co-ordination behaviour of the isosteric poly(pyrazol-1-yl)methanes has received little attention. Although some earlier papers[2] described the synthesis of several mono- or bi-nuclear niobium or tantalum complexes with N-donor ligands, for instance 2,2'-bipyridine (bipy) or related ligands, little is known of the chemistry of heavier Group 5 metals with poly(pyrazol-1-yl) ligands. In addition to several poly(pyrazol-1-yl)methane–[3] and poly(pyrazol-1-yl)borato[4]–vanadium complexes, some hydridopoly(pyrazol-1-yl)borato–niobium and –tantalum derivatives have been described.[5] Arising from our research in the field of poly(pyrazol-1-yl)methane derivatives,[6] and with the aim of exploring the chemistry of niobium complexes towards this type of ligand, we have decided to try routes for the synthesis of poly(pyrazol-1-yl)methane niobium complexes. We now present full details concerning the syntheses and spectroscopic properties of several such derivatives.

Results and Discussion

First, the reactions of bis(pyrazol-1-yl)methane, bpzm, bis(3,5-dimethylpyrazol-1-yl)methane, bdmpzm, and bis(5-trimethylsilylpyrazol-1-yl)methane, btpzm, with $[\{NbCl_3(dme)\}_n]$ **1** (dme = 1,2-dimethoxyethane) were investigated. The standard reaction procedure involved the addition of the ligand (L–L), in a slight excess of the 1:1 molar ratio, to a solution of **1** in CH_2Cl_2 at room temperature to give, after stirring for 5 h, a suspension for bpzm and solutions for bdmpzm and btpzm. The products were isolated after appropriate work-up, as air-sensitive purple, brown and violet solids corresponding to the complexes $[\{NbCl_3(L\text{–}L)\}_2]$ [L–L = bpzm **2**, bdmpzm **3** or btpzm **4**; equation (1)]. They have consistent microanalyses

$$\frac{1}{n}[\{NbCl_3(dme)\}_n] + L\text{–}L \xrightarrow{CH_2Cl_2} \underset{\mathbf{1}}{} \quad \underset{\mathbf{2}\text{–}\mathbf{4}}{\tfrac{1}{2}[\{NbCl_3(L\text{–}L)\}_2]} + dme \qquad (1)$$

and the mass spectrum of **4** indicates a binuclear formulation (see Experimental section). Their IR spectra show a strong band at *ca.* 320 cm^{-1} in the region between 400 and 200 cm^{-1} which has been assigned to the ν(Nb–Cl) terminal for a D_{2h} binuclear disposition with the terminal chloride ligands *trans* in an octahedral environment for each niobium atom. This structural geometry has been described[7] as more propitious in analogous binuclear complexes with both terminal and bridging halide ligands.

Nuclear magnetic resonance spectroscopy has proved a useful tool for the characterization of these and the remaining complexes (see below). Proton NMR data for free L–L have been published[8] and it has been found[6,9] that complexation shifts all the ligand resonances to lower field in a similar way to that noted for quaternization.[10] For the present complexes a similar behaviour has been observed. Complex **2** is insoluble in both polar and non-polar solvents and this lack of solubility has prevented the recording of its ^1H and ^{13}C NMR spectra. However we have recorded the ^1H NMR spectra for complexes **3** and **4** (see Table 1). The ^1H NMR spectrum of **3** shows the resonance for the CH_2 group as well as two resonances which correspond to the methyl groups bound to the C^3 and C^5 pyrazole atoms and H^4 of two equivalently co-ordinated pyrazol-1-yl groups (Fig. 1).

In previous work[6] we applied the method of homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy[11] to the assignment of the H^3 and H^5 resonances of co-ordinated unsubstituted poly(pyrazol-1-yl)alkane ligands in several ruthenium complexes. Using this method we have observed that irradiation of the methylene group leads to an enhancement of the resonance which must correspond to the methyl group attached to the C^5 atom, due to the spacial

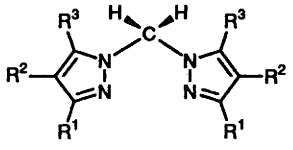
† *Non-SI unit employed:* cal = 4.184 J.

proximity of this group to the CH_2 moiety. This method has been extensively used in this work (see below) in order to assign the ^1H NMR resonances of protons or methyl groups bound to the C^5 and C^3 atoms of pyrazole rings. The ^1H NMR spectrum of complex **4** is much simpler due to the presence of a $SiMe_3$ group in the 5 position of the pyrazole rings. The resonances for CH_2 and H^4 appear at values comparable to those for complex **3** (see Table 1).

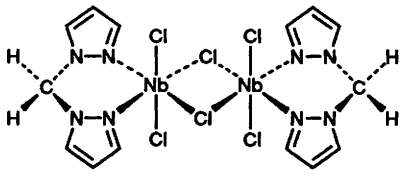
With the aim of preparing mononuclear species from complexes **2–4**, we have tested their behaviour toward diphenylacetylene. A mixture of complex **2**, **3** or **4** and PhC≡CPh, in a 1:2 molar ratio in refluxing toluene, affords the corresponding complex $[NbCl_3(L\text{–}L)(PhC{\equiv}CPh)]$ **5–7**, after appropriate work-up (see Experimental section), equation (2).

$$[\{NbCl_3(L\text{–}L)\}_2] + 2PhC{\equiv}CPh \xrightarrow[\text{Heat}]{\text{Toluene}} 2[NbCl_3(L\text{–}L)(PhC{\equiv}CPh)] \quad (2)$$

2–4 → **5–7**



bpzm $R^1 = R^2 = R^3 = H$
bdmpzm $R^1 = R^3 = Me$, $R^2 = H$
btpzm $R^1 = R^2 = H$, $R^3 = SiMe_3$



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The complexes were isolated in low yields (*ca.* 25%). However, an alternative method has allowed the isolation of a family of this type of complexes $[NbCl_3(L\text{–}L)(RC{\equiv}CR')]$ (L–L = bpzm, R = R′ = Ph **5** or Me **9**; L–L = bdmpzm, R = R′ = Ph **6** or Me **10**; L–L = btpzm, R = R′ = Ph **7**, CO_2Me **8** or Me **11**) by treating the complexes $[NbCl_3(dme)(RC{\equiv}CR')]$ with the appropriate bis(pyrazol-1-yl)methane ligands in a 1:1 molar ratio, equation (3). Starting from the complex with R = R′ = Ph, reaction with bdmpzm gave a mixture of the binuclear complex **3**, with loss of the free acetylene, and the mononuclear alkyne complex **6** (molar ratio 2.3:1 monitored by ^1H NMR spectroscopy); however, the same reaction using but-1-yne afforded the expected alkyne complex **10** as the major product. Steric effects have been proposed to be responsible for this different behaviour, since an appreciable steric hindrance may occur in the molecule when both the bdmpzm and a bulky acetylene ligand are simultaneously present. In the remaining preparations the complexes were isolated after appropriate work-up in quite high yields (*ca.* 75%) as air-stable powdery or crystalline materials. The lack of solubility of some of them has prevented spectroscopic studies (see below).

$$[NbCl_3(dme)(RC{\equiv}CR')] + L\text{–}L \xrightarrow{CH_2Cl_2} [NbCl_3(L\text{–}L)(RC{\equiv}CR')] + dme \quad (3)$$

5–11

Finally, we have investigated the reaction of $[NbCl_3(dme)(RC{\equiv}CR')]$ with tris(pyrazol-1-yl)methanes in the presence of a halide-abstraction agent, such as $AgBF_4$. Thus, the complexes react with tris(pyrazol-1-yl)methane (tpzm) or tris(3,5-dimethylpyrazol-1-yl)methane (tdmpzm) and $AgBF_4$, molar ratio 1:1:1, giving rise to the corresponding cationic complexes $[NbCl_2(L\text{–}L\text{–}L)(RC{\equiv}CR')]BF_4$ (L–L–L = tpzm, R = R′ = Ph **12** or Me **14**; L–L–L = tdmpzm, R = R′ = Ph **13** or Me **15**), from both the abstraction of one halide ligand and subsequent coordination of the N-donor ligand, equation (4). The complexes

$$[NbCl_3(dme)(RC{\equiv}CR')] + L\text{–}L\text{–}L + AgBF_4 \xrightarrow{-AgCl} [NbCl_2(L\text{–}L\text{–}L)(RC{\equiv}CR')]BF_4 + dme \quad (4)$$

12–15

Table 1 Proton NMR data (δ, *J*/Hz) for the complexes $[\{NbCl_3(L\text{–}L)\}_2]$ and $[NbCl_3(L\text{–}L)(RC{\equiv}CR')]$

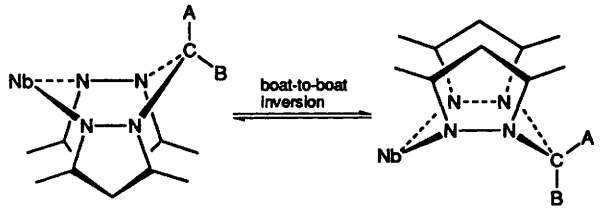
Complex	Solvent	RC≡	CH_2	H^3 or Me^3	H^4	H^5 or Me^5 or $SiMe_3$
3	$CDCl_3$	—	6.53 (s)	2.31 (s, 6 H)	5.96 (s, 2 H)	2.59 (s, 6 H)
4	$(CD_3)_2CO$	—	6.63 (s)	7.76 (s, 2 H)	6.64 (s, 2 H)	0.45 (s, 18 H)
5	$(CD_3)_2CO$	7.44–8.00 (m, 10 H)	7.32 (s)	8.63 (d, 1 H, ^3J = 2.6), 7.41 (d, 1 H, ^3J = 2.6)	6.65 (t, 1 H, ^3J = 2.5), 6.44 (t, 1 H, ^3J = 2.4)	8.27 (d, 1 H, ^3J = 2.6), 8.34 (d, 1 H, ^3J = 2.4)
6	$CDCl_3$	7.40–7.70 (m, 10 H)	A 8.07, B 5.96	2.49 (s, 3 H), 2.33 (s, 3 H)	6.07 (s, 1 H), 5.98 (s, 1 H)	2.60 (s, 3 H), 2.48 (s, 3 H)
7	$CDCl_3$	7.40–8.00 (m, 10 H)	7.08 (s)	8.70 (d, 1 H, ^3J = 2.5), 7.50 (d, 1 H, ^3J = 2.5)	6.90 (d, 1 H, ^3J = 2.5), 6.62 (d, 1 H, ^3J = 2.5)	0.61 (s, 9 H), 0.55 (s, 9 H)
8	$CDCl_3$	3.95 (s, 6 H)	6.86 (s)	8.85 (d, 1 H, ^3J = 1.7), 8.21 (d, 1 H, ^3J = 2.7)	6.71 (d, 1 H, ^3J = 2.4), 6.62 (d, 1 H, ^3J = 2.6)	0.51 (s, 18 H)
9	$(CD_3)_2CO$	3.18 (s, 6 H)	7.16 (s)	8.40 (d, 1 H, ^3J = 2.2), 7.70 (d, 1 H, ^3J = 2.4)	6.65 (t, 1 H, ^3J = 2.6), 6.58 (t, 1 H, ^3J = 2.4)	8.20 (d, 1 H, ^3J = 2.6), 8.32 (d, 1 H, ^3J = 2.6)
10	$CDCl_3$	3.13 (s, 6 H)	A 7.66, B 5.92	2.62 (s, 3 H), 2.01 (s, 3 H)	6.03 (s, 1 H), 5.98 (s, 1 H)	2.42 (s, 3 H), 2.40 (s, 3 H)
11	$CDCl_3$	3.14 (s, 6 H)	6.83 (s)	7.55 (d, 1 H, ^3J = 2.2), 8.57 (d, 1 H, ^3J = 2.2)	6.60 (d, 1 H, ^3J = 2.2), 6.63 (d, 1 H, ^3J = 2.2)	0.48 (s, 9 H), 0.47 (s, 9 H)

were isolated as air-stable solids and they are more soluble in polar solvents, such as dichloromethane, chloroform or acetone, than the neutral alkyne complexes.

Complexes **5**–**15** have been characterized spectroscopically. All the efforts to obtain suitable crystals for X-ray study were unfortunately unsuccessful. In the IR spectra absorptions of different intensities (medium to weak) located between 1692 and 1719 cm^{-1} have been assigned to the $\nu(C{\equiv}C)$ mode of the bound alkynes. This is a drop of roughly 500 cm^{-1} from free alkyne values, consistent with substantial weakening of the triple bond on co-ordination. Nevertheless, the NMR spectral data are most valuable in establishing the structures of the complexes. We will start by considering the data for the neutral alkyne complexes of stoichiometry $[NbCl_3(L{-}L)(RC{\equiv}CR')]$ **5**–**11**. The ^1H NMR spectra show two resonances for the H^3, H^4 and H^5 pyrazole protons indicating that the two pyrazole rings from the bpzm ligand are non-equivalent, a behaviour which has also been observed for complexes with the substituted pyrazoles in bdmpzm and btpzm (see Table 1). For some complexes, **5** and **10**, the assignment of H^3 and H^5 or Me^3 and Me^5 resonances (methyl groups bound to C^3 and C^5 in bdmpzm) was made by NOE experiments, and in the remaining complexes with bpzm and bdmpzm a tentative assignment was made by comparison. An interesting point is the nature of the CH_2 resonance. In most cases, it appears at room temperature as a singlet indicating that a dynamic behaviour in solution takes place, involving a boat-to-boat inversion in the six-membered metallacycle (see Scheme 1), a mechanism which has been proposed for several complexes containing poly(pyrazol-1-yl)alkane ligands, for instance in $[PdCl_2\{(C_5H_4N)_2CH_2\}]$.[12] However, in complexes **6** and **10** the presence of the two methyl groups in the bdmpzm ligand creates steric hindrance high enough to render boat-to-boat inversion difficult, and the CH_2 protons display an AB system at room temperature, similar to that previously found for substituted pyrazole complexes, such as $[PdCl_2(bdmpzm)]$. Several variable-temperature NMR studies have demonstrated the boat-to-boat inversion mechanism.[13]

In an attempt to elucidate the dynamic behaviour of complexes **10** and **11** in solution and to obtain NMR parameters for the static structure at the slow-exchange limit, variable-temperature NMR studies were carried out. At room temperature, **11** and **10** displayed a singlet and a non-resolvable AB system respectively for the CH_2 group. For complex **11** when the temperature was lowered below 218 K an AB system for the methylene was observed with a coalescence temperature at 243 K (see Fig. 1). For complex **10**, raising the temperature above ambient caused a change in the shape of the signal, which finally coalesced at 333 K. From these studies we could calculate free activation energy values, $\Delta G^{\ddagger}$, of 10.92 and 14.84 kcal mol^{-1} for **11** and **10** respectively at the coalescence temperatures.[14] We can conclude that for complexes with the less sterically demanding bpzm and btpzm a dynamic behaviour in solution for the metallacycle corresponding to a boat-to-boat inversion is established, while the steric hindrance of the bulky bdmpzm may introduce a static structure even at room temperature.

Finally, we have recorded the ^{13}C NMR spectra of the majority of these complexes and an expected downfield shift for the resonances corresponding to the carbons of the pyrazole ring with respect to the free pyrazole is observed (see Table 2). No assignment of the C^3 and C^5 resonances has been made for complexes **5** and **10**, as the lack of solubility prevented the recording of a ^1H–^{13}C heteronuclear correlation (HETCOR) spectrum. With regard to the alkyne moiety, the ^{13}C NMR data for the $[NbCl_3(L{-}L)(RC{\equiv}CR')]$ complexes (see Table 2) indicate that this ligand behaves as a four-electron donor. An empirical correlation between the alkyne π donation and ^{13}C chemical shift for the bound alkyne carbons has been observed.[15] The chemical shift values for complexes **5**–**11** appear at *ca.* δ 250, which is a clear indication that the number



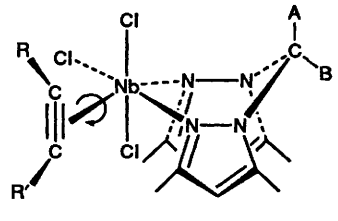
I **II**

Scheme 1

of electrons donated per alkyne is four in such a way that the role of both bonding $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals in donating electrons is not in conflict with acceptance of electron density from the niobium centre into the antibonding $\pi_{\parallel}^*$ orbital of the alkyne. It is noteworthy that in the starting complexes, $[NbCl_3(dme)(RC{\equiv}CR')]$, the alkyne moieties also behave as four-electron donors.[16] Proton and ^{13}C NMR spectra of complexes **5**–**11** indicate that both halves of the alkyne ligands are equivalent (see Tables 1 and 2); for instance, in the ^1H spectra for complexes containing methyl groups in the alkyne, such as $[NbCl_3(bpzm)(MeC{\equiv}CMe)]$ **9**, a singlet attributed to the methyl group is observed. However for complex **10** with the bulky bdmpzm ligand the variable-temperature ^1H NMR spectra indicate that some dynamic behaviour in solution might be taking place. The results seem to indicate that the alkyne ligand in the complexes is fluxional. In contrast, static structures have been described[5d] for the complexes $[NbCl_2\{HB(pz)_3\}(RC{\equiv}CR')]$ and high energy barriers to alkyne rotation about the niobium–alkyne axis were calculated. Assuming that a six-co-ordinate description of the complex in which the alkyne occupies a single site is perhaps preferable to the alternative seven-co-ordinate model where each alkyne carbon is considered to occupy a separate co-ordination position, we propose a simple rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle to explain the observed fluxional behaviour, in accordance with structure **A**. Several examples have been described, mainly for d^4 alkyne complexes of Mo^{II} or W^{II}, where a fluxional behaviour by rotation of the alkyne ligand was considered.[15]

In the variable-temperature NMR study for complex **10** (see above), when the temperature was lowered below 213 K, distinct chemical shifts were observed for the acetylenic methyl groups, with a coalescence temperature near 243 K (see Fig. 2). The rotational activation barrier, $\Delta G^{\ddagger}$, was calculated[14] to be 11.34 kcal mol^{-1} at the coalescence temperature, in accord with those previously reported for several four-electron alkyne ligands in d^4 Group 6 metal complexes.[15] In contrast, the variable-temperature NMR study for **11** (see above) indicates that the methyl alkyne ligand is fluxional even at 183 K. Both electronic and steric factors were proposed to be responsible for the values of the rotational activation barrier.[15] In our complexes we conclude that steric effects may play an important role in the proposed rotation of the alkyne ligand.

Finally, the NMR spectroscopic data for the cationic complexes **12**–**15** will be discussed. With regard to the N-donor ligands, the ^1H spectra show two resonances for the H^3, H^4 and H^5 pyrazole protons in a 1:2 ratio indicating that two equivalent rings and a third non-equivalent one are present. The assignment of the H^5, H^3 or Me^5, Me^3 (in tdmpzm) resonances



A

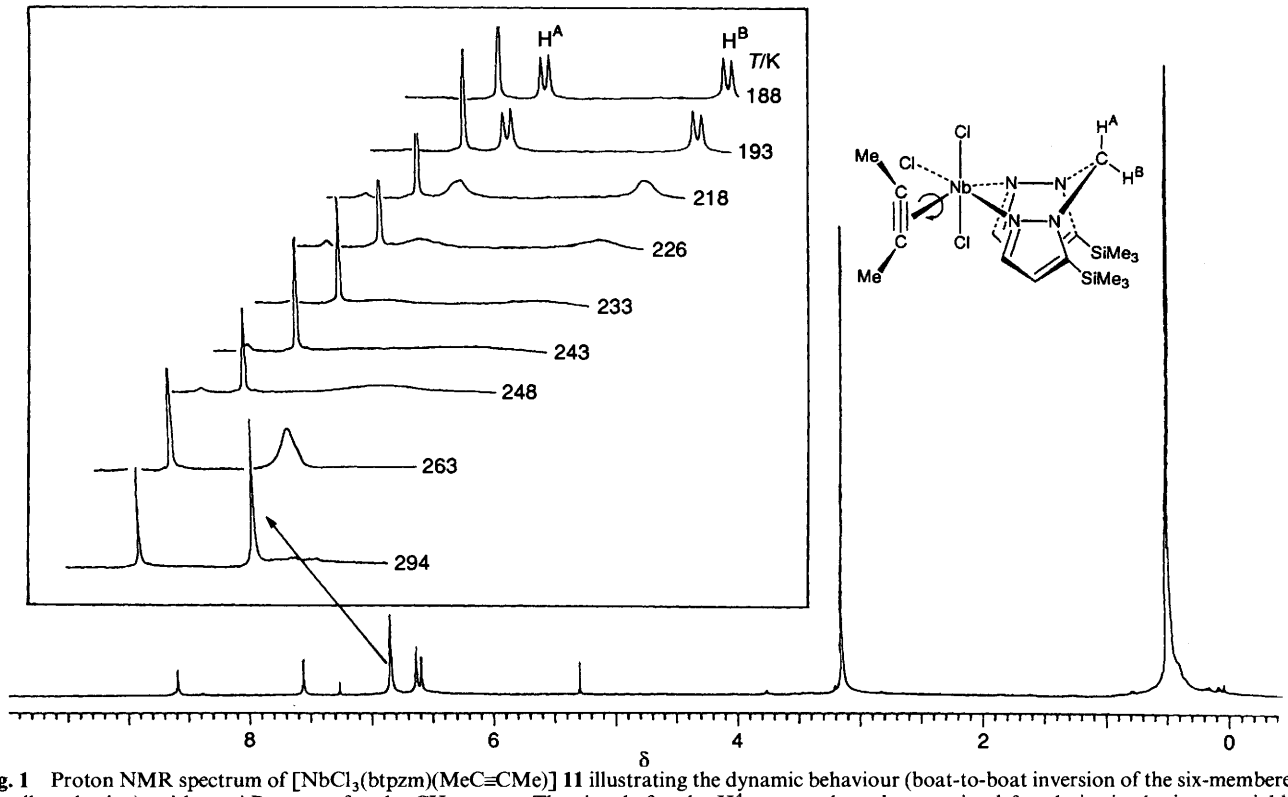


Fig. 1 Proton NMR spectrum of $[NbCl_3(btpzm)(MeC{\equiv}CMe)]$ **11** illustrating the dynamic behaviour (boat-to-boat inversion of the six-membered metallacycle ring), with an AB system for the CH_2 group. The signals for the H^4 protons have been omitted for clarity in the inset variable-temperature spectra

Table 2 Carbon-13 NMR data for complexes $[NbCl_3(L{-}L)(RC{\equiv}CR')]$

Complex	RC≡	C≡C	$C(CH_2)$	C^4	C^3 or C^5		$C(R^1)$	$C(R^3)$
5[a]	131.16–129.28	238.61	63.58	108.09, 107.61	148.64, 145.58	135.64, 134.39	—	—
7[b]	130.22–128.38 (m)	240.70 (s)	64.49 (t, ^1J = 55.0)	116.92 (dd, ^1J = 184.2), ^2J = 9.9), 116.21 (dd, ^1J = 189.6, ^2J = 10.0)	147.73 (dd, ^1J = 222.9, ^2J = 8.1), 144.87 (dd, ^1J = 223.8, ^2J = 8.1)	148.14 (s), 146.54 (s)	—	0.29 (q, ^1J = 120.4), −0.03 (q, ^1J = 122.5)
10[c]	23.80	254.00 (br)	55.66	109.11, 109.07	141.16, 140.11	155.55, 153.85	11.54, 11.23	16.11, 15.65
11[b]	22.94 (q, ^1J = 129.4)	251.61 (s)	64.12 (t, ^1J = 155.3)	116.62 (dd, ^1J = 179.7, ^2J = 9.4), 116.4 (dd, ^1J = 180.0, ^2J = 8.9)	146.17 (dd, ^1J = 191.1, ^2J = 6.8), 144.40 (dd, ^1J = 192.6, ^2J = 6.8)	147.71 (s), 146.63 (s)	—	−0.05 (q, ^1J = 120.5), −0.34 (q, ^1J = 120.5)

[a] Decoupled spectrum in $(CD_3)_2CO$. [b] Coupled spectrum in $CDCl_3$. [c] Decoupled spectrum in $CDCl_3$.

was made by NOE experiments (Table 3). The ^{13}C pyrazole resonances were also assigned by ^1H–^{13}C heteronuclear correlations (HETCOR) for complexes **13** and **14** (Table 4). Considering that the proton resonances were unambiguously assigned by NOE experiments, the ^{13}C resonances are consequently determined with certainty. The ^{13}C NMR spectra indicate also that the alkyne ligands behave as four-electron donors. The NMR data show again that dynamic behaviour in solution might be present. For complexes **12** and **14**, with the less sterically demanding tpzm ligand, the ^1H and ^{13}C NMR at room temperature indicate that both halves of the alkyne ligand are equivalent; thus for instance the alkyne carbons appear as a singlet. However, with the bulky tdmpzm ligand, the ^1H spectrum shows two kinds of phenyl and methyl resonances for **13** and **15** respectively and the ^{13}C spectrum two resonances for the alkyne carbons. The dynamic process can be viewed again as a simple rotation of the alkyne ligand around the axis passing through the metal and the midpoint of the alkyne triple bond in the proposed six-co-ordinated complex (see structure **B**).

The variable-temperature NMR study for complex **15** allowed us to calculate a value of 14.79 kcal mol^{-1} for the rotational activation barrier, $\Delta G^{\ddagger}$, at the coalescence temperature (323 K). Once again we propose that steric effects may be implicated in the fluxional behaviour of the alkyne ligand in this class of complexes.

Experimental

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyser. Mass spectra were recorded on a VG Autospec

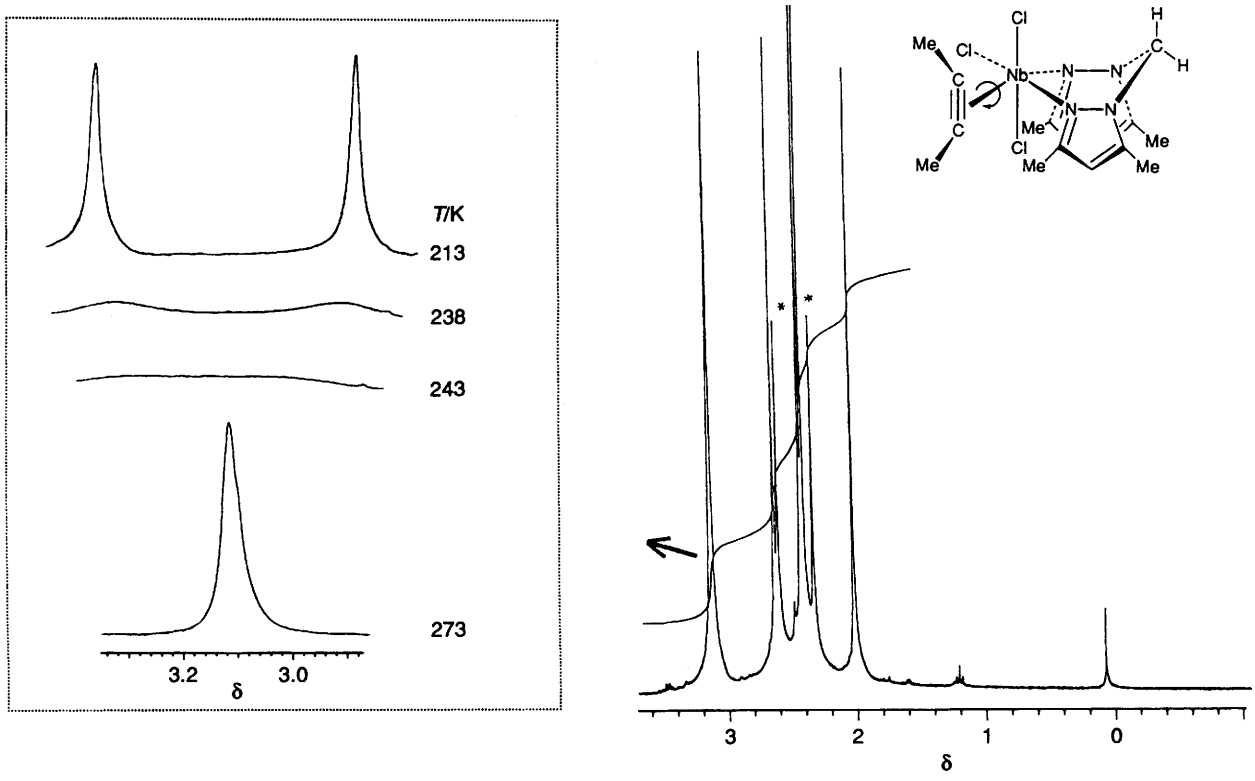


Fig. 2 Proton NMR spectrum of $[NbCl_3(bdmpzm)(MeC{\equiv}CMe)]$ **10** illustrating the temperature dependence of the acetylenic methyl resonance (solvent: $CDCl_3$). The asterisks indicate peaks corresponding to the methyl groups of $[\{NbCl_3(bdmpzm)\}_2]$

Table 3 Proton NMR data for the complexes $[NbCl_2(L\text{–}L\text{–}L)(RC{\equiv}CR')]BF_4$ in $CDCl_3$

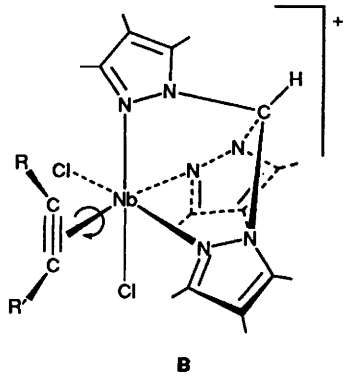
Complex	RC≡	CH	H^3 or Me^3	H^4	H^5 or Me^5
12	7.52–7.38 (m, 10 H)	10.24 (s)	7.51 (d, 2 H, ^3J = 2.2), 8.35 (d, 1 H, ^3J = 2.2)	6.50 (t, 2 H, ^3J = 2.5), 6.68 (t, 1 H, ^3J = 2.5)	8.78 (d, 2 H, ^3J = 2.7), 8.65 (d, 1 H, ^3J = 2.7)
13	8.12–7.67 (m, 5 H) 7.37–6.84 (m, 5 H)	8.44 (s)	1.77 (s, 6 H), 2.68 (s, 3 H)	6.10 (s, 2 H), 6.68 (s, 1 H)	2.91 (s, 6 H), 2.81 (s, 3 H)
14	2.99 (s, 6 H)	9.98 (s)	8.21 (d, 1 H, ^3J = 2.2), 7.62 (d, 2 H, ^3J = 2.2)	6.63 (t, 3 H, ^3J = 1.8)	8.76 (d, 2 H, ^3J = 3.0), 8.66 (d, 1 H, ^3J = 2.4)
15	3.50 (s, 3 H) 2.50 (s, 3 H)	8.25 (s)	2.82 (s, 6 H), 2.76 (s, 3 H)	6.26 (s, 2 H), 6.17 (s, 1 H)	2.03 (s, 6 H), 2.55 (s, 3 H)

Table 4 Carbon-13 NMR data for complexes $[NbCl_2(L\text{–}L\text{–}L)(RC{\equiv}CR')]BF_4$

Complex	RC≡	C≡C	C(CH)	C^3	C^4	C^5	$C(R^1)$	$C(R^3)$
12[a]	134.21–128.15	239.41	75.48	148.42, 146.03	109.19, 109.09	135.00, 134.21	—	—
13[a]	133.15–128.24	225.90 (s), 252.80 (s)	69.71	157.73, 157.12	110.73, 110.41	146.31, 144.62	11.74, 11.28	15.71, 15.49
14[b]	22.71 (q, ^1J = 130.2)	248.10 (s)	74.30	147.09 (dd, ^1J = 193.1, ^2J = 6.6), 145.58 (dd, ^1J = 193.1, ^2J = 6.7)	109.21 (dt, ^1J = 186.4, ^2J = 8.0), 108.90 (dt, ^1J = 184.0, ^2J = 7.8)	135.20 (dd, ^1J = 193.7), 132.81 (^1J = 194.0)	—	—
15[c]	23.60, 23.38	235.74, 216.43	69.42	156.47, 156.31	110.08, 109.82	145.60, 144.98	11.47, 11.10	15.33, 15.21

[a] Decoupled spectrum in $CDCl_3$. [b] Coupled spectrum in $CDCl_3$. [c] Decoupled spectrum in $(CD_3)_2CO$, at 193 K.

instrument using the FAB technique and nitrobenzyl alcohol as matrix, infrared spectra in the region 4000–200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer, and ^1H and ^{13}C NMR spectra on Varian Unity FT-300 and Varian Gemini FT-200 spectrometers referenced to the residual deuteriated solvent. The NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB, number of scans 120. Two-dimensional NMR spectra were acquired using standard VARIAN-FT software, and processed using an IPC-Sun computer. The NMR probe temperatures were varied using an Oxford Instruments VTC 4 unit, measured by a thermocouple and calibrated with CD_3OD. The free activation energies were calculated by the following



B

expression:[14] $\Delta G^{\ddagger} = 1.914 \times 10^{-2} T_c\{9.972 + \log[T_c/(\Delta\nu^2 + 6J_{AB}^2)^{\frac{1}{2}}]\}$.

The poly(pyrazol-1-yl)methanes and the complexes $[\{NbCl_3(dme)\}_n]$ **1** and $[NbCl_3(dme)(RC{\equiv}CR')]$ were prepared as reported previously.[16,17]

Preparations.—$[\{NbCl_3(bpzm)\}_2]\cdot 2CH_2Cl_2$ **2**. The compound bpzm (0.651 g, 4.38 mmol) was added to a dichloromethane suspension (60 cm^3) of $[NbCl_3(dme)]$ (1.242 g, 4.29 mmol) and the mixture stirred for 5 h. The suspension changed from red to purple. It was then filtered and the purple solid washed with Et_2O and dried under vacuum. Yield 0.961 g (64%) (Found: C, 22.55; H, 2.60; N, 12.60. $C_8H_{10}Cl_5N_4Nb$ requires C, 22.25; H, 2.30; N, 12.95%).

$[\{NbCl_3(bdmpzm)\}_2]$ **3**. The compound bdmpzm (1.000 g, 4.89 mmol) was added to a dichloromethane suspension (60 cm^3) of $[NbCl_3(dme)]$ (1.331 g, 4.59 mmol) and the mixture was stirred for 5 h. The suspension gradually darkened, finally turning brown-grey. It was then filtered and the brown solution evaporated to dryness. The residue was washed with Et_2O and dried under vacuum. Complex **3** was obtained as a brown solid. Yield 1.443 g (78%) (Found: C, 32.55; H, 3.85; N, 13.60. $C_{11}H_{16}Cl_3N_4Nb$ requires C, 32.75; H, 3.95; N, 13.90%).

$[\{NbCl_3(btpzm)\}_2]$ **4**. The compound btpzm (1.374 g, 4.70 mmol) was added to a dichloromethane suspension (60 cm^3) of $[NbCl_3(dme)]$ (1.331 g, 4.59 mmol) and the mixture stirred for 5 h. Immediately on addition the colour changed to violet and a solution was obtained. The solution was filtered and evaporated to dryness. Complex **4** was obtained as a violet solid, after washing with Et_2O and drying under vacuum. Yield 2.070 g (92%) (Found: C, 31.30; H, 4.85; N, 11.45. $C_{13}H_{24}Cl_3N_4NbSi_2$ requires C, 31.75; H, 4.90; N, 11.40%). Mass spectrum: *m/z* 981 (0.4, $M + 1$), 676 (24), 589 (5), 418 (22) and 383 (100%).

$[NbCl_3(bpzm)(PhC{\equiv}CPh)]$ **5**. *Method* (*a*). Two equivalents of PhC≡CPh (0.150 mg, 0.84 mmol) were added to a suspension of $[\{NbCl_3(bpzm)\}_2]$ (0.292 mg, 0.42 mmol) in toluene (45 cm^3). The mixture was refluxed for 8 h and then filtered; the solution was evaporated to dryness and the residue was washed with Et_2O. The complex was obtained as an orange-yellow solid. Yield 0.066 g (15%).

Method (*b*). The compound bpzm (0.640 g, 4.30 mmol) was added over a solution of $[NbCl_3(dme)(PhC{\equiv}CPh)]$ (2.020 g, 4.30 mmol) in CH_2Cl_2 (40 cm^3) and the mixture was stirred for 9 h at room temperature then washed with Et_2O. It was filtered and the solvent evaporated to dryness. Yield 1.544 g (68%) (Found: C, 48.35; H, 3.85; N, 10.30. $C_{21}H_{18}Cl_3N_4Nb$ requires C, 48.00; H, 3.40; N, 10.65%).

$[NbCl_3(bdmpzm)(PhC{\equiv}CPh)]$ **6**. A mixture of complexes **3** and **6** was isolated using both methods (*a*) and (*b*) for **5**. Attempts to prepare a pure sample of **6** by fractional crystallization were unsuccessful and the isolated complex was always contaminated by complex **3**.

$[NbCl_3(btpzm)(PhC{\equiv}CPh)]\cdot 0.5CH_2Cl_2$ **7**. *Method* (*a*). The procedure was as that used for complex **5** [method (*a*)], with $[\{NbCl_3(btpzm)\}_2]$ (0.413 g, 0.42 mmol) in toluene (45 cm^3). The complex was obtained as an orange solid. Yield 0.101 g (36%).

Method (*b*). The procedure was as that used for complex **5** [method (*b*)]. Yield 85% (Found: C, 46.75; H, 5.10; N, 7.90. $C_{27.5}H_{35}Cl_4N_4Nb$ requires C, 46.35; H, 4.90; N, 7.85%).

$[NbCl_3(btpzm)(MeO_2CC{\equiv}CCO_2Me)]$ **8**. To a solution of $[NbCl_3(dme)(MeO_2CC{\equiv}CCO_2Me)]$ (0.500 g, 1.16 mmol) in dichloromethane (30 cm^3) was added btpzm (0.338 g, 1.16 mmol). After 10 h of stirring the solution was filtered and evaporated to dryness. The residue was washed with Et_2O and dried under vacuum. Complex **8** was obtained as a brown-orange solid. Yield 0.536 g (73%) (Found: C, 35.70; H, 4.70; N, 8.60. $C_{19}H_{30}Cl_3N_4NbO_4Si_2$ requires C, 36.00; H, 4.75; N, 8.85%).

$[NbCl_3(bpzm)(MeC{\equiv}CMe)]$ **9**. The compound bpzm (0.250 g, 1.68 mmol) was added to a CH_2Cl_2 solution (30 cm^3) of $[NbCl_3(dme)(MeC{\equiv}CMe)]$ (0.579 g, 1.68 mmol) and the mixture was stirred for 10 h. The resulting suspension was filtered through Celite then evaporated to dryness and the residue was washed with Et_2O. The complex was obtained as a rose-coloured solid. Yield 0.449 g (67%) (Found: C, 33.15; H, 3.60; N, 13.60. $C_{11}H_{14}Cl_3N_4Nb$ requires C, 32.90; H, 3.50; N, 13.95%).

$[NbCl_3(bdmpzm)(MeC{\equiv}CMe)]$ **10**. This complex was prepared by a similar procedure to that used for **9**. A mixture of complexes **3** and **10** was isolated. Attempts to prepare a pure sample of **10** by fractional crystallization were unsuccessful and the isolated complex was always contaminated by complex **3**, although the ratio of monomer to dimer is about 7:3.

$[NbCl_3(btpzm)(MeC{\equiv}CMe)]\cdot 0.5CH_2Cl_2$ **11**. This complex was prepared by a similar procedure to that used for **9**. A brown solid was obtained (yield 82%) (Found: C, 35.45; H, 4.95; N, 9.45. $C_{17.5}H_{31}Cl_4N_4NbSi_2$ requires C, 35.75; H, 5.25; N, 9.50%).

$[NbCl_2(tpzm)(PhC{\equiv}CPh)]BF_4\cdot CH_2Cl_2$ **12**. To a solution of $[NbCl_3(dme)(PhC{\equiv}CPh)]$ (0.500 g, 1.07 mmol) in dichloromethane (30 cm^3) was added tpzm (0.229 g, 1.07 mmol). After 8 h of stirring the resulting suspension was filtered through Celite and the filtate concentrated to 5 cm^3. Pentane (10 cm^3) was added to precipitate compound **12** as an orange solid, which was washed with Et_2O and crystallized from dichloromethane–diethyl ether. Yield 0.426 g (62%) (Found: C, 41.15; H, 3.40; N, 11.95. $C_{25}H_{22}BCl_4F_4N_6Nb$ requires C, 41.25; H, 3.00; N, 11.55%).

$[NbCl_2(tdmpzm)(PhC{\equiv}CPh)]BF_4\cdot CH_2Cl_2$ **13**. This complex was prepared by a similar procedure to that used for **12**. An orange solid was obtained after crystallizing from dichloromethane–diethyl ether. Yield 72% (Found: C, 45.85; H, 4.25; N, 10.20. $C_{31}H_{34}BCl_4F_4N_6Nb$ requires C, 45.85; H, 4.20; N, 10.35%). Mass spectrum: *m/z* 639 ($M^+ - BF_4$, 100%).

$[NbCl_2(tpzm)(MeC{\equiv}CMe)]BF_4$ **14**. This complex was prepared by a similar procedure to that used for **12**. A rose-coloured solid was obtained. Yield 58% (Found: C, 31.95; H, 3.20; N, 15.85. $C_{14}H_{16}BCl_2F_4N_6Nb$ requires C, 32.40; H, 3.10; N, 16.20%).

$[NbCl_2(tdmpzm)(MeC{\equiv}CMe)]BF_4\cdot 0.5CH_2Cl_2$ **15**. This complex was prepared by a similar procedure to that used for **12**. A rose-coloured solid was obtained after recrystallizing from dichloromethane–pentane. Yield 86% (Found: C, 37.70; H, 4.45; N, 13.00. $C_{20.5}H_{29}BCl_3F_4N_6Nb$ requires C, 38.15; H, 4.50; N, 13.00%).

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