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A new type of monoanionic “scorpionate” ligand. Synthesis, spectroscopic characterisation and dynamic behaviour of some niobium(III) complexes

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The syntheses of novel scorpionate ligands in the form of the lithium derivative [{Li(H_2O)(bdmpza)}$_4$] **1** [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate] or as the alcohol derivative 2,2-bis(3,5-dimethylpyrazol-1-yl)-ethanol **2** (Hbdmpze) have been studied. These compounds are excellent precursors for the introduction of these scorpionate ligands into transition metal complexes. The complex [{$NbCl_3$(dme)}$_n$] (dme = 1,2-dimethoxyethane) reacted with **1** and **2**, the latter with prior addition of Bu^{n}Li, to give the binuclear complexes [{$NbCl_2$(bdmpzx)}$_2$] (x = a, **3**; x = e, **4**) [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide]. Complex **3** reacted with **1** to give the complex [{NbCl(bdmpza)$_2$}$_2$] **5**. In the same way the reaction of the mononuclear species [$NbCl_3$(dme)(RC≡CR′)] with **1** and **2**, the latter with prior addition of Bu^{n}Li, gave the appropriate [$NbCl_2$(bdmpzx)(RC≡CR′)] complexes [x = a, R = R′ = Me, **6**; Et, **7**; Ph, **8**; or $SiMe_3$, **9**; R = Ph, R′ = Me, **10**; R = Ph, R′ = Et, **11**; R = Ph, R′ = $SiMe_3$, **12**; x = e, R = R′ = Me, **13**; Et, **14**; or Ph, **15**; R = Ph, R′ = Me, **16**; R = Ph, R′ = Et, **17**; R = Ph, R′ = $SiMe_3$, **18**]. The structures of these complexes have been determined by spectroscopic methods. Variable-temperature NMR studies were carried out in order to study their dynamic behaviour in solution. The barriers to alkyne rotation have also been calculated. Reaction of **10** with LiCp′ (Cp′ = $C_5H_4SiMe_3$) gave the mixed Cp–bdmpza complex [NbCp′Cl(bdmpza)] **19**.

Introduction

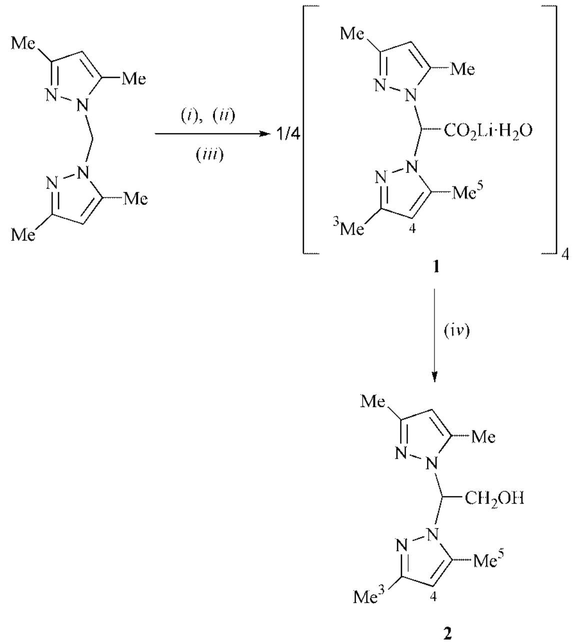
Since the initial development of tris(pyrazolyl)borate or “scorpionate” ligands by Trofimenko in the late 1960s a significant number of complexes using most metals of the Periodic Table has been prepared with these ligands.[1] As a result of our research in the field of niobium complexes with Tp or Tp* ligands [Tp = hydridotris(pyrazol-1-yl)borate and Tp* = tris(3,5-dimethylpyrazol-1-yl)hydridoborate], some of us reported the preparation of several complexes of the type [NbTp(Cl)$_2$(RC≡CR′)] or [NbTp*(O)(Cl)(OR)].[2]

We are now interested, as are other research groups, in the synthesis of “heteroscorpionate” ligands.[3–5] Our new ligands are related to the tris(pyrazol-1-yl)methane system,[4,6] but in this case one of the pyrazole groups is replaced by a carboxylate or ethoxy group to give a small degree of steric hindrance and considerable co-ordinative flexibility. With this aim in mind, we have developed a synthetic route that can be used to isolate a useful lithium compound containing a new class of tridentate ligand as precursor for the introduction of these ligands into transition metal complexes.

Following our research on alkyne-containing niobium(III) complexes,[7] and in order to gain more insight into their dynamic behaviour, we have undertaken new studies on the synthesis of heteroscorpionate-containing niobium species. Preliminary results of this work have been published previously.[3]

Results and discussion

A mixture of a cooled (−70 °C) solution of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[8] in THF and 1 equivalent of Bu^{n}Li was treated with CO_2. This reaction gave rise to the lithium carboxylate compound [{Li(H_2O)(bdmpza)}$_4$] **1** [bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate] as an air-stable colourless solid in good yield (96%) after the appropriate work-up (see Scheme 1). Although the reaction was carried out under rigorously anhydrous experimental conditions, the presence of



Scheme 1 Summary of reactions leading to the compounds **1** and **2**. Reagents and conditions: (i) Bu^{n}Li, THF, −70 °C, 45 min under an atmosphere of dry nitrogen; (ii) CO_2, THF, 0 °C, 1 h under an atmosphere of dry nitrogen; (iii) crystallisation from THF–hexane; (iv) $(CH_3)_2S\cdot BH_3$, THF, reflux, 12 h under an atmosphere of dry nitrogen.

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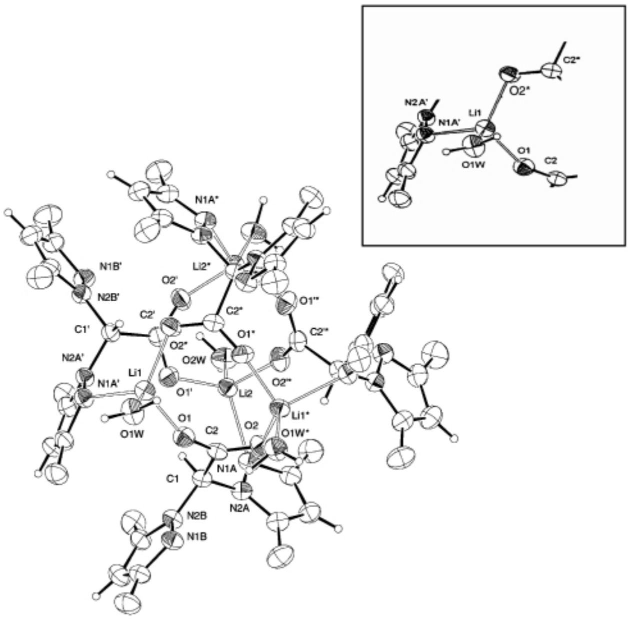


Fig. 1 Structure for complex **1**. Selected bond distances [Å] and angles [°] from a crystal structure determination:[3] Li1–O1 1.877(4), Li1–O1W 1.929(4), Li1–N1A′ 2.156(4) and Li1–O2* 1.934(4); O1–Li1–O1W 106.5(2), O1–Li1–O2* 116.1(2), O1W–Li1–O2* 107.4(2), O1–Li1–N1A′ 99.0(2), O1W–Li1–N1A′ 112.6(2) and O2*–Li1–N1A′ 115.0(2).

adventitious moisture in the reaction mixture during the work-up procedure was probably responsible for the presence of the co-ordinated water molecule. Reduction of the lithium compound **1** with a 2.0 M solution of $(CH_3)_2S{\cdot}BH_3$ (borane–dimethyl sulfide complex) in THF at reflux and in a 1 : 1 molar ratio (see Scheme 1) gave rise to the alcohol 2,2-bis(3,5-dimethylpyrazol-1-yl)ethanol **2** (Hbdmpze) as a colourless air-stable solid.

The ^1H NMR spectrum of compound **1** shows four singlets, which are assigned to CH, H^4, Me^3 and Me^5 of the pyrazole rings. However, in the spectrum of **2** the signal corresponding to the CH group appears as a triplet due to coupling with the two protons of the CH_2OH methylene group. Homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy was also applied to compounds **1** and **2** in order to confirm the assignment of the signal for the Me^3 and Me^5 groups. The ^{13}C-{H} NMR spectra exhibit only one set of resonances, as would be expected for the presence of two equivalent pyrazole rings in the molecule in solution. A ^1H–^{13}C heteronuclear correlation (HETCOR) experiment carried out for these complexes allowed us to assign the resonances corresponding to C^4, Me^3 and Me^5 of the pyrazole ring and carbon atoms of the ethanol group of **2** (see Experimental section). Finally, the ^7Li NMR spectrum of **1** exhibits a singlet at δ 1.50 for the lithium atom.

The IR spectrum of compound **1** shows two strong bands at 1641 and 1461 cm^{-1}, which are assigned to $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, respectively.[9] A characteristic band at 3194 cm^{-1} is observed in the IR spectrum of **2** and this corresponds to ν(OH) of the alcohol. The mass spectrum (FAB) of **1** indicates a tetranuclear formulation (see Experimental section), which was corroborated by means of a crystal structure determination. The structure for **1** (see Fig. 1)[3] consists of tetrameric units with a cubane-like[10] array in which the vertices are alternately occupied by four Li atoms and four bridging carboxylate groups. The two independent "scorpionate" ligands act in a tridentate fashion, bridging three Li atoms through the two oxygen atoms of the carboxylate and a nitrogen atom of a pyrazole ring. Each Li atom has a distorted tetrahedral co-ordination, binding two oxygen atoms from adjacent carboxylate groups, a nitrogen atom from a pyrazole ring and an oxygen atom from a water molecule.

Compounds **1** and **2** were used in the complexation of some niobium fragments in order to test their co-ordinative capacity as scorpionate ligands. First, we considered the reactivity of these systems with $[\{NbCl_3(dme)\}_n]$ (dme = 1,2-dimethoxyethane).[11] Thus, **1** and **2** (the latter with prior addition of Bu^{n}Li) reacted with a solution of $[\{NbCl_3(dme)\}_n]$ [eqn. (1)] in THF to give, after stirring for 12 or 1 h, respectively a suspension from which the complexes $[\{NbCl_2(bdmpzx)\}_2]$ (x = a, **3**; x = e, **4**) [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide] were isolated as violet and brown solids, respectively, after the appropriate work-up.

The complexes were characterised spectroscopically. The ^1H NMR spectra of **3** and **4** each show a set of resonances for H^4, Me^3 and Me^5, indicating that both pyrazole rings are equivalent. In addition, all the resonances for **3** are shifted to lower field in comparison with those of lithium compound **1**. The resonances of **4** are not comparable with those of **2** because the NMR spectrum was obtained from a sample in a different solvent. The ^{13}C-{H} NMR spectra exhibit the corresponding signals for C^3, C^4, C^5, Me^3 and Me^5 (see Experimental section).

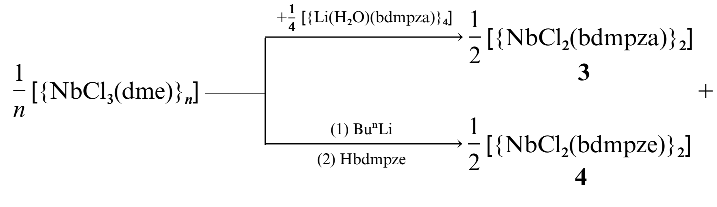
The mass spectra of complexes **3** and **4** indicate a binuclear formulation (see Experimental section). The IR spectrum of **3** shows two strong bands at 1699 and 1460 cm^{-1}, which are assigned to $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, respectively. For the lithium compound **1** the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ bands differ ($\Delta\nu_{as\text{-}s}$) by 180 cm^{-1} and in this complex the carboxylate is involved in a co-ordination bridge at two lithium atoms (Fig. 1). IR spectroscopy has previously proven to be a good indicator of the bonding mode of carboxylate ligands.[9] Bonding through the two oxygen atoms (chelate mode) leads to a decrease in $\Delta\nu_{as\text{-}s}$ in comparison to a bridge mode and bonding through the single oxygen atom leads to an increase in $\Delta\nu_{as\text{-}s}$ again in comparison to a bridge mode. For compound **3** the value of $\Delta\nu_{as\text{-}s}$ (239 cm^{-1}) is in accordance with oxygen co-ordination (monodentate). In the IR spectra of **3** and **4** a strong band at 725 and 798 cm^{-1} is observed, which is assigned to ν(Nb–O). The complexes show a band of interest at *ca.* 330 cm^{-1} and this has been assigned to ν(Nb–Cl) of the terminal group for a binuclear disposition with an octahedral environment for each niobium atom (see Fig. 2).

Compound **3** reacted with half an equivalent of **1** in THF to give, after the appropriate work-up procedure, the air-sensitive orange-yellow solid $[\{NbCl(bdmpza)_2\}_2]$ **5** [eqn. (2)]. The ^1H and

$$[\{NbCl_2(bdmpza)\}_2] + \tfrac{1}{2}[\{Li(H_2O)(bdmpza)\}_4] \xrightarrow{THF}$$

$$\underset{\mathbf{5}}{[\{NbCl(bdmpza)_2\}_2]} + 2\,LiCl \qquad (2)$$

^{13}C-{H} NMR spectra of **5** show a single set of resonances for proton and carbon atoms, indicating that both pyrazole rings are equivalent (see Experimental section). The mass spectrum



$$\frac{1}{n}[\{NbCl_3(dme)\}_n] \begin{cases} \xrightarrow{+\frac{1}{4}[\{Li(H_2O)(bdmpza)\}_4]} \frac{1}{2}\underset{\mathbf{3}}{[\{NbCl_2(bdmpza)\}_2]} \\ \xrightarrow[(2)\ Hbdmpze]{(1)\ Bu^nLi} \frac{1}{2}\underset{\mathbf{4}}{[\{NbCl_2(bdmpze)\}_2]} \end{cases} + LiCl \qquad (1)$$

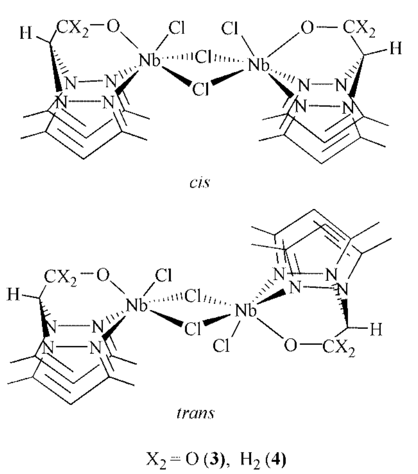


Fig. 2 Proposed structure for complexes **3** and **4** (*cis* and *trans* dispositions).

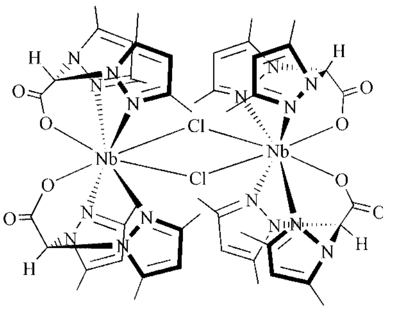


Fig. 3 Proposed structure for complex **5**.

indicates a binuclear formulation. In the IR spectrum the value of $\Delta\nu_{as\text{-}s}$ is 239 cm^{-1}, which is in accordance with oxygen co-ordination. A strong band is also observed at 250 cm^{-1} and this has been assigned to ν(Nb–Cl) of the bridge. The proposed structure for **5** is a binuclear arrangement with two scorpionate ligands acting in a tridentate fashion for each niobium atom and two chlorine atom bridges (see Fig. 3).

In this study we also used another niobium(III) precursor. Thus, the lithium compound **1** reacted at room temperature in a 1:1 molar ratio [eqn. (3)] with the complexes $[NbCl_3(dme)(RC\equiv CR')]$[11] in THF to give, after the appropriate work-up, $[NbCl_2(bdmpza)(RC\equiv CR')]$ (R = R′ = Me, **6**; Et, **7**; Ph, **8**; or SiMe$_3$, **9**; R = Ph, R′ = Me, **10**; R = Ph, R′ = Et, **11**; R = Ph, R′ = SiMe$_3$, **12**), which were isolated as orange, red or blue solids. Compound **2** also reacts with $[NbCl_3(dme)(RC\equiv CR')]$ after prior addition of 1 equivalent of Bu^{n}Li [eqn. (3)] to give $[NbCl_2(bdmpze)(RC\equiv CR')]$ (R = R′ = Me, **13**; Et, **14**; or Ph, **15**; R = Ph, R′ = Me, **16**; R = Ph, R′ = Et, **17**; R = Ph, R′ = SiMe$_3$, **18**).

The ^{1}H NMR spectra of these complexes **6**–**18** exhibit two resonances for each of the H^4, Me^3 and Me^5 pyrazole protons, indicating that the two pyrazole rings are non-equivalent. These results agree with a proposed octahedral disposition in which the two pyrazole rings are located in *cis* and *trans* positions with respect to the alkyne ligand (see Fig. 4). NOE experiments were carried out in order to confirm this situation. For example, irradiation in complex **6** or **13** of the alkyne Me group enhances only one of the Me^3 signals, which is clearly the Me group (Me$^{3'}$) of the *cis* pyrazole ring as it is in closer spatial proximity to the alkyne ligand. In addition, the ^{13}C-{H} NMR spectra of complexes **6**–**18** exhibit two resonances for the different pyrazole carbon atoms, C^3, C^4, C^5, Me^3, Me^5 and their assignments were made on the basis of ^{1}H–^{13}C HMQC (heteronuclear multiple quantum correlation) and HETCOR correlation experiments. The ^{13}C NMR resonances for the carbon atoms of the alkyne ligands appear at *ca.* δ 250, indicating that the alkyne ligand behaves as a four-electron donor (see Experimental section). An empirical correlation between the alkyne π donation and ^{13}C chemical shift for the bound alkyne carbons has previously been observed.[12] This proposed structure for these complexes was confirmed by means of a crystal structure determination for complex **10** (see Fig. 4).[3] The ^{1}H and ^{13}C NMR spectra of these complexes with symmetrical alkynes exhibit only one set of signals for the substituted groups. This is due to rotation of the alkyne ligand, as was previously observed for other alkyne-containing niobium complexes.[6,7] We assume that a six-co-ordinate description of the complexes (see Fig. 4) in which the alkyne occupies a single site is preferable to the alternative seven-co-ordinate model in which each alkyne carbon is considered to occupy a separate co-ordination position. Based on this assumption we propose a single rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle (see Fig. 4). Free energy values, $\Delta G^{\ddagger}$, for the complexes **6**–**18** were calculated[13] from variable-temperature NMR studies. The values allow us to establish a relationship between the steric demand of the alkyne and the rotation phenomenon. In fact, as can be seen in Fig. 5, the higher $\Delta G^{\ddagger}$ values and coalescence temperatures were found in the cases of the bulkier alkyne substituents.

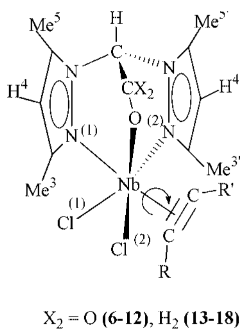


Fig. 4 Proposed structure for complexes **6**–**18**. Selected bond distances [Å] and angles [°] for **10**, from a crystal structure determination:[3] Nb–N1 2.377(4), Nb–N2 2.263(3), Nb–O 2.098(3), Nb–Cl1 2.404(1) and Nb–Cl2 2.377(1); N1–Nb–N2 78.6(1), N1–Nb–O 80.3(1), N2–Nb–O 78.4(1), O–Nb–Cl2 159.0(1), N2–Nb–Cl2 85.8(1), O–Nb–Cl1 87.2(1), Cl1–Nb–Cl2 104.03(5), N1–Nb–Cl1 84.5(1) and N1–Nb–Cl2 83.2(1).

Another factor that influences the rotation of the alkyne ligand is the nature of the scorpionate ligand. Thus, in the complexes $[NbTp^*Cl_2(RC\equiv CR')]$ (R = R′ = Me or Ph; R = Ph, R′ = Me, Et or Pr^n)[14] where the carboxylate or ethoxy groups of the scorpionate ligands are replaced by a pyrazole ring, the alkyne ligands are static at room temperature and this different behaviour is probably due to steric factors. However, for the complexes $[NbCl_2(bdmpza)(RC\equiv CR')]$ **6**–**12** and $[NbCl_2(bdmpze)(RC\equiv CR')]$ **12**–**18** there is a little difference in the values of $\Delta G^{\ddagger}$, *ca.* 0.5–1 kcal mol^{-1} (see Fig. 5). This fact is probably due to electronic effects because the steric difference between a carboxylate group and an ethoxy group is not particularly large. We will now discuss an example of the variable-temperature NMR study for a complex with a symmetrical and an unsymmetrical alkyne ligand. It can be seen from Fig. 6 that

$$[NbCl_3(dme)(RC\equiv CR')] \begin{cases} \xrightarrow{+\frac{1}{4}[\{Li(H_2O)(bdmpza)\}_4]} \underset{\mathbf{6–12}}{[NbCl_2(bdmpza)(RC\equiv CR')]} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad + LiCl \\ \xrightarrow{Bu^nLi\ +\ Hbdmpze} \underset{\mathbf{13–18}}{[NbCl_2(bdmpze)(RC\equiv CR')]} \end{cases} \qquad (3)$$

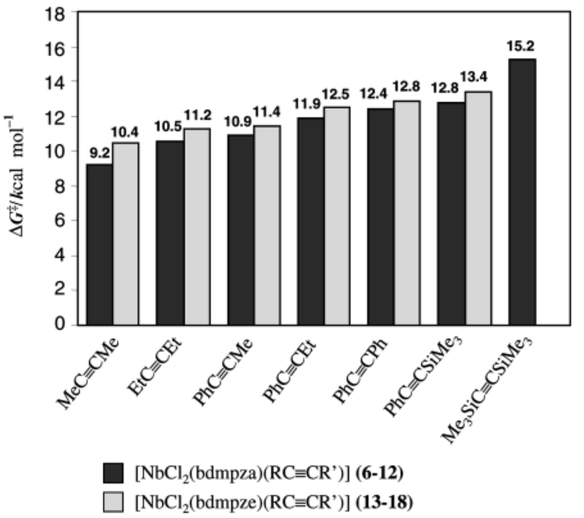


Fig. 5 Graphic representation of free energy values, $\Delta G^‡$, for rotation of the alkyne ligands for complexes **6**–**18**. Coalescence temperature values for these complexes are: 163, **6**; 181, **7**; 213, **8**; 263, **9**; 193, **10**; 203, **11**; 223, **12**; 223, **13**; 238, **14**; 263, **15**; 243, **16**; 248, **17** and 263, **18**.

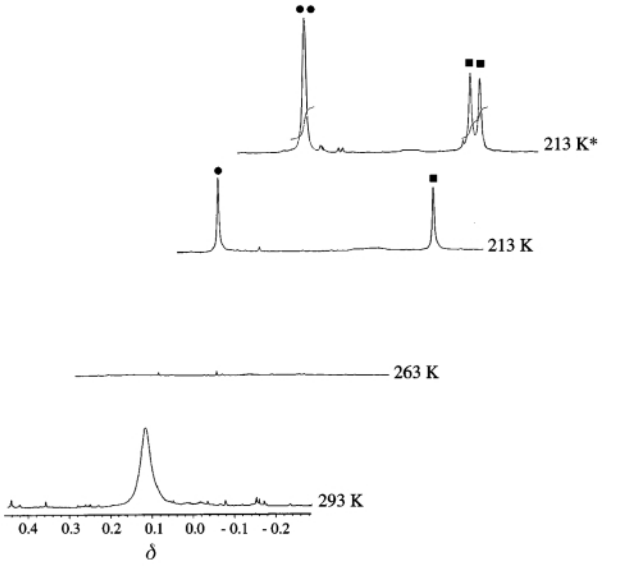
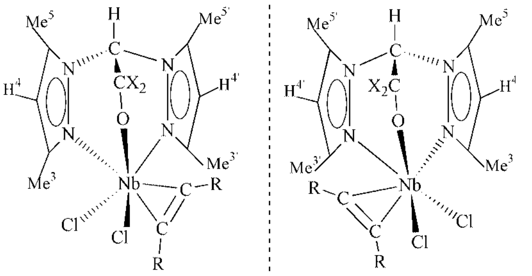


Fig. 6 Variable-temperature ^{1}H NMR spectra in the region of the $SiMe_3$ alkyne groups of the complex [$NbCl_2$(bdmpza)($Me_3SiC\equiv CSiMe_3$)] **9**. * With chiral shift reagent.

a singlet is observed for the $SiMe_3$ alkyne groups in the variable-temperature ^{1}H NMR spectra of **9** at room temperature (293 K). However, when the temperature is lowered to below 213 K, distinct chemical shifts are observed for the $SiMe_3$ alkyne groups. This is due to the static position of the alkyne where the two $SiMe_3$ substituents exhibit different chemical environments. These data clearly indicate that the alkyne lies in the molecular mirror plane, which bisects the Cl–Nb–Cl angle and contains a pyrazole ring (see Fig. 4). In this geometry one of the alkyne substituents sits between the pyrazole ring and the carboxylate group, whereas the other one is directed towards the chlorines. In the former position the electronic effects exerted by the pyrazole and carboxylate lead to a shielding of the $SiMe_3$ protons. NOE experiments were carried out in order to confirm this proposal. Thus, we assign the shielded ^{1}H NMR signal at δ −0.13 to the protons of the alkyne $SiMe_3$ group in close proximity to the pyrazole ring. Addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of **9** at 213 K gives rise to the appearance of four singlets (two coincide) for the $SiMe_3$ groups (see Fig. 6) that correspond to the two diastereoisomers from the corresponding two enantiomers (see Scheme 2).



Scheme 2 Proposed structures for the two enantiomers of complexes with a symmetrical alkyne ligand.

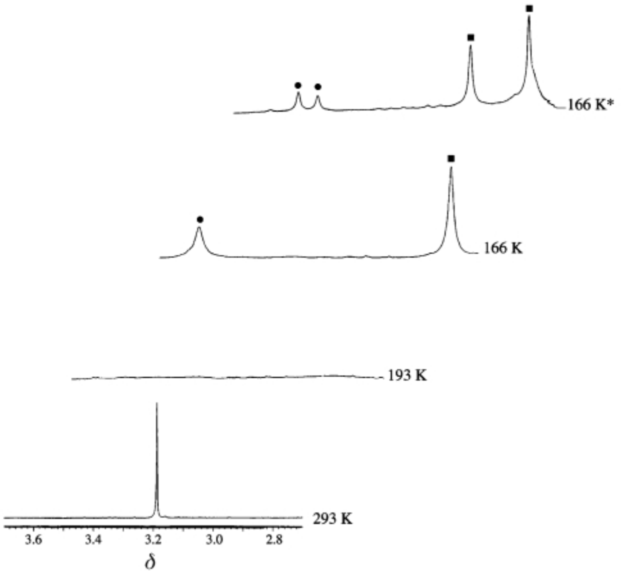
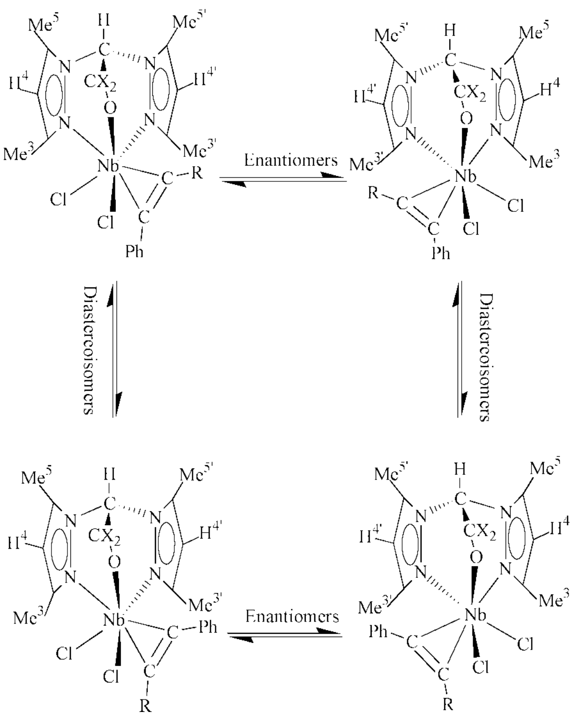


Fig. 7 Variable-temperature ^{1}H NMR spectra in the region of the Me alkyne group of the complex [$NbCl_2$(bdmpza)(PhC≡CMe)] **10**. * With chiral shift reagent.

The variable-temperature NMR study for complex **10** illustrates a good example of a system with an unsymmetrical alkyne. In Fig. 7 it can be seen that a singlet appears for the Me alkyne groups at 293 K. When the temperature was lowered below 166 K two signals (relative intensities 3 : 1) were observed for each of the diastereoisomers present (see Scheme 3). Following a similar analysis to that made in the case of symmetrical alkynes based on NOE experiments, we have established that the major isomer is the one in which the Me group lies between the pyrazole ring and carboxylate group, and the phenyl group lies between two chlorine atoms (see Fig. 4). This structure is not consistent with that found for the complex [$NbTp^*Cl_2$(PhC≡CMe)] where the phenyl group lies between the two proximal *cis*-pyrazole rings. This preference was explained on the basis of the interaction between pyrazoles and phenyl π systems.[15] The relative ratio of the two isomers in our complexes depends on the nature of the alkyne substituent. These ratios are 3 : 1 and 3 : 2 for the phenyl/methyl and phenyl/ethyl systems in complexes **10**, **11**, **16**, **17** respectively. However, for the phenyl/trimethylsilyl system in complexes **12** and **18** the ratio is 3 : 1, although the major isomer is probably the one in which the Ph group lies between the pyrazole ring and the carboxylate group because the $SiMe_3$ group is bulkier than the Ph group. NOE experiments were carried out in order to confirm this proposed situation but were not conclusive. The addition of (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol to a solution of **10** gave rise to the appearance of four singlets for the Me group of the alkyne ligand in the ^{1}H NMR spectrum at 166 K (see Fig. 7). These four signals correspond to the four diastereoisomers from the corresponding four stereoisomers (see Scheme 3).



Scheme 3 Proposed structures for the four enantiomers of complexes with an unsymmetrical alkyne ligand.

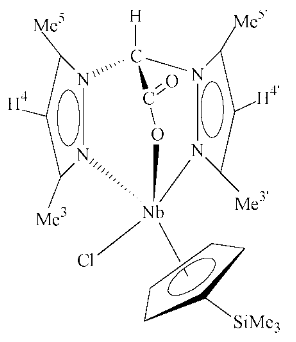


Fig. 8 Proposed structure for complex **19**.

As part of our investigation we also previously prepared mixed TpCp complexes.[2] The preparation of a new mixed Cp–scorpionate ligand complex is now described. Compound **10** reacts at room temperature in a 1 : 1 molar ratio with a THF solution of LiCp′ ($Cp' = C_5H_4SiMe_3$) [eqn. (4)] to give the

$$[NbCl_2(bdmpza)(PhC{\equiv}CMe)] + LiCp' \xrightarrow[-LiCl]{THF} \underset{\mathbf{19}}{[NbCp'Cl(bdmpza)]} + PhC{\equiv}CMe \quad (4)$$

complex [NbCp′Cl(bdmpza)] **19** as a yellow solid. This reaction gives a mixture of mononuclear Cp′–bdmpza complex and free acetylene. Such a reaction does not occur with LiCp or LiCp* ($Cp^* = C_5Me_5$).

The ^1H and ^{13}C NMR spectra for complex **19** show that Cp′ and the bdmpza are η^5- and κ^3-bound respectively. Two resonances can be observed in these spectra for each of the Me^3, Me^5 and H^4 pyrazole protons and for each of the carbon atoms, indicating that the two pyrazole rings from the bdmpza are not equivalent. The mass spectrum indicates a mononuclear formulation and the IR spectrum shows a strong band at 321 cm^{-1}, which is assigned to ν(Nb–Cl) of the terminal Cl group. A five-co-ordinate niobium disposition, depicted in Fig. 8, was proposed for this complex.

In conclusion, we have explored a method for the synthesis of novel compounds that contain new scorpionate ligands. These compounds are excellent precursors for the introduction of these ligands into transition metal complexes. This fact has been confirmed by reactions with different niobium complexes. New binuclear and mononuclear niobium species with two new scorpionate ligands have been isolated. The scorpionate niobium alkyne complexes present a dynamic behaviour in solution, which corresponds to alkyne rotation. This behaviour has been studied by variable-temperature NMR spectroscopy and the data obtained suggest that the main influence on the alkyne rotation barriers is steric factors. New efforts to enlarge the scope of this field are in progress.

Experimental

All reactions were performed using standard Schlenk-tube techniques under 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 instrument using the FAB technique and 3-nitrobenzyl alcohol as matrix, infrared spectra in the region 4000–200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer, ^1H, ^{13}C and ^7Li NMR spectra on a Varian Unity FT-300 spectrometer referenced to the residual deuteriated solvent. The NOE difference spectra were recorded with the following acquisition parameters: spectrum 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 CH_3OH.

The complexes $[\{NbCl_3(dme)\}_n]$, $[NbCl_3(dme)(RC{\equiv}CR')]$ and the compound bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) were prepared as reported previously.[8,11]

Preparations

$[\{Li(H_2O)(bdmpza)\}_4]$ 1. In a 250 cm^3 Schlenk tube, bdmpzm (4 g, 20 mmol) was dissolved in dry THF (150 cm^3) and the solution cooled to −70 °C. A 1.6 M solution of Bu^nLi (12.50 cm^3, 20 mmol) in hexane was added and the solution stirred for 45 min, CO_2 bubbled through the reaction mixture and the temperature slowly allowed to reach 0 °C. After 1 h the solvent was removed under vacuum and a white solid obtained. This solid was crystallised from a mixture of THF–hexane. Yield 96% (Found: C, 52.64; H, 6.46; N, 20.23. $C_{12}H_{17}LiN_4O_3$ requires C, 52.94; H, 6.28; N, 20.58%). ^1H NMR (DMSO, 297 K): δ 6.35 (s, 1 H, CH), 5.72 (s, 2 H, H^4), 2.03 (s, 6 H, Me^3) and 2.25 (s, 6 H, Me^5). ^{13}C-{^1H} NMR (DMSO): δ 73.9 (CH), 140.1 (C^3), 105.1 (C^4), 145.2 (C^5), 11.5 (Me^3), 13.4 (Me^5) and 164.7 (CO_2^-). ^7Li NMR (DMSO): δ 1.50 (s). IR (Nujol mull, cm^{-1}), 1557 ν(C=N), 1641 $\nu_{asym}(CO_2^-)$ and 1461 $\nu_{sym}(CO_2^-)$. Mass spectrum [FAB (*m*/*z* assignment, % intensity)]: 769 $[Li_4(bdmpza)_3]$, 20; 515 $[Li_3(bdmpza)_2]$, 19; and 261 $[Li_2(bdmpza)]$, 100.

Hbdmpze 2. In a 250 cm^3 Schlenk tube, $[\{Li(H_2O)(bdmpza)\}_4]$ **1** (3 g, 2.75 mmol) was dissolved in dry THF (150 cm^3) and a 2.0 M solution of $(CH_3)_2S{\cdot}BH_3$ (5.50 cm^3, 11 mmol) in THF added. The resulting solution was stirred for 12 h under reflux. The suspension was treated dropwise with CH_3CO_2H–water (1 : 2) to pH 5. After 1 h the solution was treated dropwise with a saturated solution of Na_2CO_3 to pH 7. The mixture was separated and the organic layer dried ($MgSO_4$) and concentrated to afford the white solid **2**, which was washed with hexane and crystallised from a mixture of THF–hexane. Yield 46% (Found: C, 61.25; H, 7.81; N, 23.82. $C_{12}H_{18}N_4O$ requires C, 61.51; H, 7.74; N, 23.91%). ^1H NMR ($CDCl_3$, 297 K): δ 6.28 (t, $^3J_{HH}$ = 5.8, 1 H, CH), 4.39 (d, $^3J_{HH}$ = 5.8 Hz, 2 H, CH_2OH), 5.82 (s, 2 H, H^4), 1.94 (s, 6 H, Me^3) and 2.21 (s, 6 H, Me^5). ^{13}C-{^1H}

NMR ($CDCl_3$): δ 72.5 (CH), 63.2 (CH_2OH), 148.2 (C^3), 106.9 (C^4), 140.3 (C^5), 10.5 (Me^3) and 13.5 (Me^5). IR (Nujol mull, cm^{-1}): 3194 ν(OH) and 1554 ν(C=N).

[{$NbCl_2$(bdmpza)}$_2$] 3. To a THF (50 cm^3) solution of [$NbCl_3$(dme)] (1.2 g, 4.20 mmol) was added [{Li(H_2O)(bdmpza)}$_4$] **1** (1.129 g, 1.04 mmol). The suspension was stirred for 12 h at room temperature. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2. A violet solid was obtained after removal of the solvents. Yield 78% (Found: C, 35.58; H, 3.98; N, 13.24. $C_{12}H_{15}Cl_2N_4O_2Nb$ requires C, 35.04; H, 3.68; N, 13.63%). ^1H NMR (DMSO, 297 K): δ 7.32 (s, 2 H, CH), 6.06 (s, 4 H, H^4), 2.27 (s, 12 H, Me^3) and 2.37 (s, 12 H, Me^5). ^{13}C-{^1H} NMR (DMSO): δ 71.4 (CH), 140.5 (C^3), 106.4 (C^4), 146.8 (C^5), 10.8 (Me^3), 13.2 (Me^5) and 165.9 (CO_2^-). IR (Nujol mull, cm^{-1}): 1557 ν(C=N), 1699 ν_{asym}(CO_2^-), 1460 ν_{sym}(CO_2^-), 725 ν(Nb–O) and 333 ν(Nb–Cl). Mass spectrum [FAB (*m*/*z* assignment)]: 752 (M − 2Cl).

[{$NbCl_2$(bdmpze)}$_2$] 4. To a cooled (−70 °C) solution of Hbdmpze (0.3 g, 1.28 mmol) in dry THF (150 cm^3) was added a 1.6 M solution of Bu^nLi (0.80 cm^3, 1.28 mmol) in hexane and the mixture stirred for 30 min. A solution of [$NbCl_3$(dme)] (0.370 g, 1.28 mmol) in THF (30 cm^3) was added. After 1 h the solvent was removed under vacuum and the solid extracted with CH_2Cl_2. A brown solid was obtained after removal of the solvent. The solid was washed with hexane and crystallised from a mixture of THF–hexane. Yield 82% (Found: C, 36.58; H, 4.28; N, 14.24. $C_{12}H_{17}Cl_2N_4NbO$ requires C, 36.30; H, 4.31; N, 14.11%). ^1H NMR (DMSO, 297 K): δ 6.27 (br s, 2 H, CH), 4.21 (d, $^3J_{HH}$ = 6.5 Hz, 4 H, CH_2O), 5.78 (s, 4 H, H^4), 2.04 (s, 12 H, Me^3) and 2.21 (s, 12 H, Me^5). ^{13}C-{^1H} NMR (DMSO): δ 70.3 (CH), 61.4 (CH_2O), 146.3 (C^3), 105.6 (C^4), 139.6 (C^5), 10.6 (Me^3) and 13.6 (Me^5). IR (Nujol mull, cm^{-1}): 1553 ν(C=N), 798 ν(Nb–O) and 309 ν(Nb–Cl). Mass spectrum [FAB (*m*/*z* assignment)]: 794 (M + 1).

[{NbCl(bdmpza)$_2$}$_2$] 5. To a THF (50 cm^3) suspension of [{$NbCl_2$(bdmpza)}$_2$] **3** (0.200 g, 0.24 mmol) was added [{Li(H_2O)(bdmpza)}$_4$] **1** (0.132 g, 0.12 mmol). The suspension was stirred for 20 h at room temperature. The solvent was removed *in vacuo* and an orange-yellow solid obtained. Yield 30% (Found: C, 46.78; H, 5.03; N, 17.72. $C_{24}H_{30}ClN_8NbO_4$ requires C, 46.27; H, 4.85; N, 17.98%). ^1H NMR ($CDCl_3$, 297 K): δ 6.79 (s, 4 H, CH), 5.69 (s, 8 H, H^4), 2.35 (s, 24 H, Me^3) and 1.99 (s, 24 H, Me^5). ^{13}C-{^1H} NMR ($CDCl_3$): δ 68.1 (CH), 141.5 (C^3), 106.4 (C^4), 146.4 (C^5), 11.7 (Me^3), 13.5 (Me^5) and 169.6 (CO_2^-). IR (Nujol mull, cm^{-1}): 1553 ν(C=N), 1701 ν_{asym}(CO_2^-), 1462 ν_{sym}(CO_2^-), 712 ν(Nb–O) and 250 ν(Nb–Cl). Mass spectrum [FAB (*m*/*z* assignment)]: 1246 (M + 1).

[$NbCl_2$(bdmpza)(MeC≡CMe)] 6. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(MeC≡CMe)] (0.600 g, 1.74 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.465 g, 0.43 mmol), to give **6** as a red solid. Yield 75% (Found: C, 41.38; H, 4.74; N, 11.98. $C_{16}H_{21}Cl_2N_4NbO_2$ requires C, 41.31; H, 4.55; N, 12.04%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.58 (s, 1 H, CH), 6.09 (s, 1 H, H^4), 6.18 (s, 1 H, $H^{4'}$), 2.52 (s, 3 H, Me^3), 2.11 (s, 3 H, $Me^{3'}$), 2.49 (s, 3 H, Me^5), 2.47 (s, 3 H, $Me^{5'}$) and 2.94 [s, 6 H, (MeC≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 67.9 (CH), 109.3, 109.2 ($C^{4\text{ or }4'}$), 155.0, 153.7, 142.3, 141.9 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.0, 15.4 (Me^3, $Me^{3'}$), 11.5, 11.1 (Me^5, $Me^{5'}$), 21.6 (*Me*C≡), 242.5 (C≡C) and 163.4 (CO_2^-). IR (Nujol mull, cm^{-1}): 1548 ν(C=N), 1693 ν_{asym}(CO_2^-), 1463 ν_{sym}(CO_2^-), 1672 ν(C≡C), 725 ν(Nb–O), 370, 342 cm^{-1} ν(Nb–Cl).

[$NbCl_2$(bdmpza)(EtC≡CEt)] 7. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(EtC≡CEt)] (1.000 g, 2.70 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.733 g, 0.67 mmol), to give **7** as a violet solid. Yield 70% (Found: C, 43.90; H, 5.37; N, 11.04. $C_{18}H_{25}Cl_2N_4NbO_2$ requires C, 43.83; H, 5.11; N, 11.35%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.59 (s, 1 H, CH), 6.08 (s, 1 H, H^4), 6.17 (s, 1 H, $H^{4'}$), 2.53 (s, 3 H, Me^3), 2.14 (s, 3 H, $Me^{3'}$), 2.50 (s, 3 H, Me^5), 2.47 (s, 3 H, $Me^{5'}$), A 3.36, B 3.24, X 1.26 [ABX_3, J_{AB} = 17.0, $J_{AX} = J_{BX}$ = 7.5 Hz, (CH_3CH_2C≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 67.9 (CH), 109.3, 109.1 ($C^{4\text{ or }4'}$), 154.8, 154.4, 141.9, 141.6 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.0, 15.5 (Me^3, $Me^{3'}$), 11.5 (Me^5, $Me^{5'}$), 31.29 ($CH_3C\mathit{H}_2C$≡), 13.5 ($C\mathit{H}_3CH_2C$≡), 247.9 (C≡C) and 161.4 (CO_2^-). IR (Nujol mull, cm^{-1}): 1550 ν(C=N), 1671 ν_{asym}(CO_2^-), 1458 ν_{sym}(CO_2^-), 1660 ν(C≡C), 717 ν(Nb–O), 360, 340 ν(Nb–Cl).

[$NbCl_2$(bdmpza)(PhC≡CPh)] 8. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(PhC≡CPh)] (1.000 g, 2.14 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.582 g, 0.53 mmol), to give **8** as an orange solid. Yield 73% (Found: C, 52.47; H, 4.35; N, 9.45. $C_{26}H_{25}Cl_2N_4NbO_2$ requires C, 52.99; H, 4.27; N, 9.50%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.74 (s, 1 H, CH), 6.01 (s, 1 H, H^4), 6.15 (s, 1 H, $H^{4'}$), 2.65 (s, 3 H, Me^3), 1.83 (s, 3 H, $Me^{3'}$), 2.54 (s, 3 H, Me^5), 2.53 (s, 3 H, $Me^{5'}$) and 7.64–7.20 [m, 10 H, (PhC≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 68.0 (CH), 109.4, 109.3 ($C^{4\text{ or }4'}$), 155.3, 155.1, 142.2, 141.7 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.2, 15.4 (Me^3, $Me^{3'}$), 11.6, 11.2 (Me^5, $Me^{5'}$), 131.8, 131.2, 130.5, 128.1 (*Ph*C≡), 252.2 (C≡C) and 161.6 (CO_2^-). IR (Nujol mull, cm^{-1}): 1552 ν(C=N), 1698 ν_{asym}(CO_2^-), 1465 ν_{sym}(CO_2^-), 1687 ν(C≡C), 722 ν(Nb–O), 329, 302 ν(Nb–Cl).

[$NbCl_2$(bdmpza)(Me_3SiC≡$CSiMe_3$)] 9. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(Me_3SiC≡$CSiMe_3$)] (1.000 g, 2.17 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.592 g, 0.54 mmol), to give **9** as a blue solid. Yield 75% (Found: C, 41.28; H, 5.92; N, 9.75. $C_{20}H_{33}Cl_2N_4NbO_2Si_2$ requires C, 41.31; H, 5.71; N, 9.50%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.55 (s, 1 H, CH), 6.10 (s, 1 H, H^4), 6.14 (s, 1 H, $H^{4'}$), 2.47 (s, 3 H, Me^3), 2.19 (s, 3 H, $Me^{3'}$), 2.44 (s, 3 H, Me^5), 2.46 (s, 3 H, $Me^{5'}$) and 0.12 [s, 18 H, (Me_3SiC≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 67.8 (CH), 109.3, 109.1 ($C^{4\text{ or }4'}$), 154.7, 154.6, 141.6, 141.5 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.2, 16.3 (Me^3, $Me^{3'}$), 11.4, 11.2 (Me^5, $Me^{5'}$), −0.3 (Me_3SiC≡), 248.2 (C≡C) and 160.5 (CO_2^-). IR (Nujol mull, cm^{-1}): 1555 ν(C=N), 1698 ν_{asym}(CO_2^-), 1462 ν_{sym}(CO_2^-), 1678 ν(C≡C), 709 ν(Nb–O), 377, 329 ν(Nb–Cl).

[$NbCl_2$(bdmpza)(PhC≡CMe)] 10. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(PhC≡CMe)] (1.000 g, 2.46 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.661 g, 0.61 mmol), to give **10** as an orange solid. Yield 85% (Found: C, 47.98; H, 4.85; N, 10.08. $C_{21}H_{23}Cl_2N_4NbO_2$ requires C, 47.83; H, 4.39; N, 10.62%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.78 (s, 1 H, CH), 6.10 (s, 1 H, H^4), 6.12 (s, 1 H, $H^{4'}$), 2.60 (s, 3 H, Me^3), 1.93 (s, 3 H, $Me^{3'}$), 2.55 (s, 3 H, Me^5), 2.51 (s, 3 H, $Me^{5'}$), 3.20 [s, 3H, (MeC≡)], 7.60–7.32 [m, 5 H, (PhC≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 68.1 (CH), 109.4, 109.2 ($C^{4\text{ or }4'}$), 155.0, 154.7, 142.1, 141.8 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.2, 15.3 (Me^3, $Me^{3'}$), 11.6, 11.2 (Me^5, $Me^{5'}$), 132.8, 131.4, 130.2, 127.9 (*Ph*C≡), 22.9 (*Me*C≡), 248.6, 232.7 (C≡C), 161.8 (CO_2^-). IR (Nujol mull, cm^{-1}): 1554 ν(C=N), 1690 ν_{asym}(CO_2^-), 1454 ν_{sym}(CO_2^-), 1676 ν(C≡C), 721 ν(Nb–O), 369, 323 ν(Nb–Cl).

[$NbCl_2$(bdmpza)(PhC≡CEt)] 11. The synthetic procedure was the same as for complex **3**, using [$NbCl_3$(dme)(PhC≡CEt)] (1.000 g, 2.38 mmol) and [{Li(H_2O)(bdmpza)}$_4$] **1** (0.650 g, 0.59 mmol), to give **11** as an orange solid. Yield 75% (Found: C, 48.92; H, 4.40; N, 10.50. $C_{22}H_{25}Cl_2N_4NbO_2$ requires C, 48.81; H, 4.65; N, 10.35%). ^1H NMR (CD_2Cl_2, 297 K): δ 6.67 (s, 1 H, CH), 6.09 (s, 1 H, H^4), 6.11 (s, 1 H, $H^{4'}$), 2.59 (s, 3 H, Me^3), 1.95 (s, 3 H, $Me^{3'}$), 2.53 (s, 3 H, Me^5), 2.50 (s, 3 H, $Me^{5'}$), 7.49–7.39 [m, 5 H, (PhC≡)], A 3.74, B 3.55, X 1.26 [ABX_3, J_{AB} = 16.0, $J_{AX} = J_{BX}$ = 7.6 Hz, (CH_3CH_2C≡)]. ^{13}C-{^1H} NMR (CD_2Cl_2): δ 68.0 (CH), 109.4, 109.2 ($C^{4\text{ or }4'}$), 155.0, 154.9, 142.1, 141.6 ($C^{3\text{ or }3'}$ or $C^{5\text{ or }5'}$), 15.2, 15.5 (Me^3, $Me^{3'}$), 11.6, 11.2 (Me^5, Me$^{5'}$), 132.7, 130.7, 130.1, 128.9 (*Ph*C≡), 31.7 (≡C*C*H$_2$CH$_3$), 12.6 (≡CCH$_2$*C*H$_3$), 251.3, 232.7 (C≡C) and 161.5 (CO$_2^-$). IR (Nujol mull, cm^{-1}): 1541 ν(C=N), 1680 ν_{asym}(CO$_2^-$), 1463 ν_{sym}(CO$_2^-$), 1672 ν(C≡C), 715 ν(Nb–O), 367, 330 ν(Nb–Cl).

[NbCl$_2$(bdmpza)(PhC≡CSiMe$_3$)] 12. The synthetic procedure was the same as for complex **3**, using [NbCl$_3$(dme)(PhC≡CSiMe$_3$)] (1.000 g, 2.15 mmol) and [{Li(H$_2$O)(bdmpza)}$_4$] **1** (0.587 g, 0.53 mmol), to give **12** as a violet solid. Yield 65% (Found: C, 47.31; H, 5.01; N, 9.81. $C_{23}H_{29}Cl_2N_4NbO_2Si$ requires C, 47.19; H, 4.99; N, 9.57%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.72 (s, 1 H, CH), 6.08 (s, 1 H, H^4), 6.13 (s, 1 H, H$^{4'}$), 2.56 (s, 3 H, Me^3), 1.98 (s, 3 H, Me$^{3'}$), 2.52 (s, 3 H, Me^5), 2.51 (s, 3 H, Me$^{5'}$), 7.76–7.28 [m 5 H, (PhC≡)] and 0.31 [s, 9 H, (≡CSiCH$_3$)]. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 67.9 (CH), 109.3, 109.2 (C$^{4 \text{ or } 4'}$), 154.9, 154.8, 142.0, 141.7 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.3, 15.7 (Me^3, Me$^{3'}$), 11.5, 11.2 (Me^5, Me$^{5'}$), 132.6, 130.7, 131.2, 128.9 (*Ph*C≡), −0.4 (≡CSi*C*H$_3$), 252.0, 244.8 (C≡C) and 161.42 (CO$_2^-$). IR (Nujol mull, cm^{-1}): 1551 ν(C=N), 1675 ν_{asym}(CO$_2^-$), 1460 ν_{sym}(CO$_2^-$), 1657 ν(C≡C), 723 ν(Nb–O), 368, 340 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(MeC≡CMe)] 13. To a cooled (−70 °C) solution of Hbdmpze (0.300 g, 1.28 mmol) in dry THF (150 cm^3) was added a 1.6 M solution of Bu^{n}Li in hexane (0.80 cm^3, 1.28 mmol). After 30 min a solution of [NbCl$_3$(dme)(MeC≡CMe)] (0.440 g, 1.28 mmol) in THF (30 cm^3) was added and the reaction mixture stirred for 1 h at room temperature. The solvent was removed under vacuum and, after extraction with toluene, a brown solid was obtained. This solid was crystallised from a mixture of THF–hexane. Yield 60% (Found: C, 42.39; H, 5.12; N, 12.22. $C_{16}H_{23}Cl_2N_4NbO$ requires C, 42.59; H, 5.14; N, 12.42%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.46 (br s, 1 H, CH), 4.53 (d, $^3J_{\mathrm{HH}}$ = 11.7 Hz, 2 H, CH$_2$O), 6.04 (s, 1 H, H^4), 6.22 (s, 1 H, H$^{4'}$), 2.59 (s, 3 H, Me^3), 2.32 (s, 3 H, Me$^{3'}$), 2.43 (s, 3 H, Me^5), 2.50 (s, 3 H, Me$^{5'}$) and 2.75 [s, 6 H, (MeC≡)]. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 68.1 (CH), 72.5 (CH$_2$O), 108.4, 108.9 (C$^{4 \text{ or } 4'}$), 154.6, 153.8, 140.4, 139.1 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.1, 15.2 (Me^3, Me$^{3'}$), 10.8, 11.2 (Me^5, Me$^{5'}$), 18.7 (*Me*C≡) and 208.1 (C≡C). IR (Nujol mull, cm^{-1}): 1561 ν(C=N), 1680 ν(C≡C), 846 ν(Nb–O), 374, 348 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(EtC≡CEt)] 14. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), Bu^{n}Li (0.80 cm^3, 1.28 mmol) and [NbCl$_3$(dme)(EtC≡CEt)] (0.475 g, 1.28 mmol), to give **14** as a brown solid. Yield 60% (Found: C, 45.22; H, 5.51; N, 11.72. $C_{18}H_{27}Cl_2N_4NbO$ requires C, 45.11; H, 5.68; N, 11.69%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.47 (br s, 1 H, CH), A 4.54, B 4.31 [AB, J_{AB} = 11.7, CH$_2$O], 6.02 (s, 1 H, H^4), 6.20 (s, 1 H, H$^{4'}$), 2.58 (s, 3 H, Me^3), 2.30 (s, 3 H, Me$^{3'}$), 2.43 (s, 3 H, Me^5), 2.50 (s, 3 H, Me$^{5'}$), A 3.42, B 3.02, X 1.16 [ABX$_3$, J_{AB} = 12.6, J_{AX} = J_{BX} = 7.5 Hz, (CH$_3$-CH$_2$C≡)]. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 68.1 (CH), 72.5 (CH$_2$O), 108.3, 108.7 (C$^{4 \text{ or } 4'}$), 154.6, 153.6, 140.3, 139.1 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.1, 16.4 (Me^3, Me$^{3'}$), 11.2, 11.7 (Me^5, Me$^{5'}$), 28.1 (CH$_3$*C*H$_2$C≡), 13.7 (*C*H$_3$CH$_2$C≡) and 213.5 (C≡C). IR (Nujol mull, cm^{-1}): 1575 ν(C=N), 1690 ν(C≡C), 790 ν(Nb–O), 344, 334 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(PhC≡CPh)] 15. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), Bu^{n}Li (0.80 cm^3, 1.28 mmol) and [NbCl$_3$(dme)(PhC≡CPh)] (0.600 g, 1.28 mmol), to give **15** as a brown solid. Yield 65% (Found: C, 54.31; H, 4.58; N, 9.71. $C_{26}H_{27}Cl_2N_4NbO$ requires C, 54.28; H, 4.73; N, 9.74%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.52 (br s, 1 H, CH), A 4.83, B 4.65 [AB, J_{AB} = 12.3 Hz, CH$_2$O], 5.94 (s, 1 H, H^4), 6.05 (s, 1 H, H$^{4'}$), 2.77 (s, 3 H, Me^3), 1.80 (s, 3 H, Me$^{3'}$), 2.45 (s, 3 H, Me^5), 2.51 (s, 3 H, Me$^{5'}$) and 7.56–7.13 (m, 10 H, PhC≡). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 66.6 (CH), 73.2 (CH$_2$O), 108.6, 108.9 (C$^{4 \text{ or } 4'}$), 155.5, 154.1, 140.2, 139.1 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.4, 15.6 (Me^3, Me$^{3'}$), 11.2, 11.7 (Me^5, Me$^{5'}$), 131.8, 130.2, 129.5, 127.1 (*Ph*C≡) and 223.5 (C≡C). IR (Nujol mull, cm^{-1}): 1575 ν(C=N), 1687 ν(C≡C), 810 ν(Nb–O), 356, 337 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(PhC≡CMe)] 16. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), Bu^{n}Li (0.80 cm^3, 1.28 mmol) and [NbCl$_3$(dme)(PhC≡CMe)] (0.520 g, 1.28 mmol), to give **16** as an orange solid. Yield 70% (Found: C, 49.21; H, 4.81; N, 10.77. $C_{21}H_{25}Cl_2N_4NbO$ requires C, 49.14; H, 4.91; N, 10.92%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.57 (br s, 1 H, CH), A 4.67, B 4.53 [AB, J_{AB} = 12.0 Hz, CH$_2$O], 6.05 (s, 1 H, H^4), 6.07 (s, 1 H, H$^{4'}$), 2.64 (s, 3 H, Me^3), 1.85 (s, 3 H, Me$^{3'}$), 2.46 (s, 3 H, Me^5), 2.53 (s, 3 H, Me$^{5'}$), 7.36–7.18 (m, 5 H, PhC≡) and 3.20 (s, 3H, ≡CMe). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 66.6 (CH), 73.0 (CH$_2$O), 108.5, 108.9 (C$^{4 \text{ or } 4'}$), 155.4, 153.9, 140.3, 139.2 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.3, 15.8 (Me^3, Me$^{3'}$), 11.3, 11.8 (Me^5, Me$^{5'}$), 135.8, 129.2, 128.5, 127.1 (*Ph*C≡), 18.9 (≡C*Me*), 216.0 and 234.5 (C≡C). IR (Nujol mull, cm^{-1}): 1565 ν(C=N), 1667 ν(C≡C), 840 ν(Nb–O), 345, 317 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(PhC≡CEt)] 17. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), Bu^{n}Li (0.80 cm^3, 1.28 mmol) and [NbCl$_3$(dme)(PhC≡CEt)] (0.537 g, 1.28 mmol), to give **17** as a brown solid. Yield 75% (Found: C, 50.21; H, 5.21; N, 10.51. $C_{22}H_{27}Cl_2N_4NbO$ requires C, 50.11; H, 5.16; N, 10.63%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.49 (br s, 1 H, CH), A 4.71, B 4.54 [AB, J_{AB} = 12.0, CH$_2$O], 6.02 (s, 1 H, H^4), 6.08 (s, 1 H, H$^{4'}$), 2.65 (s, 3 H, Me^3), 1.85 (s, 3 H, Me$^{3'}$), 2.46 (s, 3 H, Me^5), 2.51 (s, 3 H, Me$^{5'}$), 7.32–7.18 (m, 5 H, PhC≡), A 3.81, B 3.52, X 1.33 [ABX$_3$, J_{AB} = 12.7, J_{AX} = J_{BX} = 7.4 Hz, CH$_3$CH$_2$C≡]. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 66.4 (CH), 72.8 (CH$_2$O), 108.6, 108.9 (C$^{4 \text{ or } 4'}$), 155.5, 154.0, 140.2, 139.0 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.3, 15.8 (Me^3, Me$^{3'}$), 11.2, 11.7 (Me^5, Me$^{5'}$), 134.8, 128.2, 126.5, 125.1 (*Ph*C≡), 30.1 (≡C*C*H$_2$CH$_3$), 12.7 (≡CCH$_2$*C*H$_3$), 236.0, 246.7 (s, C≡C). IR (Nujol mull, cm^{-1}): 1563 ν(C=N), 1654 ν(C≡C), 835 ν(Nb–O), 357, 321 ν(Nb–Cl).

[NbCl$_2$(bdmpze)(PhC≡CSiMe$_3$)] 18. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), Bu^{n}Li (0.80 cm^3, 1.28 mmol) and [NbCl$_3$(dme)(PhC≡CSiMe$_3$)] (0.595 g, 1.28 mmol), to give **18** as a brown solid. Yield 70% (Found: C, 48.41; H, 5.52; N, 9.81. $C_{23}H_{31}Cl_2N_4NbOSi$ requires C, 48.34; H, 5.47; N, 9.80%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 6.49 (br s, 1 H, CH), A 4.67, B 4.47 [AB, J_{AB} = 12.4 Hz, CH$_2$O], 6.07 (s, 1 H, H^4), 5.98 (s, 1 H, H$^{4'}$), 2.64 (s, 3 H, Me^3), 1.84 (s, 3 H, Me$^{3'}$), 2.44 (s, 3 H, Me^5), 2.49 (s, 3 H, Me$^{5'}$), 7.31–7.22 (m, 5 H, PhC≡) and 0.42 [s, 9 H, ≡CSiMe$_3$]. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 66.4 (CH), 73.0 (CH$_2$O), 108.5, 108.9 (C$^{4 \text{ or } 4'}$), 155.6, 153.8, 140.2, 139.1 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 15.4, 16.0 (Me^3, Me$^{3'}$), 11.3, 11.7 (Me^5, Me$^{5'}$), 130.7, 129.8, 128.5, 126.2 (*Ph*C≡), 1.1 (≡CSi*Me*$_3$), 217.5, 235.2 (C≡C). IR (Nujol mull, cm^{-1}): 1555 ν(C=N), 1666 ν(C≡C), 873 ν(Nb–O), 345, 311 ν(Nb–Cl).

[NbCp′Cl(bdmpza)] 19. To a THF (50 cm^3) solution of [NbCl$_2$(bdmpza)(PhC≡CMe)] **10** (0.845 g, 1.60 mmol) was added an equimolar quantity of LiCp′ (0.231 g, 1.60 mmol). The suspension was stirred for 5 h at room temperature. The solvent was removed *in vacuo* and, by extraction with hexane, a yellow solid was obtained. Yield 70% (Found: C, 46.52; H, 5.52; N, 10.78. $C_{20}H_{28}ClN_4NbO_2Si$ requires C, 46.83; H, 5.50; N, 10.92%). ^{1}H NMR (CD$_2$Cl$_2$, 297 K): δ 7.45 (s, 1 H, CH), 5.79 (s, 1 H, H^4), 6.02 (s, 1 H, H$^{4'}$), 1.92 (s, 3 H, Me^3), 2.60 (s, 3 H, Me$^{3'}$), 2.46 (s, 3 H, Me^5), 2.55 (s, 3 H, Me$^{5'}$), 6.81–6.45 (m, 4 H, C$_5$*H*$_4$SiMe$_3$) and −0.07 (s, 9 H CH$_4$Si*Me*$_3$). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 63.9 (CH), 108.2, 107.8 (C$^{4 \text{ or } 4'}$), 152.9, 152.4, 139.2, 139.0 (C$^{3 \text{ or } 3'}$ or C$^{5 \text{ or } 5'}$), 14.6, 17.5 (Me^3, Me$^{3'}$), 14.1, 13.5 (Me^5,

$\mathrm{Me}^{5'}$), 125.9, 123.8, 119.2, 115.8, 106.4 ($\mathit{C}_5\mathrm{H}_4\mathrm{SiMe}_3$), 1.2 ($\mathrm{C}_5\mathrm{H}_4\mathrm{Si}\mathit{Me}_3$) and 162.3 ($\mathrm{CO}_2^-$). IR (Nujol mull, cm^{-1}): 1554 ν(C=N), 1680 $\nu_{\mathrm{asym}}(\mathrm{CO}_2^-)$, 1460 $\nu_{\mathrm{sym}}(\mathrm{CO}_2^-)$, 735 ν(Nb–O) and 321 ν(Nb–Cl). Mass spectrum [FAB (*m*/*z* assignment)]: 512 (M).

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