

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

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Received 6th April 2000, Accepted 31st May 2000

Published on the Web 30th June 2000

The syntheses of novel scorpionate ligands in the form of the lithium derivative $[\{\text{Li}(\text{H}_2\text{O})(\text{bdmpza})\}_4]$ **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 $[\{\text{NbCl}_3(\text{dme})\}_n]$ (dme = 1,2-dimethoxyethane) reacted with **1** and **2**, the latter with prior addition of Bu^nLi , to give the binuclear complexes $[\{\text{NbCl}_2(\text{bdmpzx})\}_2]$ ($x = \text{a}$, **3**; $x = \text{e}$, **4**) [bdmpze = 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide]. Complex **3** reacted with **1** to give the complex $[\{\text{NbCl}(\text{bdmpza})_2\}_2]$ **5**. In the same way the reaction of the mononuclear species $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]_n$ with **1** and **2**, the latter with prior addition of Bu^nLi , gave the appropriate $[\text{NbCl}_2(\text{bdmpzx})(\text{RC}\equiv\text{CR}')]_n$ complexes [$x = \text{a}$, $\text{R} = \text{R}' = \text{Me}$, **6**; Et, **7**; Ph, **8**; or SiMe_3 , **9**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$, **10**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Et}$, **11**; $\text{R} = \text{Ph}$, $\text{R}' = \text{SiMe}_3$, **12**; $x = \text{e}$, $\text{R} = \text{R}' = \text{Me}$, **13**; Et, **14**; or Ph, **15**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$, **16**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Et}$, **17**; $\text{R} = \text{Ph}$, $\text{R}' = \text{SiMe}_3$, **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' ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) gave the mixed Cp–bdmpza complex $[\text{NbCp}'\text{Cl}(\text{bdmpza})]$ **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 $[\text{NbTp}(\text{Cl})_2(\text{RC}\equiv\text{CR}')]_n$ or $[\text{NbTp}^*(\text{O})(\text{Cl})(\text{OR})]_n$.²

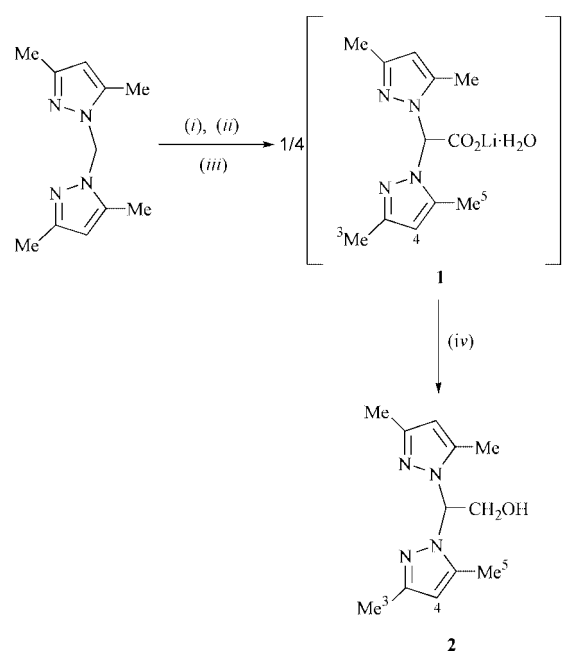
We are now interested, as are other research groups, in the synthesis of “heteroscorpionate” ligands.^{3–5} Our new ligands are related to the tris(pyrazol-1-yl)methane system,^{4,6} but in this case one of the pyrazole groups is replaced by a carboxylate or ethoxy group to give a small degree of steric 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^nLi was treated with CO_2 . This reaction gave rise to the lithium carboxylate compound $[\{\text{Li}(\text{H}_2\text{O})(\text{bdmpza})\}_4]$ **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^nLi , 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) $(\text{CH}_3)_2\text{S}\cdot\text{BH}_3$, THF, reflux, 12 h under an atmosphere of dry nitrogen.

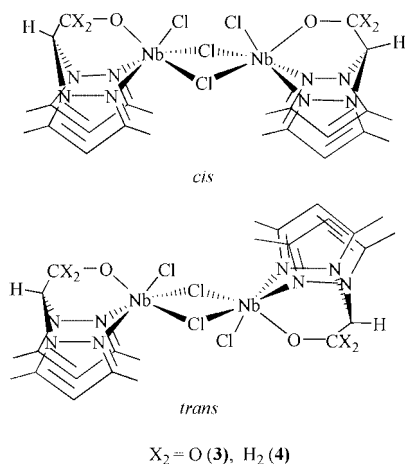


Fig. 2 Proposed structure for complexes 3 and 4 (*cis* and *trans* dispositions).

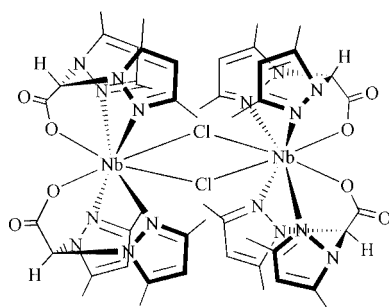
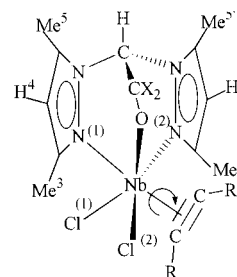


Fig. 3 Proposed structure for complex 5.

indicates a binuclear formulation. In the IR spectrum the value of $\Delta\nu_{as-s}$ 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 $\nu(\text{Nb}-\text{Cl})$ 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 $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]^{11}$ in THF to give, after the appropriate work-up, $[\text{NbCl}_2(\text{bdmpza})(\text{RC}\equiv\text{CR}')]$ ($R = R' = \text{Me}$, 6; Et, 7; Ph, 8; or SiMe_3 , 9; $R = \text{Ph}$, $R' = \text{Me}$, 10; $R = \text{Ph}$, $R' = \text{Et}$, 11; $R = \text{Ph}$, $R' = \text{SiMe}_3$, 12), which were isolated as orange, red or blue solids. Compound 2 also reacts with $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]^{11}$ after prior addition of 1 equivalent of Bu^nLi [eqn. (3)] to give $[\text{NbCl}_2(\text{bdmpze})(\text{RC}\equiv\text{CR}')]$ ($R = R' = \text{Me}$, 13; Et, 14; or Ph, 15; $R = \text{Ph}$, $R' = \text{Me}$, 16; $R = \text{Ph}$, $R' = \text{Et}$, 17; $R = \text{Ph}$, $R' = \text{SiMe}_3$, 18).

The ^1H 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 $^{13}\text{C}\{-\text{H}\}$ NMR spectra of

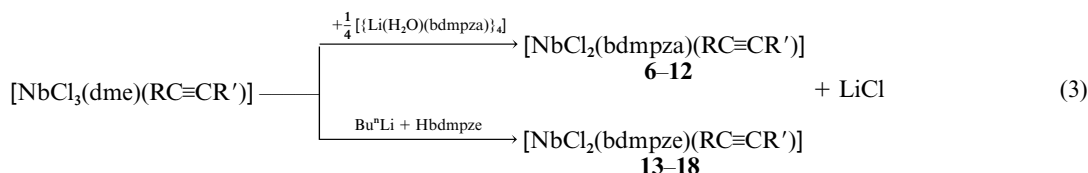


$X_2 = O$ (6–12), H_2 (13–18)

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).

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 $^1\text{H}\text{-}^{13}\text{C}$ 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 ^1H 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, ΔG^\ddagger , for the complexes 6–18 were calculated¹³ 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 ΔG^\ddagger values and coalescence temperatures were found in the cases of the bulkier alkyne substituents.

Another factor that influences the rotation of the alkyne ligand is the nature of the scorpionate ligand. Thus, in the complexes $[\text{NbTp}^*\text{Cl}_2(\text{RC}\equiv\text{CR}')]^{14}$ ($R = R' = \text{Me}$ or Ph; $R = \text{Ph}$, $R' = \text{Me}$, 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 $[\text{NbCl}_2(\text{bdmpza})(\text{RC}\equiv\text{CR}')]^{12-18}$ there is a little difference in the values of ΔG^\ddagger , *ca.* $0.5\text{--}1\text{ kcal mol}^{-1}$ (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



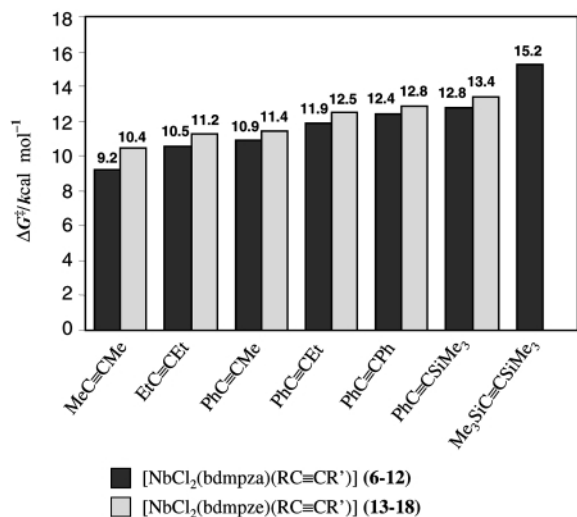


Fig. 5 Graphic representation of free energy values, ΔG^\ddagger , for rotation of the alkyne ligands for complexes **6–18**. Coalescence temperature values for these complexes are: 163, **6**; 181, **7**; 213, **8**; 263, **9**; 193, **10**; 203, **11**; 223, **12**; 223, **13**; 238, **14**; 263, **15**;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

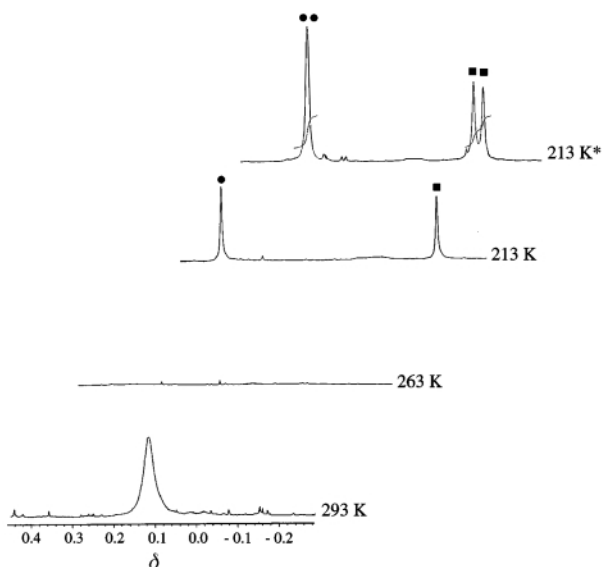
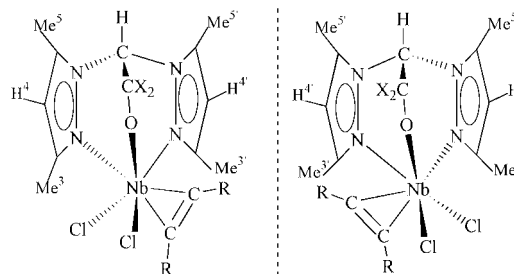


Fig. 6 Variable-temperature ^1H NMR spectra in the region of the SiMe_3 alkyne groups of the complex $[\text{NbCl}_2(\text{bdmpza})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ **9**. * With chiral shift reagent.

a singlet is observed for the SiMe_3 alkyne groups in the variable-temperature ^1H 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 ^1H NMR signal at $\delta -0.13$ 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.

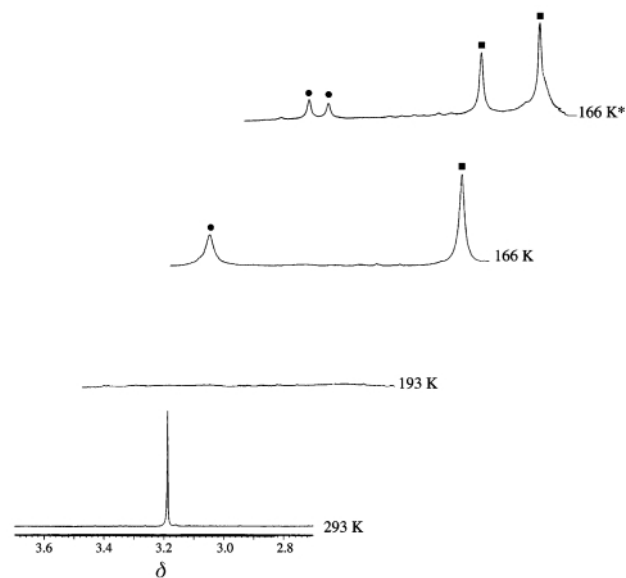
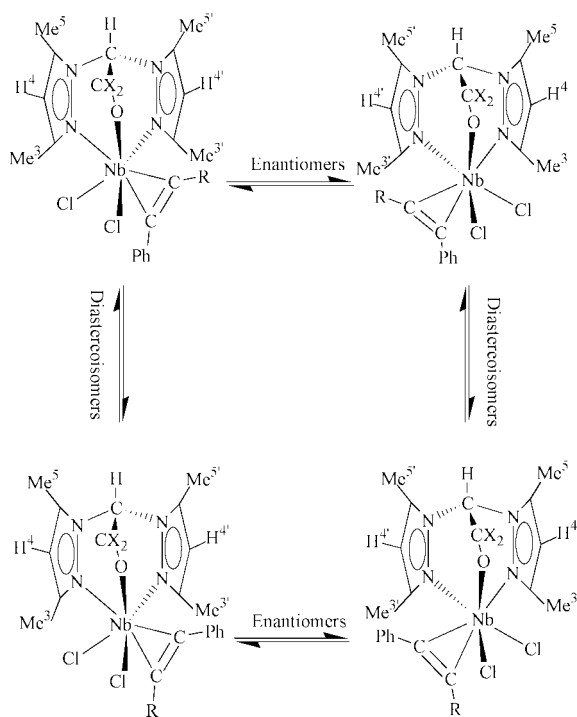


Fig. 7 Variable-temperature ^1H NMR spectra in the region of the Me alkyne group of the complex $[\text{NbCl}_2(\text{bdmpza})(\text{PhC}\equiv\text{CMe})]$ **10**. * With chiral shift reagent.

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 $[\text{NbTp}^*\text{Cl}_2(\text{PhC}\equiv\text{CMe})]$ 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 ^1H 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.

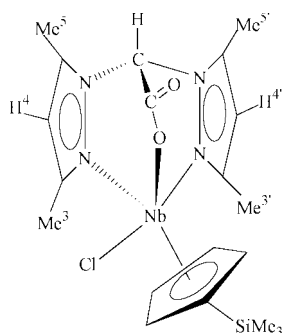
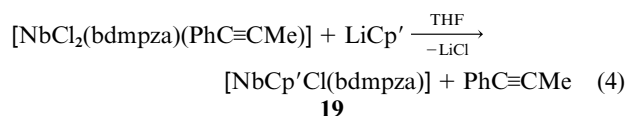


Fig. 8 Proposed structure for complex **19**.

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' = C₅H₄SiMe₃) [eqn. (4)] to give the



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* = C₅Me₅).

The ¹H and ¹³C NMR spectra for complex **19** show that Cp' and the bdmpza are η⁵- and κ³-bound respectively. Two resonances can be observed in these spectra for each of the Me³, Me⁵ and H⁴ 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 introduc-

tion 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, ¹³C and ⁷Li NMR spectra on a Varian Unity FT-300 spectrometer referenced to the residual deuterated 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 CH₃OH.

The complexes [{NbCl₃(dme)}_n], [NbCl₃(dme)(RC≡CR')] and the compound bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm) were prepared as reported previously.^{8,11}

Preparations

[{Li(H₂O)(bdmpza)}₄] **1.** In a 250 cm³ Schlenk tube, bdmpzm (4 g, 20 mmol) was dissolved in dry THF (150 cm³) and the solution cooled to -70 °C. A 1.6 M solution of BuⁿLi (12.50 cm³, 20 mmol) in hexane was added and the solution stirred for 45 min, CO₂ 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. C₁₂H₁₇LiN₄O₃ 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, H⁴), 2.03 (s, 6 H, Me³) and 2.25 (s, 6 H, Me⁵). ¹³C-¹H NMR (DMSO): δ 73.9 (CH), 140.1 (C³), 105.1 (C⁴), 145.2 (C⁵), 11.5 (Me³), 13.4 (Me⁵) and 164.7 (CO₂⁻). ⁷Li NMR (DMSO): δ 1.50 (s). IR (Nujol mull, cm⁻¹), 1557 ν(C=N), 1641 ν_{asym}(CO₂⁻) and 1461 ν_{sym}(CO₂⁻). Mass spectrum [FAB (*m/z* assignment, % intensity)]: 769 [Li₄(bdmpza)₃], 20; 515 [Li₃(bdmpza)₂], 19; and 261 [Li₂(bdmpza)], 100.

Hbdmpze **2.** In a 250 cm³ Schlenk tube, [Li(H₂O)(bdmpza)₄] **1** (3 g, 2.75 mmol) was dissolved in dry THF (150 cm³) and a 2.0 M solution of (CH₃)₂S·BH₃ (5.50 cm³, 11 mmol) in THF added. The resulting solution was stirred for 12 h under reflux. The suspension was treated dropwise with CH₃CO₂H–water (1:2) to pH 5. After 1 h the solution was treated dropwise with a saturated solution of Na₂CO₃ to pH 7. The mixture was separated and the organic layer dried (MgSO₄) 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. C₁₂H₁₈N₄O requires C, 61.51; H, 7.74; N, 23.91%). ¹H NMR (CDCl₃, 297 K): δ 6.28 (t, ³J_{HH} = 5.8, 1 H, CH), 4.39 (d, ³J_{HH} = 5.8 Hz, 2 H, CH₂OH), 5.82 (s, 2 H, H⁴), 1.94 (s, 6 H, Me³) and 2.21 (s, 6 H, Me⁵). ¹³C-¹H

NMR (CDCl₃): δ 72.5 (CH), 63.2 (CH₂OH), 148.2 (C³), 106.9 (C⁴), 140.3 (C⁵), 10.5 (Me³) and 13.5 (Me⁵). IR (Nujol mull, cm⁻¹): 3194 ν (OH) and 1554 ν (C=N).

[NbCl₂(bdmpza)₂]₂ 3. To a THF (50 cm³) solution of [NbCl₃(dme)] (1.2 g, 4.20 mmol) was added [{Li(H₂O)(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 CH₂Cl₂. A violet solid was obtained after removal of the solvents. Yield 78% (Found: C, 35.58; H, 3.98; N, 13.24. C₁₂H₁₅Cl₂N₄O₂Nb 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, H⁴), 2.27 (s, 12 H, Me³) and 2.37 (s, 12 H, Me⁵). ¹³C-¹H NMR (DMSO): δ 71.4 (CH), 140.5 (C³), 106.4 (C⁴), 146.8 (C⁵), 10.8 (Me³), 13.2 (Me⁵) and 165.9 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1557 ν (C=N), 1699 ν_{asym} (CO₂⁻), 1460 ν_{sym} (CO₂⁻), 725 ν (Nb–O) and 333 ν (Nb–Cl). Mass spectrum [FAB (*m/z* assignment)]: 752 (M – 2Cl).

[NbCl₂(bdmpze)₂]₂ 4. To a cooled (–70 °C) solution of Hbdmpze (0.3 g, 1.28 mmol) in dry THF (150 cm³) was added a 1.6 M solution of BuⁿLi (0.80 cm³, 1.28 mmol) in hexane and the mixture stirred for 30 min. A solution of [NbCl₃(dme)] (0.370 g, 1.28 mmol) in THF (30 cm³) was added. After 1 h the solvent was removed under vacuum and the solid extracted with CH₂Cl₂. 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. C₁₂H₁₇Cl₂N₄NbO 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, CH₂O), 5.78 (s, 4 H, H⁴), 2.04 (s, 12 H, Me³) and 2.21 (s, 12 H, Me⁵). ¹³C-¹H NMR (DMSO): δ 70.3 (CH), 61.4 (CH₂O), 146.3 (C³), 105.6 (C⁴), 139.6 (C⁵), 10.6 (Me³) and 13.6 (Me⁵). 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).

[NbCl₂(bdmpza)₂]₂ 5. To a THF (50 cm³) suspension of [NbCl₂(bdmpza)₂]**3** (0.200 g, 0.24 mmol) was added [{Li(H₂O)(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. C₂₄H₃₀Cl₂N₈NbO₄ requires C, 46.27; H, 4.85; N, 17.98%). ¹H NMR (CDCl₃, 297 K): δ 6.79 (s, 4 H, CH), 5.69 (s, 8 H, H⁴), 2.35 (s, 24 H, Me³) and 1.99 (s, 24 H, Me⁵). ¹³C-¹H NMR (CDCl₃): δ 68.1 (CH), 141.5 (C³), 106.4 (C⁴), 146.4 (C⁵), 11.7 (Me³), 13.5 (Me⁵) and 169.6 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1553 ν (C=N), 1701 ν_{asym} (CO₂⁻), 1462 ν_{sym} (CO₂⁻), 712 ν (Nb–O) and 250 ν (Nb–Cl). Mass spectrum [FAB (*m/z* assignment)]: 1246 (M + 1).

[NbCl₂(bdmpza)(MeC≡CMe)] 6. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(MeC≡CMe)] (0.600 g, 1.74 mmol) and [{Li(H₂O)(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. C₁₆H₂₁Cl₂N₄NbO₂ requires C, 41.31; H, 4.55; N, 12.04%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.58 (s, 1 H, CH), 6.09 (s, 1 H, H⁴), 6.18 (s, 1 H, H⁴), 2.52 (s, 3 H, Me³), 2.11 (s, 3 H, Me³), 2.49 (s, 3 H, Me⁵), 2.47 (s, 3 H, Me⁵) and 2.94 [s, 6 H, (MeC≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 67.9 (CH), 109.3, 109.2 (C⁴ or 4'), 155.0, 153.7, 142.3, 141.9 (C³ or 3' or C⁵ or 5'), 15.0, 15.4 (Me³, Me³), 11.5, 11.1 (Me⁵, Me⁵), 21.6 (MeC≡), 242.5 (C≡C) and 163.4 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1548 ν (C=N), 1693 ν_{asym} (CO₂⁻), 1463 ν_{sym} (CO₂⁻), 1672 ν (C≡C), 725 ν (Nb–O), 370, 342 cm⁻¹ ν (Nb–Cl).

[NbCl₂(bdmpza)(EtC≡CEt)] 7. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(EtC≡CEt)] (1.000 g, 2.70 mmol) and [{Li(H₂O)(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. C₁₈H₂₅Cl₂N₄NbO₂ requires C, 43.83; H, 5.11; N, 11.35%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.59 (s, 1 H, CH), 6.08 (s, 1 H, H⁴), 6.17 (s, 1 H, H⁴), 2.53 (s, 3 H, Me³), 2.14 (s, 3 H, Me³), 2.50 (s, 3 H, Me⁵), 2.47 (s, 3 H, Me⁵), A 3.36, B 3.24, X 1.26 [ABX₃, J_{AB} = 17.0, J_{AX} = J_{BX} = 7.5 Hz, (CH₃CH₂C≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 67.9 (CH), 109.3, 109.1 (C⁴ or 4'), 154.8, 154.4, 141.9, 141.6 (C³ or 3' or C⁵ or 5'), 15.0, 15.5 (Me³, Me³), 11.5 (Me⁵, Me⁵), 31.29 (CH₃CH₂C≡), 13.5 (CH₃CH₂C≡), 247.9 (C≡C) and 161.4 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1550 ν (C=N), 1671 ν_{asym} (CO₂⁻), 1458 ν_{sym} (CO₂⁻), 1660 ν (C≡C), 717 ν (Nb–O), 360, 340 ν (Nb–Cl).

[NbCl₂(bdmpza)(PhC≡CPh)] 8. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(PhC≡CPh)] (1.000 g, 2.14 mmol) and [{Li(H₂O)(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. C₂₆H₂₅Cl₂N₄NbO₂ requires C, 52.99; H, 4.27; N, 9.50%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.74 (s, 1 H, CH), 6.01 (s, 1 H, H⁴), 6.15 (s, 1 H, H⁴), 2.65 (s, 3 H, Me³), 1.83 (s, 3 H, Me³), 2.54 (s, 3 H, Me⁵), 2.53 (s, 3 H, Me⁵) and 7.64–7.20 [m, 10 H, (PhC≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 68.0 (CH), 109.4, 109.3 (C⁴ or 4'), 155.3, 155.1, 142.2, 141.7 (C³ or 3' or C⁵ or 5'), 15.2, 15.4 (Me³, Me³), 11.6, 11.2 (Me⁵, Me⁵), 131.8, 131.2, 130.5, 128.1 (PhC≡), 252.2 (C≡C) and 161.6 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1552 ν (C=N), 1698 ν_{asym} (CO₂⁻), 1465 ν_{sym} (CO₂⁻), 1687 ν (C≡C), 722 ν (Nb–O), 329, 302 ν (Nb–Cl).

[NbCl₂(bdmpza)(Me₃SiC≡CSiMe₃)] 9. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(Me₃SiC≡CSiMe₃)] (1.000 g, 2.17 mmol) and [{Li(H₂O)(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. C₂₀H₃₃Cl₂N₄NbO₂Si₂ requires C, 41.31; H, 5.71; N, 9.50%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.55 (s, 1 H, CH), 6.10 (s, 1 H, H⁴), 6.14 (s, 1 H, H⁴), 2.47 (s, 3 H, Me³), 2.19 (s, 3 H, Me³), 2.44 (s, 3 H, Me⁵), 2.46 (s, 3 H, Me⁵) and 0.12 [s, 18 H, (Me₃SiC≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 67.8 (CH), 109.3, 109.1 (C⁴ or 4'), 154.7, 154.6, 141.6, 141.5 (C³ or 3' or C⁵ or 5'), 15.2, 16.3 (Me³, Me³), 11.4, 11.2 (Me⁵, Me⁵), –0.3 (Me₃SiC≡), 248.2 (C≡C) and 160.5 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1555 ν (C=N), 1698 ν_{asym} (CO₂⁻), 1462 ν_{sym} (CO₂⁻), 1678 ν (C≡C), 709 ν (Nb–O), 377, 329 ν (Nb–Cl).

[NbCl₂(bdmpza)(PhC≡CMe)] 10. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(PhC≡CMe)] (1.000 g, 2.46 mmol) and [{Li(H₂O)(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. C₂₁H₂₃Cl₂N₄NbO₂ requires C, 47.83; H, 4.39; N, 10.62%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.78 (s, 1 H, CH), 6.10 (s, 1 H, H⁴), 6.12 (s, 1 H, H⁴), 2.60 (s, 3 H, Me³), 1.93 (s, 3 H, Me³), 2.55 (s, 3 H, Me⁵), 2.51 (s, 3 H, Me⁵), 3.20 [s, 3H, (MeC≡)], 7.60–7.32 [m, 5 H, (PhC≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 68.1 (CH), 109.4, 109.2 (C⁴ or 4'), 155.0, 154.7, 142.1, 141.8 (C³ or 3' or C⁵ or 5'), 15.2, 15.3 (Me³, Me³), 11.6, 11.2 (Me⁵, Me⁵), 132.8, 131.4, 130.2, 127.9 (PhC≡), 22.9 (MeC≡), 248.6, 232.7 (C≡C), 161.8 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1554 ν (C=N), 1690 ν_{asym} (CO₂⁻), 1454 ν_{sym} (CO₂⁻), 1676 ν (C≡C), 721 ν (Nb–O), 369, 323 ν (Nb–Cl).

[NbCl₂(bdmpza)(PhC≡CEt)] 11. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(PhC≡CEt)] (1.000 g, 2.38 mmol) and [{Li(H₂O)(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. C₂₂H₂₅Cl₂N₄NbO₂ requires C, 48.81; H, 4.65; N, 10.35%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.67 (s, 1 H, CH), 6.09 (s, 1 H, H⁴), 6.11 (s, 1 H, H⁴), 2.59 (s, 3 H, Me³), 1.95 (s, 3 H, Me³), 2.53 (s, 3 H, Me⁵), 2.50 (s, 3 H, Me⁵), 7.49–7.39 [m, 5 H, (PhC≡)], A 3.74, B 3.55, X 1.26 [ABX₃, J_{AB} = 16.0, J_{AX} = J_{BX} = 7.6 Hz, (CH₃CH₂C≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 68.0 (CH), 109.4, 109.2 (C⁴ or 4'), 155.0, 154.9, 142.1, 141.6 (C³ or 3' or C⁵ or 5'), 15.2, 15.5 (Me³, Me³), 11.6, 11.2 (Me⁵,

Me⁵), 132.7, 130.7, 130.1, 128.9 (*PhC*≡), 31.7 (≡CCH₂CH₃), 12.6 (≡CCH₂CH₃), 251.3, 232.7 (C≡C) and 161.5 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1541 ν(C=N), 1680 ν_{asym}(CO₂⁻), 1463 ν_{sym}(CO₂⁻), 1672 ν(C≡C), 715 ν(Nb–O), 367, 330 ν(Nb–Cl).

[NbCl₂(bdmpza)(PhC≡CSiMe₃)] 12. The synthetic procedure was the same as for complex **3**, using [NbCl₃(dme)(PhC≡CSiMe₃)] (1.000 g, 2.15 mmol) and [Li(H₂O)(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. C₂₃H₂₉Cl₂N₄NbO₂Si requires C, 47.19; H, 4.99; N, 9.57%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.72 (s, 1 H, CH), 6.08 (s, 1 H, H⁴), 6.13 (s, 1 H, H⁴), 2.56 (s, 3 H, Me³), 1.98 (s, 3 H, Me³), 2.52 (s, 3 H, Me⁵), 2.51 (s, 3 H, Me⁵), 7.76–7.28 [m 5 H, (PhC≡)] and 0.31 [s, 9 H, (≡CSiCH₃)]. ¹³C-¹H NMR (CD₂Cl₂): δ 67.9 (CH), 109.3, 109.2 (C⁴ or ^{4'}), 154.9, 154.8, 142.0, 141.7 (C³ or ^{3'} or C⁵ or ^{5'}), 15.3, 15.7 (Me³, Me³), 11.5, 11.2 (Me⁵, Me⁵), 132.6, 130.7, 131.2, 128.9 (*PhC*≡), -0.4 (≡CSiCH₃), 252.0, 244.8 (C≡C) and 161.42 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1551 ν(C=N), 1675 ν_{asym}(CO₂⁻), 1460 ν_{sym}(CO₂⁻), 1657 ν(C≡C), 723 ν(Nb–O), 368, 340 ν(Nb–Cl).

[NbCl₂(bdmpze)(MeC≡CMe)] 13. To a cooled (-70 °C) solution of Hbdmpze (0.300 g, 1.28 mmol) in dry THF (150 cm³) was added a 1.6 M solution of BuⁿLi in hexane (0.80 cm³, 1.28 mmol). After 30 min a solution of [NbCl₃(dme)(MeC≡CMe)] (0.440 g, 1.28 mmol) in THF (30 cm³) 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. C₁₆H₂₃Cl₂N₄NbO requires C, 42.59; H, 5.14; N, 12.42%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.46 (br s, 1 H, CH), 4.53 (d, ³J_{HH} = 11.7 Hz, 2 H, CH₂O), 6.04 (s, 1 H, H⁴), 6.22 (s, 1 H, H⁴), 2.59 (s, 3 H, Me³), 2.32 (s, 3 H, Me³), 2.43 (s, 3 H, Me⁵), 2.50 (s, 3 H, Me⁵) and 2.75 [s, 6 H, (MeC≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 68.1 (CH), 72.5 (CH₂O), 108.4, 108.9 (C⁴ or ^{4'}), 154.6, 153.8, 140.4, 139.1 (C³ or ^{3'} or C⁵ or ^{5'}), 15.1, 15.2 (Me³, Me³), 10.8, 11.2 (Me⁵, Me⁵), 18.7 (MeC≡) 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).

[NbCl₂(bdmpze)(EtC≡CEt)] 14. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), BuⁿLi (0.80 cm³, 1.28 mmol) and [NbCl₃(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. C₁₈H₂₇Cl₂N₄NbO requires C, 45.11; H, 5.68; N, 11.69%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.47 (br s, 1 H, CH), A 4.54, B 4.31 [AB, J_{AB} = 11.7, CH₂O], 6.02 (s, 1 H, H⁴), 6.20 (s, 1 H, H⁴), 2.58 (s, 3 H, Me³), 2.30 (s, 3 H, Me³), 2.43 (s, 3 H, Me⁵), 2.50 (s, 3 H, Me⁵), A 3.42, B 3.02, X 1.16 [ABX₃, J_{AB} = 12.6, J_{AX} = J_{BX} = 7.5 Hz, (CH₃-CH₂-C≡)]. ¹³C-¹H NMR (CD₂Cl₂): δ 68.1 (CH), 72.5 (CH₂O), 108.3, 108.7 (C⁴ or ^{4'}), 154.6, 153.6, 140.3, 139.1 (C³ or ^{3'} or C⁵ or ^{5'}), 15.1, 16.4 (Me³, Me³), 11.2, 11.7 (Me⁵, Me⁵), 28.1 (CH₃CH₂C≡), 13.7 (CH₃CH₂C≡) 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).

[NbCl₂(bdmpze)(PhC≡CPh)] 15. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), BuⁿLi (0.80 cm³, 1.28 mmol) and [NbCl₃(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. C₂₆H₂₇Cl₂N₄NbO requires C, 54.28; H, 4.73; N, 9.74%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.52 (br s, 1 H, CH), A 4.83, B 4.65 [AB, J_{AB} = 12.3 Hz, CH₂O], 5.94 (s, 1 H, H⁴), 6.05 (s, 1 H, H⁴), 2.77 (s, 3 H, Me³), 1.80 (s, 3 H, Me³), 2.45 (s, 3 H, Me⁵), 2.51 (s, 3 H, Me⁵) and 7.56–7.13 (m, 10 H, PhC≡). ¹³C-¹H NMR (CD₂Cl₂): δ 66.6 (CH), 73.2 (CH₂O), 108.6, 108.9 (C⁴ or ^{4'}), 155.5, 154.1, 140.2,

139.1 (C³ or ^{3'} or C⁵ or ^{5'}), 15.4, 15.6 (Me³, Me³), 11.2, 11.7 (Me⁵, Me⁵), 131.8, 130.2, 129.5, 127.1 (*PhC*≡) 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).

[NbCl₂(bdmpze)(PhC≡CMe)] 16. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), BuⁿLi (0.80 cm³, 1.28 mmol) and [NbCl₃(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. C₂₁H₂₅-Cl₂N₄NbO requires C, 49.14; H, 4.91; N, 10.92%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.57 (br s, 1 H, CH), A 4.67, B 4.53 [AB, J_{AB} = 12.0 Hz, CH₂O], 6.05 (s, 1 H, H⁴), 6.07 (s, 1 H, H⁴), 2.64 (s, 3 H, Me³), 1.85 (s, 3 H, Me³), 2.46 (s, 3 H, Me⁵), 2.53 (s, 3 H, Me⁵), 7.36–7.18 (m, 5 H, PhC≡) and 3.20 (s, 3H, ≡CMe). ¹³C-¹H NMR (CD₂Cl₂): δ 66.6 (CH), 73.0 (CH₂O), 108.5, 108.9 (C⁴ or ^{4'}), 155.4, 153.9, 140.3, 139.2 (C³ or ^{3'} or C⁵ or ^{5'}), 15.3, 15.8 (Me³, Me³), 11.3, 11.8 (Me⁵, Me⁵), 135.8, 129.2, 128.5, 127.1 (*PhC*≡), 18.9 (≡CMe), 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).

[NbCl₂(bdmpze)(PhC≡CEt)] 17. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), BuⁿLi (0.80 cm³, 1.28 mmol) and [NbCl₃(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. C₂₂H₂₇Cl₂-N₄NbO requires C, 50.11; H, 5.16; N, 10.63%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.49 (br s, 1 H, CH), A 4.71, B 4.54 [AB, J_{AB} = 12.0, CH₂O], 6.02 (s, 1 H, H⁴), 6.08 (s, 1 H, H⁴), 2.65 (s, 3 H, Me³), 1.85 (s, 3 H, Me³), 2.46 (s, 3 H, Me⁵), 2.51 (s, 3 H, Me⁵), 7.32–7.18 (m, 5 H, PhC≡), A 3.81, B 3.52, X 1.33 [ABX₃, J_{AB} = 12.7, J_{AX} = J_{BX} = 7.4 Hz, CH₃CH₂C≡]. ¹³C-¹H NMR (CD₂Cl₂): δ 66.4 (CH), 72.8 (CH₂O), 108.6, 108.9 (C⁴ or ^{4'}), 155.5, 154.0, 140.2, 139.0 (C³ or ^{3'} or C⁵ or ^{5'}), 15.3, 15.8 (Me³, Me³), 11.2, 11.7 (Me⁵, Me⁵), 134.8, 128.2, 126.5, 125.1 (*PhC*≡), 30.1 (≡CCH₂CH₃), 12.7 (≡CCH₂CH₃), 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).

[NbCl₂(bdmpze)(PhC≡CSiMe₃)] 18. The synthetic procedure was the same as for complex **13**, using Hbdmpze (0.300 g, 1.28 mmol), BuⁿLi (0.80 cm³, 1.28 mmol) and [NbCl₃(dme)(PhC≡CSiMe₃)] (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. C₂₃H₃₁Cl₂-N₄NbOSi requires C, 48.34; H, 5.47; N, 9.80%). ¹H NMR (CD₂Cl₂, 297 K): δ 6.49 (br s, 1 H, CH), A 4.67, B 4.47 [AB, J_{AB} = 12.4 Hz, CH₂O], 6.07 (s, 1 H, H⁴), 5.98 (s, 1 H, H⁴), 2.64 (s, 3 H, Me³), 1.84 (s, 3 H, Me³), 2.44 (s, 3 H, Me⁵), 2.49 (s, 3 H, Me⁵), 7.31–7.22 (m, 5 H, PhC≡) and 0.42 [s, 9 H, ≡CSiMe₃]. ¹³C-¹H NMR (CD₂Cl₂): δ 66.4 (CH), 73.0 (CH₂O), 108.5, 108.9 (C⁴ or ^{4'}), 155.6, 153.8, 140.2, 139.1 (C³ or ^{3'} or C⁵ or ^{5'}), 15.4, 16.0 (Me³, Me³), 11.3, 11.7 (Me⁵, Me⁵), 130.7, 129.8, 128.5, 126.2 (*PhC*≡), 1.1 (≡CSiMe₃), 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 cm³) solution of [NbCl₂(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. C₂₀H₂₈ClN₄NbO₂Si requires C, 46.83; H, 5.50; N, 10.92%). ¹H NMR (CD₂Cl₂, 297 K): δ 7.45 (s, 1 H, CH), 5.79 (s, 1 H, H⁴), 6.02 (s, 1 H, H⁴), 1.92 (s, 3 H, Me³), 2.60 (s, 3 H, Me³), 2.46 (s, 3 H, Me⁵), 2.55 (s, 3 H, Me⁵), 6.81–6.45 (m, 4 H, C₅H₄SiMe₃) and -0.07 (s, 9 H CH₄SiMe₃). ¹³C-¹H NMR (CD₂Cl₂): δ 63.9 (CH), 108.2, 107.8 (C⁴ or ^{4'}), 152.9, 152.4, 139.2, 139.0 (C³ or ^{3'} or C⁵ or ^{5'}), 14.6, 17.5 (Me³, Me³), 14.1, 13.5 (Me⁵,

Me⁵), 125.9, 123.8, 119.2, 115.8, 106.4 (C₅H₄SiMe₃), 1.2 (C₅H₄SiMe₃) and 162.3 (CO₂⁻). IR (Nujol mull, cm⁻¹): 1554 ν(C=N), 1680 ν_{asym}(CO₂⁻), 1460 ν_{sym}(CO₂⁻), 735 ν(Nb-O) and 321 ν(Nb-Cl). Mass spectrum [FAB (m/z assignment)]: 512 (M).

Acknowledgements

We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica, Spain (Grant. No. PB95-0023-C02-01 and PB97-0425).

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