

Niobium complexes containing a new chiral heteroscorpionate ligand and the reactivity of such a complex with O₂ to give the first gem-diolate niobium complex

A. Otero,* J. Fernández-Baeza, A. Antiñolo, J. Tejada, A. Lara-Sánchez, L. Sánchez-Barba, M. T. Expósito and A. M. Rodríguez

Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, 13071-Ciudad Real, Spain. E-mail: antonio.otero@uclm.es

Received 13th January 2003, Accepted 25th February 2003

First published as an Advance Article on the web 10th March 2003

The synthesis of a novel unsymmetrical bis(pyrazol-1-yl) ligand, (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)methane (dpmpzm), **1**, has been studied. Deprotonation at the methylene group of **1** with BuⁿLi, followed by reaction with carbon dioxide yielded a racemic mixture of [$\{Li(dpmpza)(H_2O)\}_4$], **2** [dpmpza = (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)acetate], which is a novel chiral monoanionic NNO tripod ligand. This compound is an excellent precursor for the introduction of this scorpionate ligand into transition metal complexes. The complexes [NbCl₃(dme)(RC≡CR')] (dme = 1,2-dimethoxyethane) reacted with **2**, to give the corresponding [NbCl₂(dpmpza)-(RC≡CR')] complexes (R = R' = Me, **3**; R = R' = SiMe₃, **4**; R = Ph, R' = Me, **5**; R = Ph, R' = Et, **6**). The structures of these complexes have been determined by spectroscopic methods. Variable-temperature NMR studies of these complexes were carried out in order to study their dynamic behaviour in solution. The barriers to alkyne rotation have also been calculated. The reactivity of [NbCl₂(dpmpza)(Me₃SiC≡CSiMe₃)], **4**, toward molecular oxygen is particularly noteworthy since it led to the formation of the first gem-diolate niobium species, [(NbCl₂O)₂(μ-η¹-O,O'-tpzpdo)], **7** [tpzpdo = 1,3-bis(3,5-diphenylpyrazol-1-yl)-1,3-bis(3',5'-dimethylpyrazol-1-yl)-2,2'-propanediolate], in a process that has no precedent in the literature. The molecular structure of this gem-diolate has been determined crystallographically.

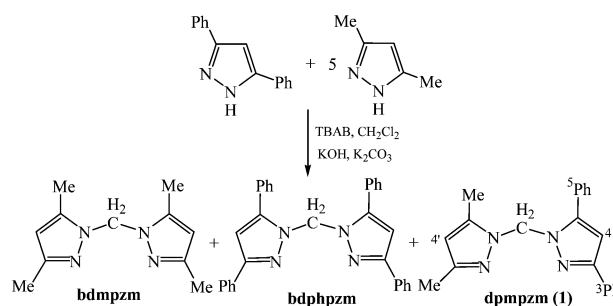
Introduction

We have recently been interested in the synthesis of new "heteroscorpionate" ligands¹ with pyrazole rings. The target compounds are related to the tris(pyrazol-1-yl)methane system,² where one of the pyrazole groups has been replaced by a carboxylate, dithiocarboxylate or ethoxide group, namely bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzda) and 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide (bdmpze). The aim of these changes is to provide a small degree of steric hindrance and considerable coordinative flexibility. These compounds were found to be excellent reagents for the introduction of scorpionate ligands into niobium complexes and a series of alkyne-containing niobium complexes was isolated and characterized.³ These compounds have an interesting dynamic behaviour in solution and this was studied by variable-temperature NMR techniques. More recently, we extended the range of complexes to include group 4 metals.⁴ We describe here the synthesis and characterization of niobium complexes with a new chiral heteroscorpionate ligand and the reactivity of one such complex with molecular oxygen to give the first gem-diolate niobium compound. Gem-diolate organometallic species are very rare and, to date, only three classes of complex in this area have been reported in the literature. One such example is a dioxomethylene species, Cp₂Zr(Cl)-OCH₂O-Zr(Cl)Cp₂, which was spectroscopically characterized as a reactive intermediate in the reaction between Schwartz's reagent [Cp₂Zr(Cl)H] and CO₂.⁵ The second class is derived from the gem-diol (C₅H₄N)₂-C(OH)₂ and a number of mononuclear⁶ and polynuclear⁷ complexes of late transition metals are known. Finally, a third type of late transition metal complex incorporating the dianion of hexafluoropropane-2,2-diol, (CF₃)₂C(OH)₂⁸ has been described.

Results and discussion

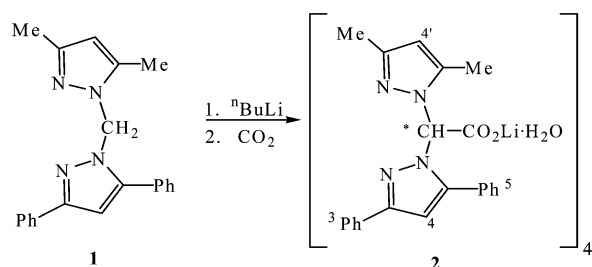
Based on the synthesis of bdmpzm published by Elguero *et al.*,⁹ we have prepared a new bis(pyrazol-1-yl)methane, which

possesses two different pyrazolyl rings. The unsymmetrical (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)methane (dpmpzm), **1**, was obtained by reaction of 3,5-dimethylpyrazole with 3,5-diphenylpyrazole, dichloromethane and base (Scheme 1). The compounds were separated by exploiting the differences in solubility and **1** could be isolated in up to 25% yield from the reaction mixture containing the three possible products (bdmpzm + bdphpzm + **1**). The ¹H and ¹³C{¹H} NMR spectra of **1** exhibit two set of signals for the two different pyrazole rings (see Experimental).



Scheme 1 Synthesis of unsymmetrical (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)methane, **1**.

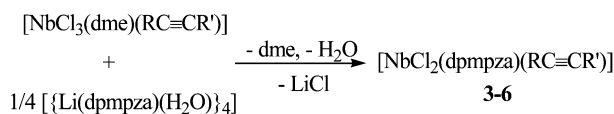
Deprotonation at the methylene group of **1** with BuⁿLi, followed by reaction with carbon dioxide yielded a racemic mixture of [$\{Li(dpmpza)(H_2O)\}_4$], **2** [dpmpza = (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)acetate] (Scheme 2). Although the reaction was carried out under rigorously anhydrous experimental conditions, the presence of adventitious moisture in the reaction mixture during the work-up procedure was probably responsible for the presence of the coordinated water molecule. The mass spectrum (FAB) of **2** indicates a tetranuclear formulation (see Experimental) and, in accordance with the structure found for [$\{Li(bdmpza)-(H_2O)\}_4$],³ we propose in solid state, an analogous arrangement consisting of tetrameric units. Their IR spectrum shows two



Scheme 2 Synthesis of complex $[\{\text{Li}(\text{dpmpza})(\text{H}_2\text{O})\}_4]$, **2**.

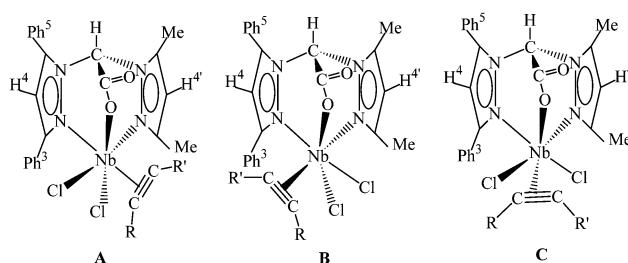
strong bands at 1649 and 1456 cm^{-1} , which are assigned to $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$, respectively. In the lithium compound $[\{\text{Li}(\text{bdmpza})(\text{H}_2\text{O})\}_4]$,³ the $\nu_{\text{as}}(\text{CO}_2^-)$ and $\nu_{\text{s}}(\text{CO}_2^-)$ ($\Delta\nu_{\text{as-s}}$) bands differ by 180 cm^{-1} and in this complex the carboxylate is involved in a coordination bridge at two lithium atoms. For compound **2** the value of $\Delta\nu_{\text{as-s}}$ (193 cm^{-1}) is also in accordance with an O-coordination bridge.¹⁰ A structurally analogous cubane-like array, in which the vertices are alternately occupied by four Li atoms and four bridging carboxylate groups can be also proposed for **2**.

The ^1H NMR spectrum contains six singlets (CH , H^4 , $\text{H}^{4'}$, Me^3 and Me^5 of the pyrazole rings and H_2O) and one multiplet (Ph^3 and Ph^5 of the one pyrazole ring). Homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy was also performed in order to confirm the assignment of the signals for the Me^3 , Me^5 , H^4 and $\text{H}^{4'}$ groups. The ^{13}C - $\{^1\text{H}\}$ NMR spectrum exhibits two set of resonances, as one would expect for the presence of two different pyrazole rings. A ^1H - ^{13}C heteronuclear correlation (HETCOR) experiment was carried out and allowed us to assign the resonances corresponding to C^4 , Me^3 and Me^5 of the pyrazole ring (see Experimental). Finally, the ^7Li NMR spectrum exhibits a singlet at δ 1.59 for the lithium atom. In this compound, the carbon atom bridge is a chiral centre and we have confirmed the presence in solution of the corresponding two enantiomers by addition of a chiral shift reagent, namely (*R*)-(-)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of complex **2**. This process gives rise to the appearance in the ^1H NMR spectrum of two signals for each proton as a result of the presence of the two diastereoisomers from the corresponding two enantiomers. Compound **2** was used in the formation of some niobium complexes in order to test its coordinative capacity as scorpionate ligand. Thus, the lithium compound **2** reacted at room temperature in a 1/4 : 1 molar ratio (Scheme 3) with the complexes $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]^{11}$ (dme = 1,2-dimethoxyethane) in THF to give, after the appropriate work-up, the complexes $[\text{NbCl}_2(\text{dpmpza})(\text{RC}\equiv\text{CR}')]^{11}$ ($\text{R} = \text{R}' = \text{Me}$, **3**; $\text{R} = \text{R}' = \text{SiMe}_3$, **4**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$, **5**; $\text{R} = \text{Ph}$, $\text{R}' = \text{Et}$, **6**), which were isolated as red, blue, orange and brown solids, respectively.



Scheme 3 Synthesis of complexes **3–6**

The mass spectra of complexes **3–6** indicate a mononuclear formulation (see Experimental). In the IR spectra the value $\Delta\nu_{\text{as-s}}$ is *ca.* 230 cm^{-1} , which is in accordance with a single oxygen coordination. Two strong bands are also observed at *ca.* 330 and 370 cm^{-1} and these have been assigned to $\nu(\text{Nb-Cl})$. These results agree with a proposed octahedral disposition in which the metal atom is surrounded by an NNO-coordinated “scorpionate” ligand, an alkyne and two chloride ligands (see Scheme 4). The alkyne ligand can be located in the *cis* position with respect to the 3,5-dimethylpyrazole ring (isomer A), in a



Scheme 4 Proposed structures for the three diastereoisomers of complexes **3–7**.

cis disposition with respect to the 3,5-diphenylpyrazol ring (isomer B) or the *trans* position with respect to the oxygen atom (isomer C).

For complexes **3** and **4** which contain symmetrical alkynes, two sets of NMR signals for both pyrazole and alkyne ligands are observed at room temperature a situation in accordance with the presence of two isomers. In the ^1H NMR spectra, each set of signals shows a 1 : 3 intensity pattern for the scorpionate and the alkyne ligands. NOE experiments were carried out in order to know the disposition of the two isomers. Thus, irradiation in major signals of the alkyne (**3**) or SiMe_3 (**4**) groups enhances only the Me^3 signal, which is clearly the Me group of the 3,5-dimethylpyrazole ring as it is in closer spatial proximity to the alkyne ligand in the *cis* position (isomer A). When the same irradiation were carried out on the minor signals, a response was not observed in the NOE experiments. This result suggests a *trans* disposition of alkyne ligands with respect to oxygen atom in the minor isomer (isomer C). Only one set of NMR signals is observed for the unsymmetrical alkyne complexes **5** and **6**, a fact that is consistent with the presence of only one isomer. Isomer (A) is proposed to be present in these complexes on basis of NOE experiments. The ^{13}C - $\{^1\text{H}\}$ NMR spectra of complexes **3–6** agree with these proposed structures. 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). An empirical correlation between the alkyne π donation and ^{13}C chemical shift for the bound alkyne carbons has previously been observed.¹² The ^1H - and ^{13}C -NMR spectra of these complexes with symmetrical alkynes exhibit only one set of signals for the substituted groups. This observation is due to rotation of the alkyne ligand, as previously observed for other alkyne-containing niobium complexes.^{2,3} We assume that a six-coordinate description of the complexes (see Fig. 1) in which the alkyne occupies a single site is preferable to the alternative seven-coordinate model in which each alkyne carbon is considered to occupy a separate coordination position. Based on this assumption we propose a single rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle. Free energy values, ΔG^\ddagger , for the complexes **3–6** 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. 2, the higher ΔG^\ddagger values and coalescence temperatures were found in the cases of the bulkier alkyne substituents.

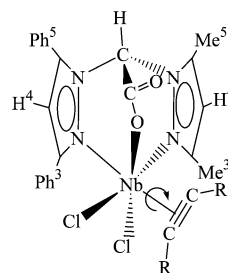


Fig. 1 Proposed structure for complexes **3**, **4** (major isomer), **5** and **6**.

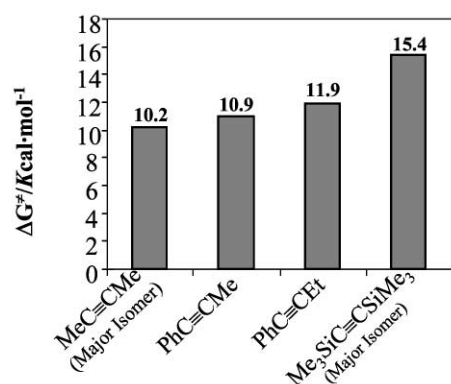


Fig. 2 Graphic representation of free energy values, ΔG^\ddagger , in the rotation of the alkyne ligands for the complexes 3–6. Coalescence temperature values for these complexes are: 180, 3 (major isomer); 263, 4 (major isomer); 193, 5; 203 K, 6.

The variable-temperature NMR study for complex 6 illustrates a good example of a system with an unsymmetrical alkyne. In Fig. 3 it can be seen that a triplet appears for the CH₃ groups in PhCCEt at 293 K. When the temperature was lowered below 170 K two signals (relative intensities 3 : 1) were observed for each of the diastereoisomers present (see Scheme 5). By NOE experiments, we have established that, the major isomer is the one in which the Et group lies between the pyrazole ring and carboxylate group, and the phenyl group lies between two chlorine atoms (see Fig. 1). The addition of (*R*)-(-)-(9-anthryl)-2,2,2-trifluoroethanol to a solution of 6 gave rise to the appearance of four triplets for the Et group of the alkyne ligand in the ¹H-NMR spectrum at 170 K. These four signals correspond to the four diastereoisomers from the corresponding four stereoisomers (see Scheme 5).

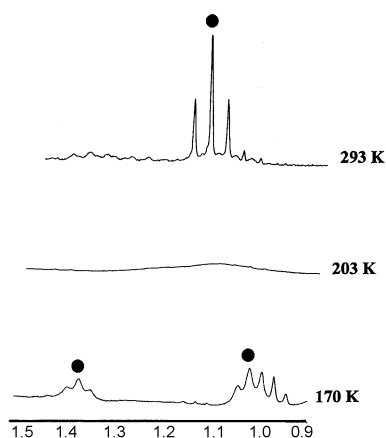
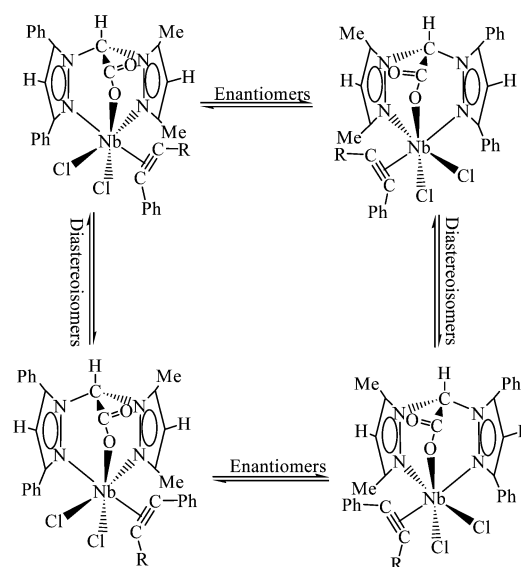
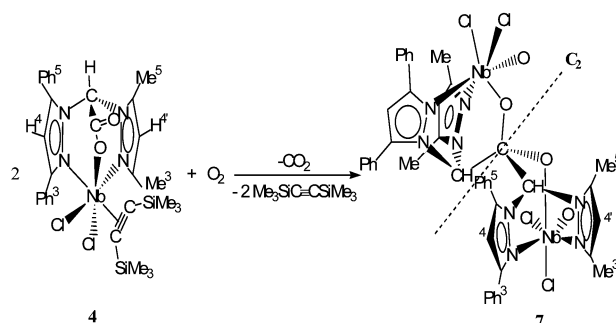


Fig. 3 Variable-temperature ¹H NMR spectra in the region of the Et, alkyne group of the complex [NbCl₂(dpmpza)(PhC≡CEt)], 6. ● = Central signal of the triplet.

The reactivity of [NbCl₂(dpmpza)(Me₃SiC≡CSiMe₃)], 4, toward molecular oxygen is particularly noteworthy since it led to the formation of the first gem-diolate niobium species, [(NbCl₂O)₂(μ-η¹-O,O'-tpzpdo)], 7 [tpzpdo = 1,3-bis(3,5-diphenylpyrazol-1-yl)-1,3-bis(3',5'-dimethylpyrazol-1-yl)-2,2'-propanediolate], in a process that has no precedent in the literature. In fact, the reaction of complex 4 with molecular oxygen in CH₂Cl₂ at room temperature renders complex 7, which was isolated as a white solid in good yield (85%) after the appropriate work-up (Scheme 6). It is thought that an initial oxidation process from SNb^{III} to Nb^V occurs and, after the loss of CO₂, a novel anionic gem-diolate bridging two metal centres is present in complex 7. In addition, this unusual ligand contains two chiral centres as well as two bis(pyrazol-1-yl) moieties, which are also coordinated to both metals in such a way that the



Scheme 5 Proposed structures for the four enantiomers of complexes with an unsymmetrical alkyne ligand.



Scheme 6 Synthesis of [(NbCl₂O)₂(μ-η¹-O,O'-tpzpdo)], 7.

ligand behaves as a tripod in its coordination to each niobium atom. An oxo and two chloride ligands complete the coordination sphere of each metal.

The molecular structure of complex 7 was determined by X-ray diffraction and it was found that this complex crystallizes in the trigonal space group *R*3̄c with 18 molecules per unit cell. The asymmetric unit contains only half a molecule of complex gem-diolate. As illustrated in Fig. 4, the structure consists of a dimeric unit possessing a crystallographic 2-fold axis passing through the C2 atom. As a result of the symmetry of the space group, the crystal shows a racemic mixture (*aR,R,R* + *aS,S,S*)¹⁴ for this compound (the *aS,S,S* form refers to the complex shown in Fig. 4).

Each niobium centre has a distorted octahedral environment with the “tpzpdo” ligand coordinated in a tridentate fashion through the oxygen atom and the two pyridinic nitrogen atoms of the pyrazole rings. The major distortion appears in the Cl2–Nb1–O1 angle, which has a value of 156.0(2)°. The Nb1–N1 bond distance of 2.243(7) Å is as one would expect for an Nb pyrazolyl complex¹⁵ but the elongated Nb1–N3 distance of 2.568(8) Å indicates that the oxygen atom O₂ exerts a strong *trans* influence. The Nb1–O₂ distance of 1.711(5) Å is as expected for a double bond.¹⁶

The ¹H and ¹³C{¹H} NMR spectra of 7 show two sets of signals, one for each of the two different pyrazolyl groups of the 1,3-bis(3,5-diphenylpyrazol-1-yl)-1,3-bis(3',5'-dimethylpyrazol-1-yl)-2,2'-propanediolate ligand. This observation indicates the equivalence of the same type of pyrazole ring and the existence in solution of either a single diastereoisomer [*rac*(*aR,R,R* + *aS,S,S*)] (found in the X-ray

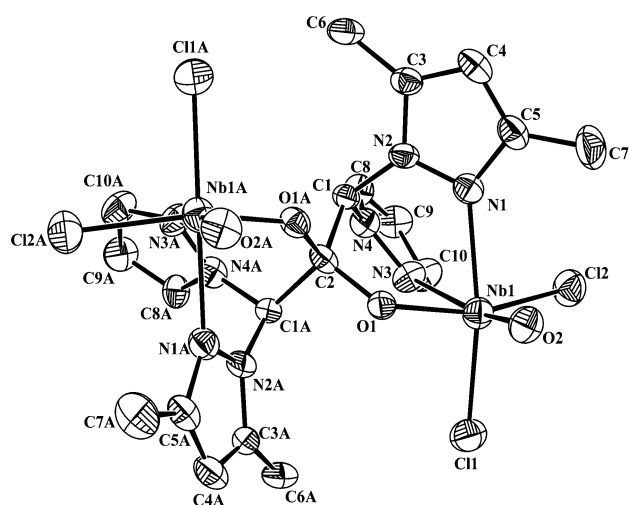
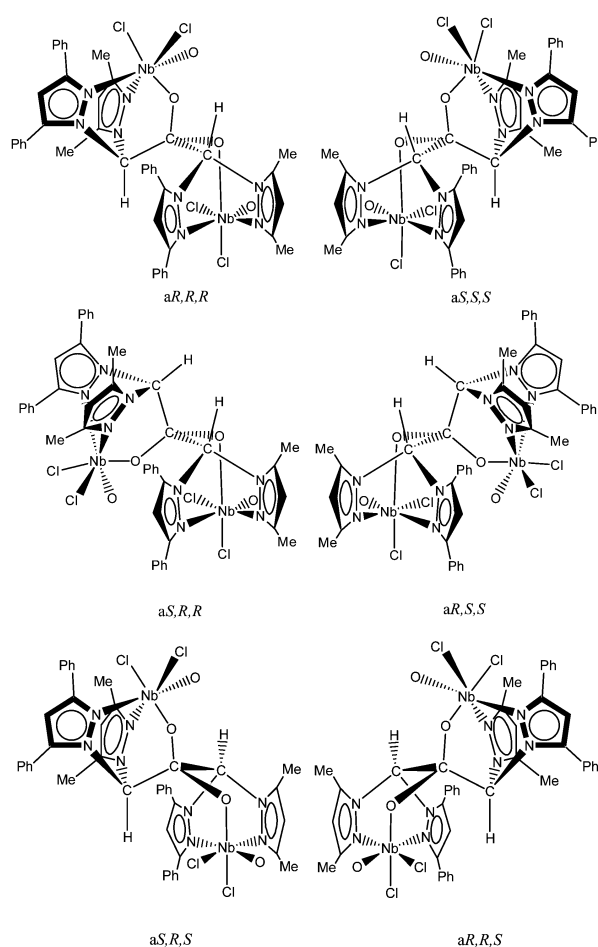


Fig. 4 Structure of complex **7** (30% probability ellipsoids). The phenyl rings are omitted for clarity. Selected bond lengths [Å] and angles [°]: Nb1–O₂ 1.711(5); Nb1–O1 1.906(5); Nb1–N1 2.243(7); Nb1–Cl1 2.327(3); Nb1–Cl2 2.350(3); Nb1–N3 2.568(8); O1–C2 1.387(8); N2–C1 1.44(1); N4–C1 1.44(1); C1–C2 1.56(1); N1–Nb1–Cl1 167.0(2); O1–Nb1–Cl2 156.0(2); O₂–Nb1–N3 170.1(3); C2–O1–Nb1 137.0(4); O1A^a–C2–O1 112(1); O1A^a–C2–C1A^a 110.7(4); O1–C2–C1A^a 105.9(4); O1A^a–C2–C1 105.9(4); O1–C2–C1 110.7(4); C1A^a–C2–C1 111(1). Symmetry transformations used to generate equivalent atoms: a $x - y + 1/3$, $-y + 2/3$, $-z + 1/6$.

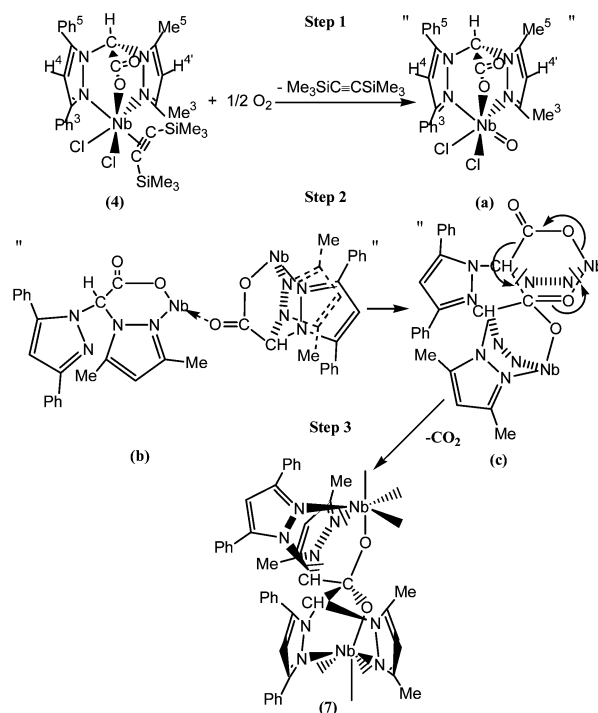
crystal study in the solid state) or a rapid isomerization equilibrium between the two diastereoisomers [*rac*(a*R,R,R* + a*S,S,S*) and *rac*(a*S,R,R* + a*R,S,S*)] (see Scheme 7). A third diastereoisomer is possible [*rac*(a*S,R,S* + a*R,R,S*)] but this would give rise to four sets of signals in the ¹H and ¹³C{¹H} NMR spectra, one for each of the pyrazolyl groups. The resonance in the ¹³C NMR spectrum attributed to the gem-diolate group (CO₂²⁻) is observed at $\delta = 101.0$, which is similar to the value found for the gem-diolate-containing zirconium complex.⁵ A homonuclear NOE study and a ¹H–¹³C correlation experiment (HETCOR) allowed us to assign the resonances corresponding to the different types of protons and carbon atoms.

Scheme 8 shows our proposed reaction pathway leading to complex **7**. We assume that complex **4** (Nb^{III}) is initially oxidized by molecular oxygen to give a new and unstable Nb^V complex, [NbCl₂(O)(κ^3 -dmpza)] (a), with the loss of an alkyne and the incorporation of an oxo ligand (step 1). Similar complexes have previously been prepared and isolated as very stable species; for example, the reaction between [NbCl₂(κ^3 -bdmpze)(PhC≡CMe)] [bdmpze = bis(3,5-dimethylpyrazol-1-yl)ethoxide]³ and molecular oxygen leads to the formation of [NbCl₂(O)(κ^3 -bdmpze)], which was characterized by an X-ray diffraction study.¹⁷

One point that must be addressed is the reason for the different behaviour of (a) in comparison to other similar complexes. On considering our proposed route the answer to this question lies in the different basic strengths of the pyrazole rings. Indeed, the p*K*_a values¹⁸ for aqueous 3,5-diphenylpyrazole and 3,5-dimethylpyrazole are 1.74 and 4.12, respectively, and this suggests that the coordination ability of the first pyrazole at the niobium centre is less than for the latter. Therefore, we propose that in the second step the oxygen atom of a carboxylate group from a neighbouring molecule can displace the 3,5-diphenylpyrazole from the metal centre of the other molecule and give rise to a binuclear intermediate such as (b). Finally, a concerted decarboxylation through a six-membered cyclic transition state (c)¹⁹ would give complex **7** (step 3). Attempts to isolate and characterize some of the different proposed intermediates on a preparative scale were unsuccessful, although the formation of CO₂ was confirmed. A study of the course of the reaction on a small scale by means of NMR spectroscopy was also carried



Scheme 7 In complex **7** it is possible to obtain three diastereoisomers: [*rac*(a*R,R,R* + a*S,S,S*)] (as corroborated by X-ray diffraction in the solid state), [*rac*(a*S,R,R* + a*R,S,S*)] and [*rac*(a*S,R,S* + a*R,R,S*)].



Scheme 8 Different steps proposed for the synthesis of complex **7**.

out. However, informative results were not obtained and the only species detected were complexes **4** and **7**. It should be noted that other possible mechanisms based on a decarboxylation process can not be excluded.

In conclusion, we describe the synthesis of a novel unsymmetrical bis(pyrazol-1-yl) ligand, which by reaction with Bu^nLi and carbon dioxide yielded a lithium compound containing is a novel chiral monoanionic NNO tripod. This compound is excellent precursor for the introduction of this heteroscorpionate ligand into transition metal complexes. This fact has been confirmed by reactions with different niobium complexes. New mononuclear niobium species with a new scorpionate ligand have been isolated. These alkyne complexes present a dynamic behaviour in solution, which corresponds to alkyne rotation. This behaviour has been studied by variable-temperature NMR spectroscopy. The reaction of one alkyne complex with molecular oxygen to give the first gem-diolate niobium complex in a process that has no precedent in the literature, has been also carried out.

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 were recorded in the region 4000–200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^1H , ^{13}C and ^7Li NMR spectra were registered 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 VARIANT-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 $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]_n$ were prepared as reported previously.¹¹

Preparations

Dpmpzm, 1. In a 1000 cm^3 three neck flask provided with a reflux condenser 3,5-diphenylpyrazole (5.00 g, 22.69 mmol), 3,5-dimethylpyrazole (10.90 g, 113.45 mmol), potassium carbonate (18.93 g, 137.00 mmol), finely ground potassium hydroxide (7.68 g, 137 mmol), TBAB (1.30 g, 4.04 mmol) and 500 cm^3 of CH_2Cl_2 were added. The reaction mixture was stirred for 12 h at reflux temperature. Salts were removed by filtration and the filtrate was concentrated under vacuum to dryness yielding a crude mixture of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm), bis(3,5-diphenylpyrazol-1-yl)methane (bdphpm) and (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)methane (dpmpzm). Extraction with cold Et_2O yielded a mixture of compounds bdmpzm and dpmpzm, **1**. This mixture was washed with hexane and a white residue of pure dpmpzm, **1**, was isolated. Yield 25%. (Found: C, 76.23; H, 6.10; N, 17.33. $\text{C}_{21}\text{H}_{20}\text{N}_4$ requires C, 76.80; H, 6.10; N, 17.06%.) ^1H -NMR (CDCl_3 , 297 K): δ 6.15 (s, 2 H, CH_2), 6.62 (s, 1 H, H^4), 5.83 (s, 1 H, H^4), 2.19 (s, 3 H, Me^3), 2.52 (s, 3 H, Me^5), 7.32–7.85 (m, 10 H, Ph). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3), δ 60.1 (CH_2), 141.0, 145.9, 148.6, 151.5 (C^3 or 5), 103.8 (C^4), 106.2 (C^4), 13.6 (Me^3), 11.1 (Me^5), 125.6–133.1 (Ph). IR (Nujol) 1557 cm^{-1} $\nu(\text{C}=\text{N})$.

$[\{\text{Li}(\text{dpmpza})(\text{H}_2\text{O})\}_4]$, 2. In a 250 cm^3 Schlenk tube, dpmpzm, [dpmpzm = (3,5-diphenylpyrazol-1-yl-3',5'-dimethylpyrazol-1-yl)methane, **1**] (4.00 g, 12.20 mmol) was dissolved in dry THF (70 cm^3) and cooled to -70°C . A 1.6 M solution of Bu^nLi (7.80 cm^3 , 12.20 mmol) in hexane was added and the solution was stirred for 1 h. The reaction mixture was warmed to 0°C and the resulting yellow solution was then treated with

gaseous CO_2 , after which the solution was colourless. The solvent was removed and on addition of hexane (70 cm^3) a white solid was obtained. This solid was crystallised from a mixture of THF–hexane. Yield 96%. (Found: C, 66.58; H, 5.21; N, 14.10. $\text{C}_{22}\text{H}_{21}\text{Li N}_4\text{O}_3$ requires C, 66.58; H, 5.34; N, 14.14%.) ^1H NMR (DMSO, 297 K), δ 6.51 (s, 1 H, CH), 6.77 (s, 1 H, H^4), 5.74 (s, 1 H, H^4), 1.96 (s, 3 H, Me^3), 2.57 (s, 3 H, Me^5), 7.26–7.77 (m, 10 H, Ph), 3.36 (s, 2 H, H_2O). ^{13}C - $\{^1\text{H}\}$ -NMR (DMSO), δ 75.4 (CH), 142.4, 145.5, 145.9, 149.3 (C^3 or 5), 103.0 (C^4), 106.7 (C^4), 13.8 (Me^3), 13.4 (Me^5), 134.2–125.6 (Ph), 165.3 (CO_2^-). ^7Li NMR (DMSO), δ 1.59 (s). IR (Nujol) 1557 $\nu(\text{C}=\text{N})$, 1649 $\nu_{\text{as}}(\text{CO}_2^-)$, 1456 cm^{-1} $\nu_{\text{s}}(\text{CO}_2^-)$. Mass spectrum (m/z assignment, % intensity, D = Daltons): 1141 D [$\text{Li}_4(\text{bdmpza})_3$], 20; 763 D [$\text{Li}_3(\text{bdmpza})_2$], 19; 385 D [$\text{Li}_2(\text{bdmpza})$], 100.

$[\text{NbCl}_3(\kappa^3\text{-dpmpza})(\text{MeC}\equiv\text{CMe})]$, 3. To a THF (100 cm^3) solution of $\text{NbCl}_3(\text{dme})(\text{MeC}\equiv\text{CMe})$ (1.00 g, 2.91 mmol) was added an equimolar quantity of $[\{\text{Li}(\text{dpmpza})(\text{H}_2\text{O})\}_4]$, **2** (1.10 g, 0.73 mmol). The solution was stirred for 18 h at room temperature. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2 . A red solid was obtained after removal of the solvents. Yield 65%. (Found: C, 52.68; H, 4.32; N, 9.31. $\text{C}_{26}\text{H}_{25}\text{Cl}_2\text{N}_4\text{NbO}_2$ requires C, 52.99; H, 4.27; N, 9.50%.) ^1H NMR (CD_2Cl_2 , 297 K), major isomer δ 6.91 (s, 1 H, CH), 6.58 (s, 1 H, H^4), 6.09 (s, 1 H, H^4), 2.04 (s, 3 H, Me^3), 1.77 (s, 3 H, Me^5), 7.86–7.41 (m, 10 H, Ph), 2.85 (s, 6 H, $\text{MeC}\equiv$); minor isomer δ 6.86 (s, 1 H, CH), 6.60 (s, 1 H, H^4), 6.05 (s, 1 H, H^4), 1.87 (s, 3 H, Me^3), 1.73 (s, 3 H, Me^5), 7.86–7.41 (m, 10 H, Ph), 2.78 (s, 6 H, $\text{MeC}\equiv$). ^{13}C - $\{^1\text{H}\}$ -NMR (CD_2Cl_2), major isomer δ 67.9 (CH), 159.0, 158.6, 156.3, 154.2, 147.2, 146.9, 143.9, 142.0 (C^3 or 5 for both isomers), 109.0 (C^4), 110.6 (C^4), 15.2 (Me^3), 10.2 (Me^5), 131.0–126.4 (Ph for both isomers), 161.3, 161.4 (CO_2^- for both isomers), 13.5 ($\text{MeC}\equiv$), 247.6, 243.5 ($\text{C}\equiv\text{C}$ for both isomers); minor isomer δ 66.9 (CH), 109.2 (C^4), 110.0 (C^4), 15.3 (Me^3), 10.9 (Me^5), 15.2 ($\text{MeC}\equiv$). IR (Nujol) 1554 $\nu(\text{C}=\text{N})$, 1692 $\nu_{\text{as}}(\text{CO}_2^-)$, 1462 $\nu_{\text{s}}(\text{CO}_2^-)$, 370, 329 cm^{-1} $\nu(\text{Nb}-\text{Cl})$. Mass spectrum (m/z assignment, % intensity, D = Daltons): 590 D [$\text{M} + 1$], 10; 554 D [$\text{M} - \text{Cl}$], 100.

$[\text{NbCl}_3(\kappa^3\text{-dpmpza})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$, 4. The synthetic procedure was the same as for complex **3**, using $\text{NbCl}_3(\text{dme})(\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ (1.00 g, 2.21 mmol) and $[\{\text{Li}(\text{dpmpza})(\text{H}_2\text{O})\}_4]$, **2** (0.87 g, 0.55 mmol), to give **4** as a blue solid. Yield 60%. (Found: C, 51.04; H, 5.28; N, 7.94. $\text{C}_{30}\text{H}_{37}\text{Cl}_2\text{N}_4\text{NbO}_2\text{Si}_2$ requires C, 51.10; H, 5.31; N, 7.82%.) ^1H NMR (CD_2Cl_2 , 297 K), major isomer δ 6.87 (s, 1 H, CH), 6.70 (s, 1 H, H^4), 5.86 (s, 1 H, H^4), 2.24 (s, 3 H, Me^3), 1.69 (s, 3 H, Me^5), 7.94–7.32 (m, 10 H, Ph), 0.16 (s, 18 H, $\text{Me}_3\text{SiC}\equiv$); minor isomer δ 6.82 (s, 1 H, CH), 6.67 (s, 1 H, H^4), 5.98 (s, 1 H, H^4), 2.21 (s, 3 H, Me^3), 1.68 (s, 3 H, Me^5), 7.94–7.32 (m, 10 H, Ph), 0.15 (s, 18 H, $\text{Me}_3\text{SiC}\equiv$). ^{13}C - $\{^1\text{H}\}$ -NMR (CD_2Cl_2), major isomer δ 67.6 (CH), 158.5, 154.6, 152.7, 149.3, 147.2, 146.7, 142.2, 141.7 (C^3 or 5 for both isomers), 109.8 (C^4), 110.7 (C^4), 13.3 (Me^3), 10.3 (Me^5), 131.0–126.1 (Ph for both isomers), 165.4, 160.6 (CO_2^- for both isomers), 1.1 ($\text{Me}_3\text{SiC}\equiv$), 259.1, 250.4 ($\text{C}\equiv\text{C}$ for both isomers); minor isomer δ 68.0 (CH), 108.9 (C^4), 110.3 (C^4), 13.6 (Me^3), 10.1 (Me^5), -0.4 ($\text{Me}_3\text{SiC}\equiv$). IR (Nujol) 1558 $\nu(\text{C}=\text{N})$, 1692 $\nu_{\text{as}}(\text{CO}_2^-)$, 1463 $\nu_{\text{s}}(\text{CO}_2^-)$, 379, 330 cm^{-1} $\nu(\text{Nb}-\text{Cl})$. Mass spectrum (m/z assignment, % intensity, D = Daltons): 705 D [$\text{M} + 1$], 18; 670 D [$\text{M} - \text{Cl}$], 100.

$[\text{NbCl}_3(\kappa^3\text{-dpmpza})(\text{PhC}\equiv\text{CMe})]$, 5. The synthetic procedure was the same as for complex **3**, using $\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CMe})$ (1.00 g, 2.47 mmol) and $[\{\text{Li}(\text{dpmpza})(\text{H}_2\text{O})\}_4]$, **2** (0.93 g, 0.62 mmol), to give **5** as an orange solid. Yield 85%. (Found: C, 57.10; H, 4.32; N, 8.49. $\text{C}_{31}\text{H}_{27}\text{Cl}_2\text{N}_4\text{NbO}_2$ requires C, 57.16; H, 4.17; N, 8.60%.) ^1H NMR (CD_2Cl_2 , 297 K), δ 7.01 (s, 1 H, CH), 6.59 (s, 1 H, H^4), 5.92 (s, 1 H, H^4), 1.86 (s, 3 H, Me^3), 1.78 (s, 3 H, Me^5), 7.97–7.37 (m, 15 H, Ph), 3.23 (s, 3 H, $\text{C}\equiv\text{CMe}$). ^{13}C - $\{^1\text{H}\}$ -NMR (CD_2Cl_2), δ 67.7 (CH), 158.8, 154.4, 146.5,

141.3 (C^3 or 5), 110.1 (C^4), 110.3 (C^4), 15.2 (Me^3), 10.2 (Me^5), 130.6–127.6 (Ph), 161.5 (CO_2^-), 22.9 ($\equiv CMe$) 248.5, 232.4 ($C\equiv C$); IR (Nujol) 1559 $\nu(C=N)$, 1693 $\nu_{as}(CO_2^-)$, 1462 $\nu_s(CO_2^-)$, 367, 332 cm^{-1} $\nu(Nb-Cl)$. Mass spectrum (m/z assignment, % intensity, D = Daltons): 652 D [$M + 1$], 21; 616 D [$M - Cl$], 100.

[NbCl₂(κ^3 -dpmpza)(PhC \equiv CEt)], 6. The synthetic procedure was the same as for complex 3, using NbCl₃(dme)(PhC \equiv CEt) (1.00 g, 2.38 mmol) and [Li(dpmpza)(H₂O)]₄, 2 (0.90 g, 0.60 mmol), to give 6 as a brown solid. Yield 75%. (Found: C, 57.50; H, 4.32; N, 8.49. C₃₂H₂₉Cl₂N₄NbO₂ requires C, 57.76; H, 4.39; N, 8.41.) ¹H NMR (CD₂Cl₂, 297 K), δ 6.99 (s, 1 H, CH), 6.61 (s, 1 H, H⁴), 5.97 (s, 1 H, H⁴), 1.86 (s, 3 H, Me³), 1.79 (s, 3 H, Me⁵), 7.96–7.35 (m, 15 H, Ph), A 3.58, B 3.40, X 1.33 [ABX₃, $J_{AB} = 17.0$ Hz, $J_{AX} = J_{BX} = 7.5$ Hz, ($\equiv CCH_2CH_3$)]. ¹³C-{¹H}-NMR (CD₂Cl₂), δ 67.9 (CH), 158.8, 154.8, 147.0, 142.3 (C^3 or 5), 109.3 (C^4), 110.7 (C^4), 15.5 (Me^3), 10.4 (Me^5), 132.5–126.0 (Ph), 161.5 (CO_2^-), 31.6 ($\equiv CCH_2CH_3$), 12.6 ($\equiv CCH_2CH_3$) 251.5, 232.7 ($C\equiv C$); IR (Nujol) 1555 $\nu(C=N)$, 1687 $\nu_{as}(CO_2^-)$, 1457 $\nu_s(CO_2^-)$, 368, 329 cm^{-1} $\nu(Nb-Cl)$. Mass spectrum (m/z assignment, % intensity, D = Daltons): 665 D [$M + 1$], 15; 630 D [$M - Cl$], 100.

[(NbCl₂O)₂(μ - η^1 -O, O'-tpzpdo)], 7. A CH₂Cl₂ (100 cm³) solution of NbCl₂(κ^3 -dpmpza)(Me₃SiC \equiv CSiMe₃), 4 (0.15 g, 0.20 mmol), was treated with dry O₂. The solution was stirred for 4 h at room temperature. The solvent was removed under vacuum and a white solid was obtained. Yield 85%. Crystals were grown from a solution in toluene by slow evaporation of the solvent. (Found: C, 48.82; H, 3.71; N, 10.21. C₄₃H₃₈Cl₄N₈Nb₂O₄ requires C, 48.79; H, 3.61; N, 10.59.) ¹H NMR (CD₂Cl₂, 297 K), δ 7.21 (s, 2 H, CH), 6.78 (s, 2 H, H⁴), 5.94 (s, 2 H, H⁴), 2.51 (s, 6 H, Me³), 1.69 (s, 6 H, Me⁵), 6.64–7.94 (m, 20 H, Ph). ¹³C-{¹H}-NMR (CD₂Cl₂), δ 69.2 (CH), 149.3, 148.4, 143.8, 142.5 (C^3 or 5), 108.6 (C^4), 110.8 (C^4), 15.6 (Me^3), 10.0 (s, Me⁵), 139.1–126.5 (Ph), 101.0 (s, CO₂²⁻). IR (Nujol) 1554 $\nu(C=N)$, 348, 290 cm^{-1} $\nu(Nb-Cl)$.

Crystal data for 7. C₄₃H₃₈N₈O₄Cl₄Nb₂ (1058.44); crystal size 0.4 × 0.3 × 0.1 mm; trigonal, space group $R\bar{3}c$, $a = 36.442(5)$, $b = 36.442(8)$, $c = 19.618(3)$ Å, $Z = 18$, $V = 22563(7)$ Å³, $\rho_{calc} = 1.402$ g cm⁻³, $T = 293$ K, $\mu = 7.16$ cm⁻¹, 17979 reflections measured, 5954 were unique ($R_{int} = 0.1485$) and 1184 observed [$I > 2\sigma(I)$]; Nonius-Mach3 diffractometer, MoK α radiation ($\lambda = 0.71073$ Å) graphite monochromated; ω scans technique to a maximum value of $2\theta = 56^\circ$. The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0531$, $wR_2 = 0.0912$ for [$I > 2\sigma(I)$], GOF = 0.831; data/parameters: 5954/265; largest diff. peak and hole, 0.294 and -0.359 e Å⁻³.

CCDC reference number 188238.

See <http://www.rsc.org/suppdata/dt/b3/b300497j/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación, Spain (Grant No. PB98-0159-C02-01).

References

- A. Otero, J. Fernández-Baeza, J. Tejada, A. Antiñolo, F. Carrillo-Hermosilla, E. Diez-Barra, A. Lara-Sánchez, M. Fernández-López, M. Lanfranchi and M. A. Pellinghelli, *J. Chem. Soc., Dalton Trans.*, 1999, 3537; T. C. Higgs and C. J. Carrano, *Inorg. Chem.*, 1997, **36**, 291; T. C. Higgs and C. J. Carrano, *Inorg. Chem.*, 1997, **36**, 298; T. C. Higgs, K. Spartalian, C. J. O'Connor, B. F. Matzanke and C. J. Carrano, *Inorg. Chem.*, 1998, **37**, 2263; T. C. Higgs, D. Ji, R. S. Czernuszewicz, B. F. Matzanke, V. Schunemann, A. X. Trautwei, M. Helliwell, W. Ramirez and C. J. Carrano, *Inorg. Chem.*, 1998, **37**, 2383; B. S. Hammes and C. J. Carrano, *Inorg. Chem.*, 1999, **38**, 3562; B. S. Hammes and C. J. Carrano, *J. Chem. Soc., Dalton Trans.*, 2000, 3304; P. Ghosh and G. J. Parkin, *Chem. Commun.*, 1998, 413; C. Kimblin, T. Hascall and E. Parkin, *Inorg. Chem.*, 1997, **36**, 5680; C. Dowling and G. Perkin, *Polyhedron*, 1996, **15**, 2463; P. Ge, B. S. Haggerty, A. L. Rheingold and C. G. Riordan, *J. Am. Chem. Soc.*, 1994, **116**, 8406; R. T. Stibrany, S. Knapp, J. A. Potenza and H. J. Schugar, *Inorg. Chem.*, 1999, **38**, 132; N. Burzlaff, I. Hegelmann and B. Weibert, *J. Organomet. Chem.*, 2001, **626**, 16; A. Beck, B. Weibert and N. Burzlaff, *Eur. J. Inorg. Chem.*, 2001, 521.
- J. Fernández-Baeza, F. A. Jalón, A. Otero and M. E. Rodrigo, *J. Chem. Soc., Dalton Trans.*, 1995, 1015; A. Antiñolo, F. Carrillo-Hermosilla, E. Diez-Barra, J. Fernández-Baeza, M. Fernández-López, A. Lara-Sánchez, A. Moreno, A. Otero, A. M. Rodríguez and J. Tejada, *J. Chem. Soc., Dalton Trans.*, 1998, 3737.
- A. Otero, J. Fernández-Baeza, J. Tejada, A. Antiñolo, F. Carrillo-Hermosilla, E. Diez-Barra, A. Lara-Sánchez and M. Fernández-López, *J. Chem. Soc., Dalton Trans.*, 2000, 3267.
- A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejada, E. Diez-Barra, A. Lara-Sánchez, L. Sánchez-Barba, I. López-Solera, M. R. Ribeiro and J. M. Campos, *Organometallics*, 2001, **20**, 2428; A. Otero, J. Fernández-Baeza, A. Antiñolo, F. Carrillo-Hermosilla, J. Tejada, A. Lara-Sánchez, L. Sánchez-Barba, M. Fernández-López, A. M. Rodríguez and I. López-Solera, *Inorg. Chem.*, 2002, **41**, 5193.
- N. E. Schlörer and S. Berger, *Organometallics*, 2001, **20**, 1703; N. E. Schlörer, E. J. Cabrita and S. Berger, *Angew. Chem., Int. Ed.*, 2002, **41**, 107.
- G. Annibale, L. Canovesi, L. Cattalini, G. Natile, M. Biagini-Cingi, A. Manotti-Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1981, 2280; S. Wang, J. W. Richardson, S. J. Briggs, R. A. Jacobson and W. P. Jensen, *Inorg. Chim. Acta*, 1986, **111**, 67; S. Sommerer, W. P. Jensen and R. A. Jacobson, *Inorg. Chim. Acta*, 1990, **172**, 3.
- V. Tangoulis, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, C. P. Raptopoulou and A. Terzis, *J. Chem. Soc., Chem. Commun.*, 1996, 1297; V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes and A. Terzis, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1083; M.-L. Tong, H. K. Lee, Y.-X. Tong, X.-M. Chen and T. C. W. Mak, *Inorg. Chem.*, 2000, **39**, 4666.
- P. Bradford, R. C. Hynes, N. C. Payne and C. J. Willis, *J. Am. Chem. Soc.*, 1990, **112**, 2647.
- J. Sebastián, P. Sala, J. Del Mazo, M. Sancho, C. Ocho, J. Elguero, J. P. Fayet and M. C. Vertut, *J. Heterocycl. Chem.*, 1982, **19**, 1141; E. Diez-Barra, A. De la Hoz, A. Sánchez-Migallon and J. Tejada, *J. Chem. Soc., Perkin Trans.*, 1993, **1**, 1079.
- K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-VCH, New York, 1997.
- E. J. Roskamp and S. F. Pedersen, *J. Am. Chem. Soc.*, 1987, **109**, 6551.
- See J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.
- J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
- For axial chirality see: E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley-Interscience, New York, 1994, 1119–1190.
- A. Antiñolo, F. Carrillo-Hermosilla, J. Fernández-Baeza, M. Lanfranchi, A. Lara-Sánchez, A. Otero, E. Palomares, M. A. Pellinghelli and A. M. Rodríguez, *Organometallics*, 1998, **17**, 3015.
- S. Minhas, A. Devlin, D. T. Richens, A. C. Benyei and P. Lightfoot, *J. Chem. Soc., Dalton Trans.*, 1998, 953.
- A. Otero, J. Fernández-Baeza, A. Lara-Sánchez, M. Fernández-López and L. Sánchez-Barba, unpublished results.
- J. Elguero, E. González and R. Jacquier, *Bull. Soc. Chim. Fr.*, 1968, **707**, 5009.
- F. A. Carey, *Organic Chemistry*, McGraw-Hill, New York, 1987, 732–773.