DALTON
FULL PAPER

Chemistry of bulky tetrakis(pyrazolyl)borate ligands $[B(pz^R)_4]^-$ (R = *p*-$CH_3OC_6H_4$ or C_6H_{11})†

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The ligands $[B(pz^R)_4]^-$ [R = *p*-$CH_3OC_6H_4$ (An) or C_6H_{11} (Cy)] and their corresponding complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ (R = An **1** or Cy **2**) and $[MoCl_2(pz^RTp^R)(NO)]$ (R = An **3** or Cy **4**) have been prepared. The molecular structures determined by NMR and X-ray crystallography reveal in all cases the formation of only one isomer having a three-co-ordinated tetrakis(pyrazolyl)borate ligand with the R substituents at the 3 position of the pyrazolyl rings, *i.e.* the symmetric form (3R,3R,3R,3R). The incorporation of the fourth pyrazolyl arm coupled to the use of different bulky substituents on the pyrazolyl rings has been analysed over the cavities produced around the molybdenum centres, and the results compared to those for related tris(pyrazolyl)borate derivatives. A greater protection of the molybdenum atom is provided by the *p*-$CH_3OC_6H_4$ substituents, which also give rise to more rigid frameworks.

Although the poly(pyrazolyl)borate ligands were discovered more than 30 years ago, their importance and significance in modern co-ordination chemistry has only recently been appreciated. Anionic ligands $[R_{4-n}B(pz^*)_n]^-$ (R = non-co-ordinating substituent; pz* = pyrazol-1-yl or pyrazol-1-yl derivative; *n* = 2, 3 or 4), namely bis-, tris- and tetrakis-(pyrazol-1-yl)borate, respectively, have been described and much effort has been devoted to the development of new derivatives for a variety of applications in inorganic and organometallic chemistry.[1] Tris(pyrazolyl)borates have become particularly popular, but the related bis and, especially, the tetrakis analogues have received much less attention.

Bidentate or tridentate co-ordination is characteristic of the bis- and tris-(pyrazolyl)borate derivatives, respectively, but the tetrakis(pyrazolyl)borates can adopt either the bi- or the tridentate forms depending on the specific system.[1–6]

Several isomers, depending on the position of substituents on the pyrazolyl rings, could be found in poly(pyrazolyl)borate derivatives. However, a regiospecific character is commonly observed. This may be illustrated by reference to the reaction of KBH_4 with a 3(5)-substituted pyrazole which produces a specific tris(pyrazolyl)borate isomer in which the R substituents are located at the less-hindered positions with respect to the boron atom, *i.e.* the symmetric isomer $[HB(pz^{3R})_3]^-$ (Tp^{3R}) represented as (3R,3R,3R).[1] The same behaviour is observed with 3R,5R′-disubstituted pyrazolyl groups, and their corresponding $[HB(pz^{3R,5R'})_3]^-$ ($Tp^{3R,5R'}$) derivatives are those having the bulkiest R substituents in the 3 positions. Some exceptions to this rule have been observed for compounds with very bulky substituents such as mesityl, anthracen-9-yl or neopentyl on the pyrazolyl ring. In these cases, asymmetric forms $[HB(pz^{3R,5R'})_2(pz^{3R',5R})]^-$ (R is the bulkier substituent) have been isolated.[7–10] However, rearrangement reactions converting the asymmetric into the symmetric form have been observed in several complexes containing some of these ligands,[9–11] although, in a previous paper, the opposite rearrangement has also been observed in complexes containing the $Tp^{3Pr^i,5Me}$ ligand.[12]

In contrast to the well established behaviour of the tris(pyrazolyl)borate ligands, no related steric requirements have been described for the tetrakis(pyrazolyl)borates, $[B(pz^R)_4]^-$, although the molecular structures of some of their complexes have revealed the symmetric (3R,3R,3R,3R) form in all cases.[11,13–16] However there is no evidence of regiospecific co-ordination of these ligands.

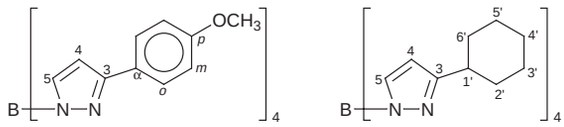
The chemistry of new $[B(pz^R)_4]^-$ derivatives offers opportunities to explore the co-ordination modes towards specific metal-containing systems, the more stable isomeric forms and, finally, the potential regiospecificity by co-ordination.

Molybdenum complexes containing substituted tris(pyrazolyl)borato ligands of the type $[Mo(Tp^R)(NO)X(Y)]$ have been widely investigated because of their interesting properties and applications.[17–21] In previous work[22] we have described the structure of $[Mo(Tp^{An})(CO)_2(NO)]$ {Tp^{An} = hydrotris[3-(*p*-methoxyphenyl)pyrazol-1-yl]borate}, in which the *p*-$MeOC_6H_4$ substituents on the 3 position of the pyrazolyl rings of the tripodal Tp^{An} ligand seemed to be an appropriate functionalisation to construct a simple bowl-shaped cavity on the ligand within which the molybdenum centre is accommodated. This shape could be interesting in the design of compounds having liquid crystal properties and, indeed, the compound having a hexyloxy group in place of the methoxy substituent exhibited metastable mesogenic behaviour.[23]

In developing related tripodal ligand systems we have begun to investigate the co-ordination behaviour of bulky substituted tetrakis(pyrazolyl)borate derivatives. The incorporation of a fourth pyrazolyl ring coupled to the use of different substituents on the 3 position of the pyrazolyl rings could generate unusual structures and/or cavities which may be interesting within themselves, may provide unusual co-ordination modes,

† The abbreviation system used in this paper is that adopted in the most recent review[1] of the poly(pyrazolyl)borate area, pz^RTp^R used in the complexes indicates a tridentate co-ordination of the $[B(pz^R)_4]^-$ ligands.

Table 1 Proton and ^{13}C-{^{1}H} NMR data (δ, J Hz)



Compound	^{1}H NMR [a] H4	H5	R	^{13}C NMR CO	C3	C4	C5	R
$[B(pz^{An})_4]^-$ [b]	6.44 (d) J = 2.0	7.55 (d)	H_o 7.50 (d) H_m 6.71 (d) J = 8.7 CH_3O 3.76		147.2	100.7	134.2	C_α 121.6 C_o 126.6 C_m 116.2 C_p 159.5 CH_3O 55.1
$[B(pz^{Cy})_4]^-$ [c]	5.76 (d) J = 2.0	7.15 (d)	CH 2.6 (br) CH_2 1.2–1.8 (m)		151.9	94.1	129.3	C1′ 32.1 C2′, C6′ 28.3 C3′, C5′ 20.9 C4 20.8
1 [d]	6.90 (d) 6.34 (d) 6.18 (d) J = 2.4	8.10 (d) 8.05 (d) 7.79 (d)	H_o 7.96 (d), 7.44 (d), 7.22 (d) H_m 7.01 (d), 6.94 (d), 6.87 (d) J = 8.7 CH_3O 3.88, 3.80, 3.79	222.1	158.7 158.0 154.0	107.3 107.0 104.1	137.9 136.7 136.2	C_α 126.1, 125.8, 125.0 C_o 131.2, 131.0, 127.2 C_m 114.1, 113.5, 113.2 C_p 160.3, 159.9, 159.6 CH_3O 55.3, 55.2
2 [d]	6.34 (d) 6.08 (d) 5.95 (d) J = 2.4	7.86 (d) 7.64 (d) 7.33 (d)	CH 3.15 (qnt), 3.04 (qnt), 2.80 (qnt) J = 11.6 CH_2 2.2–1.2 (m)	223.1	163.1 162.6 161.0	104.1 102.6 102.2	136.9 136.5 136.0	C1′ 39.1, 38.9, 37.7 C2′, C6′ 34.6, 34.0, 33.9, 33.4 C3′, C4′, C5′ 26.5, 26.4, 26.3, 26.2, 26.0, 25.8
3 [d]	6.63 (br)	7.58 (br)	H_o 7.96 (br), 7.85 (br) H_m 6.96 (br) CH_3O 3.84		152.9 152.1	104.8 103.6	138.2 138.0	C_α 123.0 C_o 128.1, 127.2 C_m 114.3, 114.1 C_p 160.4, 159.8 CH_3O 55.4, 55.2
4 [d]	6.39 (br) 6.16 (br) 6.09 (br)	7.88 (br) 7.71 (br) 7.61 (br)	CH 3.1–2.6 (m) CH_2 2.2–1.2 (m)		164.0 161.3 159.5	104.6 104.4 104.0	137.3 137.2 137.1	C1′ 38.3, 37.7, 37.6 C2′, C6′ 36.1, 35.2, 34.3, 33.3, 32.7, 32.0 C3′, C4′, C5′ 26.3, 26.2, 26.1, 25.9, 25.7, 25.6

[a] d = Doublet, qnt = quintuplet, m = multiplet, br = broad. Other signals are singlets. [b] Data in $(CD_3)_2SO$ solution, have been taken from ref. 15. [c] In $(CD_3)_2SO$ solution. [d] In $CDCl_3$ solution.

and which may be compared with those of related tris(pyrazolyl)borate derivatives.

We report here a study of the ligands $[B(pz^R)_4]^-$ where R = p-$CH_3OC_6H_4$ (An) or C_6H_{11} (Cy), and their molybdenum complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ and $[MoCl_2(pz^RTp^R)(NO)]$. The NMR spectral data of $[B(pz^{An})_4]^-$ have been described but the synthesis of the anion has not.[15] The molecular structures of the dicarbonyl complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ (R = An or Cy), determined crystallographically, are compared with that of $[Mo(Tp^{An})(CO)_2(NO)]$.[22]

Results and discussion

Synthetic and spectroscopic studies

The ligands $[B(pz^R)_4]^-$ (R = An or Cy) were synthesized by reaction of Hpz^R and KBH_4 in a way similar to that previously described for related compounds.[11,13,14,24,25] The reaction mixtures were heated for several hours until the temperature reached *ca.* 220 °C. Both compounds were isolated as potassium salts.

Reaction of $[B(pz^R)_4]^-$ with $[Mo(CO)_6]$ in tetrahydrofuran gave the intermediate $[Mo(pz^RTp^R)(CO)_3]^-$, which was not isolated, but after gas CO evolution has ceased $Me(CH_2)_3ONO$ was added, affording the dicarbonyl nitrosyl complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ (R = An **1** or Cy **2**), which were isolated and crystallised, affording suitable crystals for X-ray crystallography which revealed the regiospecificy of the tetrakis(pyrazolyl)borate ligands. These dicarbonyls are yellow-orange solids stable towards air as solids and in solution. Their reaction with NOCl afforded the dichlorides $[MoCl_2(pz^RTp^R)(NO)]$ (R = An **3** or Cy **4**) as brown-violet solids which are slightly unstable towards air and decompose in the presence of air in solution.

The IR spectra of $K[B(pz^R)_4]$ show no absorptions in the ν_{max}(BH) region indicating the full substitution of the hydrogen atoms on KBH_4. The IR spectra of compounds **1** and **2** contain bands at *ca.* 2010 and 1930 cm^{-1} due to ν_{max}(CO) and at *ca.* 1670 cm^{-1} due to ν_{max}(NO). The dichlorides **3** and **4** exhibit ν_{max}(NO) at *ca.* 1710 cm^{-1}.

The ^{1}H and ^{13}C NMR spectra of $K[B(pz^R)_4]$ in $(CD_3)_2SO$ solution (Table 1) are consistent with the presence of only one isomer. In both cases only one single H5 and H4 pyrazolyl signal, as well as one type of resonance for the R substituents, are observed in the ^{1}H NMR spectra, indicating the equivalence of the four pyrazolyl rings in keeping with tetrahedral symmetry around the boron atom. Similar behaviour is observed in the ^{13}C NMR spectra: a signal for each type of carbon atom in each molecule is present in characteristic regions. From these data it seems that the isolated anions probably have the bulky substituent in the 3 position of each of the pyrazolyl rings thereby minimising steric hindrance around the boron atom, *i.e.* they are the (3R,3R,3R,3R) isomer.

The ^{1}H NMR spectra of the complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ (R = An **1** or Cy **2**) in $CDCl_3$ solution (Table 1) contain two sets of doublets of relative area 2 : 1 : 1, each corresponding to the H4 and H5 pyrazolyl protons, respectively. The coupling constants between these protons (*ca.* 2.4 Hz) are consistent with the substituents occupying the 3 position of the rings; lower values (*ca.* 1.5 Hz) are associated with substitution at the 5

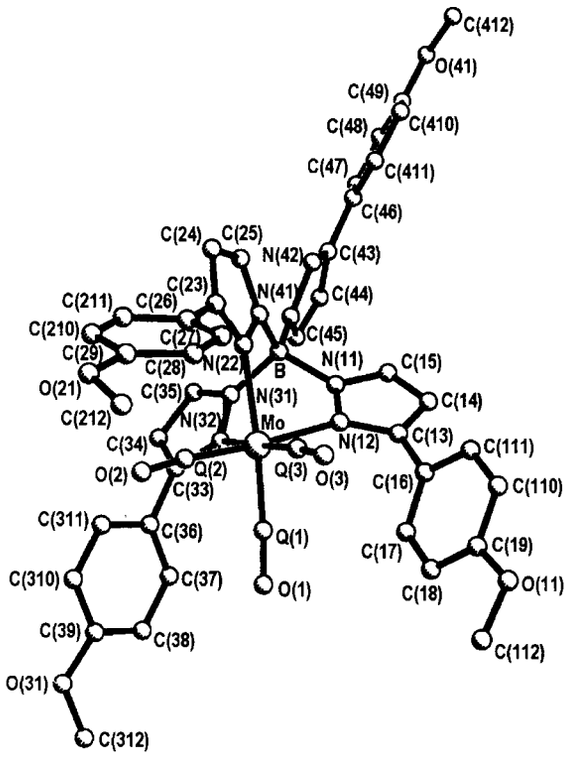


Fig. 1 Molecular structure of $[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ **1** showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

position.[15,26] In addition, the proton signals of the R substituents are observed with the same relative area. Thus the aryl derivative **1** shows two sets of doublets for the *ortho* and *meta* aryl protons with relative intensities 4 : 2 : 2, and three singlets for the CH_3O protons with relative area 6 : 3 : 3. For the cyclohexyl derivative **2** the CH signals appear as three quintuplets with relative area 2 : 1 : 1.

The ^{13}C NMR spectra of compounds **1** and **2** in $CDCl_3$ solution (Table 1) show signals for all carbon atoms of the molecules. For each type of carbon atom of the tetrakis(pyrazolyl)borate ligand there are three signals of relative intensities 2 : 1 : 1, and the carbonyl signal appears as a singlet at δ *ca.* 222.

These NMR spectral results are consistent with the occurrence of only one isomer for compounds **1** and **2**. This form should have a plane of symmetry which renders equivalent two pyrazolyl groups of a three-co-ordinated tetrakis(pyrazolyl)borate ligand. The fourth pyrazolyl group should not be co-ordinated, and the ring probably lies in the same molecular mirror plane referred to above. The aryl groups in **1** should have free rotation on the NMR timescale.

The ^1H and ^{13}C NMR spectra of the dichlorides **3** and **4** are poorly resolved because of their lower solution stability. However results related to those obtained from the dicarbonyls **1** and **2** were obtained (Table 1).

Electrochemical studies

The cyclic voltammetry of $[MoCl_2(pz^{Cy}Tp^{Cy})(NO)]$ **4** in dichloromethane showed a quasi-reversible reduction process at +0.10 V *vs.* Ag–AgCl reference electrode ($i_p^c/i_p^a = 1.1:1$), whereas $[MoCl_2(pz^{An}Tp^{An})(NO)]$ **3** showed an irreversible reduction at +0.09 V. These data may be compared with those obtained from $[MoCl_2(Tp^{An})(NO)]$[22] and $[MoCl_2(Tp^{Cy})(No)]$[27] which show quasi-reversible reduction waves at +0.11 and +0.14 V, respectively. The differences between these potentials are marginal suggesting that the presence or otherwise of pz^R in place of H at boron has little effect on the redox behaviour of the $[Mo(NO)]^{3+}$ core.

Table 2 Selected bond lengths (Å) and angles (°) for $[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ **1** and $[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ **2**

1			
Mo–Q(1)	1.886(8)	B–N(21)	1.53(1)
Mo–Q(2)	1.910(10)	B–N(31)	1.56(1)
Mo–Q(3)	1.904(8)	B–N(41)	1.52(1)
Mo–N(12)	2.219(8)	Q(1)–O(1)	1.19(1)
Mo–N(22)	2.264(7)	Q(2)–O(2)	1.17(1)
Mo–N(32)	2.219(6)	Q(3)–O(3)	1.18(1)
B–N(11)	1.56(1)		
N(22)–Mo–N(32)	81.9(2)	Q(2)–Mo–N(12)	175.1(3)
N(12)–Mo–N(32)	82.7(3)	Q(2)–Mo–Q(3)	85.0(4)
N(12)–Mo–N(22)	82.3(3)	Q(1)–Mo–N(32)	94.3(3)
Q(3)–Mo–N(32)	176.1(4)	Q(1)–Mo–N(22)	175.1(3)
Q(3)–Mo–N(22)	98.2(3)	Q(1)–Mo–N(12)	100.3(4)
Q(3)–Mo–N(12)	93.5(3)	Q(1)–Mo–Q(3)	85.9(4)
Q(2)–Mo–N(32)	98.9(3)	Q(1)–Mo–Q(2)	84.3(4)
Q(2)–Mo–N(22)	93.3(3)		
2			
Mo–Q(1)	1.931(7)	B–N(21)	1.571(8)
Mo–Q(2)	1.913(6)	B–N(31)	1.546(8)
Mo–Q(3)	1.937(7)	B–N(41)	1.501(8)
Mo–N(12)	2.249(4)	Q(1)–O(1)	1.165(7)
Mo–N(22)	2.211(5)	Q(2)–O(2)	1.158(7)
Mo–N(32)	2.230(5)	Q(3)–O(3)	1.172(7)
B–N(11)	1.53(9)		
N(22)–Mo–N(32)	82.0(2)	Q(2)–Mo–N(12)	94.2(2)
N(12)–Mo–N(32)	83.0(2)	Q(2)–Mo–Q(3)	87.8(3)
N(12)–Mo–N(22)	83.0(2)	Q(1)–Mo–N(32)	94.3(3)
Q(3)–Mo–N(32)	96.0(3)	Q(1)–Mo–N(22)	175.1(3)
Q(3)–Mo–N(22)	117.1(2)	Q(1)–Mo–N(12)	100.3(4)
Q(3)–Mo–N(12)	94.8(2)	Q(1)–Mo–Q(3)	87.3(2)
Q(2)–Mo–N(32)	175.4(2)	Q(1)–Mo–Q(2)	88.0(3)
Q(2)–Mo–N(22)	94.1(2)		

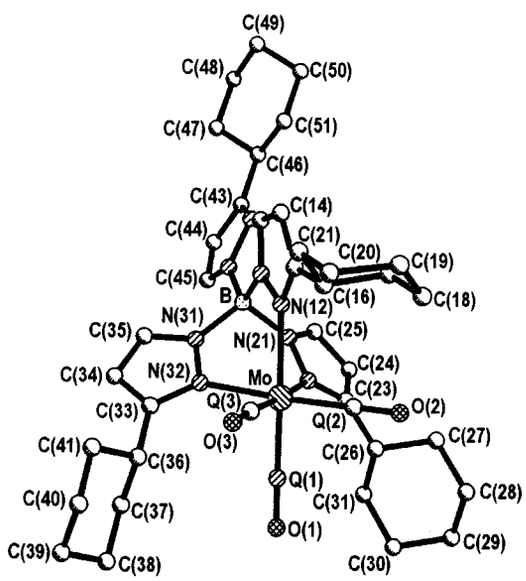


Fig. 2 Molecular structure of $[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ **2**. Details as in Fig. 1.

X-Ray studies

There are eight possible isomers of complexes $[Mo(pz^RTp^R)(CO)_2(NO)]$ having a plane of symmetry as deduced by their NMR spectra. Therefore, the crystal structure determinations of **1** and **2** were undertaken to establish unequivocally which isomer is produced. The molecular structures are depicted in Figs. 1 and 2 respectively, and Table 2 shows selected bond distances and angles for both compounds.

Both derivatives are monomeric with no short intermolecular contacts, and all substituents are located at the 3 position of the pyrazolyl rings. That is, the formation of the symmetric

(3R,3R,3R,3R) isomer is confirmed. The cyclohexyl substituents in **2** adopt the chair configuration.

Each tetrahedral tetrakis(pyrazolyl)borate group is tridentate with respect to the molybdenum atom, bonding *via* the nitrogen atoms in the 2 position of three pyrazolyl groups having approximate C_{3v} symmetry analogous to that observed for related compounds containing tris(pyrazolyl)borate ligands.[12,22,28,29] The boron atom is tetrahedral with N–B–N angles in the range 107–115°. The fourth pyrazolyl ring is located away from the pyramidal hole containing the metal centres, and each of the four pyrazolyl rings is approximately planar.

The geometry about the molybdenum atom is best described as distorted octahedral, with three facial positions occupied by three nitrogen atoms of the co-ordinated pyrazolyl rings, and the other three by the structurally indistinguishable NO and CO groups. The two sets of facial groups form two staggered triangular faces in the octahedron, and the planes so defined are inclined to each other by 1.1(3)° in compound **1** and 1.57(5)° in **2**, which may be compared with that obtained from [Mo(Tp^{An})(CO)$_2$(NO)] where the inclination is 2.1°.[22]

In compound **1** the aryl rings of the co-ordinated pyrazolyl groups are inclined at angles of 52.5(3) [C(16) to C(111)], 65.1(2) [C(26) to C(211)] and 89.4(4)° [C(36) to C(311)] (average 69.0°) with respect to their own pyrazolyl ring planes. Thus not all the rings of the co-ordinated pyrazolyl groups are truly orthogonal to the mirror planes of a strict C_{3v} point symmetry, so they do not form a perfect trigonal cavity. The aryl ring on the unco-ordinated pyrazolyl group deviates 18.2(3)° from its pyrazolyl ring plane.

In comparison compound **2** shows some differences. The best planes formed by the six carbon atoms of the cyclohexyl substituents of the co-ordinated pyrazolyl groups are almost orthogonal to their respective pyrazolyl rings {72.3(3) [C(16) to C(21)], 8.0(3) [C(36) to C(41)] and 86.4(3)° [C(26) to C(31)]; average 82.2°}, suggesting a better-defined trigonal cavity. The fourth cyclohexyl plane deviates 31.0(6)° from its pyrazolyl ring plane.

On the other hand, compounds **1** and **2** show deviations from the ideal *cis*-octahedral angle of 90° at molybdenum [N (pz)–Mo–N (pz)] with values of 81.9(2), 82.7(3) and 82.3(2)° (average 82.3°) and 82.0(2), 83.0(2) and 83.0(2)° (average 82.7°), respectively (Table 2). In addition, the angles *cis*-(OQ)–Mo–N (pz) (Q = C or N) fall in the range 93–100° (Table 2). We observe two groups of values for **1** (average 93.7 and 99.1°), but only one for **2** (average 94.8°). It is possible that for **1** these deviations are due to preferred orientations of the *p*-$CH_3OC_6H_4$ substituents, the larger angles relieving steric interactions between Q–O and the aryl group the *o*-H–C bonds of which are orientated towards Q–O as was also observed in the related [Mo(Tp^{An})(CO)$_2$(NO)].[22] No preferred orientations could be established for the cyclohexyl substituents in **2**.

The steric consequences of the fourth pyrazolyl group in the tetrakis(pyrazolyl)borato complexes may be assessed by comparing the structure of compound **1** with that of its counterpart having Tp^{An} as a ligand.[22] No significant differences are observed between them as far as the Mo–N (pz) and Mo–QO distances {average 2.23 and 1.90 Å for **1**, and 2.25 and 1.91 Å for [Mo(Tp^{An})(CO)$_2$(NO)], respectively} and the *cis*-Q–Mo–Q angles (average 85.1° for **1** and 85.0° for [Mo(Tp^{An})(CO)$_2$(NO)]} are concerned. This suggests that the steric compression of the Mo(QO)$_3$ moiety is not modified by the introduction of the fourth group.

On the other hand, some differences are observed in the angles between co-ordinated pyrazolyl planes for compound **1** and [Mo(Tp^{An})(CO)$_2$(NO)], *viz*. 59.6(3), 41.2(3) and 81.1(3)° (average 60.6°) and 60.2(3), 66.6(4) and 53.5(4)° (average 60.1°), respectively. These angles could be considered to be as a consequence of the orientation of the *p*-$CH_3OC_6H_4$ substituents towards the adjacent aryl group in [Mo(Tp^{An})(CO)$_2$(NO)], giving rise to shorter dihedral pyrazolyl/pyrazolyl angles than in **1**. However, there are no significant differences in the dihedral angles between co-ordinated pyrazolyl planes in the structure of **2** [59.7(2), 68.0(3) and 52.8(2)°; average 60.2°]. It therefore appears that the inclusion of the more flexible cyclohexyl substituents in comparison to the anisyls in the fourth pyrazolyl group should minimise that group's steric effect.

Finally, the most interesting structural feature relates to the greater protection of the molybdenum centre provided by the pyrazolyl substituents in compound **1** compared to **2**. This is evident from the *cis*-Q–Mo–Q angles: 85.0(4), 85.9(4) and 84.3(4)° in **1** *vs.* 88.0(3), 87.8(3) and 87.3(2)° in **2**, respectively (Table 2). The larger deviation of these angles in **1** from the ideal of 90° is related to the protective nature of the anisyl groups. The structure can be likened to an 'umbrella', the structural data indicating that the frame of the 'umbrella' is more rigid in **1** than in **2**.

Conclusion

The spectroscopic and X-ray diffraction studies of tetrakis(pyrazolyl)borate compounds reveal a special feature of the [B(pz^R)$_4$]$^-$ ligands. The tridentate co-ordination observed does not modify the steric requirements of the ligands which maintain the bulky substituents on the 3 position of all pyrazolyl rings.

The results obtained here demonstrate that the steric selectivity exerted in the preparation of tris(pyrazolyl)borate ligands having bulky substituents at the 3 position can probably be extended to tetrakis(pyrazolyl)borates. The influence of the substituents on the cavity produced by the tris(pyrazolyl)borate ligands is also observed in the tetrakis(pyrazolyl)borate derivatives. Thus the appropriate selection of the substituent groups can engender greater protection of the molybdenum core in complexes of the type [MoX$_2$(pz^{R}Tp^R)(NO)].

Experimental

Materials

All commercial reagents were used as supplied. The 3-(*p*-methoxyphenyl)pyrazole and 3-cyclohexylpyrazole compounds were prepared by procedures previously described.[22,30] All reaction solvents were dried and degassed according to standard methods prior to use.

All reactions involving molybdenum complexes were carried out under an atmosphere of dry oxygen-free dinitrogen, but the reaction products were handled in air. Silica gel 60 (70–230 mesh) was used for column chromatography.

Physical measurements

Elemental analyses were carried out by the Center for Elemental Microanalysis at the Complutense University. The FAB mass spectra were obtained on a VG AutoSpec spectrometer, infrared spectra on a FTIR Nicolet Magna-550 spectrophotometer with samples as KBr discs in the 4000–350 cm^{-1} region.

Proton and ^{13}C-{^{1}H}NMR spectra were performed on a Varian VXR-300 (299.88 and 75.40 MHz for ^{1}H and ^{13}C respectively) or a Bruker AM-300 (300.13 and 75.43 MHz for ^{1}H and ^{13}C respectively) spectrophotometers from solutions in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts δ are listed in parts per million relative to tetramethylsilane. The ^{1}H and ^{13}C chemical shifts are accurate to 0.01 and 0.1 ppm respectively; coupling constants are accurate to ±0.3 Hz for ^{1}H NMR spectra.

Cyclic voltammetric measurements were carried out on an Autolab apparatus equipped with a PSTA10 potentiostat using a three-electrode cell with platinum wire as working and auxiliary electrodes and an Ag–AgCl electrode as a reference, with a solution (*ca.* 10^{-3} mol dm^{-3}) of the complex in dichloro-

methane containing $[NBu_4][BF_4]$ (0.2 mol dm^{-3}) as the base electrolyte, using a scan rate of 200 mV s^{-1}. Values are referred to an Ag–AgCl electrode, but ferrocene was used as internal standard.

Synthetic methods

Potassium tetrakis[3-(*p*-methoxyphenyl)pyrazol-1-yl]borate. A mixture of KBH_4 (0.27 g, 5 mmol) and Hpz^{An} (4.35 g, 25 mmol) (ratio 1 : 5) was heated with stirring. Hydrogen evolution commenced when the mixture reached *ca.* 130 °C. The temperature was increased to *ca.* 210 °C and maintained until hydrogen evolution ceased. The white solid obtained on cooling the mixture was suspended in hexane (100 cm^3) and collected by filtration. The solid was washed repeatedly with diethyl ether to eliminate the excess of pyrazole (1.90 g, 50%) (Found: C, 64.3; H, 4.5; N, 14.8. Calc. for $C_{40}H_{36}BKN_8O_4$: C, 64.7; H, 4.9; N, 15.1%); $\tilde{\nu}_{max}/cm^{-1}$ 1611 (CN).

Potassium tetrakis(3-cyclohexylpyrazol-1-yl)borate. A mixture of KBH_4 (0.27 g, 5 mmol) and Hpz^{Cy} (3.75 g, 25 mmol) (ratio 1 : 5) was heated with stirring. Hydrogen evolution commenced when the mixture reached *ca.* 130 °C. The temperature was increased to *ca.* 210 °C and maintained until hydrogen evolution ceased. The white solid obtained on cooling the mixture was suspended in hexane (100 cm^3) and collected by filtration (1.45 g, 45%) (Found: C, 66.2; H, 7.9; N, 17.0. $C_{36}H_{52}BKN_8$ requires C, 66.9; H, 8.1; N, 17.3%); $\tilde{\nu}_{max}/cm^{-1}$ 1630 (CN).

$[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ 1. To a solution of $K[B(pz^{An})_4]$ (2.25 g, 3 mmol) in dry tetrahydrofuran (100 cm^3) was added $[Mo(CO)_6]$ (0.8 g, 3 mmol). The mixture was heated under reflux with stirring until no further gas evolution was observed and the reddish orange solution cooled with a slight stream of dinitrogen. An excess of $Me(CH_2)_3ONO$ (0.41 g, 0.48 cm^3, 4 mmol) was then added and the mixture gently heated until gas evolution ceased. The solution was poured into water (100 cm^3) and the product extracted into dichloromethane. The extracts were dried over sodium sulfate and then chromatographed on silica gel using dichloromethane as the eluent. The major yellow-orange band was collected and afforded a yellow solid, which was recrystallised from methanol (1.60 g, 60%) (Found: C, 56.5; H, 4.2; N, 13.9. $C_{42}H_{36}BMoN_9O_7$ requires C, 57.0; H, 4.1; N, 14.2%); $\tilde{\nu}_{max}/cm^{-1}$ 2009 and 1917 (CO), 1672 (NO) and 1595 (CN); *m*/*z* 886 (M^+), 859 (M − CO and M − NO), 831 (M − 2CO) and (M − NO − CO) (both ions are encompassed by the *m*/*z* range of the ion clusters at 859 and 831).

$[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ 2. The compound was prepared in a way similar to that of **1** using $K[B(pz^{Cy})_4]$ (0.65 g, 1 mmol), $[Mo(CO)_6]$ (0.26 g, 1 mmol) and $Me(CH_2)_3ONO$ (1.55 g, 1.81 cm^3, 1.5 mmol). A yellow solid was obtained (0.50 g, 65%) (Found: C, 57.3; H, 6.6; N, 15.7. $C_{38}H_{52}BMoN_9O_3$ requires C, 57.8; H, 6.6; N, 16.0%); $\tilde{\nu}_{max}/cm^{-1}$ 2012 and 1925, 1915 (CO), 1669 (NO) and 1600 (CN); *m*/*z* 792 (M^+), 733 (M − 2CO) and (M − CO − NO) (both ions are encompassed by the *m*/*z* range).

$[MoCl_2(pz^{An}Tp^{An})(NO)]$ 3. Into a suspension of $[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ (1 g, 1.1 mmol) in dichloromethane (100 cm^3) was bubbled nitrosyl chloride. The solution changed from orange to violet after *ca.* 10 min. Then a dinitrogen stream was passed through it to eliminate the excess of nitrosyl chloride. The solvent was evaporated off and the violet solid obtained washed repeated times with hexane and dried *in vacuo* (0.80 g, 81%) (Found: C, 53.4; H, 3.9; N, 13.6. $C_{40}H_{36}BCl_2MoN_9O_5$ requires C, 53.4; H, 4.0; N, 14.0%); $\tilde{\nu}_{max}/cm^{-1}$ 1727 (NO) and 1613 (CN); *m*/*z*. 867 (M − Cl) and 831 (M − 2Cl); E_p^c (irreversible, CH_2Cl_2 *vs.* Ag–AgCl) 0.09 V.

$[MoCl_2(pz^{Cy}Tp^{Cy})(NO)]$ 4. This compound was prepared in a way similar to that of **3** using $[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ (0.53 g, 0.67 mmol). A brown-violet solid was obtained (0.40 g, 72%) (Found: C, 53.4; H, 6.4; N, 15.4. $C_{36}H_{52}BCl_2MoN_9O$ requires C, 53.7; H, 6.5; N, 15.7%); $\tilde{\nu}_{max}/cm^{-1}$ 1709 (NO) and 1635 (CN); *m*/*z* 806 (M^+), 770 (M − Cl) and 732 (M − 2Cl); E_f (quasi-reversible, CH_2Cl_2 *vs.* Ag–AgCl) 0.10 V, ΔE_p 180 mV, $i_p^c/i_p^a = 1.1 : 1$.

Table 3 Crystal and refinement data for $[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ **1** and $[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ **2**

	1	**2**
Formula	$C_{42}H_{36}BMoN_9O_7$	$C_{38}H_{52}BMoN_9O_3$
M	739.39	789.64
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.728(2)	12.379(1)
b/Å	12.770(8)	13.013(1)
c/Å	13.765(3)	14.362(1)
α/°	113.13(3)	113.419(1)
β/°	97.43(2)	107.655(2)
γ/°	90.12(2)	92.372(2)
U/Å^3	2037(1)	1988.1(3)
Z	2	2
T/K	295	295
D_c/g cm^{-3}	1.44	1.319
μ(Mo-Kα)/mm^{-1}	0.372	0.377
Crystal size/mm	0.25 × 0.1 × 0.25	0.2 × 0.15 × 0.15
Scan technique	ω–2θ	ω
θ/°	1–28	1.65–23.31
Unique data	9816	7544
Unique data [$I > 2\sigma(I)$]	4509 (R_{int} = 0.007)	5431 (R_{int} = 0.0438)
Data, parameters	4509, 541	5431, 619
$R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$	0.063	0.060
wR*	0.10	0.14

* $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w^2(F_o^2)^2]^{\frac{1}{2}}$.

Crystallography

Yellow prismatic single crystals of $[Mo(pz^{An}Tp^{An})(CO)_2(NO)]$ **1** and $[Mo(pz^{Cy}Tp^{Cy})(CO)_2(NO)]$ **2** were obtained from dichloromethane–diethyl ether. Data for compound **1** were collected on an Enraf-Nonius CAD4 diffractometer, and unit cell constants refined from least-squares fitting of the θ values of 25 reflections with 2θ of 13–26°. The data of **2** were obtained on a Smart CCD area detector system. A summary of the fundamental crystal data for the two crystals is given in Table 3.

The intensities were corrected for Lorentz-polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from ref. 31. The structure was solved by Patterson and Fourier methods for **1** and by direct and Fourier methods for **2**. They were refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. For **1** the hydrogen atoms were situated in fixed gometrically calculated positions, for **2**, they were included from a ΔF map and their coordinates refined.

The largest residual peak in the final difference map was 1.10 and 0.50 e Å^{-3} for compounds **1** and **2** respectively, in the vicinity of the Rh atom. Most of the calculations for **1** were carried out with the X-RAY 80 system[32] and for **2** with SHELXTL.[33]

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