Boratropic Rearrangements in Tris(pyrazolyl)borate Molybdenum Mononitrosyl Complexes: Effects of Co-ligands†

Mercedes Cano,[a] Jose V. Heras,[a] Angeles Monge,[b] Elena Pinilla,[a,b] Elena Santamaria,[a] Helen A. Hinton,[c] Christopher J. Jones*[,c] and Jon A. McCleverty*[,d]

[a] *Departamento de Quimica Inorganica, Facultad Quimicas, Universidad Complutense, Madrid 28040, Spain*

[b] *Insto. de Ciencias de los Materiales sede D.C.S.I.C., Serrano 113, Laboratorio de Diffracion de Rayos-X, Facultad Quimicas, Universidad Complutense, Madrid 28040, Spain*

[c] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

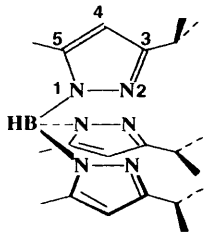
[d] *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

The complexes $[Mo(NO)\{HB(impz)_3\}I(ER)]$ [impz = isopropylmethylpyrazol-1-yl; E = O; R = Pr^i, Bu^t, CH_2SiMe_3, $(CH_2)_4I$, Ph or C_6H_4Me-4: E = NH; R = Ph or C_6H_4Me-4] have been prepared from a mixture of isomers of $[Mo(NO)\{HB(impz)_3\}I_2]$; in the cases where ER = OPh, $O(CH_2)_4I$ or OCH_2SiMe_3 the products could only be obtained as mixtures of isomers, but where ER = OPr^i, OBu^t, NHPh or NHC_6H_4Me-4 the products could be thermally converted into compounds containing a single isomer of the ligand $HB(impz)_3$. Reactions involving REH (E = O; R = Me, Pr^i or Bu^t; E = NH; R = Et, CH_2Ph or Ph) and a single isomer of $[Mo(NO)\{HB(impz)_3\}I_2]$ produced $[Mo(NO)\{HB(impz)_3\}I(ER)]$ containing a single isomer of the ligand $HB(impz)_3$ and which did not rearrange on heating. The locations of the methyl and isopropyl groups in the $HB(impz)_3$ ligand in $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}Me\text{-}C_3N_2H)_3\}(OPr^i)_2]$ have been determined by X-ray crystallographic methods.

The tris(pyrazolyl)borate ligand system, first described by Trofimenko,[1] has assumed an important role in modern co-ordination chemistry.[2] Owing to their tripodal nature the tris(pyrazolyl)borates can act as passive co-ligands occupying three facial co-ordination sites on a metal ion. As a consequence they are often used to regulate the co-ordination sphere of metal ions in studies of chemical reactivity. Furthermore, it is possible to exert some control over the steric environment at the metal ion through the incorporation of substituents on the pyrazolyl groups. Many examples of such derivatives have been reported[2] and, in particular, the methylated ligand tris(3,5-dimethylpyrazolyl)borate $HB(dmpz)_3^-$ has found a variety of applications. These include rhodium complexes which exhibit photochemical reactivity and alkane activation reactions,[3] models for bioinorganic systems,[4–7] complexes used to study intramolecular electron-transfer processes[8] and derivatives which exhibit second-order non-linear optical properties.[9]

In studying the chemistry of complexes in which a tris(pyrazolyl)borate ligand is present, it is important to note that tris(pyrazolyl)borates themselves can undergo reactions and that these may be a complicating factor in the chemistry observed. These ligand-based reactions may involve deboronation, examples being provided by the reaction of $K[HB(dmpz)_3]$ with $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ to give[10] $[Ru(\eta^6\text{-}C_6H_6)\{NH{=}CMe(dmpz)\}(Hdmpz)]^{2+}$ and in the reaction of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ with catechol to give $[Mo(NO)(O_2C_6H_4)(Hdmpz)_2(dmpz)]$.[11] A less-complete degradation may involve the displacement of one pyrazolyl from a tris(pyrazolyl)borate ligand as found in the reactions between $[Mo(NO)\{HB(dmpz)_3\}I_2]$ and 2-aminobenzenethiol or 1,2-diaminobenzene which result in the replacement of one dimethylpyrazolyl group in the tripodal ligand by the aminoaryl moiety.[12]

Further evidence of the non-passive behaviour of tris(pyrazolyl)borate ligands comes from the observation of boratropic rearrangements involving ligand reorganisation without the loss of any pyrazolyl groups. Thus the regiospecifically pure



$HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3$

$HB(3\text{-}Pr^iC_3N_2H_2)_3$ and $HB(3\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)_3$ rearrange to the isomers $HB(3\text{-}Pr^iC_3N_2H_2)_2(5\text{-}Pr^iC_3N_2H_2)$ and $HB(3\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)_2(5\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)$ when incorporated into octahedral complexes.[13] Although such asymmetrically substituted tris(pyrazolyl)borates are usually obtained as single isomers, $K[HB(impz)_3]$ (impz = isopropylmethylpyrazol-1-yl) is obtained as a mixture of isomers which cannot readily be converted into a single isomer by heating.[14] Reaction of $K[HB(impz)_3]$ with $[Mo(CO)_6]$ followed by nitrosylation affords $[Mo(CO)_2(NO)\{HB(impz)_3\}]$ which may be iodinated to give $[Mo(NO)\{HB(impz)_3\}I_2]$, both compounds being isolated as mixtures of isomers. We have previously reported[14] that the reactions of the mixed isomers of $[Mo(NO)\{HB(impz)_3\}I_2]$ with the alcohols ROH (R = Me, Et, Pr^i or Bu^t) afford monoalkoxide derivatives $[\{Mo(NO)\{HB(impz)_3\}I(OR)]$ containing the $HB(impz)_3$ ligand in a mixture of isomeric forms. In the cases where R = Pr^i or Bu^t it proved possible to convert the isomeric mixture into a *single isomer*‡ by heating. These *single isomers* result from boratropic rearrangements of the $HB(impz)_3$ ligand which are apparently promoted by the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

‡ These monosubstituted derivatives also contain a chiral molybdenum centre and are isolated as racemic mixtures. No attempt was made to resolve these mixtures, or to separate the diastereoisomers, so that the term *single isomer* refers only to the $HB(impz)_3$ ligand and not to the complex as a whole.

more sterically demanding co-ligands OR. Owing to the potential importance of such boratropic rearrangements in studies involving tris(pyrazolyl)borate complexes, we have investigated the synthesis and isomerisation of several complexes of formula [Mo(NO){HB(impz)$_3$}I(ER)] (E = O or NH; R = alkyl or aryl) and report our findings here. We have also isolated a more isomerically pure form of [Mo(NO){HB(impz)$_3$}I$_2$] and examined its reactions with methanol and organoamines.

Results and Discussion

Synthetic Studies.—A mixture of isomers of [Mo(NO){HB(impz)$_3$}I$_2$] reacts with ROH (R = Pr^i or Bu^t) to give [Mo(NO){HB(impz)$_3$}I(OR)]. The ^{1}H NMR spectra of the purified products obtained initially contained duplicated signals, as observed previously[14] for [Mo(NO){HB(impz)$_3$}I(OR)] (R = Me or Et), indicating the presence of isomeric mixtures. There are two sources of isomerism in these complexes. The first is associated with the locations of the methyl and isopropyl groups on the pyrazolyl rings and the second arises from the chirality of the metal centre (Fig. 1). After drying samples of these compounds to 80–90 °C for *ca.* 20 h the ^{1}H NMR spectra were found to exhibit only three resonances, each of relative area 3, attributable to the pyrazolyl methyl groups indicating that a complex containing a single isomer of the HB(impz)$_3$ ligand had been produced (Scheme 1). In order to establish whether a *single isomer* ‡ might be similarly obtained with an alcohol carrying a sterically bulky group one atom removed from the oxygen donor atom, the reaction of [Mo(NO){HB(impz)$_3$}I$_2$] with Me$_3$SiCH$_2$OH was investigated. Again the initial reaction product was found to contain a mixture of isomers but, in this case, heating at 80 °C for 20 h failed to produce a *single isomer*. This observation suggests that, if a *single isomer* is to be obtained, it is necessary for the sterically bulky group of the alkoxide to be attached directly to the co-ordinated oxygen atom.

In order further to investigate the effects of co-ligands containing aryl groups on the isomer distributions in compounds containing the {Mo(NO){HB(impz)$_3$}I} moiety, the reactions of [Mo(NO){HB(impz)$_3$}I$_2$] with REH (E = O or NH, R = Ph or C$_6$H$_4$Me-4) were also carried out. The results obtained from these experiments are summarised in Scheme 1. In all cases the monosubstituted products [Mo(NO){HB(impz)$_3$}I(ER)] were isolated as mixtures of isomers but, after heating *in vacuo*, at 80 °C for several hours, the arylamide derivatives were converted into *single isomers* whereas the phenoxide derivatives were not. This difference in behaviour could arise from steric or electronic effects. The presence of the amide hydrogen atom leads to the amide ligands having a greater steric bulk close to the metal centre than that of their aryloxo counterparts, so that steric effects might be invoked to account for the differing behaviour of the phenoxide and arylamide compounds. However, electrochemical data indicate that arylamide ligands are stronger electron donors to molybdenum than are their phenoxide counterparts, since their reduction potentials are more cathodic and reflect a higher electron density at the metal centre.[15] Thus it could be argued that it is this electronic difference which leads to the differing behaviour of the phenoxide and amide derivatives. However, while the alkoxide derivatives [Mo(NO){HB(impz)$_3$}I(OR)] (R = Me, Et, CH$_2$SiMe$_3$, Pr^i or Bu^t) all exhibit similar reduction potentials (see below),* which approach the values found for the arylamide derivatives, *single isomers* are obtained when R = Pr^i and Bu^t but not when R = Me, Et or CH$_2$SiMe$_3$. This would appear to confirm that the rearrangements of the

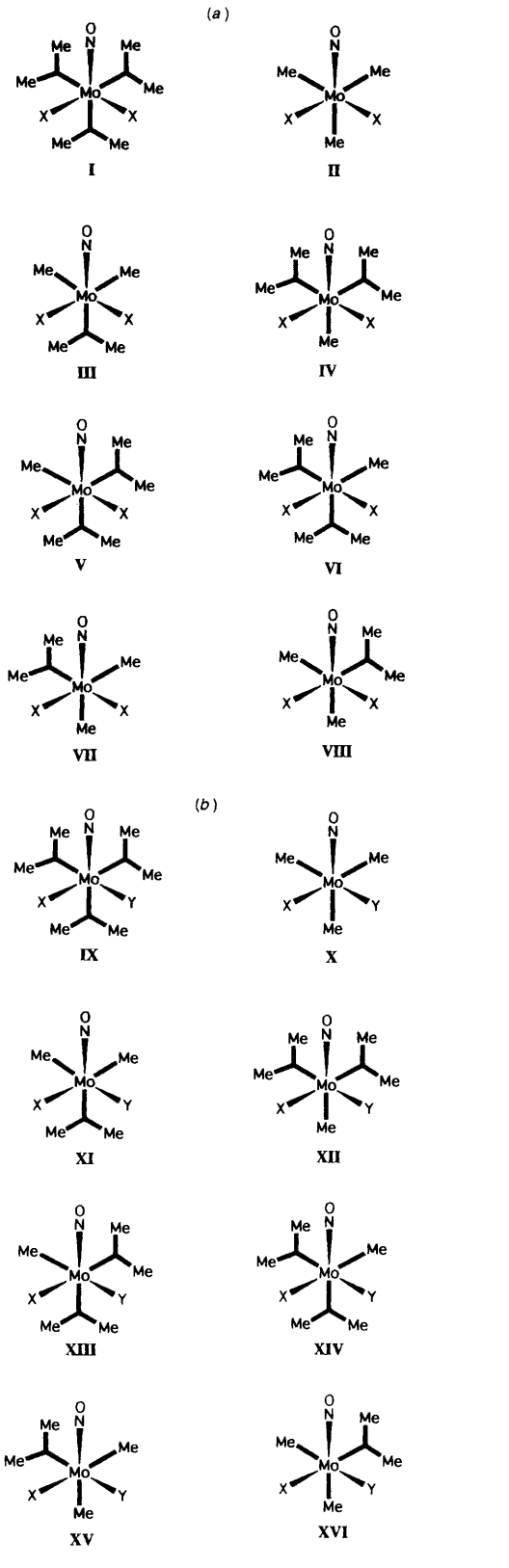
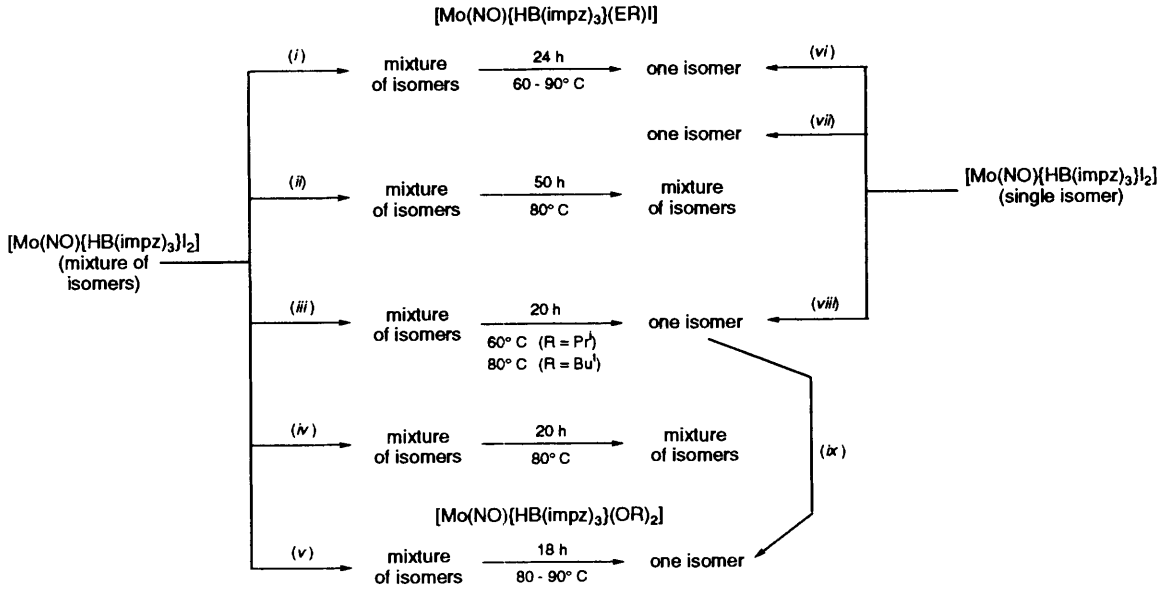


Fig. 1 The various isomeric possibilities for complexes of formulae (*a*) [Mo(NO){HB(impz)$_3$}X$_2$] and (*b*) [Mo(NO){HB(impz)$_3$}X(Y)]. To simplify the structural representations the diagrams show the complex as if viewed down the Mo–B axis with only the groups NO, X and Y bound to Mo and the substituent in the 3 position of the pyrazolyl ring shown. Structures **I**–**IV** are not chiral but **V** and **VI** constitute a pair of enantiomers, as do **VII** and **VIII**. Each of the structures **IX**–**XVI** has a corresponding enantiomeric form so that, in principle, 16 isomers of [Mo(NO){HB(impz)$_3$}X(Y)] are possible

* Electrochemical data (thf, *vs.* saturated calomel electrode) for [Mo(NO){HB(impz)$_3$}I(OR)]: R = Me, E_p^c = −0.69, −1.55; R = Et, E_p^c = −0.68, −1.52; E_f\{[Fe(C$_5$H$_5$)$_2$]$^+$ − [Fe(C$_5$H$_5$)$_2$]\} = +0.58 V.



Scheme 1 (*i*) NH_2R (R = Ph or C_6H_4Me-4); (*ii*) ROH (R = Ph or C_6H_4Me-4); (*iii*) ROH (R = Pr^i or Bu^t); (*iv*) Me_3SiCH_2OH, ROH (R = Me or Et) or tetrahydrofuran (thf); (*v*) 2ROH (R = Pr^i or Bu^t)–$Ag(O_2CMe)$; (*vi*) NH_2Ph; (*vii*) NH_2Et; (*viii*) ROH (R = Me, Pr^i or Bu^t); (*ix*) ROH, $Ag(O_2CMe)$

$HB(impz)_3$ ligand are promoted by steric rather than electronic effects.

Two other types of reaction were also investigated. The first involves the use of $Ag(O_2CMe)$ as a halide abstractor to promote alkoxide formation.[16] This reagent was used to prepare the bis(alkoxide) $[Mo(NO)\{HB(impz)_3\}(OPr^i)_2]$ either directly from the reaction of Pr^iOH and the mixed isomers of $[Mo(NO)\{HB(impz)_3\}I_2]$, or from Pr^iOH and the mixed isomers of $[Mo(NO)\{HB(impz)_3\}I(OPr^i)]$. These reactions afforded a mixture of isomers of $[Mo(NO)\{HB(impz)_3\}(OPr^i)_2]$ but, as with the monoalkoxide complex, heating this mixture affords a *single isomer* (Scheme 1). The second type of reaction involves the formation of an alkoxide through the ring opening of a cyclic ether. The reaction of $[Mo(NO)\{HB(dmpz)_3\}I_2]$, which contains the symmetric dimethylpyrazolyl group, with tetrahydrofuran effects such a ring opening to form the iodoalkoxide complex $[Mo(NO)\{HB(dmpz)_3\}I\{O(CH_2)_4I\}]$.[17] A similar reaction with tetrahydrofuran was carried out using the mixed isomers of $[Mo(NO)\{HB(impz)_3\}I_2]$ to determine whether it might proceed selectively to give a particular isomeric form of the product. In this case the product, $[Mo(NO)\{HB(impz)_3\}I\{O(CH_2)_4I\}]$, was again isolated as a mixture of isomers which, as in the case of the iodoethoxide complex,[14] was not converted into one isomer on heating.

Since it proved possible to rearrange some of the derivatives $[Mo(NO)\{HB(impz)_3\}I(ER)]$ to *single isomers* by heating, the mixed isomers of $[Mo(NO)\{HB(impz)_3\}I_2]$ were also heated *in vacuo* for several hours. The ^1H NMR spectrum of the product obtained is much simplified and indicates that a *single isomer* predominates to the extent of *ca.* 9:1. It was subsequently found that samples of similar isomeric purity can also be obtained by fractional crystallisation. Reaction of this isomerically enriched $[Mo(NO)\{HB(impz)_3\}I_2]$ with ROH (R = Pr^i or Bu^t) afforded samples of $[Mo(NO)\{HB(impz)_3\}I(OR)]$ of similar isomeric composition to the precursor and with ^1H NMR spectra corresponding with those previously obtained for the *single isomers* of the iodo alkoxide derivatives. In an attempt to determine whether any rearrangements would occur during the substitution of halide by alkoxide, the reaction of the isomerically enriched $[Mo(NO)\{HB(impz)_3\}I_2]$ with MeOH was monitored by ^1H NMR spectroscopy. Unfortunately, the formation of by-products during the reaction resulted in signal overlap which precluded unambiguous comment on the progress of the reaction. However, when the reaction products were separated the methoxide complex, $[Mo(NO)\{HB(impz)_3\}I(OMe)]$, was found to be in the form of a *single isomer* which could not be converted into a mixture of isomers by heating to 100 °C for 24 h, suggesting that it was already in the more thermodynamically stable form. The isomerically purified form of $[Mo(NO)\{HB(impz)_3\}I_2]$ also reacted with NH_2R (R = Et or CH_2Ph) to give $[Mo(NO)\{HB(impz)_3\}I(NHR)]$ as *single isomers* which did not produce a mixture of isomers on heating to 100 °C for 24 h.

The new compounds were characterised by their elemental analyses and spectroscopic properties. The IR spectra contained ν_{BH} in the region 2550–2560 cm^{-1}, in addition to other bands attributable to the presence of the $HB(impz)_3$ ligand. The alkoxide and phenoxide complexes exhibited $\nu_{max}(NO)$ in the region 1675–1680 cm^{-1}, values close to those found for $[Mo(NO)\{HB(dmpz)_3\}Cl(OR)]$.[18] Also, as expected, the arylamide complexes exhibit $\nu_{max}(NO)$ at 1665 cm^{-1} in addition to $\nu_{max}(NH)$ in the region 3275–3280 cm^{-1}.[18]

The 270 MHz ^1H NMR spectra of the new compounds contained three groups of signals attributable to the $HB(impz)_3$ ligand. The pyrazolyl 4-H protons appear in the region δ 5.7–6.0, the isopropyl CH protons at δ 3.2–3.9, the pyrazolyl methyl signals at δ 2.3–2.5 and the isopropyl methyl protons at δ 1.2–1.5. In addition signals due to the appropriate co-ligand protons are observed and, for the arylamide complexes, the amide proton resonance is observed at *ca.* δ 13. The ^1H NMR spectrum of the isomerically purified sample of $[Mo(NO)\{HB(impz)_3\}I_2]$ is consistent with the presence of a plane of symmetry in the molecule. The pyrazolyl 4-H protons appear as two singlets of relative area 1:2, the pyrazolyl methyl protons as two singlets of relative area 3:6 and the pyrazolyl isopropyl groups as three doublets of relative area 6:6:6. The isomerically pure complexes $[Mo(NO)\{HB(impz)_3\}I(ER)]$ (E = O; R = Me, Pr^i or Bu^t; E = NH; R = Et, CH_2Ph, Ph or C_6H_4Me-4) do not contain a molecular symmetry plane. In these cases the pyrazolyl 4-H protons generally appear as three singlets of relative area 1:1:1, the pyrazolyl methyl protons as three singlets of relative area 3:3:3 and the pyrazolyl isopropyl methyls as six doublets of relative area 3:3:3:3:3:3, although at 270 MHz signal overlap occurs in some cases. The spectra of the complexes $[Mo(NO)\{HB(impz)_3\}I(OR)]$ [R = CH_2SiMe_3, $(CH_2)_4I$, OPh or OC_6H_4Me-4] isolated as mixed isomers were more complex and contained a greater number of

signals. In the case of [Mo(NO){HB(impz)$_3$}I(OCH$_2$SiMe$_3$)], for example, a total of nine signals attributable to the pyrazolyl methyl protons is observed, indicating the presence of at least three different isomers.

The mass spectra of all the compounds [Mo(NO){HB(impz)$_3$}I(ER)] were consistent with their formulations and contained molecular ions in addition to fragment ions corresponding to the loss of the iodide or ER ligands.

Electrochemical Studies.—The electrochemistry of [Mo(NO){HB(impz)$_3$}I(ER)] in tetrahydrofuran solutions was investigated using cyclic voltammetry. The behaviour of the new complexes was generally similar to that of their counterparts containing the dmpz ligand.[15,19] The complexes containing aryloxo substituents, ER, exhibit a single reversible reduction process at potentials of −0.34 (ER = OPh) and −0.37 V (ER = OC$_6$H$_4$Me-4). These reduction waves exhibit well defined cathodic and anodic peaks with peak-current ratios i_{pc}/i_{pa} close to 1:1. The high internal resistance of the solutions gave rise to high values for ΔE_p but these were comparable to those obtained for ferrocene oxidation at similar diffusion currents (see Experimental section). The reduction potentials of the arylamide complexes are some 500 mV more cathodic than those of the aryloxo derivatives and are not completely reversible, having i_p^c/i_p^a ratios in excess of 1:1 (ER = NHPh; E_f = −0.80 V, i_p^c/i_p^a = 1.23:1; ER = NHC$_6$H$_4$Me-4; E_f = −0.85 V, i_p^c/i_p^a = 1.78:1). On repeated scans i_p^c decreased and small product waves, which appear to be reversible, were observed at −0.27 (ER = NHPh) and −0.31 V (ER = NHC$_6$H$_4$Me-4). These may be associated with the dissociation of iodide from the reduced species as has been observed earlier in related compounds.[20]

The alkoxide complexes exhibit only irreversible reduction processes the first having E_p^c in the range −0.64 to −0.74 V. A subsequent reduction process was also observed and may correspond to the reduction of a 17-electron solvated derivative [Mo(NO){HB(impz)$_3$}(OR)(thf)] [R = Pr^i, Bu^t, CH$_2$SiMe$_3$ or (CH$_2$)$_4$I] to its corresponding 18-electron monoanion. In accord with this proposal, repeated scans revealed new oxidation processes at +0.44 and +0.78 V. These were enhanced by the addition of NBu$_4$I to the solution, showing that the liberation of free iodide occurs following reduction.[20] The alkylamide complexes [Mo(NO){HB(impz)$_3$}I(NHR)] (R = Et or CH$_2$Ph) similarly only exhibited irreversible reductions at *ca.* −1.1 V in accord with previous findings for related alkylamide complexes containing the HB(dmpz)$_3$ ligand.[21]

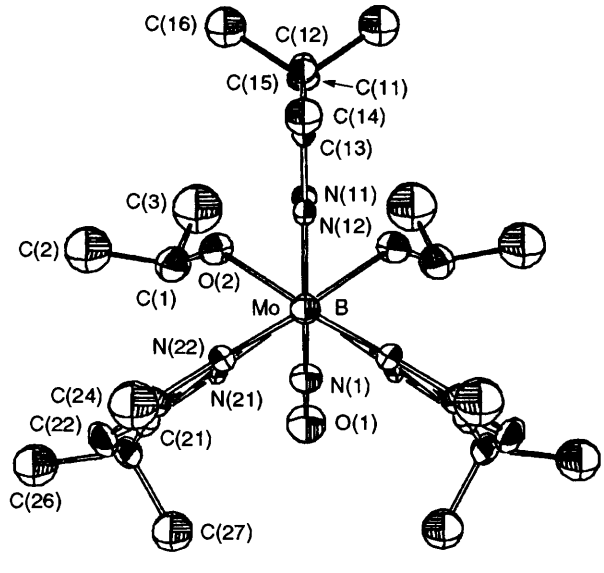


Fig. 2 Crystal structure of [Mo(NO){HB(impz)$_3$}(OPr^i)$_2$] viewed down the B–Mo axis and showing the atom numbering with 20% probability ellipsoids.[22] Hydrogen atoms have been omitted for clarity

Structural Studies.—In order to determine whether, compared to the {(NO)(OEt)$_2$} ligand set, the increased steric demands of the {(NO)(OPr^i)$_2$} ligand set might favour a different isomeric structure, the crystal stucture of [Mo(NO){HB(impz)$_3$}(OPr^i)$_2$] was determined. The molecular structure of the compound is shown in Fig. 2.[22] Atomic parameters are given in Table 1 and selected bond distances and angles in Table 2. The complex exhibits a distorted-octahedral co-ordination geometry around the formally 16-electron molybdenum centre and, as in [Mo(NO){HB(impz)$_3$}(OEt)$_2$],[14] all of the pyrazolyl isopropyl groups occupy the 3 position next to the Mo-bound nitrogen atoms. The most significant differences between these two structures involve the alkoxide ligands and, compared to the (Et)O–Mo–O(Et) angle of 99.3(5)° in [Mo(NO){HB(impz)$_3$}(OEt)$_2$], the (Pr^i)O–Mo–O(Pr^i) angle in [Mo(NO){HB(impz)$_3$}(OPr^i)$_2$] is increased to 102.0(4)°, with a corresponding reduction in the N(21)–Mo–N(21′) angle to 75.8(3)°. The average value of the (Pr^i)O–C(Pr^i)–C(Pr^i) angles is

Table 1 Atomic parameters for [Mo(NO){HB(impz)$_3$}(OPr^i)$_2$]

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.8185(1)	0.2500	0.6345(1)
N(1)	0.8437(8)	0.2500	0.7895(13)
O(1)	0.8636(8)	0.2500	0.8971(13)
O(2)	0.8740(4)	0.1587(5)	0.5852(8)
N(11)	0.7901(6)	0.2500	0.4306(12)
N(12)	0.7222(6)	0.2500	0.3966(11)
N(21)	0.7279(5)	0.1653(5)	0.6565(8)
N(22)	0.6711(5)	0.1733(5)	0.5771(8)
B	0.6646(10)	0.2500	0.4942(18)
C(1)	0.9225(9)	0.1089(11)	0.6546(16)
C(2)	0.9118(12)	0.0212(15)	0.6169(22)
C(3)	0.9910(15)	0.1322(17)	0.6120(26)
C(11)	0.8277(8)	0.2500	0.3277(14)
C(12)	0.7836(9)	0.2500	0.2277(16)
C(13)	0.7168(8)	0.2500	0.2700(14)
C(14)	0.6512(10)	0.2500	0.2038(17)
C(15)	0.9070(9)	0.2500	0.3261(15)
C(16)	0.9358(9)	0.3274(10)	0.2614(17)
C(21)	0.7137(7)	0.0968(7)	0.7274(11)
C(22)	0.6514(8)	0.0621(8)	0.6880(13)
C(23)	0.6243(7)	0.1119(9)	0.5977(11)
C(24)	0.5562(10)	0.1045(11)	0.5304(17)
C(25)	0.7586(8)	0.0704(8)	0.8313(11)
C(26)	0.7549(10)	−0.0230(12)	0.8491(17)
C(27)	0.7354(10)	0.1127(11)	0.9506(16)

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Mo–N(1)	1.74(1)	N(12)–B	1.52(2)
Mo–O(2)	1.88(1)	N(22)–B	1.52(1)
Mo–N(11)	2.26(1)	O(2)–C(1)	1.43(2)
Mo–N(21)	2.21(1)	C(1)–C(2)	1.48(3)
N(1)–O(1)	1.22(2)	C(1)–C(3)	1.43(3)
N(21)–Mo–N(21′)	75.8(3)	N(1)–Mo–N(21)	96.5(2)
N(11)–Mo–N(21′)	85.2(2)	N(1)–Mo–N(11)	177.8(6)
N(11)–Mo–N(21)	85.2(2)	N(1)–Mo–O(2′)	96.6(3)
O(2′)–Mo–N(21′)	89.6(3)	N(1)–Mo–O(2)	96.6(3)
O(2′)–Mo–N(21)	161.3(3)	Mo–N(1)–O(1)	178(1)
O(2′)–Mo–N(11)	82.0(3)	Mo–O(2)–C(1)	130.5(9)
O(2)–Mo–N(21′)	161.3(3)	N(12)–B–N(22)	110.3(3)
O(2)–Mo–N(21)	89.6(3)	O(2)–C(1)–C(3)	106(2)
O(2)–Mo–N(11)	82.0(3)	O(2)–C(1)–C(2)	107(1)
O(2)–Mo–O(2′)	102.0(4)	C(2)–C(1)–C(3)	107(2)
N(1)–Mo–N(21′)	96.5(2)		

Primed atoms are related to unprimed ones by the relation $x, \frac{1}{2} - y, z$.

107(2)°, somewhat smaller than the value of 117(2)° found for the (Et)O–C(Et)–C (Et) angles in $[Mo(NO)\{HB(impz)_3\}(OEt)_2]$. The Mo–O bond distance of 1.88(1) Å is comparable with those of 1.88(1), 1.91(1), 1.863(7) and 1.886(12) Å found respectively in the alkoxide complexes $[Mo(NO)\{HB(impz)_3\}(OEt)_2]$,[14] $[Mo(NO)\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}Cl(OPr^i)]$[23] and $[Mo(NO)\{HB(dmpz)_3\}I(OC_3H_6Br)]$.[19] The isopropyl groups of the $HB(impz)_3$ ligand are oriented to present the isopropyl CH hydrogen towards the B–Mo axis so that the steric demands of this ligand are little different from those of $HB(dmpz)_3$ within the tripodal ligand cavity. However, the methyl groups on these isopropyl substituents do produce substantial steric protection round the outer surface of the metal-bound end of the $HB(impz)_3$ ligand. The isopropoxide isopropyl groups are oriented to minimise steric interactions between these groups and the substituents in the pyrazolyl 3 positions.

At first sight it might seem surprising that the presence of more sterically bulky alkoxide ligands bound to the metal should favour the relocation of the isopropyl substituents to the 3 positions of the $HB(impz)_3$, where they are in closer proximity to these bulky co-ligands. However, in the complexes $[Mo(NO)\{HB(impz)_3\}X(Y)]$ it is the pyrazolyl 5 position closest to the smaller boron atom that is the most prone to steric congestion (Fig. 3). Thus if an increase in co-ligand steric bulk at the Mo end of the $\{HB(impz)_3Mo\}$ moiety leads to an opening out of the (pz)N–B–N(pz) or (pz)N–N(pz)–B angles, this will bring the substituents in the 5 positions of the pyrazolyl rings into closer contact, increasing still further the steric congestion in this region of the tripodal ligand. Relocation of the isopropyl groups to the 3 positions of the pyrazolyl rings can relieve steric congestion at the boron end of the ligand and, by presenting the CH face of the pyrazolyl-bound isopropyl groups towards the Mo atom, may produce little or no additional steric congestion with respect to the co-ligands. The major difference between the steric demands of the pyrazole-bound methyl and isopropyl substituents in these systems will arise from the interactions between the methyl groups of adjacent isopropyl substituents. This will be most pronounced at the boron end of the molecule. Comparing the (pz)N–N(pz)–B and (pz)N–B–N(pz) angles in $[Mo(NO)\{HB(impz)_3\}(OR)_2]$ (R = Et or Pr^i) with those in $[Mo(NO)\{HB(dmpz)_3\}(ER)_2]$ (ER = OPr^i,[24] $NHBu^n$[25] or NHC_5H_4N[26]) reveals no significant differences with (pz)N–N(pz)–B angles in the range 118.7–121.2° and (pz)N–B–N(pz) angles in the range 106.4–112° for these structures. This suggests that the OPr^i co-ligands do not produce significantly more steric congestion in $[Mo(NO)\{HB(impz)_3\}(OPr^i)_2]$ than in its counterpart $[Mo(NO)\{HB(dmpz)_3\}(OPr^i)_2]$ which contains only methyl groups in the pyrazolyl 3 position.

Conclusion

Although the ^1H NMR data do not uniquely define the structures of the compounds isolated as *single isomers*, the crystal structures of $[Mo(NO)\{HB(impz)_3\}(OR)_2]$ (R = Et[14] or Pr^i), suggest that the 3 position of the pyrazolyl ring is the most favourable location for the isopropyl substituents in these complexes. This indicates that, provided the co-ligand set $\{X(Y)\}$ is not too sterically demanding, the $[Mo(NO)\{HB(impz)_3\}X(Y)]$ structure can accommodate at least one isopropyl group in a pyrazolyl ring 5 position without being prone to boratropic rearrangement. However, if the $\{X(Y)\}$ co-ligand set is bulky and drives apart the pyrazolyl 3 substituents, this can lead to an increase in the steric interaction between substituents in the pyrazolyl 5 positions of the $HB(impz)_3$ ligand. Rearrangements to place the isopropyl groups on the pyrazolyl rings in the less confined pyrazolyl 3 positions will then become favoured.

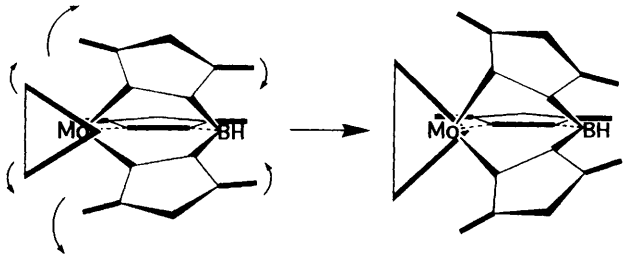


Fig. 3 A schematic diagram to show how, in complexes of the form $[Mo(NO)\{HB(impz)_3\}X(Y)]$, increasing the steric bulk of co-ligands bound to the molybdenum may increase steric congestion at the boron end of the $HB(impz)_3$ ligand

Experimental

All commercial reagents were used as supplied; $[Mo(NO)\{HB(impz)_3\}I_2]$ was prepared as a mixture of isomers according to the previously described method and used in this form.[14] Toluene and thf used as reaction media were dried and freed of oxygen before use by distillation from sodium–benzophenone under dinitrogen. Reactions were carried out under dinitrogen but purification procedures were carried out in air. Silica Gel 60 (70–230 mesh) was used as the stationary phase for column chromatography. Elemental analyses were carried out by the Microanalytical Laboratories in the School of Chemistry at the University of Birmingham.

Infrared spectra were recorded using KBr pellets and a Perkin-Elmer PE297 spectrometer, 270 MHz ^1H NMR spectra from solutions in $CDCl_3$ using a JEOL GX 270 spectrometer and FAB mass spectra* were recorded from a 3-nitrobenzyl alcohol matrix using a Kratos MS80 spectrometer. Cyclic voltammetric measurements were made using a platinum-bead electrode with a PAR 174A polarograph and 10^{-3} mol dm^{-3} solutions of complex in thf containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$ as base electrolyte. Values are referred to the SCE but ferrocene was used as an internal standard and typically exhibited $E_f\{[Fe(C_5H_5)_2]^+ - [Fe(C_5H_5)_2]\} = +0.58$ V.

Synthetic Studies.—$[Mo(NO)\{HB(impz)_3\}I(OPr^i)]$. A solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (200 mg, 0.26 mmol) in Pr^iOH (20 cm^3) was heated under reflux for 2 h during which time it became green. The resulting mixture was cooled, filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was extracted with hexane and the extract purified by column chromatography on silica gel using hexane–CH_2Cl_2 (1:1 v/v) as the eluent, the major green band being collected (yield 30 mg, 20%) (Found: C, 41.5; H, 5.6; N, 13.9. $C_{24}H_{41}BIMoN_7O_2$ requires C, 41.5; H, 5.9; N, 14.1%); ν_{max} 2550 (BH) and 1675 cm^{-1} (NO); $\delta_H(CDCl_3, 270$ MHz)† 6.41 [1 H, m, J(HH) = 6, $OCHMe_2$], 5.89, 5.84 (2 H, s; 1 H, s; $C_3N_2HMePr^i$), 3.84, 3.57, 3.23 [1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; $C_3N_2HMe(CHMe_2)$], 2.42, 2.39, 2.35 [3 H, s; 3 H, s; 3H, s; $C_3N_2HCH_3(Pr^i)$], 1.74, 1.36 [3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; $OCH(CH_3)_2$], 1.25, 1.22, 1.19, 1.15, 1.14, 1.10 {3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6 Hz; $C_3N_2HMe[CH(CH_3)_2]$}. m/z 694, M^+; 636, $[M - OCH(CH_3)_2]^+$; 622, $[M - \{CH_3 + OCH(CH_3)_2\}]^+$; and 566, $[M - I]^+$. E_p^c (thf, *vs.* SCE) = −0.74, −1.56 V; $E_f\{[Fe(C_5H_5)_2]^+ - [Fe(C_5H_5)_2]\} = +0.57$ V and $\Delta E_p\{[Fe(C_5H_5)_2]^+ - [Fe(C_5H_5)_2]\} = 100$ mV.

$[Mo(NO)\{HB(impz)_3\}I(OBu^t)]$. This compound was prepared in a similar manner to $[Mo(NO)\{HB(impz)_3\}I(OPr^i)]$ using *tert*-butyl alcohol (20 cm^3) as the reaction solvent (yield 50 mg, 30%) (Found: C, 42.7; H, 6.1; N, 14.0. $C_{25}H_{43}BIMoN_7O_2$

* The presence of B, Mo and I atoms in the molecules gives rise to complex isotope distribution patterns in which the highest-intensity ion does not always appear exactly at the calculated m/z value.

requires C, 42.5; H, 6.1; N, 13.9%); ν_{max} 2555 (BH) and 1675 cm^{-1} (NO); $\delta_H(CDCl_3$, 270 MHz)† 5.91, 5.90, 5.88 (1 H, s; 1 H, s; 1 H, s; $C_3N_2HMePr^i$), 3.91, 3.60, 3.25 [1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; $C_3N_2HMe(CHMe_2)$], 2.42, 2.37 [6 H, s; 3 H, s; $C_3N_2HCH_3(Pr^i)$], 1.71 [9 H, s, $OC(CH_3)_3$], 1.50, 1.25, 1.23, 1.21, 1.19, 1.16 [3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6 Hz, $C_3N_2HMe\{CH(CH_3)_2\}$]. m/z 708, M^+; 636, $[M - OC(CH_3)_3]^+$; 622, $[M - \{CH_3 + OC(CH_3)_3\}]^+$; and 582, $[M - I]^+$. E_p^c (thf, *vs.* SCE) = −0.64 V; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.58 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 180 mV.

$[Mo(NO)\{HB(impz)_3\}I(OCH_2SiMe_3)]$. A solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (100 mg, 0.13 mmol) and an excess of $HOCH_2SiMe_3$ (0.2 cm^3, 2 mmol) was heated under reflux in methylcyclohexane (25 cm^3) for 24 h during which time the solution became green. The resulting mixture was cooled, filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was extracted with hexane and the extract purified by column chromatography on silica gel using hexane–CH_2Cl_2 (1:1 v/v) as the eluent, the major green band being collected (yield 20 mg, 20%) (Found: C, 41.0; H, 6.3; N, 12.8. $C_{25}H_{45}BIMoN_7O_2Si$ requires C, 40.7; H, 6.2; N, 13.3%); ν_{max} 2550 (BH) and 1675 cm^{-1} (NO); $\delta_H(CDCl_3$, 270 MHz) 6.13, 5.50 [1 H, d, J(HH) = 13; 1 H, d, J(HH) = 13 Hz; OCH_2SiMe_3], 5.89, 5.81 (2 H, s; 1 H, s; $C_3N_2HMePr^i$), 3.85 [3 H, m, $C_3N_2HMe(CHMe_2)$], 2.55, 2.49, 2.46, 2.43, 2.41, 2.39, 2.38, 2.36, 2.35 [9 H, 9 s, $C_3N_2HCH_3(Pr^i)$], 1.29–1.09 {18 H, overlapping signals, $C_3N_2HMe[CH(CH_3)_2]$}; 0.28, 0.22, 0.20 [9 H, 3 s (intensity ratio 2.36:1:1.78), $Si(CH_3)_3$]. m/z 738, M^+; 636, $[M - OCH_2Si(CH_3)_3]^+$; 622, $[M - \{CH_3 + OCH_2Si(CH_3)_3\}]^+$; and 612, $[M - I]^+$. E_p^c (thf, *vs.* SCE) = −0.74, −1.52 V; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.58 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 110 mV.

$[Mo(NO)\{HB(impz)_3\}I\{O(CH_2)_4I\}]$. A solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (100 mg, 0.13 mmol) in dry thf (50 cm^3) was stirred at room temperature for 3 d during which time it became green. The resulting mixture was filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The resulting green powder was purified by recrystallisation from thf–hexane at −10 °C (yield 50 mg, 50%) (Found: C, 36.2; H, 5.1; N, 11.4. $C_{25}H_{42}BI_2MoN_7O_2$ requires C, 36.0; H, 5.1; N, 11.8%); ν_{max} 2550 (BH) and 1680 cm^{-1} (NO); $\delta_H(CDCl_3$, 270 MHz) 5.90, 5.88 (3 H, overlapping signals, $C_3N_2HMePr^i$), 5.55 (2 H, m, OCH_2), 3.75, 3.35 [2 H, m; 1 H, m; $C_3N_2HMe(CHMe_2)$], 3.25 (2 H, m, CH_2I), 2.5–2.3 [9 H, overlapping signals, $C_3N_2HCH_3(Pr^i)$], 2.02, 1.55 (2 H, m; 2 H, m; CH_2CH_2), 1.30–1.00 {18 H, overlapping signals, $C_3N_2HMe[CH(CH_3)_2]$}. m/z 707, $[M - I]^+$; 635, $[M - O(CH_2)_4I]^+$; 619, $[M - \{CH_3 + O(CH_2)_4I\}]^+$; and 612, $[M - I]^+$. E_p^c (thf, *vs.* SCE) = −0.67, −1.66 V; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.59 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 260 mV.

$[Mo(NO)\{HB(impz)_3\}I(OPh)]$. A solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (500 mg, 0.65 mmol) and phenol (60 mg, 0.64 mol) in toluene (25 cm^3) was stirred at room temperature for 3 d during which time it became red-brown. The resulting mixture was filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The resulting brown powder was purified by recrystallisation from ethanol–pentane at −10 °C to give the product as dark red microcrystals (yield 190 mg, 40%) (Found: C, 45.2; H, 5.6; N, 12.7. $C_{27}H_{39}BIMoN_7O_2$ requires C, 44.6; H, 5.4; N, 13.5%); ν_{max} 2550 (BH) and 1680 cm^{-1} (NO); $\delta_H(CDCl_3$, 270 MHz) 7.4 (5 H, m, overlapping signals, OC_6H_5), 5.99, 5.81, 5.79 (3 H, overlapping signals, $C_3N_2HMePr^i$), 3.90, 3.30 [3 H, overlapping signals, $C_3N_2HMe(CHMe_2)$], 2.53–1.97 [9 H, overlapping signals, $C_3N_2HCH_3(Pr^i)$], 1.34–0.81 [18 H, overlapping signals, $C_3N_2HMe\{CH(CH_3)_2\}$]. m/z 727, M^+; 635, $[M - OC_6H_5]^+$; and 602, $[M - (NO + OC_6H_5)]^+$. E_f (thf, *vs.* SCE) = −0.34 V, ΔE_p = 145 mV; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.58 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 170 mV.

$[Mo(NO)\{HB(impz)_3\}I(OC_6H_4Me\text{-}4)]$. This compound was prepared in a similar manner to $[Mo(NO)\{HB(impz)_3\}I(OPh)]$ using *p*-cresol (70 mg, 0.65 mmol) in place of phenol to give a brown microcrystalline product (yield 200 mg, 43%) (Found: C, 45.6; H, 5.5; N, 12.7. $C_{25}H_{43}BIMoN_7O_2$ requires C, 45.4; H, 5.6; N, 13.2%); ν_{max} 2550 (BH) and 1680 cm^{-1} (NO); $\delta_H(CDCl_3$, 270 MHz) 7.3 (4 H, m, overlapping signals, OC_6H_4Me), 5.93, 5.89, 5.85 (3 H, overlapping signals, $C_3N_2HMePr^i$), 3.95, 3.20 [3 H, overlapping signals, $C_3N_2HMe(CHMe_2)$], 2.58–1.98 [12 H, overlapping signals, $C_3N_2HCH_3(Pr^i)$, $OC_6H_4CH_3$], 1.33–0.81 [18 H, overlapping signals, $C_3N_2HMe\{CH(CH_3)_2\}$]. m/z 741, M^+; 713, $[M - NO]^+$, 636, $[M - OC_6H_4Me]^+$; and 616, $[M - (CH_3 + OC_6H_4Me)]^+$. E_f (thf, *vs.* SCE) = −0.37 V, ΔE_p = 180 mV; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.59 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 215 mV.

$[Mo(NO)\{HB(impz)_3\}I(NHPh)]$. A solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (200 mg, 0.26 mmol) and redistilled aniline (0.1 cm^3, 1.1 mol) in dichloromethane (25 cm^3) was stirred at room temperature for 4 h during which time it became brown. The solvent volume was reduced to *ca.* 10 cm^3 by evaporation and diethyl ether added to precipitate the NH_3PhI present. The mixture was filtered and the filtrate evaporated to dryness then heated *in vacuo* for 6 h to remove any residual aniline. The resulting brown powder was purified by recrystallisation from ethanol–pentane at −10 °C to give the product as dark brown microcrystals (yield 80 mg, 45%) (Found: C, 45.3; H, 5.6; N, 14.9. $C_{27}H_{40}BIMoN_8O$ requires C, 44.6; H, 5.6; N, 15.4%); ν_{max} 2550 (BH), 1665 (NO) and 3280 cm^{-1} (NH); $\delta_H(CDCl_3$, 270 MHz)† 13.2 (1 H, s, NHPh), 7.39, 7.59 [2 H, d, J(HH) = 6 Hz; 3 H, m, overlapping signals; NHC_6H_5], 6.02, 5.90, 5.82 (1 H, s; 1 H, s; 1 H, s; $C_3N_2HMePr^i$), 4.20, 3.52, 2.89 [1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; $C_3N_2HMe(CHMe_2)$], 2.48, 2.45, 2.38 [3 H, s; 3 H, s; 3 H; s; $C_3N_2HCH_3(Pr^i)$], 1.28, 1.21, 1.19, 1.17, 0.95, 0.69 {3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6 Hz, $C_3N_2HMe[CH(CH_3)_2]$}. m/z 727, M^+; 601, $[M - I]^+$; and 571, $[M - (NO + I]^+$. E_f (thf, *vs.* SCE) = −0.80 V, ΔE_p = 160 mV; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.59 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 180 mV.

$[Mo(NO)\{HB(impz)_3\}I(NHC_6H_4Me\text{-}4)]$. This compound was prepared in a similar manner to $[Mo(NO)\{HB(impz)_3\}I(NHPh)]$ using *p*-toluidine (70 mg, 0.65 mmol) in place of aniline to give a brown microcrystalline product (yield 100 mg, 43%) (Found: C, 47.6; H, 6.0; N, 14.4. $C_{25}H_{43}BIMoN_7O_2{\cdot}0.5C_5H_{12}$ requires C, 47.1; H, 6.1; N, 14.4%); ν_{max} 2555 (BH), 1665 (NO) and 3275 cm^{-1} (NH); $\delta_H(CDCl_3$, 270 MHz)† 13.3 (1 H, s, NHC_6H_4Me), 7.49, 7.18 [2 H, d, J(HH) = 6; 2 H, d, J(HH) = 6, NHC_6H_4Me], 6.00, 5.91, 5.82 (1 H, s; 1 H, s; 1 H, s; $C_3N_2HMePr^i$), 4.16, 3.48, 2.92 [1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; 1 H, m, J(HH) = 6; $C_3N_2HMe(CHMe_2)$], 2.48, 2.41, 2.39 [3 H, s; 3 H, s; 3 H, s; $C_3N_2HCH_3(Pr^i)$], 2.29 (3 H, s, $NHC_6H_4CH_3$), 1.28, 1.21, 1.18, 0.98, 0.71 [3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 6 H, d, J(HH) = 6; 3 H, d, J(HH) = 6; 3 H, d, J(HH) = 6 Hz, $C_3N_2HMe\{CH(CH_3)_2\}$]. m/z 741, M^+; and 615, $[M - I]^+$. E_f (thf, *vs.* SCE) = −0.85 V, ΔE_p = 90 mV; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.58 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 110 mV.

$[Mo(NO)\{HB(impz)_3\}(OPr^i)_2]$. Silver acetate (36 mg, 0.215 mmol) was added to a solution of $[Mo(NO)\{HB(impz)_3\}I_2]$ (82 mg, 0.107 mmol) in Pr^iOH (60 cm^3) and the mixture heated under reflux for 2 h during which time it became pink. The resulting mixture was cooled, filtered through Keiselguhr, the solvent removed from the filtrate by evaporation under reduced pressure and purified by column chromatography on silica gel

† Spectrum obtained after heating the compound to produce a single isomer as indicated in Scheme 1.

using hexane–CH_2Cl_2 (1:1 v/v) as the eluent, the major pink band being collected (yield 19 mg, 28%) (Found: C, 51.5; H, 7.4; N, 15.9. $C_{27}H_{48}BMoN_7O_3$ requires C, 51.9; H, 7.7; N, 15.2%); ν_{max} 2550 (BH) and 1640 cm^{-1} (NO); $\delta_H(CDCl_3, 300\ MHz)$† 5.85 [2 H, m, $J(HH) = 6$, $OCHMe_2$], 5.79 (3 H, s, $C_3N_2HMePr^i$), 3.52, 3.75 [2 H, m, $J(HH) = 6$; 1 H, m, $J(HH) = 6$; $C_3N_2HMe(CHMe_2)$], 2.38, 2.33 [3 H, s; 6 H, s; $C_3N_2HCH_3(Pr^i)$], 1.46, 1.27 [6 H, d, $J(HH) = 6$; 6 H, d, $J(HH) = 6$; $OCH(CH_3)_2$], 1.15, 1.12 [12 H, d, $J(HH) = 6$; 6 H, d, $J(HH) = 6$ Hz; $C_3N_2HMe\{CH(CH_3)_2\}$].

A single isomer of $[Mo(NO)\{HB(impz)_3\}I_2]$. A sample of $[Mo(NO)\{HB(impz)_3\}I_2]$ (142 mg, 0.2 mmol) was heated *in vacuo* at 80 °C for 30 h then purified by recrystallisation from dichloromethane–pentane (Found: C, 33.0; H, 4.4; N, 12.3. $C_{21}H_{34}BI_2MoN_7O$ requires C, 33.1; H, 4.5; N, 12.9%); ν_{max} 2575 (BH) and 1705 cm^{-1} (NO); $\delta_H(CDCl_3, 270\ MHz)$ 6.16, 5.86 (1 H, s; 2 H, s; $C_3N_2HMePr^i$), 3.56 [3 H, m, $C_3N_2HMe(CHMe_2)$], 2.57, 2.29 [3 H, s; 6 H, s; $C_3N_2HCH_3(Pr^i)$], 1.30, 1.05, 0.98 {6 H, d, $J(HH) = 6.7$; 6 H, d, $J(HH) = 6.9$; 6 H, d, $J(HH) = 6.7$ Hz, $C_3N_2HMe[CH(CH_3)_2]$}.

$[Mo(NO)\{HB(impz)_3\}I(OMe)]$. This compound was prepared from the *single isomer* of $[Mo(NO)\{HB(impz)_3\}I_2]$ using the procedure described previously.[14] After purification the product was found, by ^1H NMR spectroscopy, to contain one major isomer. $\delta_H(CDCl_3, 270\ MHz)$† 5.90, 5.88 (1 H, s; 2 H, s; $C_3N_2HMePr^i$), 5.39 (3 H, s, OCH_3), 3.80, 3.35, 3.15 [1 H, m, $J(HH) = 7$; 1 H, m, $J(HH) = 7$; 1 H, m, $J(HH) = 7$; $C_3N_2HMe(CHMe_2)$], 2.41, 2.40, 2.37 [3 H, s; 3 H, s; 3 H, s; $C_3N_2HCH_3(Pr^i)$], 1.18, 1.16, 1.08, 1.05 {9 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$ Hz; $C_3N_2HMe[CH(CH_3)_2]$}.

$[Mo(NO)\{HB(impz)_3\}I(NHEt)]$. A solution of the *single isomer* of $[Mo(NO)\{HB(impz)_3\}I_2]$ (500 mg, 0.66 mmol) in toluene (25 cm^3) was cooled to in an ice–salt bath to *ca.* −5 °C and a solution of ethylamine (60 mg, 1.32 mmol) in cold toluene (10 cm^3 at *ca.* −5 °C) added. The mixture was then stirred for 52 h while warming to room temperature. It was filtered to remove the precipitated ethylammonium iodide and the brown filtrate evaporated to dryness. The crude product was purified by column chromatography using hexane–CH_2Cl_2 (1:1) and the first major red-orange band was collected (yield 278 mg, 62%) (Found: C, 40.7; H, 5.9; N, 16.2. $C_{23}H_{40}BIMoN_8O$ requires C, 40.7; H, 5.9; N, 16.5%); ν_{max} 2546 (BH), 1668 (NO) and 3280 cm^{-1} (NH); $\delta_H(CDCl_3, 270\ MHz)$† 12.7 (1 H, s, NHEt), 5.96, 5.85 (1 H, s; 2 H, s; $C_3N_2HMePr^i$), 4.81, 4.04 (1 H, m; 1 H, m; $NHCH_2Me$), 4.04, 3.65, 3.30 [1 H, m; 1 H, m; 1 H, m; $C_3N_2HMe(CHMe_2)$], 2.38, 2.36, 2.35 [3 H, s; 3 H, s; 3 H, s; $C_3N_2HCH_3(Pr^i)$], 1.36 [3 H, t, $J(HH) = 7$, $NHCH_2CH_3$], 1.27, 1.26, 1.24, 1.21, 1.17, 1.15 {3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$; 3 H, d, $J(HH) = 7$ Hz, $C_3N_2HMe[CH(CH_3)_2]$}. *m/z* 678, M^+; 551, $[M - I]^+$; and 506, $[M - I - NHEt]^+$. E_p^c (thf, *vs.* SCE) = −1.21 V, $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.54 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 65 mV.

$[Mo(NO)\{HB(impz)_3\}I(NHCH_2Ph)]$. Benzylamine (80 mg, 0.74 mmol) was added to a solution of the *single isomer* of $[Mo(NO)\{HB(impz)_3\}I_2]$ (284 mg, 0.37 mmol) in toluene (25 cm^3) and the mixture stirred at room temperature for 72 h. The mixture was then filtered to remove the precipitated benzylammonium iodide and the brown filtrate evaporated to dryness. The crude product was purified by column chromatograhy using hexane–CH_2Cl_2 (1:1) and the first red-orange band was collected (yield 166 mg, 60%) (Found: C, 45.7; H, 5.6; N, 14.7. $C_{28}H_{42}BIMoN_8O$ requires C, 45.4; H, 5.7; N, 15.1%); ν_{max} 2544 (BH), 1665 (NO) and 3275 cm^{-1}(NH); $\delta_H(CDCl_3, 270\ MHz)$† 12.5 (1 H, s, $NHCH_2Ph$), 7.44–7.29 (5 H, m, C_6H_5), 6.09, 4.80 [1 H, dd, $^2J(HH) = 14$, $^3J(HH) = 10$; 1 H, dd, $^2J(HH) = 14$, $^3J(HH) = 6$ Hz; CH_2Ph], 5.87, 5.86, 5.84 (1 H, s; 1 H, s; 1 H, s; $C_3N_2HMePr^i$), 4.08, 3.42, 3.20 [1 H, m, $J(HH) = 7$; 1 H, m, $J(HH) = 7$; 1 H, m, $J(HH) = 7$; $C_3N_2HMe(CHMe_2)$], 2.38, 2.37, 2.35 [3 H, s; 3 H, s; 3 H, s; $C_3N_2HCH_3(Pr^i)$], 2.29 (3 H, s, $NHC_6H_4CH_3$), 1.28, 1.21, 1.18, 0.98, 0.71 {3 H, d, $J(HH) = 6$; 3 H, d, $J(HH) = 6$; 6 H, d, $J(HH) = 6$; 3 H, d, $J(HH) = 6$; 3 H, d, $J(HH) = 6$ Hz; $C_3N_2HMe[CH(CH_3)_2]$}. *m/z* 740, M^+; 613, $[M - I]^+$; and 506, $[M - I - NHCH_2Ph]^+$. E_p^c (thf, *vs.* SCE) = −1.14 V; $E_f\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = +0.56 V and $\Delta E_p\{[Fe(C_5H_5)_2]^+-[Fe(C_5H_5)_2]\}$ = 67 mV.

Structural Studies of $[Mo(NO)\{HB(impz)_3\}(OPr^i)_2]$.—Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer operating in the ω–2θ mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) up to θ = 25° from a red-purple crystal of dimensions 0.5 × 0.3 × 0.3 mm coated with epoxy resin. Three standard reflections were monitored hourly to check the stability of the system. 2299 Unique reflections were scanned, *hkl* (0, 0, 0) to (22, 19, 12), and 1532 with $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis.

Crystal data. $C_{27}H_{48}BMoN_7O_3$, $M_r = 625.47$, orthorhombic, space group *Pnma*, $a = 19.06(1)$, $b = 16.013(3)$, $c = 10.762(1)$ Å, $U = 3285(2)$ Å^3, $Z = 4$, $D_c = 1.192$ g cm^{-3}, μ(Mo-Kα) = 4.24 cm^{-1}, $F(000) = 1320$.

The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from ref. 27. The structure was solved by MULTAN and Fourier methods using the X-RAY 80 system.[28] An empirical absorption correction[29] was applied at the end of the isotropic refinement and final refinement was carried out using fixed isotropic thermal parameters for hydrogen atoms. A slight disorder was found for the terminal carbon atoms and, consequently, these were refined isotropically. The maximum and minimum absorption factors were 1.096 and 0.762 respectively. Refinement led to $R = 0.077$ and $R' = 0.081$. Average shift-to-error ratios were < 0.02:1. Final atomic parameters are presented in Table 1 and the plotting routine used to generate the structure shown in Fig. 1 was ORTEP.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to the Direccion General de Investigaccion Cientifica y Technica of the Ministry of Education and Science of Spain for the support of this work on project PB/890127, and to Dr. S. Trofimenko for providing a sample of $[Mo(NO)\{HB(impz)_3\}(CO)_2]$. We are also grateful to Mr. D. D. Petters for experimental assistance.

References

1 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
2 S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115; *Chem. Rev.*, 1993, **93**, 943.
3 C. K. Ghosh and W. A. G. Graham, *J. Am. Chem. Soc.*, 1987, **109**, 4726; 1989, **111**, 375.
4 S. A. Roberts, C. G. Young, W. E. Cleland, R. B. Ortega and J. H. Enemark, *Inorg. Chem.*, 1988, **27**, 3044; S. A. Roberts, C. G. Young, C. A. Kipke, W. E. Cleland, K. Yamanouchi, M. D. Carducci and J. H. Enemark, *Inorg. Chem.*, 1990, **29**, 3650.
5 W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 3653; W. H. Armstrong and S. J. Lippard, *J. Am. Chem. Soc.*, 1985, **107**, 3730; P. N. Turowski, W. H. Armstrong, M. E. Roth and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 681.
6 R. Alsfasser, S. Trofimenko, A. Looney, G. Parkin and H. Varhenkamp, *Inorg. Chem.*, 1991, **30**, 4098.

† See footnote on p. 2286.

7 N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S.Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1992, **114**, 1277.
8 A. Das, J. A. McCleverty, M. D. Ward, C. J. Jones and A. M. W. Cargill Thompson, *Polyhedron*, 1992, **11**, 2119; N. M. Rowley, S. S. Kurek, M. W. George, S. M. Hubig, J. M. Kelly, P. D. Beer, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Chem. Commun.*, 1992, 497.
9 B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor, R. J. Jones and P. V. Kolinsky, *J. Chem. Soc., Chem. Commun.*, 1992, 497; B. J. Coe, J.-D. Foulon, T. A. Hamor, C. J. Jones, J. A. McCleverty, D. Bloor, G. H. Cross and T. L. Axon, *J. Chem. Soc., Dalton Trans.*, 1994, 3427.
10 C. J. Jones, J. A. McCleverty and A. S. Rothin, *J. Chem. Soc., Dalton Trans.*, 1986, 109.
11 H. Adams, N. A. Bailey, A. S. Drane and J. A. McCleverty, *Polyhedron*, 1983, **2**, 465.
12 N. AlObaidi, C. J. Jones and J. A. McCleverty, *Polyhedron*, 1989, **8**, 1033.
13 S. Trofimenko, J. C. Calabrese, P. J. Domaille and J. S. Thompson, *Inorg. Chem.*, 1989, **28**, 1091; M. D. Olson, S. J. Rettig, A. Storr, J. Trotter and S. Trofimenko, *Acta Crystallogr., Sect. C*, 1991, **47**, 1543.
14 M. Cano, J. V. Heras, C. J. Jones, J. A. McCleverty and S. Trofimenko, *Polyhedron*, 1990, **9**, 619; M. Cano, J. V. Heras, S. Trofimenko, A. Monge, E. Gutierrez, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1990, 3577.
15 N. AlObaidi, D. Clague, M. Chaudhury, C. J. Jones, J. A. McCleverty, J. C. Pearson and S. S. Salam, *J. Chem. Soc., Dalton Trans.*, 1987, 1733.
16 J. A. McCleverty, A. S. Drane, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 91.
17 N. AlObaidi, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1990, 3329.
18 J. A. McCleverty, *Chem. Soc. Rev.*, 1983, **12**, 331.
19 C. J. Jones, J. A. McCleverty, B. D. Neaves and S. J. Reynolds, *J. Chem. Soc., Dalton Trans.*, 1986, 733.
20 T. N. Briggs, H. Colquhoun, N. El Murr, C. J. Jones, J. A. McCleverty, B. D. Neaves, H. Adams and N. A. Bailey, *J. Chem. Soc., Dalton Trans.*, 1985, 1249.
21 N. J. AlObaidi, C. J. Jones and J. A. McCleverty, *Polyhedron*, 1990, **9**, 693.
22 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
23 J. A. McCleverty, D. Seddon, N. A. Bailey and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.
24 J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1982, 951.
25 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc., Dalton Trans.*, 1986, 1525.
26 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc., Dalton Trans.*, 1987, 1063.
27 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–98.
28 J. M. Stewart, The X-RAY 80 System, Computer Science Centre, University of Maryland, College Park, 1985.
29 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Received 1*st March* 1995; *Paper* 5/01237F