Syntheses of Some Transition-metal Complexes containing the Tripodal Ligand $HB(Pr^iMeC_3N_2H)_3$ and the *X*-Ray Crystal Structure of $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(OEt)_2]$[†]

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The new complexes $[M\{HB(Pr^iMeC_3N_2H)_3\}X]$ (M = Tl, X = nothing; M = Ni or Co, X = NCS or NCO; M = Zn, X = NCS or N_3), $[M\{HB(Pr^iMeC_3N_2H)_3\}_2]$ (M = Fe, Co, Ni, or Zn), $[Mo\{HB(Pr^iMeC_3N_2H)_3\}\{\eta^3\text{-}CH_2C(Me)CH_2\}(CO)_2]$, and $[Mo(NO)\{HB(Pr^iMeC_3N_2H)_3\}X(Y)]$ (X = Y = CO, I, OMe, or OEt; X = I, Y = OMe or OEt) have been synthesised. The compounds $[Mo(NO)\{HB(Pr^iMeC_3N_2H)_3\}X(Y)]$ (X = Y = CO or I; X = I, Y = OMe or OEt); were isolated as a mixture of at least two isomers. A single-crystal *X*-ray diffraction study of $[Mo(NO)\{HB(Pr^iMeC_3N_2H)_3\}(OEt)_2]$ shows that the molybdenum atom is in an approximately octahedral co-ordination environment. The bulky Pr^i groups on the tripodal ligand are all in the 3 position closest to the ethoxide ligands with Mo–O distances of 1.86(1) and 1.91(1) Å and Mo–O–C(Et) angles both of 129(1)°.

The formal analogy between the hydrotris(pyrazolyl)borate and cyclopentadienide ligands is now well established.[1–6] However, there are significant steric[7] and electronic[8] differences between these two types of ligand. In particular the 3 substituents on the pyrazolyl rings of a hydrotris(pyrazolyl)borate ligand, bound to a metal, project across the metal co-ordination sphere towards the trigonal-prismatic sites. Thus they can produce a more pronounced structural effect than similar groups attached to a cyclopentadienyl ligand.[9,10] An example of this is provided by the $HB(3\text{-}Bu^tC_3N_2H_2)_3^-$ ligand which enforces tetrahedral co-ordination on a bound first-row *d*-block metal centre.[10] More recently the less sterically demanding ligands $HB(3\text{-}Pr^iC_3N_2H_2)_3^-$ and $HB(3\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H_2)_3^-$ have been used to prepare metal complexes.[11] In 1:1 complexes with first-row *d*-block metals these ligands also favour tetrahedral four-co-ordination but will form octahedral six-co-ordinate 2:1 ligand:metal complexes following rearrangement of the ligands to $HB(3\text{-}Pr^iC_3N_2H_2)_2(5\text{-}Pr^iC_3N_2H_2)^-$ or $HB(3\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)_2(5\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)^-$ respectively. These rearrangements relieve steric congestion, in the region of the metal co-ordination sphere where the ligand 3 substituents interact, by placing a sterically less-demanding hydrogen atom in one pyrazolyl 3 position in each ligand. In a continuation of these studies of complexes containing substituted hydrotris(pyrazolyl)borate ligands we have synthesised the new ligand $HB(Pr^iMeC_3N_2H\text{-}4)_3^-$ in which the 3 and 5 positions of the pyrazolyl ligand are occupied by either methyl or isopropyl substituents. Some aspects of the co-ordination chemistry of this ligand have been explored.

Results and Discussion

Synthetic Studies.—Following now well established precedents[12] the new tripodal ligand $HB(Pr^iMeC_3N_2H\text{-}4)_3^-$ was prepared as its potassium salt in the reaction between KBH_4 and excess of $3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H_2$. Because of the high solubility of $K[HB(Pr^iMeC_3N_2H\text{-}4)_3]$, even in non-polar solvents, the solid salt was not isolated but instead a solution in tetrahydrofuran (thf) was prepared which was suitable for use in reactions with metal salts to produce complexes. Ligands such as $HB(3\text{-}Pr^iC_3N_2H_2)_3^-$ and $HB(3\text{-}Pr^i\text{-}4\text{-}BrC_3N_2H)_3^-$ are formed regiospecifically in the reaction between BH_4^- and the appropriately substituted pyrazole.[9–13] A boratropic rearrangement to relocate one Pr^i group in each ligand in the 5 position only occurs during the formation of octahedral complexes, which cannot accommodate six Pr^i groups in the equatorial belt.[11] In contrast $3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H_2$ reacts with BH_4^- to give a mixture of isomers. Heating of this mixture in excess of $3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H_2$ under reflux for 17 h does not result in the formation of a single isomer. Thus when the thallium(I) complex of this ligand is prepared and recrystallised from methanol the ^1H n.m.r. spectrum of the product contains two Me resonances in the area ratio 3.7:1. A small amount of a second fraction could be obtained from the filtrate and this exhibited Me resonances in the area ratio 1:1, the ratio of the Me resonances in the combined products being 73:27.

It might be expected that the reaction between BH_4^- and a pyrazole carrying different substituents in the 3 and 5 positions would afford a pyrazolylborate product with the bulkiest substituent occupying the 3 position. Certainly this is the case when there is a substantial disparity in the size of the 3 and 5 substituents as with H *versus* alkyl or aryl and with Me *versus* Bu^t.[9–13] However, in the case of $HB(Pr^iMeC_3N_2H)_3^-$ the Pr^i

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[†] Diethoxotris[hydrido(3-isopropyl-5-methylpyrazol-1-yl)borato]-nitrosylmolybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

group does not exclusively occupy the 3 position. A crude quantitative rationalisation for this finding may be offered on the basis of the expected steric interactions which might arise during B–N bond formation. The conformations offered by the $\mathrm{Pr^i}$ or Me groups to an approaching $\mathrm{BH_4^-}$ ion are illustrated in Figure 1. All of the conformations of the $\mathrm{Pr^i}$ group, except (**d**), offer more hindrance in the pyrazolyl plane than would be the case for Me. Assuming that the distribution of conformations is statistical, then only 1/6 of the $\mathrm{Pr^i}$ conformations can compete with Me in B–N bond formation. Furthermore, if conformation (**d**) has an equal chance of success in forming a B–N bond as compared to an Me group, the overall probability of B–N bond formation next to $\mathrm{Pr^i}$ will be 1/12 and next to Me, 11/12. The proportions of the different isomers of $\mathrm{HB(Pr^iMeC_3N_2H)_3^-}$ containing three, two, one or no 3-$\mathrm{Pr^i}$ groups may be predicted according to the equation: $(3\text{-Pr})^3 + 3(3\text{-Pr})^2(5\text{-Pr}) + 3(3\text{-Pr})(5\text{-Pr})^2 + (5\text{-Pr})^3 = 1$, where '3-Pr' = 11/12 and '5-Pr' = 1/12. Thus the respective relative proportions of $\mathrm{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3^-}$, $\mathrm{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_2(3\text{-}Me\text{-}5\text{-}Pr^iC_3N_2H)^-}$, $\mathrm{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)(3\text{-}Me\text{-}5\text{-}Pr^iC_3N_2H)_2^-}$, and $\mathrm{HB(3\text{-}Me\text{-}5\text{-}Pr^iC_3N_2H)_3^-}$ are calculated to be 77.0:21.0:1.9:0.05. In practice it might be expected that *ca.* 80% of the ligand formed would be $\mathrm{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3^-}$ and *ca.* 20% would be $\mathrm{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_2(3\text{-}Me\text{-}5\text{-}Pr^iC_3N_2H)^-}$ with the other two isomers being present in insufficiently large proportions to isolate. When forming complexes with the isomeric mixture the situation will be further complicated by the differing abilities of the two isomers to form stable complexes, and by the possibility that complexation may be associated with ligand-rearrangement reactions.[11]

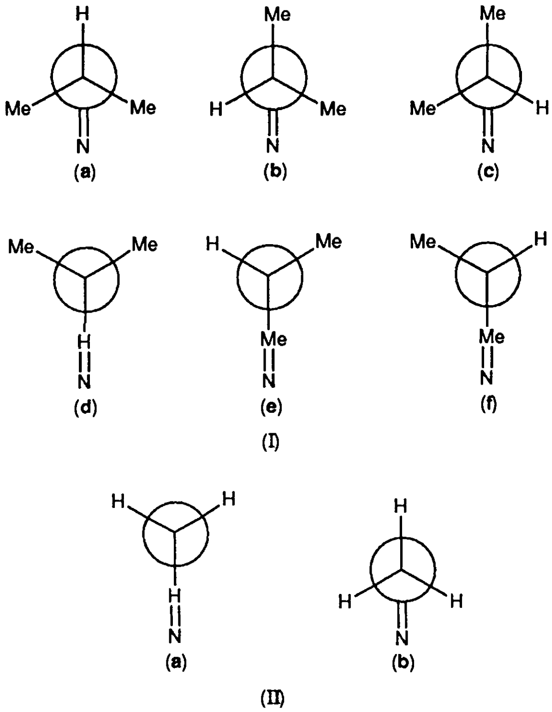

Figure 1. Conformational arrangements presented by $\mathrm{3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H_2}$ to an approaching $\mathrm{BH_4^-}$ ion as viewed in the pyrazolyl plane (represented by =N) along the vector joining C(3) and C(5): (**I**) approaching the 3-$\mathrm{Pr^i}$ group; (**II**) approaching the 5-Me group

A solution of $\mathrm{K[HB(Pr^iMeC_3N_2H)_3]}$ (KL) reacts with $\mathrm{TlNO_3}$ to give a 1:1 complex, [TlL], and with $\mathrm{M(NO_3)_2}$ (M = Fe, Co, Ni, or Zn) to give 2:1 complexes, $\mathrm{[ML_2]}$. The colours, melting points, and elemental analyses of the new complexes are presented in Table 1. The ^{1}H n.m.r. spectrum (reference $\mathrm{SiMe_4}$) of [TlL] exhibits signals at δ 5.77, 3.10, 2.37, and 1.23 of relative area 1:1:3:6 in accord with the symmetrical structure $\mathrm{[Tl\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}]}$. Signals due to an isomeric species present to the extent of *ca.* 20% are also observed at δ 2.30 and 1.19 in accord with expectations. The spectrum of $\mathrm{[ZnL_2]}$ contains signals attributable to more than one isomer. The signals of the major component have relative areas in the ratio 1:2:2:3:1:6:12:6 corresponding with the structure $\mathrm{[Zn\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_2(5\text{-}Pr^i\text{-}3\text{-}MeC_3N_2H)\}_2]}$. This is in accord with the structural precedent set by octahedral complexes containing the ligand $\mathrm{HB(Pr^iC_3N_2H_2)_3^-}$ in which rearrangement to give $\mathrm{[Zn\{HB(3\text{-}Pr^iC_3N_2H_2)_2(5\text{-}Pr^iC_3N_2H_2)\}_2]}$ occurs.[11] Attempts to separate the isomers of $\mathrm{ML_2}$ by fractional crystallisation were unsuccessful. The reaction between the solution of KL and $\mathrm{M(NO_3)_2}$ (M = Co, Ni, or Zn) in the presence of an excess of $\mathrm{X^-}$ (X = NCO, NCS, or

Table 1. Yields, melting points, i.r. bands, and elemental analyses of complexes containing $\mathrm{HB(Pr^iMeC_3N_2H\text{-}4)_3}$ (L)

Complex (Colour)	Yield (%)	M.p. (°C)	ν(BH), ν(coligand) (cm^{-1})	Analysis (%)[a] C	H	N
[TlL] (White)	58	104—106	2 530	43.1 (43.1)	5.8 (5.8)	14.3 (14.4)
$\mathrm{[FeL_2]}$ (Pale green)	63	196—198	2 528	61.5 (61.7)	8.0 (8.2)	20.7 (20.6)
$\mathrm{[CoL_2]}$ (Pale yellow)	82	188—190	2 525	61.6 (61.4)	8.7 (8.8)	20.2 (20.4)
$\mathrm{[NiL_2]}$ (Pale lilac)	75	233—235	2 528	61.3 (61.4)	8.5 (8.8)	20.4 (20.4)
$\mathrm{[ZnL_2]}$ (White)	68	266—268	2 522	59.5 (60.9)	8.8 (8.2)	19.9 (20.3)
[CoL(NCS)] (Blue)	48	207—209	2 550, 2 070	53.5 (53.0)	6.9 (6.9)	19.3 (19.7)
[CoL(NCO)] (Blue)	52	240—242	2 550, 2 230	54.9 (54.8)	7.3 (7.1)	20.4 (20.3)
[NiL(NCS)] (Green)	65	213—215	2 525, 2 135	53.2 (53.0)	6.9 (6.9)	20.0 (19.7)
[NiL(NCO)] (Red)	49	262—264	2 540, 2 210	54.9 (54.8)	7.1 (7.1)	20.1 (20.3)
[ZnL(NCS)] (White)	65	220—222	2 550, 2 082	52.4 (52.3)	6.9 (6.8)	19.4 (19.4)
$\mathrm{[ZnL(N_3)]}$ (White)	68	231—233	2 555, 2 100	51.3 (51.6)	6.9 (7.0)	25.7 (25.8)
$\mathrm{[Mo(NO)L(CO)_2]}$ (Yellow-orange)	64	268—273	2 542, 1 990, 1 900, 1 650	49.3 (49.0)	5.9 (6.0)	17.3 (17.4)
$\mathrm{[MoL(C_4H_7)(CO)_2]}$ (Yellow)	77	187—189	2 530, 1 925, 1 835	55.0 (55.1)	7.1 (7.0)	14.3 (14.3)
$\mathrm{[Mo(NO)LI_2]}$ (Black)	62		2 560, 1 700	33.0 (33.1)	4.5 (4.4)	12.3 (12.8)
[Mo(NO)L(I)(OMe)][b] (Green)	20		2 555, 1 670	41.0 (41.0)	6.8 (5.9)	14.6 (14.2)
[Mo(NO)L(I)(OEt)][b] (Green)	40		2 555, 1 670	40.7 (40.6)	6.0 (5.6)	14.1 (14.2)
$\mathrm{[Mo(NO)L(OMe)_2]}$ (Pink)	50		2 540, 1 640	48.2 (48.5)	6.7 (7.0)	16.9 (17.2)
$\mathrm{[Mo(NO)L(OEt)_2]}$ (Pink)	54		2 550, 1 642	49.9 (50.2)	7.4 (7.3)	16.7 (16.4)

[a] Calculated values in parentheses. [b] Contains 0.25 mol of hexane.

N_3) affords the tetrahedral complexes [ML(X)] (M = Co or Ni, X = NCO or NCS; M = Zn, X = NCS or N_3). In these cases the mixture of isomeric complexes could be separated by fractional crystallisation from methanol. The complexes containing symmetrically substituted L were less soluble than those containing unsymmetrically substituted L, thus being the major component of the mixture these could be obtained in pure form by recrystallisation.

The solution of KL also reacted with $[MoCl\{\eta^3\text{-}CH_2C(Me)CH_2\}(CO)_2(MeCN)_2]$ to give $[MoL\{CH_2C(Me)CH_2\}(CO)_2]$ and with $[Mo(CO)_6]$, followed by treatment with butyl nitrite, to give $[Mo(NO)L(CO)_2]$. The ^1H n.m.r. spectra of these complexes indicate that two principal isomers are present. Following the precedent[14] provided by the synthesis of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$, the reaction of $[Mo(NO)L(CO)_2]$ with iodine was investigated and $[Mo(NO)LI_2]$ obtained as a mixture of isomers as indicated by the ^1H n.m.r. spectral data.

Since the reactions of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ with alcohols have been found to afford air-stable alkoxide derivatives[3] we were interested in establishing whether a similar derivative chemistry could be developed from $[Mo(NO)LI_2]$. The reaction between the isomeric mixture of $[Mo(NO)LI_2]$ and methanol proceeds smoothly over a period of 2 h under reflux. The reaction product was found to be primarily the green complex [Mo(NO)L(I)(OMe)] contaminated with a small proportion of pink $[Mo(NO)L(OMe)_2]$ which could be separated by column chromatography. The ^1H n.m.r. spectrum of [Mo(NO)L(I)(OMe)] was extremely complex. The molecule has no element of symmetry and contains a chiral molybdenum centre so that all the carbon centres with their attached groups of protons are unique. When this situation is combined with the presence of at least two isomeric forms of L, and signal multiplicity in some cases, a large number of spectral lines result. For example the simplest case is that of the signal due to the methoxy methyl group. This appears at δ *ca.* 5.4 and would be a singlet in the case of a single isomer but actually appears as three major lines. The combination of the two chiral forms of [Mo(NO)L(I)(OMe)] with $HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3$ would result in enantiomers which would be indistinguishable by n.m.r. spectroscopy, whilst with $HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_2(5\text{-}Pr^i\text{-}3\text{-}MeC_3N_2H)$ two distinguishable isomers would arise, thus giving a total of three distinct n.m.r. signals. Attempts to separate this mixture and obtain a single isomer were unsuccessful. A similar reaction occurs with EtOH and [Mo(NO)L(I)(OEt)] is obtained as a mixture of isomers which, again, could not be separated. The i.r. spectra of the complexes [Mo(NO)L(I)Y] (Y = I, OMe, or OEt) contain ν(BH) in addition to other bands attributable to the presence of L. The values of ν(NO) are similar to those found[3] for related complexes containing $HB(3,5\text{-}Me_2C_3N_2H)_3$ in place of L. The mass spectra of the new compounds contain molecular ions at *m/z* 760 (Y = I), 663 (OMe), and 678 (OEt) in addition to a strong ion at *m/z* 633 attributable to $[Mo(NO)L(I)]^+$.

The monoalkoxide complexes can be converted into the bis(alkoxide) derivatives $[Mo(NO)(OR)_2]$ (R = Me or Et) by allowing a solution in the appropriate alcohol to stand at room temperature for several days. However, these compounds can also be prepared directly from $[Mo(NO)LI_2]$ by carrying out the reaction with ROH in the presence of silver acetate.[3] Again the i.r. spectra of the products $[Mo(NO)L(OR)_2]$ contain ν(BH) and exhibit ν(NO) values similar to those found previously[3] for $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(OR)_2]$. The mass spectra of $[Mo(NO)L(OR)_2]$ contained weak molecular ions at *m/z* 570 (R = Me) and 597 (Et) in addition to strong ions attributable to $MoL(OR)_2$ at *m/z* 539 (R = Me) and 569 (Et). The ^1H n.m.r. spectra of the bis(alkoxide) complexes are simplified by the absence of chirality and show that these compounds can be isolated as single isomers in which a plane of symmetry is present. Thus the spectrum of $[Mo(NO)L(OMe)_2]$ shows a single singlet at δ 5.00 attributable to the methoxy methyl protons, two singlets of relative areas 2:1 at δ 5.85 and 5.79 attributable to the pyrazolyl 4 protons, and three doublets of equal area attributable to the isopropyl methyl protons which occupy three magnetically distinct environments. The isopropyl CH protons appear as two septets of relative areas 2:1 at δ 3.57 and 3.06 and finally there is single resonance at δ 2.35 attributable to the pyrazolyl methyl protons. The spectrum of $[Mo(NO)L(OEt)_2]$ is broadly similar except that a triplet is present at δ 1.36 attributable to the ethoxy methyl protons, the singlet observed for the methoxy methyl protons is replaced by two multiplets from the diastereotopic ethoxy methylene protons, and the pyrazolyl methyl protons now appear as two signals of relative area 6:3 at δ 2.34 and 2.35. The *X*-ray study described below confirms that these bis(alkoxide) complexes may be formulated as $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(OR)_2]$ (R = Me or Et).

Structural Studies.—There are four isomers of $[Mo\{HB(MePr^iC_3N_2H\text{-}4)_3\}(OR)_2]$ which contain a plane of symmetry as required by the n.m.r. data. Although two of these may be deemed unlikely on steric grounds the spectroscopic data alone are still insufficient to define the structures of $[Mo(NO)L(OR)_2]$ unequivocally. Accordingly a single-crystal *X*-ray diffraction study of the complex with R = Et was undertaken. The molecular structure of $[Mo(NO)L(OEt)_2]$ is shown in Figure 2. Atomic co-ordinates are presented in Table 2 and selected bond distances and angles in Table 3. The isopropyl substituents are all located in the 3 positions of the pyrazolyl rings and the molybdenum is in an approximately octahedral co-ordination environment. The largest deviation from the ideal *cis*-octahedral angle of 90° at Mo is for N(11)–Mo–N(31) which is reduced to 78.1(4)° and is adjacent to the nitrosyl ligand. This value is slightly larger than the corresponding value of 76.0(2)° found in the related complex $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(OPr^i)_2]$. The *trans*-octahedral angle N(1)–Mo–N(21) involving the nitrosyl ligand is close to the ideal at 179.1(4)°, but *trans*-octahedral angles involving the alkoxy-oxygen atoms are reduced to 161.0(5) and 165.9(4)°, a similar geometric distortion having been observed[15] in $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}$-

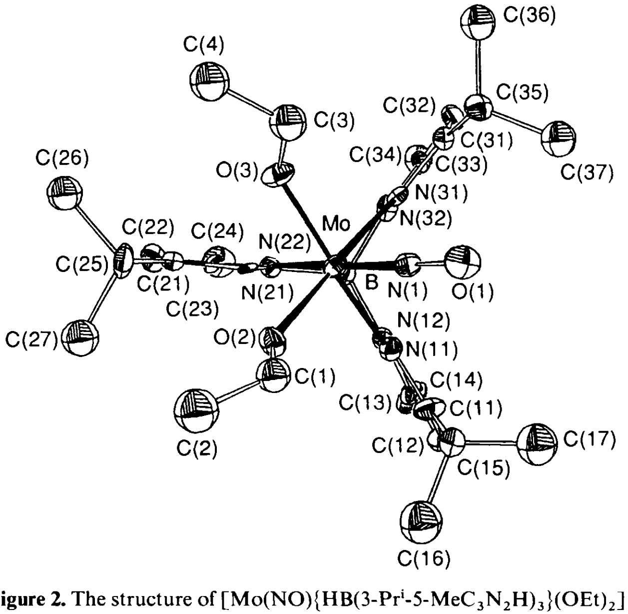

Figure 2. The structure of $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(OEt)_2]$ showing the atom labelling. Hydrogen atoms have been omitted for clarity

Table 2. Fractional atomic co-ordinates for $[\text{Mo(NO)}\{\text{HB(3-Pr}^i\text{-5-MeC}_3\text{N}_2\text{H)}_3\}\text{(OEt)}_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	0.818 9(1)	0.168 1(1)	0.250 4(0)	C(14)	0.605 9(12)	0.025 5(21)	0.011 2(13)
O(1)	0.839 4(7)	0.433 2(8)	0.267 0(10)	C(15)	0.805 5(11)	0.338 6(19)	0.046 6(12)
O(2)	0.903 3(5)	0.141 0(9)	0.186 5(8)	C(16)	0.850 1(14)	0.315 0(27)	−0.030 4(19)
O(3)	0.853 6(6)	0.123 9(11)	0.363 0(7)	C(17)	0.764 6(15)	0.451 8(25)	0.037 0(18)
N(1)	0.830 8(5)	0.323 0(10)	0.259 2(15)	C(21)	0.848 9(8)	−0.128 8(12)	0.258 0(14)
N(11)	0.751 7(7)	0.173 1(12)	0.130 9(8)	C(22)	0.810 6(9)	−0.234 1(11)	0.248 9(20)
N(12)	0.696 5(6)	0.088 4(11)	0.122 6(8)	C(23)	0.742 0(8)	−0.202 9(11)	0.224 0(8)
N(21)	0.805 3(5)	−0.032 3(8)	0.239 6(8)	C(24)	0.680 2(14)	−0.282 1(14)	0.207 5(13)
N(22)	0.738 1(6)	−0.079 2(10)	0.221 3(7)	C(25)	0.927 7(9)	−0.108 8(15)	0.279 6(12)
N(31)	0.706 2(6)	0.167 5(11)	0.304 4(7)	C(26)	0.950 6(11)	−0.176 8(21)	0.361 9(14)
N(32)	0.657 3(6)	0.082 6(11)	0.277 6(8)	C(27)	0.970 9(13)	−0.152 0(21)	0.199 9(16)
B	0.676 8(11)	0.002 6(15)	0.198 4(10)	C(31)	0.670 6(8)	0.230 9(12)	0.367 1(10)
C(1)	0.961 0(12)	0.217 3(18)	0.171 6(13)	C(32)	0.605 8(9)	0.180 7(16)	0.381 0(11)
C(2)	1.032 3(15)	0.169 1(26)	0.155 3(17)	C(33)	0.594 3(8)	0.090 3(14)	0.322 7(10)
C(3)	0.883 7(12)	0.197 7(19)	0.426 7(14)	C(34)	0.531 4(8)	0.011 5(18)	0.312 1(14)
C(4)	0.937 4(13)	0.133 9(22)	0.481 7(16)	C(35)	0.703 9(9)	0.342 1(15)	0.409 1(10)
C(11)	0.752 2(11)	0.238 2(16)	0.060 4(11)	C(36)	0.690 4(12)	0.343 9(21)	0.505 2(14)
C(12)	0.701 8(11)	0.193 8(16)	0.001 4(10)	C(37)	0.671 6(12)	0.452 3(21)	0.365 8(15)
C(13)	0.666 4(9)	0.100 0(14)	0.042 9(10)				

$(\text{OPr}^i)_2]$ to give N–Mo–O angles of 161.5(2) and 161.8(2) Å. The Mo–O(Et) distances of 1.86(1) and 1.91(1) Å may be compared with values of 1.908(4) and 1.900(4) Å in $[\text{Mo}\{\text{HB(3,5-Me}_2\text{C}_3\text{N}_2\text{H)}_3\}(\text{OPr}^i)_2]$, whilst the Mo–O–C(Et) angles of 129(1)° are smaller than the Mo–O–C(Pr^i) angles of 133.4(4)° in $[\text{Mo}\{\text{HB(3,5-Me}_2\text{C}_3\text{N}_2\text{H)}_3\}(\text{OPr}^i)_2]$. The short Mo–O distances and large Mo–O–C angles are in accord with the presence of $p_\pi \rightarrow d_\pi$ charge donation from filled *p* orbitals on the alkoxy oxygens to an empty *d* orbital on Mo as has been noted previously.[3,15] The modest differences between the structures of $[\text{Mo(NO)L(OEt)}_2]$ and $[\text{Mo}\{\text{HB(3,5-Me}_2\text{C}_3\text{N}_2\text{H)}_3\}(\text{OPr}^i)_2]$ probably arise from the replacement of the OEt ligands by the more bulky OPr^i groups. The pyrazolyl 3-Pr^i groups are oriented so as to present C–H groups to the alkoxy ligands in a similar fashion to a pyrazolyl 3-Me substituent. Consequently the replacement of the pyrazolyl 3-methyl groups with Pr^i would not be expected to contribute substantially to the steric crowding around the molybdenum centre with respect to unbranched hydrocarbyl ligand substituents. More substantial interligand interactions might be expected in complexes containing ligands such as pyrrolyl[16] or piperidyl[17] where parts of the ligand are interposed between the pyrazolyl 3 substituents in the $\text{Mo}\{\text{HB(3,5-Me}_2\text{C}_3\text{N}_2\text{H)}_3\}$ moiety.

Experimental

Synthetic and Spectroscopic Studies.—Commercial reagents were used as supplied. 3-Isopropyl-5-methylpyrazole was prepared by condensing 3-methyl-2-butanone with excess of ethyl acetate in the presence of KOBu^t and reacting the isolated dione with hydrazine.[18] Solvents used as reaction media were dried according to standard methods and freed of oxygen before use. All reactions involving molybdenum complexes were carried out under nitrogen but purification procedures were carried out in air. Activated alumina UGI (100 mesh) or silica gel 60 (70—230 mesh) were used as the stationary phase for column chromatography.

Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham or by Microanalysis, Inc., Wilmington, DE. Infra-red spectra were recorded using a PE 297 spectrometer with samples as KBr discs or with a Perkin-Elmer 283-B spectrometer with samples as Nujol mulls. 360-MHz Proton n.m.r. spectra were obtained using a Nicolet NT360WB spectrometer and 270-MHz ^{1}H n.m.r. spectra using a JEOL GX 270 spectrometer. Mass spectra were recorded using a Kratos MS80 spectrometer.

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Mo–O(2)	1.86(1)	O(1)–N(1)	1.25(1)
Mo–O(3)	1.91(1)	O(3)–C(1)	1.37(2)
Mo–N(1)	1.73(1)	O(3)–C(3)	1.39(2)
Mo–N(11)	2.22(1)	B–N(12)	1.55(2)
Mo–N(21)	2.24(1)	B–N(22)	1.49(2)
Mo–N(31)	2.23(1)	B–N(32)	1.55(2)
C(1)–C(2)	1.43(3)	C(3)–C(4)	1.48(3)
N(21)–Mo–N(31)	85.5(4)	O(2)–Mo–N(11)	91.6(5)
N(11)–Mo–N(31)	78.1(4)	O(2)–Mo–N(1)	95.5(5)
N(11)–Mo–N(21)	84.3(4)	O(2)–Mo–O(3)	99.3(5)
N(1)–Mo–N(31)	95.2(5)	Mo–O(2)–C(1)	129(1)
N(1)–Mo–N(21)	179.1(4)	Mo–O(3)–C(3)	129(1)
N(1)–Mo–N(11)	96.34(6)	Mo–N(1)–O(1)	179(2)
O(3)–Mo–N(31)	88.2(4)	N(22)–B–N(32)	110(1)
O(3)–Mo–N(21)	81.4(4)	N(12)–B–N(32)	107(1)
O(3)–Mo–N(11)	161.0(5)	N(12)–B–N(22)	112(1)
O(3)–Mo–N(1)	98.1(6)	O(2)–C(1)–C(2)	120(2)
O(2)–Mo–N(31)	165.9(4)	O(3)–C(3)–C(4)	113(2)
O(2)–Mo–N(21)	83.9(4)		

*Potassium hydrotris(isopropylmethylpyrazol-*1*-yl)borate.* A mixture of KBH_4 (5.4 g, 0.1 mol) and $\text{3-Pr}^i\text{-5-MeC}_3\text{N}_2\text{H}_2$ (62 g, 0.5 mol) was heated with stirring. Hydrogen evolution commenced when the mixture reached *ca.* 140 °C and continued up to 210 °C. When 7.4 dm^3 of hydrogen had been evolved the excess of $\text{3-Pr}^i\text{-5-MeC}_3\text{N}_2\text{H}_2$ was removed by distillation *in vacuo.* The residue was then dissolved in tetrahydrofuran (500 cm^3) to give a solution (*ca.* 0.2 mol dm^{-3}) of $\text{K[HB(Pr}^i\text{-MeC}_3\text{N}_2\text{H-4)]}_3$.

$\text{Tl[HB(Pr}^i\text{MeC}_3\text{N}_2\text{H-4)}_3]$. A solution of TlNO_3 in water (10 cm^3, 0.5 mol dm^{-3}) was added to a solution of $\text{K[HB(Pr}^i\text{-MeC}_3\text{N}_2\text{H-4)}_3]$ in thf (50 cm^3, 0.2 mol dm^{-3}) and the mixture was stirred rapidly for 15 min. After this time water (200 cm^3) was added and the product extracted from this mixture into CH_2Cl_2 (50 cm^3). The extract was passed through alumina (2 × 10 cm) and mixed with MeCN (35 cm^3). Evaporation of the CH_2Cl_2 caused the product to precipitate. $\delta_\text{H}(\text{CDCl}_3$, 360 MHz) 1.23 [18 H, d, $(\text{C}H_3)_2\text{CHC(pz)}$], 2.37 [9 H, s, $\text{C}H_3\text{C(pz)}$], 3.10 [3 H, m, $\text{Me}_2\text{C}H\text{C(pz)}$], and 5.77 [3 H, s, HC(pz)].

$[M\{HB(Pr^iMeC_3N_2H\text{-}4)_3\}_2]$ (M = Fe, Co, Ni, *or* Zn). To a solution of $K[HB(Pr^iMeC_3N_2H\text{-}4)_3]$ in thf (50 cm^3, 0.2 mol dm^{-3}) was added MZ_2 (M = Fe, Z = ClO_4; M = Co, Ni, or Zn, Z = NO_3) (10 cm^3, 0.5 mol dm^{-3}) with rapid stirring. After 15 min water (200 cm^3) was added and the product extracted from this mixture into CH_2Cl_2 (50 cm^3). The extract was passed through alumina (2 × 10 cm) and mixed with MeCN (35 cm^3). Evaporation of the CH_2Cl_2 caused the product to precipitate: $[Zn\{HB(Pr^iMeC_3N_2H\text{-}4)_3\}_2]$, $\delta_H(CDCl_3$, 360 MHz) 0.70, 1.20 [12 H, d; 24 H, d, $(CH_3)_2CHC(pz)$], 1.34, 2.44 (12 H, s; 6 H, s, $CH_3C(pz)$], 1.75, 3.52 [2 H, spt; 4 H, spt, $Me_2CHC(pz)$], and 5.51, 5.65 [4 H, s; 2 H, s, HC(pz)].

$[M\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}X]$ (M = Co *or* Ni, X = NCS *or* NCO; M = Zn, X = NCS *or* N_3). A solution of $K[HB(Pr^iMeC_3N_2H\text{-}4)_3]$ in thf (50 cm^3, 0.2 mol dm^{-3}) was mixed with an aqueous solution of K_2MX_4 (40 cm^3, 0.5 mol dm^{-3}). Methanol (50 cm^3) was then added and the mixture was stirred rapidly for 15 min. Water (200 cm^3) was added and the product extracted from this mixture into CH_2Cl_2 (50 cm^3). The extract was passed through alumina (2 × 10 cm) and mixed with MeCN (35 cm^3). Evaporation of the CH_2Cl_2 caused the product to precipitate. Further purification was carried out by recrystallisation from heptane: $[Zn\{HB(Pr^iMeC_3N_2H\text{-}4)_3\}(NCS)]$, $\delta_H(CDCl_3$, 360 MHz) 1.24 [18 H, d, $(CH_3)_2CHC(pz)$], 2.36 [9 H, s, $CH_3C(pz)$], 3.10 [3 H, m, $Me_2CHC(pz)$], and 5.79 [3 H, s, HC(pz)]; $[Zn\{HB(Pr^iMeC_3N_2H\text{-}4)_3\}N_3]$, δ_H 1.25 [18 H, d, $(CH_3)_2CHC(pz)$], 2.39 [9 H, s, $CH_3C(pz)$], 3.14 [3 H, m, $Me_2CHC(pz)$], and 5.83 [3 H, s, HC(pz)].

$[Mo(NO)\{HB(Pr^iMeC_3N_2H\text{-}4)_3\}(CO)_2]$. A solution of $K[HB(Pr^iMeC_3N_2H\text{-}4)_3]$ in thf (50 cm^3, 0.2 mol dm^{-3}) containing $[Mo(CO)_6]$ (2.64 g, 0.01 mol) was heated under reflux until 3 equivalents of CO had been evolved (*ca.* 2 h). Butyl nitrite (3 cm^3, 0.03 mol) was then added and the mixture heated for 1 h. After this time the mixture was poured into ice–water (200 cm^3) and the product extracted with CH_2Cl_2 (2 × 30 cm^3). The solvent was removed by evaporation under reduced pressure and the orange product purified by column chromatography on alumina (10 × 2 cm) using CH_2Cl_2 as the eluant. Further purification was effected by recrystallisation from amyl acetate. $\delta_H(CDCl_3$, 270 MHz) 1.18—1.28 [18 H, nl, $(CH_3)_2CHC(pz)$], 2.34—2.48 [9 H, nl, $CH_3C(pz)$], 3.34—3.45 [3 H, m, $Me_2CHC(pz)$], and 5.78—5.89 [3 H, nl, HC(pz)].*

$[Mo\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}\{CH_2C(Me)CH_2\}(CO)_2]$. To a solution of $K[HB(Pr^iMeC_3N_2H\text{-}4)_3]$ in thf (50 cm^3, 0.2 mol dm^{-3}) was added $[MoCl\{\eta^3\text{-}CH_2C(Me)CH_2\}(CO)_2(MeCN)_2]$ (3.24 g, 0.01 mol) with stirring. The solvent was then removed under reduced pressure to afford the solid product which was purified by column chromatography on alumina (10 × 2 cm) using CH_2Cl_2 as the eluant. Further purification was effected by recrystallisation from Pr^iOH. $\delta_H(CDCl_3$, 270 MHz) 1.00—1.40 [21 H, nl, $(CH_3)_2CHC(pz)$, $CH_3C_3H_4$], 2.52, 3.19 [2 H, s; 2 H, s, MeC_3H_4], 2.06, 2.33 [3 H, nl; 6 H, nl, $CH_3C(pz)$], 2.76, 4.36 [2 H, m; 1 H, m, $Me_2CHC(pz)$], and 5.64, 5.83 [1 H, nl; 2 H, nl, HC(pz)].

$[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}I_2]$. Iodine (1.36 g, 5.4 mmol) was placed in a Soxhlet thimble and extracted under reflux into a solution of $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(CO)_2]$ (3.0 g, 5.3 mmol) in methylcyclohexane (100 cm^3) over a period of 48 h. After this time the solution was allowed to cool and a black solid was deposited. This was collected by filtration and the volume of the filtrate reduced by evaporation to afford more of the black product on cooling. The combined solids obtained were dissolved in hot toluene (50 cm^3), the solution filtered, and pentane (50 cm^3) added to the cool filtrate to precipitate the purified product (2.5 g). $\delta_H(CDCl_3$, 270 MHz) 0.97—1.40 [18 H, nl, $(CH_3)_2CHC(pz)$], 2.29—2.58 [9 H, nl, $CH_3C(pz)$], 3.28—3.61 [3 H, m, $Me_2CHC(pz)$], and 5.87—6.16 [3 H, nl, HC(pz)].

$[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}I(OMe)]$. A solution of $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}I_2]$ (0.2 g, 0.26 mmol) in methanol (20 cm^3) was heated under reflux for 2 h. The solution was then cooled and the solvent removed under reduced pressure. The solid residue was extracted with hexane (10 cm^3) and the product purified by column chromatography on silica gel (50 × 3 cm) using 1:1 CH_2Cl_2–hexane as the eluant. The major dark green band was collected. This deposited the product as a dark green microcrystalline solid upon concentration and cooling (0.03 g). $\delta_H(CDCl_3$, 270 MHz) 1.09—1.54 [18 H, nl, $(CH_3)_2CHC(pz)$], 2.35—2.56 [9 H, nl, $CH_3C(pz)$], 3.08—3.85 [3 H, m, $Me_2CHC(pz)$], 5.36—5.46 [3 H, nl, CH_3O], and 5.84—5.91 [3 H, nl, HC(pz)].

$[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}I(OEt)]$. This compound was prepared in an identical manner to its methoxy-substituted homologue using dry EtOH (20 cm^3) in place of MeOH as the reaction medium. The product was obtained as a dark green microcrystalline solid (0.07 g). $\delta_H(CDCl_3$, 270 MHz) 1.09—1.30 [18 H, nl $(CH_3)_2CHC(pz)$], 1.53—1.58 (3 H, nl, CH_3CH_2O), 2.36—2.52 [9 H, nl, $CH_3C(pz)$], 3.15—3.85 [3 H, m, $Me_2CHC(pz)$], 5.45—5.85 (2 H, mnl, $MeCH_2O$), and 5.87—5.91 [3 H, nl, HC(pz)].

$[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(OMe)_2]$. Silver acetate (0.1 g, 0.6 mmol) was added to a solution of $[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}I_2]$ (0.2 g, 0.26 mmol) in methanol (50 cm^3) and the mixture heated under reflux for 24 h. Precipitated AgI was removed by filtration through Kieselguhr and the volume of the filtrate reduced (to *ca.* 20 cm^3) by evaporation. The pink product deposited upon standing for several days (0.07 g). $\delta_H(CDCl_3$, 270 MHz) 1.12, 1.19, 1.26 [6 H, d; 6 H, d; 6 H, d, $(CH_3)_2CHC(pz)$], 2.35 [9 H, s, $CH_3C(pz)$], 3.06, 3.57 [1 H, m; 2 H, m, $Me_2CHC(pz)$]; 5.00 [6 H, s, CH_3O], and 5.79, 5.85 [1 H, s; 2 H, s, HC(pz)].

$[Mo(NO)\{HB(3\text{-}Pr^i\text{-}5\text{-}MeC_3N_2H)_3\}(OEt)_2]$. This compound was prepared in an identical manner to its methoxy-substituted homologue using dry EtOH (50 cm^3) in place of MeOH as the reaction medium. The product was obtained as a pink microcrystalline solid (0.08 g). $\delta_H(CDCl_3$, 270 MHz) 1.12, 1.16, 1.26 [6 H, d; 6 H, d; 6 H, d, $(CH_3)_2CHC(pz)$], 1.36 (6 H, t, CH_3CH_2O), 2.34, 2.35 [6 H, s; 3 H, s, $CH_3C(pz)$], 3.31, 3.59 [1 H, m; 2 H, m, $Me_2CHC(pz)$], 5.27, 5.52 [2 H, m; 2 H, m, $MeCH_2O$], and 5.80, 5.85 [1 H, s; 2 H, s, HC(pz)].

Structural Studies.—Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer operating in the ω—2θ mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) up to θ = 25° from crystals of size 0.4 × 0.2 × 0.2 mm. Three standard reflections were monitored periodically to check the stability of the system. 4 703 Unique reflections were scanned and 1 984 with $I > 2\sigma(I)$ were considered observed and used in the analyses.

Crystal data. $C_{25}H_{44}BMoN_7O_3$, M = 597.4, orthorhombic, space group $Pna2_1$, a = 18.336(2), b = 11.061(2), c = 15.402(3) Å, U = 3 123.8(9) $Å^3$, Z = 4, D_c = 1.27 g cm^{-3}, μ(Mo-K_α) = 4.43 cm^{-1}, $F(000)$ = 1256.

The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The structure was solved by Patterson and Fourier methods using the *X*-Ray 80 system[19] and refined by least squares using unit weights. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from ref. 20. An empirical absorption correction[21] was applied at the end of the isotropic refinement and final

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* Shifts are approximations as signals attributable to another isomer were also present; nl = several lines observed due to the presence of a mixture of isomers.

refinement was carried out using fixed isotropic thermal parameters, and co-ordinates 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 1.12 and 0.57 respectively. Refinement was terminated when all shift/e.s.d. ratios were <0.1 and R, $R' = 0.058, 0.062$.

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

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