Nitrosyl Complexes of Molybdenum and Tungsten. Part 16.[1] Symmetrical and Unsymmetrical Bis-alkoxo- and Mixed Alkoxo-amido-complexes of Tris(3,5-dimethylpyrazolyl)boratomolybdenum, Related Tungsten Species, and the Structure of Bis(ethoxo)-, Bis(isopropoxo)-, and Ethoxo(isopropoxo)-nitrosyl[tris(3,5-dimethylpyrazolyl)borato]-molybdenum

By **Jon A. McCleverty**,*† **A. Elizabeth Rae**, **Iwona Wołochowicz**, **Neil A. Bailey**,* and **John M. A. Smith**, Department of Chemistry, The University, Sheffield S3 7HF

The complex $[Mo\{HB(Me_2pz)_3\}(NO)X(Y)]$ [Me_2pz = 3,5-dimethylpyrazolyl; X = I, Y = OH, OC_6H_{11}, and $OCH_2C_2CH_2OH$; X = Y = OR (R = H, Me, Et, Pr^i, and Bu^t); X = OEt, Y = OPr^i; X = OPr^i, Y = OBu^t; X = OR, Y = NHR′ (R = Me, R′ = H, Me, and Et; R = Et, R′ = H, Me, Et, Pr^n, C_6H_{11}, and CH_2Ph; R = Pr^i, R′ = H, Me, Et, Pr^i, and C_6H_{11})] and $[W\{HB(Me_2pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)X(Y)]$ (X = Br, Y = OMe, OEt, and OPr^i; X = Y = OEt) have been prepared and characterised spectroscopically. The complexes $[Mo\{HB(Me_2pz)_3\}(NO)(OR)(NH_2)]$ (R = Me, Et, or Pr^i) react with acetone affording $[Mo\{HB(Me_2pz)_3\}(NO)(N{=}CMe_2)(OR)]\cdot n(CH_3)_2CO$. The structures of $[Mo\{HB(Me_2pz)_3\}(NO)(OR)(OR')]$ (R = R′ = Et or Pr^i; R = Et, R′ = Pr^i) have been determined crystallographically. For R = Et, R′ = Pr^i, crystals are monoclinic, with a = 14.46(4), b = 21.67(6), c = 8.015(14) Å, β = 96.08(3)°, space group $P2_1/n$, and R 0.0388; for R = R′ = Pr^i, crystals are triclinic, with a = 11.758(8), b = 14.403(9), c = 8.173(14) Å, α = 97.970(16), β = 77.30(3), γ = 96.523(7)°, space group $P\bar{1}$, and R 0.0398; for R = R′ = Et, crystals are monoclinic, with a = 14.73, b = 21.09, c = 8.00 Å, β = 94.80°, and space group $P2_1/n$. The molecules are six-co-ordinate, with linear Mo–N–O groups and short Mo–O bond lengths (1.90 Å).

In an earlier paper we reported [2] the syntheses of mono-alkoxo-complexes $[Mo\{HB(Me_2pz)_3\}(NO)X(Y)]$, (1; X = Cl, Br, or I; Y = OR, where R = alkyl; Me_2pz = 3,5-dimethylpyrazolyl) and the bis-alkoxide (1; X = Y = OEt). These compounds are of interest because they represent one of the very few examples of alkoxo-derivatives of the early transition metals which are air- and moisture-stable. Also, they are six-co-ordinate and therefore the metal appears to be co-ordinatively unsaturated. The complexes do not, however, react with ' small ' molecules such as CO, pyridine, isonitrile, or nitriles forming adducts.

From an *X*-ray crystallographic examination of a representative member of this group of alkoxides, $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OPr^i)]$ we established [2] that there was considerable steric crowding at the metal caused by the pyrazolylborato-ligand. This has the effect of preventing the approach of another ligand which could increase the co-ordination number from six to seven, thereby relieving the metal's unsaturation. Furthermore, we found that the Mo–O bond was very short (1.86 Å) which suggested that there is a significant degree of $p_\pi \rightarrow d_\pi$ donation from O to the metal atom. This suggestion of Mo=O bonding was supported by the observation of a relatively large Mo–O–C bond angle (132°) which we would have expected to have been smaller if no π bonding was present. Thus the stability of (1; X = halide, Y = OR) and, presumably, (1; X = Y = OEt) could be rationalised in terms of the steric protection afforded by the tris(3,5-dimethylpyrazolyl)borato-ligand, and the short Mo–O bond.

Our somewhat adventitious isolation of (1; X = Y = OEt), by ' reduction ' of (1; X = Y = I) with zinc dust in ethanol, encouraged us to look for more logical synthetic routes to bis-alkoxides, and therefore to the possibility of making compounds containing two different alkoxy-ligands. Mixed alkoxo-species are known,[3] but they are not easy to prepare specifically because of the tendency to form all possible combinations of $M(OR)_x(OR')_y$; few such species have been structurally characterised.[4]

If a reliable route to (1; X = OR, Y = OR′) could be developed, then it might also be possible to prepare (1; X = OR, Y = NHR′). Mixed alkoxodialkylamido-complexes, *e.g.* $[Cr(NO)(NPr^i{}_2)(OBu^t)_2]$,[5] $[Mo(NHR)_2(OSiMe_3)_4]$ (R = 1-adamantyl),[6] and $[W(NMe_2)_3(OMe)_3]$,[7] are known but these usually contain bulky NR_2 and OR groups, and prior to our work [8] there were no examples of well characterised mixed alkoxo-*monoalkylamido*-complexes.

Finally, we were able to prepare $[W\{HB(Me_2pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)Br_2]$,[1] (2; X = Y = Br), and we decided to attempt to prepare mono- and bis-alkoxo- and mixed alkoxo-amido-complexes for comparison with their molybdenum analogue.

RESULTS AND DISCUSSION

Synthetic Studies.—The green complexes (1; X = I, Y = OR where R = Me, Et, Pr^i, CH_2Pr^i, and C_3H_5) were previously obtained [2] by refluxing (1; X = Y = I) in the appropriate alcohol. We have extended this series of complexes by making (1; X = I, Y = $OCH_2C{\equiv}CCH_2OH$ or OC_6H_{11}) by treating (1; X = Y = I) with $HOCH_2C{\equiv}CCH_2OH$ or cyclohexanol diluted in methylcyclohexane. The purple tungsten complexes (2; X =

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† *Present address:* Department of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT.

Br, Y = OMe, OEt, and OPr^{i}) were prepared similarly. Analytical data are given in Table 1.

TABLE 1

Analytical and molecular-weight data obtained from [Mo{HB($Me_2pz)_3$}(NO)X(Y)], (1) and [W{HB($Me_2pz)_2$-3,5-Me_2-4-BrC_3N_2)}(NO)X(Y)], (2)

Compound			Analytical data (%)								
			Found				Calc.				
M	X	Y	C	H	N	X [a]	C	H	N	X [a]	*M* [b]
Mo	I	OH	31.8	4.1	17.3	21.3	31.8	4.1	17.3	22.4	—
	I	OC_6H_{11}	38.8	5.1	15.0	19.7	38.8	5.1	15.1	19.6	—
	I	$OCH_2C_2CH_2OH$	35.7	4.3	15.3	19.6	35.9	4.3	15.4	20.0	—
W	Br	OMe	27.5	3.7	13.9	23.4 [c]	27.4	3.4	14.0	22.8	—
	Br	OEt	29.0	3.5	13.8	19.5 [c]	28.6	3.6	13.7	22.4	—
	Br	OPr^{i}	29.6	3.9	13.3	22.6 [c]	29.9	4.4	13.5	22.1	—
Mo	OH	OH	39.3	5.5	21.3	—	39.4	5.3	21.5	—	—
	OMe	OMe	42.0	5.6	20.6	—	42.1	5.8	20.4	—	—
	OEt	OEt	44.2	6.1	18.8	—	44.5	6.2	19.1	—	541(513)
	OPr^{i}	OPr^{i}	46.5	6.5	17.9	—	46.6	6.7	18.1	—	526(541)
	OBu^{i}	OBu^{i}	48.2	5.5	17.3	—	48.5	5.5	17.2	—	—
	OEt	OPr^{i}	45.5	6.5	18.7	—	45.6	6.5	18.6	—	524(527) 572(527) [d]
	OPr^{i}	OBu^{i}	47.5	7.1	17.8	—	47.6	6.9	17.7	—	—
W	OEt	OEt	.38.6	5.3	15.9	—	38.0	5.3	16.3	—	—
Mo	OMe	NH_2	40.7	5.3	23.7	—	40.9	5.8	23.8	—	483(470)
	OMe	NHMe	42.2	6.0	22.9	—	42.2	6.0	23.1	—	464(486)
	OMe	NHEt	43.4	5.9	22.3	—	43.4	6.2	22.5	—	—
	OEt	NH_2	41.8	5.6	22.8	—	42.2	6.0	23.1	—	—
	OEt	NHMe	43.2	6.1	22.6	—	43.4	6.2	22.5	—	562(497)
	OEt	NHEt	44.2	6.5	21.5	—	44.5	6.3	21.9	—	475(511) [d]
	OEt	NHPr^{n}	45.8	6.3	21.2	—	45.6	6.7	21.3	—	—
	OEt	$NHCH_2Ph$	50.2	6.1	19.4	—	50.2	6.1	19.5	—	—
	OEt	NHC_6H_{11}	48.6	7.1	19.8	—	48.8	6.9	19.8	—	—
	OPr^{i}	NH_2	43.7	6.2	22.7	—	43.4	6.2	22.5	—	—
	OPr^{i}	NHMe	44.4	6.4	21.8	—	44.5	6.5	21.9	—	—
	OPr^{i}	NHEt	45.9	6.9	21.3	—	45.6	6.7	21.3	—	514(526)
	OPr^{i}	NHPr^{i}	46.4	6.4	20.3	—	44.7	6.7	20.8	—	—
	OPr^{i}	NHC_6H_{11}	48.6	7.1	19.8	—	48.8	6.9	19.8	—	—

[a] Iodide, unless otherwise stated. [b] Molecular weight determined osmometrically in $CHCl_3$ unless otherwise stated. [c] Bromide. [d] In acetone.

The bis-alkoxides (1; X = Y = OR, R = Me, Et, Pr^{i}, and CH_2Pr^{i}) were conveniently obtained by treatment of (1; X = I, Y = OR) with either silver acetate or triethylamine in a mixture of the appropriate alcohol and methylcyclohexane. Use of AgOCOMe was preferred and we presume that the reaction occurs by abstraction of I^- from (1; X = I, Y = OR), and its removal as AgI, and formation of the transient (1; X = OCOMe, Y = OR).* Treatment of this acetato-intermediate with an alcohol could cause elimination of acetic acid and formation of the desired alkoxide. When NEt_3 is used, we presume that it serves to facilitate elimination of HI from the reaction system and, indeed, we have occasionally isolated [$NHEt_3$]I. The mixed alkoxo-species (1; X = OPr^{i}, Y = OR', R' = Et or CH_2Pr^{i}) were similarly prepared from (1; X = OPr^{i}, Y = I), silver acetate, and either ethanol or 2-butyl alcohol. We were unable, however, to isolate the mixed alkoxides where R = Me and R' = Et or Pr^{i}, our attempts to do so affording only the symmetrical species (1; X = Y = OR'). The bis-alkoxides were obtained as pink crystalline solids which dissolved in organic solvents giving deep pink solutions.

The tungsten bis-alkoxide [W{HB($Me_2pz)_3$}(NO)-$(OEt)_2$], which was obtained as a yellow-brown solid, was obtained by first forming what we presumed to be [W{HB($Me_2pz)_3$}(NO)I_2] (see Experimental section) and then treating this species *in situ* in solution with ethanol. The preparation of other bis(alkoxo)tungsten complexes was not attempted.

While the mixed alkoxo-amido-complexes (1; X = OR, Y = NHR') could be prepared from (1; X = OR, Y = I), AgOCOMe, and the appropriate primary amine, we found that treatment of the iodo-alkoxide precursor with at least two equivalents of the amine proved a more convenient route to the desired compounds. A full list of the complexes prepared is given in Table 1.

In the formation of (1; X = OR, Y = NH_2 or NHMe) from (1; X = OR, Y = I), ammonia and methylamine were used as their aqueous solutions. The water apparently plays no role in this reaction, although it is possible to prepare (1; X = I, Y = OH) by treatment of (1; X = Y = I) with silver acetate followed by water. These mixed-ligand species could also be prepared by treating (1; X = NHR, Y = I) with AgOCOMe in the presence of ROH, and it is interesting to note that the Mo–NHR bond is not cleaved by ROH, in contrast to the normal behaviour of alkylamido-complexes.[9] The

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* An attempt was made to isolate this acetate. It was formed as a dark olive green microcrystalline solid which, in air (moist), smelled strongly of acetic acid. Due to its instability it could not be satisfactorily characterised, ν(NO) 1 670 cm^{-1}.

mixed alkoxo-amido-complexes were obtained as yellow-orange crystalline solids.

In a previous paper we have observed[10] that [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$] seems to react with alcohols and amines *via* a redox process apparently involving the transient formation of [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$]$^-$ and [Mo{HB(Me$_2$pz)$_3$}(NO)I(solvent)$_x$]. While the simple alkoxide (1; X = I, Y = OR) may be formed by this route, it is obvious that such a reaction pathway cannot be followed in the formation of (1; X = Y = OR) *via* (1; X = I, Y = OR), AgOCOMe, and ROH. The behaviour of these molybdenum complexes with Ag$^+$ is very complex. Indeed, the *monocation* [Mo{HB(Me$_2$pz)$_3$}-(NO)(NCMe)$_2$]$^+$ is formed when (1; X = Y = I) is treated with *two* molar equivalents of Ag$^+$ in acetonitrile.[11] The behaviour of (1; X = Y = I) and (1; X = I, Y = OR) in the presence of Ag$^+$ and the general redox properties of (1; X = I, Y = OR, NHR, SR, *etc.*) and (1; X = OR, Y = NHR, SR, *etc.*) are being investigated electrochemically, and a full report of this study and how it relates to the mechanism of formation of the alkoxides, amides, *etc.*, will be given shortly.

Reactions.—Treatment of (1; X = I, Y = OR), (1; X = OR, Y = OR′), (1; X = OR, Y = NHR′), and their tungsten analogues with HCl caused cleavage of the M–O and M–N bonds and formation of (1; X = I, Y = Cl), (1; X = Y = Cl), and (2; X = Y = Cl). This behaviour has been observed previously,[1,2] and the metal-containing products of these reactions were identified by i.r. and ^{1}H n.m.r. spectroscopy.

In acetone, (1; X = OR, Y = NH$_2$; R = Me, Et, or Pr^i) formed (1; X = OR, Y = N=CMe$_2$) which were isolated as pink-red acetone solvates. Because of the difficulty of obtaining pure samples for analytical and ^{1}H n.m.r. spectral purposes, these compounds could only be identified by their i.r. spectra (see below). Trimethylamine was not required to promote this reaction, in contrast to the behaviour of (1; X = I, Y = NH$_2$) with acetone.[1]

It is well known that [Co$_2$(CO)$_8$] reacts with acetylenes, RC$_2$R′, affording the μ-acetylenic species [Co$_2$(CO)$_6$-(RC$_2$R′)]. We attempted to prepare a mixed molybdenum–cobalt carbonyl complex {1; X = I, Y = OCH$_2$-C$_2$CH$_2$OH[Co$_2$(CO)$_6$]} either by reaction of [Co$_2$(CO)$_6$-(HOCH$_2$C$_2$CH$_2$OH)] with (1; X = Y = I), or by treatment of (1; X = I, Y = OCH$_2$C$_2$CH$_2$OH) with [Co$_2$(CO)$_8$]. In each case, extensive decomposition occurred, and we could not obtain the mixed-metal compound, although treatment of the cobalt carbonyl acetylene complex with (1; X = Y = I) afforded a small amount of (1; X = I, Y = OCH$_2$C$_2$CH$_2$OH).

Spectroscopic Studies.—The i.r. spectra of the new complexes (Table 2) exhibit the expected absorptions due to the HB(Me$_2$pz)$_3$ ligand [*ca.* 2 500 cm^{-1} due to ν(BH) and 1 400 cm^{-1} associated with the pyrazolyl ring]. The NO stretching frequencies of (1; X = I, Y = OR) occur at 1 675 cm^{-1}, although (1; X = I, Y = OH) exhibits ν(NO) 10 cm^{-1} lower (this may be a solid-state effect). The corresponding tungsten complexes (2; X = Br, Y = OR), have ν(NO) at 1 635 cm^{-1}, 40 cm^{-1} lower than in their molybdenum analogues. This drop in NO stretching frequency, representing greater back donation from W to NO, may be a reflection of the enhanced overlap between the more diffuse *d* orbitals in W and the *p* orbitals in O and/or the π* orbitals in NO. The NO stretching frequencies of (1; X = Y = OR, R = H or alkyl) occur at 1 640 cm^{-1}, and the decrease in ν(NO) relative to that in (1; X = I, Y = OR) is to be expected because of the increase in donation to Mo occasioned by two rather than one OR group. The related species (2; X = Y = OEt) has the lowest recorded NO absorption (1 595 cm^{-1}) of this class of compound. Those species containing OH groups exhibit characteristic absorptions near 3 500 cm^{-1} due to ν(OH).

The i.r. spectra of the mixed alkoxo-amido-complexes, (1; X = OR, Y = NHR′), are very similar to those of their bis-alkoxide analogues. The value of ν(NO) falls between 1 630 and 1 640 cm^{-1}, and ν(NH) can be detected between 3 250 and 3 450 cm^{-1}. As mentioned earlier, (1; X = OR, Y = NH$_2$, R = Me, Et, or Pr^i) reacted with acetone giving (1; X = OR, Y = N=CMe$_2$). This was established by i.r. spectroscopy, the two ν(NH) of the precursor having disappeared after reaction, while ν(NO) occurred at 1 640 cm^{-1} and a new band at 1 700 cm^{-1} was assigned to ν(CO) of solvating acetone.

The ^{1}H n.m.r. spectra of the new complexes are presented in Table 2. Generally, the complexes exhibit a group of signals around δ = 2.5 p.p.m. due to the methyl groups of the HB(Me$_2$pz)$_3$ ligand. Resonances due to the proton attached to C-4 of the pyrazolyl groups occur near δ = 5.8 p.p.m. and these signals usually appear as three singlets for (1; X = I, Y = OR), (1; X = OR, Y = OR′), and (1; X = OR, Y = NHR′), and as two singlets (intensity 1 : 2) for (1; X = Y = OR). The occurrence of three signals for the asymmetric species is due to the lack of a plane of symmetry in these six-co-ordinate species, although, occasionally, only two lines were observed. We attribute this lack of expected multiplicity to accidental degeneracy. For the species (2; X = Br, Y = OR, NHR), only two H-4 proton signals are detected, because one pyrazolyl ring is brominated at C-4. Two H-4 resonances are also observed for (2; X = Y = OEt) indicating that this complex has no plane of symmetry and thus must have a structure as represented in Figure 1.

The protons attached to the α-C atoms of the OR and NHR groups in the complexes described here resonate at fields significantly lower than in the free alcohols and amines. This effect has been observed before[1,2] and is due to the strongly electron-withdrawing effect of the Mo{HB(Me$_2$pz)$_3$}(NO) group. However, these protons and, to a lesser extent, the β-protons in the bis-alkoxides and in (1; X = OR, Y = NHR′) resonate at frequencies slightly to higher field of their mono-alkoxide analogues. This probably reflects a slight reduction in the electronegativity of the metal in the bis-substituted species relative to (1; X = I, Y = OR) and (2; X = Br, Y = OR). We were unable to detect signals due to the

TABLE 2

Infrared and ^1H n.m.r. spectral data obtained from $[Mo\{HB(Me_2C_3HN_2)_3\}(NO)X(Y)]$

Complex			I.r. data (cm^{-1})		^1H N.m.r. data		
	X	Y	ν(NO)	Other	δ [a]	A [b]	Assignments
(1)	I	OH	1 665 [c]	3 500 (OH)	5.89 [d] 5.86 5.78	3	s s s $C_3\textit{H}Me_2N_2$
					2.52 2.50 2.40 2.32	18	s s s s $C_3H(C\textit{H}_3)_2N_2$
(1)	I	OC_6H_{11}	1 675 [c]		2.91	1	m OCH of OC_6H_{11}
					2.87 2.84	3	s s $C_3\textit{H}Me_2N_2$
					2.56 2.49 2.42 2.40 2.37 2.36	18	s s s s s s $C_3H(C\textit{H}_3)_2N_2$
					2.10—1.30	10	m C_6H_{10} of C_6H_{11}
(1)	I	$OCH_2C{\equiv}CH_2OH$	1 675 [c]	3 490 (OH)	6.00	2	m $OCH_2C_2CH_2OH$
					5.85 5.80 5.77	3	s s s $C_3\textit{H}Me_2N_2$
					3.00 [e]	1	br s $OCH_2C_2CH_2O\textit{H}$
					2.46 2.39 2.36 2.30	20	s s s s $C_3H(C\textit{H}_3)_2N_2$ and $OCH_2C_2C\textit{H}_2OH$
(2)	Br	OMe	1 635 [c]		5.95 5.91	2	s s $C_3\textit{H}Me_2N_2$
					5.49	3	s OCH_3
					2.58 2.51 2.39 2.34	18	s s s s $C_3H(C\textit{H}_3)_2N_2$
(2)	Br	OEt	1 635 [c]		5.93 5.88	2	s s $(C_3\textit{H}Me_2N_2)_2$
					5.80	2	m $OC\textit{H}_2Me$
					2.60 2.52 2.48 2.40 2.35	18	s s s s s $[C_3H(C\textit{H}_3)_2N_2]_2[C_3Br(CH_3)_2N_2]$
					1.48	3	t $OC\textit{H}_2CH_3$ ^3J(HH) 6.5 Hz
(2)	Br	OPr^i	1 635 [c]		6.33	1	qnt $OC\textit{H}Me_2$, ^3J(HH) 6.0 Hz
					5.93 5.87	2	s s $C_3\textit{H}Me_2N_2$
					2.58 2.53 2.47 2.39 2.34 2.32	18	s s s s s s $C_3H(C\textit{H}_3)_2N_2$
					1.46	6	dd $OCH(C\textit{H}_3)_2$, separation 32 Hz, ^3J(HH) 6.0 Hz
(1)	OH	OH	1 640 [c]	3 510 (OH)	5.80 (2) [d] 5.72 (1)	1	s s $C_3\textit{H}Me_2N_2$
					2.46 2.36 2.28	6	s s s $C_3H(C\textit{H}_3)_2N_2$
(1)	OMe	OMe	1 640 [c]		5.80 (2) 5.69 (1)	1	s s $C_3\textit{H}Me_2N_2$
					5.14	2	s OCH_3
					2.53 2.31 2.29 2.22	6	s s s s $C_3H(C\textit{H}_3)_2N_2$
(1)	OEt	OEt	1 640 [c]		5.82 (2) 5.76 (1)	3	s s $C_3\textit{H}Me_2N_2$
					5.53	4	m AB pair, $OC\textit{H}_2Me$, δ(A) 5.65, δ(B) 5.40, J(AB) 10.5, ^3J(HH) 7.0 Hz
					2.55 2.31	18	s s $C_3H(C\textit{H}_3)_2N_2$
					1.43		t $OCH_2C\textit{H}_3$, ^3J(HH) 7.0 Hz

TABLE 2 (*continued*)

Complex			I.r. data (cm^{-1})		^{1}H N.m.r. data		
	X	Y	ν(NO)	Other	δ ^{a}	A ^{b}	Assignments
(1)	OPr^i	OPr^i	1 640 ^{c}		5.82	2	m $\mathrm{OC\mathit{H}Me_2}$, ^3J(HH) 6.3 Hz
					5.92 (1) 5.77 (2)	3	s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					2.52 2.33 2.30 2.28	18	s s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
					1.39	12	dd $\mathrm{OCH(C\mathit{H}_3)_2}$, separation 59 Hz, ^3J(HH) 6.8 Hz
(1)	OBu^i	OBu^i	1 640 ^{c}		5.80 (2) 5.74 (1)	3	s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					5.15	4	d $\mathrm{OC\mathit{H}_2CHMe_2}$, ^3J(HH) 6.5 Hz
					2.53 2.31 2.21	18	s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
					1.90	2	q $\mathrm{OCH_2C\mathit{H}Me_2}$, ^3J(HH) 7.0 Hz
					0.95	6	dd $\mathrm{OCH_2CH(C\mathit{H}_3)_2}$, separation 10.0 Hz, ^3J(HH) 7.0 Hz
(1)	OEt	OPr^i	1 640 ^{c}		5.97	1	m $\mathrm{OC\mathit{H}Me_2}$ ^3J(HH) 6.1 Hz
					5.79 5.77 5.71	1 1 1	s s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					5.52	2	AB pair, J(AB) 12.0 Hz, δ(A) 5.59, δ(B) 5.45, ^3J(HH) 7.0 Hz, $\mathrm{OC\mathit{H}_2Me}$
					2.54 2.50 2.30 2.29	18	s s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
					1.40	3	t $\mathrm{OCH_2C\mathit{H}_3}$, ^3J(HH) 7.0 Hz
					1.38	6	dd separation 57.2 Hz, ^3J(HH) 5.9 Hz, $\mathrm{OCH(C\mathit{H}_3)_2}$
(1)	OPr^i	OBu^i	1 640 ^{c}		5.95	1	m $\mathrm{OC\mathit{H}Me_2}$, ^3J(HH) 6.4 Hz
					5.80 5.73	2 1	s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					5.17	2	AB pair poorly resolved; $\mathrm{OC\mathit{H}_2CHMe_2}$
					2.56 2.32	18	s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
					1.90	1	m $\mathrm{OCH_2C\mathit{H}Me_2}$
					1.39	6	dd separation 59.4 Hz, ^3J(HH) 6.6 Hz, $\mathrm{OCH(C\mathit{H}_3)_2}$
					0.95	6	dd separation 12 Hz, ^3J(HH) 6.9 Hz, $\mathrm{OCH_2CH(C\mathit{H}_3)_2}$
(2)	OEt	OEt	1 595 ^{c}		5.80 5.75	2 1	s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					5.54	4	AB pair, J(AB) 12 Hz, δ(A) 5.41, δ(B) 5.67, ^3J(HH) 7.0 Hz, $\mathrm{OC\mathit{H}_2Me}$
					2.63 2.36 2.29	18	s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
					1.39	6	t $\mathrm{OCH_2C\mathit{H}_3}$, ^3J(HH) 7.0 Hz
(1)	OMe	NH$_2$	1 635 ^{c} 1 637 ^{f}	3 380w ^{c} (NH) 3 280s ^{c} (NH) 3 340w ^{f} (NH) 3 340s ^{f} (NH)	8.40	2	br s NH$_2$
					5.80 5.77 5.73	3	s s s $\mathrm{C_3\mathit{H}Me_2N_2}$
					4.71	3	s OCH$_3$
					2.58 2.41 2.32 2.31 2.30 2.28	18	s s s s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$
(1)	OMe	NHMe	1 625 ^{c}	3 302 (NH)	9.68	1	br s $\mathrm{N\mathit{H}Me}$
					5.82	3	s $\mathrm{C_3\mathit{H}Me_2N_2}$
					4.70	3	s OCH$_3$
					4.34	3	d $\mathrm{NHC\mathit{H}_3}$, ^3J(HH) 7.0 Hz
					2.63 (1) 2.54 (1) 2.38 (3) 2.32 (1)	18	s s s s $\mathrm{C_3H(C\mathit{H}_3)_2N_2}$

TABLE 2 (*continued*)

Complex			I.r. data (cm^{-1})		^{1}H N.m.r. data		
	X	Y	ν(NO)	Other	δ [a]	A [b]	Assignments
(1)	OMe	NHEt	1 633 [c]	3 300 [c] (NH)	9.70	1	br s $N\mathit{H}Et$
			1 628 [f]	3 300 [f] (NH)	5.80	3	s $C_3\mathit{H}Me_2N_2$
					5.78		s
					5.77		s
					5.02 (1)	2	m ill defined AB pair, $NHC\mathit{H}_2Me$
					4.26 (1)		m
					4.64	3	s OCH_3
					2.58	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.47		s
					2.33		s
					2.31		s
					2.27		s
					1.30	3	t $NHCH_2C\mathit{H}_3$, ^3J(HH) 7.3 Hz
(1)	OEt	NH_2	1 630 [c]	3 400w (NH)	8.30	2	br s NH_2
				3 310s (NH)	5.81	3	s $C_3\mathit{H}Me_2N_2$
					5.79		s
					5.74		s
					5.07	2	q $OC\mathit{H}_2Me$, ^3J(HH) 7.8 Hz
					2.58	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.42		s
					2.38		s
					2.32		s
					2.30		s
					2.29		s
					1.37	3	t $OCH_2C\mathit{H}_3$, ^3J(HH) 7.3 Hz
(1)	OEt	NHMe	1 628 [e]	3 300 [c] (NH)	9.45	1	br s $N\mathit{H}Me$
			1 628 [f]	3 300 [f] (NH)	5.81	3	s $C_3\mathit{H}Me_2N_2$
					5.79		s
					5.04	2	m $OC\mathit{H}_2Me$
					4.28	3	d $NHC\mathit{H}_3$, J(HH) 7.3 Hz
					2.58	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.52		s
					2.37		s
					2.33		s
					2.32		s
					2.29		s
					1.31	3	t $OCH_2C\mathit{H}_3$, ^3J(HH) 7.4 Hz
(1)	OEt	NHEt	1 630 [e]	3 300 [c] (NH)	9.42	1	br s $N\mathit{H}Et$
			1 627 [f]	3 300 [f] (NH)	5.80	3	s $C_3\mathit{H}Me_2N_2$
					5.77		d
					5.01	2	q $OC\mathit{H}_2Me$, ^3J(HH) 7.0 Hz
					4.65	2	AB pair, ill defined, δ(A) 4.95, δ(B) 4.35, J(AB) 7.0, ^3J(HH) 7.0 Hz
					2.56	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.48		s
					2.37		s
					2.32		s
					2.30		s
					2.26		s
					1.29	6	2 t, overlapping, $OCH_2C\mathit{H}_3$ + $NHCH_2C\mathit{H}_3$, ^3J(HH) 7.0 Hz
					1.25		
(1)	OEt	$NHPr^n$	1 630 [e]	3 300 (NH)	9.56	1	br s $N\mathit{H}Pr^n$
					5.80	3	s $C_3\mathit{H}Me_2N_2$
					5.77		s
					5.01	2	AB pair, δ(A) 5.06, δ(B) 4.95, J(AB) 6.6 Hz, $OC\mathit{H}_2Me$, ^3J(HH) 7.0 Hz
					4.57	2	AB pair, m, δ(A) 4.90, δ(B) 4.23, $NHC\mathit{H}_2Et$
					2.57	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.50		s
					2.38		s
					2.33		s
					2.31		s
					2.27		s
					1.64	2	m $NHCH_2C\mathit{H}_2Me$
					1.30	3	t $OCH_2C\mathit{H}_3$, ^3J(HH) 6.9 Hz
					1.00	3	t $NHCH_2CH_2C\mathit{H}_3$, ^3J(HH) 6.8 Hz
(1)	OEt	$NHCH_2Ph$	1 625 [c]	3 290 (NH)	9.40	1	br s $N\mathit{H}CH_2Ph$
					7.20	5	m $NHCH_2C_6\mathit{H}_5$
					5.79	3	s $C_3\mathit{H}Me_2N_2$
					5.50		s
					5.69	2	AB pair, δ(A) 5.95, δ(B) 5.43, ^3J(HH) 7.0 Hz, J(AB) 16.0 Hz, $NHC\mathit{H}_2Ph$
					5.05	2	AB pair, δ(A) 5.11, δ(B) 4.99, J(AB) 5.8 Hz, $OC\mathit{H}_2Me$
					2.60	18	s $C_3H(C\mathit{H}_3)_2N_2$
					2.55		s
					2.33		s
					2.27		s
					2.14		s
					1.19	3	t $OCH_2C\mathit{H}_3$, ^3J(HH) 7.3 Hz

TABLE 2 (*continued*)

Complex			I.r. data (cm^{-1})		^{1}H N.m.r. data		
	X	Y	ν(NO)	Other	δ [a]	A [b]	Assignments
(1)	OEt	$\mathrm{NHC_6H_{11}}$	1 625 [c]	3 280 (NH)	9.41	1	br s $\mathrm{N}\mathit{H}\mathrm{C_6H_{11}}$
					5.80 5.74	3	s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					4.92	3	m $\mathrm{OC}\mathit{H}_2\mathrm{Me}$ and CH of $\mathrm{NHC_6H_{11}}$
					2.57 2.46 2.37 2.33 2.30 2.25	18	s s s s s s $\mathrm{C_3H(C}\mathit{H}_3)_2\mathrm{N_2}$
					1.85—1.10	10	m $\mathrm{C_6}\mathit{H}_{10}$ of $\mathrm{NHC_6H_{11}}$
					1.23	3	t $\mathrm{OCH_2C}\mathit{H}_3$, ^3J(HH) 7.2 Hz
(1)	OPr^i	$\mathrm{NH_2}$	1 637 [c]	3 410w (NH) 3 320s (NH)	8.10 [g]	1	br s $\mathrm{N}\mathit{H}_2$
					5.76 5.73 5.67	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					5.60	1	spt $\mathrm{OC}\mathit{H}\mathrm{Me_2}$, ^3J(HH) 6.0 Hz
					2.54 2.40 2.36 2.30 2.27	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3)_2\mathrm{N_2}$
					1.24	6	dd separation 10 Hz, $\mathrm{OCH(C}\mathit{H}_3)_2$, ^3J(HH) 6.0 Hz
(1)	OPr^i	NHMe	1 637 [c]	3 300 (NH)	9.22	1	br s $\mathrm{N}\mathit{H}\mathrm{Me}$
					5.79 5.77 5.75	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					5.55	1	spt $\mathrm{OC}\mathit{H}\mathrm{Me_2}$, ^3J(HH) 6.4 Hz
					4.19	3	d $\mathrm{NHC}\mathit{H}_3$, ^3J(HH) 8.3 Hz
					2.55 2.52 2.37 2.33 2.31	18	s s s s s $\mathrm{C_3H(C}\mathit{H}_3)_2\mathrm{N_2}$
					1.28	6	dd separation 22 Hz, $\mathrm{OCH(C}\mathit{H}_3)_2$, ^3J(HH) 6.6 Hz
(1)	OPr^i	NHEt	1 631 [c] 1 626 [f]	3 300 (NH) [c] 3 300 (NH) [f]	9.05	1	br s $\mathrm{N}\mathit{H}\mathrm{Et}$
					5.83 5.78 5.76	3	s s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					5.55	1	spt $\mathrm{OC}\mathit{H}\mathrm{Me_2}$, ^3J(HH) 5.90 Hz
					4.63	2	m ill defined AB pair, δ(A) 4.80, δ(B) 4.45, $\mathrm{NHC}\mathit{H}_2\mathrm{Me}$
					2.56 2.52 2.40 2.36 2.32 2.29	18	s s s s s s $\mathrm{C_3H(C}\mathit{H}_3)_2\mathrm{N_2}$
					1.30	6	dd, separation 35 Hz, $\mathrm{OCH(C}\mathit{H}_3)_2$, ^3J(HH) 6.8 Hz
					1.20	3	t $\mathrm{NHCH_2C}\mathit{H}_3$, ^3J(HH) 7.0 Hz
(1)	OPr^i	NHPr^i	1 638 [c] 1 638 [f]	3 280 (NH) [c] 3 250 (NH) [f]	8.95	1	br s $\mathrm{N}\mathit{H}\mathrm{Pr^i}$
					5.80 5.70	3	s s $\mathrm{C_3}\mathit{H}\mathrm{Me_2N_2}$
					5.44	1	spt $\mathrm{OC}\mathit{H}\mathrm{Me_2}$, ^3J(HH) 6.4 Hz
					5.14	1	m $\mathrm{NHC}\mathit{H}\mathrm{Me_2}$, ^3J(HH) 6.0 Hz
					2.53 2.50 2.38 2.36 2.29 2.25	18	s s s s s s $\mathrm{C_3H(C}\mathit{H}_3)_2\mathrm{N_2}$
					1.28	6	dd separation 44 Hz, $\mathrm{OCH(C}\mathit{H}_3)_2$, ^3J(HH) 6.4 Hz
					1.21	6	dd separation 74.8 Hz, $\mathrm{NHCH(C}\mathit{H}_3)_2$, ^3J(HH) 6.0 Hz

TABLE 2 (*continued*)

Complex			I.r. data (cm^{-1})		^1H N.m.r. data		
	X	Y	ν(NO)	Other	δ [a]	A [b]	Assignments
(1)	OPr^i	NHC_6H_{11}	1 633 [c] 1 624 [f]	3 270 (NH) [c] 3 290 (NH) [f]	9.11	1	br s NHC_6H_{11}
					5.84	3	s $C_3HMe_2N_2$
					5.76		s
					5.73		s
					5.44	1	spt $OCHMe_2$, ^3J(HH) 5.9 Hz
					4.73	1	m CH of NHC_6H_{11}
					2.57	18	s $C_3H(CH_3)_2N_2$
					2.50		s
					2.40		s
					2.38		s
					2.32		s
					2.28		s
					1.90—0.80	10	m C_6H_{10} of NHC_6H_{11}
					1.30	6	dd separation 35 Hz, $OCH(CH_3)_2$, ^3J(HH) 6.0 Hz

[a] In $CDCl_3$ solution at 220 MHz unless otherwise stated; relative intensities in parentheses. [b] Relative area. [c] In KBr disc. [d] Signals due to OH not observed because of exchange. [e] OH signal disappears on shaking with D_2O. [f] In $CHCl_3$. [g] At 100 MHz.

OH groups in (1; X = I, Y = OH) and (1; X = Y = OH), presumably because of rapid exchange between the hydroxyl proton and water in the solvent. However, the NH signal of (1; X = OR, Y = NHR′) was observed in the range δ = 8.95—9.70 p.p.m. which is significantly to higher field of that of (1; X = I, Y = NHR) (δ 12.40—12.90 p.p.m.). Furthermore, δ(NH) in (1; X = NH_2, Y = OR) occurs between 8.10 and 8.30 p.p.m., in contrast to (1; X = I, Y = NH_2) where δ(NH) = 11.64 p.p.m. These shifts also reflect the decrease in the electron-withdrawing properties of the metal as iodine in (1; X = I, Y = NHR) is replaced by OR.

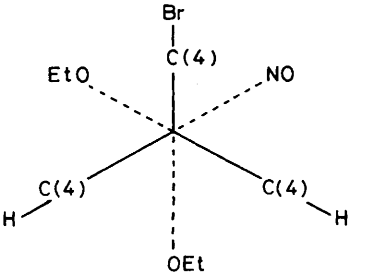

FIGURE 1 Idealised projection of (2; X = Y = OEt)

The spectra of the mixed alkoxides (1; X = OR, Y = OR′) and of the alkoxo-amido-species (1; X = OR, Y = NHR′) are consistent with their formulations, and cannot readily be interpreted as 1 : 1 mixtures of (1; X = Y = OR) and (1; X = Y = OR′) or of (1; X = Y = OR) and (1; X = Y = NHR).

Crystallographic Studies.—The structures of three bis-(alkoxo)-compounds have been determined (1; X = OR, Y = OR′; R = Et, R′ = Pr^i; R = R′ = Pr^i and Et). The structures of the two fully investigated molecules are illustrated in Figures 2 and 3, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables 5—8.

Both (1; X = OEt, Y = OPr^i) and (1; X = Y = OPr^i) exhibit a distorted octahedral co-ordination geometry around the molybdenum atom: each of the six pyrazolyl rings of the two tris(3,5-dimethylpyrazolyl)-borato-ligands is approximately planar with small out-of-plane deviations of the methyl groups and more variable deviations of the molybdenum: the metal-nitrosyl linkages are linear with normal bond lengths. The mixed alkoxo-compound shows intramolecular disorder of the alkoxy-groups but the existence of a distinct, triclinic crystalline form for the bis(isopropoxo)-complex strongly suggests that the mixed alkoxo-crystal does indeed comprise molecules as formulated and is not a 1 : 1

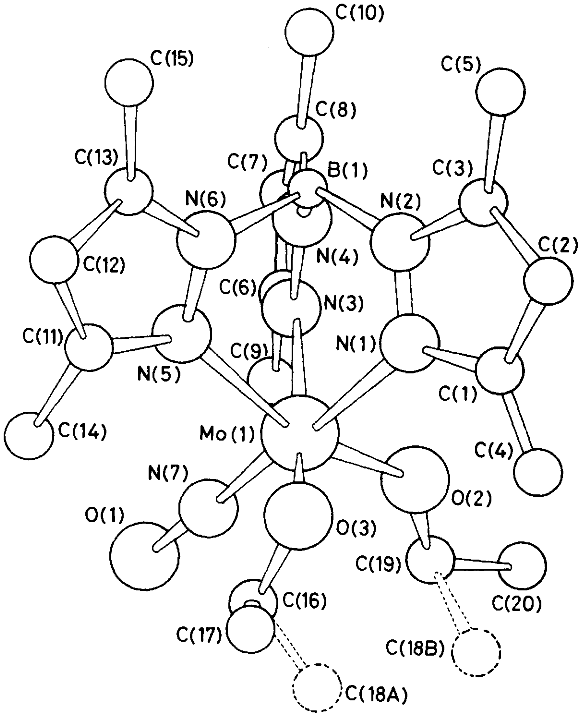

FIGURE 2 Molecular geometry of [Mo{HB($Me_2pz)_3$}(NO)-(OEt)(OPr^i)], (1; X = OEt, Y = OPr^i) with atom labelling

mixture of bis(ethoxo)- and bis(isopropoxo)-complexes. This conclusion is further strengthened by the observation that the positions for the two half-occupancy methyl groups are well within the van der Waals diameter at 3.0 Å; if the crystal were a mixture of bis complexes, both half-occupancy carbon atoms would need to be present in the bis(isopropoxy)-components. The corresponding intramolecular contact in the triclinic bis(isopropoxo)-complex is 3.8 Å. The geometry of the alkoxy-residues is rather better defined in the case of the bis(isopropoxo)-compound where no disorder effects occur.

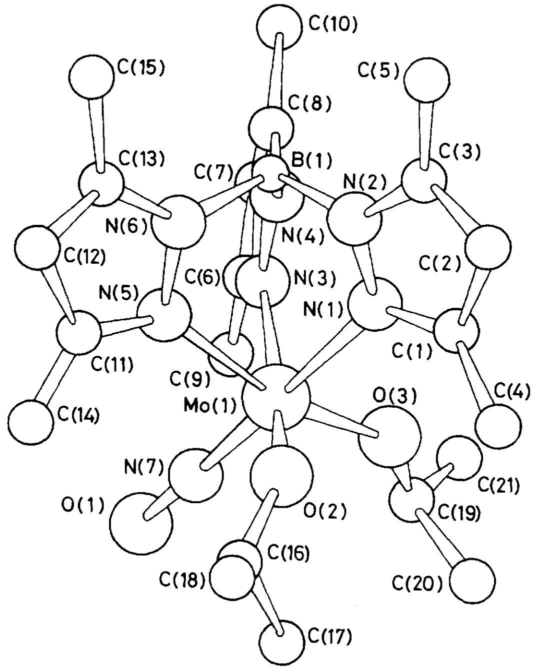

FIGURE 3 Molecular geometry of [Mo{HB(Me_2pz)$_3$}(NO)(OPr^i)$_2$], (1; X = Y = OPr^i) with atom labelling

It is thus possible to conclude that the structure of the isomorphous bis(ethoxo)-complex (see Experimental section) is derived from that of the mixed alkoxo-complex by the replacement of the two half-occupancy methyl groups by hydrogen atoms and a consequent but limited relaxation of the intramolecular structure to fill the vacancy left. That this interpretation is substantially correct was verified by the calculation of structure amplitudes for a selection of 17 {*hk*0} diffraction maxima for the two isomorphous crystal structures, including many which were, on a relative scale, detectably different from photographic data. The model for the bis(ethoxo)-complex was derived from the mixed alkoxo-complex by the removal of the two half-occupancy carbon atoms; the semi-quantitative relative changes in magnitude are substantially in agreement (Table 9).

The disordered mixed alkoxo-complex has approximate C_s symmetry, as would the proposed model for the bis(ethoxo)-complex. In order to prevent the close

TABLE 3

Fractional co-ordinates of all non-hydrogen atoms with their estimated standard deviations in parentheses for [Mo{HB(Me_2pz)$_3$}(NO)(OEt)(OPr^i)]

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	−0.224 64(3)	−0.111 85(3)	−0.006 25(6)
N(1)	−0.338 3(3)	−0.070 1(2)	0.125 2(5)
N(2)	−0.347 3(3)	−0.007 8(2)	0.138 1(5)
N(3)	−0.248 5(3)	−0.031 0(2)	−0.177 1(5)
N(4)	−0.272 5(3)	0.025 0(2)	−0.115 1(5)
N(5)	−0.136 6(3)	−0.038 6(2)	0.122 6(5)
N(6)	−0.175 4(3)	0.017 3(2)	0.157 4(5)
N(7)	−0.135 0(3)	−0.145 0(3)	−0.110 5(6)
B(1)	−0.273 5(4)	0.034 8(3)	0.074 0(8)
O(1)	−0.074 7(3)	−0.169 3(3)	−0.180 8(6)
O(2)	−0.325 8(3)	−0.152 8(2)	−0.130 5(5)
O(3)	−0.205 7(3)	−0.161 6(2)	0.189 7(5)
C(1)	−0.410 2(4)	−0.095 8(3)	0.193 8(7)
C(2)	−0.465 0(4)	−0.049 2(3)	0.250 5(7)
C(3)	−0.425 3(4)	0.005 7(3)	0.213 0(7)
C(4)	−0.425 0(5)	−0.164 4(3)	0.200 6(9)
C(5)	−0.457 3(4)	0.069 9(3)	0.242 1(9)
C(6)	−0.247 1(4)	−0.023 7(3)	−0.343 4(7)
C(7)	−0.269 3(4)	0.036 4(4)	−0.384 7(8)
C(8)	−0.284 6(4)	0.066 4(3)	−0.239 8(7)
C(9)	−0.222 5(5)	−0.074 5(4)	−0.456 2(8)
C(10)	−0.308 0(5)	0.131 9(4)	−0.212 9(10)
C(11)	−0.047 3(4)	−0.036 2(3)	0.189 5(7)
C(12)	−0.030 1(4)	0.019 9(3)	0.265 9(8)
C(13)	−0.110 5(4)	0.053 5(3)	0.243 0(7)
C(14)	0.019 6(4)	−0.088 8(4)	0.175 5(9)
C(15)	−0.128 1(5)	0.117 6(4)	0.295 7(9)
C(16)	−0.146 7(5)	−0.213 1(4)	0.223 0(10)
C(17)	−0.139 1(10)	−0.230 7(7)	0.387 2(13)
C(18A)	−0.192 6(15)	−0.268 4(7)	0.134(4)
C(18B)	−0.350 8(18)	−0.267 5(11)	−0.126(4)
C(19)	−0.325 4(5)	−0.201 3(5)	−0.246 7(12)
C(20)	−0.402 9(8)	−0.217 9(7)	−0.325 6(17)

TABLE 4

Fractional co-ordinates of all non-hydrogen atoms with their estimated standard deviations in parentheses for [Mo{HB(Me_2pz)$_3$}(NO)(OPr^i)$_2$]

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.280 52(5)	0.207 55(4)	0.072 60(7)
B(1)	0.555 7(6)	0.279 5(5)	−0.094 2(9)
N(1)	0.354 8(4)	0.327 7(3)	−0.076 6(6)
N(2)	0.472 9(4)	0.346 2(3)	−0.128 8(6)
N(3)	0.422 6(4)	0.129 3(3)	−0.097 9(6)
N(4)	0.524 3(4)	0.177 9(3)	−0.170 6(6)
N(5)	0.435 3(4)	0.247 7(3)	0.193 5(6)
N(6)	0.541 2(4)	0.277 9(3)	0.096 4(6)
N(7)	0.225 0(4)	0.113 5(3)	0.191 2(6)
O(1)	0.186 9(4)	0.049 6(3)	0.273 7(6)
O(2)	0.199 9(4)	0.303 0(3)	0.225 1(5)
O(3)	0.187 3(3)	0.178 1(3)	−0.093 4(5)
C(1)	0.303 1(6)	0.394 4(4)	−0.125 2(8)
C(2)	0.389 9(6)	0.455 3(4)	−0.210 0(8)
C(3)	0.494 5(6)	0.424 4(4)	−0.209 7(8)
C(4)	0.174 5(6)	0.399 8(5)	−0.083 3(11)
C(5)	0.614 8(7)	0.466 4(5)	−0.277 2(10)
C(6)	0.429 3(6)	0.038 8(4)	−0.162 7(8)
C(7)	0.532 7(6)	0.029 8(4)	−0.277 6(9)
C(8)	0.592 8(6)	0.117 4(4)	−0.279 3(8)
C(9)	0.337 7(7)	−0.038 0(4)	−0.108 6(9)
C(10)	0.711 4(7)	0.146 7(5)	−0.373 3(9)
C(11)	0.453 2(6)	0.248 9(4)	0.349 5(7)
C(12)	0.568 3(6)	0.279 4(4)	0.352 5(8)
C(13)	0.622 0(5)	0.295 6(4)	0.192 5(8)
C(14)	0.361 2(7)	0.219 9(5)	0.493 0(8)
C(15)	0.747 1(6)	0.324 7(5)	0.124 1(11)
C(16)	0.116 8(6)	0.301 7(6)	0.378 7(9)
C(17)	0.003 3(10)	0.260 4(12)	0.353 7(17)
C(18)	0.113 4(12)	0.395 2(8)	0.472 0(15)
C(19)	0.094 4(5)	0.106 7(4)	−0.116 8(8)
C(20)	−0.016 3(7)	0.152 8(6)	−0.092 4(13)
C(21)	0.124 0(8)	0.054 5(6)	−0.289 5(10)

TABLE 5

Bond lengths and angles with estimated standard deviations in parentheses for [Mo{HB($Me_2pz)_3$}(NO)(OEt)(OPr^i)]

Bond lengths (Å)

	Ring 1 [N(1), N(2), C(1)—C(5)]	Ring 2 [N(3), N(4), C(6)—C(10)]	Ring 3 [N(5), N(6), C(11)—C(15)]
Mo(1)–N(1)	2.235(5)	2.229(5)	2.221(5)
N(2)–B(1)	1.540(8)	1.532(8)	1.550(8)
N(1)–N(2)	1.362(6)	1.370(7)	1.376(6)
N(2)–C(3)	1.364(7)	1.341(8)	1.352(8)
C(3)–C(2)	1.368(9)	1.370(9)	1.368(9)
C(3)–C(5)	1.493(9)	1.482(10)	1.482(10)
C(2)–C(1)	1.390(8)	1.374(9)	1.373(9)
C(1)–N(1)	1.347(7)	1.344(8)	1.345(8)
C(1)–C(4)	1.504(9)	1.492(10)	1.507(10)

Bond angles (°)

	Ring 1	Ring 2	Ring 3
Mo(1)–N(1)–N(2)	121.2(3)	120.1(3)	119.9(3)
Mo(1)–N(1)–C(1)	131.5(4)	133.1(4)	133.8(4)
N(2)–N(1)–C(1)	107.1(4)	106.7(5)	106.3(4)
N(1)–N(2)–C(3)	109.7(4)	109.9(5)	109.7(5)
B(1)–N(2)–C(3)	130.7(5)	129.1(5)	129.1(5)
N(1)–N(2)–B(1)	119.6(5)	120.8(5)	120.2(4)
N(1)–C(1)–C(2)	108.9(5)	108.8(6)	109.4(5)
N(1)–C(1)–C(4)	122.8(5)	123.0(6)	122.5(6)
C(2)–C(1)–C(4)	128.3(6)	128.2(6)	128.1(6)
C(1)–C(2)–C(3)	107.1(5)	107.5(6)	107.5(6)
C(2)–C(3)–C(5)	129.2(6)	129.7(6)	129.0(6)
N(2)–C(3)–C(5)	123.6(5)	123.2(6)	123.9(6)
N(2)–C(3)–C(2)	107.2(5)	107.1(5)	107.1(5)

Other lengths and angles

Mo(1)–N(7)	1.768(5)	Mo(1)–N(7)–O(1)	178.1(5)
N(7)–O(1)	1.207(7)		

	Alkoxy 1 [O(3), C(16), C(17), C(18A)]	Alkoxy 2 [O(2), C(19), C(20), C(18B)]
Mo(1)–O(3)	1.901(4)	1.900(4)
O(3)–C(16)	1.415(9)	1.404(10)
C(16)–C(17)	1.36(2)	1.28(2)
C(16)–C(18A)	1.51(2)	1.79(3)
Mo(1)–O(3)–C(16)	129.5(4)	129.8(5)
O(3)–C(16)–C(17)	112.8(8)	118.3(10)
O(3)–C(16)–C(18A)	108.1(10)	103.1(10)
C(17)–C(16)–C(18A)	102.7(12)	79.8(12)

Angles around Mo and B

N(1)–Mo(1)–N(7)	179.9(2)	N(2)–B(1)–N(4)	109.1(5)
N(3)–Mo(1)–O(3)	162.39(17)	N(4)–B(1)–N(6)	106.7(5)
N(5)–Mo(1)–O(2)	161.74(17)	N(6)–B(1)–N(2)	110.2(5)

TABLE 6

Equations of least-squares planes in the molecule [Mo{HB($Me_2pz)_3$}(NO)(OEt)(OPr^i)] and deviations (Å) from the planes (in square brackets)

(*a*) Ring 1: N(1), N(2), C(1)—C(3)

$$-0.452X + 0.016Y - 0.892Z - 1.345 = 0$$

R.m.s. deviation: 0.0043

[N(1) 0.0017, N(2) −0.0049, C(1) 0.0020, C(2) −0.0050, C(3) 0.0061; C(4) 0.0288, C(5) 0.0416, Mo(1) 0.1274]

(*b*) Ring 2: N(3), N(4), C(6)—C(8)

$$0.957X + 0.248Y + 0.149Z + 3.674 = 0$$

R.m.s. deviation: 0.0030

[N(3) 0.0035, N(4) −0.0043, C(6) −0.0013, C(7) −0.0013, C(8) 0.0035; C(9) 0.0227, C(10) 0.0426, Mo(1) −0.0376]

(*c*) Ring 3: N(5), N(6), C(11)—C(13)

$$-0.358X - 0.367Y + 0.859Z - 1.891 = 0$$

R.m.s. deviation: 0.0049

[N(5) −0.0002, N(6) 0.0043, C(11) −0.0039, C(12) 0.0065, C(13) −0.0067; C(14) −0.0319, C(15) −0.0497, Mo(1) 0.1174]

TABLE 6 *continued*

Angles (°) between planes:

(*a*)—(*b*)	124.2
(*b*)—(*c*)	107.8
(*c*)—(*a*)	127.5

In the above plane definitions, the equations are in the form $lX + mY + nZ + p = 0$ where X, Y, and Z are Ångstrom co-ordinates referred to crystal axes *a*, *b*, and *c**.

approach of the two additional methyl groups, the two alkoxy-residues do not comply with the otherwise approximate C_s symmetry of the bis(isopropoxo)-complex.

The detailed geometries around the metal atoms in the two determined structures differ slightly in a manner entirely consistent with the greater steric considerations in the bis(isopropoxo)-complex. In these alkoxo-compounds (and in related amido-complexes), which approximate to D_{3d} (or to O_h) symmetry at the metal site, the

TABLE 7

Bond lengths and angles with estimated standard deviations in parentheses for [Mo{HB(Me$_2$pz)$_3$}(NO)(OPr^i)$_2$]

	Ring 1 [N(1), N(2), C(1)—C(5)]	Ring 2 [N(3), N(4), C(6)—C(10)]	Ring 3 [N(5), N(6), C(11)—C(15)]
Bond lengths (Å)			
Mo(1)–N(1)	2.240(5)	2.230(5)	2.240(5)
N(2)–B(1)	1.536(9)	1.547(8)	1.532(9)
N(1)–N(2)	1.367(7)	1.374(7)	1.381(7)
N(2)–C(3)	1.355(8)	1.351(8)	1.342(8)
C(3)–C(2)	1.356(9)	1.375(10)	1.361(9)
C(3)–C(5)	1.492(10)	1.483(10)	1.489(10)
C(2)–C(1)	1.395(9)	1.370(9)	1.379(9)
C(1)–N(1)	1.339(8)	1.341(8)	1.335(8)
C(1)–C(4)	1.484(10)	1.495(10)	1.481(10)
Bond angles (°)			
Mo(1)–N(1)–N(2)	121.2(3)	119.6(3)	119.4(3)
Mo(1)–N(1)–C(1)	131.4(4)	133.1(4)	134.3(4)
N(2)–N(1)–C(1)	107.3(5)	107.0(5)	106.3(5)
N(1)–N(2)–C(3)	109.4(5)	109.2(5)	109.5(5)
B(1)–N(2)–C(3)	131.4(5)	129.7(5)	129.4(5)
N(1)–N(2)–B(1)	119.2(5)	119.4(5)	120.9(5)
N(1)–C(1)–C(2)	108.5(6)	109.3(6)	109.5(6)
N(1)–C(1)–C(4)	122.7(6)	123.5(6)	123.6(6)
C(2)–C(1)–C(4)	128.8(6)	127.2(6)	126.9(6)
C(1)–C(2)–C(3)	107.2(6)	107.2(6)	107.0(6)
C(2)–C(3)–C(5)	129.0(6)	129.8(6)	129.3(6)
N(2)–C(3)–C(5)	123.4(6)	122.9(6)	123.0(6)
N(2)–C(3)–C(2)	107.6(5)	107.3(6)	107.7(6)

Other bond lengths and angles

Mo(1)–N(7)	1.757(5)	Mo(1)–N(7)–O(1)	179.4(5)
N(7)–O(1)	1.203(7)		
N(2)–B(1)–N(4)	109.9(5)	N(6)–B(1)–N(2)	110.2(5)
N(4)–B(1)–N(6)	107.0(5)	O(2)–Mo(1)–O(3)	102.7(2)
N(1)–Mo(1)–N(3)	85.2(2)	N(7)–Mo(1)–O(3)	98.0(2)
N(3)–Mo(1)–N(5)	76.0(2)	N(7)–Mo(1)–N(1)	178.8(2)
N(5)–Mo(1)–N(1)	83.9(2)	O(2)–Mo(1)–N(3)	161.8(2)
N(7)–Mo(1)–O(2)	97.0(2)	O(3)–Mo(1)–N(5)	161.5(2)

	Alkoxy 1 [O(2), C(16)—C(18)]	Alkoxy 2 [O(3), C(19)—C(21)]
Mo(1)–O(2)	1.908(4)	1.900(4)
O(2)–C(16)	1.412(9)	1.439(7)
C(16)–C(17)	1.442(16)	1.490(11)
C(16)–C(18)	1.453(15)	1.492(11)
Mo(1)–O(2)–C(16)	133.4(4)	133.4(4)
O(2)–C(16)–C(17)	112.2(8)	108.6(6)
O(2)–C(16)–C(18)	110.3(7)	109.4(5)
C(18)–C(16)–C(17)	113.1(7)	111.1(6)

three metal *d* orbitals which are formally σ-non-bonding comprise A_{1g} (d_{z^2} with opportunity for some mixing with *s*) and E_g (mainly $d_{x^2-y^2}/d_{xy}$) which become degenerate (T_{2g}) as D_{3d} approaches O_h. The lifting of this approximate degeneracy, resulting from the trigonal distortion of the molecule from local O_h symmetry,[12] is enhanced by the preferential use of one set of these orbitals in π-bond formation between metal and ligand. The orientation of the tris(dimethylpyrazolyl)borato-ligand permits metal(*d*)→ligand (π*) donation only *via* the metal E_g orbitals, since the pyrazolyl rings lie approximately parallel to the *z* axis. Thus, a spin-paired ground state is favoured and the A_{1g} orbital remains available for π donation from the alkoxy-ligands, as evidenced here by the short molybdenum–oxygen bond lengths. Such donation from the in-plane oxygen lone pair, rather than from the lone pair which lies perpendicular to the Mo–O–C plane, would result in the observed increase in the Mo–O–C bond angle; comparable bond-angle increases are observed in a monoisopropoxo-complex [2] and in a related monoethylamido-complex.[1] The orientations of the alkoxy-residues are such that the oxygen–carbon bonds all approximately eclipse the nitrosyl groups, as evidenced by the four molybdenum–oxygen torsion angles [+9.7 and −8.2° in the mixed alkoxo-complex; −3.5 and +3.5° in the bis(isopropoxy)-complex].* This alignment allows the alkoxy in-plane π donation to be enhanced by sharing a common molybdenum orbital (*e.g.* d_{xz} in an O_h co-ordinate axis system) with the strongly π-accepting nitrosyl ligand: thus, the advantageous π donation by the alkoxy-groups is facilitated.[1,2] The molybdenum–nitrogen(pyrazolyl) bond lengths in both

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* Similar conformations (Mo–N torsion angles +7.4 and −8.2°) are found in both independent molecules of a monoethylamido-complex previously reported [1] and in a related monoisopropoxo-complex (Mo–O torsion angle +8.2°).[2]

TABLE 8

Equations of least-squares planes in the molecule [Mo{HB($Me_2pz)_3$}(NO)($OPr^i)_2$] and deviations (Å) from the planes (in square brackets)

(*a*) Ring 1: N(1), N(2), C(1)—C(3)

$-0.166X - 0.569Y - 0.805Z = -2.300$

R.m.s. deviation: 0.0025

[N(1) 0.0009, N(2) 0.0013, C(1) −0.0027, C(2) 0.0035, C(3) −0.0030; C(4) −0.0675, C(5) −0.0562, Mo(1) −0.0788]

(*b*) Ring 2: N(3), N(4), C(6)—C(8)

$0.629X - 0.170Y + 0.759Z = 1.813$

R.m.s. deviation: 0.0071

[N(3) −0.0031, N(4) −0.0032, C(6) 0.0081, C(7) −0.0099, C(8) 0.0081; C(9) 0.0828, C(10) 0.0717, Mo(1) −0.1986]

(*c*) Ring 3: N(5), N(6), C(11)—C(13)

$-0.303X + 0.947Y + 0.106Z = 1.919$

R.m.s. deviation: 0.0063

[N(5) −0.0024, N(6) 0.0071, C(11) −0.0030, C(12) 0.0073, C(13) −0.0090; C(14) −0.0318, C(15) −0.0741, Mo(1) −0.0392]

Angles (°) between planes:

(*a*)—(*b*)	128.2
(*b*)—(*c*)	105.8
(*c*)—(*a*)	125.0

The equations defining the planes are in the form $lX + mY + nZ = p$ where X, Y, and Z are Ångstrom co-ordinates referred to crystal axes a, b^*, and c'.

TABLE 9

Comparison of observed and calculated structure amplitudes of a selection of {*hk*0} diffraction maxima for the bis(ethoxy)- and the ethoxoisopropoxo-compounds

		Calculated		Observed
h	k	$\lvert F_{hk0}$ (mixed)$\rvert$	$\lvert F_{hk0}$ $(OEt)_2\rvert$	$K(\lvert F_{hk0}$ $(OEt)_2\rvert - \lvert F_{hkl}$ (mixed)$\rvert)$
1	3	16.8	16.2	0.0
2	2	57.4	67.8	+12.2
2	3	13.6	11.2	−5.6
2	6	18.3	12.4	−5.8
2	8	101.8	97.0	−6.8
3	2	70.2	71.0	+2.0
3	5	51.9	51.4	0.0
3	9	33.2	34.0	0.0
4	0	90.2	95.2	0.0
4	4	62.0	58.4	0.0
4	7	75.4	72.8	−2.2
5	2	61.9	61.4	−7.2
5	8	26.7	24.2	−7.6
5	9	89.4	91.6	+4.0
6	0	69.4	74.6	+8.6
7	5	73.6	71.8	0.0
8	0	19.1	21.2	0.0

Intensities were estimated visually from photographic data and scaled together such that ΣI_{hkl} was the same from each set of 17 reflections; both sets of $\lvert F_{hkl}$ obs.$\rvert$ were scaled by $K = \Sigma\lvert F_{hkl}$ calc.$\rvert/\Sigma\lvert F_{hkl}$ obs.$\rvert$ for the mixed alkoxo-compound.

molecules are very similar and are at the long end of the range of lengths of bonds to such ligands. This reflects the more competitive π bonding (either forward or back donation) of each of the types of *trans* ligand and further confirms the substantial π involvement of alkoxides and of related alkylamido-ligands.[1]

EXPERIMENTAL

All reagents were used as purchased without further purification, except K[HB($Me_2pz)_3$] [11] and [W{HB(3,5-Me_2-4-BrC_3N_2)($Me_2pz)_2$}(NO)Br_2] [1] which were prepared as described elsewhere.

Molecular weights were determined osmometrically and i.r. spectra were measured using infracord 457, 297, and PE 180 spectrophotometers. Proton and ^{13}C n.m.r. spectra were obtained using PE R34 and JEOL PFT 90 instruments. Microanalyses were performed by the Microanalytical Laboratory of this Department, and all yields are quoted relative to the metal-containing starting materials.

All reactions were carried out under N_2 in degassed solvents.

[Mo{HB($Me_2pz)_3$}(NO)I(OH)].—A solution of [Mo{HB($Me_2pz)_3$}(NO)I_2] (0.5 g) and AgOCOMe (0.1 g) in acetone was stirred at room temperature for *ca.* 1 h, giving [Mo{HB($Me_2pz)_3$}(NO)I(OCOMe)] *in situ.* The precipitate of AgI was filtered off, six drops of water added, and the reaction mixture allowed to stir overnight. The reaction mixture was then filtered and the solvent removed *in vacuo* yielding the crude product. The *complex* was recrystallised from a dichloromethane–di-isopropyl ether mixture yielding dull green crystals (0.2 g, 55%).

[Mo{HB($Me_2pz)_3$}(NO)I(OC_6H_{11})].—A solution of [Mo{HB($Me_2pz)_3$}(NO)I_2] (0.5 g) and an excess of cyclohexanol (0.2 g) in methylcyclohexane (40 cm^3) was stirred and refluxed for *ca.* 1.5 h. The solution was then cooled, partially evaporated *in vacuo*, filtered, and stored at −15 °C to aid crystallisation. The *complex* was obtained after filtration as dark green crystals (0.1 g, 21%).

[Mo{HB($Me_2pz)_3$}(NO)I($OCH_2C{\equiv}CCH_2OH$)].—A solution of [Mo{HB($Me_2pz)_3$}(NO)I_2] and an excess of but-2-yne-1,4-diol (0.2 g) in methylcyclohexane (30 cm^3) was stirred and refluxed for 2 h. The solution was filtered while hot, partially evaporated *in vacuo*, and allowed to stand overnight, when the product precipitated. The complex was obtained after filtration as lime green microcrystals (0.26 g, 55%).

[Mo{HB($Me_2pz)_3$}(NO)$(OH)_2$].—A mixture of [Mo{HB($Me_2pz)_3$}(NO)I_2] (0.5 g), AgOCOMe (0.15 g), and water (six drops) was stirred in acetone (30 cm^3) at room temperature overnight. The AgI was filtered from the pink-brown solution which was then partially evaporated *in vacuo*. Addition of n-heptane (10 cm^3) caused the product to precipitate as a pale brown-pink powder. The excess of water in the compound was removed by pumping *in vacuo* on the powder overnight (yield 0.18 g, 53%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OMe)_2}]$.—Silver acetate (0.1 g) was added to $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OMe)}]$ in methanol–methylcyclohexane (20 cm^3 : 40 cm^3) and the mixture was stirred and refluxed gently for 24 h. The precipitate of AgI was filtered off and the solvent evaporated *in vacuo* yielding the crude product. Purification was effected by crystallisation from methanol–methylcyclohexane giving deep pink crystals of the *complex* which were collected by filtration (yield 0.3 g, 72%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)_2}]$.—*Method* 1. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ and AgOCOMe (0.1 g) in ethanol–methylcyclohexane (20 cm^3 : 60 cm^3) was stirred at room temperature for 24 h. The precipitate of AgI was filtered off and the solution was left to stand yielding deep pink crystals of the *complex* which were collected by filtration (yield 0.3 g, 69%).

Method 2. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ and triethylamine (0.1 cm^3) in methylcyclohexane–ethanol (40 cm^3 : 20 cm^3) was stirred and refluxed for *ca.* 2 h. The mixture was then cooled and the solvent removed *in vacuo*. The residue was dissolved in hot methylcyclohexane (40—50 cm^3) and filtered to remove any triethylammonium iodide. The desired *compound* then slowly crystallised from the filtrate as dark pink crystals which were collected by filtration (yield 0.16 g, 30%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)_2}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.5 g) and AgOCOMe (0.1 g) in methylcyclohexane–isopropyl alcohol (40 cm^3 : 20 cm^3) was stirred and refluxed for 24 h. The AgI was filtered off and the filtrate was left to stand for a few days, the desired product crystallising out as bright pink needle-like crystals. The *complex* was collected by filtration (yield 0.31 g, 70%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OCH_2Pr^i)_2}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2Pr^i)}]$ (0.3 g) and AgOCOMe (0.1 g) in n-heptane–isobutyl alcohol (40 cm^3 : 10 cm^3) was stirred and refluxed for 3 h. The precipitate of AgI was filtered off and the product crystallised from the filtrate over a couple of weeks as pink crystals. The *complex* was isolated by filtration (yield 0.14 g, 52%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(OPr^i)}]$.—Silver acetate (0.1 g) was added to a solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.5 g) in a mixture of methylcyclohexane–ethanol (40 cm^3 : 10 cm^3) and the mixture was stirred for *ca.* 24 h. The AgI was filtered off and the solvent removed *in vacuo* affording the crude product. The desired compound was obtained from this by recrystallisation from methylcyclohexane, and the *complex* was isolated by filtration as pink crystals (0.3 g, 69%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)(OCH_2Pr^i)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.3 g) and AgOCOMe (0.1 g) was stirred at room temperature for 20 h in a mixture of n-heptane (40 cm^3) and $\mathrm{Bu^iOH}$ (10 cm^3). The AgI was filtered off and the solvent removed *in vacuo*. The *complex* was recrystallised from methylcyclohexane over a long period giving a dark pink microcrystalline compound which was collected by filtration (yield 0.17 g, 63%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OMe)(NH_2)}]$.—Ammonia (*d* 0.88, 0.1 cm^3) was added to a solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OMe)}]$ (0.25 g) in di-isopropyl ether and the reaction mixture stirred at room temperature for *ca.* 1 h. The resulting orange solution was filtered under nitrogen and evaporated slowly until precipitation commenced. The *complex* was obtained as a yellow microcrystalline compound and was isolated by filtration (yield 0.13 g, 65%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(NH_2)}]$.—This compound was prepared by treating $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ (0.25 g) with ammonia solution (0.1 cm^3) using the same method as described in the preceding preparation, the reaction time being *ca.* 15 h. The desired *product* was obtained as bright orange microcrystals (0.09 g, 45%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)(NH_2)}]$.—This compound was prepared from $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.25 g) using a method similar to that outlined for the methoxo-derivative above, the reaction time being *ca.* 40 h. The *complex* was isolated as a dull yellow powder (0.1 g, 50%).

The three preparations outlined above can also be carried out using dichloromethane as a solvent. However, it was found very difficult to repeat these experiments consistently.

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OMe)(NHMe)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OMe)}]$ (0.3 g) and an excess of methylamine (33% aqueous solution, 0.1 cm^3) in dichloromethane (40 cm^3) was stirred for 30 min at room temperature. The solution was concentrated to *ca.* 10 cm^3 *in vacuo*, and on addition of di-isopropyl ether (20 cm^3) the desired *complex* precipitated as deep orange crystals which were collected by filtration (yield 0.18 g, 72%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(NHMe)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ (0.25 g) in di-isopropyl ether was stirred at room temperature for *ca.* 24 h with methylamine (33% aqueous solution, 0.15 cm^3). The mixture was filtered and slowly evaporated until crystallisation commenced. The *complex* was isolated by filtration as an orange microcrystalline product (0.13 g, 62%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)(NHMe)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.2 g) and an excess of methylamine (33% aqueous solution, 0.08 cm^3) in dichloromethane (30 cm^3) was stirred at room temperature for *ca.* 20 h. After addition of di-isopropyl ether the solution was filtered to remove any methylammonium iodide. The solvent was removed *in vacuo* yielding the crude product which was recrystallised from di-isopropyl ether–n-pentane giving orange crystals (0.11 g, 65%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OMe)(NHEt)}]$.—Ethylamine (0.1 cm^3) was added to a dichloromethane solution (30 cm^3) of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OMe)}]$ (0.3 g) and the reaction mixture was stirred at room temperature for 2—3 h. The solvent was removed *in vacuo* and the product extracted into di-isopropyl ether (30 cm^3). The extract was filtered, n-pentane was added, and the mixture was concentrated *in vacuo*. The *product* slowly crystallised on standing giving a bright orange microcrystalline compound (0.15 g, 57%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(NHEt)}]$.—The compound was prepared by the method described above, but using only 1 h for the reaction. The *product* was similarly isolated as orange microcrystals (0.1 g, 57%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)(NHEt)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.3 g) and ethylamine (0.15 cm^3) in di-isopropyl ether (30 cm^3) was stirred at room temperature for *ca.* 30 h. The solution was filtered and the filtrate concentrated *in vacuo* yielding the *product* as a yellow powder (0.11 g, 42%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(NHPr^n)}]$.—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ (0.3 g) and an excess of n-propylamine (0.2 cm^3) in dichloromethane (30 cm^3) was stirred for *ca.* 1.5 h at room temperature. The solvent was removed *in vacuo* and the residue treated with di-isopropyl ether (20 cm^3). The mixture was filtered and the *product* formed as a dark yellow powder. Recrystallisation was effected from an ethanol–di-isopropyl ether mixture (yield 0.15 g, 57%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)(NHPr^i)}]$.—Isopropylamine (0.2 cm^3) was added to a solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OPr^i)}]$ (0.5 g) in dichloromethane (40 cm^3) and was stirred at room temperature for 7 d. The solvent was removed *in vacuo*, the residue extracted in di-isopropyl ether, and the extract filtered. The *product* was isolated as a lemon-yellow powder upon concentration of the filtrate and was collected by filtration (yield 0.14 g, 32%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OR)(NHC_6H_{11})}]$ (R = Et *or* Pr^i).—A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OR)}]$ (R = Et or Pr^i) (0.4, 0.3 g) and an excess of cyclohexylamine (0.15 cm^3) in dichloromethane (40 cm^3) was stirred at room temperature (R = Et, 65 h; R = Pr^i, 6 d). The solvent was concentrated to a few cm^3 *in vacuo*, an excess of di-isopropyl ether was added, and the mixture then filtered. The process was repeated using n-pentane leading to the isolation of the *product*. Where R = Et the *product* precipitated as orange microcrystals from the n-pentane (yield 0.1 g, 26%). Where R = Pr^i, the compound was isolated as a lemon-yellow powder (0.08 g, 28%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(NHCH_2Ph)}]$.—This compound was prepared by treating $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ (0.3 g) with an excess of benzylamine (0.1 cm^3) using the method described above. The reaction was left for 3.5 h, and the *product* was isolated from di-isopropyl ether–n-pentane as an orange-brown powder (0.11 g, 38%).

$[\mathrm{W\{HB(Me_2pz)_2(C_3BrMe_2N_2)\}(NO)Br(OMe)}]$.—A mixture of $[\mathrm{W\{HB(Me_2pz)_2(C_3BrMe_2N_2)\}(NO)Br_2}]$ (2.0 g) and methanol (20 cm^3) in methylcyclohexane (100 cm^3) was refluxed for 4 h, during which time the mixture became homogeneous, and its colour changed from green to violet. After cooling and filtration, the solvent was evaporated *in vacuo* giving a purple solid. This solid was recrystallised from a mixture of dichloromethane and methanol affording the *complex* as purple crystals (0.3 g, 16%).

$[\mathrm{W\{HB(Me_2pz)_2(C_3BrMe_2N_2)\}(NO)Br(OEt)}]$.—The complex $[\mathrm{W\{HB(Me_2pz)_2(C_3BrMe_2N_2)\}(NO)Br_2}]$ (2.6 g) was refluxed in ethanol (60 cm^3) for 30 min. The ethanol was then partially evaporated *in vacuo* and then cooled at 5 °C. The *complex* was formed as purple crystals which were collected by filtration (yield 1.7 g, 68%).

$[\mathrm{W\{HB(Me_2pz)_2(C_3BrMe_2N_2)\}(NO)Br(OPr^i)}]$.—This compound was prepared in the same way as its methoxide analogue, using (2; X = Y = Br) (1.5 g) and propan-2-ol (15 cm^3). The *complex* was obtained as purple crystals (0.35 g, 24%).

Reaction of $[\mathrm{W\{HB(Me_2pz)_3\}(NO)(CO)_2}]$ *with Iodine, and Reaction of the Product with Ethanol:* $[\mathrm{W\{HB(Me_2pz)_3\}(NO)(OEt)_2}]$.—Iodine (3.0 g) was Soxhlet-extracted into a partial solution of $[\mathrm{W\{HB(Me_2pz)_3\}(NO)(CO)_2}]$ (6.6 g) in methylcyclohexane (150 cm^3). After 74 h, the mixture was cooled to -10 °C, and the dark brown solid which precipitated was filtered off, washed with n-pentane (to remove residual iodine), and dried *in vacuo*. The *product* was obtained as a chocolate-brown microcrystalline powder (6.3 g). However, this complex did not analyse closely as $[\mathrm{W\{HB(Me_2pz)_3\}(NO)I_2}]$ nor as its likely ring-iodinated analogues, although its i.r. and n.m.r. spectra were reasonably consistent with its formulation as a di-iodo-product. I.r. spectrum (KBr disc): 1 675 cm^{-1}, ν(NO). Proton n.m.r. spectrum (CDCl$_3$), δ (relative area): 6.12(s) and 5.89(s) (1 : 2, overall 1), and 2.83(s), 2.52(s), 2.35(s), and 2.31(s) (overall 6).

The brown product of the above reaction was refluxed in ethanol (100 cm^3) for 1 h, during which time a green-brown solution was formed. On cooling, filtration, and evaporation of the filtrate *in vacuo*, a yellow-brown precipitate of $[\mathrm{W\{HB(Me_2pz)_3\}(NO)(OEt)_2}]$ (0.5 g) was obtained.

X-*Ray Crystallographic Studies.*—*Crystal data.* $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)(OPr^i)}]$, (1; X = OEt, Y = OPr^i), $\mathrm{C_{20}H_{34}BMoN_7O_3}$, $M = 527.3$, crystallises from methylcyclohexane as orange, elongated crystals, crystal dimensions 0.10 × 0.09 × 0.34 mm, monoclinic, $a = 14.46(4)$, $b = 21.67(6)$, $c = 8.015(14)$ Å, $\beta = 96.08(3)°$, $U = 2\,497(10)$ Å^3, $D_m = 1.36$, $Z = 4$, $D_c = 1.36$ g cm^{-3}, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14 C^5_{2h}), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 5.4 cm^{-1}, $F(000) = 1096$.

Three-dimensional X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stöe Stadi-2 diffractometer by the omega-scan method. 2 503 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. On each alkoxide group there appeared one methyl group with full occupancy and one with half occupancy. Hydrogen atoms were placed in calculated positions (C–H 0.95, B–H 1.10 Å); those of the methyl groups were not resolved and their contributions were approximated by inclusion of six half-population hydrogen atoms distributed around the annulus (C–C–H 110 °). Their contributions were included in structure-factor calculations ($B = 10.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0388 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum. Table 3 lists the atomic positional parameters with estimated standard deviations.

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OPr^i)_2}]$, (1; X = Y = OPr^i), $\mathrm{C_{21}H_{36}BMoN_7O_3}$, $M = 541.3$, crystallises from methylcyclohexane–isopropyl alcohol as orange plate-like needles, crystal dimensions 0.12 × 0.03 × 0.37 mm, triclinic, $a = 11.758(8)$, $b = 14.403(9)$, $c = 8.173(14)$ Å, $\alpha = 97.970(16)$, $\beta = 77.30(3)$, $\gamma = 96.523(7)°$, $U = 1\,332(2)$ Å^3, $D_m = 1.36$, $Z = 2$, $D_c = 1.31$ g cm^{-3}, space group $P\bar{1}$ (assumed and confirmed by the analysis), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 5.1 cm^{-1}, $F(000) = 548$.

The data were collected ($6.5 < 2\theta < 50°$) and processed (2 605 independent reflections) and the structure solved and refined (R 0.0398) as for the mixed alkoxo-compound above (hydrogen isotropic thermal parameters $B = 7.0$ Å^2). Table 4 lists atomic positions and estimated standard deviations.

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)_2}]$, (1; X = Y = OEt), $M = 513.3$, crystallises from methylcyclohexane–ethanol as orange needles, monoclinic, $a = 14.73$, $b = 21.09$, $c = 8.00$ Å, $\beta = 94.80°$, $U = 2\,476$ Å^3, $D_m = 1.36$, $Z = 4$, $D_c = 1.38$ g cm^{-3}, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14, C^5_{2h}), $F(000) = 1\,064$.

The similarities of unit-cell constants and only small but detectable differences in photographically collected diffraction data as compared with those of the mixed alkoxo-compound above clearly show that the structures are isomorphous. In view of the determined structure of the mixed alkoxo-compound (see Discussion section), an independent structural determination of the bis(ethoxo)-complex was not undertaken.

For both structures, tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters, and observed structure amplitudes and calculated structure factors are deposited in Supplementary Publication No. SUP 23246 (56 pp.).* Scattering factors were taken from ref. 13; unit weights were used throughout both refinements. Computer programs formed part of the Sheffield *X*-ray system.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.