The Chemistry of Cyclopentadienyl and Related Nitrosyl Complexes of Molybdenum. Part V.[1] Dihalogenonitrosyl[tris(pyrazolyl)borato]molybdenum Complexes, their Alcoholysis, and the Crystal Structure of Chloronitrosylisopropoxo[tris(4-chloro-3,5-dimethylpyrazolyl)borato]molybdenum

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Halogenation of $[Mo\{HB(3,5\text{-}R_2C_3HN_2)_3\}(NO)(CO)_2]$ gives $[\{Mo[HB(3,5\text{-}R_2\text{-}4\text{-}XC_3N_2)_3](NO)Y_2\}_n]$ (R = X = H, Y = Cl, Br, or I, *n* = 2; R = Me, X = H, Y = Cl, Br, or I; *n* = 1; R = Me, X = Cl or Br, Y = Cl or Br, *n* = 1). These halides react with alcohols affording $[Mo\{HB(3,5\text{-}R_2\text{-}4\text{-}XC_3N_2)_3\}(NO)Y(OR')]$ (R' = Me, Et, Pr^i, Bu^s, or $CH_2CH{:}CH_2$), the ^1H and ^{13}C n.m.r. spectra of which are discussed. The crystal structure of $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OPr^i)]$ has been determined by *X*-ray diffraction methods using counter data and refined by block-diagonal least-squares procedures, to *R* 0.047 for 2 450 reflections. The monoclinic unit-cell, space-group $P2_1/n$, has dimensions *a* = 12 268(4), *b* = 16.041(4), *c* = 15.033(5) Å, β = 91.44(4)° for *Z* = 4. The molybdenum atom has octahedral co-ordination and both the Mo–Cl and, particularly, the Mo–O distances are short. The Mo–O bond length (1.86 Å) indicates significant Mo=OR bonding and $p_\pi \rightarrow d_\pi$ donation from the alkoxy-group to the metal is discussed in terms of the apparent co-ordinative unsaturation of the alkoxide complexes.

It has been shown [2] that there are strong analogies between the behaviour of metal complexes containing tris-pyrazolylborato-anions, $[RB(C_3R'R''_2N_2)_3]^-$, and those containing the η^5-cyclopentadienyl ligand. Thus $[HB(C_3HR_2N_2)_3]^-$ reacts [3] with $[Mo(CO)_6]$ affording the carbonylate ion $[Mo\{HB(C_3HR_2N_2)_3\}(CO)_3]^-$, the chemistry of which is very similar to that of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$. Indeed, acidification followed by nitrosylation of the pyrazolylborate complex afforded $[Mo\{HB(C_3HR_2N_2)_3\}(NO)(CO)_2]$, in a way entirely similar to the preparation of $[Mo(\eta^5\text{-}C_5H_5)(NO)(CO)_2]$.

It has been reported [4] that the reaction of $[Mo\{HB(C_3HR_2N_2)_3\}(NO)(CO)_2]$ with NOCl gave initially $[Mo\{HB(C_3HR_2N_2)_3\}(NO)_2Cl]$ and then $[\{Mo[HB(C_3HR_2N_2)_3](NO)Cl_2\}_n]$. Although the former has no reported analogue in η^5-cyclopentadienyl molybdenum chemistry,† the latter is directly comparable to $[\{Mo(\eta\text{-}C_5H_5)(NO)Cl_2\}_2]$.[5] Whilst this cyclopentadienyl complex, like its bromo- [5] and iodo- [6] analogues, has an extensive chemistry (reacting readily with tertiary phosphines,[5,6] isocyanides,[7] hydrazines,[8] and thiols [6,9]), the chemistry of the pyrazolylborate has not been explored. The potential existence of these two parallel series of compounds thus presented a unique opportunity to compare the relative steric and electronic properties of the $HB(C_3HR_2N_2)_3$ and $\eta^5\text{-}C_5H_5$ ligands.

In this paper, we describe the synthesis of dihalogeno-complexes, their reactions with alcohols and with some Lewis bases, and the structure of a representative member of the general group of compounds $[\{Mo[HB(C_3HR_2N_2)_3](NO)XY\}_n]$ (R = H, *n* = 2; R = Me, *n* = 1). Since we began our work, alternative syntheses of $[\{Mo[HB(C_3H_3N_2)_3](NO)X_2\}_2]$ (M = Mo or W) have been briefly mentioned.[10]

RESULTS

Synthetic Studies.—Halogenation at room temperature of $[Mo\{HB(3,5\text{-}C_3HR_2N_2)_3\}(NO)(CO)_2]$ (R = H or Me) in CCl_4 (X = Cl or Br) or hexane (X = I) afforded $[\{Mo[HB(C_3HR_2N_2)_3](NO)X_2\}_n]$ (R = H, *n* = 2; R = Me, *n* = 1). In CCl_4, $[Mo\{HB(C_3HMe_2N_2)_3\}(CO)_2(NO)]$ reacted with iodine giving only $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Cl_2]$ (see Experimental section). It was essential that the reaction stoicheiometry was strictly adhered to, otherwise halogenation of the pyrazole rings occurred. Indeed, reaction of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ with an excess of Cl_2 or Br_2 afforded $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}X\text{-}C_3N_2)_3\}(NO)X_2]$. Apparently, specific metal halogenation can also be achieved in dichloromethane at −70 °C.[10] All the complexes could be recrystallised from hot toluene without decomposition, and only $[\{Mo[HB(C_3H_3N_2)_3](NO)Cl_2\}_2]$ retained solvent of crystallisation; satisfactory analytical data were obtained (Table 1).

Unlike their η^5-cyclopentadienyl analogues, the new tris-pyrazolylborato-complexes did not form adducts with PPh_3, $AsPh_3$, $PMePh_2$, or pyridine. Unstable and uncharacterisable adducts were apparently formed with methyl isocyanide, and although reactions occurred with hydrazines, pure products could not be isolated. However, in neat $P(OEt)_3$, the adduct $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)\{P(OEt)_3\}Br_2]$ was formed. The reasons for this

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† $[(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl]$ is, however, well characterised; T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 28; **3**, 104.

Note added in proof: $[Mo(\eta^5\text{-}C_5H_5)(NO)_2Cl]$ has recently been synthesised (R. P. Stewart and G. T. Moore, *Inorg. Chem.*, 1975, **14**, 2699).

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[2] S. Trofimenko, *Accounts Chem. Res.*, 1971, **4**, 17.

[3] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588 and 1967, **89**, 3904.

[4] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

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[6] R. B. King, *Inorg. Chem.*, 1967, **6**, 30; T. A. James and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1941, 1068.

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[8] W. G. Kita, J. A. McCleverty, B. E. Mann, D. Seddon, G. A. Sim, and D. I. Woodhouse, *J.C.S. Chem. Comm.*, 1974, 132; N. A. Bailey, P. D. Frisch, J. A. McCleverty, N. W. J. Walker, and J. Williams, *ibid.*, 1975, 350.

[9] J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2588.

[10] M. E. Deane and F. J. Lalor, *J. Organometallic Chem.*, 1974, **67**, C19.

relative inability to form stable adducts are presumably steric, especially with respect to complexes containing $[HB(C_3HMe_2N_2)_3]$. It is notable that $P(OEt)_3$ is sterically less bulky than PPh_3, having a significantly smaller ‘ cone angle ’.[11]

We discovered that the dihalides dissolved in alcohols to give deep green or blue solutions from which green or blue crystals of the alkoxo-halides $[Mo\{HB(C_3HR_2N_2)_3\}(NO)(OR')X]$ ($R' =$ Me, Et, Pr^i, Bu^t, Bu^s, or C_3H_5) were isolated. During attempts to recrystallise from ethanol the pyrazolylborate with X = Br, R = Me, and $R' = C_3H_5$, alkoxide exchange occurred, giving $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(OEt)Br]$. On prolonged refluxing of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br_2]$ in ethanol, or on treatment of the ethoxobromide with zinc dust in ethanol (in an attempt to form $[\{Mo[HB(C_3HMe_2N_2)_3](NO)(OEt)\}_2]$), the diethoxide, $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(OEt)_2]$ was formed.

TABLE 1

Analytical (%) and molecular-weight data obtained from $[\{Mo[HB(3,5\text{-}R_2\text{-}4\text{-}XC_3N_2)_3](NO)YZ\}_n]$

				Calc.				Found				*M*
R	X	Y	Z	C	H	N	Hal	C	H	N	Hal	(calc.) [a]
H	H	CO	CO	33.4	2.5	24.8		33.8	2.7	25.2		
Me	H	CO	CO	42.6	4.6	20.5		42.9	4.9	20.8		
H	H	Cl	Cl [b]	32.8	3.9	21.0	15.6	32.4	3.3	21.3	15.6	
H	H	Br	Br	21.6	2.0	19.5	32.1	20.9	2.1	20.0	31.9	
H	H	I	I	18.2	1.7	16.5	*c*	18.4	1.8	15.3	*c*	
Me	H	Cl	Cl	36.4	4.5	19.8	14.4	36.2	4.7	19.6	14.1	529 (494)
Me	Cl	Cl	Cl	30.1	3.2	16.4	29.7	30.0	3.4	16.3	29.1	
Me	H	Br	Br	30.9	3.8	16.8	27.4	31.3	3.9	16.7	27.1	634 (583)
Me	Br	Br	Br	22.0	2.3	12.0	48.8	21.4	2.2	11.6	47.0	
Me	H	I	I	26.6	3.2	14.5	37.5	27.3	3.3	14.8	37.8	761 (677)
H	H	Br	OMe	26.7	2.9	21.8	17.8	26.6	3.0	21.6	17.9	
Me	H	Cl	OEt	40.5	5.4	19.5	7.1	40.6	5.6	19.4	7.2	531 (504)
Me	H	Cl	OPr^i	41.7	5.6	18.9	6.9	41.6	5.9	18.5	6.9	
Me	Cl	Cl	OPr^i	35.5	3.9	14.8	21.4	35.4	3.9	14.2	20.8	
Me	H	Br	OEt	37.2	4.9	17.9	14.6	38.0	5.3	17.8	17.3	557 (548)
Me	Br	Br	OEt	26.0	3.1	12.5	40.8	25.4	3.0	12.0	41.2	
Me	H	Br	OPr^i	38.4	5.2	17.4	14.2	38.5	5.3	17.1	14.5	
Me	H	Br	OC_3H_5	38.6	4.8	17.5	14.3	39.9	5.4	18.0	15.8	562 (562)
Me	H	I	OEt	34.3	4.5	16.5	21.3	36.3	4.9	16.7	20.0	633 (595)
Me	H	I	OPr^i	35.5	4.8	16.1	20.9	35.7	5.1	16.0	21.0	
Me	H	OEt	OEt	44.4	6.2	19.1		43.7	6.0	18.6		
Me	H	Br	Br [d]	37.7	5.5	14.6	11.9	37.6	5.1	14.9	12.2	

[a] Osmometric determination in $CHCl_3$. [b] This molecule contains a mole equivalent of toluene. [c] Not determined. [d] Complex containing one mole equivalent of $P(OEt)_3$.

The complexes containing $[HB(C_3H_3N_2)_3]$ were generally too insoluble in suitable solvents for molecular-weight determinations. However, those species containing $[HB(C_3HMe_2N_2)_3]$ were apparently monomeric in chloroform (Table 1) although, generally, the observed molecular weight (osmometric) was always higher (*ca.* 6%) than that calculated for a monomeric unit. This suggested that the complexes, particularly those containing $[HB(C_3H_3N_2)_3]$, might be dimeric in the solid state but dissociated substantially in solution. Such a situation was observed in the species $[\{Mo(\eta^5\text{-}C_5H_5)(NO)XY\}_n]$ ($n = 1$ or 2; X = Y = halide;[5,6] X = halide, Y = SR and possibly X = Y = SR).[9] These observations are supported to some extent by mass spectral information which indicates the presence of bimetallic ions derived by fragmentation of $[\{Mo[HB(C_3H_3N_2)_3](NO)X_2\}_2]$ (X = Cl or Br) $[\{M\}_2]$. Thus, ions corresponding to m/e values such as $[\{M - X\}_2]^+$, $[\{M - NO - X\}_2X]^+$, $[\{M - NO - X\}_2]^+$, $[\{M - NO - X\}NO]^+$, and $[\{M - NO - 2X\}X]^+$, together with fragments derived from $[M]^+$ ($n = 1$), were detected. All of the other complexes described herein exhibited only monometallic ions, and this is consistent with our *X*-ray structural determination.

Spectral Studies.—The BH stretching frequencies in the i.r. spectra of $[\{Mo[HB(C_3HR_2N_2)_3](NO)XY\}_n]$ (R = H, $n = 2$; R = Me, $n = 1$; X = Y = halide; X = halide, Y = OR') occurred at *ca.* 2 496 cm^{-1}, with a shoulder at 2 504 cm^{-1} ($CHCl_3$ solution) when R = H and at *ca.* 2 550 cm^{-1} when R = Me. In the chlorinated species $[Mo\{HB(C_3ClMe_2N_2)_3\}(NO)Cl(OPr^i)]$, ν_{BH} occurred at 2 558 cm^{-1} (2 570 sh; CH_2Cl_2 soln.) while in $[Mo\{HB(C_3BrMe_2N_2)_3\}(NO)Br_2]$, $\nu_{BH} = 2\,561$ cm^{-1}. The NO stretching frequencies (Table 2) in these complexes occurred in the range 1 727—1 636 cm^{-1} (*cf.* their η^5-cyclopentadienyl analogues, 1 670 cm^{-1} in KBr), and were influenced by the electron-withdrawing or -releasing properties of the X and Y groups. However, ν_{NO} in $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)X_2]$ was insensitive to X. Perhaps this may be related to the steric interactions between X and the pyrazolylborato-ligand. The value of ν_{NO} reflects, *inter alia*, the relative basicity of $[HB(C_3HMe_2N_2)_3]$ and the electronegativity of the chlorine atom in the species X = Cl. The replacement of Cl by Br increases the electron density at Mo, but the steric effect on the pyrazolylborato-ligand would be to reduce its basicity by lengthening the Mo–N bonds. These compensating effects could account for the shifts in ν_{NO}.

The unsubstituted pyrazolylborate complexes, with the exception of $[Mo\{HB(C_3H_3N_2)_3\}(NO)Br(OEt)]$, were too insoluble in suitable solvents for effective ^1H n.m.r.

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[11] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

spectral measurements. However, the spectra of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)XY]$, where X = Y = halide, were characterised (Table 2) by a group of resonances of overall intensity 1 and relative intensity 2 : 1 or 1 : 2, at *ca.* $\tau = 4.0$ (due to the 4-H protons), and a further group of signals, of overall intensity 6 and relative intensity 1 : 1 : 2 : 2 or 1 : 2 : 1 : 2 depending on solvent, in the range τ = 7.40—7.80 (due to the methyl protons). The spectra are consistent with an overall octahedral geometry for the complexes, a consequence of which is that one pyrazolyl ring is magnetically inequivalent to the other two (Figure 1a). Other structures are possible, such as trigonal prismatic (unlikely on steric grounds) or seven-co-ordination, the seventh ligand being a solvent molecule. The spectra of these complexes, and their alkoxide derivatives, exhibited a marked solvent dependence, but this does not require co-ordination by the solvent which, in any case, seems unlikely on the basis of molecular models.

At −60 °C, some changes in chemical shift occurred, but there was no evidence of significant line broadening. It may be noted that in $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Cl_2]$ the methyl resonances are apparently accidentally degenerate, occurring as a sharp singlet ($W_{\frac{1}{2}}$ = 5.0 Hz); at −60 °C in $CDCl_3$, this signal broadened only slightly.

While the spectra of the alkoxides, [Mo{HB(3,5-

TABLE 2

NO Stretching frequency and ^1H n.m.r. spectral data obtained from tris(pyrazolyl)borato-molybdenum complexes, $[\{MoXY(NO)[HB(3,5\text{-}R_2C_3HN_2]_3\}_n]$

Complex			I.r. data	^1H n.m.r. data				
X	Y	R	(ν_{NO}/cm^{-1})	Solvent	θ_c/°C	τ	A [a]	Comment
Cl	Cl	H	1 727 [b]					
			1 710 } [c]					
			1 700					
Cl	Cl	Me	1 720 [b]	$CDCl_3$	+30	4.04	2 } 3	s } $C_3HMe_2N_2$
			1 702 [c]				1	s
						7.60	18	s; $C_3H(CH_3)_2N_2$
				$(CD_3)_2CO$	+30	3.84	2 } 3	s } $C_3HMe_2N_2$
						4.12	1	s
						7.50	1 }	s } $C_3H(CH_3)_2N_2$
						7.55	2	s
						7.60	1	s
						7.66	2	s
				C_6D_6	+30	4.56	1 } 3	s } $C_3HMe_2N_2$
						4.69	2	s
						7.43	1 } 18	s } $C_3H(CH_3)_2N_2$
						7.60	2	s
						8.00	1	s
						8.17	2	s
Cl	Cl	Me (4-Cl)	1 705 [c]	$CDCl_3$	+30	7.58		s } $C_3Cl(CH_3)_2N_2$
						7.60		s
						7.63		s
						7.77		s
Br	Br	H	1 724 [b]					
			1 710 } [c]					
			1 700					
Br	Br	Me	1 720 [b]	$CDCl_3$	+30	4.00	2 } 3	s } $C_3HMe_2N_2$
			1 702 [c]			4.05	1	s
						7.41	1 } 18	} $C_3H(CH_3)_2N_2$
						7.48	1	s
						7.55	2	s
						7.58	2	s
				$CDCl_3$	−60	4.00	2 } 3	s } $C_3HMe_2N_2$
						4.05	1	s
						4.8—5.8	1	br; B*H*
						7.47	1 } 18	s } $C_3H(CH_3)_2N_2$
						7.54	1	s
						7.60	2	s
						7.67	2	s
				$CDCl_3$/ $(CD_3)_2CO$	+30	4.02	2 } 3	s } $C_3HMe_2N_2$
						4.13	1	s
						7.52	1 } 18	s } $C_3H(CH_3)_2N_2$
						7.60	1	s
						7.68	1	s
					−60	3.91	} 3	s } $C_3HMe_2N_2$
						4.06		s
						7.49	} 18	s } $C_3H(CH_3)_2N_2$
						7.51		s
						7.54		s
						7.69		s
				C_6D_6	+30	4.46	1 } 3	s } $C_3HMe_2N_2$
						4.76	2	s
						7.30	1 } 18	s } $C_3H(CH_3)_2N_2$
						7.60	2	s
						7.98	1	s
						8.23	2	s

TABLE 2 (*Continued*)

Complex			I.r. data	^{1}H n.m.r. data				
X	Y	R	(ν_{NO}/cm^{-1})	Solvent	θ_c/°C	τ	A ^{a}	Comment
Br	Br	Me (4-Br)	1 722 ^{b}					(4-bromodimethylpyrazolide)
I	I	H	1 716s 1 680sh } ^{b}					
			1 700s 1 656sh } ^{c}					
I	I	Me	1 710 ^{b}	$\mathrm{CDCl_3}$	+30	3.96	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						4.18	2	s
			1 705 1 656sh } ^{c}			7.25	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.44	1	s
						7.73	2	s
						7.83	2	s
				$\mathrm{CDCl_3}$	−60	3.87	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						4.07	2	s
						4.65—5.60	1	br; B*H*
						7.24	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.39	1	s
						7.67	2	s
						7.82	2	s
				$\mathrm{(CD_3)_2CO}$	+30	3.84	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						3.96	1	s
						7.28	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.38	1	s
						7.65	2	s
						7.84	2	s
Cl	OEt	Me	1 676 ^{b}	$\mathrm{CDCl_3}$	+30	3.8—4.3	5	m; $\mathrm{C}H_2\mathrm{Me}$ and $\mathrm{C_3}H\mathrm{Me_2N_2}$
						7.44	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.54	1	s
						7.59	2	s
						7.60	2	s
						8.45	3	t; $\mathrm{CH_2C}H_3$(J_{HH} = 6.0 Hz)
Cl	OEt	Me (4-Cl)	1 704	$\mathrm{CDCl_3}$	+30	4.03	2	m; AB pair, J_{AB} = 11.0 Hz; τ_{A} = 4.12, τ_{B} = 3.94; $\mathrm{C}H_2\mathrm{Me}$ (J_{HH} = 7.0 Hz)
						7.48	} 18	s } $\mathrm{C_3Cl(C}H_3)_2\mathrm{N_2}$
						7.58		s
						7.62		s
						7.65		s
						7.70		s
						8.41	3	t; $\mathrm{CH_2C}H_3$ (J_{HH} = 7.0 Hz)
Cl	OPr^i	Me	1 674 ^{b}	$\mathrm{CDCl_3}$	+30	3.50	2	quintet, $\mathrm{C}H\mathrm{Me_2}$ (J_{HH} = 6.0 Hz)
						4.15	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						4.21	1	s
						4.30	1	s
						7.48	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.58	1	s
						7.63	2	s
						7.64	2	s
						8.45	6	dd, sepn. 25.0 Hz, $\mathrm{CH(C}H_3)_2$ (J_{HH} = 6.0 Hz)
Cl	OPr^i	Me (4-Cl)	1 682 ^{b} 1 681 ^{c}	$\mathrm{CDCl_3}$	+30	3.47	1	quintet, $\mathrm{C}H\mathrm{Me_2}$ (J_{HH} 6.0 Hz)
						7.50	} 18	s } $\mathrm{C_3Cl(C}H_3)_2\mathrm{N_2}$
						7.58		s
						7.62		s
						7.66		s
						7.68		s
						8.46	6	dd, sepn. 25.0 Hz, $\mathrm{CH(C}H_3)_2$ (J_{HH} = 6.1 Hz)
Br	OEt	Me	1 673 ^{b}	$\mathrm{CDCl_3}$	+30	3.9—4.4	5	m; $\mathrm{C}H_2\mathrm{Me}$ and $\mathrm{C_3}H\mathrm{Me_2N_2}$
						7.52	} 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.64		s
						7.70		s
						8.45	3	t; $\mathrm{CH_2C}H_3$ (J_{HH} = 7.2 Hz)
Br	OPr^i	Me	1 674 ^{b}	$\mathrm{CDCl_3}$	+30	3.67	1	quintet., $\mathrm{C}H\mathrm{Me_2}$ (J_{HH} = 6.0 Hz)
						4.25	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						4.30	1	s
						4.34	1	s
						7.48	1 } 18	s } $\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
						7.60	2	s
						7.64	2	s
						7.67	1	s
						8.43	6	dd, sepn. 29.0 Hz, $\mathrm{CH(C}H_3)_2$ (J_{HH} = 6.0 Hz)
				$\mathrm{(CD_3)_2CO}$	+30	3.56	1	quintet, $\mathrm{C}H\mathrm{Me_2}$(J_{HH} = 6.5 Hz)
						3.97	1 } 3	s } $\mathrm{C_3}H\mathrm{Me_2N_2}$
						4.08	1	s
						4.17	1	s

Table 2 (*Continued*)

Complex			I.r. data (ν_{NO}/cm^{-1})	¹H n.m.r. data				
X	Y	R		Solvent	θc/°C	τ	A[a]	Comment
						7.52	} 18	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.57		s
						7.59		s
						7.62		s
						8.46	6	dd, sepn. 28.0 Hz, $CH(C\mathit{H}_3)_2$ (J_{HH} = 6.0 Hz)
Br	OC_3H_5	Me	1 679[b]	$CDCl_3$	+30	3.82	2	m; $C\mathit{H}_2CH{=}CH_2$
						4.16	2 } 3	brs } $C_3\mathit{H}Me_2N_2$
						4.27	1	s
						4.60—4.90	3	m; $CH_2C\mathit{H}{=}CH_2$ and $CH_2CH{=}C\mathit{H}_2$
						7.48	3	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.64	12	s
						7.67	3	s
Br	OBu[i]	Me	1 676[b]	$CDCl_3$	+30	4.15	1 } 3	s } $C_3\mathit{H}Me_2N_2$
						4.20	1	s
						4.27	1	s
						4.48	2	dd, sepn. 3.0 Hz, $C\mathit{H}_2CHMe_2$ (J_{HH} = 7.0 Hz)
						7.49	} 18	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.62		s
						7.65		s
						7.95—8.05		1 brm; $CH_2C\mathit{H}Me_2$
						8.98	6	dd, sepn. 5.0 Hz, $CH_2CH(C\mathit{H}_3)_2$ (J_{HH} = 6.0 Hz)
Br	OMe	H	1 677[b]	$CDCl_3$	+30	2.06 }	2 { d	(J = 2.0 Hz) } 3,5 protons of $C_3H_3N_2$
						2.21	dd	
						2.33	dd	
						3.65 }	1 { t	(J = 2.0 Hz) } 4-protons of $C_3H_3N_2$
						3.74	t	
						3.78	t	
						4.50	1 s	O-$C\mathit{H}_3$
Br	OEt	H		$CDCl_3$	+30	2.07	1 } 6	d } 3,5-protons of $C_3H_3N_2$
						2.21	1	d
						2.27	2	d
						2.37	2	dd
						3.68	1 } 3	t, J = 2.0 Hz } 4-proton of $C_3H_3N_2$
						3.70—3.84	2	two overlapping t J = 2.0 Hz
						4.26	2	AB pair, J_{AB} = 11.0 Hz; τ_A = 4.15 τ_B = 4.37; $C\mathit{H}_2Me$ (J_{HH} = 6.5 Hz)
						8.44	3	t, $CH_2C\mathit{H}_3$ (J_{HH} = 6.5 Hz)
I	OEt	Me	1 678[b]	$CDCl_3$	+30	4.17	1 } 5	s } $C_3\mathit{H}Me_2N_2$
						4.20	1	s
						4.22	1	s
						4.35	2	AB pair, J_{AB} = 11.5 Hz, τ_A = 4.20 τ_B = 4.49; $C\mathit{H}_2CH_3$ (J_{HH} = 7.0 Hz)
						7.50	1 } 18	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.57	1	s
						7.62	1	s
						7.66	3	s
						8.43	3	t, $CH_2C\mathit{H}_3$ (J = 7.0 Hz)
I	OPr[i]	Me	1 673[b]	$CDCl_3$	+30	3.74	1	quintet, $C\mathit{H}Me_2$ (J_{HH} = 6.0 Hz)
						4.19	} 3	s } $C_3\mathit{H}Me_2N_2$
						4.21		s
						7.49	} 18	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.54		s
						7.61		s
						7.66		s
						7.67		s
						8.41	6	dd, sepn. 35.0 Hz, $CH(C\mathit{H}_3)_2$ (J_{HH} = 6.0 Hz)
OEt	OEt	Me	1 636[b]	$CDCl_3$	+30	4.26	2 } 3	s } $C_3\mathit{H}Me_2N_2$
						4.33	1	s
						4.55	4	AB pair, J_{AB} = 10.5 Hz, τ_A = 4.67, τ_B = 4.43; $C\mathit{H}_2Me$ (J_{HH} = 7.0 Hz)
						7.48	6	s } $C_3H(C\mathit{H}_3)_2N_2$
						7.72	12	s
						8.59	6	t; $CH_2C\mathit{H}_3$ (J_{HH} = 7.0 Hz)

[a] Relative intensity. [b] $CHCl_3$ solution. [c] KBr disc.

$Me_2C_3HN_2)_3\}(NO)X(OR)]$, have an overall similarity to their dihalide precursors, with the addition of resonances due to the R groups, their detailed appearances vary significantly. These changes may be attributed to the inequivalence of all three pyrazolyl rings which is a consequence of ‘ octahedral ’ geometry (Figure 1b) (and also of seven-co-ordination if that occurred). Thus, for example, there are three, rather than two, signals due to

4-H in the spectra of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X(OR)]$ ($X = Cl$, Br, or I; $R = Et$, Pr^i, or Bu^i). No attempt was made to assign precisely the methyl group resonances, but it was clear from their relative intensities and chemical shifts that they too differed significantly from those of their dihalide precursors.

The lack of a plane of symmetry in the alkoxo-halide causes the methylene proton resonances in $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}X(OR)]$ ($R = CH_2Me$ or CH_2CHMe_2) to appear as AB pairs. While full analysis of these signals is complicated by their overlap with the 4-H signals of the pyrazolyl ring, in the halogenated species $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OEt)]$ and in $[Mo\{HB(C_3H_3N_2)_3\}(NO)Br(OEt)]$ these multiplets may be clearly seen and assigned. In the isopropoxides, the methyl resonances of the alkoxide group occur as a double doublet, the separation between the two doublets increasing in the order $Cl < Br < I$. The spectra of the diethoxo-species, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(OEt)_2]$, were distinctly different, particularly in the form of the ethyl group resonances, to those of the mono-ethoxo-complexes. Of singularity in the spectra of the alkoxides is the occurrence of the α-proton resonances of the alkoxo-group at τ-values in the range 3.5—4.5. These protons do not exchange with D_2O, and although their signals broaden somewhat at −60 °C they do not show a significant increase of J_{AB} or changes in the values of τ_A and τ_B.

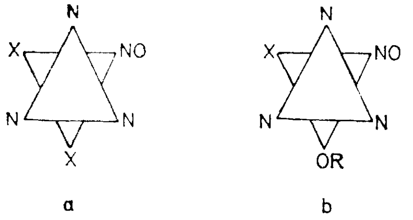

FIGURE 1

(i) The shifts could occur because of proton interaction with the metal. Indeed, unusual shifts of proton resonances have been observed in the spectra of *trans*-$[PdBr\{C_4(CO_2Me)_4\}(PPh_3)_2]$ (low field),[12] $[PtCl_2(MeN{:}S{:}NMe)(PEt_3)]$ (low field),[13] and $[Mo\{Et_2B(C_3H_3N_2)_2\}(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)(CO)_2]$ ($R = H$ or Ph) (high field).[14,15] In all these compounds, interaction between the unique hydrogen(s) and the metal has been substantiated crystallographically. If such an interaction were to occur in the compounds reported in this paper, the metal atoms configuration would increase from 16 to 18 by virtue of the association of the electrons of one α-C–H bond with the Mo atoms. This would be analogous, but not identical, to the situation in $[Mo\{Et_2B(C_3H_3N_2)_2\}(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)(CO)_2]$ ($R = H$ or Ph).[14] In these diethyl bispyrazolylborates, there is an interaction between one hydrogen atom of a methylene group and the metal, and variable-temperature ^1H n.m.r. spectral studies have established [15] that there is a rapid exchange of sites between the proton which is close to the metal and the other which is more distant. It must be observed that in these compounds the methylene resonances were shifted to *high* field and were split into relatively higher- and lower-field components as the temperature was lowered. In the alkoxides, however, the shifts are to *low* field and do not apparently split as the temperature is lowered. A further point is that the τ-value of the α-proton in the isopropoxide does ***not*** occur at an average of τ_A and τ_B of the α-CH_2 resonances in the comparable ethoxides. This does not, of course, militate entirely against a Mo · · · H–C interaction.

(ii) The protons on the α-C atom could be deshielded by neighbour anisotropy effects associated with the NO or X groups but, again, some form of methylene proton exchange process, as mentioned in (i), would be expected.

(iii) The protons could be deshielded because of ring-current effects associated with the pyrazolyl rings. This can probably be discounted, however, since molecular models of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X(OPr^i)]$ suggested that the required conformation would be severely sterically strained.

(iv) Since the metal atom in the compounds under discussion is electron deficient (formally a 16-electron system), and is bonded to the strong π-acceptor NO and the electronegative X, the group $[Mo\{HB(C_3HR_2N_2)_3\}(NO)X]$ must be strongly electron withdrawing. Consequently, there should be a net withdrawal of electron density from the alkoxo-group, the effect manifesting itself in a substantial deshielding of the α-C and α-hydrogen atoms. Indeed, in species such as $[WF_5(OMe)]$ and *cis*-$[WF_4(OMe)_2]$,[16] the fluorometallic group is strongly electron withdrawing, and the protons resonate at low fields ($\tau = 4.3$—4.7 depending upon solvent). Similar, but less dramatic, effects have been observed [17] in $\tau_{\alpha\text{-}CH_2}$ of $[\{M(OCH_2CH{:}CH_2)_x\}_n]$ ($M = Ge$, $x = 4$, $n = 1$; $M = Ti$, $x = 4$, $n = 2$; $M = Ta$, $x = 5$, $n = 2$), the low-field shift (with respect to the free alcohol) being greatest in the transition-metal alkoxides. The ^{13}C n.m.r. spectra of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(CO)_2]$ and $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br(OPr^i)]$ were obtained in $CDCl_3$, that of the first at ambient temperature and at −60 °C. The spectral assignments are listed in Table 3. The spectrum of the dicarbonyl nitrosyl is, in fact, better resolved at −60 °C than at ambient temperature, and although the positions of the carbon nuclei shifted slightly as the temperature was lowered the appearance of the spectrum as a whole does not change, indicating that the compound is not fluxional. The expected inequivalences of the ^{13}C resonances of the

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pyrazolylborate ligand in this compound were observed, *e.g.* the 4-C atom of the pyrazolide group appeared as a doublet, of approximate ratio 2 : 1. The major differences between the spectrum of the dicarbonyl nitrosyl and that of $[Mo\{HB(3,5-Me_2C_3HN_2)_3\}(NO)Br(OPr^i)]$ were, of course, the lack of carbonyl signals and the occurrence of isopropoxy-carbon nuclei resonances in the latter. Furthermore, the patterns of resonances of the carbon atoms in the pyrazolide rings were more complex, in accord with the lower symmetry of the compound. For the unique C atom of the OPr^i group, $\delta = 88.40$, while that of the free alcohol occurs nearly 25 p.p.m. nearer to $SiMe_4$. Thus extensive deshielding of this atom occurred, presumably because the *effective* electronegativity of the O atom to which it is bound has been increased by the electron-withdrawing $[Mo\{HB(C_3R_2HN_2)_3\}(NO)Br]$ group.

TABLE 3

^{13}C N.m.r. spectra[a] of $[\{HB(3,5-Me_2C_3HN_2)_3\}Mo(NO)(CO)_2]$, A, and $[\{HB(3,5-Me_2C_3HN_2)_3\}Mo(NO)Br(OPr^i)]$, B

Compound	A (Room temp.) δ (p.p.m.) (peak ht.)	A (−60 °C) δ (p.p.m.) (peak ht.)	B δ (p.p.m.) (peak ht.)
$HB[3,5-(CH_3)_2(C_3HN_2)]_3$	12.49 (32.5%)	12.80 (37.1%)	12.50 (34.7%)
	12.68 (18.3)	12.98 (19.5)	12.68 (57.1)
	14.37 (26.1)	14.50 (36.8)	12.86 (54.6)
	14.74 (13.5)	14.86 (17.4)	13.89 (39.6)
			14.56 (36.5)
			15.41 (35.2)
$OCH(CH_3)_2$			24.39 (42.9)
			(25.30) (14.8)
			25.85 (46.0)
			88.40 (72.5)
$HB[3,5-Me_2C_3HN_2]_3$, 4-C	106.42 (88.6)	106.23 (65.4)	107.45 (101.8) 107.63 (99.4)
$HB(3,5-Me_2C_3HN_2)_3$, 3,5-C	144.52 (8.9)	144.52 (30.5)	143.48 (21.3)
		145.06 (17.7)	144.94 (24.6)
			146.22 (23.8)
	151.31 (8.9)	151.07 (8.8)	152.77 (49.2)
	151.68 (16.6%)	151.31 (42.6)	154.23 (32.0)
Carbonyl CO		225.33 (16.2)	

[a] Chemical shifts ±0.2 p.p.m. at 22.62 MHz with reference to internal $SiMe_4$ in $CDCl_3$; chemical shifts increase to low field w.r.t. internal reference.

X-Ray Structural Studies.—Because of the unusual ^1H and ^{13}C n.m.r. spectral features of these alkoxide complexes, and their potential structural implications, and in view of the interest in this class of pyrazolylborate compounds,[2,14,15] we have undertaken a single-crystal *X*-ray diffraction study of a representative complex, $[Mo\{HB(3,5-Me_2-4-ClC_3N_2)_3\}(NO)Cl(OPr^i)]$ (see Experimental section for details).

Final atomic co-ordinates and anisotropic temperature factors (with e.s.d.s in parentheses) are given in Tables 4 and 5, interatomic distances and angles in Table 6, and final observed and calculated structure factors in a Supplementary publication No. SUP 21774 (23 pp., 1 microfiche).*

The molecular structure is shown in Figure 2. The molybdenum atom has an octahedral environment involving a tridentate tris-pyrazolylborate ligand, a linear metal–nitrosyl system, a chlorine atom, and an isopropoxo-group. The three pyrazolyl rings, A *trans* to Cl(2), B *trans* to N(3), and C *trans* to O(2), are each coplanar, with a maximum deviation from planarity of 0.006 Å, excluding substituents; the maximum deviation of a terminal substituent is 0.045 Å. The bond lengths and angles within the pyrazolylborate ligand compare very well with those surveyed by Guggenberger *et al.*,[18] and the

TABLE 4

Final atomic co-ordinates for $[Mo\{HB(3,5-Me_2-4-ClC_3N_2)_3\}_3(NO)Cl(OPr^i)]$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo(1)	−0.024 64(7)	0.212 90(6)	0.111 14(6)
Cl(1A)	0.413 8(3)	0.060 6(3)	0.063 1(3)
Cl(1B)	−0.218 1(3)	0.200 6(2)	−0.263 6(2)
Cl(1C)	0.126 9(3)	0.569 6(2)	0.116 7(2)
Cl(2)	−0.185 4(2)	0.290 9(2)	0.138 5(2)
N(1A)	0.136 3(6)	0.175 2(5)	0.069 6(5)
N(2A)	0.179 9(6)	0.210 6(5)	−0.004 2(5)
C(1A)	0.280 5(8)	0.177 8(7)	−0.016 9(7)
C(2A)	0.299 4(8)	0.121 7(7)	0.049 9(7)
C(3A)	0.208 1(8)	0.120 2(6)	0.102 6(6)
C(4A)	0.351 8(9)	0.201 0(9)	−0.092 9(8)
C(5A)	0.186 7(10)	0.067 2(8)	0.184 7(8)
N(1B)	−0.065 7(6)	0.222 6(5)	−0.034 5(5)
N(2B)	0.012 1(6)	0.250 5(5)	−0.092 3(5)
C(1B)	−0.025 3(8)	0.248 2(6)	−0.177 1(6)
C(2B)	−0.130 5(8)	0.217 3(7)	−0.174 8(6)
C(3B)	−0.154 7(8)	0.201 1(6)	−0.085 1(6)
C(4B)	0.038 0(10)	0.277 4(9)	−0.255 2(7)
C(5B)	−0.259 7(9)	0.168 4(8)	−0.048 8(8)
N(1C)	0.056 2(6)	0.334 6(5)	0.092 6(5)
N(2C)	0.101 4(6)	0.351 7(5)	0.011 2(5)
C(1C)	0.132 5(8)	0.432 6(6)	0.007 6(6)
C(2C)	0.106 2(8)	0.468 1(6)	0.089 4(7)
C(3C)	0.059 9(8)	0.406 8(6)	0.141 7(7)
C(4C)	0.184 2(9)	0.472 6(7)	−0.072 2(8)
C(5C)	0.020 6(9)	0.414 1(7)	0.233 6(6)
B(1)	0.121 1(9)	0.280 4(8)	−0.055 8(7)
N(3)	0.009 5(6)	0.207 1(6)	0.225 7(5)
O(1)	0.032 5(7)	0.202 6(6)	0.301 9(4)
O(2)	−0.084 7(6)	0.106 8(4)	0.097 7(4)
C(6)	−0.111 4(10)	0.042 7(7)	0.161 1(7)
C(7)	−0.232 1(13)	0.049 0(10)	0.182 1(12)
C(8)	−0.078 9(13)	−0.041 3(7)	0.121 4(10)
HC(6)	−0.073(9)	0.049(7)	0.216(7)
HB(1)	0.170(9)	0.301(8)	−0.112(7)

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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TABLE 5

Anisotropic temperature factors

$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)]$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Mo(1)	0.005 70(1)	0.003 16(0)	0.003 47(1)	−0.000 11(1)	0.001 55(1)	0.000 33(2)
Cl(1A)	0.008 26(4)	0.008 27(4)	0.008 78(4)	0.000 41(6)	0.000 76(6)	0.007 87(6)
Cl(1B)	0.009 06(4)	0.008 48(3)	0.005 03(2)	−0.000 33(5)	−0.004 25(5)	−0.002 34(7)
Cl(1C)	0.012 43(5)	0.003 19(2)	0.007 92(3)	−0.001 65(4)	−0.003 51(7)	−0.000 64(5)
Cl(2)	0.006 48(3)	0.004 63(2)	0.006 36(2)	−0.000 51(4)	0.002 47(4)	0.001 70(5)
N(1A)	0.005 4(1)	0.003 6(1)	0.003 6(1)	0.000 2(1)	0.001 5(1)	0.001 3(1)
N(2A)	0.005 1(1)	0.003 8(1)	0.004 0(1)	−0.000 8(1)	0.002 3(1)	0.001 2(1)
C(1A)	0.005 9(1)	0.004 2(1)	0.005 0(1)	−0.002 5(1)	0.002 2(2)	−0.001 1(2)
C(2A)	0.006 6(1)	0.004 2(1)	0.005 3(1)	−0.001 4(2)	−0.000 6(2)	0.002 7(2)
C(3A)	0.005 5(1)	0.004 1(1)	0.004 3(1)	−0.001 2(1)	−0.000 1(2)	0.001 8(2)
C(4A)	0.007 5(1)	0.007 9(1)	0.007 1(1)	0.002 6(2)	0.008 2(2)	0.001 0(2)
C(5A)	0.010 9(2)	0.005 5(1)	0.005 3(1)	0.003 1(2)	−0.000 5(2)	0.005 8(2)
N(1B)	0.006 1(1)	0.003 2(1)	0.004 2(1)	0.001 1(1)	0.001 2(1)	−0.000 6(1)
N(2B)	0.005 8(1)	0.003 1(1)	0.003 3(1)	−0.000 1(1)	0.000 8(1)	−0.000 6(1)
C(1B)	0.007 1(1)	0.003 8(1)	0.003 8(1)	−0.001 1(1)	−0.000 2(2)	0.000 8(2)
C(2B)	0.007 1(1)	0.004 6(1)	0.003 8(1)	−0.000 7(2)	−0.000 9(1)	0.001 3(2)
C(3B)	0.006 1(1)	0.003 0(1)	0.005 2(1)	−0.000 7(1)	−0.001 7(2)	0.000 5(1)
C(4B)	0.001 0(2)	0.007 8(1)	0.003 5(1)	0.001 7(2)	0.002 7(2)	−0.002 4(3)
C(5B)	0.006 8(1)	0.007 4(1)	0.006 2(1)	0.000 2(2)	0.001 7(2)	−0.006 1(2)
N(1C)	0.005 7(1)	0.003 3(1)	0.003 8(1)	−0.000 1(1)	0.001 8(1)	0.000 9(1)
N(2C)	0.006 4(1)	0.003 2(1)	0.003 6(1)	0.000 6(1)	0.000 3(1)	−0.000 3(1)
C(1C)	0.005 5(1)	0.003 5(1)	0.004 6(1)	0.000 6(1)	−0.002 2(2)	−0.000 8(1)
C(2C)	0.006 7(1)	0.003 1(1)	0.005 4(1)	−0.000 3(1)	−0.003 0(2)	0.000 4(2)
C(3C)	0.004 5(1)	0.003 7(1)	0.005 4(1)	−0.000 6(1)	−0.002 3(2)	0.000 7(1)
C(4C)	0.008 9(2)	0.004 8(1)	0.005 8(1)	0.003 6(2)	0.000 6(2)	−0.002 8(2)
C(5C)	0.009 5(2)	0.004 7(1)	0.003 4(1)	−0.002 1(1)	0.007 2(2)	0.004 6(2)
B(1)	0.006 1(1)	0.003 7(1)	0.003 6(1)	−0.000 3(2)	0.002 7(2)	0.000 3(2)
N(3)	0.007 6(1)	0.004 4(1)	0.003 7(1)	0.000 7(1)	0.002 6(1)	0.001 7(2)
O(1)	0.012 9(1)	0.007 2(1)	0.003 3(1)	0.000 8(1)	0.001 8(1)	0.002 8(2)
O(2)	0.008 0(1)	0.003 4(1)	0.004 1(1)	0.000 0(1)	0.002 3(1)	−0.000 9(1)
C(6)	0.011 0(2)	0.003 3(1)	0.005 9(1)	0.001 7(1)	0.002 9(2)	−0.001 9(2)
C(7)	0.015 1(3)	0.007 7(2)	0.014 0(2)	0.007 1(3)	0.020 2(4)	0.000 9(3)
C(8)	0.015 9(3)	0.003 2(1)	0.009 3(2)	−0.000 7(2)	0.000 6(1)	0.000 1(3)

Mo $\cdots$ B distance of 3.30 Å is typical of tridentate pyrazolylborate ligands where the B atom cannot interact with the metal atom for steric reasons. The nitrosyl group is linear [179.4(8)°] and the Mo–N and N–O bond lengths [1.764(8) and 1.176(11) Å, respectively] are typical values for molybdenum nitrosyls of the type $Mo(NO)^{3+}$.[8,19]

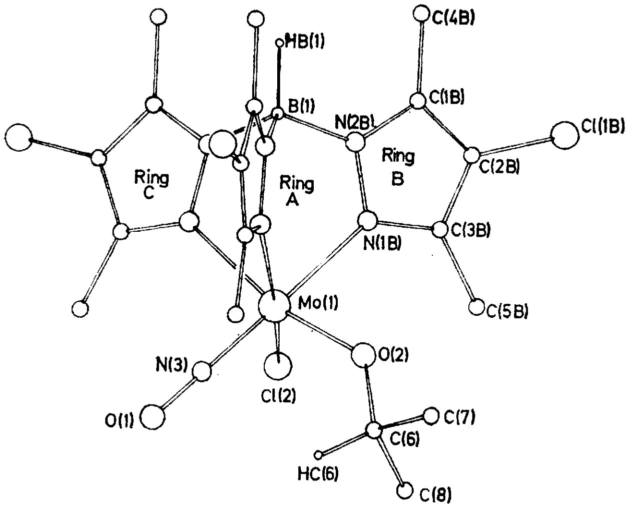

FIGURE 2

The Mo–O bond length [1.863(7) Å] is considerably shorter than the formal Mo^{II}–O single bond found in $[Mo_2(O_2CCF_3)_4(pyr)_2]$[20] [2.116(6) Å] and the metal-terminal oxygen single-bond lengths in the Mo^{III} complex $K[Mo_2(OH)_2(O_2CMe)(C_{10}H_{12}O_2N_2)]$ (2.11—2.14 Å).[21] Indeed this length is also shorter than Mo–O single-bond distances observed in other carboxylate and related compounds of Mo^V and Mo^{VI}.[22] This shortening of the Mo–O bond implies a significant degree of bond-order multiplicity, presumably arising from $p_\pi \longrightarrow d_\pi$ donation from O to the co-ordinatively unsaturated Mo atom. This idea is supported by the occurrence of a relatively large bond angle at O(2) [132.4(6)°] which might be expected to be substantially smaller if no π-donation was present; a similar situation has been observed in $[WCl_4(OMe)_2]$.[23] The Mo–Cl bond length [2.380(3) Å] is shorter than published data for Mo^{II}–Cl distances (2.42—2.56 Å),[24] but is comparable to the Mo–Cl (terminal) bond length in $Cs_3[Mo_2Cl_9]$ (2.38 Å).[25] This,

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again, may imply some degree of π-donation from Cl to Mo.*

While the alkoxides appear to be formally co-ordinatively unsaturated, the electron deficiency at the metal is compensated for, to some extent, by p_π-donation from the alkoxo-group. This donation from the O atom is thus responsible for the n.m.r. spectral deshielding of the C and H atoms, as discussed earlier.

TABLE 6

Interatomic distances and angles in $[Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl(OPr^i)]$

Bond lengths (Å), with estimated standard deviations in parentheses

Mo(1)–Cl(2)	2.380(3)	O(2)–C(6)	1.445(13)
Mo(1)–N(3)	1.764(8)	C(6)–C(7)	1.525(20)
Mo(1)–O(2)	1.863(7)	C(6)–C(8)	1.532(18)
N(3)–O(1)	1.176(11)		

Bond lengths within pyrazolyl rings

	Ring A	Ring B	Ring C
Mo(1)–N(1)	2.172(8)	2.239(8)	2.211(8)
N(1)–N(2)	1.368(11)	1.382(10)	1.383(11)
N(2)–C(1)	1.358(13)	1.344(12)	1.353(12)
C(1)–C(2)	1.364(15)	1.384(14)	1.399(14)
C(2)–C(3)	1.389(14)	1.413(14)	1.390(14)
C(3)–N(1)	1.333(12)	1.360(12)	1.373(12)
C(1)–C(4)	1.503(16)	1.499(16)	1.514(15)
C(2)–Cl(1)	1.719(11)	1.713(10)	1.698(11)
C(3)–C(5)	1.527(16)	1.506(16)	1.479(15)
N(2)–B(1)	1.533(14)	1.510(14)	1.546(14)

Bond angles within pyrazolyl rings (°), with e.s.d.s in parentheses

	Ring A	Ring B	Ring C
Mo(1)–N(1)–N(2)	119.7(5)	119.7(5)	118.5(5)
Mo(1)–N(1)–C(3)	132.4(6)	133.4(6)	133.2(6)
N(2)–N(1)–C(3)	107.9(7)	106.8(7)	107.5(7)
N(1)–N(2)–C(1)	109.2(7)	111.2(7)	110.1(7)
N(1)–N(2)–B(1)	121.6(7)	119.6(7)	120.1(7)
C(1)–N(2)–B(1)	129.0(8)	129.2(8)	129.4(8)
N(2)–C(1)–C(2)	106.9(9)	106.5(8)	106.5(8)
N(2)–C(1)–C(4)	123.9(9)	124.2(9)	124.2(9)
C(2)–C(1)–C(4)	129.2(10)	129.3(9)	129.3(9)
C(1)–C(2)–C(3)	107.8(9)	107.9(9)	108.4(9)
C(1)–C(2)–Cl(1)	125.8(8)	127.2(8)	124.5(8)
C(3)–C(2)–Cl(1)	126.3(8)	124.9(8)	127.0(8)
C(2)–C(3)–N(1)	108.1(9)	107.6(8)	107.4(8)
C(2)–C(3)–C(5)	128.9(9)	127.7(9)	128.3(9)
N(1)–C(3)–C(5)	123.0(9)	124.6(9)	124.2(9)

Other bond angles

Mo(1)–N(3)–O(1)	179.4(8)	C(7)–C(6)–C(8)	113.8(11)
Mo(1)–O(2)–C(6)	132.4(6)	N(2A)–B(1)–N(2B)	110.7(8)
O(2)–C(6)–C(7)	109.0(10)	N(2A)–B(1)–N(2C)	106.9(8)
O(2)–C(6)–C(8)	107.7(9)	N(2B)–B(1)–N(2C)	108.7(8)

Some non-bonding distances (Å)

Mo(1) · · · B(1)	3.300(11)	N(3) · · · HC(6)	2.69(12)
Mo(1) · · · HC(6)	3.17(12)	O(1) · · · HC(6)	2.97(12)

HC(6) position used for geometry assumes a C(6)–HC(6) of 1.08 Å.

It appears, therefore, that the only known pyrazolylborate complexes of molybdenum which are likely to be co-ordinatively unsaturated are $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)X_2]$ and $[Mo\{Ph_2B(C_3H_3N_2)_2\}(CO)_2(2\text{-}Ph\text{-}\eta^3\text{-}C_3H_4)]$.[27] In the former, however, some p_π–d_π donation from X to the metal must be expected and even in the latter it has been proposed that the π-electrons of a (boron) phenyl group may interact, albeit weakly, with the metal.

Finally, it may be noted that while the species $[\{Mo[HB(C_3R_2HN_2)_3](NO)X_2\}_n]$ readily react with alcohols, affording alkoxides, such a reaction had not previously been observed in the comparable η^5-cyclopentadienyl compounds, although $[\{(\eta^5\text{-}C_5H_5)Mo(NO)X_2\}_2]$ reacts with thiols affording [5,6] $[\{(\eta^5\text{-}C_5H_5)Mo(NO)X(SR)\}_2]$. However, we have observed recently that $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I\}_2]$ reacts with methanol or benzyl alcohol affording $[\{(\eta^5\text{-}C_5H_5)Mo(NO)I(OR)\}_2]$ (R = Me or CH_2Ph),[28] and that the chemical shifts of the α-protons occur at normal positions.

EXPERIMENTAL

All reagents were used as purchased without further purification, except $K[HB(C_3H_3N_2)_3]$ and $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ which were prepared as described in the literature.[29]

Molecular weights were determined osmometrically. I.r. spectra were obtained using Infracord 457 and PE 180 spectrophotometers and n.m.r. spectra were obtained with Varian HA100 and Jeol PFT100 instruments.

Microanalyses were performed by the Microanalytical Laboratory of this Department. All yields are quoted relative to the starting material.

Dicarbonylnitrosyl[tris(pyrazolyl)borato]molybdenum, $[Mo\{HB(C_3H_3N_2)_3\}(NO)(CO)_2]$.—A solution of $K[HB(C_3H_3N_2)_3]$ (13.5 g) and $[Mo(CO)_6]$ (10.5 g) in dry tetrahydrofuran (thf) (200 ml) was refluxed, with stirring, under N_2 overnight. After cooling, acetic acid (3.0 g) was added and stirring continued for 10 min. *N*-Methyl-*N*-nitrosotoluene-*p*-sulphonamide (mnts) (8.6 g) in thf (100 ml) was then added, stirring being maintained for a further hour, and refluxing being recommenced after that for a further 30 min. The mixture was then cooled, filtered, through Hyflosupercel, and the filtrate was evaporated to dryness *in vacuo*. The residue was washed with hot ethanol and the *product* obtained by recrystallisation from chloroform–ethanol as orange crystals (10.8 g, 65%).

Dicarbonylnitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(CO)_2]$.—A solution of $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ (71.0 g) and $[Mo(CO)_6]$ (55.0 g) in dry thf (500 ml) was stirred and refluxed overnight. The solution was then cooled and acidified with acetic acid (15.0 g). This mixture was stirred for 1.5 h, and then treated with mnts (45.0 g) in dry thf (150 ml). The solution was again stirred overnight, and the solvent was then evaporated *in vacuo*. The orange–yellow residue was dissolved in chloroform, and the solution filtered, the filtrate being evaporated *in vacuo*. The crude product could be obtained by washing the residue with ethanol, and purification was effected by crystallisation from chloroform–ethanol. The *product* was obtained as orange crystals (84.0 g, 82%).

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* Assuming that the covalent radius of Cl is 0.99 Å, whereas that of sp^3- and sp^2-hybridised O is 0.74 and 0.57 Å, respectively,[26] the calculated Mo–O single bond distance, assuming no p_π–d_π bonding in the Mo–Cl bond and therefore calculating the Mo values to be 1.39 Å, is *ca.* 2.11 Å (sp^3-O). If the O atom is sp^2 hybridised, the Mo–O distance would be *ca.* 1.94 Å, in reasonable agreement with that observed.

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Dichloro(nitrosyl)[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[\{Mo[HB(3,5\text{-}Me_2C_3HN_2)_3](NO)Cl_2\}_n]$.—Chlorine gas (1 l) in an N_2-stream was bubbled through a solution of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ (2.0 g) in CCl_4 (100 ml). After 2 h, the yellow solid which had precipitated was filtered off, washed with CCl_4 and n-pentane, and recrystallised from toluene. The *product* was obtained as fine yellow needles (1.0 g, 45%).

The compound was also prepared by Soxhlet extraction of iodine (2.0 g) over 2 days into a solution of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ (4.0 g) in CCl_4 (200 ml). The precipitate which had formed was then filtered off and dried *in vacuo* (2.0 g, 45%). The tris(pyrazolyl)borato-analogue, $[\{Mo[HB(C_3H_3N_2)_3](NO)Cl_2\}_n]$, was prepared similarly (45%).

Dibromo(nitrosyl)[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br_2]$.—To a carbon tetrachloride solution (100 ml) of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ (3.0 g) was added a solution of bromine (1.0 g) in CCl_4 (50 ml). After stirring for 1 h, light petroleum (10 ml, b.p. 40—60 °C) was added, and the mixture was stirred overnight. The precipitate which had formed was filtered off, washed with CCl_4 and n-pentane, and dried *in vacuo*. A further amount of the complex was obtained by evaporation of the filtrate obtained above, and washing of the residue as described. The product was obtained as an orange–brown microcrystalline powder (3.1 g, 81%).

Dibromo(nitrosyl)[tris(pyrazolyl)borato]molybdenum, $[Mo\{HB(C_3H_3N_2)_3\}(NO)Br_2]$.—A mixture of bromine (1.0 ml) and $[Mo\{HB(C_3H_3N_2)_3\}(NO)(CO)_2]$ (7.2 g) in dichloromethane (150 ml) was stirred under N_2 for 30 min. To this was added n-pentane (50 ml) and the mixture was stirred for a further 30 min. The *product*, which precipitated, was filtered off and washed with dichloromethane, being then air-dried, and was obtained as an orange powder (6.5 g, 70%).

Di-iodo(nitrosyl)[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)I_2]$.—Iodine (3.0 g) was Soxhlet-extracted into a solution of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ (6.0 g) in methylcyclohexane (250 ml). After 12 h, the mixture was cooled to *ca.* −10 °C, and the black solid which precipitated was filtered off and dried *in vacuo*. The product was obtained as a black microcrystalline powder (7.5 g, 88%).

Di-iodo(nitrosyl)[tris(pyrazolyl)borato]molybdenum, $[Mo\{HB(C_3H_3N_2)_3\}(NO)I_2]$.—To a stirred solution of $[\{HB(C_3H_3N_2)_3\}Mo(NO)(CO)_2]$ (1.8 g) in dichloromethane (100 ml) was added, slowly, iodine (1.2 g) dissolved in dichloromethane (250 ml). After the addition was complete, the mixture was stirred for a further 10 min, then evaporated to dryness *in vacuo*. The residue was maintained *in vacuo* until all iodine had sublimed away from it, and the *product* was isolated as a black solid (2.1 g, 78%).

Dibromo(nitrosyl)[tris(4-bromo-3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(4\text{-}Br\text{-}3,5\text{-}Me_2C_3N_2)_3\}(NO)Br_2]$.—The complex was prepared in the same way as $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br_2]$ using a slight excess of bromine (3.0 g). Excess of bromine was removed from the complex by washing with n-pentane. The product was obtained as a dark brown solid (3.0 g, 59%).

Dichloro(nitrosyl)[tris(4-chloro-3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(4\text{-}Cl\text{-}3,5\text{-}Me_2C_3N_2)_3\}(NO)Cl_2]$.—This complex was obtained in a similar way from $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2]$ using a slight excess of Cl_2.

Chloro(ethoxo)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Cl(OEt)]$.—The dichloride, $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Cl_2]$, was refluxed in ethanol for 30 min. On cooling, large blue crystals of the *complex* formed, which were analytically pure and were not recrystallised (yield quantitative). The corresponding complexes $[Mo\{HB(3,5\text{-}Me_2C_3XN_2)_3\}(NO)Y_2]$ (X = 4-H or 4-Cl, Y = Cl, R = Pr^i; X = 4-H, Y = Br, R = Et or Pr^i) were prepared similarly. The species where X = 4-H, Y = Br, R = Et could not be obtained pure despite several attempted recrystallisations. $[Mo\{HB(C_3H_3N_2)_3\}(NO)(OMe)Br]$ was prepared in the same way.

Bromo(ethoxo)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br(OEt)]$.—A mixture of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br_2]$ (2.0 g) and ethanol (20 ml) was refluxed for 4 h in methylcyclohexane (100 ml). After cooling, filtration, and evaporation of the filtrate, the *complex* was obtained as blue crystals (1.0 g, 50%). The compound could be recrystallised from ethanol. $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br(OR)]$ where R = Bu^i or Bu^s were prepared similarly.

Alternatively, a mixture of $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br_2]$ and allyl alcohol (10 ml) in methylcyclohexane (100 ml) was refluxed for 3 h. On cooling and evaporation of the deep green solution, a green microcrystalline complex, probably $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br(OC_3H_5)]$, was formed. Recrystallisation of this from dichloromethane–ethanol afforded $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br(OEt)]$ as sky-blue crystals.

Allyloxo(bromo)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br(OC_3H_5)]$.—This complex was prepared as described above and was purified chromatographically on alumina using light petroleum (b.p. 40—60 °C) as eluant. After evaporation of the eluant, the *complex* was obtained as green crystals (*ca.* 20%).

Diethoxo(nitrosyl)[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)(OEt)_2]$. The preparation of this complex was similar to that of $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Cl(OEt)]$ except that zinc dust was added. After refluxing the mixture for 3 h, it was filtered while hot and the filtrate partially evaporated *in vacuo* until crystallisation began. The *product* was isolated as brown crystals (*ca.* 50%).

Dibromo(nitrosyl)(triethyl phosphite)[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)\{P(OEt)_3\}Br_2]$.—This complex was prepared in the same way as $[Mo\{HB(C_3HMe_2N_2)_3\}(NO)Br(OEt)]$, using $P(OEt)_3$ instead of ethanol as the solvent/reactant. The complex was isolated as a brown insoluble powder.

Mass Spectral Data.—The mass spectra were obtained using AEI MS9 and MS12 spectrometers at 200 °C and 70 eV ionising voltages. The spectral data of selected compounds are shown here, with *m/e* values, relative intensities (in parentheses) and tentative peak assignments (peaks based on ^{92}Mo).

$[\{Mo[HB(C_3H_3N_2)_3](NO)Cl_2\}_n]$, $[M]_n$: *m/e* = 738 (10), $[M_2 - 2Cl]^+$; 708 (6) $[M_2 - 2Cl - NO]^+$; 678 (8), $[M_2 - 2Cl - 2NO]^+$; 641 (5), $[M_2 - 3Cl - 2NO]^+$; 464 (40) $[M + NO]^+$; 404 (24), $[M]^+$; 374 (100), $[M - NO]^+$; 339,334 (42), $[M - NO - Cl]^+$ and $[M - 2Cl]^+$; 304 (25), $[M - NO - 2Cl]^+$. Metastable ions at *m/e* = 588 and 689 established the fragmentation processes $[M_2 - 2Cl - NO]^+ \rightarrow [M_2 - 3Cl - 2NO]^+$ and $[M_2 - 2Cl]^+ \rightarrow [M_2 - 2Cl - NO]^+$.

$[\{Mo[HB(C_3H_3N_2)_3](NO)Br_2\}_n]$, $[M]_n$: *m/e* = 954 (5),

$[M_2 - \mathrm{NO}]^+$; 905 (2), $[M_2 - \mathrm{Br}]^+$; 875 (3), $[M_2 - \mathrm{NO} - \mathrm{Br}]^+$; 845 (10) $[M_2 - 2\mathrm{NO} - \mathrm{Br}]^+$; 826 (15), $[M_2 - 2\mathrm{Br}]^+$; 796 (27), $[M_2 - \mathrm{NO} - 2\mathrm{Br}]^+$; 782 (16), $[M_2 - 2\mathrm{Br} - 2\mathrm{NO} + \mathrm{O}]^+$; 766 (13), $[M_2 - 2\mathrm{Br} - 2\mathrm{NO}]^+$; 717$\rightarrow$520, $[M_2 - \mathrm{NO} - 3\mathrm{Br}]^+$ and fragmentation of pyrazolide residues; 492 (32), $[M]^+$; 462 (100), $[M - \mathrm{NO}]^+$; 413 (27), $[M - \mathrm{Br}]^+$; 395 (30), $[M - \mathrm{NO} - \mathrm{C_3H_3N_2}]^+$; 382 (50), $[M - \mathrm{NO} - \mathrm{Br} - \mathrm{H}]^+$ and subsequent fragmentation of pyrazolide residues. Metastable ions at $m/e = 433$ and 315 established the fragmentation processes $[M]^+ \rightarrow [M - \mathrm{NO}]^+$ and $[M - \mathrm{NO}]^+ \rightarrow [M - \mathrm{NO} - \mathrm{Br} - \mathrm{H}^+]$, respectively.

$[\{\mathrm{Mo[HB(C_3H_3N_2)_3](NO)I_2}\}_n]$, $[M]_n$: $m/e = 588$, $[M]^+$; 461, $[M - \mathrm{I}]^+$; 431, $[M - \mathrm{NO} - \mathrm{I}]^+$; 334, $[M - 2\mathrm{I}]^+$; 304, $[M - \mathrm{NO} - 2\mathrm{I}]^+$ (all peaks of approximately equal intensity).

The general mass-spectral fragmentation behaviour of these complexes is strongly reminiscent of that of $[\{(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mo(NO)X_2}\}_2]$ (X = Cl, Br, or I).

$[\mathrm{Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(NO)Br(OPr^i)}]$, $[M]$: $m/e = 556$ (30), $[M]^+$; 526 (30), $[M - \mathrm{NO}]^+$; 497 (<10), $[M - \mathrm{OPr^i}]^+$; 483 (100), $[M - \mathrm{NO} - \mathrm{Pr^i}]^+$, 434 (30), $[M - \mathrm{Br} - \mathrm{Pr^i}]^+$; 418 (10), $[M - \mathrm{Br} - \mathrm{OPr^i}]^+$; 404 (40), $[M - \mathrm{NO} - \mathrm{Br} - \mathrm{Pr^i}]^+$; 388 (40), $[M - \mathrm{NO} - \mathrm{Br} - \mathrm{OPr^i}]^+$.

Crystal Data.—$\mathrm{C_{18}H_{26}BMoN_7O_2Cl_4}$, $M = 621$, monoclinic, $a = 12.268(4)$, $b = 16.041(4)$, $c = 15.033(5)$ Å, $\beta = 91.44(4)°$, $U = 2\,957.5$ Å^3, $D_\mathrm{m} = 1.386$ (by flotation), $Z = 4$, $D_\mathrm{c} = 1.39$. The space-group was $P2_1/n$ (non-standard $P2_1/c$, No. 14, C^5_{2h}) from systematic absences, $h0l - h + l = 2n + 1$, $0k0 - k = 2n + 1$. Mo-K_α radiation ($\lambda = 0.710\,69$ Å) was used; $\mu(\text{Mo-}K_\alpha) = 8.22$ cm^{-1}.

Preliminary Weissenberg and precession photographs established the space-group. A crystal, from propan-2-ol, of dimensions 0.4 × 0.1 × 0.2 mm, was mounted along the unique axis on a STOE-STADI-2 two-circle diffractometer and the data collected using graphite monochromated Mo-K_α radiation. All reflections within the sphere $2\theta < 50°$ were collected using the stationary counter–moving crystal technique, producing 2 522 independent reflections of greater than 3σ significance. Lorentz and polarisation corrections were applied, but no correction for absorption was made.

Determination of the Structure, and Refinement.—The molybdenum atom was located from a Patterson synthesis and three cycles of least-squares refinement gave R 0.398. The remaining 31 non-hydrogen atoms were determined from a difference-Fourier based upon structure factors phased by the Mo atom. Four cycles of block-diagonal least-squares on these positions with all atoms assigned isotropic temperature factors gave R 0.091. The Mo and four Cl atoms were then assigned anisotropic temperature factors and three cycles of refinement gave R 0.068; all other atoms were then allowed anisotropic thermal parameters giving R 0.060. A further difference-Fourier based upon limited low-angle data showed the two non-methyl hydrogens, and these were included in subsequent structure-factor calculations in an assumed tetrahedral geometry with C–H = 0.95 Å[30] and B–H = 1.11 Å.[31]

The molybdenum and chlorine atomic scattering factors were corrected for anomalous dispersion reducing R to 0.057. At this stage an output analysis revealed some large discrepancies between the calculated and observed structure factors of a few low-angle reflections. Although during data collection there had been no evidence for crystal decay, an examination of more recent Weissenberg films showed a development of a secondary diffuse Bragg lattice which overlapped with some of the low-angle data. 72 Potentially affected reflections were removed and subsequent refinement was performed using the remaining 2 450 reflections giving a final R of 0.047.

Final shifts of parameters were less than 0.1σ and a final difference Fourier showed no peak larger than 0.6 e Å^{-1}.[3,32] The structure analysis and refinement described was carried out using programs from the Sheffield University X-ray system on an I.C.L. 1907 computer.

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