Molybdenum and Tungsten Nitrosyl Complexes containing Bulky Alkoxy, Aryloxy, and Arylamido Ligands: Their Electrochemical Behaviour and the Structure of $[Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2CH_2CH_2Br)]$†

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The complexes $[Mo\{HB(Me_2pz)_3\}(NO)X(NHR')]$ (X = I, R' = o-C_6H_4Me, 2,5-$Me_2C_6H_3$, $CHPh_2$, p-C_6H_4CN, p-$C_6H_4N_2Ph$, p-$C_6H_4N_2C_6H_4NO_2$-p; X = Cl, R' = p-C_6H_4I), $[W\{HB(Me_2pz)_3\}(NO)Cl(NHR')]$ (R' = $CHPh_2$ or p-C_6H_4I), $[Mo\{HB(Me_2pz)_3\}(NO)I(OR)]$ (R = $CH_2CH_2CH_2Br$, p-$CH_2C_6H_4Br$, or p-C_6H_4CN), and $[W\{HB(Me_2pz)_3\}(NO)Cl(OR)]$ (R = Ph, $CH_2CH_2CH_2Br$, or p-$CH_2C_6H_4Br$) (Me_2pz = 3,5-dimethylpyrazolyl) have been prepared and characterised spectroscopically. Electrochemical studies (cyclic voltammetry, coulometry) of these complexes in acetonitrile established that all underwent at least one one-electron reduction process, some of which were reversible. The $E_{\frac{1}{2}}$ values for the reduction were dependent on the nature of the metal, the halide, and the NHR' or OR group. The structure of $[Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2CH_2CH_2Br)]$ was determined crystallographically. The six-co-ordinate nature of the complex was confirmed and the Mo–O bond distance was 1.89 Å, comparable to that in other related compounds.

The compounds reported in this paper were prepared for two reasons: (*a*) to probe the nature of the co-ordination site when $[M\{HB(Me_2pz)_3\}(NO)X_2]$ (X = halide, Me_2pz = 3,5-dimethylpyrazolyl) underwent substitution by Y^- to give $[M\{HB(Me_2pz)_3\}(NO)XY]$, and (*b*) to establish that species of the type $[M\{HB(Me_2pz)_3\}(NO)XY]$ [X = halide, Y = OR or NHR' (R,R' = alkyl or aryl)] would undergo one-electron reduction as observed previously for $[M\{HB(Me_2pz)\}(NO)X_2]^z$ (z = 0, M = Mo, X = Cl, Br, or CO; or M = W, X = Cl; z = +1, M = Mo, X = NCMe).[1]

We have observed that the metal in $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (X = I, Y = OEt; X = I, Y = NHEt, NHC_6H_4Me-*p*, or NHC_6H_4OMe-*p*; X = Y = OEt or OPr^i; X = OEt, Y = OPr^i) enjoys considerable steric protection and, indeed, the existence of six-co-ordinate species of this type and even their apparent stability towards hydrolysis and oxidation, can be attributed to the tight ligand packing caused by the very bulky $HB(Me_2pz)_3$ group.[2] Our attitude to this rationalisation was strengthened by our *apparent* difficulties in isolating $[Mo\{HB(Me_2pz)_3\}(NO)I(NR_2)]$,[3] and the observation that the secondary alkylamido group NR_2 was very readily replaced by a primary alkylamido group, in contrast to general observations in the chemistry of metal–amido species. In order more fully to establish the steric factors relevant to the replacement of I^- in $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ by bulky amines, we have studied its reactions with *o*-methylaniline, 2,5-dimethylaniline, and methyldiphenylamine.

It is now fully established that $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$ (M = Mo, X = Cl, I, or CO; M = W, X = Cl) can undergo a facile one-electron reduction,[1] forming $[M\{HB(Me_2pz)_3\}(NO)X_2]^-$ whose stability depends on M and X. In order to establish the generality of one-electron reduction in systems of the type $[M\{HB(Me_2pz)_3\}(NO)]^{2+}$ we have investigated a representative selection of such species by cyclic voltammetry and coulometry.

Experimental

All reactions were carried out in purified, dry, oxygen-free solvents, under nitrogen. $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$ (X = Cl or I) and $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$ were synthesised as described elsewhere.[4,5] For column chromatography, silica gel 60 (70—230 mesh) was used with dichloromethane as eluant. I.r. spectra were obtained using a Perkin-Elmer 297 spectrophotometer, and ^1H n.m.r. spectra were measured using JEOL JMN-PMX-60, Varian HA 100, and Bruker WH400 (S.E.R.C. Warwick n.m.r. Service) spectrometers. All elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Birmingham.

Cyclic voltammetry (c.v.) was carried out using a system based on a Hitek DT2101 potentiostat and a PPR1 waveform generator; measurements were made in dry acetonitrile or tetrahydrofuran (thf) under N_2. In all experiments $[NBu^n_4][PF_6]$ (0.2 mol dm^{-3}) was used as supporting electrolyte with a Pt wire as test electrode. Solutions were *ca.* 10^{-3} mol dm^{-3} in the complex. Controlled potential electrolyses were performed in stirred solutions of the complexes in acetonitrile with $[NBu^n_4][PF_6]$ as supporting electrolyte.

Preparations.—$[Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4Me\text{-}o)]$. A mixture of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (1.0 g, 1.5 mmol) and *o*-toluidine (0.32 g, 3.0 mmol) in dichloromethane (40 cm^3) was stirred at room temperature for *ca.* 1.5 h during which time a dark brown solution formed. After filtration, the solvent was removed *in vacuo* until only 5 cm^3 remained. On addition of n-hexane, a brown compound formed which was purified by chromatography using dichloromethane as eluant. The main fraction was collected, the solvent evaporated *in vacuo*, and the

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† 3-Bromopropoxy(iodo)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]-molybdenum.

Supplementary data available (No. SUP 56434, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

residue recrystallised from dichloromethane–n-hexane affording the *complex* as brown microcrystals (0.68 g, 70%).

Complexes $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(NHCHPh_2)}]$ (pink, 78% yield) and $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4N_2Ph}\text{-}p)]$ (purple, 54% yield) were prepared similarly using a two-fold excess of the appropriate amine. $[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl(NHCHPh_2)}]$ was also obtained in this way, after refluxing in dichloromethane overnight, as orange crystals (59% yield).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_3Me_2\text{-}2,5)}]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (0.5 g, 0.75 mmol) and 2,5-dimethylaniline (0.68 g, 5.6 mmol) in toluene (40 $\mathrm{cm^3}$) was refluxed overnight. The reaction mixture was then cooled, filtered, and the filtrate evaporated *in vacuo*. The pure *complex* was obtained by chromatography as described above, and by recrystallisation from dichloromethane–n-hexane, being isolated as brown crystals (0.40 g, 80%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(}p\text{-}\mathrm{NHC_6H_4N_2C_6H_4NO_2}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (1.0 g, 1.5 mmol) and $p\text{-}\mathrm{NH_2C_6H_4N{=}NC_6H_4NO_2}\text{-}p$ (Disperse-orange-3) (0.71 g, 3 mmol) in dichloromethane (60 $\mathrm{cm^3}$) was refluxed for 3 h. The reaction mixture was cooled, filtered, and the filtrate partially evaporated *in vacuo* until only 5 $\mathrm{cm^3}$ remained. Addition of n-hexane caused the product to precipitate as a purple powder, purification being effected by chromatography (as above) and recrystallisation from dichloromethane–n-hexane. The *complex* was obtained as purple crystals (0.42 g, 36%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)Cl(NHC_6H_4I}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)Cl_2}]$ (0.5 g, 0.75 mmol) and *p*-iodoaniline (0.88 g, 4 mmol) in dichloromethane (100 $\mathrm{cm^3}$) was refluxed overnight. The brown solution was filtered, partially evaporated *in vacuo* and, on addition of n-hexane, the *complex* precipitated as brown microcrystals (0.43 g, 63%).

Complexes $[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl(OPh)}]$ and $[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl(NHC_6H_4I}\text{-}p)]$ were obtained similarly after refluxing for 3 d, and were isolated as green microcrystals (64% yield) and dull yellow powder (64%), respectively.

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OC_6H_4N_2Ph}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (1.0 g, 1.5 mmol) and *p*-phenylazophenol (0.58 g, 2.9 mmol) in toluene (40 $\mathrm{cm^3}$) was refluxed overnight. The reaction mixture was cooled and filtered, the filtrate being evaporated *in vacuo* to give a deep blue solid. The *complex* was obtained as deep blue microcrystals after recrystallisation from dichloromethane–n-hexane (0.5 g, 45%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2CH_2CH_2Br)}]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (1.0 g, 1.5 mmol) and 3-bromopropan-1-ol (0.40 g, 2.8 mmol) in dichloromethane (40 $\mathrm{cm^3}$) containing silver acetate (0.25 g) was stirred at room temperature for 1 h. The resulting green solution was filtered, the filtrate partially evaporated *in vacuo* to *ca.* 5 $\mathrm{cm^3}$, and the mixture treated with n-hexane. The *complex* was filtered off and obtained as green microcrystals (0.73 g, 72%).

$[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl(OCH_2CH_2CH_2Br)}]$. A solution of $[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl_2}]$ (0.5 g, 0.8 mmol) in dichloromethane (60 $\mathrm{cm^3}$) containing an excess of 3-bromopropan-1-ol was refluxed overnight. The purple solution was evaporated *in vacuo* and the *complex* obtained as a purple powder by recrystallisation from dichloromethane–n-hexane (0.23 g, 39%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2C_6H_4Br}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (0.5 g, 0.8 mmol) and *p*-bromobenzyl alcohol (0.28 g, 1.5 mmol) in toluene (40 $\mathrm{cm^3}$) was refluxed overnight. The brown solution was cooled and filtered, and the filtrate evaporated *in vacuo*. The *complex* was obtained by chromatography and recrystallisation of the main fraction from dichloromethane–n-hexane, and isolated as green crystals (0.26 g, 48%).

$[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl(OCH_2C_6H_4Br}\text{-}p)]$. A solution of $[\mathrm{W\{HB(Me_2pz)_3\}(NO)Cl_2}]$ (1.0 g, 1.6 mmol) in toluene (60 $\mathrm{cm^3}$) containing an excess of *p*-bromobenzyl alcohol was refluxed for 2 d. The purple solution was evaporated *in vacuo* and the residue chromatographed, the *second* fraction being collected (the first fraction was starting material). After filtration and evaporation the residue was recrystallised from dichloromethane–n-hexane, the *complex* being isolated as a purple powder (0.31 g, 25%).

Table 1. Atomic positional parameters with estimated standard deviations in parentheses for $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2CH_2CH_2Br)}]$

Atom	*X/a*	*Y/b*	*Z/c*
I(1)	0.519 28(21)	0.199 68(13)	0.275 93(8)
Mo(1)	0.390 86(19)	0.127 82(11)	0.170 58(7)
Br(1)	−0.129 7(6)	−0.010 3(3)	0.398 40(19)
O(1)	0.596 1(15)	−0.022 7(9)	0.185 7(7)
O(2)	0.189 7(15)	0.085 7(9)	0.217 7(6)
N(1)	0.519 1(21)	0.036 6(11)	0.179 1(7)
N(2)	0.241 1(17)	0.248 4(9)	0.162 1(7)
N(3)	0.255 3(17)	0.290 5(10)	0.103 0(6)
N(4)	0.589 9(17)	0.193 7(10)	0.104 1(7)
N(5)	0.543 2(16)	0.245 9(9)	0.053 2(7)
N(6)	0.320 4(16)	0.094 5(9)	0.075 8(6)
N(7)	0.298 6(17)	0.159 1(10)	0.033 1(6)
C(1)	0.074 8(25)	0.266 0(15)	0.274 9(9)
C(2)	0.129 0(21)	0.294 8(13)	0.203 0(9)
C(3)	0.072 0(24)	0.363 2(12)	0.171 5(10)
C(4)	0.152 2(22)	0.359 9(12)	0.108 2(10)
C(5)	0.139 7(29)	0.421 3(14)	0.053 2(12)
C(6)	0.860 0(21)	0.141 6(16)	0.139 2(10)
C(7)	0.760 7(19)	0.193 0(12)	0.094 8(9)
C(8)	0.818 5(24)	0.242 8(15)	0.042 0(9)
C(9)	0.680 6(22)	0.274 6(12)	0.016 1(10)
C(10)	0.679 4(27)	0.332 4(15)	−0.042 3(10)
C(11)	0.283 7(30)	−0.064 5(14)	0.083 1(10)
C(12)	0.275 3(21)	0.019 9(12)	0.049 6(8)
C(13)	0.230 5(26)	0.037 8(17)	−0.010 0(10)
C(14)	0.244 6(21)	0.125 1(13)	−0.021 2(8)
C(15)	0.208 0(26)	0.174 8(16)	−0.080 0(9)
C(16)	0.158(3)	0.018 8(17)	0.263 1(12)
C(17)	−0.010(4)	−0.018 9(19)	0.264 8(14)
C(18)	−0.069(4)	−0.078 9(22)	0.316 9(15)
B(1)	0.358 7(27)	0.253 4(16)	0.043 6(11)

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(NHC_6H_4CN}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (0.27 g, 0.4 mmol) and *p*-aminobenzonitrile (0.10 g, 0.8 mmol) in dichloromethane (30 $\mathrm{cm^3}$) was refluxed *in vacuo*, and the residue chromatographed. The second, brown-red fraction was collected and treated with n-hexane, the bulk of the solvent being reduced *in vacuo*. The complex was obtained as dark red-brown microcrystals which were recrystallised from dichloromethane–n-hexane (0.15 g, 51%).

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OC_6H_4CN}\text{-}p)]$. A solution of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ (0.27 g, 0.4 mmol) and *p*-hydroxybenzonitrile (0.05 g, 0.4 mmol) in thf (25 $\mathrm{cm^3}$) was stirred overnight at room temperature. The solution was evaporated *in vacuo*, the residue redissolved in dichloromethane and the mixture filtered. On addition of n-hexane followed by slow evaporation of the solvent mixture *in vacuo*, a red-brown powder formed. This was filtered off and chromatographed, the first, red-brown fraction being collected. The *complex* was isolated after partial evaporation and filtration, as dark red-brown crystals (0.17 g, 64%).

Crystal Structure Determination of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OCH_2CH_2CH_2Br)}]$.—*Crystal data.* $\mathrm{C_{18}H_{28}BBrIMoN_7O_2}$, $M = 687.98$ (crystallises from dichloromethane as small, very dark green, irregular bricks), crystal dimensions 0.20 × 0.12 × 0.20 mm, monoclinic, $a = 8.069(3)$, $b = 15.453(7)$,

Table 2. Analytical data for $[M\{HB(Me_2pz)_3\}(NO)XY]$

			Analysis[a] (%)			
M	X	Y	C	H	N	I
Mo	I	NHC_6H_4Me-*o*	40.6 (40.3)	4.9 (4.6)	17.3 (17.1)	19.5 (19.3)
	I	NHC_6H_3Me-2,5	41.2 (42.3)	4.9 (4.8)	16.7 (16.7)	19.2 (18.9)
	I	$NHCNPh_2$	46.1 (45.9)	4.4 (4.7)	15.3 (15.3)	17.3 (17.3)
	I	NHC_6H_4CN-*p*	37.0 (36.7)	3.9 (3.9)	16.8 (16.8)	—
	I	$NHC_6H_4N_2Ph$-*p*	44.5 (43.5)	4.6 (4.3)	18.2 (18.8)	16.9 (17.0)
	I	*p*-$NHC_6H_4N_2C_6H_4NO_2$-*p*[b]	41.9 (41.8)	4.5 (4.1)	18.8 (19.3)	15.9 (15.8)
	Cl	NHC_6H_4I-*p*[c]	40.0 (40.1)	4.9 (4.6)	15.8 (15.6)	17.9 (17.7)
W	Cl	$NHCHPh_2$[b]	46.7 (46.1)	4.7 (4.9)	15.8 (15.4)	—
	Cl	NHC_6H_4I-*p*[c]	36.3 (35.7)	4.3 (4.1)	13.9 (13.9)	—
Mo	I	$OCH_2CH_2CH_2Br$	31.3 (31.4)	3.8 (4.1)	14.4 (14.3)	17.9 (18.4)
	I	$OCH_2C_6H_4Br$-*p*[d]	37.1 (37.3)	4.2 (4.1)	12.8 (13.0)	—
	I	OC_6H_4CN-*p*	39.6 (39.6)	4.1 (3.9)	16.5 (16.8)	—
W	Cl	OPh[d]	40.7 (40.9)	4.6 (4.6)	15.0 (14.8)	—
	Cl	$OCH_2CH_2CH_2Br$	31.9 (31.6)	4.3 (4.1)	14.5 (14.3)	—
	Cl	$OCH_2C_6H_4Br$-*p*	36.4 (36.1)	3.6 (3.9)	13.4 (13.4)	—

[a] Calculated values in parentheses. [b] With $\frac{1}{6}$ mole of C_6H_{14}. [c] With $\frac{1}{2}$ mole of C_6H_{14}. [d] With $\frac{1}{4}$ mole of C_6H_{14}.

$c = 20.563(6)$ Å, $\beta = 81.91(20)°$, $U = 2\,538.5(16)$ Å^3, $D_m = 1.84$, $Z = 4$, $D_c = 1.800$ g cm^{-3}, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14, C_{2h}^5), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 32.94 cm^{-1}, $F(000) = 1\,344$.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntax R3 diffractometer by the ω-scan method. 1 918 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 methods. Hydrogen atoms were detected and placed in calculated positions [C–H 0.96, B–H 1.13 Å, C–C–H(methyl) 111°]; their contributions were included in structure factor calculations ($B = 8.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at *R* 0.067 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of molybdenum, iodine, and bromine. Table 1 lists atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 6; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

Results and Discussion

Synthesis and Spectroscopic Studies.—The alkyl- and aryl-amido (NHR′), and the alkyl- and aryl-oxy (OR) complexes $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (**1**) and $[W\{HB(Me_2pz)_3\}(NO)ClY]$ (**2**) were prepared by reaction of $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$ (X = Cl or I) and $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$ with an excess of the appropriate amine, phenol, or alcohol (analytical data are given in Table 2). With the amines a 1:2 mol ratio was usually a sufficient excess to effect a reasonable yield. In general, the conditions required to form (**1**; X = I, Y = NHR′) were milder than those used to produce (**1**; X = Cl, Y = NHR′), (**1**; X = I, Y = OR), and (**2**; Y = NHR′ or OR). These last required either refluxing conditions in dichloromethane or toluene, but to prepare (**1**; X = I, Y = $OCH_2CH_2CH_2Br$) it was necessary first to treat $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ with one mole equivalent of AgO_2CMe before adding the alcohol. However the conditions necessary to afford a reasonable yield of (**1**; X = I, Y = $NHC_6H_3Me_2$-2,5) were relatively vigorous, *i.e.* refluxing toluene overnight, compared to dichloromethane at room temperature for (**1**; X = I, Y = NHC_6H_4Me-*o*, $NHCHPh_2$, or $NHC_6H_4N_2Ph$-*p*) or under reflux for (**1**; X = I, Y = *p*-$NHC_6H_4N_2C_6H_4NO_2$-*p*). However, the fact that the complex *can* be prepared, together with its NHC_6H_4Me-*o* and $NHCHPh_2$ analogues, indicates that the tris(3,5-dimethyl)pyrazolylborate ligand can accommodate such bulky species. This may occur *via* alignment of the aromatic rings parallel to the cleft between two adjacent $Me_2C_3HN_2$ groups (*i.e.* parallel to the pseudo-three-fold axis defined by HB ··· Mo). Such an alignment would be analogous to that adopted by the carbonyl group in $[Mo\{HB(Me_2pz)_3\}(CO)_2(\eta^2\text{-}COPh)]$.[7]

The i.r. spectra of the complexes exhibited ν(BH) at *ca.* 2 500 cm^{-1}. The NH stretching frequency in the spectra of the amido complexes occurs at *ca.* 3 300 cm^{-1} (Table 3). The values of ν(NO) reflect the nature of the metal and the oxy or nitrogen ligand. Thus, generally ν(NO) for the Mo complexes was 30—34 cm^{-1} to higher frequency than their W analogues. The molybdenum iodo-alkylamido and -arylamido complexes exhibited ν(NO) in the range 1 650—1 659 cm^{-1} while the corresponding alkoxy species showed ν(NO) in the range 1 659—1 686 cm^{-1}, as was expected from previous studies.[1] The range of tungsten complexes was too small to permit a reasonable correlation between ν(NO) and ligand type.

The ^{1}H n.m.r. spectra (Table 3) of the complexes were consistent with the formulation of the complexes. Thus all species (except those whose spectra were determined at field strengths of 100 MHz or lower) exhibited six methyl proton signals and three resonances due to the proton on C(4) of the three inequivalent pyrazole rings. This indicated that the complexes had the expected six-co-ordinate structure and there was no plane of symmetry in the species. The amido species exhibited δ(NH) in the range 10—13.5 p.p.m., and the N–H proton was not exchanged by treatment with D_2O under neutral conditions. The ^{1}H n.m.r. spectrum of (**1**; X = I, Y = $NHC_6H_3Me_2$-2,5) exhibited eight resonances in the methyl region, consistent with the expected inequivalence of the 2- and 5- methyl groups in the anilido ligand. The chemical shifts of the α-methylene protons in (**1**; X = I, Y = $OCH_2CH_2CH_2Br$ or $OCH_2C_6H_4Br$-*p*) and (**2**; Y = $OCH_2CH_2CH_2Br$ or $OCH_2C_6H_4Br$-*p*) occurred at low field with respect to their δ values in the free ligand. This effect has been observed previously, and is attributed to the strong electronegativity of the $M\{HB(Me_2pz)_3\}(NO)X$ group (X = halide).[2,4]

Table 3. I.r. and ^{1}H n.m.r. spectral data obtained from $[\mathrm{M\{HB(Me_2pz)_3\}(NO)XY}]$

			I.r./cm^{-1} [a]		^{1}H N.m.r.		
M	X	Y	ν(NO)	ν(NH)	δ_H (*A*) [b]	Multiplicity and assignments [c]	
Mo	I	$\mathrm{NHC_6H_4Me}$-*o*	1 658	3 320	13.35 (1)	s; $\mathrm{NHC_6H_4Me}$	
					8.31 (1)	d [J(HH) 7.96]	$\mathrm{NHC_6}H_4\mathrm{Me}$
					7.36 (1)	t [J(HH) 7.36]	
					7.27 (1)	t [J(HH) 7.24]	
					7.14 (1)	t [J(HH) 7.40]	
					5.96 (1)	s	$\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.89 (1)	s	
					5.79 (1)	s	
					2.66 (3)	s	$\mathrm{C_3H(C}H_3)_2\mathrm{N_2} + \mathrm{NHC_6H_4C}H_3$
					2.48 (3)	s	
					2.42 (3)	s	
					2.39 (3)	s	
					2.38 (3)	s	
					2.00 (3)	s	
					1.89 (3)	s	
Mo	I	$\mathrm{NHC_6H_3Me_2}$-2,5	1 650	3 280	13.42 (1)	s; $\mathrm{N}H\mathrm{C_6H_3Me_2}$	
					7.19 (1)	d [J(HH) 7.52]	$\mathrm{NHC_6}H_3\mathrm{Me_2}$
					7.05 (1)	t [J(HH) 7.50]	
					6.84 (1)	d [J(HH) 7.32]	
					5.97 (1)	s	$\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.80 (1)	s	
					5.68 (1)	s	
					3.01 (3)	s	$\mathrm{C_3H(C}H_3)_2\mathrm{N_2} + \mathrm{NHC_6H_3(C}H_3)_2$
					2.67 (3)	s	
					2.63 (1)	s	
					2.48 (3)	s	
					2.35 (3)	s	
					2.33 (3)	s	
					1.81 (3)	s	
					1.51 (3)	s	
Mo	I	$\mathrm{NHCHPh_2}$	1 659	3 300	12.63 (1)	d [^3J(HH) 11.8]; $\mathrm{N}H\mathrm{CHPh_2}$	
					7.49 (1)	d [^3J(HH) 12.2]; $\mathrm{NHC}H\mathrm{Ph_2}$	
					7.26 (10)	m; $\mathrm{NHCH(C_6}H_5)_2$	
					5.84 (1)	s	$\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.76 (1)	s	
					5.69 (1)	s	
					2.61 (3)	s	$\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
					2.43 (3)	s	
					2.35 (3)	s	
					2.30 (3)	s	
					2.01 (3)	s	
					1.84 (3)	s	
Mo	I	$\mathrm{NHC_6H_4CN}$-*p*	1 666 2 224 [e]	3 227	12.48 (1) [d]	s; $\mathrm{N}H\mathrm{C_6H_4CN}$	
					7.72 (4)	s; $\mathrm{NHC_6}H_4\mathrm{CN}$	
					5.96 (1)	s	$\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.88 (1)	s	
					5.81 (1)	s	
					2.67 (3)	s	$\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$
					2.49 (3)	s	
					2.47 (3)	s	
					2.42 (3)	s	
					2.40 (3)	s	
					1.96 (3)	s	
Mo	Cl	$\mathrm{NHC_6H_4I}$-*p*	1 650	3 270	12.30 (1) [d]	s; $\mathrm{N}H\mathrm{C_6H_4I}$	
					7.50 (4)	A_2B_2 system, δ_A 7.75, δ_B 7.25, J(AB) 9.0; $\mathrm{NHC_6}H_4\mathrm{I}$	
					5.89 (2)	s	$\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.81 (1)	s	
					2.67 (3)	s	$\mathrm{C_3H(C}H_3)_2\mathrm{N_2}$ [f]
					2.44 (3)	s	
					2.40 (9)	s	
					2.02 (3)	s	

Table 3 (*continued*)

			I.r./cm$^{-1\,a}$		^{1}H N.m.r.		
M	X	Y	ν(NO)	ν(NH)	δ_H (*A*)^b	Multiplicity and assignments^c	
Mo	I	$NHC_6H_4N_2Ph$-*p*	1 658	3 250	12.97 (1)	s; $NHC_6H_4N_2Ph$	
					7.97 (2)	d [*J*(HH) 8.76]	$NHC_6H_4N_2C_6H_5$
					7.93 (2)	d [*J*(HH) 6.56]	
					7.75 (2)	d [*J*(HH) 8.68]	
					7.50 (3)	m	
					5.95 (1)	s	$C_3HMe_2N_2$
					5.86 (1)	s	
					5.79 (1)	s	
					2.70 (3)	s	$C_3H(CH_3)_2N_2$
					2.49 (3)	s	
					2.47 (3)	s	
					2.38 (3)	s	
					2.37 (3)	s	
					1.99 (3)	s	
Mo	I	*p*-$NHC_6H_4N_2C_6H_4NO_2$-*p*	1 658	3 260	12.85 (1)	s; $NHC_6H_4N_2C_6H_4NO_2$	
					8.38 (2)	d [*J*(HH) 9.0]	$NHC_6H_4N_2C_6H_4NO_2$
					8.05 (2)	d [*J*(HH) 9.0]	
					8.02 (2)	d [*J*(HH) 8.88]	
					7.76 (2)	d [*J*(HH) 8.76]	
					5.96 (1)	s	$C_3HMe_2N_2$
					5.88 (1)	s	
					5.80 (1)	s	
					2.70 (3)	s	$C_3H(CH_3)_2N_2$^{f}
					2.49 (3)	s	
					2.48 (3)	s	
					2.40 (3)	s	
					2.38 (3)	s	
					2.00 (3)	s	
W	Cl	$NHCHPh_2$	1 625	3 280	10.10 (1)	d [^{3}*J*(HH) 11.96]; $NHCHPh_2$	
					7.65 (1)	d [^{3}*J*(HH) 12.1]; $NHCHPh_2$	
					7.25 (10)	m; $NHCN(C_6H_5)_2$	
					5.83 (1)	s	$C_3HMe_2N_2$
					5.80 (1)	s	
					5.75 (1)	s	
					2.64 (3)	s	$C_3H(CH_3)_2N_2$
					2.39 (3)	s	
					2.35 (3)	s	
					2.29 (3)	s	
					2.04 (3)	s	
					1.94 (3)	s	
W	Cl	NHC_6H_4I-*p*	1 618	3 260	10.54 (1)^g	br; NHC_6H_4I	
					7.43 (4)	A_2B_2, δ_A 7.71, δ_B 7.15, *J*(AB) 8.4; NHC_6H_4I	
					5.90 (3)	br; $C_3HMe_2N_2$	
					2.74 (3)	s	$C_3H(CH_3)_2N_2$^{f}
					2.44 (6)	s	
					2.40 (6)	s	
					2.18 (3)	s	
Mo	I	$OCH_2CH_2CH_2Br$	1 659	—	5.87 (1)	s	$C_3HMe_2N_2$
					5.84 (1)	s	
					5.82 (1)	s	
					5.68 (2)	m; $OCH_2CH_2CH_2Br$	
					3.53 (2)	m; $OCH_2CH_2CH_2Br$	
					2.50 (20)	s	$C_3H(CH_3)_2N_2$ + $OCH_2CH_2CH_2Br$
					2.41	s	
					2.40	s	
					2.37	s	
					2.36	s	
					2.35	s	
W	Cl	$OCH_2CH_2CH_2Br$	1 625	—	5.92 (1)	s	$C_3HMe_2N_2$
					5.86 (1)	s	
					5.82 (1)	s	
					5.86 (2)	m; $OCH_2CH_2CH_2Br$	
					3.55 (2)	m; $OCH_2CH_2CH_2Br$	

Table 3. (*continued*)

			I.r./cm^{-1} [a]		^{1}H N.m.r.	
M	X	Y	ν(NO)	ν(NH)	δ_H (A)[b]	Multiplicity and assignments[c]
W	Cl	$\mathrm{OCH_2CH_2CH_2Br}$	1 625	—	2.58 (20)	s $\mathrm{C_3H(C}H_3\mathrm{)_2N_2}$ + $\mathrm{OCH_2C}H_2\mathrm{CH_2Br}$
					2.57	s
					2.39	s
					2.36	s
					2.35	s
					2.34	s
Mo	I	$\mathrm{OCH_2C_6H_4Br}$-*p*	1 665	—	7.36 (4)	A_2B_2, δ_A 7.44, δ_B 7.28, J(AB) 8.4; $\mathrm{OCH_2C_6}H_4\mathrm{Br}$
					6.49 (2)	AB, δ_A 6.55, δ_B 6.41, J(AB) 14.0; $\mathrm{OC}H_2\mathrm{C_6H_4Br}$
					5.86 (1)	s $\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.85 (1)	s
					5.77 (1)	s
					2.52 (3)	s $\mathrm{C_3H(C}H_3\mathrm{)_2N_2}$[f]
					2.40 (3)	s
					2.37 (3)	s
					2.36 (3)	s
					2.25 (3)	s
					2.19 (3)	s
W	Cl	$\mathrm{OCH_2C_6H_4Br}$-*p*	1 635	—	9.39 (4)	A_2B_2, δ_A 7.46, δ_B 7.32 J(AB) 8.36; $\mathrm{OCH_2C_6}H_4\mathrm{Br}$
					6.70 (2)	AB, δ_A 6.75, δ_B 6.64, J(AB) 14.0; $\mathrm{OC}H_2\mathrm{C_6H_4Br}$
					5.92 (1)	s $\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.88 (1)	s
					5.75 (1)	s
					2.61 (3)	s $\mathrm{C_3H(C}H_3\mathrm{)_2N_2}$
					2.51 (3)	s
					2.37 (3)	s
					2.35 (3)	s
					2.34 (3)	s
					2.06 (3)	s
W	Cl	OPh	1 640	—	7.25 (5)[d]	m; $\mathrm{OC_6}H_5$
					5.90 (2)	s $\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.81 (1)	s
					2.61 (3)	s $\mathrm{C_3H(C}H_3\mathrm{)_2N_2}$[f]
					2.39 (9)	s
					2.30 (3)	s
					2.19 (3)	s
Mo	I	$\mathrm{OC_6H_4CN}$-*p*	1 686	—	7.57 (4)[d]	A_2B_2, δ_A 7.66, δ_B 7.47, J(AB) 9.0; $\mathrm{OC_6}H_4\mathrm{CN}$
					5.90 (1)	s $\mathrm{C_3}H\mathrm{Me_2N_2}$
					5.87 (1)	s
					5.84 (1)	s
					2.48 (3)	s $\mathrm{C_3H(C}H_3\mathrm{)_2N_2}$
					2.43 (3)	s
					2.39 (3)	s
					2.35 (3)	s
					2.23 (3)	s
					1.95 (3)	s

[a] In KBr discs. [b] In $CDCl_3$ at 400 MHz unless otherwise stated; A = relative intensity. [c] J values in Hz. [d] In $CDCl_3$ at 100 MHz. [e] ν(CN). [f] Signals due to C_6H_{14} also detected but not assigned. [g] In $CDCl_3$ at 60 MHz.

Electrochemical Studies.—The redox behaviour of most of the new complexes and the already known [1; X = I, Y = NHEt, NHPh, $NH(CH_2)_3PPh_2$, or NHC_6H_4Cl-*p*] was investigated by a combination of cyclic voltammetry and coulometry. The data, together with those already known for $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (X = Y = Cl or I) and $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$ are summarised in Table 4.

The data obtained from the Mo complexes were obtained with an electrochemical cell different from those used for their W analogues. For the former, we anticipated that E (the separation between anodic and cathodic peaks in the cyclic voltammograms) should be 59 mV, and we accepted an experimental variation of up to +80 mV on the basis of solvent effects (in acetonitrile) and cell design. For the W complexes, by a combination of repeated cyclic voltammetry, electrolysis just beyond the reduction potential and redetermination of the conventional and cyclic voltammogram, we established that $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$ underwent a chemically and electrochemically reversible one-electron reduction, with ΔE = 80 mV. The data reported herein represent a preliminary survey of the general electrochemical behaviour of $[M\{HB(Me_2pz)_3\}(NO)XY]$ (X = Y = halide), and more thorough and detailed studies will be reported elsewhere.

In general, for the species $[Mo\{HB(Me_2pz)_3\}(NO)IY]$ the $E_{\frac{1}{2}}$

Table 4. Electrochemical data obtained from $[M\{HB(Me_2pz)_3\}(NO)XY]$

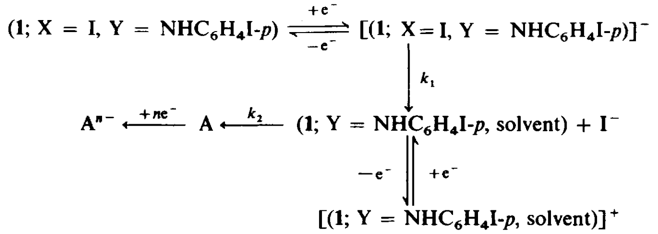
			MeCN Solution			thf Solution	
M	X	Y	$E_{\frac{1}{2}}{}^{a}$ (V)	ΔE (mV)	n^{b}	$E_{\frac{1}{2}}{}^{a}$ (V)	ΔE (mV)
Mo	I	I				+0.22	120
Mo	Cl	Cl	+0.09	70	1.0	−0.09	90
W	Cl	Cl	−0.42	80	1.0	−0.46	200
Mo	I	NHPh	−0.83	100	0.6		
Mo	I	$NHCHPh_2$	-1.14^{c}	—	0.8	-1.12^{c}	—
Mo	I	NHEt	-1.21^{c}	—	0.8	-1.34^{c}	—
Mo	I	$NH(CH_2)_3PPh_2$				-1.29^{b}	—
Mo	I	NHC_6H_4I-*p*	−0.68	80	0.9		
Mo	I	NHC_6H_4Cl-*p*	−0.73	80	0.8		
Mo	Cl	NHC_6H_4I-*p*	−0.78	120	0.9		
W	Cl	NHC_6H_4I-*p*	−1.20	110	0.8		
Mo	I	$NHC_6H_4N_2Ph$-*p*	−0.57	80	1.1		
			-1.64^{c}	—	—		
Mo	I	*p*-$NHC_6H_4N_2C_6H_4NO_2$-*p*	−0.45	70	1.2		
			−0.94	80	0.9		
Mo	I	OEt	−0.61	70	1.2		
Mo	I	$OCH_2CH_2CH_2Br$	−0.54	80	0.7		
W	Cl	$OCH_2CH_2CH_2Br$	−1.14	180	0.8		
Mo	I	$OCH_2C_6H_4Br$-*p*	−0.50	100	0.7		
W	Cl	$OCH_2C_6H_4Br$-*p*	−1.10	240	0.6		
Mo	I	$OC_6H_4N_2Ph$-*p*	−0.14	60	1.0		

[a] Solutions 0.2 mol dm^{-3} $[NBu^{n}{}_4][BF_4]$, *ca.* 10^{-3} mol dm^{-3} in complex, using Pt electrode, *vs.* saturated calomel electrode (s.c.e.); different cells used for Mo and W complexes. [b] Number of electrons, by comparison with $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$, $i_p\mu^{-\frac{1}{2}}[\text{complex}]^{-1} = 5.20 \times 10^2$ A $V^{-\frac{1}{2}}$ $S^{-\frac{1}{2}}$ dm^3 mol^{-1}. [c] E_{pc} value only, irreversible process.

values (*vs.* s.c.e. in MeCN) follow the order of increasing difficulty of reduction where Y = aryloxy (*ca.* −0.10 V) < alkoxy (−0.50 ⟶ −0.65 V) < arylamido (−0.60 ⟶ −1.10 V) < alkylamido (−1.10 ⟶ −1.22 V).[2] This broadly parallels the electron-releasing/accepting capabilities of the group Y, and is consistent with the effect of these substituents on ν(NO).[2]

The stability of the W-containing species upon reduction was generally greater than those of their Mo analogues. This may be illustrated by the behaviour of (**1**; X = I, Y = $OCH_2CH_2CH_2Br$) and (**2**; Y = $OCH_2CH_2CH_2Br$). On sweeping the potential of the former in acetonitrile from +0.2 to −1.0 V (at 0.3 V s^{-1} sweep rate), the cathodic peak due to reduction of the alkoxide was observed. However, on holding the reduction potential at −1.0 V for *ca.* 0.5 min and then reversing the sweep, the anodic scan revealed *two* peaks, the first due to reoxidation of $[(\mathbf{1}; X = I, Y = OCH_2CH_2CH_2Br)]^-$, the second caused by formation of a new electroactive species which exhibited quasi-reversible behaviour. From our inspection of peak heights most of (**1**; X = I, Y = $OCH_2CH_2CH_2Br$) at the electrode was converted to this new product. In contrast cyclic voltammetric reduction of (**2**; Y = $OCH_2CH_2CH_2Br$) was electrochemically and chemically stable and no new products were formed after reduction.

The systems (**1**; X = I, Y = NHR′) also exhibited irreversible electrode behaviour, and on reoxidation following reduction did not show E_{pa}. A study was made of the behaviour of (**1**; X = Cl or I, Y = NHC_6H_4Cl-*p* or NHC_6H_4I-*p*). Controlled potential reduction of (**1**; X = I, Y = NHC_6H_4I-*p*), which underwent an irreversible one-electron reduction, was carried out at −1.4 V *vs.* s.c.e. That the parent species was reduced in a one-electron step to $[(\mathbf{1}; X = I, Y = NHC_6H_4I\text{-}p)]^-$ was established by plotting a graph of cell current *vs.* charge passed. By investigating the cyclic voltammogram of the solution after reduction was complete it was shown that dissociation of I^- had occurred (the $I^- \longrightarrow \frac{1}{2}I_2$ and $I^- \longrightarrow I_3{}^-$ oxidation peaks were detected). The metal-containing species, presumably $[Mo\{HB(Me_2pz)_3\}(NO)(NHC_6H_4I\text{-}p)(\text{solvent})]$ underwent a quasi-reversible oxidation ($E_{\frac{1}{2}} = +0.04$ V). This, in turn, was observed to undergo a chemical reaction to form a product A which was irreversibly reduced, $E_p = -0.94$ V. The overall electrochemical process may be summarised as in the Scheme.



Scheme.

In order to establish that I^- liberated in this reaction originated from the metal and not from the NC_6H_4I-*p* ligand, the electrochemistry of (**1**; X = I, NHC_6H_4Cl-*p*) and (**1**; X = Cl, Y = NHC_6H_4I-*p*) was investigated. The former species exhibited electrode characteristics very similar to that of its NHC_6H_4I-*p* analogue, $E_{\frac{1}{2}}$ being more cathodic, presumably reflecting the change of *para* substituent on the aromatic ring (this will be discussed elsewhere). The electrochemistry of (**1**; X = Cl, Y = NHC_6H_4I-*p*)], however, revealed a quasi-reversible wave at −0.78 V and no trace of liberated I^- was detected. This confirms that electrochemical reduction of species containing Mo–I bonds leads to cleavage of that bond with release of I^-.

Only two complexes exhibited two one-electron reductions, (**1**; X = I, Y = $NHC_6H_4N_2Ph$-*p*) and (**1**; X = I, Y = *p*-$NHC_6H_4N_2C_6H_4NO_2$-*p*). The second wave in the cyclic voltammogram of the first complex was irreversible but the

Table 5. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [Mo{HB($Me_2pz)_3$}(NO)I($OCH_2CH_2CH_2Br$)]

Mo(1)–I(1)	2.763(2)	Mo(1)–N(2)	2.240(14)	O(1)–N(1)	1.127(21)	C(17)–C(18)	1.45(4)
Mo(1)–O(2)	1.886(12)	Mo(1)–N(4)	2.206(14)	O(2)–C(16)	1.39(3)	C(18)–Br(1)	1.98(3)
Mo(1)–N(1)	1.772(16)	Mo(1)–N(6)	2.167(13)	C(16)–C(17)	1.47(4)		

I(1)–Mo(1)–O(2)	97.3(4)	O(2)–Mo(1)–N(1)	98.4(6)	N(1)–Mo(1)–N(4)	92.5(6)	Mo(1)–N(1)–O(1)	177.7(15)
I(1)–Mo(1)–N(1)	87.4(5)	O(2)–Mo(1)–N(2)	83.8(5)	N(1)–Mo(1)–N(6)	97.5(6)	Mo(1)–O(2)–C(16)	131.8(13)
I(1)–Mo(1)–N(2)	89.6(4)	O(2)–Mo(1)–N(4)	167.6(5)	N(2)–Mo(1)–N(4)	85.5(5)	O(2)–C(16)–C(17)	113.2(20)
I(1)–Mo(1)–N(4)	88.9(4)	O(2)–Mo(1)–N(6)	93.7(5)	N(2)–Mo(1)–N(6)	85.1(5)	C(16)–C(17)–C(18)	118.4(25)
I(1)–Mo(1)–N(6)	167.3(4)	N(1)–Mo(1)–N(2)	176.4(6)	N(4)–Mo(1)–N(6)	79.2(5)	C(17)–C(18)–Br(1)	107.5(21)

Tris(3,5-dimethylpyrazolyl)borate geometry

	Ring A [N(2), N(3), C(1)—C(5)]	Ring B [N(4), N(5), C(6)—C(10)]	Ring C [N(6), N(7), C(11)—C(15)]
N(2)–N(3)	1.369(20)	1.414(20)	1.358(19)
N(2)–C(2)	1.352(23)	1.365(22)	1.344(22)
N(3)–B(1)	1.494(27)	1.533(27)	1.560(27)
N(3)–C(4)	1.353(23)	1.330(24)	1.360(23)
C(1)–C(2)	1.547(28)	1.521(27)	1.481(28)
C(2)–C(3)	1.353(27)	1.359(27)	1.356(29)
C(3)–C(4)	1.371(27)	1.389(28)	1.370(29)
C(4)–C(5)	1.490(30)	1.497(29)	1.496(28)
Mo(1)–N(2)–N(3)	119.1(10)	118.4(10)	118.8(10)
Mo(1)–N(2)–C(2)	135.6(12)	135.7(11)	133.2(11)
N(3)–N(2)–C(2)	105.4(13)	105.7(13)	107.7(13)
N(2)–N(3)–B(1)	120.8(14)	120.2(14)	121.7(14)
N(2)–N(3)–C(4)	109.5(14)	109.1(14)	109.4(14)
B(1)–N(3)–C(4)	129.4(16)	130.4(16)	128.1(15)
N(2)–C(2)–C(1)	121.1(16)	121.8(16)	122.5(16)
N(2)–C(2)–C(3)	111.1(16)	109.5(16)	108.0(16)
C(1)–C(2)–C(3)	127.8(17)	128.7(17)	129.5(18)
C(2)–C(3)–C(4)	106.2(17)	107.7(18)	109.1(19)
N(3)–C(4)–C(3)	107.9(16)	108.1(17)	105.8(16)
N(3)–C(4)–C(5)	123.5(17)	124.0(17)	126.0(16)
C(3)–C(4)–C(5)	128.6(18)	127.9(18)	128.2(18)
N(3)–B(1)–N(5)	111.4(16)		
N(3)–B(1)–N(7)	108.8(16)		
N(5)–B(1)–N(7)	105.9(16)		

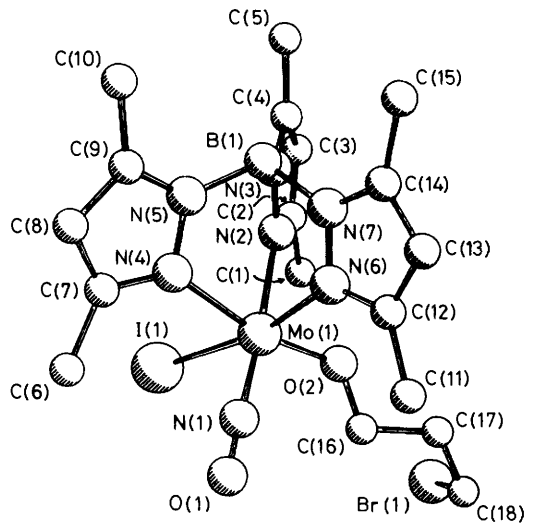


Figure. The molecular structure of [Mo{HB($Me_2pz)_3$}(NO)I($OCH_2CH_2CH_2Br$)] showing the atom labelling

second complex revealed two reversible one-electron processes. We were not able, however, to identify the reduction products. The species (1; X = I, Y = $OC_6H_4N_2Ph$-*p*), unlike its anilido analogues, revealed only one electrode process, a reversible one-electron transfer at −0.14 V, by far the easiest compound to reduce both chemically and electrochemically. In general, it would appear that species containing electron-withdrawing phenolic ligands may give rise to well behaved electrode behaviour, and to reduction potentials which make the reduced species accessible by chemical as well as electrochemical techniques. Efforts to prepare reduced species are currently underway.

Crystal Structure of [Mo{HB($Me_2pz)_3$}(NO)I($OCH_2CH_2CH_2Br$)].—The structure is illustrated in the Figure 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 and 6.

The co-ordination polyhedron of the molybdenum atom is essentially octahedral, comprising a linear nitrosyl, a terminal iodine, a 3-bromopropoxy ligand, and a tris(3,5-dimethylpyrazolyl)borato ligand with geometries which are very similar to those previously reported for other similar molecules (ref. 2). Features include a short Mo–N(nitrosyl), slightly short Mo–I, Mo–N(pyrazolyl) lengths which reflect the extent of competitive σ-bonding by the *trans* ligand, and a short Mo-O bond indicating substantial σ-donor bonding from the alkoxy residue to the molybdenum atom in order to utilise a vacant σ-nonbonding orbital in π-bond formation. The angles between the mean pyrazole planes differ from 120° in a way which reflects the bulk of the adjacent unidentate ligand. The conformations adopted along the carbon chain of the 3-bromopropoxy ligand are approximately antiperiplanar with the exception that the terminal bromine substituent is very skew (see Table 6 for torsion angles); this seems to be a consequence of crystal packing since there are two, short (3.75 Å) intermolecular contacts from this bromine to pyrazole methyl groups. All ligand bond lengths are unexceptional.

Table 6. Details of planar fragments. Equations of mean planes are of the form $pX + qY + rZ = d$, where p, q, and r are direction cosines referred to orthogonal axes a, b, c^*. Deviations (Å) of atoms from mean planes are given in parentheses

	p	*q*	*r*	*d*
Plane A: N(2), N(3), C(2)—C(4)	0.7832	0.5641	0.2614	4.9230
[N(2) −0.004, N(3) 0.004, C(2) 0.002, C(3) 0.000, C(4) −0.003, Mo(1) −0.044, C(1) −0.046, C(5) 0.036, B(1) −0.116]				
Plane B: N(4), N(5), C(7)—C(9)	−0.0816	−0.8050	−0.5877	−4.0642
[N(4) −0.003, N(5) −0.001, C(7) 0.006, C(8) −0.006, C(9) 0.004, Mo(1) 0.136, C(6) 0.038, C(10) −0.001, B(1) 0.144]				
Plane C: N(6), N(7), C(12)—C(14)	−0.8937	0.1259	0.4307	−1.6477
[N(6) −0.010, N(7) 0.009, C(12) 0.008, C(13) −0.003, C(14) −0.004, Mo(1) 0.132, C(11) −0.010, C(15) −0.007, B(1) −0.177]				

Angles (°) between planes:		
	A–B	132.2
	A–C	121.1
	B–C	106.4

Torsion angles (°):		
	Mo(1)–O(2)–C(16)–C(17)	−152.9
	O(2)–C(16)–C(17)–C(18)	−170.1
	C(16)–C(17)–C(18)–Br(1)	+75.0

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