Electrochemical and Chemical Properties of Di-iodonitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum, $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$, and Related Complexes†

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Cyclic voltammetric (c.v.), coulometric, and e.s.r. spectroscopic studies have established that $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$, (**A**) ($Me_2pz$ = 3,5-dimethylpyrazolyl), can be reduced reversibly to a paramagnetic monoanion in tetrahydrofuran (thf) solution, and that $(\mathbf{A})^-$ dissociates I^- giving $[Mo\{HB(Me_2pz)_3\}(NO)I(solvent)]$, (**B**). The latter undergoes a reversible one-electron oxidation process. The electrochemical behaviour (c.v.) of $[W\{HB(Me_2pz)_3\}(NO)(CO)_2]$ and $[Mo\{HB(Me_2pz)_3\}(NO)L_2]^z$ (L = NCMe, $z = +1$; L = CO, $z = 0$) has also been briefly examined. Reduction of complex (**A**) by $Li(C_6H_4Me\text{-}p)$ in diethyl ether afforded the complex $[Mo\{HB(Me_2pz)_3\}(NO)I_2\{Li(OEt_2)_2\}]$, (**E**), whose characterisation and properties are described. It is thought that (**E**) contains the $\{Mo^-(\mu\text{-}I)_2Li^+\}$ group.

The di-iodo-complex $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (Me_2pz = 3,5-dimethylpyrazolyl) is a convenient precursor for the preparation of remarkably stable monomeric alkoxy-, amido-, thiolato-, and hydrazido(1−)-species of the type $[Mo\{HB(Me_2pz)_3\}(NO)I(X)]$ (X = OR, NHR, SR, or NHNRR′).[1] We have attributed the unusual stability of these compounds, particularly towards aerial oxidation and hydrolysis, to the steric bulk, and therefore protective nature, of the tris(3,5-dimethylpyrazolyl)borato-ligand, and there is substantial evidence to support this view.[1] However, the assumption that the parent di-iodide was itself monomeric, and therefore co-ordinatively unsaturated, has not been confirmed, although there is sufficient circumstantial experimental data to indicate that this is so. There is a well established analogy between the chemistry of cyclopentadienyl and tris(pyrazolyl)borato complexes, which has a useful predictive function.[2] It is known that the corresponding di-iodo(η-cyclopentadienyl) complex, $[\{Mo(\eta\text{-}C_5H_5)(NO)I_2\}_2]$ is dimeric (with two I bridges), and is readily reduced to the Mo–Mo bonded species $[\{Mo(\eta\text{-}C_5H_5)(NO)I\}_2]$. It does not appear, however, that the tris(3,5-dimethylpyrazolyl)borate complex behaves similarly, which is presumably due to the steric hindrance of the heterocyclic ligand.

Our reinvestigation of the nature of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ and related species was prompted by two observations: (*i*) that the di-iodide became green in several oxygen-containing solvents, including water, although it could be recovered usually quantitatively, and (*ii*) that attempts to prepare aryl complexes of the type $[Mo\{HB(Me_2pz)_3\}(NO)I(R)]$ led not to the formation of Mo–C containing species, but to reduced forms of the di-iodide. In this paper we give an account of our observations, dealing with (*a*) the electrochemical properties of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ and related compounds, and spectral identification of reduced species obtained therefrom, and (*b*) attempts to isolate reduced species based on $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$. Some preliminary results of our work have been published.[3]

Experimental

Electrochemical studies were carried out using a Hitek galvanostat/potentiostat and wave-form generator, using platinum-wire electrodes. I.r. spectral data were obtained using a PE 297 spectrophotometer, ^1H n.m.r. spectra using a PE R34 instrument, and e.s.r. spectra were recorded on a Hilger-Watts Microspin *X*-band spectrometer using a 100-MHz modulation (*g* values were determined from frequency measurements with a proton-resonance head); diphenylpicrylhydrazyl (dpph) was used as reference.

Tolyl-lithium, $[Mo\{HB(Me_2pz)_3\}(NO)X_2]$[2,4] (X = CO, Cl, or I), and $[W\{HB(Me_2pz)_3\}(NO)Cl_2]$[2] were prepared as described earlier, and all reactions were carried out under dry nitrogen. Elemental analyses were determined by the Microanalytical Laboratory, University of Birmingham.

$[Mo\{HB(Me_2pz)_3\}(NO)I_2\{Li(OEt_2)_2\}]$.—An excess of tolyl-lithium (3 cm^3), synthesised from lithium metal (0.95 g) and *p*-bromotoluene (10.8 g) in diethyl ether (40 cm^3), was added to a stirred suspension of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (2.0 g) in diethyl ether (100 cm^3). A magenta solid quickly formed in a magenta-green solution. After 1 h the mixture was filtered under N_2, washed thoroughly with ether, and small magenta crystals formed in the washings. Alternatively, a small amount of diethyl ether (20 cm^3) could be added to the crude magenta powder isolated after filtration, and on standing for 2 d, magenta crystals formed (Found: C, 33.5; H, 5.1; I, 30.4; N, 11.9. $C_{23}H_{42}BI_2LiMoN_7O_3$ requires C, 33.2; H, 5.1; I, 30.5; N, 11.8%). I.r. (KBr disc): ν(BH) 2 250w, ν(NO) 1 630m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ = 3.54 (br) and 1.24 (br). E.s.r.: g = 2.024 (powder), 2.027 (tetrahydrofuran solution).

Results

Electrochemical Studies of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ *and Related Species:* $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$, (**A**).—A polarographic study of complex (**A**) in tetrahydrofuran (thf) (dropping mercury electrode, $[NBu^n{}_4][PF_6]$ as supporting electrolyte) revealed, immediately after addition of (**A**) to the electrolyte

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† *Non-S.I. unit employed:* G = 10^{-4} T.

solution, two cathodic waves of equal peak current, at E_p^c = +0.35 and −1.9 V (*vs.* saturated calomel electrode, s.c.e.). After *ca.* 3 min the polarogram had changed in the presence of Hg, some of the first cathodic wave became anodic, and after 1 h the wave at +0.35 V was completely anodic, without alteration of the potential. These observations indicated that there was an electron transfer and reaction between (**A**) and mercury, and, on shaking (**A**) with Hg in thf, dark green solids were isolated. However, characterisation of these solids proved impossible and further investigations along this line were abandoned.

The cyclic voltammogram (c.v.) of an unstirred solution of complex (**A**) in dry thf (using a platinum wire or vitreous carbon electrode) also showed two cathodic electrode processes. The first, $E_{\frac{1}{2}}$ = +0.22 V, was completely reversible [$\Delta E\,(E_p^a - E_p^c)$ = 120 mV at a scan rate of 100 mV s^{-1}], whereas the second, E_p^c = −2.0 V, was irreversible and not further investigated. The reversibility of the first wave was established by comparison with the ferrocene–ferricenium couple (ΔE = 120 mV at 100 mV s^{-1} scan rate) over a wide range of c.v. scan rates (500—10 mV s^{-1}), and by generation of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]^-$, (**A**)$^-$, by electrolysis followed by voltammetry, where the electrode process was now anodic but at the same potential as before. Coulometric studies in thf established that (**A**) consumed 1 faraday mol^{-1} and peak-current functions ($i_p/v^{\frac{1}{2}}$) for the complex at several scan rates at 298 K were consistent with a one-electron stoicheiometry for the electrode process. On electrolysis, the initially red-brown solution became dark green.

Electrochemical studies of complex (**A**) in acetonitrile established that the di-iodide was unstable in this medium, and on reduction provided several uncharacterised products.

We noticed that the c.v. of (**A**) in thf was significantly affected by traces of water. Thus, the peak current of the wave corresponding to the generation of (**A**)$^-$ in thf decreased very slowly with time, and after 12 h under argon had been reduced by *ca.* 35%. A c.v. at this time revealed additional anodic peaks, at +0.48, +0.66, and +0.86 V (*vs.* s.c.e.). The two peaks at +0.48 and +0.86 V were irreversible and were identified as due to oxidation of I$^-$ ($\mathrm{I^- \longrightarrow \frac{1}{2}I_2;\ I_3^- \longrightarrow \frac{3}{2}I_2}$) and this was confirmed by enhancement of the appropriate peak currents on addition of $[\mathrm{NBu^n_4}]$I. If small amounts of water were added to initially dry electrolyte solutions of (**A**), this more complex wave pattern was established very rapidly and, if the electrolyte itself was damp, then it was observed immediately on recording the first *i*/*E* sweep.

We suggest that the first electron-transfer process is due to one-electron reduction of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$, *e.g.* (**A**) + e$^-$ $\rightleftharpoons$ (**A**)$^-$. However, dissociation of I$^-$ can occur from (**A**), equation (1), a process clearly accelerated, if not initiated, by traces of water. The new mono-deiodinated species, (**B**), is presumably solvated and is itself redox-active. Thus the third anodic peak described above, at +0.66 V, is due to the reversible one-electron oxidation of (**B**) (ΔE = 160 mV at scan rates 30 mV s^{-1}).

$$(\mathbf{A})^- \longrightarrow \underset{(\mathbf{B})}{[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I}]} + \mathrm{I}^- \qquad (1)$$

$[\mathrm{M\{HB(Me_2pz)_3\}(NO)Cl_2}]$ (M = Mo *or* W). The c.v.s of these dichlorides were obtained in thf and in MeCN. Both species exhibited a reversible cathodic one-electron transfer in both solvents (see Table 1 for electrode characteristics). A comparison of half-wave potentials from these species with that for the couple (**A**)–(**A**)$^-$ reveals that both the metal and the halide significantly influence the $E_{\frac{1}{2}}$ value. It is also noticeable that the reduced dichlorides are substantially more stable in solution than (**A**)$^-$. There was no detectable evidence for the generation of Cl$^-$ in solutions containing the dichlorides either in the presence or absence of water. This trend towards greater stability of the chloro-species has also been detected in mixed alkoxy-, amido-, and phenoxychloro-species, as will be reported separately.

$[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(NCMe)_2}][\mathrm{PF_6}]$, (**C**)$^+$, *and* $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(CO)_2}]$, (**D**). The paramagnetic, 17-electron species $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(NCMe)_2}][\mathrm{PF_6}]$, (**C**)$^+$,[5] underwent a one-electron reduction in acetonitrile which is reversible at fast scan rates (⩾ 500 mV s^{-1} at 298 K). The $E_{\frac{1}{2}}$ value for the process is −0.81 V (ΔE = 110 mV at scan rate 500 mV s^{-1}), which presumably corresponds to the formation of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(NCMe)_2}]$, which is isoelectronic with $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(CO)_2}]$. The reduced acetonitrile-containing complex was unstable, and we were unable to characterise its decomposition products.

The species $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(CO)_2}]$, (**D**), underwent solvent-dependent redox processes as established by cyclic voltammetry (see Table 2) in acetonitrile; an irreversible one-electron oxidation was detected at +0.92 V (scan rate < 300 mV s^{-1}). However, at fast scan rates (> 300 mV s^{-1}) this

Table 1. Electrochemical data obtained from $[\mathrm{M\{HB(Me_2pz)_3\}(NO)X_2}]$

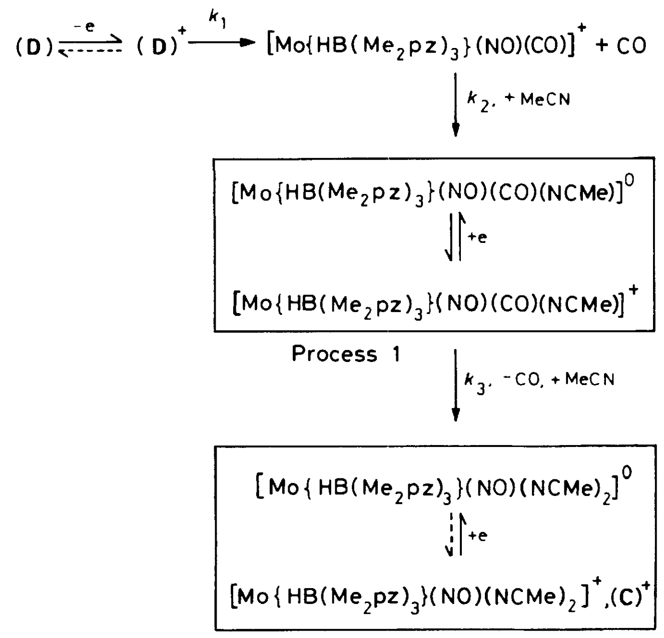
M	X	Solvent	$E_{\frac{1}{2}}{}^a$/V	ΔE/mV	n^b
Mo	I	thf	+0.22	120	1.0
Mo	Cl	thf	−0.09	90	
		MeCN	+0.09	70	1.0
W	Cl	thf	−0.46	200	
		MeCN	−0.46	80	1.0

[a] Using platinum wire, $[\mathrm{NBu^n_4}][\mathrm{PF_6}]$ as supporting electrolyte; data measured by comparison with $[\mathrm{Fe(C_5H_5)_2}]$–$[\mathrm{Fe(C_5H_5)_2}]^+$ couple. [b] Number of electrons consumed in electrolysis.

Table 2. Electrochemical properties of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(NCMe)_2}]^+$, (**C**)$^+$, and $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(CO)_2}]$, (**D**)

		$E_{\frac{1}{2}}$/V				
Complex	Solvent	ox	red	ΔE/mV	n^a	Process assignment
(**C**)$^+$	MeCN		−0.81	110	1	$(\mathbf{C})^+ \overset{+e}{\rightleftharpoons} (\mathbf{C})^0$
(**D**)	MeCN	+0.92		70	1	$(\mathbf{D})^0 \overset{-e}{\rightleftharpoons} (\mathbf{D})^+$
Product of process 1^b	MeCN		+0.18	70		$(\mathbf{D})^+ \overset{+e}{\rightleftharpoons} (\mathbf{X})^0$
Product of process 2^b	MeCN		−0.87^c			$(\mathbf{C})^+ \overset{+e}{\rightleftharpoons} (\mathbf{C})^0$
(**D**)	thf	+1.24^d	−1.98	190^e	1	$(\mathbf{D}) \overset{-e}{\rightleftharpoons} (\mathbf{D})^+$ $(\mathbf{D}) \overset{+e}{\rightleftharpoons} (\mathbf{D})^-$

[a] Number of electrons involved in process, by coulometry. [b] See text for description. [c] E_p wave, enhanced by addition of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(NCMe)_2}]^+$, and then oxidation portion of couple can be observed. [d] E_p value, as process is irreversible. [e] ΔE for reduction process.



Scheme.

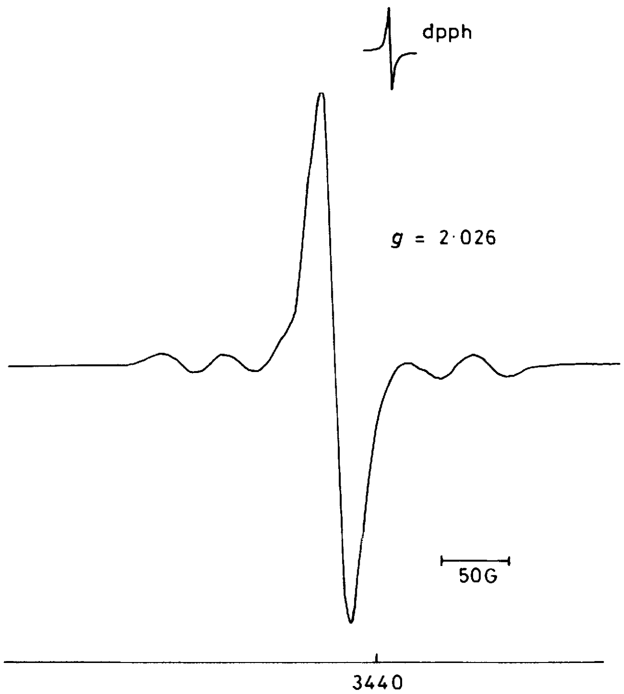


Figure 1. E.s.r. spectrum in thf of complex (**A**)$^-$ on electrolysis of (**A**)

process was shown to be reversible, and the current function $i_p/v^{\frac{1}{2}}$ × concentration is consistent with this view. Upon scan reversal following the first anodic sweep, two waves were detected down to −1.4 V, processes 1 and 2. These waves were attributed to products resulting from reactions involving [Mo{HB(Me$_2$pz)$_3$}(NO)(CO)$_2$]$^+$, (**D**)$^+$, and both product waves showed a degree of reversibility at scan rates of 300 mV s^{-1} (data in Table 2). We suggest that the electrode behaviour of (**D**) in acetonitrile may be described as in the Scheme.

We propose that process 2 is due to the formation of (**C**)$^+$ and this was supported by addition of authentic [Mo{HB(Me$_2$pz)$_3$}(NO)(NCMe)$_2$]$^+$, when the wave at −0.87 V was significantly enhanced. The stepwise loss of CO may be concerted as attempts to establish rate constants for the first step (k_1) indicated that this was not a first-order process.

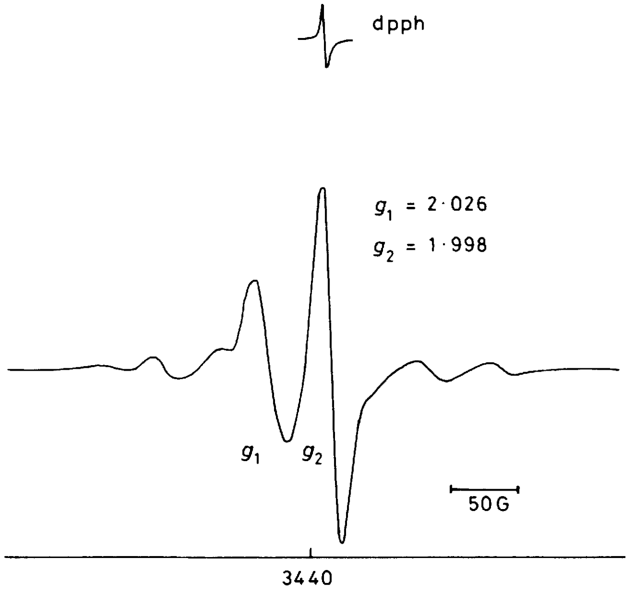


Figure 2. E.s.r. spectrum of electrolytically reduced (**A**) after 6 h in thf

A c.v. of complex (**D**) in thf established that there was a reversible one-electron reduction at −1.98 V, and an irreversible one-electron oxidation at +1.24 V. Product waves were observed following oxidation and scan reversal, but we were not able to identify the species produced.

Spectroscopic Study of Electrochemically Reduced [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$].—(*a*) *Spectral characteristics of* (**A**)$^-$ *and* (**B**). The e.s.r. spectrum of electrolytically reduced complex (**A**) in thf revealed a strong central resonance at g = 2.026 ±0.0005, and five broad satellite signals due to ^{95}Mo and ^{97}Mo hyperfine coupling ($I = \frac{5}{2}$ relative abundances 15.9 and 9.6% respectively) (Figure 1). An analysis of the spectrum will be reported elsewhere. On standing for 6 h the e.s.r. spectrum of electrolytically reduced (**A**) showed a new, additional signal, centred at g = 1.998 ±0.0005 (Figure 2). After a further 4 h, this new signal had almost completely replaced that at g = 2.026 (Figure 3).

It may be recalled from the electrochemical study, that, over this time-scale, the c.v. of complex (**A**) revealed dissociation of I$^-$ from (**A**)$^-$ and generation of (**B**). We conclude, therefore, that the resonance at g = 2.026 is due to (**A**), whereas that at g = 1.998 is due to (**B**). This last assignment was confirmed by synthesis of (**B**) [from (**A**) + ferrocene in thf, see below] and observation of a signal at g = 1.998 (Figure 4).

(*b*) *E.s.r. studies of reactions of complex* (**A**) *with 'reducing agents'.* On electrochemical reduction of complex (**A**) in pure dry thf, (**A**)$^-$ is clearly formed, as described above. Over a few hours, however, the presence of (**B**) can be detected also (g = 1.988) and the strength of this signal is gained at the expense of that due to (**A**)$^-$ (see Table 3, experiment 1). Addition to thf solutions of various salts (Table 3, experiments 2—5) also gave rise to signals associated with (**A**)$^-$ and (**B**). However, treatment of (**A**)$^-$ in thf solution with AgPF$_6$ resulted in a new signal, at g = 1.966, and no (**A**)$^-$ or (**B**) could be detected. We have not so far been able to identify the species giving rise to this new signal.

The observations that complex (**A**) reacted with a number of

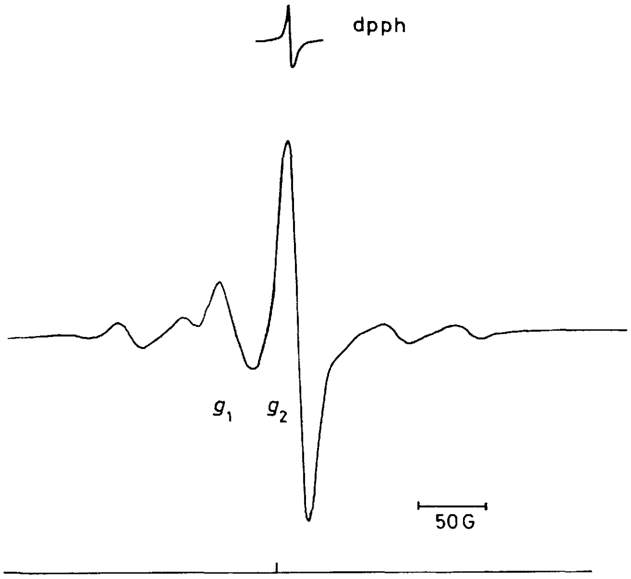


Figure 3. E.s.r. spectrum of electrolytically reduced (**A**) after 10 h in thf

species giving rise to transient green solutions prompted an examination of the e.s.r. spectra of several mixtures. Thus, while (**A**) did not apparently react immediately with thf under N_2, over 12 h [Table 3, experiment 7 (ii)] signals due to (**B**) and at 1.966 were detected. Tetrahydrofuran solutions of (**A**) in moist air gave, over several hours, similar data (Table 3, experiment 9). These observations, coupled with the fact that over several hours in an electrolyte cell, where contact with water *via* aqueous reference electrodes separated from the test solution only by porous discs was entirely possible, led us to the conclusion that water was intimately involved in the generation of (**B**), if not of $(\mathbf{A})^-$ as well. Indeed, treatment of complex (**A**) with water in thf caused immediate formation of signals due to (**B**) (Table 3, experiment 8), and it may be recalled from our electrochemical studies that generation of (**B**) from $(\mathbf{A})/(\mathbf{A})^-$ was greatly accelerated by water.

From $E_{\frac{1}{2}}$ values it was clear that complex (**A**) should be reduced by I^-, and addition of $[NBu^n{}_4]I$ to the neutral di-iodide did indeed afford a signal, in dry thf, due to $(\mathbf{A})^-$ alone (Table 3, experiment 10). Similar data were obtained in dichloromethane, but not in toluene, but this result has not been further investigated. Treatment of (**A**) with $[NBu^n{}_4]Br$ in dichloromethane, however, afforded only (**B**) (Table 3, experiment 11).

An e.s.r. spectrum of complex (**A**) taken immediately after dissolution in ethanol afforded a signal due to (**B**) (Table 3, experiment 12). We may also note that n.m.r. spectra of solutions made up under similar conditions gave rise to broadened signals, but after some time these sharpened and eventually $[Mo\{HB(Me_2pz)_3\}(NO)I(OEt)]$ could be detected. Reaction of (**A**) with $PhCH_2SH$ also afforded (**B**), whereas with PPh_3 and NEt_3 both $(\mathbf{A})^-$ and (**B**) were initially detected, the signals of the former gradually being replaced by those of the latter (Table 3, experiments 13—15).

Ferrocene was also able to effect reduction of complex (**A**) to (**B**), presumably with concomitant formation of $[Fe(C_5H_5)_2]I$, although we have not yet confirmed this (Table 3, experiment 16). Finally, the phthalimide anion was able to reduce (**A**) to $(\mathbf{A})^-$, and a signal at 2.009 was also detected; this may have been due to phthalimide radical (Table 3, experiment 17).

From these data it is quite clear that complex (**A**) is readily reduced, first to $(\mathbf{A})^-$, and that (**B**) is formed rapidly if water is present. Indeed, reduction of (**A**) to (**B**) is rapidly and apparently most efficiently achieved by water in thf. The extreme facility with which (**A**) may be reduced is reflected in, for example, its reactions with ethanol. The oxidation potential of ethanol is > 1.00 V whereas the reduction potential of complex (**A**) is +0.2 V (in thf). However, reduction of (**A**) does occur, possibly through reaction with dissociated I^-. Further studies of this point are in progress.

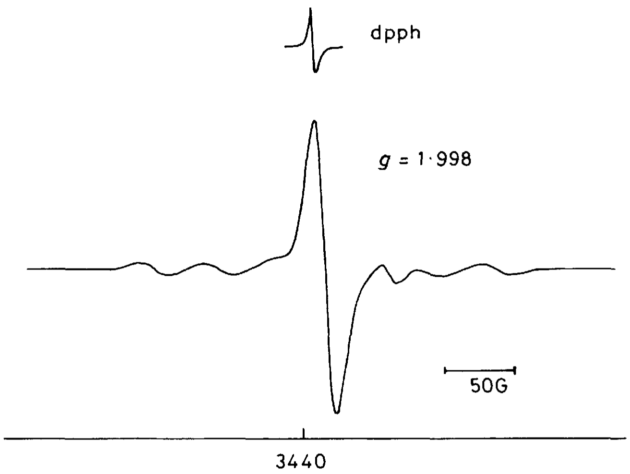


Figure 4. E.s.r. spectrum of complex (**B**)

(*c*) *Attempts to synthesise reduced forms of* $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$. From the $E_{\frac{1}{2}}$ data obtained for complex (**A**) (Table 1) it seemed highly probable that reduction to give $(\mathbf{A})^-$ should be fairly easy to achieve. In fact, attempts to isolate products obtained after stoicheiometric treatment of (**A**) with Hg, Na–Hg, or $[NBu^n{}_4]I$ failed because intractable mixtures were obtained, the product decomposed, or the starting material was recovered unchanged.

However, during an attempt to prepare arylmolybdenum complexes, by reaction of (**A**) with $Li(C_6H_4Me\text{-}p)$ in diethyl ether, we were able to isolate air- and moisture-sensitive magenta crystals. While these crystals did not analyse as $[Mo\{HB(Me_2pz)_3\}(NO)I(C_6H_4Me)]$, their microanalyses did provide an extremely good fit for $[Mo\{HB(Me_2pz)_3\}(NO)I_2\{Li(OEt_2)_2\}]$, (**E**). This compound was partially soluble in toluene and in diethyl ether, affording magenta solutions, but in thf, acetone, alcohols, and chlorinated hydrocarbons it afforded green solutions.

The ^1H n.m.r. spectrum of complex (**E**) in $CDCl_3$ exhibited two broad signals associated with the protons of the pyrazolyl group, but we could not obtain clear evidence for the methyl protons, although weak and poorly resolved signals were observed in the appropriate region. However, the broadness of these resonances suggested that the species was paramagnetic, and this was confirmed by e.s.r. spectroscopy. The compound exhibited a strong central signal in the solid state, with five weak satellite signals, at $g = 2.024$, and in thf a similar resonance was observed at $g = 2.027$. These observations are consistent with a species having one unpaired electron. The i.r. spectrum of (**E**) (in KBr discs) exhibited ν(NO) at 1 630 cm^{-1}, 70 cm^{-1} lower than that of its precursor, (**A**). An electrochemical examination of complex (**E**) in thf solution showed a reversible one-electron *oxidation* step at a potential identical to the one-electron *reduction* of (**A**) in the same solvent. A mass-spectral examination of the magenta complex afforded, as highest mass ion, peaks consistent with the formulation $[Mo\{HB(Me_2pz)_3\}(NO)I]$ (m/e = 532 based on ^{92}Mo).

Dissolution of (**E**) in ethanol afforded a green solution, and if this was rapidly evaporated (**E**) was recovered almost

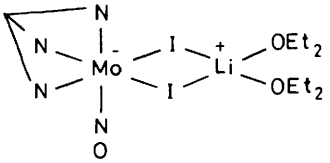
Table 3. E.s.r. spectral data obtained from solutions containing [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$]

Reagent	Experiment	Solvent	Time-scale[a]	g	Assignment[b]
Electrolytic reduction (1 F mol^{-1})	1	Dry thf	(i) Immediately	2.027	**(A)**$^-$
			(ii) 12 h (e.s.r. tube)	2.027	**(A)**$^-$
				1.988w	**(B)**
			(iii) 20 h (e.s.r. tube)	2.028w	**(A)**$^-$
				1.988vs	**(B)**
	2	Dry thf + NaBPh$_4$	(i) Immediately	2.025	**(A)**$^-$
			(ii) 24 h	2.025	**(A)**$^-$
				1.998	**(B)**
			(iii) 72 h	2.025vw	**(A)**$^-$
				1.988vs	**(B)**
	3	Dry thf + [NMe$_3$Ph]PF$_6$	Immediately	2.028	**(A)**$^-$
				1.998	**(B)**
	4	Dry thf + [NBu$^n_4$]ClO$_4$	Immediately	2.027	**(A)**$^-$
				1.998	**(B)**
	5	Dry thf + LiClO$_4$		2.022	**(A)**$^-$
				1.998	**(B)**
	6	Dry thf + AgPF$_6$		1.966	Unknown
thf	7	Dry thf	(i) Immediately		No reduction
			(ii) 12 h	1.998	**(B)**
				1.966w	Unknown
Water	8	Dry thf	Immediately	1.998	**(B)**
				1.966w	Unknown
thf	9	Dry thf exposed to air	(i) Immediately		No reduction
			(ii) 7 h	1.988	**(B)**
				1.966w	Unknown
			(iii) 12 h	1.966	Unknown
[NBu$^n_4$]I	10	(i) thf	Immediately	2.029	**(A)**$^-$
		(ii) CH$_2$Cl$_2$	Immediately	2.029	**(A)**$^-$
		(iii) Toluene	Immediately	2.018	Unknown
[NBu$^n_4$]Br	11	CH$_2$Cl$_2$	Immediately	1.998	**(B)**
EtOH	12	EtOH	Immediately	1.998	**(B)**
PhCH$_2$SH	13	thf	Immediately	1.988	**(B)**
PPh$_3$	14	(i) thf	Immediately	2.027s	**(A)**$^-$
				1.998w	**(B)**
		(ii) thf	12 h	1.998	**(B)**
NEt$_3$	15	(i) Toluene	Immediately	2.025s	**(A)**$^-$
				1.998w	**(B)**
		(ii) Toluene	48 h	2.025w	**(A)**$^-$
				2.000s	**(B)**
		(iii) Toluene	7 d	1.999	**(B)**
[Fe(C$_5$H$_5$)$_2$]	16	(i) thf	Immediately	1.998	**(B)**
		(ii) thf + LiClO$_4$	Immediately	1.998	**(B)**
		(iii) thf	12 h	1.998	**(B)**
				1.965	Unknown
Phthalimide anion	17	(i) thf	Immediately	2.026s	**(A)**$^-$
				2.009w	**(P)**?
		(ii)	7 min	2.026m	
				2.009m	
		(iii)	25 min	2.028w	**(A)**$^-$
				2.009s	**(P)**?
		(iv)	4 h	2.009	**(P)**?
				2.000	**(B)**?

[a] Spectra were recorded as soon as the reagents were mixed or electrolysis complete, unless otherwise stated. [b] **(A)** = [Mo{HB(Me$_2$pz)$_3$}(NO)I$_2$], **(B)** = [Mo{HB(Me$_2$pz)$_3$}(NO)I(solvent)]; **(P)** = phthalimide radical.

quantitatively. However if the solution was allowed to stand in the air overnight, evaporation afforded a green-pink solid which was shown, by thin-layer chromatography and i.r. spectral comparison with authentic samples, to be a mixture of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OEt)}]$ (green) and $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)(OEt)_2}]$ (pink). On passing CO through a refluxing toluene solution containing complex (**E**), the dicarbonyl complex (**D**) was produced in low yields. Treatment of (**E**) with HCl, $\mathrm{PhCH_2Br}$, or $\mathrm{I_2}$ afforded $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)X_2}]$, where X = Cl, Br, or I, respectively.

The combination of microanalytical, spectroscopic, electrochemical, and chemical data strongly suggests that (**E**) contains the reduced form of (**A**), *i.e.* $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]^-$. However, because of the compound's partial solubility in toluene and its magenta colour, whereas electrochemically generated $(\mathbf{A})^-$ is green, it seems reasonable that (**E**) is best described as $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2\{Li(OEt_2)_2\}}]$. The interaction between the Mo and Li atoms *via* iodine bridges is therefore analogous to the arrangement suggested in $[\mathrm{Yb(\eta\text{-}C_5Me_5)_2I_2\{Li(OEt_2)_2\}}]$[6] and identified crystallographically in $[\mathrm{Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\}(\mu\text{-}Cl)_2\{Li(thf)_2\}}]$.[7]



If the structure is correct, then dissolution of complex (**E**) in co-ordinating solvents to give green solutions can be explained by dissociation of the $\mathrm{Mo(\mu\text{-}I)_2Li}$ system, with generation of solvated $\mathrm{Li^+}$ and $(\mathbf{A})^-$. The e.s.r. and i.r. spectral data are consistent with the existence of $(\mathbf{A})^-$, and mass-spectral decomposition of (**E**) presumably leaves involatile LiI on the probe while the volatile fragment (**B**) is detected. Our failure to obtain pure samples of $(\mathbf{A})^-$ in the absence of $\mathrm{Li^+}$ indicates that $\mathrm{Li^+}$ plays an important role in stabilising $(\mathbf{A})^-$ and facilitating its isolation.

The reaction of complex (**E**) with ethanol, to give mono- and bis-alkoxide species, can be explained as in equations (2)—(8) $[\{\mathrm{Mo}\} = \mathrm{Mo\{HB(Me_2pz)_3\}(NO)}]$. Similarly, with CO, the dicarbonyl, (**D**) was formed, perhaps as in equations (9)—(12). The reaction with benzyl bromide (RBr) may proceed in a somewhat similar way [equations (13)—(17)]. The reaction with HCl, in which $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)Cl_2}]$ is formed, may proceed similarly, and that with iodine, in which (**A**) is regenerated, may be viewed as a simple oxidation reaction.

$$(\mathbf{E}) \rightleftharpoons \mathrm{Li(solvent)}_n^{\ +} + (\mathbf{A})^- \qquad (2)$$

$$(\mathbf{A})^- \rightleftharpoons (\mathbf{B}) + \mathrm{I}^- \qquad (3)$$

$$(\mathbf{B}) + \mathrm{EtOH} \longrightarrow [\{\mathrm{Mo}\}\mathrm{I(EtOH)}] \qquad (4)$$

$$[\{\mathrm{Mo}\}\mathrm{I(EtOH)}] \xrightarrow[\text{oxidation}]{-\mathrm{H}^{\cdot}} [\{\mathrm{Mo}\}\mathrm{I(OEt)}]\ \text{(green)} \qquad (5)$$

$$[\{\mathrm{Mo}\}\mathrm{I(EtOH)}] \xrightarrow{-\mathrm{HI}} [\{\mathrm{Mo}\}\mathrm{(OEt)}] \qquad (6)$$

$$[\{\mathrm{Mo}\}\mathrm{(OEt)}] + \mathrm{EtOH} \longrightarrow [\{\mathrm{Mo}\}\mathrm{(OEt)(EtOH)}] \qquad (7)$$

$$[\{\mathrm{Mo}\}\mathrm{(OEt)(EtOH)}] \xrightarrow[\text{oxidation}]{-\mathrm{H}^{\cdot}} [\{\mathrm{Mo}\}\mathrm{(OEt)_2}]\ \text{(pink)} \qquad (8)$$

$$(\mathbf{A})^- + \mathrm{CO} \longrightarrow [\{\mathrm{Mo}\}\mathrm{I(CO)}] + \mathrm{I}^- \qquad (9)$$

$$[\{\mathrm{Mo}\}\mathrm{I(CO)}] \longrightarrow [\{\mathrm{Mo}\}\mathrm{(CO)}] + \mathrm{I}^{\cdot} \qquad (10)$$

$$\mathrm{I}^{\cdot} \longrightarrow \tfrac{1}{2}\mathrm{I_2} \qquad (11)$$

$$[\{\mathrm{Mo}\}\mathrm{(CO)}] + \mathrm{CO} \longrightarrow (\mathbf{D}) \qquad (12)$$

$$(\mathbf{A})^- + \mathrm{RBr} \longrightarrow [\{\mathrm{Mo}\}\mathrm{IBr}] + \mathrm{R}^{\cdot} + \mathrm{I}^- \qquad (13)$$

$$\mathrm{R}^{\cdot} \longrightarrow \tfrac{1}{2}\mathrm{R_2} \qquad (14)$$

$$[\{\mathrm{Mo}\}\mathrm{IBr}] + \mathrm{RBr} \longrightarrow [\{\mathrm{Mo}\}\mathrm{IBr}]^- + \mathrm{RBr}^{\cdot +} \qquad (15)$$

$$\mathrm{RBr}^{\cdot +} \longrightarrow \mathrm{R}^+ + \mathrm{Br}^{\cdot} \qquad (16)$$

$$[\{\mathrm{Mo}\}\mathrm{IBr}]^- + \mathrm{Br}^{\cdot} + \mathrm{R}^+ \longrightarrow [\{\mathrm{Mo}\}\mathrm{Br_2}] + \mathrm{RI} \qquad (17)$$

Attempts to obtain suitable crystals of complex (**E**) for an *X*-ray structure determination were completely unsuccessful, as were attempts to replace the ether groups attached to Li in (**E**) by other ligands, such as $\mathrm{Me_2NCH_2CH_2NMe_2}$ or $\mathrm{MeOCH_2CH_2OMe}$.

Conclusions

A crystallographic study of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I_2}]$ was undertaken, but a satisfactory refinement of the data could not be obtained.[8] However, the preliminary results show that the di-iodide, (**A**), is monomeric in the solid state, which would be generally consistent with the solution properties of the molecule. Thus the metal is co-ordinatively unsaturated and, perhaps because of the protective nature of the $\mathrm{HB(Me_2pz)_3}$ which prevents effective expansion of the co-ordination sphere, is unable to reach saturation (*i.e.* ideally an 18-electron configuration) except (*i*) (partially) by reduction, to a 17-electron species, or (*ii*) by reaction with ligands which can function as powerful donors without an increase of co-ordination number, *e.g.* OR, NHR, or SR *via* σ and $p(\pi)$ donation. The easy reduction of (**A**) to $(\mathbf{A})^-$ with subsequent dissociation of $\mathrm{I^-}$ to form (**B**) must have implications for the mechanism of reaction of (**A**) with ROH, $\mathrm{RNH_2}$, and RSH in which substitution of one iodine atom by an OR, NHR, or SR group is readily achieved. However, a detailed discussion of the mechanism of formation of $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)I(OR)}]$ and its amido- and thiolato-analogues must await a kinetic study which is in progress.

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