Steric and Electronic Effects on the Chemistry of Molybdenum Octahedrally Co-ordinated by Six Nitrogen Atoms. The Molecular Structure of $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)(pyrollide)_2]$†

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$[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)I_2]$ reacts with the nitrogen heterocycles Z to give $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)Z_2]^+$, where Z = pyridine, imidazole, *N*-methylimidazole, or pyrazole, with monosodium organoamides to give $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)Y_2]$ where Y = $NHEt^-$, $NHPh^-$, *p*-$NHC_6H_4Me^-$, or pyrollide, and with moist tetrahydrofuran to give $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)I\{O[CH_2]_4I\}]$; the molecular structure of $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)(pyrollide)_2]$ has been determined.

The complexes $[MoL(NO)I_2]_2$, (**1**), where $L^- = \eta^5\text{-}C_5H_5^-$ or $HB(C_3N_2H_3)_3^-$, are isolated as iodide-bridged dimers containing 18-electron, 7-co-ordinate Mo centres.[1,2] In contrast the analogous complex $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)I_2]$, (**2**), is isolated as a monomeric 16-electron complex because the steric demands of the tris(3,5-dimethylpyrazolyl)hydroborate ligand, L^{*-}, restrict the Mo centre to octahedral six-co-ordination.[3,4] The electron-deficient Mo centre in (**2**) is highly reactive and undergoes facile electrochemical reduction to a paramagnetic 17-electron complex which slowly dissociates I^- in polar solvents.[5] E.s.r. and ^1H n.m.r. studies indicate that paramagnetic species are also formed from (**2**) in the presence of such weak reducing agents as amines, alcohols, and pyridine.[6] In the case of primary amines and alcohols the final reaction products are the air stable complexes $[Mo(L^*)(NO)IY]$, (**3**), where Y is alkoxide, phenoxide, monoalkylamide, or monoarylamide.[4,7,8] Further treatment of (**3**) with $AgPF_6$ in the presence of alcohols then affords $[Mo(L^*)(NO)XY]$, (**4**), where X is alkoxide.[7] However, similar reactions of (**3**) in the presence of primary amines did not afford bisamido derivatives of (**2**). We have now isolated and characterised the final paramagnetic products formed from the reaction of (**2**) with pyridine and several other unsaturated nitrogen-containing heterocycles. A synthetic route to bisamido derivatives of (**2**) has also been found. Although the nature of the paramagnetic species observed when (**2**) is dissolved in moist tetrahydrofuran, THF, remains uncertain, we have now isolated a THF derivative of (**2**) in which the THF ring has opened to give an alkoxide.

$[MoL(NO)I_2]_2$ (**1**)

$[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)I_2]$ (**2**)

$[Mo(L^*)(NO)IY]$ (**3**)

$[Mo(L^*)(NO)XY]$ (**4**)

$[Mo(L^*)(NO)Z_2]^+$ (**5**)

$[Mo(L^*)(NO)Y_2]$ (**6**)

In the presence of an excess of Z, where Z = pyridine, imidazole, *N*-methylimidazole, or pyrazole, (**2**) reacts to produce the paramagnetic green complexes $[Mo(L^*)(NO)Z_2]^+$, (**5**), which were isolated as their BPh_4^- salts. These complexes are formally 17-electron systems containing an $\{Mo(NO)\}^{2+}$ moeity and are air stable as solids. The i.r. spectral and electrochemical properties of these compounds are summarised in Table 1. Mono-substituted derivatives of (**2**) with Z also exist but, provided an excess of Z is present, the reaction proceeds smoothly to give (**5**). Since these reactions involving ligands containing 2-co-ordinate N readily

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† Bispyrollyl{tris(3,5-dimethylpyrazolyl)hydroborato}nitrosylmolybdenum.

Table 1. I.r. and electrochemical data for $[Mo(L^*)(NO)Z_2]^+$,[a] (**5**), and $[Mo(L^*)(NO)Y_2]$, (**6**).

Y_2 or Z_2	$\nu(N\text{-}H)^b/cm^{-1}$	$\nu(NO)^b/cm^{-1}$	$E_{\frac{1}{2}}^c/V$	$\Delta Ep^d/mV$
For (**6**)				
$(NHEt)_2$	3315	1620	-1.50^e	—
$(NHPh)_2$	3310	1632	-1.32	80
$(NHPh)(p\text{-}NHC_6H_4Me)$	3310	1638	-1.35	140
	3330			
$(p\text{-}NHC_6H_4Me)_2$	3320	1628	-1.35	100
$(Pyrollide)_2$	—	1682	-0.46	80
For (**5**)				
$(Pyridine)_2$	—	1630	-1.00	60
$(Imidazole)_2$	3325	1632	-1.54^e	—
	3375			
$(N\text{-}Methylimidazole)_2$	—	1612	-1.56	70
$(Pyrazole)_2$	—	1633	-1.12^e	—
			-1.68	90

[a] All the new compounds gave satisfactory microanalyses for C, H, and N. The cationic species had solution conductivities in MeCN consistent with their formulation as 1 : 1 electrolytes. [b] KBr disc. [c] Electrochemical measurements performed in MeCN containing 0.2 M $[Bu^n_4N][BF_4]$ as supporting electrolyte. [d] ΔEp = Separation between anodic and cathodic peak potentials. [e] Cathodic peak potentials for an irreversible process.

proceeded to bis derivatives, the reactions of (**2**) with monosodium organoamides, which also contain 2-co-ordinate N, were investigated. In the presence of an excess of NaY these proceeded directly to form the complexes $[Mo(L^*)(NO)Y_2]$, (**6**), where Y = $NHEt^-$, $NHPh^-$, $p\text{-}NHC_6H_4Me^-$, or pyrollide. These compounds were diamagnetic air-stable solids whose ^1H n.m.r. spectra were consistent with the presence of a plane of symmetry as required for bis substitution. Their i.r. and electrochemical properties are summarised in Table 1. The reaction of (**3**), Y = alkyl- or aryl-amide, with sodium organoamides provides a potential route to mixed bisamide complexes but some ligand exchange appears to occur during the reaction. This was especially apparent when mixed alkyl–aryl bisamide derivatives were the desired product. The formation of bisarylamides appeared to be favoured over the formation of the mixed alkyl–aryl bisamides. Unlike their counterparts (**5**), these complexes, (**6**), are formally 16-electron compounds containing the $\{Mo(NO)\}^{3+}$ moiety.

Despite the pronounced electronic differences between the complexes of series (**5**) and (**6**), their electrochemical properties were remarkably similar. The cyclic voltammograms of both series revealed only irreversible oxidation processes at potentials more anodic than +0.6 V. Except for the pyrollide derivative, the compounds all exhibited a reduction wave in the region −1.0 to −1.7 V. Well defined cathodic and anodic peaks were present except in the complexes containing ethylamide, imidazole, or pyrazole. In the latter two cases this lack of reversibility may be associated with the loss of hydrogen from the imidazole or pyrazole which are present in their protonated forms. Thus it appears that the trinegative ligand set containing L^{*-} and two strong σ-donor amide ligands is effective in stabilising the $\{Mo(NO)\}^{3+}$ configuration. In contrast the uninegative ligand set containing L^{*-} and two neutral unsaturated nitrogen heterocycles was effective in stabilising the $\{Mo(NO)\}^{2+}$ configuration. In the complex (**6**) with Y = pyrollide an intermediate situation was apparent in so far as the $\{Mo(NO)\}^{3+}$ configuration was stable but its reduction to $\{Mo(NO)\}^{2+}$ was significantly more facile than for the other complexes (**6**). This anodic shift in reduction potential was associated with an increase of *ca.* 50 cm^{-1} in nitrosyl stretching frequency.

The steric demands of L^{*-} usually prevent the formation of complexes (**3**) in which Y is a secondary amide. Only where Y = NMe_2^- has such a compound been isolated and this was found to decompose. In order to confirm the formulation of the secondary amine complex (**6**) with Y = pyrollide, and to investigate the steric compatibility of L^{*-} with pyrollide, an *X*-ray diffraction study was carried out. The complex crystallises as dark green needles.

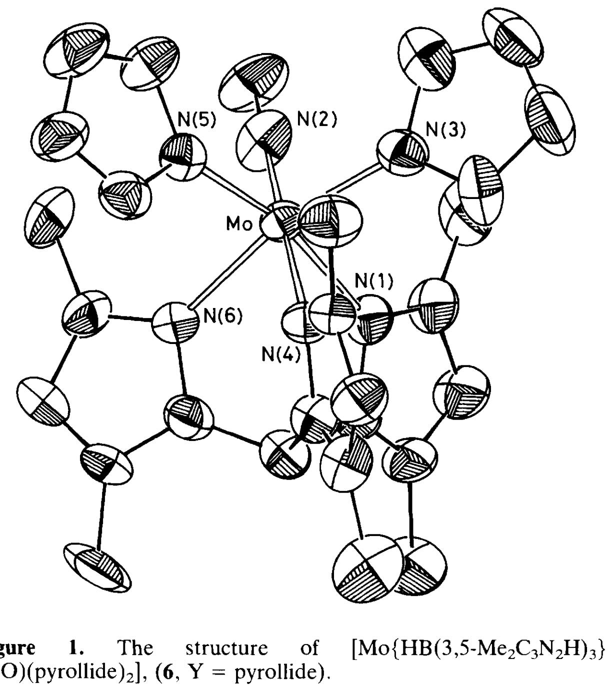

Figure 1. The structure of $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)(pyrollide)_2]$, (**6**, Y = pyrollide).

Crystal data: $C_{23}H_{30}BMoN_9O$, M = 555.3, triclinic, space group $P\bar{1}$, a = 8765(5), b = 10.224(3), c = 15.137(5) Å, α = 92.95(2), β = 97.85(3), γ = 101.57(3)°, U = 1312 Å^3, Z = 2, D_c = 1.41 g cm^{-3}, *X*-ray data were collected using an Enraf–Nonius CAD4 diffractometer of the Crystallography Unit, Universities of Aston and Birmingham, and Mo-K_α radiation, with 2998 unique observed reflections [with $I > 3\sigma(I)$] having $2\theta < 50°$. The structure was solved by

Patterson–Fourier methods and refined by full-matrix least-squares to a current residual R of 0.072.‡

The molecular structure is shown in Figure 1. The geometry of the complex is similar overall to that[9] of $[Mo(L^*)(NO)(MeCN)_2]^+$, but the two pyrollide ligands are orientated to fit between the projecting methyl groups of L^*. The steric interaction results in an opening of the N–N 'bite' on L^* to 2.972 and 2.992 Å, where the pyrollide ligands are involved, compared with 2.789 Å for N–N opposite NO.

The average Mo–N distance in the present complex has slightly decreased (0.02 Å) compared with that in the MeCN compound, in line with the increased formal oxidation state of molybdenum. The N–O distance of 1.163 Å is shorter than the distance of 1.213 Å in the MeCN compound, in agreement with the increase in ν(NO). The average Mo–N (pyrollide) distance of 2.01 Å (2.045 and 1.982 Å) is shorter than the average Mo–N (MeCN) distance of 2.142 Å, but longer than the Mo–N (amide) distance of 1.959 Å (average) in $[Mo(L^*)(NO)I(NHEt)]$.

In addition to the reaction of (**2**) with unsaturated nitrogen heterocycles we have also investigated its reaction with the saturated oxygen heterocycle THF. As with alcohols or amines, (**2**) is known to form paramagnetic species in moist THF, but not in dry THF. We have confirmed that (**2**) is stable in rigorously dried THF at reflux for 3 days under nitrogen. However, if air or water are present a green alkoxy complex is ultimately formed. This was first isolated following an attempt to prepare (**5**) with Z = pyrazine and was found, on the basis of C, H, N microanalyses and i.r. and ^{1}H n.m.r. spectral data, to be $[Mo(L^*)(NO)I\{O[CH_2]_4I\}]$. A compound with identical spectral properties was obtained in almost quantitative yield by refluxing (**2**) in moist THF for 3 days.

These reactions provide additional evidence for the unusual reactivity of the Mo centre in (**2**). It is of special interest that, although primary amines react more rapidly with (**2**) than alcohols to substitute the first iodide, only alcohols or thiols have previously been found to substitute for the second. The reactions described here show that, although 3-co-ordinate nitrogen is ineffective in substituting the second iodide, 2-co-ordinate nitrogen reacts readily to substitute both iodides. These observations provide support for the proposal that the mechanism of the first iodide substitution by primary amines involves the abstraction of hydrogen from the amine.[5] The ligand L^{*-} is able to discriminate sterically between RQH; Q = O, S, N$^\bullet$, and RNH_2 in these reactions.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.