Bis-organoamide Complexes of Nitrosyl[tris(3,5-dimethylpyrazolyl)borato]-molybdenum and -tungsten. The Crystal and Molecular Structure of $[Mo(NO)\{HB(Me_2pz)_3\}(NHBu^n)_2]$†

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The reaction between $[Mo(NO)L(I)(NHR^1)]$ [L = tris(3,5-dimethylpyrazolyl)borate, $HB(Me_2pz)_3^-$; R^1 = Et, Pr^n, or Bu^n] and R^1NH^- afforded $[Mo(NO)L(NHR^1)_2]$ but did not provide a route to derivatives in which R^1 = aryl. A similar approach using $[W(NO)L(Cl)(NHR^1)]$ and R^1NH^- afforded the tungsten analogues $[W(NO)L(NHR^1)_2]$ (R^1 = Et, Pr^n, or Bu^n). The reaction of $[Mo(NO)L(I)(NHR^1)]$ (R^1 = Et, Ph, or C_6H_4Me-*p*) with $NaC_{10}H_8$ in tetrahydrofuran, followed by the addition of R^2NH_2 (R^2 = Ph or C_6H_4Me-*p*), led to the formation of the arylamide derivatives $[Mo(NO)L(NHR^1)(NHR^2)]$ ($R^1 = R^2$ = Ph or C_6H_4Me-*p*; R^1 = C_6H_4Me-*p*, R^2 = Ph; and R^1 = Et, R^2 = C_6H_4Me-*p*). Bis-arylamide derivatives of tungsten could not be prepared in this manner but $[W(NO)L(NHEt)(NHC_6H_4Me\text{-}p)]$ was prepared from the reaction of $NHC_6H_4Me\text{-}p^-$ and $[W(NO)L(Cl)(NHEt)]$. The electrochemistry of the new complexes has been investigated and, while the bis-arylamide derivatives exhibited reversible reduction behaviour, the alkylamide complexes reduced irreversibly. The molecular structure of $[Mo(NO)\{HB(Me_2pz)_3\}(NHBu^n)_2]$ has been determined by a single-crystal *X*-ray diffraction study and was found to contain a linear nitrosyl ligand. The average Mo–N(butylamido) distance was 1.940 Å and the average Mo–N–Bu^n angle 129.9°.

The preparation of air- and moisture-stable molybdenum nitrosyl complexes of the types $[Mo(NO)L(X)(OR^1)]$ (**1**) and $[Mo(NO)L(X)(NHR^1)]$ (**2**) [X = Cl, Br, or I; R^1 = alkyl or aryl; and L = tris(3,5-dimethylpyrazolyl)borate, $HB(Me_2pz)_3^-$], have been described previously.[1,2] Treatment of (**1**) with Ag^+ in the presence of alcohols, R^2OH, where R^2 = alkyl or aryl, was found to produce[3] the complexes $[Mo(NO)L(OR^1)(OR^2)]$ (**3**). In the presence of an excess of alkylamine, R^2NH_2, (**1**) also reacted to produce[4] the alkoxy–amide complexes $[Mo(NO)L(OR^1)(NHR^2)]$ (**4**) and, like their precursors these complexes were found to be remarkably stable towards air and moisture. However, attempts to produce bis-amide complexes $[Mo(NO)L(NHR^1)(NHR^2)]$ (**5**) by similar means were unsuccessful. This observation was surprising in view of the ease of formation and stability of the complexes (**1**)—(**4**). Other studies[5] have shown that $[Mo(NO)LI_2]$ (**6**) reacts readily with unsaturated nitrogen heterocycles to give bis-substituted derivatives directly. This suggested that compounds containing two-co-ordinate nitrogen centres, as found in the amide ions R^2NH^-, might be more effective reagents for forming bis-amide derivatives than the amines R^2NH_2 which contain three-co-ordinate nitrogen. Accordingly we have investigated the reactions of (**2**) and (**6**) with R^2NH^-, generated from R^2NH_2 by reaction with sodium hydride, in an attempt to prepare the bis-amides (**5**). Similar reactions have also been carried out with the previously unreported complexes $[W(NO)L(Cl)(NHR^1)]$ (**7**) in an attempt to prepare $[W(NO)L(NHR^1)(NHR^2)]$ (**8**). The isolation of the bis-amide species completes the possible series of alkoxide and amide derivatives (**1**)—(**5**) based on the $[Mo(NO)L]^{2+}$ moiety. This work also extends the known range of tungsten amide complexes revealing a parallel, but subtly different, chemistry compared with that of molybdenum.

Results and Discussion

Synthetic Studies.—Our initial attempts to prepare the bis-amide complexes $[Mo(NO)L(NHR^1)(NHR^2)]$ (**5**) utilised conditions similar to those known to afford the bis-alkoxides (**3**) and alkoxy–amides (**4**). However, we were unable to isolate bis-amides (**5**) from the reactions of $[Mo(NO)L(X)(NHR^1)]$ (**2**) with AgO_2CMe in the presence of an excess of alkyl- or aryl-amine. More promising results were obtained by refluxing (**2**; R^1 = Ph or C_6H_4Me-*p*) in tetrahydrofuran (thf) with aniline or *p*-toluidine, in that traces of purple bis-amide were found to have formed. Unfortunately such reactions proved to be of little synthetic use since the bulk of the reactant (**2**) was recovered unchanged. An effective route to the bis-alkylamides (**5**) was provided by the reaction of (**2**; R^1 = Et, Pr^n, or Bu^n) with R^2NH_2 (R^2 = Et, Pr^n, or Bu^n) respectively, in the presence of NaH. However, this approach did not afford the bis-arylamides when R^1 and R^2 were aryls. This finding may reflect the less basic character of the arylamides as compared with their alkyl counterparts.

Since the reduction of some monoamides (**2**; X = I) was known from electrochemical studies[6,7] to result in I^- dissociation, we next investigated the use of sodium naphthalenide to stimulate the reaction of (**2**) with organoamines in thf. This approach was successful in affording the bis-arylamide complexes (**5**; $R^1 = R^2$ = Ph or C_6H_4Me-*p*; R^1 = Ph, R^2 = C_6H_4Me-*p*). However we were unable to prepare the molybdenum bis-alkylamides by this means. In view of our observation, discussed below, that the complexes (**5**; R^1, R^2 = Ph or C_6H_4Me-*p*) exhibit more cathodic reduction potentials than (**2**; R^1 = Ph or C_6H_4Me-*p*),[6] the formation of (**5**; R^1, R^2 = aryl) may be rationalised in terms of the reactions shown in the Scheme.

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† Bis(n-butylamido)nitrosyl[tris(3,5-dimethylpyrazolyl)borato]-molybdenum(III).

Supplementary data available (No. SUP 56521, 15 pp.): i.r., ^1H n.m.r., electronic, and mass spectroscopic data, elemental analyses, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Electrochemical[a] and i.r. data for the complexes $[\mathrm{M(NO)\{HB(Me_2pz)_3\}XY}]$

M	X	Y	$E_{\frac{1}{2}}$/V	ΔE_p/mV[b]	n[c]	Solvent	ν_{NO}/cm^{-1}[d]
Mo	NHPh	NHPh	−1.32	80	1.19	MeCN	1 632
Mo	NHPh	NHC_6H_4Me-*p*	−1.35	140	1.09	MeCN	1 638
Mo	NHC_6H_4Me-*p*	NHC_6H_4Me-*p*	−1.35	100	1.30	MeCN	1 628
Mo	NHC_6H_4Me-*p*	NHEt	−1.50[e]	—	1.29	MeCN	1 640
			−0.98[e]	—	1.21		
Mo	NHEt	NHEt	−1.50	—	1.05	MeCN	1 620
Mo	$NHPr^n$	$NHPr^n$	−1.46[e]	—	1.22	thf	1 618
			−2.48[e]	—	0.92		
Mo	$NHBu^n$	$NHBu^n$	−1.28[e]	—	0.78	thf	1 622
			−2.41[e]	—	1.20		
W	Cl	NHEt	−1.76[e]	—	0.75	thf	1 622
			−2.24[e]	—	0.92		
W	Cl	$NHPr^n$	−1.92[e]	—	1.30	thf	1 620
W	Cl	$NHBu^n$	−1.30[e]	—	0.80	thf	1 610
W	Cl	NHC_6H_4Me-*p*	−1.34	120	1.12	thf	1 626
W	NHEt	NHEt	−1.12[e]	—	0.97	thf	1 582
W	$NHPr^n$	$NHPr^n$	−1.46[e]	—	1.05	thf	1 580
W	$NHBu^n$	$NHBu^n$	−1.40[e]	—	1.06	thf	1 588
W	NHEt	NHC_6H_4Me-*p*	−2.20	120	0.87	thf	1 618, 1 610
			−2.44	—	1.01		

[a] 0.2 mol dm^{-3} $[\mathrm{NBu_4}][\mathrm{BF_4}]$ in acetonitrile, or thf, at a platinum bead electrode. [b] Scan rate 0.3 V s^{-1}. [c] Number of electrons involved in the reduction process as determined by comparison with $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}Cl_2}]$; based on the diffusion current at the cathodic peak potential. [d] Recorded on a PE 297 instrument as KBr discs. [e] Cathodic peak potentials for an irreversible process.

$$[\mathrm{Mo(NO)L(I)(NHR^1)}] + \mathrm{C_{10}H_8}^- \longrightarrow [\mathrm{Mo(NO)L(I)(NHR^1)}]^- + \mathrm{C_{10}H_8}$$

$$[\mathrm{Mo(NO)L(I)(NHR^1)}]^- + \mathrm{thf} \longrightarrow [\mathrm{Mo(NO)L(thf)(NHR^1)}] + \mathrm{I}^-$$

$$\mathrm{Na}^+ + \mathrm{I}^- \longrightarrow \mathrm{NaI}\downarrow$$

$$\mathrm{C_{10}H_8}^- + \mathrm{R^2NH_2} \longrightarrow \mathrm{C_{10}H_8} + \mathrm{R^2NH}^- + \mathrm{H_2}$$

$$[\mathrm{Mo(NO)L(thf)(NHR^1)}] + \mathrm{R^2NH}^- \longrightarrow [\mathrm{Mo(NO)L(NHR^1)(NHR^2)}]^- + \mathrm{thf}$$

$$[\mathrm{Mo(NO)L(NHR^1)(NHR^2)}]^- + [\mathrm{Mo(NO)L(I)(NHR^1)}] \longrightarrow [\mathrm{Mo(NO)L(NHR^1)(NHR^2)}] + [\mathrm{Mo(NO)L(I)(NHR^1)}]^-$$

Scheme.

Such a scheme would seem less credible in the case of (**2**; R^1 = alkyl) which have more cathodic reduction potentials and exhibit quite irreversible reduction behaviour.[6,7] This is in accord with our failure to prepare (**5**; R^1,R^2 = alkyl) using $C_{10}H_8^-$, although, it did prove possible to prepare (**5**; R^1 = Et, R^2 = C_6H_4Me-*p*) using this procedure.

During the reaction of (**2**; R^1 = Ph) with $NaC_{10}H_8$ we observed that the purple colour of the bis-arylamide began to develop before any additional arylamine was present. This prompted us to investigate the reaction of (**2**; R^1 = Ph) with $NaC_{10}H_8$ in the absence of added amine. In this way we were able to prepare (**5**; R^1 = R^2 = Ph) in 45% yield. Such a product would be consistent with the Scheme if $PhNH^-$ arises from ligand dissociation as shown below.

$$[\mathrm{Mo(NO)L(I)(NHPh)}]^- + \mathrm{thf} \longrightarrow [\mathrm{Mo(NO)L(thf)I}] + \mathrm{PhNH}^-$$

We were unable to determine the fate of the proposed [Mo(NO)L(thf)I] species. However, this complex is also proposed[8] to arise from the reduction of $[\mathrm{Mo(NO)LI_2}]$ (**6**) in thf and previous attempts to isolate it have failed owing to its lability and reactivity. Although we cannot completely rule out the possibility that R^2NH^- may react directly with (**2**) when R^1 and R^2 are aryl, our failure to prepare bis-arylamide derivatives of (**2**) using R^2NH^- alone would mitigate against such a proposal. Attempts to prepare bis-amide complexes directly from (**6**) were only partially successful. The reaction between (**6**), $C_{10}H_8^-$, and $PhNH_2$ did afford (**5**; R^1 = R^2 = Ph). However, the reaction of (**6**) with organoamide ions, or with $C_{10}H_8^-$ and alkylamines, failed to give the bis-amide complexes.

Tungsten exhibited a chemistry parallel to, but not identical with, that of molybdenum in this series of compounds. The mono-organoamide complexes $[\mathrm{W(NO)L(Cl)(NHR^1)}]$ (**7**) could be prepared from the reaction between $[\mathrm{W(NO)LCl_2}]$ and R^1NH_2 (R^1 = Et, Pr^n, or Bu^n) in a manner similar to their molybdenum analogues. However, the reaction with *p*-toluidine was much slower and sodium hydride was added to stimulate the substitution of chloride. We also found that, in the presence of $C_{10}H_8^-$ or sodium hydride, (**7**; R^1 = C_6H_4Me-*p*) did not react with arylamines to give bis-arylamide complexes. In contrast the bis-alkylamide complexes $[\mathrm{W(NO)L(NHR^1)(NHR^2)}]$ (**8**; R^1 = R^2 = Et, Pr^n, or Bu^n) could be prepared from the reactions of (**7**; R^1 = Et, Pr^n, or Bu^n) respectively with the corresponding amide R^1NH^-. It also proved possible to prepare (**8**; R^1 = C_6H_4Me-*p*, R^2 = Et) from (**7**; R^1 = Et) and *p*-$MeC_6H_4NH^-$. Attempts to prepare the bis-amides (**8**) directly from $[\mathrm{W(NO)LCl_2}]$ using $C_{10}H_8^-$ and organoamines, or organoamides, R^1NH^-, were unsuccessful.

*Spectral Studies.**—All the new compounds exhibited bands in their i.r. spectra attributable to the tris(3,5-dimethylpyrazolyl)borate ligand and the appearance of ν_{BH} at 2 500 cm^{-1} indicated that this ligand remained intact in the reaction products. The complexes exhibited bands attributable to ν_{N-H} in the region 3 270—3 350 cm^{-1} and values of ν_{NO} are shown in Table 1. The nitrosyl stretching frequencies of the alkylamide complexes were generally lower than those of the arylamide complexes in accord with the more basic character of the alkylamide ligands. The values of ν_{NO} in the tungsten complexes were typically some 40 cm^{-1} lower than in their molybdenum analogues. There was a decrease of 20—30 cm^{-1} in ν_{NO} on

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* Spectroscopic and microanalytical data are deposited in Supplementary Publication No. SUP 56521.

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of $[Mo(NO)\{HB(Me_2pz)_3\}(NHBu^n)_2]$

Atom	*x*	*y*	*z*
Mo	159(2)	899(2)	7 637(1)
N(1)	−1 019(15)	1 028(17)	6 876(14)
O(1)	−1 832(13)	1 144(17)	6 361(12)
N(2)	454(16)	2 356(15)	7 735(14)
C(1)	−133(26)	3 195(26)	7 380(20)
C(2)	−269(22)	3 867(27)	8 090(29)
C(3)	−909(28)	4 702(33)	7 843(26)
C(4)	−1 005(27)	5 359(32)	8 537(34)
N(3)	−94(15)	610(16)	8 729(14)
C(5)	−930(31)	679(24)	8 861(20)
C(6)	−960(27)	1 490(35)	9 459(34)
C(7)	−1 588(39)	1 650(34)	9 719(37)
C(8)	−1 711(34)	2 545(46)	10 204(27)
N(4)	1 668(14)	719(17)	8 641(12)
N(5)	2 210(17)	18(18)	8 453(12)
C(9)	1 840(17)	1 910(22)	9 915(16)
C(10)	2 191(23)	1 105(19)	9 472(17)
C(11)	3 040(20)	616(21)	9 817(17)
C(12)	3 066(22)	−87(23)	9 189(20)
C(13)	3 791(19)	−784(30)	9 236(19)
N(6)	221(13)	−812(16)	7 424(10)
N(7)	1 032(13)	−1 230(12)	7 439(10)
C(14)	−1 341(18)	−1 406(20)	7 246(17)
C(15)	−412(16)	−1 563(18)	7 281(15)
C(16)	41(19)	−2 466(22)	7 165(14)
C(17)	893(17)	−2 260(19)	7 256(14)
C(18)	1 663(17)	−2 944(19)	7 243(16)
N(8)	722(14)	795(18)	6 548(13)
N(9)	1 494(16)	199(14)	6 695(10)
C(19)	−314(18)	1 896(17)	5 300(14)
C(20)	529(19)	1 197(16)	5 708(16)
C(21)	1 155(20)	901(23)	5 351(15)
C(22)	1 778(21)	265(21)	5 995(22)
C(23)	2 601(20)	−243(21)	5 929(16)
B	1 852(22)	−564(21)	7 531(18)

substituting the halide of (**2**) with a second amide ligand. This is indicative of increased π-bonding interactions with the amide ligand compared to halide. Such effects have been observed previously and the successive substitution of Cl^- by alkoxide in $[Mo(NO)LCl_2]$, for example, results in successive reductions of *ca.* 20 and *ca.* 40 cm^{-1} in the value of ν_{NO}.[9] The overall order of ν_{NO} values in [Mo(NO)L(X)Y] is thus X = Y = halide > X = halide, Y = alkoxide > X = halide, Y = alkylamide > X = Y = alkoxide > X = alkoxide, Y = alkylamide > X = Y = alkylamide. The same order is found in the related tungsten series but with an overall bathochromic shift of 25—45 cm^{-1} compared with the molybdenum series.

The 100-MHz ^1H n.m.r. spectra of the new complexes (**5**) and (**8**) where $R^1 = R^2$ were consistent with the presence of a plane of symmetry in the molecule. The pyrazolyl H^4 protons appeared as two resonances of intensity ratio 2:1 in the region δ 5.7—5.9 p.p.m., while the pyrazolyl methyl protons appeared as four signals of intensity ratio 6:6:3:3 in the region δ 2.0—2.6 p.p.m. The α-CH_2 protons of the alkylamide complexes appeared at low field in the region δ 3.9—5.0 and as AB pairs coupled to the adjacent methylene protons. In the molybdenum complexes the alkylamide N–H protons were generally observed as a broad resonance at *ca.* δ 6.6 which disappeared after contact with D_2O. In the tungsten compounds these protons appeared at higher field in the region of δ 5.4 p.p.m. The N–H protons in the arylamide complexes appeared at lower field than in their alkyl counterparts; in the region δ 8.6—9.0 p.p.m. for the molybdenum complexes. Other signals consistent with the presence of the appropriate alkyl or aryl substituents were also observed. The spectra of (**5**) and (**8**) where R^1 = Et, $R^2 = C_6H_4Me$-*p* exhibited three distinct resonances of area 1 for the pyrazolyl H^4 protons, consistent with the absence of a plane of symmetry in the molecule. However, the pyrazolyl methyl environments were not fully distinguished. In combination with the tolyl methyl resonance they gave rise to six signals of intensity ratio 6:3:3:3:3:3 in the region δ 2.2—2.7 p.p.m. for (**8**; R^1 = Et, $R^2 = C_6H_4Me$-*p*). In the case of (**5**; R^1 = Et, $R^2 = C_6H_4Me$-*p*) five methyl signals of intensity ratio 3:3:6:6:3 were observed in the region δ 2.2—4.5 p.p.m. In the spectrum of (**5**; R^1 = Ph, $R^2 = C_6H_4Me$-*p*) the methyl environments were poorly resolved giving rise to only three signals of relative intensity 9:9:3 in the region δ 2.2—2.5 p.p.m. The pyrazolyl H^4 protons gave rise to two signals of relative intensity 2:1 at δ 5.68 and 5.69 p.p.m. presumably as a result of the similarity between the $PhNH^-$ and *p*-$MeC_6H_4NH^-$ ligands. However, the integration of the signals for this complex was consistent with the presence of one phenyl and one tolyl substituent. Two distinct amide proton resonances were also observed at δ 8.49 and 8.96 p.p.m.

The electronic spectra of the molybdenum complexes generally showed three absorption bands, although these were not fully resolved in the alkylamide complexes. The arylamide systems absorbed at longer wavelengths than their alkylamide counterparts and were more intensely coloured. In the tungsten complexes only one absorption band could be resolved.

The mass spectra of the complexes all exhibited a molecular ion along with ions attributable to the sequential loss of the amide ligands and nitric oxide. In the lower mass region, ions attributable to the amide ligands themselves were observed. There was also a complex pattern of ions attributable to the fragmentation of the MoL or WL moieties along with an intense ion at *m*/*e* = 96 attributable to 3,5-dimethylpyrazole derived from the destruction of L.

Microanalytical data for the new complexes were in accord with their formulations as bis- or mono-amide complexes. Some of these compounds showed a marked tendency to crystallise with solvent in the lattice. In certain cases this could not be removed completely even by heating *in vacuo* for extended periods. However, the ^1H n.m.r. spectra of such compounds exhibited signals at δ 0.9 and 1.25 p.p.m. attributable to hexane which integrated for the appropriate mol ratio of hexane in accord with the microanalytical data.

Electrochemical Studies.—The electrochemical properties of the new complexes were investigated in acetonitrile or thf solution using cyclic voltammetry and the results obtained are presented in Table 1. The bis-arylamide complexes of molybdenum (**5**; $R^1 = R^2$ = Ph or C_6H_4Me-*p*; R^1 = Ph, $R^2 = C_6H_4Me$-*p*) all exhibited a one-electron reduction process between −1.3 and −1.4 V. This was found to be reversible on the cyclic voltammetry time-scale and linear plots of i_p against $v^{\frac{1}{2}}$ could be obtained where v was the scan rate in V s^{-1} and i_p was the peak current in mA. These compounds also exhibited an irreversible oxidation process at *ca.* +0.6 V. The molybdenum complexes (**5**; $R^1 = R^2$ = Et, Pr^n, or Bu^n; R^1 = Et, $R^2 = C_6H_4Me$-*p*) containing alkylamide ligands exhibited only irreversible reduction waves in their cyclic voltammograms. This behaviour is in accord with that obtained for the monoamide complexes (**2**; X = I, R^1 = Et or Ph) in which reversible behaviour was found[7] for the arylamide but not the

Table 3. Selected bond lengths (Å) and angles (°) in [Mo(NO){HB($Me_2pz)_3$}($NHBu^n)_2$]

Mo–N(1)	1.748(21)	Mo–N(6)	2.260(20)
Mo–N(2)	1.945(19)	Mo–N(8)	2.204(21)
Mo–N(3)	1.935(20)	N(1)–O(1)	1.206(18)
Mo–N(4)	2.254(19)		
N(1)–Mo–N(2)	96.3(10)	N(2)–Mo–N(8)	88.2(9)
N(1)–Mo–N(3)	95.5(9)	N(3)–Mo–N(4)	83.3(8)
N(1)–Mo–N(4)	178.8(8)	N(3)–Mo–N(6)	88.5(7)
N(1)–Mo–N(6)	95.1(9)	N(3)–Mo–N(8)	161.9(9)
N(1)–Mo–N(8)	96.2(8)	N(4)–Mo–N(6)	84.7(7)
N(2)–Mo–N(3)	104.1(9)	N(4)–Mo–N(8)	84.9(7)
N(2)–Mo–N(4)	84.2(8)	N(6)–Mo–N(8)	76.9(7)
N(2)–Mo–N(6)	162.1(8)		
Mo–N(1)–O(1)	178.2(22)	Mo–N(3)–C(5)	130.1(20)
Mo–N(2)–C(1)	129.7(19)		

Table 4. Deviations (Å) of atoms from the planes of the pyrazolyl rings; e.s.d.s are *ca.* 0.02 Å for Mo and 0.04 Å for the lighter atoms

Plane 1: N(4), N(5), C(10)—C(12)
N(4) 0.02, N(5) −0.02, C(10) −0.01, C(11) 0.00, C(12) 0.01, Mo 0.254, C(9) 0.00, C(13) 0.03, B −0.05

Plane 2: N(6), N(7), C(15)—C(17)
N(6) −0.02, N(7) 0.01, C(15) 0.01, C(16) 0.00, C(17) −0.01, Mo −0.083, C(14) 0.02, C(18) 0.05, B −0.09

Plane 3: N(8), N(9), C(20)—C(22)
N(8) 0.01, N(9) −0.01, C(20) −0.01, C(21) 0.00, C(22) 0.01, Mo 0.107, C(19) −0.02, C(23) 0.04, B −0.25

Interplanar angles (°): 1—2 124.7(10), 1—3 128.6(10), 2—3 105.3(10)

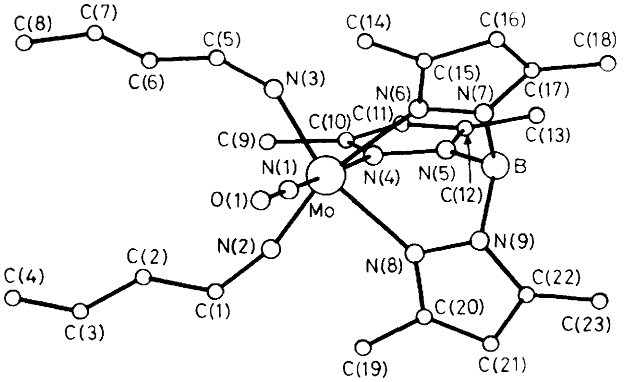

Figure 1. The structure of [Mo(NO){HB($Me_2pz)_3$}($NHBu^n)_2$] with atom numbering but excluding hydrogen atoms

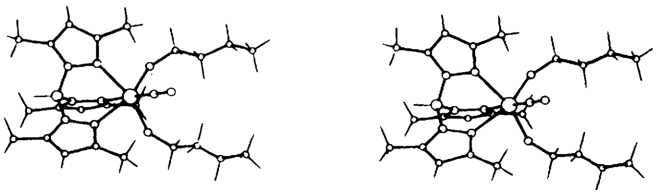

Figure 2. Stereoscopic view of [Mo(NO){HB($Me_2pz)_3$}($NHBu^n{}_2$)]

alkylamide complexes. The bis-alkylamides also exhibited irreversible oxidation waves but at more anodic potentials than their arylamide counterparts.

The tungsten bis-alkylamide complexes [W(NO)L(NHR^1)(NHR^2)] (**8**) exhibited irreversible one-electron reduction processes in the region −1.1 to −1.5 V. This observation is unusual in that, where reversible couples are involved, the tungsten compounds in this series have shown reduction potentials some 400—500 mV more cathodic than their molybdenum analogues.[7] The reduction process in the case of the alkylamide derivatives may thus be ligand- rather than metal-based.

*Structural Studies.**—In order to characterise an example of this new series of compounds a single-crystal *X*-ray diffraction study was carried out on (**5**; $R^1 = R^2 = Bu^n$). Atomic co-ordinates are listed in Table 2 and selected bond lengths and angles are given in Table 3. The structure of the complex is illustrated in Figure 1, which also shows the atomic numbering, and Figure 2. The complex has approximate mirror (C_s) symmetry, the pseudo plane passing through the Mo–N–O group, the boron atom, and the N(4), N(5), C(10)—C(12) pyrazolyl ring.

The co-ordination about the molybdenum atom is distorted octahedral, similar to that observed in a number of related complexes.[1–4,10,11] The maximum angular distortion from ideal octahedral is 18.1° and the mean distortion is 7.5°. Of the Mo–N linkages, the Mo–N(nitrosyl) is the shortest and the Mo–N=O fragment is essentially linear. The bonds to the n-butylamido groups at 1.935(20) and 1.945(19) Å are similar to those found[2,3,10] previously for Mo–N(arylamido and alkylamido) bonds. The bonds to the pyrazolyl rings are some 0.3 Å longer.

The observed lengths of the Mo–N(butylamido) bonds indicate a significant degree of p_π–d_π donation from the ligands. The large Mo–N–C angles (130° for both ligands) noted previously[2,3] are also consistent with this, but may be due also to steric effects.[3] Close intramolecular non-bonded contacts N(1)···C(1) and N(1)···C(5) [observed values 3.10(3) and 3.09(4) Å respectively] are alleviated by the large angles at N(2) and N(3). The torsion angles N(1)–Mo–N(2)–C(1) and N(1)–Mo–N(3)–C(5) are small, 6(2) and −10(2)° respectively, similar to the values found[1–4,10,11] in other structures of this type. A small increase of these angles would also reduce crowding with the nitrosyl group; such an increase may however be energetically unfavourable due to the steric requirements of the p_π–d_π ligand–molybdenum interaction.[4]

The pyrazolyl rings are effectively planar (Table 4) with the molybdenum atom out of the ring plane by distances of 0.1—0.25 Å. The N(6), N(7) and N(8), N(9) rings are inclined at 125(1) and 129(1)°, respectively, to the N(4), N(5) ring. The dihedral angle between the former rings is 105(1)°. The geometry of the tris(3,5-dimethylpyrazolyl)borato ligand is thus similar to that in related structures,[3,4] the range of values found for the two categories of dihedral angle being 124—128 and 106—110°. The larger angles in each case appear to result from steric interactions between the 5-methyl substituents and adjacent bulky ligands ($NHBu^n$ in the present structure). The smaller angle is between the pyrazolyl ligands embracing the less bulky nitrosyl ligand.

Experimental

Structural Studies.—A crystal (0.3 × 0.2 × 0.1 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer; cell

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* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

dimensions and intensities were measured by $\omega/2\theta$ scans with graphite-monochromated Mo-K_α radiation and scan range $(\omega) = (1.0 + 0.35 \tan \theta)^\circ$. The scan speed varied from 0.9 to 3.5° min^{-1} depending on the intensity. 5 549 Reflections were scanned within $2 < \theta < 25^\circ$. Two standard reflections measured every 2 h showed a slight (*ca.* 13%) decrease in intensity and appropriate scaling factors were applied.

Lorentz and polarization corrections were applied and 1 142 structure amplitudes with $F > 5\sigma(F)$ were considered observed and used in the analysis.

Crystal data. $C_{23}H_{42}BMoN_9O$, $M = 567.4$, monoclinic, space group $P2_1/n$, $a = 15.508(7)$, $b = 13.025(4)$, $c = 15.639(5)$ Å, $\beta = 113.38(3)^\circ$, $U = 2\,899.6$ Å^3, $Z = 4$, $D_c = 1.300$ g cm^{-3}, $F(000) = 1\,192$, $\mu(\text{Mo-}K_\alpha) = 0.474$ mm^{-1}, $\lambda = 0.710\,69$ Å.

The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for the heavier atoms except for those of one of the pyrazolyl rings and the boron atom which were refined isotropically. Hydrogen atoms were placed in calculated positions riding on their respective bonded atom. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.001F^2]$ and the refinement converged to $R = 0.063$, $R' = 0.075$ (maximum shift/error ratio in final cycle 0.21). The residual electron density in a final difference map was within ± 0.4 e Å^{-3}.

Complex neutral-atom scattering factors were employed. Computations were carried out on the University of Birmingham Honeywell computer and on the CDC 7 600 at the University of Manchester Regional Computer Centre with the SHELX[12] and PLUTO[13] programs.

Owing to the relatively small number of significant data, high accuracy was not achieved and detailed discussion of bonding geometry within the organic ligands is not possible.

Synthetic Studies.—All reactions were carried out in an atmosphere of dry nitrogen. Tetrahydrofuran (thf), for use as a reaction medium, was redistilled from sodium benzophenone under nitrogen prior to use.[14] Other solvents were dried over molecular sieves or sodium, as appropriate, prior to use. $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I_2}]$,[15] $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHR')}]$ ($R' = Et$, Pr^n, Bu^n, Ph, or C_6H_4Me-*p*), and $[\mathrm{W(NO)\{HB(Me_2pz)_3\}Cl_2}]$ were prepared by methods described elsewhere.[2,3] Other reagents were used as received except for Pr^nNH_2 and Bu^nNH_2 which were dried over $CaCl_2$ before use. Column chromatography was carried out using 70—230 mesh silica gel.

Infrared spectra were recorded using a PE 297 spectrometer, 100-MHz ^1H n.m.r. spectra using a PE R34 spectrometer, and electronic spectra using a Perkin-Elmer M330 spectrophotometer. Microanalyses were carried out by the University of Birmingham Microanalytical Laboratory. Yields were calculated on the basis of the metal-containing starting material. Electrochemical measurements were made using a Hiteck potentiostat and wave-form generator.

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHEt)_2}]$. Sodium hydride (0.1 g) and sodium metal (0.1 g) were dispersed in thf (80 cm^3) and a solution of ethylamine (0.2 cm^3) in thf (20 cm^3) was added. The mixture was stirred at room temperature for 2 h by which time effervescence had ceased. $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHEt)}]$ (1.0 g) was then added and the mixture stirred at ambient temperature for a further 48 h. At this stage the solution was yellow-orange. The solution was then filtered under nitrogen and the solvent evaporated from the filtrate *in vacuo* to afford the crude product. This was redissolved in dichloromethane and the solution filtered in air. Partial removal of the dichloromethane by evaporation followed by the addition of n-hexane then caused the product to precipitate. Further recrystallisation from dichloromethane–hexane gave the yellow microcrystalline complex (0.60 g, 80%).

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHPr^n)_2}]$. This complex was prepared in an identical manner to the ethylamide derivative using n-propylamine (0.3 cm^3) and $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHPr^n)}]$ (1.0 g). An orange crystalline product (0.54 g, 64%) was obtained.

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHBu^n)_2}]$. This complex was prepared in an identical manner to the ethylamide derivative described above using n-butylamine (0.3 cm^3) and $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHBu^n)}]$ (1.0 g). An orange crystalline product was obtained (0.42 g, 53%).

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHPh)_2}]$. Sodium metal (0.1 g) was added to a solution of naphthalene (0.2 g) in thf (100 cm^3). The mixture was stirred overnight at ambient temperature during which time a dark green solution developed. $[\mathrm{Mo(NO)\{HB(Me_2pz_2)_3\}I(NHPh)}]$ (1.0 g) was then added, the mixture stirred for 1 h then aniline (0.15 cm^3) was added and the mixture stirred for a further 1 h. The resulting purple solution was then filtered and the solvent removed from the filtrate *in vacuo* to afford the crude product. This was redissolved in dichloromethane and filtered. Partial evaporation of the dichoromethane followed by the addition of n-hexane caused the product to precipitate as a purple microcrystalline solid (0.72 g, 80%). Further purification could be effected by column chromatography on silica gel using thf as the eluant, followed by recrystallisation from dichloromethane–hexane.

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHC_6H_4Me\text{-}\mathit{p})_2}]$. This complex was prepared in an identical manner to the bis-anilide complex described above using $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHC_6H_4Me\text{-}\mathit{p})}]$ (1.0 g) and *p*-toluidine (0.16 g). A purple microcrystalline product (0.7 g, 75%) was obtained.

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHPh)(NHC_6H_4Me\text{-}\mathit{p})}]$. This complex was prepared in an identical manner to the bis-toluidine derivative described above using aniline (0.15 g) in place of *p*-toluidine. A purple microcrystalline product (0.78 g, 85%) was obtained.

$[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHEt)(NHC_6H_4Me\text{-}\mathit{p})}]$. Sodium metal (0.1 g) was added to a solution of naphthalene (0.21 g) in thf (100 cm^3) and the mixture stirred overnight at room temperature during which time it became dark green. $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHEt)}]$ (1.0 g) was then added, the mixture stirred for a further 0.5 h, and then *p*-toluidine (0.17 g) added. The mixture was stirred for a further 48 h without heating. The mixture was then filtered and the filtrate evaporated to dryness *in vacuo* to give a red-purple solid. This was redissolved in dichloromethane, filtered and the solvent partially removed by evaporation before adding hexane to precipitate the product as a red-purple powder (0.64 g, 76%). Further purification could be effected by column chromatography on silica gel using thf as the eluant, followed by recrystallisation from dichloromethane–hexane.

Reaction of $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}I(NHPh)}]$ *with sodium naphthalenide.* The procedure for preparing $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHPh)_2}]$ was followed using half quantities except that no aniline was added to the mixture. A purple product (0.2 g, 45%) with identical spectral properties to $[\mathrm{Mo(NO)\{HB(Me_2pz)_3\}(NHPh)_2}]$ was isolated.

$[\mathrm{W(NO)\{HB(Me_2pz)_3\}Cl(NHC_6H_4Me\text{-}\mathit{p})}]$. A solution of $[\mathrm{W(NO)\{HB(Me_2pz)_3\}Cl_2}]$ (0.5 g) in dichloromethane (50 cm^3) was stirred at reflux with sodium hydride (0.1 g) and *p*-toluidine (0.3 g) for 3 d. The reaction mixture was then cooled, filtered, and the filtrate evaporated to dryness giving the crude brown product. This was purified by column chromatography using dichloromethane as eluant and collecting the major brown fraction. Further purification was effected by recrystallisation from dichloromethane–hexane mixtures to give the brown product (0.43 g, 77%).

$[\mathrm{W(NO)\{HB(Me_2pz)_3\}Cl(NHEt)}]$. Ethylamine (1 cm^3) was added to a solution of $[\mathrm{W(NO)\{HB(Me_2pz)_3\}Cl_2}]$ (0.5 g) in dichloromethane (40 cm^3) and the mixture was then stirred at room temperature for 10 min. During this time the solution became red and was subsequently filtered and evaporated to dryness. The solid obtained was then purified by column chromatography using dichloromethane as the eluant and collecting the first major orange fraction. This afforded the orange product (0.38 g, 74%) which could be further purified by recrystallisation from dichloromethane–hexane mixtures.

$[W(NO)\{HB(Me_2pz)_3\}Cl(NHPr^n)]$. This compound was prepared in an identical manner to its ethylamide analogue using n-propylamine (1 cm^3). An orange microcrystalline product (0.3 g, 55%) was obtained.

$[W(NO)\{HB(Me_2pz)_3\}Cl(NHBu^n)]$. This compound was prepared in an identical manner to its ethylamide analogue using n-butylamine (1 cm^3). An orange microcrystalline product (0.25 g, 45%) was obtained.

$[W(NO)\{HB(Me_2pz)_3\}(NHEt)_2]$. Sodium hydride (0.2 g) and sodium metal (0.05 g) were added to a solution of ethylamine (0.5 cm^3) in thf (100 cm^3). The resulting mixture was stirred at room temperature for 2 h during which time effervescence ceased. $[W(NO)\{HB(Me_2pz)_3\}Cl(NHEt)]$ (1.0 g) was then added and the mixture stirred for a further 48 h at room temperature. During this time the mixture became orange-yellow. The reaction mixture was next filtered and the solvent removed *in vacuo* to afford the crude yellow product. This was recrystallised from dichloromethane (0.8 g, 79%).

$[W(NO)\{HB(Me_2pz)_3\}(NHPr^n)_2]$. This material was prepared in a similar manner to its ethylamide analogue using n-propylamine (1.0 cm^3) and $[W(NO)\{HB(Me_2pz)_3\}Cl(NHPr^n)]$ (1.0 g) and a reaction time of 24 h. Recrystallisation was again effected using dichloromethane–hexane to give a yellow product (0.48 g, 47%).

$[W(NO)\{HB(Me_2pz)_3\}(NHBu^n)_2]$. This material was prepared in a similar manner to its ethylamide analogue using n-butylamine (1.0 cm^3) and $[W(NO)\{HB(Me_2pz)_3\}Cl(NHBu^n)]$ (1.0 g). Recrystallisation from dichloromethane–hexane afforded the yellow product (0.58 g, 55%).

$[W(NO)\{HB(Me_2pz)_3\}(NHEt)(NHC_6H_4Me\text{-}p)]$. Sodium hydride (0.2 g) and sodium metal (0.1 g) were dispersed in thf (100 cm^3) and *p*-toluidine (0.18 g) added. The mixture was refluxed for 1 h and then $[W(NO)\{HB(Me_2pz)_3\}Cl(NHEt)]$ (1.0 g) was added. The mixture was refluxed for a further 3 d during which time the solution became red-purple. The mixture was then filtered and the solvent evaporated *in vacuo*. The crude product was recrystallised from dichloromethane–hexane to give a red-brown powder. Further purification could be effected by column chromatography using thf as the eluant and collecting the principal orange fraction. This product was further recrystallised using dichloromethane–hexane (0.56 g, 50%).

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