Reactions of $[M(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}X_2]$ (M = Mo, X = I; M = W, X = Cl) with Some Amine-substituted Pyridines. The Molecular Structures of $[M(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$†

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The 16-electron complex $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ reacted with an excess of 2-aminopyridine to produce the diamagnetic bis(amide) derivative $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$, whereas with 2-aminomethylpyridine the 17-electron complex $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NH_2CH_2C_5NH_4)_2]^+$ was formed. Similar reactions with $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ in the presence of NaH afforded only the bis(amide) derivatives. The molecular structures of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$ (M = Mo or W) were determined by *X*-ray diffraction methods. Both complexes contain metal ions in an approximately octahedral co-ordination environment with linear nitrosyl ligands. In neither case was evidence found for any interaction between the pyridyl nitrogen atom and the electron-deficient metal centre. The metal–nitrogen (amide) bond distances are 1.987(3) and 1.990(3) Å (Mo), and 1.97(1) and 2.00(1) Å (W). The corresponding M–NH–C(pyridyl) angles are 135.5(2), 135.4(2), 141(1), and 134(1)°, respectively.

The sterically bulky ligand tris(3,5-dimethylpyrazolyl)borate, L, has been found to restrict metal centres to which it is co-ordinated to octahedral six-co-ordination.[1–4] In the case of compounds containing the $\{Mo(NO)\}^{3+}$ core this leads to formal co-ordinative unsaturation and electron deficiency at the metal centre. This effect is exemplified by the related complexes $[\{Mo(NO)(\eta^5\text{-}C_5H_5)I_2\}_2]$ and $[Mo(NO)LI_2]$, (**1**). The former is an iodide-bridged dimer[5,6] containing 18-electron, nominally seven-co-ordinate, molybdenum centres while the steric demands of L result in (**1**) being a monomer containing a 16-electron, six-co-ordinate molybdenum centre.[7]

The compound (**1**) reacts readily with primary amines, alcohols, or thiols to produce the 16-electron complexes [Mo(NO)L(I)Y] (Y = amide, alkoxide, or thiolate) which are surprisingly air stable in view of their nominal co-ordinative unsaturation.[1] This stability may in part be attributed to the protective effects of the sterically bulky ligand L, but also arises from electron stabilisation by ligand to metal $p_\pi \longrightarrow d_\pi$ charge donation as indicated by the short Mo–X (X = O, S, or NH) bond distances found in the alkoxide, thiolate, and amide derivatives.[8–11] Like (**1**), these derivatives will undergo reduction reactions to produce 17-electron complexes without expanding the metal co-ordination number, but do not appear to accept an additional monodentate ligand to give an 18-electron, seven-co-ordinate species.[7,12]

The observation by Lalor and co-workers[13] that an η^2-acyl ligand could be accommodated by L in $[Mo(\eta^2\text{-}OCC_6H_4Me\text{-}p)(CO)_2L]$, to give a nominally seven-co-ordinate complex, prompted us to investigate whether L might also accommodate a sterically compact bidentate, uninegative, four-electron ligand in place of I^- in (**1**). This would afford a co-ordinatively saturated 18-electron complex. Since the complex $[Mo(NO)L(I)(NHC_6H_4Me\text{-}p)]$ had already been structurally characterised,[8] we chose 2-aminopyridine as a ligand which might form a related complex in which the pyridyl nitrogen also binds to molybdenum. In order to be accommodated by L, we anticipated that the pyridyl ligand would have to be oriented to lie in the cleft between two pyrazolylmethyl groups as seen in the structurally characterised[12,14] pyrrolyl complex, $[Mo(NO)L(NC_4H_4)_2]$. Other studies in our laboratory have shown[12,14] that $[Mo(NO)LI_2]$, (**1**), reacts with excess of pyridine to form the 17-electron complex $[Mo(NO)L(NC_5H_5)_2]^+$. Thus, should the formation of a chelated species not occur the experiment might still indicate the preference of the molybdenum centre in these systems for an anionic amide nitrogen by complexing with $NC_5NH_4NH^-$, or for a neutral pyridine nitrogen by complexing with $NC_5H_4NH_2$. Further to test this point we also investigated the reactivity of (**1**) towards 2-aminomethylpyridine, $2\text{-}NH_2CH_2C_5NH_4$. The reactions of these two potentially bidentate ligands with $[W(NO)LCl_2]$, (**2**), were also studied to compare the related molybdenum and tungsten chemistry.

Results and Discussion

Synthetic Studies.—The monoamide complex $[Mo(NO)LI(NHC_5NH_4)]$, (**3**), was prepared by treating (**1**) with a slight excess of 2-aminopyridine in the presence of NaH, which served to destroy the HI liberated in the reaction. In the presence of a three-fold excess of 2-aminopyridine in refluxing tetrahydrofuran (thf), (**1**) reacted, in the absence of NaH, to form the bis(amide) derivative $[Mo(NO)L(NHC_5NH_4)_2]$, (**4**). This finding was surprising since the reaction of (**1**) with excess of NH_2Ph produces only the monoamide [Mo(NO)L(I)(NHPh)]. Furthermore, quite forcing conditions (reduction with $NaC_{10}H_8$ in the presence of NH_2Ph) were necessary to convert this product into $[Mo(NO)L(NHPh)_2]$. The reaction of (**1**) with excess of 2-aminomethylpyridine, $2\text{-}NH_2CH_2C_5NH_4$, in refluxing tetrahydrofuran (thf) also led to the substitution of both iodides, but in this case the paramagnetic green complex $[Mo(NO)L(NC_5H_4CH_2NH_2)_2]^+$, (**5**), was obtained. This reaction would appear to be directly analogous to the reaction between (**1**) and an excess of pyridine which produces only $[Mo(NO)L(NC_5H_5)_2]^+$.

The reactions of 2-aminopyridine and 2-aminomethylpyridine with (**2**) were also investigated. Tungsten complexes containing the $\{W(NO)L\}^{2+}$ moiety are generally less readily

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† Nitrosylbis(2-pyridylamido)[tris(3,5-dimethylpyrazolyl)borato]-molybdenum or -tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Selected spectroscopic and electrochemical data

Compound L = {$HB(3,5-Me_2C_3N_2H)_3$}	ν_{NO}[a]/cm^{-1}	$E_{\frac{1}{2}}$[b]/V	ΔE_p[c]/mV	n[d]	$\lambda_{max.}$/nm	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	Solvent
[$Mo(NO)LI(NHC_5NH_4)$]	1 660	−0.59	60	1.07	452	18 210	MeCN
					385	16 100	
[$Mo(NO)L(NHC_5NH_4)_2$]	1 640[e]	−1.05	100	1.13	530	9 250	
					440	9 880	thf
					360	12 000	
					295	11 300	
[$Mo(NO)L(NC_5H_4CH_2NH_2)_2$]I	1 620	−1.31	60	1.03	720	211	MeCN
[$W(NO)L(Cl)(NHC_5NH_4)$]	1 625	−1.18	100	0.97	440	3 420	thf
[$W(NO)L(NHC_5NH_4)_2$]	1 610	−1.50	60	1.12	395	6 460	MeCN
					320	4 750	
[$W(NO)L(Cl)(NHCH_2C_5NH_4)$]	1 605	−1.70	160	0.86			thf
[$W(NO)L(NHCH_2C_5NH_4)_2$]	1 580	−1.08[f]		0.73			thf

[a] As KBr disc unless otherwise specified. [b] Obtained in solutions containing 0.1 mol dm^{-3} $NBu^n_4BF_4$ as supporting electrolyte and using a platinum bead electrode. Values are referred to the saturated calomel electrode. [c] Separation between cathodic and anodic peak potentials, typical values for ferrocene being 80 mV under similar conditions. [d] Calculated by comparison with the diffusion current for [$Mo(NO)LCl_2$]. [e] Obtained in CH_2Cl_2 solution. [f] Cathodic peak potential for a chemically irreversible process.

reduced than their molybdenum analogues[9] and no 17-electron compounds were isolated from these reactions. When an equimolar quantity of 2-$NH_2C_5NH_4$ was reacted with (**2**) in the presence of NaH, the monoamide derivative [$W(NO)L(Cl)(NHC_5NH_4)$], (**6**), was obtained. However, when a three-fold excess of 2-$NH_2C_5NH_4$ was used, again in the presence of NaH, the bis(amide) [$W(NO)L(NHC_5NH_4)_2$], (**7**), was formed. As with its molybdenum analogue, (**4**), this finding was quite unexpected since all previous attempts to prepare tungsten bis(arylamide) derivatives of this type using aniline or *p*-toluidine had failed.[6] Only the bis(alkylamide) derivatives [$W(NO)L(NHR)_2$] (R = Et, Pr^n, or Bu^n) had been obtained from [$W(NO)L(Cl)(NHR)$] by reaction with additional NH_2R in the presence of NaH.

The reactions of (**2**) with 2-$NH_2CH_2C_5NH_4$ followed the pattern previously observed for alkylamines. When equimolar quantities of reagent were used the mono(alkylamide) [$W(NO)L(Cl)(NHCH_2C_5NH_4)$], (**8**), was formed, while using an excess of amine in the presence of NaH led to the formation of [$W(NO)L(NHCH_2C_5NH_4)_2$], (**9**). Thus, while 2-$NH_2CH_2C_5NH_4$ reacted with (**1**) in a manner analogous to pyridine, its reactions with (**2**) were akin to those of an alkylamine. The reaction of an excess of 2-$NH_2C_5NH_4$ with both (**1**) and (**2**) was remarkable in the facility with which the bis(arylamide) derivatives (**4**) and (**7**) were produced.

Spectral Studies.—All the new complexes exhibited bands in their i.r. spectra consistent with the presence of the polypyrazolylborate ligand, L, and ν_{NH} were observed in the region 3 100—3 350 cm^{-1} for all the complexes. The values of ν_{NO} are listed in Table 1 and were in accord with the formulations of the complexes as mono- or bis-amide derivatives or, in the case of (**5**), as a 17-electron complex.[1,12,14–16] In particular, the values of ν_{NO} provided no evidence for chelation by 2-$NHC_5NH_4^-$ or 2-$NHCH_2C_5NH_4^-$ ligands to produce 18-electron molybdenum complexes. If such compounds had formed, a marked decrease in the value of ν_{NO} would be expected as compared to the related 16-electron compounds. No such effect was observed, typical values for ν_{NO} in [$M(NO)L(X)Y$] being[1,15] 1 660 cm^{-1} for M = Mo, X = I, Y = NHR; 1 635 cm^{-1} for M = Mo, X = Y = NHR; 1 626 cm^{-1} for M = W, X = Cl, Y = NHR; 1 620 cm^{-1} for M = W, X = Y = NHR′, where R = aryl and R′ = alkyl. The electronic spectra of the complexes similarly provided no evidence for the presence of 18-electron species (Table 1).

The complexes (**3**), (**6**), (**7**), and (**8**) exhibited molecular ions in their mass spectra but (**4**) and (**9**) exhibited only [$M - NHC_5NH_4$]$^+$ and [$M - NHCH_2C_5NH_4$]$^+$ respectively as their heaviest detected ions.

The 100-MHz ^1H n.m.r. spectra of all the diamagnetic complexes exhibited signals consistent with their formulations. In the case of (**4**) signals due to a molecule of free 2-$NH_2C_5NH_4$ were also detected, the presence of this material being subsequently confirmed by an *X*-ray diffraction study. The signals attributable to the ligand L appeared as two groups of singlets in the regions δ 2.0—2.7 p.p.m., assigned to the pyrazolyl methyl protons, and δ 5.6—6.0 p.p.m. assigned to the pyrazolyl ring C–H protons. In the spectra of (**4**), (**7**), and (**9**) the methyl signals appeared in the intensity ratio 3:3:6:6, and the pyrazolyl C–H protons in the intensity ratio 2:1, as required for a plane of symmetry in the molecule. These observations militate against a structure involving chelation by one of the aminopyridine ligands but do not rule out the possibility that both ligands might be chelating alternately as part of a dynamic process which was fast on the n.m.r. time-scale.* However, an *X*-ray diffraction study (see later) established that chelation did not occur in the solid state.

The pyridine ring protons in the complexes (**3**), (**4**), (**6**), and (**7**) appeared as a group of multiplets in the region δ 6.4—8.3 p.p.m. The methylene protons of the $NHCH_2C_5NH_4^-$ ligand in (**8**) and (**9**) appeared as an AB system in the region δ 5.4—6.5 p.p.m. as has been noted previously for compounds of this type.[1,8] All the complexes except (**5**) exhibited a broad resonance in the region δ 6—13 p.p.m. assigned to the amide NH protons. The paramagnetic complex, (**5**), exhibited an e.s.r. signal at room temperature in CH_2Cl_2 solution (g = 1.9822 ± 0.0003) which also exhibited satellite signals (A = 5.33 mT) attributable to hyperfine interactions with ^{95}Mo (15.9% abundance, $I = \frac{5}{2}$) and ^{97}Mo (9.6% abundance, $I = \frac{5}{2}$). This may be compared with the values g = 1.9974, A = 4.89 mT obtained[8] under similar conditions for [$Mo(NO)L(NC_5H_5)_2$]$^+$.

Electrochemical Studies.—The electrochemical properties of the new complexes were investigated by cyclic voltammetry in thf or acetonitrile solutions and the results obtained are

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* Low-temperature studies were inhibited by the limited solubility of these complexes in suitable solvents.

presented in Table 1. Only irreversible oxidation processes were observed and for the complexes (**3**), (**4**), and (**6**)—(**8**) these were at potentials more anodic than +0.9 V. The 17-electron complex (**5**) exhibited two irreversible oxidation processes at +0.38 and +0.76 V attributable to the presence of I^-. All the complexes exhibited a one-electron reduction process in the region −0.5 to −2.0 V but in the cases of (**8**) and (**9**) this was not reversible and no anodic peak was observed for (**9**). The reduction potential for (**4**) was 0.27 V more anodic than that of its analogue $[Mo(NO)L(NHPh)_2]$, while for (**3**) the anodic shift was *ca.* 0.19 V compared to [Mo(NO)L(I)(NHPh)]. A similar shift of *ca.* 0.12 V was apparent in the case of the tungsten derivative (**6**), but no comparable species exists for (**7**).

These differences presumably reflect the higher electronegativity of the nitrogen in the pyridine ring compared to -CH- in phenyl. This exerts an inductive effect on the metal centre and facilitates reduction as found with electron-withdrawing substituents in related arylamide complexes.[17] Such an effect would also account for the small increase in ν_{NO} found in these complexes as compared to their anilide analogues.[1,14,15] As has been noted previously the tungsten complexes are typically reduced at potentials some 500 mV more cathodic than their molybdenum analogues, although the irreversible nature of the reduction processes for the alkylamide derivatives precludes comparisons. The reduction potential of (**5**) is *ca.* 300 mV more cathodic than that of the related complex $[Mo(NO)L(NC_5H_5)_2]^+$ and presumably reflects the electron-releasing properties of the aminomethyl substituents present in the *ortho* positions of the two pyridine ligands. The reduction potentials of the 17-electron bis(pyridine) derivatives would thus appear to show a marked sensitivity to ring substituents as has already been noted in the case of 16-electron arylamide or phenoxide complexes.[17]

Structural Studies.—In order to establish unequivocally that chelation[18] was not occurring in the bis(2-aminopyridine) derivatives, *X*-ray diffraction studies of (**4**) and (**7**) were undertaken. This work also provided the first structural

Table 2. Fractional atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$[Mo(NO)\{HB(3,5-Me_2C_3N_2H)_3\}(2-NHC_5NH_4)_2]$							
Mo	7 588(1)	−917(1)	7 375(1)	C(15)	9 445(4)	−2 557(4)	3 757(3)
N(1)	8 118(2)	392(2)	7 595(2)	N(8)	7 087(3)	−1 458(2)	8 820(2)
O	8 522(3)	1 266(2)	7 777(2)	C(16)	6 974(3)	−973(3)	9 726(2)
N(2)	6 959(2)	−2 620(2)	7 071(2)	C(17)	6 717(4)	207(3)	9 698(3)
N(3)	7 716(2)	−3 354(2)	6 587(2)	C(18)	6 643(4)	658(4)	10 620(3)
C(2)	5 938(3)	−3 133(3)	7 264(3)	C(19)	6 793(4)	−81(4)	11 542(3)
C(3)	6 026(3)	−4 192(3)	6 910(3)	C(20)	6 997(4)	−1 239(4)	11 517(3)
C(4)	7 151(3)	−4 313(3)	6 486(3)	N(9)	7 084(3)	−1 706(3)	10 633(2)
C(1)	4 874(3)	−2 607(3)	7 783(4)	N(10)	6 057(2)	−213(2)	6 680(2)
C(5)	7 724(4)	−5 290(3)	5 991(4)	C(21)	5 466(3)	885(3)	6 523(2)
N(4)	9 337(2)	−1 920(2)	7 686(2)	C(22)	4 593(3)	1 135(3)	5 796(3)
N(5)	9 713(2)	−2 772(2)	7 112(2)	C(23)	4 023(4)	2 230(4)	5 633(3)
C(7)	10 182(3)	−1 911(3)	8 407(3)	C(24)	4 338(4)	3 053(3)	6 189(4)
C(8)	11 095(3)	−2 758(3)	8 300(3)	C(25)	5 201(4)	2 749(3)	6 928(4)
C(9)	10 776(3)	−3 278(3)	7 475(3)	N(11)	5 791(3)	1 675(3)	7 110(3)
C(6)	10 086(4)	−1 113(4)	9 202(3)	B	8 952(3)	−2 990(3)	6 192(3)
C(10)	11 431(4)	−4 255(4)	7 033(4)	N(12) *	6 240(4)	5 831(3)	10 536(4)
N(6)	8 368(2)	−839(2)	5 756(2)	C(26) *	6 966(4)	5 188(3)	9 935(4)
N(7)	8 782(2)	−1 847(2)	5 412(2)	C(27) *	8 137(4)	5 469(4)	9 681(4)
C(12)	8 377(3)	8(3)	4 922(3)	C(28) *	8 834(5)	4 792(4)	9 111(4)
C(13)	8 783(3)	−455(4)	4 051(3)	C(29) *	8 387(5)	3 827(4)	8 808(4)
C(14)	9 025(3)	−1 628(3)	4 381(3)	C(30) *	7 231(5)	3 612(4)	9 088(3)
C(11)	7 962(4)	1 243(3)	4 979(3)	N(13) *	6 513(3)	4 272(3)	9 629(3)
$[W(NO)\{HB(3,5-Me_2C_3N_2H)_3\}(2-NHC_5NH_4)_2]$							
W	2 505(1)	4 242(1)	1 526(1)	C(12)	1 624(8)	3 048(7)	1 700(11)
N(1)	1 798(6)	4 315(6)	363(9)	C(13)	1 757(10)	2 414(9)	2 179(12)
O(1)	1 290(6)	4 347(7)	−449(8)	C(14)	2 402(8)	2 265(8)	2 620(11)
N(2)	3 410(6)	4 151(6)	3 026(9)	C(15)	2 747(11)	1 679(9)	3 169(16)
N(3)	3 699(7)	3 526(7)	3 356(10)	N(8)	3 017(7)	4 967(7)	1 403(9)
C(1)	3 651(9)	5 316(9)	3 683(13)	C(16)	2 935(11)	5 525(9)	790(14)
C(2)	3 772(8)	4 587(8)	3 740(12)	C(17)	2 378(11)	5 624(8)	−102(14)
C(3)	4 302(9)	4 239(10)	4 536(13)	C(18)	2 289(13)	6 167(10)	−663(14)
C(4)	4 242(9)	3 578(10)	4 255(14)	C(19)	2 846(17)	6 572(13)	−308(19)
C(5)	4 679(12)	2 995(11)	4 886(18)	C(20)	3 424(16)	6 437(13)	598(21)
N(4)	2 979(6)	3 480(6)	1 104(9)	N(9)	3 463(9)	5 940(9)	1 158(13)
N(5)	3 370(6)	2 993(7)	1 765(11)	N(10)	2 129(6)	4 712(6)	2 208(9)
C(6)	2 633(11)	3 814(12)	−547(15)	C(21)	1 545(8)	5 034(7)	1 899(11)
C(7)	2 982(9)	3 412(9)	305(14)	C(22)	1 170(8)	5 345(8)	993(11)
C(8)	3 384(10)	2 869(12)	414(17)	C(23)	576(10)	5 621(9)	791(15)
C(9)	3 608(9)	2 594(11)	1 314(18)	C(24)	349(9)	5 579(10)	1 362(16)
C(10)	4 019(11)	1 998(12)	1 789(20)	C(25)	749(9)	5 307(12)	2 239(16)
N(6)	2 206(6)	3 274(6)	1 869(9)	N(11)	1 347(7)	4 996(8)	2 546(9)
N(7)	2 679(6)	2 798(6)	2 449(9)	B	3 385(10)	2 894(10)	2 688(15)
C(11)	1 013(8)	3 413(9)	1 103(14)				

* Atom of the 2-aminopyridine molecule.

Table 3. Selected bond lengths (Å) and angles (°) for [$M(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2$] (M = Mo or W)

	M = Mo	M = W		M = Mo	M = W
M-N(1)	1.751(3)	1.746(12)	M-N(8)	1.987(3)	1.968(13)
M-N(2)	2.242(3)	2.243(13)	M-N(10)	1.990(3)	2.001(11)
M-N(4)	2.210(3)	2.210(12)	N(1)-O(1)	1.203(4)	1.230(16)
M-N(6)	2.231(3)	2.216(11)			
N(1)-M-N(2)	178.4(1)	179.6(4)	N(4)-M-N(6)	78.4(1)	77.6(5)
N(1)-M-N(4)	94.0(1)	94.4(5)	N(4)-M-N(8)	89.3(1)	90.2(5)
N(1)-M-N(6)	95.6(1)	94.8(5)	N(4)-M-N(10)	163.3(1)	162.4(5)
N(1)-M-N(8)	96.1(1)	97.5(5)	N(6)-M-N(8)	163.5(1)	163.4(5)
N(1)-M-N(10)	96.1(1)	95.5(5)	N(6)-M-N(10)	87.4(1)	87.3(4)
N(2)-M-N(4)	84.4(1)	85.5(5)	N(8)-M-N(10)	102.8(1)	102.6(5)
N(2)-M-N(6)	84.3(1)	85.1(4)	M-N(1)-O	177.4(2)	177.7(11)
N(2)-M-N(8)	83.7(1)	82.7(5)	M-N(8)-C(16)	135.5(2)	140.6(13)
N(2)-M-N(10)	85.5(1)	84.1(5)	M-N(10)-C(21)	135.4(2)	134.0(10)

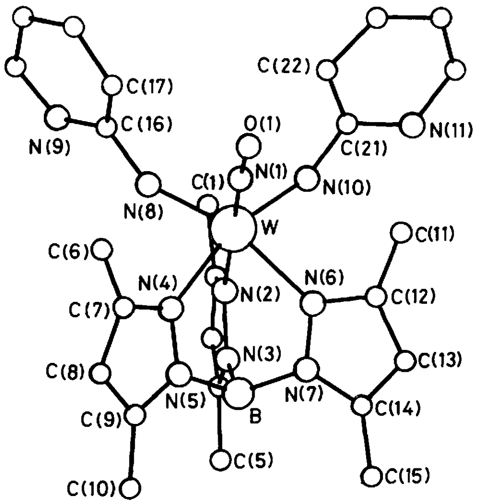
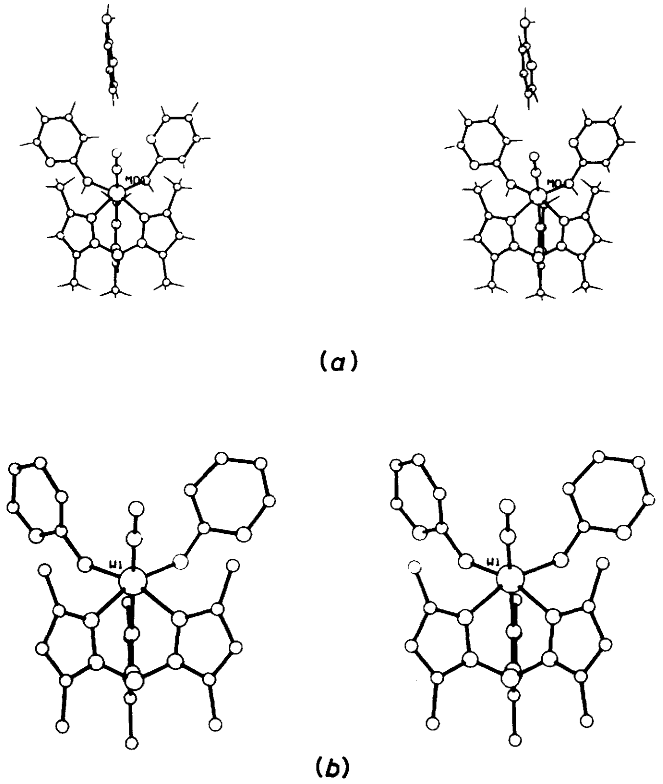


Figure 1. The structure of the tungsten complex, showing the atom numbering. The same numbering scheme is used for the molybdenum complex



(a)

(b)

Figure 2. Stereoscopic views of (a) the molybdenum and (b) the tungsten complex

characterisations of bis(arylamide) derivatives containing the $\{M(NO)L\}^{2+}$ (M = Mo or W) core.* The molybdenum complex (4) crystallised with an equimolar proportion of 2-$NH_2C_5NH_4$ in the lattice, but this did not occur in the case of its tungsten analogue (7). Both complexes contained metal ions in an approximately octahedral co-ordination environment and carrying linear nitrosyl ligands. In neither case was any interaction between the metal and a pyridine nitrogen atom apparent, the closest contact distance being Mo ••• N 3.474(3) Å. The other pyridine ring in the molybdenum complex, and both pyridine rings in the tungsten complex, are oriented so that the closest contact involves a carbon atom, M ••• C 3.58—3.70 Å. These relatively large distances are a consequence of the large bond angle at the amido nitrogen atoms (see later) rather than the orientation of the pyridine rings.

Atomic co-ordinates for both structures are listed in Table 2 and selected bond lengths and angles in Table 3. The structures of the complexes are illustrated in Figures 1 and 2.

The co-ordination geometries in the two complexes are similar, corresponding angles differing by an average of only 0.8°, with a maximum difference of 1.4°. The maximum metal–ligand bond-length difference is 0.03 Å. The maximum angular distortion from an ideal octahedron is 16.7 (Mo complex) and 17.6° (W complex); mean distortions are 7.1 and 7.2° respectively. Comparison with the corresponding bis(butylamido) complex[15] shows that its co-ordination geometry is very similar, the maximum difference in the ligand–Mo–ligand angles being 2.2°. The bonds to the pyrazolyl rings (2.21—2.24 Å) are within the range previously found for this type of bond in molybdenum complexes. As has been generally found previously, the bond *trans* to the nitrosyl group is the longest of these. This has been attributed[8] to the *trans* effect of the strongly π-accepting nitrosyl group.

The geometry of the M–N(pyridine-2-amido) linkage is also similar to that found previously.[8,9,15] The shortness of the metal–ligand bonds (1.97—2.00 Å) and the large M–N–C angles (135—141°) are consistent with $p_\pi \rightarrow d_\pi$ donation from the ligands. Compared with the bis(butylamido) complex,

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

Table 4. Deviations (Å) of atoms from the planes of the heterocyclic rings

Plane	$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$ E.s.d.s are *ca.* 0.003 Å for Mo and 0.01 Å for the lighter atoms	$[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$ E.s.d.s are *ca.* 0.003 Å for W and 0.02 Å for the lighter atoms
(1): N(2), N(3), C(2)—C(4)	Atoms defining plane <0.001; Mo -0.021, C(1) -0.01, C(5) 0.00, B -0.09	Atoms defining plane $\leqslant 0.01$; W -0.037, C(1) -0.06, C(5) 0.06, B 0.03
(2): N(4), N(5), C(7)—C(9)	Atoms defining plane <0.004; Mo 0.070, C(6) 0.02, C(10) 0.02, B -0.03	Atoms defining plane $\leqslant 0.02$; W 0.065, C(6) -0.04, C(10) -0.08, B -0.17
(3): N(6), N(7), C(12)—C(14)	Atoms defining plane $\leqslant 0.01$; Mo -0.337, C(11) -0.03, C(15) -0.06, B 0.08	Atoms defining plane $\leqslant 0.01$; W 0.146, C(11) -0.04, C(15) -0.03, B -0.11
(4): N(9), C(16)—C(20)	Atoms defining plane $\leqslant 0.02$; N(8) -0.04	Atoms defining plane $\leqslant 0.04$; N(8) -0.02
(5): N(11), C(21)—C(25)	Atoms defining plane $\leqslant 0.01$; N(10) -0.03	Atoms defining plane $\leqslant 0.03$; N(10) -0.08

however, the M–N distances and the N(amido) angles are greater by an average of 0.05 Å and 6°, respectively. These differences may be a manifestation of additional electron delocalisation involving the aromatic rings in the complexes **(4)** and **(7)**, which compete with the nitrogen to metal $p_\pi \longrightarrow d_\pi$ donation. In both structures the pyridine rings are fairly close to coplanarity with their respective M–N–C planes [maximum deviation 29(1)°] consistent with this model.[9]

Steric effects may however also play a role in increasing the M–N–C angle, in order to relieve potentially close contacts between the nitrosyl nitrogen atom [N(1)] and C(16) and C(21); the actual distances are 3.259(4) and 3.258(4) Å in the complex of Mo, and 3.41(2) and 3.21(2) Å in that of W, somewhat longer than the corresponding distances in the bis(butylamido)molybdenum complex (3.10 and 3.09 Å). The corresponding N(1)–M–N–C torsion angles are small (5—14°), again similar to previously found[8,9,15] values.

The pyrazolyl rings are planar to within the limits of experimental error (Table 4); the methyl groups lie close to their respective ring planes (maximum deviation 0.08 Å). The metal and boron atoms deviate by greater amounts, up to 0.34 and 0.17 Å, respectively. The pattern of interplanar angles previously noted[9,15] (105—119° between pyrazolyl rings encompassing the relatively small nitrosyl ligand, 124—129° between pyrazolyl rings involved in steric interactions with adjacent bulky ligands) is observed in the tungsten complex but not in the molybdenum complex.

Conclusions

These studies have produced no evidence for the formation of chelate complexes of the $\{Mo(NO)L\}^{2+}$ moiety with the 2-$NHC_5NH_4^-$ ligand. Both steric and electronic reasons may be advanced to account for this finding. The methyl substituents on L sterically preclude chelation in a manner which would lead to a geometry approaching the normal 'piano stool' arrangement found in related seven-co-ordinate molybdenum complexes[1] such as $[Mo(NO)(NC_5H_5)(\eta^5\text{-}C_5H_5)Cl_2]$. Instead the chelating ligand would be obliged to adopt an unusual position between the pyrazolyl groups of L to give a near face-capped octahedral geometry about the molybdenum atom. Such a structure may be energetically less favourable than the normal piano stool arrangement and calculations indicate[19] that this is so in the case of compounds such as $[Mo(CO)_3(CH_3)(\eta^5\text{-}C_5H_5)]$. Furthermore, although the complexes described here are formally 16-electron systems, this electron deficiency is alleviated by amide nitrogen to molybdenum $p_\pi \longrightarrow d_\pi$ donation. This effect is manifest in the change in ν_{NO} from 1 700 to 1 660, then 1 640 cm^{-1} in going from **(1)** to **(3)** then **(4)**. A good example of such stabilisation of a formally electron-deficient molybdenum centre is provided by $[Mo(NO)(\eta^5\text{-}C_5H_5)(SPh)_2]$.[20] In this molecule there is no steric blocking which would preclude dimerisation or binding of a Lewis base to produce a seven-co-ordinate 18-electron complex. However, it is the 16-electron monomer which is isolated as a stable compound in which sulphur to molybdenum $p_\pi \longrightarrow d_\pi$ charge donation may be invoked to account for its structural properties. Such considerations suggest that if 2-aminopyridine had been found to chelate this would have been the more surprising result of our studies.

Although definitive comments on complex stability cannot be made solely on the basis of the products isolated from reaction mixtures, some qualitative observations can be made on the basis of the results described here. In the complexes involving the $\{Mo(NO)L\}^{2+}$ moiety it would appear that bis(arylamide) formation is preferred over reduction and co-ordination to two pyridine ligands. This, in turn, would appear to be favoured over formation of a bis(alkylamide) derivative. In the case of complexes containing the $\{W(NO)L\}^{2+}$ moiety it seems that the formation of bis(alkyl- or aryl-amide) derivatives is favoured over reduction and co-ordination to pyridine. This may merely reflect the absence of a sufficiently powerful reducing agent in the reaction medium, but comparisons with molybdenum chemistry and electrochemistry[12] suggest that facile reduction in the presence of pyridine ligands should be possible. Consequently we feel that these results demonstrate a genuine preference for amide co-ordination by the $\{W(NO)L\}^{2+}$ moiety.

Experimental

The complexes $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ **(1)** and $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ **(2)** were prepared by previously described methods.[21,22] Other reagents were used as supplied and reaction solvents were redistilled from drying agents according to standard methods prior to use. All reactions were performed under an atmosphere of dry nitrogen but the reaction products were air stable. Infrared, electronic, mass, and 100-MHz ^1H n.m.r. spectra were recorded on PE 197, PEM 330, Kratos MS 80, and PE R34 instruments respectively. Electrochemical measurements were made using a Hitek galvanostat/potentiostat and waveform generator with a platinum-bead working electrode and saturated calomel reference electrode. Elemental analyses were performed by the Microanalytical Laboratory, University of Birmingham.

Syntheses.—$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I(2\text{-}NHC_5NH_4)]$, **(3)**. A solution of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ (1.0 g, 1.5 mmol) and 2-aminopyridine (0.15 g, 1.9 mmol) in dichloromethane (100 cm^3) was stirred at room temperature for 2 d in the presence of NaH (0.10 g, 4 mmol). The mixture was then filtered and the solvent removed *in vacuo*. The product thus obtained was purified by column chromatography on silica gel using CH_2Cl_2 as eluant. The main dark brown band which developed was collected. Further purification was effected by recrystallisation from CH_2Cl_2–hexane (yield 0.6 g, 63%)

(Found: C, 37.5; H, 4.4; N, 19.4. $C_{20}H_{27}BIMoN_9O$ requires C, 37.4; H, 4.2; N, 19.6%). $\delta_H(CDCl_3)$: 12.63 (1 H, s, $N\mathit{H}C_5NH_4$), 8.20, 7.70, 7.10 (2 H, t; 1 H, t; 1 H, t, $NHC_5N\mathit{H}_4$), 5.80, 5.76, 5.66 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N\mathit{H})_3$], 2.60, 2.40, 2.30, and 1.86 [3 H, s; 6 H, s; 6 H, s; 3 H, s, $(\mathit{Me}_2C_3NH)_3$].

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]\cdot 2\text{-}NH_2\text{-}C_5NH_4$, (**4**). A solution of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ (0.8 g, 1.2 mmol) and 2-aminopyridine (0.3 g, 3.8 mmol) in tetrahydrofuran (thf) (100 cm^3) was refluxed overnight (20 h) to give a red solution. The solvent was then removed *in vacuo* to give a crude product which was redissolved in CH_2Cl_2, the solution filtered, and hexane added to induce crystallisation of the purple product (yield 0.54 g, 65%). Further purification could be effected by column chromatography on silica gel using thf as eluant, followed by recrystallisation from CH_2Cl_2–hexane (Found: C, 51.4; H, 4.3; N, 25.2. $C_{30}H_{38}BMoN_{13}$ requires C, 51.3; H, 5.4; N, 25.9%). $\delta_H(CDCl_3)$: 9.30 [2 H, s, $(N\mathit{H}C_5NH_4)_2$], 8.1—7.3, 6.8—6.4 [8 H, m; 4 H, m, $(NHC_5N\mathit{H}_4)_2$ and $NH_2C_5N\mathit{H}_4$], 5.84, 5.70 [1 H, s; 2 H, s, $(Me_2C_3N_2\mathit{H})_3$], 2.42, 2.34, and 2.16 [3 H, s; 9 H, s; 6 H, s, $(\mathit{Me}_2C_3N_2H)_3$].

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NC_5H_4CH_2NH_2)_2]I$, (**5**). A solution of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2]$ (1.0 g, 1.5 mmol) and 2-aminomethylpyridine (1 cm^3, 9.3 mmol) in thf (60 cm^3) was refluxed for 4 h during which time a green precipitate formed. This was collected by filtration and recrystallised from CH_2Cl_2–hexane to give a green powder (yield 0.63 g, 62%) (Found: C, 41.9; H, 5.8; N, 18.5. $C_{27}H_{38}BIMoN_{11}O$ requires C, 42.3; H, 5.0; N, 20.1%). Molar conductivity (MeCN): 120 S cm^{-2} mol^{-1}.

$[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl(2\text{-}NHC_5NH_4)]$, (**6**). This complex was prepared in a similar manner to its molybdenum analogue using $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ (1.0 g, 1.7 mmol) and 2-aminopyridine (0.16 g, 2 mmol). A brown microcrystalline product was obtained (yield 0.54 g, 49%) (Found: C, 37.5; H, 4.1; N, 19.7. $C_{20}H_{27}BClN_9OW$ requires C, 37.5; H, 4.4; N, 19.7%). $\delta_H(CDCl_3)$: 10.82 (1 H, s, $N\mathit{H}C_5NH_4$), 8.3—8.0, 7.9—7.6, 7.1—6.8 (2 H, t; 1 H, t; 1 H, t, $NHC_5N\mathit{H}_4$), 5.90, 5.81 [2 H, s; 1 H, s, $(Me_2C_3N_2\mathit{H})_3$], 2.70, 2.44, 2.40, 2.35, and 2.08 [3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, $(\mathit{Me}_2C_3N_2H)_3$].

$[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHC_5NH_4)_2]$,(**7**). A solution of $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ (0.8 g, 1.4 mmol) and 2-aminopyridine (0.28 g, 3.5 mmol) in thf (10 cm^3) was refluxed for 3 d in the presence of NaH (0.1 g, 4 mmol). The solution was then filtered and the solvent removed *in vacuo*. The product thus obtained was purified by column chromatography on silica gel using thf as eluant, the main red-orange fraction being collected. Further purification could be effected by recrystallisation from CH_2Cl_2–hexane to give an orange microcrystalline solid (yield 0.58 g, 61%) (Found: C, 43.6; H, 5.1; N, 20.5. $C_{25}H_{32}BN_{11}OW$ requires C, 43.1; H, 4.6; N, 21.1%). $\delta_H(CDCl_3)$: 8.40 [2 H, s, $(N\mathit{H}C_5NH_4)_2$], 8.1—8.0, 7.8—7.6, 6.8—6.6 [4 H, t; 2 H, t; 2 H, t, $(NHC_5N\mathit{H}_4)_2$], 5.94, 5.75 (1 H, s; 2 H, s, $(Me_2C_3N_2\mathit{H})_3$], 2.44, 2.33, and 2.66 [6 H, s; 6 H, s; 6 H, s, $(\mathit{Me}_2C_3N_2H)_3$].

$[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl(2\text{-}NHCH_2C_5NH_4)]$, (**8**). A solution of $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ (0.5 g, 0.9 mmol) and 2-aminomethylpyridine (0.2 cm^3, 1.9 mmol) in thf (60 cm^3) was refluxed overnight (20 h). The solution was then filtered and the solvent removed *in vacuo*. The resulting product was purified by recrystallisation from CH_2Cl_2–hexane to give a brown powder (yield 0.3 g, 68%) (Found: C, 39.2; H, 3.8; N, 18.8. $C_{21}H_{29}BClN_9OW$ requires C, 38.6; H, 4.4; N, 19.3%). $\delta_H(CDCl_3)$: 10.42 (1 H, s, $N\mathit{H}CH_2C_5NH_4$), 8.50, 7.8—7.5, 7.3—7.1 (1 H, d; 2 H, m; 1 H, m, $NHCH_2C_5N\mathit{H}_4$), 6.5—6.0 (2 H, m, $NHC\mathit{H}_2C_5NH_4$), 5.84 [3 H, s, $(Me_2C_3N_2\mathit{H})_3$], 2.66, 2.50, 2.38, 2.35, 2.32, and 2.26 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(\mathit{Me}_2C_3N_2H)_3$].

$[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(2\text{-}NHCH_2C_5NH_4)_2]$, (**9**). A solution of $[W(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ (0.5 g, 0.9 mmol) and 2-aminomethylpyridine (0.5 cm^3, 4.6 mmol) in toluene (60 cm^3) was refluxed overnight (20 h) in the presence of NaH (0.1 g, 4 mmol). The solution was then filtered and the solvent removed *in vacuo*. The crude product thus obtained was recrystallised from CH_2Cl_2–hexane to give a yellow microcrystalline solid (yield 0.31 g, 50%) (Found: C, 44.7; H, 4.7; N, 21.4. $C_{27}H_{36}BN_{11}OW$ requires C, 44.6; H, 5.0; N, 21.3%). $\delta_H(CDCl_3)$: 8.40, 7.6—7.0, 7.1—6.9 [2 H, d; 4 H, t; 2 H, t, $(NHCH_2C_5N\mathit{H}_4)_2$], 6.25 [2 H, s, $(N\mathit{H}CH_2C_5NH_4)_2$], 5.70—5.10 [4 H, m, $(NHC\mathit{H}_2C_5NH_4)_2$], 5.80, 5.72 [1 H, s; 2 H, s, $(Me_2C_3N_2\mathit{H})_3$], 2.58, 2.35, 2.26, and 2.19 [6 H, s; 3 H, s; 6 H, s; 3 H, s, $(\mathit{Me}_2C_3N_2H)_3$].

Crystallographic Studies.—Crystal data for (**4**). $M = 703.5$, triclinic, space group $P\bar{1}$, $a = 11.166(12)$, $b = 11.668(5)$, $c = 12.947(9)$ Å, $\alpha = 80.92(6)$, $\beta = 89.33(7)$, $\gamma = 85.67(5)°$, $U = 1\,661$ Å^3, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 728$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $\mu = 0.427$ mm^{-1}.

A crystal (0.3 × 0.3 × 0.2 mm) was mounted on an Enraf–Nonius CAD-4 diffractometer; cell dimensions and intensities were measured by ω—2θ scans with graphite-monochromated Mo-K_α radiation. 6 113 Reflections were scanned within $2 < \theta < 25°$. Two standard reflections were measured every 2 h to monitor the stability of the system. Lorentz polarisation corrections were applied. 5 076 Structure amplitudes with $I > 2.50\sigma(I)$ were considered observed and used in the analysis.

The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atom. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.0005F^2]$ and the refinement converged to $R = 0.039$, $R' = 0.056$. The residual electron density in a final difference map was within the range 0.6 to -0.9 e Å^{-3}.

Crystal data for (**7**). $M = 697.3$, monoclinic, space group $C2/c$, $a = 24.135(12)$, $b = 19.720(10)$, $c = 16.310(7)$ Å, $\beta = 122.56(4)°$, $U = 6\,543$ Å^3, $Z = 8$, $D_c = 1.42$ g cm^{-3}, $F(000) = 2\,768$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $\mu = 3.769$ mm^{-1}.

Data collection and structure determination procedures were similar to those used for the molybdenum complex (see above). Crystal size was 0.2 × 0.2 × 0.15 mm. 8 792 Reflections were scanned, of which 3 533 [$I > 3.5\sigma(I)$] were used in the analysis. The weighting scheme used in the least-squares refinement was $w = 1/[\sigma^2(F) + 0.001\ F^2]$. Final $R = 0.055$, $R' = 0.079$.

The final difference map showed a few relatively large (up to 2.5 e Å^{-3}) maxima, remote from the metal complex. It was not possible to interpret these maxima in terms of a chemical entity, but they may indicate the presence of a disordered molecule of solvent of crystallisation. The maximum negative electron density was -0.75 e Å^{-3}.

Complex neutral-atom scattering factors were employed for both structures. Computations were carried out on the University of Birmingham Honeywell computer and on the CDC 7600 at the University of Manchester Regional Computer Centre with the SHELX[23] and PLUTO[24] programs.

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