In memory of S. M. Nelson and T. A. Stephenson

Monometallic, Homo- and Hetero-bimetallic Complexes based on Redox Active Tris(3,5-dimethylpyrazolyl)borato Molybdenum and Tungsten Nitrosyls. Part 6.† Synthesis and Electrochemistry of Complexes containing Saturated Heterocyclic Amide Ligands. *X*-Ray Crystal and Molecular Structure of $[\{Mo(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$‡

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The co-ordinatively unsaturated complexes $[M(NO)\{HB(Me_2pz)_3\}Cl(Y)]$ [M = Mo or W; Y = $NC_3H_6^-$, $NC_4H_8^-$, or $NC_5H_{10}^-$; $HB(Me_2pz)_3$ = hydrotris(3,5-dimethylpyrazolyl)borate] have been prepared and characterised. All exhibit reversible one-electron reduction processes in their cyclic voltammograms. The bimetallic species $[\{M(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$ (M = Mo or W) were also prepared, and the molybdenum complex structurally characterised by an *X*-ray diffraction study which revealed a chair conformation for the bridging piperazine-1,4-diyl ligand (NC_4H_8N). The molybdenum atoms are oriented essentially equatorially with Mo $\cdots$ Mo separation 6.773(2) Å. These bimetallic species appear to behave as 'strongly interacting' redox systems. In the case of M = Mo two one-electron reduction processes, separated by 560 mV, were observed by cyclic voltammetry.

The $[Mo(NO)]^{3+}$ and $[W(NO)]^{3+}$ moieties have been found to constitute versatile redox centres in complexes of the type $[M(NO)L(X)(ER)]$ [E = O, S, or NH; L = hydrotris(3,5-dimethylpyrazolyl)borate, $HB(Me_2pz)_3$; R = aryl; M = Mo and X = Cl or I, M = W and X = Cl].[1–4] Such complexes undergo one-electron reduction reactions at potentials which vary depending upon the nature of M, X, E, and R. Thus the complexes in which E = NH were found to reduce at potentials some 500 mV more cathodic than their counterparts in which E = O or S. Similarly the tungsten complexes were found to reduce at potentials some 450 mV more cathodic than their molybdenum analogues.[3] The reduction potentials have also been found to vary in a broadly linear manner with the Hammett σ parameter of substituents attached to the aryl ring, R, of the complexes in which E = O or NH.[4] The sensitivity of the $[M(NO)]^{3+}$ redox centres to the nature of the ligating group ER has also been exploited in the study of bimetallic complexes of the type $[\{Mo(NO)L(X)\}_2(Z)]$ in which Z is a bridging ligand such as *m*- and *p*-NHC_6H_4NH, *m*- and *p*-OC_6H_4O, $C_{10}H_6(NH)$-1,5, *p*-$NHC_6H_4CH_2C_6H_4NH$-*p* or $Fe(\eta^5\text{-}C_5H_4S)_2$.[5–8] The cyclic voltammograms of such compounds reveal two one-electron reduction processes at potentials whose separation depends upon the extent of interaction between the metal centres as transmitted across the bridging ligand Z. In cases where there is a strong interaction the reduction waves may be separated by several hundred mV; thus when X = Cl and Z = *p*-NHC_6H_4NH– the separation is 850 mV.[5] However, when the bridging ligand effectively insulates the two redox centres from one another much smaller separations are found, and in the example where X = Cl and Z = –$NHC_6H_4CH_2CH_2C_6H_4NH$– the separation was less than 50 mV.[6]

In order to make meaningful measurements on systems of this type it is necessary to use complexes whose electrochemical properties exhibit reversible behaviour. In the complexes in which X = I this may not be the case since a coupled chemical reaction involving I^- dissociation may occur.[9] On the cyclic voltammetry time-scale this effect appears most pronounced in complexes having more cathodic potentials, that is with the amide derivatives. This problem does not arise when X = Cl since the chloride ligand in the reduced complex is less labile. Unfortunately, the reversible behaviour exhibited by the chloro(arylamide) complexes is not found with chloro(alkylamide) complexes. This has precluded the extension of our studies to bimetallic complexes in which the bridging ligand Z is fully saturated. Other studies of 17-electron complexes containing the $[Mo(NO)L]^+$ moiety have shown that the presence of N–H protons in these systems leads to irreversible reduction behaviour.[10,11] A similar effect may be responsible for the irreversible reduction observed for the alkylamide derivatives and the use of secondary amide ligands might provide complexes exhibiting reversible reduction behaviour. Earlier studies,[12] which showed the dimethylamide complex $[Mo(NO)L(I)(NMe_2)]$ to be of limited stability, suggested that bridging ligands such as $MeNCH_2CH_2NMe$ might not offer stable bimetallic species. In an attempt to define dialkylamine ligands which might be more compatible with the sterically demanding ligand L, while affording derivatives which exhibit reversible reduction behaviour, we have investigated the formation of chloro-complexes containing saturated cyclic amide ligands.[13]

Results and Discussion

Synthetic Studies.—$[Mo(NO)LCl_2]$ reacted with an excess of the cyclic amines (HY) azetidine, pyrrolidine, or piperidine to produce the mono-amide derivatives $[Mo(NO)L(Cl)(Y)]$ (Y = $NC_3H_6^-$, $NC_4H_8^-$, or $NC_5H_{10}^-$) respectively. Despite the excess of amine used no evidence for the formation of bis-amido complexes was found. This is in accord with previous ob-

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† Part 5 is ref. 4.

‡ μ-Piperazine-1,4-diyl-bis{chloro(nitrosyl)[tris(3,5-dimethylpyrazolyl)borato]molybdenum}.

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

Table 1. Infrared and n.m.r. spectral data for $[\{M(NO)L(Cl)\}_z(Y)]$

Complex			ν_{NO}[a]/ cm^{-1}	Shift[b] (p.p.m.)	Area[c]	Assignment
M	Y	z				
Mo	NC_3H_6	1	1 655	5.90	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.81	1 (s)	
				5.78	1 (s)	
				5.87	1 (m)	$\mathrm{NC}H_2\mathrm{CH_2C}H_2$
				5.29	1 (m)	
				4.81	1 (m)	
				4.00	1 (m)	
				2.58	2 (m)	$\mathrm{NCH_2C}H_2\mathrm{CH_2}$
				2.62	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.47	3 (s)	
				2.42	3 (s)	
				2.38	6 (s)	
				2.31	3 (s)	
W	NC_3H_6	1	1 620	5.92	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.85	1 (s)	
				5.79	1 (s)	
				5.96	1 (m)	$\mathrm{NC}H_2\mathrm{CH_2C}H_2$
				5.44	1 (m)	
				4.80	1 (m)	
				4.00	1 (m)	
				2.50	2 (m)	$\mathrm{NCH_2C}H_2\mathrm{CH_2}$
				2.65	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.60	3 (s)	
				2.45	3 (s)	
				2.36	6 (s)	
				2.29	3 (s)	
Mo	NC_4H_8	1	1 630	5.86	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.75	1 (s)	
				5.74	1 (s)	
				5.60	1 (m)	$\mathrm{NC}H_2\mathrm{CH_2C}H_2\mathrm{C}H_2$
				4.78	1 (m)	
				4.34	1 (m)	
				3.24	1 (m)	
				2.66	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.39	6 (s)	
				2.32	3 (s)	
				2.24	3 (s)	
				2.16	3 (s)	
				1.96	2 (m)	$\mathrm{NCH_2C_2}H_4\mathrm{CH_2}$
				1.72	2 (m)	
W[d]	NC_4H_8	1	1 605	5.90	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.86	1 (s)	
				5.80	1 (s)	
				5.60	1 (m)	$\mathrm{NC}H_2\mathrm{CH_2CH_2C}H_2$
				4.95	1 (m)	
				4.20	1 (m)	
				3.30	1 (m)	
				2.68	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.38	6 (s)	
				2.32	9 (s)	
				1.85	2 (m)	$\mathrm{NCH_2C_2}H_4\mathrm{CH_2}$
				1.62	2 (m)	
Mo	NC_5H_{10}	1	1 640	5.87	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.80	1 (s)	
				5.77	1 (s)	
				4.99	2 (m)	$\mathrm{NC}H_2\mathrm{C_3H_6C}H_2$
				4.05	1 (m)	
				3.45	1 (m)	
				2.65	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.43	3 (s)	
				2.40	3 (s)	
				2.39	3 (s)	
				2.35	3 (s)	
				2.28	3 (s)	
				1.92	2 (m)	$\mathrm{NCH_2C_3}H_6\mathrm{CH_2}$
				1.80	1 (m)	
				1.60	3 (m)	
				1.30	1 (m)	
W	NC_5H_{10}	1	1 610	5.90	1 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.86	1 (s)	
				5.78	1 (s)	
				5.03	2 (m)	$\mathrm{NC}H_2\mathrm{C_3}H_6\mathrm{C}H_2$
				3.87	1 (m)	
				3.38	1 (m)	
				2.68	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.50	3 (s)	
				2.47	3 (s)	
				2.39	6 (s)	
				2.28	3 (s)	
				1.88	1 (m)	$\mathrm{NCH_2C_3}H_6\mathrm{CH_2}$
				1.68	2 (m)	
				1.55	1 (m)	
				1.22	1 (m)	
Mo	NC_4H_8N	2	1 650	5.90	2 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.88	2 (s)	
				5.78	2 (s)	
				5.03	2 (m)	$\mathrm{NC_4}H_8\mathrm{N}$
				4.85	2 (m)	
				4.25	2 (m)	
				3.49	2 (m)	
				2.62	6 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.48	6 (s)	
				2.43	12 (s)	
				2.30	12 (s)	
W	NC_4H_8N	2	1 620	5.92	2 (s)	$(\mathrm{Me_2C_3N_2}H)_3$
				5.90	2 (s)	
				5.77	2 (s)	
				5.05	2 (m)	$\mathrm{NC_4}H_8\mathrm{N}$
				4.69	2 (m)	
				3.99	2 (m)	
				3.37	2 (m)	
				2.62	3 (s)	$(Me_2\mathrm{C_3N_2H})_3$
				2.50	3 (s)	
				2.43	12 (s)	
				2.41	12 (s)	
				2.29	6 (s)	

[a] KBr disc. [b] Measured at 400 MHz in $CDCl_3$ solution unless otherwise indicated. Shifts quoted to the nearest 0.01 p.p.m. [c] Multiplicity given in parentheses by s = singlet and m = multiplet. [d] Measured at 100 MHz.

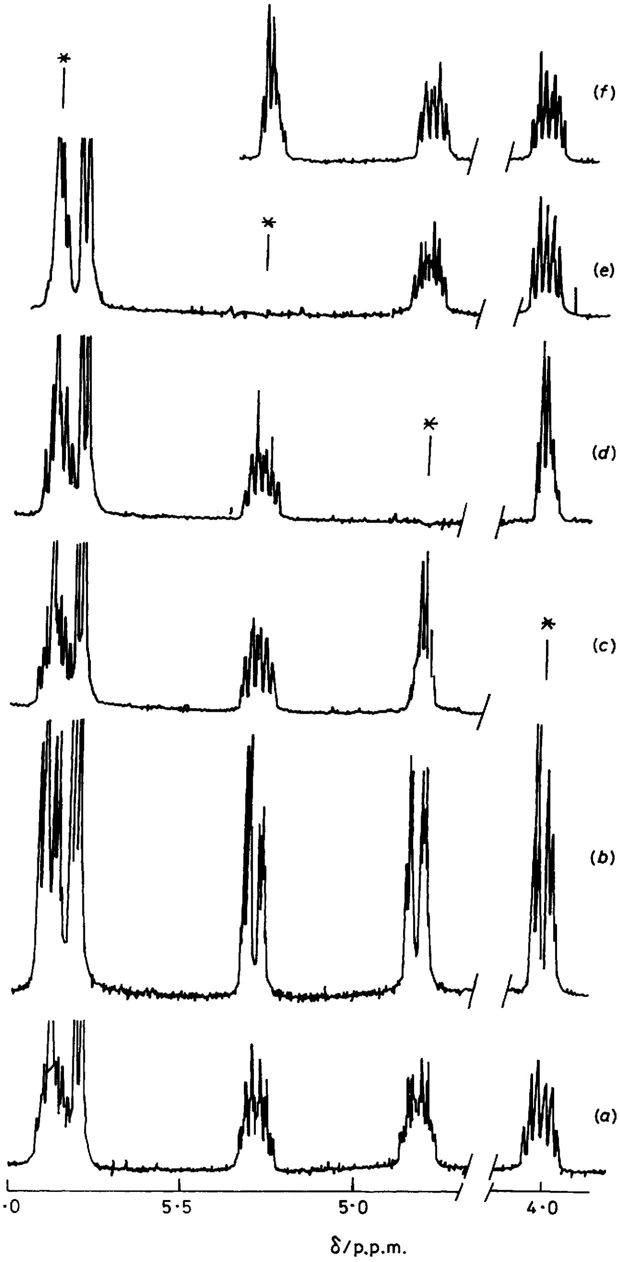

Figure 1. A part of the 400-MHz ^1H n.m.r. spectrum of $[Mo(NO)L(Cl)(NC_3H_6)]$ showing the α-methylene proton signals of the NC_3H_6 ligand and the results of proton double-resonance experiments labelled as follows. (*a*) The normal spectrum. (*b*) The spectrum recorded while irradiating at the frequency of the β-methylene protons. (*c*)—(*f*) Spectra recorded while irradiating at the frequencies of individual α-methylene protons at the positions indicated by *

servations made with primary amines, in that bis-substitution of the halide ligand in $[Mo(NO)LI_2]$ could only be achieved in two reaction steps. In the reactions described here are least a 2:1 molar ratio of amine to $[Mo(NO)LCl_2]$ was used so that the HCl liberated would be absorbed in the form of $[H_2Y]Cl$. However, in preparing the bimetallic derivative a two-fold excess of $[Mo(NO)LCl_2]$ was used and NaH added to promote complete reaction and suppress the formation of $[Mo(NO)L(Cl)(NC_4H_8NH_2)]^+$. The tungsten-containing precursor $[W(NO)LCl_2]$ was found to be less reactive than its molybdenum counterpart and NaH was added to all the preparations involving tungsten to promote reaction. All of the new complexes could be purified by column chromatography.

Spectral Studies.—All the new complexes exhibited ν_{BH} at *ca.* 2 550 cm^{-1} in their i.r. spectra, along with other bands attributable to the presence of the ligand L. The nitrosyl stretching frequencies of the molybdenum complexes (Table 1) were in the range 1 630—1 655 cm^{-1} as expected for mono-amide derivatives. The values for their tungsten counterparts were *ca.* 30 cm^{-1} lower, as has been noted previously.[1] All of the monometallic complexes exhibited molecular ions at the appropriate *m*/*z* value in their mass spectra in addition to peaks corresponding to $[M - NO]^+$ and $[M - (NO + \text{cyclic amide})]^+$.

The 400-MHz ^1H n.m.r. spectra of the new compounds were in accord with their formulation as mono-amide derivatives and exhibited three groups of signals. First, those due to the pyrazolyl H^4 protons generally appeared as three resonances of area ratio 1:1:1 in the region δ 5.7—6.0 p.p.m. Secondly, the pyrazolyl methyl protons appeared as five or six signals in the region δ 2.1—3.2 p.p.m. Finally, the signals attributable to the cyclic amide ligand protons appeared as complex multiplets in the range δ 1.2—6 p.p.m. and were the most notable feature of these spectra. It has been reported previously that the α-methylene protons in alkylamide or alkoxide derivatives of this type appear as AB pairs shifted to low field by the proximity of the electron-deficient metal centre.[1] In the case of these heterocyclic amide complexes there are two α-methylene groups attached to the amide nitrogen and all four protons on these groups are in different environments close to the chiral metal centre. The signals attributable to these protons appear as complex multiplets consisting of up to 20 lines. It would thus appear that each proton is coupled, not only to its complementary proton in the AB pair and to the β-methylene protons, but also to the other α-methylene protons across the amide nitrogen. The simplest examples are provided by $[M(NO)L(Cl)(NC_3H_6)]$ (M = Mo or W), and in the case of the molybdenum complex the signals attributable to the α-methylene protons appear as resonances of area 1 at δ 5.87, 5.29, 4.81, and 4.00 p.p.m. while the two β-methylene protons appear at δ 2.58 p.p.m. (Figure 1). Irradiation of the β-methylene proton resonance in this complex leads to the simplification of the α-methylene signals into doublets of multiplets from which J_{AB} may be estimated at 16 MHz. Additional couplings of *ca.* 2 and *ca.* 4 Hz could also be resolved in these decoupled signals and may be attributed to the effects of the complementary sets of α-methylene protons. Irradiation of the proton resonating at δ 4.00 p.p.m. resulted in the simplification of the other three α-methylene proton resonances. In particular the resonance at δ 4.81 p.p.m. was significantly narrowed by the loss of J_{AB} at 16 Hz indicating that the protons resonating at δ 4.00 and 4.81 are associated with the same methylene group. The other two resonances in the set showed some loss of fine structure but the larger couplings were still present. Irradiation of the proton resonating at δ 4.81 p.p.m. similarly led to a significant narrowing of the signal at δ 4.00 p.p.m. and a loss of some fine structure from the signals at δ 5.29 and 5.87 p.p.m. In accord with these observations irradiation of the proton resonating at δ 5.29 p.p.m. caused a narrowing of the signal at δ 5.87 p.p.m. and a loss of some fine structure from the signals at δ 4.00 and 4.81 p.p.m. Conversely irradiation of the proton resonating at δ 5.87 p.p.m. caused a narrowing of the signal at δ 5.29 p.p.m. and again some loss of fine structure from the δ 4.81 and 4.00 p.p.m. signals. Decoupling experiments on the related tungsten complex produced an entirely similar pattern of results establishing that the resonances at δ 4.00 and 4.80 p.p.m. were associated with the protons of one α-methylene group and the signals at δ 5.44 and 5.96 p.p.m. with the other.

Similar decoupling experiments were carried out on [Mo(NO)L(NC_4H_8)] and [Mo(NO)L(NC_5H_{10})] and broadly similar results obtained, although the presence of two sets of β-methylene protons resulted in only one set of α-methylene proton signals being simplified by irradiation of a particular set of β-methylene protons.

The 400-MHz ^1H n.m.r. spectrum of [{Mo(NO)L(Cl)}$_2$(NC_4H_8N)] exhibited four resonances of area 2 at δ 5.03, 4.85, 4.25, and 3.49 p.p.m. attributable to four pairs of equivalent protons on the piperazine-1,4-diyl bridging ligand. The signals at δ 5.03 and 3.49 p.p.m. appeared as broadened triplets with $J_{HH} \approx 8$ Hz, while those at δ 4.85 and 4.25 p.p.m. appeared as doublets of triplets with $J_{HH} = 12$ and 4 Hz. These signals may be assigned to symmetry related pairs of axial and equatorial protons in accord with the chair conformation of the piperazine-1,4-diyl ligand carrying two chiral molybdenum based substituents as found in the *X*-ray diffraction study described below. The resonances at δ 5.03 and 3.49 p.p.m. may be associated with the axial protons and those at δ 4.85 and 4.25 p.p.m. with the equatorial protons of the six-membered ring. Similar spectral data were obtained from the related bimetallic tungsten complex.

Electrochemical Studies.—The electrochemical properties of the new complexes were investigated by cyclic voltammetry and the results are summarised in Table 2. In accord with earlier findings for this type of compound, all the complexes exhibited only poorly defined irreversible oxidation processes at potentials more anodic than +0.5 V. The monometallic complexes exhibited a one-electron reversible or quasireversible * reduction process at potentials more cathodic than −1.0 V. In the case of the molybdenum complexes this occurred in the range −1.3 to −1.5 V. These values are significantly more cathodic than those found for arylamide complexes of the type [Mo(NO)L(Cl)(NHR)] (R = aryl), in accord with the more basic nature of the alkylamide ligand as compared to arylamide. Unlike the primary alkylamide derivatives [Mo(NO)L(NHR′)] (R′ = alkyl), which reduced irreversibly, exhibiting no peak on the anodic scan of their cyclic voltammograms, these secondary amide complexes exhibited reversible reduction behaviour. It is thus tempting to implicate the amide proton as the cause of the irreversible reduction of the primary alkylamide derivatives. Similar observations have been made with related formally 17-electron complexes in that the protonated complex [Mo(NO)L(im)$_2$]$^+$ (im = imidazole) underwent an irreversible reduction process while the compounds which did not carry an exchangeable proton, [Mo(NO)L(mim)$_2$]$^+$ (mim = *N*-methylimidazole) and [Mo(NO)L(py)$_2$]$^+$ (py = pyridine), reduced reversibly. We have no direct evidence of the role of the proton in these reduction reactions but its loss as H$^\bullet$ from the reduced species could account for the irreversible nature of the reduction. In the case of arylamide derivatives such as [Mo(NO)L(Cl)(NHPh)], which reduce at more anodic potentials than their alkylamide counterparts, reversible reduction behaviour is observed.[4] However, when an acidic proton is present these too may undergo irreversible reduction. Thus the thiol substituted complex [Mo(NO)L(Cl)(NHC_6H_4SH-*p*)] was found to undergo irreversible reduction whereas [Mo(NO)L(Cl)(NHC_6H_4SMe-*p*)] reduced reversibly.

The monometallic tungsten complexes reduced at potentials some 350 mV more cathodic than their molybdenum counterparts. This figure may be compared with an average 450 mV difference in the case of related molybdenum and tungsten arylamide complexes.[3]

Table 2. Electrochemical data for [{M(NO)L(Cl)}$_z$(Y)]

Complex						
M	Y	z	$E_{\frac{1}{2}}{}^a$/V	$\Delta E_p{}^b$/mV	n^c	Solvent
Mo	NC_3H_6	1	−1.44	80	1.17	MeCN
Mo	NC_4H_8	1	−1.38	80	1.09	MeCN
Mo	NC_5H_{10}	1	−1.33	60	1.10	MeCN
Mo	NC_4H_8N	2	−1.10	110	1.12	CH_2Cl_2
			−1.66^d	—	1.10	CH_2Cl_2
W	NC_3H_6	1	−1.78	120	1.26	MeCN
W	NC_4H_8	1	−1.72	110	0.95	thf
W	NC_5H_{10}	1	−1.71	60	1.07	MeCN
W	NC_4H_8N	2	−1.59	100	0.91	CH_2Cl_2

[a] Obtained from cyclic voltammetry studies in the specified solvent containing 0.2 mol dm^{-3} [NBu$^n{}_4$]BF$_4$ as supporting electrolyte. Solutions were *ca.* 2 × 10^{-3} mol dm^{-3} in complex and measurements were made at 21 ± 1 °C at 0.3 V s^{-1} scan rate using a Pt-bead working electrode and saturated calomel reference electrode. [b] Separation between anodic and cathodic peak potentials, typical values for ferrocene under similar conditions being 60—100 mV in MeCN and 100—200 mV in thf or CH_2Cl_2. No compensation for internal cell resistance was made but linear plots of $i_p{}^c v^{-\frac{1}{2}}$ against v, where $i_p{}^c$ is the cathodic peak current and v the scan rate, could be obtained. [c] Calculated on the basis of the current function for [Mo(NO)LCl$_2$] in the same cell and confirmed by coulometry in the cases of M = W, z = 1, Y = NC_3H_6; M = Mo, z = 2, Y = NC_4H_8N; or M = Mo, z = 1, Y = NC_5H_{10}. [d] Cathodic peak potential for an irreversible process.

A point of particular interest was the reduction behaviour of the bimetallic complexes and whether or not they would behave as complexes in which there were strong interactions between the redox active metal centres as manifest in their electrochemical properties. In both the molybdenum and tungsten complexes a one-electron reduction was observed at more anodic potentials than for their monometallic counterparts. In the case of molybdenum the anodic shift was 230 mV while in the case of tungsten it was reduced to 120 mV. This reduced effect of the 16-electron tungsten centre as compared to the molybdenum centre has been noted previously.[4,5] In the case of the bimetallic molybdenum complex a second one-electron reduction process was observed at a potential 560 mV more cathodic than the first. Unfortunately, this second process was irreversible so that the exact reduction potential remains in doubt. However, the 560 mV separation is consistent with the presence of strongly interacting metal centres. In the case of the bimetallic tungsten complex no second reduction process was resolved. This process might be expected to occur at *ca.* −1.9 to −2.0 V and interference from the solvent background at these cathodic potentials precluded meaningful observations in this region.

The one-electron nature of the first reduction process for the bimetallic molybdenum complex was confirmed by coulometry in dichloromethane solution at −1.39 V which indicated that 1.08 × 10^5 C were consumed per mole of complex. The blue solution produced by electrolysis exhibited an e.s.r. signal centred at g = 1.973 99 (±0.0003) which exhibited hyperfine coupling (⟨A⟩ = 4.89 mT) attributable to the presence of ^{95}Mo (15.9% abundance, $I = \frac{5}{2}$) and ^{97}Mo (9.6% abundance, $I = \frac{5}{2}$). No changes were apparent in this spectrum after a period of 24 h at room tempeature. The electronic spectrum of the solution exhibited $\lambda_{max.}$ at 803 nm. A blue compound could also be isolated from the reaction between [Co(η-C_5H_5)$_2$] and [{Mo(NO)L(Cl)}$_2$(NC_4H_8N)] in dry CH_2Cl_2 under N_2. This material exhibited $\lambda_{max.}$ at 806 nm and g = 1.973 06 (⟨A⟩ = 5.19 mT) in dichloromethane solution. The blue solid exhibited

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* This term is used here to describe a process in which well defined reduction and oxidation peaks are present, with similar limiting diffusion currents, but the shape parameter ΔE_p is significantly greater than expected from comparisons with ferrocene.

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for [$\{Mo(NO)L(Cl)\}_2(NC_4H_8N)$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	2 049(1)	1 446(1)	−433(1)	C(10)	5 084(7)	193(8)	2 339(7)
Cl(1)	1 027(2)	2 751(2)	−1 123(2)	N(6)	3 466(5)	2 388(5)	−330(4)
N(1)	2 288(6)	1 016(6)	−1 581(6)	N(7)	4 025(5)	2 471(4)	532(5)
O(1)	2 394(6)	805(6)	−2 303(5)	C(11)	3 485(9)	3 085(10)	−1 890(7)
N(2)	1 789(5)	2 096(4)	933(4)	C(12)	3 887(6)	2 994(7)	−915(6)
N(3)	2 629(5)	2 124(5)	1 625(4)	C(13)	4 743(7)	3 450(7)	−434(7)
C(1)	−136(6)	2 588(7)	812(7)	C(14)	4 795(6)	3 129(6)	467(7)
C(2)	942(6)	2 452(6)	1 345(6)	C(15)	5 535(8)	3 423(8)	1 296(8)
C(3)	1 224(7)	2 655(6)	2 264(6)	N(8)	963(4)	509(4)	−219(4)
C(4)	2 278(7)	2 461(6)	2 421(6)	C(16)	314(7)	1(7)	−958(6)
C(5)	2 966(9)	2 587(9)	3 305(7)	C(17)	864(7)	44(8)	674(7)
N(4)	3 209(5)	495(5)	297(4)	B(1)	3 736(7)	1 870(6)	1 378(6)
N(5)	3 782(4)	813(4)	1 099(4)	C(18)*	2 335(13)	4 524(9)	613(12)
C(6)	3 054(8)	−1 013(7)	−636(7)	Cl(2)*	2 923(4)	4 944(3)	1 620(4)
C(7)	3 499(6)	−416(6)	150(6)	Cl(3)*	2 077(7)	5 359(6)	−261(6)
C(8)	4 261(6)	−677(6)	858(6)	Cl(3A)*	1 424(15)	5 224(12)	212(13)
C(9)	4 408(6)	111(6)	1 448(6)				

* Atoms of dichloromethane molecule: Cl(3) site occupancy 0.63(2), Cl(3A) site occupancy 0.35(3).

Table 4. Selected bond lengths (Å), bond angles (°), and torsion angles (°) for [$\{Mo(NO)L(Cl)\}_2(NC_4H_8N)$]*

Mo–Cl(1)	2.408(2)	Mo–N(8)	1.942(6)
Mo–N(1)	1.804(10)	N(1)–O(1)	1.097(9)
Mo–N(2)	2.212(6)	N(8)–C(16)	1.473(10)
Mo–N(4)	2.188(6)	N(8)–C(17)	1.453(10)
Mo–N(6)	2.222(6)	C(16)–C(17′)	1.577(12)
N(1)–Mo–N(2)	175.1(3)	N(4)–Mo–N(8)	88.2(2)
N(1)–Mo–N(4)	94.6(3)	N(4)–Mo–Cl(1)	168.0(2)
N(1)–Mo–N(6)	93.8(3)	N(6)–Mo–N(8)	165.5(2)
N(1)–Mo–N(8)	95.2(3)	N(6)–Mo–Cl(1)	88.9(2)
N(1)–Mo–Cl(1)	90.0(2)	N(8)–Mo–Cl(1)	102.4(2)
N(2)–Mo–N(4)	88.1(2)	Mo–N(1)–O(1)	175.2(8)
N(2)–Mo–N(6)	82.7(2)	Mo–N(8)–C(16)	125.0(5)
N(2)–Mo–N(8)	88.9(2)	Mo–N(8)–C(17)	123.6(5)
N(2)–Mo–Cl(1)	86.6(2)	C(16)–N(8)–C(17)	109.8(6)
N(4)–Mo–N(6)	79.8(2)		
Mo–N(8)–C(16)–C(17′)	−138.4(7)	C(17)–N(8)–C(16)–C(17′)	55.6(9)
Mo–N(8)–C(17)–C(16′)	135.3(7)	N(8)–C(16)–C(17′)–N(8′)	−57.8(8)
C(16′)–C(17)–N(8)–C(16)	−58.5(9)		

* Primed atoms are related to the others by the centre of symmetry.

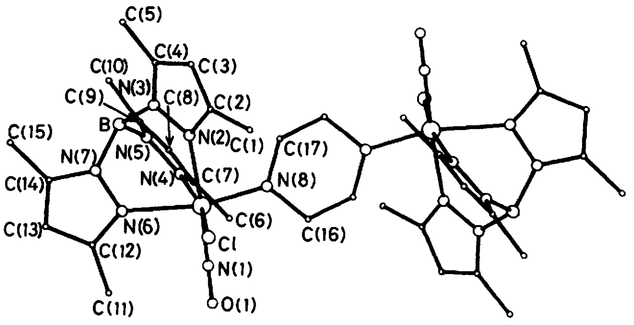

Figure 2. Molecular structure of [$\{Mo(NO)L(Cl)\}_2(NC_4H_8N)$] showing the atom labelling

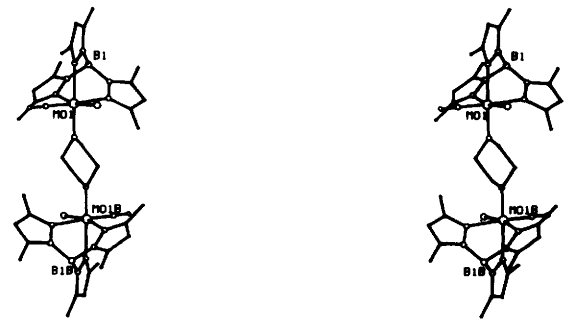

Figure 3. A stereoview of [$\{Mo(NO)L(Cl)\}_2(NC_4H_8N)$]

a broad ν_{NO} band at 1 635 cm^{-1} in its i.r. spectrum, in accord with its formulation as the reduced complex [$Co(\eta^5-C_5H_5)_2$][$\{Mo(NO)L(Cl)\}_2(NC_4H_8N)$]. The e.s.r. and electronic spectral data suggest that the same mixed-valence complex may be produced by both electrochemical reduction and chemical reduction using cobaltocene.

*Structural Studies.**—In order unambiguously to characterise the bimetallic species [$\{M(NO)L(Cl)\}_2(NC_4H_8N)$] (M = Mo or W), the crystal structure of the molybdenum complex was determined. Atomic co-ordinates are listed in Table 3 and selected geometrical parameters are in Table 4. The structure of the complex, which possesses crystallographic inversion symmetry, is shown in Figures 2 and 3.

The co-ordination about molybdenum is essentially octahedral {maximum angular deviation from ideal octahedral 14.5° [N(6)–Mo–N(8) 165.5(2)°], mean deviation 5.6°}, and is similar to that in the analogous bis(pyridine-2-amido) complex[14] [$Mo(NO)L(2-NHC_5H_4N)_2$], mean angular difference 2.4°, and in the bis(butylamido) complex[15] [$Mo(NO)L(NHBu^n)_2$], mean difference 2.8°. The co-ordination geometries of [$Mo(NO)L(2-NHC_5H_4N)_2$] and [$Mo(NO)L(NHBu^n)_2$] agree much more closely (maximum angular difference 1.6°, mean difference 0.8°).

The Mo–N(piperazin-1,4-diyl) bond length, 1.942(6) Å, is similar to the Mo–N(butylamido) lengths of 1.935 and 1.945 Å in [$Mo(NO)L(NHBu^n)_2$],[15] and is indicative of $p\pi \rightarrow d\pi$ donation from the ligand. The large Mo–N(8)–C angles of 125.0(5) and 123.6(5)° are consistent with this. The piperazine-1,4-diyl ring is in the normal, slightly flattened chair conformation, with ring torsion angles in the range ±55.6—±58.5°. The molybdenum atom, although essentially equatorial, lies close to

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

Table 5. Mean-plane calculations

(*a*) Deviations (Å) of atoms from ring planes[a]

Plane (1): N(2), N(3), C(2)—(4)
Atoms defining plane $\leqslant$0.015 Å; Mo 0.213, C(1) −0.07, C(5) −0.02, B −0.12

Plane (2): N(4), N(5), C(7)—(9)
Atoms defining plane $\leqslant$0.006 Å; Mo 0.066, C(6) 0.02, C(10) 0.09, B −0.20

Plane (3): N(6), N(7), C(12)—(14)
Atoms defining plane $\leqslant$0.013 Å; Mo 0.147, C(11) 0.01, C(15) 0.07, B −0.01

(*b*) Dihedral angles (°)[b]

1—2	129.9
1—3	116.5
2—3	113.5

[a] E.s.d.s are *ca.* 0.005 Å for Mo and 0.02 Å for the lighter atoms. [b] E.s.d.s are *ca.* 0.3°.

the plane of the nitrogen atom and the two adjacent ring carbon atoms [sum of bond angles at N(8), 358.4°; Mo–N(8)–C–C torsion angles, −138.4 and 135.3°].

The bonds to the pyrazolyl rings (2.19—2.22 Å) fall within the range of lengths commonly observed in this type of complex. As had been generally found previously, the bond *trans* to the nitrosyl group tends to be long (2.212 Å in the present structure) and this has been attributed[12] to the *trans* effect of the strongly π-accepting nitrosyl group. The shortest Mo–N(pyrazolyl) bond is *trans* to the chloro substituent. This appears to be a general phenomenon in this class of complexes. If a halogen (I or Cl) is co-ordinated to molybdenum, then the Mo–N(pyrazolyl) bond *trans* to the halogen is invariably the shortest of these three bonds.[12,16—18] The Mo–Cl length, 2.408(2) Å, is similar to that found (2.380 Å) in the only analogous chloro complex whose crystal structure has been determined, *viz.* chloro[hydrotris(4-chloro-3,5-dimethylpyrazolyl)borato](isopropoxo)nitrosylmolybdenum.[16]

The pyrazolyl rings are each planar to within the limits of experimental error (Table 5). The molybdenum and boron atoms lie on opposite sides of each of the three ring planes, deviating by up to 0.2 Å. The dihedral angles between the pyrazolyl rings are in the range 113.5—129.9°, the largest angle being between the pair of rings encompassing the relatively bulky piperazine-1,4-diyl ring.

Conclusions

The results described here indicate that a substantial interaction between the metal centres in $[\{Mo(NO)L(Cl)\}_2(NC_4H_8N)]$ is possible despite the saturated nature of the bridging ligand. The absence of π bonds in the piperazine-1,4-diyl ligand, and the Mo–Mo separation of 6.773(2) Å, preclude any significant delocalisation of the added electron between the metal centres in the mixed oxidation state (I and II) complex. This expectation is borne out by the e.s.r. data which are consistent with the unpaired electron being located in a substantially metal based orbital. The hyperfine coupling constant of 4.89 mT is identical with those found in the monometallic 17-electron complexes $[Mo(NO)L(Cl)(NHC_nH_{2n})]$ (n = 4 or 5). It is also similar to those found in the reduced monometallic arylamide complexes[4] $[Mo(NO)L(Cl)(NHR)]^-$ (R = p-substituted phenyl) or the paramagnetic complexes $[Mo(NO)L(L')_2]^+$ (L′ = py, im, mim, or pyrazole) in which the electron is in a metal based orbital of axial symmetry.[11] In the absence of direct metal orbital overlap or mesomeric effects, the interaction between the molybdenum centres must be attributable to polar effects transmitted across the bridging ligand. The inductive effect transmitted through the σ-bond framework will be small since two sets of three bonds separate the ligating nitrogen atoms.[19] Consequently, it would appear that a substantial proportion of the observed interaction must be attributed to through-space electrostatic field effects. As noted by Richardson and Taube,[20] mixed oxidation state complex stabilisation by electron delocalisation is not a necessary prerequisite for strong metal–metal interactions as expressed in electrochemical properties. Mesomeric[5] and polar effects can lead to substantial interactions across bridging ligands. The results presented here indicate that polar effects can make a substantial contribution to the comproportionation constants of mixed oxidation state bimetallic species and in the case of $[\{Mo(NO)L(Cl)\}_2(NC_4H_8N)]$ a value of 3×10^9 is found. This figure shows that, although the two Mo centres in the molecule are chemically equivalent, the mixed oxidation state compound is greatly stabilised with respect to a mixture of the doubly oxidised and doubly reduced species. In the case of completely non-interacting Mo centres a comproportionation constant of only 4 would be expected. Thus far all our attempts to prepare a pyrazine bridged analogue of the Creutz–Taube ion based on the molybdenum system have failed. The results presented here would suggest that, if such a species existed, it would exhibit very substantial interactions between the molybdenum redox centres.

Experimental

Synthetic Studies.—Commercial reagents were used as received and all reactions were carried out under nitrogen in redistilled, dry, oxygen-free solvents. The compound $[Mo(NO)\{HB(Me_2pz)_3\}Cl_2]$ and $[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ were prepared according to previously described methods.[16] Silica gel 60 (70—230 mesh) was used as the stationary phase for column chromatography. Infrared spectra were recorded on a PE 297 instrument, and 100-MHz ^1H n.m.r. spectra on a Varian XL100 instrument. 400-MHz ^1H N.m.r. spectra were recorded on a Bruker WH 400 spectrometer of the S.E.R.C. high-field n.m.r. service, University of Warwick. Mass spectra were recorded on a Kratos MS80 instrument. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Birmingham.

Cyclic voltammetry measurements were carried out using a Hi-tek Potentiostat DT2101 and Waveform Generator PPR1.

Preparation.—$[Mo(NO)\{HB(Me_2pz)_3\}Cl(NC_5H_{10})]$. $[Mo(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1.0 g, 2.0 mmol) and piperidine (1 cm^3, 10 mmol) in CH_2Cl_2 (60 cm^3) were refluxed for 16 h. The reaction mixture was then filtered and evaporated *in vacuo*. The solid residue was purified by column chromatography using CH_2Cl_2 as eluant and collecting the principal red fraction. The compound was further purified by recrystallisation from CH_2Cl_2–hexane. Yield: 0.70 g (64%) (Found: C, 44.2; H, 6.2; N, 20.7. Calc. for $C_{20}H_{32}BClMoN_8O$: C, 44.3; H, 5.9; N, 20.7%).

$[Mo(NO)\{HB(Me_2pz)_3\}Cl(NC_4H_8)]$. This compound was prepared in an identical manner to its piperidyl analogue using pyrrolidine (1 cm^3) in place of piperidine. Yield: 0.58 g (54%) (Found: C, 43.0; H, 5.1; N, 21.0. Calc. for $C_{19}H_{30}BClMoN_8O$: C, 43.2; H, 5.7; N, 21.2%).

$[Mo(NO)\{HB(Me_2pz)_3\}Cl(NC_3H_6)]$. A solution of $[Mo(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1.0 g, 2 mmol) and azetidine (0.28 cm^3, 2 mmol) in dichloromethane (60 cm^3) was stirred with NaH (0.2 g) at room temperature for 24 h. The resulting red solution was filtered and the filtrate evaporated to dryness.

The solid obtained was purified by column chromatography, using dichloromethane as the eluant, the main red fraction being collected. Recrystallisation from dichloromethane–hexane gave the product as pink microcrystals. Yield: 0.43 g (41.4%) (Found: C, 42.3; H, 5.3; N, 21.9. Calc. for $C_{18}H_{28}BClMoN_8O$: C, 42.0; H, 5.4; N, 21.8%).

$[\{Mo(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$. $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2]$ (1.0 g, 2.0 mmol) and piperazine (0.1 g, 0.87 mmol) were refluxed in CH_2Cl_2 (60 cm^3) for 2 d in the presence of excess NaH. The reaction mixture was then filtered and the solvent removed *in vacuo*. The crude product was purified by column chromatography using CH_2Cl_2 as the eluant, the principal red-purple band being collected. This could be further purified by recrystallisation from CH_2Cl_2–hexane. Yield: 0.32 g (32%) (Found: C, 40.3; H, 5.1; N, 22.0. Calc. for $C_{34}H_{52}B_2Cl_2Mo_2N_{16}O_2$: C, 40.8; H, 5.2; N, 22.4%). Further elution of the column with MeCN developed a second red-purple band which was found to be the monometallic complex $[Mo(NO)\{HB(Me_2pz)_3\}Cl(NC_4H_8NH)]$. This material could also be further purified by recrystallisation from CH_2Cl_2–hexane. Yield: 0.3 g (54%) (Found: C, 39.9; H, 5.6; N, 21.5. Calc. for $C_{19}H_{31}BClMoN_9O \cdot 0.5CH_2Cl_2$: C, 40.2; H, 5.3; N, 21.3%).

$[W(NO)\{HB(Me_2pz)_3\}Cl(NC_5H_{10})]$. $[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (0.7 g, 1.2 mmol) and piperidine (1.0 cm^3, 10 mmol) were refluxed in CH_2Cl_2 (60 cm^3) for 3 h in the presence of excess NaH (0.2 g). During this time the solution became red. After filtration the reaction mixture was evaporated *in vacuo* until *ca.* 5 cm^3 remained. The addition of hexane caused a dark pink powder to precipitate and this was further purified by column chromatography using CH_2Cl_2 as the eluant. The principal red-purple band was collected and could be further purified by recrystallisation from CH_2Cl_2–hexane. Yield: 0.54 g (72%) (Found: C, 38.0; H, 5.1; N, 17.5. Calc. for $C_{20}H_{32}BClN_8OW$: C, 38.1; H, 5.1; N, 17.8%).

$[W(NO)\{HB(Me_2pz)_3\}Cl(NC_4H_8)]$. $[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1.0 g, 1.7 mmol) and pyrrolidine (5.0 cm^3, 70 mmol) were stirred in the presence of NaH (0.2 g) in CH_2Cl_2 (60 cm^3) for 16 h at room temperature during which time the solution became red. After filtration the reaction mixture was evaporated *in vacuo* until *ca.* 5 cm^3 remained. Addition of hexane caused a red powder to precipitate. This product was purified by column chromatography using CH_2Cl_2 as the eluant and collecting the principal red fraction. The product was further purified by recrystallisation from CH_2Cl_2–hexane. Yield: 0.46 g (43%) (Found: C, 36.9; H, 4.9; N, 18.1. Calc. for $C_{19}H_{30}BClN_8OW$: C, 37.0; H, 4.9; N, 18.2%).

$[W(NO)\{HB(Me_2pz)_3\}Cl(NC_3H_6)]$. A solution of $[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1 g, 1 mmol) and azetidine (0.23 cm^3, 2 mmol) in dichloromethane (60 ml) was refluxed with NaH (0.2 g) for 2 d. The resulting brown mixture was filtered and the filtrate evaporated to dryness. The solid obtained was purified by column chromatography using dichloromethane as the eluant and collecting the main orange fraction. Recrystallisation from dichloromethane–hexane gave the product as orange microcrystals. Yield: 0.42 g (41%) (Found: C, 36.2; H, 4.7; N, 18.4. Calc. for $C_{18}H_{28}BClN_8OW$: C, 35.9; H, 4.7; N, 18.6%).

$[\{W(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$. $[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1.0 g, 1.7 mmol) and piperazine (75 mg, 0.9 mmol) were refluxed for 4 d in CH_2Cl_2 (60 cm^3) in the presence of excess NaH (0.2 g). The reaction mixture was then filtered and evaporated *in vacuo*. The red residue was purified by column chromatography using CH_2Cl_2 as the eluant and collecting the principal red-pink fraction. Further purification was effected by recrystallisation from CH_2Cl_2–hexane mixtures. Yield: 0.45 g (45%) (Found: C, 34.8; H, 4.5; N, 18.1. Calc. for $C_{34}H_{52}B_2Cl_2N_{16}O_2W_2$: C, 34.6; H, 4.5; N, 19.0%).

Cobaltocene Reduction of $[\{Mo(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$.—An excess of cobaltocene was added to a stirred solution of $[\{Mo(NO)[HB(Me_2pz)_3]Cl\}_2(NC_4H_8N)]$ (0.1 g) in dry tetrahydrofuran (5 cm^3). A blue solution formed immediately. The reaction mixture was stirred for a further 3 h and then filtered under N_2. The volume of the filtrate was reduced by evaporation to precipitate the blue, air-sensitive product. This was collected by filtration under N_2 and redissolved in a mixture of dichloromethane and thf. Evaporation of the solvent caused the blue product to precipitate (Found: C, 42.9; H, 5.2; N, 17.8. Calc. for $C_{44}H_{62}B_2Cl_2CoMoN_{16}O_2 \cdot CH_2Cl_2$: C, 43.3; H, 5.1; N, 18.2%).

X-Ray Crystallographic Analysis of $[\{Mo(NO)L(Cl)\}_2(NC_4H_8N)]$.—A crystal (0.4 × 0.4 × 0.3 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer; cell dimensions and intensities were measured by $\omega/2\theta$ scans with graphite-monochromated Mo-K_α radiation and scan range $(\omega) = (1.0 + 0.35 \tan\theta)^\circ$. Scan speed varied from 1.2 to 3.5° min^{-1} depending on the intensity. 8 638 Reflections scanned within $2 < \theta < 25^\circ$. Of these 4 468 were unique (merging $R_{int} = 0.039$). Two standard reflections measured every 2 h showed significant but similar decrease in intensity and appropriate scaling factors were applied to the data. 2 830 Structure amplitudes with $F > 5\sigma(F)$ were considered observed and used in the analysis.

Crystal data. $C_{34}H_{52}B_2Cl_2Mo_2N_{16}O_2 \cdot CH_2Cl_2$, M = 1 086.2, monoclinic, space group $P2_1/n$, $a = 12.655(5)$, $b = 14.007(3)$, $c = 14.370(5)$ Å, $\beta = 94.54(3)^\circ$, $U = 2\,539$ Å^3, $Z = 2$, $D_c = 1.421$ g cm^{-3}, $F(000) = 1\,108$, μ(Mo-K_α) = 0.744 mm^{-1}, $\lambda = 0.710\,69$ Å.

The structure was determined by Patterson and Fourier methods and refined by least-squares methods using anisotropic thermal parameters for the heavier atoms except for one of the chlorine atoms of the dichloromethane molecule which was disordered over two sites and which was refined isotropically. Hydrogen atoms were placed in calculated positions riding on their respective bonded atom. Those of the CH_2Cl_2 molecule were, however, not included. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.001F^2]$ and the refinement converged to $R = 0.059$, $R' = 0.075$. The residual electron density in a final difference map was within ± 0.9 e Å^{-3}, apart from two maxima of 1.2 e Å^{-3} close to Mo.

Complex neutral-atom scattering factors were employed. 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[21] and PLUTO[22] programs.

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