

Monometallic, Homo- and Hetero-bimetallic Complexes Based on Redox-active Tris(3,5-dimethylpyrazolyl)borato Molybdenum and Tungsten Nitrosyls. Part 7.† Compounds containing Strongly Interacting Redox Centres derived from *para*-Substituted Anilines and Phenols‡

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The compounds $[ML(NO)X(NHC_6H_4ZH)]$ [$L = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{borate}$; $Z = \text{NH}$; $M = \text{Mo}$, $X = \text{I}$; $M = \text{W}$, $X = \text{Cl}$; $Z = \text{O}$; $M = \text{Mo}$, $X = \text{I}$; $M = \text{W}$, $X = \text{Cl}$; $Z = \text{S}$, $M = \text{Mo}$, $X = \text{Cl}$], $[\{ML(NO)X\}_2(NHC_6H_4NH)]$ ($M = \text{Mo}$, $X = \text{Cl}$ or I ; $M = \text{W}$, $X = \text{Cl}$), $[\{ML(NO)X\}_2(NHC_6H_4O)]$ ($M = \text{Mo}$, $X = \text{Cl}$ or I ; $M = \text{W}$, $X = \text{Cl}$), $[\{MoL(NO)Cl\}_2(OC_6H_4O)]$, and $[MoL(NO)I(YC_6H_4Z)WL(NO)Cl]$ ($Y = Z = \text{NH}$; $Y = \text{O}$, $Z = \text{NH}$; $Y = \text{NH}$, $Z = \text{O}$) have been prepared. Cyclic voltammetric and coulometric studies established that the monometallic species undergo a one-electron reduction, whereas the bimetallic species are reduced in two one-electron steps. The electrochemical data suggest that the redox centres in the bimetallic complexes influence each other strongly.

There is considerable interest in bimetallic complexes which are redox active. Such species, especially those in which the redox centres are not directly attached by metal-metal bonds or separated by single-atom bridges, but are connected by polyatomic bridging ligands, like pyrazine or 4,4'-bipyridyl, provide a number of challenging theoretical and practical problems.¹ Two of the most interesting facets of this class of compound are (i) the possibility that such species can give rise to mixed-valence complexes with unusual spectroscopic, magnetic, and/or electrical properties, and (ii) the way in which one redox centre may be influenced by the redox activity of its adjacent partner. There has been continuing and substantial interest in (i), which may be exemplified by the extensive studies of the Creutz-Taube ion, $[\{Ru(NH_3)_5\}_2(N_2C_4H_4)]^{5+}$ ($N_2C_4H_4 = \text{pyrazine}$) and related complexes.² The majority of species of this type which have been investigated thoroughly are 'valence-trapped' containing, for example, $Ru^{II}Ru^{III}$, $Ru^{II}Rh^{III}$, or $Ru^{II}Co^{III}$ redox pairs. The Creutz-Taube ion itself may be a rare example of a delocalised system, although this remains uncertain.³ However, the influence of one redox centre on the electrochemical properties of its partner has been less extensively examined,⁴ although an effective theory for the behaviour of pairs of redox centres exists.⁵

We have already demonstrated that the sterically hindered, formally co-ordinatively unsaturated tris(3,5-dimethylpyrazolyl)borato $[HB(Me_2pz)_3]$ compounds $[ML(NO)XY]$ [$L = HB(Me_2pz)_3$; $M = \text{Mo}$ or W ; $X, Y = \text{halide, OR, SR, SR}', \text{NHR, NHR}', \text{NR}_2, \text{or NR}'_2$ ($R = \text{alkyl}$, $R' = \text{aryl}$)] are redox active,⁶⁻⁹ undergoing a one-electron reduction formally associated with the process $M(NO)^{3+} + e^- \rightleftharpoons M(NO)^{2+}$. The facility with which these complexes can be made, together with their apparent reluctance to form chelated species with ligands such as $NH_2CH_2CH_2OH$ ¹⁰ or $HOCH_2CH_2OH$,¹¹ suggested to us that it should be possible to construct bimetallic redox-active compounds linked by polyatomic bridges based either on bifunctionalised saturated hydrocarbons, e.g. 1,2-

diaminoethane, or related aromatic ring systems, e.g. *p*-phenylenediamine.

We have previously demonstrated that it was possible to prepare heterobimetallic complexes using $NH_2(CH_2)_3PPh_2$ and *p*- $NH_2C_6H_4I$ as bridging ligands, but these complexes possessed only one redox-active centre.¹² We therefore adopted a relatively simple strategy of either forming, by well established routes, a simple *p*-functionalised anilino or phenolato complex, e.g. $[ML(NO)X(YC_6H_4ZH)]$ ($X = \text{halide}$; $Y = \text{O}$ or NH ; $Z = \text{O}$, NH , or S) and reacting this with a further equivalent of $[ML(NO)X_2]$, or of treating two molar equivalents of $[ML(NO)X_2]$ with one molar equivalent of a *p*-bifunctionalised aromatic.¹³ We have presented a brief preliminary report of our work,¹⁴ showing that bimetallic complexes can be prepared from a large variety of *p*-bifunctionalised aromatic ligands and that they exhibit a range of electrochemical behaviour, being typified by strong, intermediate, and weak interaction between redox centres. We also noted that the $E_{1/2}$ values of the redox processes in these bimetallic species and their monometallic progenitors were strongly affected by the *p* substituent.

In this paper we concentrate on strongly interacting bimetallic species, based on *para*-diamino-, -dihydroxy- and related benzene rings, describing the synthesis of the monometallic precursors, their bimetallic derivatives, and a simple voltammetric study of the new compounds. In subsequent papers we will report on related results obtained from intermediate- and weakly-interacting systems, and in later papers the synthesis and spectral characterisation of reduced species obtained from these bimetallic compounds.

Experimental

The complexes $[M\{HB(Me_2pz)_3\}(NO)X_2]$ ($M = \text{Mo}$, $X = \text{Cl}$ or I ; $M = \text{W}$, $X = \text{Cl}$) were prepared as described in the literature.^{15,16} All ligands were used as received, and all complexes were stable enough to be purified using column chromatography, under N_2 , if necessary. Silica gel 60 (70–230 mesh) was used to prepare the columns, and dichloromethane was employed as eluant. All reactions were carried out under nitrogen and all yields are quoted relative to the metal-containing starting material.

† Part 6 is ref. 21.

* Supplementary data available (No. SUP 56685, 10 pp.): i.r. and 1H n.m.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

I.r. spectra were obtained using PE 297 and SP 180 spectrophotometers. ^1H N.m.r. spectra were measured using JEOL JNM-PMX-60, PE R-14-100 MHz, JEOL GFX270, or Bruker 400 MHz spectrometers, the last courtesy of the S.E.R.C. high-field n.m.r. service at Warwick University. Electrochemical data were obtained using a Hitek DT2101 potentiostat, a Hitek PPR1 waveform generator, and a Philips XY-recorder or a PAR 174 instrument. Cyclic voltammetry was carried out in dry acetonitrile or tetrahydrofuran (thf) under dry N_2 . In all experiments $[\text{NBu}^+_4][\text{PF}_6^-]$ was used as the base electrolyte and a Pt wire as the test electrode.

Preparations.— $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]\cdot 0.5\text{CH}_2\text{Cl}_2$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.27 g, 0.4 mmol) and *p*-phenylenediamine (0.09 g, 0.8 mmol) in dichloromethane (40 cm^3) was stirred at room temperature (r.t.) for 90 min. After filtration of the dark purple solution (removal of white $\text{C}_6\text{H}_8\text{N}_2\cdot\text{HI}$), addition of *n*-hexane (30 cm^3) to the filtrate and partial evaporation *in vacuo* (ca. 20 cm^3), black crystals of the complex separated. The complex was filtered off and obtained as black microcrystals (0.27 g, 95%). The compound could be recrystallised from dichloromethane–diethyl ether mixtures.

$[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{NH}_2)]$. A solution of $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2]$ (1.0 g, 1.7 mmol) and *p*-phenylenediamine (0.36 g, 3 mmol) in dichloromethane (100 cm^3) was stirred at r.t. for 3 d. The orange-brown solution was filtered and the filtrate evaporated to dryness *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed, the main orange fraction being collected. After evaporation of the solvent and recrystallisation of the solid from dichloromethane–*n*-hexane mixtures the complex was obtained as an orange microcrystalline powder (0.92 g, 82%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{NH}_2)]$ was prepared similarly, and was isolated as deep purple microcrystals (86%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{OH})]\cdot 0.5\text{CH}_2\text{Cl}_2$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.27 g, 0.4 mmol) and *p*-aminophenol (0.09 g, 0.8 mmol) in thf (50 cm^3) was stirred at r.t. for 90 min. The dark red-brown solution was evaporated *in vacuo*, the residue dissolved in dichloromethane (40 cm^3), the solution filtered and the filtrate treated with *n*-hexane (30 cm^3). After evaporation *in vacuo* to ca. 20 cm^3 , the compound separated as a black solid. This was filtered off, redissolved in dichloromethane, and chromatographed. The first two fractions (blue and purple, respectively) were discarded, but the main red-brown fraction was collected, treated with *n*-hexane, and partially evaporated as before. The complex was filtered off and isolated as black microcrystals (0.23 g, 81%).

$[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{OH})]$. This compound was prepared in a way similar to that of the $\text{NHC}_6\text{H}_4\text{NH}_2$ derivative above, using *p*-aminophenol (0.38 g) in refluxing dichloromethane (60 cm^3) over 5 d. The complex was obtained as an orange powder (0.67 g, 60%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{SH})]$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2]$ (0.50 g, 1 mmol) and *p*-aminothiophenol (0.24 g, 1.9 mmol) in dichloromethane (75 cm^3) was refluxed for 2 d. The resulting maroon mixture was filtered and the filtrate evaporated *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed, the main purple-maroon fraction being collected. After evaporation of the solvent and recrystallisation of the solid from dichloromethane–*n*-pentane mixtures, the complex was isolated as black microcrystals (0.11 g, 19%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{SH})]$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.27 g, 0.4 mmol) and *p*-aminothiophenol (0.1 g, 0.8 mmol) in chloroform (40 cm^3) was stirred for 1 h at -10 to -15 °C. The dark red solution was filtered

rapidly and the filtrate evaporated *in vacuo*. The residue was redissolved in benzene, the solution filtered and *n*-heptane added, the bulk of the mixture being reduced *in vacuo* until precipitation began. The complex was filtered off and isolated as a black powder (0.16 g, 61%). The colour of this complex is strongly influenced by the nature of the solvent, behaviour which is probably associated with the acidity of the thiophenolic proton. Thus addition of base can cause the colour to change from deep red through purple-blue to dark blue.

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2(\text{NHC}_6\text{H}_4\text{NH})]$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2]$ (1.0 g, 2 mmol) and *p*-phenylenediamine (0.11 g, 1 mmol) in dichloromethane (50 cm^3) was refluxed for 4 d. The resulting purple solution was filtered, the filtrate evaporated *in vacuo* to low bulk, and purified by chromatography. The purple-violet band was collected, the solvent evaporated *in vacuo*, and the residue recrystallised from dichloromethane–*n*-hexane mixtures, giving the complex as a purple powder (0.43 g, 21%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2(\text{NHC}_6\text{H}_4\text{NH})]\cdot 0.5\text{CH}_2\text{Cl}_2$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.14 g, 0.2 mmol) and $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]\cdot 0.5\text{CH}_2\text{Cl}_2$ (0.14 g, 0.2 mmol) in dichloromethane (40 cm^3) was stirred at r.t. for 4 d. To the dark blue solution *n*-hexane (40 cm^3) was added, and the volume reduced to ca. 20 cm^3 by evaporation *in vacuo*. The complex, which precipitated, was collected by filtration giving a black microcrystalline solid (0.21 g, 84%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2(\text{NHC}_6\text{H}_4\text{O})]$. This complex was obtained in the same way as its chloro $\text{NHC}_6\text{H}_4\text{NH}$ analogue above, using $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2]$ (1.00 g, 2 mmol) and *p*-aminophenol (0.11 g, 1 mmol), as a violet powder (0.42 g, 20%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2(\text{NHC}_6\text{H}_4\text{O})]$. A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (0.14 g, 0.2 mmol) and $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{OH})]\cdot 0.5\text{CH}_2\text{Cl}_2$ (0.15 g, 0.2 mmol) in dichloromethane (50 cm^3) was treated with a suspension of NaH (0.01 g in 50% dispersion in oil) in dichloromethane (15 cm^3), and the mixture was stirred at r.t. for 3 d. The resulting purple solution was filtered and the filtrate evaporated *in vacuo*. The residue was chromatographed using dichloromethane–*n*-hexane mixtures (with increasing amounts of the polar solvent starting at 1:1 v/v). The blue and pale yellow fractions were discarded and the main purple fraction collected. To the solution *n*-heptane was added and the bulk of the mixture reduced *in vacuo*, giving the complex as black microcrystals (0.09 g, 39%).

$[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2(\text{NHC}_6\text{H}_4\text{O})]$. A solution of $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2]$ (0.44 g, 0.8 mmol) and $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{OH})]$ (0.5 g, 0.8 mmol) in dichloromethane (60 cm^3) was refluxed for 3 d. The brown solution was filtered and the filtrate evaporated *in vacuo*. The residue was chromatographed giving a brown fraction which was collected, the solvent evaporated *in vacuo* and the solid recrystallised from dichloromethane–*n*-hexane mixtures. The complex was isolated as a brown powder (0.35 g, 39%).

The complex $[\text{W}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2(\text{NHC}_6\text{H}_4\text{NH})]$ was obtained in the same way, as a pink solid (20%).

$[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2(\text{OC}_6\text{H}_4\text{O})]$. *Method 1.* A solution of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{I}_2]$ (1.00 g) and AgPF_6 (0.37 g) in dichloromethane (50 cm^3) was stirred at r.t. for 1 h. *p*-Dihydroxybenzene (0.16 g) was added and the mixture refluxed for 2 d. The resulting violet solution was filtered through Kieselguhr and evaporated *in vacuo*. The residue was chromatographed and the main violet fraction collected. After evaporation of the solvent and recrystallisation of the solid from dichloromethane–*n*-hexane mixtures, the complex was isolated as a violet powder (0.54 g, 30%).

The compound $[\text{Mo}\{\text{HB}(\text{Me}_2\text{pz})_3\}(\text{NO})\text{Cl}_2(\text{OC}_6\text{H}_4\text{O})]$ was prepared similarly using *p*-dihydroxybenzene (0.22 g) and

AgPF₆ (0.52 g) and was isolated as a purple powder (0.4 g, 19%).

Method 2. A solution of [Mo{HB(Me₂pz)₃}(NO)I₂] (0.27 g, 0.4 mmol) in thf (20 cm³) was treated with a mixture of *p*-dihydroxybenzene (0.04 g, 0.4 mmol) and NaH (0.02 g of 50% dispersion in oil, 0.4 mmol) in thf (15 cm³). The mixture was stirred for 3 h at r.t. and then evaporated *in vacuo*. The residue was extracted into chloroform, the solution filtered and to the blue-purple filtrate *n*-heptane (*ca.* 1:1 v/v) was added, the mixture being partially evaporated *in vacuo*. A blue powder was filtered off, dissolved in the minimum volume of dichloromethane, and chromatographed using dichloromethane as eluant. The first blue fraction was collected, partially evaporated and treated with *n*-heptane, affording [Mo{HB(Me₂pz)₃}(NO)I₂}(OC₆H₄O)] as black microcrystals (0.07 g, 30%). The second blue fraction was then collected and worked-up similarly, giving [Mo{HB(Me₂pz)₃}(NO)I(OC₆H₄OH)]·CH₂Cl₂ as black microcrystals (0.11 g, 35%). Both products could be recrystallised from dichloromethane-*n*-hexane.

[Mo{HB(Me₂pz)₃}(NO)I(NHC₆H₄NH)W{HB(Me₂pz)₃}(NO)Cl]. A solution of [Mo{HB(Me₂pz)₃}(NO)I₂] (0.66 g, 1 mmol) and [W{HB(Me₂pz)₃}(NO)Cl(NHC₆H₄NH₂)] (0.65 g, 0.9 mmol) in dichloromethane (100 cm³) was stirred at r.t. for 3 d. The solution was filtered, the filtrate evaporated *in vacuo*, and the residue chromatographed, the main purple fraction being collected. After evaporation of the solvent and recrystallisation of the solid from dichloromethane-*n*-hexane mixtures, the complex was isolated as a purple powder (0.64 g, 55%).

[Mo{HB(Me₂pz)₃}(NO)I(OC₆H₄NH)W{HB(Me₂pz)₃}(NO)Cl]. This complex was prepared in the same way as that above, using [Mo{HB(Me₂pz)₃}(NO)I₂] (0.52 g) and [W{HB(Me₂pz)₃}(NO)Cl(NHC₆H₄OH)] (0.50 g) in dichloromethane to which NaH (0.02 g) had been added. Chromatography effected separation of a main blue band which afforded, after work-up as described above, the complex as a blue powder (0.49 g, 53%).

[Mo{HB(Me₂pz)₃}(NO)I(NHC₆H₄O)W{HB(Me₂pz)₃}(NO)Cl] was obtained in the same way using [Mo{HB(Me₂pz)₃}(NO)I(NHC₆H₄OH)] (0.50 g) and [W{HB(Me₂pz)₃}(NO)Cl₂] (0.44 g) and was obtained as a purple powder (0.21 g, 23%).

Results and Discussion

Synthetic Studies.—The synthetic strategy for the production of bimetallic species was that described above: (a) preparation of appropriately *p*-functionalised anilino or phenolato species, e.g. [ML(NO)X(YC₆H₄ZH)] (M = Mo, X = Cl or I; M = W, X = Cl; Y = NH, Z = NH, O, or S; Y = O, Z = O) and (b) reaction of these monometallic species with an equivalent of [ML(NO)X₂], to give [ML(NO)X(YC₆H₄Z)ML(NO)X].

(a) The monomeric species were obtained as previously,¹⁷ by reaction of [ML(NO)X₂] with two equivalents of NH₂C₆H₄ZH. The excess of the aniline is necessary to absorb the liberated HX: [ML(NO)X₂] + 2NH₂C₆H₄ZH → [ML(NO)X(NHC₆H₄ZH)] + [H₃NC₆H₄ZH]⁺ + X⁻. The reactions were carried out in dichloromethane and most occurred smoothly at room temperature. Only in the formation of [WL(NO)Cl(NHC₆H₄OH)] and [MoL(NO)Cl(NHC₆H₄SH)] was it necessary for the mixture to be refluxed. It proved difficult to isolate [MoL(NO)X(OC₆H₄OH)] and, indeed, we failed to obtain the chloro complex (X = Cl), although traces of it could be detected during chromatography. However, the iodo complex (X = I) was separated from the bimetallic [MoL(NO)I₂}(OC₆H₄O)] by column chromatography.

The complexes were obtained as microcrystalline powders (elemental analyses, Table 1), which gave strongly coloured solutions in dichloromethane. A number of these species changed colour on treatment with base, an observation which caused confusion during work-up procedures. Thus [MoL(NO)I(NHC₆H₄OH)] and [MoL(NO)I(NHC₆H₄SH)] are red-brown and purple-blue in dichloromethane, but on addition of an excess of NEt₃ the colours changed to claret red and dark blue, respectively. The original colour was partly restored on addition of an excess of acetic acid and we attribute these phenomena to the reaction: [MoL(NO)I(NHC₆H₄ZH)] + base ⇌ [MoL(NO)I(NHC₆H₄Z)]⁻ + [H base]⁺. The colour changes are certainly not associated with redox phenomena, as is clear from the potential data (see later), in contrast to the behaviour of [MoL(NO)I₂] in the presence of mild reducing agents, including bases.⁶

(b) The bimetallic complexes were obtained by two routes. The first, that of our original strategy, afforded the desired species either at room temperature [MoL(NO)I species] or

Table 1. Analytical data

Complex· <i>n</i> C ₆ H ₁₄ ^a	Analysis (%) ^b			
	C	H	N	<i>n</i>
[Mo{HB(Me ₂ pz) ₃ }(NO)I(NHC ₆ H ₄ NH ₂)]	37.2 (36.9)	4.4 (4.3)	18.1 (18.0)	0.5 ^c
[Mo{HB(Me ₂ pz) ₃ }(NO)Cl(NHC ₆ H ₄ NH ₂)]	42.2 (42.4)	4.9 (4.9)	19.3 (20.7)	0.5 ^c
[W{HB(Me ₂ pz) ₃ }(NO)Cl(NHC ₆ H ₄ NH ₂)]	39.3 (39.6)	4.7 (4.7)	18.9 (18.9)	0.17
[Mo{HB(Me ₂ pz) ₃ }(NO)I(NHC ₆ H ₄ OH)]	35.7 (35.6)	4.1 (4.1)	14.8 (15.1)	1.0 ^c
[W{HB(Me ₂ pz) ₃ }(NO)Cl(NHC ₆ H ₄ OH)]	39.7 (39.5)	4.2 (4.5)	17.0 (16.8)	0.17
[Mo{HB(Me ₂ pz) ₃ }(NO)Cl(NHC ₆ H ₄ SH)]	42.9 (43.3)	4.8 (4.8)	19.2 (19.2)	0
[Mo{HB(Me ₂ pz) ₃ }(NO)I(NHC ₆ H ₄ SH)]	35.6 (37.4)	4.2 (4.2)	16.8 (16.6)	0
[{Mo[HB(Me ₂ pz) ₃ }(NO)Cl] ₂ (NHC ₆ H ₄ NH)]	43.1 (43.9)	5.4 (5.4)	19.5 (21.0)	0.5
[{Mo[HB(Me ₂ pz) ₃ }(NO)I] ₂ (NHC ₆ H ₄ NH)]	34.2 (34.0)	4.1 (4.0)	16.9 (17.4)	0.5 ^c
[{W[HB(Me ₂ pz) ₃ }(NO)Cl] ₂ (NHC ₆ H ₄ NH)]	35.6 (36.1)	4.0 (4.2)	16.9 (16.7)	0
[{Mo[HB(Me ₂ pz) ₃ }(NO)Cl] ₂ (NHC ₆ H ₄ O)]	42.2 (42.2)	4.4 (4.8)	19.1 (20.5)	0
[{Mo[HB(Me ₂ pz) ₃ }(NO)I] ₂ (NHC ₆ H ₄ O)]	36.3 (35.8)	3.9 (4.1)	17.3 (17.4)	0
[{W[HB(Me ₂ pz) ₃ }(NO)Cl] ₂ (NHC ₆ H ₄ O)]	38.4 (38.3)	4.5 (4.6)	16.3 (16.7)	0.67
[{Mo[HB(Me ₂ pz) ₃ }(NO)Cl] ₂ (OC ₆ H ₄ O)]	41.9 (42.2)	5.6 (4.7)	18.3 (19.1)	0
[{Mo[HB(Me ₂ pz) ₃ }(NO)I] ₂ (OC ₆ H ₄ O)]	36.2 (35.7)	4.2 (4.0)	16.4 (16.2)	0
[Mo{HB(Me ₂ pz) ₃ }(NO)I(NHC ₆ H ₄ NH)W{HB(Me ₂ pz) ₃ }(NO)Cl]	38.7 (38.2)	5.2 (4.6)	17.5 (17.8)	0.67
[Mo{HB(Me ₂ pz) ₃ }(NO)I(OC ₆ H ₄ NH)W{HB(Me ₂ pz) ₃ }(NO)Cl]	35.3 (35.9)	4.1 (4.1)	17.4 (17.1)	0
[Mo{HB(Me ₂ pz) ₃ }(NO)I(NHC ₆ H ₄ O)W{HB(Me ₂ pz) ₃ }(NO)Cl]	37.2 (37.1)	4.7 (4.4)	16.7 (17.1)	0.33

^a Complexes may be isolated containing *n* moles of *n*-hexane of crystallisation as determined by elemental analysis, and confirmed by several independent ¹H n.m.r. spectral determinations. ^b Calculated values are given in parentheses. ^c No. of moles of CH₂Cl₂ of crystallisation, confirmed by independent ¹H n.m.r. spectroscopy.

under refluxing conditions in dichloromethane [ML(NO)Cl species, M = Mo or W]. In reactions involving [ML(NO)X(NHC₆H₄OH)] the formation of the desired bimetallic was assisted by addition of NaH to the reaction mixture, presumably forming [ML(NO)X(NHC₆H₄O)]⁻, a more effective nucleophile.

The second route involved reaction of two mole equivalents of [ML(NO)X₂] with *p*-HYC₆H₄ZH. In this way [{MoL(NO)Cl}₂](NHC₆H₄Z) (Z = NH or O) and [{MoL(NO)X}₂](OC₆H₄O) (X = Cl or I) were produced, the complexes containing [OC₆H₄O]²⁻ being formed by the assistance of AgPF₆ which caused precipitation of AgX from the reaction mixture.

The heterobimetallic complexes were obtained by treatment of [MoL(NO)L₂] with [WL(NO)Cl(NHC₆H₄ZH)] (Z = NH or O), or by reaction of [WL(NO)Cl₂] with [MoL(NO)I(NHC₆H₄OH)]. Thus we were able to obtain the related pair of complexes [MoL(NO)I(NHC₆H₄O)WL(NO)Cl] and [MoL(NO)I(OC₆H₄NH)WL(NO)Cl], by appropriate choice of metal dihalide and anilino complex. It should be recalled that in all reactions between [ML(NO)X₂] with NH₂QOH or NH₂QSH (Q is any bridging group), the metal preferentially selects the amino group for initial reaction.¹⁰

These complexes were obtained as microcrystalline powders and, despite exhaustive attempts, we have so far failed to obtain crystals suitable for X-ray studies. In solution, the complexes have colours significantly different to those of their monometallic precursors. For example, [MoL(NO)I(NHC₆H₄NH₂)] is purple whereas [{MoL(NO)I}₂](NHC₆H₄NH) is dark blue, [MoL(NO)I(NHC₆H₄OH)] is red-brown while [{MoL(NO)I}₂](NHC₆H₄O) is purple, [WL(NO)Cl(NHC₆H₄OH)] is orange and [{WL(NO)Cl}₂](NHC₆H₄O) is brown, and [MoL(NO)I(OC₆H₄OH)] is purple whereas [{MoL(NO)I}₂](OC₆H₄O) is dark blue.

Spectroscopic Studies.—The i.r. spectra of the monometallic species were characterised by ν(BH) (*ca.* 2 550 cm⁻¹) and absorptions typical of the pyrazolyl groups. The NH stretching

frequencies of the anilino groups occurred at *ca.* 3 300 cm⁻¹. The positions of ν(NO) are dependent on the metal and the donor atom NH or O, as we have noted previously.¹³ Thus [MoL(NO)X(NHR')] (R' = aryl) exhibits ν(NO) in the range 1 635—1 660 cm⁻¹, whereas that for [MoL(NO)X(OR')] occurs in the range 1 665—1 680 cm⁻¹. There are similar trends in the tungsten complexes, although these are less fully documented.

The symmetrical homobimetallic complexes show i.r. spectra generally similar to their monometallic progenitors. Thus there is only one ν(NO), at a value not usually significantly different from the comparable monometallic species. It is unlikely that there would be vibrational coupling between the two symmetrical ML(NO)X groups across the YC₆H₄Z group. In spectra of the asymmetric bimetallic complexes, two ν(NO) were expected, and were observed for [{MoL(NO)Cl}₂](NHC₆H₄O)] and its W analogue. In the molybdenum complex the band at 1 650 cm⁻¹ could be associated with the MoL(NO)(NHC₆H₄O)Mo fragment, whereas that at 1 670 cm⁻¹ may be due to the MoL(NO)(OC₆H₄NH)Mo residue. Similar assignments may be made of the NO stretching frequencies in [{WL(NO)Cl}₂](NHC₆H₄O)]; the band at lower frequency may be associated with WL(NO)(NHC₆H₄O)W and that at higher frequency with WL(NO)(OC₆H₄NH)W. The NO stretching frequencies in [{MoL(NO)X}₂](NHC₆H₄Z)] (X = I, Z = O; X = Cl, Z = S) were broad and could not be resolved into two components in KBr discs.

The ¹H n.m.r. spectra of the new complexes were generally unexceptional and are consistent with our formulations. There are two sets of characteristic resonances, two or three closely spaced signals in the range δ 5—6 p.p.m. due to the H⁴ protons of the pyrazolyl rings, and a set of lines in the range δ 2—3 due to the pyrazolyl methyl protons. In all of these complexes, three 4 H proton signals would be expected because of the asymmetry of the complexes and the observation of only two can be attributed either to accidental degeneracy or the recording of the spectra at low field where the signals were too close in chemical shift to be resolved.

In the monometallic complexes, the aromatic proton signals

Table 2. Electrochemical data for [ML(NO)X(YC₆H₄ZQ)]

M	X	Y	Z	Q ^a	E ₁ ^b (V)	E ₂ ^b (V)	ΔE _p ^{1c} (mV)	ΔE _p ² (mV)	n ^{1d}	n ²	Remarks ^e
Mo	Cl	NH	NH	H	-1.05	—	80	—	1.0	—	R
Mo	I	NH	NH	H	-1.03	—	—	—	1.0	—	I
W	Cl	NH	NH	H	-1.44	—	120	—	1.0	—	R
Mo	I	NH	O	H	-1.01	—	—	—	0.7	—	I
Mo	Cl	NH	O	Me	-0.96 ^f	—	90	—	1.0	—	R
W	Cl	NH	O	H	-1.38	—	90	—	1.0	—	R
Mo	Cl	NH	S	Me	-0.84 ^f	—	80	—	1.0	—	R
Mo	Cl	NH	S	H	+0.02	—	—	—	—	—	I
					-0.74	—	—	—	1.0	—	I
					-1.25	—	100	—	1.0	—	R
					-0.42 ^f	—	90	—	1.0	—	R
Mo	Cl	O	O	Me	-0.61	-1.46	70	80	1.0	1.0	R, R
Mo	Cl	NH	NH	'MoCl'	-0.61	-1.46	70	80	1.0	1.0	R, R
Mo	I	NH	NH	'MoI'	-0.49	-1.52	60	—	0.5	—	R, I
W	Cl	NH	NH	'WCl'	-1.16	-1.72	80	—	0.6	—	R, I
Mo	Cl	NH	O	'MoCl'	-0.24	-1.24	70	120	1.0	1.0	R
Mo	I	NH	O	'MoI'	-0.15	-1.16	100	70	1.0	0.7	R, R
Mo	Cl	NH	S	'MoCl'	-0.31	-1.10	100	120	1.0	1.0	R, R
Mo	Cl	O	O	'MoCl'	-0.26	-0.72	80	120	1.0	1.0	R, R
Mo	I	NH	NH	'WCl'	-0.74	-1.66	60	—	0.8	—	R, I
Mo	I	O	NH	'WCl'	-0.28	-1.60	70	—	1.0	0.7	R, I

^a 'MoCl' = MoL(NO)Cl, 'MoI' = MoL(NO)I, and 'WCl' = WL(NO)Cl. ^b In V vs. saturated calomel electrode (s.c.e.) in MeCN at Pt bead with [NBu₄]⁺[PF₆]⁻ (0.2 mol dm⁻³) as base electrolyte and 0.3 V s⁻¹ scan rate. ^c Difference between anodic and cathodic peak potentials. For [Fe(η-C₅H₅)₂]-[Fe(η-C₅H₅)₂]⁺ couple, ΔE_p = 80 mV. ^d Number of electrons involved in electrode process. Determined by comparison with [MoL(NO)Cl₂]; *i*_pv⁻¹[concn.]⁻¹ = 6.5 × 10⁻² A V⁻¹ s¹ dm³ mol⁻¹; [concn.] = concentration of electroactive species. ^e R = Fully reversible process, checked by plotting scan rate *v* versus *i*_pv⁻¹, where straight line is obtained; I = irreversible process. ^f Obtained from S. C. Charsley, Ph.D. Thesis, University of Birmingham, 1985.

in the group $M(YC_6H_4ZH)$ appear essentially as A_2B_2 -type spectra. In the anilino spectra, $\delta(NH)$ in the Mo complexes occurred at chemical shifts in the range 12–14 p.p.m., whereas that in the W complexes appears between 10 and 12 p.p.m.

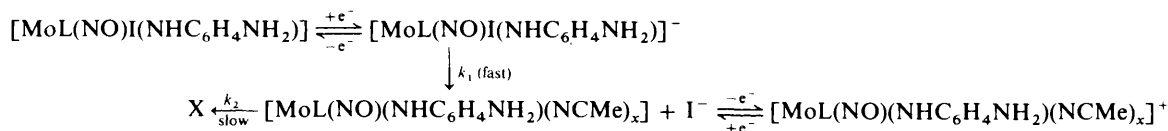
In the spectra of the bimetallic species, the intensities of the pyrazolyl protons relative to those of the aromatic ring were close to 21:2, consistent with the bimetallic nature of the complexes. In the symmetric species, the YC_6H_4Z protons occurred as a singlet, whereas in the asymmetric complexes the aromatic proton resonances usually appeared as a complex multiplet.

The 1H n.m.r. spectra of the heterobimetallic complexes were generally similar to those of their homobimetallic analogues. The aromatic signals appeared as A_2B_2 -type multiplets, and $\delta(NH)$ of the various complexes could be assigned to either $Mo(NHC_6H_4O)$ or $W(NHC_6H_4O)$ on the basis of the data obtained from their monometallic progenitors.

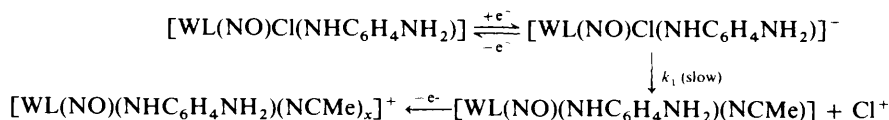
Electrochemical Studies.—All of the complexes were investigated by cyclic voltammetry (c.v.) in acetonitrile using a Pt bead electrode. The monomeric species exhibited one reduction process and the bimetallic complexes two (data summarised in Table 2). A number of the electrode processes were reversible or nearly so, this being established by comparison of wave shape with that of the electrode behaviour of ferrocene under the same conditions. The separation of peaks in reversible systems varied from 70 to 120 mV depending on the solvent and the cells used for the measurements, and all the data obtained were reproducible, the experimental error being ± 15 mV. Reversibility was also established in a number of cases by plotting c.v. scan rate v , versus $i_p v^{1/2}$, a straight line being obtained. The number of electrons in a number of selected electrode processes was established by coulometry.

We have noted previously¹⁷ that the reduction potentials for $[MoL(NO)I(NHR')]^-$ occur in the range -0.60 to -1.10 V and those for the corresponding aryloxy derivatives in the range -0.10 to -0.34 V. In general, the reduction potentials of the tungsten chloro complexes were substantially more cathodic than their molybdenum iodo counterparts (390–600 mV). We also observed generally that the redox processes of the chloro complexes were electrochemically reversible, whereas the iodo complexes, especially those containing NHR' , gave rise often to irreversible electrode behaviour. This is almost certainly due to the dissociation of I^- following electron transfer as we have described previously, and which we indicate below.

Monometallic complexes. Controlled potential electrolysis of $[MoL(NO)I(NHC_6H_4NH_2)]^-$ was carried out in acetonitrile. The neutral species was reduced irreversibly in a one-electron step, giving $[MoL(NO)I(NHC_6H_4NH_2)]^-$ (Scheme 1). Dissociation of I^- then rapidly occurred (the $I^- \rightarrow \frac{1}{2}I_2$ and $I^- \rightarrow I_3^-$ oxidation peaks being detected), $[MoL(NO)(NHC_6H_4NH_2)(NCMe)_x]$ presumably being formed. This solvated species underwent a reversible oxidation ($E = -0.79$ V) but



Scheme 1.



Scheme 2.

slowly reacted to form a new unidentified species, X. The related tungsten complex $[WL(NO)Cl(NHC_6H_4NH_2)]^-$ was similarly investigated (Scheme 2), and it was noted that dissociation of Cl^- was very slow indeed in comparison to that of I^- from $[MoL(NO)I(NHC_6H_4NH_2)]^-$. The solvated species $[WL(NO)(NHC_6H_4NH_2)(NCMe)_x]$ exhibited an oxidation peak at $E_p = -0.72$ V, and a reduction peak at -0.94 V. However the peak separation between these two waves (220 mV) is too large for the electrode behaviour to be that of a reversible one-electron transfer.

The electrochemical behaviour of $[MoL(NO)Cl(NHC_6H_4SH)]^-$ was complex. On sweeping the potential range from 0 to -2.0 V, an irreversible apparently one-electron reduction at -0.74 V and a reversible one-electron process at -1.25 V were detected. By comparison with the redox behaviour of the closely related $[MoL(NO)Cl(NHC_6H_4SMe)]^-$ (reversible one-electron reduction at -0.84 V) we might reasonably have assigned the wave in the thiol species at -0.74 to the formation of $[MoL(NO)Cl(NHC_6H_4SH)]^-$. However, our experience with chloromolybdenum complexes has been that the reduction process is reversible or nearly so, and that dissociation of Cl^- , which might give rise, as in the iodo analogues, to irreversible electrode behaviour, is very slow indeed. An alternative explanation for this irreversible process could be the generation of $[MoL(NO)Cl(NHC_6H_4SH)]^-$ with loss of H_2 , giving $[MoL(NO)Cl(NHC_6H_4S)]^-$. The reversible wave at -1.25 V could then be due to subsequent reduction of this, which would be at significantly more cathodic potentials because of the negative charge. The anodic process, at $+0.02$ V, may be due to oxidation of the thiol, giving $[MoL(NO)Cl(NHC_6H_4S-SC_6H_4NH)MoL(NO)Cl]$. However, a more detailed study of these species is necessary before firm conclusions as to the nature of their redox characteristics can be drawn.

Bimetallic complexes. The electrode behaviour of the bimetallic species will be discussed under three headings: (i) that of the symmetrical species $[ML(NO)X]_2(YC_6H_4Z)]$ ($Y = Z$), (ii) the asymmetric complexes $[ML(NO)X]_2(YC_6H_4Z)]$ ($Y \neq Z$), and (iii) that of the heterobimetallic compounds $[MoL(NO)I(NHC_6H_4NH)WL(NO)Cl]$ and $[MoL(NO)I(NHC_6H_4O)WL(NO)Cl]$.

(i) *Symmetric complexes.* The species $[MoL(NO)Cl]_2(NHC_6H_4NH)]^-$ underwent two reversible one-electron reductions, corresponding to the formation of $[MoL(NO)Cl]_2(NHC_6H_4NH)]^-$ and $[MoL(NO)Cl]_2(NHC_6H_4NH)]^{2-}$. The separation between these two waves (ΔE , Table 3) is 850 mV. The values of E_1 and E_2 may be compared with that of the monometallic progenitor, E_m , at -1.05 V, the separation between this wave and E_1 and E_2 being 440 and 410 mV, respectively. Reduction of $[WL(NO)Cl]_2(NHC_6H_4NH)]^-$ was similar, ΔE being 560 mV, although there must be some uncertainty in this value since E_2 was irreversible. The separation between E_m and E_1 and E_2 was 280 mV in each case. Reduction of $[MoL(NO)Cl]_2(OC_6H_4O)]^-$ occurred in two

Table 3. Comparative half-wave potentials for mono- and bi-metallic complexes, $[ML(NO)X(YC_6H_4Z)]$

M	X	Y	Bimetallic species				Monometallic species			
			Z	E_1^a	E_2^a	ΔE^b	Z	E_m	$(E_m - E_1)^b$	$(E_m - E_2)^b$
Mo	Cl	NH	NHMoL(NO)Cl	-0.61	-1.46	850	NH ₂	-1.05	440	410
Mo	I	NH	NHMoL(NO)I	-0.49	-1.52	1 030	NH ₂	-1.03	540	490
W	Cl	NH	NHWL(NO)Cl	-1.16	-1.72	560	NH ₂	-1.44	280	280
Mo	Cl	O	OMoL(NO)Cl	-0.26	-0.72	460	OMe	-0.42	160	300
Mo ^c	Cl	NH	OMoL(NO)Cl	-0.24			OMe	-0.42		180
Mo ^c	I	NH	OMoL(NO)I	-0.15						
					-1.24					
Mo ^c	Cl	NH	SMoL(NO)Cl	-0.31			OH	-1.01		150
					-1.16					
Mo ^c	I	NH	NHWL(NO)Cl	-0.74			SMe	-0.84		260
					-1.10		NH ₂	-1.03	290	260
Mo ^c	I	NH	NHWL(NO)Cl	-0.74			NH ₂	-1.44		220
					-1.66		OMe	-0.42	140	220
Mo ^c	I	O	NHWL(NO)Cl	-0.28			OH	-1.38		160
					-1.60					

^a In V. ^b In mV, $E_m = E_1$ of monometallic species for comparison. ^c Upper figures relate to redox centre ML(NO)X, lower figures to redox centre Z.

steps at potentials significantly more anodic than those of the related $NHC_6H_4NH_2^{2-}$ species, as expected. ΔE in this complex was 460 mV and the separations between E_m {estimated from $[MoL(NO)Cl(OC_6H_4OMe)]$ since $[MoL(NO)Cl(OC_6H_4OH)]$ was not available} and E_1 and E_2 were 160 and 300 mV respectively.

These electrochemical results indicate that the molybdenum centres in $[MoL(NO)Cl_2(YC_6H_4Z)]$; (Y = Z, O or NH), interact strongly and the nature of this interaction warrants some comment.

In order to account for strong metal-metal interactions in 'valence-trapped' systems containing bridging aryl groups it is perhaps most simple initially to use a substituent effect model. Thus in the compounds described here the electron 'deficient' $MoL(NO)ClY-$ moiety might be regarded as an electron-withdrawing substituent which facilitates reduction of the complementary $MoL(NO)ClZ-$ moiety through both polar and mesomeric effects. Once the first reduction has occurred, the reduced substituent $MoL(NO)ClZ-$ acts as an electron releasing group so that the second reduction potential of the complex is substantially more cathodic than the first. The sensitivity of the $Mo(NO)^4$ centre to such substituent effects is well established^{14,18} and reaction constants for the reduction of such species fall in the range 5—7. The separations of E_1 and E_2 from each other and from E_m may thus be regarded as a measure of the substituent effects exerted by the oxidised or reduced molybdenum-containing substituents.

Preliminary e.s.r. studies have shown that such a model would be appropriate in the homobimetallic complexes containing *meta*-substituted aryl bridges.^{19,20} The e.s.r. spectrum of $[MoL(NO)Cl_2(OC_6H_4O-m)]^-$, produced by cobaltocene reduction of the diamagnetic species in CH_2Cl_2 solution, exhibited a signal at $g = 1.969$ with a hyperfine coupling constant (to ⁹⁵Mo and ⁹⁷Mo each spin $\frac{1}{2}$ at 15.9% and 9.6% abundancies respectively) $\langle A_{Mo} \rangle = 4.78$ mT. This may be compared with the values of $g = 1.968$ and $\langle A_{Mo} \rangle = 4.69$ mT found for $[MoL(NO)Cl(OC_6H_4OMe-p)]^-$ under similar conditions and indicates that this mixed-valence species is 'valence trapped'. Further comparisons may be made with e.s.r. data for other 17-electron complexes containing the $MoL(NO)^+$ moiety. In the electrochemically reduced monometallic species $[MoL(NO)Cl(NHC_6H_4Z-p)]^-$ (Z = H, Me, CO₂Me, CH, Cl, or NO₂), e.s.r. signals are found in the region $g = 1.969$ —1.973 with hyperfine couplings in the range $\langle A_{Mo} \rangle = 4.89$ —5.19 mT.²⁰ Similarly the electrochemically reduced bimetallic complex $[MoL(NO)Cl_2\{N(CH_2CH_2)_2N\}]^-$, in

which a saturated bridge precludes electron delocalisation between the metal centres, exhibits an e.s.r. spectrum with $g = 1.974$ and $\langle A_{Mo} \rangle = 4.89$ mT.²¹ The air-stable monometallic 17-electron complexes $[MoL(NO)A_2]^+$ (A = pyridine, imidazole, *N*-methylimidazole, or pyrazole) exhibit e.s.r. signals in the region $g = 1.974$ —1.997 with hyperfine couplings in the range $\langle A_{Mo} \rangle = 4.89$ —5.08 mT.²² Detailed studies of these latter compounds indicate that the unpaired electron occupies an orbital of axial symmetry, being substantially metallic in character with no evidence of delocalisation onto the heterocyclic ligands.

A rather different picture emerges from e.s.r. spectral investigations of the homobimetallic complexes containing *para*-substituted aryl bridges. The e.s.r. spectra of $[MoL(NO)Cl_2(YC_6H_4Y-p)]^-$ (Y = O or NH) generated by cobaltocene reduction of the diamagnetic species in CH_2Cl_2 solution, exhibit signals at $g = 1.969$ (Y = O) and $g = 1.972$ (Y = NH) with reduced hyperfine coupling constants of $\langle A_{Mo} \rangle = 2.53$ mT (Y = O) and $\langle A_{Mo} \rangle = 2.58$ mT (Y = NH) attributable to the 24% of molecules containing either ⁹⁵Mo or ⁹⁷Mo. Weak satellites were also observed for the 1.5% of molecules containing both ⁹⁵Mo and ⁹⁷Mo. These results indicate that these species are not 'valence trapped' on the e.s.r. time-scale. Further studies of these systems are in progress to determine whether they might be genuinely delocalised. If such were to be the case the use of a 'substituent effect' model, as outlined earlier, would be inappropriate since the substituent and the reaction site could no longer be distinguished. Under these circumstances a model for the mixed-valence species involving direct coupling of the metal-based redox orbitals through delocalised bridge ligand orbitals becomes necessary. However, in 'valence-trapped' systems we believe that the inherent simplicity of a substituent effect model for rationalising the electrochemical properties of bimetallic species has much to commend it.

(ii) *Asymmetric complexes.* Two clearly defined one-electron reductions were again observed, but ΔE (790—1 000 mV) cannot be treated in the same way as for the symmetric species in (i) above.

Recalling that E_1 values for the reductions of phenolato species are substantially more anodic than their arylamido counterparts, it is likely that the E_1 value at -0.24 V in $[MoL(NO)Cl_2(NHC_6H_4O)]^-$ and at -0.15 V in the related iodo complex are associated with the $MoL(NO)X(OR')$ redox centre. Those waves in the region of -1.20 V may therefore be due to the $MoL(NO)X(NHR')$ moiety. These assignments are

consistent¹⁷ with E_3 for $[\text{MoL}(\text{NO})\text{X}(\text{NHC}_6\text{H}_4\text{NH}_2)]$ (ca. -1.04 V) and $[\text{MoL}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{OMe})]$ (-0.42 V).

It may also be noted that the E_3 values for the first reduction process in these bimetallics are significantly more anodic than that for $[\text{MoL}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{OMe})]$, whereas those for the second reduction waves are more cathodic than those for $[\text{MoL}(\text{NO})\text{X}(\text{NHR}')]$. This again could be regarded as a reflection of the influence of the electron-withdrawing effect of neutral $\text{MoL}(\text{NO})\text{X}$ and the electron-releasing influence of anionic $\text{MoL}(\text{NO})\text{X}^-$ on the adjacent redox centre.

(iii) *Heterobimetallic complexes.* Again, two well separated one-electron reductions are observed, but, as in (ii), ΔE is not especially significant. However, in the voltammogram of $[\text{MoL}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH})\text{WL}(\text{NO})\text{Cl}]$, the reduction at -0.74 V may be associated with the $\text{MoL}(\text{NO})\text{I}$ fragment, by comparison with E_3 from $[\text{MoL}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{NH}_2)]$ (-1.03 V) and that at -1.66 V with the $\text{WL}(\text{NO})\text{Cl}$ fragment (-1.44 V in the corresponding monometallic). Thus there is an anodic shift of 290 mV in E_1 with respect to the Mo-containing monometallic, and a cathodic shift of 220 mV in E_2 with respect to $[\text{WL}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{NH}_2)]$. A similar but smaller effect is observed in the c.v. of $[\text{MoL}(\text{NO})\text{I}(\text{OC}_6\text{H}_4\text{NH})\text{WL}(\text{NO})\text{Cl}]$ where $E_m(\text{W}) - E_2 = 160$ mV. The assignment of the first reduction wave ($E_1 = -0.28$ V) to the $\text{MoL}(\text{NO})\text{I}(\text{OR}')$ fragment and not to $\text{MoL}(\text{NO})\text{I}(\text{NHR}')$ (the other possible isomeric fragment of the bimetallic) is consistent with the method of preparation of the compound, the position of E_1 relative to E_3 in $[\text{MoL}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{OMe})]$ (-0.42 V), $[\text{MoL}(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{OH})]$ (-1.01 V), and $[\text{WL}(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{OH})]$ (-1.38 V).

The anodic and cathodic shifts of E_1 and E_2 above relative to E_m are again in accord with the electronegativity of the $\text{WL}(\text{NO})\text{Cl}(\text{NHR}')$ and $\text{MoL}(\text{NO})\text{Cl}(\text{OR}')$ fragments.

Conclusions. We may note that the reduction potentials of a number of the complexes reported above are such that reduction should be possible chemically, giving relatively stable monoanionic species. This is likely to be possible with $[\text{MoL}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{OMe})]$, $[\{\text{MoL}(\text{NO})\text{X}\}_2(\text{NHC}_6\text{H}_4\text{Z})]$ ($\text{X} = \text{Cl}, \text{I}$ and $\text{Z} = \text{O}; \text{X} = \text{Cl}, \text{Z} = \text{S}$), $[\{\text{MoL}(\text{NO})\text{Cl}\}_2(\text{OC}_6\text{H}_4\text{O})]$, and $[\text{MoL}(\text{NO})\text{I}(\text{OC}_6\text{H}_4\text{NH})\text{WL}(\text{NO})\text{Cl}]$, where the monoanionic species are generated at potentials more anodic than -0.4 V vs. s.c.e. The syntheses and spectroscopic properties of these reduced species are under investigation and will be described in a future paper.

Acknowledgements

We are grateful to the S.E.R.C. (S. M. C., B. D. N., and S. J. R.) and to the Italian C.N.R. (G. D.) for support, and to Mr. T. C. Green for technical assistance.

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Received 9th January 1987; Paper 7/059