Monometallic, Homo- and Hetero-bimetallic Complexes Based on Redox-active Tris(3,5-dimethylpyrazolyl)borato Molybdenum and Tungsten Nitrosyls. Part 8.[1] Complexes exhibiting Weak or Intermediate Interaction between Two Redox Centres †

Stephen M. Charsley, Christopher J. Jones, Jon A. McCleverty,* Bryan D. Neaves, and Sarah J. Reynolds
Department of Chemistry, The University of Birmingham, P. O. Box 363, Birmingham B15 2TT

The complexes [ML(NO)X(NHQNH$_2$)] [L = tris(3,5-dimethylpyrazolyl)borate; M = Mo, X = I, Q = (C$_6$H$_4$)$_2$Y where Y = O, SO$_2$, CH$_2$, or CH$_2$CH$_2$; M = W, X = Cl, Q = (C$_6$H$_4$)$_2$O], [MoL(NO)I(NHCH$_2$CH$_2$C$_6$H$_4$NH$_2$)], [ML(NO)X(OQOH)] [M = Mo, X = I, Q = (C$_6$H$_4$)$_2$Y where Y = nothing or S; X = Cl, Q = (C$_6$H$_4$)$_2$S], and [ML(NO)X(OCH$_2$C$_6$H$_4$CH$_2$OH)] (M = Mo, X = I; M = W, X = Cl) have been prepared. The bimetallic complexes [{ML(NO)X}$_2$(NHQNH)] [M = Mo, X = I, Q = (C$_6$H$_4$)$_2$Y where Y = O, SO$_2$, CH$_2$, or CH$_2$CH$_2$; M = W, X = Cl, Q = (C$_6$H$_4$)$_2$O], [{MoL(NO)I}$_2$(NHCH$_2$CH$_2$C$_6$H$_4$NH)], [{MoL(NO)X}$_2$(OQO)] [X = I, Q = (C$_6$H$_4$)$_2$Y where Y = nothing or S; X = Cl, Q = (C$_6$H$_4$)$_2$Y where Y = nothing, S, SO$_2$, CO, or COC$_6$H$_4$C$_6$H$_4$CO], and [{ML(NO)X}$_2$(OCH$_2$C$_6$H$_4$CH$_2$O)] (M = Mo, X = I; M = W, X = Cl) were obtained either from the monometallics by reaction with [ML(NO)X$_2$] or by direct reaction of the latter with the appropriate arylamine or phenol. The heterobimetallic [MoL(NO)I(NHC$_6$H$_4$OC$_6$H$_4$NH)WL(NO)Cl] was also prepared and all compounds were characterised spectroscopically. The monometallic species underwent a single, usually reversible, one-electron reduction determined by cyclic voltammetry (in CH$_3$CN using a Pt electrode). Values of $E_{\frac{1}{2}}$ were dependent on M, X, and the nature of the heteroatom ligand. The bimetallic species underwent two one-electron reductions, investigated by differential pulse polarography. The separation between the redox potentials ($\Delta E_{\frac{1}{2}}$) varied from 45 mV (negligible interaction between redox centres) to 138 mV (weak interaction), depending on the nature of the bridging ligand.

In the previous paper[1] we described the synthesis and electrochemical characteristics of the bimetallic species [{ML(NO)X}$_2$Q] {L = tris(3,5-dimethylpyrazolyl)borate [HB(Me$_2$pz)$_3$]; M = Mo or W; X = Cl or I; M = W, X = Cl; Q = NHC$_6$H$_4$NH, OC$_6$H$_4$NH, OC$_6$H$_4$O, *etc.*}. The cyclic voltammetric data obtained from these compounds were analysed in terms of two strongly interacting redox centres ML(NO)$^{2+}$ *via* a polar and mesomeric effect. We noted that each bimetallic species exhibited two one-electron transfer processes, and that the extent of interaction between the two centres was reflected in the separation, in mV, between these two one-electron transfers: this being in the range 400—1 000 mV. We also observed that the $E_{\frac{1}{2}}$ values for the two reductions in the bimetallics were displaced significantly from $E_{\frac{1}{2}}$ for the comparable monometallic [ML(NO)X(QH)]. Thus the first reduction potential is significantly anodic and the second substantially cathodic with respect to $E_{\frac{1}{2}}$ (monometallic).

In this paper, we describe our further exploration of the electrochemical behaviour of this class of bimetallic compound. Our intention was to determine the effect of increasing the complexity of the aromatic ligand bridging the two redox centres, with a view to establishing whether, and at what point, interaction between the two redox centres would cease. A preliminary account of some of this work has been given.[2]

Experimental

All commercial reagents were used as supplied. [Mo{HB(Me$_2$pz)$_3$}(NO)X$_2$] (X = Cl[3] or I[4]) and [W{HB(Me$_2$pz)$_3$}(NO)Cl$_2$][4] were synthesised as described previously. All the complexes formed were stable for short periods in solution in the presence of air, and could be purified by column chromatography using silica gel 60 (70—230 mesh) and dichloromethane as eluant. The main fraction was collected.

I.r. spectra were obtained using a PE 357 spectrophotometer, and ^{1}H n.m.r. data were measured using Varian XL 100, JEOL JNMGX 270, and Bruker 400 spectrometers. Cyclic voltammetric data were obtained using a Hitek PPR1 waveform generator and DT2101 potentiostat, and a PAR 174 instrument. Solutions in acetonitrile were *ca.* 10^{-3} mol dm^{-3} in the complex, and [NBu$^n_4$][BF$_4$] (0.2 mol dm^{-3}) was used as the base electrolyte. A Pt wire was employed as the test electrode, and controlled potential electrolyses were performed in stirred solutions of the complexes in acetonitrile under nitrogen. Differential pulse polarography (d.p.p.) was carried out using the PAR 174 A instrument, using acetonitrile as solvent and [NBu$^n_4$][BF$_4$] (0.2 mol dm^{-3}) as supporting electrolyte. A pulse amplitude of 10 mV was used, and [MoL(NO)Cl$_2$] employed as a standard exhibiting a one-electron reversible wave.

In d.p.p. the current *vs.* potential curve is a Δi *vs.* E relationship. To obtain $\Delta E_{\frac{1}{2}}$ values from these waves the relationships developed by Richardson and Taube[5] were used. A graph of $w_{\frac{1}{2}}$ (d.p.p. peak width at half-height) *vs.* $\Delta E_{\frac{1}{2}}$ was constructed as shown previously.[5] The value for $w_{\frac{1}{2}}$ for [MoL(NO)Cl$_2$] was 98 mV and the theoretical value for a one-electron process is 91 mV.

Preparations.—[MoL(NO)I(NHC$_6$H$_4$SO$_2$C$_6$H$_4$NH$_2$)]. A solution of [MoL(NO)I$_2$] (0.5 g) and bis(*p*-aminophenyl) sulphone (0.37 g) in dichloromethane (60 cm^3) was stirred for 3 d at room temperature (r.t.). The solution was filtered and the dark brown filtrate was evaporated *in vacuo* until only *ca.* 5 cm^3

---

† *Supplementary data available* (No. SUP 56686, 12 pp.): i.r. and ^{1}H n.m.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

remained. Addition of n-hexane caused the *complex* to precipitate as a brown powder (0.28 g, 48%).

$[MoL(NO)I(NHCH_2CH_2C_6H_4NH_2)]$. This complex was prepared in the same way as that described above, using $[MoL(NO)I_2]$ (1.0 g) and *p*-(2-aminoethyl)phenylamine (0.4 g). The pink powder which was obtained was further purified using column chromatography, the solid ultimately obtained being recrystallised from dichloromethane–n-hexane (0.6 g, 59%). It was isolated as a red-brown solid.

The complexes $[MoL(NO)I(NHC_6H_4CH_2C_6H_4NH_2)]$ (59%), $[MoL(NO)I(NHC_6H_4CH_2CH_2C_6H_4NH_2)]$ (58%), and $[MoL(NO)I(NHC_6H_4OC_6H_4NH_2)]$ (59%) were obtained in the same way, all as red-brown solids.

$[WL(NO)Cl(NHC_6H_4OC_6H_4NH_2)]$. A solution of $[WL(NO)Cl_2]$ (1.0 g) and bis(*p*-aminophenyl) ether (0.68 g) in dichloromethane (60 cm^3) was refluxed for 3 d. The mixture was then cooled, filtered, and the orange-brown filtrate evaporated *in vacuo*. The solid so obtained was taken up in the minimum volume of dichloromethane, and chromatographed. The main orange fraction was collected and, after work-up and recrystallisation from dichloromethane–n-hexane mixtures afforded the *complex* as an orange solid (1.08 g, 84%).

$[MoL(NO)I(OC_6H_4C_6H_4OH)]$ *and* $[\{MoL(NO)I\}_2(OC_6H_4C_6H_4O)]$. A solution of $[MoL(NO)I_2]$ (1.0 g) and 4,4′-biphenyldiol (0.28 g) in toluene (60 cm^3) was refluxed overnight. The mixture was evaporated *in vacuo* giving a deep purple solid. Thin-layer chromatography showed this to be a mixture of two compounds. Using column chromatography, the first purple fraction was collected and identified as $[\{MoL(NO)I\}_2(OC_6H_4C_6H_4O)]$ and the second purple fraction was similarly collected and shown to be $[MoL(NO)I(OC_6H_4C_6H_4OH)]$. Both species were recrystallised from dichloromethane–n-hexane mixtures giving purple solids (0.15 g, 27% for the monometallic; 0.17 g, 17% for the bimetallic).

The complexes $[MoL(NO)I(OC_6H_4SC_6H_4OH)]$ (purple, 22%), $[\{MoL(NO)I\}_2(OC_6H_4SC_6H_4O)]$ (purple, 18%), $[MoL(NO)I(OCH_2C_6H_4CH_2OH)]$ (red-brown, 20%), and $[\{MoL(NO)I\}_2(OCH_2C_6H_4CH_2O)]$ (red-brown, 33%) were obtained similarly.

$[MoL(NO)Cl(OC_6H_4SC_6H_4OH)]$. A solution of $[MoL(NO)Cl_2]$ (0.5 g), bis(*p*-hydroxyphenyl) sulphide (0.22 g), and NaH (an excess, 0.1 g) in dichloromethane (75 cm^3) was refluxed for 2 d. The resulting purple mixture was filtered and the filtrate evaporated *in vacuo*. The solid obtained was purified by chromatography using tetrahydrofuran (thf)–dichloromethane mixtures (10% thf) as eluant. The main purple fraction was collected and recrystallisation of the solid from dichloromethane–n-pentane afforded the *complex* as a purple powder (0.3 g, 44%).

$[WL(NO)Cl(OCH_2C_6H_4CH_2OH)]$. This complex was prepared in the same way as $[MoL(NO)I(OCH_2C_6H_4CH_2OH)]$. The complex was obtained as a purple solid on recrystallisation from dichloromethane–n-hexane mixtures (0.25 g, 21%).

$[\{MoL(NO)I\}_2(NHCH_2CH_2C_6H_4NH)]$. A solution of $[MoL(NO)I_2]$ (2.0 g) and *p*-(2-aminoethyl)phenylamine (0.2 g) in dichloromethane (60 cm^3) was stirred at r.t. for *ca.* 1.5 h, during which time the solution changed to red-brown. The solution was filtered and the filtrate evaporated to *ca.* 5 cm^3 *in vacuo*. Addition of n-hexane afforded the *complex* as a brown precipitate (1.01 g, 58%).

$[\{MoL(NO)I\}_2(NHC_6H_4CH_2C_6H_4NH)]$. *Method 1.* A solution of $[MoL(NO)I_2]$ (0.4 g) and $[MoL(NO)I(NHC_6H_4CH_2C_6H_4NH_2)]$ (0.44 g) in dichloromethane (50 cm^3) was stirred at r.t. overnight. The solution was filtered and the dark brown filtrate evaporated *in vacuo* to *ca.* 5 cm^3. Addition of n-hexane afforded the *complex* as a brown powder (0.43 g, 56%).

Method 2. A solution of $[MoL(NO)I_2]$ (1.0 g) and 4,4′-methylenedianiline (0.14 g) in dichloromethane (60 cm^3) was stirred at r.t. overnight. The *complex* was isolated by the procedure described above as a brown solid (0.72 g, 75%).

The complexes $[\{MoL(NO)I\}_2(NHC_6H_4CH_2CH_2C_6H_4NH)]$ (72%), $[\{MoL(NO)I\}_2(NHC_6H_4OC_6H_4NH)]$ (59%), and $[\{MoL(NO)I\}_2(NHC_6H_4SO_2C_6H_4NH)]$ (42%) could be obtained either by Method 1 or 2, as red-brown solids.

$[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$. A solution of $[MoL(NO)I_2]$ (0.45 g) and $[WL(NO)Cl(NHC_6H_4OC_6H_4NH_2)]$ (0.5 g) in dichloromethane (100 cm^3) was stirred at r.t. for 3 d. The solution was then filtered and the solvent evaporated *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed, the main red fraction being collected. After evaporation and recrystallisation from dichloromethane–n-hexane mixtures, the *complex* was obtained as a red solid (0.28 g, 33%).

$[\{WL(NO)Cl\}_2(NHC_6H_4OC_6H_4NH)]$ was prepared similarly.

$[\{MoL(NO)Cl\}_2(OC_6H_4SC_6H_4O)]$. A solution of $[MoL(NO)Cl_2]$ (0.5 g), bis(*p*-hydroxyphenyl) sulphide (0.11 g), and NaH (0.2 g, an excess) in dichloromethane (75 cm^3) was refluxed for 2 d. The resulting purple mixture was filtered and the filtrate evaporated *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed, using dichloromethane as eluant. The main purple fraction was collected, the solvent evaporated, and the solid recrystallised from dichloromethane–n-pentane mixtures giving the *complex* as black microcrystals (0.2 g, 34%).

The complexes $[\{MoL(NO)Cl\}_2(OC_6H_4C_6H_4O)]$ (25%; black microcrystals) and $[\{MoL(NO)Cl\}_2(OC_6H_4COC_6H_4C_6H_4COC_6H_4O)]$ (46%, black crystals) were obtained similarly, the latter being purified by chromatography using dichloromethane containing thf (10% by volume). The former was purple in solution while the latter was orange-red.

$[\{WL(NO)Cl\}_2(OCH_2C_6H_4CH_2O)]$. This complex was prepared in the same way as $[\{MoL(NO)I\}_2(OC_6H_4C_6H_4O)]$ using $[WL(NO)Cl_2]$ in place of $[MoL(NO)I_2]$. The solid obtained was recrystallised from dichloromethane–n-hexane affording the *complex* as a purple solid (0.11 g, 21%).

$[\{MoL(NO)Cl\}_2(OC_6H_4SO_2C_6H_4O)]$. A solution of $[MoL(NO)Cl_2]$ (0.5 g), 4,4′-sulphonyldiphenol (0.13 g) and NaH (0.2 g, an excess) in a 1:1 mixture of dichloromethane and thf (80 cm^3) was refluxed for 2 d. The resulting dark red-brown mixture was filtered and the filtrate evaporated *in vacuo*. The solid obtained was purified by chromatography using dichloromethane as eluant. The main red-brown fraction was collected and after evaporation of the solvent and recrystallisation from dichloromethane–n-pentane mixtures, the *complex* was isolated as a red-brown powder (0.2 g, 54%).

The complex $[\{MoL(NO)Cl\}_2(OC_6H_4COC_6H_4O)]$ was obtained similarly using a 4:1 mixture of dichloromethane and thf, and was obtained as black microcrystals (0.28 g, 50%; orange-red in solution).

Results and Discussion

Synthetic Studies.—The monometallic arylamido species $[MoL(NO)I(NHR')]$ ($R' = C_6H_4YC_6H_4NH_2$, where $Y = CH_2$, CH_2CH_2, O, or SO_2) and $[MoL(NO)I(NHCH_2CH_2C_6H_4NH_2)]$ were obtained by reaction of $[MoL(NO)I_2]$ with a two-fold excess of the appropriate amine in dichloromethane at room temperature. The bimetallic arylamido species $[\{MoL(NO)I\}_2(NHQNH)]$ [$Q = (C_6H_4)_2Y$, where $Y = CH_2$, CH_2CH_2, O, or SO_2] and $[\{MoL(NO)I\}_2(NHCH_2CH_2C_6H_4NH)]$ could be obtained by two routes: either addition of a molar equivalent of $[MoL(NO)I_2]$ to $[MoL(NO)I(NHR')]$ (R' as above) in dichloromethane at room temperature, or reaction of two molar equivalents of $[MoL(NO)I_2]$ with one of the appropriate amine in refluxing dichloromethane. The related

Table 1. Elemental analyses for $[ML(NO)XY]\cdot nC_6H_{14}$ and $[ML(NO)X(\text{-}Y\text{-})M'L(NO)X']\cdot nC_6H_{14}$ [L = $HB(Me_2pz)_3$]

						Analysis (%)[b]			
M	M′	X	X′	Y	*n*[a]	C	H	N	I
Mo	—	I	—	$NHC_6H_4OC_6H_4NH_2$	0	43.2 (43.3)	4.6 (4.4)	16.4 (14.4)	16.6 (16.9)
Mo	—	I	—	$NHC_6H_4SO_2C_6H_4NH_2$	$\frac{1}{6}$	41.7 (41.5)	4.7 (4.4)	15.3 (15.5)	16.1 (15.6)
Mo	—	I	—	$NHC_6H_4CH_2C_6H_4NH_2$	0	44.6 (45.0)	4.9 (4.7)	17.1 (16.9)	16.8 (17.0)
Mo	—	I	—	$NHC_6H_4CH_2CH_2C_6H_4NH_2$	0	45.2 (45.8)	5.0 (5.0)	16.5 (16.6)	16.4 (16.7)
Mo	—	I	—	$NHCH_2CH_2C_6H_4NH_2$	$\frac{1}{6}$	41.2 (41.2)	5.3 (5.0)	18.1 (18.0)	18.2 (18.1)
W	—	Cl	—	$NHC_6H_4OC_6H_4NH_2$	0	43.3 (43.5)	4.6 (4.5)	16.7 (16.9)	—
Mo	—	I	—	$OC_6H_4C_6H_4OH$	0	44.8 (44.1)	4.4 (4.3)	13.7 (13.3)	17.7 (17.3)
Mo	—	I	—	$OC_6H_4SC_6H_4OH$	$\frac{1}{6}$	43.3 (43.0)	4.7 (4.3)	12.7 (12.6)	—
Mo	—	Cl	—	$OC_6H_4SC_6H_4OH$	0	48.2 (48.0)	4.4 (4.6)	13.6 (14.5)	—
Mo	—	I	—	$OCH_2C_6H_4CH_2OH$	$\frac{1}{6}$	41.3 (41.1)	4.3 (4.7)	14.6 (14.0)	—
W	—	Cl	—	$OCH_2C_6H_4CH_2OH$	$\frac{1}{6}$	41.1 (41.3)	5.2 (4.8)	13.8 (14.1)	—
Mo	Mo	I	I	$NHC_6H_4OC_6H_4NH$	$\frac{1}{6}$	39.5 (39.4)	4.7 (4.3)	17.0 (17.1)	19.6 (19.3)
Mo	Mo	I	I	$NHC_6H_4SO_2C_6H_4NH$	$\frac{1}{6}$	38.2 (38.0)	4.6 (4.2)	16.3 (16.9)	18.1 (18.7)
Mo	Mo	I	I	$NHC_6H_4CH_2C_6H_4NH$	0	40.3 (39.8)	4.5 (4.4)	17.4 (17.3)	19.7 (19.6)
Mo	Mo	I	I	$NHC_6H_4CH_2CH_2C_6H_4NH$	0	40.1 (40.3)	4.2 (4.5)	16.8 (17.1)	19.7 (19.4)
W	W	Cl	Cl	$NHC_6H_4OC_6H_4NH$	$\frac{1}{6}$	40.2 (39.6)	4.8 (4.3)	16.9 (17.2)	—
Mo	W	I	Cl	$NHC_6H_4OC_6H_4NH$	$\frac{1}{3}$	40.2 (40.1)	4.8 (4.4)	16.9 (17.0)	—
Mo	Mo	I	I	$NHCH_2CH_2C_6H_4NH$	0	37.0 (37.0)	4.6 (4.4)	17.9 (18.2)	20.2 (20.6)
Mo	Mo	I	I	$OC_6H_4C_6H_4O$	0	39.5 (39.3)	4.4 (4.1)	15.6 (15.3)	19.5 (19.8)
Mo	Mo	Cl	Cl	$OC_6H_4C_6H_4O$	[c]	45.4 (45.8)	5.1 (4.0)	16.8 (16.6)	—
Mo	Mo	I	I	$OC_6H_4SC_6H_4O$	0	38.4 (38.3)	4.2 (4.0)	15.2 (14.9)	19.3 (19.3)
Mo	Mo	Cl	Cl	$OC_6H_4SC_6H_4O$	1[d]	42.4 (42.4)	4.3 (4.4)	15.8 (16.1)	—
Mo	Mo	Cl	Cl	$OC_6H_4SO_2C_6H_4O$	1[e]	44.8 (44.5)	4.6 (4.8)	16.6 (16.3)	—
Mo	Mo	Cl	Cl	$OC_6H_4COC_6H_4O$	1[d]	43.0 (43.5)	4.1 (4.5)	15.4 (16.1)	—
Mo	Mo	Cl	Cl	$(OC_6H_4COC_6H_4)_2$	0.5[e]	52.5 (52.2)	4.9 (4.9)	15.2 (14.6)	—
Mo	Mo	I	I	$OCH_2C_6H_4CH_2O$	$\frac{1}{6}$	37.6 (37.5)	3.8 (4.4)	15.7 (15.7)	—
W	W	Cl	Cl	$OCH_2C_6H_4CH_2O$	$\frac{2}{3}$	39.0 (39.0)	4.6 (4.7)	15.4 (15.2)	—

[a] Number of moles of C_6H_{14}; this factor was confirmed by independent ^1H n.m.r. spectral integration. [b] Calculated values are given in parentheses. [c] 0.5 mole CH_2Cl_2, 0.5 mole C_5H_{12}. [d] Number of moles of CH_2Cl_2. [e] Number of moles of C_5H_{12}.

tungsten complexes $[WL(NO)Cl(NHC_6H_4OC_6H_4NHR)]$ [R = H or WL(NO)Cl] were prepared similarly but in refluxing dichloromethane.

The monometallic phenolic species, $[ML(NO)X(OR')]$ ($R' = C_6H_4C_6H_4OH$ or $C_6H_4SC_6H_4OH$; M = Mo, X = Cl or I; M = W, X = Cl) and $[MoL(NO)I(OCH_2C_6H_4CH_2OH)]$ were prepared by refluxing the appropriate metal-containing dihalide with the phenol in toluene. They were invariably isolated in low yields together with significant quantities of the bimetallic compounds $[\{MoL(NO)I\}_2(OC_6H_4C_6H_4O)]$, $[\{MoL(NO)I\}_2(OC_6H_4SC_6H_4O)]$, and $[\{ML(NO)X\}_2(OCH_2C_6H_4CH_2O)]$ (M = Mo, X = I; M = W, X = Cl), and the two types of complex were separated by column chromatography. $[MoL(NO)Cl(OC_6H_4SC_6H_4OH)]$ was prepared by treatment of $[MoL(NO)Cl_2]$ with a molar equivalent of bis(*p*-hydroxyphenyl) sulphide and a slight excess of NaH in dichloromethane. The species $[\{MoL(NO)Cl\}_2(OQO)]$ [$Q = (C_6H_4)_2Y$, where Y = S, SO_2, CO, $COC_6H_4C_6H_4CO$, or $C_6H_4C_6H_4$] were obtained by treatment of the biphenol with a two-fold excess of $[MoL(NO)Cl_2]$ and an excess of NaH in refluxing dichloromethane or dichloromethane–thf mixtures. The mixed-metal complex $[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$ was obtained by reaction of $[WL(NO)Cl(NHC_6H_4OC_6H_4NH_2)]$ with $[MoL(NO)I_2]$ in dichloromethane at room temperature. The analytical data for these new compounds are given in Table 1.

Spectroscopic Studies.—The i.r. spectra of the new complexes exhibited bands due to the tris(3,5-dimethylpyrazolyl)borato ligand and also bands associated with arylamido or phenolato ligands. The NO stretching frequencies of the mono- and bimetallic molybdenum arylamido iodo complexes occurred in the range 1 648—1 660 cm^{-1}, and the related phenolic species exhibited ν(NO) in the range 1 670—1 675 cm^{-1}, both consistent with earlier observations.[6,7] The mono- and bi-metallic molybdenum species containing $OCH_2C_6H_4CH_2O(H)$ showed ν(NO) at 1 660 cm^{-1}, whereas ν(NO) in the related tungsten complexes occurred at 1 630 cm^{-1}. The chloro molybdenum species containing bridging phenolato ligands showed ν(NO) in the range 1 678—1 685 cm^{-1}.

In the heterobimetallic complex $[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$, two NO stretching frequencies were observed. That at 1 650 cm^{-1} is assigned to the Mo(NO) fragment, and that at 1 630 cm^{-1} to the W(NO) moiety, this being consistent with the data from their mono- and homobimetallic analogues.

The ^1H n.m.r. spectra of the new complexes exhibited resonances associated with L. In particular, almost all gave rise to three signals in the region δ 5—6 p.p.m. associated with the H^4 protons in the pyrazolyl rings, and five or six signals in the range δ 1.5—3.0 p.p.m. due to the pyrazolyl methyl protons. Occasionally, the H^4 protons appeared as two signals, of relative intensity 2:1. This is either due to incomplete resolution of the spectrum at relative low field (60 MHz), or to accidental degeneracy, since species of the type [ML(NO)XY] have no plane of symmetry and should give rise to a 1:1:1 pattern. The signals due to the N–H proton in the molybdenum arylamido iodo complexes occurred in the range δ 12.7—13.2 p.p.m., whereas that for the W complexes was at δ *ca.* 10.8 p.p.m., as previously observed.[6,7]

The ^1H n.m.r. spectrum of $[MoL(NO)I(NHCH_2CH_2C_6H_4NH_2)]$ exhibited an A_2B_2-type pattern at δ 6.84 p.p.m. [*J*(AB) = 8.4 Hz] which is assigned to the aromatic protons. A broad signal at δ 3.58 p.p.m. (relative area 2) disappeared when the solution was shaken with D_2O, and is assigned to the uncomplexed NH_2 protons. Two complex multiplets appeared at δ 4.49 and 2.99 p.p.m. These are assigned to the methylene protons, and on the basis of earlier studies of alkylamido species, $[MoL(NO)I(NHCH_2R)]$ (R = Me, Et, *etc.*),[8] we suggest that the resonances at δ 4.69 p.p.m. are due to the protons on the C atom α to the NH group. Significant deshielding of these protons relative to their 'normal' position would be expected on the grounds of the strongly electron-withdrawing character of the MoL(NO)I moiety. In the related bimetallic species $[\{MoL(NO)I\}_2(NHCH_2CH_2C_6H_4NH)]$, the aromatic protons again appeared as an A_2B_2-multiplet at δ 7.44 p.p.m. [J(AB) = 8 Hz] and the methylene protons were observed at δ 4.76 and 3.08 p.p.m. The signal in the monometallic at δ 3.58 p.p.m. had disappeared, and a broad resonance, of relative intensity 2, appeared at δ 13.10 p.p.m., being assigned to the two NH protons. These data, of themselves, do not confirm the formulation of the monometallic species as being an alkylamido complex, rather than $[MoL(NO)I(NHC_6H_4CH_2CH_2NH_2)]$. However, the relative positions of the methylene proton resonances are consistent with our proposed structure.

The ^1H n.m.r. spectra of $[MoL(NO)I(NHQNH_2)]$ [$Q = (C_6H_4)_2Y$, where $Y = CH_2$, CH_2CH_2, O, or SO_2] are all similar. They give rise to A_2B_2 multiplets due to the aromatic protons [J(AB) = *ca.* 8 Hz], and to a broad singlet at δ *ca.* 3.57 p.p.m. which disappears on treatment of the solutions with D_2O. This latter signal is due to the uncomplexed NH_2 protons. The methylene protons in the complexes containing $Y = CH_2$ or CH_2CH_2 appeared as singlets (the latter as two sharp single resonances). The related bimetallic species $[\{MoL(NO)I\}_2(NHQNH)]$ showed similar spectra, with the exception of the signal at δ *ca.* 3.57 p.p.m. which was absent, as expected. In general, the aromatic A_2B_2 multiplets resonated at fields lower than in their monometallic precursors. The ^1H n.m.r. spectrum of $[\{MoL(NO)I\}_2(NHC_6H_4CH_2CH_2C_6H_4NH)]$ at 400 MHz exhibited two sets of aromatic A_2B_2 multiplets corresponding to eight protons. These protons did not appear to be coupled to the NH or to the CH_2CH_2 protons and the total integration of proton signals indicated that there was only one compound of the formula shown present. Accordingly, we conclude that this species exists as a mixture of two isomers in equal amounts. In the absence of a crystal-structure determination, we are unable to draw firm conclusions as to the possible nature of the isomers. The ^1H n.m.r. spectrum of the heterobimetallic $[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$ was consistent with our formulation, the NH protons appearing at δ 13.13 and 10.77 p.p.m. The former signal is probably due to the MoN*H*R′ group and the latter to WN*H*R′.

In general, the ^1H n.m.r. spectra of the phenolic complexes were similar to those of their arylamido analogues. The monometallic species exhibited a singlet in the region δ 4.6—5.0 p.p.m. which disappeared when the solutions were treated with D_2O. Hence these resonances are attributed to the OH proton and are, of course, absent in the spectra of the corresponding bimetallic species. The majority of complexes, both mono- and bi-metallic, revealed characteristic A_2B_2 multiplets due to the aromatic ring protons. However, the spectrum of $[MoL(NO)Cl(OC_6H_4SC_6H_4OH)]$ exhibited a singlet at δ 7.22 p.p.m. of relative intensity 4, and an A_2B_2 multiplet at δ 7.10 p.p.m., also of relative intensity 4. We were unable to assign these signals to the appropriate aromatic ring, although the one at lower field could be due to that adjacent to the metal. The spectrum of $[\{MoL(NO)I\}_2(OC_6H_4COC_6H_4C_6H_4COC_6H_4O)]$ exhibited a multiplet of lines, of overall intensity 16, in the aromatic region. Again, no definitive assignment could be made.

Table 2. Cyclic voltammetric data obtained from molybdenum and tungsten complexes, [ML(NO)XZ]

M	X	Z	$E_{\frac{1}{2}}$[a] (V)	ΔE[b] (mV)	n[c]	E_c[d]
Mo	I	$NHC_6H_4OC_6H_4NH_2$	−0.86	70	1.0	
		$NHC_6H_4CH_2C_6H_4NH_2$	−0.85	60	0.9	
		$NHC_6H_4CH_2CH_2C_6H_4NH_2$	−0.85	80	1.2	
		$NHC_6H_4SO_2C_6H_4NH_2$	−0.54	80	0.8	
		$NHCH_2CH_2C_6H_4NH_2$	−1.22[e]	—	0.6	
W	Cl	$NHC_6H_4OC_6H_4NH_2$	−1.30	100	1.0	
Mo	I	$NHC_6H_4OC_6H_4NHMoI(NO)L$	−0.88[f]	240	2.1	−0.85
		$NHC_6H_4CH_2C_6H_4NHMoI(NO)L$	−0.84[f]	150	—	−0.82
		$NHC_6H_4CH_2CH_2C_6H_4NHMoI(NO)L$	−0.84[f]	120	—	−0.84
		$NHC_6H_4SO_2C_6H_4NHMoI(NO)L$	−0.49	60	1.0	−0.54
			−0.60	80	1.3	
Mo	I	$NHC_6H_4OC_6H_4NHWCl(NO)L$	−0.81	70	0.7	
			−1.37[d]	—	—	
Mo	I	$NHCH_2CH_2C_6H_4NHMoI(NO)L$	−0.85	80	1.1	
			−1.26[e]			
Mo	Cl	$OC_6H_4SC_6H_4OH$	−0.32	120	—	
	I	$OC_6H_4SC_6H_4OH$	−0.25	50	1.5	
	I	$OCH_2C_6H_4CH_2OH$	−0.53	60	0.9	
W	Cl	$OCH_2C_6H_4CH_2OH$	−1.13	120	0.9	
Mo	I	$OC_6H_4C_6H_4OH$	−0.28	80	1.3	
		$OC_6H_4C_6H_4OMoI(NO)L$	−0.26[f]	160	1.5	−0.24
		$OC_6H_4SC_6H_4OMoI(NO)L$	−0.25[f]	180	1.2	
		$OCH_2C_6H_4CH_2OMoI(NO)L$	−0.52[f]	160	—	
W	Cl	$OCH_2C_6H_4CH_2OWCl(NO)L$	−1.16	190	1.1	

[a] In CH_3CN 10^{-3} mol dm^{-3} in complex, 0.2 mol dm^{-3} in $[NBu^n_4][PF_6]$ using Pt wire electrode; scan rate 50 mV s^{-1}; $E_{\frac{1}{2}} \pm 20$ mV. [b] Separation between cathodic and anodic c.v. peaks; for one-electron process value is 80 ± 20 mV for $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ couple. [c] Number of electrons involved in reduction process; determined by comparison with $[WL(NO)Cl_2]$, $i_p v^{-\frac{1}{2}}[\text{concn.}]^{-1} = 5.20 \times 10^{-2}$ A $V^{-\frac{1}{2}}$ $s^{\frac{1}{2}}$ dm^3 mol^{-1}. [d] Centre of symmetry of d.p.p. curve (see Table 3), in V; included for comparison. [e] E_p (cathodic) only, irreversible process. [f] Shoulder seen on cathodic and anodic peaks.

Table 3. Differential pulse polarographic data and comproportionation constants for mono- and bi-metallic molybdenum complexes, [MoL(NO)X(QR)]

X	QR	$w_{\frac{1}{2}}$[a] (mV)	$\Delta E_{\frac{1}{2}}$[b] (mV)	E_c[c] (V)	$E_{\frac{1}{2}}(1)$[d] (V)	$E_{\frac{1}{2}}(2)$[d] (V)	k_c[e]
Cl	Cl	98	—	+0.11	+0.110	—	—
I	$OC_6H_4C_6H_4OH$	98	—	−0.24	−0.240	—	—
I	$NHC_6H_4CH_2CH_2C_6H_4NHMoL(NO)I$	105	45	−0.84	−0.812	−0.858	5.9
Cl	$OC_6H_4COC_6H_4C_6H_4COC_6H_4OMoL(NO)Cl$	120	56	−0.18	−0.142	−0.198	8.8
I	$NHC_6H_4CH_2C_6H_4NHMoL(NO)I$	145	62	−0.82	−0.784	−0.846	11
Cl	$OC_6H_4SO_2C_6H_4OMoL(NO)Cl$	150	75	−0.25	−0.207	−0.272	18
I	$OC_6H_4C_6H_4OMoL(NO)I$	158	80	−0.24	−0.194	−0.275	23
Cl	$OC_6H_4COC_6H_4OMoL(NO)Cl$	165	85	−0.22	−0.170	−0.255	27
Cl	$OC_6H_4C_6H_4OMoL(NO)Cl$	200	110	−0.34	−0.280	−0.390	72
I	$NHC_6H_4OC_6H_4NHMoL(NO)I$	200	111	−0.85	−0.788	−0.900	76
I	$NHC_6H_4SO_2C_6H_4NHMoL(NO)I$	225	135	−0.54	−0.468	−0.603	191
Cl	$OC_6H_4SC_6H_4OMoL(NO)Cl$	230	138	−0.32	−0.250	−0.388	215

[a] Linewidth at half-height of d.p.p. curve; theoretical value for one-electron reversible process 91 mV. [b] Separation between $E_{\frac{1}{2}}^1$ and $E_{\frac{1}{2}}^2$ determined graphically (ref. 5); for two one-electron reversible processes in non-interacting systems within the same molecule, $\Delta E_{\frac{1}{2}} = 36.5$ mV, probable error ± 10 mV. [c] Centre of symmetry of d.p.p. curve; $E_{\frac{1}{2}}^1 = E_c + (\Delta E_{\frac{1}{2}} + E_{pul})/2$; E_{pul}, pulse potential, = 10 mV. [d] Half-wave potentials in CH_3CN solution, *vs.* s.c.e., Pt electrode, $[NBu^n{}_4][BF_4]$ (0.2 mol dm^{-3}) as base electrolyte; $E_p = E_{\frac{1}{2}} - E_{pul}/2$; E_p = d.p.p. peak position, $E_{pul} = 10$ mV. [e] Comproportionation constant; $k_c = \exp(\Delta E_{\frac{1}{2}}/25.69)$.

The species $[ML(NO)X(OCH_2C_6H_4CH_2OH)]$ (M = Mo, X = I; M = W, X = Cl) gave rise to similar spectra. The methylenic protons attached to the C atom α to the metal-containing fragment resonated, as expected by analogy with related alkoxides,[9] at low field (δ *ca.* 6.6 p.p.m.). The other methylenic signals were more difficult to identify but in the Mo complex appeared as a singlet at δ 4.6 p.p.m., whereas in the W complex a broad signal, of relative intensity 3, was observed at δ 4.64 p.p.m. The latter diminished in intensity when its solutions were treated with D_2O so it appears that the CH_2 and OH signals overlap. In the bimetallic species, the α-methylenic protons were all observed in the range δ 6.5—6.9 p.p.m.

In all of the spectra of the complexes, solvent of crystallisation was detected, when expected on the basis of elemental analytical data (Table 1), the relative intensity of these signals being consistent with the analytical data.

Electrochemical Studies.—The electrochemical behaviour of the new complexes was investigated by cyclic voltammetry (Table 2) and by differential pulse polarographic techniques (Table 3). In a number of selected cases, the number of electrons involved in charge-transfer processes was determined directly by coulometry (Table 2).

Cyclic voltammetry (c.v.) was used principally to determine the extent of the redox activity, and to determine the $E_{\frac{1}{2}}$ values and the influences upon them. Differential pulse polarography (d.p.p.) was employed primarily to facilitate the analysis of two-step electron-transfer processes whose $E_{\frac{1}{2}}$ values were very close ($\Delta E_{\frac{1}{2}}$ *ca.* 100 mV), and thereby to permit an evaluation of the extent of interaction between the two redox centres.

From the c.v. data it is clear that the monometallic species underwent a single, usually reversible, one-electron reduction, consistent with our earlier observations.[2,10] The bimetallic complexes underwent two one-electron reduction processes, often with $E_{\frac{1}{2}}$ values separated by 100 mV or less. When separation between the two redox processes is so small, the c.v. appears as a single broad wave and, as such, one cannot readily distinguish between two single electron transfers, where $E_{\frac{1}{2}}^1 < E_{\frac{1}{2}}^2$ or $E_{\frac{1}{2}}^1 > E_{\frac{1}{2}}^2$ (> means more cathodic than) or a single two-electron transfer, although the ΔE_p value is substantially larger than the 29 mV expected for a two-electron process. In chemical terms it seems extremely unlikely that $E_{\frac{1}{2}}^1$ is more cathodic than $E_{\frac{1}{2}}^2$, but d.p.p. techniques can significantly assist in unravelling this problem. Small values of $\Delta E_{\frac{1}{2}}$ can be interpreted in terms of very weak or negligible interactions between the two redox centres, and in the cases under study, $\Delta E_{\frac{1}{2}}$ values are substantially smaller than those observed in related species containing $[YC_6H_4Z]^{2-}$ as bridging ligands where the interaction is regarded as being very strong.[1]

The $E_{\frac{1}{2}}$ values for the arylamido complexes generally occurred at *ca.* −0.85 V [*vs.* saturated calomel electrode (s.c.e.) in CH_3CN], except for those species containing $NHC_6H_4SO_2C_6H_4NH$ (*ca.* −0.55 V). The divergence of this latter species may be a reflection of the strongly electron-withdrawing nature of the sulphonyl group. The molybdenum iodo phenoxides exhibited $E_{\frac{1}{2}}$ in the range −0.25 to −0.28 V, whereas the chloro analogues have $E_{\frac{1}{2}}$ *ca.* 70 mV more cathodic. The complexes containing $OCH_2C_6H_4CH_2O$ underwent reduction at potentials *ca.* 200 mV more cathodic than the aryloxy species, again consistent with earlier observations.[6] The $E_{\frac{1}{2}}$ values of the tungsten complexes were, in general, 400—600 mV more cathodic than their iodo molybdenum counterparts, as expected.[2,6]

Within the series of complexes $[\{MoL(NO)Cl\}_2(OC_6H_4YC_6H_4O)]$, $E_{\frac{1}{2}}$ varied significantly as a function of Y. Thus the half-wave potentials became more cathodic in the order Y = $(COC_6H_4)_2$ < CO < SO_2 < S < nothing. This trend, which reflects the decreasing ease of reduction of these species, may be related to the electron releasing/withdrawing propensities of aromatic ring substituents, as mentioned elsewhere.[2]

The monometallic species $[MoL(NO)I(NHCH_2CH_2C_6H_4NH_2)]$ exhibited a single reversible reduction with $E_{\frac{1}{2}} = -1.22$ V. This is at a position *vs.* s.c.e. entirely consistent with $E_{\frac{1}{2}}$ for other alkylamido complexes.[6] In the bimetallic, $[\{MoL(NO)I\}_2(NHCH_2CH_2C_6H_4NH)]$, however, two waves were observed, at −0.85 and −1.26 V. The former, reversible, process is clearly due to the MoL(NO)I(NHR′) entity, consistent with the data mentioned above, whereas the latter is, as in the monometallic species, due to the alkylamido moiety, $MoL(NO)I(NHCH_2CH_2R')$. The positions of these $E_{\frac{1}{2}}$ values are not significantly different from those expected or observed in the cyclic voltammograms of their monometallic analogues (alkyl- or aryl-amido), and so there seems to be little interaction between the redox centres.

In the c.v. of the heterobimetallic complex $[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$, two waves were detected, the first, at −0.81 V, being reversible, and the second, at −1.37 V, being irreversible. From a comparison of the data in Table 2 we can suggest that the first charge transfer may be associated with the molybdenum-containing redox centre. It is, however, slightly more anodic than $E_{\frac{1}{2}}$ for its monometallic analogue (−0.86 V). The second process may therefore be associated with the WL(NO)Cl(NHR′) moiety, but it too is shifted, although cathodically, relative to its monometallic precursor ($E_{\frac{1}{2}}$ = −1.30 V). We have discussed interpretations of the shifts in $E_{\frac{1}{2}}$ in bimetallic species relative to their monometallic precursors.[1] Compounds containing *meta*-$C_6H_4O_2$ or *meta*-$C_6H_4(NH)_2$ exhibit electrochemical behaviour which can be rationalised in terms of simple polar and mesomeric effects, and the e.s.r. spectral data from $[\{MoL(NO)X\}_2(YC_6H_4Y\text{-}m)]^-$ can be interpreted by a 'valence-trapped' model.[11] However such explanations appear inappropriate for the analogous compounds containing *para*-$C_6H_4Y_2$ (Y = O or NH) since e.s.r. spectral data obtained from $[\{MoL(NO)Cl\}_2(OC_6H_4O\text{-}p)]^-$ seem to indicate either that the unpaired electron is delocalised or at least undergoing extremely rapid intramolecular exchange between the two metal centres. In the complexes described here where there is an extended two-ring bridge system, it seems unlikely that a delocalised model would be appropriate and that a 'valence-trapped' description may be more realistic. As yet, we have no e.s.r. spectral data to test this hypothesis, so our explanations for the electrochemical behaviour must be tentative.

Accordingly, in the neutral species, $[MoL(NO)I(NHC_6H_4OC_6H_4NH)WL(NO)Cl]$, reduction of the molybdenum centre may be influenced by the *para*-substituent effect of the arylamido ring *via* polar and mesomeric influences. In this system, that substituent is the electron-withdrawing $WL(NO)Cl(NHC_6H_4O\text{–})$ and so, relative to the unsubstituted species $[MoL(NO)I(NHC_6H_4OC_6H_4NH_2)]$, the $E_{\frac{1}{2}}$ will be shifted anodically. Once reduced, the bimetallic anion undergoes reduction at the second, tungsten-containing centre. In this instance, the *para* substituent on the W–NHR′ ring system is the negatively-charged $MoL(NO)I(NHC_6H_4O\text{–})^-$ moiety, and so, relative to the monometallic tungsten precursor, the second reduction potential in the bimetallic is shifted cathodically. The movements of $E_{\frac{1}{2}}$, relative to those in the monometallic precursors, imply some interaction between the redox centres.

From the data in Table 2, it is apparent that most of the bimetallic species undergo a two-electron reduction where the separation between the two redox processes, assuming that two distinct one-electron transfers do occur, is *ca.* 100 mV or less. It is extremely difficult to analyse cyclic voltammograms in such circumstances and hence we resorted to d.p.p. techniques in an effort to analyse the nature of the electron-transfer process.

In systems which can undergo multi-step electron-transfer reactions of the type (1), the relationship of the concentrations

$$A \xrightarrow{n_1e,\ E_1^\circ} B \xrightarrow{n_2e,\ E_2^\circ} C \tag{1}$$

of A and C (the product of *two* electron additions to A) to B at equilibrium can be given in terms of the comproportionation constant, k_c[5] [equation (2)]. In the situation under discussion

$$k_c = [B]^{n_1+n_2}/[C]^{n_1}[A]^{n_2} = \exp[(E_1 - E_2)_{n_1n_2}F/RT] \tag{2}$$

here, $n_1 = n_2 = 1$ and, to a first approximation and since comparative and not absolute values are being used, we can substitute $E_1^\circ - E_2^\circ$ by $E_{\frac{1}{2}}^1 - E_{\frac{1}{2}}^2$, *i.e.* $\Delta E_{\frac{1}{2}}$. Hence $k_c = \exp(\Delta E_{\frac{1}{2}}/25.69)$. In our study of the redox behaviour of these bimetallic molybdenum and tungsten complexes, a knowledge of k_c for the reaction (3) can give a simple indication

$$[ML(NO)X(ZQZ)ML(NO)X] + [ML(NO)X(ZQZ)ML(NO)X]^{2-} \rightleftharpoons 2[ML(NO)X(ZQZ)ML(NO)X]^- \tag{3}$$

of the concentration of the monoreduced species. Richardson and Taube[5] have derived a relationship between $\Delta E_{\frac{1}{2}}$ and the form of the d.p.p. curve in systems where the interaction between two redox centres in the same molecule is small. The derivation requires determination of the d.p.p. peak-width at half-height ($w_{\frac{1}{2}}$), and its conversion to $\Delta E_{\frac{1}{2}}$ values can be made using curves derived by the procedures of Richardson and Taube.[5] In the d.p.p. work described here, the pulse amplitude was 10 mV, and the curves were used for $\Delta E_{\frac{1}{2}}$ < 180 mV. For two non-interacting redox centres within one molecule k_c = 4 and hence $\Delta E_{\frac{1}{2}}$ [$(RT/n_1n_2F)\ln 4$] is 35.6 mV if $n_1 = n_2 = 1$. While these relationships were devised for application to aqueous solutions, they appear reasonably valid for polar non-aqueous solvents, *e.g.* CH_3CN, assuming that the *iR* drop in the cell system is small.

In Table 3 we report $w_{\frac{1}{2}}$ values determined directly from d.p.p. curves obtained from the complexes listed. This permitted an evaluation of $\Delta E_{\frac{1}{2}}$ and, in the case of most of the phenoxy complexes where cyclic voltammograms were not recorded, $E_{\frac{1}{2}}^1$ and $E_{\frac{1}{2}}^2$ could be readily calculated. The value of k_c was determined using the relationship above.

From the data in Table 3, it is clear that the two redox centres in $[\{MoL(NO)I\}_2(NHC_6H_4CH_2CH_2C_6H_4NH)]$ (k_c = 5.9, $\Delta E_{\frac{1}{2}}$ = 45 mV) are essentially non-interacting since, under the experimental conditions used, these values cannot be distinguished from k_c = 4 and $\Delta E_{\frac{1}{2}}$ = 36 mV. A small but detectable increase in $\Delta E_{\frac{1}{2}}$ is found when the length of the saturated bridge is reduced to give $[\{MoL(NO)I\}_2(NHC_6H_4CH_2C_6H_4NH)]$ (k_c = 11, $\Delta E_{\frac{1}{2}}$ = 62 mV). A more significant two-redox-centre interaction is found when the methylene group in this complex is replaced by –O– (k_c = 76, $\Delta E_{\frac{1}{2}}$ = 111 mV) or $\text{–}SO_2\text{–}$ (k_c = 191, $\Delta E_{\frac{1}{2}}$ = 135 mV). A similar trend is found for the phenoxide compounds in that there is only a slight interaction across the long conjugated bridge in $[MoL(NO)Cl(OC_6H_4COC_6H_4C_6H_4COC_6H_4O)]$ (k_c = 8.8, $\Delta E_{\frac{1}{2}}$ = 56 mV), while stronger interactions are found in the complexes $[\{MoL(NO)Cl\}_2Q]$ in which Q = $\text{–}OC_6H_4COC_6H_4O\text{–}$ (k_c = 27, $\Delta E_{\frac{1}{2}}$ = 85 mV), $\text{–}OC_6H_4SO_2C_6H_4O\text{–}$ (k_c = 18, $\Delta E_{\frac{1}{2}}$ = 75 mV), $\text{–}OC_6H_4C_6H_4O\text{–}$ (k_c = 72, $\Delta E_{\frac{1}{2}}$ = 110 mV), and $\text{–}OC_6H_4SC_6H_4O\text{–}$ (k_c = 215, $\Delta E_{\frac{1}{2}}$ = 138 mV). The increase in interaction from $\Delta E_{\frac{1}{2}}$ = 110 mV to 138 mV on interposing a sulphur between the two phenyl rings in $[\{MoL(NO)Cl\}_2(OC_6H_4C_6H_4O)]$ could be rationalised in stereochemical terms. In the biphenyl system steric interactions result in a tilt of the plane of one phenyl ring with respect to the other thereby minimising the mesomeric transmission of effects across the bridge. The insertion of the sulphur would relieve these steric constraints allowing the transmission of effects between coplanar rings *via* the involvement of *p* or *d* orbitals on the sulphur. The data obtained suggest that the less polarisable –O– or –CO– linking groups are less effective than –S– in transmitting effects between the metal centres.

In all these species the coupling between the metal centre, as detected electrochemically, is substantially smaller than that observed in $[\{MoL(NO)Cl\}_2(ZC_6H_4Z\text{-}p)]$ where Z = O ($\Delta E_{\frac{1}{2}}$ = 460 mV) or NH ($\Delta E_{\frac{1}{2}}$ = 850 mV). Consequently we would classify them as showing a weak or intermediate interaction between the metal centres. The observation that $\Delta E_{\frac{1}{2}}$ is smaller in $[\{MoL(NO)Cl\}_2(ZC_6H_4SO_2C_6H_4Z)]$ when Z = –O– than when Z = –NH– may be associated with the more cathodic reduction potentials of the arylamide as compared to the phenoxide complexes. This would seem to indicate a stronger Mo–Z interaction in the amide complexes allowing a more effective transmission of effects from the bridging group. This view is supported by the observation that the reaction constants for the one-electron reductions of aryl substituted phenoxide complexes containing the $MoL(NO)Cl^+$ moiety are smaller than for their arylamido counterparts.[2] Thus we may conclude that the extent of two-redox-centre interactions in bimetallic complexes of formula $[\{MoL(NO)Cl\}_2(ZC_6H_4{-}Y{-}C_6H_4Z)]$ varies not only with the nature of Y, but also with the nature of Z.

Acknowledgements

We are grateful to the S.E.R.C. for personnel support (S. M. C., B. D. N., and S. J. R.) and for provision of funds to buy equipment, and to Dr. H. M. Colquhoun, New Science Group, ICI, Runcorn, for gifts of some phenols.

References

1 S. M. Charsley, C. J. Jones, J. A. McCleverty, B. D. Neaves, S. J. Reynolds, and G. Denti, preceding paper.

2 G. Denti, C. J. Jones, J. A. McCleverty, B. D. Neaves, and S. J. Reynolds, *J. Chem. Soc., Chem. Commun.*, 1983, 474.

3 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3904; 1969, **91**, 588.

4 S. J. Reynolds, C. F. Smith, C. J. Jones, and J. A. McCleverty, *Inorg. Synth.*, 1985, **23**, 4.

5 D. E. Richardson and H. Taube, *Inorg. Chem.*, 1981, **20**, 1278.

6 C. J. Jones, J. A. McCleverty, B. D. Neaves, S. J. Reynolds, H. Adams, N. A. Bailey, and G. Denti, *J. Chem. Soc., Dalton Trans.*, 1986, 743.

7 J. A. McCleverty, G. Denti, S. J. Reynolds, A. S. Drane, N. El Murr, A. E. Rae, N. A. Bailey, H. Adams, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 81.

8 J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey, and J. M. A. Smith, *J. Chem. Soc., Dalton Trans.*, 1982, 429.

9 J. A. McCleverty, D. Seddon, N. A. Bailey, and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.

10 T. N. Briggs, C. J. Jones, J. A. McCleverty, B. D. Neaves, N. El Murr, and H. M. Colquhoun, *J. Chem. Soc., Dalton Trans.*, 1985, 1249.

11 N. M. Atherton, D. Collinson, and F. E. Mabbs, personal communication.

Received 24*th November* 1986; *Paper* 6/2258