Monometallic, Homo- and Hetero-bimetallic Complexes based on Redox Active Tris(3,5-dimethylpyrazolyl)borato-molybdenum and -tungsten Nitrosyls. Part 4.[†] The Effects of Ligating Atom Type on the Reduction Potentials of Monometallic Complexes[‡]

Najat Al Obaidi, Muktimoy Chaudhury, Diane Clague, Christopher J. Jones,[*] Julie C. Pearson, Jon A. McCleverty, and Sithy S. Salam
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

The complexes [M(NO)(L)X(Y)] [L = tris(3,5-dimethylpyrazolyl)borate; M = Mo, X = Cl, Y = OPh; M = W, X = Cl, Y = SPh; or M = W, X = Y = NC_4H_4, OPh, or SPh] have been prepared and characterised. The electrochemical properties of these compounds were investigated by cyclic voltammetry and compared with those of others in the series [M(NO)(L)X(Y)] (M = Mo or W; X = Cl, Y = OPh, NHPh, or SPh; or X = Y = NC_4H_4, OPh, NHPh, or SPh). It was found that the thiophenolate complexes reduced at slightly more anodic potentials than their phenolate analogues while the arylamide complexes reduced at significantly more cathodic potentials. In general the tungsten complexes reduced at potentials *ca.* 0.45 V more cathodic than their molybdenum analogues.

The formally 16-electron complexes [$M(NO)(L)Cl_2$] [L = tris(3,5-dimethylpyrazolyl)borate, $HB(Me_2pz)_3^-$; M = Mo or W] have been found to undergo a one-electron reduction which is reversible on the cyclic voltammetry time-scale.[1] The chloride ligands in these complexes may be substituted by arylamide, phenoxide, or thiolate ligands to produce air-stable derivatives which are also formally 16-electron complexes. Several of these derivatives have also been found to undergo electrochemical reductions at potentials which depend on the nature of both the ligating atoms and the substituents attached to them.[2–5] Such complexes thus provided a useful basis for studying the effects of donor atom type on the reduction potentials of 16-electron complexes containing the $\{Mo(NO)\}^4$ and $\{W(NO)\}^4$ cores. In particular it was of interest to determine whether sulphur-containing ligands would stabilise the lower oxidation state of the complexes as compared to oxygen donor ligands. Since ligand to metal $p\pi$–$d\pi$ donation has been proposed to account for the short Mo–S and Mo–O bond distances observed in alkoxide and thiolate complexes of this type,[6,7] the π-acceptor properties of sulphur might not be expected to be a dominant feature in the bonding of these complexes.

A comparison of the reduction potentials of analogous molybdenum and tungsten complexes would also provide a test of whether the higher oxidation state were stabilised for the third row transition metal as compared to the second row metal in these $\{M(NO)\}^4$ systems. Such an effect is apparent in the reduction potentials of the hexachlorometalates[8] and amounts to a difference of 650 mV between molybdenum and tungsten for the d^1–d^2 couple and 870 mV for the d^2–d^3 couple. Such comparisons are difficult when unsaturated organic ligands are present since these may themselves be redox active. Thus in the tris(dithiolene) complexes $[M\{S_2C_2(CN)_2\}_3]^z$ a difference of 370 mV was observed between molybdenum and tungsten for the $z = -2/-3$ couple but for the $z = -1/-2$ couple of these and several related complexes no substantial difference in redox potential was found.[9] The observation of ^{95}Mo and ^{97}Mo hyperfine coupling in the e.s.r. spectra of a number of reduced complexes containing the $\{Mo(NO)\}^5$ core indicates that the orbital carrying the added electron has significant metal character,[1,10] so that some differences would be expected on replacing the $\{Mo(NO)\}^4$ core with $\{W(NO)\}^4$ in the examples presented here.

Results and Discussion

Synthetic Studies.—The molybdenum complexes used in this study have, with the exception of [Mo(NO)(L)Cl(OPh)], been reported previously.[1,5,11–14] The chloro-phenolato derivative was obtained from the direct reaction of phenol with [$Mo(NO)(L)Cl_2$] in toluene at reflux over a period of 2 d. The tungsten chloro-thiophenolato derivative could similarly be prepared from the direct reaction of [$W(NO)(L)Cl_2$] with thiophenol, the phenolate analogue [W(NO)(L)Cl(OPh)] having been reported previously.[3] To prepare the disubstituted tungsten complexes it was necessary to add sodium hydride to generate the PhO^- or PhS^- anions *in situ*. Unlike phenol or thiophenol, pyrrole did not react directly with [$W(NO)(L)Cl_2$]. However, the $NC_4H_4^-$ ion, produced in the presence of NaH, reacted smoothly to give a disubstituted derivative, as was found in preparing the related molybdenum complex.[5,10]

Spectroscopic Studies.—All of the new complexes exhibited bands in their i.r. spectra consistent with the presence of the tris(3,5-dimethylpyrazolyl)borate ligand L and in particular ν_{BH} was present at *ca.* 2 500 cm^{-1}. The values of ν_{NO} were in accord with expectation (see SUP 56676). As has been noted previously[15] the values for the tungsten complexes were lower than those of their molybdenum counterparts. In the case of the bis(phenolate) derivatives this difference amounted to *ca.* 35 cm^{-1} compared to 60 cm^{-1} in the case of the bis(pyrrolide) derivatives.

The ^1H n.m.r. spectral data for the new complexes were consistent with their formulations (see SUP 56676). All exhibited signals in the region δ 8.1—5.8 p.p.m. attributable to the pyrrolide, phenolate, or thiophenolate ligands. The pyrazolyl methyl signals appeared in the region δ 1.3—2.7 p.p.m. while the pyrazolyl C^4 protons appeared in the region δ

[‡] Part 3, S. M. Charsley, C. J. Jones, J. A. McCleverty, B. D. Neaves, and S. J. Reynolds, *Transition Met. Chem. (Weinheim Ger)*, 1986, **11**, 329.

[†] *Supplementary data available* (No. SUP 56676, 4 pp.): ^1H n.m.r. data and ν_{NO} stretching frequencies. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table. Electrochemical data for [M(NO)(L)X(Y)]

		M = Mo		M = W			
X	Y	$E_{\frac{1}{2}}$/V[a]	ΔE_p/mV[b]	$E_{\frac{1}{2}}$/V[a]	ΔE_p/mV[b]	$\Delta E_{\frac{1}{2}}$/V[c]	Ref.
Cl	Cl	+0.09[d]	70	−0.42[d]	80	0.51	1
Cl	OPh	−0.42[d]	110	−0.86[d]	120	0.44	—
OPh	OPh	−0.74[d]	100	−1.20[d]	110	0.46	12
Cl	SPh	−0.37[d]	60	−0.83	60	0.46	11
SPh	SPh	−0.64[d]	90	−1.04[d]	80	0.40	7
Cl	NHPh	−0.85[d]	100	−1.30[d,e]	100	0.45[f]	11
NHPh	NHPh	−1.32[d]	80	—	—	—	5
NHC_5H_4N[g]	NHC_5H_4N[g]	−1.05[d,e]	100	−1.50[d]	60	0.45[f]	14
NC_4H_4	NC_4H_4	−0.46[d]	80	−0.96	80	0.50	4, 10

[a] Obtained from *ca.* 10^{-3} mol dm^{-3} solutions in MeCN, unless otherwise specified, containing 0.2 mol dm^{-3} $[NBu^n{}_4]BF_4$ as supporting electrolyte with a platinum bead working electrode at scan rates between 0.2 and 0.5 V s^{-1}. Errors in $E_{\frac{1}{2}}$ measurement are estimated at less than ±25 mV. Values are uncompensated for *IR* drop and are quoted relative to the saturated calomel electrode at 0.3 V s^{-1}. [b] Separation between anodic and cathodic peak potentials with typical values for ferrocene under similar conditions falling in the range 60—100 mV. [c] Difference in $E_{\frac{1}{2}}$ values for analogous Mo and W complexes. [d] Shown by coulometry to be a one-electron process. All other reduction processes were also found to be one electron by comparison with $[Mo(NO)(L)Cl_2]$. [e] Obtained using thf as solvent. [f] $\Delta E_{\frac{1}{2}}$ value includes the effects of a change in solvent. [g] NHC_5H_4N = 2-pyridylamide.

5.6—6.0 p.p.m. In the disubstituted complexes the signals due to L appeared in area ratios consistent with the presence of a plane of symmetry in the molecule as seen by ^1H n.m.r. spectroscopy.

Electrochemical Studies.—The electrochemical properties of the new complexes were investigated by cyclic voltammetry in acetonitrile solution. The electrochemistry of [Mo(NO)(L)X(Y)] (X = Cl, Y = SPh; X = Y = OPh or SPh) and of [W(NO)(L)Cl(OPh)] was also studied. All the complexes exhibited only poorly defined irreversible oxidation processes, but all underwent a single reversible or quasireversible one-electron reduction at potentials which varied with the nature of M, X, and Y. The data obtained are presented in the Table along with some previously reported results for [M(NO)(L)X(Y)] (M = Mo or W, X = Y = Cl;[1] M = Mo, X = Cl, Y = NHPh,[11] X = Y = NC_4H_4[4,10] or NHPh;[5] and M = W or Mo, X = Y = NHC_5H_4N[14]) which are provided for comparison.

The results obtained indicate that the reduction potentials of [M(NO)(L)X(Y)] are shifted to increasingly cathodic potentials by substitution of chloride with other ligands in the order Cl < NC_4H_4 < SPh ≈ OPh < NHPh. To some extent this order reflects the increasing basicity in the series Cl < OPh < NHPh but relatively anodic reduction potentials were found for $[M(NO)(L)(NC_4H_4)_2]$ as compared to $[M(NO)(L)(NHR')_2]$ (M = Mo or W, R′ = C_5H_4N; M = Mo, R′ = Ph). This reflects the reduced availability of the nitrogen *p* electrons in $NC_4H_4^-$ for *p*π donation because of their involvement in the aromatic system of the unsaturated heterocyclic ring. The importance of the $p\pi \rightarrow d\pi$ donation in such systems may be judged by comparison with $[Mo(NO)(\eta^5\text{-}C_5H_5)(SPh)_2]$. This complex is monomeric, the metal formally having a 16-electron configuration, despite the absence of steric factors which might preclude expansion of the molybdenum coordination sphere to attain an 18-electron configuration by dimerisation. Molecular orbital calculations[16] indicate that $S \rightarrow Mo$ $p\pi \rightarrow d\pi$ charge donation destabilises the lowest unoccupied molecular orbital (l.u.m.o.) and inhibits the addition of nucleophiles to the molybdenum centre. Such an effect would also shift the reduction potential of the complex to more cathodic values, so that the observed potential reflects not only the σ-base character of the donor atoms, but also the π-base character.

The effect of replacing oxygen by sulphur in the compounds described here may be assessed by comparing the reduction potentials of related phenolate and thiophenolate complexes. Under the experimental conditions used little significance can be attached to differences in potential below *ca.* 50 mV. Accordingly no significant change in reduction potential is observed for [W(NO)(L)Cl(EPh)] in going from E = O to E = S. In the case of molybdenum the difference of 50 mV is barely significant and not experimentally distinguishable from the value found for the tungsten complex. In the disubstituted complexes, $[M(NO)(L)(EPh)_2]$, the change from E = O to E = S is accompanied by a small but significant anodic shift. This amounts to 100 mV where M = Mo and 160 mV where M = W. Taken overall the results obtained suggest that there is a small anodic shift in reduction potential on replacing O with S in these complexes. The magnitude of this shift is too small to be measured with accuracy under the conditions used here, but appears to be of the order of 50 ± 30 mV per atom changed.

The effect of changes in the nature of the ligating groups X and Y on the properties of [M(NO)(L)X(Y)] becomes more apparent if both the reduction potentials, $E_{\frac{1}{2}}$, and the nitrosyl stretching frequencies, ν_{NO}, of the complexes are considered.* In so far as ν_{NO} is a measure of electron density at the metal centre, it might be expected that lower values of ν_{NO} would be associated with more cathodic values for $E_{\frac{1}{2}}$. Using the data reported here, in conjunction with other previously reported[15] ν_{NO} values, we have investigated the correlation between $E_{\frac{1}{2}}$ and ν_{NO}. Plots of the data for [M(NO)(L)X(Y)] (M = Mo with X = Cl, Y = OPh, NHPh, or SPh and X = Y = Cl, OPh, NHPh, NHC_5H_4N, SPh, or NC_4H_4; M = W with X = Cl, Y = OPh, NHPh, or SPh and X = Y = Cl, OPh, NHC_5H_4N, SPh, or NC_4H_4) are shown in the Figure. If only the complexes in which X and Y are restricted to chloride, phenolate, or arylamide are considered, good linear correlations are found between $E_{\frac{1}{2}}$ and ν_{NO}. These may be described by the linear equation (1), in which

$$\nu_{NO} = N + a\,E_{\frac{1}{2}} \qquad (1)$$

N is the value of ν_{NO} in cm^{-1} for a hypothetical molecule in which $E_{\frac{1}{2}} = 0$ and *a* is the slope of the line in cm^{-1} V^{-1}. In the case of the molybdenum series a linear regression analysis gave a correlation coefficient, *r*, of 0.9932 with $N = 1\,698$ cm^{-1} and $a = 52$ cm^{-1} V^{-1}. Inclusion of the points for X = Cl, Y = SPh and X = Y = NC_4H_4 reduced the value of *r* to 0.9866 and further inclusion of the point for X = Y = SPh gave a still

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* We are grateful to a referee for suggesting that we examine this point in more detail.

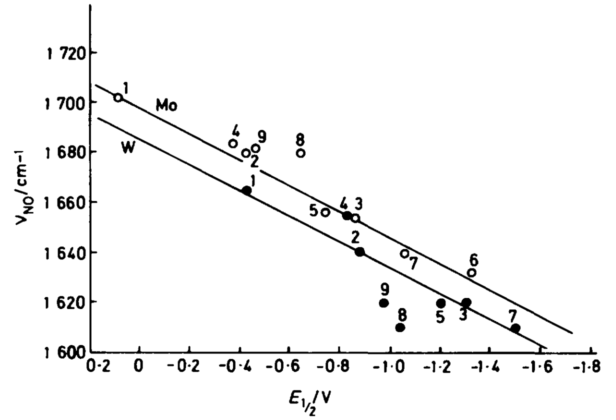

Figure. A plot of ν_{NO} against $E_{\frac{1}{2}}$ for [M(NO)(L)X(Y)] (○, Mo; ●, W) in which the line labelled Mo is for $\nu_{NO} = 1\,698 + 52E_{\frac{1}{2}}$ and that labelled W is for $\nu_{NO} = 1\,685 + 51E_{\frac{1}{2}}$. Points are labelled as follows: 1 (X = Y = Cl), 2 (X = Cl, Y = OPh), 3 (X = Cl, Y = NHPh), 4 (X = Cl, Y = SPh), 5 (X = Y = OPh), 6 (X = Y = NHPh), 7 (X = Y = NHC_5H_4N), 8 (X = Y = SPh), and 9 (X = Y = NC_4H_4)

poorer correlation with $r = 0.9643$. In the case of the tungsten series a value of 0.9944 was obtained for r with $N = 1\,685$ cm^{-1} and $a = 51$ cm^{-1} V^{-1}. Again inclusion of the points for X = Cl, Y = SPh and X = Y = SPh or NC_4H_4 gave a substantially poorer correlation with $r = 0.8551$. It is noteworthy that the slopes of the lines for the molybdenum and tungsten series are experimentally indistinguishable. The value of N is some 13 cm^{-1} lower for tungsten than for molybdenum in accord with previous observations.[15]

The anomalous behaviour of the complexes containing the thiophenolate or pyrrolide ligands may be rationalised in terms of their π-donor/acceptor properties. In the case of the thiophenolate ligand the presence of unfilled d orbitals on sulphur provides an opportunity for π-acceptor behaviour which does not exist with the phenolate or arylamide ligands. If changes in the balance of π-donor and π-acceptor properties of the ligand are not experienced equally by the l.u.m.o. of the complex and the orbital involved in donation to the π^* orbital on NO, the correlation between $E_{\frac{1}{2}}$ and ν_{NO} would be lost. In the case of the pyrrolide ligand the π-base character will be restricted by the involvement of the nitrogen p electrons in the aromatic system of the heterocyclic ring. Again the relative effects of this change on $E_{\frac{1}{2}}$ and ν_{NO} may be different when compared to the situation in primary amide complexes.

Molybdenum appears less sensitive to changes in the nature of X and Y than tungsten. Only [Mo(NO)(L)(SPh)$_2$] falls substantially away from the linear model for the molybdenum series, whilst all three complexes involving the SPh or NC_4H_4 ligands fall significantly away from the linear model for the tungsten series. Furthermore, the deviations of [M(NO)(L)(SPh)$_2$] from the linear models are in opposite senses for molybdenum and tungsten. This observation is difficult to interpret since the properties of the metal will be affected by the orientations of the aryl rings of the SPh ligands.[16] Thus the observed differences between the Mo and W complexes may reflect either structural or electronic effects or both. In spite of these complications, for complexes containing SPh or NC_4H_4 ligands, it is apparent that a good correlation between $E_{\frac{1}{2}}$ and ν_{NO} exists for complexes containing chloride, phenolate, or arylamide ligands. Based on the near identical slopes of the linear models for the Mo and W complexes it would appear that, within this series of ligands, molybdenum and tungsten are affected equally by changes in ligand type.

A comparison of the reduction potentials of related molybdenum and tungsten complexes reveals a consistent cathodic shift on going from molybdenum to tungsten. The magnitude of the shift falls in the range 400—510 mV and may be approximated as 450 ± 50 mV. This constitutes a substantial stabilisation of the higher oxidation state of the metal on going from the second to the third row of the d block. This observation would be consistent with the view that the redox orbital in these compounds has substantial metal character in accord with the e.s.r. observations mentioned earlier. The difference of 450 mV for this $\{M(NO)\}^4$–$\{M(NO)\}^5$ couple is somewhat smaller than the respective 650 and 870 mV quoted earlier[8] for the d^1–d^2 and d^2–d^3 couples in $[MCl_6]^z$ ($z = -1$ to -3).[1] However, it is larger than the 370 mV difference found for the M^{I}–M^{II} couple in the tris(1,2-dicyanoethene-1,2-dithiolate) complexes.[8] Unfortunately such comparisons can only be of a qualitative nature since the effect of the ligands cannot be quantified, but the results obtained here do confirm that a significant difference in oxidation state stabilities between molybdenum and tungsten is also present in these lower oxidation state nitrosyl complexes.

Experimental

All reactions were carried out in redistilled, dry, oxygen-free solvents under nitrogen. The complexes [Mo(NO){HB(Me$_2$pz)$_3$}Cl$_2$] and [W(NO){HB(Me$_2$pz)$_3$}Cl$_2$] were prepared according to previously reported methods.[13] Silica gel 60 (70—230 mesh) was used for column chromatography and, unless otherwise specified, reaction products were purified by chromatography, using CH_2Cl_2 as eluant, followed by recrystallisation from CH_2Cl_2–hexane. I.r. spectra were recorded using a Perkin-Elmer 297 spectrophotometer and ^{1}H n.m.r. spectra on a Varian XL 100 instrument. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Birmingham.

Cyclic voltammetric measurements were made using a Hitek DT2101 potentiostat and PPR1 waveform generator or PAR 174 potentiostat. Measurements were made in redistilled MeCN under nitrogen using 0.2 mol dm^{-3} [NBu$^n{}_4$]BF$_4$ as the supporting electrolyte and a standard calomel reference electrode at 21 ± 1 °C. The cell characteristics were calibrated using [Mo(NO){HB(Me$_2$pz)$_3$}Cl$_2$], and all electron-transfer processes reported were found to involve one electron by comparison with this reference compound which is known to undergo a reversible one-electron reduction, or directly by coulometry.

[Mo(NO){HB(Me$_2$pz)$_3$}Cl(OPh)].—[Mo(NO){HB(Me$_2$pz)$_3$}Cl$_2$] (0.5 g, 1 mmol) and phenol (0.095 g, 1 mmol) were refluxed in toluene (50 cm^3) for 2 d. The reaction mixture was then purified by column chromatography using tetrahydrofuran(thf) as eluant, the principal dark brown band being collected. Further purification was effected by recrystallisation from CH_2Cl_2–pentane, yield 0.32 g (56%) (Found: C, 46.0; H, 5.2; N, 17.4. Calc. for $C_{21}H_{27}BClMoN_7O_2$: C, 45.7; H, 4.9; N, 17.9%).

[W(NO){HB(Me$_2$pz)$_3$}Cl(SPh)].—[W(NO){HB(Me$_2$pz)$_3$}Cl$_2$] (0.5 g, 0.86 mmol) and PhSH (1.0 cm^3, 10 mmol) were refluxed in toluene (100 cm^3) for 2 d. The reaction mixture was then purified by column chromatography, the principal dark green band being collected, yield 0.27 g (48%) (Found: C, 39.3; H, 4.8; N, 15.4. Calc. for $C_{21}H_{27}BN_7OW$: C, 38.5; H, 4.1; N, 15.0%).

[W(NO){HB(Me$_2$pz)$_3$}(SPh)$_2$].—[W(NO){HB(Me$_2$pz)$_3$}Cl$_2$] (0.5 g, 0.86 mmol) and PhSH (2.0 cm^3, 20 mmol) were refluxed in toluene (100 cm^3) in the presence of excess NaH for a period of 4 d. After this time the reaction mixture was purified by column chromatography, the principal purple band being collected, yield 0.29 g (46%) (Found: C, 46.0; H, 5.0; N, 12.2. Calc. for $C_{27}H_{32}BN_7OS_2W{\cdot}0.5C_6H_{14}$: C, 46.6; H, 5.0; N, 12.7%).

$[W(NO)\{HB(Me_2pz)_3\}(NC_4H_4)_2]$.—$[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (1.0 g, 1.7 mmol) and pyrrole (1 cm^3, 16 mmol) were refluxed in thf for 3 d in the presence of excess NaH. After this time the reaction mixture was purified by column chromatography, collecting the principal dark green band, yield 0.68 g (62%) (Found: C, 42.4; H, 5.4; N, 18.8. Calc. for $C_{23}H_{30}BN_9OW$: C, 42.9; H, 4.7; N, 19.6%).

$[W(NO)\{HB(Me_2pz)_3\}(OPh)_2]$.—$[W(NO)\{HB(Me_2pz)_3\}Cl_2]$ (0.5 g, 0.86 mmol) and phenol (0.16 g, 1.7 mmol) in toluene (60 cm^3) were refluxed for 2 d in the presence of excess NaH. The resulting brown solution was then filtered, evaporated to dryness and the crude product chromatographed, the principal brown fraction being collected, yield 0.26 g (44%) (Found: C, 46.7; H, 4.9; N, 14.3. Calc. for $C_{27}H_{32}BN_7O_3W$: C, 46.5; H, 4.6; N, 14.1%).

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