Synthesis and Electrochemical Properties of Homo- and Hetero-bimetallic Complexes not containing M-M' or M–X–M' Bridges (X = Single Atom)

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A series of air- and moisture-stable homo- and hetero-bimetallic complexes have been prepared which contain two metal centres separated by a variety of *para*-disubstituted bifunctional aromatic ligands and whose electrochemical properties indicate strong, intermediate, and weak interactions between the metal centres.

There has been considerable recent interest in the preparation and electrochemical study of bimetallic complexes.[1] In many of the systems studied the metal centres are linked by metal–metal bonds or single atom bridges. There are relatively few examples in which polyatomic bridging ligands,[2] such as pyrazine,[3] separate the metals. In mixed-valence complexes of this latter type the metal centres are thought to be essentially 'valence trapped'.[4] Their interaction appears to be largely explicable in terms of inductive effects transmitted through the bridging ligand. Here we describe the synthesis and electrochemical study of several bimetallic complexes in which the metal centres may influence one another to a greater or lesser extent. On the basis of $E_{1/2}$ values we have attempted to quantify the inductive effects of Mo and W centres in compounds containing *para*-substituted arylamido-ligands.

$$[M\{HB(Me_2pyz)_3\}(NO)XY]$$

(**1**) M = Mo

(**2**) M = W

We have recently described the syntheses of a series of air- and moisture-stable molybdenum alkoxides, phenoxides, alkyl- and aryl-amides, and thiolates of the type $[Mo\{HB(Me_2pyz)_3\}(NO)XY]$(**1**)[X = I, Y = OR, OAr, NHR, NHAr, SR, or SAr, R = H or alkyl, $HB(Me_2pyz)_3$ = $HB(3,5\text{-}Me_2C_3HN_2)_3$ = tris(3,5-dimethylpyrazolyl)borate].[5] We have also observed that in reactions of (**1**; X = Y = I) with bifunctional, potentially chelating, ligands, *e.g.* $NH_2[CH_2]_nOH$ and $HO[CH_2]_nOH$, only compounds in which the bifunctional ligand was *monodentate* with respect to Mo, *i.e.* (**1**; X = I, Y = $NHCH_2CH_2OH$) or (**1**; X = I, Y = $O[CH_2]_nOH$), could be obtained.[6] Furthermore, we have reported that (**1**; X = Y = I) is redox-active, readily undergoing an electrochemically reversible one-electron reduction to give a paramagnetic mono-anion.[7] On the basis of these observations, we have developed a route to redox-active homo- and hetero-bimetallic species by (a) prior attachment of a potentially bifunctional ligand, *e.g.* $NH_2[CH_2]_3PPh_2$ or *p*-HOC_6H_4I, *via* one donor atom (N or O) to $[M\{HB(Me_2pyz)_3\}(NO)X_2]$ (**1**; M = Mo, X = Y = I) or (**2**; M = W, X = Y = Cl), and (b) subsequent attachment of the unbound functional group to another metal complex.

The preparation of 'functionalised' metal complexes, as indicated in (a) above, has been achieved using a variety of potentially bridging ligands. These complexes are similar to their more simple 'unfunctionalised' alkoxy, aryloxy, or amido analogues, and, like them, are air- and moisture-stable.

The formation of bimetallic species,[‡] as suggested in (b) above, can be achieved in a number of ways, but we have so far used only three techniques.

Table 1. Reduction potentials for bimetallic complexes and their monometallic analogues.

Complex[a]	$E_{\frac{1}{2}}/V$[b]	$\Delta E_p/mV$
$\{Mo\}NHC_6H_4CH_2C_6H_4NH_2$	−0.85	60
$\{Mo\}NHC_6H_4CH_2C_6H_4NH\{Mo\}$	−0.84[c]	150
$\{Mo\}NHC_6H_4CH_2CH_2C_6H_4NH_2$	−0.85	80
$\{Mo\}NHC_6H_4CH_2CH_2C_6H_4NH\{Mo\}$	−0.84[c]	120
$\{Mo\}NHC_6H_4SO_2C_6H_4NH_2$	−0.54	80
$\{Mo\}NHC_6H_4SO_2C_6H_4NH\{Mo\}$	−0.49	60
	−0.60	80
$\{Mo\}NHC_6H_4OC_6H_4NH_2$	−0.86	70
$\{Mo\}NHC_6H_4OC_6H_4NH\{Mo\}$	−0.88[c]	240
$\{W\}NHC_6H_4OC_6H_4NH_2$	−1.30	100
$\{W\}NHC_6H_4OC_6H_4NH\{W\}$	−1.32[c]	160
$\{Mo\}NHC_6H_4OC_6H_4NH\{W\}$	−0.81	70
	−1.37[b]	—
$\{Mo\}NHC_6H_4NH_2$	−0.98[b]	—
$\{Mo\}NHC_6H_4NH\{Mo\}$	−0.48	60
	−1.52[d]	—
$\{W\}NHC_6H_4NH_2$	−1.44	120
$\{W\}NHC_6H_4NH\{W\}$	−1.16	80
	−1.72[d]	
$\{Mo\}NHC_6H_4NH\{W\}$	−0.74	60
	−1.66[d]	—
$\{Mo\}NHC_6H_4OH$	−1.01[d]	—
$\{Mo\}NHC_6H_4O\{Mo\}$	−0.15	100
	−1.16	70
$\{Mo\}NHC_6H_4O\{W\}$	−0.28	70
	−1.60[d]	—

[a] {Mo} = $\{HB(Me_2pyz)_3\}Mo(NO)I$; {W} = $\{HB(Me_2pyz)_3\}W(NO)Cl$. [b] For a 1-electron process unless otherwise stated. [c] 2-Electron process, broadened wave observed. [d] E_p reduction quoted. Oxidation peak shifted by a chemical reaction following the reduction.

(i) Reaction of a 'metallo-amine' or 'metallo-alcohol/phenol' with (**1**; X = Y = I) or (**2**; X = Y = Cl), thereby forming homo- and hetero-bimetallic complexes. Thus, addition of (**1**; X = Y = I) to purple (**1**; X = I, Y = *p*-$NHC_6H_4NH_2$) in solution afforded the deep blue $[Mo\{HB(Me_2pyz)_3\}(NO)I(NHC_6H_4NH)Mo\{HB(Me_2pyz)_3\}(NO)I]$, *i.e.* $[\{MoI\}(NHC_6H_4NH)\{MoI\}]$. Similarly, treatment of orange (**2**; X = Cl, Y = *p*-NHC_6H_4OH) with (**1**; X = Y = I) in solution afforded the deep orange-brown hetero-bimetallic $[\{WCl\}(NHC_6H_4O)\{MoI\}]$.

(ii) Reaction of a complex containing *p*-halide atoms in an aromatic derivative with co-ordinatively unsaturated compounds *via* oxidative addition. Thus, reaction of (**1**; X = I, Y = NHC_6H_4I) with $Pd(PPh_3)_4$ afforded the purple heterobimetallic species [**1**; X = I, Y = $NHC_6H_4Pd(PPh_3)_2I$]. Similar Pt complexes have been made but, as expected, there was no reaction between (**1**; X = I, Y = NHC_6H_4I) and $[Ir(CO)(PPh_3)_2Cl]$.

(iii) Reaction of 'metallo-phosphine' complexes with metal halides. For example (**2**; X = Cl, Y = $NH[CH_2]_3PPh_2$)

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[‡] Elemental analyses (C,H,N,halide,S) and ^1H n.m.r. and i.r. spectral results are all consistent with the formulation of these compounds.

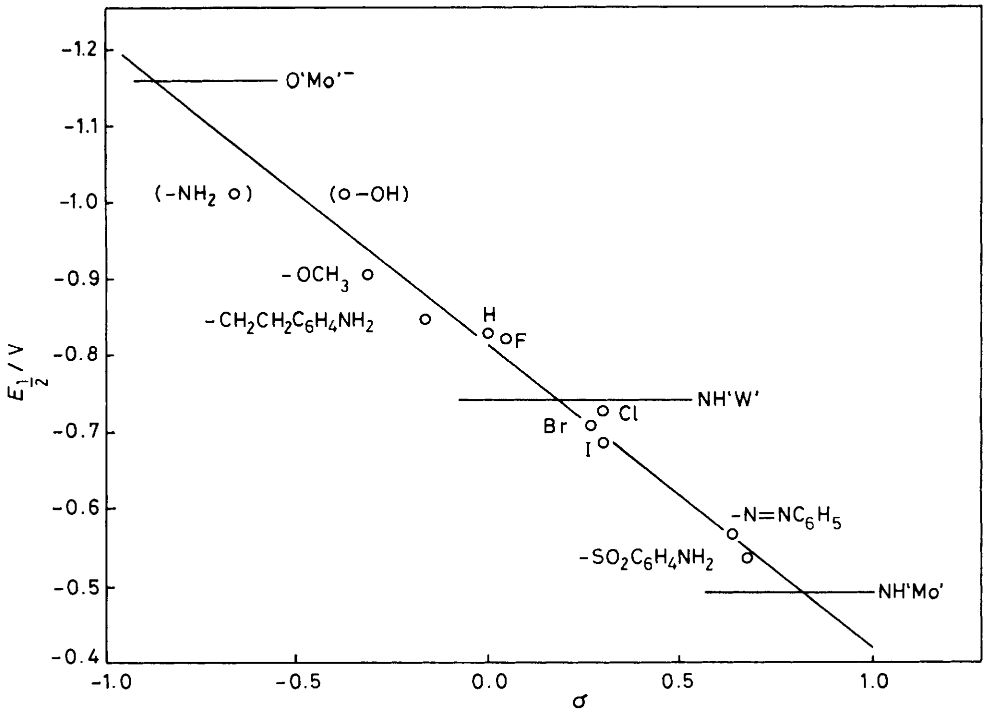

Figure 1. Plot of $E_{1/2}$ values against the Hammett *σ para* constant for a series of *para*-substituted complexes (**1**; X = I, L = NHC_6H_4Z) Z being shown on the graph. (Points in parentheses are E_p reduction values for a chemically irreversible reduction.)

reacted with $[Rh(CO)_2Cl]_2$ giving the trimetallic $[\{W\{HB(Me_2pyz)_3\}(NO)Cl(NH[CH_2]_3PPh_2)\}_2Rh(CO)Cl]$, while (**1**; X = I, Y = $NH[CH_2]_3PPh_2$) reacted with HgI_2 giving $[\{Mo\{HB(Me_2pyz)_3\}(NO)I(NH[CH_2]_3PPh_2)\}_2HgI_2]$.

We have made a preliminary study of the electrochemical properties of the bimetallic complexes prepared by route (i) and have compared the results with those obtained from some monometallic analogues. All the complexes undergo at least one one-electron reduction in acetonitrile or tetrahydrofuran. This has been detected using cyclic voltammetry and coulometry. Some complexes undergo two one-electron reductions and often these electrode processes are reversible, especially the less cathodic ones. The $E_{1/2}$ values for the first reduction waves depend on both the metal atom, W complexes being reduced at potentials *ca.* 500 mV more cathodic than their Mo analogues, and the donor atoms. Typically iodophenoxide molybdenum complexes reduce at *ca.* −0.3 V, iodoalkoxide molybdenum at *ca.* −0.6 V and iodoarylamide molybdenum at *ca.* −0.9 V. In the case of the phenoxide and arylamide complexes, the exact value of $E_{1/2}$ also depends upon the substituents present on the aromatic ring. So far our most comprehensive data have been obtained for complexes of type (**1**; X = I, Y = *p*-NHC_6H_4Z) where Z is one of a variety of *para*-substituents. There is a broadly linear correlation between the Hammett *σ para*-substituent constant[8] for Z and the $E_{1/2}$ value for the complex, as shown in Figure 1. The line shown has a slope of −400 mV so that the most electron-releasing Z groups give rise to the most cathodic $E_{1/2}$ values. A coupled chemical reaction, which can be shown by peak matching methods to be dissociation of I^- from the reduced complex, is observed for all Z groups.

The electrochemical data for the bimetallic complexes provide evidence of strong, intermediate, or weak interactions between the metal centres, depending on the nature of the bridging ligand. These data are summarised in Table 1. In symmetric homo-bimetallic complexes in which $-CH_2-$ or $-CH_2CH_2-$ groups link the two halves of the molecule a single broad two-electron reduction wave is observed at potentials virtually identical§ to those observed for the related monometallic species, *e.g.* (**1**; X = I, Y = NHPh; $E_{1/2}$ = −0.83 V). Thus there is *no* electrochemically detectable interaction between the metal centres in such systems. If, instead, the two halves of the molecule are linked by O, S, or SO_2 groups two overlapping waves are observed by cyclic voltammetry and the two reduction processes are separated by *ca.* 100 mV in each case. As the potential separation between two successive reductions becomes less than 100/*n* mV, the individual waves merge into one distorted wave.[9] Where the two metal centres are more directly linked, for example by $-NHC_6H_4NH-$ or $-NHC_6H_4O-$ bridging ligands, two one-electron reduction processes are observed. The potentials of these processes straddle that of the related monometallic species and suggest a *strong* interaction between the metal centres.

A similar state of affairs exists for the hetero-bimetallic species except that two one-electron processes are observed, corresponding to reduction at each of the two different metal centres. The potentials of these processes again differ from those of the related monometallic species by an amount dependent on the extent to which the metal centres influence one another.

If we accept that the relationship between $E_{1/2}$ and the Hammett *σ para* constant in the arylamido systems is valid, then it is possible to assign *σ para* values to the metal centres on the basis of the $E_{1/2}$ values of the bimetallic compounds. In this way *σ para* values of +0.83, +0.20, −0.81, and −1.74 may be assigned, respectively, to the substituents (**1**; X = I, Y

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§ A 36 mV separation would be expected on statistical grounds if both redox centres in the homo-bimetallic species had identical $E_{1/2}$ values; J. B. Flanagan, S., Margal, A. J. Bard, and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.

=NH–), (**2**; X = Cl, Y = NH–), (**1**; X = I, Y = O–; –1 charge), and (**1**; X = I, Y = NH–; –1 charge). These figures suggest that the replacement of a *p*-amino hydrogen atom by a molybdenum centre in (**1**; X = I, Y = $NHC_6H_4NH_2$) exerts a powerfully electron-withdrawing effect on the original metal atom. However, once an Mo centre has been reduced it appears to become powerfully electron-releasing towards the unreduced metal centre.

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