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Electrochemistry of dimolybdenum complexes containing oxo, imido, and sulphido moieties. A measure of their relative π-donor abilities?

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Abstract

The electrochemistry of dimolybdenum complexes $[(RC_5H_4)Mo(X)(\mu\text{-}X)]_2$ (X = multiply bonded ligand) has been investigated by cyclic voltammetry. The tetraoxo complex $[(MeC_5H_4)MoO(\mu\text{-}O)]_2$ (1) which adopts a *cis*-puckered geometry shows two reversible one electron reduction waves in THF. The substitution of oxo by imido moieties results in the adoption of a *trans*-planar geometry which substantially effects the electrochemistry such that complexes show oxidation chemistry. The trisimido-oxo complex $[(MeC_5H_4)_2Mo_2O(NPh)(\mu\text{-}NPh)_2]$ (2) shows an irreversible oxidation wave at +815 mV which becomes reversible at high scan rates indicative of an EC mechanism. The trisimido-sulphido complex $[(MeC_5H_4)_2Mo_2S(NPh)(\mu\text{-}NPh)_2]$ (3) shows a quasi-reversible oxidation at +620 mV and the tetraimido complex $[(MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$ (4) shows a reversible one electron oxidation at +525 mV together with a second irreversible oxidation at higher potential. A comparison of the oxidation potentials of 2, 3, and 4 gives a measure of the relative π-donor abilities of oxo, sulphido, and imido ligands at a Mo^V centre.

Introduction

The isoelectronic oxo, imido, and sulphido ligands bind to transition metal centres utilising both σ and π interactions, the latter involving the overlap of filled ligand *p*-orbitals with vacant metal *d*-orbitals. Productive π-bonding thus requires that the metal centre be in a high oxidation state with a low *d*-electron count and thus in the vast majority of complexes containing these ligands bound to a single metal centre the metal has a d^0, d^1, or d^2 electronic configuration. The extent to which this π-donation is developed, however, is difficult to ascertain. For the imido ligand, the valence bond description suggests that the metal–nitrogen bond order can, to a first approximation, be inferred from the position of the substituent [1], however for other multiply bonded ligands this probe is not available.

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Infrared data have previously been used as a measure of the relative π-donor abilities of multiply bonded ligands [2]. This can be achieved either directly via the measurement of multiply bonded metal–ligand vibrations or, indirectly, by monitoring the variation in stretching frequency of a secondary ligand, for example a carbonyl group, upon substitution of one multiply bonded ligand for another. Thus, successive substitutions of imido for oxo ligands at an Os^{VIII} centre results in a shift of the remaining Os=O vibrations to lower wavenumbers indicating that the imido moiety is a better π-donor than the oxo ligand at this centre [3]. Alternatively, for the complexes $[W(X)Cl_2(CO)L_2]$, changes in the carbonyl stretching frequency upon variation of X suggests that π-donation decreases in the order $NR^{2-} > S^{2-} > O^{2-}$ at the tungsten(V) centre [4].

During the course of our studies on high oxidation state cyclopentadienyl stabilised dimolybdenum complexes we have synthesised a number of compounds of the type $[(RC_5H_4)MoX(\mu\text{-}X)]_2$ containing oxo, imido, and sulphido moieties [5]. X-ray crystallographic studies reveal that while the tetraoxo complex, $[(C_5H_5)MoO(\mu\text{-}O)]_2$ [6] adopts a *cis*-puckered geometry, substitution of an oxo by an imido moiety results in a conformational change to a *trans*-planar form [5,7]. While we can not eliminate the possibility that the steric requirements of the more bulky arylimido ligand may be the cause of this effect, we considered that this pronounced change in structure may be a consequence of the better π-donor ability of the imido versus the oxo moiety. Electrochemical measurements should be a useful probe of the relative π-donor abilities of multiply bonded ligands since oxidation and reduction potentials are sensitive to ligand environments. This probe may be especially useful when considering complexes containing imido ligand(s) since absorptions in the infrared commonly assigned to this moiety contain both M–N and N–C character [8] and thus are not a direct measure of the former. We have thus measured, utilising cyclic voltammetry, the solution electrochemistry of a number of dimolybdenum complexes containing multiply bonded ligands in order to access both the electronic consequences of these different geometrical forms and the application of electrochemical measurements towards accessing the relative π-donor ability of oxo, imido, and sulphido ligands at a molybdenum(V) centre.

Results and discussion

The electrochemical properties of a number of cyclopentadienyl stabilised dimolybdenum complexes containing multiply bonded π-donor ligands have been studied utilising cyclic voltammetry at a platinum-disc electrode with 0.1 *M* tetra-n-butylammonium hexafluorophosphate as electrolyte at a scan speed of 50 mV s^{-1}. The results, summarised in Table 1, are relative to the saturated calomel electrode (s.c.e.) and have been measured using as internal reference the couple $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E_{1/2} = +355$ mV; $\Delta E_{1/2} = 60$ mV).

The tetraoxo complex $[(MeC_5H_4)MoO(\mu\text{-}O)]_2$ (1) undergoes two one-electron diffusion controlled reversible reductions in THF at -845 and -905 mV respectively, but did not show oxidation chemistry in THF up to the limit of detection ($+750$ mV). Upon substitution of all oxo by phenylimido ligands a substantial change in the redox chemistry is observed. Thus, the tetraimido complex $[(MeC_5H_4)Mo(NPh)(\mu\text{-}NPh)]_2$ (4) shows no reduction chemistry in either THF, acetonitrile, or dichloromethane (-2 V) but rather shows oxidation chemistry. In

Table 1

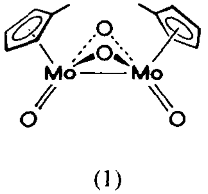
Electrochemical data for $[(MeC_5H_4)_2Mo_2(X)(X')(\mu\text{-}Y)(\mu\text{-}Y')]$ ($E_{1/2}$; $\nu = 50$ mV s^{-1})

	Complex				Solvent	Reduction (mV)		Oxidation (mV)	
	X	X′	Y	Y′		−2	−1	+1	+2
1	O	O	O	O	THF	−905 [r]	−845 [r]	–	–
2	O	NPh	NPh	NPh	CH_2Cl_2	–	–	−815 [ia]	–
3	S	NPh	NPh	NPh	CH_2Cl_2	–	–	+620 [qb]	–
4	NPh	NPh	NPh	NPh	CH_2Cl_2	–	–	+525 [rc]	+915 [id]
					MeCN	–	–	+805 [r]	+1175 [id]
					THF	–	–	+365 [r]	+645 [id]

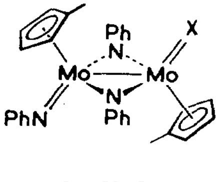
[a] An EC mechanism indicated by behaviour at high ν. [b] $\Delta E_{1/2} = 65$ mV. [c] $\Delta E_{1/2} = 65$ mV. [d] E_{pA}.
[i] Irreversible. [q] Quasi-reversible. [r] Reversible.

THF, a one electron reversible oxidation wave at +345 mV and a second irreversible oxidation at +645 mV are observed, the reversibility of the former being confirmed by the value of peak current ratio, ip_C/ip_A being close to unity, and a plot of ip against $\nu_{1/2}$ giving a straight line through the origin, in agreement with the Randles–Sevcik equation. The differences in redox chemistry exhibited by the quasi-electronic complexes **1** and **4** is indicative of the electron deficient nature of the former in contrast to the electron rich nature of the latter, a consequence of the better π-donor properties of the phenylimido versus the oxo moiety. This effect can be traced back to their adoption of different geometrical forms as shown by X-ray crystallography. Thus, the tetraoxo complex (**1**), by analogy with the unsubstituted derivative $[(C_5H_5)MoO(\mu\text{-}O)]_2$, contains a puckered metallacyclic core arrangement and *cis*-cyclopentadienyl ligands [6]. In this form the two molybdenum atoms show a close approach [2.602(1) Å in the unsubstituted complex] as a result of their electron deficient nature. In contrast, the tetraimido complex (**4**) contains a planar $Mo_2(\mu\text{-}N)_2$ core arrangement with *trans*-methylcyclopentadienyl ligands [5]. In this latter geometry, the two metal atoms are more distant at 2.7175(5) Å, representing the better π-donor ability of the phenylimido versus oxo group. While this is clearly reflected in the redox chemistry an insight into the relative π-donor properties of these ligands is precluded since the two complexes adopt widely differing geometrical forms.

Complexes **2**–**4** adopt the *trans*-planar geometrical form and differ only in the nature of one of the terminally bonded ligands at a molybdenum(V) centre. Thus a



(1)



(2) X=O
(3) X=S
(4) X=NPh

comparison of their electrochemical properties should allow for measure of the relative π-donor abilities of these ligands. The trisimido-oxo complex $[(MeC_5H_4)_2Mo_2O(NPh)(\mu\text{-}NPh)_2]$ (**2**) showed an irreversible oxidation at +805 mV (scan rate 50 mV s^{-1}), which developed return wave characteristics at higher scan speeds ($\nu = 500$ mV s^{-1}; $ip_C/ip_A = 0.46$), behaviour indicative of an EC mechanism [9] (*vide infra*), while the analogous trisimido-sulphido complex $[(MeC_5H_4)_2Mo_2S(NPh)(\mu\text{-}NPh)_2]$ (**3**) showed a one-electron quasi-reversible oxidation at +620 mV. As already discussed, upon full oxo substitution for phenylimido ligands this oxidation process becomes reversible, being observed at +525 mV in dichloromethane. These results suggest that the relative π-donor abilities of these ligands at the molybdenum(V) centre follow the order $NPh^{2-} > S^{2-} > O^{2-}$, a similar trend to that noted at a tungsten(V) centre [4].

The electrochemical data also lend insight into the stability of radical cations formed during oxidative processes. Thus, the trisimido-oxo (**2**) complex exhibits reversible behaviour at high scan rates. Measuring the cyclic voltammagrams at different scan speeds showed that an EC mechanism [9] was responsible for these observations. The rate of decomposition of the oxidised species was such that at faster scan speeds, some oxidised material remained for reduction. For both the tetraimido complex (**4**) and the trisimidosulphido complex (**3**) decomposition of the oxidised species does not occur (or is extremely slow) on the voltammetric time scale. Thus, the stability of the oxidised species is enhanced by strong π-donor ligands. Attempts to isolate the radical cation of the tetraimido complex (**4**) have, to date, been unsuccessful. Thus, chemical oxidation of (**4**) with a stoichiometric amount of $AgPF_6$ resulted in a rapid colour change from orange to yellow. Work-up, however, using rigorously dried and degassed solvents, led only to the isolation of the hydrolysis products $[(MeC_5H_4)MoO(\mu\text{-}NPh)]_2$ and **2** [5]. Clearly, oxidation of **4** renders it especially susceptible to hydrolysis.

As might be expected [8], infrared data for these complexes (Table 2) do not reflect the differences observed electrochemically, with bridging and terminal imido stretches lying within 3 and 5 cm^{-1} ranges respectively. Hence it appears that electrochemical data provide a sensitive probe of the relative π-donor properties of these ligands. A similar effect has been noted in a series of mixed oxo-sulphido dimolybdenum dithiocarbamate complexes where the ease of production and chemical stability of one- and two-electron reduction products was found to increase with increasing sulphur substitution [10]. These complexes which electrochemically behave very similar to **1** also adopt a puckered metallacore geometry [11]. Thus it appears to be a general observation that in dimolybdenum(V) systems supporting both bridging and terminal multiply bonded ligands the geometry adopted (*cis*-

Table 2

Infrared data (cm^{-1}) (KBr)

Complex	Mo=O	μ-O	Mo=NPh	μ-NPh
1	927	715	–	–
2	884	–	1327	1263
3	474 [a]	–	1324	1264
4	–	–	1322	1266

[a] Mo=S.

puckered or *trans*-planar) dominates the electrochemistry. These considerations may prove critical when trying to design such complexes to be oxygen transfer, oxyamination, or amination reagents, since the transfer of the multiply bonded ligand to, for example, an unsaturated organic necessarily involves the reduction of the metal centre.

Experimental

Compounds **1**–**4** were prepared as previously described [5]. Solvents were pre-dried over activated molecular sieves and distilled under nitrogen from potassium (THF), phosphorus pentoxide (dichloromethane), calcium hydride followed by phosphorus pentoxide (acetonitrile). Tetra-n-butylammonium hexafluorophosphate (Aldrich) was recrystallised from THF and dried *in vacuo* for several hours. Cyclic voltammetry experiments were performed using ca. 5 mg of sample in ca. 20 cm^3 of 0.1 *M* tetra-n-butylammonium hexafluorophosphate solution at ca. 20 °C. Voltammograms were recorded using an Oxford Instruments Potentiostat and a Rikadenki X–Y chart recorder. A two compartment cell was used. The working compartment contained the working and counter electrodes, and was separated from the one containing the reference electrode by a medium grade porous frit. A platinum disc (diameter 3 mm) sealed in glass, a platinum gauze, and a platinum "pigtail" electrode served as the working, counter, and quasi-reference electrodes respectively. Sample loading was by Schlenk line techniques. Ferrocene was added at the end of each experiment as an internal reference [12]; its potential against the saturated calomel electrode (s.c.e.) being taken as +355 mV [13]. All potentials are quoted relative to s.c.e.

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