

Electrochemistry of Dinuclear, Thiolato-bridged Transition-metal Compounds. Part 2.¹ Reductive Electrochemistry of Metal–Metal Bonded Complexes

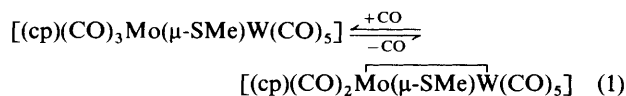


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The compounds $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_4\text{L}}$ (**1**) (L = CO) and (**2**) [L = P(OMe)₃] have been studied by electrochemical methods (cyclic voltammetry, controlled-potential electrolysis, and coulometry) in propylene carbonate. The substitution of P(OMe)₃ for CO at the tungsten centre is shown to have various effects on the electrochemical behaviour. Both (**1**) and (**2**) are reduced according to an e.c.-disp. process (second electron transfer is homogeneous) which differs depending on the nature of L. The results reported are consistent with the presence of an acceptor–donor metal–metal bond in both compounds.

The aim of the studies in this series is to contribute to the electron-transfer chemistry of sulphur- and thiolato-bridged transition-metal complexes.^{2–4} In the preceding paper, we described the electrochemistry of octacarbonyl complexes which reversibly lose a CO ligand at the Mo centre with the concomitant formation of a metal–metal bond,⁵ e.g. reaction (1).† Several examples of such a reaction have been reported by

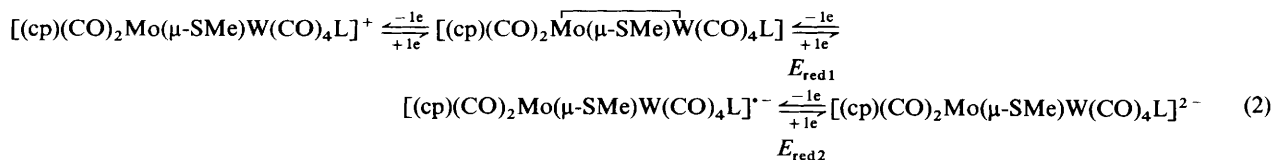


us and others.^{5–14}

The metal–metal bond in the complexes $[(\text{cp})(\text{CO})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_4\text{L}}$ [L = CO (**1**) or P(OMe)₃ (**2**)] has been viewed initially as a covalent bond.⁵ However, several studies showed that the metal–metal interaction can have a significant donor–acceptor character.^{8,10–16} The metal–metal bonding and antibonding orbitals contain a stronger character of one metal centre than of the other (see Scheme 1 in ref. 13). For complexes containing such polar metal–metal bonds, the crystal structure determination often shows the presence, at the donor metal centre, of a semi-bridging or bent carbonyl group,^{16–25} the role of which is to redress the charge imbalance that would result from the metal–metal interaction.¹⁶ The occurrence of a semi-bridging CO at the W centre in both (**1**) and (**2**) lends support to the assignment of a dative Mo←W bond to these compounds (Figure 1). However, theoretical calculations indicate the absence of direct M–M interaction in such complexes.²⁶

The results we report here concern the electrochemical behaviour of the title compounds as well as changes in reactivity resulting from the substitution of a donor ligand for CO at the tungsten centre.

This study may have relevance to the wider area of catalysis *via* transition-metal complexes.



† Throughout this paper, cp stands for $\eta^5\text{-C}_5\text{H}_5$ and $\overline{\text{MM}}$ represents a metal–metal bonded species.

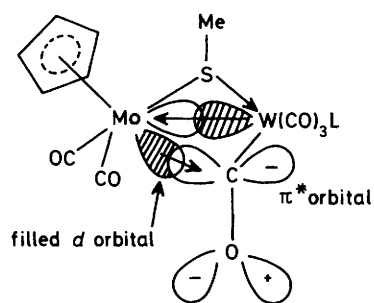


Figure 1. Illustration of the bonding scheme in complexes $[(\text{cp})(\text{CO})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_4\text{L}}$ (only one lobe of the metal-centred orbitals is represented)

A part of the present work has been the subject of a previous brief conference report.²⁷

Experimental

Synthesis.—Compounds (**1**) and (**2**) were prepared as described previously.⁵

Solvents, Reagents, Electrochemical Apparatus, and Measurements.—The purification of the solvents [propylene carbonate (pc), tetrahydrofuran (thf), PhCN, and CH₂Cl₂] and reagents, as well as the experimental techniques have been described previously.¹ All the potentials are quoted against the ferrocenium–ferrocene couple.

Results and Discussion

The complexes $[(\text{cp})(\text{CO})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_4\text{L}}$ [L = CO (**1**) or P(OMe)₃ (**2**)] are stable members of four-membered electron-transfer series, equation (2).

Thus cyclic voltammetry (c.v.) of complex (**2**) in various non-aqueous electrolytes shows that it undergoes two successive one-electron reductions and a one-electron oxidation, as

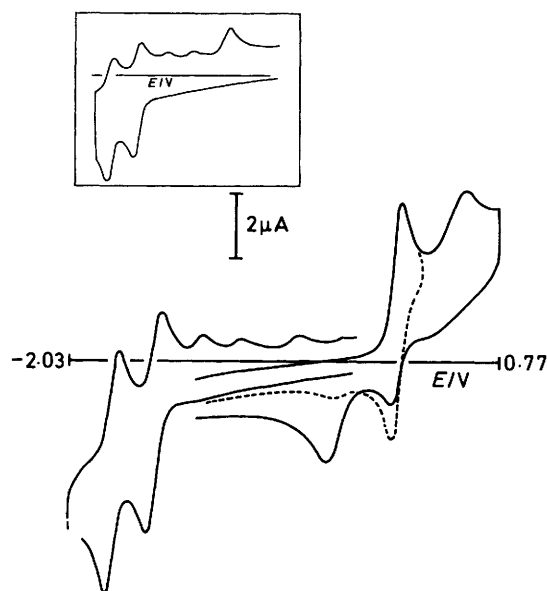


Figure 2. Cyclic voltammetry of (2) ($ca. 10^{-3}$ mol dm^{-3}) in pc -0.1 mol dm^{-3} $[NBu_4][PF_6]$. Insert: ramp-clamp cyclic voltammetry; potential held 20 s at -2.0 V. Scan rate 0.2 V s^{-1}

exemplified by the cyclic voltammogram of Figure 2, recorded in a pc electrolyte.

The stabilities of the extreme members of the electron-transfer series for the complex in which $L = CO$ are decidedly less than for the $P(OMe)_3$ analogue: the oxidation tends towards an irreversible two-electron process, the second reduction step shows reversibility only at low temperatures or fast scan rate (Figure 3). The difference in stabilities of the corresponding $P(OMe)_3$ and CO species is electronic rather than steric in origin. Tables 1 and 2 list the redox potential data for complexes (1) and (2), from which it can be seen that the $P(OMe)_3$ group exerts a considerable inductive effect on the redox orbitals relative to the CO substituent. Studies of the behaviour of the complexes at a rotating disc electrode (r.d.e.) confirm the monotonic nature of the electron-transfer steps.

The results reported here concern the reduction of the complexes, the oxidation processes have not been investigated in detail.

For both complexes (1) and (2) the cathodic current functions are independent of scan rate (v) only for $v > 0.1$ V s^{-1} , as illustrated in Figure 4 for complex (1). This demonstrates that at the first wave, reduction of complexes (1) and (2) is complicated by chemical reactions.

Coulometric measurements during controlled-potential electrolyses (c.p.e.) at the potential of either wave of complex (2) lead to $n_{app} = 2$ electrons per molecule, a value entirely consistent with the current-function data. Therefore, at E_p^{red1} , complex (2) undergoes an e.c.e. or e.c.-disp.²⁸ mechanism.*

On the contrary, the coulometric data for complex (1) are in contrast with those expected for an e.c.e. mechanism, since 0.9 electron is exchanged per molecule of complex at the first wave while $n_{app} = 1.3$ electrons per molecule when the electrolysis is performed at E_p^{red2} .

Two types of mechanism, to our knowledge, could be invoked

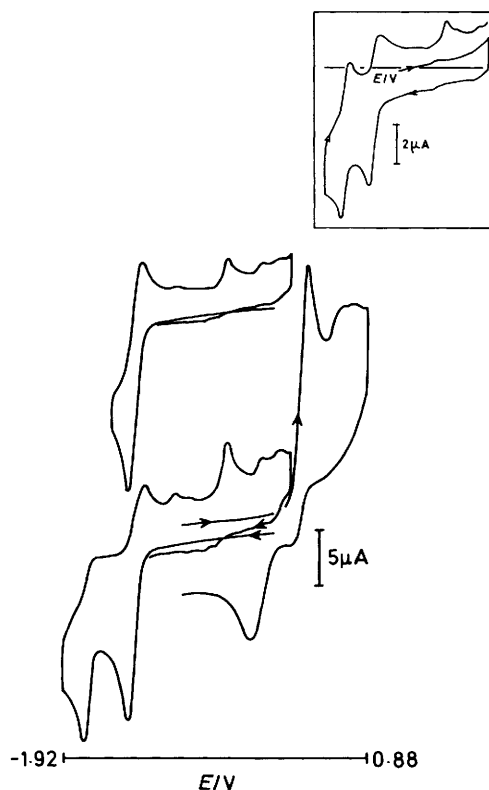


Figure 3. Room-temperature and low-temperature (-15 °C, insert) cyclic voltammogram of complex (1) ($ca. 10^{-3}$ mol dm^{-3}) in pc -0.1 mol dm^{-3} $[NBu_4][PF_6]$. Scan rate 0.2 V s^{-1}

to explain the scan-rate dependence of the peak currents (Figure 4) and the number of electrons involved in the overall reduction at the first wave ($n_{app} < 1.0$) for complex (1): (i) an e.c.e. (or e.c.-disp.) process, in which a product resulting from the primary electronation and the subsequent rate-determining step would react with the parent complex, and (ii) a c.e. process, in which both the species in equilibrium would be reducible. This might be the case for a mixture of isomers²⁹⁻³¹ or for a compound which undergoes a geometrical isomerization accompanying the metal-metal bond cleavage.³² (For a detailed discussion of the scan-rate dependence of the peak currents for a c.e. mechanism with both species electroactive see ref. 30.)

Although the cathodic current functions would be qualitatively similar for the reduction occurring following either scheme (Figure 5), the e.c.e. and c.e. processes may be distinguished by a comparison of $i_p/v^{1/2}c$ (i_p = peak current, c = concentration of the complex) for the compound under study and for a reversible one-electron system, without any chemical complication of the electronic step (Figure 5). The anodic current function of $[Fe(CO)(cp)(\mu-SMe)_2]^\ddagger$ is plotted in Figure 4, curve 3: this situation corresponds to an e.c.e.-type mechanism.

Intermediates and Products of the Two-electron Reduction of (1) and (2).—Detection of intermediates. The reduction of

* An e.c.e. mechanism comprises a chemical reaction (c) coupled between two electron-transfer steps (e). The second electron transfer may either be heterogeneous (e.c.e. mechanism) or homogeneous (e.c.-disp. mechanism). Likewise, in a c.e. process, a chemical reaction precedes an electron transfer.

$\ddagger [Fe(CO)(cp)(\mu-SMe)_2]$ has been shown to oxidize without chemical complication on the c.v. time-scale.³³⁻³⁵ This complex was preferred to ferrocene since potential-step experiments show that the diffusion coefficient (D) of the former is close to that of compound (2). Complexes (1) and (2) are assumed to have identical D values.

Table 1. Electrochemical data^a for [(cp)(CO)₂Mo(μ-SMe)W(CO)₅] (1)

Solvent	First reduction					Second reduction					First oxidation			
	$\frac{1}{2}(E_{pa} + E_{pc})/V$	$E_p - E_{p/2}/mV$	$E_{\frac{1}{2}}(r.d.e.)/V$	Slope	n^b	k_c^c/s^{-1}	$E_{p/2}/V$	$E_p - E_{p/2}/mV$	$E_{\frac{1}{2}}(r.d.e.)/V$	Slope	n^b	$E_{p/2}/V$	$E_{\frac{1}{2}}(r.d.e.)/V$	n^b
pc	-1.26	60	-1.26	64	0.85	0.10 ± 0.02	-1.66	60	-1.67	50	1.3	0.21	0.25	2
thf	-1.38	70	-1.40	115	0.85	0.10 ± 0.02	-1.90	70	-1.88	110		+0.29		
CH ₂ Cl ₂	-1.41	65	-1.41	70		0.09 ± 0.02	-1.79	65	-1.83	70		+0.30 ^d	0.30	
PhCN	-1.35	60	-1.36	80		0.10 ± 0.02	-1.81	60	-1.88	67		0.13	0.17	

^a Potentials quoted vs. ferrocene-ferrocenium couple; cyclic voltammetry, $v = 0.2 \text{ V s}^{-1}$. Slope = slope of line (in mV) $E = f[\log(i/i_d - i)]$ where i_d is the diffusion current and i is the current at potential E . ^b Number of electrons (coulometric experiments). ^c Rate constant of the rate-determining step. ^d $\frac{1}{2}(E_{pa} + E_{pc})$.

Table 2. Electrochemical data^a for [(cp)(CO)₂Mo(μ-SMe)W(CO)₄{P(OMe)₃}] (2)

Solvent	First reduction						Second reduction					First oxidation		
	$\frac{1}{2}(E_{pa} + E_{pc})/V$	$E_p - E_{p/2}/mV$	$E_{\frac{1}{2}}(r.d.e.)/V$	Slope	n	k_c/s^{-1}	$\frac{1}{2}(E_{pa} + E_{pc})/V$	$E_p - E_{p/2}/mV$	$E_{\frac{1}{2}}(r.d.e.)/V$	Slope	n	$\frac{1}{2}(E_{pa} + E_{pc})/V$	$E_{\frac{1}{2}}(r.d.e.)/V$	Slope
pc	-1.47	60	-1.48	80	2.0	0.06 ± 0.02^b	-1.75	60	-1.77	82	2.0	+0.10	+0.09	62.5
thf	-1.65	70				0.10 ± 0.02^c	-2.05	70				+0.11		
CH ₂ Cl ₂	-1.60	80	-1.64	84			-1.83 ^d	50	-1.88	78		+0.08	+0.08	71

^a See comments in Table 1. ^b At 20 °C. ^c At 30 °C. ^d Irreversible system; value of $E_{p/2}$.

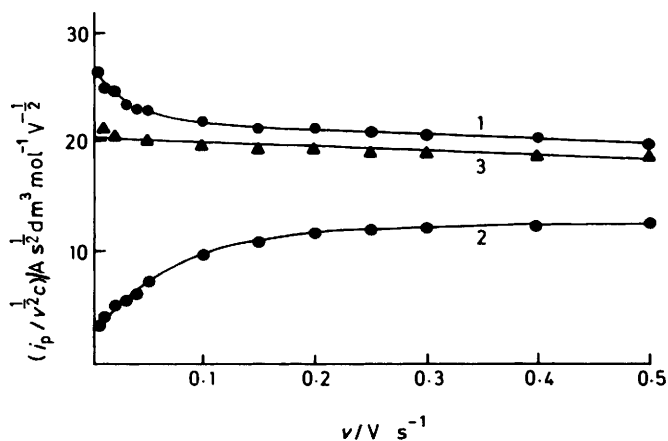


Figure 4. Scan-rate dependence of the peak currents of complex (1) in a pc electrolyte. Curve 1: first reduction peak; curve 2: second reduction peak; curve 3: oxidation peak of [(Fe(CO)(cp)(μ-SMe))₂]

complex (1) [or complex (2)] at the first or at the second wave leads to the same species, either stable products or unstable intermediates. One of the species resulting from the reduction of (1) (Figure 3) is easily identified as [W(CO)₅(SMe)]⁻¹. The major peak in the cyclic voltammogram of (2) (Figure 2, insert) is assigned to the corresponding [W(CO)₄{P(OMe)₃}(SMe)]⁻ anion, the potential of which is consistent with the negative shift in oxidation potential expected on substitution of P(OMe)₃ for CO in 18-electron compounds.

A small peak, which occurs at the same potential for complexes (1) and (2), is shifted depending on the solvent (S'). From the ligand constants reported for thf^{36,37} and PhCN³⁸ and from the oxidation potentials of various [Mo(CO)₂(cp)L]⁻ anions,¹ the oxidation of [Mo(CO)₂(cp)(S')]⁻ is expected

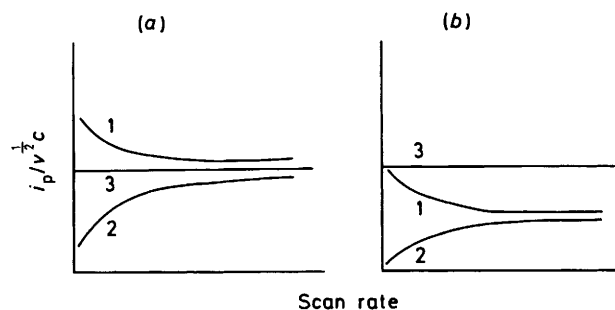
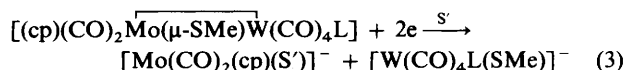


Figure 5. Schematic illustration of the scan-rate dependence of the peak currents for an e.c.e. (a) or c.e. mechanism (b) (see text). Curve 1: first reduction peak; curve 2: second reduction peak; curve 3: current peak (oxidation or reduction) for an uncomplicated one-electron system

between -1.2 and -1.5 V in thf, and at -1.0 V in PhCN. These values are entirely consistent with the potential of the solvent-dependent peak (-1.46 in thf, -1.0 in PhCN, and -1.16 V in pc), which we assign to the oxidation of [Mo(CO)₂(cp)(S')]⁻.

The occurrence of intermediates resulting from a two-electron exchange, e.g. equation (3), at the potential of the first



wave demonstrates that an e.c.e.-type process is operative at this potential, which is fully supported by the current-function data.

Fate of the intermediates. The major peak observed in the cyclic voltammogram of complex (1), and absent for complex (2), is due to the oxidation of the tricarbonyl species [Mo(CO)₃(cp)]⁻¹. The occurrence of this anion, even in non-

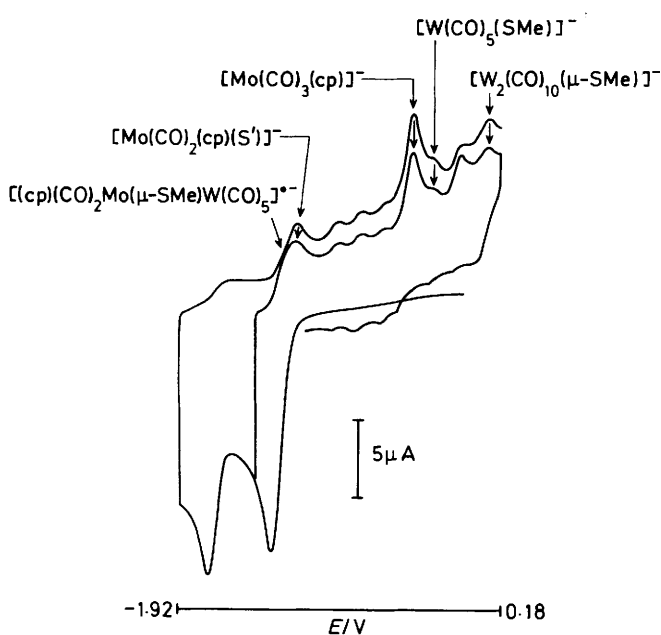
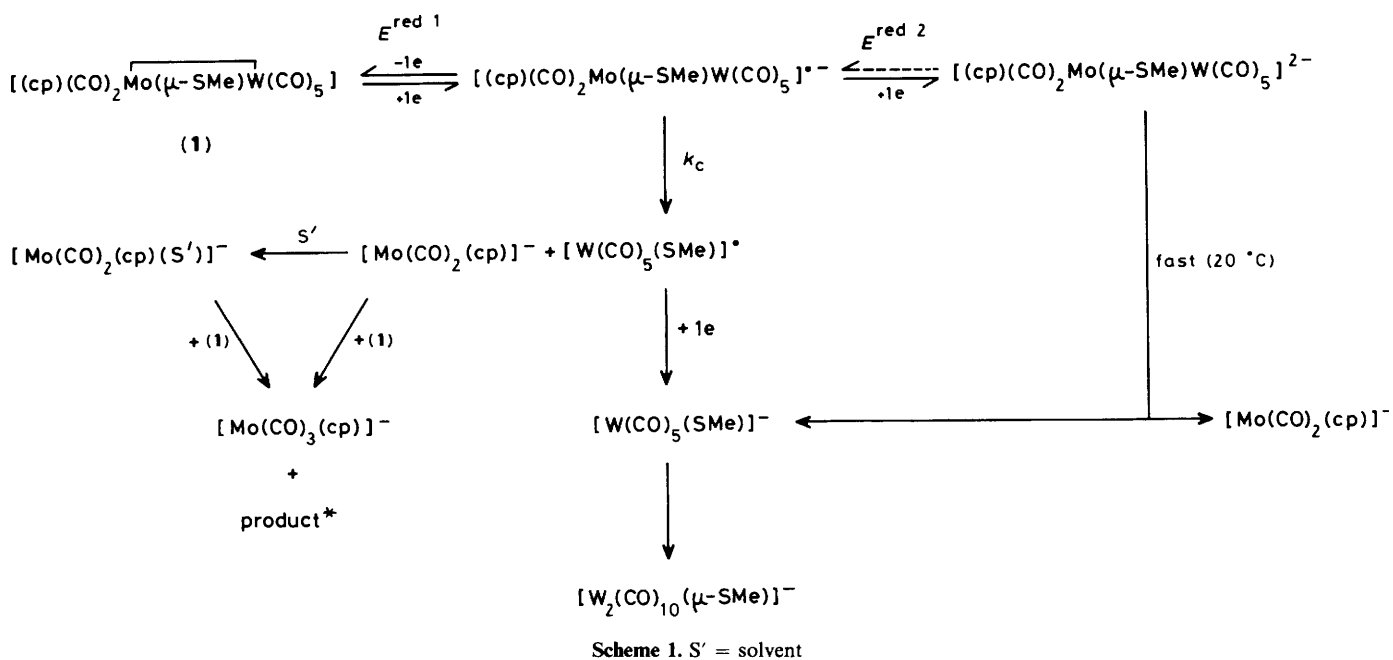


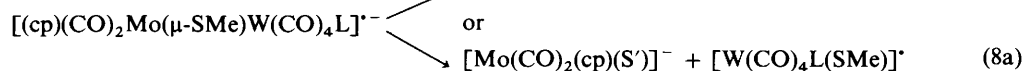
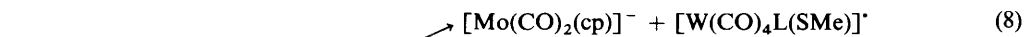
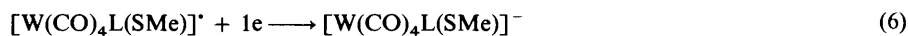
Figure 8. Ramp-clamp cyclic voltammetry of complex (1) in pc-0.1 mol dm⁻³ [NBu₄][PF₆]. Potential held 20 s, scan rate 0.2 V s⁻¹

involve kinetic effects of the chemical step [(F_c^{red1})_k at v < 0.1 V s⁻¹] or not [(F_c^{red1})_d at v > 0.1 V s⁻¹]. Mean values of k_c are listed in Tables 1 and 2. These values demonstrate that the rate-determining step does not involve attack by the solvent as k_c is solvent-independent (pc, thf, CH₂Cl₂, or PhCN; Table 1). However, this does not preclude the possibility of a fast reaction between the solvent and the radical anion, preceding the rate-determining cleavage of the product (Scheme 2). The rate constant calculated for complex (2) in the presence of CO, k_c = 1.5 s⁻¹, demonstrates that CO favours the disruption of the radical anion (2)^{·-} (Figure 7).

The secondary electronation. The rate-determining cleavage of the radical anion generates the [W(CO)₄L(SMe)][·] species (Schemes 1 and 2), which was shown to reduce at a potential less negative than E_p^{red1}, L = CO.¹ Although the substitution of P(OMe)₃ for CO makes the radical harder to reduce, this reaction undoubtedly occurs at a potential less negative than E_p^{red1} [-1.47 V for complex (2)].

Whether the secondary electronation occurs at the electrode [equation (6), e.c.e. mechanism] or in the bulk of the solution [e.c.-disp. mechanism, equation (7)] will depend on the relative rates of reaction (7) and of the rate-determining step, e.g. equation (8) or (8a).

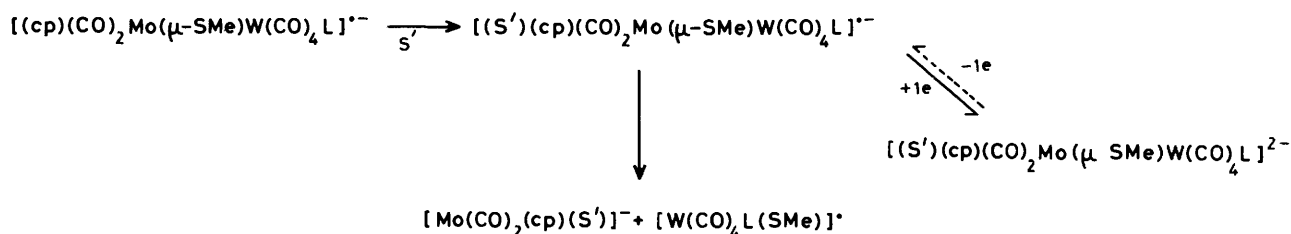
Owing to the half-lives of (1)^{·-} and (2)^{·-} (Tables 1 and 2), the disruption of the radical anion does not take place in the electrode vicinity. It is therefore likely that the [W(CO)₄L-



F_c = i_p/v^{1/2}c, F = Faraday constant] of the equation established by Nicholson and Shain.⁴³ In this equation, (F_c^{red1})_k and (F_c^{red1})_d are the values of the cathodic current functions for the first reduction process at scan rates (v) which were shown to

(SMe)][·] fragment undergoes a homogeneous electron transfer before it diffuses back to the electrode.

The Reduction of (1) at E_p^{red2}.—After a c.p.e. at E_p^{red1}, cyclic

Scheme 2. S' = solvent, L = CO or P(OMe)₃

voltammetry of the catholyte shows the presence of a reduction peak at the same potential as the second reduction of the starting material. This peak is associated with the oxidation process at -0.12 V since both are absent when the electrolysis is performed at $E_p^{\text{red}2}$, or disappear when a c.p.e. at $E_p^{\text{red}2}$ follows a reduction at $E_p^{\text{red}1}$. The suppression of the oxidation peak at -0.12 V is also apparent in ramp-clamp experiments (Figure 8) with the potential held beyond $E_p^{\text{red}2}$.

We believe that the reduction process at -1.7 V and the oxidation at -0.12 V are due to a by-product (product* in Scheme 1), of the attack of $[\text{Mo}(\text{CO})_2(\text{cp})]^-$ {or $[\text{Mo}(\text{CO})_2(\text{cp})(S')]^-$ } on the parent complex (1). The reduction of this by-product at $E_p^{\text{red}2}$ accounts for the number of electrons exchanged per molecule of complex during electrolyses at $E_p^{\text{red}2}$ ($n_{\text{app}} = 1.3$ electrons per molecule).

Conclusions

The electrochemical investigation of complexes $[(\text{cp})(\text{CO})_2\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_4\text{L}]$ [L = CO (1) or P(OMe)₃ (2)] has shown that both reduce according to an e.c.-disp.-type mechanism, at the potential of the first reductive step.

The results are entirely consistent with the presence of an acceptor-donor Mo←W bond in the complexes. The two one-electron reductions of the formal Mo^{II}W⁰ compounds result in the generation of (Mo^IW⁰)⁻ and (Mo⁰W⁰)²⁻ species. The substitution of P(OMe)₃ for CO exerts a strong influence on the redox orbital: the electronic charge at the W centre is transmitted to the adjacent metal centre through the polar metal-metal bond. This is in complete agreement with the results reported by Honrath and Vahrenkamp⁴⁴ for a series of similar compounds.

The effects of the substitution of P(OMe)₃ for CO, i.e. (a) the harder reduction of the phosphite-substituted derivative, (b) the increased stability of the radical anion and dianion for (2), (c) the simpler reduction mechanism of (2) relative to (1), and (d) the lower reactivity of (2) with CO or other two-electron donor ligands,²⁷ are all electronic in origin as they arise from the increased electron density at the W centre upon substitution.

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