Electrochemistry of Dinuclear, Thiolato-bridged Transition-metal Compounds. Part 1. Electrochemical Behaviour of $[(\eta^5\text{-}C_5H_5)(CO)_3M(\mu\text{-SR})W(CO)_5]$ (R = Me, M = Mo or W; R = Ph, M = W) Complexes in Non-aqueous Media

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The compounds $[(\eta^5\text{-}C_5H_5)(CO)_3M(\mu\text{-SR})W(CO)_5]$ have been studied by usual electrochemical methods (cyclic voltammetry, controlled-potential electrolysis, and coulometry). They undergo a destructive two-electron reduction according to an electrochemical–chemical–electrochemical process with a diffusion-controlled intervening chemical step. The $[W(CO)_5(SMe)]^-$ anion generated by the reduction of the complexes undergoes chemical reactions leading to the dinuclear species $[W_2(CO)_{10}(\mu\text{-SMe})]^-$ on the time-scale of controlled-potential electrolyses.

In a previous report[1] we described the synthesis, the crystal structure determination, and some aspects of the reactivity of dinuclear, thiolato-bridged complexes which were shown to react according to reaction (1).†

$$[(cp)(CO)_2LM(\mu\text{-SR})W(CO)_5] \underset{-L}{\overset{+L}{\rightleftharpoons}} [(cp)(CO)_2\overline{M(\mu\text{-SR})W}(CO)_5] \quad (1)$$

$$L = P(OMe)_3, P(OPh)_3, PPh_3, CO \ldots$$
$$M = \text{Mo or W}, R = Me$$

This prompted us to investigate the electrochemical behaviour of both partners in reaction (1) since they possess some desirable properties from the point of view of their possible use as catalysts:[2–5] (*i*) the co-ordinatively saturated complexes $[(cp)(CO)_3M(\mu\text{-SR})W(CO)_5]$ possess labile ligands at the M centre (M = Mo or W), thus liable to exchange with a substrate; and (*ii*) the metal–metal bonded complexes undergo cleavage of the M–W bond under mild conditions in the presence of CO, $P(OMe)_3$, $P(OPh)_3$ *etc.* [*e.g.* reaction (1)], a reaction which may be reversed by thermally inducing L dissociation.[1]

We now report the results concerning the reductive electrochemistry of the saturated species $[(cp)(CO)_3M(\mu\text{-SR})W(CO)_5]$ (R = Me, M = Mo or W; R = Ph, M = W). The electrochemical behaviour of the metal–metal bonded species will be described in the following paper.

Experimental

Synthesis.—The thiolate precursors $[M(CO)_3(cp)(SR)]$ (M = Mo or W, R = Me or Ph) of the dinuclear complexes were synthesised according to published procedures.[6] The preparation of the compounds $[(cp)(CO)_3M(\mu\text{-SR})W(CO)_5]$ was described in an earlier report.[1] The dinuclear complex $[W_2(CO)_{10}(\mu\text{-SMe})]^-$ was prepared according to the literature[7] method [i.r. data:[7] 2 060w, 2 047m, 1 968w (sh), 1 936vs, 1 907m, 1 874m cm^{-1}].

Solvents.—The purification of propylene carbonate (pc) was as described in the literature.[8] Phenyl cyanide (PhCN) and tetrahydrofuran (thf) were purified according to published procedures.[9,10] Dichloromethane (refluxed over CaH_2) and thf were collected immediately before use.

Reagents.—Tetrabutylammonium hexafluorophosphate, $[NBu_4][PF_6]$ (Fluka), was used as supporting electrolyte. The purification of the salt was carried out as described in the literature.[8] The solutions were 0.1 mol dm^{-3} in supporting electrolyte in the solvents pc and PhCN, and 0.2 mol dm^{-3} in CH_2Cl_2 and thf.

Electrochemical Apparatus and Measurements.—The electrochemical apparatus has been described in earlier reports.[8] All the experiments were conducted under a nitrogen atmosphere, at room temperature, in a three-electrode cell. The working electrode was made of a vitreous carbon disc (area 0.063 cm^2, Tacussel EDI electrode). The secondary electrode was a vitreous carbon rod. The reference electrode was either a Ag-wire/Ag[PF$_6$]–pc–0.1 mol dm^{-3} $[NBu_4][PF_6]$ half-cell (measurements in pc) or a Ag-wire pseudo-reference electrode. When the Ag pseudo-reference was used, ferrocene was added as an internal standard at the end of the experiments. All potentials are quoted against the ferrocene–ferrocenium cation couple.

Results and Discussion

The Primary Reduction of the Binuclear Complexes.—Figure 1 shows a typical cyclic voltammogram of $[(cp)(CO)_3Mo(\mu\text{-SMe})W(CO)_5]$ in pc–0.1 mol dm^{-3} $[NBu_4][PF_6]$. It is qualitatively the same in the other solvents used for this study (thf, CH_2Cl_2, or PhCN). The complex shows a totally irreversible reduction on the time-scale of cyclic voltammetry (c.v.), scan rate $v \leqslant 2$ V s^{-1}. At low temperature (−45 °C in a thf electrolyte) the reduction process remains irreversible.

The peak current, i_p^{red}, for the reduction increases linearly with increasing concentration of the complex ($2 \times 10^{-4} < c < 2 \times 10^{-3}$ mol dm^{-3}). The cathodic current function, $i_p^{red}/v^{\frac{1}{2}}c$, is essentially independent of scan rate, and its magnitude corresponds to that calculated for a two-electron reduction‡ [equation (2)].

$$[(cp)(CO)_3M(\mu\text{-SR})W(CO)_5] + 2e \longrightarrow \text{products} \quad (2)$$

In rotating disc electrode (r.d.e.) voltammetry, the limiting

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† Throughout this work, cp stands for $\eta^5\text{-}C_5H_5$ and $\overline{MM}$ represents a metal–metal bonded complex.

‡ The number of electrons exchanged in the reduction process was calculated according to[11–13] $n_{irr} = 0.9\{[(i_p/v^{\frac{1}{2}}c)_{irr}]/[(i_p/v^{\frac{1}{2}}c)_{rev}]\}\{(n_{rev})^{\frac{3}{2}}/(\alpha n_a)_{irr}{}^{\frac{1}{2}}]$, where $(i_p/v^{\frac{1}{2}}c)_{rev}$ is the current function for an uncomplicated one-electron couple, *i.e.* $[\{Fe(cp)(CO)(\mu\text{-SMe})\}_2]$ oxidation;[14–16] $\alpha n_a = 0.0477\,(E_p - E_{p/2})$ (in V); n_a = number of electrons, α = transfer coefficient for the rate-determining step.

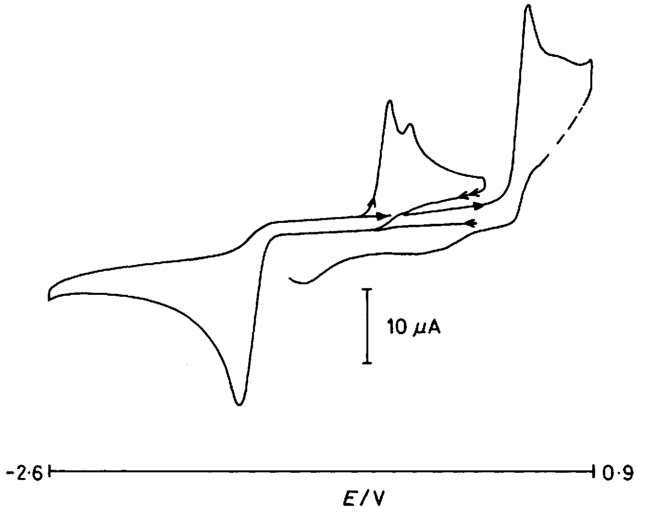

Figure 1. Cyclic voltammetry of $[(cp)(CO)_3Mo(\mu\text{-}SMe)W(CO)_5]$ (1.2 mmol dm^{-3}) in pc–0.1 mol dm^{-3} $[NBu_4][PF_6]$. Scan rate 0.2 V s^{-1}

Table 1. Electrochemical data for $[(cp)(CO)_3MX]$ complexes

M	X	Solvent	Reduction* E_p	Reduction* $E_{p/2}$	Oxidation* E_p	Oxidation* $E_{p/2}$
W	Cl	pc	−1.30	−1.21	0.61	0.53
	SMe	pc	−1.82	−1.73	0.35	0.26
		thf	−1.93	−1.86		
	SPh	pc	−1.60	−1.52	0.40	0.36
	(SMe)W(CO)$_5$	pc	−1.39	−1.32	0.42	0.37
		thf	−1.51	−1.41	0.49	0.40
	(SPh)W(CO)$_5$	pc	−1.20	−1.13		
Mo	(SMe)W(CO)$_5$	pc	−1.35	−1.27	0.49	0.41
		thf	−1.43	−1.34	0.47	0.39
		CH_2Cl_2	−1.49	−1.41	0.45	0.40
		PhCN	−1.35	−1.29	0.44	0.38

* Irreversible process. Values of E_p and $E_{p/2}$ (half-peak potential) measured at scan rate v = 0.2 V s^{-1}. Potentials are in volts against ferrocene.

Table 2. Cyclic voltammetry* data concerning the reduction of $[(cp)(CO)_2LMo(\mu\text{-}SMe)W(CO)_5]$ and the oxidation of $[Mo(CO)_2(cp)L]^-$

L	Solvent	$[(cp)(CO)_2LMo(\mu\text{-}SMe)W(CO)_5]$ $E_{p/2}{}^{red}$/V	$[(cp)(CO)_2LMo]^-$ $E_{p/2}{}^{ox}$/V
P(OMe)$_3$	pc	−1.59	−0.89
	thf	−1.74	−0.99
P(OPh)$_3$	pc	−1.39	−0.68
	thf	−1.57	−0.83
	CH_2Cl_2	−1.62	−0.84
PPh$_3$	pc	−1.54	−0.98
	thf	−1.80	−1.16
Bu^{t}NC	pc	−1.58	−0.92
	thf	−1.73	−1.06
	CH_2Cl_2	−1.70	−1.04

* Scan rate 0.2 V s^{-1}; potentials are in volts against ferrocene.

current of the reduction wave is proportional to the concentration of the electroactive species as well as to the square root of the revolution speed (ω) of the electrode (50 < ω < 5 000 r.p.m.). These criteria demonstrate the diffusion-controlled nature of the electron-transfer event.

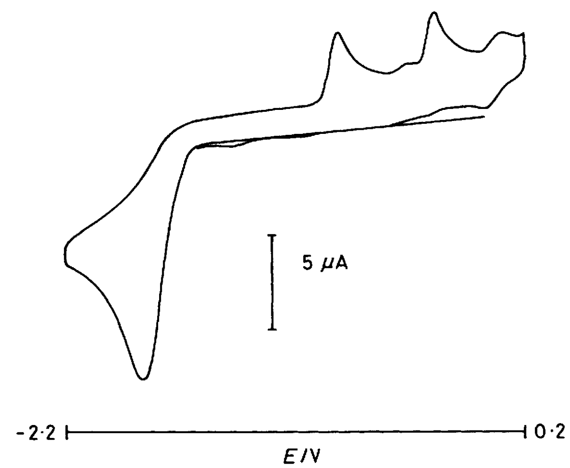

Figure 2. Cyclic voltammetry of $[(cp)(CO)_2\{P(OMe)_3\}Mo(\mu\text{-}SMe)W(CO)_5]$ in pc–0.1 mol dm^{-3} $[NBu_4][PF_6]$. Scan rate 0.2 V s^{-1}

The closely related complexes (M = W, R = Me or Ph) show essentially identical cyclic voltammetric behaviour. Thus we find that they undergo an irreversible, diffusion-controlled, two-electron reduction, equation (2).

Structural Effects on the Primary Reduction Potential.—The influence of the metal centre on the reduction potential of otherwise analogous complexes is small. The $[(cp)(CO)_3W(\mu\text{-}SMe)W(CO)_5]$ species is harder to reduce (by *ca.* 40 mV) than is its molybdenum analogue (Table 1). The nature of the bridging thiolate has a more substantial effect, $[(cp)(CO)_3W(\mu\text{-}SMe)W(CO)_5]$ is harder to reduce than is its phenylthiolate analogue by some 190 mV in accord with a significant inductive effect on the redox orbital.

The replacement of one CO ligand on the $Mo(CO)_3(cp)$ group by another ligand results in significant shifts in $E_p{}^{red}$. Comparatively good donor ligands such as $P(OMe)_3$ and Bu^{t}NC cause a shift in $E_p{}^{red}$ to values *ca.* 300 mV more negative than that of the parent carbonyl complex (Tables 1—2). The effect of the solvent on the reduction potentials is not directly related to the acceptor or donor properties of the solvents.[17] We attribute the solvent dependence of the potentials to changes in the solvation energies.

Nature of the Reduction Products.—The c.v. of complexes containing the $M(CO)_3(cp)$ moiety, *e.g.* $[W(CO)_3(cp)Cl]$, $[W(CO)_3(cp)(SMe)]$, $[W(CO)_3(cp)(SPh)]$, and $[\{M(CO)_3(cp)\}_2]$ (M = Mo or W), demonstrates for all of them the presence of an oxidation peak at the same potential as the first one observed in Figure 1 after scan reversal. The electrochemical reductions of $[M(CO)_3(cp)Cl]$ and $[\{M(CO)_3(cp)\}_2]$ (M = Mo or W) are known processes which were shown to generate the $[M(CO)_3(cp)]^-$ anion.[18–20] Accordingly, the peak detected at *ca.* −0.5 V in pc–0.1 mol dm^{-3} $[NBu_4][PF_6]$ we assign to the irreversible oxidation of $[M(CO)_3(cp)]^-$.*

For complexes $[(cp)(CO)_2LMo(\mu\text{-}SMe)W(CO)_5]$, the oxidation process at −0.5 V is essentially absent and replaced by a peak, the potential of which depends on the nature of L (Figure 2, Table 2). This clearly indicates that the ligand L is retained in the fragment, *i.e.* $[Mo(CO)_2(cp)L]^-$.

The second oxidation peak due to the reduction products

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* In contrast to the results reported by Dessy *et al.*[21] but in agreement with others,[22–24] we observed virtually no difference in the oxidation potentials of $[Mo(CO)_3(cp)]^-$ and $[W(CO)_3(cp)]^-$.

Table 3. Electrochemical data[a] for the species generated by reduction of $[(cp)(CO)_3M(\mu\text{-SR})W(CO)_5]$

		$[M(CO)_3(cp)]^-$		$[W(CO)_5(SR)]^-$		$[W_2(CO)_{10}(\mu\text{-SMe})]^-$		
Complex	Solvent	E_p^{ox}	$E_{p/2}^{ox}$	E_p^{ox}	$E_{p/2}^{ox}$	$E_{\frac{1}{2}}^{ox}$	E_p^{red}	$E_{p/2}^{red}$
$[(cp)(CO)_3W(\mu\text{-SMe})W(CO)_5]$	pc	−0.44	−0.50	−0.28	−0.32	0.05	−2.35	−2.23
	thf	−0.59	−0.65	−0.40	−0.45	0	−2.63	−2.51
$[(cp)(CO)_3W(\mu\text{-SPh})W(CO)_5]$	pc	−0.42	−0.50	−0.15	−0.19			
$[(cp)(CO)_3Mo(\mu\text{-SMe})W(CO)_5]$	pc	−0.43	−0.49	−0.28	−0.32	0.05	−2.37	−2.27 (2.32)[b]
	thf	−0.58	−0.65	−0.38		0	−2.58	−2.48
	CH_2Cl_2	−0.57	−0.61	−0.45				
	PhCN	−0.53	−0.59	−0.37				

[a] Values obtained from c.v. experiments, scan rate 0.2 V s^{-1}; potentials are in volts against ferrocene. [b] $E_{\frac{1}{2}}$ at the rotating disc electrode.

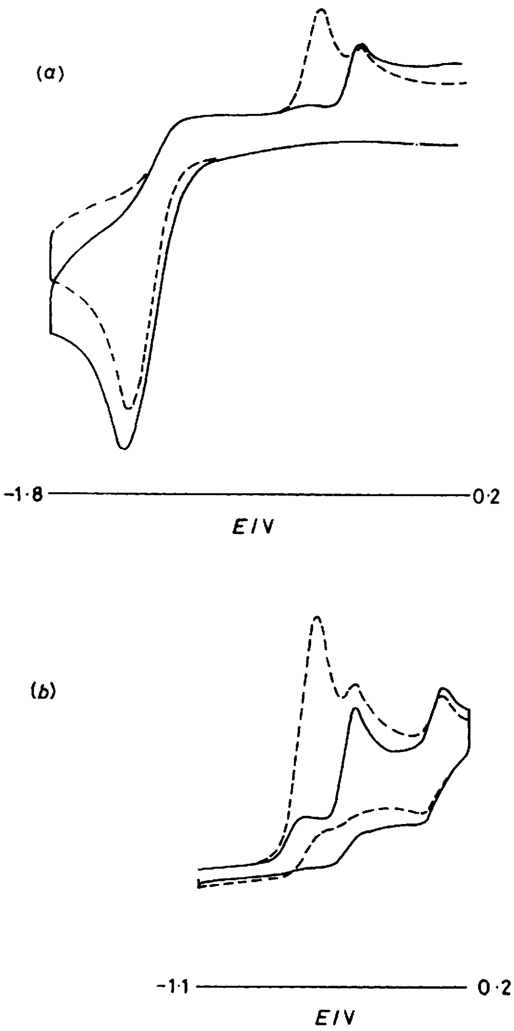

Figure 3. (*a*) Cyclic voltammetry of $[(cp)(CO)_3Mo(\mu\text{-SMe})W(CO)_5]$ (1 mmol dm^{-3}) under N_2 (— — —) and under air (——) in thf–0.2 mol dm^{-3} $[NBu_4][PF_6]$. (*b*) Cyclic voltammetry of the catholyte after controlled-potential electrolysis (1.52 F mol^{-1}) of $[(cp)(CO)_3Mo(\mu\text{-SMe})W(CO)_5]$ (0.78 mmol dm^{-3}) in thf–0.2 mol dm^{-3} $[NBu_4][PF_6]$ under N_2 (— — —) or after air-oxidation (——)

(Figure 1) shifts to more positive potential by *ca.* 150 mV on substitution of Ph for Me (Table 3), thus indicating that this fragment contains the –SR group. This shift compares well with that reported for $[Mo(SR)_2(dppe)_2]$,[25] $[Mo(SR)(dppe)_2]^-$,[25] and $[Mo(cp)_2(SR)_2]$[26] (R = alkyl or aryl; dppe = $Ph_2PCH_2CH_2PPh_2$).

The second anodic peak on the reverse scan in the cyclic voltammograms of $[(cp)(CO)_2LM(\mu\text{-SR})W(CO)_5]$ [L = CO or $P(OMe)_3$; $P(OPh)_3$ *etc.*] (Figures 1, 2) arises from the irreversible oxidation of the $[W(CO)_5(SR)]^-$ anion. This was confirmed by a comparison with the c.v. of a sample of the anion (R = Me).

The oxidation peak of $[W(CO)_5(SMe)]^-$ is much smaller than that of $[M(CO)_3(cp)]^-$ (Figure 1), which is unexpected from the reaction representing the reduction of the complex [equation (3)].

$$[(cp)(CO)_3M(\mu\text{-SMe})W(CO)_5] + 2e \longrightarrow [M(CO)_3(cp)]^- + [W(CO)_5(SMe)]^- \quad (3)$$

The discrepancy in the oxidation peak currents of one-electron systems [*e.g.* equations (4) and (5)] is shown to arise

$$[M(CO)_3(cp)]^- - 1e \longrightarrow [M(CO)_3(cp)]^{\cdot} \quad (4)$$

$$[W(CO)_5(SMe)]^- - 1e \longrightarrow [W(CO)_5(SMe)]^{\cdot} \quad (5)$$

from the fact that oxidation of $[M(CO)_3(cp)]^-$ occurs according to an electrochemical–chemical–electrochemical (e.c.e.) process in the presence of $[W(CO)_5(SMe)]^-$. Our evidence for this is as follows. (*i*) Tentative calculations of the yield of $[M(CO)_3(cp)]^-$ from the oxidation current in cyclic or rotating disc electrode (r.d.e.) voltammetry, after exhaustive electrolyses of $[(cp)(CO)_3M(\mu\text{-SMe})W(CO)_5]$, lead to inconsistent results {yield of $[M(CO)_3(cp)]^-$ > 100%}.* Whereas $[M(CO)_3(cp)]^-$ undergoes a one-electron oxidation when generated from $[\{M(CO)_3(cp)\}_2]$, the presence of $[W(CO)_5(SMe)]^-$, SMe^-, or Cl^- leads to a more complicated process. (*ii*) An increase in the scan rate (up to 1 V s^{-1}) or the dilution of the solution of $[(cp)(CO)_3M(\mu\text{-SMe})W(CO)_5]$ result in a less pronounced difference in the peak currents for the oxidation of $[M(CO)_3(cp)]^-$ and $[W(CO)_5(SMe)]^-$. The scan rate- and concentration-dependence are in agreement with the oxidation of $[M(CO)_3(cp)]^-$ according to an e.c.e. mechanism in the presence of $[W(CO)_5(SMe)]^-$, SMe^-, or Cl^-. (*iii*) When $[M(CO)_3(cp)]^-$ is removed from the electrode surface, the $[W(CO)_5(SMe)]^-$ oxidation peak current is consistent with that for a one-electron process. This is illustrated in Figure 3 after $[M(CO)_3(cp)]^-$ has been removed from the electrode surface [Figure 3(*a*)] or from the solution [Figure 3(*b*)] by air-oxidation.[27] Since no peak is detected at −0.3 V in the absence of $[W(CO)_5(SMe)]^-$, the change in the c.v. curve cannot be due to the oxidation of any by-product of the reaction between $[M(CO)_3(cp)]^-$ and O_2. (*iv*) The c.v. curves of $[(cp)(CO)_2LMo(\mu\text{-SMe})W(CO)_5]$ (Figure 2) do not show such a discrepancy in the oxidation peak currents

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* For these experiments, the calibration plot was constructed from known-concentration (amperometric titrations with acid) solutions of $[M(CO)_3(cp)]^-$, generated by the two-electron reduction of $[\{M(CO)_3(cp)\}_2]$.

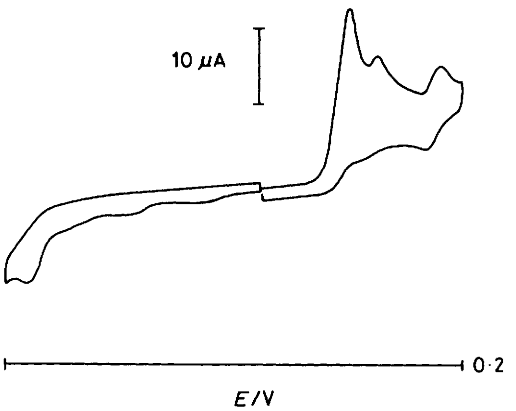

Figure 4. Cyclic voltammetry of the catholyte after c.p.e. (1.52 F $\mathrm{mol^{-1}}$) of $[(cp)(CO)_3Mo(\mu\text{-}SMe)W(CO)_5]$ (0.78 mmol $\mathrm{dm^{-3}}$) in thf–0.2 mol $\mathrm{dm^{-3}}$ $[NBu_4][PF_6]$. Scan rate 0.2 V $\mathrm{s^{-1}}$

for $[Mo(CO)_2(cp)L]^-$ and $[W(CO)_5(SMe)]^-$, although the former is more important. The intervening chemical step of the e.c.e. process is slower in this case than for L = CO. The substitution of a donor ligand $[P(OMe)_3$, $P(OPh)_3$, PPh_3, or $Bu^tNC]$ for CO results in an increase in the electronic density at the Mo centre, and in a poorer electrophilicity of $[Mo(CO)_2(cp)L]^\bullet$ as compared to $[Mo(CO)_3(cp)]^\bullet$. This makes the former more reluctant to react with $[W(CO)_5(SMe)]^-$. Although points (*i*)—(*iv*) are fully consistent with an e.c.e. oxidation of $[M(CO)_3(cp)]^-$ in the presence of $[W(CO)_5(SMe)]^-$, *e.g.* reaction (6), repetitive cyclic scanning did not allow the

$$[M(CO)_3(cp)]^- - 1e \longrightarrow [M(CO)_3(cp)]^\bullet \xrightarrow[{[W(CO)_5(SMe)]^-}]{-1e} [(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5] \quad (6)$$

observation of $[(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5]$ regeneration since it and $[\{M(CO)_3(cp)\}_2]$ are reduced at very similar potentials.

The Reduction Mechanism of Complexes $[(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5]$.—A comparison of the electrochemistry of closely related compounds, *i.e.* $[(cp)(CO)_3M(\mu\text{-}AsMe_2)M'(CO)_5]$ (M,M′ = Cr, Mo, or W)[28] and $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]$, allows the analysis of the reduction mechanism for the latter series of complexes.

As reported by Madach and Vahrenkamp,[28] $[M(CO)_3(cp)]^-$ and $[(CO)_5M'(\mu\text{-}AsMe_2AsMe_2)M'(CO)_5]$ were recovered after the *one-electron reduction* of $[(cp)(CO)_3M(\mu\text{-}AsMe_2)M'(CO)_5]$. This demonstrates that $[M'(CO)_5(AsMe_2)]^\bullet$ is not reducible at the potential of electrolysis or that it is removed by a very fast coupling reaction.* On the contrary, $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]$ undergo a *two-electron reduction*, leading to $[M(CO)_3(cp)]^-$ and $[W(CO)_5(SR)]^-$, detected on the c.v. time-scale and after exhaustive electrolyses (see later, Figure 4). The results reported by Madach and Vahrenkamp[28] and here suggest that in both cases the primary electronation occurs at the $M[M(CO)_3(cp)]$ centre. The disruption of the resulting radical anion, $[(cp)(CO)_3M(\mu\text{-}L')M'(CO)_5]^-$ (L′ = ligand), leads to $[M(CO)_3(cp)]^-$ and $[M'(CO)_5(L')]^\bullet$, which undergoes a further one-electron reduction for L′ = SR. Therefore complexes $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]$ reduce according to an e.c.e. mechanism† with a very fast intervening chemical step.

The presence of a bridging ligand does not prevent the cleavage of the molecule of complex on one-electron reduction. This suggests that in these $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]$ complexes, the lowest unoccupied molecular orbital has an M–S antibonding character.

The Reactivity of the $[W(CO)_5(SMe)]^\bullet$ *Radical.*—The c.v. of a solution of $[(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5]$ after an exhaustive reduction shows that $[W(CO)_5(SMe)]^-$ is partially involved in chemical reactions on the time-scale of controlled potential electrolyses (c.p.e.). The reversible couple at 0 V and the reduction peak at −2.6 V (thf electrolyte) (Table 3, Figure 4) result from the formation of $[W_2(CO)_{10}(\mu\text{-}SMe)]^-$. This was ascertained by comparisons with the c.v. and the i.r. spectrum (*cf.* Experimental section) of the dinuclear anion. Coulometric experiments during c.p.e. of $[(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5]$ in either pc or thf electrolytes lead to *n* values (number of electrons involved in the reduction process) less than 2 ($n = 1.7$, M = Mo and W; pc or thf electrolytes). The difference between the experimental values derived from coulometry and those calculated from cyclic voltammetry ($n = 1.96$, M = Mo; $n = 2.03$, M = W; see above) is attributed to the reactivity of the $[W(CO)_5(SMe)]^\bullet$ radical which undergoes fast reactions consuming this electroactive material.‡ This is supported by the fact that the oxidation of $[W(CO)_5(SMe)]^-$ is a totally irreversible process, $v \leqslant 2$ V $\mathrm{s^{-1}}$.

The formation of a stable MeSSMe-bridged dimer, $[(CO)_5W(\mu\text{-}MeSSMe)W(CO)_5]$, appears very unlikely since attempts to prepare this complex from $[W(CO)_5(thf)]$ and MeSSMe under mild conditions[30] were unsuccessful. However, the detection of MeSSMe in the catholyte (gas chromatographic analysis) is consistent with the transient formation of the dimer and a subsequent, fast elimination of MeSSMe, *e.g.* equation (7)

$$2[W(CO)_5(SMe)]^\bullet \longrightarrow [(CO)_5W(\mu\text{-}MeSSMe)W(CO)_5] \xrightarrow[\text{fast}]{S'} 2[W(CO)_5(S')] + MeSSMe \quad (7)$$

(S′ = solvent), or with reductive elimination of $SMe^\bullet$ from $[W(CO)_5(SMe)]^\bullet$ and dimerization of the thiolate radical [equations (8) and (9)]. Examples of such reactions have already been reported.[26,31]

$$[W(CO)_5(SMe)]^\bullet \xrightarrow{S'} [W(CO)_5(S')] + SMe^\bullet \quad (8)$$

$$2SMe^\bullet \longrightarrow MeSSMe \quad (9)$$

Although it has been reported that no reaction takes place between $[W(CO)_5(SMe)]^-$ and $[W(CO)_5(thf)]$,[32] we strongly believe that $[W_2(CO)_{10}(\mu\text{-}SMe)]^-$ would form in a reaction similar to that leading to $[W_2(CO)_{10}(\mu\text{-}H)]^-$ from $[W(CO)_5(thf)]$ and $[WH(CO)_5]^-$,[33] equation (10) (S′ = pc or thf).

$$[W(CO)_5(S')] + [W(CO)_5(SMe)]^- \longrightarrow [W_2(CO)_{10}(\mu\text{-}SMe)]^- + S' \quad (10)$$

Reaction (7) or the sequence (8), (9) would contribute to lower the experimental value of *n* with respect to the theoretical one, $n = 2$, since MeSSMe and $[W(CO)_5(S')]$ (S′ = pc or thf)

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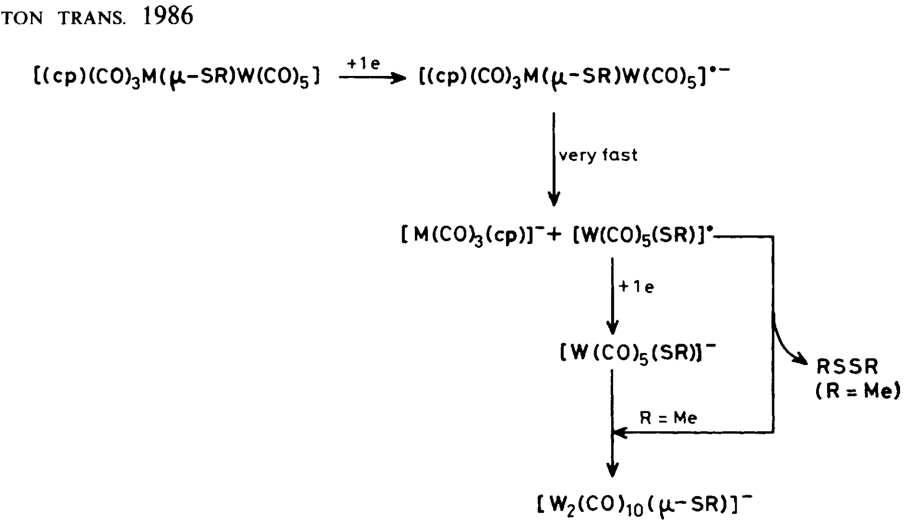
* $[(CO)_5Mo(\mu\text{-}AsMe_2AsMe_2)Mo(CO)_5]$ was shown to be harder to reduce than $[(cp)(CO)_3Mo(\mu\text{-}AsMe_2)Mo(CO)_5]$ by 0.3 V.[28]

† Owing to the extreme instability of $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]^{\bullet -}$, its cleavage occurs in the vicinity of the electrode, thus making an e.c.-disp. mechanism (second electron transfer is homogeneous)[29] unlikely.

‡ Although $[W(CO)_5(SMe)]^-$ reacts with acids, the addition of water in large excess (0.3—0.5 mol $\mathrm{dm^{-3}}$) has no effect on the value of *n*, thus suggesting that the side reaction does not consist of an attack of the anion {or $[W(CO)_5(SMe)]^\bullet$} on adventitious water. However, SMe^- loss from $[W(CO)_5(SMe)]^-$ would produce the observed effects ($n < 2$, MeSSMe produced) since SMe^- reduces the starting material $[(cp)(CO)_3Mo(\mu\text{-}SMe)W(CO)_5]$.



Scheme. R = Me, M = Mo or W; R = Ph, M = W

are both harder to reduce than the starting material $[(cp)(CO)_3M(\mu\text{-}SMe)W(CO)_5]$.

Because of the reactivity of the sulphur-containing fragments, the reduction of the dinuclear-bridged complexes is not a clean reaction. The yields of the major products identified by cyclic voltammetry $\{[M(CO)_3(cp)]^-, [W(CO)_5(SMe)]^-, [W_2(CO)_{10}(\mu\text{-}SMe)]^-\}$, i.r. spectroscopy $\{[W_2(CO)_{10}(\mu\text{-}SMe)]^-\}$, or gas chromatography (MeSSMe) were not calculated.

Our interpretation of the reduction mechanism of $[(cp)(CO)_3M(\mu\text{-}SR)W(CO)_5]$ complexes is summarized in the Scheme.

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References

1 J. E. Guerchais, J. L. Le Quéré, F. Y. Pétillon, Lj. Manojlovic-Muir, K. W. Muir, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1982, 283; J. L. Le Quéré, F. Y. Pétillon, J. E. Guerchais, Lj. Manojlovic-Muir, K. W. Muir, and D. W. A. Sharp, *J. Organomet. Chem.*, 1983, **249**, 127.
2 J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.
3 D. A. Roberts, W. C. Mercer, S. M. Zahurak, G. L. Geoffroy, C. W. De Bross, M. E. Cass, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1982, **104**, 910.
4 H. C. Foley, W. C. Finch, C. G. Pierpont, and G. L. Geoffroy, *Organometallics*, 1982, **1**, 1379.
5 T. S. Targos, R. P. Rosen, R. R. Whittle, and G. L. Geoffroy, *Inorg. Chem.*, 1985, **24**, 1375.
6 P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720; R. Havlin and G. R. Knox, *Z. Naturforsch., Teil B*, 1968, **21**, 1108; D. D. Watkins, jun., and T. A. George, *J. Organomet. Chem.*, 1975, **102**, 71.
7 J. K. Ruff and R. B. King, *Inorg. Chem.*, 1969, **8**, 180.
8 J. Talarmin and J. Courtot-Coupez, *Electrochim. Acta*, 1984, **29**, 967; J. Talarmin, Y. Le Mest, M. L'Her, and J. Courtot-Coupez, *ibid.*, p. 957.
9 Y. Le Mest, M. L'Her, J. Courtot-Coupez, J. P. Collman, E. R. Evitt, and S. Bencosme, *J. Electroanal. Chem.*, 1985, **84**, 331.
10 C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 1975, 879.
11 R. N. Adams, 'Electrochemistry at Solid Electrodes,' Marcel Dekker, New York, 1969, pp. 115—139.
12 D. A. Smith, J. W. McDonald, H. O. Finkka, V. R. Ott, and F. A. Schultz, *Inorg. Chem.*, 1982, **21**, 3825.
13 M. Chaudhury, *Inorg. Chem.*, 1984, **23**, 4434.
14 J. A. De Beer, R. J. Haines, R. Greatrex, and J. A. Van Wyk, *J. Chem. Soc., Dalton Trans.*, 1973, 2341.
15 P. D. Frisch, M. K. Lloyd, J. A. McCleverty, and D. Seddon, *J. Chem. Soc., Dalton Trans.*, 1973, 2268.
16 R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1968, **88**, 471.
17 V. Gutmann, 'The Donor-Acceptor Approach to Molecular Interactions,' Plenum Press, New York, 1978.
18 R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, 1966, **88**, 5112.
19 R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, 1966, **88**, 5117.
20 L. I. Denisovich, S. P. Gubin, Yu. A. Chapovskii, and N. A. Ustynyuck, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, **4**, 924.
21 R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, 1966, **88**, 5121.
22 T. Madach and H. Vahrenkamp, *Z. Naturforsch., Teil B*, 1979, **34**, 573.
23 A. Chaloyard and N. El Murr, *Inorg. Chem.*, 1980, **19**, 3217.
24 A. Giraudeau, P. Lemoine, M. Gross, and P. Braunstein, *J. Organomet. Chem.*, 1980, **202**, 455.
25 T. I. Al Salih and C. J. Pickett, *J. Chem. Soc., Dalton Trans.*, 1985, 1255.
26 J. C. Kotz, W. Vining, W. Coco, R. Rosen, A. R. Dias, and M. H. Garcia, *Organometallics*, 1983, **2**, 68.
27 M. D. Curtis and K. R. Han, *Inorg. Chem.*, 1985, **24**, 378.
28 T. Madach and H. Vahrenkamp, *Z. Naturforsch., Teil B*, 1979, **34**, 1195.
29 C. Amatore and J. M. Savéant, *J. Electroanal. Chem.*, 1978, **86**, 227.
30 P. M. Treichel, L. D. Rosenheim, and M. S. Schmidt, *Inorg. Chem.*, 1983, **22**, 3960.
31 J. R. Bradbury, A. F. Masters, A. C. McDonell, A. W. Brunette, A. M. Bond, and A. G. Wedd, *J. Am. Chem. Soc.*, 1981, **103**, 1959.
32 W. J. Schlientz and M. K. Ruff, *Inorg. Chem.*, 1972, **11**, 2265.
33 L. Arndt, T. Delord, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1984, **106**, 456.

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