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Electrochemistry of Carbonyl(fulvalene)dimetal Complexes ($M_2 = Cr_2, Mo_2, W_2, Ru_2, Mo-Ru$) in Aprotic Media

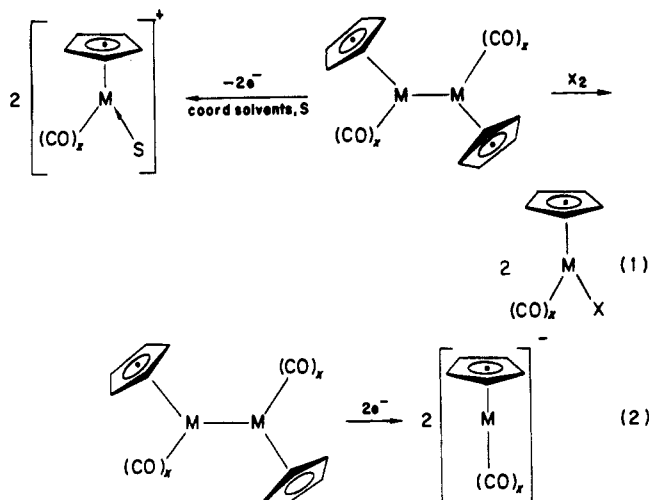
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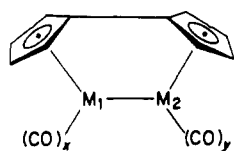
Electrochemical studies were carried out on a series of fulvalene-bridged metal-metal-bonded carbonyl complexes. The compounds are oxidized and reduced in 2e processes. The oxidation process is irreversible on the time scale of the CV experiment. The reduction of the compounds occurs with cleavage of the metal-metal bond in an ECE or ECEC mechanism; the resulting dianion is oxidized at relatively positive potentials to re-form the metal-metal bond. Scan rate and wave shape studies of the chromium and molybdenum dimers were carried out to study the heterogeneous-electron-transfer rates. Computer simulations of cyclic voltammetry data based on the ECE mechanism show that radical-anion intermediates of the homonuclear compounds disproportionate at a fast rate. The electrochemistry of the products of the reaction of the dichromium and dimolybdenum dimers with I_2 and the products of the reactions of the diruthenium dimer with I_2 and Br_2 was examined. The dichromium diiodide and diruthenium dibromide reduce in a 2e process to the metal-metal-bonded dimers, releasing 2 equiv of halide. The dimolybdenum and diruthenium diiodides reduce to unknown products.

Introduction

The oxidation (eq 1) and reduction (eq 2) reactions of cyclopentadienylmetal carbonyl dimers have been extensively employed for the preparation of reactive homonuclear complexes.

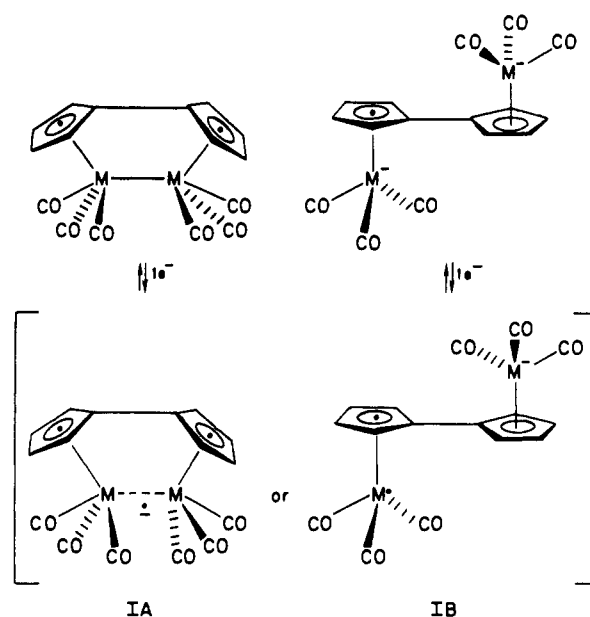


The development of an efficient synthesis^{1,2} of the fulvalene-bridged metal-metal-bonded carbonyl complexes 1-5 allowed us to explore the related redox chemistry and electrochemistry in a system expected to retain its dinuclear character. Of particular

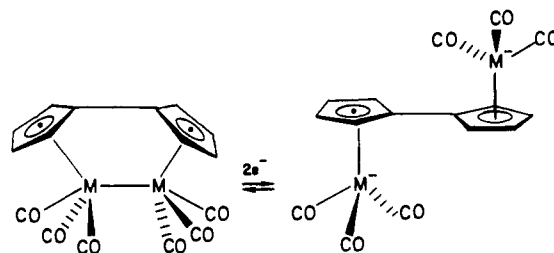


compd	M ₁	M ₂	x	y
1	Cr	Cr	3	3
2	Mo	Mo	3	3
3	W	W	3	3
4	Ru	Ru	2	2
5	Mo	Ru	3	2

interest was the extent to which the bridging fulvalene ligand would affect electron-transfer processes, i.e., whether the compounds would undergo two discrete one-electron or concerted two-electron oxidations and reductions. An example of each possibility follows for the reduction of a fulvalene-bridged group VI metal hexacarbonyl:



A two-step process implies that the potential for the transfer of the first electron would be less negative than that for the transfer of the second, predicting the intermediacy of an odd-electron monoanion (IA or IB). Alternatively, if the hypothetical monoanion possessed a less negative reduction potential than the neutral complex, facile transfer of a second electron should occur at the same potential, producing the dianion as the only detectable product:



Such a mechanism is implied in a previous brief electrochemical study of the (fulv)Rh₂(CO)₂(PPh₃)₂²⁺ complex (fulv = fulvalene) formed during oxidation of (η-C₅H₅)Rh(CO)(PPh₃).³

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(1) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* 1977, 16, 1788.

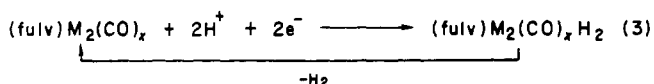
(2) (a) Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* 1983, 105, 1676 and references therein. (b) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* 1984, 3, 82.

Table I. Peak Potential^a vs. NHE (V)

M-M'	compd	E_{pa} $M_2 \rightarrow M_2^{2+}$	$E_{pc}(\text{redn})$ $M_2 \rightarrow M_2^{2-}$	$E_{pa}(\text{reox})$ $M_2^{2-} \rightarrow M_2$	ΔE_p , ^b V	λ_{max} , ^c eV	M-M, ^{2a,16,17} Å
Cr-Cr	1	+1.02	-0.43	-0.28	0.15	2.76	3.471
Mo-Mo	2	+1.08	-0.77	-0.08	0.69	3.28	3.371
W-W	3	+1.02	-0.82	-0.075	0.75	3.51	3.347
Ru-Ru	4	+1.05	-1.65	-0.50	1.15	3.73	2.821
Mo-Ru	5	+1.03	-1.25	-0.54	0.71	3.28	

^a Peak potentials were measured relative to an internal standard, ferrocene/ferrocenium, which was taken to be +0.547 V vs. NHE. Peaks are scan rate and solvent dependent. Listed values are for $v = 100$ mV/s in 1 M (TBA)BF₄/acetone. Concentration = 1.5 mM. ^b $\Delta E_p = E_{pa}(\text{reox}) - E_{pc}(\text{redn})$. ^c λ_{max} refers to absorption peak assigned to the promotion of metal-metal bonding electron to the antibonding orbital.^{2b}

We were further encouraged to explore the electrochemistry of these compounds because, in contrast to the bis(cyclopentadienyl) analogues, hydridic forms of the fulvalene complexes are unstable and undergo a fast H₂ extrusion process.^{1,2a} Thus, these compounds might be useful as hydrogen evolution catalysts via reduction of the metal-metal bond followed by protonation to form the dihydride, which then decomposes to starting material with the evolution of H₂ (eq 3). In addition, there has been



interest in the general use of electrochemical reduction of bridged bimetallic species and the nature of the reactions that follow electron transfer.⁴

Experimental Section

Materials. Reagent grade solvents were dried over 4-Å molecular sieves for at least 24 h before use. Reagent grade tetrahydrofuran (THF) was distilled once from CaH₂ and twice from sodium benzophenone ketyl and then was deaerated by several freeze-pump-thaw cycles before being passed into a drybox and stored under a He atmosphere. Liquid SO₂ was collected by condensation into an oven-dried cell on a vacuum line and purged with nitrogen. Traces of moisture were removed by passing the SO₂ through a column of P₂O₅, as described previously.⁵ The supporting electrolyte, tetra-*n*-butylammonium tetrafluoroborate ((TBA)BF₄), purchased from Southwestern Analytical Chemicals (Austin, TX), was recrystallized from ethyl acetate/ether and air-dried at room temperature. The following compounds were prepared according to literature procedures:² (fulv)Cr₂(CO)₆ (1); (fulv)Mo₂(CO)₆ (2); (fulv)W₂(CO)₆ (3); (fulv)Ru₂(CO)₄ (4); (fulv)MoRu(CO)₅ (5).

Electrochemical Measurements. Cyclic voltammetry was carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter and a high-impedance voltage amplifier (Model 178) mounted externally to the potentiostat as a follower. Voltammograms were recorded either directly on a Houston Series 2000 X-Y recorder or indirectly on a Nicolet 1090A digital oscilloscope for higher scan rates. Chronocoulometry was carried out with a BAS-100 (Bioanalytical Systems, West Lafayette, IN) electrochemical system. The electrochemical cells were of the same three-compartment design, as described previously.⁶

The reference electrode was an Ag quasi-reference electrode (QRE); the silver wire was pretreated by immersion in 10 M HNO₃ for 5 min before use. The counter electrode was a Pt flag or mesh. The working electrode was a polished platinum disk embedded in glass (area 0.026 cm²). After a series of experiments, the QRE potential was calibrated by adding ferrocene (Fc) to the solution and taking voltammograms of the Fc/Fc⁺ couple. Potentials for the waves were then referred to this couple, which has been recommended as a standard reference couple in nonaqueous solvents.⁷

Results and Discussion

The $\eta^5:\eta^5$ -fulvalene-bridged metal carbonyl complexes are soluble and stable in a wide variety of organic solvents. The most reproducible electrochemical results were obtained with THF and

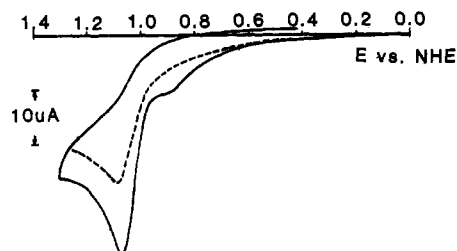


Figure 1. Cyclic voltammogram of a 1.98 mM solution of **2** in PC/0.2 M (TBA)BF₄ (scan rate 100 mV/s): first scan, solid line; second scan, dotted line.

acetone. Other solvents examined included propylene carbonate (PC), dimethyl sulfoxide (Me₂SO), dimethoxyethane (DME), SO₂, and butyronitrile (BuCN). The compounds are insoluble in NH₃ and water. A CO atmosphere and protection from light helped to preserve the stability of solutions during longer experiments. All of the compounds can be electrochemically oxidized and reduced and were studied by cyclic voltammetry (CV) and other techniques as described below.

Electrochemical Oxidation. Compounds 1-5 behaved similarly, all being oxidized at potentials near +1.0 V vs. NHE (see Table I). A typical cyclic voltammogram for the oxidation of **2** is shown in Figure 1. All of the compounds exhibited a prewave to the main oxidation wave on the first scan toward positive potentials. This wave was absent on second and subsequent scans and may result from the formation of an adsorption product of the oxidized species on the electrode. The number of electrons involved in the first oxidation process for compounds 1-5 could be estimated from the CV anodic peak current, i_{pa} , by comparison with the peak current for the associated reduction, which was shown to be a two-electron step, as will be discussed later. Therefore, we suggest that the oxidation is a two-electron process. Coulometry could not be used to determine the overall number of electrons transferred in this process (n_{app}), since the oxidation process passivates the electrode (see below).

The irreversibility of the oxidation wave probably stems from a reaction of the oxidized species with the solvent. Even when cyclic voltammetry was carried out in BuCN at temperatures as low as -108 °C,⁶ the oxidation wave showed no reverse cathodic wave for scan rates as high as 10 V/s, suggesting a low activation barrier for subsequent reaction. However, studies of molecules isoelectronic with the fulvalene complexes⁸ have shown that the ligands of 17-electron metal complexes can be displaced by donor molecules relatively easily. Therefore, reaction with the solvent in this case seems to be a reasonable conclusion.

Since the potentials for the oxidation of all the compounds studied were between +1.0 V and +1.1 V vs. NHE, independent of the metals in the complex (Table I), we suggest that the electron is removed from an orbital that is primarily ligand-localized. Unfortunately, no experiment in any solvent produced any evidence

(3) See also: Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.
 (4) See, e.g.: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888.
 (5) Tinker, L. A.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 2316.
 (6) Van Duyn, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.
 (7) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527.

(8) (a) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (c) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (d) Shi, Q.; Richmond, T. G.; Troglor, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (e) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

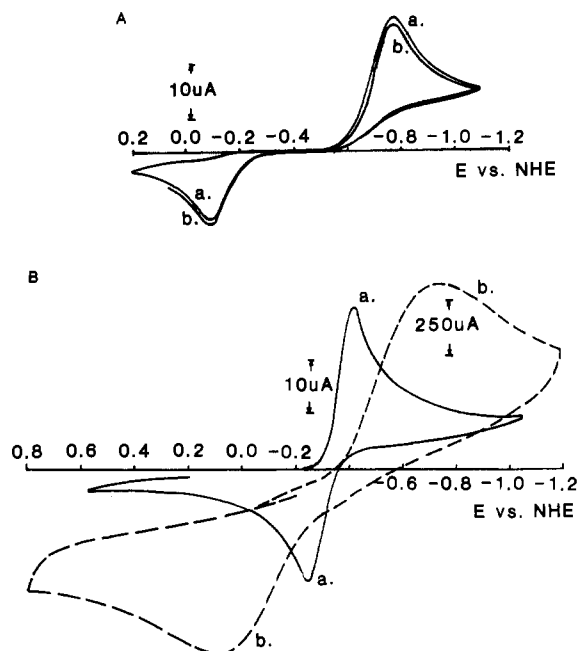


Figure 2. (A) Cyclic voltammogram of the reduction of 2.1 mM **2** in THF/0.5 M (TBA)BF₄ (scan rate 100 mV/s). The first (a) and second (b) scans are shown. (B) Cyclic voltammogram of a 1.2 mM solution of **1** in THF/1.5 M (TBA)BF₄. Scan rates are 100 mV/s (a) and 100 V/s (b).

of reversible electron transfer for the oxidation waves. Therefore, pathway and kinetic studies were not carried out.

The oxidation process appears to cause some filming of the electrode. When a clean, polished Pt-disk electrode was placed in a PC solution of the series **1–5**, reproducible CV reduction waves were obtained. However, if a scan was taken first over the oxidation wave, changes in the electrode surface occurred, resulting in small changes in the peak potentials, currents, and wave shapes of the reduction waves. This filming on the anodic scan may explain the occurrence of the small prewave 100 mV negative of the main oxidation peak, only on the first scan. The integrated current of the prewave corresponds roughly to monolayer coverage. However, when the electrode was held at a potential positive of the main oxidation wave, additional material appeared to coat the surface, leading to a passivation of the electrode.^{9a} Once the electrode was filmed in this manner, the surface could not be cleaned by sweeps to potentials as negative as -1.0 V. Only polishing restored the original behavior.

Electrochemical Reduction of 1–5. All of the compounds were reduced at potentials that strongly depended upon the metal centers involved. A typical CV curve is given in Figure 2 for the reduction of the dimolybdenum compound, **2**, in THF/0.5 M (TBA)BF₄. Compounds **1**, **3**, and **4** behave similarly, but **5** exhibits a different behavior that will be discussed separately. The reduction process involves a cathodic wave to form a reduced species that is oxidized at more positive potentials on an anodic scan (Table I). The overall number of electrons transferred in these waves was determined coulometrically. In a typical experiment, 3.3 mg of **2** was dissolved in 1 M (TBA)BF₄ in THF (10 mL) and reduced at a Pt-flag electrode (1.5 cm²) held at -0.9 V vs. NHE, well within the diffusion-limited region of the reduction wave. The current decayed to background (less than 50 μ A) within 1 h, with the consumption of 1.36 C. Subtraction of the contribution attributable to background current gave a value of 1.25 C for reduction of substrate to the product, corresponding to an n_{app} of 1.94 faradays/mol. Similar experiments showed that **1**, **4**, and **5** were also reduced in a two-electron process. The dianion products could be oxidized coulometrically ($n_{app} = 2$). Such oxidation produced the starting substance, since a cyclic

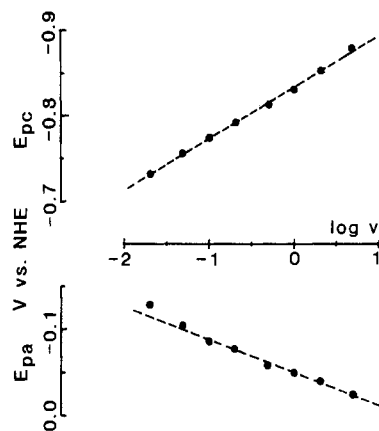
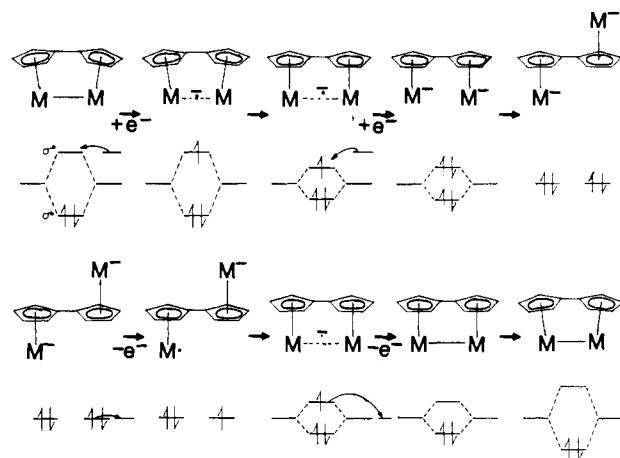


Figure 3. Plots of peak potential for the reduction of 0.94 mM **2** and the oxidation of the dianion of **2** vs. $\log v$ in THF/0.4 M (TBA)BF₄. For cathodic scan, slope = 56 mV; for anodic scan, slope = 39 mV.

Scheme I



voltammogram taken after this reduction and oxidation was identical with the original one.

The cyclic voltammetry and coulometry experiments are consistent with an ECE type mechanism^{9b} for the reduction (see Scheme I). We propose that the first electron is introduced into the metal-metal antibonding orbital, reducing the bond order and yielding an anion radical in an unfavorable geometry; i.e., the metal-metal distance is too short. The molecule then relaxes to a less strained geometry. This results in a shift in the orbital energies so that the reduction of the relaxed anion radical occurs more easily than the starting material. Therefore, an overall 2e transfer is observed. After the second electron transfer occurs, the molecule may relax to the preferred conformation (probably a trans configuration) of the dianion. Geometric isomerization of this nature has been postulated for isoelectronic species.¹⁰

Experiments were performed in an attempt to decrease the time scale of the reduction process and obtain evidence for radical-anion intermediates. For example, CV at high scan rates (up to 200 V/s) of a THF solution of **1** produced no qualitative change in the shapes of the voltammograms, suggesting that the rate constant for the rearrangement is greater than 600 s⁻¹ (see Figure 2B). Reduction and reoxidation of a solution of **2** in BuCN at -108 °C (see above) also gave results similar to those at room temperature, suggesting a low activation barrier to the rearrangement.

A systematic shift in the peak potentials for the oxidation (E_{pa}) and reduction (E_{pc}) waves with scan rate, v , was observed. A plot of peak potential vs. $\log v$ for **2** was linear for v up to 5 V/s (Figure

(9) Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods*; Wiley: New York, 1980: (a) p 525; (b) p 455; (c) p 92; (d) p 675.

(10) (a) Rausch, M. D.; Kovar, R. F.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1969**, *91*, 1259. (b) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 29. (c) Freeman, M. S.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2283.

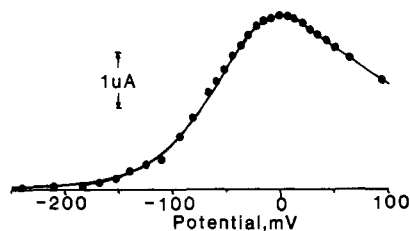


Figure 4. Comparison of theoretical (line) and experimental wave shapes (points) for the oxidation of the dianion of **2**. $(1 - \alpha)n_a$ was assumed to be 0.68 (scan rate 100 mV/s).

3). The slope of this plot can be used to determine the relative rates of heterogeneous electron transfer and the metal-metal bond formation and scission reactions.¹¹ If the heterogeneous reaction is fast and the homogeneous reactions are slow, the peak potentials will be independent of scan rate. However, when the homogeneous reactions are also fast, the reduction wave is shifted to less negative potentials (slope, $dE_p/d \log v$, of $29.6/n$ mV at 25 °C). In that case, the rate constant of the heterogeneous reaction decreases. In the limit, when the rate of the heterogeneous reaction is controlling, the slope will be $30/\alpha n_a$ mV, where α is the electron-transfer coefficient and n_a is the number of electrons transferred in the rate-limiting step.^{9c}

A plot of peak potential vs. $\log v$ shown in Figure 3 shows that $dE_p/d \log v$ is 56 mV, which is consistent with the slow heterogeneous kinetics case described above, with $n_a = 1$ and $\alpha = 0.53$. The peak potential of the anodic wave shifts 42.2 mV/decade of scan rate, suggesting $(1 - \alpha)$ for this oxidation is 0.70.

An analysis of the shapes of the reduction and reoxidation waves can give an independent estimate of the electron-transfer kinetics. The wave shape of a totally irreversible charge transfer (i.e., one totally controlled by slow heterogeneous kinetics) is a tabulated function ($\chi(bt)$)¹¹ and is characteristically broader than the Nernstian wave shape. The transfer coefficient can be found by comparing the tabulated function to the normalized experimental CV wave. The experimentally observed wave shape for the oxidation most closely matched that of the irreversible-charge-transfer current function with $(1 - \alpha)n_a = 0.68$ (see Figure 4). This value is consistent with the peak potential vs. scan rate study discussed above.

The scan rate and wave shape studies show that the electron-transfer processes are characterized by irreversible charge transfer, suggesting that the value of the standard heterogeneous rate constant k_f° ($=k^\circ \exp(\alpha n_a f(E - E_0'))$) is small. This can arise if the rate is intrinsically slow (i.e., a small k°) or if the homogeneous reaction is sufficiently fast to shift the wave so that it occurs at a potential where the exponential term is small. Since the rate of the bond-forming and -scission reactions is known to be greater than 600 s^{-1} (see above), it seems reasonable that the electron transfer is not intrinsically slow; rather, the fast following chemical reaction causes the electron transfer to occur at a potential where k_f° is small. Previous studies of analogous reactions support this conclusion.⁴

The behavior of the mixed-metal species **5** (Ru-Mo) is somewhat different from that of **2** (Mo₂) and **4** (Ru₂). A solution of **5** in freshly distilled THF was reduced in a single wave determined by coulometry again to involve 2 faradays/mol. On the anodic scan a large oxidation wave was observed at roughly the same potential (-0.54 V vs. NHE) as the oxidation of the dianion of **4** (-0.50 V vs. NHE). A smaller oxidation wave was observed near 0.06 V vs. NHE (see Figure 5). A chronocoulometric experiment in which the electrode was stepped past the reduction wave and then positive of the main oxidation wave is shown in Figure 6. The nearly equal Q vs. $t^{1/2}$ slopes suggest that the same number of electrons is transferred in each electron-transfer reaction. This implies that the main oxidation wave is a 2e oxidation of the dianion, presumably to afford the original metal-metal-bonded material.

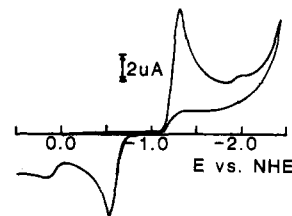


Figure 5. Cyclic voltammogram of a 1.61 mM solution of **5** in freshly distilled THF/1 M (TBA)BF₄ (scan rate 100 mV/s).

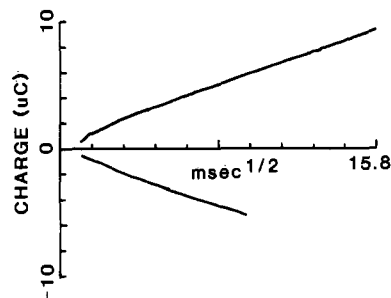


Figure 6. Chronocoulometric Q vs. $t^{1/2}$ plot of a 1.61 mM solution of **5** in freshly distilled THF/1 M (TBA)BF₄. The electrode was pulsed from -0.2 to -2.1 V and back. Forward scan: slope = $0.547 \mu\text{C}/\text{ms}^{1/2}$; intercept = $0.734 \mu\text{C}$. Reverse scan: slope = $0.524 \mu\text{C}/\text{ms}^{1/2}$; intercept = $0.388 \mu\text{C}$.

The proximity of the second oxidation wave to the potential for oxidation of **2** under similar conditions suggests a Mo-centered anion is being oxidized. If traces of air are introduced into the cell, the second oxidation wave grows at the expense of the first, so that the second oxidation wave may be caused by an irreversible chemical oxidation of the Ru-centered anion by traces of O₂ present in the cell.

The observed CV pattern was simulated, by assuming an ECE mechanism and employing the usual digital simulation methods.^{4,9c,12} A successful simulation requires that the relative peak currents and potentials follow the experimentally observed behavior for the second cycle, as a function of scan rate and switching potential (E_λ). For example, the relative values of i_{pa} and i_{pc} depend upon E_λ . i_{pc} is generally larger than i_{pa} , even though both involve 2e reactions, because, during the time the electrode is scanning in the region between the peaks, the dianion is neither consumed nor produced and the concentration at the electrode surface drops as it diffuses away. Therefore, the surface concentration of the dianion is decreased when the electrode scans over the oxidation wave.

The cyclic voltammetry of **2** was simulated with a program based on an ECE mechanism for the reduction process and an EE_i for the reoxidation.⁴ Several parameters must be chosen to achieve the best fit to the experimental data. The heterogeneous rate constants, standard potentials, and transfer coefficients were estimated from the observed CV E_p vs. v results discussed above. The homogeneous rate constant for the rearrangement was set at the highest possible value the simulation would allow for reasonable computer times (19 s^{-1}). Since the ECE mechanism assumes the second electron transfer for the reduction occurs at a potential positive of the first, any trace amounts of the radical-anion intermediate that are not reduced immediately after formation stay in solution and can be reduced on the anodic scan at potentials positive of the reduction wave. This can result in a crossover pattern that was not observed experimentally. This crossover will not occur when a disproportionation reaction of the radical anions can occur (the ECE-DISP mechanism).¹³ The crossover was found to disappear in the simulation when the bimolecular rate constant exceeded $6000 \text{ M}^{-1} \text{ s}^{-1}$ in the forward direction.

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(12) Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *48*, 113.

(13) Amatore, C.; Gueil, M.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *147*, 1.

Table II. Comparison between Observed and Computer-Simulated Values of Cathodic and Anodic Peak Current Ratios for 1.51 mM 3^a

E_{λ} , V vs. NHE	$(i_{pc}/i_{pa})_{obsd}$	$(i_{pc}/i_{pa})_{sim}$	E_{λ} , V vs. NHE	$(i_{pc}/i_{pa})_{obsd}$	$(i_{pc}/i_{pa})_{sim}$
-1.18	2.22	2.07	-1.32	1.64	1.59
-1.22	2.21	1.89	-1.42	1.50	1.43
-1.27	1.96	1.72	-1.52	1.32	1.22

^a Simulated current ratios were based on the following experimental parameters: $\alpha_c n_a = 0.25(1 - \alpha_a) n_a = 0.55$; $v = 50$ V/s. E_1° and E_2° were adjusted so that $E_{pc} = -1.121$ V and $E_{pa} = +0.071$ V. $\psi_1 = 0.002$, $\psi_2 = 0.1$, $\psi_3 = 100$, and $k_f = 6000$ /s. Experimental results were derived from a 1.51 mM solution of 3 in PC/0.4 M (TBA)BF₄. Potentials were measured relative to ferrocene as an internal standard.

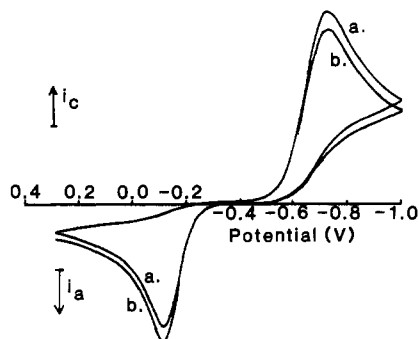


Figure 7. Simulated cyclic voltammogram of 2 based on an ECE/EE₁ (DISP) mechanism. $E_1 = -0.18$ V, $E_2 = 0.0$ V, $E_3 = -2.5$ V, $\psi_1 = 0.002$, $\psi_2 = 0.1$, $\psi_3 = 100$, $\alpha_1 = 0.52$, $\alpha_2 = 0.30$, $\alpha_3 = 0.5$. First (a) and second (b) scans are shown.

Typical results of the simulation are shown in Figure 7. On the first scan, a large reduction wave and smaller reoxidation wave are observed. The reduction wave decreases and the oxidation wave increases with repeated scans, and in general the simulations were in qualitative agreement with the experimental results. To investigate the extent of quantitative agreement, the experimental i_{pa}/i_{pc} was compared to the simulated one as a function of v and E_{λ} . Generally $(i_{pa}/i_{pc})_{exptl}$ was less than $(i_{pa}/i_{pc})_{sim}$. This implies that the dianion leaves the electrode at a greater rate than that caused by diffusion. We attribute this to the effect of natural convection; i.e., the density of the solution of the dianion is greater than that of the bulk solution, and at the downward oriented disk electrode, convection caused by gravity occurs to remove dianion from the electrode surface. Such effects are well-known in electrochemical studies.¹⁴ In an effort to decrease the effect of this convection, fast CV scans (50 V/s) were taken in a relatively viscous solvent (PC/0.2 M (TBA)BF₄) at a J-shaped electrode with the electrode surface oriented upward.¹⁵ Values of i_{pa}/i_{pc} of a 1.51 mM solution of 3 as a function of switching potential E_{λ} are shown in Table II. The simulated values are still consistently slightly higher than those observed experimentally, but the agreement is quite good. There is some uncertainty in measuring the actual peak currents relative to the background charging current, which could account for some of the error.

Interestingly, the simulation shows no scan rate dependence on the i_{pa}/i_{pc} ratio as long as the peak potentials are relatively independent of v . This is analogous to the i_{pa}/i_{pc} independence of v for a Nernstian process.

Reduction of Dihalide Products. The metal-metal bond of the compounds is cleaved upon reaction with I₂ and Br₂ to give dihalide products (eq 4).^{2a} Cyclic voltammograms of THF/(TBA)BF₄ (fulv)M₂(CO)_x + X₂ → (fulv)M₂(CO)_xX₂ (4)

solutions of the dibromo and diiodo products of 4 are shown in Figure 8a,b, respectively. The reduction of the dibromo product involves multiple steps and at least two distinct electron-transfer processes. 4 appears to be a product of the electrochemical reduction of the dibromide at -0.8 V, since the second reduction wave appears at the potential where 4 is reduced (-1.65 V) and there is an oxidation on the anodic scan corresponding to the dianion of 4. The peak size of the reduction wave implies that

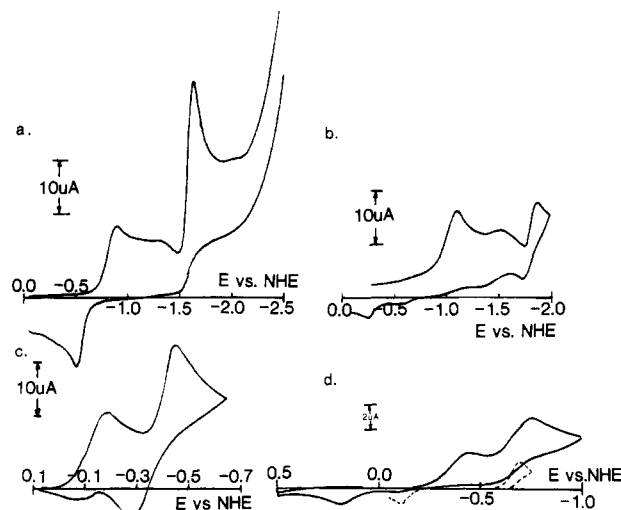


Figure 8. Cyclic voltammograms of dihalide products of 1, 2, and 4 (scan rate 100 mV/s): (a) 2.88 mM (fulv)Ru₂(CO)₄Br₂ in THF/0.2 M (TBA)BF₄; (b) 2.0 mM (fulv)Ru₂(CO)₄I₂ in THF/0.4 M (TBA)BF₄; (c) 5.75 mg of 1 and 3.50 mg of I₂ (1.92 equiv) in 5 mL of THF/0.4 M (TBA)BF₄; (d) 1.45 mM (fulv)Mo₂(CO)₆I₂ in THF/0.5 M (TBA)BF₄ (dotted line—CV of 2 for comparison).

4 is formed in high yield by reduction of the dibromide.

Reduction of the diiodo product of 4 occurs at a potential negative of the dibromo compound (see Figure 8b). Although the shapes of the cyclic voltammograms were similar, these lines shapes indicate a complicated stepwise electron transfer. However, in contrast to that of the dibromide, reduction of the diiodide afforded only a low yield of 4, as indicated by the absence of a reduction peak at -1.65 V. A peak was observed at -0.15 V on the anodic scan, corresponding to the product of the first reduction wave of the diiodide at -1.05 V. An oxidation wave at +0.6 V corresponding to the evolution of iodine was also observed.

The electrochemistry of diiodo derivatives of 1 and 2 was also explored. (fulv)Mo₂(CO)₆I₂ was isolated from the reaction of 2 with I₂ in THF. The dichromium analogue was made from 1 and I₂, but it resisted isolation as a pure solid. The dichromium diiodide complex did appear stable in solution in the absence of light, so the reaction of 1 and iodine was carried out in an electrochemical cell and the electrochemistry was performed without any attempt at purification or isolation of product. Cyclic voltammetry of solutions prepared in this fashion did not change significantly over several hours.

The results of studies on the Cr and Mo diiodide derivatives are shown in Figure 8c,d. (fulv)Cr₂(CO)₆I₂ was reduced at -0.2 V vs. NHE in a process that showed only a small oxidation wave on the anodic reversal scan at -0.07 V. This produced the metal-metal-bonded dimer 1, since reduction to the dianion is observed at -0.28 V.

Cyclic voltammetry of (fulv)Mo₂(CO)₆I₂ is shown in Figure 8d. A reduction at -0.5 V is followed by a second reduction at -0.8 V. The product of the second reduction was oxidized at 0.2 V. The small anodic peak near -0.1 V could be attributed to the presence of a small amount of the dianion of 2 produced by the reduction of the diiodide. However, the major reduction product is a material oxidized at +0.2 V. In an effort to explore the nature of this unknown product, a Pt-flag electrode was held at -1.0 V in a stirred THF solution of the dimolybdenum diiodide. However, long before the electrolysis was complete, the current being passed

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(17) Structures of 1 and 2 will be included in a later publication.

at the electrode had dropped to less than 10% of its initial value and the solution turned from orange to brown, suggesting a more complex decomposition reaction. In contrast, when (fulv)Mo₂(CO)₆I₂ was reduced by sodium amalgam in THF, the solution changed rapidly from orange to violet to yellow. TLC analysis shows that the violet and yellow compounds are **2** and its dianion, respectively.

Conclusion

All of the metal-metal-bonded compounds behave analogously: they can be oxidized near +1.0 V vs. NHE, are reduced in a single wave (ECE) to dianions, and are reoxidized to starting materials in 2e processes. The relative strength of the metal-metal bond in compounds **1-3** can be inferred from the CV data. As previously discussed, the reduction and reoxidation potentials are taken to correspond to the energy levels of the σ antibonding and nonbonding orbitals, respectively (Scheme 1). The thermodynamic potentials and the corresponding energy levels of the orbitals cannot be determined from the CV data, because the kinetics of the metal-metal bond formation and scission reactions shifts the peak potentials away from the reversible (E°) values. However, if we assume that the effects of the homogeneous and heterogeneous kinetics on the peak potentials are similar for all the reductions and reoxidations of **1-3**, then a stronger metal-metal bond would show a larger difference in E_p values, $\Delta E_p = [E_{pa}(\text{reox}) - E_{pc}(\text{redn})]$, under similar conditions. The ΔE_p values in Table I suggest that the metal-metal bond strengths follow the trend **1** < **2** < **3**. This is consistent with the greater ability of the 5d orbitals of the W atoms in **3** to overlap with each other to form a strong metal-metal bond as compared to the less extended 3d orbitals of the Cr atoms in **1**.

The spectroscopic and crystallographic data (Table I) also support the bond strength trend. The metal-metal bond lengths among **1-3** show an unusual trend in that the Cr-Cr distance in **1** is larger than the bond lengths in either **2** or **3**. In fact, the Cr-Cr distance is perhaps the largest ever observed for a metal-metal single bond. The long bond length is a reflection of the inability of the smaller d orbitals of the Cr in **1** to overlap significantly and induce a distortion in the fulvalene bridge. In a recent electrochemical study,^{3,10c} the reduction of (fulv)Rh₂(CO)₂(PPh₃)₂²⁺ in CH₂Cl₂ was described as an essentially Nernstian two-electron reduction ($\Delta E_p \sim 35$ mV) and was ascribed to single-electron transfers to essentially noninteracting

metal centers. However, cyclic voltammetry with electron transfers to multiple noninteracting centers are usually associated with ΔE_p values of ca. 59 mV,¹⁸ and the observed results with the fulvalene-Rh₂ species would be more consistent with an ECE reaction scheme where the intervening reaction (e.g., isomerization) is fast and reversible.¹⁹ Thus, the Rh₂ species seems to undergo the same ECE reaction sequence as we observe on reduction, but with a reversible, rather than irreversible, intervening reaction. The electrochemistry of **1-5** differs substantially from that of bis(fulvalene) compounds.²⁰ Bis(fulvalene) complexes are inflexible and unable to isomerize through bond rotation. Oxidized forms of the bis(fulvalene) compounds are also more stable than the "half-sandwich" complexes studied here because complexation by the η^5 -cyclopentadienyl moiety blocks a ligand displacement in the oxidized state.

Reduction of the dihalide complexes occurs 200-400 mV positive of the corresponding metal-metal-bonded dimers and is easier for the bromides than for the iodides. In the cases where the metal-halide bond is weak (i.e., (fulv)Cr₂(CO)₆I₂ and (fulv)Ru₂(CO)₄Br₂), the product of the reduction at the electrode is the corresponding metal-metal-bonded dimer. When the metal-halide bond is stronger, the reduction results in a decomposition reaction. Note that the dimers react with I₂ despite the fact that iodide is oxidized 500 mV negative of the peak potential for the oxidation of the dimers at the electrode. This implies that the strength of the M-I bond provides significant driving force for the reaction.

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