

Heterogeneous Electron-Transfer Rate Constants for $M_2(O_2CR)_4^{0/+}$, Where $M = Mo, W, Ru,$ or Rh and $R =$ Alkyl or Aryl

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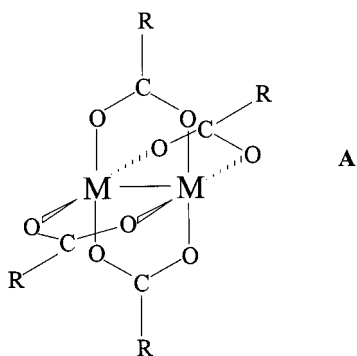
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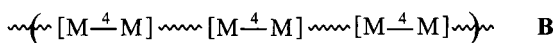
By the use of Nicholson's method, the heterogeneous electron-transfer rate constants (k_s) for the oxidation of a series of $M_2(O_2CR)_4$ complexes have been determined in benzonitrile, where the metal $M = Mo, W, Ru,$ or Rh and $R =$ alkyl or aryl. For $R = tBu$, the values of k_s follow the order $M = Mo > W > Ru > Rh$. No simple influence of R on k_s was observed, although added ligands that are known to reversibly bind to the dinuclear center were shown to influence the $E_{1/2}$ values in order of their basicity and to suppress the rate of electron transfer. The reported data are compared with those obtained for $Cp_2Fe^{0/+}$, $Cp_2^*Fe^{0/+}$, and $Ru(bpy)_2^{2+/3+}$ and with earlier work on dirhenium multiply bonded compounds.

Introduction

Compounds of the type $M_2(O_2CR)_4$ are known for a wide variety of transition metals and adopt a D_{4h} lantern- or paddle-wheel-like molecular structure as shown in **A** below.¹ Depending

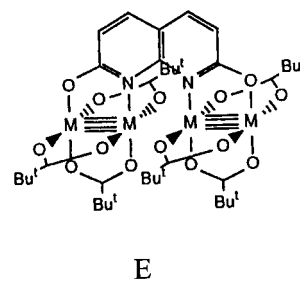
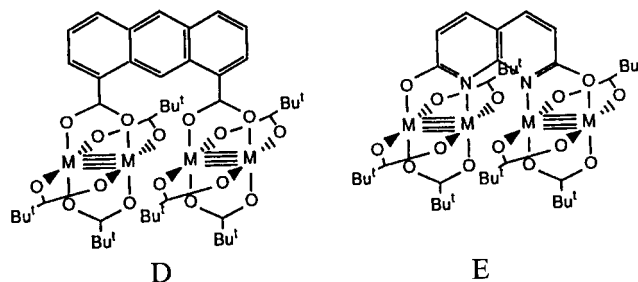


upon the metal, these compounds can have a variety of $M-M$ electronic configurations, including the now-famous quadruple bond $M-M \sigma^2\pi^4\delta^2$ ($M = Cr, Mo,$ or W) as well as double ($M = Ru$) and single ($M = Rh$) bonds.² We have recently embarked upon studies aimed at incorporating the $M-M$ quadruple bond into "ordered assemblies" such as 1-D polymers of the type depicted by **B** and **C** and aligned liquid crystalline mesophases.³



Studies of the electronic communication within linked "dimers of dimers" provide valuable information concerning the properties of the extended arrays. In our earlier work, we noted that

the electronic communication, as evidenced by both electronic spectroscopy and electrochemical measurements, occurs through the ligand bridge even when the $[M_2] \cdots [M_2]$ units are brought into close proximity.⁴ For example, in the anthracene dicarboxylate and 2,7-dioxynaphthyridine complexes shown in **D** and **E**, respectively, the $Mo_2 \cdots Mo_2$ distance is only 3.1 Å in the solid state. However, their cyclic voltammetric behavior varies greatly, such that the $[M_2 \cdots M_2]^{+*}$ species can be viewed as valence-trapped for **D** but delocalized for **E**.



When we obtained these data, we realized that although the compounds $M_2(O_2CR)_4$ are known to undergo reversible one-electron oxidations ($M = Mo, W, Ru,$ or Rh), nothing was known about the kinetics of electron transfer for this series. It seemed to us that this information was conspicuously lacking for an otherwise well-studied class of compounds having a common geometry, **A**, and varying electronic configurations. In this paper, we report our studies of the kinetics of electron transfer for the $M_2(O_2CR)_4^{0/+}$ redox couple, which were aimed at elucidating the role, if any, of the metal and the $M-M$ electronic configuration, for example, $M^4-M \sigma^2\pi^4\delta^2$ versus $M = M \sigma^2\pi^4\delta^2\delta^*\pi^*2$, and the nature of (1) R , which could be potentially an insulating or conducting ligand, and (2) added donor ligands, which are known to bind along the $M-M$ axis. Our method of analysis employs the Nicholson method, which has long been known as a reliable method for the determination of rates of heterogeneous electron transfer for redox couples that exhibit ideal reversible electrochemical behavior.⁵

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Table 1. Half-Wave Potentials, Diffusion Coefficients, and Heterogeneous Electron-Transfer Rate Constants for Selected Electrochemical Standards^a

standard	$E_{1/2}$ (V vs SCE)	D_o (cm ² s ⁻¹) × 10 ⁶	k_s (cm s ⁻¹) × 10 ³
Cp ₂ Fe	+0.51	1.67	20(3)
Cp ₂ *Fe	-0.01	2.39	11(3)
Ru(bpy) ₃ ²⁺	+1.43	2.56	12(2)

^a All measurements were made for 1 mM concentrations of the electroactive species in benzonitrile containing 0.10 M TBAPF₆ at 25 ± 2 °C.

Results and Discussion

Electrochemical Measurements. A standard operating procedure involved the use of 1 mM concentrations of M₂(O₂CR)₄ in rigorously dried and deoxygenated benzonitrile, with 0.1 M ⁿBu₄N⁺PF₆⁻ as the supporting electrolyte. The single-compartment voltammetric cell was equipped with a glassy carbon working electrode of known area, a Pt wire counter electrode, and a cadmium-amalgam reference electrode. Cyclic voltammograms were collected with scan rates varying from 50 to 6000 mV s⁻¹.

The selection of benzonitrile as solvent was based on the desire for a high dielectric constant and good solubility of the M₂(O₂CR)₄ compounds. In this regard, CH₂Cl₂ proved unsatisfactory because of the low solubility of the aryl carboxylates as well as its lower dielectric constant. In CH₃CN, we observed poorer solubility relative to PhCN, and we found some irreversible electrochemistry in dimethylformamide (DMF). Although the strong trans effect of the M⁴-M bond in M₂(O₂CR)₄ (M = Mo or W) complexes results in the very weak binding of σ donor ligands in the axial site, we were concerned that the benzonitrile solvent may form stronger axial interactions with Ru₂(O₂CR)₄ and Rh₂(O₂CR)₄ complexes, which have M-M bond orders of 2 and 1, respectively. However, the determination of k_s for Rh₂(O₂CR)₄ in CH₂Cl₂ revealed no rate enhancement over the identical measurement using benzonitrile as the solvent. We therefore conclude that although benzonitrile may not be an innocent solvent, it is probably undergoing very rapid exchange and hence does not impede our measurements.

In applying the Nicholson method, we determined the peak separation for the anodic and cathodic waves as a function of scan rate. From this information, we calculated the heterogeneous rate constants (k_s) for electron transfer. Because such rate constants may vary greatly with the electrochemical system, that is, the electrode surface, solvent, and supporting electrolyte, we evaluated the rate constants for the well-known one-electron oxidation-reduction processes for the ferrocene-ferrocinium couple and the Ru(bpy)₃^{2+/3+} couple. We also examined decamethylferrocene (Cp₂*Fe^{0/+}) in relation to ferrocene (Cp₂Fe^{0/+}). Table 1 provides a compilation of $E_{1/2}$ ⁶ and k_s values for these species.

We recognize that the k_s values for the Cp₂Fe^{0/+} and Ru(bpy)₃^{2+/3+} couples reported in Table 1 are significantly smaller than those found in some other studies, primarily because of the effects of uncompensated solution resistance that are associated with the use of macroelectrodes.⁷⁻⁹ Although Weaver and co-workers¹⁰ have cited a value of k_s as large as 5 cm s⁻¹ for the oxidation of Cp₂Fe at an annealed gold electrode in acetonitrile containing 0.1 M tetraethylammonium perchlorate,

(5) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(6) The formal redox potential for each redox couple in a particular solvent-electrolyte combination with a specified electrode is more accurately defined as $E^{0'}$; in this paper, we use the more general term $E_{1/2}$ to denote this measurement.

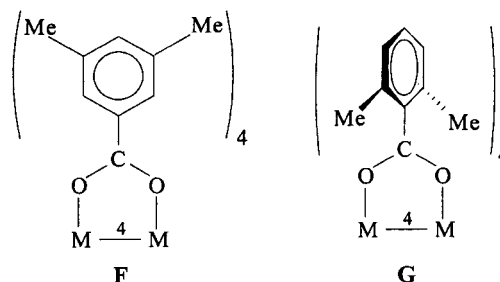
Table 2. Effect of Carboxylate R Groups on Rates of Oxidation of Mo₂(O₂CR)₄^a

R	$E_{1/2}$ (V vs SCE)	k_s (cm s ⁻¹) × 10 ³
tBu	0.48	7.6(8)
C ₇ H ₁₅	0.49	7.0(4)
C ₆ H ₅ ^b	0.58	4.3(6)
2,6-(CH ₃) ₂ C ₆ H ₃	0.61	2.6(4)
3,5-(CH ₃) ₂ C ₆ H ₃ ^b	0.53	14(3)
2,4,6-(CH ₃) ₃ C ₆ H ₂	0.57	16(2)
4-H ₃ COC ₆ H ₄ ^b	0.42	10(2)

^a All measurements were made for 1 mM concentrations of the electroactive species in benzonitrile containing 0.10 M TBAPF₆ at 25 ± 2 °C. ^b Carboxylates that show conjugation with the metal d orbitals.

values as low as 0.02 cm s⁻¹ have been determined by Sharp,¹¹ using vitreous carbon electrodes in the same solvent-supporting electrolyte. However, the aim of the present investigation was not to obtain highly refined rate constants but only to establish trends among the various compounds chosen for examination.

Mo₂(O₂CR)₄ Compounds. Both heterogeneous rate constants and $E_{1/2}$ values for a set of Mo₂⁴⁺ carboxylates are recorded in Table 2. The selection of R was made in order to examine the influence of aromatic versus alkyl groups. In the case of the latter, we considered that tBu and *n*-octanoate represent insulating hydrocarbon shields, whereas for aryl groups there is the possibility of conjugation. Specifically, it is known from crystallography and visible spectroscopy for R = Ph, 3,5-Me₂C₆H₃-, and *p*-MeOC₆H₄- that the aromatic ring aligns itself with the M-M axis.^{12,13} In this way, one observes a dramatic red shift in the metal-to-ligand charge-transfer $\delta \rightarrow$ CO₂ π^* transition because of its conjugation with the aromatic π system.¹² However, for the bulky 2,6-Me₂C₆H₃- and 2,4,6-Me₃C₆H₂- groups, the aromatic rings are twisted out of the M₂O₂C plane such that this electronic coupling is not possible and the $\delta \rightarrow$ CO₂ π^* transition is essentially as it is in alkylcarboxylates.¹³ Pictorially, we show these limiting situations in **F** and **G** below; the twisting shown in **G** relieves an otherwise unfavorable O...Me interaction involving the ortho methyl and carboxylate oxygen atoms.



In reviewing the data presented in Table 2, one can see that the $E_{1/2}$ values span a narrow range from +0.4 to +0.6 V and

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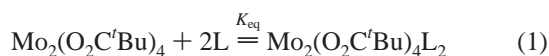
Table 3. Effect of Added Base (100 equiv) on Rates of Oxidation of $\text{Mo}_2(\text{O}_2\text{C}'\text{Bu})_4^a$

added base	$E_{1/2}$ (V vs SCE)	k_s (cm s^{-1}) $\times 10^3$
(none)	0.48	7.6(8)
pyrazine	0.44	6.1(5)
PPh ₃	0.39	3.5(4)
PPh ₂ Me	0.35	2.3(3)
PPhMe ₂	0.33	1.6(3)

^a All measurements were made for 1 mM concentrations of the electroactive species in benzonitrile containing 0.10 M TBAPF₆ at 25 \pm 2 °C.

that there is little correlation between alkyl versus aryl substituents. Furthermore, one can see that the k_s values do not parallel the $E_{1/2}$ values. Indeed, the observed k_s values span roughly 1 order of magnitude but do not show any obvious trends with respect to alkyl versus aryl, and for the aryl groups there is no significant trend with respect to conjugation. The largest rate constant is observed for the mesityl carboxylate, which contains aromatic rings that are both alkylated and out of the plane of the $\text{Mo}_2\text{O}_2\text{C}$ units. We have measured the rate constants for several of these compounds on different occasions and find that the values reported are accurate to $\pm 15\%$, an uncertainty which is numerically less than the differences seen between members of the series. The k_s values are similar to those for the $\text{Cp}_2\text{Fe}^{0/+}$ and $\text{Cp}_2^*\text{Fe}^{0/+}$ redox couples.

The next phenomenon we examined was the influence of added donor ligands that are known to bind reversibly along the M–M axis.¹⁴ Because the equilibrium constants for the ligation of σ donors are known to be small,¹⁵ 100 equiv of added base was used to encourage complex formation. Data shown in Table 3 reveal that the values of k_s decrease with the nucleophilicity of the added ligand, which clearly implies that an equilibrium of the type shown in eq 1 is operative and that axial ligation suppresses electron transfer. Also of significance is the trend in $E_{1/2}$ values, which reveals that ligation alters the oxidation potential in the expected



manner. So, even though it is thermodynamically easier to oxidize an $\text{M}_2(\text{O}_2\text{C}'\text{Bu})_4\text{L}_2$ complex, the process is kinetically slower. Pyrazine is a poor nucleophilic base and could act as an electron conduit through its π^* system; this is more likely for $\text{Ru}_2(\text{O}_2\text{CR})_4$ complexes, as described later. However, no evidence for an enhancement of k_s is seen when pyrazine is added.

Finally, we must emphasize that we were limited in the addition of nucleophiles in reaction 1 because of two factors: (1) pyridine, 4,4'-bipyridine, quinuclidine, and PMe_3 gave rise to irreversible electrochemical behavior and (2) chemical reactions can occur wherein the $\mu\text{-O}_2\text{C}'\text{Bu}$ moiety is displaced, as is well documented in the case of O_2CCF_3 ligands.¹⁶

Varying the Nature of M and the M–M Electronic Configuration. Taking pivalate as a standard carboxylate (one with good solubility in PhCN), we compared the heterogeneous rates of electron transfer for a series $\text{M}_2(\text{O}_2\text{C}'\text{Bu})_4^{0/+}$, where M = Mo, W, Ru, or Rh. In this series, we can compare k_s for second- and third-row metals having a quadruple bond; also

Table 4. Effect of the Identity of the Metal Atom on the Rate of Oxidation of $\text{M}_2(\text{O}_2\text{C}'\text{Bu})_4^a$

metal	electronic configuration	$E_{1/2}$ (V vs SCE)	k_s (cm s^{-1}) $\times 10^3$
Mo	$\sigma^2\pi^4\delta^2$	+0.48	7.6(8)
W	$\sigma^2\pi^4\delta^2$	−0.22	4.8(6)
Ru	$\sigma^2\pi^4\delta^2\delta^*\pi^*2$	+0.06	2.2(5)
Rh	$\sigma^2\pi^4\delta^2\delta^*\pi^*4$	+1.02	1.3(8)
Ru ^b	$\sigma^2\pi^4\delta^2\delta^*\pi^*2$	+0.87	0.9(6)

^a All measurements were made for 1 mM concentrations of the electroactive species in benzonitrile containing 0.10 M TBAPF₆ at 25 \pm 2 °C. ^b In the presence of 100 equiv of added pyrazine.

for the second-row metals, we can examine the effect of the M–M quadruple, double, and single bonds, where M = Mo, Ru, or Rh. The M–M electronic configuration for $\text{Ru}_2(\text{O}_2\text{CR})_4$ compounds is now well-known to be $\sigma^2\pi^4\delta^2\delta^*\pi^*2$, whereas that for $\text{Rh}_2(\text{O}_2\text{CR})_4$ is $\sigma^2\pi^4\delta^2\delta^*\pi^*4$.² Thus, formation of $[\text{Ru}_2]^{5+}$ removes an antibonding electron and leads to an increase in the M–M bond order to 2.5. Similarly, oxidation of the Rh_2^{4+} core removes a π^* electron. Rate data and $E_{1/2}$ values for this series are given in Table 4. The $E_{1/2}$ values follow the now-expected trend, revealing that it is easier to oxidize a W–W quadruple bond than its Mo–Mo analogue by more than 0.5 V. Moreover, the oxidation of the Ru_2^{4+} core is easier because of the removal of a π^* electron, but oxidation of the Rh_2^{4+} core is more difficult, presumably because of the increase in electronegativity of the metal atoms (which increases with increasing atomic number across a given row). The $E_{1/2}$ values correlate well with the first ionization potentials determined in the gas phase by means of photoelectron spectroscopy for the compounds $\text{M}_2(\text{O}_2\text{CCF}_3)_4$, where M = Mo, W, Ru, or Rh.¹⁷ What is striking is that the k_s values do not correlate in any simple manner with the $E_{1/2}$ values. Thus, although it is thermodynamically easier to oxidize both $\text{W}_2(\text{O}_2\text{C}'\text{Bu})_4$ and $\text{Ru}_2(\text{O}_2\text{C}'\text{Bu})_4$ than $\text{Mo}_2(\text{O}_2\text{C}'\text{Bu})_4$, removal of an electron from the latter species is fastest.

Because pyrazine is known to coordinate to $\text{Ru}_2(\text{O}_2\text{CR})_4$ compounds and because the $\text{Ru}_2^{4+}\pi^*$ orbitals are of the appropriate symmetry to interact with axial pyrazine π^* orbitals,¹⁸ we obtained cyclic voltammetric data for the oxidation of $\text{Ru}_2(\text{O}_2\text{C}'\text{Bu})_4$ in PhCN in the presence of 100 equiv of pyrazine (Table 4). Added pyrazine is seen to make the $E_{1/2}$ value more positive, which is consistent with its acting as a π^* acceptor ligand; compare the effect of added pyrazine on the oxidation of $\text{Mo}_2(\text{O}_2\text{C}'\text{Bu})_4$, as shown in Table 3. However, the k_s value for either the Mo_2 or Ru_2 carboxylates is suppressed by the addition of pyrazine, indicating that it does not act as an electron conduit.

Conclusions

When treated according to the Nicholson method, our electrochemical data show that the heterogeneous electron-transfer rate constants for oxidation of $\text{M}_2(\text{O}_2\text{CR})_4$ compounds are influenced by the nature of both M and R as well as by added ligands. However, there is no evidence that electronic coupling of the M_2 δ orbitals with the CO_2 π^* orbitals in aryl carboxylates in any way facilitates the electron-transfer process. This is clearly evident from a comparison of the 3,5-xylyl and the 2,4,6-mesityl complexes, which adopt very different structures but have nearly identical values of k_s . Furthermore, we

(14) For example, $\text{W}_2(\text{O}_2\text{C}'\text{Bu})_4\cdot 2\text{PPh}_3$; Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985**, *24*, 371.

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note that the relative k_s values do not correlate with the size of the R group. From these observations, we can state that carboxylate orbital pathways do not appear to be controlling the rate of electron transfer.

The influence of changing M on k_s is not what we might have expected. Tungsten's 5d orbitals are more diffuse than the Mo 4d orbitals, yet k_s for M = W is less than that for M = Mo. Likewise, removal of the Ru₂⁴⁺ π^* electron is slower than removal of the Mo₂ δ electron. Clearly, kinetic parameters do not track thermodynamic effects within this series. For the series M₂(O₂C'Bu)₄^{0/+}, changes in M–M distance and solution effects are expected to be small and similar. The result that k_s for the Mo species is greater than k_s for the W and Ru species is not in any way intuitively obvious to us.

However, the effect of added ligand is understandable, as axial ligation will block access of the M₂ moiety to the electrode; we would expect k_s to fall off with distance. A similar relationship was seen when a platinum electrode was used under identical conditions. The absence of a major effect on measured k_s values upon changing the electrode material suggests that there is not appreciable interaction between the electrode and the base. Therefore, we are disinclined to the view that the suppression of relative k_s values in the presence of added base is due merely to a modification of the electrode surface by the base.

There are, to our knowledge, only two previous studies of the rates of electron transfer involving metal–metal multiply bonded species, one of which was conducted by Coddington and Wherland¹⁹ on the self-exchange of Re₂X₄(PMe₂Ph)₄^{0/+}, where X = Cl or Br, as determined by NMR line broadening. The other, by Walton and Weaver and their co-workers,²⁰ was an investigation of the heterogeneous electron-transfer rate constants of Re₂^{4+/5+} and Re₂^{5+/6+} couples. A common finding of the latter work and this study is that the rates of electron transfer differ by less than 5-fold relative to those of Cp₂Fe^{0/+}. Collectively, these studies support the view that the kinetics of electron transfer are dominated by the solvent-mediated reorganizational energies of an outer-sphere process. The notion that the relative k_s values for a series of M₂(O₂CR)₄ complexes is dependent on the nature of M (and hence M–M electronic configuration) and R is thus proven to be incorrect by these studies of heterogeneous electron-transfer kinetics. This finding may, however, be irrelevant to electron mobility within polymers (or oligomers) of the type depicted by **B** and **C** because ligand bridges denoted by \curvearrowright provide an intramolecular pathway by orbital mixing with the M–M electrons.

Experimental Section

General Procedures. Benzonitrile was dried over P₂O₅, distilled, and stored over 4-Å molecular sieves. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆), ferrocene, and decamethylferrocene were purchased from Aldrich and used without further purification. Tris-(bipyridyl)ruthenium(II) chloride, obtained from Aldrich, was converted into the perchlorate salt by metathesis with sodium perchlorate. The complexes Mo₂(O₂CR)₄,²¹ W₂(O₂C'Bu)₄,²² Ru₂(O₂C'Bu)₄,²³ and Rh₂(O₂C'Bu)₄²⁴ were prepared according to literature procedures. Inert

atmosphere techniques were used throughout the sample preparations and electrochemical measurements. Electrochemical samples were prepared inside a He-filled glovebox and placed into an airtight cyclic voltammetric cell. The cell was then removed from the glovebox, and the electrodes were inserted into the cell under positive N₂ pressure. Solutions of W₂(O₂C'Bu)₄ were prepared in a glovebox, removed from the glovebox in a Schlenk flask, and then transferred via cannula into a thoroughly purged (Ar) electrochemical cell.

Electrochemistry. Cyclic voltammetric and chronoamperometric data were collected with the aid of a Princeton Applied Research (PAR) 173A potentiostat–galvanostat equipped with a PAR 176 current-to-voltage converter with *iR* compensation capability. A single-compartment voltammetric cell was equipped with a glassy carbon working electrode (area = 0.077 cm²), a platinum wire auxiliary electrode, and a reference electrode consisting of a saturated cadmium amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; the potential of this reference electrode is –0.76 V versus the aqueous saturated calomel electrode (SCE) at 25 °C. All potentials cited in this paper are given with respect to the SCE. A Faraday cage was used to screen out stray electrical noise.

In a typical cyclic voltammetric experiment, a 1.0 mM solution of the desired metal complex was prepared in benzonitrile containing 0.10 M TBAPF₆. For a given redox couple, the potential was initially scanned in a positive-going direction from 200 mV negative of the cathodic peak potential to 200 mV positive of the anodic peak potential at scan rates ranging from 50 mV s^{–1} to 6 V s^{–1}. In experiments with added base, the benzonitrile solution contained 0.10 M base. Measurements were repeated several times and on different occasions to check for reproducibility; it was determined that small changes in ambient temperature and solute concentration had a negligible effect on the experimental results.

Chronoamperometry was employed to determine the diffusion coefficients for the various metal complexes from background-subtracted plots of current (A) versus $t^{-1/2}$ (s^{–1/2}). To acquire the chronoamperograms, the potential of the working electrode was stepped from 200 mV negative to 200 mV positive of the formal potential for the redox couple. As a check on the validity of the chronoamperometric procedure, hydrodynamic voltammetry²⁵ with a rotating glassy carbon disk electrode (area = 0.459 cm²) was employed to determine the diffusion coefficient for Ru(bpy)₃²⁺.

Data obtained from the cyclic voltammetric and chronoamperometric experiments for the various metal complexes were then treated by means of the Nicholson method⁵ to calculate the heterogeneous electron-transfer rate constants, k_s (cm s^{–1}).

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Supporting Information Available: Primary data pertaining to the determination of k_s for ferrocene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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