achieve this, it is necessary to carefully control the temperature and nature of the colloid surface coating. This latter condition is well met by using citrate-reduced sols. Adsorbed citrate ions coat the silver surface and confer a protein-compatible surface. This organic layer may prevent the heme approaching too closely to the silver surface, especially when a pH < p*I* is used to activate a protein/colloid interaction. This is critical in avoiding denaturation by heme extraction, in cytochrome P-420 formation, or in avoiding undesirable low- to high-spin-state conversion. The main features of the spectra of each of four P-450s studied are summarized in Table I. That the cytochromes P-450 are relatively intact and biologically active on the sol surface is exemplified by the response to substrate of the adsorbed proteins.

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Registry No. Ag, 7440-22-4; cytochrome P450, 9035-51-2; benzphetamine, 156-08-1; citric acid, 77-92-9; heme, 14875-96-8.

Intrinsic Barriers to Atom Transfer: Self-Exchange Reactions of $CpM(CO)_3X/CpM(CO)_3^-$ Halide Couples

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Abstract: Rate constants and activation parameters were measured for the self-exchange of $CpM(CO)_3^-$ with $CpM(CO)_3X$ in CD_3CN solvent:

$$CpM(CO)_3^- + CpM(CO)_3X \rightleftharpoons CpM(CO)_3X + CpM(CO)_3^-$$

The self-exchange reactions were followed by ^1H NMR spectroscopy: For the X = I complexes, standard line width measurements yield (M = Mo) $k(298) = 1.5 \times 10^4\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 6.4\ (\pm 0.4)$ kcal mol^{-1}, $\Delta S^\ddagger = -18\ (\pm 1.5)$ cal K^{-1} mol^{-1}) and (M = W) $k(298) = 4.5 \times 10^3\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 7.5\ (\pm 0.1)$ kcal mol^{-1}, $\Delta S^\ddagger = -16.8\ (\pm 0.5)$ cal K^{-1} mol^{-1}). For the X = Br complexes, magnetization-transfer experiments yield (M = Mo) $k(298) = 1.6 \times 10^1\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 12.1\ (\pm 4.5)$ kcal mol^{-1}, $\Delta S^\ddagger = -12\ (\pm 15)$ cal K^{-1} mol^{-1}) and (M = W) $k(298) = 1.5\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 15.1\ (\pm 5.2)$ kcal mol^{-1}, $\Delta S^\ddagger = -7\ (\pm 16)$ cal K^{-1} mol^{-1}); ^1H NMR longitudinal relaxation times T_1 for the Cp groups of the reactants are typically 40 s. The X = Cl systems were studied by conventional techniques, with the rates of "transfer" of Cp-d_5 from $(Cp\text{-}d_5)W(CO)_3^-$ to $CpW(CO)_3Cl$ being monitored; for M = Mo, $k(298) = 9.0 \times 10^{-2}\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 18.9\ (\pm 1.0)$ kcal mol^{-1}, $\Delta S^\ddagger = 0\ (\pm 4)$ cal K^{-1} mol^{-1}) and for M = W, $k(298) = 2.1 \times 10^{-3}\ M^{-1}\ s^{-1}$ ($\Delta H^\ddagger = 17.7\ (\pm 3.3)$ kcal mol^{-1}, $\Delta S^\ddagger = -11\ (\pm 11)$ cal K^{-1} mol^{-1}). For X = CH_3, the $CpW(CO)_3^-/CpW(CO)_3CH_3$ self-exchange rate constant, also determined by monitoring rates of "transfer" of Cp-d_5 from $(Cp\text{-}d_5)W(CO)_3^-$ to $CpW(CO)_3X$, is $\approx 1 \times 10^{-5}\ M^{-1}\ s^{-1}$ at 335 K. The latter self-exchange reaction is discussed in terms of the intrinsic barrier for oxidative addition to the anion. For the X = halogen exchanges, the role of the M(I) ("metal radical") state is considered, and it is concluded that the latter isovalent state is not an intermediate for these systems. However, the isovalent state may serve to stabilize the transition state for two-electron transfer between the metal centers through configuration interaction. Our results, taken with those for other X = halogen systems, indicate that effective transfer of X^+ may be intrinsically rapid when both reactants are 18-electron species and steric factors are favorable.

Introduction

The concept of factoring the kinetic barrier to a reaction into intrinsic and thermodynamic components has proven remarkably powerful for outer-sphere electron-transfer reactions.[1] In recent years, this approach has also been applied to proton-transfer, methyl (CH_3^+)-transfer, and other "atom"-transfer reactions.[2,3] In these applicatons, a crucial parameter is the free energy barrier to the self-exchange ($\Delta G^\circ = 0$) reaction, $\Delta G^\ddagger_{ex}$. While $\Delta G^\ddagger_{ex}$ values have been inferred from kinetic data for net ($\Delta G^\circ \neq 0$) reactions, only rarely (with the exception of outer-sphere electron-transfer reactions) have the intrinsic barriers been evaluated by direct study of the self-exchange process. It is becoming apparent that transition-metal complexes are excellent substrates for such studies. In this paper we describe our studies of "atom-transfer" self-exchange reactions of $CpM(CO)_3^-/CpM(CO)_3X$ couples. In our experiments a range of ^1H NMR techniques provide a probe of the self-exchange process analogous to that of radioisotopes in the earliest self-exchange measurements.

Following Taube[4] we adopt the term "atom transfer" for reactions in which an atom originating in either the oxidizing or reducing agent is transferred to the reaction partner so that in the activated complex both oxidizing and reducing centers are attached to the atom being transferred. In this sense, "atom transfer" is intended as a broad reaction class and is not restricted to reactions in which a single neutral atom is transferred (for example, a hydrogen atom or halogen atom abstraction). Reactions falling within this class include one-electron and two-electron inner-sphere electron-transfer reactions,[5] halogen- and hydrogen-atom abstractions, hydride-transfer reactions, and certain proton-transfer and nucleophilic substitution reactions. With, perhaps, one[6] exception, all known two-electron-transfer reactions

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in solution involve atom transfer. Such reactions are central to many catalytic changes effected by transition-metal centers and, indeed, to much chemistry in general. Self-exchange studies of only a few atom-transfer couples have been made. One of the earliest and most comprehensive was of the Pt(II)/Pt(IV)[7-9] exchange (eq 1). However, these systems are complicated by

$$trans\text{-}\mathbf{Pt}^{IV}(NH_3)_4Cl_2^{2+} + Cl^- + Pt^{II}(NH_3)_4^{2+} \rightleftharpoons [Cl\mathbf{Pt}(NH_3)_4ClPt(NH_3)_4Cl]^{3+}$$

$$[Cl\mathbf{Pt}(NH_3)_4ClPt(NH_3)_4Cl]^{3+} \rightleftharpoons \mathbf{Pt}^{II}(NH_3)_4^{2+} + Cl^- + trans\text{-}Pt^{IV}(NH_3)_4Cl_2^{2+} \quad (1)$$

the intrinsic coordination number mismatch of the 16-electron Pt(II) and 18-electron Pt(IV) complexes, since electron "exchange" requires loss of two ligands from reactant Pt(IV) and the gain of two ligands by reactant Pt(II). Recently self-exchange rate constants were determined[10] for a series of 18-electron ruthenium and osmium MCp_2 complexes (eq 2) where X = I or Br and Cp

$$M^{IV}Cp_2X^+ + \mathbf{M}^{II}Cp_2 \rightleftharpoons M^{II}Cp_2 + \mathbf{M}^{IV}Cp_2X^+ \quad (2)$$

= cyclopentadienide; the pressure dependence of the rate constants for M = Ru, X = Br has also been reported.[11] These systems, which (at least formally) involve two-electron transfer coupled to atom transfer, have distinct advantages over previously studied two-electron systems since they are not complicated by possible solvent coordination and differing electron counts. The proton-transfer self-exchange studies of 18-electron metal hydrides and their 18-electron, conjugate bases (e.g., eq 3; M = Cr, Mo, W) reported by Norton and colleagues[12] also fall within the broad definition of atom transfer. Recently oxo-transfer self-exchange

$$CpM^0(CO)_3^- + Cp\mathbf{M}^{II}(CO)_3H \rightleftharpoons CpM^{II}(CO)_3H + Cp\mathbf{M}^0(CO)_3^- \quad (3)$$

reactions have been studied,[13] and a reversible three-electron transfer between manganese porphyrins accompanied by nitrogen-atom transfer has been recorded.[14]

In the present work we have measured rate constants and activation parameters for the self-exchange reactions of metal anions with their metal halide or methyl complexes (eq 4) with

$$CpM^0(CO)_3^- + Cp\mathbf{M}^{II}(CO)_3X \rightleftharpoons CpM^{II}(CO)_3X + Cp\mathbf{M}^0(CO)_3^- \quad (4)$$

M = W or Mo and X = Cl, Br, or I (the M = Cr members of the series being omitted because the $CpCr(CO)_3X$ complexes are not stable). These 18-electron, d^6–d^4 systems are isoelectronic with the Ru and Os MCp_2 systems[10] in eq 2 and are also related to the proton exchanges in eq 3 (eq 4, X = H). As will be seen, the self-exchange rate constants determined for eq 4 in this study span many orders of magnitude and require the exploitation of a wide range of ^{1}H NMR techniques, including line broadening, magnetization transfer, and conventional kinetic techniques.

Experimental Section

Materials. PPN[$CpMo(CO)_3$] (PPN = bis(triphenylphosphine)-iminium cation and Cp = cyclopentadienyl anion) was prepared by a slight modification of the literature method,[15] with NaK[16] instead of Na/Hg being used to reduce the dimer $[CpMo(CO)_3]_2$. PPN[$CpW(CO)_3$] was prepared from Na[$CpW(CO)_3$] and PPNCl as described for the Mo analogue.[15] Deuterated cyclopentadiene, C_5D_6, was prepared by a slight modification of the literature procedure,[17] by using three exchanges of cyclopentadiene with deaerated NaOD/D_2O. The C_5D_6 was converted to $[(Cp\text{-}d_5)M(CO)_3]_2$,[18] (M = Mo, W). Reduction of the dimers followed by counterion exchange gave PPN[$(Cp\text{-}d_5)M(CO)_3$] (M = Mo, W). The iodides, $CpM(CO)_3I$ (M = Mo, W), were prepared by I_2 oxidation of $[CpM(CO)_3]_2$ in CH_2Cl_2.[19] The bromides, $CpM(CO)_3Br$, were prepared[20] from the reaction of $CpM(CO)_3H$ with $CHBr_3$ instead of CBr_4. The chlorides, $CpM(CO)_3Cl$, were prepared from $CpM(CO)_3H$ and CCl_4.[21] $CpW(CO)_3CH_3$ was prepared by reaction of CH_3I and Na[$CpW(CO)_3$] in THF.[21]

CD_3CN (Aldrich) was dried over P_4O_{10}, then vacuum transferred, and stored over 3Å molecular sieves.

Sample Preparation. Samples were prepared in one of two ways. (1) A weighed sample of the compound was placed in an NMR tube in an argon drybox. On a vacuum line, CD_3CN was transferred into the NMR tube and the tube was flame sealed. The volume of the solution was calculated from the height of solvent in the NMR tube.[22] (2) In an argon drybox, known quantities of compound were placed in a volumetric flask and diluted to the mark with CD_3CN. A portion was transferred by pipet to an NMR tube. The tubes were then flame sealed under vacuum. Prepared NMR tubes were stored in a −81 °C freezer until used.

^{1}H NMR Measurements. The NMR data (300 MHz) were collected on a Bruker AM-300 NMR equipped with an Aspect 3000 computer and a VT-1000 variable temperature unit. The variable temperature unit was calibrated with MeOH (0.1% HCl)[23] and ethylene glycol[24] over the temperature range 235–350 K. The unit was calibrated with the appropriate solution, before each NMR run. The NMR instrument was allowed to temperature equilibrate for 2 h prior to any single accumulation experiments in order to maintain an unvarying lock. The lock unit was found to be intolerant of room temperature changes greater than ±1 °C for the single-accumulation experiments.

Line broadening experiments were performed on the iodo systems over a range of temperatures and varying $CpM(CO)_3I$ concentration with constant PPN[$CpM(CO)_3$] concentration. Line widths were determined by measuring the full width at half-height (FWHH) of the Cp resonances. The line widths in the absence of exchange for the individual compounds were 0.5 ± 0.2 Hz, and their variation with temperature was found to be negligible. Dioxane was used as an internal line width standard.

Magnetization-transfer experiments were performed on the bromide systems with a DANTE pulse sequence.[25] This pulse sequence has the form

$$D_1\text{–}(\text{–}P_1\text{–}D_2\text{–})_n\text{–}\tau\text{–FID}$$

where D_1 is a long delay of 5 times the longest T_1 value, P_1 is $1/n$ of the 180° pulse width, D_2 is a short delay, τ is a variable delay, and FID is the free induction decay. The pulse sequence selectively inverts by excitation one of the resonances; then, the observed pulse being delayed by a specified interval τ, the change in magnetization of the other exchange-coupled resonance is followed with time. In this study n = 10 was used. This resulted in a coarse digitization parameterization[26] and possibly some small errors in the baseline, but none were readily apparent. The 180° pulse width was measured prior to each run. A 90° pulse width was used in collecting the FID. The short delay D_2 was 1 ms, and the τ value varied over a range of 0.5–400 s. Only one accumulation was taken at each delay because of the long T_1 values and the long delays needed between data points. The intensity data were input into a four-parameter nonlinear least-squares fit program written by Perkin[27] and

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modified by Brunschwig. An important input parameter is the true T_1 value for each component at each temperature. These were determined separately with use of an inversion recovery pulse sequence on the Aspect 3000. The T_1's were evaluated by using the T_1 fit program on the NMR, or, in some cases, the T_1's were calculated from plots[28] of ln $[I(\infty) - I(t)]$ vs τ, where the slope is $-1/T_1$.

The chloro systems were monitored by conventional NMR techniques. The growth of the Cp resonance for $CpM(CO)_3^-$ was followed with time after mixing $CpM(CO)_3Cl$ with the perdeuterated Cp complex, $(Cp\text{-}d_5)M(CO)_3^-$ (eq 5, M = Mo, W). This method was also used to investigate the rate of methyl exchange, X = CH_3 with M = W.

$$(Cp\text{-}d_5)M(CO)_3^- + CpM(CO)_3X \rightleftharpoons (Cp\text{-}d_5)M(CO)_3X + CpM(CO)_3^- \quad (5)$$

Results

The room-temperature 300-MHz proton NMR spectra of the complexes in CD_3CN exhibit a single resonance for the cyclopentadienyl protons. The resonances of the anion and halo complexes are well separated. The anion resonances lie at 5.04 ppm for Mo and at 5.08 for W. The resonances for the halo complexes $CpM(CO)_3X$ lie, respectively, at 5.83, 5.72, and 5.73 ppm for X = I, Br, and Cl when M = Mo and at 5.82, 5.84, and 5.84 ppm for X = I, Br, and Cl when M = W.

The second-order rate constants k_{ex} and the activation parameters for the $CpM(CO)_3^-/CpM(CO)_3X$ self-exchange reactions were measured with use of three different NMR techniques.

$$CpM(CO)_3^- + CpM(CO)_3X \underset{k_{ex}}{\overset{k_{ex}}{\rightleftharpoons}} CpM(CO)_3X + CpM(CO)_3^- \quad (4)$$

Line Broadening. The relatively rapid exchange rates for the $CpM(CO)_3I$ systems were best determined by standard line width measurements. The spectrum of a solution 0.05 M in $CpM(CO)_3I$ and in $(PPN)[CpM(CO)_3]$ in CD_3CN at room temperature shows two very broad and overlapping resonances. As the solution is cooled, the peaks sharpen and separate (Figure 1). For both the W and Mo complexes, the corrected line width (experimental line width minus the line width in the absence of exchange) increases with increasing temperature, placing these systems in the slow-exchange regime.[29] The analysis of the data thus takes the simple form given in eq 6.[30] In eq 6, $\Delta\nu_{1/2M,MI}$ is the FWHH of $CpM(CO)_3^-$ (M) in the presence of a given concentration [MI] of $CpM(CO)_3I$ (MI) and $\Delta\nu_{1/2M}$ is the FWHH of $CpM(CO)_3^-$ in the absence of $CpM(CO)_3I$. Similarly, $\Delta\nu_{1/2MI,M}$ is the FWHH of $CpM(CO)_3I$ in the presence of a given concentration [M] of $CpM(CO)_3^-$, and $\Delta\nu_{1/2MI}$ is the FWHH of $CpM(CO)_3I$ in the absence of $CpM(CO)_3^-$. Corrected line widths obtained at a single temperature were plotted against the concentration of the reaction partner, and k_{ex} was determined from the slope. Line width data are summarized in Table I, and k_{ex} values extracted from the concentration dependences of the line widths are listed in Table II. Figure 2 shows the behavior of $CpW(CO)_3^-$ and $CpW(CO)_3I$ resonances as a function of $CpW(CO)_3I$ concentration at 290 K. Small amounts of impurities which form as the solution ages over the course of the measurements do not interfere with the determination.

$$k_{ex} = [\Delta\nu_{1/2M,MI} - \Delta\nu_{1/2M}]\pi/[MI] = [\Delta\nu_{1/2MI,M} - \Delta\nu_{1/2MI}]\pi/[M] \quad (6)$$

Table I. Corrected Line Widths $\Delta\nu_{1/2}$ Obtained for $PPN[CpM(CO)_3]$ in CD_3CN in the Presence of $CpM(CO)_3I$ as a Function of Temperature

$[CpM(CO)_3^-]$, M	$[CpM(CO)_3I]$, M	temp,[a] K	$\Delta\nu_{1/2}(CpM(CO)_3^-)$,[b] Hz
	M = Mo		
0.0614	0.0621	235	12.4
		246	22.4
		257	50.4
		269	89.4
		279	122.4
0.0613	0.0333	235	8.6
		246	12.1
		257	23.7
		269	41.5
		279	61.0
0.0635	0.0101	235	2.11
		246	3.27
		257	5.68
		269	11.4
		279	18.9
0.0615	0.0070	235	1.33
		246	2.15
		257	4.62
		269	8.46
		279	13.8
	M = W		
0.0489	0.0460	246	3.67
		257	7.84
		269	15.6
		279	25.8
		290	45.0
		300	71.7
0.0488	0.0200	246	1.66
		257	3.46
		269	6.46
		279	11.4
		290	19.5
		300	31.6
0.0485	0.0076	246	0.79
		257	1.51
		269	2.63
		279	4.89
		290	8.02
		300	12.4
0.0492	0.0030	246	0.21
		257	0.51
		269	0.97
		279	1.76
		290	2.30
		300	3.38

[a] Temperature calculated from calibration curve. [b] Line width corrected by line width in the absence of exchange.

Table II. Bimolecular Rate Constants for the $CpM(CO)_3^-/CpM(CO)_3I$ Self-Exchange

temp, K	M = Mo k_{ex}, M^{-1} s^{-1}	M = W k_{ex}, M^{-1} s^{-1}
235	0.64×10^3	
246	1.2×10^3	0.25×10^3
257	2.6×10^3	0.53×10^3
269	4.6×10^3	1.1×10^3
279	6.2×10^3	1.7×10^3
290		3.1×10^3
300		4.9×10^3

Magnetization Transfer. The rates of exchange in the $CpM(CO)_3Br$ and $CpM(CO)_3Cl$ systems were too slow for measurement by a simple line broadening technique. However, the $CpM(CO)_3Br$ systems did prove amenable to study by magnetization-transfer techniques, although the data are less precise than those obtained from the other techniques used here. The magnetization-transfer or spin-saturation-transfer method is a double resonance NMR technique initially developed by Forsen and Hoffman[31] for measuring rates of exchange between magnetically inequivalent sites within a single molecule. Associated with each site in a molecule are a characteristic lifetime for each spin state and a time constant associated with the recovery of populations expected at thermal equilibrium. The time constant associated with the restoration of the resonance intensity is known

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Table III. T_1 Values Determined for PPN[CpM(CO)$_3$] and CpM(CO)$_3$Br Complexes in CD$_3$CN

compound	temp, K	T_1, s
(PPN)[CpMo(CO)$_3$]	294	39
	301	44
	306	44
	314	55
CpMo(CO)$_3$Br	294	43
	298	42
	309	48
	314	38
(PPN)[CpW(CO)$_3$]	298	50
	310	61
	313	57
	319	50
	326	60
CpW(CO)$_3$Br	310	36
	313	39
	320	42
	326	45

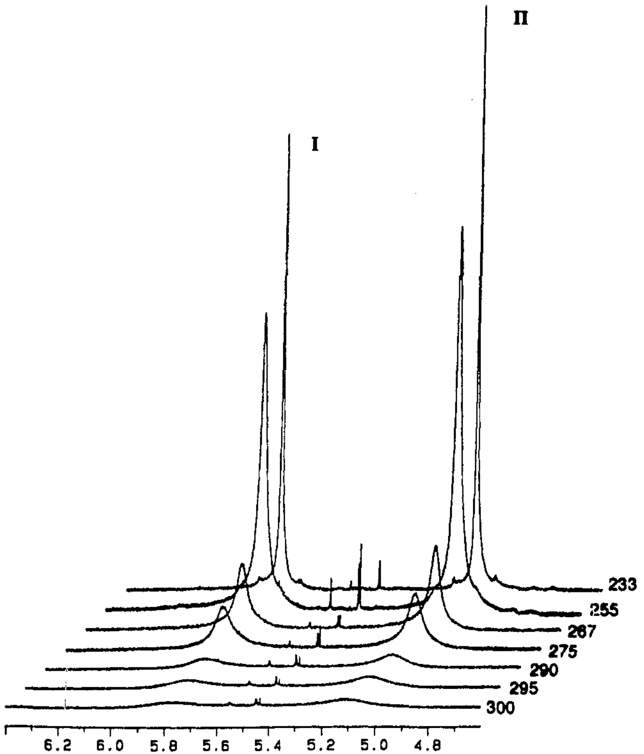

Figure 1. Stacked plot of NMR spectra from a linebroadening experiment with CpW(CO)$_3$I (0.046 M) (I) and CpW(CO)$_3^-$ (0.049 M) (II) in CD$_3$CN at different temperatures. Small peaks are due to impurities.

as the longitudinal relaxation time, T_1. When chemical exchange occurs, the nuclei are transferred from one (magnetically inequivalent) site to another. The exchange takes place without relaxation occurring in the transfer process. Consequently, when the exchange rate is comparable to the relaxation rates at both sites, complete saturation of one resonance results in partial saturation of the other. Saturation can be obtained by a "soft" pulse used to selectively negate or invert one of the exchanging resonances. In the DANTE sequence used in this study, saturation occurs as the excited resonance is nulled. When it is allowed to relax, the signal intensity at the other site recovers.

T_1 values determined in this study for CpM(CO)$_3^-$ and CpM(CO)$_3$Br are listed in Table III. They are typically of the order of 40 s, and $1/T_1$ is of the order of 2.5×10^{-2} s^{-1}. Thus if the self-exchange time scale can be brought into this range, either by choosing the appropriate concentration level or temperature, magnetization transfer should be observed. Figure 3 illustrates the behavior observed for 3 mM molybdenum complexes at 29 °C.

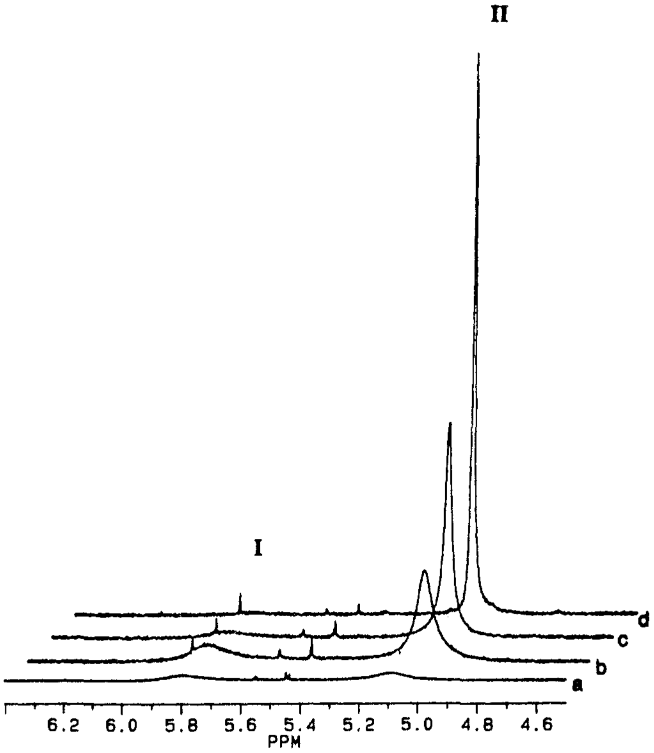

Figure 2. Stacked plot of NMR spectra for the linebroadening experiments with CpW(CO)$_3$I (I) and CpW(CO)$_3^-$ (II) in CD$_3$CN at 290 K. The concentration of CpW(CO)$_3^-$ was kept constant at 0.049 M, and the CpW(CO)$_3$I concentrations are (a) 0.046, (b) 0.020, (c) 0.008, and (d) 0.003 M.

The sequence of events occurring in a magnetization-transfer experiment involving a bimolecular exchange is summarized in Scheme I. In the magnetization-transfer sequence, A is selectively excited to A* (i). In the presence of B, exchange (ii) occurs with a bimolecular rate constant k_{ex} to yield partial saturation of B (B*). Similarly, since B is undergoing self-exchange with A, the B* population can be depleted through (iii). In parallel, both A* and B* decay to A and B by their respective time constants, T_{1A} and T_{1B} (iv and v). Scheme I yields eqs 7 and 8 for [A*] and [B*]. The solution to the time-dependent Bloch equations describing the magnetization at each site yields eq 9, which contains the two characteristic time constants λ_1 and λ_2 (eq 10). C_2 is a constant of integration, and the λ expression contains T_1 values for both A and B as well as k_A and k_B.[32] The intensity data and

Scheme I

$$A \xrightarrow{\text{pulse}} A^* \tag{i}$$

$$A^* + B \xrightarrow{k_{ex}[B] = k_A} A + B^* \tag{ii}$$

$$A + B^* \xrightarrow{k_{ex}[A] = k_B} A^* + B \tag{iii}$$

$$A^* \xrightarrow{1/T_{1A}} A \tag{iv}$$

$$B^* \xrightarrow{1/T_{1B}} B \tag{v}$$

$$\frac{-d[A^*]}{dt} = k_{ex}[A^*][B] + \frac{1}{T_{1A}}[A^*] - k_{ex}[B^*][A] \tag{7}$$

$$\frac{d[B^*]}{dt} = k_{ex}[A^*][B] - \frac{1}{T_{1B}}[B^*] - k_{ex}[B^*][A] \tag{8}$$

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[32] Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

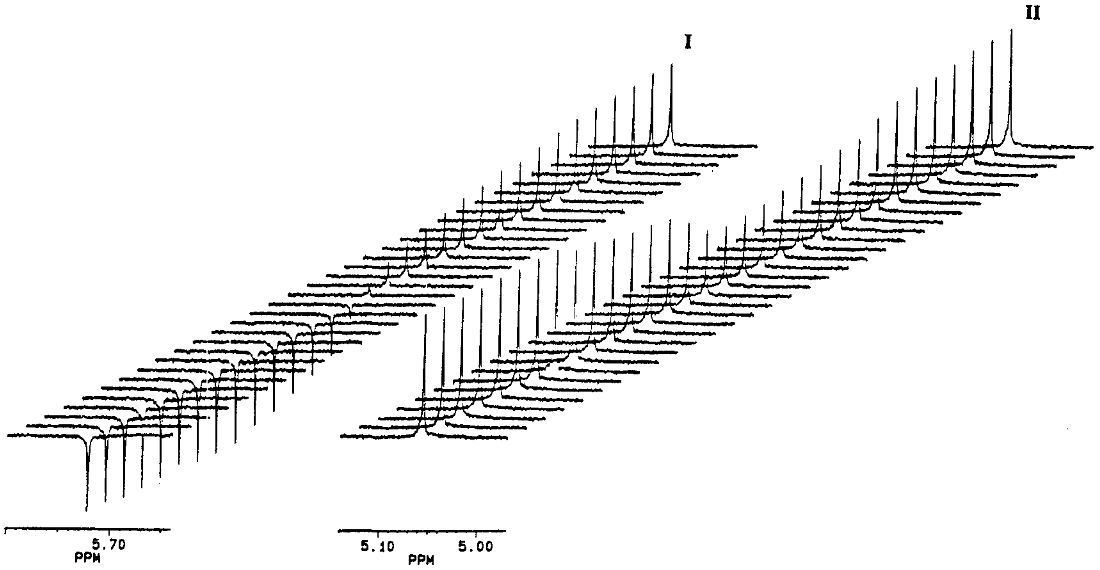


Figure 3. Stacked plot of magnetization-transfer results for CpMo(CO)$_3$Br (0.0025 M) (I) and CpMo(CO)$_3^-$ (0.0036 M) (II) in CD$_3$CN at 303 K. Each spectrum was obtained at a different value of τ: the value of τ at the bottom of the plot is 0.0002 s, and at the top it is 250 s.

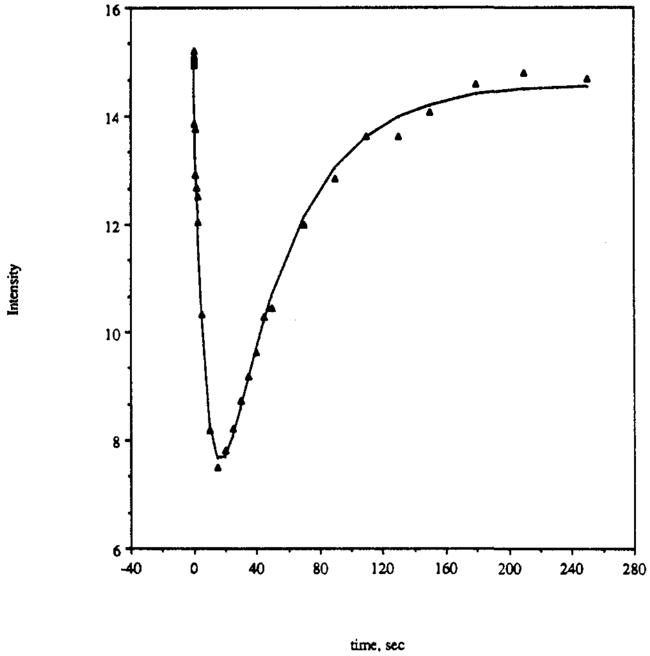


Figure 4. Fit of CpMo(CO)$_3^-$ intensity data from magnetization-transfer experiment with CpMo(CO)$_3^-$ and CpMo(CO)$_3$Br in CD$_3$CN at 303 K.

other parameters were fit to eq 9 to yield values of the pseudo-first-order rate constant k_A.

$$\Delta M_z = \Delta M_\infty + \left((\Delta M_0 - \Delta M_\infty) - C_2\left(1 - \frac{\left(\frac{1}{T_{1A}} + k_A\right) - \lambda_2}{k_B}\right)\right)e^{-\lambda_1 t} + \left(C_2\left(1 - \frac{\left(\frac{1}{T_{1A}} + k_A\right) - \lambda_2}{k_B}\right)\right)e^{-\lambda_2 t} \quad (9)$$

$$\lambda_{1,2} = \frac{1}{2}\left(\left(\frac{1}{T_{1A}} + k_A\right) + \left(\frac{1}{T_{1B}} + k_B\right)\right) \pm \frac{1}{2}\left(\left(\left(\frac{1}{T_{1A}} + k_A\right) - \left(\frac{1}{T_{1B}} + k_B\right)\right)^2 + 4k_Ak_B\right)^{1/2} \quad (10)$$

Table IV. Magnetization-Transfer Rate Constants for PPN[CpM(CO)$_3$]/CpM(CO)$_3$Br in CD$_3$CN

[CpM(CO)$_3^-$], M	[CpM(CO)$_3$Br], M	temp, K	k_{fit}, s^{-1}	k_{ex}, M^{-1} s^{-1}
		M = Mo		
0.0036	0.0023	293	0.019	8.2
0.0036	0.0026	298	0.043	1.7×10^1
0.0034	0.0070	302	0.30	4.4×10^1
0.0034	0.0018	302	0.040	2.2×10^1
0.0036	0.0025	303	0.044	1.7×10^1
0.0037	0.0019	309	0.047	2.5×10^1
0.0038	0.0027	313	0.11	4.4×10^1
		M = W		
0.0032	0.0034	308	.015	4.4
0.0032	0.0067	310	.017	2.5
0.0032	0.0092	310	.030	3.2
0.0032	0.0034	313	.029	8.9
0.0032	0.0034	318	.026	7.5
0.0034	0.0033	315	.030	8.8
0.0032	0.0033	326	.044	1.3×10^1

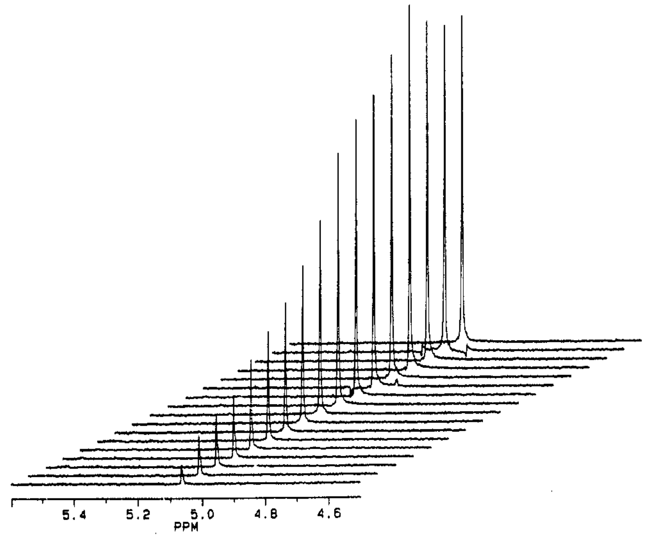


Figure 5. Stacked plot of exchange results for CpW(CO)$_3$Cl (0.057 M) and (Cp-d_5)W(CO)$_3^-$ (0.040 M) in CD$_3$CN at 298 K. Plot shows the growth of CpW(CO)$_3^-$.

A typical data set and fit are shown in Figure 4. The bimolecular exchange rate constants were determined from the fitted pseudo-first-order rate constants corrected for the concentration

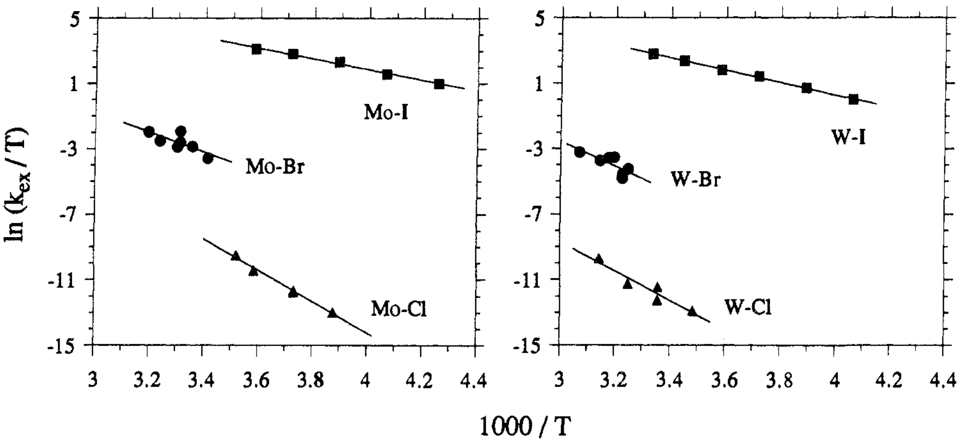


Figure 6. Plots of ln (k_{ex}/T) vs $1/T$ for $CpMo(CO)_3^-/CpMo(CO)_3X$ and $CpW(CO)_3^-/CpW(CO)_3X$, where X = I (■), Br (●), and Cl (▲).

Table V. Rate Constants for Reaction of $PPN[(Cp\text{-}d_5)M(CO)_3]$ with $CpM(CO)_3Cl$ in CD_3CN

$[(Cp\text{-}d_5)M(CO)_3^-]$, M	$[CpM(CO)_3Cl]$, M	temp, K	k, s^{-1}	k_{ex}, M^{-1} s^{-1}
		M = Mo		
0.056	0.056	258	6.7×10^{-5}	6.0×10^{-4}
0.065	0.065	268	3.0×10^{-4}	2.3×10^{-3}
0.065	0.067	268	2.8×10^{-4}	2.1×10^{-3}
0.074	0.072	279	1.2×10^{-4}	8.3×10^{-3}
0.058	0.058	284	2.4×10^{-3}	2.1×10^{-2}
		M = W		
0.037	0.035	287	5.1×10^{-5}	7.1×10^{-4}
0.047	0.058	298	3.3×10^{-4}	3.1×10^{-3}
0.057	0.039	298	1.3×10^{-4}	1.4×10^{-3}
0.036	0.032	308	2.6×10^{-4}	3.9×10^{-3}
0.066	0.048	318	2.1×10^{-3}	1.9×10^{-2}

of the reaction partner. In most cases, $CpM(CO)_3Br$ was irradiated so that A = $CpM(CO)_3Br$ and B = $CpM(CO)_3^-$. The range of temperatures over which these reactions could be studied was limited by a slow rate of exchange at lower temperatures and decomposition of the reactants to the more insoluble dimer species at higher temperatures. The results for X = Br are given in Table IV.

Conventional Techniques. The rates of exchange were determined for the $CpM(CO)_3Cl$ systems by conventional NMR techniques. Solutions containing both $CpM(CO)_3Cl$ and the perdeuterated complex $(Cp\text{-}d_5)M(CO)_3^-$ were monitored with time until the reaction had reached equilibrium (eq 5) and k_{ex} was evaluated from eq 11.[33] The semilog plots of the intensity-time data were linear for the 4–5 half-lives monitored (12–18 time points). Figure 5 shows the NMR results for one of the slow exchange experiments, and all of the results are summarized in Table V.

$$(Cp\text{-}d_5)M(CO)_3^- + CpM(CO)_3X \rightleftharpoons (Cp\text{-}d_5)M(CO)_3X + CpM(CO)_3^- \quad (5)$$

$$k_{obsd} = k_{ex}([M^-] + [MCl]) \quad (11)$$

The errors on the derived bimolecular rate constants are generally ±10% but larger for the X = Br systems studied by the magnetization-transfer method. For all three types of experiments activation parameters were determined from plots of ln (k_{ex}/T) vs $1/T$ as shown in Figure 6, and values for k_{ex} at 298 K, calculated from the least-squares fit of the data, are given in Table VI. As expected, the errors on the activation parameters for the X = Br systems are much greater than for the others.

In a single exploratory experiment, the exchange of $(Cp\text{-}d_5)W(CO)_3^-$ with $CpW(CO)_3(CH_3)$ was followed in CD_3CN at 335 K. The half-life for eq 12 with $[CpW(CO)_3CH_3]$ = 0.010 M and $[(Cp\text{-}d_5)W(CO)_3^-]$ = 0.012 M was approximately 1 month. The exchange rate constant was estimated to be 8 (±1) × 10^{-6} M^{-1} s^{-1}.

Table VI. Activation Parameters and Self-Exchange Rate Constants at 298 K for $CpM(CO)_3^-$ or $(Cp\text{-}d_5)M(CO)_3^-$ with $CpM(CO)_3X$[a]

reaction pair	k_{ex}(298 K), M^{-1} s^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal K^{-1} mol^{-1}
$CpMo(CO)_3^-/CpMo(CO)_3I$	1.5×10^4	6.4 (±0.4)	−17.8 (±1.5)
$CpMo(CO)_3^-/CpMo(CO)_3Br$	16	12.1 (±4.5)	−12 (±15)
$(Cp\text{-}d_d)Mo(CO)_3^-/CpMo(CO)_3Cl$	9.0×10^{-2}	18.9 (±1.0)	0 (±4)
$CpW(CO)_3^-/CpW(CO)_3I$	4.5×10^3	7.5 (±0.1)	−16.8 (±0.5)
$CpW(CO)_3^-/CpW(CO)_3Br$	1.5	15.1 (±5.2)	−7 (±16)
$(Cp\text{-}d_5)W(CO)_3^-/CpW(CO)_3Cl$	2.1×10^{-3}	17.7 (±3.3)	−11 (±11)

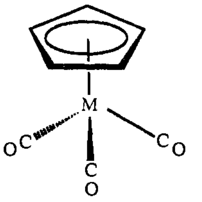
[a] Values in parentheses are standard deviations.

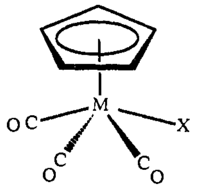
$$(Cp\text{-}d_5)W(CO)_3^- + CpW(CO)_3CH_3 \rightleftharpoons CpW(CO)_3^- + (Cp\text{-}d_5)W(CO)_3CH_3 \quad (12)$$

As a probe of the substitution kinetics of compounds in this series, the potential reaction of PMe_3 with $CpM(CO)_3^-$ in CD_3CN was investigated by ^1H NMR: at room temperature, no reaction to form phosphine-substituted complexes was observed over a 7 month period ($[PMe_3]/5 = [CpM(CO)_3^-] > 3$ mM).

Discussion

The $CpM(CO)_3^-$ and $CpM(CO)_3X$ complexes used in this study have structures based on the three- and four-legged piano stool. In the course of the self-exchange the X group is transferred from one "leg" site to another, and only small changes in the intramolecular $CpM(CO)_3$ distances and angles ensue: In the anion,[34a] the OC–M–CO angles and Cp–M–CO angles are typically 86 and 128°, respectively; in $CpM(CO)_3X$, both angles are somewhat smaller (for X = Cl, 78 and 110–125°, respectively).[34b] The Mo–Cl and W–Cl distances are 2.498 (1) and 2.490 (2) Å.[34b]





Homolytic bond dissociation enthalpies for $CpMo(CO)_3X$ are[35] 72.4 (Cl), 60.5 (Br), 51.8 (I), and 47 (CH_3) kcal mol^{-1}. Met-

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[33] McKay, H. A. C. *Nature* **1938**, *142*, 997; *J. Am. Chem. Soc.* **1943**, *65*, 702.

[34] (a) For the Mo complex: Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3020. (b) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197.

[35] Nolan, S. P.; De La Vega, R. L.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1491.

Table VII. Properties of $CpM(CO)_3$ Species

reaction		M: Cr	Mo	W
$CpM(CO)_3 + e^- = CpM(CO)_3^-$	$E°$, V vs sce[a]	−0.38	−0.078	−0.022
$CpM(CO)_3^+ + 2e^- = CpM(CO)_3^-$	$E°$, V, vs sce[b]		(−0.37)	(−0.39)
$CpM(CO)_3^- + H^+ = CpM(CO)_3H$	log K (pK_a M–H)[c]	13.3	13.9	16.1
$CpM(CO)_3^- + CH_3I \rightarrow CpM(CO)_3CH_3 + I^-$	k ($M^{-1}\ s^{-1}$)[d]	7.5×10^{-2}	1.5	2.4
$CpM(CO)_3H = CpM(CO)_3 + H$	$\Delta H°$, kcal mol^{-1} [a]	62	70	73
$[CpM(CO)_3]_2 = 2CpM(CO)_3$	$\Delta H°$, kcal mol^{-1}	15.8[e]	32.5[f]	56.1[g]

[a] Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711; **1990**, *112*, 2843. [b] Estimated from the anodic peak for the anion and the cathodic peak for the cation reported by Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246. [c] Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. [d] Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541 (solvent: tetrahydrofuran). [e] McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. [f] Amer, S.; Kramer, G.; Pöe, A. *J. Organomet. Chem.* **1981**, *209*, C28. [g] Krause, J. R.; Bidinosti, D. R. *Can. J. Chem.* **1975**, *53*, 628.

al–metal[35,36] and metal–hydrogen[37] bond dissociation energies are given in Table VII. As is summarized in Table VII, the anions are rather weak proton bases[12] and reducing agents.[37–41] On the basis of their reactivity with respect to methyl iodide,[42] they are also moderate nucleophiles (roughly 10^3 times more reactive than triethylamine, roughly 10^3 times less reactive than $CpFe(CO)_2^-$).[42b] In the parlance of traditional coordination chemistry, both the M(0) and M(II) complexes are substitution inert—synthetic substitution chemistry generally being carried out only at elevated temperatures where CO loss occurs[43] or under conditions where catalysis by M(I) can be achieved.[44] Interestingly, $CpM(CO)_3^-/CpM(CO)_3X$ mixtures, used here to determine self-exchange rates, can be used synthetically (at higher temperatures) to prepare the metal–metal bonded M(I) dimers $(CpM(CO)_3)_2$. However, this "comproportionation" reaction is much slower than self-exchange under conditions used here.

Within the definition given in the Introduction, the systems studied here meet the criteria for an atom-transfer reaction: The halide (or methyl group, eq 12) originating in the oxidant $CpM(CO)_3X$ is transferred to the reducing agent $CpM(CO)_3^-$. For these systems, this observation requires that both metal centers be bound to the group being transferred in the activated complex. Self-exchange is the only reaction observed: solvolysis of $CpM(CO)_3X$ to yield $CpM(CO)_3(CH_3CN)^+$ is negligible on the time scales of the various NMR experiments; furthermore, replacement of CO by PMe_3 is not observed for $CpM(CO)_3^-$. Thus sequences such as the following are ruled out.

$$M\text{–}X \rightarrow M^+ + X^-$$

$$M^- + M^+ \rightarrow M^+ + M^-$$

$$M^+ + X^- \rightarrow M\text{–}X$$

Table VIII. Activation Parameters and Self-Exchange Rate Constants for Electron-, "Atom"-, and Proton-Transfer Reactions[a]

reaction pair	$k_{ex}(298)$, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Cp_2Fe/Cp_2Fe^+ [b]	7.5×10^6	4.7	−12
Cp_2Co/Cp_2Co^+ [b]	3.8×10^7	4.0	−10.6
Cp_2Ru/Cp_2RuI^+ [c]	9.8×10^5	5.4	−13
Cp_2Ru/Cp_2RuBr^+ [d]	2.0×10^3	8.5	−14.9
Cp_2Os/Cp_2OsI^+ [e]	1.8×10^4	7.6	−13.3
$CpMo(CO)_3^-/CpMo(CO)_3I$ [f]	1.5×10^4	6.47	−17.7
$CpMo(CO)_3^-/CpMo(CO)_3Br$ [f]	1.4×10^1	12.3	−12
$(Cp\text{-}d_5)Mo(CO)_3^-/CpMo(CO)_3Cl$ [f]	8.6×10^{-2}	18.5	−1
$CpW(CO)_3^-/CpW(CO)_3I$ [f]	4.5×10^3	7.5	−17
$CpW(CO)_3^-/CpW(CO)_3Br$ [f]	2.8	10.4	−22
$(Cp\text{-}d_5)W(CO)_3^-/CpW(CO)_3Cl$ [f]	2.1×10^{-3}	17.9	−11
$(Cp\text{-}d_5)W(CO)_3^-/CpW(CO)_3CH_3$ [f,g]	$\approx 1 \times 10^{-5}$		
$CpCr(CO)_3^-/CpCr(CO)_3H^4$h	1.8×10^4	4.9	−22.6
$CpCr(CO)_3^-/CpCr(CO)_3D$ [h]	5.0×10^3	6.4	−20.0
$CpMo(CO)_3^-/CpMo(CO)_3H$ [h]	2.5×10^3	5.3	−25.3
$CpMo(CO)_3^-/CpMo(CO)_3D$ [h]	6.7×10^2	6.3	−24.0
$CpW(CO)_3^-/CpW(CO)_3H$ [h]	6.5×10^2	5.2	−28.0
$CpW(CO)_3^-/CpW(CO)_3D$ [h]	1.7×10^2	6.2	−27.4

[a] In CD_3CN. [b] Nielson, R. M.; McManis, G. E.; Goloving, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. [c] Reference 10; $CF_3SO_3^-$ salt. [d] Reference 11; ClO_4^- salt. [e] Kirchner, K.; Han, L.-F.; Dodgen, H. W.; Wherland, S.; Hunt, J. P. *Inorg. Chem.* Submitted for publication. [f] This work; $N(PPh_3)_2^+$ salt. [g] From one experiment at 335 K. [h] Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945; K^+ salts.

At 25 °C, the self-exchange reactions (eq 4, X a halogen) proceed with rate constants ranging from 8.6×10^{-2} to 1.5×10^4 $M^{-1}\ s^{-1}$ for molybdenum and 2.1×10^{-3} to 4.5×10^3 $M^{-1}\ s^{-1}$ for tungsten. At 335 K, the $CpW(CO)_3^-/CpW(CO)_3CH_3$ self-exchange rate constant is $\approx 1 \times 10^{-5}$ $M^{-1}\ s^{-1}$. In Table VIII, rate constants and activation parameters for these self-exchange reactions are compared with those for outer-sphere electron exchange reactions (eq 13), the Cp_2Ru/Cp_2RuX^+ self-exchanges (eq 2), and the $CpM(CO)_3^-/CpM(CO)_3H$ (eq 3) proton-transfer self-exchanges. All of the data tabulated were obtained in acetonitrile

$$MCp_2 + MCp_2^+ \rightleftharpoons MCp_2^+ + MCp_2 \qquad (13)$$

$$CpM(CO)_3^- + CpM(CO)_3X \rightleftharpoons CpM(CO)_3X + CpM(CO)_3^- \qquad (4)$$

$$MCp_2 + MCp_2X^+ \rightleftharpoons MCp_2X^+ + MCp_2 \qquad (2)$$

$$CpM(CO)_3^- + CpM(CO)_3H \rightleftharpoons CpM(CO)_3H + CpM(CO)_3^- \qquad (3)$$

solvent, and the data set is confined to structurally related complexes. Not surprisingly, the outer-sphere electron-transfer couples exhibit the greatest rate constants and the smallest enthalpic barriers to self-exchange. Both Cp_2Fe/Cp_2Fe^+ and Cp_2Co/Cp_2Co^+ couples are subject only to rather small inner-shell barriers to electron transfer, the bulk of the barriers for these couples being due to the solvent-reorganization barrier.[45a] The volumes of

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(36) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643.

(37) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(38) Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

(39) Madfach, T.; Vahrenkamp, H. *Z. Naturforsch.* **1979**, *34b*, 573.

(40) Denisovich, L. I.; Gubin, S. P.; Chapovskii, Yu, A.; Ustynok, N. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. Engl. Transl.* **1968**, 891.

(41) (a) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (b) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5117. (c) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (d) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5124.

(42) (a) Lai, C.-K.; Feighery, W. G.; Zhen, Y.; Atwood, J. D. *Inorg. Chem.* **1989**, *28*, 3929 (solvent, acetonitrile). (b) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541 (solvent, tetrahydrofuran). (c) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121 (solvent, dimethoxyethane). (d) Richardson, D. E.; Christ, C. S.; Sharpe, P.; Eyler, J. R. *Organometallics* **1987**, *6*, 1819 (gas phase).

(43) (a) In one of the few kinetics studies of substitution processes of M(II) complexes of this family, rate constants for dissociative replacement of CO by phosphines were typically 1×10^{-4} s^{-1} at 40 (Cl), 60 (Br), and 80 (I) °C. White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (b) There is no evidence that the anions undergo "ring slippage" to yield η^3-Cp species through which associative substitution pathways might occur although there is evidence for this in related systems (see: Angelici, R. J.; Graham, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 5590. Brodie, N. M. J.; Chen, L.; Poe, A. J. *Int. J. Chem. Kinet.* **1988**, *20*, 467).

(44) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613.

Table IX. Reactivity Ratios as a Function of Halogen

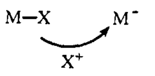
reactants	k_X/k_{Br} at 298 K Cl	Br	I
Outer-Sphere One-Electron Transfer			
$Ru(NH_3)_6^{2+} + Co(NH_3)_5X^{2+}$[a]	1.6×10^{-1}	1	4.2
Inner-Sphere One-Electron Transfer			
$Co(CN)_5^{3-} + Co(NH_3)_5X^{2+}$[b]	2.5×10^{-2}	1	
$Cr(OH_2)_6^{2+} + Co(NH_3)_5X^{2+}$[c]	4×10^{-1}	1	>2.1
$Cr(OH_2)_6^{2+} + Cr(NH_3)_5X^{2+}$[d]	1.6×10^{-1}	1	17
$CoN_4(OH_2)^{2+} + CoN_4(OH_2)X^{2+}$[e]	$\approx 3 \times 10^{-1}$	1	
$Cr(OH_2)_6^{2+} + Cr(H_2O)_5X^{2+}$[f]	$<1.5 \times 10^{-1}$	1	
Halogen Abstraction			
"$Cr(en)_2^{2+}$" + CR_3X[g]	7×10^{-3}	1	8×10^{1}
$Re(CO)_4PMe_3 + C_3H_3X$[h]	4×10^{-4}	1	3.2
$Re(CO)_4P(OMe)_3 + C_3H_3X$[h]	7×10^{-4}	1	21
$(n\text{-}Bu)_3Sn + t\text{-}(CH_3)_3CX$[i]	2×10^{-4}	1	
$C_8H_{17}^{\bullet} + (CH_3)_3CX$[j]	1.3×10^{-1}	1	6.5×10^{2}
$c\text{-}C_3H_5^{\bullet} + Cl_3CX$[k]	5.4×10^{-4}	1	
Nucleophilic Displacement			
$X^-_g + CH_3X_g$[l] (S_N2)	5	1	
$X^-_{aq} + CH_3X_{aq}$[m]	8×10^{-3}	1	2.3
$X^-_{DMF} + CH_3X_{DMF}$[m]	8×10^{-4}	1	35
Redox/Nucleophilic Displacement			
$HOOH + X^-$[n]	4×10^{-3}	1	2.5×10^{4}
$H_3O_2^+ + X^-$[o]	3×10^{-3}	1	7.9×10^{2}
Coupled Two-Electron Halogen-Transfer Self-Exchange			
$RuCp_2 + RuCp_2X^+$[p]	1.1×10^{-3}	1	4.9×10^{3}
$OsCp_2 + OsCp_2X^+$[o]		1	5×10^{2}
$CpMo(CO)_3X + CpMo(CO)_3^-$[q]	5.6×10^{-3}	1	9.4×10^{2}
$CpW(CO)_3X + CpW(CO)_3^-$[q]	1.3×10^{-3}	1	3×10^{3}

[a] In water. Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1686. [b] In water. Candlin, J. P.; Halpern, J.; Nakamura, S. *J. Am. Chem. Soc.* **1963**, *85*, 2517. [c] In water. Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766. [d] In water. Ogard, A. E.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1084. [e] "N_4" is a tetraazamacrocycle. Endicott, J. F. *Prog. Inorg. Chem.* **1983**, *30*, 141. [f] Ball, D. L.; King, E. L. *J. Am. Chem. Soc.* **1958**, *80*, 1091. [g] Espenson, J. H. *Adv. Inorg. Bioinorganic Mechanisms* **1982**, *1*, 1. [h] In toluene at 295 K. Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269. [i] In cyclohexane. Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047. [j] In benzene at 323 K. Newcomb, N.; Sanchez, R. M.; Kaplan *J. Am. Chem. Soc.* **1987**, *109*, 1195. [k] In benzene. Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877. [l] In the gas phase. Pelerite, M. J.; Brauman, J. I. *Mechanistic Aspects of Inorganic Reactions*, ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; p 81; *J. Am. Chem. Soc.* **1983**, *105*, 2672. [m] In water or DMF. Albery, W. J. *Ann Rev. Phys. Chem.* **1980**, *31*, 227. [n] Edwards, J. O. *Inorganic Reaction Mechanisms, An Introduction*; W. A. Benjamin, Inc.: New York, 1964. [o] Reference 10. In CD_3CN. [p] Reference 11. In CD_3NO_2 at 366 K. [q] This work.

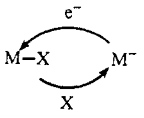
activation for the outer-sphere Cp_2Fe/Cp_2Fe^+ couple[45b] and Cp_2Ru/Cp_2RuBr^+ atom-transfer couple[11] have been determined to be -5 to -8 cm³ mol⁻¹ and -3.0 ± 0.2 cm³ mol⁻¹, respectively, in acetonitrile. The slowest self-exchange studied here, the $CpW(CO)_3^-/CpW(CO)_3CH_3$ exchange (eq 12) followed only at 63 °C, is by several orders of magnitude the slowest of any of the self-exchanges studied to date. The ΔS^* values are most negative for the proton-transfer self-exchange systems, consistent, perhaps, with some contributions to the rate from proton tunneling.[46] The ΔH^* values are greaters for the halogen-transfer couples and increase in the order I < Br < Cl. As discussed later, M–X bond stretching probably contributes significantly to the barriers to these self-exchanges. The halogen-transfer self-exchanges seem to be intrinsically more rapid for the second transition series metal center (Mo or Ru) than for the third transition series metal center (W or Os). The analogous ordering, Cr > Mo > W, is also seen for the proton exchanges probed by Norton.[12] By contrast, the order W > Mo has been inferred for chlorine atom abstraction by the metal radicals $CpM(CO)_3^{\bullet}$ from CCl_4.[47]

As noted above, both $CpM(CO)_3^-/CpM(CO)_3X$ and MCp_2X^+/MCp_2 (M = Ru, Os)[10,11] atom-transfer self-exchange (eqs 4 and 2) rate constants follow the order I > Br > Cl. This is also the so-called "normal" order observed for inner-sphere, one-electron-transfer reactions.[48] As is illustrated in Table IX, this reactivity order is found for inner-sphere reductions of $Co(NH_3)_5X^{2+}$ by $Cr(OH_2)_6^{2+}$ and $Co(CN)_5^{3-}$ and of $Fe(OH_2)_5X^{2+}$ by $Cr(OH_2)_6^{2+}$ and for $Cr(OH_2)_6^{2+}/Cr(OH_2)_5X^{2+}$ (but not $Fe(OH_2)_6^{2+}/Fe(OH_2)_5X^{2+}$) self-exchanges. The "normal order" is also found for halogen atom abstraction reactions, for S_N2 peroxide oxidations of halides, and even for certain outer-sphere electron-transfer reactions. For the net (as opposed to self-exchange) reactions listed, the normal order is favored by the fact that the driving force for the reaction also follows the order I > Br > Cl. Thus only the data for self-exchange reactions, for which $\Delta G^\circ = 0$ by definition, are truly comparable. The most striking feature of the data in Table IX is the exceptional sensitivity of the rate constant for the coupled two-electron/halogen-transfer self-exchange reactions to the identity of the halogen. The rate constants are five to six orders of magnitude greater for X = I than for X = Cl. A comparable range of relative rates is found only for the halide-peroxide reactions, for which, as noted above, the driving force varies, and for Pt(II)/Pt(IV)[9] self-exchanges. By contrast, the range spanned is only about two orders of magnitude for inner-sphere one-electron-transfer reactions.

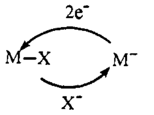
The self-exchange reactions studied here all formally belong to the class of redox self-exchange processes, with the redox site being the M(0)/M(II) centers. In addition, as noted earlier, all involve atom (or methyl) transfer. However, as will be seen, these reactions pose a classification problem at the level of purely descriptive chemistry. Depending upon the nature of X, reasonable descriptions encompass a remarkable range—from I, which might be denoted as X^+ transfer (analogous with H^+ transfer) or I′ nucleophilic displacement by M^-, to II, coupled one-electron and atom transfer, to III, two-electron transfer accompanied by X^- transfer. These limiting descriptions will now be discussed with reference to the reactants' properties.



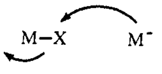
I



II



III



I′

The nucleophilic displacement mechanism I′ finds precedent in redox reactions of nonmetals,[49] for example, peroxide oxidations of halides[49a] and the recently investigated[49b] transfer of Cl^+ from HOCl to CN^-. As recognized by Edwards,[49a] "That such an S_N2 step occurs ... is not surprising, for reducing agents are species with available electrons, just as are nucleophiles." Indeed, in some coupled two-electron/atom-transfer systems the demarcation between redox and substitution processes is strictly formal.[4] For example, the S_N2 displacement of bromide by chloride is classified as a substitution reaction when IBr is the substrate, but the

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(45) (a) Nielson, R. M.; McManis, G. E.; Goloving, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441. (b) Dang, S. Q.; Stebler, M.; Dodgen, W. H.; Wherland, S.; Hunt, J. P. Unpublished work cited as footnote 2 in ref 11.

(46) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 2418.

(47) Abrahamson, H. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510. Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388. However, this result may be deceptive if interpreted as reflecting intrinsic reactivity: the CCl_4 BDE (73 kcal mol⁻¹) is nearly the same as the Mo–Cl bond energy. Since the W–Cl bond energy is almost certainly several kcal mol⁻¹ greater than for M = Mo, Cl abstraction by the W complex is more strongly favored by the thermodynamics.

(48) Sutin, N. *Ann. Rev. Phys. Chem.* **1966**, *17*, 119.

(49) (a) Edwards, J. O. *Inorganic Reaction Mechanisms, An Introduction*; W. A. Benjamin, Inc.: New York, 1964. (b) Gerritsen, C. M.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2757.

Table X. Methyl-Transfer Reactions

reactants	*T*	*k*, M^{-1} s^{-1}	$\Delta G^{\ddagger}$
$(Cp\text{-}d_5)W(CO)_3^-/CpW(CO)_3CH_3$[a]	335	$\approx 1 \times 10^{-5}$	27.2
$CpW(CO)_3^- + CH_3I$[b]	298	2.4	
S_N2			
X^-_g/CH_3X_g[c]			
X = F			[26.2]
X = Cl			[10.2]
X = Br			[11.2]
X^-_{aq}/CH_2X_{aq}[d,e]			
X = F	298	2×10^{-11}	31.8
X = Cl	298	3×10^{-7}	26.6
X = Br	298	3×10^{-5}	23.7
X = I	298	8×10^{-5}	23.2
X^-_S/CH_3X_S[e,f] (S = DMF)			
X = Cl	298	8×10^{-4}	21.8
X = Br	298	1	17.6
X = I	298	4×10^{1}	15.5
S_H2			
$CoN_4^{2+}/CoN_4(CH_3)^{2+}$[d,g]	298		18
$Cr(H_2O)_6^{2+} + Co(dmgBF_2)_2(CH_3)$[d,h]	298	5.1×10^{1}	
$Co(dmgBF_2)_2 + Cr(H_2O)_5(CH_3)^{2+}$[d,h]	298	2.1×10^{2}	(14)

[a] This work, in acetonitrile at 335 K. [b] In THF. Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541. [c] Pelerite, M. J.; Brauman, J. I. *Mechanistic Aspects of Inorganic Reactions*; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; p 81; *J. Am. Chem. Soc.* **1983**, *105*, 2672. The barriers listed are $\Delta E^{\ddagger}$ for the X^-/CH_3X complex in the gas phase. [d] In water. [e] Albery, W. J. *Ann. Rev. Phys. Chem.* **1980**, *31*, 227. [f] In *N*,*N*-dimethylformamide. [g] Endicott, J. F.; Wong, C.-L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 2100. N_4 is the tetraene macrocycle. [h] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.

displacement of chloride by iodide is classified as a redox reaction when BrCl is the substrate. By contrast, S_N2 halide displacements

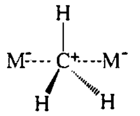
$$IBr + Cl^- = ICl + Br^- \qquad \text{substitution}$$

$$BrCl + I^- = IBr + Cl^- \qquad \text{redox}$$

at carbon centers are always classified as substitution reactions but can be seen to be related to the reactions above. By analogy

$$CH_3I + Cl^- = CH_3Cl + I^- \qquad \text{substitution}$$

with these examples, the present systems might be considered to proceed by nucleophilic displacements of $CpM(CO)_3^-$ (M^-) from $CpM(CO)_3X$ (M–X).[50,51] For example, with X = CH_3, the nucleophile M^- attacks the C–M bond to displace M^-. (Note

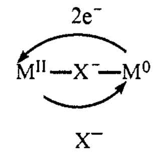


that X, not M, is the substrate for substitution. By contrast, M is formally the S_N2 substrate in the reaction,[51b] $M'^- + M\text{–}M \rightarrow M'\text{–}M + M^-$.) From the viewpoint of M^-, such a pathway resembles oxidative addition, a reaction which $CpMo(CO)_3^-$ and $CpW(CO)_3^-$ undergo fairly readily (Table VII). In fact, for X = CH_3 the barrier for the self-exchange eqs 4 or 12 may sensibly be regarded[3b] as providing a measure of the intrinsic barrier for oxidative addition of CH_3^+, also providing a measure of the kinetic nucleophilicity (and leaving group ability) of $CpW(CO)_3^-$.

Data for CH_3^+ and CH_3 transfers are compared in Table X. It is evident that the barrier for eq 12 is large—larger than for methyl halides[2,3] and much greater than for S_H2 methyl radical transfer between two cobalt(II) centers[52] or between[53] cobalt(II) and chromium(II) complexes. While CH_3^+ transfers have been extensively studied for organic systems in both solution[2] and the gas phase,[3] CH_3^+ transfers between transition-metal centers have received little attention. Thus the generality of the result obtained here cannot be judged. Clearly the area of CH_3^+ transfer between transition-metal centers warrants more extensive study.

The analogy with nucleophilic displacements in nonmetal systems is of potential utility in a number of cases[51] but, for reasons to be outlined now, does not appear to be appropriate for the halo self-exchanges. For X = Cl, Br, or I, the nucleophilic displacement mechanism would require the use of empty halogen orbitals to accept electron density from M^-. That is, the halogen ligand must act as a Lewis acid toward M^-. Halogen centers are commonly found to serve the role of Lewis acids when the halogen is in a high oxidation state and, as noted earlier, halogen(I) or -(0) centers are the substrates for S_N2 peroxide displacements.[49] In addition, halogen(0) centers act as Lewis acids in the interhalide anions such as I_3^-, I_2Cl^-, etc., and the stability of the polyhalides Y_2X^- increases in the order Y = Cl < Br < I. It thus might be expected that the ability of a halogen(−I) ligand to accept M^- electron density would also increase in the order Cl < Br < I. However, no precedent appears to exist for halides or halogen ligands acting as Lewis acids with respect to transition-metal nucleophiles. Thus I′ does not seem an appealing framework in which to discuss eq 4 for the halide complexes.

Another mechanistic limit to be considered for the X = halogen reactions is IIIa, in which inner-sphere two-electron transfer from M^0 to M^{II}, with halide transfer proceeding in the opposite direction, occurs via a binuclear $M^{II}\text{–}X^-\text{–}M^0$ intermediate. This is the



III a

analogue of inner-sphere, one-electron transfer reactions of more classical coordination complexes. However, there are significant differences between the systems considered here (and in ref 10) and the systems that undergo classical inner-sphere reactions. The mechanism typically observed for inner-sphere, one-electron transfer reactions[5] is outlined in Scheme II. Step a in Scheme

Scheme II

$$M^{III}\text{–}X^{2+} + M^{2+} \rightleftharpoons \{M^{III}\text{–}X\text{–}M^{II}\}^{4+} \qquad a$$

$$\{M^{III}\text{–}X\text{–}M^{II}\}^{4+} \rightleftharpoons \{M^{II}\text{–}X\text{–}M^{III}\}^{4+} \qquad b$$

$$\{M^{II}\text{–}X\text{–}M^{III}\}^{4+} \rightleftharpoons M^{2+} + M^{III}\text{–}X^{2+} \qquad c$$

II is associated with a conventional substitutional or addition step: Attack of $M^{III}\text{–}X^{2+}$ on M^{2+} leads to $M^{II}\text{–}X$ bond formation, yielding a binuclear $\{M^{III}\text{–}X\text{–}M^{II}\}^{4+}$ species in which X occupies a normal coordination site on each metal center. Formation of the precursor complex as the rate-determining step corresponds to substitutional control of the "electron-transfer" rate—a limit found, for example, in many reductions by $V(H_2O)_6^{2+}$. However, in the $CpM(CO)_3^-/CpM(CO)_3X$ (and $M(Cp)_2/M(Cp)_2X$, M = Ru, Os) halide systems, the observed self-exchange rates are many orders of magnitude greater than normal substitution rates. Thus

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(50) (a) Note that the present systems are, without question, correctly categorized as *net* redox self-exchange reactions of M(0) and M(II). Following oxidation-state conventions, the M(II) complexes contain X^- ligands since the electronegativity of X is significantly greater than that of Mo(II) or W(II) (but see ref 50b); furthermore, there is experimental evidence for an effective negative charge on the halogen atoms in related systems.[50c] Rather, the ambiguity lies in the nature of the critical activation events. (b) Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926. (c) Sundberg, P.; Andersson, C.; Folkesson, B.; Larsson, R. J. *Electron Spectroscopy and Related Phenomena* **1988**, *46*, 85 and references cited therein.

(51) (a) Interestingly, effective two-electron transfer from metal carbonyl cations to metal carbonyl anions has recently been demonstrated to take place via nucleophilic attack at bound CO. Zhen, Y.; Feighery, W. G.; Lai, C.-K.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 7832. (b) Reactions constituting formal nucleophilic displacement of M^- in M_2 by M'^- have also been studied. Corraine, M. S.; Atwood, J. D. *Inorg. Chem.* **1989**, *28*, 3782.

(52) Endicott, J. F.; Wong, C.-L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 2100.

(53) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197.

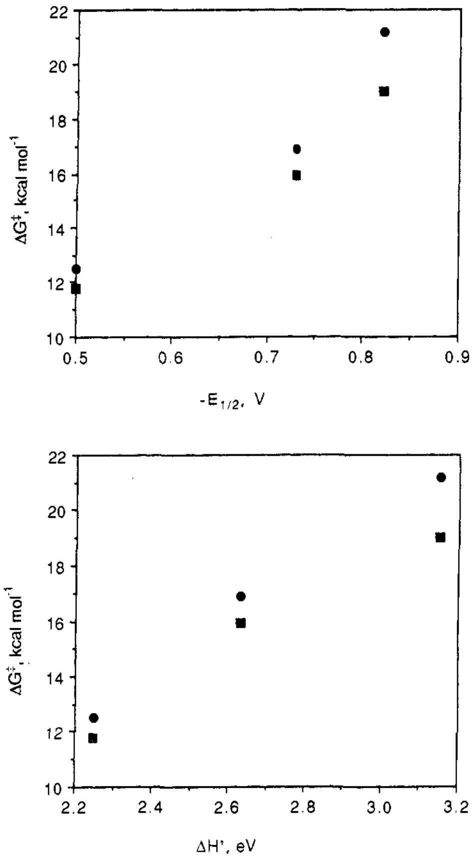
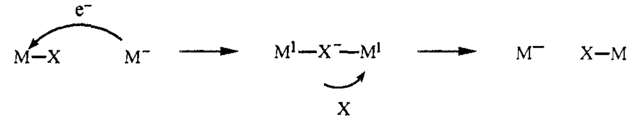


Figure 7. Plot of $\Delta G(298)^{\ddagger}$ for the $CpMo(CO)_3^-/CpMo(CO)_3X$ (■) and $CpW(CO)_3^-/CpW(CO)_3X$ (●) self-exchanges vs (top) the half-wave potential ($E_{1/2}$)[40] for $CpW(CO)_3X$ and (bottom) the $CpMo(CO)_3X$ bond dissociation energies[35] $\Delta H°$.

it is concluded that transfer of the halogen via such a mechanism cannot be a significant reaction pathway.[54]

The above considerations lead to the conclusion that the $CpM(CO)_3^-/CpM(CO)_3X$ self-exchanges cannot proceed through a binuclear M^0–X–M^{II} intermediate. An alternative that must be considered is involvement of an "isovalent"[10] M^I–X^-–M^I species, formed through comproportionation of the reactants. Thus in one limit of II, one-electron transfer[55-57] from the anion to $CpM(CO)_3X$ forms 17 and 19 electron M(I) species which associate in an M^I–X^-–M^I complex. Dissociation of M^I–X^-–M^I to M^- and M–X effects the halogen transfer and completes the "self-exchange" process.[58] An attractive aspect of such a scheme is



II

that it is consistent with the known reactivity of $CpM(CO)_3$ radicals with respect to both normal substitutional processes and atom abstraction. For a given M, the thermodynamic tendency of the reactant pair to undergo comproportionation will parallel the reducibility of the M–X complex. As is shown in Figure 7,

$$M^- + M\text{–}X \rightleftharpoons M^{\bullet} + M\text{–}X^- \qquad K_{com}$$

both molybdenum and tungsten self-exchange rates do correlate with the reducibility of the tungsten halides as ascertained from polarographic studies. Note that they also parallel the bond dissociation energies for the molybdenum complexes.[59a] However, the thermodynamics of the comproportionation appear to be extremely unfavorable (see Appendix)[59b]—so unfavorable that an M^I–X^-–M^I intermediate cannot be involved unless there is a particularly strong stabilization of M^I associated with the formation of the M^I–X^-–M^I complex.

The above considerations strongly suggest that no chemistry leading to stabilized intermediates is likely to be found for these systems since neither the bound halogen groups nor the metal anions function effectively as Lewis acids,[60] and pathways involving the M(I) radical appear to lie at prohibitively high activation energy. We thus arrive at the curious position of needing to consider a weak (ground-state) interaction mechanism for a reaction in which chemical bonds are broken and made: The last

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[54] This is expected to be true in general when *both* reactants are 18-electron species: Substitution reactions of 18-electron complexes generally proceed by (slow) dissociative pathways. The behavior to be expected for 18-electron/18-electron couples may be contrasted with that to be expected for 16-electron/18-electron (usually d^8/d^6) couples such as the Pt(II)/Pt(IV) ammine couples (eq 1) mentioned in the Introduction. These have a relatively facile pathway to a bridged binuclear species through the tendency of the 16-electron species to increase its coordination number.

$$trans\text{-}Pt^{IV}(NH_3)_4Cl_2^{2+} + Pt^{II}(NH_3)_4^{2+} \rightleftharpoons [Pt(NH_3)_4ClPt(NH_3)_4Cl]^{4+}$$

However, the formation of a symmetric binuclear intermediate again requires that an 18-electron species (e.g., five-coordinate Pt(II)) increase its coordination number.

$$[Pt^{II}(NH_3)_4ClPt^{IV}(NH_3)_4Cl]^{4+} + Cl^- \rightleftharpoons [ClPt(NH_3)_4ClPt(NH_3)_4Cl]^{3+}$$

[55] Brown has proposed that outer-sphere electron transfer is a significant component in the net halogen transfer from alkyl halides to the metal radical $Re(CO)_4L$ in solution,[56] i.e.

$$Re(CO)_4L + R\text{–}X \rightarrow \{Re(CO)_4L/R\text{–}X\}$$

$$\{Re(CO)_4L/R\text{–}X\} \rightarrow \{Re(CO)_4L^+/R\text{–}X^-\} \qquad \text{electron transfer}$$

$$\{Re(CO)_4L^+/R\text{–}X^-\} \rightarrow \{Re(CO)_4LX/R\} \qquad \text{X transfer}$$

$$\{Re(CO)_4LX/R\} \rightarrow Re(CO)_4LX + R$$

and similar conclusions have emerged from work in the gas phase.[57] Following the rate-determining electron-transfer event, the "halogen" is transferred as halide to the resulting metal cation.

[56] Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269.

[57] Jones, M. T.; McDonald, R. N.; Schell, P. L.; Ali, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 5983.

[58] An extreme limit of such a scheme is the two step mechanism shown below.

$$M^- + M\text{–}X \rightleftharpoons M^{\bullet} + M\text{–}X^- \qquad K_1$$

$$M^{\bullet} + M\text{–}X^- \rightarrow M\text{–}X + M^- \qquad k_2$$

$$k_{obsd} = \{k_2k_1/(k_{-1} + k_2)\}$$

In the first step, an outer-sphere electron transfer, the metal radicals are formed. In the second, X transfer results in exchanged products. The operation of such a stepwise mechanism can be ruled out for the present systems on the following basis: first, the fact that, unless the second step is faster than diffusion-controlled, metal dimer formation,

$$M^{\bullet} + M^{\bullet} \rightarrow M\text{–}M$$

rather than, or in addition to, self-exchange, should be observed. Furthermore, the self-exchange itself is likely to involve a chain mechanism through the operation of

$$M^{\bullet} + M\text{–}X \rightarrow M\text{–}X + M^{\bullet}$$

[59] (a) Note that (not shown) neither $X = CH_3$ nor $X = H$ complex falls on these plots. (b) Given the presently available thermodynamic data (see Appendix) this can be done even roughly for only the $CpMo(CO)_3^-/CpMo(CO)_3Cl$ couple; the estimates $K'_{com} = 2 \times 10^{-20}$, $\Delta G'_{com}° = 26.5$ kcal mol^{-1} are obtained at 25 °C for

$$M^- + M\text{–}X \rightleftharpoons M^{\bullet} + M^{\bullet} + X^- \qquad K'_{com}$$

(Since $k(298) = 8.6 \times 10^{-2}$ M^{-1} s^{-1}, within this mechanism k_2 is required to have the impossibly large value of 10^{18} M^{-1} s^{-1}. Thus these considerations also rule out the stepwise mechanism given earlier.[58])

[60] We have not discussed here, what we consider to be the very unlikely possibility that CO or Cp ligands serve as Lewis acid substrates for the anion. The similarity of the data for the $CpM(CO)_3^-/CpM(CO)_3X$ and $M(Cp)_2/M(Cp)_2X$ systems would seem to exclude a role for the CO groups in the former couples.

mechanism to be considered for the halogen systems is a weak interaction, electron-transfer mechanism[1] (the weak interaction limit of III) as outlined in Scheme III. If no special interaction between the reactants takes place, step a in Scheme III is associated with the formation of a weakly associated ($K_a \approx 10^{-1}$ M^{-1}) precursor complex of the type invoked for outer-sphere one-electron-transfer reactions and also recently considered[46] for proton transfer between transition-metal centers. Step a is simply a diffusional step—and, by symmetry, so is step c. All of the chemical action—two-, one-, or zero-electron transfer between the metal centers, transfer of the halogen as X$^-$, X$^\bullet$, or X$^+$—must take place in step b.

Scheme III

$$\text{M—X} + \text{M}^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \{\text{M—X} \mid \text{M}^-\} \qquad \text{a}$$

$$\{\text{M—X} \mid \text{M}^-\} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} \{\text{M}^- \mid \text{X—M}\} \qquad \text{b}$$

$$\{\text{M}^- \mid \text{X—M}\} \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \text{M}^- + \text{M—X} \qquad \text{c}$$

If step b in Scheme III occurs by two-electron transfer, it may be broken down as shown[1,61] in Scheme IV. The reactants are an $\{\text{M-X/M}^-\}$ pair at one[61a] reactant-separation r, for example, a van der Waals contact (M···M ≈ 5.6 Å for X = Cl). This pair is denoted $\{\text{M-X/M}^-\}_r$. The M–X bond stretches by $\Delta d_r^{\ddagger}$ to give $\{\text{M-X}\cdots\text{M}^-\}^{\ddagger}_r$ in which the M$^{\text{II}}$–X and M^0···X distances are identical. Electron transfer takes place to give $\{\text{M}^-\cdots\text{X-M}\}^{\ddagger}$, and relaxation of the newly formed M–X bond to its equilibrium distance gives $\{\text{M}^-/\text{M-X}\}_r$.

Scheme IV

$$\{\text{M—X} \mid \text{M}^-\} \rightleftharpoons \{\text{M}^-\text{—X--M}\}$$

$$\{\text{M}^-\text{—X--M}\} \rightleftharpoons \{\text{M}^-\text{--X—M}\}$$

$$\{\text{M}^-\text{--X—M}\} \rightleftharpoons \{\text{M}^- \mid \text{X—M}\}$$

Figure 8 depicts reactant/product surfaces for the process outlined in Scheme IV. The intersection point of the parabolas occurs at[61] $\Delta G_r^{\circ\ddagger}$, the intrinsic barrier in the zero-order reactant–product-interaction limit at this M···M separation. At the intersection point, the M$^{\text{II}}$–X and X–M^0 distances must be equal. Thus the M$^{\text{II}}$–X bond distance is considerably greater than its equilibrium value. The enthalpy change required for this deformation $\Delta d_r^{\ddagger}$ is likely to dominate $\Delta G_r^{\circ\ddagger}$, but, in addition, since the curves depicted are for exchange via two-electron transfer, there is also a substantial contribution from the solvent barrier to electron transfer. From the zero-order surfaces, the exchange via such a pathway is expected to have an extremely large $\Delta H_r^{\circ\ddagger}$ (the bulk of the M–X deformation and solvent reorganization barriers are enthalpic) and an extremely negative $\Delta S_r^{\circ\ddagger}$ (the probability of crossing from reactant to product surface is extremely small).

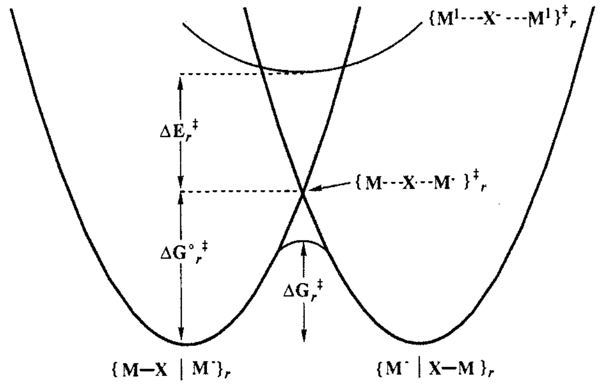

Figure 8. Reactant–product surfaces for the M–X/M$^-$ self-exchange. The reactants are an $\{\text{M-X/M}^-\}_r$ pair at one reactant separation, r. The diagram depicts the free-energy of the reactants (products) as a function of reaction coordinate (which is dominated by the M$^{\text{II}}$–X stretch, Δd_r). The M–X bond stretches by $\Delta d_r^{\ddagger}$ to give $\{\text{M-X}\cdots\text{M}^-\}^{\ddagger}_r$ in which the M$^{\text{II}}$–X and M^0···X distances are identical. Electron transfer takes place to give $\{\text{M}^-\cdots\text{X-M}\}^{\ddagger}$, and relaxation of the newly formed M–X bond to its equilibrium distance gives $\{\text{M}^-/\text{M-X}\}_r$. The intersection point of the parabolas occurs at[61] $\Delta G_r^{\circ\ddagger}$, the intrinsic barrier in the zero-order reactant–product-interaction limit at this M···M separation. At this nuclear configuration, interaction with electronically excited states such as M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ may mix the reactant–product states and, for significant mixing, substantially lower the activation barrier to the self-exchange reaction $\Delta G_r^{\ddagger}$. Within the model depicted here, the critical parameter is $\Delta E_r^{\ddagger}$, the energy difference between the M$^{\text{II}}$–X$^-$/M^0 and M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ states at the nuclear configuration associated with $\Delta d_r^{\ddagger}$.

The zero-order surfaces represent an extreme situation. In reality, configuration interaction with other states is likely to mix the reactant–product surfaces and significantly lower the barrier to reaction. In particular, for the present systems, mixing with the M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ state is most likely to be significant.[10,62–64] Within the model depicted in Figure 8, the critical parameter is $\Delta E_r^{\ddagger}$, the energy difference between the M$^{\text{II}}$–X$^-$/M^0 and M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ states at the nuclear configuration[61d] associated with $\Delta d_r^{\ddagger}$. If $\Delta E_r^{\ddagger}$ is small, mixing of the M$^{\text{II}}$–X$^-$/M^0 and M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ states will be considerable. For the $CpMo(CO)_3Cl/CpMo(CO)_3^-$ couple, we estimate $\Delta E_r^{\ddagger}$ to be of the order of 1 eV.[59] Since $\Delta G(298)^{\ddagger}$ is determined to be 0.83 eV for the $CpMo(CO)_3Cl/CpMo(CO)_3^-$ self-exchange, the energetics seem reasonable on the whole.

At a qualitative level, the above model[65] provides a useful framework for interpreting the halogen self-exchanges. It incorporates negligible "ground-state" interaction, and it offers a reasonable role for the "isovalent" state, which serves to lower the activation barrier to exchange through configuration interaction. Finally, it accounts for the extreme sensitivity of the rates to halogen identity: both $\Delta H_r^{\circ\ddagger}$ and $\Delta E_r^{\ddagger}$ diminish in the order Cl > Br > I. The $\Delta H_r^{\circ\ddagger}$ values are expected to decrease in this order because the M–X bond strengths do (however the solvent barrier increases in this order because of the greater size of the X atom). The $\Delta E_r^{\ddagger}$ "energy gaps" follow the order because the M–X/M–X$^-$ reduction potentials follow this order, as well.

Concluding Remarks. In this work we have exploited ^{1}H NMR techniques to determine bimolecular self-exchange rates ranging (at 298 K) from ≪10^{-5} to 10^4 M^{-1} s^{-1}. With the combination of line width, saturation transfer, and conventional techniques used, it is apparent that NMR methods can provide an extraordinarily

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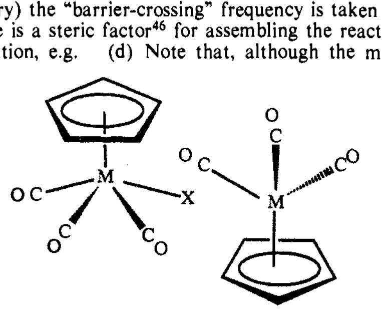
(61) The treatment given here is oversimplified but adequate for the present qualitative discussion. (a) Reaction is actually expected to occur at a significant rate over a range of reactant–reactant separations. (b) By denoting the barrier as $\Delta G_r^{\circ\ddagger}$ (an activation free-energy based on transition-state theory) the "barrier-crossing" frequency is taken as kT/h.[1] (c) Neglected here is a steric factor[46] for assembling the reactant pair in the correct orientation, e.g. (d) Note that, although the minimum in the M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ state is shown to lie at $r^{\ddagger}$ in Figure 8, the latter is not necessarily the true minimum in the M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ surface. For a symmetric M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ state, the minimum lies at $r^{\ddagger}$ when r is such that $d_r^{\ddagger}$ is equal to the equilibrium M$^{\text{I}}$–X bond length of d°(M$^{\text{I}}$–X). If the ground state of M$^{\text{I}}$–X$^-$–M$^{\text{I}}$ is not symmetric, its potential minimum never lies above $r^{\ddagger}$.



(62) For applications of this approach to one-electron transfer reactions see refs 63 and 64.

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(65) A referee has drawn our attention to the discussion of S_N2 processes given in Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; 3rd ed.; Harper and Row: pp 356–360. That discussion is indeed complementary to ours; it would seem that some combination of the two could provide a unified model for atom-transfer processes in general.

versatile and powerful probe of self-exchange processes in appropriately selected systems. We have learned that transfer of methyl cation between "$\mathrm{CpW(CO)_3^-}$" centers is intrinsically quite slow in comparison with either methyl-cation transfer between other (nontransition-metal) nucleophiles or in comparison with methyl-radical transfer between certain transition-metal centers. In contrast to the $\mathrm{CpW(CO)_3^-/CpW(CO)_3CH_3}$ self-exchange, with X = halogen, the $\mathrm{CpM(CO)_3^-/CpM(CO)_3X}$ self-exchange reactions are relatively rapid, with the activation barriers roughly paralleling both M–X bond dissociation energies and M–X reducibilities. The relative rapidity of the X = halogen exchanges studied so far suggests that relatively rapid halogen transfer might be observable in other organometallic self-exchange systems and indicate that effective transfer of $\mathrm{X^+}$ may be intrinsically rapid when both reactants are 18-electron species and steric factors are favorable. We have concluded that, despite the potential similarity of the present systems to classic inner-sphere one-electron-transfer systems in which binuclear, halogen-bridged intermediates play a significant role, negligible interaction between the $\mathrm{CpM(CO)_3^-}$ and $\mathrm{CpM(CO)_3X}$ reactants is likely to take place when the reactants are in their ground states. Thus the halo self-exchanges are ultimately considered in terms of a "weak interaction" ground-state mechanism in which configuration interaction with the "isovalent" $\mathrm{M^I{-}X^-{-}M^I}$ states at the nuclear configuration of the transition state serves to significantly lower the barrier to the reaction.

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Appendix

The available data allow rough estimates for the thermodynamics of several comproportionation processes. Here we outline the cycles and the assumptions required in obtaining these estimates. The following abbreviations are used: "$\mathrm{M^-}$" $\mathrm{CpM(CO)_3^-}$; "M–X" $\mathrm{CpM(CO)_3X}$; "$\mathrm{M^\bullet}$" $\mathrm{CpM(CO)_3^\bullet}$; "$\mathrm{M^+}$" $\mathrm{CpM(CO)_3^+}$; "$E_{\rm pc}$,$E_{\rm pa}$" cathodic/anodic peak potential (of a cyclic voltammogram); "$E_{1/2}$" half-wave potential (of a polarogram); "E°" reversible potential under the prevailing conditions (usually denoted "$E_{1/2}$").

I. The free-energy change for the comproportionation eq 1A for M = Mo, X = Cl is estimated as follows: Bond dissociation

$$\mathrm{M^- + M{-}X \rightleftharpoons M^\bullet + M^\bullet + X^-} \qquad \Delta G'^\circ_{\rm com} \tag{1A}$$

enthalpies for the halo-molybdenum complexes were determined in THF.[66] We assume the bond dissociation enthalpy to be solvent independent and to be equal to the bond dissociation free energy. Thus for the chloro complex

$$\mathrm{M{-}X \rightleftharpoons M^\bullet + X^\bullet} \qquad \Delta G^\circ_{\rm BDE} = 3.15\ \mathrm{eV\ (Mo,Cl)} \tag{2A}$$

We take the reduction potential estimated by Tilset and Parker[67] for the $\mathrm{M^\bullet/M^-}$ couple in acetonitrile vs ferricinium/ferrocene ($\mathrm{Fc^+/Fc}$) (eq 3A)

$$\mathrm{M^\bullet + e^- \rightleftharpoons M^-} \qquad E^\circ = -0.39\ \mathrm{V\ vs\ Fc^+/Fc\ (Mo)} \tag{3A}$$

To close the cycle we require the reduction potential for the $\mathrm{Cl^\bullet/Cl^-}$ couple vs $\mathrm{Fc^+/Fc}$ in acetonitrile (eq 4A). (We assume the potential of the $\mathrm{Fc^+/Fc}$ couple to be solvent invariant.) To estimate the latter, we take the reduction potential for the couple in water[68] (+2.41 V vs SHE, 2.04 V vs $\mathrm{Fc^+/Fc}$), the free energy of transfer of $\mathrm{Cl^-}$ from water to acetonitrile (+0.44 eV),[69] and assume the free-energy of transfer of $\mathrm{Cl^\bullet}$ from water to acetonitrile to be negligible. We thus obtain for eq 1A, $\Delta G'^\circ_{\rm com} = +1.16$ eV (26.5 kcal mol^{-1}).

$$\mathrm{Cl^\bullet + e^- \rightleftharpoons Cl^-} \qquad E^\circ = 1.60\ \mathrm{V\ vs\ Fc^+/Fc} \tag{4A}$$

II. The free-energy change for the comproportionation reaction eq 5A in acetonitrile can also be estimated. The reduction

$$\mathrm{M^- + M^+ \rightleftharpoons M^\bullet + M^\bullet} \qquad \Delta G''^\circ_{\rm com} \tag{5A}$$

potentials for the $\mathrm{M^+/M^\bullet}$ (eq 6A) and $\mathrm{M^\bullet/M^-}$ (eq 3A) couples vs SCE in acetonitrile are estimated from peak potential data reported by Kadish.[70] As discussed by Tilset and Parker,[67] metal-radical dimerization to give $\mathrm{[CpM(CO)_3]_2}$ introduces chemical irreversibility in these systems. However, comparison of the anion-oxidation data in refs 67 and 70 suggests that the required correction to Kadish's data is not large. Thus we subtract eq 3A from eq 6A to estimate the free-energy change for comproportionation of $\mathrm{M^+}$ and $\mathrm{M^-}$ to yield two $\mathrm{M^\bullet}$ radicals (eq 5A). For M = Mo, $\Delta G''^\circ_{\rm com} = +0.62$ eV is obtained. A similar analysis of the data for the tungsten complexes gives $\Delta G''^\circ_{\rm com} = +0.67$ eV for M = W. Note that the affinity of the metal cation (M

$$\mathrm{M^+ + e^- \rightleftharpoons M^\bullet} \qquad E_{\rm pc}(\mathrm{M^+/M^\bullet}) = -0.68\ \mathrm{Vvs\ SCE^{70}\ (Mo)} \tag{6A}$$

$$\mathrm{M^\bullet + e^- \rightleftharpoons M^-} \qquad E_{\rm pa}(\mathrm{M^-/M^\bullet}) = -0.06\ \mathrm{V\ vs\ SCE^{70}\ (Mo)} \tag{3A}$$

= Mo) for chloride ion calculated by subtracting eq 1A from that of eq 5A is −0.54 eV (−12.4 kcal mol^{-1}).

$$\mathrm{M^+ + Cl^- \rightleftharpoons M{-}Cl}$$

III. The free-energy change for the comproportionation eq 1A as a function of X is useful to the interpretation of the plot shown in Figure 8. Our treatment of this process is unfortunately the

$$\mathrm{M + M{-}X \rightleftharpoons M^\bullet + M^\bullet + X^-} \qquad \Delta G'^\circ_{\rm com} \tag{1A}$$

most speculative. We use polarographic half-wave data reported by Denisovich et al.[71] for the tungsten complexes on a mercury electrode in acetonitrile. These data reflect[71] the driving force for the process given in eq 7A. We use cyclic voltammetric data

$$\mathrm{M{-}X + e^- + \tfrac{1}{2}Hg \rightleftharpoons \tfrac{1}{2}M_2Hg + X^-} \tag{7A}$$

for M–M obtained with a platinum electrode in acetonitrile[70] (eq 8A) to compensate for eq 10A, that is—we take the difference

$$\mathrm{M{-}M + e^- \rightleftharpoons M^\bullet + M^-} \qquad E_{\rm pc}(\mathrm{M_2}) \tag{8A}$$

$$\mathrm{M{-}M + e^- + \tfrac{1}{2}Hg \rightleftharpoons \tfrac{1}{2}M_2Hg + M^-} \qquad E_{1/2}(\mathrm{M_2}) \tag{9A}$$

$$\mathrm{M^\bullet + \tfrac{1}{2}Hg \rightleftharpoons \tfrac{1}{2}M_2Hg} \qquad \Delta G^\circ \tag{10A}$$

between $E_{\rm pc}(\mathrm{M_2}) = -1.33$ V[70] and $E_{1/2}(\mathrm{M_2}) = -0.89$ V[71] to estimate $\Delta G^\circ = -0.44$ eV for eq 10A. This correction is then applied to $E_{1/2}$ values for the M–X complexes to give the following estimated $E_{\rm pc}$(M–X) values for eq 11A (X, $E_{\rm pc}$(M–X)): $\mathrm{CH_3}$, −2.44; H, −2.15; Cl, −1.26; Br, −1.17; I, −0.94 V vs SCE. For M = Mo, X = I[72] the value −0.82 V vs SCE is obtained. Then treating

$$\mathrm{M{-}X + e^- \rightleftharpoons M^\bullet + X^-} \tag{11A}$$

the latter $E_{\rm pc}$ values as E° values for eq 11A and combining them with the E° value for the tungsten anion/radical couple (−0.08 V vs SCE, eq 3A, M = W)[67] we obtain the following ΔG° values for eq 1A with M = W (X, ΔG° eV): $\mathrm{CH_3}$, 2.36; H, 2.07; Cl, 1.18; Br, 1.09; I, 0.86. With M = Mo and X = I, the value 0.76 eV is obtained. Note that the affinity of the metal cation (M = W) for chloride ion calculated by subtracting eq 11A (M = W) from eq 6A (M = W) is −0.46 eV (−10.6 kcal mol^{-1}).

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