# Electron-Transfer Reactions of $Re(CO)_5$: Atom-Transfer-Concerted Mechanism *vs* Bimetallic Intermediate Formation

**M. Sarakha and G. Ferraudi***

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

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Flash photochemically generated $Re(CO)_5$ reacts with halide complexes, $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+$, $Cu(Me_2pyo[14]trieneN_4)X^+$, and $Ni(Me_2pyo[14]trieneN_4)X^+$ (X = Cl, Br, I) and ion pairs, $[Co(bipy)_3^{3+}, X^-]$. The rate constants for the electron transfers have values, $k \approx 10^9\ M^{-1}\ s^{-1}$, close to expectations for processes with diffusion-controlled rates. Reaction intermediates, probably bimetallic species, were detected in electron-transfer reactions of $Re(CO)_5$ with $Cu(Me_6[14]dieneN_4)X^+$, (X = Cl, Br, I). In the absence of the halides $X^-$, the electron-transfer reactions between $Re(CO)_5$ and these complexes are slow, $k < 10^6\ M^{-1}\ s^{-1}$. The results are discussed in terms of inner-sphere pathways, namely an atom-transfer-concerted mechanism. The mediation of bimetallic intermediates in the electron transfer is also considered.

## Introduction

Reactions of various metallocarbonyls, e.g., $Re(CO)_5$, and organic compounds with halogen−carbon bonds, eq 1, have

$$M(CO)_5 + CCl_4 \rightarrow M(CO)_5Cl + CCl_3^{\bullet} \qquad (1)$$

received some attention in the past.[1−5] On the basis of the rate constants with $CCl_4$ or $IC_5H_{11}$, a reactivity order

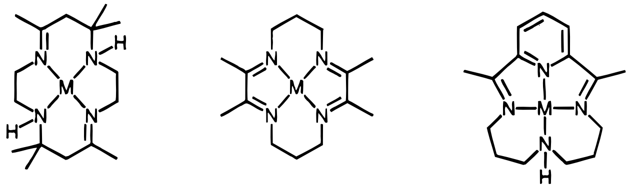
$$Re(CO)_5 > Mn(CO)_5 > (\eta^5\text{-}C_5H_5)W(CO)_3 >$$
$$(\eta^5\text{-}C_5H_5)Mo(CO)_3 > (\eta^5\text{-}C_5H_5)Fe(CO)_2 > Co(CO)_4$$

was established for these radical-like species. These processes were regarded as analogous of the abstraction of iodine by $Co(CN)_5^{3-}$, eq 2.[6] It has been proposed that the reactions

$$Co(CN)_5^{3-} + ICH_3 \rightarrow Co(CN)_5I^- + CH_3^{\bullet} \qquad (2)$$

proceed by the concerted and synchronous motion of nuclei and electronic density, i.e., one that "appropriately balances bond breaking with bond making".[5] The intermediacy of binuclear complexes in inner-sphere electron transfers of the metallocarbonyls has not been previously investigated as an alternate mechanism. Outer-sphere pathways may become available for reactions of metallocarbonyls in strongly coordinating solvents, e.g., phosphines. Indeed, the coordination of the solvent to monomeric metallocarbonyls may circumvent the need to form pentacoordinated cations via energetically expensive electron transfers.[5,7,8] The outer-sphere reductions of pyridinium ions by $Mn(CO)_5(CH_3CN)$ have been presented as examples of this chemical behavior.[9]

The role of the halide bridge and the intermediacy of binuclear species in the inner-sphere reactions of $Re(CO)_5$ with $Co(bipy)_3^{3+}$ and various Ni(II) and Cu(II) macrocyclic complexes (**1**) were investigated in this work.



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## Experimental Section

**Time-Resolved Optical Measurements.** Time-resolved optical spectra and reaction kinetics were investigated by flash photolysis and pulse radiolysis. The experiments were carried out with a modification of the flash photolysis apparatus described in the literature. Laser pulses of 351 and 355 nm were respectively generated with an excimer laser (Lambda Physik) and with a Nd:Yag laser (Quanta Ray).[10] Changes introduced in the detection system allow time-resolved optical density measurements from 10 ns to 0.5 s on the same instrument. Rate constants for reactions between $Re(CO)_5$ and various reactants were determined as a function of a given reactant concentration, by using concentrations resulting in pseudo-first-order rates. Curve fitting of oscillographic traces were made with commercially available routines from Microcal Origin software. In flash photolysis experiments, solid $Re_2(CO)_{10}$ was added to Ar-deaerated solutions of the reactants in $CH_3CN$. The liquids placed in a gastight cell were handled under Ar in a drybox. A 15 $cm^3$ volume of solution was stirred after each flash irradiation and used for only 10 consecutive experiments. Light intensities in 351 or 355 nm laser-flash irradiations were measured with the actinometer $Co(NH_3)_5Br^{2+}$ by a literature procedure.[11] Quantum yields of $Re(CO)_5$ in flash photolysis were calculated with such intensities and the corresponding concentrations of the Re radical appraised from the oscillographic traces.

The apparatus and procedures used in puse radiolysis are described elsewhere.[12] Pulse radiolysis was used for the investigation of the reaction between $Re(CO)_5$ and $Co(bipy)_3^{3+}$ in ethanolic solutions. The technique allowed a wider range of Co(III) complex concentrations

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than flash photolysis. In these experiments, $Re(CO)_5$ was generated by reaction of the solvated electron with $Re(CO)_5Br$ according to a literature study. Concentrations of $Co(bipy)_3^{3+}$ between $10^{-3}$ and $10^{-4}$ M in a $10^{-2}$ M $Re(CO)_5Br$ solution were used for the interception of the Re radical by the Co(III) complex.

**Steady-State Photolysis Procedures.** Steady-state photolyses, $\lambda_{exc}$ 350 nm, were carried out with light from a Rayonet lamp. Solutions of $Re_2(CO)_{10}$ in $CH_3CN$ were prepared in the manner described above. The progress of the photochemical reaction was monitored by means of the UV−vis optical spectra. A reaction cell described elsewhere allowed dual measurements of the optical density with optical paths of 1.0 and 0.1 cm.[13] Actinometric measurements of the intensity with $Co(NH_3)_5Br^{2+}$ were based on the analysis of the photoproduced $Co^{2+}$ with $SCN^-$.[11] Quantum yields were calculated with these intensities and the slopes $\lim_{t\to 0} d[P]/dt$, extracted from plots of the photoproduct concentration, [P], against the irradiation time.

**Materials.** $[Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)](ClO_4)_2$, $[Cu(Me_2pyo[14]trieneN_4)](ClO_4)_2$, $[Ni(Me_2pyo[14]trieneN_4)](ClO_4)_2$, $[Cu(Me_6[14]dieneN_4)](ClO_4)_2$, and $[Co(bipy)_3](ClO_4)_3$ were available from a previous work and were used without further purification.[14,15] Vacuum sublimations were applied to the purification of $Re_2(CO)_{10}$ according to a literature procedure. Results from flash photochemical experiments with this purified material and reagent grade $Re_2(CO)_{10}$ were not different. Aldrich (Spectroquality) $CH_3CN$ and $CH_3CH_2OH$ and $O_2$-free Ar were used without further purification for the preparation of solutions.

## Results

**1. Reactions of $Re(CO)_5$ in $CH_3CN$.** Flash irradiations of $10^{-3}$ M $Re_2(CO)_{10}$ in $CH_3CN$ ($\lambda_{exc}$ 351 or 355 nm) photogenerated $Re_2(CO)_9$ ($\lambda_{max}$ ~400 nm) and $Re(CO)_5$ ($\lambda_{max}$ 550 nm), eqs 3 and 4. Because $Re_2(CO)_9$ is scavenged by the solvent in less than 10 ns, i.e., the time response of the instrument, the spectral changes observed after the irradiation can be related to the products of the two processes.[16] While $Re_2(CO)_9(CH_3CN)$ ($\lambda_{max}$ <340 nm) is a stable product, the disappearance of the pentacarbonyl product in $CH_3CN$, followed at $\lambda_{ob}$ 550 nm, was kinetically of second-order in $Re(CO)_5$ and assigned to the dimerization reaction in eq 5. A rate constant, $k_{dim} = (1.0 \pm 0.2) \times 10^{10}$ $M^{-1}$ $s^{-1}$, was calculated for such a reaction in $CH_3CN$ by using a literature value of the $Re(CO)_5$ extinction coefficient in ethanol.[17] This value of $k_{dim}$ compares well with one communicated for the same process in cyclohexane.[18] The value of $k_{dim}$ and the spectrum of $Re(CO)_5$ did not change when electrolyte ($NaClO_4$, NaCl, NaBr) was added in small concentrations, e.g., less than $10^{-2}$ M, to the solution of $Re_2(CO)_{10}$. In terms of the effect of the ionic strength on reaction rates, the results agreed with expectations for reactions between uncharged species. This observation and the lack of spectral changes show that halide anions in low concentrations do not associated with the pentacarbonyl product.

$$Re_2(CO)_{10} + h\nu \xrightarrow{-CO} Re_2(CO)_9 \xrightarrow{CH_3CN} Re_2(CO)_9CH_3CN \tag{3}$$

$$Re_2(CO)_{10} + h\nu \rightarrow 2Re(CO)_5 \tag{4}$$

$$2Re(CO)_5 \xrightarrow{k_{dim}} Re_2(CO)_{10} \tag{5}$$

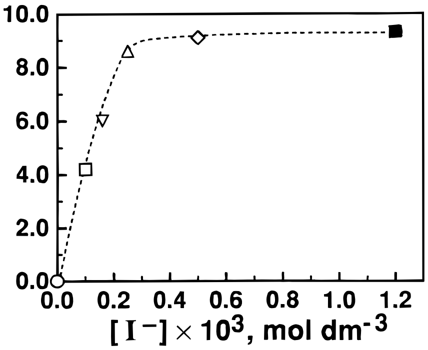

**Figure 1.** Dependence of the rate constant for the formation of $Cu^I(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ on iodide anion concentration. The molar relationships between halide and Cu(II) complex, $C_M = 2.5 \times 10^{-4}$ M, concentrations used in 351 nm flash irradiations of $Re_2(CO)_{10}$ are (□) 0.40, (▽) 0.64, (△) 1.0, (◇) 2.0, (■) 4.8.

**2. Electron-Transfer Reactions with Coordination Complexes.** Since $Re_2(CO)_9$ was rapidly scavenged by the solvent, $CH_3CN$, this process, eq 3, presented no experimental obstacles to the study of various reactions between $Re(CO)_5$ and various Cu(II), Ni(II), and Co(III) complexes. When halide ions (concentrations between $10^{-2}$ and $10^{-3}$ M) were added to solutions of the reactants, they coordinated to Cu(II) and Ni(II) macrocycles or were associated in ion pairs with $Co(bipy)_3^{3+}$. Under these conditions, the oxidations of $Re(CO)_5$ by halide adducts compete with the dimerization of $Re(CO)_5$. In the absence of halide ions, such redox reactions were not observed with concentrations of $Re(CO)_5$ about $10^{-5}$ M and millimolar concentrations of the macrocyclic complexes. The observed second-order decay of $Re(CO)_5$ revealed that electron-transfer processes are too slow to compete with the dimerization of $Re(CO)_5$, eq 5. A limiting value for the rate constant, $k \leq 10^6$ $M^{-1}$ $s^{-1}$, of these reactions was estimated from the inequality $k \leq 10k_{dim}[Re(CO)_5]_{t=0}$, where $[Re(CO)_5]_{t=0} \approx 10^{-5}$ M is the flash-generated concentration of Re complex. The experimental observations made with each oxidant are described next.

**3. Reactions of $Re(CO)_5$ with $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+$ ($X = Cl^-, Br^-, I^-$).** The kinetics of the reactions

$$Re(CO)_5 + Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+ \rightarrow Re(CO_5X + Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+ \tag{6}$$

$$X = Cl, Br, I$$

were studied by following the disappearance of $Re(CO)_5$ at wavelengths near the 550 nm absorption maximum and the growth of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ at 740 nm. When halide concentrations, $C_X$, were larger than or equal to the $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^{2+}$ concentration, $C_M$, reaction rates exhibited a zero-order dependence on the halide concentration. Concentrations $C_M$ of the Cu(II) complex were adjusted to values ≥10 times larger than those of the flash photogenerated $Re(CO)_5$ in order to approach pseudo-first-order kinetics. Mathematical functions corresponding to an exponential growth and an exponential decay, both with the same time constant, were respectively fitted to oscillographic traces recorded at 740 and 500 nm. The dependence of the reaction rate on halide concentration, Figure 1, became evident in measurements of the rate constant with solutions having halide concentrations

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(14) Ligand abbreviations: bipy, 2,2′-bipyridine; $Me_6[14]dieneN_4$, 5,7,12,14,14-$Me_6[14]$-4,11-diene-1,4,8,11-$N_4$; $Me_4[14]$-1,3,8,10-tetraene$N_4$, 2,3,9,10-$Me_4[14]$-1,3,8,10-tetraene-1,4,8,11-$N_4$; $Me_2pyo[14]trieneN_4$, 2,6-$Me_2$-3,4,5-pyo[14]-1,3,6-triene-1,4,7,11-$N_4$.

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smaller than those of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^{2+}$, i.e., $C_X < C_M$. Since the equilibrium in eq 7,[19,20] must be saturated

$$Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^{2+} + X^- \rightleftarrows Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+ \quad (7)$$

at those halide concentrations, $10^{-5} \leq C_X \leq 10^{-3}$ M, used in this study, concentrations of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+$ are given by the mass balances in eqs 8 and 9. The mass

$$[Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+] \approx C_X \text{ for } C_X < C_M \quad (8)$$

$$[Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+] \approx C_M \text{ for } C_X \geq C_M \quad (9)$$

balances dictate that the dependence of the rate on the halide concentration, $C_X$, must cease when $C_X \geq C_M$, a functional behavior that is in agreement with experimental observations in Figure 1.[20]

Continuous irradiations of $4 \times 10^{-3}$ M $Re_2(CO)_{10}$, $\lambda_{exc}$ 350 nm, in deaerated solutions of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^{2+}$ were carried out in order to corroborate experimental observations made by flash photolysis. The photogeneration of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ in these irradiations was observed only when various concentrations of halide ions, $10^{-4}$ M $< [X^-] < 5 \times 10^{-3}$ M, were present in solutions of the photolyte, Figure 2. The progress of the photochemical reaction was monitored by following the growth of the absorption band of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$, $\lambda_{max}$ 745 nm and $\epsilon_{max} = 8000$ $M^{-1}$ $cm^{-1}$. Photoinduced spectral changes, e.g., with X $= I^-$, resulted in isosbestic points at 466 and 375 nm that remained unchanged through the irradiation. When halide ion concentrations surpassed the concentration of Cu(II) complex, i.e., $C_X > C_M$, the concentration of photoproduct $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ (attained at a 95% conversion of $Cu(TIM)^{2+}$ to Cu(I)) was nearly equal to $C_M$, Figure 2a. Steady irradiations of $Re_2(CO)_{10}$ were also carried out with smaller initial concentrations of halide anion than the initial concentration of Cu(II) complex, i.e., $C_X < C_M$. Final concentrations of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ produced in such irradiations, Figure 2b, were nearly equal to $C_X$, i.e., the initial concentration of halide in the photolyte solutions. It must be noted that, for all the conditions of $C_X$ and $C_M$ indicated above, the quantum yield for $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ photogeneration has the same value when conversions of Cu(II) to Cu(I) were smaller than 50%. Quantum yields for the photogeneration of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$, $\varnothing = 0.34 \pm 0.03$, in 350 nm steady-state photolyses and $Re(CO)_5$, $\varnothing = 0.35 \pm 0.04$, measured in flash photolysis were the same and indicative of a 1:1 stoichiometry. These experimental observations show that only $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)X^+$ species (their concentrations established by mass balances in eqs 8 and 9) reacted with $Re(CO)_5$.

**4. Role of the Halide Ions.** The electron-transfer reactions of $Re(CO)_5$ with other coordination complexes, i.e., $Cu(Me_2pyo[14]trieneN_4)^{2+}$, $Ni(Me_2pyo[14]trieneN_4)^{2+}$, and $Co(bipy)_3{}^{3+}$, were also investigated at various halide concentrations, i.e., $C_X \leq 10^{-3}$ M. In the absence of halide ions, the presence of Cu(II), Ni(II), and Co(III) complexes in millimolar concentrations did not alter the disappearance of $Re(CO)_5$ *via* radical recombination, eq 5. The species $Cu(Me_2pyo[14]trieneN_4)X^+$ and $Ni(Me_2pyo[14]trieneN4)X^+$, present in solutions of halide ions, X $= Cl^-$ or $Br^-$,[20,21] reacted with $Re(CO)_5$ to give the corresponding reduction products of the macrocyclic complexes, eqs 10 and 11. Identical rate constants were determined for

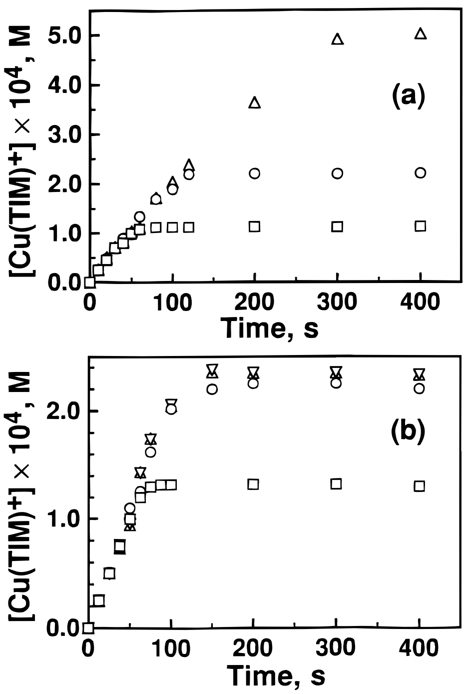

**Figure 2.** Concentrations of photogenerated $Cu^I(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^+$ as a function of irradiation time in 350 nm steady photolyses of $Re_2(CO)_{10}$. Product concentrations in (a) were measured for various values of the initial concentration of $Cu(Me_4[14]\text{-}1,3,8,10\text{-tetraeneN}_4)^{2+}$, $C_M = 1.0 \times 10^{-4}$ M (□), $2.5 \times 10^{-4}$ M (○), and $5.0 \times 10^{-4}$ M (△), and with a molar relationship $C_{I^-}/C_M = 2$ of iodide to Cu(II) complex. In (b), data were collected with various $C_M = 2.5 \times 10^{-4}$ M and with various $C_{I^-}/C_M$ molar relationships: $C_{I^-} = 1.0 \times 10^{-4}$ M (□), $2.0 \times 10^{-4}$ M (○), $4.0 \times 10^{-4}$ M (△), $1.0 \times 10^{-3}$ M (▽).

$$Re(CO)_5 + Cu(Me_2pyo[14]trieneN_4)X^+ \rightarrow Re(CO)_5X + Cu(Me_2pyo[14]trieneN_4)^+ \quad (10)$$

$$Re(CO)_5 + Ni(Me_2pyo[14]trieneN_4)X^+ \rightarrow Re(CO)_5X + Ni(Me_2pyo[14]trieneN_4)^+ \quad (11)$$

the appearance of the reduction products $Cu(Me_2pyo[14]trieneN_4)^+$ ($\lambda_{ob}$ ~670 nm) and $Ni(Me_2pyo[14]trieneN_4)^+$ ($\lambda_{ob}$ ≈ 460 nm) and for the disappearance of $Re(CO)_5$ ($\lambda_{ob}$ ~500 nm), Figure 3. The rate constants measured for these processes, eqs 6, 10, and 11, are given in Table 1 for various complexes of the macrocycles with $Cl^-$, $Br^-$, and $I^-$. It must be noted that the reaction rate constant exhibits a small but measurable dependence on the halide, a point better illustrated in Figure 4 for the rate constants of eq 10.[22] Results in Table 1 show that increments of *k* from Cl to Br to I are smaller than 1 order of magnitude and follow the "normal order of bridging efficiency".[23,24]

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(20) An equilibrium constant, $K \simeq 4 \times 10^3$ $M^{-1}$, was calculated from the slope of $k_{ob}$ *vs* [**I**] in Figure 1. The value of *K*, smaller than the one reported for the association of $Cl^-$ to the complex, leads to a saturation of the equilibrium when $[I^-] \geq 2 \times 10^{-4}$ M. See: Sarakha, M.; Ferraudi, G. Unpublished observations.

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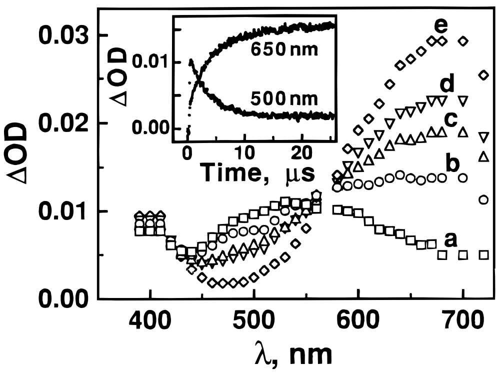

**Figure 3.** Time-resolved spectra recorded during the reaction of Re(CO)$_5$ with Cu(Me$_2$pyo[14]trieneN$_4$)Br$^+$. The pentacarbonyl was generated in (351 nm) flash irradiations of Re$_2$(CO)$_{10}$ (4× spectra were recorded with delays given in the figure following the 351 nm flash irradiation of $4 \times 10^{-3}$ M Re$_2$(CO)$_{10}$ in a solution $8 \times 10^{-4}$ M in Br$^-$ and $4 \times 10^{-4}$ M Cu(II) complex. The spectra were recorded with various delays: (a) 60 ns, (b) 360 ns, (c) 660 ns, (d) 960 ns, (e) 3660 ns, after the flash. Oscillographic traces in the inset show the same lifetimes for the disappearance of Re(CO)$_5$, $\lambda_{ob}$ 500 nm, and the appearance of the Cu(I) product, $\lambda_{ob}$ 650 nm.

**Table 1.** Dependence of the Electron-Transfer Rate Constant on the Halide Ion

| | $k/10^9$ (M$^{-1}$ s$^{-1}$) | | |
|---|---|---|---|
| oxidant | X = Cl$^-$ | X = Br$^-$ | X = I$^-$ |
| Cu(Me$_4$[14]-1,3,8,10-tetraeneN$_4$)X$^+$ | 1.5 | 2.3 | 3.6 |
| Cu(Me$_2$pyo[14]trieneN$_4$)X$^+$ | 1.8 | 2.3 | 4.7 |
| Ni(Me$_2$pyo[14]trieneN$_4$)X$^+$ | 1.9 | 2.5 | 4.5 |

Although complexes of halide appear to be the only species to react rapidly with Re(CO)$_5$, ion pairs of halide with Co(bipy)$_3$$^{3+}$ reacted equally fast. When halide ions, i.e., $10^{-3} \geq [\mathrm{Cl^-}] \geq 3 \times 10^{-4}$ M, were in solution, associated mostly as ion pairs [Co(bipy)$_3$$^{3+}$,X$^-$], $10^{-5} < C_M < 10^{-3}$ M in CH$_3$CN or CH$_3$CH$_2$OH, the Co(III) complex was reduced by Re(CO)$_5$, eqs 12 and 13. The process was kinetically pseudo-first-order

$$\mathrm{Co(bipy)_3^{3+} + X^- \rightleftharpoons [Co(bipy)_3^{3+}, X^-]} \qquad (12)$$

$$\mathrm{Re(CO)_5 + [Co(bipy)_3^{3+}, X^-] \rightarrow Re(CO)_5X + Co(bipy)_3^{2+}} \qquad (13)$$

in Re(CO)$_5$ concentration and faster than the dimerization of the Re radical, eq 5. A rate constant, $k \approx 9 \times 10^8$ M$^{-1}$ s$^{-1}$, for eq 13 was calculated by following the decay of Re(CO)$_5$ at 550 nm by pulse radiolysis or by flash photolysis. No reaction between Re(CO)$_5$ and Co(bipy)$_3$$^{3+}$, $10^{-3} < C_M < 10^{-5}$ M, was observed in the absence of halide.

**5. Intermediacy of Binuclear Complexes.** The rate law of the reactions described above is kinetically second-order, first-order in the concentration of Re(CO)$_5$ and oxidant complex. Identical rate constants have been measured for the disappearance of Re(CO)$_5$, i.e., the decay of the optical density at 550 nm, and for the formation of the reduced products. The reaction of Re(CO)$_5$ WITH Cu(Me$_6$[14]dieneN$_4$)$^{2+}$ requires the complexation of the macrocycle by halide anions, eq 14, in order

$$\mathrm{Cu(Me_6[14]dieneN_4)^{2+} + X^- \rightleftharpoons Cu(Me_6[14]dieneN_4)X^+} \qquad (14)$$

to be kinetically competitive with the second-order termination of the Re radical. In contrast to the kinetics of reactions described above, the rate of Re(CO)$_5$ consumption does not parallel the rate of Cu(Me$_6$[14]dieneN$_4$)$^+$ formation. Oscillographic traces, Figure 5, reveal that the decay of the 550 nm optical density, i.e., the decay of Re(CO)$_5$, precedes the growth of the 420 nm optical density, i.e., the formation of the Cu(I) product, by a period of several microseconds. The disappearance of Re(CO)$_5$ was kinetically pseudo-first-order, and the rate constant varied linearly with the concentration of Cu(II) complex. By contrast, a variable lifetime characterized the growth of the 420 nm optical density over the initial 15 μs of the reaction and reached a limiting value at longer times. Results in Table 2 show that the dependence of the rate constant for the decay of Re(CO)$_5$ on the halide parallels the lifetime of the Cu(I) appearance.

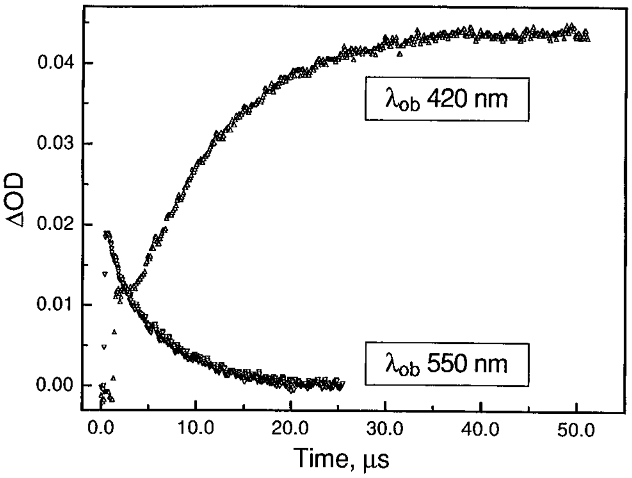

**Figure 5.** Oscillographic traces for the single-exponential disappearance of Re(CO)$_5$, $\lambda_{ob}$ 550 nm, and the multiple-step formation of Cu(Me$_6$[14]dieneN$_4$)$^+$, $\lambda_{ob}$ 420 nm. Transients were recorded in 351 nm flash irradiation of $4 \times 10^{-3}$ M Re$_2$(CO)$_{10}$ solutions that were $4 \times 10^{-4}$ M in Cl$^-$ and $2 \times 10^{-4}$ M in Cu(Me$_6$[14]dieneN$_4$)$^{2+}$.

Significant differences can be observed between time-resolved optical changes recorded when Re(CO)$_5$ respectively reacts with Cu(Me$_6$[14]dieneN$_4$)X$^+$, Figure 5, and with Cu(Me$_2$pyo[14]trieneN$_4$)Cl$^+$, eq 10 and insert to Figure 3. The various steps in the growth of the 420 nm optical density in Figure 5 signal that adducts between Re and Cu(Me$_6$[14]dieneN$_4$)X$^+$ complexes, eq 14, mediate the formation of the final products, eqs 15−17.

$$\mathrm{Re(CO)_5 + Cu(Me_6[14]dieneN_4)X^+ \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} (CO)_5Re^0XCu^{II}(Me_6[14]dieneN_4)^+} \qquad (15)$$

(precursor complex)

$$\mathrm{(CO)_5Re^0XCu^{II}(Me_6[14]dieneN_4)^+ \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} (CO)_5Re^IXCu^I(Me_6[14]dieneN_4)^+} \qquad (16)$$

(successor complex)

$$\mathrm{(CO)_5Re^IXCu^I(Me_6[14]dieneN_4)^+ \underset{k_{-17}}{\overset{k_{17}}{\rightleftharpoons}} Re^I(CO)_5X + Cu^I(Me_6[14]dieneN_4)^+} \qquad (17)$$

The initial step, i.e., from zero to several microseconds in the oscillographic trace recorded at 420 nm, can be assigned to the relaxation of the equilibrium between precursor and successor complexes, eq 16. It can also be modeled in terms of an

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(24) Haim, A. *Inorg. Chem.* **1968**, *7*, 1475.

**Table 2.** Dependence of the Rate Constant for the Decay of $Re(CO)_5$ and Lifetime for the Formation of $Cu(Me_6[14]dieneN_4)^+$ on the Halide Bridge

| X | $k/10^8$ ($M^{-1}$ $s^{-1}$) | $10^5\tau$ (s) |
|---|---|---|
| $Cl^-$ | 9.3 | 0.58 |
| $Br^-$ | 12 | 0.37 |
| $I^-$ | 31 | 0.18 |

electron-transfer step that kinetically lags behind the complexation step, i.e., $k_{15} > k_{-15} < k_{16} \approx k_{17} > k_{-16} \approx k_{-17}$.

## Discussion

The reactions of $Re(CO)_5$ described above demonstrate that $CH_3CN$ cannot stabilize a hexacoordinated $Re(CO)_5(CH_3CN)$ species to the extent that makes an outer-sphere mechanism a preferred path. Similarities between chemical properties of $Re(CO)_5$ and $Mn(CO)_5$ diverge therefore in the formation of solvent-bound complexes.

When bridging ligands are not available, ion pairs between halide ions and $Co(bipy)_3^{3+}$ are required for electron transfers to $Re(CO)_5$, eqs 12 and 13. The mediation of halide ions underlines the significance of Re−X bond making in the activated complex of a reaction that could be regarded otherwise as an outer-sphere electron transfer. With the exception of reactions of ion pairs,[25,26] the other investigated processes appear to proceed almost completely via an inner-sphere electron-transfer mechanism. Experimental observations on the reaction of $Cu(Me_6[14]dieneN_4)X^+$ with $Re(CO)_5$ suggest that a binuclear intermediate mediates the formation of the terminal products, i.e., $Cu(Me_6[14]dieneN_4)^+$ and $Re(CO)_5X$. Any interpretation of the time-resolved optical changes in Figure 5 requires two kinetically distinguishable steps and (at least) one or more additional intermediates, eqs 15−17. The nature of the products and dependence of the rate constant on the halide suggest that such an intermediate could be a bimetallic complex, e.g., with a halide bridge between Re and Cu. Concentrations of bimetallic intermediates in reactions of $Re(CO)_5$ with $Me_4[14]$-1,3,8,10-tetraene$N_4$ and $Me_2pyo[14]trieneN_4$ complexes could have quickly achieved a steady state and been undetectable in our flash photochemical experiments. However, experimental observations on the reactions of $Re(CO)_5$ with $Cu(Me_2pyo[14]trieneN_4)X^+$ and $Cu(Me_4[14]$-1,3,8,10-tetraene$N_4)X^+$ can also be rationalized in terms of the concerted atom-transfer mechanism. In this mechanism, the variation of the rate constant with halide bridge defines a trend that was associated in earlier reports with contributions to the activation energy from the breaking of X−M bonds.[23,24] Nevertheless, this contribution must be small because the magnitude of the $Re(CO)_5$ reaction rate constants nears those of diffusion-controlled processes, i.e., $k \geq 10^9$ $M^{-1}$ $s^{-1}$. Self-exchange rate constants, $10 \leq k_{exc} \leq 10^3$ $M^{-1}$ $s^{-1}$ for Cu(II)/Cu(I) and $10^7 \leq k_{exc} \leq 10^8$ $M^{-1}$ $s^{-1}$ for Ni(II)/Ni(I),[15] suggest that an inner-sphere path must have an intrinsic kinetic advantage over an outer-sphere pathway.

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**Supporting Information Available:** Figure 4, showing dependence of the rate constant on halide ($Cl^-$, $Br^-$, $I^-$) concentration for reactions of $Re(CO)_5$ with $Cu(Me_2pyo[14]trieneN_4)X^+$ (1 page). Ordering information is given on any current masthead page.

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(25) It must be noted that the effect of the anion on the reaction between $Re(CO)_5$ and $Co(bipy)_3^{3+}$ can parallel those in other outer-sphere electron transfers.[26]

(26) Przystas, T.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545.