can then be formed either by redox reaction of the $ArCH_2O_2$ with the POA^{red} catalyst, or, due to the high termination rate of the arylperoxy radicals, by disproportionation of two $ArCH_2O_2$. In this case the corresponding alcohol is also formed.[20] Subsequent oxidation of the latter may also give *p*-tolualdehyde. In turn, oxidation of the aldehyde produces the corresponding carboxylic acid. At this point, reoxidation of the reduced POA catalyst in the presence of excess oxygen is an easy and fast process, which efficiently closes the catalytic cycle.[11]

Further, we note that, after about 20 h of irradiation, the reaction performed either with **1** or **2** showed the presence of a white precipitate (ca. 3% of the starting *p*-xylene) that turned out to be analytically pure terephthalic acid. At this point, light scattering and diffusion from the heterogeneous reaction mixture considerably decreases the photocatalytic reaction rate. However, it is noteworthy that, after the first oxidation step, deactivation of the second CH_3 by the electron-withdrawing carboxylic group does not prevent complete oxidation of *p*-xylene.

Finally, we point out that recovery of the catalyst, after both the anaerobic and the aerobic reactions, gives partially insoluble products that, although retaining the intact POA structure (IR spectroscopy), contain small amounts of organics strongly bound to the inorganic acid.[23]

Investigation of this and other aspects of the reported processes are under way and will be reported at a later stage.

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(23) Preliminary results (^1H NMR) indicate that traces of CH_3CN oxidation products are present.

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Kinetics and Mechanism of Electron Transfer from Pentacarbonylrhenate to Metal Carbonyl Dimers by Infrared Stopped-Flow Spectroscopy

Single-electron transfer is a reaction of importance in organic synthesis, homogeneous catalysis, and organometallic chemistry.[1-3] Reactions of metal carbonylates with dimers involve electron transfer and offer the opportunity to study single-electron transfer between organometallic complexes.[4] These reactions occur rapidly, and we have developed an infrared stopped-flow system to examine such reactions. In this communication we report on the reactions of $Re(CO)_5^-$ with the dimers $Mn_2(CO)_{10}$, $Co_2(CO)_8$, and $Cp_2Mo_2(CO)_6$.

Product determination of reactions 1-3 was examined by infrared spectroscopy. Spectral data are given in Table I. All reactions were run in THF, the THF was removed, and the solid was extracted with hexanes to separate the dimeric species from the anions. Reactions 1-3 were quantitative; the reverse reactions

$$2Re(CO)_5^- + Mn_2(CO)_{10} \rightarrow Re_2(CO)_{10} + 2Mn(CO)_5^- \quad (1)$$

$$2Re(CO)_5^- + Co_2(CO)_8 \rightarrow Re_2(CO)_{10} + 2Co(CO)_4^- \quad (2)$$

$$2Re(CO)_5^- + Cp_2Mo_2(CO)_6 \rightarrow Re_2(CO)_{10} + 2CpMo(CO)_3^- \quad (3)$$

Table I. Infrared Spectral Data for the Anions and Dimers

$Mn_2(CO)_{10}$	2050 (m)	2015 (s)	1985 (w)	
$Co_2(CO)_8$	2070 (m) 1840 (m)	2040 (m)	1950 (m)	1885 (w)
$Cp_2Mo_2(CO)_6$	1950 (m)	1910 (m)	1775 (w)	1720 (w)
$Re_2(CO)_{10}$	2070 (s)	2010 (m)	1965 (m)	
$(PPN)Re(CO)_5$	1906 (m)	1860 (s)		
$(PPN)Mn(CO)_5$	1890 (m)	1860 (s)		
$(PPN)CpMo(CO)_3$	1893 (s)	1780 (s)		
$(PPN)Co(CO)_4$	1890 (m)			

Table II. Observed Rate Constants for Reaction of $Re(CO)_5^-$ with M_2

M_2	$[M_2]$,[a] M	k_{obsd},[b] s^{-1}
$Cp_2Mo_2(CO)_6$	2.0×10^{-3}	$1.04 \times 10^{-1} \pm 1.5 \times 10^{-3}$
	2.00×10^{-2}	$5.31 \times 10^{-1} \pm 1.2 \times 10^{-3}$
	6.00×10^{-2}	$1.12 \pm 3.6 \times 10^{-2}$
	8.00×10^{-2}	$1.78 \pm 2.0 \times 10^{-2}$
	2.00×10^{-1}	$4.08 \pm 5.7 \times 10^{-2}$
$Mn_2(CO)_{10}$	1.00×10^{-3}	$4.44 \times 10^{-2} \pm 3.3 \times 10^{-4}$
	2.00×10^{-2}	$5.04 \times 10^{-2} \pm 3.4 \times 10^{-4}$
	6.00×10^{-2}	$9.31 \times 10^{-2} \pm 3.3 \times 10^{-3}$
	8.00×10^{-2}	$1.39 \times 10^{-1} \pm 2.5 \times 10^{-3}$
	2.00×10^{-1}	$3.01 \times 10^{-1} \pm 1.9 \times 10^{-3}$
$Co_2(CO)_8$	3.0×10^{-2}	2.07 ± 0.04
	6.00×10^{-2}	2.60 ± 0.01
	8.00×10^{-2}	2.70 ± 0.02
	1.00×10^{-1}	3.00 ± 0.02

[a] Concentrations are in molarity, $[Re(CO)_5^-] = 1.00 \times 10^{-3}$ M. [b] k_{obs} values were calculated using the OLIS 4120AT computer program. The standard deviations are reported.

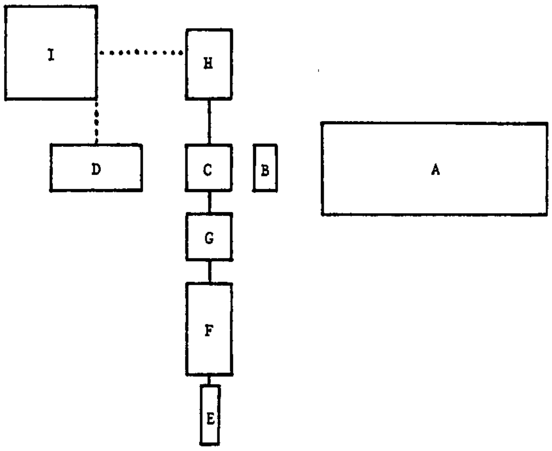

Figure 1. Schematic of the infrared stopped-flow spectrophotometer. A is a tunable CO laser (Edinburgh Instruments PL 3), B is an iris diaphragm, C is an Irtran-2 flow-through cell (Wilmad Glass Co., Inc.), D is a HgCdTe detector (Infrared Associates, Inc.), E is an air cylinder (Power Drive, Inc.), F is the syringe assembly, G is the Berger ball mixer (Research Instruments and Mfg. and Commonwealth Technology, Inc.), H is the stopping syringe assembly, and I is the stopped-flow operating system (OLIS). The dashed lines indicate an electrical connection.

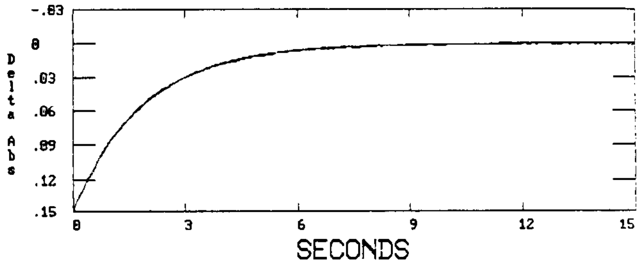

Figure 2. Plot of the kinetic data and fit for the reaction of $Re(CO)_5^-$ (1×10^{-3} M) with $Cp_2Mo_2(CO)_6$ (2×10^{-2} M) following the loss of $Re(CO)_5^-$ at 1860 cm^{-1}.

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Table III. Second-Order Rate Constants for the Reaction of $Re(CO)_5^-$ with M_2

M_2	k,[a] $s^{-1}\ M^{-1}$	$-E_{1/2}$,[b] V
$Co_2(CO)_8$	13 ± 1	0.9
$Mn_2(CO)_{10}$	1.4 ± 0.3	1.7
$Cp_2Mo_2(CO)_6$	20 ± 2	1.4

[a] Error limits are 95% confidence limits. [b] Reference 7.

did not occur—none of the anions reacted with $Re_2(CO)_{10}$.

Examination by infrared stopped-flow kinetics studies[5] showed that reactions 1–3 were first order in $[Re(CO)_5^-]$ and in dimer.[6]

$$\text{rate} = k[Re(CO)_5^-][M_2] \qquad (4)$$

$$M = Mn(CO)_5,\ CpMo(CO)_3,\ Co(CO)_4$$

A typical plot of the decrease in absorbance due to $Re(CO)_5^-$ at 1860 cm^{-1} is shown in Figure 2; plots for each dimer at different concentrations are given in the supplementary material. The fits to the plots under pseudo-first-order conditions (the dimer in at least a 10-fold excess) show a first-order dependence on $Re(CO)_5^-$. The dependence on the dimers is shown by the data in Table II. The rate constants, k, were obtained as the slope of plots (supplemental data) of k_{obs} versus $[M_2]$ and are shown in Table III.

The rate law observed is typical for electron-transfer reactions with a first-order dependence on the oxidant and the reductant. The dependence on the dimer is $Cp_2Mo_2(CO)_6 > Co_2(CO)_8 > Mn_2(CO)_{10}$, as shown in Table III. This dependence does not correlate with the reduction potentials for the dimers, which are also given in Table III. This casts doubt on an outer-sphere mechanism for the electron transfer. Possible inner-sphere mechanisms requiring dissociation of a ligand from the anion or the dimer are precluded because the electron transfer occurs more rapidly than ligand dissociation. An inner-sphere mechanism involving nucleophilic attack of the anion on the dimer is indicated. Possible sites for nucleophilic attack would be (1) the metal–metal antibonding orbital, (2) the metal center, and (3) a carbon of a carbonyl. Attack at the metal center would seem unlikely since the most sterically constrained metal (seven-coordinate) reacts more rapidly.[7,8] It is difficult to distinguish between the other two possibilities at this point. On the basis of the known preference for nucleophilic attack at CO's with less electron density and the rapid reaction of $Cp_2Mo_2(CO)_6$,[9,10] we favor attack at the carbonyl. Future studies will be directed toward this question.

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Supplementary Material Available: Plots of k_{obs} versus $[M_2]$ and of kinetic data for reactions of $Re(CO)_5^-$ with M_2 (9 pages). Ordering information is given on any current masthead page.

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(5) A schematic of the infrared stopped-flow instrument is shown in Figure 1. The infrared source is a tunable carbon monoxide laser (Edinburgh Instruments PL3). The beam passes through an iris diaphragm and the Irtran-2 cell (Wilmad Glass Co., Inc.) and into the HgCdTe detector (Infrared Associates, Inc.). The signal from the detector is processed by a stopped-flow operating system (OLIS). The stopped-flow system is composed of Teflon and KelF components. The syringes are driven by an air cylinder (Power Drive Inc.) through a Berger ball mixer (Research Instruments and Mfg. and Commonwealth Technology Inc.). The stopcocks and tubing are from Hamilton.

(6) For $M_2 = Co_2(CO)_8$ the plots of k_{obs} versus $[Co_2(CO)_8]$ have a substantial intercept. This may indicate a process that is independent of $[Co_2(CO)_8]$ or may be a result of the instability of $Co_2(CO)_8$ in THF solution. Since the other dimers do not show such an intercept, we favor the latter explanation.

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Preparation and X-ray Structure of (Tetramethyldibenzotetraaza[14]annulene)chromium Dimer, $[(tmtaa)Cr]_2$. A Multiply Bonded Complex of Dichromium(II) without Bridging Ligands

Understanding the factors that promote or inhibit the formation of metal–metal multiple bonds remains even today a very challenging and interesting goal.[1] This is especially puzzling in the chemistry of Cr(II) where the well-known ability of the d^4 electronic configuration to form unusually short Cr–Cr quadruple bonds[2] contrasts with theoretical calculations that predict for the quadruple bond either little[3] or no contribution[4] to the ground state. Furthermore, the occurrence of Cr–Cr quadruple bonds, with the only three exceptions being $Cr_2Me_8Li_4$,[5a] $Cr_2(C_4H_8)_4Li_4$,[5b] and $Cr_2(PMe_3)_2(CH_2SiMe_3)_2(\mu\text{-}CH_2SiMe_3)_2$[6] is confined to a homogeneous series of compounds containing ligands with the characteristic geometry of the bridging three-center chelating systems.[1,7] In order to identify a possible role of the ligands in forcing the formation of Cr–Cr bonds, we started an extensive study of new classes of Cr(II) compounds, containing ligands with most diverse geometries.[8-10] Herein we report an example where the formation of a Cr–Cr multiple bond without the assistance of bridging atoms is caused by the unique geometry of a macrocyclic ligand.

Reaction of $Me_8Cr_2(LiTHF)_4$[5] with 2 equiv of tetramethyldibenzotetraaza[14]annulene ($tmtaaH_2$) in toluene proceeds smoothly with evolution of methane (Scheme I)[11] and formation

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