and Macintosh SE/30 computers.[43] Norman's procedure for interpolation of overlapping-sphere sizes was used to optimize the virial coefficient at 1.[44,45] Schwarz's α_{HF} values[46] were used for the atomic exchange parameters, except for hydrogen, in which case Slater's value[47] of 0.777 25 was used. The α values for the intersphere and outer-sphere regions were weighted averages of the atomic α values, where the weights are the number of valence electrons on the different neutral free atoms.

A minimal basis set in partial wave expansion was used for all calculations.[48] Using $l = 1$ for the outer-sphere region was sufficient to generate basis function components in all representations.

The coordinates for $Co(CO)_3L_2'$ were taken from the crystal structure of the related $Co(CO)_3L_2$ complex in ref 23 and idealized to C_s symmetry. The phenyl rings bonded to the P atoms in $Co(CO)_3L_2$ were replaced by H atoms for the calculation. The coordinate system used is shown in Figure 2. The Co atom is placed at the origin, and the phosphorus, carbon, and oxygen atoms of the L_2' ligand lie in the yz plane. The axial CO ligand lies at an 11° angle from the x axis (in the positive y direction), and the two symmetry equivalent CO's are 34° below the yz plane. The coordination geometry around the cobalt atom is approximately square pyramidal. The mirror plane is the xy plane. Due to the unspherical nature of the molecule, the origin for the outer sphere was placed at the valence-electron-weighted average of all the other atom coordinates. The coordinates for all atoms, in bohrs, are found in the supplementary material.

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Supplementary Material Available: A table with the atom coordinates used in the calculation and a figure showing the linear relationship between the ν(CO) frequencies and the band maximum of the lowest energy absorption band (2 pages). Ordering information is given on any current masthead page.

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Alkyl-Transfer Reactions from Transition Metal Alkyl Complexes to $CpFe(CO)_2^-$: Rate and Mechanistic Studies

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Abstract: We have examined reactions of several alkyl complexes ($Mn(CO)_5Me$, $Mn(CO)_5CH_2Ph$, $Mn(CO)_5Ph$, $CpMo(CO)_3Me$, $CpMo(CO)_3Et$, and $CpMo(CO)_3CH_2Ph$) with $CpFe(CO)_2^-$. Each of these reactions results in transfer of the alkyl group to the iron with formation of $Mn(CO)_5^-$ or $CpMo(CO)_3^-$. The reactions were first order in the concentration of $CpFe(CO)_2^-$ and first order in the alkyl complex. The dependence on the group transferred, $H^+ > CH_2Ph^+ > Me^+ > Et^+ > Ph^+$, is consistent with a nucleophilic attack mechanism. For methyl transfer the rate correlates with the difference in nucleophilicity between the reactant and product anions. We have also evaluated the self-exchange between $CpFe(CO)_2Me$ and $CpFe(CO)_2^-$ by line-broadening experiments. Our attempt to estimate the self-exchange rate constant for $CpMo(CO)_3Me$ and $CpMo(CO)_3^-$ shows this reaction to occur very slowly through a methyl migration sequence.

Electron transfer in organic and organometallic reactions is recognized as a crucial step in many important reactions.[1,2] Atom-transfer reactions, while common for organic systems,[3] are less commonly observed for organometallic complexes. Hydrogen transfer, as a proton[4] and as an atom,[5] has been reported. The

Table I. Carbonyl Stretching Frequencies of the Alkyl Complexes in Hexane

compound	ν_{CO} (cm^{-1})
$Mn(CO)_5Me$	2110 (w), 2012 (s), 1991 (s)
$Re(CO)_5Me$	2127 (w), 2041 (w), 2013 (s), 1983 (s)
$CpFe(CO)_2Me$	2014 (s), 1960 (s)
$CpMo(CO)_3Me$	2024 (s), 1941 (s)
$CpMo(CO)_3Et$	2009 (s), 1935 (s)
$Mn(CO)_5CH_2Ph$	2107 (s), 2043 (w), 2010 (s), 1992 (s)
$CpMo(CO)_3CH_2Ph$	2019 (s), 1944 (sh), 1936 (s)
$PhMn(CO)_5$	2115 (m), 2045 (w), 2020 (s), 1998 (s), 1985 (w)

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Table II. Rate Constants for Reaction of $(PPN)CpFe(CO)_2$ with Alkyl Complexes

alkyl compd	k (s^{-1} M^{-1})
$Mn(CO)_5Me$	$(1.2 \pm 0.1) \times 10^2$
$CpMo(CO)_3Me$	$(1.1 \pm 0.1) \times 10^3$
$CpMo(CO)_3Et$	$(4.0 \pm 0.3) \times 10^2$
$Mn(CO)_5CH_2Ph$	$(9.2 \pm 1.2) \times 10^2$
$CpMo(CO)_3CH_2Ph$	fast
$CpMo(CO)_3H$	fast

most comprehensive examination of proton transfer has come from the Norton group.[4a–f] Quite recently Kristjánsdôtter and Norton reported that transfer of a proton between group 6 species $CpM(CO)_3H$ and $KCpM(CO)_3$ follows the Marcus theory for proton transfer.[4f] A few examples of halogen atom transfer have also been reported.[6] Self-exchange reactions between $CpM(CO)_3X$ and $CpM(CO)_3^-$ were reported as a measure of intrinsic barriers.[6a]

Methyl transfer between MeI and a metal carbonyl anion is used to measure nucleophilicity of the metal carbonyl anions.[7] However, examples of alkyl transfer between two transition metal centers have not been extensively studied.[8–12] Casey and coworkers examined reactions of several metal carbonyl anions with methyl complexes as a possible route to carbene complexes.[8] In several cases transfer of a methyl was observed by ^1H NMR spectroscopy, and a reactivity order based on nucleophilicity was suggested.[8]

In this paper we report the transfer of Me^+, $PhCH_2^+$, Et^+, and a proton between metal carbonyl anions and establish a reactivity order for the group transferred and for the metal carbonyl anions that is consistent with a nucleophilic attack mechanism.

Experimental Section

The metal carbonyl dimers ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$, and $Cp'_2Mo_2(CO)_6$ ($Cp' = \eta^5\text{-}C_5H_4Me$)) were purchased from Strem Chemical and used as received. Solvents (THF, hexanes, d_8-THF, and d_6-acetone) were dried and degassed prior to use. All manipulations, unless otherwise indicated, were accomplished in an inert atmosphere glovebox under an argon atmosphere. Infrared spectra were recorded on a Mattson Polaris Fourier transform infrared spectrometer in 0.5-mm cells. NMR spectra were obtained using a Varian VXR-400 NMR spectrometer. The metal carbonyl anions were prepared as previously described.[13]

Preparation of Alkyl Compounds. Methyl complexes and $CpMo(CO)_3Et$ were prepared from reaction of the alkyl iodide with the sodium salt of the metal carbonyl anion.[14] An excess of the alkyl iodide was stirred with the metal carbonyl anion in THF at 25 °C for 2 h. The THF and alkyl iodide were removed by vacuum, and the compounds were purified by sublimation. $CpFe(CO)_2Me$ and $CpMo(CO)_3Me$ were sublimed at 40 °C in dynamic vacuum; because of their volatility, $Mn(CO)_5Me$ and $Re(CO)_5Me$ were sublimed under static vacuum. The benzyl derivatives, $Mn(CO)_5(CH_2Ph)$ and $CpMo(CO)_3(CH_2Ph)$, were prepared from benzyl chloride and the sodium salt of a metal carbonyl anion in diethyl ether.[6,14] Following filtration to remove NaCl, the filtrate was cooled to −80 °C and the crystalline product was collected on a sintered-glass filter. The phenyl complex ($PhMn(CO)_5$) was prepared by a literature procedure.[15] The infrared spectra of the compounds, reported in Table I, are in good agreement with the literature values.[8a,16] The ^1H NMR spectra are also consistent with the formulation: $Mn(CO)_5Me$ (d_6-acetone) −0.13 (s) ppm; $Re(CO)_5Me$ (d_6-acetone) −0.25 (s) ppm; $CpFe(CO)_2Me$ (d_6-acetone) 0.10 (s), 4.90 (s) ppm; $CpMo(CO)_3Me$ (d_6-acetone) 0.33 (s), 5.40 (s) ppm; $Mn(CO)_5CH_2Ph$ (d_8-THF) 2.39 (s), 6.88–7.13 (m) ppm; $CpMo(CO)_3CH_2Ph$ (d_8-THF) 2.90 (s), 5.34 (s), 6.89–7.18 (m) ppm.

Table III. Products and Yields from Reaction of $CpFe(CO)_2^-$ with Alkyl Complexes

reactant	products	yield (%)
$HMoCp(CO)_3$	$CpMo(CO)_3^-$, $HFeCp(CO)_2$	100
$CH_3Mn(CO)_5$	$Mn(CO)_5^-$, $CH_3FeCp(CO)_2$	91
$CH_3MoCp(CO)_3$	$CpMo(CO)_3^-$, $CH_3FeCp(CO)_2$	93
$EtMoCp(CO)_3$	$CpMo(CO)_3^-$, $EtFeCp(CO)_2$	95
$PhCH_2Mn(CO)_5$	$Mn(CO)_5^-$, $PhCH_2FeCp(CO)_2$	100
$PhCH_2MoCp(CO)_3$	$CpMo(CO)_3^-$, $PhCH_2FeCp(CO)_2$	98

Kinetic Studies. The kinetic data were obtained on our infrared stopped-flow spectrometer with the data manipulated by the OLIS stopped-flow operating system.[17] All reactions were examined in THF solution under pseudo-first-order conditions with the alkyl complex in excess. The PPN^+ salts were used to minimize ion-pairing interactions. The rate of disappearance of $CpFe(CO)_2^-$, initially present at a concentration of 0.001 M, was determined by following the absorbance at 1790 cm^{-1}. Rate constants were determined as the slope of plots of k_{obsd} versus [RM]. Error limits of k_{obsd} are standard deviations; error limits in k values are 95% confidence limits. The rate constants are presented in Table II.

The self-exchange reaction between $CpFe(CO)_2^-$ and $CpFe(CO)_2Me$ was studied by line broadening of the Cp NMR resonances at room temperature. The exchange of Me between $CpMo(CO)_3Me$ and $Cp'Mo(CO)_3^-$ ($Cp' = \eta^5\text{-}C_5H_4Me$) was studied by integration of the ^1H NMR signals of spectra recorded for several days.

Results and Discussion

Reactions of $CpFe(CO)_2^-$ with alkyl and hydride complexes of manganese and molybdenum lead to transfer of the group quantitatively.[16]

$$CpFe(CO)_2^- + RM \rightarrow RFeCp(CO)_2 + M^- \qquad (1)$$

$$M = Mn(CO)_5;\ R = Me,\ CH_2Ph$$

$$M = CpMo(CO)_3;\ R = H,\ Me,\ Et,\ CH_2Ph$$

The reactants, products, and measured yields are shown in Table III. In addition, methyl transfer can be observed between other metal carbonyl anions, though the reactions are not as clean.

$$M'^- + MeM \rightarrow MeM' + M^- \qquad (2)$$

$$M' = CpFe(CO)_2,\ M = Re(CO)_5$$

$$M' = Re(CO)_5,\ M = Mn(CO)_5 \text{ or } CpMo(CO)_3$$

The products of reactions 1 and 2 are separated and characterized by infrared and NMR spectroscopies.

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(18) THF was the solvent for each reaction. The anions were characterized by infrared spectra in THF solution.[16] The THF was removed by vacuum, and the methyl compounds were extracted into hexanes for identification by infrared analysis.

Low-temperature ^{1}H NMR spectroscopy provides no evidence for intermediates. Even at −70 °C, $Mn(CO)_5Me$ began to react with $(PPN)CpFe(CO)_2$. As the temperature was increased, only $CpFe(CO)_2Me$ (0.10 (s) ppm) was observed. Similarly, reaction of $Mn(CO)_5CH_2Ph$ with $NaCpFe(CO)_2$ showed a smooth decrease in $Mn(CO)_5CH_2Ph$ (2.36 (s) ppm) resulting in an increase in $CpFe(CO)_2CH_2Ph$ (2.66 (s) ppm). In neither reaction were any unidentified resonances observed.

Reaction of $Mn(CO)_5Ph$ with $CpFe(CO)_2^-$ is not a clean reaction.

$$Mn(CO)_5Ph + CpFe(CO)_2^- \rightarrow Mn(CO)_5^- + CpFe(CO)_2Ph + Cp_2Fe_2(CO)_4 \quad (3)$$

This reaction is slower and involves formation of the iron dimer, $Cp_2Fe_2(CO)_4$. The $Mn(CO)_5^-$ formed represents an ~70% yield.

The reaction of $CpFe(CO)_2^-$ with $HMoCp(CO)_3$ resulting in proton transfer would not be predicted from the homolytic bond dissociation energies,[19] but is consistent with the pK_a values.[4] The lack of correlation between homolytic bond dissociation energies and pK_a values has been previously noted.[19] For the methyl complexes the reactivity would indicate that transfer of CH_3^+ between two metal carbonyl anions occurs in the following order:

$$MeFeCp(CO)_2 < MeRe(CO)_5 < MeMn(CO)_5 < MeMoCp(CO)_3$$

This order is exactly the same as observed for CO^{2+} transfer[13] and similar to the order of pK_a's of the hydrides except that for pK_a's the $HRe(CO)_5$ and $HFeCp(CO)_2$ are reversed.[4]

Kinetics. For the reactions represented by eq 1 we have examined the kinetics by stopped-flow infrared spectroscopy.[17] For each reaction examined, the rate shows a first-order dependence on the concentration of the alkyl complex and on $[CpFe(CO)_2^-]$.

$$\text{rate} = k[CpFe(CO)_2^-][RM] \quad (4)$$

The rate constants reported in Table II were obtained under pseudo-first-order conditions from plots of k_{obsd} versus [RM]. The dependence of the rate constant on the R group,

$$H > CH_2Ph > Me > Et > Ph$$

spans at least 3 orders of magnitude. The proton transfer was too rapid for examination on our system. The Ph group transfer (reaction 3) was slow and was not examined kinetically.

The effect of the countercation on reactions of the metal carbonyl anions has typically been small and variable depending on the oxidant.[20] For reaction of $CpMo(CO)_3Me$ with $NaCpFe(CO)_2$ the rate constant is substantially lower ($k = 16 \pm 2$ M^{-1} s^{-1}) than for the PPN salt. This decreased reactivity was also observed for reaction of $NaCpFe(CO)_2$ with the benzyl complex, $CpMo(CO)_3CH_2Ph$, allowing an estimate for the reactivity towards transfer of the benzyl group. Reaction of $CpMo(CO)_3H$ with $NaCpFe(CO)_2$ was too rapid to be examined on our stopped-flow system.

Mechanism. The dependence on the group transferred is a strong indication that nucleophilic attack on the organic fragment is important in the mechanism.[21] Formally one may consider the transfer to be as R^+ with the two metal carbonyl anion nucleophiles competing. The more nucleophilic anion retains the R^+. Such a competition has also been used to describe transfer (formally) of H^+ and CO^{2+} between metal carbonyl anions. The very clean formation of the new alkyl complex and metal carbonyl anion and the absence of dimers are strong evidence against a single electron transfer mechanism.

Reaction of the phenyl complex, $PhMn(CO)_5$, with $CpFe(CO)_2^-$ probably occurs by a different mechanism, as expected since nucleophilic attack on the phenyl is unlikely. In this case, formation of $Cp_2Fe_2(CO)_4$ *may* indicate a single electron transfer process.

Previous studies of methyl transfer between two metal centers have also concluded that a nucleophilic mechanism is operative.[8-12] The rate of methyl transfer between $CpMo(CO)_3^-$ and $CpFe(CO)_2^-$ lies intermediate between the rates for transfer of methyl between two iodides[3b] and between cobalt macrocycles that serve as mimics of vitamin B12.[3a] That transfer of an ethyl is slower than transfer of a methyl is also consistent with nucleophilic attack, though the magnitude of the difference is not as large as for transfer between other metal centers.[22] Methyl transfer between different metal carbonyl anions is completely consistent with the nucleophilicity of the metal carbonyl anions.[7] The rate appears to be dependent on the difference in nucleophilicity between the reactant and product metal carbonyl anions. Thus for reactions with $CpFe(CO)_2^-$, the rate of methyl transfer from $MeMoCp(CO)_3$ is faster than that for $MeMn(CO)_5$. For reaction of different anions with $MeMoCp(CO)_3$, the reactivity order for abstraction of methyl is $CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^-$. In organic terminology the first trend would be attributed to $CpMo(CO)_3^-$ being a better leaving group than $Mn(CO)_5^-$. The trend in rates for anion reaction with $MeMoCp(CO)_3$ would be interpreted as faster displacement by the more nucleophilic anion. For the metal carbonyl anions, both of these effects can be accommodated by a faster rate of CH_3^+ transfer as the difference in nucleophilicity between the metal carbonyl anions increases.

Marcus-Type Analysis. Marcus analysis of outer sphere electron transfer is quite generally used.[24] Recently a similar analysis was shown to be valid for proton transfer between transition metal systems.[4f,25] Analysis of methyl transfers by Marcus relationships has been accomplished for a few organic reactions[26] but, to our knowledge, has not been applied to transfer between transition metal complexes.

For the relative Marcus-type analysis, the rate constant is related to the rate constants for self-exchange reactions.[24]

$$k_{12} = (k_1 k_2 K_{12})^{1/2} \quad (5)$$

Thus the self-exchange reactions

$$CpFe(CO)_2^- + MeFeCp(CO)_2 \rightleftarrows \quad (6)$$

$$CpMo(CO)_3^- + MeMoCp(CO)_3 \rightleftarrows \quad (7)$$

must be evaluated. Self-exchange for the iron complex is at a rate appropriate for examination by line broadening. Such an analysis gives a rate constant of 50 ± 20 s^{-1} M^{-1} for reaction 6. The molybdenum self-exchange reactions are much slower; to obtain an estimate of the rate constant, we have examined the reaction of $Cp'Mo(CO)_3^-$ with $MeMoCp(CO)_3$ ($Cp' = \eta^5\text{-}C_5H_4Me$).

$$Cp'Mo(CO)_3^- + MeCpMo(CO)_3 \rightleftarrows MeMoCp'(CO)_3 + CpMo(CO)_3^- \quad (8)$$

This reaction equilibrated over several days. Kinetic analysis[27] shows the rate to best fit a rate law that is first order in $CpMo(CO)_3Me$ and independent of $Cp'Mo(CO)_3^-$. The rate constant of 5.3×10^{-6} s^{-1} is about 1 order of magnitude slower than the rate of methyl migration under similar conditions.[28] Thus

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$$A = \frac{[CpMo(CO)_3Me]}{[CpMo(CO)_3Me] + [CpMo(CO)_3]}$$

and plotted $\ln [(A - A_\infty)/(A_0 - A_\infty)]$.

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the rate constant is probably a reflection of the methyl migration and not an accurate measure of the self-exchange rate constant between two molybdenum centers. The self-exchange rate must be slower than the rate of methyl migration to a CO. The reported value for self-exchange of methyl between two tungsten centers is also quite slow.[6a]

The equilibrium constant for the cross reaction,

$$\mathrm{CpFe(CO)_2^- + MeMoCp(CO)_3 \rightarrow MeFeCp(CO)_2 + CpMo(CO)_3^-} \quad (9)$$

is also required. For this reaction there is no trace of the reactants by ^{1}H NMR or IR spectroscopy after the reaction, indicating an equilibrium constant that is large, at least $>10^4$. Using the pK_a values[4] as a means to approximate the equilibrium constant gives a value of $K_{eq} = 10^6$. Using this value for K_{eq} and the self-exchange values of k_1 (for Fe, reaction 6) = 50 s^{-1} M^{-1} and k_2 (for Mo, reaction 7) <5.3 × 10^{-4} s^{-1} M^{-1} gives

$$k_{12} = [(50\ \mathrm{s^{-1}\ M^{-1}})(5.3 \times 10^{-4}\ \mathrm{s^{-1}\ M^{-1}})(10^6)]^{1/2} = 200\ \mathrm{s^{-1}\ M^{-1}}$$

This value is in moderate agreement with the observed value of 1100 s^{-1} M^{-1}. Thus the methyl transfer may obey relative Marcus-type relationships, but uncertainty in the value for the CpMo(CO)$_3^-$/CpMo(CO)$_3$Me self-exchange rate constant and in the equilibrium constant for reaction 9 prohibits a more detailed analysis. Similar analysis for CH$_3^+$ transfer between two organic nucleophiles[26] indicates reasonable utility of eq 5 for methyl-transfer reactions.

Conclusion

The results reported in this paper show that transfer of alkyl groups between metal carbonyl anions is closely related to organic nucleophilic displacement reactions in reactivity and mechanism. This represents the first comparison of transfer of different alkyl groups between transition metal centers.

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Supplementary Material Available: Plots of the absorbance change at 1790 cm^{-1} for reaction of MeMn(CO)$_5$ with CpFe(CO)$_2^-$, [MeMn(CO)$_5$] versus k_{obsd}, and line width of the Cp resonance of CpFe(CO)$_2^-$ versus [MeFeCp(CO)$_2$] for the self-exchange reaction (3 pages). Ordering information is given on any current masthead page.

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Multichromophoric Cyclodextrins. 1. Synthesis of *O*-Naphthoyl-β-cyclodextrins and Investigation of Excimer Formation and Energy Hopping

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Abstract: The synthesis and photophysical properties of β-cyclodextrins bearing seven 2-naphthoyloxy chromophores in specific positions, either on the primary face or the secondary face, or 14 2-naphthoyloxy chromophores, seven on each face, are reported. These multichromophoric cyclodextrins are good models for the study of excitation energy migration among chromophores in well-defined positions. The investigation was performed in dichloromethane and in a mixture of ethanol and methanol that can form a glass at low temperature. The absorption spectra show that the interactions between chromophores in the ground state are weak, whereas the fluorescence spectra reveal the existence of excimers at room temperature but not at low temperature in a rigid glass. Further evidence of excimer formation is provided by the fluorescence decays. Since excimers act as energy traps, the energy hopping process was studied in a rigid glass at low temperature by steady-state and time-resolved fluorescence depolarization techniques. The steady-state anisotropy is found to be one seventh of the theoretical limiting anisotropy 0.4, which means that excitation energy hops between chromophores with essentially randomly oriented transition moments at a rate much higher than the chromophore intrinsic decay rate. Energy hopping is indeed very fast as shown by the fluorescence anisotropy decay which is at least as fast as the apparatus time resolution (a few tens of picoseconds).

Introduction

In recent years, there has been a great deal of activity devoted to supramolecular photophysics and photochemistry.[1-4] Among the systems investigated, cyclodextrins (CD's) (cyclic oligosaccharides composed of six (α-CD), seven (β-CD), or eight (γ-CD) D-(+)-glucopyranose units) have been the object of special attention because of their ability to form supramolecular species by enclosing various compounds undergoing specific photoprocesses.[3,5,6]

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