two energy transitions (347, 418 nm) can be assigned to a mixture of \( d \rightarrow \text{metallacycle} \) \( \pi^* \) and metallacycle \( \pi \rightarrow \pi^* \) transitions. These assignment is quite similar to those assigned to the complex \( \text{CpCo} (1,4-\text{R}_2\text{N})_6 \). The extinction coefficients (13500, 6800 \( \text{M}^{-1} \text{cm}^{-1} \)) tell us that these transition are charge-transfer bands. The transition at 642 nm is assigned to a \( d \rightarrow d \) transition.

**Electrochemistry.** Complex II displays a quasi reversible reduction in the cyclic voltammogram at a potential of \(-1.52 \text{ V vs an SCE reference. The voltammogram of complex II is shown in Figure 2. Electrochemical data for C}_{\text{p}}^* \text{M} (1,4-\text{R}_2\text{N})_6 \) is listed in Table 5. At slow scan rate (50 mV/s) the reduction of II becomes irreversible, which suggests the anion radical is unstable.

**Acknowledgement.** This work was supported by grants from the Korea Research Foundation 1993.

**References**


# Comparison of the Ligating Ability of Anionic Transition Metal Complex (Mn(CO)$_5^-$), Transition Metal Hydrides (HCr(CO)$_5^-$, HW(CO)$_5^-$, cis-HW(CO)$_4$P(OMe)$_3^-$, HFe(CO)$_4^-$, trans- HFe(CO)$_3$P(OMe)$_3^-$), and Traditional Ligands (Br$^-$, P(C$_6$H$_5$)$_3$) to M(CO)$_5^0$ (M=Cr, W)

Yong K. Park, In S. Han, and Marcetta Y. Darenbourg$^*$

$^*$Department of Chemistry, Kangwon National University, Chuncheon 200-701

Department of Chemistry, Texas A & M University, College Station, Texas 77843, U. S. A.

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Heterobimetallic complexes have a donor-acceptor metal-metal bond in which two electrons from the electron-rich metal moiety are donated to the other electron-deficient one. Based on the competition reactions, Cotton-Kraihanzel force constants, $v$(CO)IR band resolution and the relative nucleophilicity comparison of the donor ligands, the following relative ligating ability of the donor ligands toward M(CO)$_5$ (M=Cr, W) is assessed: cis-HW(CO)$_4$P(OMe)$_3^-$, HW(CO)$_5^-$ > HCr(CO)$_5^-$ > Br$^-$ > trans-HFe(CO)$_3$P(OMe)$_3^-$ > Mn(CO)$_5^-$ > HFe(CO)$_4^-$ > PPh$_3$

**Introduction**

The chemistry of the heterobimetallic complexes is a rapidly exploring area of inorganic and organometallic chemistry. Heterobimetallic complexes with substantially different chemical properties are inherently of importance due to the
possibility that they may lead to unusual bifunctional activation of organic substrates.\textsuperscript{2}

Heterobimetallic complexes can be prepared either by homolytic cleavage of dimer followed by recombination, Lewis acid-base adduct formation, or binuclear reductive elimination.\textsuperscript{18} Heterobimetallic complexes have a donor-acceptor metal-metal bond in which two electrons from the electron rich metal moiety are donated to the other electron deficient one. Thus, this electron deficient transition metal group will satisfy the EAN.\textsuperscript{10,12} It is of interest to study the formation and stability of mixed metal complex anions; $\text{Mn}M(CO)_{10}^-$ (M = Cr, W)\textsuperscript{4}, $\text{HFeM(CO)_{10}^-}$ (M = Cr, W) and $\text{HFe(CO)_{5}}P\text{(OMe)}_2\text{W(CO)_{5}}$\textsuperscript{4,5,6}, $\mu\text{-HCrW(CO)_{10}}$\textsuperscript{6}.

It is also interesting to allow such "18-electron donor (metal complex) ligand" to compete (both in terms of formation and thermodynamic stability) with traditional ligands such as PR$_3$ or X" for M(CO)$_6$ (M = Cr, W) Lewis acid acceptor. The relative reactivity of each electron donor ligand can be measured through the competition reaction as in Eq. (1).

$$L: \text{M(CO)_{6}} \rightarrow \text{M'CO}_{\text{L}} \rightarrow \text{M'CO}_{\text{L}} $$

Experimental

Materials. Solvents were distilled under nitrogen from appropriate O$_2$ scavenging and drying agents. Tetrahydrofuran (THF) and toluene were distilled under nitrogen from sodium/benzophenone ketyl. Hexane was purified by stirring over concentrated H$_2$SO$_4$ overnight, then washing with aqueous NaHCO$_3$ and distilling from sodium/benzophenone ketyl. Aconitine was purified by distillation from calcium hydride, followed by P$_2$O$_5$ drying before being stored over 3-Å molecular sieves. Methylene chloride was distilled from P$_2$O$_5$ under nitrogen. Ethanol and n-butanol were distilled from calcium hydride. Bis (triphenylphosphine) nitrogen (1+) chloride (PPN$^+$Cl$^-)$ was purchased from Aldrich. All other chemicals were purchased from commercial suppliers and used without further purification.

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer with 0.10-mm sealed CaF$_2$ or NaCl solution cells. $^1$H-NMR spectra were recorded on a Bruker WM-300 spectrometer and all the chemical shifts are referenced to CDCl$_3$. Photoreactions were performed with a 450 watt mercury vapor lamp (Hanovia). Unless stated otherwise, all reactions were carried out under nitrogen in a Vacuum Atmosphere glovebox, or in an inert atmosphere using Schlenk techniques.

Preparations. [$\text{M(CO)_{6}}$ (THF)] (M = Cr, W)\textsuperscript{18} PPN$^+$[Mn (CO$_6$)$_7$] and PPN$^+$[CrMn(CO)$_{10}$]$^4$ were prepared according to the cited literatures. The metal carbonylates were prepared from Na/Hg reduction of the corresponding metal carbonyl dimers.$^8$

PPN$^+$HM(CO)$_6$ (M = Cr, W) were synthesized by the borohydride method.$^9$ PPN$^+$cis-HW(CO)$_5$P(OMe)$_2$ and PPN$^+$HFe(CO)$_5$\textsuperscript{11} were prepared according to the literature procedures. PPN$^+$trans-HFe(CO)$_5$P(OMe)$_2$ was prepared by a procedure similar to that reported by Edens$^{10}$ and Ellis$^{15}$.

Competition Reaction of Anionic Metal Hydride and Transition Metal Anion, or Traditional Ligand Toward Group 6B Metal Pentacarbonyl. Usually two competing reactants (0.05 mmol, each) were mixed in a 10 ml volumetric flask which was then sealed tightly with a septum under N$_2$ atmosphere at room temperature. A freshly prepared THF solution (10 ml) of Cr(CO)$_5$.THF (0.05 mmol) was added quickly to this solution with stirring at ambient temperature. The competition reactions were usually monitored by v(CO) IR spectroscopy. v(CO)IR spectra were obtained successively during 3 hrs of the reaction time starting within minutes from the initiation of the reaction. The approximate % yields could be calculated, based on the Beer's law plot (absorbance vs. concentration of v (CO) peak) of the reaction(s), or the expected product(s) of the same concentration(s).

Thermal Reactions of Cr(CO)$_5$PR$_3$ (R = CH$_3$, or C$_6$H$_5$) with either PPN$^+$HCr(CO)$_5$ or -Br. THF solution (10 ml) of PPN$^+$HCr(CO)$_5$ (0.05 mmol) was added to Cr(CO)$_5$P(CH$_3$) (0.05 mmol) in a 10 ml volumetric flask via cannula. This reaction mixture was stirred for a few min. and then placed in a silicone oil bath set at 60°C for 19 hrs. The reaction was monitored by v(CO)IR spectroscopy. In case of the thermal reaction of Cr(CO)$_5$P(C$_6$H$_5$)$_3$ with PPN$^+$Br, THF solution (10 ml) of Cr(CO)$_5$ (0.05 mmol) was added to P(C$_6$H$_5$)$_3$ (0.05 mmol) in a 10 ml volumetric flask, tightly rubber-septum, via cannula and the flask was placed in a silicone oil bath where the solution was stirred at 50°C for about 18 hrs. The formation of Cr(CO)$_5$P(C$_6$H$_5$)$_3$ was confirmed by v(CO)IR. The solution was transferred to another 10 ml volumetric flask to which 9-fold excess of PPN$^+$Br (0.25 mmol) was added. This reaction mixture was then heated to 50°C in the same bath for 7 hrs. The reaction was monitored by v(CO)IR spectroscopy.

Temperature-Dependent Competition Reaction of PPN$^+$Mn(CO)$_{15}$ and PPN$^+$HFe(CO)$_5$ with Cr(CO)$_5$. THF. A THF solution (10 ml) of Cr(CO)$_5$.THF (0.05 mmol) kept in a dry-ice/acetone bath (−78°C) for a while was cannulated into a mixture of PPN$^+$Mn(CO)$_{15}$ (0.05 mmol) and PPN$^+$HFe(CO)$_5$ (0.05 mmol) in a rubber septum 10 ml volumetric flask in a dry ice/acetone bath. This reaction mixture was kept cold at −78°C for 20 min. and then an aliquot of the solution was taken for v(CO)IR spectrum. After the initial spectrum was obtained, the reaction mixture was allowed to warm up to ambient temperature. Subsequent v(CO)IR spectra were obtained at 1 hr and at about 18 hrs reaction times.

Thermal Reaction of PPN$^+$CrMn(CO)$_{10}$ with PPN$^+$HCr(CO)$_5$. A THF solution (10 ml) of Cr(CO)$_5$.THF (0.01 mmol) was added to PPN$^+$Mn(CO)$_{15}$ (0.10 mmol) in a tightly septed 100 ml Schlenk flask via cannula. This solution was then stirred at ambient temperature for 2 hrs. V(CO)IR spectra confirmed the product to be PPN$^+$CrMn(CO)$_{10}$. A THF solution (10 ml) of PPN$^+$HCr(CO)$_5$ (0.10 mmol) was added to the reaction mixture. After attaching a water-cooled condenser to the Schlenk flask, the solution was placed in a silicone oil bath set at 80°C for 4 hrs. The reaction was monitored both by v(CO)IR and $^1$H-NMR.

Reaction of PPN$^+$HFeCr(CO)$_5$ with PPN$^+$Mn(CO)$_{15}$. THF (20 ml) was added to the mixture of PPN$^+$HFeCr(CO)$_5$ (0.10 mmol) and PPN$^+$Mn(CO)$_{15}$ (0.03 mmol) in a 25 ml volumetric flask via cannula at ambient temperature. This reaction was monitored by v(CO)IR for 3 hrs.

Beer's Law Plot (Absorbance vs. Concentration).
To each species was added degassed THF (10 mL) to prepare $5 \times 10^{-3}$, $1.5 \times 10^{-3}$ and $2.0 \times 10^{-3}$ M solutions by dilution. The ν(CO)IR spectra were obtained for each solution for each compound. The transmittance base line was set to 95% initially. Attempts were made to plot the absorbance of each band of one species against its concentration.

**Cotton-Kraihanzel Force Constant.** Cotton-Kraihanzel force constants were calculated for $C_\omega$ Mn(CO)$_5$ (M = Cr, W) fragments bound to various ligands including metallas- liones. The ligands used here are THF, PPh$_3$, Br$^-$, HFe(CO)$_5$-, and Co(CO)$_5$-. All the ν(CO)IR spectra were measured in THF solution. Among ν(CO)IR stretching modes for $C_\omega$, $A_1$, $E$, and $A_1$ are IR-active bands and their relative intensities are weak, strong and medium respectively. From the corresponding approximate secular equations, $k_1$ (axial), $k_2$ (equatorial) force constants and $k_i$ (cis interaction constant) could be derived.

**Results and Discussion**

Our study is focused mainly on the formation and stability of the dimeric mixed metal complex anions: MnM(CO)$_{10}$ (M = Cr, W), HFeM(CO)$_5$ (M = Cr, W), HFe(CO)$_5$P(OMe)$_2$W(CO)$_5$-, and HCrW(CO)$_9$-. All the compounds are prepared in ligand-displacement reaction of the photochemically generated M(CO)$_5$THF (M = group 6 transition metals) complexes. These heterobimetallic species are formed through metal-metal donor-acceptor bonds Eq. (2) and (3), or through a hydride (H$^-$) bridging two metal atoms Eq. (4).

$$\text{Mn(CO)}_5^+ + \text{Cr(CO)}_5^- \text{THF} \rightarrow (\text{OC})_2\text{Mn}^- \rightarrow \text{Cr(CO)}_5^- $$ (2)

$$\text{HFe(CO)}_5^+ + \text{W(CO)}_5^- \text{THF} \rightarrow (\text{OC})_2\text{HFe}^- \rightarrow \text{W(CO)}_5^- $$ (3)

$$\text{HCr(CO)}_5^- + \text{Cr(CO)}_5^- \text{THF} \rightarrow (\text{OC})_2\text{CrH}^- \rightarrow \text{Cr(CO)}_5^- $$ (4)

Here in the above equations the metal hydrides are assumed to be nucleophiles, with a pair of electrons in the M-H bond rendering a three-center two-electron M-H-M bond.\textsuperscript{24} Bergman and coworkers found that in the competition reaction of CpV(CO)$_2$H$^-$ against PPh$_3$, CpV(CO)$_2$H$^-$ reacts more rapidly with the phosphine with transient, coordinatively unsaturated CpV(CO)$_5$, but PPh$_3$ is thermodynamically better ligand.\textsuperscript{15}

This study demonstrated that PPh$_3$ is clearly a thermodynamically better ligand for vanadium than CpV(CO)$_2$H$^-$.

**ν(CO)IR Band Resolution for HFeW(CO)$_5$-.** The ν(CO)IR spectrum for HFeW(CO)$_5$- with $C_\omega$ symmetry yields 9 active and allowed IR bands. The observation of fewer bands than is predicted by group theory suggests the bands are possibly overlapping, hence an alternate analysis (a local symmetry approach) is possible. Figure 1 shows the possible ν(CO)IR stretching modes of HFeW(CO)$_5$- analyzed in terms of the fragments 1a and 1b. A maximum of 7 bands is possible assuming the donor ligand 1a has $C_5$ symmetry and acceptor, 1b has $C_\omega$ symmetry.

X-ray structure analyses\textsuperscript{16} have shown the iron carbonyl moiety to have substantial tetrahedral character similar to H$_2$Fe(CO)$_5$ or (P$_3$P$_3$P$_3$)$_2$Fe(CO)$_5$.\textsuperscript{17} When a ν(CO)IR pattern similar to that of (P$_3$P$_3$P$_3$)$_2$Fe(CO)$_5$ is subtracted from the ν(CO)IR of HFeW(CO)$_5$-, a three-band pattern remains. This band pattern is quite similar to the ν(CO)IR of W(CO)$_5$-. THF. Based this result it is assumed that substantial negative charge is located on HFe(CO)$_5$ moiety of the heterobi- metallic complex and slightly actual electron transfer to the W(CO)$_5$ occurs.

**Attempted ν(CO)IR Band Resolution for CrMn(CO)$_{10}$-.** The heterobimetallic anion MnCr(CO)$_{10}$, originally prepared and characterized by Graham and Anders,\textsuperscript{40} is isoelectronic with the homobimetallic Mn$_2$(CO)$_{10}$ and Cr$_2$(CO)$_{10}$\textsuperscript{2}. Attempts were made to use the local symmetry approach to analyze the ν(CO)IR spectrum of CrMn(CO)$_{10}$ prepared by the reaction of Mn(CO)$_5^-$ with Cr(CO)$_5$THF photochemically generated. Graham assumed that negative charge resides on Cr(CO)$_5$ moiety of CrMn(CO)$_{10}$-. However, in analogy with the HFeW(CO)$_5$- anion it might be argued that the typically anionic fragment Mn(CO)$_5^-$ might retain much of the negative charge.

Graham assigned the bands at 2065 (w), 1950 (s), and 1925 (m) cm$^{-1}$ to $C_\omega$, Mn(CO)$_5$ fragment similar to RMn(CO)$_6$ and bands at 1900 (s), 1896 (s), 1865 (m) cm$^{-1}$ to a $C_\omega$, Cr(CO)$_5$- fragment similar to ClCr(CO)$_5$-. This assignment was accepted by others.\textsuperscript{40} However, the charge distribution in CrMn(CO)$_{10}$- assigned by Graham,\textsuperscript{40} Onaka,\textsuperscript{16} and Risen, et al.\textsuperscript{16} should be considered very cautiously because there are major differences in the ν(CO)IR intensity pattern of Cr(CO)$_5$- and Cm, Cr(CO)$_5$. The deconvolution of the ν(CO)IR spectrum for CrMn(CO)$_{10}$- into six bands does not give two sets of three bands of intensity patterns that could plausibly be assigned to two non-interacting $C_m$ centers. In fact considerable coupling of CO vibrations in this heterobimetallic complex occurs and the local symmetry approach is not applicable. The major, most intense band (band 3 in Figure 2) may not represent the band from one of the $C_m$ fragments, Cr(CO)$_5$ and Mn(CO)$_5$-. (Comparison of the deconvoluted spectrum rules out this possibility as shown in Figure 2, but rather a band arising from the discrete CrMn(CO)$_{10}$- species.

**Cotton-Kraihanzel force Constants.** The ν(CO) band maxima and Cotton-Kraihanzel force constants for the M(CO)$_5$ (M = Cr, W) component of HFeW(CO)$_5$- are compared with those of other donor ligands in Table 1. According to these results, HFe(CO)$_5$- ligand affects the M(CO)$_5$ fragment most similarly to the 8-donor, THF. The lower force constants of BrM(CO)$_5$- suggest the anionic bromide ligand transfers more electron density to M(CO)$_5$ than does HFe(CO)$_5$- or THF. But HFe(CO)$_5$- donates more electron den-
Ligating Ability Comparison of Transition Metal Complexes

Figure 2. Deconvolution of ν(CO)IR spectrum for [PPN][CrMn(CO)₅]. The total area under the six deconvoluted bands is equal to 21.84. The combined area under fragment bands 1, 4, and 3 is equal to 14.32 or 66% and the combined area under fragment bands 2, 5, and 6 is equal to 7.52 or 34%.

Table 1. ν(CO)IR Data and Cotton-Kraihanzel Force constants for C₄H₂M(CO)₅(M = Cr, W) Fragments Bound to Various Ligands Including Metalloanions

<table>
<thead>
<tr>
<th>Ligand</th>
<th>ν(CO) for M(CO)₅</th>
<th>C-K force constants</th>
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<th>M = W</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>A₁⁺ E</td>
<td>A₁⁻ K₁</td>
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<tr>
<td>Ar</td>
<td>2092 1965 1936</td>
<td>15.32 16.24 .34</td>
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<td></td>
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<tr>
<td>PPh₃</td>
<td>2061 1936 1936</td>
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<tr>
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<td>2045 1916 1850</td>
<td>13.97 15.47 .32</td>
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<td>2063 1950 1925</td>
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<td>HFe(CO)₅⁻</td>
<td>2057 1942 1880</td>
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<td>15.26 16.24 .34</td>
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<td></td>
</tr>
<tr>
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<td>2072 1927 1882</td>
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<tr>
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<td>2058 1915 1848</td>
<td>13.96 15.53 .36</td>
<td></td>
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<tr>
<td>Mn(CO)₅⁻</td>
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<td>15.15 15.91 .29</td>
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<tr>
<td>HFe(CO)₅⁻</td>
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<tr>
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<td>2063 1941 1868</td>
<td>14.23 15.84 .31</td>
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*All spectra were measured on THF solutions except for ArM(CO)₅ (Ar matrix). The A₁⁺, E, and A₁⁻ are IR allowed bands under C₄ᵥ symmetry whose relative intensities are weak, strong and medium, respectively. Band positions are 1-2 cm⁻¹. The Cotton-Kraihanzel force constants, K₁ = axial and K₃ = equatorial stretching force constants. K₄ represents the cis interaction constants, K₅ and K₆. The C-K method assumed K₅ = K₆ = K₃ and 2 K₁ = K₅. The bands assigned here are according to the local symmetry approach as discussed: An alternate assignment (A₁⁺, 990 cm⁻¹, E, 1896, and A₁⁻, 1865) yields CK force constants of K₁ = 14.1 and K₃ = 15.0 M⁻¹ cm⁻¹. †Ref. 21.

Table 2. Competition of Metalloanions as Donor Ligand for Photochemically Generated THF·M(CO)₅(M = Cr, W) in THF, 22°C. ¹

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor</th>
<th>M(CO)₅⁻·THF</th>
<th>Products²</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>HFe(CO)₅⁻</td>
<td>Cr</td>
<td>HCr(CO)₅⁻ (100%)</td>
</tr>
<tr>
<td></td>
<td>HCr(CO)₅⁻</td>
<td>Cr</td>
<td>Mn(CO)₅⁻ (70%)</td>
</tr>
<tr>
<td>2</td>
<td>HFe(CO)₅⁻</td>
<td>Cr</td>
<td>CrMn(CO)₅⁻ (70%)</td>
</tr>
<tr>
<td></td>
<td>Mn(CO)₅⁻</td>
<td>Cr</td>
<td>HFeCr(CO)₅⁻ (30%)</td>
</tr>
<tr>
<td>3</td>
<td>HCr(CO)₅⁻</td>
<td>Cr</td>
<td>μ-HCr(CO)₅⁻ (70%)</td>
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<tr>
<td></td>
<td>Mn(CO)₅⁻</td>
<td>Cr</td>
<td>CrMn(CO)₅⁻ (70%)</td>
</tr>
<tr>
<td>4</td>
<td>trans-HFe-</td>
<td>Cr</td>
<td>HFeCr(CO)₅⁻P(OMe)₅⁻</td>
</tr>
<tr>
<td></td>
<td>(CO)₅P(OMe)₅⁻</td>
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<td>CrMn(CO)₅⁻ (70%)</td>
</tr>
<tr>
<td>5</td>
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<td>Cr</td>
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<td>Cr</td>
<td>μ-HCrW(CO)₅⁻ (25%)</td>
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<td>Cr</td>
<td>HCrW(CO)₅⁻ (35%)</td>
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<tr>
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<td>W</td>
<td>HCr(CO)₅⁻ (70%)</td>
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<tr>
<td></td>
<td>HW(CO)₅⁻</td>
<td>W</td>
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</tr>
<tr>
<td>7</td>
<td>HFe(CO)₅⁻</td>
<td>W</td>
<td>HFeW(CO)₅⁻P(OMe)₅⁻</td>
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<td>(CO)₅P(OMe)₅⁻</td>
<td>W</td>
<td>μ-HFe(CO)₅⁻ (100%)</td>
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<td>μ-HFe(CO)₅⁻ (50%)</td>
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<td>Mn(CO)₅⁻</td>
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</tr>
</tbody>
</table>

¹Reactions were carried out on solutions which are 0.012 M in each reactant. ²Conversion of reactants to products in ratios was noted within 3 min. as assessed by IR except where noted. ³The product ratios were determined by ¹H-NMR 30 min after mixing.

Metalloanions to M(CO)₅ than Mn(CO)₅. HFe(CO)₅⁻ is known to have electron density localized mainly on Fe atom although there is slightly more electron density build-up on equatorial COs than axial COs. However, in traditional low-valent metal-ligand terms, Mn(CO)₅⁻ is assumed to have more back donation activity and less donor ability than HFe(CO)₅⁻ because Mn(CO)₅⁻ has 5 COs while HFe(CO)₅⁻ has 4 COs. Therefore, Mn(CO)₅⁻ is well-matched with Cr(CO)₅⁺ and the bonding here is less aptly described as donor-acceptor, or coordinate covalent, but rather mainly covalent. Extended Hückel-type molecular orbital calculation on the M₄(CO)₆ and the related systems finds the HOMO to be σ-bonding between the two metals, and suggests a small contribution from d₃ bonding character in the metal-metal bonding. The slight amount of electron density left on Cr atom, originally donated from Mn(CO)₅⁻, may be shifted to Mn(CO)₅⁺ moiety through dₓ₋dᵧ overlap. Therefore, electron density on CrMn(CO)₅⁻ system would seem to be quite delocalized. This electron delocalization is represented both by the relatively higher ν(CO)IR
and Cotton-Kraihanzel force constants \((K_1, K_2)\) of \(\text{Cr(CO)}^3_6\) moiety of \(\text{CrMn(CO)}^3_9\) compared to those of \(\text{HFeCr(CO)}^5_7\) as shown in Table 1.

Based on the \(v\) (CO) band maxima and Cotton-Kraihanzel force constants, the relative electron donating ability of the ligand to \(\text{M(CO)}^3_5\) \((\text{M} = \text{Cr}, \text{W})\) is represented below:

\[
\text{Br} \overset{>}{\text{HFe(CO)}^3_5} \text{Cr(CO)}^3_5 \overset{>}{\text{THF}} \text{PPh}_{5} \overset{>}{\text{Ar}}
\]

Therefore, this electron delocalization may be the reason why the deconvolution of \((\text{CO})\text{IR} \text{ spectrum of CrMn(CO)}^3_9\) does not work. However, the \((\text{CO})\text{IR} \text{ spectrum of CoW(CO)}^3_5\) \((2063 \text{ w}, 2012 \text{ m}, 1940 \text{ vs}, 1912 \text{ w}, 1868 \text{ m})^21\) does appear to consist of a \(\text{CO}\) fragment and a \(\text{Co(CO)}^3_5\) - donor, analogous to the \(\text{HFeW(CO)}^3_7\) case. According to the Cotton-Kraihanzel force constant, usually \(K_2\) (equatorial stretching force constant) is greater than \(K_1\) (axial stretching force constant); \(K_2 > K_1\) obviously indicates that trans influence is operating in this system.

**Competition Reactions.** Although all the mixed metal anions were prepared in this study by the displacement of labile THF ligand within time of mixing, their relative reactivities could be discerned by competition studies. Table 2 shows various competitors for \(\text{M(CO)}^3_5\cdot\text{THF} \text{ (M} = \text{Cr}, \text{W})\). In all but one case the reactions were complete before an infrared spectrum \((v\) (CO) region) could be taken (5 min.) and the product distribution did not change over the course of 3 hrs reaction time at ambient temperature (20-25°C). The exception was entry 2 in which only approximately 80% reaction occurred within 3 min. When monitored again at 3 hrs, the reaction was complete and the product distribution was the same. It should be noted that there is extensive overlap of \(v\) (CO) bands in the dimeric products and the monomer precursors therefore the product ratios are estimated with the experimental error \((\pm 5\%)\).

The products observed in Table 2, entries 1-3, are both the kinetic and thermodynamic products. Independent experiments have verified that the minor products (\(\text{HFeCr(CO)}^3_5\)) in entries 1 and 2, and \(\text{CrMn(CO)}^3_9\) in entry 3 react with excess anionic reactant slowly at room temperature (several hrs required). On the other hand, when heated in refluxing THF, the \(\text{HFeCr(CO)}^3_5\) reacts with \(\text{M(CO)}^3_5\) to yield \(\text{CrMn(CO)}^3_9\).

The product distributions in Table 2, entries 1-3 show that the hydride which is an active hydride donor, \(\text{HCr(CO)}^3_5\) is a better competitor for \(\text{Cr(CO)}^3_5\cdot\text{THF}\) than \(\text{HFe(CO)}^3_5\) does; \(\text{M(CO)}^3_5\) is between \(\text{HCr(CO)}^3_5\) and \(\text{HFe(CO)}^3_5\) in their reactivity toward \(\text{Cr(CO)}^3_5\cdot\text{THF}\). Replacement of one CO by \(\text{PO(CH}_3)_2\) in \(\text{HFe(CO)}^3_5\) enhances reactivity to \(\text{Cr(CO)}^3_5\cdot\text{THF}\) far better than \(\text{M(CO)}^3_5\) (entry 4). Ion pairing studies have indicated the extra electron density resides significantly on the metal in trans-\(\text{HFe(CO)}^3_5\text{P(O)(OMe)}^3_3\).

In the case of \(\text{cis-HW(CO)}^3_5\text{P(O)(OMe)}^3_3\), both \((\text{CO})\text{IR} \text{ and } ^1\text{H-NMR indicated that contact interaction with Na}^+ \text{ occurred solely at W-H site. Hence the electron density build-up on H}^+\text{ has enhanced its electrostatic potential in this case. However, cis-HW(CO)}^3_5\text{P(O)(OMe)}^3_3\text{ is no better than HW(CO)}^3_5\text{ in its reactivity towards W(CO)}^3_5\cdot\text{THF probably because the steric hindrance caused by P(OMe)}^3_3\text{ may dominate the electronic effect.}

The reactivities of several hydrides were compared in entries 5-10; entries 5 and 9 show that \(\text{HW(CO)}^3_5\), slightly more hydridic than \(\text{HCr(CO)}^3_5\), is a better competitor for

<table>
<thead>
<tr>
<th>Entry</th>
<th>Donor</th>
<th>M(CO)_5·THF</th>
<th>Products²</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
<tr>
<td>12</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
<tr>
<td>13</td>
<td>Mn(CO)_5^-</td>
<td>W</td>
<td>WCr(CO)_9^- (95%)</td>
</tr>
<tr>
<td>14</td>
<td>Mn(CO)_5^-</td>
<td>W</td>
<td>WCr(CO)_9^- (95%)</td>
</tr>
<tr>
<td>15</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
<tr>
<td>16</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
<tr>
<td>17</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
<tr>
<td>18</td>
<td>Mn(CO)_5^-</td>
<td>Cr</td>
<td>CrMn(CO)_9^- (95%)</td>
</tr>
</tbody>
</table>

²Reactions were carried out on solutions which are ca. 0.012 M in each reactant (i.e., a 1:1:1 molar ratio) except where noted. Products and ratios were established v(CO)IR within minutes after mixing reactants.

M(CO)_5·THF (M = Cr, W). Based on the results in Table 2, the relative reactivity of these anionic species toward M(CO)_5·THF can be ordered:

\[\text{cis-HW(CO)}^3_5\text{P(O)(OMe)}^3_3\cdot\text{HW(CO)}^3_5\cdot\text{THF} \overset{>}{\text{HCr(CO)}^3_5\cdot\text{THF}} \overset{>}{\text{trans-HFe(CO)}^3_5\text{P(O)(OMe)}^3_3 \cdot\text{HW(CO)}^3_5\cdot\text{THF}} \overset{>}{\text{Mn(CO)}^3_9\cdot\text{THF}} \overset{>}{\text{HFe(CO)}^3_5\cdot\text{THF}}
\]

Table 3 shows competitions between metalloanion and traditional ligand for Mn(CO)_5·THF. In entry 11, Table 3, Mn(CO)_5·THF is observed to be a much better kinetic ligating agent than the neutral ligand PPh_3, but with excess of PPh_3 (50 fold excess) in THF at 50°C for more than 11 hours produced Cr(CO)_5·PPh_3(95%) and Mn(CO)_5·PPh_3 (5% yield). These products suggest that Cr(CO)_5·PPh_3 is thermodynamically more stable than CrMn(CO)_9·THF.

A traditional anionic ligand, Br^-, a metal carbonyl anion Mn(CO)_9^-, and the anionic hydrides, HCr(CO)_5^- and HFe(CO)_5^- were compared in their ligating ability towards Cr(CO)_5·THF (entries 15-17). In their relative reactivities Br^- is more reactive than Mn(CO)_9^- or HFe(CO)_5^-, but is similar to HCr(CO)_5^- as summarized below:

\[\text{Br}^- \overset{>}{\text{HCr(CO)}^3_5\cdot\text{THF}} \overset{>}{\text{Mn(CO)}^3_9\cdot\text{THF}} \overset{>}{\text{HFe(CO)}^3_5\cdot\text{THF}}
\]

In entries 18-22, the PPh_3 neutral ligand is found to be the least reactive of all, and entries 19 and 20 show that HW(CO)_5 is more reactive than Br^-.
Ligating Ability Comparison of Transition Metal Complexes

Based on the results from Table 2 and 3, the following relative ligating ability of the anionic transition metal species, traditional neutral and anionic ligands was established:

\[ \text{cis-HW(CO)}_3\text{P(OMe)}_3^{-}\text{HCO(CO)}_3^{-}\text{Br}^{-}\text{trans-HFe(CO)}_3\text{P(OMe)}_3^{-}\text{Mn(CO)}_5^{-}\text{HFe(CO)}_4^{-}\text{PPh}_3 \]

**Correlation of Ligating Ability with Hydride Reactivity.** The kinetic expression describing typical ligand displacement reaction from octahedral metal carbonyls is well characterized and the two term rate law is generally accepted as representing a dissociative (D) term as well as dissociative interchange (L) term. For the chemistry described so far, the M of Eq. (5) represents M(CO)_5^− THF and L is the entering ligand, PR_3, X_−, Mn(CO)_5^−, HFe(CO)_4^− or HCr(CO)_3^−.

\[ \text{Rate} = [K_1 + K_2[L]][M] = K_{Mn} [L] \]  
(5)

In the reaction mentioned above, each entering ligand exhibits its own ligating ability; the distribution of various ligating abilities of ligands so far observed rules out the possibility that the M-THF bond dissociation is the rate determining step of the reactions. Therefore K_1 would be quite smaller than K_2. Since there is no change in coordination number of both the reactants and the products, no configurational change is expected. Therefore the ligating ability of reacting ligand can be explained in terms of its hydridic nature for the anionic metal hydride, or in terms of nucleophilicity for the anionic metal species or the traditional ligands.

The relative ligating ability of the hydrides is, on the whole, quite similar to the relative hydridic nature of hydrides in reactions with alkyl halides. The latter has been determined to obey an overall second order rate expression, first order with respect to [MH^−] and first order with respect to [RX] as in eq. 6 and 7.

\[ \text{MH}^− + \text{RX} → \text{RH} + \text{MX}^− \]  
(6)

\[ \text{Rate} = K_2 [\text{MH}^−][\text{RX}] \]  
(7)

For RX = n-BuBr,

\[ \text{cis-HW(CO)}_3\text{P}^{-}\text{cis-HCr(CO)}_3\text{P}^{-}\text{HCO(CO)}_3^{-}\text{HCr(CO)}_3^{-}\text{HFe(CO)}_4^{-} (P = \text{P(OMe)}_3) \]

Ion pairing studies show that more electron density is located on H in the anionic metal carbonyl hydrides such as HM(CO)_5^− (L = CO, P(OMe)_3); however, in case of HFe(CO)_4^− the electron density is more populated on Fe metal center.

**Factors Determining Ligation to M(CO)\text{X}^\text{−}**

Several factors determining ligation to M(CO)\text{X}^\text{−} (M = Cr, W) were considered:

**Anionic charge in ligand.** As is observed in their ligating ability of the ligands, the negatively charged ligand is more reactive than the neutral analogue, e.g., Br^− > PPh_3; MH^− > M^−H^+ (e.g., HCr(CO)_3^− reacts with Cr(CO)_3^−THF to produce μ-HCr(CO)_3^− but HCO(CO)_3^− is known to be inactive toward Cr(CO)_3^−THF).

**Electron density on MH^−.** In case of HFe(CO)_4^−, replacing CO by P(OMe)_3 makes this anion more electron rich on the Fe metal center so that this species can better ligate to M(CO)_5^− than HFe(CO)_4^−.

Steric bulkiness may overcome electronic effect as is shown here, e.g., cis-HW(CO)_3P(OMe)_3-HW(CO)_3^−. H^− on metal may provide a ligation site requiring little, if any, reorganization of the metal hydride ligand, permitting a more facile ligand displacement reaction than an anionic metalloligand that has no hydride. For example, the other of HCr(CO)_3^− > Mn(CO)_5^− in ligating ability towards M(CO)_7^− THF requires no coordination sphere rearrangement for HCr(CO)_3^− whereas the latter(Mn(CO)_5^−) requires structural reorganization.

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**References**

Transition-Metal-Mediated Cytotoxicity of Quinolones to L1210 Cells

Thong-Sung Ko*, Tae-Ik Kwon, Moon-Jip Kim†, Il-Hyun Park, and Hyeong-Won Ryu

Department of Biochemistry, Chungnam National University, Taegon 305-764
†Department of Physics, Soochnohyang University, Chunahn 330-080

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Transition metals tested, Cu
textsuperscript{2+}, and Ni
textsuperscript{2+}, were found effective in the induction of the cytotoxicity of the quinolones tested, nalidixic acid, oxolinic acid, and pipemidic acid, against L1210 leukemia cells in vitro, whereas the alkaline earth metal, Mg
textsuperscript{2+}, was not. The differential effect of the metals on the quinolone cytotoxicity can be explained by their different mode of interaction with the quinolones. Our present difference spectroscopic titration data suggest that the transition metals can form DNA-intercalating agents, with the quinolones, which can cause the cytotoxicity.

Introduction

Although the intermediation of certain metal ions in the quinolone interaction with DNA is obvious based on previous reports that 4-oxo-3-carboxylic acid moiety is essential for significant antibacterial activity and that quinolone drugs can act as chelating agents of certain divalent cations, discriminatory chelating behavior of the quinolones toward the metal ions or differential effect of metal ions on the functional activity of quinolones has not yet been extensively investigated.

Previously from our data of competitive binding experiments using ethidium bromide demonstrating intercalative binding of nalidixate to calf thymus DNA via metal chelate complex formation with Cu
textsuperscript{2+}, we proposed that a trinuclear aromatic chromophore produced from the binding of the nalidixate anion to the metal ion by the 4-oxo and 3-carboxylate groups, will be an intercalating agent with respect to DNA. The trinuclear form of the metal-quinolone complex can have a geometry better suited for the intercalative binding to the DNA double helix than the binuclear free quinolone anion. Through the formation of the metal-drug complex, the quinolone drugs may become competent intercalating agents having a flat aromatic chromophore closer to the size of a base pair and increased positive charge. Divalent transition metal mediated intercalative binding of quinolone to DNA could be further ascertained previously by our observation that the viscosity of calf thymus DNA solution is increased with increasing concentrations of bound metal-quinolone complexes until the saturation limit binding at a ratio of ~0.22 metal ions per DNA phosphate groups.

On the other hand, DNA intercalating drugs can be inhibitors of DNA topoisomerases and can induce both DNA single-strand breaks and DNA double-strand breaks in mammalian cells. Furthermore there has been a substantial body of evidence indicating that certain classes of intercalating agents cause topoisomerase-mediated DNA breaks and thereby can act as antitumor agents.

We were, therefore, tempted to examine metal-dependent cytotoxicity of quinolones to eukaryotic cells, metal-mediated intercalation reactivity of quinolones to DNA, and stability constant of the metal chelate complexes of the quinolone and the relationship of these metal-dependent properties of quinolones. Here we used L1210 leukemia cells for cytotoxicity test and report that Mg
textsuperscript{2+}, which does not form a stable chelate complex with the quinolone drugs tested, neither induce intercalation reactivity of quinolones to DNA, nor cytotoxicity of quinolones against L1210 cells in vitro, whereas the alkaline earth metals, Cu
textsuperscript{2+}, which form stable metal-chelate complex with quinolones, induced the intercalating reac-