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Table 5. Electrochemical Data^a for Other Process Observed for Cp*M(1,4-R₂N₄)

Compound	Solvent	E_{pa} V^b	I_{pa}/I_{pc}
I	DMF	−1.52	0.93
II	DMF	−1.46	0.91
III	DMF	−1.48	0.96
IV	DMF	−1.42	0.92

^{a}Measured in 0.1 M [^{n}Bu₄N][ClO₄]-DMF electrolyte solution. ^{b}Scan rate = 100 mV/s unless otherwise.

two energy transitions (347, 418 nm) can be assigned to a mixture of $d \rightarrow$ metallacycle π^* and metallacycle $\pi \rightarrow \pi^*$ transitions. These assignment is quite similar to those assigned to the complex CpCo (1,4-H₂N₄)[19]. The extinction coefficients (13500, 6800 M^{-1}cm^{-1}) tell us that these transition are charge-transfer bands. The transition at 642 nm is assigned to a d-d transition.

Electrochemistry. Complex II displays a quasi reversible reduction in the cyclic voltammogram at a potential of −1.52 V *vs* an SCE reference. The voltammogram of complex II is shown in Figure 2. Electrochemical data for Cp*M (1,4-R₂N₄) 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.

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Comparison of the Ligating Ability of Anonic Transition Metal Complex (Mn(CO)₅⁻), Transition Metal Hydrides (HCr(CO)₅⁻, HW(CO)₅⁻, cis-HW(CO)₄P(OMe)₃⁻, HFe(CO)₄⁻, trans- HFe(CO)₃P(OMe)₃⁻), and Traditional Ligands (Br⁻, P(C₆H₅)₃) to M(CO)₅⁰ (M=Cr, W)

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Heterobimetallic complexes have a donor-accepter 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, ν(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)₄P(OMe)₃⁻, HW(CO)₅⁻ >HCr(CO)₅⁻-Br⁻ >trans-HFe(CO)₃P(OMe)₃⁻ >Mn(CO)₅⁻ >HFe(CO)₄⁻ >PPh₃
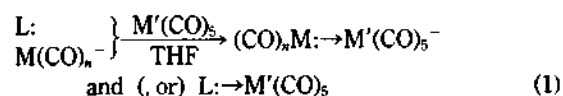
Introduction

The chemistry of the heterobimetallic complexes is a rap-

idly exploring area of inorganic and organometallic chemistry.[1] 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.[2]

Heterobimetallic complexes can be prepared either by homolytic cleavage of dimer followed by recombination, Lewis acid-base adduct formation, or binuclear reductive elimination.[1a] 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.[1c,3] It is of interest to study the formation and stability of mixed metal complex anions; $MnM(CO)_{10}^-$ $(M=Cr, W)$[4]; $HFeM(CO)_9^-$ $(M=Cr, W)$ and $HFe(CO)_3P$ $(OMe)_3W(CO)_5^{-}$ [1c,5]; μ-$HCrW(CO)_{10}^{-}$ [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 $M(CO)_5^0$ $(M=Cr, W)$ Lewis acid acceptor. The relative reactivity of each electron donor ligand can be measured through the competition reaction as in Eq. (1).

$$L: \left.\begin{matrix} \\ M(CO)_n \end{matrix}\right\}^- \xrightarrow[THF]{M'(CO)_5} (CO)_xM:\to M'(CO)_5^-$$
$$\text{and (, or) } L:\to M'(CO)_5 \qquad (1)$$

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_2SO_4 overnight, then washing with aqueous $NaHCO_3$ and distilling from sodium/benzophenone ketyl. Acetonitrile was purified by distillation from calcium hydride, followed by P_2O_5 drying before being stored over 3-Å molecular sieves. Methylene chloride was distilled from P_2O_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. ^{13}C-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. $[M(CO)_5(THF)]$ $(M=Cr, W)$,[1c] PPN$^+$[Mn $(CO)_5]^-$[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$(CO)_5^-$ $(M=Cr, W)$ were synthesized by the borohydride method.[9] PPN$^+$*cis*-HW$(CO)_4P(OMe)_3^-$ [10] and PPN$^+$ HFe$(CO)_4^-$ [11] were prepared according to the literature procedures. PPN$^+$*trans*-HFe$(CO)_3P(OMe)_3^-$ was prepared by a procedure similar to that reported by Edens[12] and Ellis.[13]

Competition Reaction of Anionic Metal Hydride and Transition Metal Anion, or Traditional Ligand

Towards Group 6B Metal Pentacarbonyl. Usually two competing reactants (0.05 mmol, each) were mixed in a 10 m*l* volumetric flask which was then sealed tightly with a septum under N_2 atmosphere at room temperature. A freshly prepared THF solution (10 m*l*) of $Cr(CO)_5 \cdot THF$ (0.05 mmol) was added quickly to this solution with stirring at ambient temperature. The competition reactions were usually monitored by $\nu(CO)$ IR spectroscope. $\nu(CO)$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 ν (CO) peak) of the reaction (s), or the expected product(s) of the same concentration(s).

Thermal Reactions of $Cr(CO)_5PR_3$ $(R=CH_3,$ or $C_6H_5)$ with either PPN$^+$-HCr$(CO)_5^-$ or -Br$^-$. THF solution (10 m*l*) of PPN$^+$HCr$(CO)_5^-$ (0.05 mmol) was added to $Cr(CO)_5P(CH_3)_3$ (0.05 mmol) in a 10 m*l* volumetric flask *via* cannula. This reaction mixture was stirred for a few min. and then placed in a silicone oil bath set at 60℃ for 19 hrs. The reaction was monitored by $\nu(CO)$IR spectroscopy. In case of the thermal reaction of $Cr(CO)_5P(C_6H_5)_3$ with PPN$^+$Br$^-$, THF solution (10 m*l*) of $Cr(CO)_5 \cdot THF$ (0.05 mmol) was added to $P(C_6H_5)_3$ (0.05 mmol) in a 10 m*l* volumetric flask, tightly rubber-septumed, *via* cannula and the flask was placed in a silicone oil bath where the solution was stirred at 50℃ for about 18 hrs. The formation of $Cr(CO)_5P(C_6H_5)_3$ was confirmed by $\nu(CO)$IR. The solution was transferred to another 10 m*l* volumetric flask to which 5-fold excess of PPN$^+$Br$^-$ (0.25 mmol) was added. This reaction mixture was then heated to 50℃ in the same bath for 7 hrs. The reaction was monitored by $\nu(CO)$IR spectroscope.

Temperature-Dependent Competition Reaction of PPN$^+$Mn$(CO)_5^-$ and PPN$^+$HFe$(CO)_4^-$ with $Cr(CO)_5 \cdot$ THF. A THF solution (10 m*l*) of $Cr(CO)_5 \cdot THF$ (0.05 mmol) kept in a dry-ice/acetone bath $(-78℃)$ for a while was cannulated into a mixture of PPN$^+$Mn$(CO)_5^-$ (0.05 mmol) and PPN$^+$HFe$(CO)_4^-$ (0.05 mmol) in a rubber septumed 10 m*l* volumetric flask in a dry ice/acetone bath. This reaction mixture was kept cold at $-78℃$ for 20 min. and then an aliquot of the solution was taken for $\nu(CO)$IR spectrum. After the initial spectrum was obtained, the reaction mixture was allowed to warm up to ambient temperature. Subsequent $\nu(CO)$ 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 m*l*) of $Cr(CO)_5 \cdot THF$ (0.01 mmol) was added to PPN$^+$Mn$(CO)_5^-$ (0.10 mmol) in a tightly septumed 100 m*l* Schlenk flask *via* cannula. This solution was then stirred at ambient temperature for 2 hrs. $\nu(CO)$IR spectra confirmed the product to be PPN$^+$CrMn $(CO)_{10}^-$. A THF solution (10 m*l*) 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℃ for 4 hrs. The reaction was monitored both by $\nu(CO)$IR and ^{1}H-NMR.

Reaction of PPN$^+$HFeCr$(CO)_9^-$ with PPN$^+$Mn$(CO)_5^-$. THF (20 m*l*) was added to the mixture of PPN$^+$HFeCr$(CO)_9^-$ (0.10 mmol) and PPN$^+$Mn$(CO)_5^-$ (0.01 mmol) in a 25 m*l* volumetric flask *via* cannula at ambient temperature. This reaction was monitored by $\nu(CO)$IR for 3 hrs.
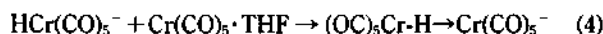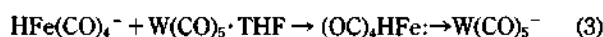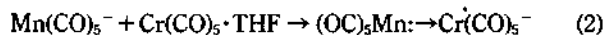
Beer's Law Plot (Absorbance vs. Concentration).

To each species was added degassed THF (10 m*l*) to prepare 5×10^{-3}, 1.5×10^{-3} and 2.0×10^{-3} M solutions by dilution. The v(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 speices against its concentration.

Cotton-Kraihanzel Force Constant.[14] Cotton-Kraihanzel force constants were calculated for C_{4v} M(CO)$_5$ (M = Cr, W) fragments bound to various ligands including metalloanions. The ligands used here are THF, PPh$_3$, Br$^-$, HFe(CO)$_4{}^-$, and Co(CO)$_4{}^-$. All the v(CO)IR spetra were measured in THF solution. Among v(CO)IR stretching modes for C_{4v}, $A_1{}^2$, E, $A_1{}^1$ 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 costants 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)$_9{}^-$ (M = Cr, W), HFe-(CO)$_3$P(OMe)$_3$W(CO)$_5{}^-$, and μ-HCrW(CO)$_{10}{}^-$. 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 speices are formed either through metal-metal donor-acceptor bonds Eq. (2) and (3), or through a hydride (H$^-$) bridging two metal atoms Eq. (4).

$$Mn(CO)_5{}^- + Cr(CO)_5 \cdot THF \to (OC)_5Mn{:}{\to}Cr(CO)_5{}^- \quad (2)$$

$$HFe(CO)_4{}^- + W(CO)_5 \cdot THF \to (OC)_4HFe{:}{\to}W(CO)_5{}^- \quad (3)$$

$$HCr(CO)_5{}^- + Cr(CO)_5 \cdot THF \to (OC)_5Cr\text{-}H{\to}Cr(CO)_5{}^- \quad (4)$$

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.[24] Bergman and coworkers found that in the competition reaction of CpV(CO)$_3$H$^-$ against PPh$_3$, CpV(CO)$_3$H$^-$ reacts more rapidly than the phosphine with transient, coordinatively unsaturated CpV(CO)$_3$, but PPh$_3$ is thermodynamically better ligand.[15]

This study demonstrated that PPh$_3$ is clearly a thermodynamically better ligand for vanadium than CpV(CO)$_3$H$^-$. However the trend of the kinetic ligating abilities of these ligands is opposite.

v (CO)IR Band Resolution for HFeW(CO)$_9{}^{-1c}$. The v (CO)IR spectrum for HFeW(CO)$_9{}^-$ with C_S 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 v (CO)IR stretching modes of HFeW(CO)$_9{}^-$ analyzed in terms of the fragments **1a** and **1b**. A maximum of 7 bands is possible assuming the donor ligand **1a** has C_S symmetry and acceptor, **1b** has C_{4v} symmetry.

X-ray structure analyses[16] have shown the iron carbonyl moiety to have substantial tetrahedral character similar to H$_2$Fe(CO)$_4{}^{17}$ or (Ph$_3$PAu)$_2$Fe(CO)$_4$.[18] When a v (CO)IR pattern similar to that of (Ph$_3$PAu)$_2$Fe(CO)$_4$ is substracted from the

1a

$C_S(3A' + A'')$

1b

$C_{4v}(2A_1 + E)$
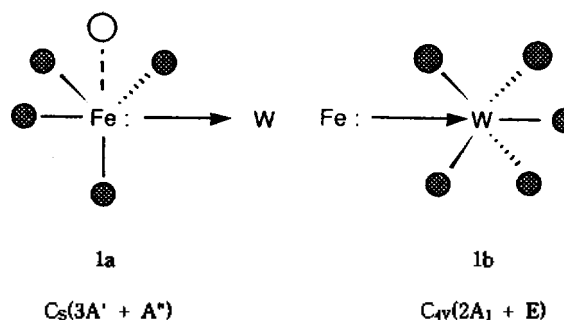
Figure 1. HFeW(CO)$_9{}^-$ has a maximum of 7 vibrational modes predicted by group theory.

v (CO)IR of HFeW(CO)$_9{}^-$, a three-band pattern remains. This band pattern is quite similar to the v (CO)IR of W (CO)$_5$· THF. Based this result it is assumed that substantial negative charge is located on HFe(CO)$_4$ moeity of the heterobimetallic complex and slightly actual electron transfer to the W(CO)$_5$ occurs.

Attempted v (CO)IR Band Resolution for CrMn(CO)$_{10}{}^-$. The heterobimetallic anion MnCr(CO)$_{10}{}^-$, originally prepared and characterized by Graham and Andrs,[4b] is isoelectronic with the homobimetallic Mn$_2$(CO)$_{10}$ and Cr$_2$(CO)$_{10}{}^{-2}$. Attempts were made to use the local symmetry approach to analyze the v (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 HFeCr(CO)$_9{}^-$ 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_{4v}, Mn(CO)$_5$ fragment similar to RMn(CO)$_5$ and bands at 1990 (s), 1896 (s), 1865 (m) cm^{-1} to a C_{4v} Cr(CO)$_5{}^-$ fragment similar to ClCr(CO)$_5{}^-$. This assignment was accepted by others.[4c,19] However, the charge distribution in CrMn (CO)$_{10}{}^-$ assigned by Graham,[4b] Onaka,[19c] and Risen, *et al.*[19a,b] should be considered very cautiously because there are major difference in the v (CO)IR intensity pattern of ClCr(CO)$_5{}^-$ and C_{4v}, Cr(CO)$_5$. The deconvolution of the v (CO)IR spectrum fo 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_{4v} 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_{4v} fragmetns, 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)$_{10}{}^-$ speices.

Cotton-Kraihanzel force Constants. The v(CO) band maxima and Cotton-Kraihanzel force constants for the M(CO)$_5$ (M = Cr, W) component of HFeM(CO)$_9{}^-$ are compared with those of other donor ligands in Table 1. According to these results, HFe(CO)$_4{}^-$ ligand affects the M(CO)$_5$ fragment most similarly to the δ-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)$_4{}^-$ or THF. But HFe(CO)$_4{}^-$ donates more electron den-

Ligating Ability Comparison of Transition Metal Complexes

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Band Area : 6 = 2.82
Band Area : 5 = 2.29
Band Area : 4 = 2.08
Band Area : 3 = 12.22
Band Area : 2 = 2.41
Band Area : 1 = 0.02
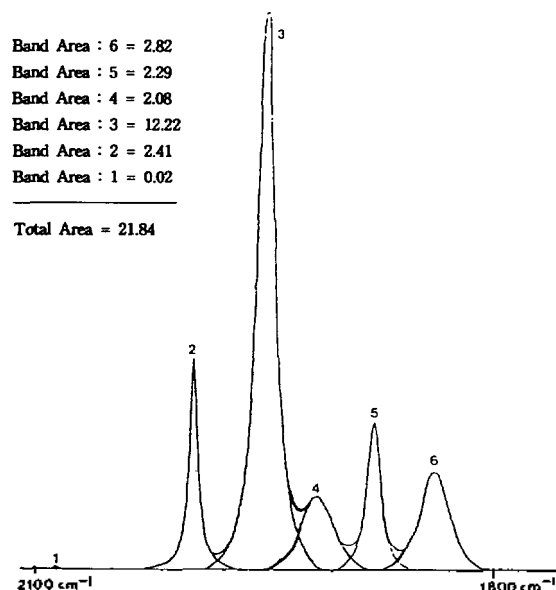
Total Area = 21.84

Figure 2. Deconvolution of ν (CO)IR spectrum fo [PPN][CrMn (CO)$_{10}$]. The total area under the six deconvoluted bands is equal to 21.8. 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 C$_{4v}$M(CO)$_5$(M = Cr, W) Fragments Bound to Various Ligands Including Metalloanions^d

Ligand	ν (CO) for M(CO)$_5^b$			C-K force constants^c		
	A_1^2	E	A_1^1	K_1	K_2	K_3
M = Cr						
Ar	2092	1965	1936	15.32	16.24	.34
THF	2074	1938	1894	14.66	15.85	.34
PPh$_3$	2061	1936	1936	15.35	15.75	.30
Br$^-$	2045	1916	1850	13.97	15.47	.32
Mn(CO)$_5^{-d}$	2063	1950	1925	15.12	15.92	.28
HFe(CO)$_4^-$	2057	1942	1880	14.40	15.81	.29
M = W						
Ar	2097	1963	1232	15.26	16.24	.34
THF	2072	1927	1882	14.49	15.72	.36
PPh$_3$	2069	1938	1938	15.39	15.81	.32
Br$^-$	2058	1915	1848	13.96	15.53	.36
Mn(CO)$_5^-$	2066	1948	1926	15.15	15.91	.29
HFe(CO)$_4^-$	2064	1941	1868	14.23	15.84	.31
Co(CO)$_4^{-c}$	2063	1941	1868	14.23	15.84	.31

^{a}All spectra were measured on THF solutions except for ArM (CO)$_5$ (Ar matrix). ^{b}The A_1^2, E, and A_1^1 are IR allowed bands under C$_{4v}$ symmertry whose relative intensities are weak, strong and medium, respectively. Band positions are 1-2 cm^{-1}. ^{c}Cotton-Kraihanzel force constants. K_1 = axial and K_2 = equatorial stretching force constants. K_3 represents the *cis* interaction constants, K_c and K_c'. The C--K method assumed $K_c = K_c' = K_i$ and 2 $K_i = K_t$. ^{d}The bands assigned here are according to the local symmetry approach as discussed: An alternate assignment (A_1^2, 1990 cm^{-1}, E, 1896, and A_1^1, 1865) yields CK force constants of $K_1 = 14.1$ and $K_2 = 15.0^{4b}$. ^{e}Ref. 21.

Table 2. Competition of Metalloanions as Donor Ligand for Photochemically Generated THF·M(CO)$_5$(M = Cr, W) in THF, 22. 1°C^a

Entry	Donor	M(CO)$_5$·THF	Products^b
1	HFe(CO)$_4^-$ HCr(CO)$_5^-$	Cr	μ-HCr$_2$(co)$_{10}^-$ (100%)
2	HFe(CO)$_4^-$ Mn(CO)$_5^-$	Cr	CrMn(CO)$_{10}^-$ (70%) HFeCr(CO)$_9^-$ (30%)
3	HCr(CO)$_5^-$ Mn(CO)$_5^-$	Cr	μ-HCr$_2$(CO)$_{10}^-$ (>90%) CrMn(CO)$_{10}^-$ (<10%)
4	*trans*-HFe- (CO)$_3$P(OMe)$_3^-$ Mn(CO)$_5^-$	Cr	HFeCr(CO)$_8$P(OMe)$_3^-$ (70%) CrMn(CO)$_{10}^-$ (30%)
5^c	HCr(CO)$_5^-$ HW(CO)$_5^-$	Cr	μ-HCr$_2$(CO)$_{10}^-$ (15%) μ-HCrW(CO)$_{10}^-$ (25%) HCrW(CO)$_5^-$ (35%) HW(CO)$_5^-$ (25%)
6	HFe(CO)$_4^-$ HW(CO)$_5^-$	W	μ-HW$_2$(CO)$_{10}^-$ (100%)
7	HFe(CO)$_4^-$ *trans*-HFe- (CO)$_3$P(OMe)$_3^-$	W	HFeW(CO)$_8$P(OMe)$_3^-$ (100%)
8	HFe(CO)$_4^-$ HCr(CO)$_5^-$	W	-HWCr(CO)$_{10}^-$ (100%)
9^c	HCr(CO)$_5^-$ HW(CO)$_5^-$	W	μ-HW$_2$(CO)$_{10}^-$ (43%) μ-HWCr(CO)$_{10}^-$ (27%) HCr(CO)$_5^-$ (30%)
10	HW(CO)$_5^-$ HW(CO)$_4$P(OMe)$_3^-$	W	μ-HW$_2$(CO)$_{10}^-$ (50%) μ-HW$_2$(CO)$_9$P(OMe)$_3^-$ (50%)

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

sity to M(CO)$_5$ than Mn(CO)$_5$. HFe(CO)$_4^-$ 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 CO[20]. 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)$_4^-$ because Mn(CO)$_5^-$ has 5 COs while HFe(CO)$_4^-$ has 4 COs. Therefore, Mn(CO)$_5^-$ is well-matched with Cr(CO)$_5^0$ and the bonding here is less aptly described as donor-acceptor, or coordinate covalent, but rather mainly covalent. Extended Huckel-type molecular orbital calculation on the M$_2$(CO)$_{10}$ and the related systems finds the HOMO to be σ-bonding between the two metals, and suggests a small contribution from d_π bonding character in the metal-metal bonding.[4c] 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 $d_\pi - d_\pi$ overlap. Therefore, electron density on CrMn(CO)$_{10}^-$ 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 $Cr(CO)_5$ moiety of $CrMn(CO)_{10}^-$ compared to those of $HFeCr(CO)_9^-$ 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 $M(CO)_5$ (M = Cr, W) is represented below:

$$Br^- > HFe(CO)_4^- \cdot -Co(CO)_4^- > THF > PR_3\text{-Ar}$$

Therefore, this electron delocalization may be the reason why the deconvolution of v (CO)IR spectrum of $CrMn(CO)_{10}^-$ does not work. However, the v (CO)IR spectrum of $CoW(CO)_9^-$ (2063 w, 2012 m, 1940 vs, 1912 w, sh, 1868 m)[21] does appear to consist of a C_{4v} $W(CO)_5$ fragment and a $Co(CO)_4^-$ donor, analogous to the $HFeW(CO)_9^-$ 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 $M(CO)_5 \cdot THF$ (M = Cr, 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 (20-23°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 (± 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 ($HFeCr(CO)_9^-$, entries 1 and 2, and $CrMn(CO)_{10}^-$, entry 3) react with excess anionic reactant slowly at room temperature (several hrs required). On the other hand, when heated in refluxing THF, the $HFeCr(CO)_9^-$ reacts with $Mn(CO)_5^-$ to yield $CrMn(CO)_{10}^-$.

The product distributions in Table 2, entries 1-3 show that the hydride which is an active hydride donor, $HCr(CO)_5^-$ better competes for $Cr(CO)_5 \cdot THF$ than $HFe(CO)_4^-$ does; Mn $(CO)_5^-$ is between $HCr(CO)_5^-$ and $HFe(CO)_4^-$ in their reactivity toward $Cr(CO)_5 \cdot THF$. Replacement of one CO by $P(OCH_3)_3$ in $HFe(CO)_4^-$ enhances reactivity to $Cr(CO)_5 \cdot THF$ far better than $Mn(CO)_5^-$ (entry 4). Ion pairing studies have indicated that the extra electron density resides significantly on the metal in *trans*-$HFe(CO)_3P(OMe)_3^-$.[20]

In the case of *cis*-$HW(CO)_4PR_3^-$, both v (CO)IR and ^{1}H-NMR indicated that contact interaction with Na^+ occurred solely at W-H site. Hence the electron density build-up on H^- has enhanced its electrostatic potential in this case. However, *cis*-$HW(CO)_4P(OMe)_3^-$ is no better than $HW(CO)_5^-$ in its reactivity towards $W(CO)_5 \cdot THF$ probably because the steric hindrance caused by $P(OMe)_3$ may dominate the electronic effect.

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

Table 3. Competition of Metalloanions and Traditional Ligands for Photochemically Generated $THF \cdot M(CO)_5$[a]

Entry	Donor	$M(CO)_5 \cdot THF$	Products[b]
11	$Mn(CO)_5^-$ PPh_3	Cr	$CrMn(CO)_{10}^-$ (~95%)
12	$Mn(CO)_5^-$ $PPh_3(\times 50)$	Cr	$CrMn(CO)_{10}^-$ (5%) $Cr(CO)_5PPh_3$ (95%)
13	$Mn(CO)_5^-$ PPh_3	W	$WMn(CO)_{10}^-$ (100%)
14	$Mn(CO)_5^-$ $PPh_3(\times 20)$	W	$W(CO)_5PPh_3$ (>90%) $WMn(CO)_{10}^-$ (<10%)
15	$Mn(CO)_5^-$ Br^-	Cr	$CrMn(CO)_{10}^-$ (12%) $BrCr(CO)_5^-$ (88%)
16	$HCr(CO)_5^-$ Br^-	Cr	μ-$HCr(CO)_{10}^-$ (52%) $BrCr(CO)_5^-$ (48%)
17	$HFe(CO)_4^-$ Br^-	Cr	$BrCr(CO)_5^-$ (90%) $HFeCr(CO)_9^-$ (10%)
18	Br^- PPh_3	Cr	$BrCr(CO)_5^-$ (100%)
19	Br^- $PPh_3(\times 50)$	Cr	$BrCr(CO)_5^-$ (66%) $Cr(CO)_5PPh_3$ (34%)
20	$HW(CO)_5^-$ $PPh_3(\times 20)$	W	μ-$HW(CO)_{10}^-$ (95%) $W(CO)_5PPh_3$ (5%)
21	$HFe(CP)_4^-$ PPh_3	W	$HFeW(CO)_9^-$ (100%)
22	$HFe(CO)_4^-$ $PPh_3(50)$	Cr	$HFeCr(CO)_9^-$ (5%) $Cr(CO)_5PPh_3$ (95%)

[a]Reactions 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. [b]Products and ratios were established v (CO)IR within minutes after mixing reactants.

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

$$cis\text{-}HW(CO)_4P(OMe)_3^- \cdot -HW(CO)_5^- > HCr(CO)_5^- > trans\text{-}HFe$$
$$(CO)_3P(OMe)_3^- > Mn(CO)_5^- > HFe(CO)_4^-$$

Table 3 shows competitions between metalloanion and traditional ligand for $Mn(CO)_5 \cdot THF$. In entry 11, Table 3, Mn $(CO)_5^-$ 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 $Cr(CO)_5PPh_3(95\%)$ and $Mn(CO)_5^-$ (5% yield). These products suggest that $Cr(CO)_5PPh_3$ is thermodynamically more stable than $CrMn(CO)_{10}^-$.

A traditional anionic ligand, Br^-, a metal carbonyl anion $Mn(CO)_5^-$, and the anionic hydrides, $HCr(CO)_5^-$ and HFe $(CO)_4^-$, were compared in their ligating ability towards Cr $(CO)_5 \cdot THF$ (entries 15-17). In their relative reactivities Br^- is more reactive than $Mn(CO)_5^-$ or $HFe(CO)_4^-$, but is similar to $HCr(CO)_5^-$ as summarized below:

$$Br^- \cdot -HCr(CO)_5^- > Mn(CO)_5^- > HFe(CO)_4^-$$

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

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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:

$$cis\text{-HW(CO)}_4\text{P(OMe)}_3^- \text{-HW(CO)}_5^- > \text{HCr(CO)}_5^- \text{-Br}^- > trans\text{-}$$
$$\text{HFe(CO)}_3\text{P(OMe)}_3^- > \text{Mn(CO)}_5^- > \text{HFe(CO)}_4^- > \text{PPh}_3$$
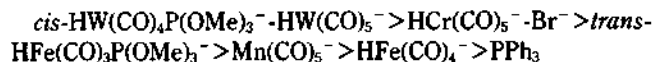
Correlation of Ligating Ability with Hydride Reactivity. The kinetic expression describing typical ligand displacement reaction from octahedral metal carbonyls is well characterized and the two term rate law is generally accepted as representing a dissociative (D) term as well as dissociative interchange (I_d) term. For the chemistry described so far, the M of Eq. (5) represents $\text{M(CO)}_5\cdot\text{THF}$ and L is the entering ligand, PR_3, X^-, Mn(CO)_5^-, HFe(CO)_4^- or HCr(CO)_5^-.

$$\text{Rate} = \{K_1 + K_2[L]\}[M] = K_{obs}[M] \tag{5}$$

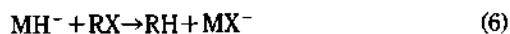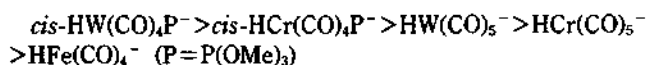In the reaction mentioned above, each entering ligand exhibits its own ligating ability; the distribution of various ligating abilities of ligands so far observed rules out the possibility that the M-THF bond dissociation is the rate determining step of the reactions. Therefore K_1 would be quite smaller 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.[22] 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.

$$\text{MH}^- + \text{RX} \rightarrow \text{RH} + \text{MX}^- \tag{6}$$

$$\text{Rate} = K_2[\text{MH}^-][\text{RX}] \tag{7}$$

For RX=n-BuBr,

$$cis\text{-HW(CO)}_4\text{P}^- > cis\text{-HCr(CO)}_4\text{P}^- > \text{HW(CO)}_5^- > \text{HCr(CO)}_5^-$$
$$> \text{HFe(CO)}_4^- \quad (\text{P}=\text{P(OMe)}_3)$$

Ion pairing studies show that more electron density is located on H in the anionic metal carbonyl hydrides such as $\text{HM(CO)}_4\text{L}^-$ (L=CO, P(OMe)$_3$); however, in case of HFe (CO)$_4^-$ the electron density is more populated on Fe metal center.[23]

Factors Determining Ligation to M(CO)$_5$°

Several factors determining ligation to $\text{M(CO)}_5°$ (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.*, $\text{Br}^- > \text{PPh}_3$; $\text{MH}^- > \text{M'H}°$ (*e.g.*, HCr(CO)_5^- reacts with $\text{Cr(CO)}_5\cdot\text{THF}$ to produce $\mu\text{-HCr}_2\text{(CO)}_{10}^-$ but HCo(CO)_4 is known to be inactive toward $\text{Cr(CO)}_5\cdot\text{THF}$).

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 $\text{M(CO)}_5°$ than $\text{HFe(CO)}_4°$.

Steric bulkiness may overcome electronic effect as is

shown here, *e.g.*, $cis\text{-HW(CO)}_4\text{P(OMe)-HW(CO)}_5^-$. 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)_5^- $> \text{Mn(CO)}_5^-$ in ligating ability towards $\text{M(CO)}_5\cdot\text{THF}$ requires no coordination sphere rearrangemet for HCr(CO)_5^- whereas the latter(Mn(CO)_5^-) requires structural reorganization.

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Transition-Metal-Mediated Cytotoxicity of Quinolones to L1210 Cells

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Transition metals tested, Cu^{2+}, and Ni^{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^{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[1] 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[2], 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[3] demonstrating intercalative binding of nalidixate to calf thymus DNA *via* metal chelate complex formation with Cu^{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[4]. 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[3,4].

On the other hand, DNA intercalating drugs can be inhibitors of DNA topoisomerases[5] and can induce both DNA single-strand breaks and DNA double-strand breaks in mammalian cells[6,7]. 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[8-14].

We were, thereupon, 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^{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^{2+}, which form stable metal-chelate complex with quinolones, induced the intercalating reac-