nature of $HRe(CO)_5$ in solution,[23] recent molecular orbital calculations,[24] and observations by Meckstroth and Ridge.[21]

The most striking result of this work is that all reference anions react with $HCo(PF_3)_4$, establishing $HCo(PF_3)_4$ as the strongest gas-phase acid known to date. $HIr(PF_3)_4$ is less acidic than $HCo(PF_3)_4$, again showing that third-row hydrides are less acidic than first-row hydrides. These results are in agreement with data showing that $HIr(PF_3)_4$ is less acidic than $HCo(PF_3)_4$ in pyridine.[25] The comparision of the PF_3-substituted manganese complexes' acidities to that of $HMn(CO)_5$ shows that even partial PF_3 substitution for CO dramatically increases the acidity of the hydride. Quantitative acidities for the reference acids FSO_3H and CF_3SO_3H are yet to be determined, so we are unable at this time to assign quantitative acidities for the PF_3-substituted complexes.

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Concurrent One- and Two-Electron Processes in Electrophile/Nucleophile Interactions of Organometallic Ion Pairs

R. E. Lehmann, T. M. Bockman, and J. K. Kochi*

Chemistry Department, University of Houston
University Park, Houston, Texas 77204-5641

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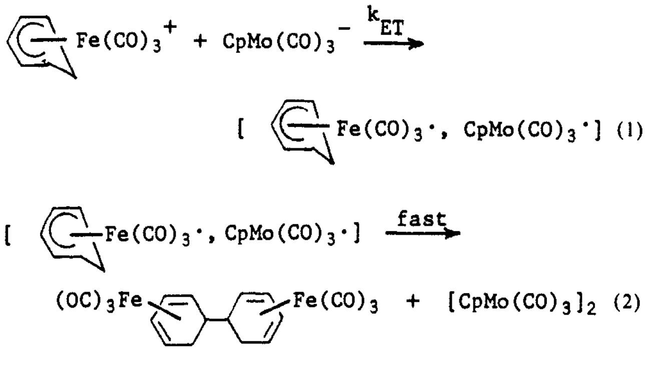
Electrophile/nucleophile combinations leading to the formation of covalent bonds (and the microscopic reverse involving bond heterolyses) are classic 2-electron processes, but their rates correlate strongly with $E°$ (redox potentials)[1-3] inherent to 1-electron transfer.[4] The resultant dichotomy between 1e and 2e organic mechanisms[5] also pertains to organometallic reactions in which cations and anions commonly play the roles of electrophiles and nucleophiles.[6] Accordingly, we wish to show how the structural variability of organometallic ion pairs can be exploited to establish the full range of 1e and 2e processes.

Table I. Electrophile/Nucleophile Interactions of $(\eta^5\text{-L})Fe(CO)_3^+$ and $CpMo(CO)_3^-$ [a]

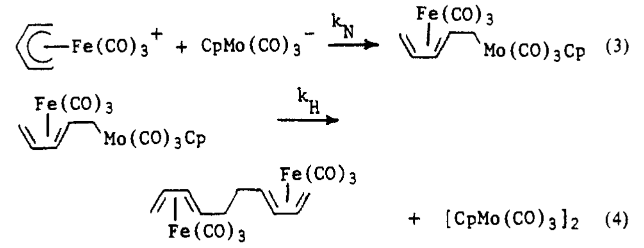
L (mmol)	E_p [b]	$CpMo(CO)_3^-$, mmol	products (%) [c]
cyclohexadienyl (0.73)	–0.31	0.73	Fe_2 (95) [73];[d] Mo_2 (95) [75]
cycloheptadienyl (0.08)	–0.35	0.08	Fe_2 (e); Mo_2 (90)
pentadienyl (0.46)	–0.24	0.46	IIa (95) [47]
hexadienyl (0.48)	–0.26	0.48	IIb (75) [46]; Mo_2 (25), Fe_2[f] (25)

[a] Reactions carried out with PF_6^- and PPN^+ salts, respectively, in 10 mL of THF at 25 °C. [b] Cathodic peak potential in V vs SCE by cyclic voltammetry at $v = 0.5$ V s^{-1} in THF. [c] Yields in parentheses based on stoichiometry in Schemes I and II by IR analysis. Isolated yields in brackets. $Fe_2 = [(\eta^4\text{-L})Fe(CO)_3]_2$, $Mo_2 = [CpMo(CO)_3]_2$. [d] Mixture of meso (43%) and *dl* (30%) Ia isomers. σ-Adduct absent (IR analysis). [e] Complex mixture of I isomers. [f] See ref 9b.

Scheme I



Scheme II



Spontaneous electron transfer occurred upon the addition of the cationic electrophile[7] $(\eta^5\text{-cyclohexadienyl})Fe(CO)_3^+$ to a THF solution of the anionic nucleophile[8] $CpMo(CO)_3^-$, as observed spectroscopically at 25 °C by the rapid disappearance of both carbonylmetal ions and the simultaneous formation of the corresponding pair of homo dimers in high yields (Table I). Particularly diagnostic is the unique carbon–carbon-bonded reductive dimer $[(\eta^4\text{-}C_6H_7)Fe(CO)_3]_2$ (Ia),[9] since it was recently demonstrated by Wrighton and co-workers to arise via the transient 19e radical $(\eta^5\text{-cyclohexadienyl})Fe(CO)_3^•$ by regiospecific coupling at the ligand center.[10] Furthermore, the 17e radical $CpMo(CO)_3^•$ is the precursor to the accompanying oxidative dimer $[CpMo(CO)_3]_2$, as judged from the anodic oxidation of the anion.[11] Such an electron-transfer process for ion-pair combination[12] (Scheme I) differs from that of the open-chain analogue $(\eta^5\text{-pentadienyl})Fe(CO)_3^+$, which afforded only the σ-adduct $(\eta^4\text{-}C_5H_7)Fe$-

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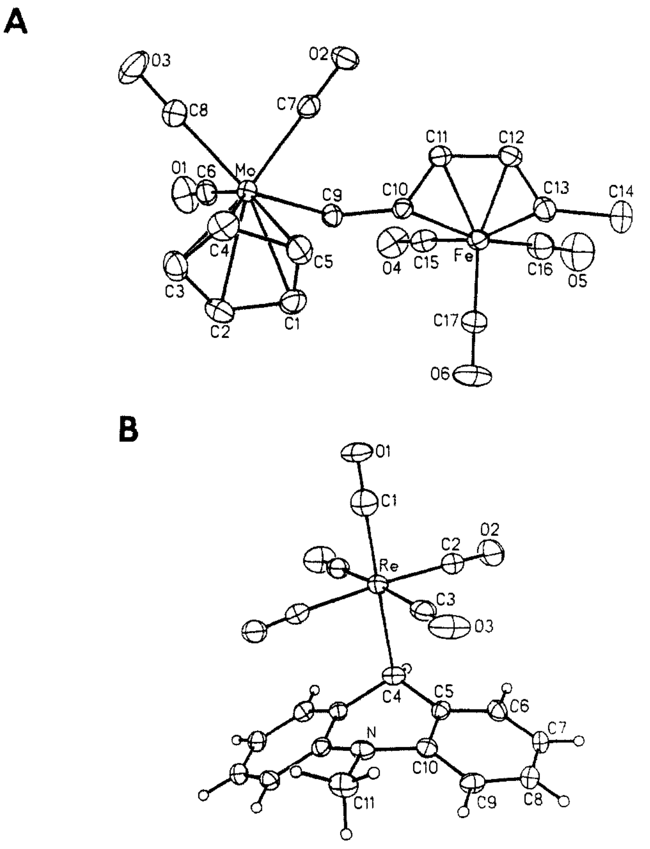
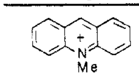
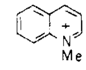
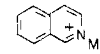


Figure 1. ORTEP view of the σ-adduct $CpMo(CO)_3Fe(CO)_3(\eta^4$-hexadiene) (IIb) (A) and $Re(CO)_5$(9-*N*-methylacridanyl) (IVa) (B).

Table II. Carbonylmetalate Nucleophiles and Cationic Heteroaromatic Electrophiles[a]

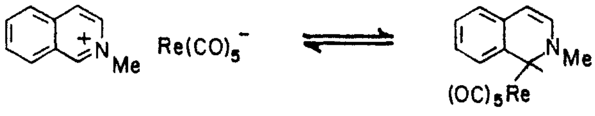
electrophile	E_p[b]	nucleophile	solv	products (%)[c]
	−0.43	$Mn(CO)_5^-$	MeCN	E_2 [86],[d] N_2 (90)
		$CpMo(CO)_3^-$	MeCN	E_2 (e),[d] N_2 (93)
		$Re(CO)_5^-$	MeCN	IVa (90); E_2 [6], N_2 (e)
	−0.90	$Mn(CO)_5^-$	THF[f]	E_2 (g),[d] N_2 (91)
		$Re(CO)_5^-$	THF[f]	IVb (20);[h] E_2 (g); N_2 (80)
	−1.08	$Mn(CO)_5^-$	THF[f]	E_2 (g);[d] N_2 (100)
		$Re(CO)_5^-$	THF[f]	E_2 (g);[i] N_2 (73)

[a] Reactions carried out with equimolar concentrations (0.01 M) of cation as triflate and anion as PPN^+ salts by mixing at −30 °C followed by warming to room temperature, unless indicated otherwise. [b] Cathodic CV peak potential in V vs SCE at $v = 0.5$ V s^{-1} in MeCN. [c] Yields in parentheses by IR analysis. Isolated yields in brackets. E_2 = 9,9′-bis(*N*-methylacridanyl). N_2 = $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, or $[CpMo(CO)_3]_2$. [d] σ-Adduct not detected. [e] Not quantified. [f] At 20 °C. [g] Not determined. [h] At 16% ion-pair conversion. [i] For σ-adduct IVc, see text.

$(CO)_3CpMo(CO)_3$ (IIa) under the same reaction conditions via the nucleophilic addition of $CpMo(CO)_3^-$ to the coordinated ligand, as in eq 3 (Scheme II).[13] The subsequent thermal decomposition of IIa at 25 °C proceeded by first-order kinetics to yield the same series of homo dimers with $k_H = 4.3 \times 10^{-6}$ s^{-1} and activation parameters $\Delta H^\ddagger = 31$ kcal mol^{-1} and $\Delta S^\ddagger = 18$ eu. Since the overall transformation in Scheme II is equivalent to that in Scheme I, the initial transformations of the ion pairs, as described in eqs 1 and 3, are clearly distinguished as 1e and 2e processes, respectively.[14] Indeed these processes occurred *concurrently* in the case of $(\eta^5$-hexadienyl)$Fe(CO)_3^+$, which produced both the σ-adduct $(\eta^4$-hexadiene)$Fe(CO)_3Mo(CO)_3Cp$ (IIb) (Figure 1a) in 75% yield and the homo dimers[9] in 25% yields (Table I). It is important to emphasize that IIb was not an intermediate in the formation of homo dimers since its rate of decomposition was much too slow[15] to account for the amounts of $[(\eta^4$-hexadiene)$Fe(CO)_3]_2$ (Ib) and $[CpMo(CO)_3]_2$ observed.

The same concurrence of 1e and 2e processes was also brought about by a slight change in the organometallic nucleophile. For example, the addition of the cationic electrophile[16] *N*-methylacridinium to an acetonitrile solution of the anionic nucleophile[17] $Mn(CO)_5^-$ at −30 °C rapidly resulted in the pair of homo dimers *N,N′*-dimethyl-9,9-biacridanyl (III)[18] and $Mn_2(CO)_{10}$ in essentially quantitative yields (Table II). In contrast, the isostructural nucleophile[19] $Re(CO)_5^-$ reacted under the same conditions, to afford the σ-adduct (*N*-methylacridanyl)$Re(CO)_5$ (IVa),[20] the identity of which was confirmed by X-ray crystallography (Figure 1B). Thus the distinctive behavior of the closely related nucleophiles $Mn(CO)_5^-$ and $Re(CO)_5^-$ in ion-pair combination exactly mirrors the 1e/2e processes outlined in Schemes I and II, respectively, for the cationic electrophiles. Moreover, the slow subsequent decomposition of the σ-adduct IVa[21] proved that it cannot be an intermediate in the formation of the small amounts (~5%) of homo dimers III and $Re_2(CO)_{10}$ observed (Table II). Extension to the related heteroaromatic cations *N*-methylquinolinium (Q^+) and isoquinolinium (iQ^+) revealed the same duality of ion-pair behavior, as listed in Table II.

The electrophile/nucleophile interactions leading to the 1e and 2e processes (Scheme I and II) were spectroscopically characterized by the appearance of charge-transfer (CT) absorption bands of contact ion pairs (CIP) of the type delineated earlier.[22] For example, the bathochromic shift in the broad, featureless absorption band of isoquinolinium (iQ^+) paired with $Mn(CO)_5^-$ at $\lambda_{max} \simeq 500$ to 650 nm for $Re(CO)_5^-$ followed the classical CT behavior,[23] as diagnosed by the parallel ease of anion oxidation.[24] Furthermore, the monotonic decrease in the CT absorbance with increasing amounts of added tetrabutylammonium perchlorate established the facile ionic exchange of the CIP.[22a] Importantly, the presence of the LMCT band ($\lambda_{sh} \sim 450$ nm) of the σ-adduct IVc and its simultaneous decrease with the CT band by added salt (TBAP) can be attributed to the equilibrium.

 (5)

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(14) As used here, the 1e/2e processes refer to redox changes.

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