

procedure, full characterization of tellurolestes, α -hydroxy ketones, and an acylsilane obtained, and a discussion on actual acylating species and main side reactions (8 pages). Ordering information is given on any current masthead page.

Effects of Metal and Ligand Substitutions on Gas-Phase Acidities of Transition-Metal Hydrides

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Gas-phase chemistry and spectroscopy of negative ions have provided important data on thermochemistry and reactivity for a wide variety of transition-metal organometallic complexes.¹⁻⁶ Despite this, since the work of Stevens Miller and Beauchamp,⁷ who determined the gas-phase acidities of HMn(CO)₅, H₂Fe(CO)₄, and HCo(CO)₄, no further acidities for transition-metal hydride complexes have been reported. This is particularly surprising since hydrides are very important in reactive and catalytic chemistry.⁸ We report here the determination of the gas-phase acidity of HRe(CO)₅, a refinement in the value for the gas-phase acidity of HMn(CO)₅, and experiments identifying HMn(CO)₃(PF₃)₂, HMn(CO)₂(PF₃)₃, HCo(PF₃)₄, and HIr(PF₃)₄ as extremely strong gas-phase acids.

The hydrides were synthesized as described in the literature.¹¹⁻¹⁶ HIr(PF₃)₄ showed an unidentified low-mass contaminant in some of the samples we prepared, but all other compounds gave pure samples. The ion-molecule reactions were studied at the Geophysics Laboratory, using a selected-ion flow tube described elsewhere.¹⁷ Proton abstraction reactions by the metal anions were not studied since the metal compounds decompose in the ion source.

The hydride HMn(CO)₅ proton transfers to F⁻, Cl⁻, Br⁻, and CCl₃CO₂⁻, at rates near the collision frequency.¹⁸ No reaction is observed with I⁻. HRe(CO)₅ reacts rapidly by proton transfer

Table I. Gas-Phase Acidity Scale Used for This Work, with the Relative Positions of the Transition-Metal Hydrides Given^a

acid	ΔH_{acid}	ΔG_{acid}
HF	371.5 ± 0.2	365.7 ± 0.5
HCO ₂ H	345.2 ± 2.3	338.2 ± 2.0
HNO ₂	338.2 ± 4.3	330.5 ± 4.6
HCl	333.4 ± 0.2	328.0 ± 0.5
HRe(CO) ₅	position according to this work	
CHF ₂ CO ₂ H	330.0 ± 2.3	323.5 ± 2.0
CF ₃ COCH ₂ COCH ₃	328.4 ± 4.1	322.0 ± 2.0
CHCl ₂ CO ₂ H	327.3 ± 2.6	320.8 ± 2.0
HBr	323.5 ± 0.1	318.2 ± 0.4
CCl ₃ CO ₂ H	319.9 ± 2.9	312.8 ± 2.0
HMn(CO) ₅	position according to this work	
HI	314.4 ± 0.1	309.3 ± 0.4
HPO ₃	311 ± 3 ^b	
HMn(CO) ₃ (PF ₃) ₂ , HMn(CO) ₂ (PF ₃) ₃	positions according to this work	
FSO ₃ H	b	
HIr(PF ₃) ₄	position according to this work	
CF ₃ SO ₃ H	b	
HCo(PF ₃) ₄	position according to this work	

^aThe acidity data, in kilocalories per mole, are from refs 9 and 10 except as noted. ^bReference 19.

to F⁻, HCO₂⁻, NO₂⁻, and Cl⁻. In the reaction with F⁻, ligand displacement also occurs, with ion products (CO)₅Re⁻ (65%) and HRe(CO)₃F⁻ (35%). HRe(CO)₅ reacts by proton transfer with CHF₂CO₂⁻, but at a rate about a factor of 3 less than collisional. No reaction is observed with CF₃COCHCOCH₃⁻, CHCl₂CO₂⁻, Br⁻, or I⁻.

A mixture of HMn(CO)₃(PF₃)₂ and HMn(CO)₂(PF₃)₃ reacts rapidly with Br⁻, I⁻, and PO₃⁻, and a factor of 30 more slowly with FSO₃⁻. Proton transfer occurs to all the ions, but the mixture also shows product masses 455 ± 10 amu and 475 ± 10 amu from reaction with PO₃⁻, and ion products of mass 325 ± 10 amu and 403 ± 10 amu from reaction with FSO₃⁻. No reaction occurs with CF₃SO₃⁻.

HCo(PF₃)₄ proton transfers at collision frequency to I⁻, PO₃⁻, FSO₃⁻, and CF₃SO₃⁻. HIr(PF₃)₄ proton transfers rapidly to Br⁻, I⁻, PO₃⁻, and FSO₃⁻, and a factor of 1000 more slowly to CF₃SO₃⁻.

Table I gives the gas-phase acidity scale^{9,10,19} used for this work. The positions of the hydride acidities are determined by assuming that the reaction is exothermic if the proton-transfer rate is equal to the ion-molecule collision rate,¹⁸ and endothermic if the rate is much smaller than the collisional rate.²⁰

The acidity of HMn(CO)₅ was previously bracketed between the acidities of HI and CF₃CO₂H.⁷ The present work confirms that result, but narrows the bracketing slightly, to between HI and CCl₃CO₂H ($\Delta H_{\text{acid}} = 314$ – 320 kcal/mol). The third-row complex HRe(CO)₅ has an acidity, ΔH_{acid} , between 330 and 333 kcal/mol, or about 10–19 kcal/mol less acidic than HMn(CO)₅. Meckstroth and Ridge²¹ presented evidence that the electron affinities of (CO)₅Mn and (CO)₅Re are equal. The acidity difference between HMn(CO)₅ and HRe(CO)₅ therefore is a result of the homolytic bond energy $D[(\text{CO})_5\text{Re}-\text{H}]$ being 10–19 kcal/mol stronger than $D[(\text{CO})_5\text{Mn}-\text{H}]$. Using $D[(\text{CO})_5\text{Mn}-\text{H}] = 60$ kcal/mol²² gives $D[(\text{CO})_5\text{Re}-\text{H}] = 70$ – 79 kcal/mol. These energetics are in keeping with the less acidic

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nature of $\text{HRe}(\text{CO})_5$ 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 $\text{HCo}(\text{PF}_3)_4$, establishing $\text{HCo}(\text{PF}_3)_4$ as the strongest gas-phase acid known to date. $\text{Hr}(\text{PF}_3)_4$ is less acidic than $\text{HCo}(\text{PF}_3)_4$, again showing that third-row hydrides are less acidic than first-row hydrides. These results are in agreement with data showing that $\text{Hr}(\text{PF}_3)_4$ is less acidic than $\text{HCo}(\text{PF}_3)_4$ in pyridine.²⁵ The comparison of the PF_3 -substituted manganese complexes' acidities to that of $\text{HMn}(\text{CO})_5$ 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 $\text{CF}_3\text{-SO}_3\text{H}$ 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

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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 mechanisms⁵ 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

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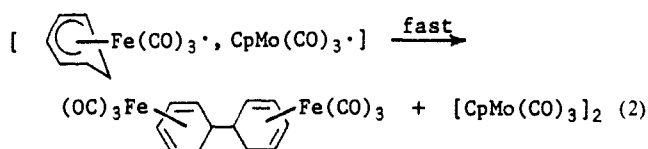
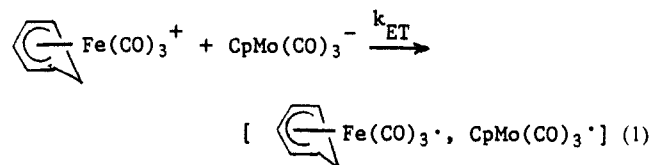
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Table 1. Electrophile/Nucleophile Interactions of $(\eta^5\text{-L})\text{Fe}(\text{CO})_3^+$ and $\text{CpMo}(\text{CO})_3^-$

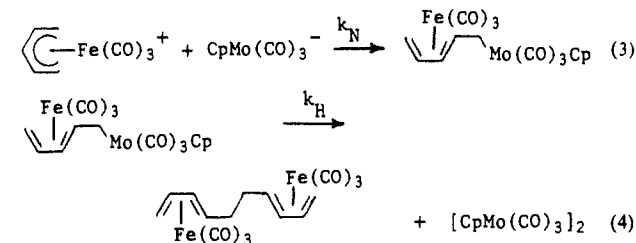
L (mmol)	E_p^b	$\text{CpMo}(\text{CO})_3^-$, mmol	products (%) ^c
cyclohexadienyl (0.73)	-0.31	0.73	Fe_2 (95) [73]; ^d Mo_2 (95) [75]
cycloheptadienyl (0.08)	-0.35	0.08	Fe_2 (e); Mo_2 (90)
pentadienyl (0.46)	-0.24	0.46	Ia (95) [47]
hexadienyl (0.48)	-0.26	0.48	IIb (75) [46]; Mo_2 (25), Fe_2^f (25)

^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 $v = 0.5 \text{ V s}^{-1}$ in THF. ^c Yields in parentheses based on stoichiometry in Schemes I and II by IR analysis. Isolated yields in brackets. $\text{Fe}_2 = [(\eta^5\text{-L})\text{Fe}(\text{CO})_3]_2$, $\text{Mo}_2 = [\text{CpMo}(\text{CO})_3]_2$. ^d Mixture of meso (43%) and dl (30%) Ia isomers. ^e σ -Adduct absent (IR analysis). ^f Complex mixture of I isomers. ^g See ref 9b.

Scheme I



Scheme II



variability of organometallic ion pairs can be exploited to establish the full range of 1e and 2e processes.

Spontaneous electron transfer occurred upon the addition of the cationic electrophile $(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3^+$ to a THF solution of the anionic nucleophile $\text{CpMo}(\text{CO})_3^-$, as observed spectroscopically at 25 °C by the rapid disappearance of both carbonylmethyl 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 $[(\eta^4\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]_2$ (Ia),⁹ since it was recently demonstrated by Wrighton and co-workers to arise via the transient 19e radical $(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3 \cdot$ by regiospecific coupling at the ligand center.¹⁰ Furthermore, the 17e radical $\text{CpMo}(\text{CO})_3 \cdot$ is the precursor to the accompanying oxidative dimer $[\text{CpMo}(\text{CO})_3]_2$, as judged from the anodic oxidation of the anion.¹¹ Such an electron-transfer process for ion-pair combination¹² (Scheme I) differs from that of the open-chain analogue $(\eta^5\text{-pentadienyl})\text{Fe}(\text{CO})_3^+$, which afforded only the σ -adduct $(\eta^4\text{-C}_5\text{H}_7)\text{Fe}$

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