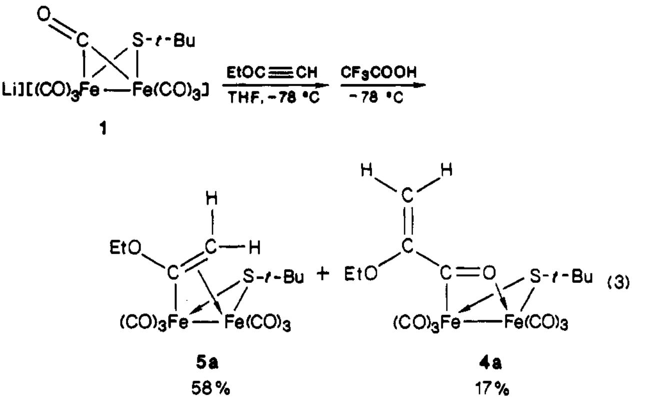
framework. However, in this instance it functions as a μ-bridging acyl. The acetylenic portion of the ligand is no longer bound to iron as in **2** but is now attached by the same α-carbon atom to the acyl bridge. Net protonation at the β-carbon atom of the acetylenic moiety thus gives rise to the pendant vinyl substituent. Typically, these acyl products are isolated as an inseparable mixture of two isomers, presumably resulting from either an axial or equatorial orientation of the thiolate group. Figure 3 shows the structure of the axial isomer of **4a** only.

Certainly, the chemistry of the Li[1]/ethoxyacetylene system is dominated by complex rearrangement mechanisms operating at room temperature. However, at lower temperature, this complex chemistry is considerably retarded. For instance, reaction of Li[1] (R = *t*-Bu) with ethoxyacetylene at −78 °C followed by quenching at −78 °C with CF_3COOH and warming to room temperature gave (μ-EtOC(=CH_2)C=O)(μ-*t*-BuS)$Fe_2(CO)_6$ (**4a**) in only 17% yield with the major product being (μ-σ,π-EtOC=CH_2)(μ-*t*-BuS)$Fe_2(CO)_6$ (**5a**) in 58% yield (eq 3). Presumably, **5a** arises via the direct protonation at the β-position of the assumed intermediate vinylic anion [(EtOC=CH)(μ-CO)(μ-*t*-BuS)$Fe_2(CO)_6$]$^-$ (**6**) in the absence of rearrangement.



All new compounds have been characterized by carbon/hydrogen combustion analysis, mass spectrometry, and NMR and IR spectroscopy. Characterizing data are provided as supplementary material.

Acknowledgment. We are grateful to the National Science Foundation for generous support of this work. We thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment, NIH Grant S10RR02243-01.

Registry No. **1a**, 107099-49-0; **1b**, 107114-70-5; **2a**, 109151-74-8; **2b**, 109151-75-9; **2c**, 109151-76-0; **4a**, 109151-77-1; **4b**, 109151-78-2; **5a**, 109151-73-7; $Fe_3(CO)_{12}$, 17685-52-8; Fe, 7439-89-6; ethoxyacetylene, 927-80-0; *tert*-butylmercaptan, 75-66-1.

Supplementary Material Available: Tables of final positional and thermal parameters for **2a** and **4a** and characterization data for compounds **2a–c** and **4a,b** (9 pages); tables of final observed and calculated structure factors for **2a** and **4a** (26 pages). Ordering information is given on any current masthead page.

Nucleophilicities of Organometallic Anions in the Gas Phase

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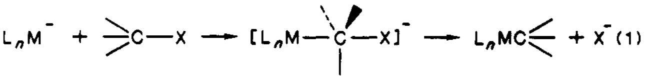
Summary: The nucleophilicities of four organometallic anions in the gas phase are examined via reactions with $CH_3SO_3CF_3$, $C_6H_5CH_2Br$, and CH_3X ($X = Cl^-, Br^-, I^-$). The trends in the solution rate constants for the displacement reactions were also found for the rate constants of the gas-phase reactions, where no ion pairing or solvent effects are present; i.e., $k((C_5H_5)Fe(CO)_2^-) > k((C_5H_5)Ni(CO)^-) > k((C_5H_5)Mo(CO)_3^-) \simeq k(Mn(CO)_5^-)$.

Alkylation of organometallic anions via nucleophilic displacement reactions is a common method for the synthesis of metal–carbon bonds,[1-3] and the kinetics and mechanisms of these reactions have received much attention in the literature.[4-7] Two pathways are generally believed to be prevalent:[4-7] direct attack at the carbon to form an S_N2 transition state (eq 1) and an electron-transfer mechanism in which the metal–carbon bond forms via radical coupling following an electron-transfer step (eq 2 and 3). Reaction 3 may occur within a solvent cage between geminate radical pairs.[5] The kinetic nucleophilicities of a number of organometallic nucleophiles have been compiled, and reactivity differences of several orders of magnitude have been noted.[4] For some of the more potent nucleophiles, such as $CpFe(CO)_2^-$ and SnR_3^-, a contribution by the radical pathway (eq 2 and 3) has been established.[5]



$$L_nM^- + RX \rightarrow L_nM^\bullet + R^\bullet + X^- \qquad (2)$$

$$L_nM^\bullet + R^\bullet \rightarrow L_nMR \qquad (3)$$

We have undertaken a study of the kinetic nucleophilicities of common organometallic anions in the gas phase by using the Fourier transform ion cyclotron resonance technique.[8] Through the study of these reactions in the absence of complicating solvation, we hope to identify the sources of the large variations in nucleophilicities and establish the thermodynamics for formation of possible mechanistic intermediates and transition states. A variety of R groups (methyl, benzyl) and leaving groups X^- (Cl^-, Br^-, I^-, $CF_3SO_3^-$) have been used. This report

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Table I. Rate Constants for Displacement of X^- from RX by Organometallic Anions in the Gas Phase[a]

RX	k_f(CpFe-(CO)$_2^-$)	k_f(CpNi-(CO)$^-$)	k_f(CpMo-(CO)$_3^-$)	k_f(Mn-(CO)$_5^-$)
$CH_3SO_3CF_3$	2.8×10^{11}	2.2×10^{11}	3.6×10^8	1.3×10^8
CH_3I	5.8×10^{10}	1.2×10^{10}	$\lesssim 3 \times 10^7$	$\lesssim 3 \times 10^7$
$C_6H_5CH_2Br$	$\sim 2.7 \times 10^{10}$	$\lesssim 3 \times 10^7$	$\lesssim 3 \times 10^7$	$\lesssim 3 \times 10^7$

[a] Rate constants k_f given in $M^{-1}\ s^{-1}$. Temperature ~375 K. Estimated errors in rate constants are ±30%. To obtain rate constants in cm^3 molecules^{-1} s^{-1}, multiply the given values by 1.66×10^{-21}.

summarizes our findings for the nucleophiles $CpFe(CO)_2^-$, $CpNi(CO)^-$, $CpMo(CO)_3^-$, and $Mn(CO)_5^-$.[9] The rate constants for displacement of I^- from CH_3I by these anions have been determined at 25 °C in THF and are 2.8×10^6, 2.2×10^5, 1.5, and 7.4 $M^{-1}\ s^{-1}$, respectively.[4] The nature of the barriers that result in the lower nucleophilicity of Mp^- and $Mn(CO)_5^-$ in comparison to Fp^- and Np^- is not clear. Much of this uncertainty arises from the unknown mechanisms encountered and the sparsity of applicable thermodynamic data.[10] In addition, the role of ion pairing in determining reactivity must be considered before meaningful comparisons of nucleophilicity can be made.[11] The study of displacement reactions in the gas phase can potentially provide considerable insight into the relationship of intrinsic kinetic nucleophilicities to activation barriers and exoergicities. Such factors have been incorporated with much success into interpretation of the kinetics of displacement reactions involving non-metallic anions in the gas phase.[12,13]

The gas-phase anions used in this study were prepared by dissociative electron attachment to $[CpFe(CO)_2]_2$, $[CpNi(CO)]_2$, $[CpMo(CO)_3]_2$, and $Mn_2(CO)_{10}$.[14] The RX substrates were introduced to give total pressures in the range 5×10^{-7} to 2×10^{-6} torr. At these pressures substantial thermalization via ion/molecule collisions occurs in the early stages of the reaction, so we assume the anions are thermal in the time over which the reaction kinetics were followed. The rate constants were determined by using ratio techniques described elsewhere.[15] The data from all reactions yielded linear first-order kinetic plots, and all but two reactions were followed for 1.5–3 half-lives.[16]

The rate constants are summarized in Table I. The general trends observed in solution are found in the gas phase where no ion pairing or solvent effects are present; i.e., $k(Fp^-) > k(Np^-) > k(Mp^-) \approx k(Mn(CO)_5^-)$. The order of reactivity in solution then results in part from intrinsic properties of the nucleophiles and can be ultimately related to differences in overall exoergicities, activation barriers, and the energies of mechanistic intermediates. With respect to the nature of the leaving groups X^-, the observed reactivity trends are not unexpected on the basis of solution results. The superior methylating agent $CH_3SO_3CF_3$ reacts detectably with all four nucleophiles, and CH_3I is somewhat less reactive. Displacement of X^- from CH_3Br and CH_3Cl was not observed in any case, but Br^- displacement was observed in the reaction of Fp^- with $C_6H_5CH_2Br$. The unobserved displacement reactions may be too slow to be measured by using our technique because of large activation barriers or may be endoergic.

In general, the gas-phase rate constants are several orders of magnitude higher than those for the same reactions in solution, and the rate constants for the reaction of Fp^- and Np^- with $CH_3SO_3CF_3$ approach typical collision rates ($\sim 1 \times 10^{12}\ M^{-1}\ s^{-1}$).[12] These gas-phase reactions are best understood in terms of a double-well potential surface where stabilizing ion/molecule interactions lower the activation barrier relative to separated thermal reactants. Such potential surfaces have been used to interpret the kinetics of a variety of ion/molecule reactions, including nucleophilic displacement,[12] proton transfer,[13] and electron transfer.[15,17] In addition, the different solvation energies for reactants and the transition state will typically result in a higher condensed-phase barrier.[12]

The mechanisms of the reactions in Table I cannot be fully established by using the present data. However, some thermodynamic data available for $Mn(CO)_5^- + RX$ indicate that a radical mechanism is unlikely in that case. The electron affinity of $Mn(CO)_5^\bullet$ (~2.3 ± 0.2 eV)[18,19] can be used to estimate ΔH values for eq 4 of 39 ± 5 kcal mol^{-1} (X = I), 45 ± 5 kcal mol^{-1} (X = Br), and 54 ± 5 kcal mol^{-1} (X = Cl). The overall endothermicity of forming the

$$Mn(CO)_5^- + CH_3X \rightleftarrows Mn(CO)_5^\bullet + CH_3^\bullet + X^- \quad (4)$$

gas-phase electron-transfer products of eq 4 as an intermediate ternary successor complex will be reduced from these values by the stability associated with the anion/neutral complex $[Mn(CO)_5,CH_3,X^-]$.[12] These stabilities are not known for the present reactants, but they can be significant for anion/neutral complexes (~5–20 kcal mol^{-1}).[23] We have not reliably measured displacement of I^- from CH_3I by $Mn(CO)_5^-$, which is consistent with $D[(CO)_5Mn{-}CH_3] \lesssim 39$ kcal mol^{-1} (literature estimates[18,21] give values of ~35–45 kcal mol^{-1}). In the case of $Fp^- + CH_3I$, the lower electron affinity[22] of $CpFe(CO)_2^\bullet$ will lower, but is not likely to overcome, the endothermicity of forming radical intermediates. The known contribution of radical mechanisms for Fp^- displacements at certain RI substrates

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(9) Abbreviations: Cp = cyclopentadienyl; $CpFe(CO)_2^-$, Fp^-; $CpNi(CO)^-$, Np^-; $CpMo(CO)_3^-$, Mp^-.

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(16) The reactions of $Mn(CO)_5^-$ and $CpMo(CO)_3^-$ with $CF_3SO_3CH_3$ were particularly slow and could only be followed for approximately $^1/_2$ of a half-life. This corresponds to trapping times of up to 25 s at pressures between 2 and 3×10^{-6} torr. The average rate constant and standard deviation from the kinetic plots for the slowest reaction ($Mn(CO)_5^- + CF_3SO_3CH_3$) using three experimental runs is $(2.2 \pm 0.8) \times 10^{-13}\ cm^3\ s^{-1}$. Appropriate control experiments were used to show the absence of contributions from impurities. Note that we have reliably measured reaction efficiencies (k_{obsd}/k_{coll}) in the range of 10^{-4}, while the usual range is typically cited as $\gtrsim 10^{-3}$.

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(19) The value of electron affinity (EA) for $Mn(CO)_5^\bullet$ was obtained in ref 18 via a thermochemical cycle. We have observed rapid electron transfer from $Mn(CO)_5^-$ to tetracyanoethylene (EA = 73 ± 2 kcal mol^{-1})[20] and do not observe transfer to *p*-cyanonitrobenzene (EA = 39 ± 2 kcal mol^{-1})[20] or other acceptors with EA < 1.7 eV. These observations are consistent with 1.7 eV < EA($Mn(CO)_5^\bullet$) < 3.2 eV. Further refinement of this value is underway via bracketing techniques.[20]

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in solution[5] is most likely increased in comparison to the gas phase by higher solvation energies for the leaving group (I^-) compared to the larger Fp^-. Available thermodynamic data for $CH_3SO_3CF_3$ are inadequate to evaluate thermodynamics for reactions involving that substrate.

Further evaluation of thermochemistry and mechanisms in these organometallic reactions will be possible when further data for electron affinities of organometallic radicals and reverse reactions (i.e., $X^- + RML_x$) become available. Such gas-phase experiments can also provide data on fundamental quantities such as metal-carbon bond strengths for comparison to the expanding literature for solvated reactants.[24] Studies directed toward these goals are underway in our laboratories.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (D.E.R.). Additional support was also provided by Research Corp. (D.E.R.). Helpful discussions with J. Boncella are gratefully acknowledged.

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Synthesis of a Molybdenum-Substituted Furan from $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+$ and Epibromohydrin in the Presence of Triphenylphosphine: *trans*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}2\text{-furan}]$

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Summary: The reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ Na^+ and epibromohydrin ($BrCH_2CHOCH_2$) in the presence of an excess of triphenylphosphine leads to the isolation of *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)$-2-furan. In the absence of phosphine a σ–π allyl ester complex is formed, $(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{—CO—O—}CH_2CH\text{=}CH_2$. The structure of the furan complex is provided along with a suggested mechanism of formation.

The chemistry of furans plays a pivotal role in modern heterocyclic chemistry, and this chemistry, along with the various modes of synthesis of these compounds have recently been reviewed.[1]

We wish to report the first example of the use of the simple molecule carbon monoxide as a reagent in the one-step synthesis of furans, namely, by coupling a coordinated CO with epibromohydrin. The reaction (eq 1) occurs in the coordination sphere of a molybdenum complex.

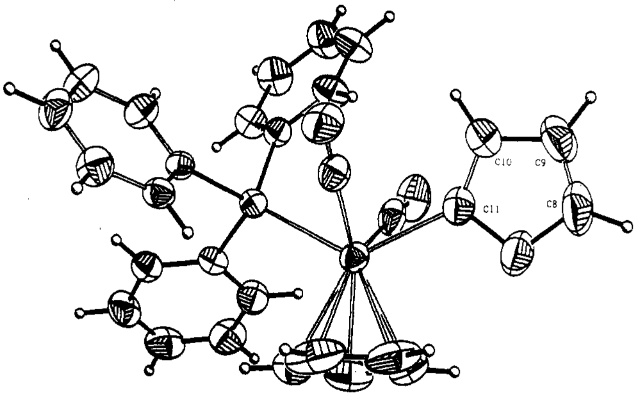
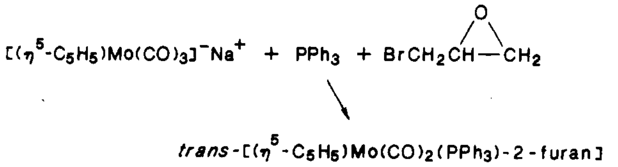


Figure 1. Crystal structure of $C_{29}H_{23}O_3PMo$: space group $P\bar{1}$ with $a = 9.150$ (5) Å, $b = 12.028$ (5) Å, $c = 12.716$ (8) Å, $\alpha = 112.67$ (3) °, $\beta = 100.97$ (3) °, $\gamma = 98.83$ (8) °, and $Z = 2$. The data were collected on a Nicolet R3M four-circle diffractometer, and refinement using SHELXTL gave a final R of 0.0348. Selected bond lengths (Å): Mo–C_{11} = 2.233 (4), C_{10}–C_{11} = 1.331 (7), C_9–C_8 = 1.298 (9), C_{10}–C_9 = 1.414 (7).



$$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-Na^+ + PPh_3 + BrCH_2CH\overset{O}{\text{—}}CH_2 \longrightarrow trans\text{-}[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)\text{-}2\text{-furan}] \quad (1)$$

In a typical reaction, 1.0 g (3.8 mmol) of $Mo(CO)_6$ was heated at reflux in 100 mL of THF with an equivalent of NaC_5H_5 for 24 h. After this time period, infrared monitoring indicated that a high yield of the molybdenum carbonylate had formed.[2] To this solution at room temperature was added initially 1.4 g (5.3 mmol) of triphenylphosphine (infrared monitoring showed that no chemical reaction took place at this stage) and then 3.0 g (17 mmol) of epibromohydrin. The resulting mixture was stirred for 12 h during which period the solution slowly changed color from clear yellow to brown-orange. After removal of the solvent a waxy solid was obtained from which unreacted $Mo(CO)_6$ was removed by sublimation at 45 °C and 10^{-1} mmHg. The residue was dissolved in the minimum of a 30:70 methylene chloride/hexane mixture and placed upon a neutral alumina column, 20 × 2.5 cm. Initial elution with hexane removed any residual phosphine and $Mo(CO)_6$, and subsequent elution with a 70:30 methylene chloride/hexane mixture led to the slow elution of a yellow band of the title complex (0.4 g, 0.7 mmol, 20%). The product was recrystallized from the same solvent mixture.

A single crystal X-ray structural determination was performed, and the resulting structure is illustrated in Figure 1 together with some of the pertinent bond lengths. The spectral data of the complex are in accord with the structure.[3]

The mechanism of this reaction appears to be related to the acid-catalyzed transformation of epoxide acetates

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[3] The initial structure solution, with the furan O atom regarded as C, gave an isotropic thermal parameter of 0.15, which was reduced to 0.12 upon changing to O, clearly distinguishing the unique O atom. No intramolecular H-bonding interactions were observed in the structure: orange-red solid; mp 178 °C dec; IR (CH_2Cl_2) ν(CO) 1955 (m), 1870 (s) cm^{-1}; ^{13}C NMR (ppm, C_6D_6) 92.4 (C_5H_5), 111.7, 148.6, 126.7 128.3, 128.7, 130.3, 133.6, 133.8, 148.6 (furan, phenyl), 199.3 (CO); ^1H NMR (ppm, C_6D_6) 4.69 (d, J = 0.7 Hz, C_5H_5), 7.12, 7.61 (C_6H_5), 6.70, 7.23, 7.30, 8.13 (m, C_4H_3O). Anal. Found (Calcd): C, 64.2 (63.8); H, 4.46 (4.20).

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