Similarly, the pale yellow solutions of the manganese(II) monomesityl intermediate instantly turn bright red upon addition of 1 mol of dry oxygen/mol of manganese(II). Unlike previous studies, however, the color is persistent, and removal of the solvent followed by crystallization from diethyl ether gives deep red prisms of the new manganese(III) aryl complex $\mathrm{Mn(C_6H_2Me_3)Br_2(PMe_3)_2}$.[33] This 14-electron compound is high-spin in solution ($\mu = 4.8\ \mu_B$) and is EPR silent; the ^{1}H NMR spectrum shows shifted and broadened peaks, as expected from the paramagnetism. The complex is unique in being the only σ-organomanganese(III) complex prepared to date, and there are only three other manganese(III) phosphine complexes of any kind: $\mathrm{MnI_3(PMe_3)_2}$,[26] $\mathrm{MnH_3(dmpe)_2}$,[29] and $\mathrm{[MnCl_2(dmpb)_2]^+}$,[34] where dmpb is 1,2-bis(dimethylphosphino)benzene.

The X-ray crystal structure[35] reveals that the $\mathrm{Mn(C_6H_2Me_3)Br_2(PMe_3)_2}$ molecule (Figure 1) possesses a distorted trigonal-bipyramidal structure with the phosphine ligands occupying the axial sites; the overall coordination geometry is similar to that described for the manganese complex $\mathrm{MnI_3(PMe_3)_2}$[27] and the rhenium species $\mathrm{RePh_3(PEt_2Ph)_2}$.[36,37] The phosphines are bent toward the mesityl group and away from the bromide ligands, P–Mn–P = 171.61 (10)°, evidently due to the relative sizes of C and Br. The Mn–P distances of 2.424 (3) and 2.427 (3) Å are essentially identical with those of 2.43 (1) Å reported for $\mathrm{MnI_3(PMe_3)_2}$[27] and longer than the 2.344 Å distance in the low-spin octahedral manganese(III) complex, $\mathrm{[MnCl_2(dmpb)_2]^+}$.[34] The Mn–Br distances of 2.490 (2) and 2.505 (1) Å are shorter than that of 2.666 (3) Å in the high-spin manganese(II) complex $\mathrm{MnBr_2(dmpe)_2}$.[30]

The mesityl group and the bromide ligands occupy the molecular equatorial plane, with the ortho methyl groups of the aryl ring fitting into the "notch" formed by the axial phosphines. The Mn–C(sp^2) distance of 2.089 (8) Å is somewhat short relative to the Mn–C(sp^2) contact of 2.11 (1) Å reported for the $\mathrm{Mn^{II}}$ mesityl complex[38] $\mathrm{[Mn(C_6H_2Me_3)_2]_3}$ and the 2.10–2.20 Å range reported for other $\mathrm{Mn^{II}}$ alkyl complexes[28-31] but is comparable to the 2.06–2.12 Å distances observed in the $\mathrm{Mn^{IV}}$ alkyl $\mathrm{MnMe_4(dmpe)}$.[39] These trends are fully explicable in terms of the decreasing size of the metal center with increasing oxidation state[40] and the differences in the covalent radii of sp^2 vs. sp^3 carbon atoms.[41]

The isolation of an organomanganese(III) complex is somewhat surprising in view of the tendency of $\mathrm{Mn^{III}}$ either to reduce to $\mathrm{Mn^{II}}$ or disproportionate to $\mathrm{Mn^{II}}$ and $\mathrm{Mn^{IV}}$.[13] For example, alkylation of the trivalent β-diketonate complex $\mathrm{Mn(acac)_3}$ with methyllithium and dmpe rapidly gives the disproportionation products $\mathrm{MnMe_2(dmpe)_2}$ and $\mathrm{MnMe_4(dmpe)}$ without any $\mathrm{Mn^{III}}$ intermediates being observable even at −78 °C.[39] The isolation of the present compound suggests that while the high-valent manganese species studied to date invariably react with organic substrates via electron transfer, i.e., radical pathways,[16-20] there may in fact be a significant chemistry of organic groups bound directly to a tri- or tetravalent manganese center. Such chemistry may lead to further advances in the regioselectivity possible in the oxidation of alkanes and other organic substrates by high-valent manganese reagents.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757) and the Office of Naval Research under their Young Investigator Award Program (Contract N00014-86-K-0638) for support of this research and Lubrizol for a fellowship (R.J.M.). We particularly thank Dr. Scott Wilson of the University of Illinois X-ray Crystallographic Laboratory for performing the X-ray crystal structure determination.

Supplementary Material Available: Tables of final atomic parameters and bond lengths and angles for $\mathrm{Mn(C_6H_2Me_3)Br_2(PMe_3)_2}$ (5 pages); a listing of observed and calculated structure factors for $\mathrm{Mn(C_6H_2Me_3)Br_2(PMe_3)_2}$ (8 pages). Ordering information is given on any current masthead page.

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[33] To a suspension of $\mathrm{MnBr_2}$ (0.42 g, 2.00 mmol) in diethyl ether (25 mL) at 25 °C was added trimethylphosphine (0.40 mL, 3.90 mmol) and $\mathrm{Mg(C_6H_2Me_3)_2(THF)_2}$ (0.46 g, 1.15 mmol) suspended in diethyl ether (25 mL), giving a clear yellow-orange solution. After the solution was stirred for 15 min, dry oxygen (45 mL, 2.00 mmol) was injected by syringe, immediately causing the solution to turn dark red. After the solution was stirred for 3 h, the solvent was removed under vacuum. The residue was washed with pentane (50 mL) and extracted with diethyl ether (75 mL), and the filtered solution was concentrated to ca. 50 mL. Cooling to −20 °C resulted in the formation of large clusters of small dark red prisms. Two additional crops of crystals were obtained from the supernatant. Yield: 0.11 g (11%). Anal. Calcd: C, 37.1; H, 6.01; Br, 32.9; Mn, 11.3. Found: C, 36.3; H, 5.92; Br, 34.0; Mn, 11.3. Mp. 110 °C, dec.

[34] Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126.

[35] Dark red single crystals of $\mathrm{Mn(C_6H_2Me_3)Br_2(PMe_3)_2}$ grown from diethyl ether are monoclinic, space group $P2_1/n$, with $a = 8.956$ (3) Å, $b = 25.228$ (8) Å, $c = 9.472$ (3) Å, $\beta = 100.29$ (2)°, $V = 2106$ (1) Å^3, $Z = 4$, $d_{\text{calcd}} = 1.533$ g cm^{-3}, $\mu_{\text{calcd}} = 45.04$ cm^{-1}. X-ray diffraction data were collected on a 0.3 × 0.3 × 0.4 mm crystal for 4387 independent reflections having $2\theta < 53°$ and for $\pm h,+k,+l$ on a Syntex $P2_1$ automated diffractometer using graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, and ω/θ scans. The space group was unambiguously determined from the systematic absences. Refinement proceeded after averaging of nonunique data and correcting for Lorentz, polarization, crystal decay (<10%), anomalous dispersion, and absorption effects; for the last, the maximum and minimum transmission factors were 0.324 and 0.276, respectively. The structure was solved by direct methods, followed by least-squares difference Fourier syntheses. The final residuals for 182 variables refined against the 1835 data for which $I > 2.58\sigma(I)$ were $R_F = 0.050$ and $R_{wF} = 0.048$. All non-hydrogen atoms were refined with anisotropic thermal coefficients, while a group isotropic thermal parameter was varied for the hydrogen atoms, which were included as fixed contributors in idealized positions with C–H = 0.96 Å; the hydrogen atoms of the mesityl methyl groups were placed in arbitrary rotational conformations about the C–CH$_3$ bonds.

[36] Chatt, J.; Garforth, J. D.; Rowe, G. A. *J. Chem. Soc. A* **1966**, 1834.

[37] Carroll, E. W.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825.

[38] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1129.

[39] Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1163.

[40] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

[41] Pauling, L. *The Nature of the Chemical Bond*; Cornell University: Ithaca, NY, 1960; p 224.

Ligand Rearrangements in Dinuclear Iron Carbonyl Complexes. A Novel Delocalized Bridging Vinylcarbene Complex

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Received March 30, 1987

Summary: Reaction of [Li][(μ-CO)(μ-RS)$\mathrm{Fe_2(CO)_6}$] salts with ethoxyacetylene followed by reaction of the anionic intermediate with an electrophile yields bridging vinylcarbene or bridging α,β-unsaturated acyl products resulting from unusual intramolecular rearrangement chemistry involving vinyl and carbonyl ligands.

Recently, we reported the synthesis of unusual dinuclear (σ,π-vinyl thioketal)- and (σ,π-vinyl thio ester)iron carbonyl

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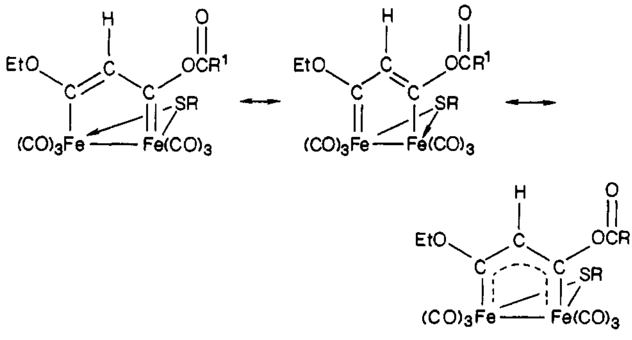
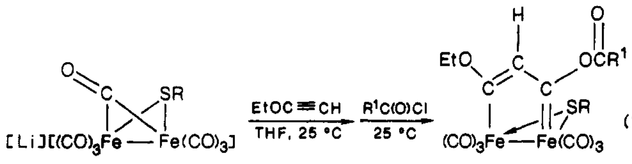


Figure 1.

complexes by the reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ salts, 1, with acetylenes.[1] Presumably, these species arise from complex intramolecular rearrangement chemistry involving vinyl, thiolate, and carbonyl ligands prior to reaction with a suitable electrophile, either an acid chloride or trifluoroacetic acid, respectively. In particular, the acetylenes utilized in these experiments were the electrophilic, carbonyl-activated acetylenes 3-butyn-2-one, methyl propiolate, and dimethyl acetylenedicarboxylate. In extending the chemistry of 1 to ethoxyacetylene (EtOC≡CH), we discovered rearrangement chemistry similar to that observed in the activated acetylene system but which ultimately yielded new and unexpected products. Herein we report these novel findings since unusual ligand transformations are involved.

Reaction of $[Li][(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]$ (1, R = *t*-Bu, Et) with ethoxyacetylene at room temperature followed by addition of an acid chloride, $R^1C(O)Cl$ (R^1 = Me, Ph), gave in generally good yields μ-vinylcarbene products of type 2 (eq 1).[2] In this reaction, a carbonyl ligand has been



(1)

1a, b 2a-c

2a	R = *t*-Bu	R¹ = Me	79%
2b	R = *t*-Bu	R¹ = Ph	71%
2c	R = Et	R¹ = Me	75%

incorporated into the acetylenic framework. However, in contrast to what had been observed with the electrophilic acetylenes,[1] further reaction with the thiolate bridge has not occurred. Instead, direct acylation of the presumed vinylic acylmetalate 3 has resulted.

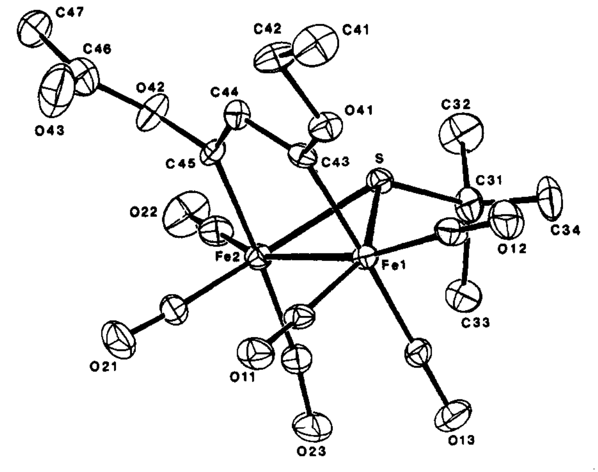
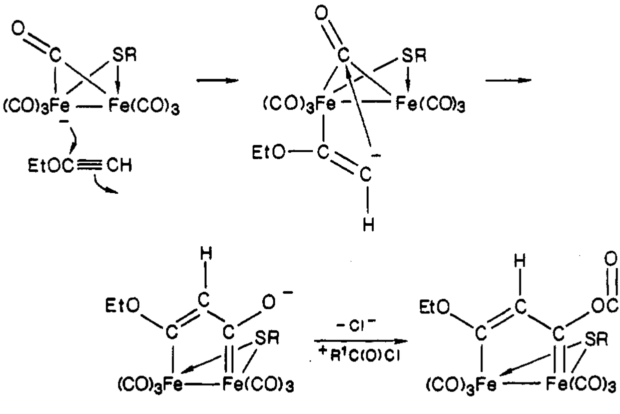


Figure 2. ORTEP diagram of **2a** showing the 20% probability thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms have been omitted. Bond lengths (in Å) are as follows: Fe1–Fe2 = 2.628 (2), Fe1–C43 = 1.976 (8), Fe1–C44 = 3.010, Fe1–C45 = 3.157, Fe2–C45 = 1.967 (8), Fe2–C44 = 2.997, Fe2–C43 = 3.169, C43–C44 = 1.392 (11), C44–C45 = 1.365 (11), C43–O41 = 1.318 (9), O41–C42 = 1.501 (11), C42–C41 = 1.515 (13), C45–O42 = 1.363 (9), O42–C46 = 1.319 (14), C46–O43 = 1.223 (14), C46–C47 = 1.477 (16), Fe1–S = 2.252 (2), Fe2–S = 2.256 (3), S–C31 : 1.875 (9), C31–CH_3(mean) = 1.558, Fe1–CO(mean) = 1.781, Fe1/C–O(mean) = 1.140, Fe2–CO(mean) = 1.787, Fe2/C–O(mean) = 1.136.

Scheme I



3 2

Complexes of type 2 are structurally interesting in that two distinct resonance forms can be drawn for the vinylcarbene bridge (Figure 1). A more accurate description of these species, therefore, may be that of a novel π-delocalized vinylcarbene system. In general, the far downfield shift of the two carbene atom resonances in the ^{13}C NMR spectra (δ_C ~267 and 284) corroborates these findings. Likewise, this delocalized nature is further verified in the crystal structure of **2a** shown in Figure 2.[3] The symmetry of the ring atoms with respect to an orthogonal plane bisecting the C43–C44–C45 angle is striking. Furthermore, the deviation from a plane defined by Fe1, Fe2,

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(1) Seyferth, D.; Hoke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895.

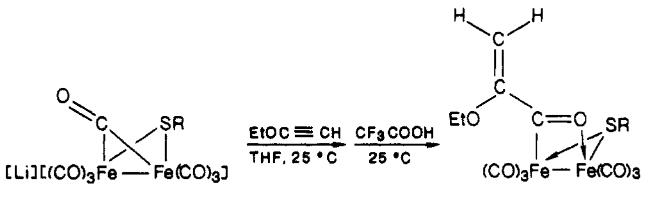
(2) (a) In a typical experiment, $Li[\mu\text{-}CO)(\mu\text{-}t\text{-}BuS)Fe_2(CO)_6]$ was prepared in situ by sequential addition of 1.00 mmol each of *t*-butylmercaptan and *n*-BuLi (in hexane) to 1.00 mmol of $Fe_3(CO)_{12}$ in 30 mL of the THF at −78 °C (under nitrogen). This mixture was stirred for 10 min and subsequently warmed to room temperature, resulting in a green to brown-red color change. One millimole of ethoxyacetylene was then added via syringe. The reaction mixture was stirred for 30 min, and then 1.50 mmol of acetyl chloride was added. After the mixture was stirred an additional 3.5 h at room temperature, the solvent was removed in vacuo to yield a red solid that was purified by filtration chromatography (silicic acid; pentane and then 4:6 pentane/CH_2Cl_2). **2a** (0.79 mmol, 79%) was obtained as a red solid, mp 111.0–113.0 °C, after recrystallization from pentane/CH_2Cl_2. (b) For **2a**: ^1H NMR ($CDCl_3$, 250 MHz) δ 1.39 (s, 9 H, $SC(CH_3)_3$), 1.42 (t, J = 6.89 Hz, 3 H, OCH_2CH_3), 2.25 (s, 3 H, $C(O)CH_3$), 4.07 (complex m, 2 H, OCH_2CH_3), 6.85 (s, 1 H, EtOC=C*H*); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 14.06 (q, J = 128.1 Hz, OCH_2CH_3), 21.64 (q, J = 130.0 Hz, $C(O)CH_3$), 33.88 (q, J = 127.0 Hz, $SC(CH_3)_3$), 50.47 (s, $SC(CH_3)_3$), 71.56 (t, J = 148.0 Hz, OCH_2CH_3), 136.06 (d, J = 159.5 Hz, EtOC=*C*H), 165.37 (s, $C(O)CH_3$), 207.99, 210.12, 214.20 (all s, Fe–CO), 267.43 (s, EtO*C*=CH), 284.82 (s, MeC(O)O*C*–CH); IR (CCl_4) 1778 s (C=O) cm^{-1}; terminal carbonyl region (pentane) 2065 vs, 2025 vs, 2000 vs, 1990 vs, 1978 m, 1968 sh, 1948, vw cm^{-1}. Anal. Calcd for $C_{17}H_{18}Fe_2O_9S$: C, 40.03; H, 3.56. Found: C, 40.03; H, 3.55.

(3) (a) Crystal data for **2a**: a = 9.583 (2) Å, b = 14.176 (3) Å, c = 16.206 (2) Å, β = 93.37 (1)°, V = 2197.8 Å^3, space group $P2_1/n$, Z = 4, μ = 14.2 cm^{-1}. A semiempirical absorption correction was applied. Data in the range 3° < 2θ < 55° were collected by using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractiometer. Data collection, reduction, and refinement procedures have been detailed elsewhere.[3b] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final R_1 = 0.069 and R_2 = 0.073 for 2360 observed reflections (+h,+k,±l) [$I_o > 2\sigma(I_o)$] and 262 variables. The largest peak on the final difference-Fourier map was 0.68 e Å^{-3}. (b) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

C43, C44, and C45 is only 0.0346 (1) Å for C43. Inclusion of O41 and O42 with these five ring atoms defines a plane with a largest deviation of 0.0799 (1) Å, and hence a degree of delocalization and, therefore, double-bond character extend to these adjacent atoms as well. Related Fischer alkoxy- and (acyloxy)carbene complexes[4] are known to display considerable carbon–oxygen double-bond character which is also in agreement with the observed C45–O42 and C43–O41 bonding distances of 1.363 (9) and 1.318 (9) Å, respectively.

A possible mechanism accounting for the formation of **2a–c** is outlined in Scheme I. Initially, addition of anion **1** to the α-carbon atom of the acetylene leads to the formation of a reactive, electron-rich vinylic anion (Li^+ cation). In analogy to known RLi reactivity,[4] this vinyl anion readily and rapidly attacks a coordinated (either bridging or terminal) carbon monoxide ligand on the adjacent iron center. Due to the electron-rich and resonance-stabilized nature of the resulting Fischer-type anionic oxycarbene species **3**, bridging of the vinyl ligand and further reaction with the nucleophilic thiolate bridge does not occur (compare ref 1). Instead, direct acylation of oxygen with $R^1C(O)Cl$ produces **2**.

Attempted interception of anion **3** by protonation rather than acylation led to unexpected results. Addition of an equimolar amount of CF_3COOH at room temperature to the Li[**1**]/ethoxyacetylene reaction mixture (with stirring for 30 min) did not yield stable hydroxyvinylcarbene analogues, but instead α,β-unsaturated bridging acyl species, **4**, were obtained in good yields (eq 2).[5] While the hydroxyvinylcarbene species may be implicated as reactive intermediates, a complex secondary rearrangement must occur which ultimately yields the new bridging acyl products (Scheme II). These μ-acyl complexes are rather unstable toward decarbonylation, readily converting to the known μ-σ,π-vinyl species (μ-EtOC=CH_2)(μ-RS)$Fe_2(CO)_6$ (**5**)[6] in nearly quantitiative yield at room temperature in THF.[7]



1a, b **4a, b**

a R = *t*-Bu 76%
b R = Et 52%

(2)

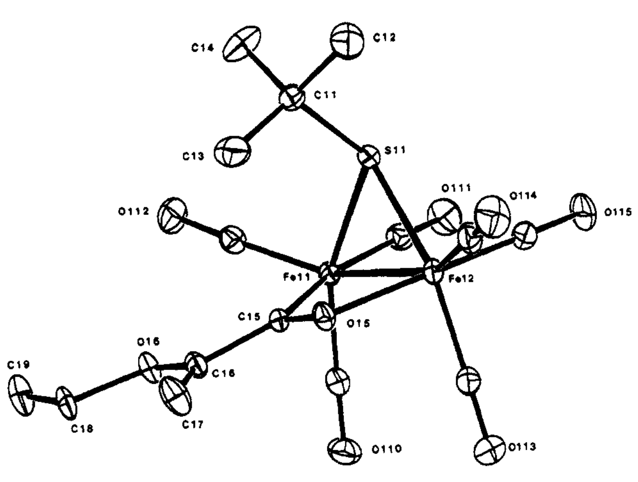
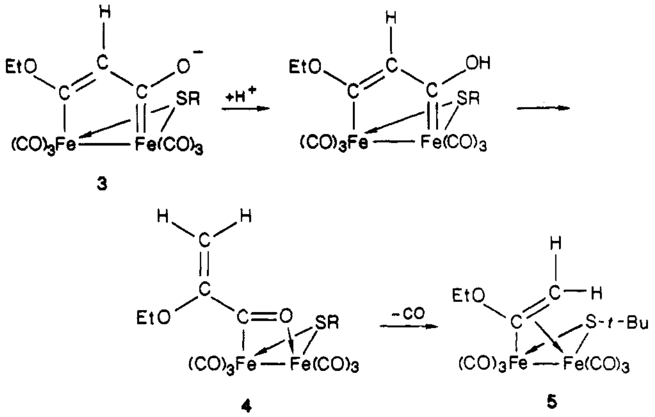


Figure 3. ORTEP diagram of **4a** showing the 30° probability thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms have been omitted. Bond lengths (in Å) are as follows: Fe11–Fe12 = 2.565 (1), Fe11–C15 = 1.930 (3), Fe11–O15 = 2.704, Fe12–O15 = 1.976 (2), Fe12–C15 = 2.586 (3), C15–O15 = 1.248 (4), C15–C16 = 1.504 (4), C16–C17 = 1.337 (5), C16–O16 = 1.351 (4), O16–C18 = 1.449 (4), C18–C19 = 1.518 (6), Fe11–S11 = 2.253 (1), Fe12–S11 = 2.243 (1), S11–C11 = 1.865 (4), C11–CH_3(mean) = 1.532, Fe11–CO(mean) = 1.806, Fe11/C–O(mean) = 1.143, Fe12–CO(mean) = 1.803, Fe12/C–O(mean = 1.137.

Scheme II



Structure proof of the unexpected α,β-unsaturated bridging acyl complexes was somewhat ambiguous so a single-crystal X-ray diffraction study of **4a** was undertaken.[8] The structure is shown in Figure 3. Here also, a carbonyl ligand has been incorporated into the organic

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[4] Review: Fischer, H. In *Transition Metal Carbene Complexes*; Dötz, K.-H.; Fischer, H.; Hofmann, P., Kreissel, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983, pp 1–68.

[5] For **4a**: ^1H NMR ($CDCl_3$, 250 MHz) δ 1.24 (s, 9 H, $SC(CH_3)_3$ major isomer), 1.42 (t, J = 7.28 Hz, 3 H, OCH_2CH_3 minor isomer), 1.45 (t, J = 7.10 Hz, 3 H, OCH_2CH_3 major), 1.54 (s, 9 H, $SC(CH_3)_3$ minor isomer), 3.76 (complex m, 2 H, OCH_2CH_3 both isomers), 3.84 (d, J = 2.26 Hz, 1 H, C=CH_2 both isomers–diastereotopic CH_2), 4.32 (d, J = 2.25 Hz, 1 H, C=CH_2 both isomers–diastereotopic CH_2), ratio major minor = 2.7/1.0; ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 13.86 (q, J = 127.0 Hz, OCH_2CH_3 both isomers), 34.23 (q, J = 125.7 Hz, $SC(CH_3)_3$ minor isomer), 34.82 (q, J = 127.4 Hz, $SC(CH_3)_3$ major isomer), 48.07 (s, $SC(CH_3)_3$ major isomer), 49.47 (s, $SC(CH_3)_3$ minor isomer), 64.04 (t, J = 142.2 Hz, OCH_2CH_3 both isomers), 84.66 (t, J = 161.6 Hz, C=CH_2 major isomer), 85.68 (t, J = 163.1 Hz, C=CH_2 minor isomer), 159.70 (s, EtOC=CH_2 both isomers), 207.26, 209.51, 210.37, 210.55, 210.72, 211.21 (all s, Fe–CO), 287.24 (s, acyl C=O both isomers); IR ($CHCl_3$) 1600 s (C=C), 1482 vs (acyl C=O) cm^{-1}; terminal carbonyl region (pentane) 2072 s, 2034 vs, 2008 vs, 2000 vs, 1989 s, 1980 s cm^{-1}; mass spectrum (EI, 70 eV) M^+ and $M^+ - nCO$ (n = 1–7). Anal. Calcd for $C_{15}H_{16}Fe_2O_8S$: C, 38.49; H, 3.44. Found: C, 38.75; H, 3.56.

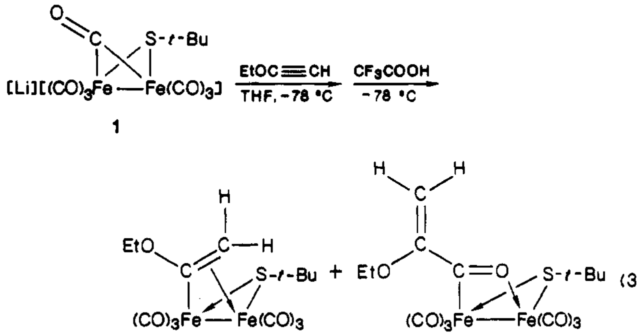
[6] Seyferth, D.; Hoke, J. B., manuscript in preparation.

[7] In a typical experiment, (μ-EtOC(=CH_2)C=O)(μ-*t*-BuS)$Fe_2(CO)_6$ (**4a**) (0.72 mmol) was stirred at room temperature under nitrogen for 6 days in 30 mL of THF. Removal of the solvent in vacuo and purification of the residue by filtration chromatography (silicic acid; pentane) gave **4a** (0.67 mmol, 92%) as a red oil. Reaction of the corresponding ethanethiolate bridged complex **4b** required only 4 days for complete conversion.

[8] Crystal data for **4a**: a = 11.125 (3) Å, b = 11.400 (2) Å, c = 7.820 (3) Å, α = 100.88 (2)°, β = 91.57 (2)°, γ = 85.37 (2)°, V = 970.7 Å^3, space group $P\bar{1}$, Z = 2, μ = 16.0 cm^{-1}. A semiempirical absorption correction was applied. Data in the range $3° < 2\theta < 55°$ were collected at −65 °C by using Mo Kα radiation on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device. Data collection, reduction, and refinement procedures have been detailed elsewhere.[3b] Hydrogen atoms were ignored while all other atoms were refined anisotropically. Final R_1 = 0.044 and R_2 = 0.060 for 3769 reflections ($\pm h$, $\pm k$, +l) [$I_o > 2\sigma(I_o)$] and 235 variables. The largest peak in the difference-Fourier map was 0.69 e Å^{-3}. The structure solution proved difficult and was initially obtained in space group $P1$ and then transformed to $P\bar{1}$.

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.



1

(3)

5a 58%

4a 17%

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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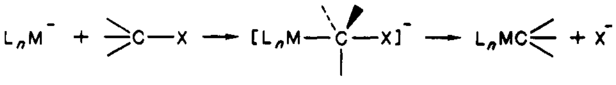
Summary: The nucleophilicities of four organometallic anions in the gas phase are examined via reactions with $CH_3SO_3CF_3$, $C_6H_5CH_2Br$, and CH_3X ($X = Cl^-, Br^-, I^-$). The trends in the solution rate constants for the displacement reactions were also found for the rate constants of the gas-phase 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]



(1)

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

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

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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