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# Synthesis, Structure, Cis–Trans Isomerization, and Reactions of Heterodinuclear Iron–Manganese Anion and Alkoxycarbyne Complexes. X-ray Crystal Structure of *cis*-($\eta^5$-Cp)(CO)Fe($\mu$-COCH$_2$CH$_3$)($\mu$-CO)Mn(CO)($\eta^5$-MeCp)

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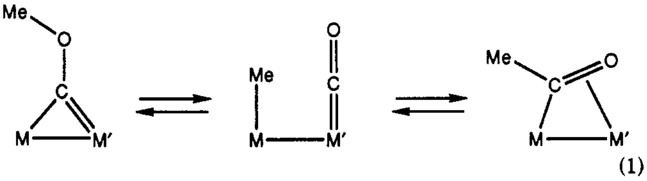
Reaction of ($\eta^5$-RC$_5$H$_4$)Fe(CO)$_2^-$Na$^+$ (R = H, CH$_3$) with ($\eta^5$-R′C$_5$H$_4$)Mn(CO)$_2$L (R′ = H, CH$_3$, L = CH$_3$CN, THF) gives the heterodinuclear anions [($\eta^5$-RC$_5$H$_4$)(CO)-Fe($\mu$-CO)$_2$Mn(CO)($\eta^5$-R′C$_5$H$_4$)]$^-$Na$^+$ (**1a**, R = H, R′ = Me; **1b**, R = R′ = Me; **1c**, R = Me, R′ = H; **1d**, R = R′ = H), which were further characterized by conversion to the (Ph$_3$P)$_2$N$^+$ (**1a**-PPN$^+$) and Ph$_3$PCH$_3^+$ (**1a**-Ph$_3$PCH$_3^+$, **1b**-Ph$_3$PCH$_3^+$) salts. Alkylation with methyl triflate or ethyl triflate gives the novel alkoxycarbynes ($\eta^5$-RC$_5$H$_4$)(CO)Fe($\mu$-CO)($\mu$-COR″)Mn(CO)($\eta^5$-R′C$_5$H$_4$) (R″ = CH$_3$: **2a**, R = H, R′ = Me; **2b**, R = R′ = Me; **2c**, R = Me, R′ = H; **2d**, R = R′ = H; R″ = CH$_2$CH$_3$: **3a**, R = H, R′ = Me; **3b**, R = R′ = Me) from the above anions in good yield. Variable-temperature $^1$H NMR spectra of **1a**-PPN$^+$, **2a**, and **3a** suggest that these compounds each exist in solution as interconverting cis–trans isomers, with a small thermodynamic preference for the cis isomer of each, and with $\Delta G^\dagger$ (300 K, cis to trans) = 15.8 ± 0.4 (**1a**, CD$_2$Cl$_2$), 16.4 ± 0.7 (**2a**, C$_6$D$_6$), 16.5 ± 0.9 (**3a**, toluene-$d_8$), and 17.2 ± 4.9 (**3a**, acetone-$d_6$) kcal/mol. The X-ray crystal structure of **3a** (space group $C2/c$, $a$ = 25.319 (3) Å, $b$ = 7.3978 (8) Å, $c$ = 17.275 (2) Å, $\beta$ = 92.135 (2)°, $V$ = 3221.1 Å$^3$, $Z$ = 8, $\rho$(calcd) = 1.63 g cm$^{-3}$, and $R$ = 0.037, $R_w$ = 0.050 for 2041 independent reflections) shows that it crystallizes as the cis isomer and contains a nearly symmetrically bound carbyne ligand (Fe–C = 1.843 (4) Å, Mn–C = 1.839 (4) Å) and a semibridging carbonyl ligand (Fe–C = 2.065 (5) Å, Mn–C = 1.883 (5) Å, ∠(Fe–C–O) = 130.4 (4)°, ∠(Mn–C–O) = 148.3 (4)°) with a short Fe–Mn single-bond distance of 2.572 (1) Å. Thermal decomposition of **2a** and **3a** occurs at 65 °C to give mainly MeCpMn(CO)$_3$ (MeCp = $\eta^5$-CH$_3$C$_5$H$_4$) and in lower yields Cp(CO)$_2$FeR″ (Cp = $\eta^5$-C$_5$H$_5$, R″ = CH$_3$, CH$_2$CH$_3$), [CpFe(CO)$_2$]$_2$, [CpFe(CO)]$_4$, CH$_4$ (for **2a**), and C$_2$H$_6$ and C$_2$H$_4$ (for **3a**); addition of phosphines can give Cp(CO)(L)FeR″ (R″ = CH$_3$, L = PPh$_3$; R″ = CH$_2$CH$_3$, L = PPh$_3$, PPh$_2$Me, PPhMe$_2$) in high yield, although demethylation of the methoxycarbynes to give back the heterodinuclear anions can also occur, for instance with PPh$_3$ and **2a** to give **1a**-Ph$_3$PCH$_3^+$. Photolysis and hydrogenation of **2a** give the same products as thermal decomposition, with the exception of a low yield of dimethyl ether in the hydrogenation reaction.

## Introduction

Mechanistic investigation of discrete transition-metal compounds, both mononuclear and polynuclear, is an accepted tool for gaining an understanding of surface-catalyzed reactions such as the Fischer–Tropsch reaction.[2] We have been investigating difunctional clusters,[3] in order to gain new insight into such complex systems where multiple organic fragments can interact with each other.[2c–e,g,3,4] Study of the simpler monofunctional clusters is necessary as a starting point, however.[5] In particular, one can imagine an equilibrium between a carbonyl/alkyl moiety and the isomeric alkoxycarbyne and acyl groups (eq 1). Reversible methyl migration from an



(1)

acyl ligand is common in mononuclear systems and recently in particular has also been shown to be facile for $\eta^2$-acyls.[6] For di- and trinuclear analogues, examples of cluster/alkyls

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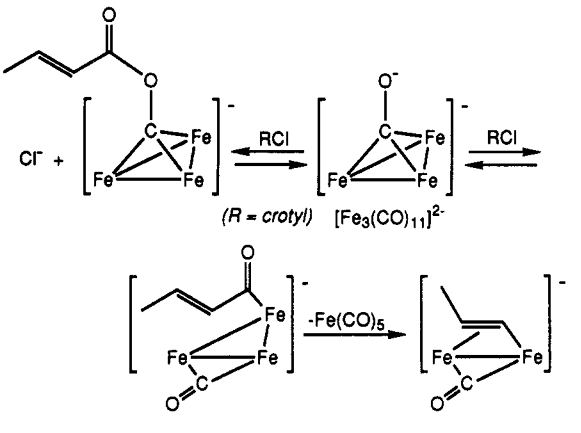
that yield acyls[7] as well as rare examples of cluster acyl deinsertion[7e,8] are also known. On the other hand, alkyl migration involving the isomeric alkoxycarbyne ligand has no precedent. For mononuclear compounds, several recently reported *aryl*oxycarbynes represent the first examples of this class of compounds[9] and, like their isolable analogues, including mononuclear siloxycarbynes[10] and thiocarbynes,[11] have not been reported to undergo migration reactions. However, the related hydroxycarbyne/carbonyl hydride equilibrium has been accorded theoretical support[12] and alkyl migration from a proposed intermediate alkoxycarbyne has been suggested as a decomposition pathway from a silyl-substituted Fischer carbene.[13] For clusters, prior to this work[5a] there were no examples of alkyl migration involving alkoxycarbynes, although subsequently Ford reported a novel reaction in which methyl migration occurs *directly* to carbon to give a $\mu$-acyl upon photolysis of the triruthenium carbyne $HRu_3(CO)_{10}(\mu\text{-}COCH_3)$.[14] More recently Watanabe reported the acylation of $Fe_3(CO)_{11}{}^{2-}$ to give a $\mu_3$-acyloxycarbyne and subsequent decomposition to a $\sigma,\pi$-vinyl complex, but while the transformations were described as an acyl group transfer from oxygen to iron, in fact the authors showed (eq 2) that the reactions are better explained as a set of equilibria between the starting cluster dianion and the kinetically favored carbyne product, and the final thermodynamically favored alkyl product;[15] that is, no direct oxygen to iron acyl migration occurred. A better characterized example of this type of reactivity is the unique system described by Gladfelter in which $Ru_2(\mu\text{-}CO)$[bis(dimethylphosphino)methane]$(CO)_4$ irreversibly gives equal amounts of M- and O-alkylation to yield cationic methyl and methoxycarbyne complexes; subsequent CO insertion to give acetyl complexes also occurs but again without reentry into the carbyne manifold.[7g]



(2)

A variety of di- and trinuclear $\mu_2$-alkoxycarbyne and $\mu_2$-thiocarbyne complexes are known. The first neutral dinuclear carbyne, reported by Mathieu, was prepared by alkylation of an anionic $\mu$-vinyl diiron complex to give $(CO)_3Fe(\mu\text{-}COCH_2CH_3)(\mu\text{-}C(Ph){=}C(Ph)H)Fe(CO)_3$.[4] Related compounds have been prepared by alkylation of neutral iron and ruthenium homonuclear dimers to give cationic homodinuclear alkoxycarbynes,[7g,16] of neutral homodinuclear (diiron) and heterodinuclear (Mn/Co, Mn/Pt) thiocarbonyl complexes to give cationic thiocarbynes,[17] and of anionic iron, ruthenium, and osmium clusters of three or more metals to give neutral and anionic edge-bridging $\mu_2$-alkoxycarbynes.[18] In this paper we describe the syntheses and solution structures of what appear to be the first examples of heterodinuclear anions in which each of the metal atoms bears a cyclopentadienyl ring, the first neutral, heterodinuclear $\mu_2$-alkoxycarbyne complexes, the X-ray crystal structure of an ethoxycarbyne complex, and some reactions of these materials. Mechanistic work on one of these reactions, the unprecedented oxygen to metal migration of the carbyne alkyl group (eq 1), will be reported separately. Some of this work has been communicated previously.[5a]

## Results

**Synthesis of Dinuclear Iron–Manganese Anions.** Refluxing a 1:1 mixture of $MeCpMn(CO)_2(CH_3CN)$ (MeCp = $\eta^5\text{-}CH_3C_5H_4$) and $CpFe(CO)_2{}^-Na^+$ (Cp = $\eta^5\text{-}C_5H_5$) in THF for 12 h gave a color change from orange to dark red. After the solvent was removed, a benzene-insoluble dark red-purple compound was obtained in 87% yield and identified as anion **1a** (eq 3), isoelectronic and isostructural to the neutral iron dimer $Cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)Cp$. A comparable yield was obtained by substituting $MeCpMn(CO)_2THF$ for the acetonitrile adduct and stirring overnight at room temperature, and for convenience this is the method of choice (eq 3). The compound is unstable in air and decomposes to $MeCpMn(CO)_3$ and $[CpFe(CO)_2]_2$, along with some insoluble solid. The infrared spectrum in THF exhibited bands at 1909, 1850, 1723, and 1647 cm$^{-1}$, indicating the presence of two terminal carbonyl ligands and two bridging carbonyl ligands. The $^1H$ NMR

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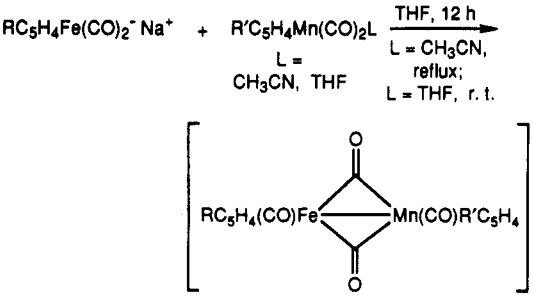
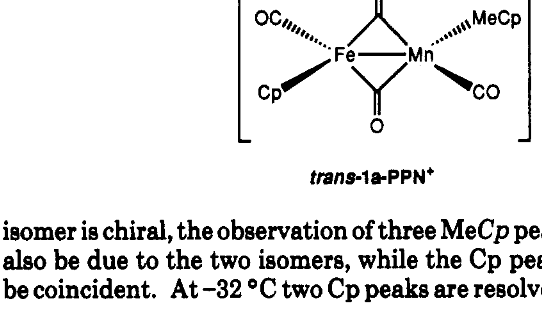


(3)

**1a** R = H, R' = Me
**1b** R, R' = Me
**1c** R = Me, R' = H
**1d** R, R' = H

($CD_3CN$) exhibited singlets at δ 4.38 (s, 5H) and 4.10 (br, 4H); the *Me*Cp resonance was presumed to be hidden under that of the solvent. Compounds **1b**, **1c**, and **1d** were synthesized in similar yields. Metathesis of the $Na^+$ salt of **1a** with $PPN^+Cl^-$ ($PPN^+$ = bis(triphenylphosphine)-nitrogen(1+)) gave the $PPN^+$ salt **1a**-$PPN^+$ as a dark purple solid in 76% yield. The infrared spectrum in $CH_2Cl_2$ simplified to three bands of equal intensity at 1899 $cm^{-1}$ for the terminal Fe carbonyl, 1832 $cm^{-1}$ for the terminal Mn carbonyl, and 1671 $cm^{-1}$ for the bridging carbonyl ligands; all are shifted ~100 $cm^{-1}$ to lower frequency from those of the iron dimer $[CpFe(CO)_2]_2$ at 1996, 1954, and 1773 $cm^{-1}$ in $CH_2Cl_2$ due to the negative charge. In the $^1H$ NMR ($CD_2Cl_2$) signals were observed at δ 4.43 (s) for the Cp hydrogens and 4.15 (br, ~2H), 4.10 (br, ~1H), and 4.01 (br, ~1H) for the Me*Cp* hydrogens, and at δ 1.98 (s) and 1.83 (s) in a 46:54 ratio for the *Me*Cp peaks. These last two peaks suggested that there were actually two isomers in solution which by analogy to the isoelectronic iron dimer are proposed to be the cis and trans isomers[19] *cis*-**1a** and *trans*-**1a** (eq 4). Since neither isomer is chiral, the observation of three Me*Cp* peaks must also be due to the two isomers, while the Cp peaks must be coincident. At −32 °C two Cp peaks are resolved at 500 MHz, at δ 4.419 and 4.414 (Δν = 2.5 Hz), as are two sets of MeCp peaks. The ratio of the *Me*Cp peaks, shifted slightly to δ 1.93 and 1.75, was reversed to 59:41, allowing the downfield peak to be assigned to the thermodynamically more stable isomer and approximate thermodynamic parameters to be derived (Table I). The $Ph_3PCH_3^+$ salts of **1a** and **1b** were similarly prepared, and the room-temperature cis/trans ratio was apparently reversed for **1a**-$Ph_3PCH_3^+$ (*Me*Cp peaks at δ 1.96, 1.81, 58:42; the ratio could not be determined by $^1H$ NMR for **1b**-$Ph_3PCH_3^+$); while this phenomenon was not investigated further, the ratio would appear to be a function of ion pairing.



*cis*-**1a**-$PPN^+$

*trans*-**1a**-$PPN^+$

(4)

Heating **1a**-$PPN^+$ in the NMR (200 MHz) probe resulted in sharpening of the MeCp cyclopentadienyl signals into two bands by 312 K and coalescence of the two MeCp methyl signals also at 312 K, consistent with rapid cis–trans isomerization, again as seen for the iron dimer.[19] Cooling back to room temperature resulted in reappearance of the original spectrum. Line-shape analysis of the *Me*Cp signals yielded rate constants for the exchange process in $CD_2Cl_2$ from 297 to 334 K (see Experimental Section for details), giving a linear Eyring plot (Figure 1) and $\Delta G^\dagger$(300 K) = 15.8 ± 0.4 kcal/mol (Table I).

The $^{13}C$ NMR spectrum of **1a**-$PPN^+$ at −32 °C (125 MHz) exhibited two sets of peaks in a 3:2 ratio, identical to the cis–trans ratio seen in the $^1H$ NMR spectrum, due to the Cp carbons (85.0, 87.3 ppm), the MeCp ipso carbons (100.7, 101.6 ppm), the 2,5 and 3,4-MeCp carbons (85.5, 84.6; 86.5, 85.4 ppm), and the MeCp methyl carbons (13.3, 12.8 ppm) of the two isomers. However, only one set of sharp carbonyl resonances, at 302.8, 232.5, and 216.4 ppm, was observed. By analogy to the iron dimer, the carbonyl bands are proposed to be due to the cis isomer; the carbonyl ligands in the trans isomer are presumed to be undergoing rapid intramolecular exchange by a mechanism unavailable to the cis isomer as proposed for the iron dimer,[19c] in which bridging–terminal ligand interconversion can occur without internal rotation about the metal–metal bond in the unbridged isomer. Due to the large chemical shift difference between the terminal Fe–CO and Mn–CO ligands, the exchanging peaks are presumably too broadened to observe. The positions of the three carbonyl bands are in complete accord with the proposed structure; the resonance at 216.4 is assigned as the Fe–CO signal[23] and that at 232.5 as the Mn–CO signal,[23a] and the resonance due to the bridging carbonyls at 302.8 ppm is typical of those in iron anions.[24] This last signal might seem unusually far downfield for a bridging carbonyl ligand—for instance that in *cis*-$[CpFe(CO)_2]_2$ is at 275 ppm[19b]—but delocalization of the negative charge onto the bridging carbonyls, perhaps in conjunction with preferential ion pairing of the μ-CO ligands to the cation like that of Lewis acids with the iron dimer,[24] will impart some carbyne character to the μ-CO ligands and result in the observed downfield shift.

**Synthesis of Iron–Manganese Alkoxycarbynes.** Alkylation of the anion **1a** was attempted with $CH_3I$, $CH_3SO_3C_6H_4CH_3$, and $(CH_3)_3O^+BF_4^-$, but the only identifiable products were $MeCpMn(CO)_3$ and $[CpFe(CO)_2]_2$. However, rapid addition of 1.1 equiv of $CH_3SO_3CF_3$ to a THF solution of **1a** gave after stirring for 15 min followed by

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**Table I. Thermodynamic and Kinetic Parameters for Cis to Trans Isomerization of 1a-PPN$^+$, 2a, 3a, and Related Compounds, in Order of Increasing $\Delta G^\dagger$ [a]**

| compd (solvent) | $\Delta G°$(300 K)[b] | $\Delta H°$ | $\Delta S°$ | $\Delta G^\dagger$(300 K)[c] | $\Delta H^\dagger$ | $\Delta S^\dagger$ | ref |
|---|---|---|---|---|---|---|---|
| $[CpFe(CO)_2]_2$ (1:3 toluene-$d_8$–$CS_2$) | –0.15 ± 0.1 | 0.9 ± 0.1 | 3.5 ± 0.5 | ~12 (220 K) | | | 19a,d[d] |
| $[\{FeMn\}(\mu\text{-}CO)_2][PPN]$[e] (**1a**-PPN$^+$, $CD_2Cl_2$) | –0.11 | 1.3 | 5 | 15.8 ± 0.4 | 16.4 ± 0.3 | 2.2 ± 0.8 | this work |
| $[CpMn(CO)(NO)]_2$ (toluene-$d_8$) | –0.44 ± 0.3 | –0.16 ± 0.1 | 0.93 ± 0.4 | 16.2 ± 3.4 | 18.5 ± 2.4 | 8 ± 8 | 19d[d] |
| $\{FeMn\}(\mu\text{-}COCH_3)(\mu\text{-}CO)$[e] (**2a**, $C_6D_6$) | 0.46[f] | ~0 | ~–1.5 | 16.4 ± 0.7 | 14.4 ± 0.5 | –7 ± 2 | this work |
| $\{FeMn\}(\mu\text{-}COCH_2CH_3)(\mu\text{-}CO)$[e] (**3a**, toluene-$d_8$) | 0.36 ± 0.16 | 1.0 ± 0.1 | 2.2 ± 0.4 | 16.5 ± 0.9 | 18.0 ± 0.7 | 5 ± 2 | this work |
| $\{FeMn\}(\mu\text{-}COCH_2CH_3)(\mu\text{-}CO)$[e] (**3a**, acetone-$d_6$) | 1.22 ± 0.96 | 3.1 ± 0.6 | 6.4 ± 2.4 | 17.2 ± 4.9 | 21 ± 3 | 13 ± 11 | this work |
| $[CpCr(NO)_2]_2$ (toluene-$d_8$) | –1.6 ± 0.3 | –2.1 ± 0.3 | –1.7 ± 1.0 | 20.8 ± 2.2 | 20.8 ± 1.3 | 0 ± 6 | 19d[d] |
| $[Cp(CO)Fe]_2(\mu\text{-}GeMe_2)(\mu\text{-}CO)$[g] (*o*-dichlorobenzene) | 1.2 ± 0.3 | 2.1 ± 0.1 | 3.0 ± 0.7 | 22.1 ± 0.9 | 21.9 ± 0.7 | –1 ± 2 | 21 |
| $[Cp(CO)Fe]_2(\mu\text{-}CH_2)(\mu\text{-}CO)$ ($C_6D_6$) | –0.6 ± 0.1 | 1.8 ± 0.1 | 4.1 ± 0.2 | 22.7 ± 1.7 | 19.0 ± 1.7 | –12.4 ± 0.5 | 22 |

[a] All values in kcal/mol and eu. [b] Calculated from least-squares fit of plot of ln (trans/cis) vs $1/T$, except as noted for **2a**. [c] Calculated from least-squares fit to Eyring plot of ln $(k/T)$ vs $1/T$. [d] Activation parameters from ref 19d converted[20] from $E_a$ and log $A$. [e] {FeMn} = Cp(CO)Fe–Mn(CO)MeCp. [f] Average % cis for the five temperatures from 274 to 294 K of 68.36 ± 0.33% was used to calculate $\Delta G°$ only, giving the approximate values shown for $\Delta H°$ and $\Delta S°$. [g] Trans to cis activation parameters from ref 21 were converted to cis to trans parameters according to the equation $k_{ct} = 2k_{tc}/(c/t)$, where the factor of 2 is derived from the detailed mechanism for this particular NMR analysis, $k_{tc} = 1/\tau$, and c/t is the calculated (extrapolated) cis/trans ratio.

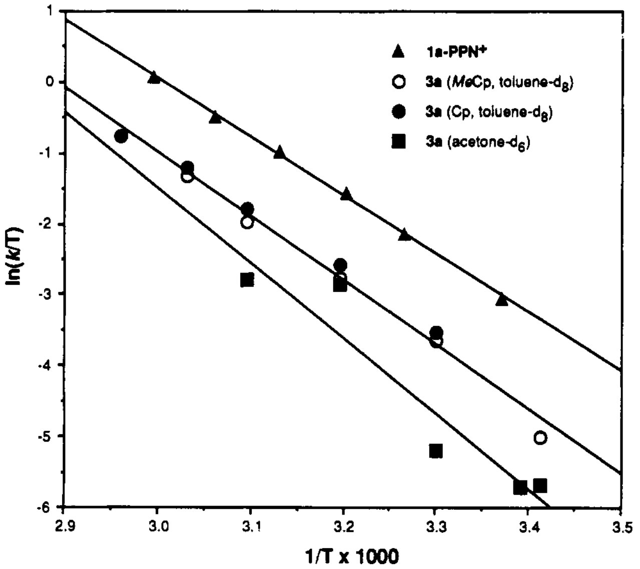
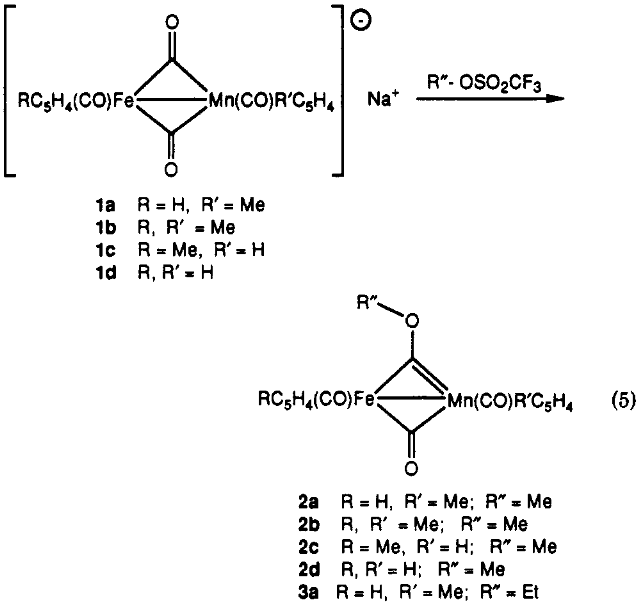


**Figure 1.** Eyring plots of ln $(k/T)$ vs $1/T$ where $k$ is the rate of cis to trans isomerization of **1a**-PPN$^+$, **3a** in toluene-$d_8$, and **3a** in acetone-$d_6$. Data for **2a** in benzene-$d_6$ overlap those for **3a** in toluene-$d_8$ and so are not shown. The least-squares-fit line for **3a** in toluene includes the rate constants measured from both *Me*CpMn and *Cp*Fe exchange.



**1a** R = H, R′ = Me
**1b** R, R′ = Me
**1c** R = Me, R′ = H
**1d** R, R′ = H

(5)

**2a** R = H, R′ = Me; R″ = Me
**2b** R, R′ = Me; R″ = Me
**2c** R = Me, R′ = H; R″ = Me
**2d** R, R′ = H; R″ = Me
**3a** R = H, R′ = Me; R″ = Et
**3b** R, R′ = Me; R″ = Et

solvent removal a new red-purple solid. Subsequent workup and recrystallization from pentane/diethyl ether gave in 60% yield a compound that was identified as the heterodinuclear methoxycarbyne complex **2a**. Methoxycarbynes **2b–d** were synthesized in similar yields (eq 5).

The carbonyl ligands are proposed to be arranged as shown on the basis of the infrared and $^{13}C$ NMR spectra. The IR for **2a**, for instance, exhibited strong bands at 1954 and 1907 cm$^{-1}$, indicative of two terminal carbonyl ligands, and a strong band at 1774 cm$^{-1}$, indicative of a bridging carbonyl ligand. The $^{13}C$ NMR spectrum (acetone-$d_6$) also exhibited signals indicative of two terminal CO ligands (228.9, Mn–CO; 214.8 ppm, Fe–CO) and a bridging CO (272.7 ppm); as with the anion, these are typical values,[23] and in particular the $\mu$-CO of the neutral iron dimer *cis*-$[CpFe(CO)_2]_2$ is observed at 275 ppm.[19b] Key NMR data in support of the methoxycarbyne formulation are the appearance of the new methyl signal in the $^1H$ NMR spectrum (acetone-$d_6$) at $\delta$ 5.02, which was absent when $CD_3OSO_2CF_3$ was used for the alkylation, and the carbyne resonance at 390.7 ppm characteristic of the bridging carbon atom in $\mu_2$-tolylidynes[25] and $\mu_2$-alkoxycarbynes[4,18a–e] and thiocarbynes,[17b] and the new methoxy signal at 73.2 ppm in the $^{13}C$ NMR spectrum. In less polar solvents **2a**, like **1a**, apparently exists as a mixture of cis and trans isomers (eq 6); observed isomer ratios at ambient temperature were 100:0 in acetone-$d_6$, 74:26 in methylene-$d_2$ chloride, and 68:32 in benzene-$d_6$, as judged by $^1H$ NMR spectroscopy. The $^{13}C$ NMR spectrum in $C_6D_6$ exhibited two resonances for several of the carbon atoms, including two peaks in a ~2:1 ratio, respectively, due to bridging carbyne carbon atoms at $\delta$ 391.2 and 394.6 ppm, bridging CO ligands at 270.8 and 269.9 ppm, and Mn–CO ligands at 228.1 and 229.0 ppm. However, only one methoxy carbon and only one Fe–CO band were seen, indicating that the chemical shifts for the two isomers are

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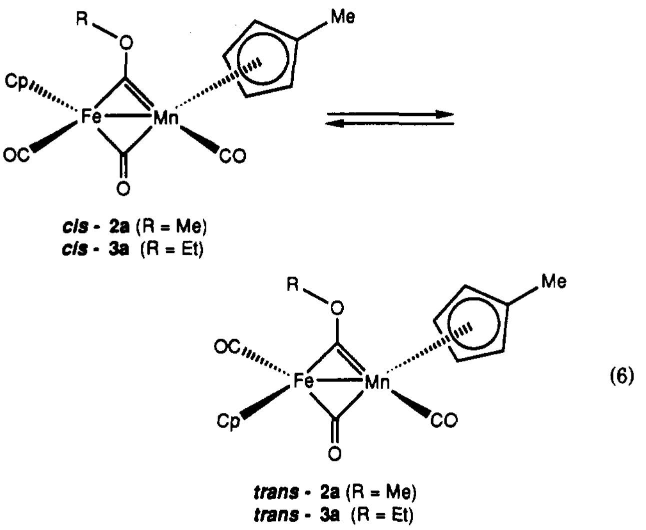
[25] (a) Chetcuti, M. J.; Green, M.; Jeffery, J. C.; Stone, F. G. A.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 948–949. (b) Stone, F. G. A. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; Washington, DC, 1983; pp 383–397.



*cis* - **2a** (R = Me)
*cis* - **3a** (R = Et)

*trans* - **2a** (R = Me)
*trans* - **3a** (R = Et)

(6)

coincident, as also was seen in the $^1$H NMR spectrum for the methoxy signal.

Alkylation of **1a** and **1b** with ethyl triflate to give ethoxycarbynes **3a** and **3b** occurred similarly to that described above with methyl triflate (eq 5). The IR spectra exhibit similar terminal and bridging CO bands, and the $^{13}$C NMR spectrum (values that follow are for **3a** in acetone-$d_6$) again confirmed the arrangement of carbonyl ligands (273.6 ($\mu$-CO), 229.6 (Mn–CO), 215.4 (Fe–CO) ppm), the presence of a carbyne carbon (388.6 ppm), and the presence of an ethoxy group (84.8 and 16.0 ppm). The low-field ethoxy $CH_2$ carbon resonates in the same region of the spectrum as the MeCp and Cp methine carbons and was identified by means of the DEPT-135 NMR spectrum. The $^1$H NMR spectrum in acetone-$d_6$ exhibited a small triplet just downfield of the large triplet due to the cis isomer, but presumably because of the low concentration of the trans isomer (~10%), no other peaks due to it were seen in that solvent. The diastereotopic hydrogens of the $CH_2$ group appeared as a 16-line $ABX_3$ multiplet. The spectrum in $C_6D_6$ consisted of a ~2:1 ratio of isomers as judged by the pairs of Cp and MeCp methyl peaks.

**Variable-Temperature $^1$H NMR Spectra of Alkoxycarbynes.** Heating a $C_6D_6$ solution of **2a** resulted in coalescence of both the MeCp methyl signals and the Cp signals of the two isomers, at ~310 K for the *Me*Cp peaks, and at ~322 K for the more widely separated Cp peaks (Figure 2). Return to room temperature gave the same ratio of isomers as at the start. No significant change in cis–trans ratio was observed over the temperature range 274–294 K as judged both by integrating the MeCp methyl peaks and by varying the cis–trans ratios in the calculated spectra, so the average value of the integrations, 68.4 ± 0.3% cis, was used for the rate calculations at all temperatures. Line-shape analyses were carried out for both sets of exchanging peaks (see Experimental Section for details) and gave similar rate constants at the same temperatures. Calculated equilibrium and activation parameters are collected in Table I.

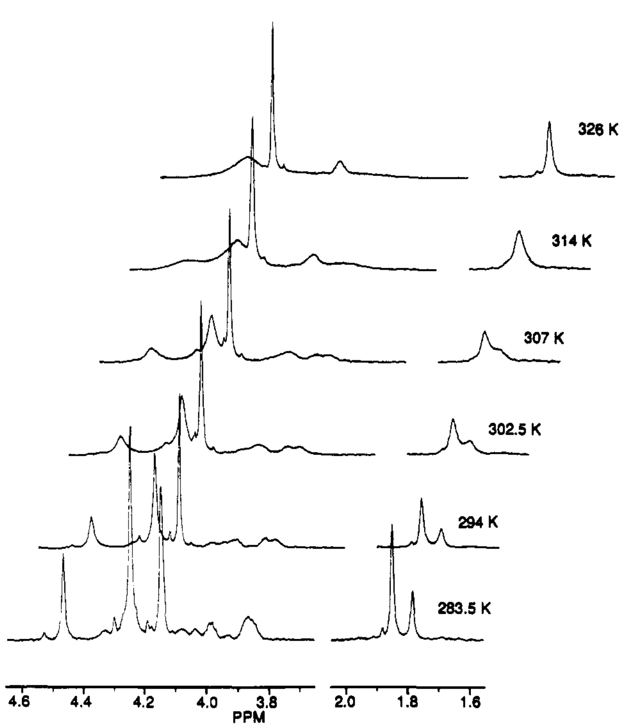


**Figure 2.** Variable-temperature $^1$H NMR (200 MHz) spectra of **2a** in $C_6D_6$, plotted at constant height of the nonexchanging methoxy signal at ~4.1 ppm. The chemical shift of this peak varies with temperature.

Variable-temperature $^1$H NMR spectra were recorded over a wide temperature range for **3a** in both toluene-$d_8$ and acetone-$d_6$. The cis–trans ratios were measured over the temperature range 253–283 K in both solvents, but even over this 30 K range the changes were small, giving large errors in the derived thermodynamic parameters. Heating **3a** in both solvents again led to coalescence of peaks due to the two isomers. In toluene, coalescence of the MeCp methyl peaks occurred by 323 K and of the Cp peaks by 330 K. As for **2a**, line-shape analyses were carried out for both sets of exchanging peaks (see Experimental Section for details) and again gave similar rate constants at the same temperatures and a linear Eyring plot (Figure 1); derived parameters are collected in Table I. The ethoxy methyl triplets were coincident above 293 K and remained visible as a triplet to the highest temperature used, 338 K. The ethoxy $CH_2$ hydrogens, however, appeared as a complex multiplet at and below room temperature due to noncoincidence of the cis–trans isomers and the fact that they are diastereotopic. Heating the sample resulted in apparent coalescence of the signals due to the cis–trans isomers but not the diastereotopic hydrogens, since at 338 K a broad *quintet*, presumed to be due to overlapping *quartets*, was observed. In acetone, the only peak visible due to the minor isomer was the ethoxy methyl peak; coalescence with the major isomer peak occurred by 323 K and allowed a line-shape analysis to be carried out, but the results (Table I) are subject to large errors due to the dissimilarity in the sizes of the exchanging peaks; these errors are reflected in the relatively poor Eyring plot obtained (Figure 1). Apparent coalescence of the diastereotopic $CH_2$ hydrogens and two of the diastereotopic MeCp cyclopentadienyl hydrogens also was observed. Two factors made it impossible to determine if the coalescence was due to chemical exchange, however. First, broadening of all signals (including the TMS reference peak) reproducibly occurred at high temperature, resulting in resolution insufficient to observe coupling of any peaks. Second, plotting the chemical shifts of the diastereotopic hydrogen atoms vs temperature at low temperature gave linear plots tending toward convergence of the $CH_2$ hydrogens and the two high-field MeCp cyclopentadienyl signals. Coalescence of the MeCp signals would occur solely from this effect; the other two MeCp signals were sufficiently separated at 360 MHz that no broadening due

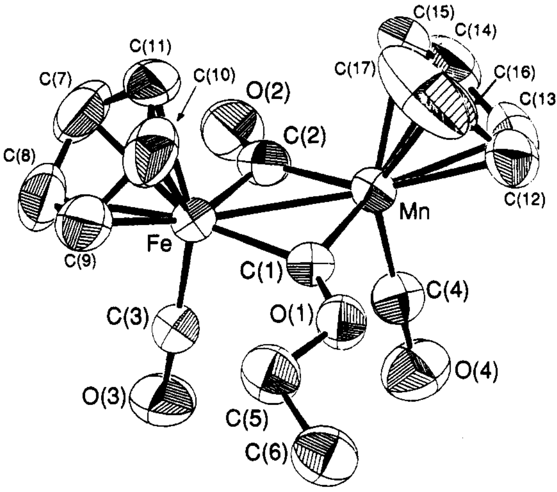


**Figure 3.** ORTEP drawing of **3a**.

**Table II. Selected Distances (Å) and Angles (deg) in 3a**

| | | | |
|---|---|---|---|
| Fe–Mn | 2.572 (1) | C(3)–Fe–Mn | 98.8 (1) |
| Fe–C(1) | 1.843 (4) | C(1)–Mn–Fe | 45.8 (1) |
| Fe–C(2) | 2.065 (5) | C(1)–Mn–C(2) | 96.9 (2) |
| Fe–C(3) | 1.745 (5) | C(1)–Mn–C(4) | 88.8 (2) |
| Mn–C(1) | 1.839 (4) | C(2)–Mn–Fe | 52.5 (2) |
| Mn–C(2) | 1.883 (5) | C(2)–Mn–C(4) | 91.3 (2) |
| Mn–C(4) | 1.763 (5) | C(4)–Mn–Fe | 99.4 (2) |
| C(1)–O(1) | 1.305 (5) | Fe–C(1)–Mn | 88.6 (2) |
| C(2)–O(2) | 1.176 (5) | Fe–C(1)–O(1) | 138.5 (3) |
| C(3)–O(3) | 1.144 (5) | Mn–C(1)–O(1) | 132.9 (3) |
| C(4)–O(4) | 1.155 (5) | C(1)–O(1)–C(5) | 120.3 (4) |
| C(5)–O(1) | 1.475 (5) | O(1)–C(5)–C(6) | 107.4 (4) |
| C(5)–C(6) | 1.492 (7) | Fe–C(2)–Mn | 81.2 (2) |
| C(1)–Fe–Mn | 45.6 (1) | Fe–C(2)–O(2) | 130.4 (4) |
| C(1)–Fe–C(2) | 90.7 (2) | Mn–C(2)–O(2) | 148.3 (4) |
| C(1)–Fe–C(3) | 91.3 (2) | Fe–C(3)–O(3) | 178.9 (4) |
| C(2)–Fe–Mn | 46.3 (1) | Mn–C(4)–O(4) | 178.0 (5) |
| C(2)–Fe–C(3) | 88.7 (2) | | |

to chemical exchange would have been visible at 338 K. While this temperature dependence of chemical shift would have been insufficient to give coalescence of the $CH_2$ peaks, the broadening of all the peaks precluded a meaningful line-shape analysis of the methylene peaks from being made.

**X-ray Structure of 3a.** Despite numerous attempts, crystals of **2a–d** suitable for X-ray analysis could not be obtained, presumably due to the presence of the cis–trans isomers. However, **3a** yielded suitable crystals one time, even though typically powders similar to those obtained from **2a** were normally obtained. Details of the structure determination are described in the Experimental Section; it is worth noting that an advantage of the use of Cp and MeCp rings is the unambiguous assignment of the iron and manganese atoms, respectively. An ORTEP drawing is shown in Figure 3, and selected bond distances and angles are given in Table II. The major features of the structure deduced from the NMR spectra—the presence of the μ-carbyne ligand and arrangement of CO ligands—are clearly confirmed. Of additional interest is that (1) the structure is of the cis isomer, (2) the carbyne ligand bridges the Fe–Mn bond fairly symmetrically, with Fe–C and Mn–C bond lengths of 1.843 (4) and 1.839 (4) Å, respectively, and Fe–C–O and Mn–C–O angles of 138.5 (3) and 132.9 (3)°, and (3) the bridging carbonyl is semibridging, with a shorter Mn–C bond length of 1.883 (5) Å and larger Mn–C–O angle of 148.3 (4)°, and a longer Fe–C bond length of 2.065 (5) Å and smaller Fe–C–O angle of 130.4 (4)°. The dihedral angle between the Fe–(μ-C)–Mn planes is 163.4°, which is comparable to related diiron compounds.[26] The $^1H$ NMR spectrum of this material exhibited the same cis–trans ratio as other samples in $C_6D_6$, despite the observation of the cis stereochemistry in the solid state.

**Reactions. Thermal Decomposition of 2a and 3a.** All of the following thermal reactions are shown in Scheme I. Heating **2a** in benzene in a sealed NMR tube at 45 °C for 13 h resulted in no visible change, although $MeCpMn(CO)_3$ was present in ~3% yield as judged by $^1H$ NMR. Heating was continued at 65 °C, resulting in a slow change in color from a dark red to a green-brown color. A precipitate began to form after 8 h, and after 130 h decomposition was complete, giving $MeCpMn(CO)_3$ (90%), $CpFe(CO)_2CH_3$ (24%), $[CpFe(CO)_2]_2$ (9%), $[CpFe(CO)]_4$ (15%), and $CH_4$ (4%) as the major decomposition products identified by $^1H$ NMR. In this and subsequent experiments, products were identified by comparison of NMR data in $C_6D_6$ to those obtained from commercially available materials or compounds prepared according to literature procedures, except as noted (see below for $[CpFe(CO)]_4$ and Experimental Section for remaining details). Heating **2a** at 65 °C in the presence of 1.2 equiv of $PPh_3$ (~0.06 M) resulted in complete consumption of **2a** within 36 h, giving a relatively light red solution and a precipitate. A simpler looking $^1H$ NMR spectrum was obtained than that in the absence of $PPh_3$, but the yields were lower: $MeCpMn(CO)_3$ (46%), $CpFe(CO)(PPh_3)CH_3$ (44%), $CpFe(CO)_2CH_3$ (11%), $[CpFe(CO)_2]_2$ (4%), and possibly $MeCpMn(CO)_2PPh_3$ (2%)[27] were obtained. Heating at 75 °C in the presence of 5 equiv or more of $PPh_3$ gave higher yields of $MeCpMn(CO)_3$ and $CpFe(CO)(PPh_3)CH_3$, lower yields of $[CpFe(CO)_2]_2$, and no detectable $CpFe(CO)_2CH_3$ and $MeCpMn(CO)_2PPh_3$.[28] The isolated precipitate was found to be soluble in $CD_2Cl_2$ and was identified as **1a**-$Ph_3PCH_3^+$. The more nucleophilic phosphines $MePh_2P$ and $Me_3P$ rapidly reacted with **2a** at 75 °C to give benzene-insoluble precipitates presumed to be the corresponding phosphonium salts of **1a**, and for $PMe_3$, no benzene-soluble products formed at all.

Ethoxycarbyne **3a** was subjected to conditions similar to those described above. After 6 h in $C_6D_6$ at 65 °C, 7% unreacted starting material remained, giving $MeCpMn(CO)_3$ (89%), $CpFe(CO)_2CH_2CH_3$ (13%), $[CpFe(CO)_2]_2$ (21%), $[CpFe(CO)]_4$ (56%), $C_2H_4$ (11%), and $C_2H_6$ (28%) as the major decomposition products identified by $^1H$ NMR. The tetrameric cluster $[CpFe(CO)]_4$ was identified by isolation from this reaction and comparison of spectral data (IR, $^1H$ NMR, MS) to those in the literature.[29] Ethane was identified by independent synthesis from EtI and $Bu_3SnH$. Reaction with $PPh_3$ (2 equiv, 0.08 M) at 45 °C led to complete consumption of starting material after 103 h, giving $MeCpMn(CO)_3$ (98%), $CpFe(CO)(PPh_3)CH_2CH_3$ (29%), $CpFe(CO)_2CH_2CH_3$ (12%), $[CpFe(CO)_2]_2$ (29%), $C_2H_4$ (13%), and $C_2H_6$ (13%), while reaction with $PPh_2Me$ (1.4 equiv $PPh_2Me$, 0.1 M) at 65 °C went to completion in 19 h and was cleaner, giving $MeCpMn(CO)_3$ (97%), $CpFe(CO)(PPh_2Me)CH_2CH_3$ (64%), $CpFe(CO)_2CH_2CH_3$ (5%), $[CpFe(CO)_2]_2$ (3%), $C_2H_4$ (8%), and $C_2H_6$ (8%). At high concentrations of $PPh_2Me$ (10.4 equiv, 0.68 M),

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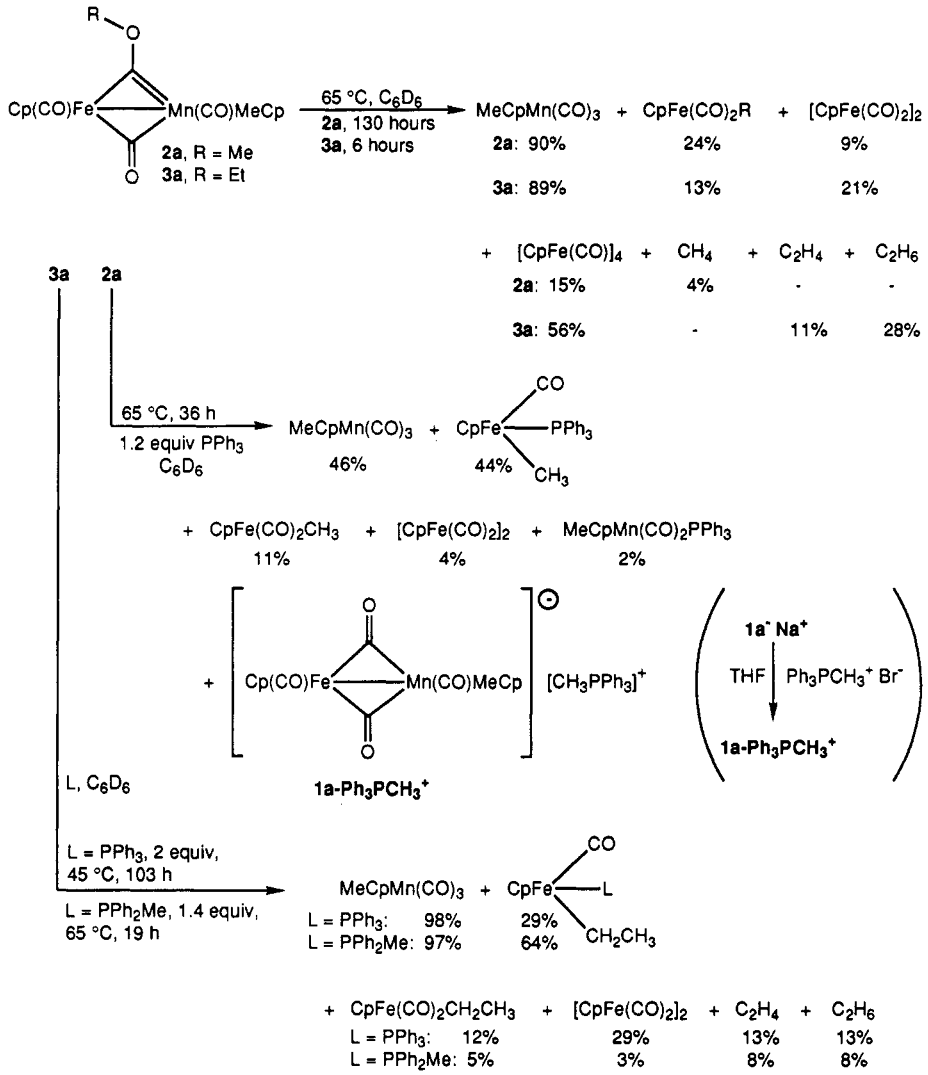
[26] Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633–1637.

[27] Nyholm, R. S.; Sandhu, S. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1963**, 5916–5919.

[28] Fong, R. H.; Hersh, W. H. Manuscript in preparation.

[29] (a) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227–2230. (b) Landon, S. J.; Rheingold, A. L. *Inorg. Chim. Acta* **1981**, *47*, 187–189.

**Scheme I**



products yields were $MeCpMn(CO)_3$ (75%), $CpFe(CO)(PPh_2Me)CH_2CH_3$ (43%), $C_2H_4$ (2%), and $C_2H_6$ (7%).[30] Reaction with $PPhMe_2$, while not quantified, was similar, while that with $PMe_3$ gave a large amount of black precipitate presumed to be due to dealkylation, like that seen for **2a**, but was not pursued further.

**Other Reactions.** Photolysis of **2a** gave results similar to thermal decomposition, in that $MeCpMn(CO)_3$, $CpFe(CO)_2CH_3$, $[CpFe(CO)_2]_2$, and $CH_4$ were observed, but the reaction was slow initially and slowed even more as the reaction proceeded, evidently due to a precipitate that formed and coated the NMR tube after about 35 h of irradiation, blocking out the light. After 162 h of photolysis, the experiment was terminated, although ~10% unreacted **2a** remained. Hydrogenation of **2a** was carried out in $C_6D_6$ at 45–65 °C under ~3 atm $H_2$. Little reaction occurred at 45 °C, after which heating was continued at 55 °C for 55 h and 65 °C for 17 h. The only identifiable organometallic products were the usual $MeCpMn(CO)_3$ (65%), $CpFe(CO)_2Me$ (12%), $[CpFe(CO)_2]$ (16%), and $[CpFe(CO)]_4$ (3%), and in addition, methane (3%) and dimethyl ether (2%) were observed by $^1H$ NMR. Singlets of comparable intensity to the last two compounds were observed at $\delta$ 2.11 and 1.84 but were not identified. Lastly, in an attempt to prepare a difunctional methylene/carbyne cluster,[3a] **2a** was combined with diazomethane; no reaction was observed at room temperature, and heating only gave thermal decomposition.

## Discussion

**Dinuclear Anions.** While the synthesis of heterodinuclear compounds is an exceedingly active area of research,[31] to the best of our knowledge **1a–d** are the first examples of dinuclear anions that have two different metal atoms and have cyclopentadienyl ligands. Displacement of a neutral ligand[31a] as shown for the preparation of **1** in eq 3 succeeds as long as the nucleophile is $CpFe(CO)_2^-$ or $CpRu(CO)_2^-$ rather than less nucleophilic anions[32] such as $CpW(CO)_3^-$.[33] In addition, as shown in eq 3, the THF adduct of $MeCpMn(CO)_2$ is more reactive than the MeCN adduct, allowing the reaction to be carried out at room temperature. Herrmann has recently reported the use of a third manganese source for the synthesis of **1a**-$PPN^+$,

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[30] Idmoumaz, H.; Lin, C.-H.; Hersh, W. H. Manuscript in preparation.

[31] (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; G. Wilkinson, Ed.; Pergamon Press: Oxford, 1982; Vol. 6; pp 763–877. (b) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41–107.

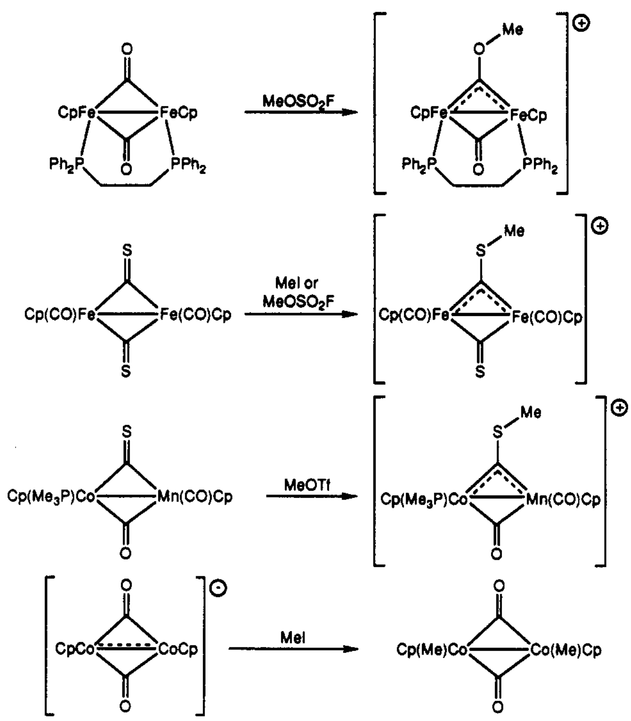
[32] (a) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541–1547. (b) Lai, C.-K.; Feighery, W. G.; Zhen, Y.; Atwood, J. D. *Inorg. Chem.* **1989**, *28*, 3929–3930.

[33] Fong, R. H.; Hersh, W. H. Unpublished results.

in which ($\mu_3$-Sn)[MeCpMn(CO)$_2$]$_3$ was refluxed with CpFe(CO)$_2^-$, but the purpose was presumably the investigation of the chemistry of the novel tin–manganese cluster, not the development of a new synthesis of heterodinuclear anions.[34] Graham described in 1967 what appear to be the first heterodinuclear anions, MM′(CO)$_{10}$ (M = Mn, Re; M′ = Cr, Mo, W), prepared by reaction of M(CO)$_5^-$ with M′(CO)$_6$ at high temperature in order to allow thermal substitution of CO.[35] Ruff described in 1968 a number of additional compounds including FeCo(CO)$_8^-$, FeMn(CO)$_9^-$, and CoW(CO)$_9^-$ prepared from Co(CO)$_4^-$ or Mn(CO)$_5^-$ and Fe(CO)$_5$ or W(CO)$_6$, for instance, where loss of CO from the neutral reactants was induced photochemically.[36] More recently, the labile ligand strategy was used to prepare H(CO)$_4$Fe–M(CO)$_5^-$ (M = Cr, W) from HFe(CO)$_4^-$ and M(CO)$_5$(THF),[37] and FeRe(CO)$_9^-$ from Re(CO)$_5^-$ and Fe(CO)$_4$(NCMe).[38] Examples of anion displacement of a *halide* are more numerous, however, to give *neutral* heterodinuclear compounds.[31a,39] Two examples of *homo*nuclear bis(cyclopentadienyl) anions are known, namely, Bergman's [($\eta^5$-C$_5$R$_5$)M(CO)]$_2^-$ (M = Co, R = H; M = Rh, R = Me) radical anions prepared by reduction of neutral precursors.[40]

**Site of Alkylation.** Alkylation of the anion 1 could be achieved only with "hard" triflates, exclusively yielding O-alkylation to give the alkoxycarbynes 2 and 3. Despite the variety of anions noted above and in the Introduction that have been alkylated, 2 and 3 appear to be only the second *neutral* alkoxycarbynes that contain only *two* metal atoms,[4] and the first *hetero*dinuclear alkoxycarbynes. Mathieu's diiron ethoxycarbyne described in the Introduction is neutral by virtue of having a second $\sigma$-bound ligand, the $\sigma,\pi$-vinyl moiety, while 2 and 3 are neutral by virtue of having different metal atoms. Use of the soft alkylating agent MeI with 1a results in oxidation to give in nonstoichiometric fashion the neutral (cyclopentadienyl)manganese and -iron carbonyls MeCpMn(CO)$_3$ and [CpFe(CO)$_2$]$_2$. While Semmelhack and later Bergman observed that the same features common to enolate O vs C alkylation can apply to mononuclear metal acylates,[41] in which hard alkylating reagents yield more O-alkylation and soft alkylating reagents more M-alkylation, metal alkylation of 1a by MeI seems unlikely since formation of CpFe(CO)$_2$Me would have been a plausible outcome. Instead, the structure of the resultant cluster seems to be a better predictor of site of alkylation than does hardness of the electrophile. That is, O-alkylation conserves the (cyclopentadienyl)dicarbonyliron dimer structure of the anion, in which two terminal and two bridging ligands are present. Similar results have been obtained for other neutral and anionic dinuclear compounds (Scheme II), as in the synthesis of the iron dimer analogue in which the $\mu_2$-bis(diphenylphosphino)ethane ligand replaces two carbonyl ligands[16] and the cationic diiron[17c] and Co/Mn[17b] thiocarbynes shown. More strikingly, the same effect is observed in the alkylation of [CpCo(CO)]$_2^-$ and the rhodium analogue,[40] where methylation occurs on both metal atoms to again give the iron dimer structure, where the two terminal ligands are now methyl groups. Other examples of M-alkylation are known where the prediction is less clear-cut. The reaction of FeW(CO)$_9^{2-}$ with MeI or MeOTs gives MeFeW(CO)$_9^-$ having the M$_2$(CO)$_{10}$ (M = Mn, Re) structure[42] rather than the methoxycarbyne which would have the Fe$_2$CO$_9$ type of structure, while as described in the Introduction Ru$_2$($\mu$-CO)[bis(dimethylphosphino)methane](CO)$_4$ reacts with MeOTf to give equal amounts of cationic methyl and methoxycarbyne adducts.[7g]

Scheme II



**Cis–Trans Isomerization.** Both the anions and carbynes studied here exist in solution as interconverting cis and trans isomers. The cis isomers are thermodynamically favored in the solvents used, although at room temperature the trans isomer predominates for 1a-PPN$^+$. Data are collected in Table I for several related compounds as well, including the carbonyl- and nitrosyl-bridged dimers [CpM(XO)(YO)]$_2$ (M = Fe, X = Y = C; M = Mn, X = C, Y = N; M = Cr, X = Y = N) and the "carbene"/carbonyl-bridged dimers ($\mu$-XR$_2$)($\mu$-CO)[CpFe(CO)]$_2$ (XR$_2$ = CH$_2$, GeMe$_2$). Of these compounds, the trans isomer is thermodynamically favored only for the nitrosyl-containing dimers. However, given the range of terminal and bridging ligands, metals, and even charge in these eight isoelectronic compounds, the steric and electronic factors must be closely

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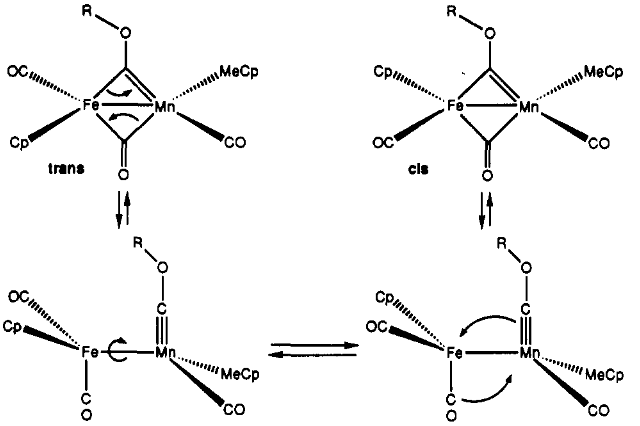
**Scheme III**



balanced, and no simple explanation of the small differences in cis–trans ratios is likely. The iron dimer has been shown to exhibit isomer-ratio dependence on solvent polarity, with the assumption that the more polar solvents favor the cis isomer on the basis of its higher dipole,[19a,d] and this is presumed to be the case for carbynes **2a** and **3a**. At room temperature, a single isomer of **2a** was observed in the most polar solvent used, acetone-$d_6$, while 3:1 and 2:1 ratios were observed for the increasingly nonpolar solvents methylene chloride and benzene. For **3a**, a 95:5 ratio was seen in acetone, and a ~2:1 ratio was seen in both benzene and toluene.

The similarity in the activation barriers for conversion of the cis to trans isomers is clear only for the three Fe–Mn compounds as well as (coincidentally) $[CpMn(CO)(NO)]_2$, where attention is focussed on $\Delta G^\dagger$ since this is likely to be the most accurate parameter. The iron dimer lies 4 kcal/mol below the ~16 ± 1 kcal/mol range of these four compounds, while the chromium dimer and the $\mu$-$CH_2$ and $\mu$-$GeMe_2$ dimers lie 4–6 kcal/mol above it. The mechanism of cis–trans isomerization for the dimeric iron, manganese, and chromium compounds is thought to be the same,[19a,c,d] involving "unbridging" of the $\mu$-CO (or $\mu$-NO) ligands, rotation about the metal–metal bond, and closure of the bridging ligands. Since **1a**-$PPN^+$ is isostructural as well as isoelectronic to these dimers, and since the activation parameters measured for it lie within the ranges of these dimers, it is reasonable to suppose that its mechanism of cis–trans isomerization is identical. While the activation parameters measured for **2a** and **3a** are essentially the same as those of **1a**-$PPN^+$, the same cis–trans isomerization mechanism would require unbridging of the carbyne ligand as shown in Scheme III to give a terminal alkoxycarbyne, stable examples of which are rare as described in the Introduction. A similar problem has been recognized for cis/trans isomerization of a variety of $\mu$-alkylidenes, where formation of the analogous intermediate with a presumably high-energy terminal alkylidene could account for the slower isomerization compared to $[CpFe(CO)_2]_2$.[21,43] As an alternative, however, it has also been suggested that the alkylidene bridge might remain intact.[22,44] Such a supposition could account for the slower cis–trans isomerization of **2a** and **3a** relative to $[CpFe(CO)_2]_2$ but would not apply to **1a**-$PPN^+$. Indeed, given the facts that the chromium dimer has nearly as high a barrier as the $\mu$-$CH_2$ and $\mu$-$GeMe_2$ adducts, and **1a**-$PPN^+$ and $[CpMn(CO)(NO)]_2$ have barriers similar to those of the carbynes, barrier height is not a convincing mechanistic criterion and we presume that all of the compounds in Table I undergo cis–trans isomerization by the *same* mechanism.

While the above arguments focus on the structural differences between these compounds, the anionic complex **1**, carbynes **2** and **3**, and nitrosyls like the Mn and Cr dimers are closely related electronically:

$$M{\equiv}C{-}OMe \qquad M{\equiv}\overset{+}{N}{-}O^- \qquad M{\equiv}C{-}O^-$$

In mononuclear complexes, terminal nitrosyls and carbynes are clearly seen to be isoelectronic, and isostructural compounds are known.[45] To the extent that the negative charge in **1** might be localized on oxygen, it too would be expected to be more similar to these complexes than to one containing only neutral carbonyl ligands as in $[CpFe(CO)_2]_2$. The rate-determining step could involve the unbridging of the carbyne, nitrosyl, or carbonylate ligands to give an intermediate that could formally contain a M≡X (X = C, N) bond, or the intermediate with this functionality could be more resistant to M–M rotation and so the rate-determining step could occur after the unbridging step. The higher barrier for $[CpCr(NO)_2]_2$ then simply follows from the fact of having one additional such group. We will not speculate on why the alkylidene and related species have higher barriers, but it is interesting to note that protonation of a diiron $\mu$-vinylidene complex to give a cationic $\mu$-ethylidyne complex was apparently accompanied by a lowering of the barrier to cis–trans isomerization.[43a] Thus, it is possible that the carbyne bridge may *promote* cis–trans isomerization in spite of the presumed instability of the proposed intermediate terminal carbyne.

The mechanism in Scheme III also accounts for the fact that **3a** does not racemize while undergoing rapid cis–trans isomerization in toluene-$d_8$. The key feature is that the carbyne must migrate to only one of the metals. That is, the Mn center shown is stereogenic, but if migration to Fe occurred as well, racemization would occur; of course, exclusive migration to Fe would be equally acceptable. If carbyne unbridging does not occur, then the absence of racemization would require that the $\mu$-CO migrate only to one metal as well. This result is a unique feature of the use of heterodinuclear compounds and illustrates the potential for highly specific reactions.

**Solid-State Structure.** Known $\mu_2$-alkylidynes exhibit both symmetrical and asymmetrical bonding to the dinuclear center that they bridge.[46] For simplicity in electron counting we have been drawing the structure of the carbynes **2** and **3** with a manganese–carbon double bond to the carbyne carbon and a symmetrically bound $\mu$-CO ligand, but the X-ray structure of **3a** clearly shows that in the solid state the electronic imbalance of having two different metals is resolved instead by the presence of an unsymmetrical CO bridge and a symmetrical carbyne. *Homo*dinuclear complexes that have different ligands on the metals typically have semibridging carbonyl ligands

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**Table III. Comparison of Bond Lengths in Bridged Iron[a] and Manganese Dinuclear Compounds**

| compd | Fe—($\mu$-C) or Fe=C | Mn—($\mu$-C) or Mn=C | Fe—Fe | Mn—Mn | Fe—Mn | terminal |  | bridging |  | ref |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Fe—CO | Mn—CO[b] | Fe—CO | Mn—CO |  |
| ($\mu$-C(H)CH$_3$)($\mu$-CO)-[Cp(CO)Fe]$_2$ | 1.987 (1) |  | 2.525 (1) |  |  | 1.742 (1) |  | 1.905 (1) |  | 50 |
| [$\mu$-C(CH$_2$CH$_2$)]($\mu$-CO)-[Cp(CO)Fe]$_2$ | 1.943 (8) |  | 2.503 (7) |  |  | 1.73 (1) |  | 1.91 (1) |  | 26 |
| ($\mu$-C=C(Ph)CH$_2$Ph)($\mu$-CO)-[Cp(CO)Fe]$_2$ | 1.940 (4) |  | 2.510 (1) |  |  | 1.74 (1) |  | 1.928 (8) |  | 51 |
| ($\mu$-CO)$_2$[CpFe(CO)]$_2$ | 1.917 (7) |  | 2.531 (2) |  |  | 1.745 (15) |  | 1.917 (7) |  | 48b |
| [($\mu$-C-C(H)=C(H)-*p*-tolyl)-($\mu$-CO)[Cp(CO)Fe]$_2$]$^+$ | 1.841 (8) |  | 2.507 (1) |  |  | 1.777 (9) |  | 1.945 (9) |  | 52 |
| ($\mu$-CH$_2$)[MeCp(CO)$_2$Mn]$_2$ |  | 2.014 (5) |  | 2.779 (1) |  |  | 1.78 (2) |  |  | 53 |
| ($\mu$-C=CH$_2$)[Cp(CO)$_2$Mn]$_2$ |  | 1.975 (7) |  | 2.759 (2) |  |  | 1.78 (1) |  |  | 54 |
| Cp(CO)Mn($\mu$-CO)($\mu$-NO)-Mn(NO)Cp |  | 1.906 (5)[c] |  | 2.571 (1) |  |  | 1.723 (4)[c] |  | 1.906 (5)[c] | 19d |
| (CO)$_4$Fe($\mu$-C=C(H)CO$_2$Me)-($\mu$-CO)Mn(CO)$_2$Cp | 1.94 (2) | 1.95 (2) |  |  | 2.703 (4) | 1.83 (2) | 1.80 (2) | 2.73 (2) | 1.75 (2) | 55 |
| Cp(CO)Fe($\mu$-CS)($\mu$-CO)-Mn(CO)$_4$ | 1.924 (4) | 1.990 (8) |  |  | 2.632 (1) | 1.760 (3) | 1.86 (1) | 1.869 (4) | 2.19 (2) | 56 |
| Cp(CO)Fe($\mu$-CH$_2$)-($\mu$-CO)Mn(CO)$_4$ | 1.919 (5) | 2.085 (5) |  |  | 2.613 (1) | 1.789 (6) | 1.86 (2) | 1.916 (5) | 2.134 (5) | 57 |
| Cp(CO)Fe($\mu$-COEt)($\mu$-CO)-Mn(CO)MeCp (**3a**) | 1.843 (4) | 1.839 (4) |  |  | 2.572 (1) | 1.745 (5) | 1.763 (5) | 2.065 (5) | 1.883 (5) | this work |
| Cp(CO)(I)Fe=C[(CH$_2$)$_3$O] | 1.86 (1) |  |  |  |  | 1.74 (1) |  |  |  | 58 |
| Cp(CO)(I)Fe=C(OEt)Ph | 1.85 (1) |  |  |  |  | 1.76 (1) |  |  |  | 59 |
| Cp(CO)$_2$Mn=CPh$_2$ |  | 1.885 (2) |  |  |  |  | 1.788 (5) |  |  | 60 |
| Cp(CO)$_2$Mn=C(OEt)Ph |  | 1.87 (1) |  |  |  |  | 1.80 (1) |  |  | 61 |

[a] Data given are for cis isomers. [b] Data for terminal CO ligands cis to bridge. [c] The CO and NO ligands are disordered in the X-ray structure, but spectral evidence supports the presence of one bridging and terminal ligand of each type; the "Mn—C" distances are therefore an average of Mn—C and shorter Mn—N distances.

in order to redistribute electron density,[47] so it is hardly surprising that this also occurs in a *hetero*dinuclear compound. In solution, the $^{13}$C chemical shift of the $\mu$-CO carbon is indistinguishable from that seen in Cp(CO)Fe($\mu$-CO)$_2$Fe(CO)Cp, however, for which the X-ray structure reveals a symmetrical $\mu$-CO ligand,[48] so it is not clear that this bonding detail will be reflected in the chemistry of the carbynes. Nonetheless, it is noteworthy that in Stone's series of heterodinuclear alkylidyne complexes, those that have bridging carbonyls exhibit asymmetry in *both* bridges. That is, the carbonyl is semibridging, and the alkylidyne carbon to metal bond lengths exhibit double-bond character to one metal and single-bond character to the other,[49] leading to Stone's "dimetallacycloprop*ene*" designation.[25b] In order to ascertain whether or not the carbyne bridge in **3a** is really symmetrical in terms of bond order, then, comparisons must be made to other Fe–C and Mn–C bond lengths where the bond order is not in doubt.

Data from a number of (cyclopentadienyl)iron and -manganese $\mu_2$-alkylidene, vinylidene, alkylidyne, and carbonyl complexes is collected in Table III. Only bridging compounds have been considered for comparisons of single-bond lengths in order to minimize structural differences from **3a**, since it has been noted that M–($\mu$-CH$_2$)–M metal–carbon bond lengths are shorter than unbridged M-C bonds.[62] The Fe–C and Mn–C single-bond lengths are quite similar, ranging from 1.917 (7) to 1.987 (1) Å and from 1.906 (5) to 2.085 (5) Å, respectively. However, direct comparison of the diiron and dimanganese $\mu$-alkylidene and $\mu$-vinylidene complexes suggests that the Fe–C bond lengths are slightly (~0.03 Å) shorter, and comparison of the terminal CpFe–CO and CpMn–CO bond lengths supports this conclusion. The bridging carbonyl bond lengths merely illustrate once again the semibridging nature of the $\mu$-CO in **3a**. The Fe–C and Mn–C carbyne bond lengths in **3a** are identical within experimental error and at 1.841 (4) Å are significantly shorter than single bonds and in fact identical to those of the Fe–C bonds of Casey's cationic alkylidyne[52] (the fifth entry in Table III), where the bond order is presumably 1.5. A comparison to *mono*nuclear iron and manganese carbenes and alkylidenes, where the compounds in Table III represent the closest structural analogues to **3a**, confirms the multiple-

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bond character of the carbyne bonding, with Fe=C and Mn=C bond lengths averaging 1.855 (10) and 1.88 (1) Å, respectively, but both are *longer* than those in **3a**. While these values for terminal ligands are therefore not helpful in assigning bond orders to the M–C carbyne bonds in **3a**, they do provide additional evidence that Mn–C bonds are *longer* than Fe–C bonds having the *same* bond order. We conclude therefore that even though the Mn–C and Fe–C bond lengths in **3a** are identical, the Mn–C bond is shortened more from the putative single-bond length than is the Fe–C bond. That is, while both bonds are short and at least of bond order 1.5, the Mn–C bond has more double-bond character than the Fe–C bond.

In addition to the metal–carbyne bond order, the carbon–oxygen bond order is of interest. Farrugia has pointed out that alkoxycarbynes typically behave as $\pi$-donors at oxygen, where the oxygen is considered to be $sp^2$-hybridized in order to allow donation of electron density from the oxygen p orbital into that of the carbyne carbon.[63] Evidence for this is found in the typical ~120° bond angle about oxygen in alkoxycarbynes. In **3a**, that angle is 120.3 (4)°, and in addition the oxygen and methylene carbon are essentially (within 0.015 Å) in the Fe–($\mu$-C)–Mn plane. Comparison of this $\mu_2$-carbyne to our related $Fe_2Mn$–$\mu_3$-alkoxycarbynes shows that the interaction is stronger in **3a**. The carbyne–metal bonds are shorter in **3a**, and so is the C–O bond of the carbyne, 1.305 (5) Å in **3a** vs an average 1.356 (9) Å in the $Fe_2Mn$–$\mu_3$-alkoxycarbynes.[3] As a point of reference, the length of the C–O bond in our $Fe_2Mn$ $\mu_2$-methoxycarb*ene* complex, which presumably is not involved in $\pi$-donation to the carbene carbon, is significantly longer at 1.385 (3) Å, and the angle about oxygen is significantly more acute, 116.0 (2)°.[3b]

A number of iron–manganese-bonded complexes are known,[3,55–57,64] including the $\mu$-vinylidene,[55] $\mu$-CS,[56] and $\mu$-methylene[57] complexes shown in Table III, and allow comparison to the Fe–Mn bond length in **3a**. The range of Fe–Mn bond lengths is relatively large, from an average 2.56 (1) Å for the MeCpMn–FeCp bonds in our $Fe_2Mn$ $\mu_3$-capped difunctional clusters,[3] to 2.843 (4) Å for $Cp(CO)_2Fe$–$Mn(CO)_5$[64a] and 2.848 (4) Å for $(CO)_4Fe(\mu_2\text{-}AsMe_2)Mn(CO)_4$.[64c] The 2.572 (1) Å bond length seen in **3a** in fact appears to be the shortest for a dinuclear Fe–Mn complex, but the length is clearly driven by the shortness of the bonds to the bridging carbyne, which are also the shortest for any Fe–Mn bridging ligands. The apparent sensitivity of Mn–Mn bond lengths to bridging ligands was illustrated in a detailed study by Bernal, Herrmann, and co-workers,[53] and this can be seen in the data in Table III: the singly bridged manganese dimers have bond lengths of 2.759 (2) and 2.779 (1) Å, but the doubly bridged dimer $[CpMn(CO)(NO)]_2$ has a bond length of 2.571 (1) Å, virtually the same as in doubly bridged **3a**.

**Reactions.** The obvious site of reactivity in **2** and **3** is the alkyl moiety of the alkoxycarbyne. The thermal reactions involve cleavage of the alkyl–oxygen bond and alkyl migration to iron, with metal–metal bond cleavage occurring at an unknown point during this process. Reactions with phosphines include the thermal reaction, in which the phosphine simply acts to trap the presumed intermediate Cp(CO)Fe–R (R = $CH_3$, $C_2H_5$) to give the alkyl phosphine/carbonyl adduct in a stoichiometric fashion,[28,30] as well as a second cleavage reaction of the alkyl–oxygen bond to regenerate the stable anion **1**. Both types of reaction depend on the electrophilic character of the carbon bound to the carbyne oxygen, which is reasonable given the apparently strong oxygen to carbyne carbon $\pi$-donation suggested by the X-ray structure. It is not obvious why the migration type of reaction has not been observed previously; clearly cationic alkoxycarbynes possess equally electrophilic alkyl groups. One possibility is simply that elimination of stable $MeCpMn(CO)_3$ provides a thermodynamic driving force for the reaction. There is no evidence of phosphine attack directly on either metal, and the absence of any reaction with diazomethane similarly suggests that no coordination sites are made available during the thermal reactions. Photolysis gives the same result, and presumably ligand loss[44] is not a factor here. Only hydrogenation, giving a trace of dimethyl ether, gives any hint of reactivity at the carbyne carbon, but even in this reaction, alkyl–oxygen cleavage to give methane is more favorable.

## Conclusions

Syntheses of novel iron–manganese anions and alkoxycarbynes have provided a number of new heterodinuclear members of the (cyclopentadienyl)dicarbonyliron dimer class of compounds. Analysis of cis–trans isomerization rates suggests that the presence of the intuitively more robust carbyne bridge does not alter the widely accepted "unbridging" mechanism, by which a terminal alkoxycarbyne is proposed as an intermediate in this case. Analysis of the X-ray structure of the ethoxycarbyne shows the presence of a tightly bound $\pi$-donor carbyne ligand with a normal, albeit short, metal–metal bond, short metal–carbon bonds of bond order ~1.5, and possibly even higher bond order for the manganese–carbon bond. Thermal decomposition occurs by a novel oxygen to metal alkyl migration reaction. A detailed description of the mechanism of this reaction will be published separately. Future work in this area will include extending the synthetic method to other metals in order to probe the generality (if any) of the alkyl migration reaction, and routes to the isomeric acyl complexes that evidently do not form from these dinuclear anions or carbynes.

## Experimental Section

**General Considerations.** All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert-atmosphere drybox under recirculating nitrogen or by using standard Schlenk techniques. NMR spectra were recorded on JEOL FX90Q, IBM AF-200, Bruker WP-200, AM-360 and AM-500, and IBM/Bruker WP-200SY spectrometers; chemical shifts are reported relative to TMS or hydrogen in $C_6D_6$ ($\delta$ 7.15), $CD_2Cl_2$ ($\delta$ 5.32), acetone-$d_6$ ($\delta$ 2.04), $CD_3CN$ ($\delta$ 1.93), and toluene-$d_8$ ($\delta$ 2.09), and to $C_6D_6$ at 128.0 ppm, $CD_2Cl_2$ at 53.8 ppm, or acetone-$d_6$ at 29.8 ppm for $^{13}C$ NMR. Infrared spectra were obtained on a Perkin-Elmer 237 spectrometer with 0.1 mm NaCl solution cells, or a Mattson Galaxy 4020 FT-IR. Elemental analyses were

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performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained on an AEI-MS902 (EI) and an AEI-MS9 with FAB gun using xenon, at 5 kV in a matrix of acetone. Photolyses were carried out with a medium-pressure 450-W mercury Hanovia lamp.

All solvents were treated under nitrogen. Acetonitrile was purified by sequential distillation from calcium hydride and phosphorus pentoxide. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexane was purified by washing successively with 5% nitric acid in sulfuric acid, water, sodium bicarbonate solution, and water and then dried over calcium chloride and distilled from *n*-butyllithium in hexane. Pentane was dried over 3-Å sieves and vacuum-transferred. Methylene chloride was distilled from phosphorus pentoxide; $CD_2Cl_2$ was vacuum-transferred from phosphorus pentoxide. Acetone-$d_6$ and $CD_3CN$ were dried over 4-Å molecular sieves and vacuum-transferred prior to use; benzene-$d_6$ and toluene-$d_8$ were vacuum-transferred from sodium benzophenone ketyl.

Silica gel (200–400 mesh) was dried for several hours under vacuum while heating with a heat gun and was transferred under vacuum into the drybox. Triphenylphosphine was recrystallized from ethanol, and $Ph_3CH$ was recrystallized form hexane. Trimethylphosphine (Strem), $Ph_2PMe$ (Pressure Chemical), $PhPMe_2$ (Pressure Chemical), $Ph_3PCH_3{}^+Br^-$ (Aldrich), MeCpMn$(CO)_3$ (Aldrich), and $[CpFe(CO)_2]_2$ (Pressure Chemical) were used as received. Methyl triflate and ethyl triflate (Aldrich) were vacuum-transferred from $CaH_2$.

**[Cp(CO)Fe(μ-CO)₂Mn(CO)MeCp]⁻Na⁺ (1a). Method 1.** In the glovebox, 125 mL of THF was added to a mixture of 2.23 g (9.67 mmol) of MeCpMn$(CO)_2(CH_3CN)$[65] and 2.09 g (92% by weight, 9.67 mmol) of solid CpFe$(CO)_2{}^-Na^+\cdot\sim$0.5THF (prepared according to the literature method[66] followed by solvent removal on a vacuum line; determination of the mole fraction of THF in the solid by $^1$H NMR in $CD_3CN$ suggests the fraction shown above, but the weight fraction is variable and should be used for accuracy). A reflux condenser capped by a rubber septum was attached, the apparatus was removed from the glovebox, and the mixture was heated at reflux overnight under a nitrogen atmosphere. After cooling to room temperature, the solvent was removed on a vacuum line, leaving a red-brown solid which was purified by stirring for 15 min with benzene, filtering, and then washing the resultant solid several times with 5-mL portions of benzene until these washes were nearly colorless, yielding 4.05 g of a dull red solid that by $^1$H NMR ($CD_3CN$) was (by weight) 81% **1a** (3.26 g, 87% yield) and 19% THF: IR (THF) 1909 (s), 1850 (s), 1648 (m), 1723 (m) cm$^{-1}$; $^1$H NMR ($CD_3CN$) δ 4.38 (s, 5H), 4.10 (br s, 4H), *Me*Cp obscured by solvent resonance.

**Method 2.** Although the synthesis of MeCpMn$(CO)_2$(THF) has been described,[67] we find that the conversion from MeCpMn$(CO)_3$ depends on the physical details of the experimental apparatus (lamp intensity, reaction flask size, concentration, photolysis time). Thus, in the glovebox, 2.52 g (11.55 mmol) MeCpMn$(CO)_3$ was placed in a 1-L round-bottom flask equipped with a magnetic stirrer, 540 mL of THF was added, and the flask was capped with a rubber septum. The mixture was placed in an ice-cooled water bath and irradiated using a 450-W Hanovia medium-pressure mercury lamp, with nitrogen bubbling through the solution via a long syringe needle and exiting via another syringe needle attached to an oil bubbler. The mixture was photolyzed until no more changes (MeCpMn$(CO)_3$ ~2020, 1930 cm$^{-1}$; MeCpMn$(CO)_2$(THF) ~ 1920, 1850 cm$^{-1}$) were observed in the IR (a small band at 2020 would still be present), typically about 4 h. The freshly prepared solution was then transferred via a cannula into a solution of CpFe$(CO)_2{}^-Na^+\cdot\sim$0.5THF (2.82 g, 77% by weight, 10.87 mmol) in 50 mL of THF, and the mixture was stirred overnight at room temperature under a nitrogen atmosphere. Workup as described for method 1 above yielded 4.09 g of product that by $^1$H NMR ($CD_3CN$) was (by weight) 83% **1a** (3.40 g, 80% yield), 4% CpFe$(CO)_2{}^-Na^+$, and 13% THF.

**[MeCp(CO)Fe(μ-CO)₂Mn(CO)MeCp]⁻Na⁺ (1b), [MeCp(CO)Fe(μ-CO)₂Mn(CO)Cp]⁻Na⁺ (1c), and [Cp(CO)Fe(μ-CO)₂Mn(CO)Cp]⁻Na⁺ (1d).** These compounds were each prepared by method 1 above, substituting CpMn$(CO)_2(CH_3CN)$ prepared from CpMn$(CO)_3$[66b] and MeCpFe$(CO)_2{}^-Na^+\cdot\sim$0.5THF (prepared from $[MeCpFe(CO)_2]_2$[66b]) as appropriate, in yields of 77% (**1b**), 72% (**1c**), and 80% (**1d**). **1b**: IR (THF) 1906 (s), 1848 (s), 1743 (m), 1643 (m) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 4.18, 4.11 (Me*Cp*Fe), 4.04, 3.95 (Me*Cp*Mn), *Me*Cp obscured by solvent resonance. **1c**: IR (THF) 1910 (s), 1848 (s), 1722 (m), 1657 (m) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 4.11 (Me*Cp*Fe), 4.21 (CpMn), *Me*Cp obscured by solvent resonance. **1d**: IR (THF) 1910 (s), 1855 (s), 1719 (m), 1651 (m) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 4.34 (CpFe), 4.21 (CpMn).

**[Cp(CO)Fe(μ-CO)₂Mn(CO)MeCp]⁻PPN⁺ (1a-PPN⁺).** In the glovebox, 25 mL of THF was added to 0.22 g of **1a** (0.50 mmol) and 0.35 g of $PPN^+Cl^-$ ($PPN^+ = (Ph_3P)_2N^+$)[68] (0.62 mmol) and stirred for 1 h. The mixture was then filtered through a medium frit and the solvent stripped in vacuo from the supernatant. The resultant solid was stirred for 10 min with 15 mL of benzene, filtered using a medium frit, and then washed three times with 2-mL portions of benzene, giving 0.34 g of red-purple **1a-PPN⁺** (76% yield). Analytically pure material was obtained by crystallization from $CH_2Cl_2$/hexane. IR ($CH_2Cl_2$): 1899 (m), 1832 (m), 1671 (m) cm$^{-1}$. $^1$H NMR (296.6 K, $CD_2Cl_2$): δ 4.43 (s, 5H, CpFe), 4.15 (br s, ~2H), 4.10 (br s, ~1H), 4.01 (br s, ~1H, Me*Cp*Mn), 1.98, 1.83 (br s, 3H, *Me*Cp, 46:54); $^1$H NMR (−32 °C, $CD_2Cl_2$) δ 4.419, 4.414 (s, 5H, CpFe), 4.183, 4.069; 4.160, 3.967 (s, 4H, Me*Cp*Mn), 1.934, 1.753 (s, 3H, *Me*Cp) in 59:41 ratio for each set. $^{13}$C NMR ($CD_2Cl_2$, −32 °C, 125 MHz): 302.75 (μ-CO), 232.53 (br, MnCO), 216.36 (FeCO), PPN⁺ at 133.60 ($C_4$), 131.98, 131.94, 131.90, 129.41, 129.37, 129.31, ($C_2$, $C_3$, coupled to P), and 126.7 (d, $J_{PC}$ = 108 Hz, $C_1$), cis (60%) at 100.74 (ipso Me*Cp*), 85.50, 84.55 (Me*Cp*), 84.96 (CpFe), 13.27 (*Me*CpMn); trans (40%) at 101.63 (ipso Me*Cp*), 86.49, 85.44 (Me*Cp*), 87.31 (CpFe), 12.75 (*Me*CpMn). Anal. Calcd for $C_{51}H_{42}NO_4P_2FeMn$: C, 67.64; H, 4.67; N, 1.55. Found: C, 67.41; H, 4.61; N, 1.55.

**[Cp(CO)Fe(μ-CO)₂Mn(CO)MeCp]⁻Ph₃PCH₃⁺ (1a-Ph₃PCH₃⁺) and [MeCp(CO)Fe(μ-CO)₂Mn(CO)MeCp]⁻Ph₃PCH₃⁺ (1b-Ph₃PCH₃⁺).** The procedure described for the synthesis of **1a-PPN⁺** was used, substituting $Ph_3PCH_3{}^+Br^-$ for $PPN^+Cl^-$, giving **1a-Ph₃PCH₃⁺** in 63% yield and **1b-Ph₃PCH₃⁺** in 39% yield; each was crystallized from $CH_2Cl_2$/hexane to give analytically pure dark purple crystals that each contained a molecule of $CH_2Cl_2$ of crystallization, on the basis of elemental analysis and $^1$H NMR in $CD_3CN$. **1a-Ph₃PCH₃⁺**: IR ($CH_2Cl_2$) 1901 (m), 1839 (m), 1672 (m) cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$) δ 7.88, 7.73, 7.60 (m, 15H, *Ph*₃PCH₃), 4.41 (s, 5H, CpFe), 4.15, 4.09, 3.97 (br s, 4H, Me*Cp*Mn), 2.84 (d, 3H, $J_{PH}$ = 13 Hz, PPh₃*CH*₃), 1.96, 1.81 (s, 3H, *Me*Cp, 58:42). Anal. Calcd for $C_{35}H_{32}O_4Cl_2PFeMn$: C, 57.64; H, 4.42. Found: C, 57.62; H, 4.34. **1b-Ph₃PCH₃⁺**: IR ($CH_2Cl_2$) 1898 (m), 1837 (m), 1671 (m) cm$^{-1}$; $^1$H NMR ($CD_2Cl_2$) δ 7.88, 7.68 (m, 15H, *Ph*₃PCH₃), 4.24–3.97 (m, 8H, Me*Cp*), 2.86 (d, 3H, $J_{PH}$ = 13 Hz, Ph₃P*CH*₃), 2.00, 1.96, 1.81 (s, 6H, cis and trans *Me*Cp, relative ratios of peaks ~1:1:2). Anal. Calcd for $C_{36}H_{34}O_4Cl_2PFeMn$: C, 58.17; H, 4.61. Found: C, 58.21; H, 4.44.

**Cp(CO)Fe(μ-CO)(μ-COCH₃)Mn(CO)MeCp (2a).** In the glovebox, 1.47 g (9.02 mmol) of $CH_3SO_3CF_3$ was added to 3.25 g (8.34 mmol) of **1a** in 100 mL of THF and stirred for 15 min. The solvent was removed under vacuum and the flask left on the vacuum line overnight in order to remove the MeCpMn$(CO)_3$ formed as a side product, giving a dark red solid. This material was stirred for 10 min with 15 mL of benzene and then filtered through Celite. Removal of solvent by vacuum and crystallization

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from 1:5 diethyl ether/pentane gave 1.96 g of **2a** (62% yield) as a fluffy red solid: IR (THF) 1954 (s), 1907 (s), 1774 (s) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 5.02 (s, 3H, $CH_3O$), 4.76 (s, 6H, CpFe, 1H of Me*Cp*Mn), 4.56, 4.46, 4.39 (br s, 1H each, Me*Cp*Mn), *Me*CpMn obscured by solvent resonance; $^1$H NMR ($C_6D_6$) δ 4.47, 4.26 (s, trans, cis CpFe), 4.19 (s, 3H, cis/trans $CH_3O$), 4.01, 3.92 (br m, cis/trans Me*Cp*Mn), 1.84, 1.78 (s, 3H, cis, trans *Me*CpMn); $^1$H NMR ($CD_2Cl_2$) δ 4.99, 4.94 (s, ~3.5H, trans-CpFe, $CH_3O$), 4.68 (s, ~5.5H, cis-CpFe, ~1H of Me*Cp*Mn), 4.44, 4.32 (br s, ~3H, Me*Cp*Mn), 2.05, 1.90 (s, 3H, cis, trans *Me*CpMn, 3:1); $^{13}$C NMR (acetone-$d_6$) 390.7 (μ-*C*O$CH_3$), 272.7 (μ-CO), 228.9 (br, MnCO), 214.8 (sharp, FeCO), 104.1 ($\eta^5$-$C_4H_4$*C*Me), 89.0, 87.8, 84.8 (Me*Cp*Mn), 86.2 (CpFe), 73.2 (μ-CO*C*$H_3$), 13.3 (*Me*CpMn) ppm; $^{13}$C NMR ($C_6D_6$) 394.6, 391.2 (trans, cis μ-*C*O$CH_3$), 270.8, 269.9 (cis, trans μ-CO), 229.0, 228.1 (br, trans, cis MnCO), 214.1 (sharp, FeCO), 104.7, 103.7 (trans, cis $\eta^5$-$C_4H_4$*C*Me), 89.4, 88.3, 87.9, 87.3, 86.9, 86.0, 84.2, 82.2, 82.0 (Me*Cp*Mn, trans CpFe), 85.5 (cis CpFe), 72.0 (μ-CO*C*$H_3$), 13.2, 12.8 (cis, trans *Me*CpMn) ppm; MS (EI) *m/e* 382 ($M^+$), 354 ($M^+$ − CO), 326 ($M^+$ − 2CO), 311 ($M^+$ − 2CO, $CH_3$), 283 ($M^+$ − 3CO, $CH_3$), 255 ($M^+$ − 4CO, $CH_3$), 200 (CpFeMeCp, base peak). Anal. Calcd for $C_{16}H_{15}O_4FeMn$: C, 50.30; H, 3.96. Found: C, 49.90; H, 3.67.

**Cp(CO)Fe(μ-CO)(μ-COCD$_3$)Mn(CO)MeCp (2a-*d*$_3$).** The same procedure as described for **2a** was used, substituting $CD_3SO_3CF_3$ prepared according to a literature procedure[69] by stirring $CD_3I$ with excess silver triflate for 1 h and then separating the deuteriomethyl triflate by vacuum transfer; this material contained 20% toluene (a contaminant in the silver triflate) by weight, as determined by integration of a $^1$H NMR spectrum containing ferrocene as an internal standard. The $^1$H NMR spectra were identical to those of **2a** except that the singlet at δ 5.02 (acetone-$d_6$) and 4.19 ($C_6D_6$) was missing in each case.

**MeCp(CO)Fe(μ-CO)(μ-COCH$_3$)Mn(CO)MeCp (2b), MeCp(CO)Fe(μ-CO)(μ-COCH$_3$)Mn(CO)Cp (2c), and Cp(CO)Fe(μ-CO)(μ-COCH$_3$)Mn(CO)Cp (2d).** The procedure described for the synthesis of **2a** was used, substituting **1b–d**, giving **2b–d** in 55%, 55%, and 60% yield, respectively. **2b**: IR (THF) 1951 (s), 1901 (s), 1767 (s) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 5.01 (s, 3H, $CH_3O$), 4.80, 4.62, 4.57, 4.42, 4.34 (br m, 8H, Me*Cp*), *Me*Cp obscured by solvent resonance; $^1$H NMR ($C_6D_6$) δ 4.34, 4.15, 4.07, 4.00, 3.95, 3.90 (br s, 8H, cis/trans Me*Cp*), 4.23 (s, 3H, cis/trans $CH_3O$), 1.89, 1.85, 1.81, 1.75 (s, 6H, cis, cis, trans, trans *Me*Cp, ~2:2:1:1); MS (EI) *m/e* 396 ($M^+$), 368 ($M^+$ − CO), 340 ($M^+$ − 2CO), 325 ($M^+$ − 2CO, $CH_3$), 297 ($M^+$ − 3CO, $CH_3$), 269 ($M^+$ − 4CO, $CH_3$), 214 ($(MeCp)_2Fe$, base peak). Anal. Calcd for $C_{17}H_{17}O_4FeMn$: C, 51.55; H, 4.33. Found: C, 50.80; H, 4.33. **2c**: IR (THF) 1950 (s), 1901 (s), 1767 (s) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 5.02 (s, 3H, $CH_3O$), 4.77 (s, 5H, CpFe), 4.66, 4.61, 4.46 (br s, 4H, Me*Cp*Mn), *Me*Cp obscured by solvent resonance; $^1$H NMR ($C_6D_6$) δ 4.33, 4.23 (s, trans, cis CpMn), 4.19 (s, 3H, cis/trans $CH_3O$), 4.14, 4.01 (br s, cis/trans Me*Cp*Fe), 1.81, 1.73 (s, 3H, cis, trans *Me*CpFe, ~2:1); MS (EI) *m/e* 382 ($M^+$), 354 ($M^+$ − CO), 326 ($M^+$ − 2CO), 311 ($M^+$ − 2CO, $CH_3$), 283 ($M^+$ − 3CO, $CH_3$), 255 ($M^+$ − 4CO, $CH_3$), 200 (CpFeMeCp, base peak). Anal. Calcd for $C_{16}H_{15}O_4FeMn$: C, 50.30; H, 3.96. Found: C, 49.92; H, 3.76. **2d**: IR (THF) 1951 (s), 1901 (s), 1771 (s) cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 5.02 (s, 3H, $CH_3O$), 4.77 (s, 5H, Cp), 4.76 (s, 5H, Cp); $^1$H NMR ($C_6D_6$) δ 4.46, 4.30 (br s, trans Cp), 4.25, 4.21 (s, cis Cp), 4.17 (s, 3H, $CH_3O$); MS (EI) *m/e* 368 ($M^+$), 340 ($M^+$ − CO), 312 ($M^+$ − 2CO), 297 ($M^+$ − 2CO, $CH_3$), 269 ($M^+$ − 3CO, $CH_3$), 241 ($M^+$ − 4CO, $CH_3$), 186 ($Cp_2Fe$, base peak). Anal. Calcd for $C_{15}H_{13}O_4FeMn$: C, 48.95; H, 3.56. Found: C, 49.07; H, 3.43.

**Cp(CO)Fe(μ-CO)(μ-COCH$_2$CH$_3$)Mn(CO)MeCp (3a).** In the glovebox, 402 mg (2.26 mmol) of $CH_3CH_2SO_3CF_3$ was added to 730 mg (1.88 mmol) of **1a** in 30 mL of THF and stirred for 10 min. The solvent was removed under vacuum and the flask left on the vacuum line overnight in order to remove the $MeCpMn(CO)_3$ formed as a side product, giving a dark red solid. This material was dissolved in 10 mL benzene, the solution was filtered through Celite, and the solvent was once again removed under vacuum. Crystallization at −40 °C from 15 mL of a 3:2 mixture of pentane–chloroform gave 472 mg (63% yield) of product as a red-brown powder: IR (THF) 1975 (s), 1938 (m), 1772 (s) cm$^{-1}$; $^1$H NMR ($C_6D_6$) δ 4.71 (q, *J* = 7.2 Hz, $CH_2$), 4.49 (s, trans-*Cp*Fe), 4.29 (s, cis-*Cp*Fe), 4.05, 3.94 (m, Me*Cp*Mn), 1.86 (s, cis-*Me*CpMn), 1.80 (s, trans-*Me*CpMn), 1.25 (t, *J* = 7.2 Hz, CH$_2$*CH*$_3$), cis:trans ≈ 2:1; $^1$H NMR (acetone-$d_6$) 5.47–5.32 (m, $CH_2$), 4.78 (s, *Cp*Fe), 4.74, 4.58, 4.47, 4.41 (s, Me*C*pMn), 1.81 (t, *J* = 7.1 Hz, trans-CH$_2$*CH*$_3$), 1.74 (t, *J* = 7.1 Hz, cis-CH$_2$*CH*$_3$); $^{13}$C NMR (acetone-$d_6$) 388.6 (μ-*C*OEt), 273.6 (μ-CO), 229.6 (MnCO), 215.4 (FeCO), 104.4, 89.3, 88.0, 86.8, 85.2 (Me*Cp*Mn), 86.8 (*Cp*Fe), 84.8 (*CH*$_2$CH$_3$, identified by DEPT-135 NMR), 16.0, 13.5 (CH$_2$*CH*$_3$ and *Me*CpMn) ppm; MS (5 kV FAB, acetone) *m/e* 396 ($M^+$, 76%), 368 ($M^+$ − CO, 100%), 340 ($M^+$ − 2CO, 12%), 312 ($M^+$ − 3CO, 46%). Anal. Calcd for $C_{17}H_{17}O_4FeMn$: C, 51.55; H, 4.33. Found: C, 50.82; H, 4.40.

**MeCp(CO)Fe(μ-CO)(μ-COCH$_2$CH$_3$)Mn(CO)MeCp (3b).** A solution of 217.8 mg (1.22 mmol) of $CH_3CH_2SO_3CF_3$ and 490 mg (1.21 mmol) of **1b** in 15 mL THF was treated as described above for **3a**. The sticky solid residue obtained from the benzene extraction was washed on a frit with hexane to give 341 mg (68% yield) of a brown-red powder: IR (THF) 1950 (s), 1897 (s), 1763 (m) cm$^{-1}$; $^1$H NMR ($C_6D_6$) δ 4.73 (q, *J* = 7.1 Hz, 2H, cis/trans-*CH*$_2$CH$_3$), 4.42, 4.37, 4.34, 4.25, 4.14, 4.09, 4.04, 3.96, 3.90 (br s, 8H, cis/trans-Me*Cp*), 1.91, 1.86, 1.83, 1.77 (s, 6H, cis, cis, trans, trans *Me*Cp, ~2:2:1:1), 1.27 (t, *J* = 7.1 Hz, cis/trans-CH$_2$*CH*$_3$); $^1$H NMR (acetone-$d_6$) 5.40 (q, *J* = 7.1 Hz), 5.30 (q, *J* = 7.2 Hz), 4.77, 4.74, 4.70, 4.58, 4.54, 4.43, 4.39, 4.34 (s, Me*Cp*), 1.897, 1.849 (*Me*Cp), 1.77 (t, *J* = 7.0 Hz, trans-$CH_3$), 1.70 (t, *J* = 7.1 Hz, cis-$CH_3$); $^{13}$C NMR (31 mg **3b** and 27 mg $Cr(acac)_3$ in 0.84 mL acetone-$d_6$) 386.9 (μ-*C*OEt), 275.6 (μ-CO), 229.7 (MnCO), 215.5 (FeCO), 104.3, 102.3, 89.45, 87.8 (2 C), 87.2, 86.4, 85.35, 85.3, 84.2 (Me*Cp*Mn), 84.4 (*CH*$_2$CH$_3$, identified by DEPT-135 NMR), 16.1 (CH$_2$*CH*$_3$), 13.56, 13.34 (*Me*CpMn, *Me*CpFe) ppm; MS (5 kV FAB, acetone) *m/e* 410 ($M^+$, 100%), 382 ($M^+$ − CO, 94%), 354 ($M^+$ − 2CO, 13%). Anal. Calcd for $C_{18}H_{19}O_4FeMn$: C, 52.71; H, 4.67. Found: C, 50.53; H, 4.44.

**$^1$H NMR Experiments. General Considerations.** In the glovebox, reactants were loaded into an NMR tube that had been sealed to a 14/20 ground glass joint; typically ~10 mg carbyne was used. For the methoxycarbynes, $Ph_3CH$ was added as an internal NMR integration standard, while for the ethoxycarbynes, TMS was added via microliter syringe in the glovebox. For the ethoxycarbynes, $C_6D_6$ was added in the glovebox (as the solvent used to transfer the weighed liquid $PPh_2Me$ into the NMR tube). The tube was fitted with a vacuum stopcock, attached to a vacuum line, and evacuated (after first freezing for the ethoxycarbynes). For the methoxycarbynes, $C_6D_6$ was then added by vacuum transfer. The tube was submitted to two freeze–pump–thaw cycles and then sealed with a torch. The hydrogenation was carried out by admitting ~550 Torr $H_2$ after the final pumping cycle, cooling as much of the tube as possible with liquid nitrogen, and sealing.

Identification of all products was carried out by $^1$H NMR; although most of the following compounds are known (unreferenced compounds below were commercially available), literature data in $C_6D_6$ are not often available and so are given here. **CpFe(CO)$_2$CH$_3$:**[66] δ 4.00 (s, 5H, Cp), 0.30 (s, 3H, Me). **CpFe(CO)$_2$CH$_2$CH$_3$:**[66a] δ 4.01 (s, 5H, Cp), 1.59 (q, *J* = 7.1 Hz, 2H, $CH_2$), 1.37 (t, *J* = 7.1 Hz, 3H, $CH_3$). **CpFe(CO)(PPh$_3$)CH$_3$:**[70a,b] δ 7.54, 6.98 (m, 15H, Ph), 4.12 (d, $J_{PH}$ = 1 Hz, 5H, Cp), 0.30 (d, $J_{PH}$ = 6.4 Hz, 3H, $CH_3$). **CpFe(CO)(PPh$_3$)CH$_2$CH$_3$:**[70b,c] δ 7.53, 6.99 (m, 15H, Ph), 4.11 (d, $J_{PH}$ = 1 Hz, 5H, Cp), 1.85 (m, approx q, *J* = 9 Hz, 2H, C*H*CH$_3$), 1.58 (dt, $J_{PH}$ = 1.8 Hz, $J_{HH}$ = 7.3 Hz, 3H, $CH_3$), 1.08 (m, C*H*CH$_3$). **CpFe(CO)(PPh$_2$Me)CH$_2$CH$_3$:**[30] δ 7.42–7.38 (m, 2H), 7.31–7.28 (m, 2H), 7.05–6.98 (m, 6H, Ph), 4.136 (d, *J* = 0.96 Hz, 5H, Cp), 1.59–1.52 (m, C*H*CH$_3$), 1.518 (t, *J* = 7.5

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Hz, $CH_2CH_3$), 1.511 (d, $J$ = 8.0 Hz, P$CH_3$, 7H for $\delta$ 1.59–1.51), 0.79–0.71 (m, 1H, C$H$CH$_3$). **[CpFe(CO)$_2$]$_2$**: $\delta$ 4.22 (s). **[CpFe(CO)]$_4$**:[29] $\delta$ 4.63 (s). **MeCpMn(CO)$_3$**: $\delta$ 3.87, 3.81 (m, 4H, Me$Cp$), 1.39 (s, 3H, $Me$Cp). **MeCpMn(CO)$_2$PPh$_3$**:[27] $\delta$ 7.60 (m, 6H), 6.99 (m, 9H), 4.01, 3.91 (br s, 2H each, Me$Cp$), 1.77 (s, 3H, $Me$Cp). **$CH_4$**: $\delta$ 0.15. **$C_2H_6$**: $\delta$ 0.79. **$C_2H_4$**: $\delta$ 5.25. **$CH_3OCH_3$**: $\delta$ 3.03. **$H_2$**: $\delta$ 4.46.

The known phosphine alkyls CpFe(CO)(PPh$_3$)R (R = $CH_3$, $CH_2CH_3$) were prepared using the general photolysis procedure in ref 71. The known tetramer [CpFe(CO)]$_4$ was isolated from the thermal reaction of **3a** in $C_6D_6$, by chromatography on silica gel (in the glovebox), with first hexane and then ether/hexane as eluent to remove mono- and dinuclear products, and then ether to elute the green tetramer. Ethane, while available, is expensive and so was prepared in situ as follows. A solution of AIBN (azoisobutyrylnitrile, 2.9 mg, 0.017 mmol), iodoethane (65.3 mg, 0.418 mmol), and tributyltin hydride (133 mg, 0.457 mmol) in 1.3 mL of $C_6D_6$ was placed in a glass vessel sealed to a vacuum stopcock, submitted to two freeze–pump–thaw cycles, and heated at 100 °C for 45 min under vacuum. The volatiles were then transferred via a vacuum line into an NMR tube, and the tube was sealed with a torch. The $^1$H NMR spectrum exhibited peaks due to ethane and unreacted $C_2H_5I$.

**Line-Shape Analysis.** Activation parameters for exchange were calculated by plotting ln ($k/T$) vs $1/T$, where the first-order rate constants were determined by visually fitting spectra calculated by the DNMR5 program to the observed spectra at each temperature. Temperatures in the NMR probe were calibrated using the chemical shifts of the methanol hydrogens according to the method of van Geet.[72] The data on anion **1a**-PPN$^+$ and methoxycarbyne **2a** were collected at 200 MHz, while for ethoxycarbyne **3a** the measurements were done at 360 MHz. At each temperature, calculation of the exchanging spectrum uses (1) values for the $T_2$ relaxation time, approximated as $T_2 = 1/w\pi$, where $w$ = width at half-height of a nonexchanging peak, (2) the chemical shift difference between the exchanging peaks, and (3) the relative populations of the exchanging peaks. For **3a** in toluene-$d_8$ as solvent, the Me peak of added MeCpMn(CO)$_3$ was used as the internal line width reference, while TMS was used for all the other samples. In all cases, the chemical shifts and cis–trans ratios were found to be temperature-dependent, so data collected in the slow exchange limit (approximately in some cases) was extrapolated to higher temperature. For the chemical shifts, plots of $\Delta\nu$ vs $T$ were found to be linear, thereby allowing direct extrapolation, while for the cis–trans ratios the theoretically justified extrapolation was carried out by plotting ln ($K$) vs $1/T$ (where $K_{\text{cis to trans}}$ = [trans]/[cis]). For **1a**-PPN$^+$, the cis–trans ratios and chemical shift differences were extrapolated from spectra taken at 241 K and 299 K, for **2a** from spectra taken from 274 to 294 K, and for **3a** from spectra taken from 253 to 283 K by integration of the ethoxy methyl triplets. All of the data used are available as supplementary material.

**X-ray Structure Determination of 3a.** About 12 mg of dark brown crystals of **3a** suitable for X-ray analysis were obtained by layering 2.5 mL of pentane onto a solution of ~30 mg of **3a** in ~1.5–1.8 mL of $CHCl_3$ and allowing the mixture to stand at -40 °C for 3 days. The mounted crystal was coated with epoxy cement to prevent oxidation, and data were collected at room temperature using equipment and procedures that have been described previously;[45] further details are described below and in Table IV. Automatic peak search and centering routines gave 52 peaks that were used for autoindexing and least-squares refinement of the lattice parameters. Inspection of the indices of the observed reflections showed that those with $h + k$ odd were absent, so data were colllected with the assumption of a $C$-centered unit cell. A total of 3151 reflections were collected; a 0.67% decay in the standard reflections was observed over the course of the data collection, and a correction was applied. Inspection of the data showed that reflections having $h0l$, $l = 2n + 1$, were systematically absent, consistent with space groups $Cc$ and $C2/c$, but the presence of eight molecules in the unit cell was consistent with the centrosymmetric space group, and the successful solution confirmed this choice. Following removal of systematically absent and redundant data, 2041 reflections with $I > 3\sigma(I)$ were used to solve the structure. Positions of the iron and manganese atoms were obtained from a Patterson map, and the positions of the remaining non-hydrogen atoms as well as one hydrogen atom on each of the two methyl groups were located on difference electron density maps. The positions of the remaining hydrogen atoms were calculated (C–H = 1.00 Å). An absorption correction using an 8 × 16 × 8 grid was applied and refinement continued with anisotropic thermal parameters for the non-hydrogen atoms to give the residuals in Table IV. The largest peaks on the final difference map were near the cyclopentadienyl hydrogen atoms and the manganese atom.

**Table IV. Crystal and Data Collection Parameters**[a]

| | |
|---|---|
| cmpd | $C_{17}H_{17}O_4FeMn$ (**3a**) |
| fw | 396.11 |
| space group | $C2/c$ |
| $a$, Å | 25.319 (3) |
| $b$, Å | 7.3978 (8) |
| $c$, Å | 17.275 (2) |
| $\beta$, deg | 92.135 (2) |
| $V$, Å$^3$ | 3221.1 |
| $Z$ | 8 |
| $\rho$(calcd), g cm$^{-3}$ | 1.63 |
| temp, °C | 25 |
| size, mm | 0.45 × 0.27 × 0.24[b] |
| abs coeff, $\mu$, cm$^{-1}$ | 16.628 |
| transmission factors | 0.6469–0.6940 |
| radiation | Mo K$\alpha$, 0.7107 Å |
| rflns measd | $h + k = 2n$, ±1 |
| no. of rflns collected[c] | 3151 |
| no. of unique rflns ($I_o > 3\sigma(I_o)$ | 2041 |
| no. of params refined | 208 |
| $R$[d] | 0.037 |
| $R_w$[e] | 0.050 |
| GOF[f] | 1.6305 |
| shift to error ratio[g] | |
| av | 0.002 |
| max | 0.041 |

[a] Diffractometer, modified Picker FACS-1 with graphite monochromator; scan type, $\theta/2\theta$; scan rate, 6° min$^{-1}$; scan range, 1.3° below K$\alpha_1$, 1.6° above K$\alpha_2$; $2\theta$ limit, 50°. [b] Boundary faces: 010, 00$\bar{1}$, $\bar{1}$00, 0$\bar{1}$0, 001, 100, at distances of 0, 0, 0, 0.4455, 0.270, 0.243 mm from a common point. [c] Standard reflections (5$\bar{1}\bar{1}$, 62$\bar{3}$, 204) were measured after every 97 reflections. [d] $R = \sum(\|F_o|-|F_c\|)/\sum|F_o|$. [e] $R_w = [\sum(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2|F_o|)$. [f] Goodness of fit = $[\sum w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where $N_o$ is the number of observations and $N_v$ is the number of variables. [g] In final refinement.

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**Supplementary Material Available:** A table of data for NMR line-shape analyses and rate constants and tables of crystallographic data for **3a** (10 pages). Ordering information is given on any current masthead page.

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