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Reactions of Organocopper Reagents with the Cationic Bridging Acylium Complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+$

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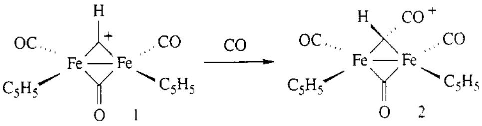
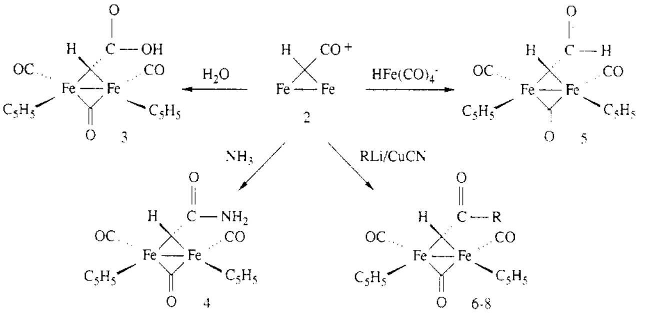
The bridging acylium complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+PF_6^-$ (**2**) reacted with organocuprates Li(RCuCN) at the acylium carbon to give the acyl-substituted μ-alkylidene complexes $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCOR)$ (**6**, R = CH_3; **7**, R = $(CH_2)_3CH_3$; **8**, R = C_6H_5). The acyl groups of complexes **6**–**8** display low carbonyl stretching frequencies indicative of strong electron donation from the $Fe_2(\mu\text{-}C)$ core onto the acyl substituents. The molecular structure of **8**, determined by X-ray crystallography, supports these observations. Crystals of **8** are triclinic, space group $P\bar{1}$, with a = 7.008 (2) Å, b = 12.392 (3) Å, c = 12.441 (3) Å, α = 118.37 (2)°, β = 91.09 (2)°, γ = 103.42 (2)°, and Z = 2. **6** reacted with $CF_3SO_3CH_3$ to give the O-methylated complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHC(CH_3)OCH_3]^+CF_3SO_3^-$ (**12**) resulting from methylation of the acetyl group of **6** at oxygen. Reaction of **2** with $Li_2[(CH_3)_2CuCN]$ afforded the μ-alkenylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}C{=}(CH_3)_2]$ (**13**) via double nucleophilic addition. **13** reacted with $Me_3O^+BF_4^-$ to give the μ-alkylidyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CC(CH_3)_3]^+BF_4^-$ (**14**).

The cationic diiron bridging methylidyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) is extremely electrophilic[1] and reacts with CO to give a 1:1 adduct, $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+PF_6^-$ (**2**). Complex **2** is best regarded as a bridging acylium species and is readily attacked by nucleophiles at the acylium carbon.[2,3] Reaction of **2** with water in CH_2Cl_2 gives the carboxylic acid $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCO_2H)$ (**3**), ammonia gives the amide $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCONH_2)$ (**4**), and the hydride donor $Et_4N^+HFe(CO)_4^-$ gives the aldehyde $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCHO)$ (**5**).

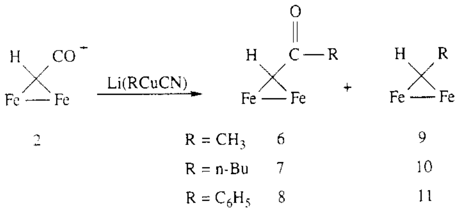




Here we report that organocuprates prepared from CuCN and alkyllithium reagents react with **2** to form new μ-alkylidene complexes containing acyl-substituted side chains (**6**, R = CH_3; **7**, R = $(CH_2)_3CH_3$; **8**, R = C_6H_5). The IR spectra, chemical properties, and in one case X-ray crystal structure of these new complexes suggest that in addition to the μ-alkylidene formulation, there is also a contributing formulation to the observed structure from a dipolar bridging alkenyl species. The latter formulation is discussed in terms of electron donation from the $Fe_2(\mu\text{-}CH)$ unit, and an analogy is drawn between the structure and bonding in **2** and that in complexes **3**–**8**.

Results and Discussion

Reaction of Organocuprates, Li(RCuCN), with 2. When a THF solution of the cuprate $Li(CH_3CuCN)$ (prepared from equimolar amounts of methyllithium and CuCN)[4] was added to a slurry of **2** in THF at −78 °C, a bright red solution rapidly formed. Chromatography of the reaction mixture afforded the new acyl-substituted μ-alkylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCOCH_3)$ (**6**) as a red crystalline solid in 63% yield. Additionally, a small quantity of the previously reported[5] alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**9**) was isolated in 8% yield.



The structure of **6** was readily established by spectroscopy. The presence of a $\mu\text{-}CHCOCH_3$ ligand is supported by the observation of a characteristic downfield singlet at δ 10.96 in the ^1H NMR spectrum, due to the hydrogen on the bridging alkylidene carbon and by the observation of a downfield signal at δ 157.3 in the $^{13}C\{^1H\}$ NMR spectrum characteristic of a bridging alkylidene carbon. The resonance for the $COCH_3$ protons appears as a singlet at δ 2.54. Additionally the IR spectrum of **6** contains a band at 1633 cm^{-1} corresponding to the C=O stretch of the acyl group.

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[1] Casey, C. P.; Crocker, M.; Vosejpka, P. C.; Fagan, P. J.; Marder, S. R.; Gohdes, U. A. *Organometallics* **1988**, *7*, 670–675.

[2] Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360–7361.

[3] Casey, C. P.; Crocker, M.; Niccolai, G. P.; Fagan, P. J.; Konings, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6070–6076.

[4] (a) Gorlier, J.-P.; Hamon, L.; Levisalles, J.; Wagnon, J. *J. Chem. Soc., Chem. Commun.* **1973**, 88 and references therein. (b) Koosha, K.; Berlan, J.; Capmau, M. L.; Chodkiewicz, W. *Bull. Soc. Chim. Fr.* **1975**, 1284.

[5] Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918.

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This unusually low ketone carbonyl stretching frequency suggests that the $Fe_2(\mu\text{-}CH)$ group is acting as a strong electron donor. The cis arrangement of the Cp and terminal CO ligands of **6** is assigned on the basis of the observation of a single C_5H_5 resonance in both the ^1H and ^{13}C NMR spectra. This assignment is confirmed by the observation of a single terminal CO resonance at δ 213.6 in the $^{13}C\{^1H\}$ NMR spectrum and by the appearance of infrared bands at 1997 (s) and 1965 (m) cm^{-1} consistent with cis terminal CO ligands. The bridging carbonyl ligand of **6** is assigned on the basis of an IR band at 1791 cm^{-1} and a $^{13}C\{^1H\}$ NMR resonance at δ 270.5. While the spectral data alone does not allow an assignment of the relative geometry of the $COCH_3$ and Cp groups, it should be noted that the X-ray crystal structure of **2** shows the carbonyl group of the acylium ligand to be trans to the Cp groups.[2] On this basis a similar geometry is assigned to **6**. This assignment is strongly supported by the X-ray structure of the related benzoyl derivative **8** (see below).

The reaction of acylium complex **2** with the cuprate $Li[CH_3(CH_2)_3CuCN]$ in THF led to the formation of the pentanoyl-substituted μ-alkylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CHCO(CH_2)_3CH_3]$ (**7**) in 75% yield. The pentylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)[\mu\text{-}CH(CH_2)_3CH_3]$ (**10**)[6] was also isolated from the reaction mixture in 14% yield. Similarly, treatment of **2** with $Li(C_6H_5CuCN)$ afforded a red crystalline material identified as the benzoyl-substituted μ-alkylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCOC_6H_5)$ (**8**) in 56% yield, together with the μ-benzylidene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC_6H_5)$ (**11**)[1] isolated in 16% yield. IR, ^1H NMR, and $^{13}C\{^1H\}$ NMR spectra of **7** and **8** showed features similar to those of **6**.

An unexpected feature of these reactions is the formation of the μ-alkylidene complexes **9–11**. At first sight these products might appear to derive from nucleophilic attack of the appropriate organocuprate on the methylidyne complex **1**, formed via CO loss from **2**. However, when a solution of **2** in CD_2Cl_2 was placed under an atmosphere of ^{13}CO (700 Torr, 99.5% ^{13}C-enriched), no significant incorporation of ^{13}CO into the acylium group of **2** was detected by NMR spectroscopy over a period of several days. The formation of acylium complex **2** from **1** and CO is therefore concluded to be irreversible. The formation of alkylidene complexes **9–11** may instead be interpreted in terms of nucleophilic attack at the bridging carbene carbon of **2** with concomitant loss of CO, an S_N2-type process. An alternative that we consider more likely involves electron transfer from the organocuprate reagent to complex **2** which would generate a radical which can lose CO and then undergo coupling with the resultant cuprate radical.[7]

Crystal Structure of 8. In order to gain insight into the structural characteristics of the acyl-substituted μ-alkylidene complexes synthesized above, a single-crystal X-ray diffraction study was carried out on the benzoyl complex **8** (Figure 1). In the solid state, **8** adopts a conformation that has cis cyclopentadienyl groups with the benzoyl unit oriented anti to these groups. This conformation might be the result of either kinetic or thermodynamic control. Attack of the phenyl cuprate on the acylium complex **2** would produce this isomer. However, since μ-alkylidene complexes can undergo cis–trans isomerizations, **8** may also be the thermodynamically most stable isomer. In the observed configuration of **8**, the bulky COC_6H_5 substituent on the bridging alkylidene carbon is directed away from the Cp groups.

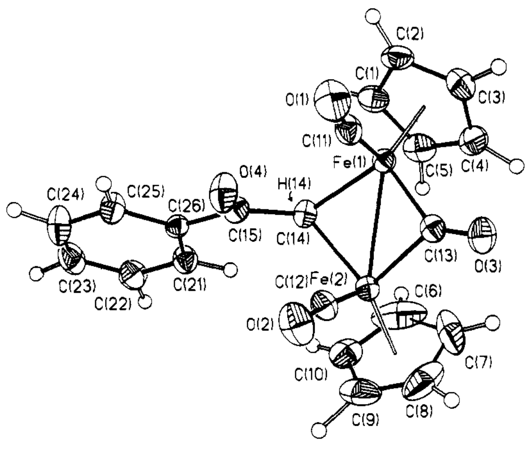
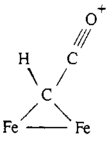


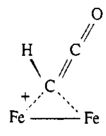
Figure 1. Molecular structure and labeling scheme for **8** drawn with 40% thermal ellipsoids.

The entire $\mu\text{-}CHCOC_6H_5$ ligand lies approximately in a plane perpendicular to the Fe–Fe axis and bisecting it. The ketone carbonyl oxygen is displaced only 0.07 Å from this plane. The plane of the ketone group defined by C14, C15, C26, and O4 is twisted 19° relative to this plane. The interplanar angle between the ketone and the phenyl ring is 15°. The ketone oxygen is directed toward the diiron system while the larger phenyl group is directed away from the diiron system.

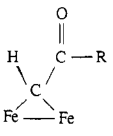
The observed conformation of **8** allows excellent overlap between the ketone carbonyl π-bond and a p orbital of the bridging carbon parallel to the iron–iron axis. This overlap results in significant electron donation from the $Fe_2(\mu\text{-}C)$ core onto the μ-alkylidene ligand and increases the C–C bond order while decreasing the C–O bond order in the μ-CHCOPh ligand. Previously, we had found similar π-bonding in the acylium complex **2** and described this in terms of ketene formulation **2k**. Fenske–Hall molecular orbital calculations also pointed out the importance of π-bonding between the carbons of the μ-CHCO ligand of **2**.[3]



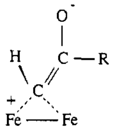
2-a



2-k



8-k



8-e

In the case of benzoyl-substituted alkylidene complex **8**, significant contribution from enolate formulation **8e** helps to explain the structure and spectral properties of **8**. The C14—C15 bond (1.481 (7) Å) is about 0.02 Å shorter than a typical sp^2–sp^3 carbon–carbon bond[8] and the C15–O4 bond (1.220 (5) Å) is about 0.02 Å longer than normal ketone C=O bonds.[9] While these bond length differences are in the direction predicted by a contribution from resonance formulation **8e**, the difference in bond lengths are only about 3σ and may not be statistically significant. A significant contribution from formulation **8e** explains the unusually low ketone carbonyl stretching frequency of 1616 cm^{-1}. Low ketone carbonyl stretching frequencies are also seen for μ-CHCHO complex **5** (1615 cm^{-1}), μ-

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(6) Casey, C. P.; Austin, E. A.; Niccolai, G. P., unpublished results.

(7) For discussions of electron transfer from cuprates see: (a) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59–67. (b) Bertz, S. H.; Dabbagh, G.; Cook, J. M.; Honkan, V. *J. Org. Chem.* **1984**, *49*, 1739–1743. (c) Casey, C. P.; Cesa, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4236–4244.

(8) Somayajulu, G. R. *J. Chem. Phys.* **1959**, *31*, 919–921 and references therein.

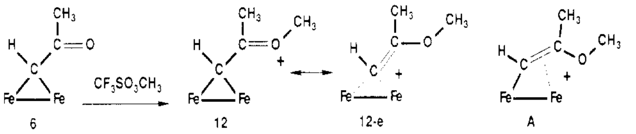
(9) Kwei, G. H.; Curl, R. F. *J. Chem. Phys.* **1960**, *32*, 1592–1594.

$CHCOCH_3$ complex **6** (1633 cm^{-1}), and μ-CHCOBu complex **7** (1638 cm^{-1}). The higher frequency of the μ-CO stretching vibration of **8** (1793 cm^{-1}) compared with other μ-alkylidene complexes such as μ-CHPh complex **11** (1781 cm^{-1})[1] and μ-$CHCH_3$ complex **9** (1784 cm^{-1} in THF)[5] can be explained in terms of the more positive iron framework suggested by formulation **8e**.

The closest analogies to complex **8** are the formyl-substituted μ-alkylidene complexes $[C_5H_5(NO)Fe]_2(\mu$-CHCHO) and $[C_5Me_5(CO)M]_2(\mu$-CHCHO) (M = CO, Rh) synthesized by Herrmann and co-workers.[10] The infrared stretching frequencies of the formyl carbonyls in these complexes are likewise shifted to low energy, indicative of similar electronic effects.

The dipolar nature of the contributing μ-enolate formulation **8e** also helps to rationalize the observed polar nature of complexes **5**–**8**. While these complexes are soluble in CH_2Cl_2 and acetone, they are insoluble in hexane and only sparingly soluble in diethyl ether. It is also likely that the carboxylic acid and amide substituted complexes **3** and **4** possess a similar bonding situation to that discussed for **5**–**8**. For these complexes the CO stretching frequency of the organic functionality is again lowered by about 50 cm^{-1} from the lower end of the range commonly observed for organic carboxylic acids and amides.[11] Thus the carbonyl group of **3** absorbs at 1630 cm^{-1}, while that of **4** absorbs at 1579 cm^{-1} (amide I band).[3] Again these low stretching frequencies are indicative of strong electron donation from the diiron core onto the alkylidene ligand.

Methylation of Acetyl Complex 6. The addition of $CF_3SO_3CH_3$ to a dichloromethane solution of **6** at room temperature resulted in a color change from red to purple-black. Addition of diethyl ether to the solution afforded the O-methylated complex $[C_5H_5(CO)Fe]_2(\mu$-CO)[μ-$CHC(OCH_3)CH_3]^+CF_3SO_3^-$ (**12**) as a purple-black solid in 73% yield. The formation of **12** arises from methylation of the oxygen of the acetyl group of **6**. This is in accord with the notion that electron donation from the $Fe_2(\mu$-C) core into the acetyl substituent of **6** leads to a buildup of negative charge on the acetyl oxygen atom.



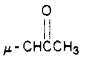
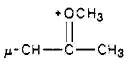
Two formulations for the O-methylated complex were considered: first, a symmetrically bridged μ-alkylidene complex with an O-methylated ketone substituent, **12**; and second, the μ-η^1,η^2-bridging alkenyl formulation **A**. The ^1H NMR resonances due to the bridging ligand consist of a singlet at δ 9.45 for the μ-CH proton and singlets at δ 3.99 and 3.05 for the OCH_3 and CH_3 groups and are consistent with either **12** or **A**. Similarly, the observation of only one Cp resonance in the ^1H NMR at −90 °C is consistent either with formulation **12** or with a rapidly fluxional μ-alkenyl structure **A**.

Table I. Selected Bond Distances and Angles for **8**

	(a) Bond Distances (Å)		
Fe(1)–Fe(2)	2.519 (1)	Fe(1)–C(11)	1.768 (5)
CNT(1)[a]–Fe(1)	1.747 (4)	Fe(2)–C(12)	1.746 (4)
CNT(2)–Fe(2)	1.748 (4)	C(11)–O(1)	1.144 (6)
Fe(1)–C(13)	1.887 (4)	C(12)–O(2)	1.149 (5)
Fe(2)–C(13)	1.934 (5)	C(14)–C(15)	1.481 (7)
Fe(1)–C(14)	1.970 (5)	C(15)–O(4)	1.220 (5)
Fe(2)–C(14)	2.001 (4)		
	(b) Bond Angles (deg)		
CNT(1)–Fe(1)–Fe(2)	134.7 (1)	C(12)–Fe(2)–C(13)	87.3 (2)
CNT(1)–Fe(1)–C(11)	121.9 (2)	C(12)–Fe(2)–C(14)	94.7 (2)
CNT(1)–Fe(1)–C(13)	122.6 (2)	C(13)—Fe(2)–Fe(1)	48.0 (1)
CNT(1)–Fe(1)–C(14)	122.9 (2)	C(13)–Fe(2)C(14)	96.2 (2)
C(11)–Fe(1)–Fe(2)	103.0 (1)	C(14)–Fe(2)–Fe(1)	50.1 (1)
C(11)–Fe(1)–C(13)	86.2 (2)	Fe(1)–C(13)–Fe(2)	82.5 (2)
C(11)–Fe(1)–C(14)	95.9 (2)	Fed(1)–C(14)–Fe(2)	78.7 (2)
C(13)–Fe(1)–Fe(2)	49.6 (1)	Fe(1)–C(3)–O(3)	141.0 (3)
C(13)–Fe(1)–C(14)	98.8 (2)	Fe(2)–C(13)–O(3)	136.6 (3)
C(14)–Fe(1)–Fe(2)	51.2 (1)	Fe(1)–C(14)–C(15)	123.0 (3)
CNT(2)–Fe(2)–Fe(1)	136.1 (1)	Fe(2)–C(14)–C(15)	117.1 (2)
CNT(2)–Fe(2)–C(12)	120.7 (2)	C(14)–C(15)–O(4)	123.5 (5)
CNT(2)–Fe(2)–C(13)	121.7 (2)	C(14)–C(15)–C(26)	119.7 (3)
CNT(2)–Fe(2)–C(14)	126.7 (2)	O(4)–C(15)–C(26)	116.8 (4)
C(12)–Fe(2)–Fe(1)	102.4 (1)		

[a] CNT = centroid of Cp ring.

Table II. Infrared Stretches for the Bridging Carbonyl Group of $[C_5H_5(CO)Fe]_2(\mu$-CO)(μ-R)

bridging hydrocarbyl ligand	$\nu_{\mu\text{-CO}}$, cm^{-1}	bridging hydrocarbyl ligand	$\nu_{\mu\text{-CO}}$, cm^{-1}
μ-CH_2	1780	μ-CHC≡O^+	1847
 μ-$CH\overset{O}{\overset{\Vert}{C}}CH_3$	1791	μ-CH^+	1856
 μ-$CH{-}\overset{^{+}OCH_3}{\overset{\Vert}{C}}{-}CH_3$	1829	μ-η^1,η^2-CH=CHR^+	1864

The ^{13}C NMR chemical shifts of the complex strongly support its formulation as the symmetrically bridged μ-alkylidene structure **12**. The α-carbon of the bridging ligand gives rise to a doublet ($J_{^{13}CH}$ = 155 Hz) at δ 132.9 and the β-carbon of the bridging ligand gives rise to a singlet at δ 205.6. The β-carbon of **12** which bears a OMe group is shifted only 6.9 ppm upfield from the ketone carbonyl of **6**. For comparison, moderate downfield chemical shifts are observed upon O-protonation of benzaldehyde (from δ 191 to 204) and acetophenone (from δ 196 to 219).[12] The estimated ^{13}C chemical shift for the β-carbon of the μ-alkenyl formulation **A** would be far upfield of the observed δ 205.6. For comparison, the ^{13}C chemical shift of the β-vinyl carbon in $[C_5H_5(CO)Fe]_2(\mu$-CO)(μ-η^1,η^2-CH=$CH_2)^+PF_6^-$ is a triplet ($J_{^{13}CH}$ = 165 Hz) at δ 65.1 while that of the α-vinyl carbon is a doublet ($J_{^{13}CH}$ = 161 Hz) at δ 185.5.[13] In vinyl ethers, the chemical shift of the vinyl carbon bearing the methoxy group appears about 30 ppm downfield from that in the corresponding alkene. Consequently, it would be unreasonable to expect the β-carbon of **A** to appear at δ 205.6 and the assignment of symmetric structure **12** to the methylated product appears reasonable.

The position of the infrared stretch of the μ-CO ligand can be used as a measure of electron donation from the $[C_5H_5(CO)Fe]_2(\mu$-CO) unit to the bridging hydrocarbyl ligand. As more electron density is transferred to the

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(10) Kalcher, W.; Herrmann, W. A.; Pahl, C.; Ziegler, M. L. *Chem. Ber.* **1984**, *117*, 69–78.

(11) See, for example: (a) Dolphin, D., Wick, A. E. *Tabulation of Infrared Spectral Data*; Wiley-Interscience: New York, 1977, Chapter 4. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; Chapter 3.

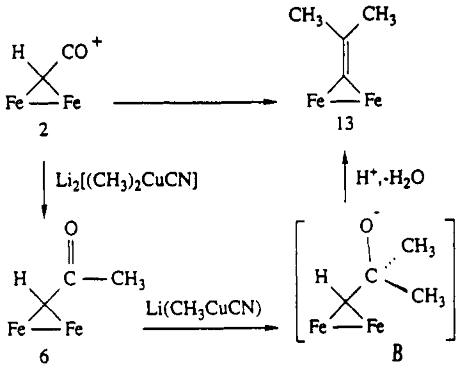
(12) Olah, G. A.; Iyer, P. S.; Surya Prakash, G. K.; Krishnamurthy, Y. V. *J. Am. Chem. Soc.* **1984**, *106*, 7068–7073.

(13) The $\{^1H\}^{13}C$ NMR of $[C_5H_5(CO)Fe]_2(\mu$-CO)(μ-η^1,η^2-CH=$CH_2)^+$-PF_6^- has been reported earlier.[14] To confirm the assignments of the α- and β-vinyl carbon resonances, we have obtained a proton-coupled spectrum: ^{13}C NMR (acetone-d_6, 126 MHz) δ 241.9 (μ-CO), 213.9, 208.2 (CO), 185.5 (d, J = 161 Hz, μ-*C*H=CH_2), 92.9 (d, J = 183 Hz, C_5H_5), 89.7 (d, J = 188 Hz, C_5H_5), 65.1 (t, J = 165 Hz, μ-CH=*C*H_2).

(14) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705.

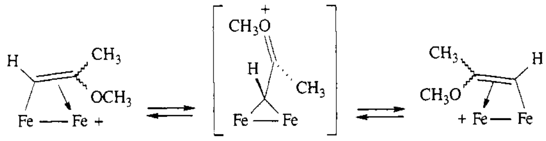
(15) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417–1426.

Scheme I



bridging hydrocarbyl ligand, the diiron unit becomes more electropositive and the μ-CO stretch increases as shown in Table II. The substantial shift in the μ-CO stretch from 1791 to 1829 cm^{-1} upon O-methylation of **6** to produce **12** indicates increased electron donation from the diiron unit to the positively charged μ-CHC(OCH$_3$)CH$_3$ ligand and is consistent with the importance of resonance structures such as **12-e**. Such electron donation was shown to be important for the bridging acylium complex **2**.[3] In the case of the μ-CHCO complex **2**, this electron donation was accompanied by an unusually far upfield ^{13}C NMR chemical shift for the bridging μ-CH carbon which appeared at δ 27 (J = 174 Hz). The ^{13}C NMR chemical shift of the bridging carbon of **12** appears at δ 133 which is 24 ppm upfield from that of the precursor ketone **6**. This is consistent with enhanced electron donation to the positively charged μ-CHC(OCH$_3$)CH$_3$ ligand of **6**.

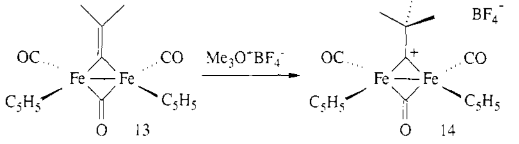
The fluxionality of μ-vinyl diiron complexes was previously suggested to proceed through a symmetric transition state in which positive charge was more localized on the β-vinyl carbon atom. The barrier to rearrangement was lowered by electron donor alkyl substituents on the β-vinyl carbon atom. The observed barriers to μ-vinyl fluxionality decreased from >14.7 kcal for μ-CH=CH$_2$, to 12.9 kcal for μ-CH=CHR, to 9.8 kcal for μ-CH=CR$_2$. It is very interesting that the strong electron-donating ability of the β-methoxy substituent in **12** has so stabilized the symmetric bridging structure that it is more stable than the μ-alkenyl structure **12**.



Reaction of Li$_2$[(CH$_3$)$_2$CuCN] with 2. The reaction of **2** with Li(CH$_3$CuCN) affords the acetyl-substituted alkylidene complex **6** as described above. However, when **2** was reacted with a slight excess of the cuprate Li$_2$[(CH$_3$)$_2$CuCN][16] and the reaction mixture subsequently quenched with ethanol, a pale red solid was isolated. A ^{1}H NMR spectrum of the product showed it to be a mixture of the bridging alkenylidene complex [C$_5$H$_5$(CO)Fe]$_2$(μ-CO)[μ-C=C(CH$_3$)$_2$] (**13**, 32% yield) and the μ-CHCH$_3$ complex **9** (8% yield). **13** had previously been prepared by Hoel[17] from the protonation of a methyl-substituted cyclopropylidene complex, followed by deprotonation of the resulting bridging alkylidyne species.

The formation of **13** may be rationalized in terms of the reaction sequence outlined in Scheme I. Transfer of 1 equiv of methyl anion from the cuprate Li$_2$[(CH$_3$)$_2$CuCN] to **2** would lead to the formation of complex **6**. **6** in turn is postulated to undergo attack by the resulting cuprate Li(CH$_3$CuCN) or by unreacted Li$_2$[(CH$_3$)$_2$CuCN] at the carbonyl carbon of the acetyl substituent, leading to the formation of anion **B**. Protonation of anion **B** at oxygen followed by elimination of water would then generate **13**. Evidence for the proposed intermediacy of complex **6** in this scheme was provided by the observation that addition of Li(CH$_3$CuCN) to a sample of **6** afforded **13** in 43% yield.

Reaction of Alkenylidene Complex 13 with Me$_3$O$^+$BF$_4^-$. Since several groups[18] have established that alkenylidene complexes undergo attack by electrophiles at the carbon α to the bridging carbon atom to generate new alkylidyne complexes, the reactivity of **13** toward the methylating agent Me$_3$O$^+$BF$_4^-$ was examined. Stirring an equimolar mixture of these reacts in CH$_2$Cl$_2$ at room temperature led to a slow reaction. IR spectroscopy indicated that consumption of **13** was complete after 7 days. Subsequent workup of the reaction mixture afforded an orange solid in 36% yield identified as the *tert*-butyl-substituted alkylidyne complex [C$_5$H$_5$(CO)Fe]$_2$(μ-CO)[μ-C(CH$_3$)$_3$]$^+$BF$_4^-$ (**14**). The formation of **14** is the result of the expected methylation of the carbon α to the bridging alkenylidene carbon of **13**. Characterization of **14** as a bridging alkylidyne complex was facilitated by its ^{13}C{^{1}H} NMR spectrum which contains a downfield resonance at δ 520.1, characteristic of a bridging alkylidyne carbon.[19]



Experimental Section

General Data. ^{1}H NMR spectra were normally obtained on a Bruker WP270 spectrometer or where indicated on a Bruker WP200 spectrometer. ^{13}C NMR spectra were normally obtained on a JEOL FX200 spectrometer (50.1 MHz) or where indicated on a Bruker AM 500 spectrometer (125.76 MHz). Cr(acac)$_3$ (0.07 M) was added to ^{13}C NMR samples as a shiftless relaxation agent. Infrared spectra were measured on a Beckman 4230 or Mattson Polaris (FT) spectrometer. Mass spectra were determined on a Kratos MS-80. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN), or by Schwarzkopf Laboratories (Woodside, NY).

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard high-vacuum and Schlenk techniques. Diethyl ether, THF, hexane and C$_6$D$_6$ were distilled immediately prior to use from purple solutions of sodium and benzophenone. CH$_2$Cl$_2$ and CD$_2$Cl$_2$ were dried over CaH$_2$. CD$_3$CN and (CD$_3$)$_2$CO were dried over CaH$_2$ and B$_2$O$_3$, respectively.

[C$_5$H$_5$(CO)Fe]$_2$(μ-CO)(μ-CHCOCH$_3$) (6). A solution of Li(CH$_3$CuCN),[1,4] prepared from CuCN (32 mg, 0.36 mmol) and CH$_3$Li (0.35 mmol) in THF (3 mL) cooled to −78 °C, was added via cannula to a slurry of **2** (180 mg, 0.35 mmol) in THF (8 mL) cooled to −78 °C. The resulting red solution was stirred at −78 °C for 15 min. Volatile material was evaporated under vacuum at room temperature. The residue was extracted into CH$_2$Cl$_2$ (3 mL) and loaded onto an alumina column (15 cm × 2 cm). Elution with 3:2 hexane/diethyl ether afforded a red material identified by ^{1}H NMR as **9**[5] (10 mg, 8%). Subsequent elution with 1:1 acetone/diethyl ether afforded a purple-red solid. The material

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[16] For recent examples of the use of cuprates of this type in organic and organometallic synthesis see: (a) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101–105. (b) Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 2305–2307.

[17] Hoel, E. L. *Organometallics* **1986**, *5*, 587–588.

[18] Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59–128 and references therein.

[19] Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053.

Table III. Crystal Parameters for 8

(a) Crystal Data			
formula	$C_{21}H_{16}O_4Fe_2$	γ, deg	103.42 (2)
fw	444.04	V, Å^3	914.0
cryst system	triclinic	Z	2
space group	$P\bar{1}$	μ(Mo Kα), cm^{-1}	16.1
a, Å	7.008 (2)[a]	D(calcd), g cm^{-3}	1.613
b, Å	12.392 (3)	temp, K	293
c, Å	12.441 (3)	cryst size, mm	0.08 × 0.30 × 0.31
α, deg	118.37 (2)	cryst color	deep red
β, deg	91.09 (2)	T(max)/T(min)	0.85/0.70
(b) Data Collection			
diffractometer	Nicolet R3m	data collected	$\pm h,\pm k,+l$
monochromator	graphite	reflns collctd	3289
radiation	Mo Kα	indpdt rflns	3045
wavelength, Å	0.71073	R(int), %	2.45
scan method	ω	indpdt rflns, $F_o \geq 4\sigma(F_o)$	2550
scan limits, deg	$4 \leq 2\theta \leq 49$		
(c) Refinement Results			
$R(F)$, %	3.93	$\Delta(\rho)$, e Å^{-3}	0.396
$R(wF)$, %	4.51	N_o/N_v	8.6
Δ/σ(max)	0.08	GOF	1.437

[a] Unit-cell parameters obtained from the least-squares fit of 25 rfeflections ($22° \leq 2\theta \leq 31°$).

was recyrstallized from CH_2Cl_2/hexane, washed with hexane (3 × 5 mL), and dried under vacuum to give **6** as red microcrystals (85 mg, 63%): ^{1}H NMR (acetone-d_6) δ 10.96 (s, μ-CH), 4.95 (s, 10 H, C_5H_5), 2.54 (s, CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 270.5 (μ-CO), 213.3 (CO), 212.5 ($COCH_3$), 157.3 (μ-CH), 88.5 (C_5H_5), 30.3 (CH_3); IR (CH_2Cl_2) 1997 (s), 1965 (m), 1791 (s), 1633 (w) cm^{-1}. HRMS Calcd for M − CO $C_{15}H_{14}Fe_2O_3$: 353.9641. Found 353.9650. Anal. Calcd for $C_{16}H_{14}Fe_2O_4$: C, 50.31; H, 3.69. Found: C, 50.04; H, 4.01.

[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-CHCO(CH_2)$_3$$CH_3$] (7). A solution of Li[$CH_3(CH_2)_3$CuCN], prepared from CuCN (37 mg, 0.41 mmol) and n-BuLi (0.39 mmol) in THF (3 mL) cooled to −78 °C, was added via cannula to a slurry of **2** (200 mg, 0.39 mmol) in THF (8 mL) at −78 °C. Workup was as described for **6**. Chromatography of the reaction mixture afforded **10**^{6} (1:1 hexane/diethyl ether) as an orange-red solid (23 mg, 14%), followed by **7** (1:1 CH_2Cl_2/ether) as a red solid (125 mg, 75%): ^{1}H NMR (acetone-d_6) δ 10.98 (s, μ-CH), 4.94 (s, 10 H, C_5H_5), 2.97 (t, J = 7.7 Hz, $COCH_2$), 1.71 (tt, J = 7.7, 7.4 Hz, $COCH_2CH_2$), 1.43 (tq, J = 7.4, 7.0 Hz, CH_2CH_3), 0.96 (t, J = 7.0 Hz, CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 270.8 (μ-CO), 214.9 ($COCH_2$), 213.4 (CO), 157.5 (μ-CH), 88.6 (C_5H_5), 43.0 ($COCH_2$) 29.0 (CH_2), 23.4 (CH_2), 14.5 (CH_3); IR (CH_2Cl_2) 1997 (s), 1973 (m), 1796 (s), 1638 (w) cm^{-1}. HRMS Calcd for M − CO $C_{18}H_{20}Fe_2O_3$: 396.0110. Found: 396.0106. Anal. Calcd for $C_{19}H_{20}Fe_2O_4$: C, 53.82; H, 4.75. Found: C, 53.61; H, 5.00.

[C_5H_5(CO)Fe]$_2$(μ-CO)(μ-CHCOC_6H_5) (8). A solution of Li(C_6H_5CuCN), prepared from CuCN (48 mg, 0.54 mmol) and C_6H_5Li (0.54 mmol) in THF (3 mL) cooled to −78 °C, was added via cannula to a slurry of **2** (247 mg, 0.48 mmol) in THF (8 mL) at −78 °C. Workup was as described for **6**. Chromatography of the reaction mixture afforded **11**^{1} (diethyl ether) as a red solid (32 mg, 16%), followed by **8** (1:1 acetone/ether) as a dark red microcrystalline solid (120 mg, 56%): ^{1}H NMR (acetone-d_6) δ 11.77 (s, μ-CH), 8.27 (m, 2 H, o-Ph), 7.55 (m, 3 H, m-, p-Ph), 4.95 (s, 10 H, C_5H_5); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 269.8 (μ-CO), 213.4 (CO), 206.7 (COC_6H_5), 150.4 (μ-CH), 141.6 (ipso C_6H_5), 131.9, 129.4, 128.7 (C_6H_5), 87.5 (C_5H_5); IR (CH_2Cl_2) 1997 (s), 1970 (m), 1793 (s), 1616 (w) cm^{-1}. HRMS Calcd for M + H $C_{21}H_{17}O_4Fe_2$: 444.9825. Found: 444.9832.

[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-CHC(OCH_3)CH_3]$^+$$CF_3SO_3^-$ (12). A solution of **6** (80 mg, 0.21 mmol) and $CF_3SO_3CH_3$ (0.04 mL, 0.35 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 6 h. Diethyl ether (10 mL) was then added to afford a purple-black solid which was isolated by filtration. The product was recrystallized from CH_2Cl_2/ether, washed with ether (3 × 10 mL), and dried under vacuum to give **12** (84 mg, 73%): ^{1}H NMR (acetone-d_6, 200 MHz) δ 9.45 (s, μ-CH), 5.45 (s, 10 H, C_5H_5), 3.99 (s, OCH_3), 3.05 (s, CH_3); ^{13}C NMR (CD_2Cl_2, 125.76 MHz) δ 253.5 (μ-CO), 210.2 (CO), 205.6 (μ-CHC), 132.9 (d, J = 155 Hz, μ-CH), 89.6 (d, J = 178 Hz, C_5H_5), 58.9 (q, J = 136 Hz, OCH_3), 27.3 (q, J = 131 Hz, CH_3); IR (CH_2Cl_2) 2014 (s), 1982 (m), 1829 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{17}F_3Fe_2O_7S$: C, 39.59; H, 3.14. Found: C, 39.54; H, 2.84.

Reaction of 2 with $Li_2[(CH_3)_2CuCN]$. A solution of $Li_2[(CH_3)_2CuCN]$ was prepared by stirring a suspension of CuCN (27 mg, 0.32 mmol) and CH_3Li (0.64 mmol) in THF (3 mL) at −20 °C until a clear solution formed. The solution was then cooled to −78 °C and was added via cannula to a slurry of **2** (151 mg, 0.29 mmol) in THF (5 mL) cooled to −78 °C. The reaction mixture was stirred at −78 °C for 20 min and then quenched with ethanol (1 mL). The mixture was warmed to room temperature, and volatile material was removed under vacuum. The residue was extracted into CH_2Cl_2 (2 mL) and chromatographed on alumina. Elution with diethyl ether afforded a red band which was recrystallized from diethyl ether/hexane at −78 °C to yield a pale red microcrystalline solid (45 mg). ^{1}H NMR spectroscopy showed the product to be a 4:1 mixture of **13**/**9** (32% yield of **13**). **13**: ^{1}H NMR (acetone-d_6, 200 MHz) δ 4.96 (s, 10 H, C_5H_5), 2.45 (s, 6 H, CH_3); IR (CH_2Cl_2) 1992 (s), 1953 (m), 1780 (s), 1623 (w) cm^{-1}.

[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-CC(CH_3)$_3$]$^+$$BF_4^-$ (14). A solution of **13** (80 mg, 0.21 mmol) and $Me_3O^+BF_4^-$ (31 mg, 0.21 mmol) in CH_2Cl_2 (8 mL) was stirred at room temperature for 7 days. The reaction mixture was then filtered through a plug of Celite and the volume of solvent reduced under vacuum to 4 mL. Diethyl ether (8 mL) was slowly added to afford an orange precipitate which was isolated by filtration. The solid was recrystallized from CH_2Cl_2/ether, washed with ether (3 × 10 mL), and dried under vacuum to give **14** (34 mg, 36%, 37:1 mixture of cis/trans Cp isomers): ^{1}H NMR (acetone-d_6, 200 MHz), cis isomer, δ 5.97 (s, 10 H, C_5H_5), 1.94 (s, 9 H, CH_3), trans isomer, δ 5.67 (s, 10 H, C_5H_5), 1.82 (s, 9 H, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6), cis isomer, δ 520.1 (μ-$CC(CH_3)_3$), 251.6 (μ-CO), 212.6 (CO), 93.3 (C_5H_5), 73.6 ($C(CH_3)_3$), 32.5 (CH_3), trans isomer, δ 87.7 (C_5H_5), 27.3 (CH_3), other carbons not observed; IR (CH_2Cl_2) 2041 (s), 2009 (m), 1851 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{19}BF_4Fe_2O_3$: C, 44.87; H, 3.97. Found: C, 44.37; H, 3.97.

Crystallographic Structural Determination of 8. Crystal, data collection, and refinement parameters are given in Table III. Platelike crystals were grown by diffusion of hexane into a CH_2Cl_2 solution. No crystal symmetry higher than triclinic was found either from axial photographs or by the cell reduction program TRACER. The centrosymmetric space group $P\bar{1}$ was assumed correct throughout; the validity of the choice is affirmed by the chemically and computationally reasonable results of refinement. The data were empirically corrected for absorption (216 data, six-parameter pseudoellipsoid model).

The Fe atom locations were obtained from a Patterson map and the remaining atoms from subsequent difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms (all found) were refined isotropically. The phenyl ring was constrained to a rigid, planar hexagon (d(C−C) = 1.395 Å) to conserve data. The Cp ring of Fe(2) is likely disordered to some extent; the thermal parameters (U) for this ring average 0.088 Å^2 compared to 0.055 Å^2 for the ring of Fe(1). We were unable to resolve individual atom positions.

All computations used the SHELXTL and P3 program libraries (Nicolet Corp., Madison, WI) which served additionally as the source of the neutral atom scattering factors.

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Registry No. 2, 117182-15-7; 6, 117182-15-7; 7, 117144-58-8; 8, 117144-59-9; 9, 75811-60-8; 10, 117144-60-2; 11, 112172-87-9; 12, 117144-66-8; 13, 99923-12-3; 14, 117144-62-4; Li(CH_3CuCN), 41753-78-0; Li[$CH_3(CH_2)_3$CuCN], 41742-63-6; Li(C_6H_5CuCN), 41742-64-7; $Li_2[(CH_3)_2CuCH]$, 80473-70-7; *trans*-[C_5H_5(CO)Fe]$_2$(μ-CO)[μ-CC(CH_3)$_3$$^+$$BF_4^-$, 117144-64-6.

Supplementary Material Available: Complete listings of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters (6 pages); a listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.