Synthesis of $\{[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)]_2(\mu\text{-}C_3H_3)\}^+PF_6^-$ by Reaction of a Diiron Bridging Methylidyne Complex with a Diiron Bridging Ethenylidene Complex

Charles P. Casey* and Seth R. Marder

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Arnold L. Rheingold*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

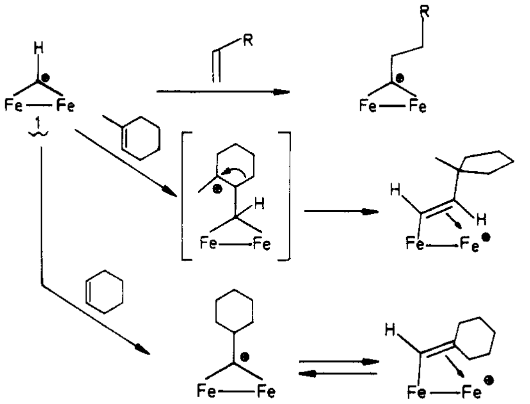
Received July 31, 1984

Reaction of $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$, **1**, with $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, **2**, produces $\{[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)]_2(\mu\text{-}C_3H_3)\}^+PF_6^-$, **3**, in 78% yield. The structure of **3** was determined by X-ray crystallography: monoclinic space group $P2_1/n$, with unit cell constants a = 9.435 (3) Å, b = 32.89 (1) Å, c = 11.285 (4) Å, β = 97.46 (2)°, and Z = 4. The unique bridging system can best be thought of as a three-carbon allyl system with two in-plane iron substituents syn to the central allylic hydrogen; in addition, a third iron sits above the allyl plane interacting strongly with the terminal allylic carbon and weakly with the central allylic carbon and a fourth iron sits below the allyl plane interacting strongly with the other terminal allylic carbon and weakly with the central carbon. A double-labeling experiment using ^{13}C methylidyne labeled **1**-^{13}CH and dideuterio ethenylidene complex **2**-d_2 gave **3** which retained the ^{13}CH bond. This labeling pattern is consistent only with electrophilic addition of the methylidyne carbon of **1** to **2** followed by a 1,2-deuterium migration to produce labeled **3**.

Introduction

Several years ago, we prepared the diiron methylidyne complex $[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$, **1**, by hydride abstraction with $C(C_6H_5)_3^+$ from the corresponding bridging methylene complex.[1] Complex **1** was the first compound in which a C–H unit bridges between two metals. It can be viewed as a secondary carbocation stabilized by two electron-donating iron substituents which make the cation **1** more stable than $C(C_6H_5)_3^+$. In spite of its high thermodynamic stability, **1** reacts rapidly with nucleophiles such as NR_3, HOR, and even CO to form 1:1 adducts.[2] Complex **1** reacts with alkenes as an electrophile to produce complexes with new carbon–carbon bonds, but the mechanism of the addition and the observed products depend strongly on the nature of the alkene.[3] With ethylene and mono- and 1,1-disubstituted alkenes, the carbon–hydrogen bond of **1** undergoes a concerted addition across the carbon–carbon double bond of the alkene (hydrocarbation) to produce a new bridging alkylidyne complex.[4] With some alkenes such as 1-methylcyclohexene and *trans*-stilbene, the carbon atom of **1** adds to the alkenes to generate a stabilized tertiary or benzylic carbocation that then undergoes subsequent carbon migration to give bridging vinyl complexes.[4,5] With 1,2-disubstituted alkenes such as 2-butene and cyclohexene, we have shown by detailed deuterium labeling experiments that the C–H bond of **1** adds across the alkene to produce an alkylidyne complex that subsequently equilibrates with a bridging vinyl complex via a 1,2 hydrogen shift.[5,6]

Since bridging (alkenylidene)diiron complexes are readily protonated,[6-8] we thought that the electrophilic methylidyne complex **1** might react with the ethenylidene complex $(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, **2**. Here we report that the reaction of **1** and **2** produces the new complex in which a C_3H_3 group bridges between four iron centers.



Results

Reaction of methylidyne complex **1** with ethenylidene complex **2** in dichloromethane led to the formation of the blue-black crystalline compound $\{[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)]_2(\mu\text{-}C_3H_3)\}^+PF_6^-$, **3**, in 78% isolated yield. The general structure of **3** was deduced from spectroscopic data, and the precise nature of the compound was established by X-ray crystallography. The IR spectrum of **3** in the carbonyl region consisted of three bands at 2013, 1979, and 1814 cm^{-1} consistent with the presence of two equivalent $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)$ units. The ^1H and ^{13}C NMR of **3** also indicated a highly symmetric or fluxional structure.

In the ^1H NMR of **3**, the observation of a one-proton triplet (J = 12 Hz) at δ 5.75 and a two-proton doublet (J = 12 Hz) at δ 11.46 established the presence of a symmetric allylic like C_3H_3 unit in which the protons on the terminal carbons were anti to the proton on the central carbon. In addition, a 20-proton singlet at δ 5.45 could be assigned either to four equivalent C_5H_5 groups or to four C_5H_5

---

(1) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.

(2) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360.

(3) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173.

(4) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950.

(5) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680.

(6) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197.

(7) Dawkins, G. M.; Green, M.; Jeffrey, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans* **1983**, 499.

(8) Alternatively, the ethenylidene group can be named methylidenecarbene. See: Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348–354.

0276-7333/85/2304-0762$01.50/0

Table I. Selected Bond Distances and Angles for 3

(a) Bond Distances (Å)

Fe(1)-Fe(2)	2.553 (3)	Fe(2)-C(3)	1.76 (2)	C(2)-O(2)	1.17 (2)
Fe(3)-Fe(4)	2.555 (3)	Fe(2)-C(7)	2.00 (1)	C(3)-O(3)	1.16 (2)
Fe(1)-CNT(1)[a]	1.728 (8)	Fe(3)-C(4)	1.75 (1)	C(4)-O(4)	1.18 (2)
Fe(2)-CNT(2)	1.744 (7)	Fe(3)-C(5)	1.96 (1)	C(5)-O(5)	1.18 (2)
Fe(3)-CNT(3)	1.718 (8)	Fe(3)-C(9)	2.03 (1)	C(6)-O(6)	1.12 (2)
Fe(4)-CNT(4)	1.748 (9)	Fe(4)-C(5)	1.89 (2)	C(7)-C(8)	1.44 (2)
Fe(1)-C(1)	1.75 (1)	Fe(4)-C(6)	1.77 (1)	C(8)-C(9)	1.39 (2)
Fe(1)-C(2)	1.91 (1)	Fe(4)-C(9)	1.95 (1)	Fe(2)· · ·C(8)	2.77 (1)
Fe(1)-C(7)	1.95 (1)	C(1)-O(1)	1.14 (2)	Fe(3)· · ·C(8)	2.55 (1)
Fe(2)-C(2)	1.95 (1)				

(b) Bond Angles (deg)

Fe(1)-Fe(2)-CNT(2)	136.6 (4)	Fe(2)-C(3)-O(3)	176 (1)	Fe(3)-C(9)-Fe(4)	79.9 (5)
Fe(2)-Fe(1)-CNT(1)	138.1 (4)	C(2)-Fe(1)-C(7)	100.2 (5)	Fe(3)-C(5)-O(5)	136 (1)
Fe(1)-C(1)-O(1)	177 (1)	C(2)-Fe(2)-C(7)	97.1 (5)	Fe(4)-C(5)-O(5)	141 (1)
Fe(1)-C(2)-Fe(2)	82.3 (5)	C(7)-C(8)-C(9)	125 (1)	Fe(3)-C(9)-C(8)	94.8 (8)
Fe(1)-C(7)-Fe(2)	79.8 (4)	Fe(3)-Fe(4)-CNT(4)	137.9 (5)	Fe(4)-C(9)-C(8)	130.6 (9)
Fe(1)-C(2)-O(2)	140 (1)	Fe(4)-Fe(3)-CNT(3)	133.8 (4)	Fe(4)-C(6)-O(6)	177 (1)
Fe(2)-C(2)-O(2)	138 (1)	Fe(3)-C(4)-O(4)	177 (1)	C(5)-Fe(3)-C(9)	95.5 (5)
Fe(1)-C(7)-C(8)	129.5 (9)	Fe(3)-C(5)-Fe(4)	83.1 (5)	C(5)-Fe(4)-C(9)	100.6 (5)
Fe(2)-C(7)-C(8)	106.1 (8)				

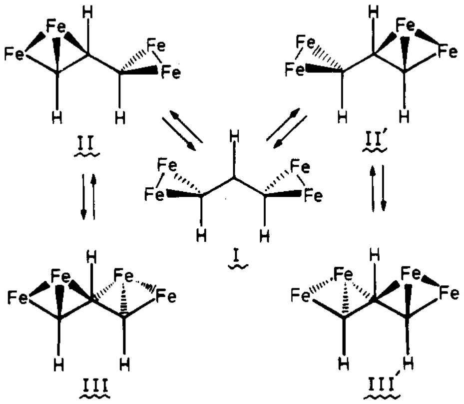
(c) Dihedral Angles (deg)

CNT(1)-Fe(1)-Fe(2)-CNT(2)	−1.2	plane[Fe(1)-Fe(2)-C(2)]-plane[Fe(1)-Fe(2)-C(7)]	8.0
CNT(3)-Fe(3)-Fe(4)-CNT(4)	0.4	plane[Fe(3)-Fe(4)-C(5)]-plane[Fe(3)-Fe(4)-C(9)]	5.1

[a] CNT = centroid of η^5-C_5H_5 ring.

groups made equivalent by a fluxional process. In the ^{13}C NMR, only single resonances were seen for the four C_5H_5 groups at δ 90.1, for the two terminal carbons of the C_3 unit at δ 159.8, for the one central carbon of the C_3 unit at δ 155.5, for the bridging CO's at δ 252.8, and for the terminal CO's at δ 212.2. No evidence for the slowing of a fluxional process was seen at −70 °C in the ^1H NMR or at −50 °C in the ^{13}C NMR.

Several possible structures that were considered for 3 included the symmetric structure I in which a carbonium ion is flanked by two bridging alkylidene iron units, a fluctional structure II in which one of the diiron centers has a bridging alkylidene group and the other has a bridging vinyl group, and a fluxional structure III in which the center carbon of the C_3 unit interacts with two iron atoms—one from each Fe_2 group. Interconversion of II with II′ and of III with III′ require passing through a symmetric intermediate or transition state of structure I.



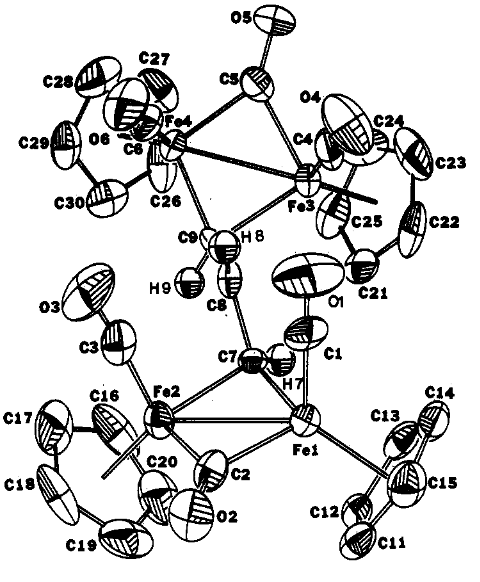


Figure 1. ORTEP of 3.

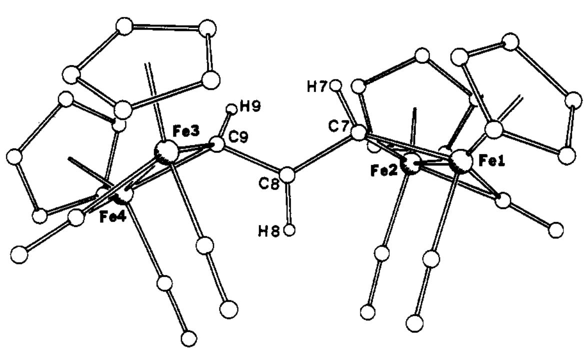


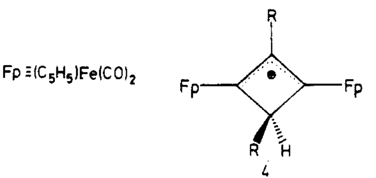
Figure 2. View emphasizing C_3H_3 portion of 3.

X-ray Structure of 3. Crystals of a monoacetone solvate of 3 were obtained from an acetone–ether solution. In spite of experimental difficulties involving weak diffraction and minor twinning effects, the structure of 3 was solved with a final R_F = 0.074. Selected bond lengths and angles are presented in Table I. Figures 1 and 2 indicate that the cation has a structure approximated by III. The cation has roughly C_2 symmetry with a C_2 axis in the plane of the C_3 unit and passing through the central carbon of the C_3 unit linking the two diiron fragments. The central C_3 unit can best be described as an allyl system with two iron atoms bonded to the terminal carbons with bond lengths of 1.95 (1) Å both for Fe(1)–C(7) and for Fe(4)–C(9). These two iron atoms are syn to the central hydrogen of the allyl unit and are nearly in the plane of the allyl carbons; Fe(1) is 0.44 Å above the plane and Fe(4) is 0.22 Å below the plane. The two remaining iron atoms are situated well above and well below the allyl plane. Fe(2), which is 1.83 Å below the allyl plane, is strongly bonded to Fe(1) [2.553 (3) Å] and to terminal allyl carbon C(7) [2.00 (1) Å] and weakly bonded to the central allyl carbon C(8) [2.77 (1) Å]. Similarly, Fe(3), which is 1.92 Å above the allyl plane, is strongly bonded to Fe(4) [2.555 (3) Å] and to terminal allyl carbon C(9) [2.03 (1) Å] and weakly bonded to the central allyl carbon C(8) [2.55 (1) Å]. The distances from the out of plane iron atoms to the central carbon of the allyl unit are substantially longer than the 2.21 Å iron to β-vinyl carbon distance observed for the bridging vinyl complex $\{(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)\}^+PF_6^-$.[9] The interactions between the out-of-plane iron atoms and the central allyl carbon atom are therefore similar to but weaker than the interactions of iron with the β-carbon of a bridging vinyl complex.

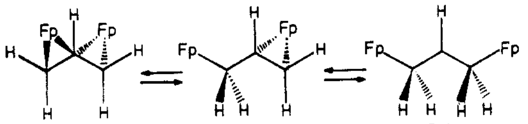
Another way of describing the bonding to the central allyl carbon in **3** is in terms of a hyperconjugative electron donation into the p orbital at the central allyl carbon from the σ bonds joining the out of plane irons to the terminal allyl carbons. This interaction is similar to the interaction that stabilizes cyclopropyl carbinyl cations. The geometry of **3** is nearly ideal for such an interaction: the dihedral angle between the bond from Fe(2) to C(7) and the p orbital at the central carbon C(8) is 23.0° and the dihedral angle between the bond from Fe(3) to C(9) and the p orbital at the central carbon is 18.4°.[10]

There are two types of iron compounds that incorporate some of the key structural features of **3**. Cationic allyl compounds with two in-plane iron atoms such as **4** have been made by reaction of iron acetylides with cationic (alkenylidene)iron complexes.[11,12] Compounds such as **5** in which a cation at the central carbon of a three-carbon chain is stabilized by interaction with two out of plane iron centers have been synthesized.[13-15] The infrared spectra of **5** indicates two different iron centers as shown for **5-I**. The X-ray structure indicates that the iron centers are nonidentical but both interact with the electron-deficient central carbon atom (2.59 and 2.72 Å).[14] In the low-temperature NMR spectrum of **5**, the two iron centers are equivalent and three different allyl resonances are seen as expected for a symmetric or fluxional structure **5-II**.[15] At room temperature, the protons on the terminal allyl carbons are NMR equivalent due to rapid rotation about the Fe–C bonds.[15] As in the case of **3**, the highest energy conformation is **5-II** in which neither iron center interacts with the central electron-deficient carbon center.

Double-Labeling Experiment. There are two possible mechanisms for the formation of **3** which can be distinguished only by a double labeling experiment. These possibilities will be discussed in the context of the reaction of the ^{13}C labeled methylidyne complex **1**-^{13}CH with the dideuterium-labeled ethenylidene complex **2**-d_2. The formation of **3** could proceed by an initial hydrocarbation

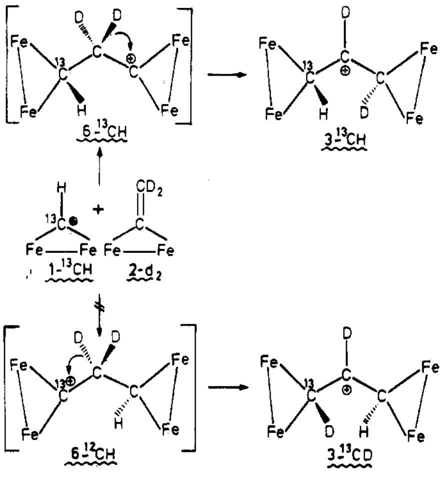


4



5 5-I 5-II

in which the ^{13}C–H bond of **1**-^{13}CH adds across the $D_2C{=}CFe_2$ double bond of **2**-d_2 to generate alkylidyne complex **6**-^{12}CH which then undergoes a 1,2 hydrogen migration to produce **3**-^{13}CD. In this mechanism, there is a net conversion of the ^{13}C–H bond in the starting material to a ^{13}C–D bond in the product. A second possible mechanism for formation of **3** would involve electrophilic addition of the methylidyne carbon of **1**-^{13}CH to the terminal carbon of **2**-d_2 to generate alkylidyne complex **6**-^{13}CH which then undergoes a 1,2 hydrogen migration to produce **3**-^{13}CH. In this mechanism, the ^{13}C–H bond in the starting material is retained as a ^{13}C–H bond in the product. A third possible outcome of the double-labeling experiment would invovle scrambling of hydrogen and deuterium labels between **3**-^{13}CH and **3**-^{13}CD via reversible 1,2 hydrogen shifts that interconvert **3** and **6**. Such a scrambling process would preclude distinguishing between a hydrocarbation and an electrophilic addition mechanism. Earlier we showed that a 1,2 hydrogen migration is a facile process for interconverting bridging alkylidyne and bridging vinyl complexes.[6]



These three possible scenarios are easily distinguished by observation of the ^1H NMR resonance at δ 11.5 due to protons on the terminal carbons of the three-carbon bridge of **3**. The hydrocarbation pathway would give rise to **3**-^{13}CD which would have a singlet (ignoring ^2H and long-range ^{13}C coupling) at δ 11.5; the electrophilic pathway would give rise to **3**-^{13}CH which would have a doublet ($J_{^{13}CH}$ = 147 Hz) centered at δ 11.5; finally, scrambling would give a superposition of the singlet and the doublet (a 1:2:1 pattern with peak separation of 74 Hz).

In the key experiment, **1**-^{13}CH with 99% ^{13}C label at the methylidyne carbon was reacted with ethenylidene complex **2**-d_2 with 83% deuterium incorporation in the $D_2C{=}CFe_2$ group. Examination of the product **3** by ^1H NMR indicated the presence of an intense doublet ($J_{\alpha^{13}CH}$ = 147 Hz) centered at δ 11.5 and a weaker doublet ($J_{\gamma^{13}CH}$ = 5 Hz) also at δ 11.5 with an integrated area ratio 1.00:0.21

---

[9] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1427.

[10] These are the angles between the vectors defined by the Fe(2)–C(7) bond and the Fe(3)–C(9) bond and a vector perpendicular to the C(7)–C(8)–C(9) plane [equivalent to a p orbital at C(8)]. The Fe(2)–C(7)–C(8) angle is 106.1°, and the Fe(3)–C(9)–C(8) angle is 94.8°.

[11] Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8.

[12] Kolobova, N. Y.; Skripkin, V. V.; Alexandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *169*, 293.

[13] King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *7*, 311.

[14] Laing, M.; Moss, J. R.; Johnson, J. *J. Chem. Soc. Chem. Commun.* **1977**, 656.

[15] Kerber, R. C.; Giering, W. P.; Bauch, T.; Waterman, P.; Chou, E. *J. Organomet. Chem.* **1976**, *120*, C31.

[16] Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31.

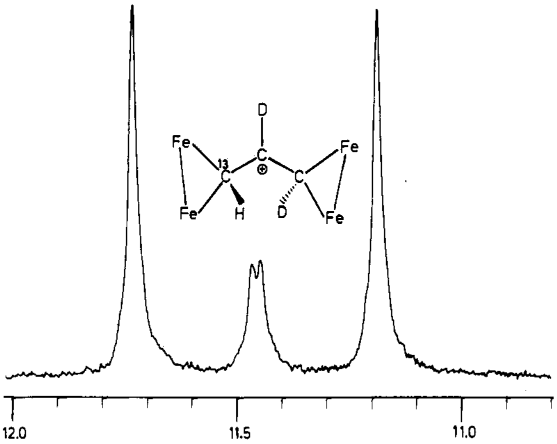
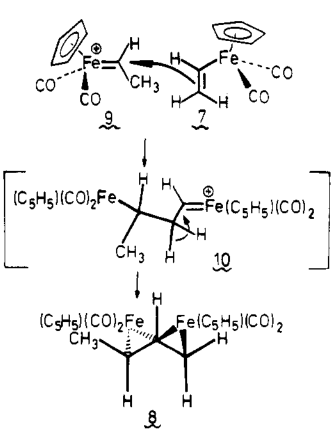


Figure 3. ^{1}H NMR of δ 11.5 region of the product of the reaction of **1**-^{13}*CH* with **2**-d_2.

(Figure 3). The intense doublet is due to the ^{13}CH terminal group on the three-carbon bridge of **3**-^{13}*CH*; the weaker finely split doublet is largely due to a ^{13}CH–CD–^{12}CH group in **3** arising from incomplete deuteration of starting material **2**-d_2. If there is no isotope effect (k_H/k_D = 1) on the migration of H or D during the rearrangement of monodeuterated **6**-d_1, Fe$_2$^{13}CH–CHD–CFe$_2$, then the observed ratio of NMR peaks is consistent with 97.5 ± 2.1% of the reaction proceeding via an electrophilic mechanism involving intermediate **6**-^{13}*CH* and 2.5 ± 2.1% of the reaction proceeding via a hydrocarbation mechanism involving **6**-^{13}*CD*. Alternatively if the entire reaction is assumed to proceed via the electrophilic pathway, then the isotope effect on the migration of H or D during the rearrangement of monodeuterated intermediate **6**-d would be k_H/k_D = 1.44.

In a second run of the double-labeling experiment using **2**-d_2 with 77% deuterium incorporation, the ratio of the ^{13}CH doublet to ^{12}CH singlet was 1.00:0.27. This corresponds either to 96.6 ± 2.7% electrophilic mechanism and 3.4 ± 2.7% hydrocarbation with no isotope effect for hydrogen migration or to 100% electrophilic mechanism with k_H/k_D = 1.48.

Cutler has observed a reaction of monoiron compounds that is analogous to the electrophilic addition leading to **3**. Cutler found that protonation of the vinyliron complex (C$_5$H$_5$)(CO)$_2$FeCH=CH$_2$, **7**, led to the formation of the cationic diiron compound **8**. Cutler proposed that protonation of **7** gives the electrophilic iron carbene complex (C$_5$H$_5$)(CO)$_2$Fe=CHCH$_3$$^+$, **9**, which electrophilically adds to a second molecule of vinyliron complex **7** to produce intermediate **10** which then undergoes a 1,2 hydrogen shift to produce **8**. Cutler's electrophilic carbene complex **9** is analogous to our methylidyne complex **1**; his vinyl complex **7** is analogous to our bridging ethenylidene complex **2**; his intermediate **10** is analogous to our intermediate **6**.



Conclusion

The reaction of methylidyne complex **1** with ethenylidene complex **2** has produced the interesting new tetrairon complex **3** by an electrophilic addition mechanism. This addition of a carbon electrophile to a bridging alkylidenecarbene complex suggests the possibility of a general mode of carbon–carbon bond formation that we are currently exploring.

Experimental Section

General Data. ^{1}H NMR spectra were recorded on a Bruker WP200 or a WP270 spectrometer. ^{13}C NMR were recorded on a JEOL FX 200 spectrometer operating at 50.10 MHz. CD$_2$Cl$_2$ was dried over P$_2$O$_5$; acetone-d_6 was dried over molecular sieves or B$_2$O$_3$; benzene-d_6 was distilled from purple solutions of sodium and benzophenone. NMR samples were prepared and sealed on a vacuum line and centrifuged prior to analysis. IR spectra were recorded on a Beckman 4230 infrared spectrometer calibrated with polystyrene film.

Air-sensitive compounds were handled by using standard Schlenk procedures and glovebox manipulations. Diethyl ether, THF, and hexane were distilled from purple solutions of sodium and benzophenone. CH$_2$Cl$_2$ was distilled from CaH$_2$. ^{13}CH$_3$P(C$_6$H$_5$)$_3$$^+I^-$ [17] (prepared from ^{13}CH$_3$I, 99% ^{13}C, Cambridge Isotope Laboratories), [(C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CH)]$^+$PF$_6^-$, **1**,[1] and [(C$_5$H$_5$)$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CCH$_3$)]$^+$PF$_6^-$, **11**,[18] were prepared as previously described.

***cis*- and *trans*-$(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, 2.** Ethylidyne complex **11** (1.50 g, 3.0 mmol) was stirred for 1 h with solid NaHCO$_3$(1 g, 11.9 mmol) in a mixture of acetone (10 mL), H$_2$O (10 mL), and diethyl ether (30 mL). An additional 10 mL of water was added, and the red ether phase was separated. The aqueous phase was extracted with 30 mL of ether, and the combined ether extracts were dried (MgSO$_4$) and evaporated under vacuum to give **2** (0.97 g, 82%) as a red crystalline solid: mp 151–154 °C dec (lit.[18] mp 153–155 °C dec); ^{1}H NMR (270 MHz, acetone-d_6) trans, δ 6.91 (s, 2 H), 4.81 (s, 10 H), cis δ 6.81 (s, 2 H), 4.91 (s, 10 H), trans:cis = 40:1; IR (hexane) 2003 (vw), 1964 (s), 1810 (s) cm^{-1}.[7,18]

$\{[(C_5H_5)_2(CO)_2Fe_2(\mu\text{-}CO)]_2(\mu\text{-}C_3H_3)\}^+PF_6^-$, 3. A mixture of methylidyne complex **1** (0.400 g, 0.84 mmol) and ethenylidene complex **2** (0.297 g, 0.84 mmol) in 30 mL of CH$_2$Cl$_2$ was stirred for 1 h at ambient temperature, and solvent was removed under vacuum. The residue was dissolved in 30 mL of acetone and filtered. The volume was reduced to 15 mL, and 35 mL of ether was added to give **3** (0.544 g, 78%) as blue-black microcrystalline solid: mp 187–189 °C dec; ^{1}H NMR (270 MHz, acetone-d_6) δ 11.46 (d, J = 12 Hz, 2 H), 5.75 (t, J = 12 Hz, 1 H), 5.45 (s, 20 H); ^{13}C NMR (acetone-d_6, 0.07 M Cr(acac)$_3$, −50 °C) δ 252.8 (bridging CO), 212.2 (terminal CO), 159.8 (d, J_{CH} = 150 Hz, FeCH), 155.5 (d, J_{CH} = 161 Hz, FeCH CH), 90.1 (d, J_{CH} = 181 Hz, C$_5$H$_5$); IR (CH$_2$Cl$_2$) 2013, 1979, 1814 cm^{-1}.

Anal. Calcd for C$_{29}$H$_{23}$F$_6$Fe$_4$O$_6$P: C, 41.67; H, 2.77; P, 3.74. Found: C, 41.63; H, 2.88; P, 3.74.

$[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}^{13}CH)]^+PF_6^-$, 1-^{13}*CH*. n-C$_4H_9$Li (2.3 mL, 1.66 M in hexane, 3.82 mmol) was added via syringe to a slurry of ^{13}CH$_3$P(C$_6$H$_5$)$_3$$^+I^-$ (1.36 g, 3.36 mmol) in 60 mL of THF until a homogeneous solution was obtained. Solid [C$_5$H$_5$Fe(CO)$_2$]$_2$ (0.600 g, 1.69 mmol) was added to the pale orange solution of CH$_2$=P(C$_6$H$_5$)$_3$, and the solution was refluxed 30 h. Silica gel (0.3 g) was added to the cooled solution, and solvent was removed on a rotary evaporator. The silica gel was washed with ether until the washings were nearly colorless. Alumina (0.3 g) was added to the ether solution, and solvent was removed on a rotary evaporator. The alumina was placed on top of an activity III alumina column (15 mm × 250 mm). A yellow band was eluted with hexane. When a second purple band began to come off the column with hexane, the solvent was changed to ether. A red band

---

(17) Atkinson, J. G.; Fisher, M. H.; Horley, D.; Morse, A. T.; Stuart, R. S.; Synnes, E. *Can. J. Chem.* **1965**, *43*, 1614.

(18) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911.

Table II. Crystal and Refinement Data

formula	$C_{32}H_{29}F_6Fe_4O_7P$
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.435 (3)
b, Å	32.89 (1)
c, Å	11.285 (4)
β, deg	97.46 (2)
V, Å^3	3472 (2)
Z	4
mol wt	893.9
D(calcd), g cm^{-3}	1.710
temp, °C	23
radiatn	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
transmissn (max/min)	0.614/0.413
diffractometer	Nicolet R3
abs coeff, cm^{-1}	18.1
scan speed, deg/min	variable 3-10
2θ scan range, deg	4-40
scan technique	Wyckoff (ω scan, peaks only)
data collected	$\pm h,+k,+l$
unique data	3714 reflctns (4043 collected)
unique data with (F_o) > $3\sigma(F_o)$	2615
least-squares parameters	416
std reflctns	3/97
R_F, R_{wF}, GOF	0.0740, 0.0750, 1.446
highest peak, final difference map, e Å^{-3}	0.634
mean shift/esd max final cycle	0.134

was then quickly eluted. Evaporation of solvent from the combined purple and red fractions gave 0.370 g of a 2.94:1.00 mixture of *cis*- and *trans*-$[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}^{13}CH_2)$:$[(C_5H_5)Fe(CO)_2]_2$.

This mixture and $(C_6H_5)_3C^+PF_6^-$ (0.298 g, 0.77 mmol) were stirred in 7 mL of CH_2Cl_2 at 0 °C for 1.5 h. The resulting red solid was isolated by filtration, washed with CH_2Cl_2 (3 × 5 mL) and dried to give 1-^{13}*CH* (0.240 g, 29% yield based on $[(C_5H_5)Fe(CO)_2]_2$): ^{1}H NMR (CD_2Cl_2, 270 MHz) cis:trans = 16:1, cis, δ 22.85 (d, $J_{^{13}CH}$ = 170.5 Hz, CH), 5.36 (s, C_5H_5), trans, δ 22.93 (d, $J_{^{13}CH}$ = 172.6 Hz, CH), 5.29 (s, C_5H_5).

$(C_5H_5)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CD_2)$, 2-$d_2$. A solution of 2 (0.540 g, 1.53 mmol) in CF_3CO_2D (2 mL, 26.0 mmol) was stirred for 10 min. D_2O (2 mL, 111 mmol) was added slowly over 5 min, and the solution was stirred for an additional 15 min. Additional D_2O (7 mL) was added and the resulting red precipitate was isolated by centrifugation and removal of the supernatant liquid via cannula. This entire exchange procedure was repeated a second time, and the resulting solid was washed with D_2O (2 mL), dried under vacuum, and stirred with $N(CH_3)_3$ (11.5 mmol) in 10 mL of Et_2O for 30 min. The ether solution was filtered and evaporated to dryness under high vacuum to give 2-d_2 (280 mg, 52%): mp 147–149 °C dec; ^{1}H NMR (200 MHz, acetone-d_6) indicated 23% residual vinylic H at δ 6.91 by comparison with the cyclopentadienyl protons at δ 4.81.

In a smaller scale procedure in which the $N(CH_3)_3$ treatment was omitted, 2-d_2 was obtained with only 17% residual vinylic H but in only 4% yield.

Double-Labeling Experiment. 1-^{13}*CH* (4 mg, 8 μmol) and 2-d_2 (5 mg, 14 μmol, 83% deuterated) were dissolved in 0.5 mL of CH_2Cl_2 in an NMR tube. After 1.5 h at room temperature, 1.0 mL of ether was added and the solids were centrifuged to the bottom of the tube. Solvent was decanted and the compacted solid was stirred in 1.5 mL of ether and centrifuged. Solvent was decanted and the residual 3-^{13}*CH* dried under vacuum. In the ^{1}H NMR (270 MHz, acetone-d_6), integration of the doublet ($J_{\alpha ^{13}CH}$ = 147 Hz) centered at δ 11.46 and a finely split doublet ($J_{\gamma ^{13}CH}$ = 5 Hz)[19] with the same chemical shift gave a ratio of 6.88:1.00 ^{13}CH:^{12}CH.

In a second run using 77% deuterated 2-d_2, NMR integration showed a 3.66:1.00 ratio of ^{13}CH:^{12}CH.

X-ray Data Collection and Structure Determination. Crystals for the diffraction study were obtained by dissolving 3 in acetone and layering with Et_2O. All of 31 crystals inspected by initial rotational photographs showed very weak diffraction and a broad mosaic spread. Additionally, minor twinning effects along the c axis of the unit cell were evident from axial photographs. A reddish brown, opaque, irregular trapazoidal plate (0.07 × 0.35 × 0.35 mm) was selected for data collection on the basis of its diffration strength and was mounted with epoxy cement on a glass fiber. Systematic absences uniquely defined the monoclinic spage group $P2_1/n$. Scans of individual peaks showed that, with few exceptions, adequate resolution existed between the diffraction intensity maxima for the major orientation and its minor twin to allow data collection on the major component only using a Wyckoff scan technique (ω scans of peaks only plus a few steps to either side of maximum intensity). Very restrictive peak shape rejection criteria were set for the processing of the intensity data to eliminate contributions from the minor twin. Of 4060 reflections collected, 17 were thus eliminated from further consideration.

Other data, including crystal parameters and data collection procedures, are collected in Table II. No intensity decay was observed during data collection; the rough, irregular shape of the crystal prevented the assignment of crystal faces for an analytical absorption correction. Programs contained in the P3, SHELXTL (3.0), and XP packages provided by the Nicolet Corp. were used throughout the collection, processing, and refinement of the data.

The direct-methods routine SOLV straightforwardly produced an E map revealing the positions of the four Fe and one P atoms, and subsequent difference Fourier syntheses located the remaining non-hydrogen atoms. Following refinement of an all-isotropic model, a partially disordered molecule of acetone was located in the lattice (one for each cation/anion pair).

Final refinement proceeded by blocked-cascade methods using anisotropic thermal parameters for all non-hydrogen atoms. The PF_6^- ions were constrained to octahedra with d(P–F) = 1.575 (3) Å, the C_5H_5 rings were treated as rigid bodies, and hydrogen atoms were added as fixed, idealized contributions, d(C–H) = 0.96 Å.

Acknowledgment. Support from the Department of Energy Division of Basic Energy Science and the National Science Foundation is gratefully acknowledged (C.P.C. and S.R.M.). We would like to thank Bill Olson for helpful discussions. Funds from the National Science Foundation to the University of Delaware for the purchase of a diffractometer is gratefully acknowledged (A.L.R.).

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates and a structure factor table (calculated vs. observed) are available as supplementary material (23 pages). Ordering information is given on any current masthead page.

---

(19) Vicinal ^{13}C–^{1}H coupling constants are smaller than the one-bond coupling constants by a factor of about 20. Gunther, H. "NMR Spectroscopy"; Wiley: Chicester, 1980; p 376.

(20) **Note Added in Proof.** The X-ray structure of an unsymmetric MeC–CH–CH ruthenium analogue of 3 indicates that it is best described as a complex with one μ-alkylidene and one μ-vinyl unit similar to formulation II. Davies, D. L.; Howard, J. A. K.; Knox, S. A. R.; Marsden, K.; Mead, K. A.; Morris, M. J.; Rendle, M. C. *J. Organomet. Chem.* **1985**, *279*, C37.