Under nitrogen atmosphere, complex $\{\eta^6\text{-}C_6H_5Si(Me)_2H\}Cr(CO)_3$ (**5**) (1.04 g, 3.8 mmol) in toluene (5 mL) was added into a toluene solution (10 mL) of $(CH_2{=}CHSiMe_2)_2O$ (0.5 g, 2.7 mmol). After addition of 0.1 mL of chloroplatinic acid solution, the reaction mixture was heated to 85–90 °C. The reaction was continued until the ν(Si–H) IR band (at 2132 cm^{-1}) had disappeared. After purification by filtration on silica and precipitation with petroleum ether, the dinuclear complex $\{\eta^6\text{-}C_6H_5SiMe_2(CH_2)_2SiMe_2\text{-}\}_2O\text{-}[Cr(CO)_3]_2$ (**20**) was isolated as a yellow solid, which was dried in vacuum for 24 h (60% yield, 0.82 g, 1.14 mmol).

Anal. Calcd for $C_{32}H_{46}O_7Si_4Cr_2$: C, 49.31; H, 5.75. Found: C, 48.95; H, 5.05.

^{1}H NMR ($CDCl_3$): δ 5.45 (t, H_p, C_6H_5), 5.38 (d, H_o, C_6H_5), 5.11 (t, H_m, C_6H_5), 2.38, 1.50 (m, H, CH_2), 0.3 (m, H, CH_3). IR (CH_2Cl_2): ν(CO) 1970, 1966 cm^{-1}. $\bar{M}_n$ (VPO, $CHCl_3$): 675 g/mol.

Following the same method, complex **6** (1.6 g, 4.84 mmol) was treated with an excess of $(CH_2{=}CHSiMe_2)_2O$, until disappearance of the ν(Si–H) band (2118 cm^{-1}), showing that all of the starting mononuclear complex had been converted into polymer **19**. After purification as above, compound $[\text{-}SiMe_2\{\eta^6\text{-}1,4\text{-}C_6H_4\}Cr(CO)_3SiMe_2(CH_2)_2SiMe_2OSi(CH_2)_2\text{-}]_n$ was isolated as a yellow gum solid, which was dried in vacuum for 24 h.

^{1}H NMR ($CDCl_3$): δ 5.38 (s, H, 1,4-C_6H_4), 1.2–1.6 (m, H, CH_2), 0.4–0.2 (m, H, CH_3). IR (CH_2Cl_2): ν(CO) 1964, 1888 cm^{-1}. $\bar{M}_n$ (VPO, $CHCl_3$): 4700 g/mol.

Preparation of SiO_2-Supported $\{\eta^6$-(Alkoxysilyl)arene$\}$-$Cr(CO)_3$ Derivatives. For the attachment of complexes **1**–**4** to silica surfaces, silica gel previously treated with dry methanol under reflux was used.[46] Modification of this silica with chromium tricarbonyl species was carried out by heating a sample (3–5 mmol) of each one of the **1**–**4** derivatives with about 1 g of methanol-treated silica, in toluene suspension, under nitrogen for about 18 h. The silica material, which was now yellow, was isolated by filtration, washed several times with toluene and then with dichloromethane, and dried in vacuum at 40 °C.

The properties of the functionalized silica so obtained are described under Results and Discussion.

Studies on Polymerization of PhC≡CH Catalyzed by $\{\eta^6$-(Organosilyl)arene$\}Cr(CO)_3$. These studies were performed by following the experimental procedures previously described.[13,17]

In homogeneous conditions, solutions of phenylacetylene (4.65 g, 45.5 mmol) in benzene (10 mL) were heated in the presence of complexes **1**–**4** (ca. 0.5 mmol). In the heterogeneous procedure, PhC≡CH was treated with ca. 0.5 g of SiO_2-supported **1**–**4** complexes. From the resulting reaction mixture the SiO_2-supported catalyst was separated by filtration. The products were isolated and purified as described.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (DGICYT) (Proyect No. 87/0123) for financial support of this work.

Registry No. **1**, 138813-88-4; **2**, 137779-62-5; **3**, 138813-89-5; **4**, 138813-90-8; **5**, 122780-39-6; **6**, 75830-40-9; **6**$^+$, 138834-40-9; **7**, 138813-91-9; **8**, 138813-92-0; **9**, 138813-93-1; **9**$^+$, 138814-01-4; **10**, 138834-39-6; **11**, 138813-94-2; **12**, 138813-95-3; **13**, 138813-96-4; **13**$^+$, 138814-02-5; **14**, 138813-97-5; **15**, 138813-98-6; **16**, 138813-99-7; **17**, 138814-04-7; **18**, 138814-03-6; **19**, 138814-05-8; **20**, 138814-00-3; $Cr(CO)_6$, 13007-92-6; $C_6H_5Si(OEt)_3$, 780-69-8; $C_6H_5Si(OMe)_2Me$, 3027-21-2; $C_6H_5(CH_2)_2Si(OMe)_3$, 49539-88-0; 1,4-C_6H_4-$[(CH_2)_2Si(OMe)_3]_2$, 60354-74-7; $C_6H_5Si(Me)_2H$, 766-77-8; 1,4-$C_6H_4[Si(Me)_2H]_2$, 2488-01-9; $C_6H_5Si(NMe_2)_2Me$, 33567-83-8; $(MeCN)_3Cr(CO)_3$, 16800-46-7; $CH_2{=}CHSi(Me)_2H$, 18243-27-1; $ClSi(NMe_2)_2Me$, 10339-02-3; $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, 12082-08-5; $(\eta^6\text{-}1,4\text{-}C_6H_4Li_2)Cr(CO)_3$, 115775-85-4; $ClSi(Me)_2H$, 1066-35-9; 1,4-$C_6H_4[Si(Me)_2OH]_2$, 2754-32-7; $(CH_2{=}CHSiMe_2)_2O$, 2627-95-4; PhC≡CH, 536-74-3; $[\{\eta^6\text{-}1,4\text{-}C_6H_4(SnBu_3)_2\}Cr(CO)_3]$, 115775-86-5; $(PhC{\equiv}CH)_n$, 25038-69-1; $P(OBu)_3$, 102-85-2.

Rearrangement, Hydride Abstraction, and Retro Ene Reactions of Dicarbonyl(η^5-cyclopentadienyl)iron Vinylidene Triflates

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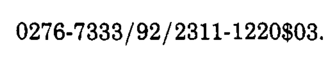
Received July 3, 1991

Several $(CO)_2CpFe$ (i.e. Fp) η^1-polymethylenevinylidene triflates, $(CH_2)_nC{=}C{=}Fp^+TfO^-$ (**3a**–**e**, n = 4–7, 10), were prepared at −78 °C from the corresponding Fp cycloalkylacyls $(CH_2)_nCHC(O)Fp$ (**1a**–**e**, n = 4–7, 10) and triflic anhydride. Solutions of **3c**–**e** in CH_2Cl_2, when warmed to 25 °C and reacted completely before being diluted with diethyl ether, are converted exclusively to Fp η^2-homocycloalkyne triflate, $\{Fp\text{–}[\eta^2\text{-}(CH_2)_n(C{\equiv}C)]\}^+TfO^-$ (**5c**–**e**, n = 7, 8, 10). This rearrangement, the organometallic analogue of an "end-to-end" alkyl shift in a vinyl cation, has not been previously observed in transition-metal vinylidenes. In contrast to **3c**–**e**, solutions of **3a**,**b** (and also **3c** at 0 °C) in CH_2Cl_2, when warmed to 25 °C and diluted with diethyl ether, react with the diluent to yield mixtures of Fp η^2-methylenecycloalkane triflates, $\{Fp\text{–}[\eta^2\text{-}(CH_2)_nC{=}CH_2]\}^+TfO^-$ (**9a**–**c**, n = 4–6), and Fp polymethyleneethoxycarbene triflates, $\{Fp\text{–}[\eta^1\text{-}C(OEt)CH(CH_2)_n]\}^+TfO^-$ (**12a**–**c**, n = 4–6). **9b** formed from **1b** and triflic anhydride in perdeuteriodiethyl ether contains ~1.6 atoms of deuterium per molecule, suggesting that, in the absence of a viable course of rearrangement or a better nucleophile, **3a**–**c** produce **9a**–**c** by abstracting a hydride from diethyl ether.

Dicarbonyl(η^5-cyclopentadienyl)iron (i.e. Fp) η^1-neopentylidene type complexes typically rearrange by shifting a carbon from the β- to the α-position, forming thereby a trisubstituted η^2-olefin complex (eq 1).[1] The rearrangement probably involves an intermediate carbocation.[1-3] If Fp η^1-alkylidenes are thought of as iron-sta-



(1)

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[1] (a) Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765. (b) Bly, R. S.; Hossain, M. M.; Lebioda, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549. (c) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723. (d) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 7730. (e) Bly, R. S.; Bly, R. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1046.

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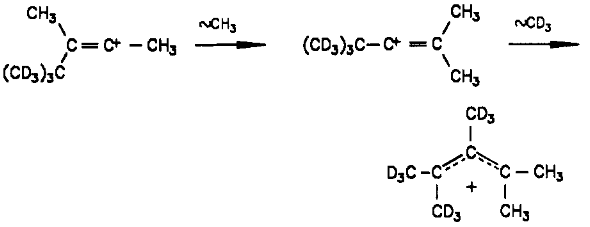
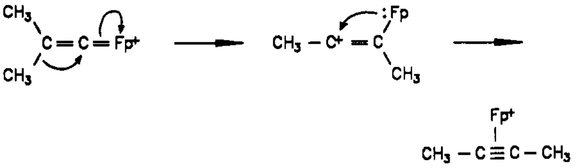
bilized carbocations,[4a] then such rearrangements are the iron-stabilized analogues of ametallic Wagner–Meerwein rearrangements.[1]

Vinyl cations also rearrange,[5a] some by shifting an alkyl group end to end on the double bond to form a different vinyl cation (eq 2).[5b,6–8] If cationic Fp η^1-vinylidenes, i.e. η^1-alkylidenemethylidenes, are equivalent to iron-stabilized vinyl cations,[9–15] their rearrangement to Fp η^2-alkynes (eq 3) might be anticipated, for it would constitute an iron-stabilized counterpart of the vinyl cation "end-to-end" shift. To our knowledge, no such disubstituted η^1-vinylidene to nonterminal η^2-alkyne rearrangements have been reported.[16] We recount here our successful search for them.

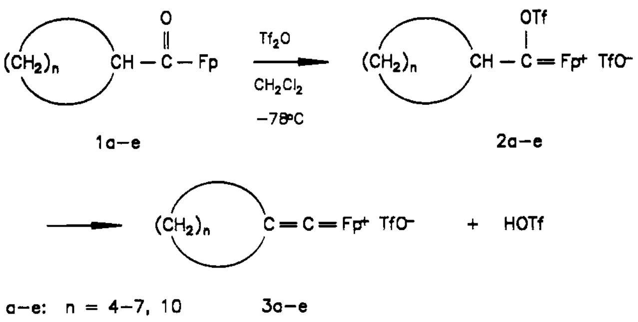


(2)

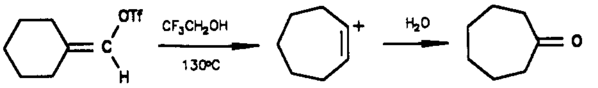


(3)

Scheme I



End-to-end alkyl shifts usually start with exocyclic, "primary" vinyl cations and form endocyclic "secondary" vinyl cations.[5b] Though it may no longer be linear, the resulting vinyl cation becomes part of a larger, usually less strained ring (e.g. eq 4).[8]



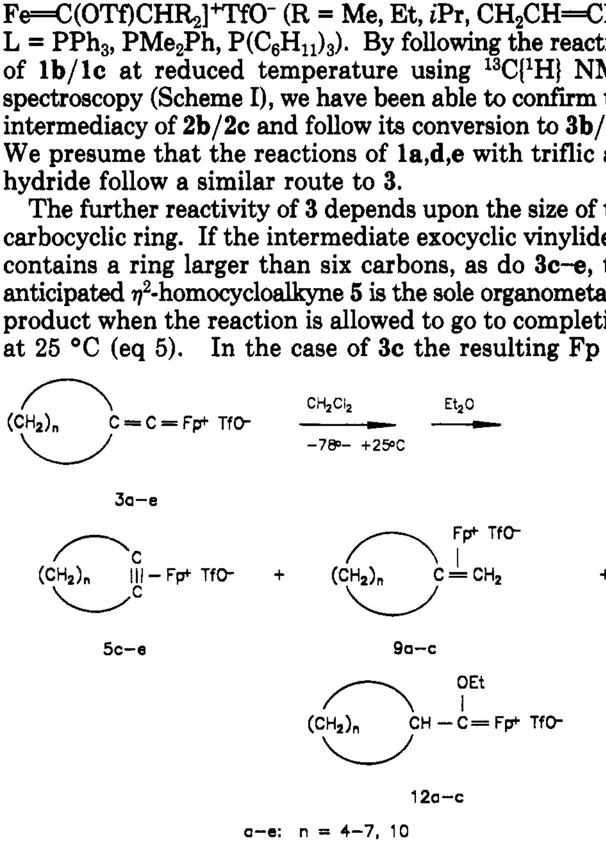
(4)

Here we describe the synthesis of several homologous Fp η^1-cycloalkylidenemethylidenes (**3**) and report their unusual reactivities, including rearrangement to medium-ring Fp η^2-cycloalkynes and/or reaction with diethyl ether.

Results

The required unstable dicarbonyl(η^1-cycloalkylidenylmethylidene)(η^5-cyclopentadienyl)iron triflates (i.e. Fp η^1-polymethylenevinylidene triflates; **3a–e**) were prepared by treating the corresponding dicarbonyl(η^1-cycloalkylcarbonyl)(η^5-cyclopentadienyl)irons (i.e. Fp acyls; **1a–e**) with triflic anhydride at −78 °C (Scheme I). Hughes et al.,[15a] who developed the method, have shown that in several acyclic carbonyl η^5-cyclopentadienyl phosphine type iron(II) acyls the reaction proceeds by way of a cationic trifluoromethanesulfonyl Fischer carbene, $[(CO)Cp(L)Fe{=}C(OTf)CHR_2]^+TfO^-$ (R = Me, Et, *i*Pr, $CH_2CH{=}CH_2$; L = PPh_3, PMe_2Ph, $P(C_6H_{11})_3$). By following the reaction of **1b**/**1c** at reduced temperature using ^{13}C{^{1}H} NMR spectroscopy (Scheme I), we have been able to confirm the intermediacy of **2b**/**2c** and follow its conversion to **3b**/**3c**. We presume that the reactions of **1a**,**d**,**e** with triflic anhydride follow a similar route to **3**.

The further reactivity of **3** depends upon the size of the carbocyclic ring. If the intermediate exocyclic vinylidene contains a ring larger than six carbons, as do **3c–e**, the anticipated η^2-homocycloalkyne **5** is the sole organometallic product when the reaction is allowed to go to completion at 25 °C (eq 5). In the case of **3c** the resulting Fp η^2-



(5)

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(2) (a) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354. (b) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

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(4) (a) This analogy is nicely drawn, especially in Table 9.4 (pp 412–413) in: Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; Chapters 9.5 and 9.6, and references included therein. (b) *Ibid.*, cf. Chapter 3.5. (c) *Ibid.* cf. Chapter 9.7.

(5) (a) Cf.: Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979; Chapter 7. (b) *Ibid.*, cf. Chapter 7.III.B for other examples. (c) *Ibid.*, Unpublished work of M. Hanack, and K. A. Fuchs; cf. Table 7.2 and Scheme 7.19, pp 464–465. (d) *Ibid.*, cf. Chapter 5.B, pp 282–285 and references cited therein. (e) *Ibid.*, cf. Chapter 2, Table 2.1, p 7, and references cited therein.

(6) (a) Imhoff, M. A.; Summerville, R. H.; Schleyer, P. v. R.; Martinez, A. G.; Hanack, M.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 3802. (b) Hanack, M.; Schleyer, P. v. R.; Martinez, A. G. *An. Quim.* **1974**, *70*, 941. (c) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 3802.

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(8) Stang, P. J.; Dueber, T. E. *Tetrahedron* **1977**, 563.

(9) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491.

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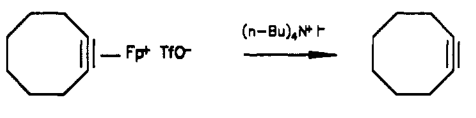
(14) Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta* **1980**, *42*, 277.

(15) (a) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (b) Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635.

(16) Cf.: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Pombeiro, A. J. L.; Richards, R. L. *Coord. Chem. Rev.* **1990**, *104*, 13. (c) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (e) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

cyclooctyne triflate (**5c**) was identified from its characteristic $^{13}C\{^1H\}$ NMR spectrum (Cp ring carbons at δ 89.92, a single aprotic two-carbon resonance at 55.1 ppm due to η^2-(–C≡C–), and three two-carbon >CH_2 resonances), its accurate-mass FAB molecular cation, and the $^{13}C\{^1H\}$ NMR spectrum of its known decomplexation product, cyclooctyne (**6c**; eq 6).[17] Though not decomplexed, η^2-cycloalkynes **5d,e** were identified from their accurate-mass FAB molecular cation and by comparison of their $^{13}C\{^1H\}$ NMR spectra with that of η^2-cyclooctyne **5c**.[18]

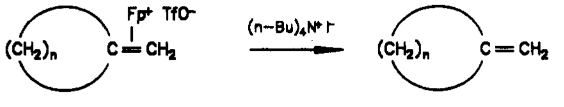


(6)

5c **6c**

When the exocyclic vinylidene **3** contains a five- (**3a**) or a six-membered ring (**3b**) (n = 4 or 5, respectively) no η^2-cycloalkyne (**5**) is formed. When diethyl ether is added at room temperature to precipitate the cationic triflate(s) (or, in fact, if the reaction itself is carried out in diethyl ether), the reaction mixture immediately darkens and the product isolated is a mixture of η^2-methylenecycloalkane (**9a,b**) and η^1-cycloalkylethoxymethylidene (**12a,b**; eq 5). When heated to about 40 °C, **3b** in CH_2Cl_2 gels without discernible rearrangement.

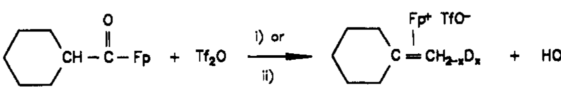
The η^2-methylenes **9a,b** were identified from their ^1H and ^{13}C NMR spectra and by decomplexation with tetra-*n*-butylammonium iodide[22] to the known methylenecycloalkanes **10a,b**, respectively (eq 7). When pentamethylenevinylidene **3b** is generated from a dilute solution of acyl **1b** and triflic anhydride in perdeuteriodiethyl ether, the exocyclic methylene **9b** which is formed incorporates ~1.6 deuterium atoms per molecule—evidence that diethyl ether is the source of one of the additional hydrogens in **9** (eq 8). The other presumably comes from an acidic species in the solution, perhaps diethyloxonium ion; the excess over one deuterium probably arises from exchange (vide infra).



(7)

9a,b **10a,b**

a, n = 4 **b**, n = 5



(8)

1b **9b**

i) $(C_2H_5)_2O$, x = 0

ii) $(C_2D_5)_2O$, x = 1·6

The η^1-cycloalkylethoxymethylidene triflates (**12a,b**) that are also formed have $^{13}C\{^1H\}$ NMR spectra which, with the exception of a quartet at δ ~119 ppm due to the CF_3 resonance of unreacted triflic anhydride that is also present, are identical with those of the corresponding tetrafluoroborates **13a,b**, synthesized independently from acyls **1a,b** as recounted in the Experimental Section.

If cold diethyl ether is added to a solution of **3c** in deuteriomethylene chloride at 0 °C and the mixture is stirred for a while at that temperature before being worked up, small amounts of exocyclic η^2-olefin **9c** and ethoxy Fischer carbene **12c** are produced as well as η^2-cyclooctyne **5c** (eq 5). This is the only Fp η^2-vinylidene in our hands to form detectable amounts of all three organometallic complexes.

Discussion

Vinylidene–Acetylene Isomerization. Many examples of transition-metal acetylene–vinylidene interconversions are known.[16] Most convert *terminal* η^2-alkynes into *monosubstituted* η^1-vinylidenes (eq 9) and involve d^6-ML$_5$ or isolobal,[23] T-shaped, d^8-ML$_3$ metal fragments (cf. eqs 10–12).[24-26] Cationic vinylidenes are often converted to, or formed from, neutral η^1-acetylides by the loss or gain of a proton during the process (eq 13).[11a] In d^4-ML$_5$ systems, when the η^2-alkyne is a four-electron donor, the isomerization is accompanied by the gain or loss of a neutral ligand such as CO (eq 14).[27]

$$L_nM(RC{\equiv}CH) \rightarrow L_nM({=}C{=}CHR) \qquad (9)$$

$$\begin{aligned}&(CO)_3(dppe)W(THF) + PhC{\equiv}CH \rightarrow \\ &\quad fac\text{-}(CO)_3(dppe)W[\eta^2\text{-}(PhC{\equiv}CH)] \xrightarrow{50\ ^\circ C} \\ &\qquad mer\text{-}(CO)_3(dppe)W{=}C{=}CHPh \qquad (10)\end{aligned}$$

$$\begin{aligned}&\underset{13\%}{\{Cp(NO)(PPh_3)Re[\eta^2\text{-}(tBuCC{\equiv}CH)]\}^+BF_4^-} \xrightleftharpoons[PhCl]{80\ ^\circ C} \\ &\qquad \underset{87\%}{\{Cp(NO)(PPh_3)Re{=}C{=}CHtBu\}^+BF_4^-} \qquad (11)\end{aligned}$$

$$\begin{aligned}&Cl(PR_3)_2Ir[\eta^2\text{-}(PhC{\equiv}CH)] \rightarrow \\ &\quad Cl(PR_3)_2Ir(H)(-C{\equiv}CPh) \rightarrow Cl(PR_3)_2Ir{=}C{=}CHPh \qquad (12)\end{aligned}$$

$$\begin{aligned}&[Cp(dppe)Fe{=}C{=}CHMe]^+ \xrightleftharpoons[+H^+]{-H^+} \\ &\qquad Cp(dppe)Fe{-}C{\equiv}CMe \qquad (13)\end{aligned}$$

$$\begin{aligned}&[(Cp)(PMe_2Ph)_2Mo(HC{\equiv}CtBu)]^+ \xrightleftharpoons[-CO]{+CO} \\ &\qquad [(Cp)(CO)(PMe_2Ph)_2Mo{=}C{=}CHtBu]^+ \qquad (14)\end{aligned}$$

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(17) Blomquist, A. T.; Liu, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 2153.

(18) π complexation increases the shielding of acetylenic carbons through back-bonding.[16c] It is interesting to note that the *shift to higher frequency* of the alkynyl carbon ^{13}C resonances, i.e. $\delta(^{13}C)_{complex} - \delta(^{13}C)_{noncomplex} = \Delta\delta(^{13}C)$, when medium- and large-ring cycloalkynes are ligated as η^2 two-electron donors to Fp$^+$ decreases and approaches that of an acyclic η^2-alkyne as the cycloalkyne ring becomes larger; i.e. **5c** (39.6 ppm) > **5e** (33.3 ppm)[19a] > [Fp(η^2-3-hexyne)]$^+$ (31.7 ppm).[19b] The implication is that, as expected,[20a] back-bonding from Fe(II) to the π^* orbital of the acetylene[21] decreases as the cycloalkyne becomes larger and the C—C≡C—C unit more linear. A similar trend in $\delta(^{13}C_{complex})$ has been noted in two-electron-donor, small-ring $(PPh_3)_2Pt$ η^2-cycloalkynes.[16c]

(19) (a) $\delta(^{13}C)$ for the alkyne carbons of cyclododecyne is 81.5 ppm; cf.: Bernassau, J. M.; Bertranne, M.; Collongues, C.; Fetizon, M. *Tetrahedron* **1985**, *41*, 3063. (b) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

(20) (a) Cf.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 156ff. and references cited therein. (b) *Ibid.*, p 305 and Table 5.1 and references cited therein. (c) *Ibid.*, p 284 and Table 5.2.

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Terminal η^2-acetylene–η^1-vinylidene interconversions could, a priori, involve intramolecular oxidative addition–reductive elimination (OARE) by way of a metal hydrido acetylide (eq 15). In several instances a hydrido acetylide

$$L_nM[\eta^2\text{-}(HC{\equiv}CR)] \rightarrow L_nM(H)[\eta^1\text{-}(C_\alpha{\equiv}C_\beta R)] \rightarrow L_nM{=}C{=}CHR \quad (15)$$

has been observed and/or isolated during the course of the isomerization.[26,28,29] Werner et al. have noted the formation of an equilibrium mixture of Rh(I) η^2-alkyne, Rh(III) [η^1-(alkynyl)] hydride, and Rh(I) η^1-vinylidene when a solution of [RhCl(P*i*Pr$_3$)$_2$] and *t*BuC≡CH in ether at 0 °C is warmed to 20 °C (eq 16).[28b] The intermediate hydrido acetylide has been isolated in this and in the corresponding iridium system[26] (eq 12) and observed spectroscopically in other cases.[28c,29] The observation of a metal hydrido acetylide has been commonly associated with an OARE sequence. The possibility of OARE also has been raised in cases where hydrido acetylides have not been observed, e.g. the conversion of Cp(CO)$_2$Mn(η^2-PhC≡CH) to Cp(CO)$_2$Mn=C=CHPh[30] and the isomerization of [Cp(PMe$_3$)$_2$Ru(η^2-MeC≡CH)]$^+$ to [Cp(PMe$_3$)$_2$Ru(=C=CHMe)]$^+$.[31]

$$\begin{aligned}
&[ClRh(PiPr_3)_2]_2 + tBuC{\equiv}CH \xrightarrow[0\text{–}20\ ^\circ C]{Et_2O} \\
&\qquad \underset{5\%}{Cl(PiPr_3)_2Rh(\eta^2\text{-}tBuC{\equiv}CH)} \rightleftharpoons \\
&\qquad \underset{75\%}{Cl(PiPr_3)_2Rh(H)(\text{-}C{\equiv}CtBu)} \rightleftharpoons \\
&\qquad\qquad \underset{20\%}{Cl(PiPr_3)_2Rh{=}C{=}CHtBu} \quad (16)
\end{aligned}$$

An alternative route for terminal η^2-acetylene–η^1-vinylidene interconversions is that of direct 1,2-hydrogen migration. This course was suggested by Clark et al. to rationalize the formation of *trans*-[CH$_3$(PMe$_2$Ph)$_2$Pt=C(OCH$_3$)C$_2$H$_5$]$^+$PF$_6^-$ when *trans*-[CH$_3$(PMe$_2$Ph)$_2$PtCl] reacts with propyne and Ag$^+$PF$_6^-$ in methanol.[10] The reaction is thought to proceed by way of *trans*-[CH$_3$(PMe$_2$Ph)$_2$Pt(η^2-HC≡CCH$_3$)]$^+$, which undergoes an intramolecular 1,2-hydrogen shift (rather than intermolecular deprotonation–reprotonation). The η^1-vinylidene that is formed adds methanol nucleophilically to give the observed Fischer carbene (eq 17).

$$\begin{aligned}
&Me(PMe_2Ph)_2PtCl + MeC{\equiv}CH \xrightarrow[MeOH]{AgPF_6} \\
&\quad [Me(PMe_2Ph)_2Pt(MeC{\equiv}CH)]^+ \xrightarrow{\sim H} \\
&\quad [Me(PMe_2Ph)_2Pt{=}C{=}CHMe]^+ \xrightarrow{MeOH} \\
&\qquad [Me(PMe_2Ph)_2Pt{=}C(OMe)Et]^+ \quad (17)
\end{aligned}$$

It is difficult experimentally to distinguish intramolecular OARE from intramolecular 1,2-hydrogen migration, especially if the reaction is reversible and produces an equilibrium mixture of reactant, intermediate, and product as in eq 16. The observation and/or isolation of a hydrido acetylide does not alone establish an OARE process.[25] Silvestre and Hoffmann have approached this distinction theoretically using "simple perturbation theory and both symmetry and overlap considerations supplemented by computations at the extended Hückel level" to model the reaction path from ML$_5$(η^2-HC≡CH) to ML$_5$(=C=CH$_2$).[32] They consider the possibility of a fully concerted reaction path as in eq 9 (R = H), of a path involving prior slippage of the metal from η^2 to η^1 of the alkyne (eq 18; R = H), and of oxidative addition followed by "migration of the hydrogen to the far carbon atom", i.e. intramolecular reductive elimination (eq 15; R = H), the reaction sequence that we term "OARE".

$$L_nM(\eta^2\text{-}HC{\equiv}CR) \rightarrow L_nM^-\ \eta^1\text{-}(\text{-}CH{=}C^+R) \xrightarrow{\sim H} L_nM{=}C{=}CHR \quad (18)$$

On the basis of their calculations Silvestre and Hoffmann reach the following conclusion:[32] "The formal 1,2 H shift must involve the prior slippage of the alkyne to a η^1 mode of coordination (e.g. eq 18). From there the vinylidene complex may be formed. The tremendous thermodynamic stability of the product and the efficient stabilization of the transition state by the metal combine to make this reaction feasible. Alternatively, oxidative addition may occur to form a hydrido acetylide complex. Our feeling is that the hydrido acetylide channel is a dead end, as far as eventual vinylidene production is concerned. We think the expenditure of energy to promote the migration from the metal to C$_\beta$ of the acetylide is prohibitive." Note, however, that while these calculations may rule out the hydrido acetylide as an intermediate in a totally intramolecular acetylene to vinylidene isomerization, they do not rule out an intermolecular deprotonation–reprotonation sequence for the conversion of hydrido acetylide to vinylidene.[29b]

We believe the formal 1,2-migration of a β-alkyl group in a metal-stabilized vinyl cation (η^1-vinylidene complex) to form a cationic, nonterminal η^2-acetylene complex (e.g. eq 5) to be a new reaction in transition-metal chemistry. The isomerizations cited above involve the conversion of *terminal* acetylenes into "*monosubstituted*" vinylidenes. The reactions appear generally to be reversible, with the vinylidene being the proponderant or exclusive product (cf. eqs 11 and 16). We know of no *nonterminal* acetylenes which rearrange in this manner. Dimethylacetylene, for example, reacts with Ag$^+$PF$_6^-$ and *trans*-[CH$_3$(PMe$_2$Ph)$_2$PtCl] in methanol to yield vinyl ether complexes (eq 19),[33] while in the absence of a nucleophilic protic solvent, the intermediate, η^2-bound dimethylacetylene, inserts instead into the methyl–platinum bond (eq 20).[10b] Acyclic "*disubstituted*" η^1-alkylidenes have also not previously been reported to rearrange in the reverse sense to *nonterminal* η^2-alkynes. Solutions of [(η^5-C$_5$H$_5$)(CO)(PPh$_3$)Fe=C=CMe$_2$]$^+$BF$_4^-$ in CH$_2$Cl$_2$ are, in fact, stable at room temperature for several hours.[15b]

$$\begin{aligned}
&Me(PMe_2Ph)_2PtCl + MeC{\equiv}CMe \xrightarrow[MeOH]{AgPF_6} \\
&\quad [Me(PMe_2Ph)_2Pt(\eta^2\text{-}MeC{\equiv}CMe)]^+ \xrightarrow{MeOH} \\
&\quad Me(PMe_2Ph)_2Pt{-}C(Me){=}C(OMe)Me + H^+ \quad (19)
\end{aligned}$$

$$\begin{aligned}
&Me(PMe_2Ph)_2PtCl + MeC{\equiv}CMe \xrightarrow[acetone]{AgPF_6} \\
&\qquad [(PMe_2Ph)_2Pt[\text{-}C(Me){=}CMe_2]]^+ \quad (20)
\end{aligned}$$

What then can we say about the path of this new intramolecular isomerization? It probably follows the course

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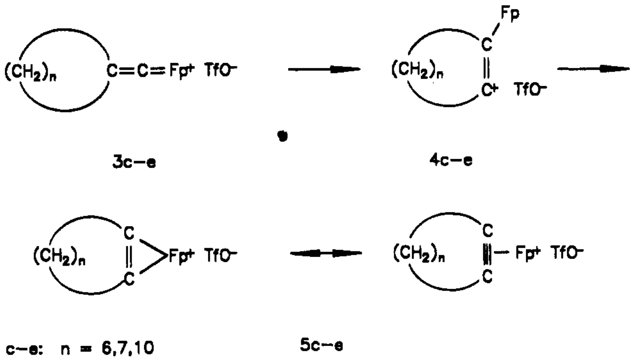
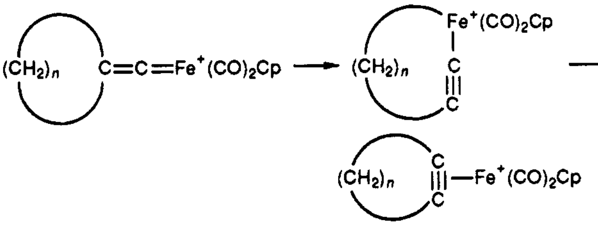
Scheme II



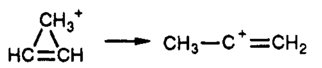
outlined in Scheme II. We see no evidence of a metallacycloalkyne, the expected intermediate of an OARE sequence (eq 21). Intramolecular oxidative additions and/or reductive eliminations of carbon–carbon bonds are generally restricted to the strained bonds of small rings,[20b] are thermodynamically less favorable than their carbon–hydrogen counterparts,[20c] and in any case are not common in iron(II) complexes.[34,35] Thus, an OARE sequence via an Fe(IV) η^1-alkyl η^1-acetylide seems unlikely in the cases reported here.



(21)

On the other hand, the ametallic analogue of a 1,2-alkyl shift is well-known: medium-ring exocyclic vinyl triflates produce homoendocyclic vinyl cations upon solvolysis (eq 4).[8] The acyclic iron(II) analogue of this rearrangement, the conversion of a Fp η^1-vinylidene to a β-Fp η^1-vinyl cation which becomes a Fp η^2-alkyne (cf. eq 3), is the microscopic reverse of the process suggested by Silvestre and Hoffmann for the conversion of acyclic η^2-terminal acetylenes to acyclic monosubstituted η^1-vinylidenes (viz. eq 18).

Silvestre and Hoffmann[32] emphasize that "upon coordination of a transition-metal fragment, the thermodynamic stability of the acetylene and vinylidene is reversed", i.e. that the rearrangement of corner-protonated cyclopropene, the isolobal equivalent of $ML_5(\eta^2\text{-}HC{\equiv}CH)$, to the 2-propenyl cation, the isolobal equivalent of $ML_5({=}C{=}CH_2)$, is endothermic (eq 22), whereas that of the η^2-acetylene complex (cf. eq 9) is exothermic. The process that we observe runs counter to this thermodynamic prediction and to the terminal acetylene rearrangements cited above. If it is reversible, i.e. thermodynamically controlled, the equilibrium lies far to the right: we detect no exocyclic vinylidene **3c** by ^{13}C NMR spectroscopy when a solution of η^2-cyclooctyne **5c** in CD_2Cl_2 is cooled to −50 °C, conditions under which **3c** is relatively stable. This is in contrast with the ametallic 1-methyl-2-tetramethylenevinyl cation, which apparently interconverts with 2-methyl-1-cyclohexenyl cation in trifluoroethanol at 50–100 °C (eq 23).[5c]



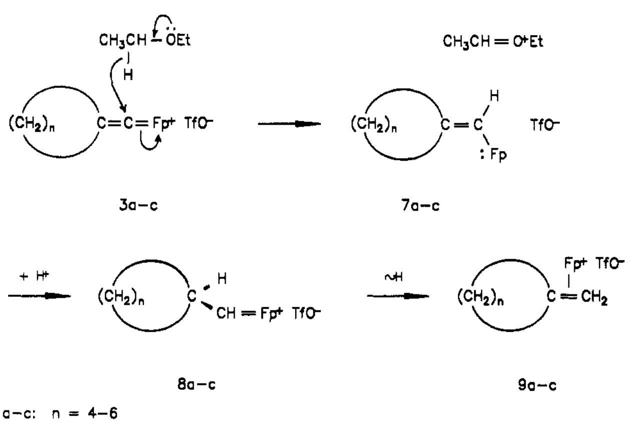
(22)

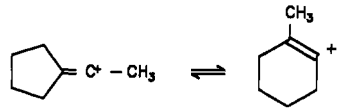
Table I. MM2 H_f°'s and Enthalpies of Reaction (ΔH) for the Conversion of Bis(polymethylenepropatrienes) (A) to Two Homocycloalkynes (B) (Eq 24)

n	est H_f°, kcal/mol A	est H_f°, kcal/mol B	~$\Delta H/2$, kcal/mol	est C—C≡C bond angles in B, deg
3	190.2	195.8	+2.8	121, 121
4	134.8	125.9	−4.5	133, 133
5	116.6	92.2	−12.2	143, 143
6	114.7	75.5	−19.6	154, 154
7	111.3	61.1	−25.1	160, 160
10	81.3	29.3	−26.0 −25.1[a]	166, 168

[a] For $(Me_2C{=}C{:})_2 \rightarrow 2MeC{\equiv}CMe$.

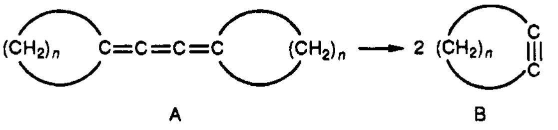
Scheme III





(23)

To assess the thermodynamic driving force for ring enlargement of exocyclic vinyl carbenes absent the metal, we used PCMODEL/MMX[36] to calculate the energetics of the isodesmic reaction (eq 24; cf. Table I). As anticipated, the larger the ring, the more favorable the rearrangement. This reaction is energetically equivalent to that of the analogous acyclic case, viz. $Me_2C{=}C{=}C{=}CMe_2 \rightarrow 2MeC{\equiv}CMe$, in rings of 8 or 11 carbons ($n = 7, 10$). Since we, in fact, observe ring enlargement in **3c** ($n = 6$), for which the ametallic enthalpy estimated in this manner ($\Delta H/2$ in kcal/mol) is −20, and not in the case of **3b** ($n = 5$; $\Delta H/2 = -12$), a Fp η^1-vinylidene must be about 12–20 kcal/mol more stable than the isomeric Fp η^2-homo-



(24)

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[34] Klemarczyk, P.; Price, T.; Preister, W.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *139*, C25.

[35] Tivakornpannarai, S.; Jones, W. M. *Organometallics* **1991**, *10*, 1827 and references cited therein.

[36] PCMODEL (88.0) and MMX (88.5) are molecular mechanics software routines designed to run on an IBM-PC; cf.: Midland, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 5042. They utilize the MMP2 (77-80) force field of N. Allinger (Georgia) (QCPE No. 395) supplemented by the generalized parameters of C. Still (Columbia) and extended to other nuclei by J. J. Gajewski and K. E. Gilbert (Indiana). MMX (88.5) uses the same force field as PCMODEL but slightly different minimization algorithms and incorporates the PI routine of Allinger (QCPE No. 318) to permit inclusion of the Pople (Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375. Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 767) semiempirical, SCF, π-orbital delocalization energies in the overall minimization and in the resulting, estimated heat of formation. The present calculations do not utilize this latter option.

cycloalkyne. This is roughly consistent with the estimates of Silvestre and Hoffmann in the acyclic, monosubstituted vinylidene cases.[32]

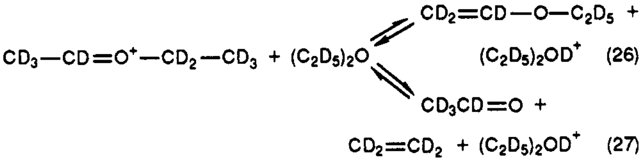
Hydride Abstraction. We formulate the conversion of exocyclic vinylidenes **3a,b** to η^2-methylenecycloalkanes **9a,b** as outlined in Scheme III.

Hydride abstractions similar to those that convert **3a–c** into **7a–c** and ultimately to **9a–c**, while hardly common, are well-precedented in both biological[37] and nonbiological systems.[4b,c,38a] Alcohol dehydrogenase, for example, catalyzes the oxidation of alcohols to aldehydes by reversibly transferring hydride from the α-carbon to nicotinamide adenine dinucleotide (NAD) cofactor.[39] Many NAD-dependent dehydrogenases operate in a similar manner.[37,39b] In nonbiological systems, carbocations have long been known to abstract hydride intermolecularly from a variety of other compounds, including saturated hydrocarbons containing secondary and/or tertiary hydrogens,[40] unsaturated hydrocarbons,[41] especially those ligated to a neutral, transition-metal moiety,[4d,42,43] cyclic ketals,[44] primary and secondary alcohols,[40,45] and formic acid.[46]

Though generally not as reactive as alcohols, ethers too are good hydride donors.[38b] Label and product studies have demonstrated that, as in the case of alcohols,[40] α- rather than β-hydrogen is lost preferentially. A well-known route to triphenylmethane, for example, employs triphenylmethyl chloride, anhydrous aluminum chloride, and diethyl ether and produces acetaldehyde and ethyl chloride in addition to triphenylmethane (eq 25).[47] Although no oxidized organic can be isolated or observed when **3a–c** are converted to **9a–c** (Scheme III), we presume that α-hydrogen is abstracted in these cases as well.

$$Ph_3C{-}Cl + AlCl_3 + Et_2O \rightarrow Ph_3C{-}H + CH_3CHO + EtCl \quad (25)$$

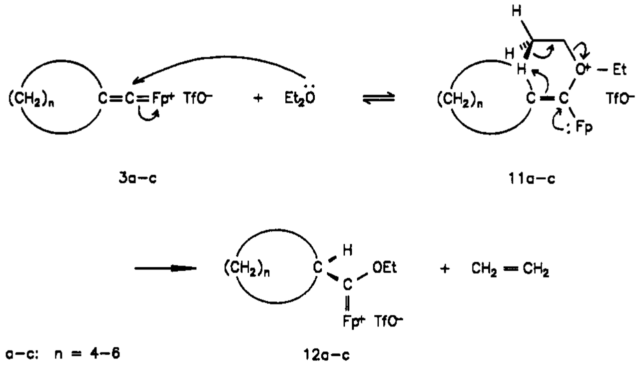
The "exchange" to which we ascribe the excess over one deuterium in the η^2-methylenecyclohexane **9b** that occurs when the reaction is carried out in perdeuteriodiethyl ether (eq 8; vide supra) must arise by transfer of a β-deuteron from the acidic putative oxidative product, $CD_3CD{=}O^+C_2D_5$, to the basic solvent, $(C_2D_5)_2O$ (cf. eq 26 and/or 27). The 7-fold excess of perdeuterio ether that is present precludes the ready isolation and/or observation of the perdeuterated ethylene, acetaldehyde, and/or ethyl vinyl ether that is also expected.



$$CD_3{-}CD{=}O^+{-}CD_2{-}CD_3 + (C_2D_5)_2O \rightarrow CD_2{=}CD{-}O{-}C_2D_5 + (C_2D_5)_2OD^+ \quad (26)$$

$$CD_3{-}CD{=}O^+{-}CD_2{-}CD_3 + (C_2D_5)_2O \rightarrow CD_3CD{=}O + CD_2{=}CD_2 + (C_2D_5)_2OD^+ \quad (27)$$

Scheme IV



Retro Ene Reaction. The pericyclic retro ene reaction[48] depicted in Scheme IV, which we offer as a possible route for the conversion of **3a–c** to ethoxy Fischer carbenes **12a–c**, is modeled after another speculatively suggested earlier by Hughes et al. to rationalize the conversion of $[(CO)(\eta^5\text{-}Cp)(PPh_3)Fe(\eta^1\text{-}C{=}CH_2)]^+BF_4^-$ to $[(CO)(\eta^5\text{-}Cp)(PPh_3)Fe(\eta^1\text{-}C(OC_2H_5)CH_3)]^+BF_4^-$ and presumably acetylene in the presence of ethyl vinyl ether.[15b]

What determines whether the exocyclic vinylidene **3** rearranges to the homocyclic alkyne **5** or whether it abstracts hydrogen from diethyl ether? We do not have the whole answer to this question, for we have not yet examined the larger ring vinylidenes **3c–e** in the presence of diethyl ether, but the smaller ring vinylidenes, viz. **3a,b** which cannot rearrange to a relatively strain-free (Table I) Fp-substituted endo vinyl cation or homocycloalkyne, are relatively stable in dichloromethane at −20 to 0 °C.[49] However, when diethyl ether is present, the very electrophilic α-carbon of these Fp vinylidenes either abstracts a hydride (Scheme III) or coordinates and facilitates a retro ene transformation (Scheme IV). In the case of **3c**, where the thermodynamic driving force for rearrangement is probably small (Table I), the intra- and intermolecular reactions are apparently competitive at 0 °C.

Experimental Section

General Procedures. All operations were carried out under dry, oxygen-free nitrogen using standard Schlenk-line or drybox techniques. Proton NMR spectra were recorded on a Bruker AM-300.13 spectrometer at 300 MHz or an AM-500.13 instrument at 500 MHz; the ^{13}C NMR spectra were recorded on an IBM NR-80 spectrometer at 20.13 MHz, on the AM-300.13 instrument at 75 MHz, or on an AM-500.13 spectrometer at 33.55 MHz. Proton chemical shifts (δ) are reported in ppm downfield from TMS; ^{13}C resonances (at all temperatures) were recorded using the δ 53.8 (CD_2Cl_2) or 77.0 ppm ($CDCl_3$) resonance of the solvent as an internal reference and are reported in ppm downfield from TMS. Some of the ^{13}C assignments were made using the refocused "insensitive nucleus enhancement through polarization transfer" (INEPT) technique[50] modified and made available to us by Dr. Ron Garber. Infrared (IR) spectra were recorded on either a Beckman IR-4210 or a Perkin-Elmer 1600 Series FTIR spectrometer. The unit-mass mass spectra were determined on a Finnigan 4021 GC-MS spectrometer using a direct probe at

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(37) Wuest, J. D., Ed. Tetrahedron Symposia-in-Print #25. *Tetrahedron* **1986**, *42*, 941–1116 and papers contained therein.

(38) (a) Nenitzescu, C. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 13 and references contained therein. (b) *Ibid.*, p 484.

(39) Cf.: Walsh, C. *Enzymatic Reaction Mechanisms*; W. H. Freeman: San Francisco, 1979; Chapter 10.C.2. (b) *Ibid.*, Chapter 10 and especially Table 10-2, p 334.

(40) Bartlett, P. D.; McCollum, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 1441.

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(48) Cf.: Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1979; pp 292–296.

(49) When Fp η^1-vinylidenes are formed by protonating or alkylating a neutral Fp η^1-alkyne, μ-1,3-cyclobutenylidene complexes are frequently observed.[15b] Cationic Fp η^2-cycloalkynes such as **5** or Fp η^2-cycloalkenes such as **9** are not electrophilic, i.e. do not serve as nucleophiles toward cationic Fp η^1-vinylidenes such as **3**.

(50) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

ionization potentials of 70 eV, and the accurate-mass and fast atom bombardment (FAB) mass spectra were run on a VG Analytical, Ltd., 70SQ high-resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system and analyzed by comparison with isotopic ion distributions calculated by the ISO program of VG Analytical, Ltd. Microanalyses were performed by Robertson Laboratory, Inc.

Solvents and Reagents. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade pentane was stirred overnight with concentrated sulfuric acid, washed with water, distilled from P_2O_5, stored over sodium ribbon, and distilled from sodium under nitrogen immediately prior to use. Solvents used for spectrochemical determinations were degassed by the freeze–pump–thaw technique and stored under vacuum. Unless otherwise indicated, column chromatography was carried out on neutral, 70–230-mesh "Merck EM aluminum oxide 90", deactivated to "Activity Stage III" by the addition of 4.6 wt % water.

Preparation of Dicarbonyl(η^1-cycloalkylcarbonyl)(η^5-cyclopentadienyl)iron (1a–e). A solution of cycloalkanecarbonyl chloride, prepared as described previously[51] from cycloalkanecarboxylic acid and oxalyl chloride and dissolved in 10–15 mL of anhydrous THF, was mixed at room temperature with 1.1–1.3 equiv of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate[52] slurried in 5–10 mL of anhydrous THF and stirred at ambient temperature for 1–4 h. The volatiles were removed at reduced pressure, the resulting residue was extracted three to five times with (9–14):1 hexane/ether, and the extracts were filtered through a short column of activity III alumina. The resulting filtrate was concentrated to dryness under vacuum and the residue then redissolved in a minimum volume of pentane and chromatographed on activity III alumina. When eluted with 19:1 pentane/ether and stripped of solvent under vacuum, the desired acyl complex **1a–e** was obtained as a yellow oil or low-melting solid.

Dicarbonyl(η^1-cyclopentylcarbonyl)(η^5-cyclopentadienyl)iron (1a), prepared in 61% yield (1.88 g, 6.8 mmol) from 1.26 g (11.1 mmol) of acid, 4 mL (5.82 g, 45.9 mmol) of oxalyl chloride, and 2.62 g (12.2 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate, is a yellow oil at room temperature. It exhibits the following spectra: IR (CH_2Cl_2) 2005, 1955 ($-C{\equiv}O$), 1645 cm^{-1} ($>C{=}O$); ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H, Cp), 3.41 (m, 1 H, $>CHCO-$), 1.67 (m, 2 H) and 1.52 (m, 2 H) ($>CH_2$'s); ^{13}C NMR ($CDCl_3$) δ 260.01 ($>C{=}O$), 214.65 ($-C{\equiv}O$'s), 86.40 (Cp), 73.78 ($>CHCO-$), 29.44, 25.66 (2 C, $>CH_2$'s). Anal. Calcd for $C_{13}H_{14}O_3Fe$: C, 56.97; H, 5.15. Found: C, 57.12; H, 5.18.

Dicarbonyl(η^1-cyclohexylcarbonyl)(η^5-cyclopentadienyl)iron (1b), prepared in 75% yield (2.75 g, 9.6 mmol) from 1.63 g (12.7 mmol) of acid, 4 mL (5.82 g, 45.9 mmol) of oxalyl chloride, and 3.12 g (14.44 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate,[52] is a yellow solid, mp 75–77 °C. It exhibits the following spectra: IR (CH_2Cl_2) 2005, 1955 ($-C{\equiv}O$), 1640 cm^{-1} ($>C{=}O$); ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H, Cp), 2.84 (m, 1 H, $>CHCO-$), 1.91 (m, 2 H) and 1.70 (m, 2 H), 1.61 (m, 1 H), 1.16 (m, 5 H) ($>CH_2$'s); ^{13}C NMR ($CDCl_3$) δ 261.35 ($>C{=}O$), 215.09 ($-C{\equiv}O$'s), 86.70 (Cp), 74.20 ($>CHCO-$), 29.02, 26.23 (2 C, $>CH_2$'s), 26.40 (1 C, $>CH_2$). Anal. Calcd for $C_{14}H_{16}O_3Fe$: C, 58.36; H, 5.60. Found: C, 58.34; H, 5.57.

Dicarbonyl(η^1-cycloheptylcarbonyl)(η^5-cyclopentadienyl)iron (1c), prepared in 90% yield (2.92 g, 9.7 mmol) from 1.529 g (10.724 mmol) of acid, 4 mL (5.82 g, 45.9 mmol) of oxalyl chloride, and 2.78 g (12.87 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate,[52] is a yellow oil at room temperature. It exhibits the following spectra: IR (CH_2Cl_2) 2000, 1950 ($-C{\equiv}O$), 1640 cm^{-1} ($>C{=}O$); ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H, Cp), 2.95 (br m, 1 H, $>CHCO-$), 1.86 (m, 2 H), 1.68 (m, 2 H), 1.60 (m, 1 H), 1.49 (br m, 3 H), and 1.36 (m, 4 H) ($>CH_2$'s); ^{13}C NMR ($CDCl_3$) δ 260.58 ($>C{=}O$), 214.74 ($-C{\equiv}O$'s), 86.40 (Cp), 75.33 ($>CHCO-$), 29.67, 27.96, 26.56 (2 C, $>CH_2$'s). Anal. Calcd for $C_{15}H_{18}O_3Fe$: C, 59.63; H, 6.00. Found: C, 59.65; H, 6.06.

Dicarbonyl(η^1-cyclooctylcarbonyl)(η^5-cyclopentadienyl)iron (1d), prepared in 54% yield (0.68 g, 2.2 mmol) from 0.625 g (4.00 mmol) of acid, 3 mL (4.37 g, 34.4 mmol) of oxalyl chloride, and 1.03 g (4.75 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate,[52] is a yellow solid, mp 36–38 °C. It has the following spectra: IR (CH_2Cl_2) 2005, 1950 ($-C{\equiv}O$), 1640 cm^{-1} ($>C{=}O$); ^1H NMR ($CDCl_3$) δ 4.85 (s, 5 H, Cp), 3.04 (m, 1 H, $>CHCO-$), 1.73 (br m, 4 H) and 1.46 (br m, 10 H) ($>CH_2$'s); ^{13}C NMR ($CDCl_3$) δ 260.64 ($>C{=}O$), 214.76 ($-C{\equiv}O$'s), 86.39 (Cp), 73.93 ($>CHCO-$), 28.02, 25.52, (2 C, $>CH_2$'s), 26.53 (1 C, $>CH_2$); MS *m/e* $[M - CO]^+$ calcd for $[FeC_{15}H_{20}O_2]^+$ 288.0813, found 288.0818. Anal. Calcd for $C_{16}H_{18}O_3Fe$: C, 60.78; H, 6.38. Found: C, 60.64; H, 6.52.

Dicarbonyl(η^1-cycloundecylcarbonyl)(η^5-cyclopentadienyl)iron (1e), prepared in 75% yield (1.33 g, 3.7 mmol) from 0.975 g (4.92 mmol) of acid, 3 mL (4.37 g, 34.4 mmol) of oxalyl chloride, and 1.35 g (6.25 mmol) of potassium dicarbonyl(η^5-cyclopentadienyl)ferrate,[52] is a yellow oil at room temperature. It exhibits the following spectra: IR (CH_2Cl_2) 2005, 1950 ($-C{\equiv}O$), 1640 cm^{-1} ($>C{=}O$); ^1H NMR ($CDCl_3$) δ 4.83 (s, 5 H, Cp), 3.08 (m, 1 H, $>CHCO-$), 1.71 (br m, 3 H) and ~1.41 (br m, 17 H) ($>CH_2$'s); ^{13}C NMR ($CDCl_3$) δ 260.55 ($>C{=}O$), 214.81 ($-C{\equiv}O$'s), 86.55 (Cp), 73.58 ($>CHCO-$), 28.31, 26.04, 25.97, 25.68, 25.06 (2 C, $>CH_2$'s). Anal. Calcd for $C_{19}H_{26}O_3Fe$: C, 63.70; H, 7.32. Found: C, 64.09; H, 7.68.

Treatment of Dicarbonyl(η^1-cycloalkylcarbonyl)(η^5-cyclopentadienyl)iron (1a,b) with Triflic Anhydride in Dichloromethane. Formation of Dicarbonyl(η^2-methylenecycloalkane)(η^5-cyclopentadienyl)iron Triflate (9a,b) and Dicarbonyl(η^1-cycloalkylethoxymethylidene)(η^5-cyclopentadienyl)iron Triflate (12a,b). To a solution of **1a**/**1b** in 2–5 mL of CH_2Cl_2 at 0 °C was added ~3 equiv of triflic anhydride ($(CF_3SO_2)_2O$). The resulting mixture was stirred at 0 °C for 30 min and for an additional 30 min at room temperature and then concentrated to dryness under vacuum to remove triflic acid and/or excess triflic anhydride. The residue was dissolved in CH_2Cl_2, this solution was filtered through a layer of Celite, and the volume of the solution was reduced to a few milliliters under vacuum. When a large excess of freshly distilled diethyl ether was added to the clear, yellow solution of **1a** or **1b** in a attempt to precipitate a cationic triflate salt, the solution darkened and a red-to-black sludge settled to the bottom. The supernatant was syringed away, the residue was dried under vacuum and taken up in 15 mL of CH_2Cl_2, and this solution was filtered through Celite. The Celite was washed with additional CH_2Cl_2, which was combined with the filtrate. The resulting solution was concentrated to ~2 mL; 40 mL of diethyl ether was added at 0 °C to yield a residue, which was separated from the supernatant and dried at reduced pressure. A ^1H NMR spectrum of this material indicates it to be a mixture of η^2-methylenecycloalkane **9a**/**9b** and Fischer carbene **12a**/**12b**.[47]

Dicarbonyl(η^5-cyclopentadienyl)(η^2-methylenecyclopentene)iron Triflate (9a). When prepared as outlined above using 0.327 g (1.19 mmol) of **1a** and 0.5 mL (0.84 g, 3.0 mmol) of triflic anhydride, 0.335 g of an ~3:2 mixture of **9a** and **12a** (as judged by the relative intensities of the Cp H's at δ 5.57 and 5.41 ppm, respectively, vide infra) was obtained.

Fractional crystallization of this mixture from CH_2Cl_2/pentane gave 0.095 g (0.23 mmol, 20%) of yellow crystalline **9a**, mp 74–76 °C: IR (CH_2Cl_2) 2035, 2015 ($-C{\equiv}O$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 5.57 (s, 5 H, Cp), 4.01 [s, 2 H, η^2-($>C{=}CH_2$)], 2.43 (br m, 2 H), 2.09 (m, 4 H) and 1.81 (br m, 2 H) ($>CH_2$'s); ^{13}C NMR (CD_2Cl_2) δ 210.16 ($-C{\equiv}O$'s), 126.90 [η^2-($>C{=}CH_2$)], 89.49 (Cp), 51.41 [η^2-($>C{=}CH_2$)], 38.23, 26.36 (2 C, $>CH_2$'s); FAB *m/e* calcd for $[C_{13}H_{15}O_2Fe]^+$ 259.0421 observed 259.0425. Anal. Calcd for $C_{14}H_{15}F_3FeO_5S$: C, 41.20; H, 3.70. Found: C, 40.43, 39.64; H, 3.56, 3.44.

The ^1H and ^{13}C NMR spectra of **12a** (the triflate) are identical with those of the corresponding tetrafluoroborate **13a**, prepared from **1a** and triethyloxonium tetrafluoroborate (vide infra).

Dicarbonyl(η^5-cyclopentadienyl)(η^2-methylenecyclohexane)iron Triflate (9b). When prepared as outlined above using 0.342 g (1.19 mmol) of **1b** and 0.5 mL (0.84 g, 3.0 mmol) of triflic anhydride, 0.357 g of an ~3:2 mixture of **9b** and **12b** (as judged by the relative intensities of the Cp H's at δ 5.62 and 5.42 ppm, respectively, vide infra) was obtained.

Fractional crystallization of this mixture from CH_2Cl_2/pentane gave 0.175 g (0.414 mmol, 35%) of yellow crystalline **9b**, mp 84–86 °C: IR (CH_2Cl_2) 2030, 2010 ($-C{\equiv}O$) cm^{-1}; ^1H NMR (CD_2Cl_2) δ

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(51) Bly, R. S.; Wu, R.; Bly, R. K. *Organometallics* **1990**, *9*, 936.

(52) Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 285.

5.62 (s, 5 H, Cp), 3.98 [s, 2 H, η^2-(>C=CH$_2$)], 2.50 (m, 2 H), 2.10 (br s, 2 H), 1.80 (br m, 1 H) and 1.54 (m, 5 H) (>CH$_2$'s); ^{13}C NMR (CDCl$_3$) δ 209.79 (–C≡O's), 129.37 [η^2-(>*C*=CH$_2$)], 89.14 (Cp), 51.87 [η^2-(>C=*C*H$_2$)], 41.17 and 34.30 (2 C, >CH$_2$'s), 25.77 (1 C, >CH$_2$); FAB *m/e* calcd for [C$_{14}$H$_{17}$O$_2$Fe]$^+$ 273.0578, observed 273.0580. Anal. Calcd for C$_{15}$H$_{17}$F$_3$FeO$_5$S: C, 42.67; H, 4.06. Found: C, 41.56, 41.80; H, 3.81, 3.92.

The ^{1}H and ^{13}C NMR spectra of **12b** (the triflate) are identical with those of the corresponding tetrafluoroborate **13b**, prepared from **1b** and triethyloxonium tetrafluoroborate (vide infra).

Dicarbonyl(η^5-cyclopentadienyl)(η^1-cycloalkylethoxymethylidene)iron Tetrafluoroborates 13a,b were prepared by treatment of the corresponding η^1-cycloalkylcarbonyl derivatives **1a,b** with excess triethyloxonium tetrafluoroborate in dichloromethane solution as described previously.[1a]

Dicarbonyl(η^5-cyclopentadienyl)(η^1-cyclopentylethoxymethylidene)iron Tetrafluoroborate (13a). The yellow crystalline solid exhibits the following spectra: IR (CH$_2$Cl$_2$) 2000, 2047 (–C≡O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.41 (s, 5 H, Cp), 5.18 (d, *J* = 7 Hz, 2 H, OC*H*$_2$CH$_3$), 4.25 [br, 1 H, >C*H*C(OEt)Fp$^+$], 2.00 (m, 2 H), 1.71 (t, *J* = 7 Hz, CH$_2$C*H*$_3$) overlapping a multiplet at ~1.8–1.6; ^{13}C{^{1}H} NMR (–50 °C, CD$_2$Cl$_2$) δ 341.2 [>CH*C*(OEt)-Fp$^+$], 208.6 (CO's), 87.5 (Cp), 83.2, 74.3, 32.1 (2 C), 26.3, (2 C), 14.0; FAB *m/e* calcd for [C$_{15}$H$_{19}$O$_3$Fe]$^+$ 303.0684, observed 303.0679.

Dicarbonyl(η^5-cyclopentadienyl)(η^1-cyclohexylethoxymethylidene)iron Tetrafluoroborate (13b). The yellow crystalline solid exhibits the following spectra: IR (CH$_2$Cl$_2$), 2002, 2050 (–C≡O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.42 (s, 5 H, Cp), 5.20 (d, *J* = 7 Hz, 2 H, OC*H*$_2$CH$_3$), 3.63 [br, 1 H, >C*H*C(OEt)Fp$^+$], 1.84 (m, 4 H), 1.72 (t, *J* = 7 Hz, 3 H, CH$_2$C*H*$_3$), ~1.4–1.1 (br m, 6 H); ^{13}C{^{1}H} NMR (–50 °C, CD$_2$Cl$_2$) δ 342.3 [>CH*C*(OEt)Fp$^+$], 209.4 (CO's), 88.0 (Cp), 84.3, 75.1, 29.7 (2 C), 25.6, 25.7 (2 C), 14.4; FAB *m/e* calcd for [C$_{16}$H$_{21}$O$_3$Fe]$^+$ 317.0840, observed 317.0843.

Treatment of Dicarbonyl(η^1-cyclohexylcarbonyl)(η^5-cyclopentadienyl)iron (1b) with Triflic Anhydride Followed by Low-Temperature ^{13}C NMR Spectroscopy. Observation of Dicarbonyl(η^1-cyclohexylidenylmethylidene)(η^5-cyclopentadienyl)iron Triflate (3b) and Dicarbonyl(η^1-cyclohexyl(((trifluoromethyl)sulfonyl)oxy)methylidene)(η^5-cyclopentadienyl)iron Triflate (2b). Three 5-mm NMR tubes, each containing 0.050 g (0.156 mmol) of **1b** in 0.6 mL of CDCl$_3$, were cooled in liquid nitrogen, and 0.075 mL (0.125 g, 0.443 mmol) of trifluoromethanesulfonic anhydride (triflic anhydride) was vacuum-transferred into each. The tubes were sealed under vacuum and warmed to –78 °C.

To obtain the spectrum of the reaction mixture at room temperature prior to its decomposition, the **first sample tube** was warmed to room temperature and placed in the probe of the AM-500.13 spectrometer and the ^{13}C{^{1}H} NMR spectrum was quickly determined at ambient temperature. The observed spectrum, δ 379.2 (>C=*C*=Fp$^+$), 203.01 (–C≡O's), 132.82 (>-*C*=C=Fp$^+$), 92.29 (Cp), 25.80, 25.04, and 22.30 (>CH$_2$'s), is that of vinylidene **3b**.

In an attempt to force the rearrangement of vinylidene **3b**, the temperature of the probe was raised to about 40 °C, at which point the contents of the NMR tube began to gel, the lock was lost, and the ^{13}C spectrum could no longer be observed. Until the loss of lock, the Cp resonance of **3b** at δ 92.29 remained the strongest organometallic signal in the mixture, and no new resonance appeared at δ 89–90, the expected position of the Cp C's of an η^2-cycloalkyne complex (vide infra).

The **second sample tube** was placed in the cooled probe of an NMR spectrometer at –50 °C and the ^{13}C{^{1}H} NMR spectrum determined. The observed spectrum, δ 339.31 [>CH*C*(OTf)=Fp$^+$], 208.63 (–C≡O's), 86.91 (Cp), 72.99 [>*C*HC(OTf)=Fp$^+$], 28.46 (1 C, >CH$_2$), 24.97 (2 C, >CH$_2$'s), is that of Fischer carbene **2b**. After this spectrum was recorded, the probe temperature was raised to about –25 °C and a second ^{13}C{^{1}H} NMR spectrum was determined. This spectrum revealed the reaction mixture to consist of an ~1:1 mixture of **2b** and **3b**. The probe temperature was then raised to ~0 °C and a third ^{13}C{^{1}H} NMR spectrum, indicating **3b** to be the preponderant organometallic present in the reaction mixture, was determined.

Finally, the tube was warmed to ambient temperature and a fourth ^{13}C{^{1}H} NMR spectrum was recorded. This spectrum is similar to that recorded at ambient temperature for the **first sample** (vide supra).

The **third sample tube** was warmed to –20 °C and held at that temperature for 60 days, and the ^{13}C{^{1}H} NMR spectrum at that temperature was determined; it is that of **3b** uncontaminated with **2b**.

Treatment of Dicarbonyl(η^1-cyclohexylcarbonyl)(η^5-cyclopentadienyl)iron (1b) with Triflic Anhydride in Protio- and in Perdeuteriodiethyl Ether. To an ice-cold solution of 40 mg (0.14 mmol) of **1b** in 0.9 mL of anhydrous **protiodiethyl ether** was added with stirring, in one portion, 50 μL (84 mg, 0.30 mmol) of triflic anhydride. The solution turned bright orange, and a dark gummy material separated after approximately 2 min. Stirring was discontinued, and the reaction mixture stood at 0 °C for an additional 10 min. The solvent was removed by syringe, and the residue was washed with two 1-mL portions of cold ether. Residual ether was removed under vacuum. A ^{1}H NMR spectrum (CDCl$_3$) of the crude product mixture, though poorly resolved, showed it to be essentially identical with that obtained when the reaction was carried out in CH$_2$Cl$_2$ instead of in ether. The yield of ether-insoluble products, a 3:2 mixture of **9b** and **12b**, was 44 mg.

The procedure was repeated using 20 mg (0.07 mmol) of **1b**, 0.5 mL (4.7 mmol) of **perdeuteriodiethyl ether** (Cambridge Isotope Laboratories, 99% D), and 30 μL (50 mg, 0.18 mmol) of triflic anhydride. The reaction was allowed to proceed at 0 °C for 20 min. The ^{1}H NMR (CDCl$_3$) spectrum of the crude mixture showed the presence of **9b** and **12b** (now ~1:1) and ~15% of **1b**. The ethoxy proton resonances, a 1:3:3:1 quartet at δ 5.20 and a 1:2:1 triplet at δ 1.72, of protiated **9b** are absent in the deuterated analogue while the resonance of the complexed, exocyclic methylene, a two-proton singlet at δ 3.98 in protiated **9b**, is greatly reduced, its integrated area now representing 0.4 H. No attempt was made to isolate either of these complexes.

Treatment of Dicarbonyl(η^1-cycloalkylcarbonyl)(η^5-cyclopentadienyl)iron (1c–e) with Triflic Anhydride in Dichloromethane. Formation of Dicarbonyl(η^2-cycloalkyne)(η^5-cyclopentadienyl)iron Triflate (5c–e). To a solution of **1** in 2–5 mL of CH$_2$Cl$_2$ at 0 °C was added ~3 equiv of triflic anhydride. The resulting mixture was stirred at 0 °C for 30 min and for an additional 30 min at room temperature and then concentrated to dryness under vacuum to remove triflic acid and/or excess triflic anhydride. The resulting residue was dissolved in CH$_2$Cl$_2$ and this solution filtered through a layer of Celite, and the volume of the solution was reduced to a few milliliters under vacuum. A large excess of freshly distilled diethyl ether was added, and the mixture was to cooled to –20 °C and held there for ~1 h to precipitate the cationic triflate salt. The microcrystalline solid **5** which separated was isolated, washed with diethyl ether, and dried under vacuum.

Dicarbonyl(η^2-cyclooctyne)(η^5-cyclopentadienyl)iron triflate (5c), prepared in 66% yield (0.335 g, 0.77 mmol) as yellow crystals, mp 110–112 °C, from 0.355 g (1.18 mmol) of **1c** and 0.5 mL (0.84 g, 3.0 mmol) of triflic anhydride, exhibits the following spectra: IR (CH$_2$Cl$_2$) 2040, 2020 (–C≡O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.69 (s, 5 H, Cp), 2.59 (br s, 4 H), 2.00 (br s, 4 H) and 1.68 (br s, 4 H) (>CH$_2$'s); ^{13}C NMR (CD$_2$Cl$_2$) δ 207.73 (–C≡O's), 89.92 (Cp), 55.10 [2 C, η^2-(–C≡C–)], 31.82, 28.41, 26.60 (2 C, >CH$_2$'s); FAB *m/e* calcd for [C$_{15}$H$_{17}$O$_2$Fe]$^+$ 285.0578, observed 285.0576. Anal. Calcd for C$_{16}$H$_{17}$F$_3$FeO$_5$S: C, 44.26; H, 3.95. Found: C, 43.98; H, 3.70.

When a CD$_2$Cl$_2$ solution of **5c** in an NMR tube is cooled to –50 °C and held there for several hours, the ^{13}C NMR spectrum is that of η^2-cyclooctyne **5c** (vide supra) uncontaminated with vinylidene **3c**.

Dicarbonyl(η^2-cyclononyne)(η^5-cyclopentadienyl)iron triflate (5d), prepared in 61% yield (0.195 g, 0.44 mmol) as yellow crystals, mp 98–100 °C, from 0.225 g (0.712 mmol) of **1d** and 0.35 mL (0.59 g, 2.1 mmol) of triflic anhydride, exhibits the following spectra: IR (CH$_2$Cl$_2$) 2040, 2015 (–C≡O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.66 (s, 5 H, Cp), 2.68 (br m, 4 H), 1.90 (br m, 4 H) and 1.61 (br m, 6 H) (>CH$_2$'s); ^{13}C NMR (CD$_2$Cl$_2$) δ 208.17 (–C≡O's), 89.57 (Cp), 51.33 [2 C, η^2-(–C≡C–)], 27.46 (1 C, >CH$_2$), 27.27, 27.04, 25.10 (2 C, >CH$_2$'s); FAB *m/e* calcd for [C$_{16}$H$_{19}$O$_2$Fe]$^+$ 299.0734, observed 299.0733. Anal. Calcd for C$_{17}$H$_{19}$F$_3$FeO$_5$S: C, 45.55; H, 4.27. Found: C, 45.25; H, 4.29.

Dicarbonyl(η^2-cyclododecyne)(η^5-cyclopentadienyl)iron triflate (5e), prepared in 69% yield (0.305 g, 0.62 mmol) as yellow crystals, mp 114–116 °C, from 0.325 g (0.908 mmol) of **1e** and 0.50 mL (0.84 g, 3.0 mmol) of triflic anhydride, exhibits the following spectra: IR (CH_2Cl_2) 2060, 2020 (–C≡O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.63 (s, 5 H, Cp), 2.83 (br m, 4 H), 1.74 (br m, 6 H) and 1.38 (br m, 10 H) (>CH_2's); ^{13}C NMR ($CDCl_3$) δ 208.12 (–C≡O's), 89.29 (Cp), 48.17 [2 C, η^2-(–C≡C–)], 28.06, 27.11, 26.99, 25.06, 23.91 (2 C, >CH_2's); FAB *m/e* calcd for $[C_{19}H_{25}O_2Fe]^+$ 341.1204; observed 341.1192. Anal. Calcd for $C_{20}H_{25}F_3FeO_5S$: C, 48.99; H, 5.14. Found: C, 47.79; H, 5.19.

Treatment of Dicarbonyl(η^1-cycloheptylcarbonyl)(η^5-cyclopentadienyl)iron (1c) with Triflic Anhydride Followed by Low-Temperature ^{13}C NMR Spectroscopy. Observation of Dicarbonyl(η^1-cycloheptyl(((trifluoromethyl)sulfonyl)oxy)methylidene)(η^5-cyclopentadienyl)iron Triflate (2c) and Dicarbonyl(η^1-cycloheptylidenylmethylidene)(η^5-cyclopentadienyl)iron Triflate (3c). A sealed 5-mm NMR tube, prepared at liquid-nitrogen temperature as described above from 0.025 g (0.083 mmol) of **1c**, 0.05 mL (0.085 g, 0.30 mmol) of triflic anhydride, and 0.6 mL of $CDCl_3$, was warmed to −78 °C and then placed in the −50 °C probe of an 80-MHz spectrometer, and the $^{13}C\{^1H\}$ NMR spectrum was determined. The observed spectrum, δ 338.00 [>CH*C*(OTf)=Fp$^+$], 208.67 (–C≡O's), 86.98 (Cp), 73.62 [>*C*HC(OTf)=Fp$^+$], 29.53, 27.08, 26.39 (2 C, >CH_2's), is that of Fischer carbene **2c**.

The probe temperature was raised to −20 °C, and the $^{13}C\{^1H\}$ NMR spectrum was redetermined. In addition to the resonances attributed to **2c** (vide supra), the following, attributable to vinylidene **3c**, are also present: δ 382.0 (>C=*C*=Fp$^+$), 203.32 (–C≡O's), 132.00 (>*C*=C=Fp$^+$), 92.10 (Cp), 29.01, 26.60, and 22.99 (>CH_2's). Intermediates **2c** and **3c** appear to be present in approximately equal amounts under these conditions.

The probe temperature was raised further to ~0 °C, and the $^{13}C\{^1H\}$ NMR spectrum was again determined. In addition to the resonances of **2c** and **3c**, those of the η^2-cyclooctyne **5c** (vide supra) are also present.

Finally, as judged by the $^{13}C\{^1H\}$ NMR spectrum at 125 MHz, **5c** is the only organometallic present in the reaction mixture after it has been warmed to room temperature.

Decomplexation of the η^2-Cycloalkene/η^2-Cycloalkyne (9/5) with Tetra-*n*-butylammonium Iodide. Approximately 3 equiv of tetra-*n*-butylammonium iodide was added to a solution of the η^2 complex in 1 mL of $CDCl_3$, the mixture was stirred at room temperature for 30 min to 2 h, and the volatiles were removed under 1 mmHg (60 °C) and collected. The resulting cycloalkene/cycloalkyne was dried over Na_2SO_4 and the $^{13}C\{^1H\}$ NMR spectrum determined.

Methylenecyclopentane (10a), recovered from 0.050 g (0.122 mmol) of **9a** and 0.125 g (0.338 mmol) of tetra-*n*-butylammonium iodide, has the following $^{13}C\{^1H\}$ NMR spectrum: δ 153.86 (>C=), 104.84 (=CH_2), 33.37, 26.96 (>CH_2's). The spectrum is identical with that of a known sample of pure **10a**.[53]

Methylenecyclohexane (10b), recovered from 0.050 g (0.118 mmol) of **9b** and 0.125 g (0.338 mmol) of tetra-*n*-butylammonium iodide, has the following $^{13}C\{^1H\}$ NMR spectrum: δ 150.67 (>C=), 106.80 (=CH_2), 35.77, 28.68, and 26.66 (>CH_2's). The spectrum is identical with that of a known pure (99%) sample of **10b**.[53]

Cyclooctyne (6c), recovered from 0.050 g (0.115 mmol) of **5c** and 0.125 g (0.338 mmol) of tetra-*n*-butylammonium iodide, has the following $^{13}C\{^1H\}$ NMR spectrum: δ 94.71 (–C≡), 34.67, 29.84, and 21.04 (>CH_2's). This spectrum is identical with that of an authentic sample of cyclooctyne prepared independently.[54]

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