Acyclic $Cp(CO)_2Fe$ Disubstituted η^1-Vinylidene–η^2-Acetylene Isomerizations[1]

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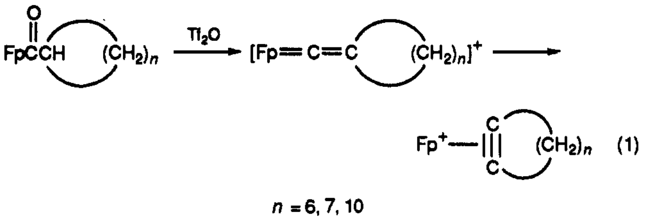
Acyclic, disubstituted vinylidene complexes, $[Cp(CO)_2Fe{=}C{=}CR^1R^2]^+TfO^-$, **3a–c** (**a**, R^1, R^2 = Me; **b**, R^1 = Ph, R^2 = Me; **c**, R^1, R^2 = Ph), isomerize to nonterminal η^2-acetylene complexes, $[Cp(CO)_2Fe(\eta^2\text{-}R^1\text{-}C{\equiv}C\text{-}R^2)]^+TfO^-$, **5a–c**, in CD_2Cl_2 above −50 °C. Carbon-13 labeling and VT ^{13}C NMR are used to track the formation of **3** and its conversion to **5**. The isomerizations are intramolecular and apparently irreversible. That of **3b** to **5b** involves only phenyl migration. It is suggested that $Cp(CO)_2Fe$ η^2-acetylenes are favored over $Cp(CO)_2Fe$ η^1-vinylidenes under these conditions by the strongly electron withdrawing COs which, relative to less π-acidic ligands, destabilize the vinylidene and stabilize the π-acetylene.

Introduction

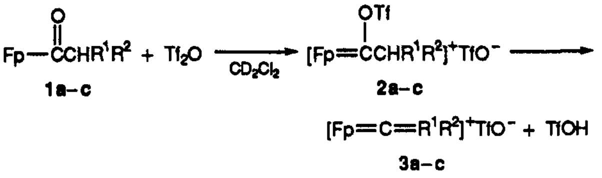
Utilizing a reaction originally developed by Hughes *et al.* to prepare stable Cp(CO)(L)Fe η^1-vinylidenes from Cp(CO)(L)Fe acyls [L = PPh_3, PMe_2Ph, $P(C_6H_{11})_3$],[2] we recently generated some cationic medium- and large-ring exocyclic $Cp(CO)_2Fe$ η^1-polymethylenevinylidene complexes, *i.e.* $[Fp{=}C{=}C(CH_2)_n]^+$ (n = 6, 7, 10), and observed their rearrangement to stable η^2-homocycloalkynes, $Fp[\eta^2\text{-}C_2(CH_2)_n]^+$, eq 1.[3] Simple molecular mechanics calculations[3,4] suggest that these isomerizations are exothermic above and beyond any strain release associated with the rings themselves. Thus, it seemed likely to us that unstrained, *acyclic* Fp η^1-vinylidene complexes might also isomerize to *acyclic* Fp η^2-acetylenes. Here we report what we believe are the first disubstituted examples of some which do.



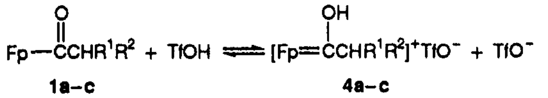
Results

Cationic disubstituted η^1-vinylidenes **3a–c** were produced by the vacuum transfer of an ~2–3 mole excess of triflic anhydride in CD_2Cl_2 into a cold (−196 °C), 5-mm NMR tube containing the Fp disubstituted acetyl, **1a–c**.[3] The tube was sealed under vacuum, warmed to −80 °C, shaken at that temperature to dissolve the acyl, and inserted in the precooled probe of a 500-MHz NMR spectrometer. The ensuing reaction was followed by periodically monitoring the integrated $^{13}C\{^1H\}$ NMR intensities of the Cp carbons of intermediates and product(s); *cf.* Table 1.

As suggested by Hughes *et al.*,[2b] the initial intermediate, Fischer carbene **2**, loses triflic acid to form vinylidene **3**, eq 2. The triflic acid reversibly protonates unreacted acyl **1**, thereby yielding Fisher carbene **4**, eq 3, and markedly decreasing the rate of vinylidene formation.[5] In time, vinylidene **3** is converted to Fp η^2-acetylene **5**, eq 4 (*cf.* Table 1). Product is formed more rapidly in the presence of 2,6-di-*tert*-butylpyridine (DTBP). This nonnucleophilic base prevents the triflic acid formed in eq 2 from protonating the starting acyl, eq 3. And, although the evidence here is less clear, it may also accelerate the conversion of triflate carbene **2** to vinylidene **3**, eq 2, thereby increasing the likelihood that the isomerization step, eq 4, is rate-limiting. It cannot affect the rate of the isomerization step *per se* for it is neither a catalyst not a reactant.



$$\underset{\mathbf{1a-c}}{Fp{-}\overset{\overset{O}{\|}}{C}CHR^1R^2} + Tf_2O \xrightarrow[CD_2Cl_2]{} \underset{\mathbf{2a-c}}{[Fp{=}\overset{\overset{OTf}{|}}{C}CHR^1R^2]^+TfO^-} \longrightarrow \underset{\mathbf{3a-c}}{[Fp{=}C{=}R^1R^2]^+TfO^-} + TfOH \quad (2)$$



$$\underset{\mathbf{1a-c}}{Fp{-}\overset{\overset{O}{\|}}{C}CHR^1R^2} + TfOH \rightleftharpoons \underset{\mathbf{4a-c}}{[Fp{=}\overset{\overset{OH}{|}}{C}CHR^1R^2]^+TfO^-} + TfO^- \quad (3)$$

$$\underset{\mathbf{3a-c}}{[Fp{=}C{=}CR^1R^2]^+TfO^-} \xrightarrow{-R} \underset{\mathbf{5a-c}}{[Fp(\eta^2\text{-}R^1\text{-}C{\equiv}C\text{-}R^2)]^+TfO^-} \quad (4)$$

a: R^1, R^2 = Me **b**: R^1 = Ph, R^2 = Me **c**: R^1, R^2 = Ph

With the possible exception of the last data set in each run, the measurements in Table 1 are not of equilibrium mixtures. Recooling a reacting mixture that has been

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[1] *Cf.*: Bly, R. S.; Zhong, Z.; Kane, C.; Bly, R. K. *Abstracts of the 205th National Meeting of the American Chemical Society*, March 28–April 2, 1993, Denver, CO; American Chemical Society: Washington, DC, 1993; ORGN #168.

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[4] We have used PCMODEL, versions 2.0 and 4.0, for these calculations. Each version utilizes the MM2 (77) force field of N. Allinger (QCPE No. 395) supplemented by the generalized parameters of C. Still and extended to other nuclei by J. J. Gajewski and K. E. Gilbert. Version 4.0 can be used with transition metals including those with π-bound ligands. For details see ref 3, footnote 36, and: Mackie, S. C.; Park, Yong-S.; Shuvell, H. F.; Baird, M. C. *Organometallics* **1991**, *10*, 2993 (footnote 5).

[5] The protonated acyl **4**, formed separately in CD_2Cl_2 from triflic acid and acyl **1**, does not yield vinylidene **3** in the absence of triflic anhydride.

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Table 1. Integrated $^{13}C\{^1H\}$ NMR Intermediate and Product Ratios in the Reactions of Fp Disubstituted Acetyls, 1, with Excess Triflic Anhydride in CD_2Cl_2 with/without Added 2,6-Di-*tert*-butylpyridine (DTBP)

run				DTBP/			ratio		
no.	acyl	R[1]	R[2]	acyl[a]	*T*, °C	Δ*t*,[b] h	(1), 2 (4)[c]	3	5
1.1	**1a**	Me	Me	0.0	−78	1.5	84	16	0
1.2					−53	1	52	48	0
1.3						7	50	50	0
1.4					−20	2.5	39	57	4
1.5					0	2.5	14	4	82
1.6						21.5	3	0	97
2.1	**1b**	Ph	Me	0.0	−78	1.5	94	6	0
2.2						6.5	66	33	<1
2.3					−53	0.5	53	37	10
2.4						2	50	20	30
2.5					−20	5	34	0	66
2.6						~2 weeks	2	0	98
3.1	**1b**	Ph	Me	1.0	−78	~0.3	97	3	0
3.2						9.5	42	58	0
3.3					−53	2.5	4	68	28
3.4						5	0	33	67
3.5					−20	1.5	0	0	100
4.1	**1c**	Ph	Ph	0.0	−78	1.5	100	0	0
4.2						6.5	>99	0	<1
4.3					−53	0.5	95	0	5
4.4						7.5	74	0	26
4.5					−20	5	30	0	70
4.6						17	24	0	76
5.1	**1c**	Ph	Ph	1.4	−57	1	92	0	8
5.2						3.5	60	0	40
5.3					−20	17	0	0	100

[a] Mole ratio of di-*tert*-butylpyridine (DTBP) to acyl. [b] Time increments are approximately *additive* within a single run, i.e. ~36 h at the temperatures listed produces a mixture containing 97% **5a** (*cf.* run 1). Times at temperatures are approximate because in most runs the temperature was raised while the sample was in the probe. [c] In a mixture containing Tf_2O, TfOH, and TfO^-, **1** is protonated; the $^{13}C\{^1H\}$NMR spectra of **2** and **4** are broadened and virtually indistinguishable. In the presence of DTBP the spectra are sharp and only **1** can be observed.

allowed to warm to a higher temperature slows but does not reverse isomerization of vinylidene **3** to acetylene **5**. Reacting mixtures maintained for extended periods at a single temperature continue to exhibit incremental increases in the product acetylene, **5**, until vinylidene **3** is no longer perceptible; *vide infra*.

The Fp disubstituted acetylene π-complexes **5** can be isolated as triflate salts by dilution of the reaction mixture with diethyl ether. They are modestly stable under nitrogen at room temperature. Alternately, the samples used for NMR can be decomplexed *in situ* by addition of tetra-*n*-butylammonium iodide. The volatiles, including the free alkyne, **6**, can be recovered by vacuum transfer, *e.g.* eq 5.

$$\underset{\textbf{5b}}{[\mathrm{Fp}(\eta^2\text{-Me—C≡C—Ph})]^+\mathrm{TfO}^-} \xrightarrow[\mathrm{CD_2Cl_2}]{(n\text{-Bu})_4\mathrm{N^+I^-}} \underset{\textbf{6b}}{\text{Me—C≡C—Ph}} + \mathrm{FpI} \quad (5)$$

Reversibility of η¹-Vinylidene Isomerizations. Monoalkyl- or aryl-substituted acyclic η^1-vinylidenes are frequently more stable in solution than isomeric terminal η^2-acetylenes. Solutions of virtually all such monometallic organotransition metal terminal η^2-acetylenes, except those ligated to dicarbonyl(η^5-cyclopentadienyl)iron (*i.e.* Fp),[6,7] isomerize to η^1-vinylidenes.[8,9] Such isomerizations, especially those that occur in the presence of base, are frequently considered to be reversible.[7n,8,9i,10] In some instances, equilibrium mixtures, containing more vinylidene than acetylene, have been observed.[10] Nonetheless, most non-Fp monoalkyl- or aryl-substituted η^1-vinylidenes, including other Fe(II) species,[2,7i,11] do not produce observable amounts of terminal η^2-acetylenes in solution.[8,9,12] Extended Hückel and nonparamaterized MO calculations support these experimental observations.[13]

In contrast to numerous examples of monosubstituted η^1-vinylidene/terminal η^2-acetylene interconversion, no non-Fp dialkyl-, alkylaryl-, or diaryl-substituted η^1-vi-

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(6) Fp terminal η^2-acetylenes, formed from Fp—CH=C=CHR and HA,[7b,c,e,f] and from $[\mathrm{Fp}(\eta^2\text{-CH}_2\text{=CMe}_2)]^+$ [7j,l] or $(\mathrm{Fp—THF})^+$ [7g,h,i,k] and HC≡CR in the presence of an alcohol or water, frequently yield products which appear to result from the corresponding $[\mathrm{Fp}(\eta^1\text{-vinylidene})]^+$, but this intermediate is not observed. There is no evidence, except for some that we will provide in a subsequent publication,[1] that a Fp η^2-vinylidene is present in an aprotic solution of a *Fp* terminal acetylene *in the absence of added nucleophile or base.*

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nylidene/nonterminal η^2-acetylene isomerization has been described. Most of the known organotransition metal, dialkyl-, alkylaryl-, or diaryl-substituted η^1-vinylidenes, other than those of dicarbonyl(η^5-cyclopentadienyl)iron, are kinetically, and perhaps thermodynamically, stable *vis-à-vis* isomerization to the corresponding η^2-acetylene.[2,7i,9j,n,o,11a–c,e,f,14] Likewise, no 18-electron transition metal, nonterminal dialkyl, alkylaryl, or diaryl η^2-acetylene complex in which the acetylene is a 2-electron ligand is reported to isomerize to a disubstituted vinylidene complex.[7j,l,n,9b,c,15]

These situations are reversed in the case of Fp η^2-acetylenes and η^1-vinylidenes. As we will detail in a subsequent paper, Fp monoalkyl- or monoaryl-substituted η^1-vinylidenes, formed in methylene chloride from the Fp acyl and triflic anhydride, isomerize readily to Fp terminal η^2-acetylenes with or without added base.[1] Solutions of Fp terminal η^2-acetylenes, though they may decomplex slowly above about 0 °C, do not contain perceptible amounts of monosubstituted η^1-vinylidene.[1,6] The Fp disubstituted acyclic η^1-vinylidenes reported here, and the exocyclic ones reported earlier,[3] isomerize readily to Fp disubstituted acyclic and cyclic η^2-acetylenes, respectively. In deuteriomethylene chloride containing excess DTBP, the acyclic cases ultimately produce solutions of Fp η^2-acetylene that contain no discernible amount of vinylidene; *cf.* Table 1, runs 3 and 5. From a ^{13}C NMR spectrum with a signal-to-noise ratio of 600-to-1, we estimate the final product mixture from **1b** at −20 °C (*cf.* Table 1, observation 3.5) to contain at least 200 times as much η^2-acetylene as η^1-vinylidene. If the isomerization, eq 4 (which is not affected by added base since none is consumed or evolved in this step), is reversible, the equilibrium constant, K, is ≥200 and [Fp(η^2-PhC≡CMe)]$^+$, **5b**, is thermodynamically at least 2.7 kcal/mol more stable than [Fp=C=C(Ph)-Me]$^+$, **3b**, at this temperature.

Clearly, it is important to know whether the isomerization of disubstituted vinylidene to nonterminal acetylene produces an equilibrium mixture that simply contains too little vinylidene to detect by NMR or whether it is, in fact, irreversible. To examine this question more carefully, we generated Fp vinylidene [1-^{13}C]-**3b** in CD$_2$Cl$_2$ as before from acyl **1b** labeled at the acyl carbon with 24.9% carbon-13.[16] The reaction mixture was allowed to stand in a sealed NMR tube at 0 °C as the ^{13}C{^{1}H} NMR spectrum was monitored periodically. After about 1 month, Fischer carbene [1-^{13}C]-**4b** was no longer evident. After 2 months, the mixture, though beginning to show some decomplexed material (as evinced by the "Cp–C" resonance of Fp$^+$ at δ ~85 ppm[7g,17]), eq 6, contained [Fp-(η^2-1-phenyl-1-propyne)]$^+$ ([^{13}C]-**5b**) labeled at a single acetylene carbon (δ ~47.4 ppm) with carbon-13. No ^{13}C-labeled acyl, carbene, vinylidene, protonated acyl, or other ^{13}C-labeled acetylene could be detected.

$$\underset{}{\mathrm{Fp}(\eta^2\text{-Me}{-}\mathbf{C}{\equiv}\mathbf{C}{-}\mathrm{Ph})^+\mathrm{TfO}^-} \rightarrow \underset{[1\text{- or }2\text{-}^{13}\mathrm{C}]\text{-}\mathbf{5b}}{} \quad \mathrm{FpOTf} + \underset{[1\text{- or }2\text{-}^{13}\mathrm{C}]\text{-}\mathbf{6b}}{\mathrm{Me}{-}\mathbf{C}{\equiv}\mathbf{C}{-}\mathrm{Ph}} \qquad (6)$$

$$\mathbf{C} = {}^{13}\mathrm{C}$$

The labeled Fp η^2-acetylene [^{13}C]-**5b** was precipitated from this mixture by addition of cold (0 °C) ether, washed several times with additional cold ether, and dried under vacuum. This "2-month" sample was dissolved in CDCl$_3$, and the ^{13}C{^{1}H} NMR spectrum was compared with that of a comparable sample isolated similarly but after 12 h at 0 °C. The ratio of the integrated intensities of the labeled (δ 47.4 ppm) and unlabeled (δ 54.6 ppm) η^2-acetylene carbon resonances is (26 ± 6)/1 in the "12-h" sample and (24 ± 5)/1 in the "2-month" sample.[18] Thus, as best we can determine, either phenyl or methyl migrates; the ^{13}C label is not scrambled between the acetylene carbons of the Fp(η^2-1-phenyl-1-propyne)$^+$, [^{13}C]-**5b**, eq 7. Either this vinylidene-to-acetylene rearrangement is irreversible under the reaction conditions or the same group migrates exclusively in the reverse sense as well.

$$\underset{[2\text{-}^{13}\mathrm{C}]\text{-}\mathbf{5b}}{[\mathrm{Fp}(\eta^2\text{-MeC}{\equiv}\mathrm{CPh})]^+} \overset{\sim\mathrm{Me}}{\rightleftharpoons} \underset{[1\text{-}^{13}\mathrm{C}]\text{-}\mathbf{3b}}{[\mathrm{Fp}{=}\mathbf{C}{=}\mathrm{C(Ph)Me}]^+} \overset{\sim\mathrm{Ph}}{\rightleftharpoons} \underset{[1\text{-}^{13}\mathrm{C}]\text{-}\mathbf{5b}}{[\mathrm{Fp}(\eta^2\text{-Ph}\mathbf{C}{\equiv}\mathrm{CMe})]^+} \qquad (7)$$

To determine the position of the label, [^{13}C]-**5b** was decomplexed, eq 5, and the resulting [^{13}C]-1-phenyl-1-propyne ([^{13}C]-**6b**) was isolated. The ^{13}C resonance of the labeled carbon appears at δ 79.8 ppm, which, according to the reported spectrum of 1-phenyl-1-propyne,[19] would place the label next to the methyl group, implying that only methyl migrates in the isomerization of **3b** to **5b**.

We were skeptical of this result and, to check it, decomplexed [^{13}C]-**5b** using tetra-*n*-butylammonium iodide in benzene, eq 5, and then oxidized the resulting [^{13}C]-**6b** *in situ*, in a two-phase system with a large excess of potassium permanganate in water,[20] eq 8. Mass and ^{13}C NMR spectra of the benzoic acid which is produced indicates that it incorporates all of the ^{13}C label initially present in the starting acyl, [1-^{13}C]-**1b**. Thus the ^{13}C

$$\underset{[1\text{- or }2\text{-}^{13}\mathrm{C}]\text{-}\mathbf{6b}}{\mathrm{Me}{-}\mathbf{C}{\equiv}\mathbf{C}{-}\mathrm{Ph}} \xrightarrow[(n\text{-Bu})_4\mathrm{N}^+\mathrm{I}^-/\mathrm{C_6H_6}]{\mathrm{KMnO_4/H_2O}} \xrightarrow[\mathrm{H_2O}]{\mathrm{H}^+} (\mathrm{MeCO_2H}) + \mathrm{C_6H_5CO_2H} \qquad (8)$$

$$\mathbf{C} = {}^{13}\mathrm{C}$$

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(18) As the standard deviations of a dozen or so intergrations imply, these two ratios are experimentally identical. The ratio is expected to be 29.6 in a sample that contains 24.9 atom % ^{13}C at one acetylene carbon and 1.1 atom % (the natural abundance) at the other.

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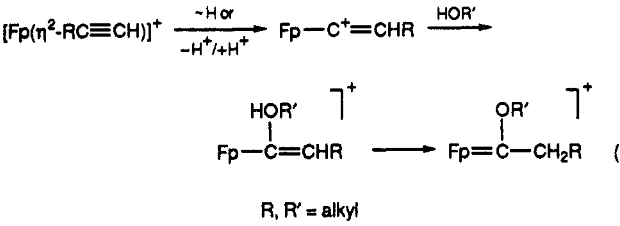
chemical shifts of the acetylene carbons of 1-phenyl-1-propyne are incorrectly assigned in the literature.[19] The product of the isomerization of vinylidene [1-^{13}C]-**3b** is π-complexed acetylene [1-^{13}C]-**5b**; phenyl, not methyl, migrates.

Relative Rates of η^1-Vinylidene Isomerizations. It is evident from a comparison of measurements of vinylidene concentration *vs* time, in both the absence of DTBP (*cf.* Table 1, runs 1, 2 and 4) and the presence of DTBP (runs 3 and 5), that the relative isomerization rate of vinylidenes 3, eq 4, is **3c** > **3b** > **3a**. This order is consistent with a migratory aptitude of Ph > R, similar to that observed in cationic η^1-alkylidene-to-η^2-alkene isomerizations,[21] migrations across the double bond of ametallic, solvolytically generated vinyl cations,[22] and "more often than not" in Wagner–Meerwein rearrangements.[23]

Trapping of Disubstituted Vinylidene with Methanol. Although Fp η^2-acetylenes in solution do not isomerize to spectroscopically observable amounts of Fp η^1-vinylidene,[1,6] Rosenblum *et al.* showed early on that terminal Fp η^2-acetylenes do react with anhydrous alcohols to produce Fp alkoxycarbenes, eq 9, and postulated



(9)

monosubstituted η^1-vinylidene as the reactive intermediate.[7f] Accordingly, it seemed appropriate to examine the reversibility of the disubstituted vinylidene–nonterminal acetylene isomerization(s) in the presence of an added alcohol.

The addition of excess MeOD (98 atom % $^2\mathrm{H}_1$) to a cold (−80 °C) solution of approximately 10% acyl [1-^{13}C]-**1b**, 88% vinylidene [1-^{13}C]-**3b**, 2% π-complexed acetylene [1-^{13}C]-**5b**, and excess DTBP in $\mathrm{CD_2Cl_2}$ causes an immediate color change from deep red to light yellow. A ^{13}C{^{1}H} NMR spectrum of the reaction mixture at −80 °C reveals that the vinylidene resonances have been replaced by those of ^{13}C-enriched methoxy Fischer carbene, incorporating ~70 atom % deuterium at the C(2) position, eq 10. Clearly, unrearranged phenylmethylvinylidene **3b** can be trapped by deuteriomethanol at low temperature in the presence of DTBP/DTBPH$^+$.

$$[\mathrm{Fp{=}\mathbf{C}{=}C(Me)Ph}]^+\mathrm{TfO}^- + [1\text{-}^{13}\mathrm{C}]\text{-}\mathbf{3b}\ \ \mathrm{DTBP/DTBPH}^+ + \mathrm{TfO}^- \xrightarrow[-80\,^\circ\mathrm{C}]{\mathrm{MeOD}} [\mathrm{Fp{=}\mathbf{C}(OMe)CD(Me)Ph}]^+\mathrm{TfO}^- + [1\text{-}^{13}\mathrm{C},2\text{-}^{2}\mathrm{H}]\text{-}\mathbf{7b}\ \ \mathrm{DTBP/DTBPH}^+ + \mathrm{TfO}^- \quad (10)$$

$$\mathbf{C} = {}^{13}\mathrm{C}$$

In a second experiment, a solution of similar initial concentration was allowed to react until acyl [^{13}C]-**1b** and vinylidene [^{13}C]-**3b** were no longer evident by ^{13}C{^{1}H} NMR. When excess MeOD was added to the cold (−80 °C) solution containing only π-complexed acetylene [1-^{13}C]-**5b** and excess DTBP, no color change was observed. A ^{13}C{^{1}H} NMR spectrum, recorded after 1 h at −53 °C and an additional 1 h at −20 °C, reveals [1-^{13}C]-**5b** to be the only organometallic present, eq 11. A reaction, presumably nucleophilic addition of MeOD to the Fp nonterminal η^2-acetylene,[7b,f] is observed above ~0 °C. The absence of [1-^{13}C,2-^{2}H]-**7b** in the reaction mixture at −20 °C confirms the irreversibility of the **3b**-to-**5b**, vinylidene-to-acetylene, isomerization under these conditions.

$$[\mathrm{Fp}(\eta^2\text{-}\mathrm{Me{-}\mathbf{C}{\equiv}C{-}Ph})]^+\mathrm{TfO}^- + [1\text{-}^{13}\mathrm{C}]\text{-}\mathbf{5b}\ \ \mathrm{DTBP/DTBPH}^+ \xrightarrow[-20\,^\circ\mathrm{C}]{\mathrm{CH_3OD}} \text{no reaction} \quad (11)$$

$$\mathbf{C} = {}^{13}\mathrm{C}$$

Discussion

Why do Fp η^1-vinylidenes isomerize to Fp η^2-alkynes whereas previously reported η^1-vinylidenes are stable, many, in fact, having been formed by isomerization of an η^2-alkyne in the first place? The reason, we suggest, in disubstituted vinylidenes—and possibly in monosubstituted cases as well—lies in the nature of the isomerization itself, in the extreme electrophilicity of vinylidene α-carbons,[24] and in the high π-acidity of carbonyl ligands relative to the phosphine-, phosphite-, or diphosphine-type ligands[25] utilized in virtually all of the prior examples.[8–12]

Isomerization of a disubstituted vinylidene complex to an acetylene complex involves a β-to-α carbon shift.[3] Such shifts in vinyl cations, and presumably in η^1-vinylidenes as well, depend upon the presence of a highly electrophilic α-carbon.[3,22,24] Because of their extreme electrophilicities, such carbons are extraordinarily sensitive to the electronic nature of substituents to which they are attached.[24b] As a consequence of its two strongly π-acidic carbonyl ligands, Fp is a much weaker electron donor than a phosphine, phosphite, or diphosphine-ligated metal moiety.[25] Hence Fp η^1-vinylidene complexes are less stable, have more electrophilic α-carbons[26] and are expected to show a greater tendency to rearrange[1,3,7f] than their phosphorus-ligated, η^1-vinylidene counterparts.[9–12,14,15]

This tendency of Fp vinylidene complexes to rearrange is further enhanced by the greater relative stability of the resulting η^2-alkyne complexes. Because of lower electron density at the metal, Fp η^2-alkynes are less strongly destabilized by repulsive interactions between the filled d orbitals of the metal and the filled $\pi_\perp$ orbital of the ligated alkyne[9u,26] than are 18-electron transition metal alkyne complexes having higher electron densities at the metal, *i.e.* those with less strongly π-acidic ligands.[25]

We suggest that electronic differences such as these cause η^1-vinylidene–η^2-acetylene isomerizations to favor

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the acetylene in the case of Fp and the vinylidene in cases where the metal is substituted by phosphine(s), by phosphite(s), or by a diphosphine ligand.

Experimental Section

General Procedures. All operations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-line and glovebox (Vacuum/Atmospheres "Dri-Lab") techniques. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. All ^{1}H NMR spectra were acquired at 300 or 500 MHz on a Bruker AM-300.13 or AM-500.13 spectrometer, respectively. Proton chemical shifts are reported in ppm relative to the residual proton resonances of the NMR solvent: CDCl$_3$ (7.24 ppm), CD$_2$Cl$_2$ (5.32 ppm). The ^{13}C NMR spectra were obtained at 125 MHz on a Bruker AM-500.13 spectrometer, and the ^{13}C resonances are reported in ppm relative to the carbon of the deuterated solvent: CDCl$_3$ (77.0 ppm), CD$_2$Cl$_2$ (53.8 ppm). High resolution FAB$^+$ and mass spectra were determined 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.

Solvents and Reagents. Reagent grade diethyl ether and 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$_2$O$_5$, stored over sodium ribbon, and distilled from sodium under nitrogen immediately prior to use. Deuterated NMR solvents, CDCl$_3$ (Aldrich) and CD$_2$Cl$_2$ (Cambridge Isotope), were purified by drying over P$_2$O$_5$, degassed by a freeze–pump–thaw technique and stored under vacuum.

General Procedure for the Preparation of Acyclic Dicarbonyl(η^5-cyclopentadienyl)iron(II) Acyls: [(CH$_3$)$_2$CHCO]Fe(η^5-C$_5$H$_5$)(CO)$_2$ (1a). A 656-mg sample of 2-methylpropanoyl chloride (6.16 mmol) was placed in a 50-mL side-arm round-bottom flask. The flask was charged with 15 mL of THF and potassium dicarbonyl (η^5-cyclopentadienyl)ferrate[27] (KFp, 1.33 g, 6.16 mmol) in a glovebox, and the solution was stirred overnight. The THF was evaporated under reduced pressure; the residue was digested in pentane and filtered through Celite and sand. The Celite was washed several times with pentane and the filtrate was concentrated to about 5 mL at reduced pressure. Column chromatography with alumina (activity III) using 5% ether/pentane as eluent provided 600 mg (39%) of **1a**, an oil. IR (CH$_2$Cl$_2$): 2010, 1955 (C$\equiv$O), 1610, 1580 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$), δ: 4.85 (s, 5H, Cp), 3.06 [heptet, $^3J_{HH}$ = 6.8 Hz, 1H, –C(O)C*H*(CH$_3$)$_2$], 0.96 ppm (d, $^3J_{HH}$ = 6.8 Hz, 6H, >CHC*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$), δ: 264.7 (>C=O), 215.1 (–C$\equiv$O), 86.8 (Cp), 63.4 [C(O)CH], 18.9 ppm (CH$_3$). MS: *m/e* [M – CO]$^+$ 220.0197 (calcd for C$_{10}$H$_{12}$O$_2$Fe: 220.0187).

(*d,l*-CH$_3$CH(Ph)CO)Fe(η^5-C$_5$H$_5$)(CO)$_2$ (1b). Complex **1b** was prepared from *d,l*-2-phenylpropanoyl chloride (289 mg, 1.71 mmol) and KFp (370 mg, 1.71 mmol). Two fractions were collected from an alumina column: the first constituted a trace amount of an unidentified product, and the second provided 383 mg (72%) of **1b** as an oil after evaporation of the solvents. The oil crystallized upon standing, mp 44–46 °C. IR (CH$_2$Cl$_2$): 2021, 1960 (C$\equiv$O), 1655, 1632 (C=O) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.2–7.4 (m, 5H, Ph), 4.70 (s, 5H, Cp), 4.29 (q, $^3J_{HH}$ = 6.9 Hz, ^{1}H, >C*H*CH$_3$), 1.24 ppm (d, $^3J_{HH}$ = 6.9 Hz, 3H, >CHC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$), δ: 257.5 (>C=O), 215.5, 214.8 (–C$\equiv$O), 140.8, 129.1, 128.9 and 127.1 (Ph), 86.6 (Cp), 75.0 [C(O)CH], 19.9 ppm (CH$_3$). MS: *m/e* [M – CO]$^+$ 282.0331 (calcd for C$_{15}$H$_{14}$O$_2$Fe: 282.0343). Anal. Calcd for C$_{16}$H$_{14}$O$_3$Fe: C, 61.97; H, 4.55. Found: C, 61.85; H, 4.18.

Carbonyl-^{13}C-labeled acyl [1-^{13}C]-1b was prepared from 1-^{13}C-enriched, *d,l*-2-phenylpropanyl chloride obtained from the reaction of oxalyl chloride with 24.9 atom % (by mass spectroscopy) 1-^{13}C-enriched, *d,l*-2-phenylpropanoic acid. This labeled acid was prepared by alkylating a mixture of 1 part 99 atom % [1-^{13}C]phenylacetic acid (MSD, Canada) and 3 parts unenriched acid with 1.1 equiv of methyl iodide in the presence of 2.0 equiv of lithium diisopropylamide (LDA) in THF.

[(C$_6$H$_5$)$_2$CHCO]Fe(η^5-C$_5$H$_5$)(CO)$_2$ (1c). This compound was obtained as a yellow microcrystalline solid from the reaction of diphenylacetyl chloride (1.0 g, 4.33 mmol) with KFp (1.0 g, 4.63 mmol) in THF. The yield was 854 mg (53%), mp 111–114 °C. IR (CH$_2$Cl$_2$): 2022, 1965 (C$\equiv$O), 1646 (C=O) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.18–7.31 (m, 10H, Ph), 4.77 (s, 5H, Cp), 2.16 ppm) s, 1H, >CH–). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$), δ: 256.2 (>C=O), 214.8 (–C$\equiv$O's), 138.9 (1C, Ph), 129.4 (2C, Ph), 129.0 (2C, Ph), 127.3 (1C, Ph), 86.8 (Cp), 86.3 ppm (>CH–). Anal. Calcd for C$_{21}$H$_{16}$O$_3$Fe: C, 67.77; H, 4.33. Found: C, 67.63; H, 4.23.

Reaction of the Dicarbonyl(η^5-cyclopentadienyl)iron Acyls (1) in Deuteriodichloromethane with Triflic Anhydride in the Absence of Added Base, Monitored by Low-Temperature ^{13}C NMR. Solutions of 25–35 mg (~0.1–0.15 mequiv) of each of the Fp–acyl complexes **1** in 0.5 mL of CD$_2$Cl$_2$ were placed in 5-mm NMR tubes, cooled in liquid nitrogen to –197 °C, and combined by vacuum transfer with an approximately 3-fold excess (~0.3–0.45 mequiv) of triflic anhydride. The tubes were sealed under vacuum and stored at –197 °C. The frozen mixtures were thawed and mixed while completely submerged in a dry ice–isopropyl alcohol (IPA) bath and then transferred quickly to the precooled probe of the Bruker 500 NMR spectrometer. Each reaction was followed by periodically monitoring the ^{13}C{^{1}H} NMR spectrum with data acquisition beginning immediately after the precooled sample had been inserted into the cold probe; *vide infra*. Our observations for each starting material are summarized below and in Table 1.

Formation and Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron [η^1-(2,2-Dimethylvinylidene)] Triflate (3a). With 2-methylpropanoyl Fp (**1a**), the first ^{13}C{^{1}H} NMR spectrum (run 1.1), determined after ~1.5 h at –78 °C, suggests that the major component is an unresolved mixture of Fischer carbene(s), (CH$_3$)$_2$CH(OY)=Fp$^+$ (**2a**, Y = OTf) and/or **4a** (Y = OH), in equilibrium with nonprotonated **1a**. All but the methyl signals are very broad: δ ~213.6–210.6 (C$\equiv$O's), ~87.5–87.0 (Cp), ~63.1–62.9 (CH's), 18.7 ppm (CH$_3$'s). Also observed are signals attributed to vinylidene **3a** [δ 387.1 (>C=*C*=Fp$^+$), 203.8 (C$\equiv$O's), 128.6 (>*C*=C=Fp$^+$), 93.0 (Cp), 11.6 ppm (CH$_3$'s)] and to a trace of an unknown material, 91.2 ppm (Cp). No carbene carbon signals are discerned at this stage of the reaction.

After an additional 8 h at –53 °C (run 1.3) the solution contained a ~50/50 mixture of **2a**/**4a** {δ: ~341.8 [broad, >CH*C*(OH, OTf)=Fp$^+$], 209.5 (C$\equiv$O's), 62.7 [>*C*HC(OH, OTf)=Fp$^+$], 87.7 (Cp), 18.7 ppm (CH$_3$'s)} and **3a**. When the temperature was raised to –20 °C and above (runs 1.4–1.6), formation of π-complexed acetylene **5a** was observed: δ (–5 °C) 208.2 (C$\equiv$O's), 89.0 (Cp), 43.7 [Fp$^+$(η^2-(–C$\equiv$C–))], 10.9 ppm (CH$_3$'s). The ^{13}C spectrum of the cation of **5a**$^+$OTf$^-$ is virtually identical to that reported by Reger[15a] for the cation of **5a**$^+$BF$_4^-$, *viz.* δ [(CD$_3$)$_2$CO] 43.8 ($\equiv$CCH$_3$), 10.3 ppm (CH$_3$).

Formation and Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron [η^1-(2-Methyl-2-phenylvinylidene)] Triflate (3b). Starting with *d,l*-2-phenylpropanoyl Fp, **1b**, the first ^{13}C{^{1}H} NMR spectrum (run 2.1), determined at –78 °C, showed very broad ($w_{1/2}$ 20–75 Hz), irregular-shaped resonances attributed to a **1b**/**2b**/**4b** mixture, *viz.* δ ~215–213 (C$\equiv$O's) (pure **1b** has sharp C$\equiv$O resonances at 215.5 and 214.8), 140.0, 129.3 (two unresolved absorptions?), and 127.7 (Ph) (pure **1b** has sharp phenyl resonances at 140.8, 129.1, 128.9, and 127.1), 86.8 (Cp) (a sharp resonance at 86.6 in pure **1b**), 74.6 (>CH–) (at 75.0 in pure **1b**), 19.9 ppm (CH$_3$) (at 19.9 in pure **1b**).

At this stage in the reaction, the resonances of the acyl carbonyl of **1b** [δ 257.5 for pure **1b** in neutral solution at this temperature] and/or the alkylidene carbon of **2b**/**4b**, [Fp$^+$=*C*(OTf, OH)CH(Ph)CH$_3$], expected at δ ~330–340, are apparently too broad to be detected. Vinylidene **3b** resonances are evident at δ 402.8 (>C=*C*=Fp$^+$), 202.9 (C$\equiv$O's), 135.4, 130.3, 129.8, and 126.7 (Ph), 126.0 (>*C*=C=Fp$^+$), 93.9 (Cp), and 9.0 ppm (CH$_3$).

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[27] Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* 1981, *20*, 285.

After 8 h at −78 °C (run 2.2), the signals of the first component(s) have sharpened somewhat and the remaining resonances are shifted slightly from their initial positions: δ 211.6, 210.1 (C≡O's), 138.2, 130.0, 129.4, and 128.8 (Ph), 87.6 (Cp), 73.7 (CH), 19.4 ppm (CH_3). Though the relative intensities of the vinylidene **3b** signals are increased, their chemical shifts are unchanged. At −53 °C (runs 2.3–2.4), the carbene carbon resonance(s) of **2b**/**4b**, $Fp^+{=}C(OTf, OH)CH(Ph)CH_3$, become evident at δ 333.7, and rearrangement of vinylidene **3b** to π-complexed acetylene **5b** is observed; *cf.* Table I.

Isolation of the η^2-Acetylene Complex: $[(\eta^2\text{-}PhC{\equiv}CCH_3)Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+OTf^-$ (5b). Complex **1b** (127 mg, 0.410 mmol) was placed in a 25-mL side-arm, round-bottom flask and charged with 4 mL of dry, degassed CH_2Cl_2. While stirring at −78 °C [(dry ice/isopropyl alcohol (IPA)], triflic anhydride (344 μL, 577 mg, 2.05 mmol) was added via a microsyringe. The resulting orange solution was held at −20 °C for 3 days. The solution was allowed to warm to room temperature and Et_2O was added via syringe. An orange precipitate formed immediately. The supernatant Et_2O was syringed away and the solids were washed with several portions of Et_2O. The product was dried at 0.01 mmHg to give 146 mg (81%) of **5b**: mp 74–76 °C dec. IR (CH_2Cl_2); 2130 (C≡C), 2085, 2048 (C≡O) cm^{-1}. ^1H NMR (CD_2Cl_2), δ: 7.61 (s, 2H, Ph), 7.51 (s, 3H, Ph), 5.68 (s, 5H, Cp), 2.72 ppm (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 208.2 (−C≡O), 133.1 (Ph), 131.1 (Ph, *para*-C), 130.1 (Ph), 122.7 (Ph, *ipso*-C), 121.2 (q, 320.1 Hz, CF_3), 90.2 (Cp), 47.0 (C≡*C*—Ph), 55.5 (C≡*C*—CH_3), 12.7 ppm (s, CH_3). MS: *m/e* $[M - OTf]^+$ 293.0280 (calcd for $C_{16}H_{13}O_2Fe$: 293.0265). Anal. Calcd for $C_{17}H_{13}O_5F_3FeS$: C, 46.18; H, 2.96. Found: C, 45.72; H, 2.67.

Formation and Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron [η^1-(2-Methyl-2-phenyl[1-^{13}C]vinylidene)] Triflate ([1-^{13}C]-3b). A sample of *d,l*-2-phenylpropanoyl Fp enriched at the acyl carbon with 25% ^{13}C, [1-^{13}C]-**1b**, was mixed with triflic anhydride in deuteriodichloromethane as before; *vide supra*. The reaction mixture was sealed under vacuum and monitored by $^{13}C\{^1H\}$ NMR as before. After 2 days at −20 °C the reaction mixture was found to contain 11% [^{13}C]-**2b** and/or [^{13}C]-**4b** and 89% [^{13}C]-**5b**. The added ^{13}C label appears exclusively at the δ 47.4 ppm acetylene carbon resonance. The sealed reaction mixture was transferred to an ice-bath and its $^{13}C\{^1H\}$ NMR spectrum determined periodically. After 60 days at 0 °C the relative intensities of the acetylene carbon resonances at δ ~54.2 and 47.7 ppm appeared to be unchanged, though some decomposition (presumably due to decomplexation) was evident. New resonances appear at δ 210 and 85.1 ppm, presumably due to the CO and Cp, respectively, of FpOTf, and at 148 ppm, attributable to the ^{13}C-labeled benzylidene carbon of PhC(OTf)═CHMe or PhCH═C(OTf)Me, the expected product(s) from the addition of triflic acid to decomplexed [1-^{13}C]-1-phenyl-1-propyne, [1-^{13}C]-**6**.

The product was isolated by addition of ether to the reaction mixture at 0 °C, withdrawal of the supernatant liquid by syringe and washing of the crystalline, ether-insoluble residue with several portions of cold ether. After drying under vacuum, the crystalline product was dissolved in deuteriodichloromethane and its $^{13}C\{^1H\}$ NMR spectrum was determined at −20 °C. The ratio of the integrated intensities of the δ 47.4 $[Fp(\eta^2\text{-}CH_3{-}C{\equiv}\mathit{C}{-}Ph)]^+$ and δ 54.6 ppm $[Fp(\eta^2\text{-}CH_3{-}\mathit{C}{\equiv}C{-}Ph)]^+$ acetylene carbon resonances (vide infra) is (26 ± 6)/1 when determined after 12 h and (24 ± 5)/1 in the isolated "2-month" product sample, confirming that scrambling of the ^{13}C label between the acetylene carbons does not occur under these reaction conditions.[18]

Decomplexation of Dicarbonyl(η^5-cyclopentadienyl)iron [η^2-([1-^{13}C]-1-phenyl-1-propyne)] Triflate ([1-^{13}C]-5b) and Isolation of [1-^{13}C]-1-phenyl-1-propyne ([1-^{13}C]-6b). To the 60-day sample in the NMR tube was added ~50 mg of tetra-*n*-butylammonium iodide. After standing for ~1 h at room temperature the volatiles were vacuum transferred to a second 5-mm NMR tube and analyzed by $^{13}C\{^1H\}$ NMR. The spectrum of the only volatile product was identical to that of 1-phenyl-1-propyne enriched exclusively at C(1): (CD_2Cl_2, 25 °C), δ: 131.5 (2C Ph), 128.2 (2C Ph), 127.5 (1C Ph), 124.1 (1C Ph), 85.8 (≡C-Me), 79.8 (Ph-C≡), 4.2 ppm (CH_3). (Note that these acetylene carbon assignments do not agree with those currently reported in the literature[19] but have been confirmed as described below.)

Decomplexation and Oxidation of Dicarbonyl(η^5-cyclopentadienyl)iron [η^2-([1-^{13}C]-1-Phenyl-1-propyne)]$^+$ ([1-^{13}C]-5b) from the Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron [η^1-(2-Methyl-2-phenyl[1-^{13}C]vinylidene)] Triflate ([1-^{13}C]-3b). The phase-transfer oxidation portion of this combined decomplexation–oxidation was modeled after that of Krapcho, Larson, and Eldridge.[20c] To a solution of 85 mg (0.19 mmol) of [1-^{13}C]-**5b** (isolated from the rearrangement of [1-^{13}C]-**3b** as described above in the nonlabeled case) in 2 mL of benzene was added 100 mg (0.27 mmol) of tetra-*n*-butylammonium iodide (to serve as both a decomplexing agent and a phase-transfer catalyst). The mixture was stirred at room temperature for 15 min and then combined with 600 mg of potassium permanganate and 3 mL of water. Stirring was continued for 11 days. The dark suspension was combined with 5 mL of water and ~3 g of sodium sulfite and acidified with dilute sulfuric acid. The now colorless mixture was extracted with three 5-mL portions of ether. The extract was dried (Na_2SO_4), and the solvent was removed under vacuum. The crystalline residue was sublimed to give 19 mg (83%) of benzoic acid having 25.1 ± 0.5% (by mass spectroscopy) ^{13}C enrichment at the carboxyl carbon: ^{13}C NMR ($CDCl_3$) δ 172.4 ppm.

This experiment confirms our ^{13}C NMR chemical shift reassignments for the acetylene carbons of 1-phenyl-1-propyne (*vide supra*)—they are reversed, *i.e.* incorrect, in the current literature.[19]

Formation and Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron (η^1-((Trifluoromethyl)sulfonyl)diphenylmethylidene) Triflate (2c). Starting with diphenylacetyl Fp, **1c**, the initial $^{13}C\{^1H\}$ NMR spectrum at −78 °C (run 4.1) is identical to that of the pure acyl except for some broadening of the >C═O signal at δ 256.7 ppm. As the temperature is gradually raised and as the concentration of triflic acid increases, the resonances broaden. The presence of **2c** and/or **4c** is indicated by slight changes in the observed chemical shifts: after about 30 min at −53 °C (run 4.3), the spectrum shows resonances at δ 212 (C≡O's), 137.5, 129.5, 129.4, 128.0 (Ph), 87.3 (Cp), and 85.3 ppm (CH) but the resonance of the carbene carbon(s) has broadened to the point that it can no longer be distinguished from the baseline. At no time can any vinylidene **3c** be detected. Formation of acetylene π-complex **5c** is observed at −53 °C: δ 207.4 (C≡O's), 133.2, 131.5, 130.2, and 123.1 (Ph), and 58.7 ppm (≡C—Ph) (*cf.* Table 1). This $^{13}C\{^1H\}$ NMR spectrum of the cationic portion of $5c^+OTf^-$ in CD_2Cl_2 is virtually identical to that reported by Reger[15a] for the cation of $5c^+BF_4^-$ in $(CD_3)_2CO$.

Reaction of the Dicarbonyl(η^5-cyclopentadienyl)iron Acyls (1) in Deuteriodichloromethane with Triflic Anhydride in the presence of 2,6-Di-*tert*-butylpyridine (DTBP), Monitored by Low-Temperature ^{13}C NMR. Solutions containing equimolar amounts of Fp acyl **1** and the nonnucleophilic base, DTBP, in 0.5 mL of deuteriodichloromethane were combined in 5-mm NMR tubes with triflic anhydride, sealed under vacuum, thawed, and mixed at the dry ice–IPA temperature as described above. The progress of each reaction was monitored by $^{13}C\{^1H\}$ NMR.

Formation and Rearrangement of Dicarbonyl (η^5-cyclopentadienyl)iron [η^1-(2-Methyl-2-phenylvinylidene)] Triflate (3b) in the Presence of Added DTBP. In the presence of 1 equiv of DTBP, the reaction of **1b** with triflic anhydride yields π-acetylene **5b** as it does in the absence of base. However, the only precursor that can be observed is the starting acyl **1b**—all carbon resonances including that of the acetyl >C═O are apparent. The rearrangement to **5b** is complete and occurs more rapidly than it does in the absence of added DTBP; *cf.* Table I.

Formation and Rearrangement of Dicarbonyl(η^5-cyclopentadienyl)iron (η^1-((Trifluoromethyl)sulfonyl)diphenylmethylidene) Triflate (2c) in the Presence of Added DTBP. In the presence of 1.4 equiv of DTBP, the reaction of

1c with triflic anhydride follows the same course that it does in the absence of base. The final π-complexed product, **5c**, is identical in each case; in neither case is the putative vinylidene **3c** observed. In the presence of DTBP the reaction goes ultimately to completion and may be somewhat more rapid. The final product, **5c**, is but sparingly soluble—orange crystals begin to precipitate before the reaction is complete. The percent compositions reported in Table 1 represent only the composition of the supernatant *solution*.

Treatment of ^{13}C-Enriched Dicarbonyl(η^5-cyclopentadienyl)iron [η^1-(2-Methyl-2-phenylvinylidene)] Triflate ([1-^{13}C]-5b) with MeOD. A solution of 27 mg (0.087 mmol) of acyl [1-^{13}C]-**1b** (containing ~25 atom % carbon-13), 72 mg (0.26 mmol) of triflic anhydride, and 17 mg (0.089 mmol) of 2,6-di-*tert*-butylpyridine (added to neutralize the TfOH produced in the conversion of [1-^{13}C]-**2b** to [1-^{13}C]-**3b** and thus prevent the formation of [1-^{1}13C]-**4b** in the reaction mixture) in 0.5 mL of CD_2Cl_2 was prepared cold (*vide supra*) and held in a dry ice–IPA bath under nitrogen for ~22 h. A ^{13}C{^{1}H} NMR at -80 °C reveals the mixture to contain ~10% acyl [1-^{13}C]-**1b**, ~88% vinylidene [1-^{13}C]-**3b**, and ~2% π-complexed acetylene [1-^{13}C]-**5b**.

The deep-red solution was returned to a dry ice–IPA bath and combined at that temperature with 50 μL (1.2 mmol) of CH_3OD. An immediate color change from red to light yellow occurred. A second ^{13}C{^{1}H} NMR spectrum at -80 °C has no vinylidene {1-^{13}C]-**3b** resonances; the only organometallic present is the ^{13}C-labeled methoxy Fischer carbene, [$CH_3CH(Ph)^{13}C(OCH_3)$=Fp]$^+$ (*vide infra*) incorporating ~70 atom % deuterium at C(2) (δ 74.8 ppm), *i.e.* ([1-^{13}C, 2-^{2}H]-**1b**.

The structure of the product was confirmed by independent synthesis of unlabeled **7b** from acyl **1b** and methyl triflate.[28] ^{13}C{^{1}H} NMR (CD_2Cl_2), δ: 338.7 [-*C*(OCH_3)=Fp$^+$], 209.8, 208.4 (C≡O's), 138.3 (=C<, Ph), 130.2, 129.3, 129.1 (=CH–, Ph), 88.1 (Cp), 74.8 [>CHC(OMe)=Fp$^+$], 73.1 (–OCH_3), 20.5 [–CH(CH_3)–].

Treatment of ^{13}C-Enriched Dicarbonyl(η^5-cyclopentadienyl)iron [η^2-([1-^{13}C]-1-Phenyl-1-propyne)] Triflate ([1-^{13}C]-5b) with MeOD. A second solution of similar composition (*vide supra*) was held at -53 °C overnight and at -29 °C for 2 h and then analyzed by ^{13}C{^{1}H} NMR. The only material detected was π-complexed acetylene [1-^{13}C]-**5b**.

The light-orange solution was cooled to -78 °C and combined with 50 μL of CH_3OD. No color change occurred; ^{13}C{^{1}H} NMR spectra, recorded after 1 h at -53 °C and after an additional 1 h -20 °C, show only unreacted {1-^{13}C]-**5b**. A reaction, presumably nucleophilic addition of CH_3OD to π-complexed acetylene [1-^{13}C]-**5b**,[7b,f] was observed at 0 °C and above; although no products were isolated and although the ^{13}C{^{1}H} NMR spectrum at this point is quite complex, it is clear that methoxy Fischer carbene [$CH_3CH(Ph)^{13}C(OCH_3)$=Fp]$^+$ ([1-^{13}C]-**7b**) (*vide supra*), either with or without deuterium, is not formed in this reaction.

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