of **4** (0.25 g, 0.27 mmol; 54%): mp 176 °C; IR (C_6H_{12}) ν_{CO} 2060 (s), 2015 (s), 2005 (s), 1980 (s), 1955 (m, br), 1650 (ester) cm^{-1}; ^1H NMR (WM-250; CD_2Cl_2; 223 K) δ 7.7–7.3 (m, 20 H), 4.58 (septet, J_{HH} = 6.3 Hz, 1 H), 2.65 (m, 1 H), 2.34 (m, 1 H), 2.01 (m, 1 H), 1.98 (m, 1 H), 1.10 (d, 3 H), 0.99 (d, 3 H); ^{13}C NMR (WM-400; CD_2Cl_2; 183 K) δ 243.1 (apical C), 210.5 (1 CO), 208.8 (1 CO), 203.5 (2 CO), 201.6 (3 CO), 182.2 (C=O), 137.7, 132.1, 130.5, 130.2, 129.2, 129.0 (Ph), 68.5 (CH), 25.4 (d, J_{CP} = 23 Hz, (CH_2–P), 23.1 (CH_2–As), 22.0 (CH_3); ^{31}P NMR (C_6D_6) 47.6 ppm. FAB mass spectrum: *m/z* (%) 914 (28) $C_{38}H_{31}Co_3O_9AsP$ (M^+); 886 (4) $(M - CO)^+$; 858 (4) $(M - 2CO)^+$; 830 (10) $(M - 3CO)^+$; 802 (4) $(M - 4CO)^+$; 774 (8) $(M - 5CO)^+$; 746 (4) $(M - 6CO)^+$; 718 (9) $(M - 7CO)^+$; 660 (14) $C_{28}H_{25}Co_3OAsP$; 632 (17) $C_{27}H_{25}Co_3AsP$; 59 (100) Co. Anal. Calcd for $C_{38}H_{31}AsCo_3O_9P$: C, 49.92; H, 3.36. Found: C, 49.88; H, 3.52.

$[C_5(CH_3)_5]MoCo_2(CO)_6CCO_2CH(CH_3)_2(Ph_2PCH_2CH_2PPh_2)$ (5). As with the synthesis of the tricobalt complex **3**, diphos and **16** in THF gave **5** in 56% yield: mp 117 °C; IR (C_6H_{12}) ν_{CO} 2090 (w), 2050 (m), 2040 (m), 2010 (m), 1990 (s), 1970 (s), 1945 (s), 1920 (w), 1910 (w), 1660 (ester) cm^{-1}; ^1H NMR (WM-250; CD_2Cl_2) δ 7.6–7.3 (m, 20 H), 4.2 (septet, J_{HH} = 6.0 Hz, 1 H), 2.80 (m, 2 H), 2.45 (m, 2 H), 2.04 (s, 15 H), 1.06 (d, 6 H); ^{13}C NMR (WM-400; CD_2Cl_2; 198 K) δ 228.0 (2 CO) (Mo–CO's), 213.2 (2 CO), 210.5 (1 CO), 207.6 (1 CO) (Co–CO's), 133.5, 129.5, 128.3, 127.9 (Ph), 102.0 (Cp–C), 68.2 (CH), 24.1 (d, J_{CP} = 24 Hz) (CH_2–P), 24.1 (CH_3) 11.2 (Cp–CH_3); ^{31}P NMR (C_6D_6) 37.4 ppm. FAB mass spectrum: *m/z* (%) 1016 (28) $C_{47}H_{46}Co_2MoO_8P_2$ (M^+); 988 (4) $(M - CO)^+$; 960 (5) $(M - 2CO)^+$; 932 (53) $(M - 3CO)^+$; 904 (100) $(M - 4CO)^+$; 876 (8) $(M - 5CO)^+$; 848 (28) $(M - 6CO)^+$; 713 (10) $(M - 6CO - C_5Me_5)^+$. Anal. Calcd for $C_{47}H_{46}Co_2MoO_8P_2$: C, 55.64; H, 4.57. Found: C, 55.32; H, 4.81.

$[C_5(CH_3)_5]MoCo_2(CO)_6CCO_2CH(CH_3)_2(Ph_2AsCH_2CH_2PPh_2)$ (6) was prepared analogously to **3**; arphos and **16** in THF gave **6** in 82% yield: mp 105 °C; IR (C_6H_{12}) ν_{CO} 2065 (s), 2020 (s), 2015 (s), 1985 (m), 1655 (ester) cm^{-1}; ^1H NMR (WM-250, CD_2Cl_2) δ 7.7–7.2 (m, 20 H), 4.1 (septet, J_{HH} = 6.2 Hz, 1 H), 3.02 (m, 1 H), 2.65 (m, 1 H), 2.44 (m, 1 H), 2.10 (m, 1 H), 2.05 (s, 15 H), 1.10 (d, 3 H), 1.03 (d, 3 H); ^{13}C NMR (WM-400; CD_2Cl_2; 213 K) δ 228.4 (1 CO), 226.9 (1 CO) (Mo–CO's), 213.1 (2 CO), 208.6 (1 CO), 208.0 (1 CO) (Co–CO's), 132.5, 130.2, 128.3, 127.8 (Ph), 101.7 (Cp–C), 67.4 (CH), 25.3 (d, J_{CP} = 24 Hz, CH_2–P), 21.2 (CH_2–As), 20.9 (CH_3) 11.0 (Cp–CH_3); at 183 K extra CO resonances appear at δ 235.5, 231.5, 209.2, 204.3, 201.0; ^{31}P NMR (C_6D_6) 41.0 ppm. Anal. Calcd for $C_{47}H_{46}AsCo_2MoO_8P$: C, 53.33; H, 4.38. Found: C, 53.40; H, 3.99.

Carbonyl Enrichments. In a typical experiment, **3** (0.1 g, 0.11 mmol) in THF (35 cm^3) was stirred under an atmosphere of ^{13}CO for 48 h. The solvent was removed in vacuo and the product analyzed mass spectrometrically; enrichment was usually of the order 25–30%. On a Bruker WM 400, an acceptable ^{13}C NMR spectrum could be obtained after 100 scans.

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Supplementary Material Available: Lists of anisotropic temperature factors and bond lengths and angles within the phenyl rings (2 pages); lists of calculated and observed structure factor amplitudes (25 pages) Ordering information is given on any current masthead page.

Reactions of Acetylenes with the Cationic Bridging Methylidyne Complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$

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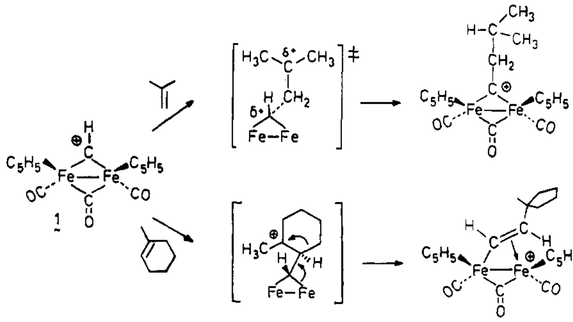
Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) with 2-butyne produced $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHC(CH_3)C(CH_3)CO)^+PF_6^-$ (**2**) in 76% yield. The structure of **2** was determined by X-ray crystallography: monoclinic space group $P2_1/c$, with cell constants a = 7.576 (3) Å, b = 19.053 (8) Å, c = 13.439 (9) Å, β = 101.03 (4)°, Z = 4, and R = 0.083 and R_w = 0.090 for 1895 reflections with $F_o \geqslant 3\sigma(F_o)$. **1** reacted regioselectively with phenylacetylene to produce $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHCHC(C_6H_5)CO)^+PF_6^-$ (**7**) in 81% yield. The reaction of **1** with *tert*-butylacetylene gave an 88% yield of an 80:20 mixture of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3){=}C(CH_3)_2)^+PF_6^-$ (**9-PF$_6$**) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CHC(CH_3)_3)^+PF_6^-$ (**10-PF$_6$**).

Introduction

The cationic diiron bridging methylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) is very electrophilic.[1] Nucleophiles such as CO and NMe_3 add to the methylidyne carbon of **1** to form stable 1:1 adducts.[1] The reactions of alkenes with **1**, which lead to either μ-alkylidyne or μ-alkenyl products, are initiated by an interaction of the alkene with the electrophilic methylidyne carbon. For ethylene, monosubstituted alkenes, and isobutylene, the transition state for reaction with **1** involves interaction of the methylidyne carbon with the least substituted alkene carbon and development of partial positive charge at the more substituted alkene carbon. After this rate-determining transition state, a 1,3-hydride shift from the methylidyne carbon to the alkene completes the formation of the μ-alkylidyne product.[2] For some alkenes such as



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

1-methylcyclohexene, *trans*-stilbene, and 1,1-diphenylethylene that are more sterically congested and capable of forming stabilized carbocation intermediates, the electrophilic addition of 1 leads to formation of an intermediate cation that then undergoes a 1,2-carbon or hydrogen shift to form a μ-alkenyl complex.[3]

Here we report that the reaction of 1 with alkynes occurs via a totally different and unanticipated third pathway that involves addition of the alkyne between the μ-CH carbon and a terminal CO carbon and produces novel μ-η^1,η^4-vinylketene complexes.

Results

Reaction of 1 with 2-Butyne. The reactions of alkynes with 1 produced 1:1 addition products, but spectroscopy indicated that the adducts were neither μ-alkylidyne nor μ-alkenyl complexes similar to those obtained from alkenes. For example, the reaction of 1 with 2-butyne in CH_2Cl_2 at 0 °C led to the isolation of a 76% yield of a brown, air-stable solid 1:1 adduct, 2. The solid-state IR spectrum of 2 has CO bands at 2010 (s), 1867 (s), and 1770 (s) cm^{-1}. The two high-energy bands are similar to those seen for the terminal and bridging CO ligands of cationic diiron μ-alkylidyne and μ-alkenyl complexes, but the 1770-cm^{-1} band indicates the presence of a new type of functional group. The ^1H NMR of 2 shows the presence of two isomers (cis and trans Cp groups) in a 74:26 ratio at 23 °C. The major isomer has a one proton singlet at δ 13.56, two cyclopentadienyl resonances at δ 5.89 and 5.36, and two methyl resonances at δ 2.80 and 1.78. The μ-alkylidyne complex A can be excluded since the one proton resonance would be expected to be a quartet near δ 8 and not the observed singlet at δ 13.56. The μ-allenyl complex B can also be excluded since a fluxional rearrangement would have been expected to give rise to only one cyclopentadienyl and only one methyl resonance.

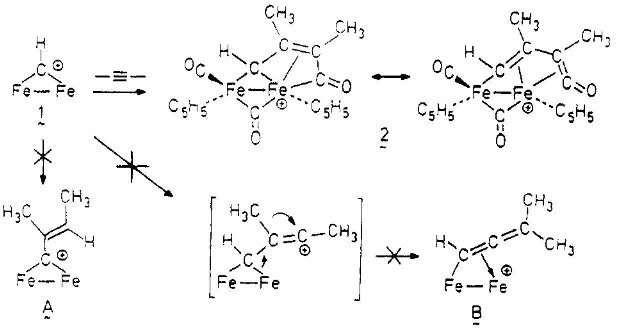

Table I. Selected Bond Distances (Å) and Angles (deg) for 2

(a) Bond Distances

Fe(1)–Fe(2)	2.597 (2)	C(1)–O(1)	1.138 (14)
Fe(1)–C(1)	1.762 (11)	C(2)–O(2)	1.166 (16)
Fe(1)–C(2)	1.847 (13)	C(3)–O(3)	1.198 (14)
Fe(1)–C(6)	1.945 (12)	C(3)–C(4)	1.440 (17)
Fe(1)–C(11)	2.132 (12)	C(4)–C(5)	1.386 (16)
Fe(1)–C(12)	2.132 (11)	C(4)–C(7)	1.526 (18)
Fe(1)–C(13)	2.129 (14)	C(5)–C(6)	1.413 (15)
Fe(1)–C(14)	2.098 (15)	C(5)–C(8)	1.509 (17)
Fe(1)–C(15)	2.108 (14)	C(11)–C(12)	1.459 (17)
Fe(2)–C(2)	2.091 (13)	C(11)–C(15)	1.407 (16)
Fe(2)–C(3)	1.955 (11)	C(12)–C(13)	1.411 (17)
Fe(2)–C(4)	2.136 (12)	C(13)–C(14)	1.366 (18)
Fe(2)–C(5)	2.148 (11)	C(14)–C(15)	1.425 (21)
Fe(2)–C(6)	2.022 (12)	C(21)–C(22)	1.414 (18)
Fe(2)–C(21)	2.106 (11)	C(21)–C(25)	1.427 (20)
Fe(2)–C(22)	2.118 (12)	C(22)–C(23)	1.365 (20)
Fe(2)–C(23)	2.120 (14)	C(23)–C(24)	1.426 (21)
Fe(2)–C(24)	2.095 (15)	C(24)–C(25)	1.409 (20)
Fe(2)–C(25)	2.121 (15)		

(b) Bond Angles

Fe(2)–Fe(1)–C(1)	99.9 (4)	Fe(1)–C(2)–Fe(2)	82.3 (5)
Fe(2)–Fe(1)–C(2)	52.9 (4)	Fe(1)–C(2)–O(2)	147.6 (10)
Fe(2)–Fe(1)–C(6)	50.4 (4)	Fe(2)–C(2)–O(2)	130.1 (10)
C(1)–Fe(1)–C(2)	92.4 (6)	Fe(2)–C(3)–O(3)	142.3 (10)
C(1)–Fe(1)–C(6)	91.8 (5)	Fe(2)–C(3)–C(4)	76.3 (7)
C(2)–Fe(1)–C(6)	102.7 (5)	C(4)–C(3)–O(3)	140.3 (11)
Fe(1)–Fe(2)–C(2)	44.8 (4)	Fe(2)–C(4)–C(3)	62.8 (6)
Fe(1)–Fe(2)–C(3)	85.6 (3)	Fe(2)–C(4)–C(5)	71.6 (6)
Fe(1)–Fe(2)–C(4)	96.7 (3)	Fe(2)–C(4)–C(7)	129.0 (8)
Fe(1)–Fe(2)–C(5)	81.1 (3)	C(3)–C(4)–C(5)	121.1 (11)
Fe(1)–Fe(2)–C(6)	47.8 (3)	C(3)–C(4)–C(7)	114.7 (11)
C(2)–Fe(2)–C(3)	73.9 (5)	C(5)–C(4)–C(7)	122.8 (11)
C(2)–Fe(2)–C(4)	109.4 (4)	Fe(2)–C(5)–C(4)	70.7 (7)
C(2)–Fe(2)–C(5)	117.6 (4)	Fe(2)–C(5)–C(6)	65.4 (6)
C(2)–Fe(2)–C(6)	92.1 (5)	Fe(2)–C(5)–C(8)	135.7 (7)
C(3)–Fe(2)–C(4)	40.9 (5)	C(4)–C(5)–C(6)	122.3 (10)
C(3)–Fe(2)–C(5)	73.6 (5)	C(4)–C(5)–C(8)	118.2 (10)
C(3)–Fe(2)–C(6)	93.0 (5)	C(6)–C(5)–C(8)	119.2 (10)
C(4)–Fe(2e–C(5)	37.8 (4)	Fe(1)–C(6)–Fe(2)	81.8 (5)
C(4)–Fe(2)–C(6)	72.2 (5)	Fe(1)–C(6)–C(5)	134.6 (9)
C(5)–Fe(2)–C(6)	39.5 (4)	Fe(2)–C(6)–C(5)	75.1 (7)
Fe(1)–C(1)–O(1)	176.8 (12)		

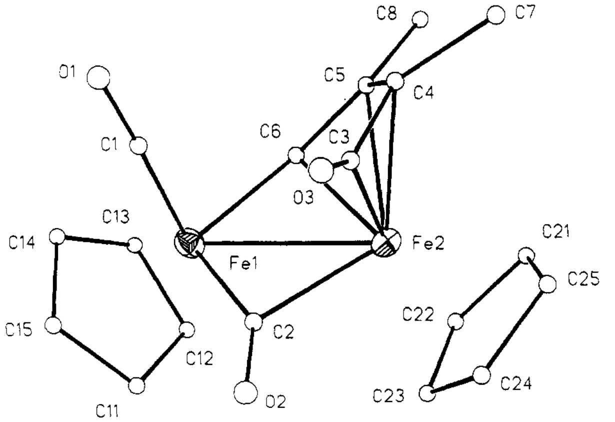

Figure 1. Perspective view of 2 showing the numbering scheme, 50% probability thermal ellipsoids for iron atoms, and arbitrarily sized circles for carbon and oxygen atoms (PF_6^- omitted for clarity).

Since neither of the two expected products was observed and a new functional group was present, we employed single-crystal X-ray diffraction for structure determination. Because of twinning and other difficulties with the X-ray structure determination, the final R_w was 0.090 and small differences between bond lengths are probably not experimentally significant. Nevertheless, the structure of 2 was clearly established as the μ-η^1,η^4-vinylketene complex $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHC(CH_3)C(CH_3)CO)^+PF_6^-$ (Table I). As seen in Figure 1, 2-butyne has been inserted between the methylidyne carbon [C(6)] and a carbonyl carbon [C(3)] and all four of these carbons are π-bonded to Fe(2). The distances from Fe(2) to the carbons derived from 2-butyne are somewhat longer [2.15 Å to C(5) and 2.14 Å to C(4)] than those to the terminal carbons of this η^4 system [2.02 Å to C(6) and 1.96 Å to C(3)]. The carbon–carbon bond lengths of this η^4 system [1.39 (2) to 1.44 (2) Å] indicate substantial double-bond character between all adjacent carbons. The bond distance from the semibridging carbonyl carbon to Fe(1) that also bears a terminal CO ligand is substantially shorter than to Fe(2) that bears the η^4 ligand [Fe(1)–C(2), 1.85 Å; Fe(2)–C(2), 2.09 Å], and the angle between Fe(1)–C(2)–O(2), 147.6°, is

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

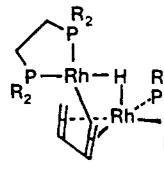
(3) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.

Table II. Summary of Crystal Data and Intensity Collection

formula (mol wt)	$C_{18}H_{17}Fe_2O_3P$ (538.02)
space group	$P2_1/c$
cryst system	monoclinic
cell consts	
a, Å	7.576 (3)
b, Å	19.053 (8)
c, Å	13.439 (9)
β, deg	101.03 (4)
crystl dimens, mm	0.72 × 0.34 × 0.07
V, Å^3	1904 (2)
Z	4
temp, K	178 (5)
radiatn	Mo Kα (λ = 0.71069 Å)
abs coeff, μ, cm^{-1}	16.80
scan type	θ–2θ
scan speed, deg/min	3.0–24.0
scan range, deg	$2\Theta_{K_{\alpha1}} - 2\Theta_{K_{\alpha2}} + 2$
bkgd/scan time ratio	0.33
data collected	3.0–30.0° ($+h,\pm k,\pm l$); 30.0–45.0° ($+h,+k,\pm l$)
unique data	2487
unique data ($F_o > 3\sigma(F_o)$)	1895
no. of variables	172
goodness of Fit	1.73
R	0.083
R_w	0.090

substantially wider than that between Fe(2)–C(2)–O(2), 130.1°.

The closest analogue of 2 that we are aware of is the η^1,η^4-diene dirhodium complex 3 reported by Fryzuk.[4]



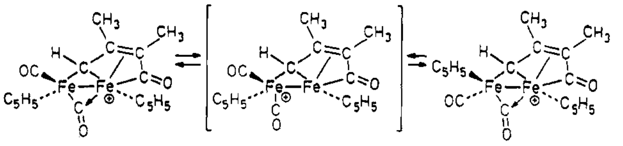
3, R = i-Pr

To obtain semiquantitative information on the relative reactivity of alkynes such as 2-butyne compared with alkenes such as *trans*-2-butene, the reaction of 1 with a fourfold excess of 2-butyne was followed by ^{1}H NMR at −55 °C until more than half of 1 was converted to 2. During this interval, the 2-butyne concentration was observed to drop by about 25%. A crude pseudo-first-order rate constant was calculated to be $k_{obsd} = (5 \pm 1) \times 10^{-5}$ s^{-1}. Using an average 2-butyne concentration, we estimated the second-order rate constant to be $k_2 = 3 \times 10^{-3}$ M^{-1} s^{-1} at −55 °C. This is similar to the rate of reaction of 1 with *trans*-2-butene which leads to a μ-alkylidyne complex ($k_2 = 9.2 \times 10^{-3}$ M^{-1} s^{-1} at −50 °C).[2]

When a sample of 2 was dissolved in acetone-d_6 at −78 °C, ^{1}H NMR spectroscopy at −77 °C showed the presence of only one (>96%) NMR-detectable isomer with singlets at δ 13.49 (CH), 6.00 (C_5H_5), 5.48 (C_5H_5), 2.80 (CH_3), and 1.77 (CH_3). Upon warming to −35 °C, a second minor isomer (16%) with singlets at δ 12.36, 5.22, 5.02, 2.74, and 1.71 was observed. Upon further warming to 23 °C, the amount of the minor isomer increased to 26%.

This mixture of isomers was shown to be in dynamic equilibrium by spin saturation transfer[5,6] studies carried out at −8 °C. This was accomplished by irradiating the δ 5.89 (Cp) resonance of the major isomer with a 2-mW saturation pulse for a variable length of time and monitoring the decay of the δ 5.02 (Cp) resonance of the minor isomer. For example, with a 0.5-s saturating pulse, the δ 5.02 resonance decreased in intensity by 25%. The first-order rate constant for the conversion of the minor isomer to the major isomer was found to be 0.6 ± 0.2 s^{-1} at −8 °C which corresponds to $\Delta G^{\ddagger}$ = 15.7 kcal mol^{-1}.

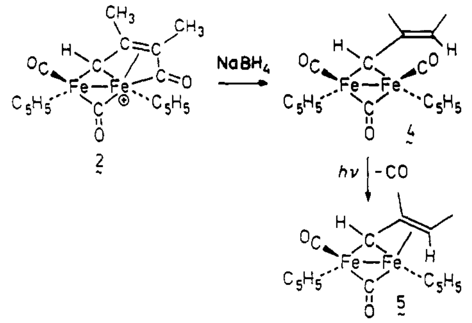
This isomerization probably occurs by release of the semibridging carbonyl from the iron bearing the η^4-ligand and then reestablishing a semibridging interaction to the other carbonyl group. The overall transformation results in conversion of the major isomer with cis Cp groups into the minor isomer with trans Cp groups.



cis-2 trans-2

Attempted deprotonation of the cationic 2-butyne adduct 2 with NMe_3, $LiN(SiMe_3)_2$, or aqueous bicarbonate led to the destruction of starting material, but we were unable to isolate neutral diiron species from the reaction mixtures.

Reaction of $NaBH_4$ with 2 led to the isolation of the neutral light-sensitive vinylcarbene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}CHC(CH_3){=}CHCH_3)$ (4) in 65% isolated yield.[7] This remarkable transformation involves hydride addition to the carbon α to the carbonyl group of the η^4-ligand of 2, cleavage of the short (1.44 Å) carbon–carbon bond linking the carbonyl group to the η^4-ligand, and conversion of this carbonyl group back to a terminal CO ligand. In the ^{1}H NMR of 4, the resonance for the proton on the bridging carbene carbon appears characteristically far downfield at δ 11.8 and the resonance for the vinyl hydrogen of the uncomplexed double bond appears as a quartet at δ 6.2 coupled to the methyl group that appears as a doublet at δ 1.82.



Exposure of 4 to fluorescent laboratory light led to loss of CO and formation of the η^3-vinylcarbene complex $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}(E)\text{-}CHC(CH_3){=}CHCH_3)$ (5).[8] Pure 5 was obtained in 22% isolated yield by photolysis of an ether solution of 4. Upon complexation of the double bond, the quartet for the vinyl hydrogen is shifted far upfield to δ −0.69. A similar upfield chemical shift seen previously for the terminal vinyl hydrogen with a large trans vinylic coupling constant in $(C_5H_5)_2(CO)Ru_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}CH_2)$[9] suggested that 5 possessed the

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[4] Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *J. Chem. Soc., Chem. Commun.* **1984**, 1556–1558.

[5] Martin, M. L.; Delpuch, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heydon: London 1980; pp 315–322.

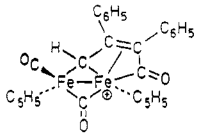
[6] Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705.

[7] 4 was previously observed as one component of the product mixture obtained from reaction of 1 with 2-butene followed by deprotonation with NMe_3.[8]

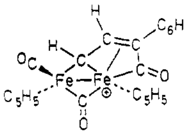
[8] Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Bly, R. K.; Fagan, P. J. *Organometallics* **1986**, *5*, 1873–1879.

E configuration of the complexed double bond. The *E* configurational assignment of **5** was confirmed by observation of nuclear Overhauser effects in the NMR of **5**. Irradiation of the methyl singlet at δ 1.8 led to a 9.4% enhancement of the resonance at δ 11.4 due to the proton on the bridging carbon and only a 2.0% enhancement of the vinyl resonance at δ –0.69.

Reaction of 1 with Diphenylacetylene, Phenylacetylene, and Propyne. The reaction of methylidyne complex 1 with diphenylacetylene in CH_2Cl_2 also produced a solid μ-η^1,η^4-vinylketene complex. A 62:38 ratio of the cis and trans cyclopentadienyl isomers of $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHC(C_6H_5)C(C_6H_5)CO)^+PF_6^-$ (6) was isolated in 81% yield as an olive green monoacetone solvate, after crystallization from acetone–hexane. The ^1H NMR resonances at δ 13.7 and 12.7 for the protons on the bridging carbons of the two isomers of 6 and the IR band at 1770 cm^{-1} established that 6 possessed an η^1,η^4-vinylketene functionality similar to that found for 2.



6



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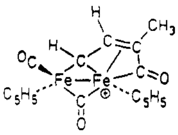


8

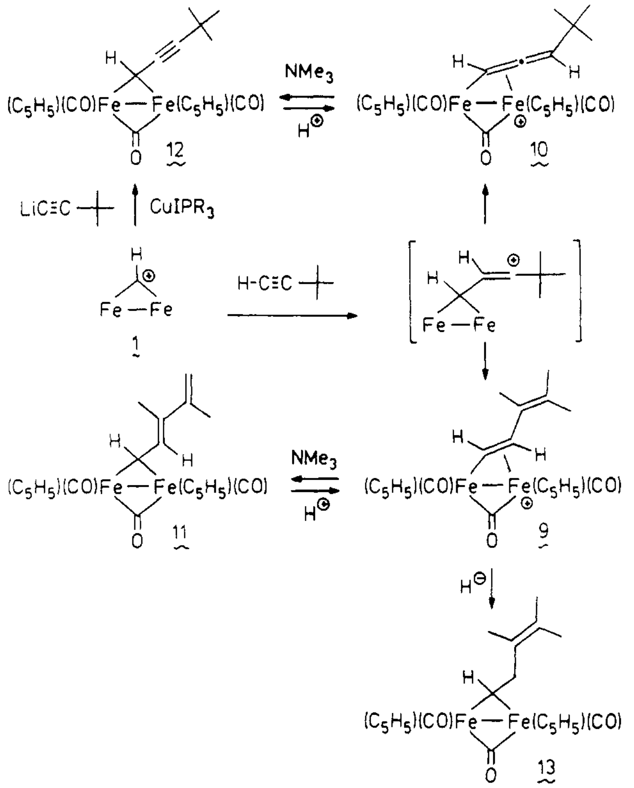
Phenylacetylene reacted with 1 to form the η^1,η^4-vinylketene complex $(C_5H_5)_2(CO)Fe_2(\eta\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHCHC(C_6H_5)CO)^+PF_6^-$ (7) in which the methylidyne carbon added regioselectively to the unsubstituted alkyne carbon. A 75:25 ratio of the cis and trans cyclopentadienyl isomers of 7 was isolated as a brown powder in 79% yield. The presence of vicinal coupling (J = 7.5 Hz) between the proton on the bridging carbon at δ 13.7 and the proton on the adjacent carbon at δ 8.2 established the regiochemistry of the reaction product. The regioselective addition of the methylidyne carbon of 1 to the less substituted carbon of alkenes was seen previously.[2,3]

The reaction of 1 with propyne in CD_2Cl_2 was examined by ^1H NMR. The presence of major resonances at δ 13.58 (d, J = 7.3 Hz) and at δ 7.58 (d, J = 7.3 Hz) was consistent with the formation of the regioisomer $(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHCHC(CH_3)CO)^+PF_6^-$ (8) in which the methylidyne carbon added to the unsubstituted alkyne carbon. ^1H NMR indicated that 8 constituted approximately 16% of the mixture of products. 8 was not isolated from this complex mixture.

Reaction of 1 with *tert*-Butylacetylene. In contrast to the reactions of 1 with 2-butyne, diphenylacetylene, phenylacetylene, and propyne that produced μ-η^1,η^4-vinylketene complexes, the reaction of 1 with *tert*-butylacetylene gave an 80:20 ratio of two quite different products in 88% isolated yield. The major product was shown to be the μ-η^1,η^2-dienyl complex $[(C_5H_5)(CO)Fe]_2(\eta\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3){=}C(CH_3)_2)^+PF_6^-$ (**9-PF$_6$**) and the minor product was shown to be the μ-η^1,η^2-allenyl complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CHC(CH_3)_3)^+PF_6^-$ (**10-PF$_6$**). While **9-PF$_6$** and **10-PF$_6$** were not directly separable, each was isolated as a pure material by sequences of reactions outlined in Scheme I.

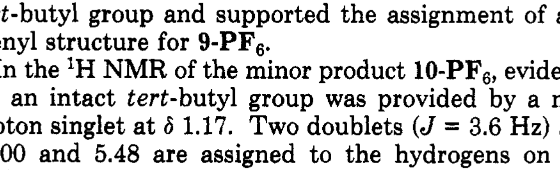
The formation of the major product **9-PF$_6$** involves the regioselective electrophilic addition of the methylidyne carbon of 1 to the unsubstituted acetylenic carbon of *tert*-butylacetylene and migration of a methyl group from the *tert*-butyl moiety to the substituted alkyne carbon. The formation of the minor product **10-PF$_6$** also involves regioselective addition of the methylidyne carbon of 1 to *tert*-butylacetylene, but in this case hydrogen migrates from the unsubstituted acetylenic carbon to the substituted alkyne carbon to produce a μ-allenyl system.

Scheme I



In the ambient-temperature ^1H NMR of the major product **9-PF$_6$**, doublets (J = 12.8 Hz) at δ 12.16 and 5.15 and a single broad cyclopentadienyl resonance at δ 5.62, all characteristic of a fluxional μ-alkenyl complex,[8] were observed. In addition, the observation of three singlets at δ 2.18, 1.94, and 1.88 for methyl groups attached to double-bonded carbons attested to the disruption of the *tert*-butyl group and supported the assignment of a μ-dienyl structure for **9-PF$_6$**.

In the ^1H NMR of the minor product **10-PF$_6$**, evidence for an intact *tert*-butyl group was provided by a nine proton singlet at δ 1.17. Two doublets (J = 3.6 Hz) at δ 12.00 and 5.48 are assigned to the hydrogens on the bridging carbon and terminal carbon of a μ-allenyl system. The small 3.6-Hz coupling of the allenyl protons is similar to that seen for other allene complexes.[10] The two cyclopentadienyl singlets seen for **10-PF$_6$** at δ 5.85 and 5.60 cannot be taken as evidence for a static μ-allenyl unit since a fluxional μ-allenyl isomerization would not exchange the environment of the two C_5H_5 groups.



10 10

When the mixture of **9-PF$_6$** and **10-PF$_6$** obtained from reaction of 1 with *tert*-butylacetylene was treated with NMe_3, the ^1H NMR spectrum of the product mixture showed that deprotonation had occurred to give an 82:18

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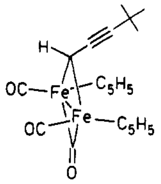
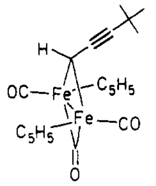
mixture of the two neutral diiron complexes $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}C(CH_3)C(CH_3){=}CH_2)$ (**11**) and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC{\equiv}CC(CH_3)_3)$ (**12**).

The major neutral product **11** was obtained as a pure maroon powder in 39% yield after flash chromatography. **11** is the product of deprotonation at a remote methyl group of **9-PF$_6$**. The structure of **11** was established by ^1H NMR and IR spectroscopy. The observation of a doublet ($J = 1.7$ Hz) at δ 5.16 and a broad singlet at δ 4.98 was taken as evidence for a $C{=}CH_2$ unit.

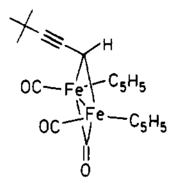
There are three possible geometric isomers of the alkyne–carbene complex **12**: *cis,anti*-**12** in which the alkyne unit is anti to cis carbonyl groups on iron, *cis,syn*-**12** in which the alkyne unit is syn to cis carbonyls on iron, and *trans*-**12** which has trans carbonyls on iron. All three isomers were observed by ^1H NMR. *trans*-**12** was present as 12% of the mixture, and its structure was readily assigned since it has two Cp resonance at δ 4.80 and 4.75. The two cis isomers were present in 82 and 6%, respectively. The major cis isomer has a Cp singlet at δ 4.86, a carbene CH singlet at δ 10.57, and a *t*-Bu singlet at δ 1.13 and is tentatively assigned as the less crowded *cis,syn*-**12** structure. The minor cis isomer has a Cp resonance at δ 4.84.



cis, anti-12



trans-12



cis, syn-12

The assignment of **12** as an alkyne carbene complex was confirmed by independent synthesis. Treatment of a CH_2Cl_2 solution of **1** and a catalytic amount of $CuIP(n\text{-}C_4H_9)_3$ with a diethyl ether solution of $LiC{\equiv}CC(CH_3)_3$ produced **12** in 20% isolated yield. The initially isolated product consisted of a 75:13:12 ratio of the *cis,anti*-**12**:*trans*-**12**:*cis,syn*-**12** isomers. This mixture reached an equilibrium ratio of 31:11:58 after 9 h at 35 °C.

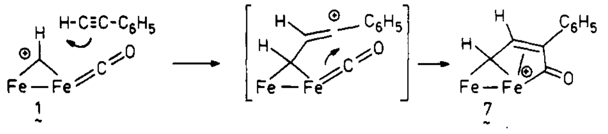
Protonation of the diene carbene complex **11** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 occurred at the remote double bond to produce the μ-dienyl complex **9-BF$_4$** which was isolated as a pure red-brown powder in 69% yield. The IR and ^1H NMR spectra of **9-PF$_6$** and **9-BF$_4$** were very similar.

Protonation of the acetylene carbene complex **12** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 afforded the μ-allenyl complex **10-BF$_4$** in 61% isolated yield. The ^1H NMR spectra of **10-BF$_4$** and **10-PF$_6$** were very similar.

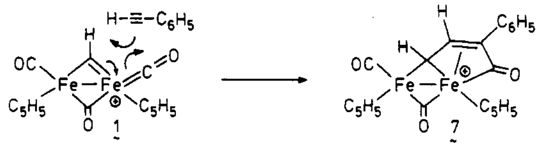
When the mixture of products obtained from the reactions of **1** with *tert*-butylacetylene was treated with $NEt_4{}^+HFe(CO)_4{}^-$, the major μ-dienyl product **9-PF$_6$** was converted to the allyl carbene complex **13** in 53% yield by regioselective hydride addition to the complexed double bond.

Discussion

Phenylacetylene, diphenylacetylene, and 2-butyne all reacted cleanly with **1** to form 1:1 addition products in which the alkyne was inserted between the methylidyne carbon and a terminal CO ligand to produce a novel η^1,η^4-vinylketene unit. The regiochemistry of the addition of the methylidyne carbon of **1** to the unsubstituted carbon of phenylacetylene is similar to the regiochemistry of the addition of **1** to alkenes[2,3] and suggests that the reaction of **1** with alkynes is initiated by an electrophilic addition of the methylidyne carbon to the alkyne to produce a vinyl cation-like intermediate or transition state. In the case of the reaction of **1** with alkenes, the carbocation intermediate is trapped either by a 1,3 migration of hydrogen from the methylidyne carbon to the cationic center to produce a μ-alkylidyne complex or by a 1,2 migration of carbon or hydrogen to the cationic center to produce a μ-alkenyl complex. For these alkyne reactions, the vinyl cation intermediate is trapped by a terminal carbonyl on iron. This trapping reaction can be viewed as an electrophilic attack of a vinyl cation on the iron–carbon double bond of an $Fe{=}CO$ system. Ordinarily, electrophiles attack terminal metal carbonyls at oxygen[11] and nucleophiles such as RLi[12] and R_3BH^-[13] attack carbonyls at carbon. The fact that the alkyne ends up π-complexed to iron (in addition to the two new carbon–carbon σ-bonds) may be responsible or this reversal of a normal reactivity pattern. It should be mentioned that $M{=}CR_2$ double bonds of carbene complexes are attacked by coordinatively unsaturated metal complexes acting as electrophiles[14] and that bridging carbonyl groups can be formed by addition of electrophilic coordinatively unsaturated metals to $M{=}CO$ units.



Alternatively, the reaction of **1** with alkynes may be viewed as a concerted 2 + 2 + 2 cycloaddition. Examination of models indicates that one approach of the alkyne to **1** would allow simultaneous formation of both new carbon–carbon σ-bonds and the new π-complex to the iron center. Indeed, very little movement of the methylidyne and terminal carbonyl ligands of **1** is required for the formation of the η^1,η^4-vinylketene system.



In the case of the reaction of **1** with *tert*-butylacetylene, the steric bulk of the *tert*-butyl group apparently prevents cyclization onto a terminal carbonyl group and two other processes are observed. In the first, the initially formed vinyl cation intermediate undergoes a 1,2-hydride shift to form the new μ-allenyl complex **10-PF$_6$**. Similar 1,2-hydride shifts were observed in the reaction of **1** with some alkenes that formed μ-alkenyl complexes.[3] In a second competing process, a methyl group migrates from the *tert*-butyl group to the vinyl cation center to produce the μ-dienyl product **9-PF$_6$**. In the reactions of alkenes with **1**, migrations to the cationic center from the carbon between the bridging carbon and the cationic carbon have been observed; this migration leads directly to a μ-alkenyl complex.[3] In the case of the formation of **9-PF$_6$**, migration occurs from a center remote from the bridging carbon but again a stable μ-alkenyl complex is formed.

The η^1,η^4-vinylketene system formed in these reactions is very unusual and is difficult to formulate in simple

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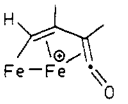
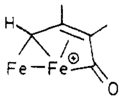
(13) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1–38.

(14) (a) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A.; *J. Chem. Soc., Dalton Trans.* **1980**, 1593–1600. (b) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward P. *J. Chem. Soc., Dalton Trans.* **1981**, 743–750.

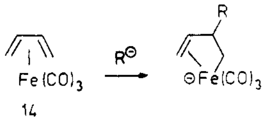
valence-bond terms that can adequately explain the observed bond lengths and the site of reaction of **2** with BH_4^-. The resonance structures I and II can for the similar bond lengths seen for the three carbon–carbon bonds of the η^1,η^4 system. However, neither formulation helps to explain the site of hydride addition to the ligand that occurs at the carbon α to the carbonyl. The α,β-unsaturated ketone formulation II would suggest attack at the carbonyl carbon or at the carbon β to the carbonyl group; vinylketene formulation I would suggest attack at the ketene carbonyl group. The only remote analogy to the regiochemistry observed here is Semmelhack's observation that diene iron complexes such as **14** are attacked by powerful nucleophiles at an internal carbon of the diene.[15]



I



II



14

The regiochemistry of hydride attack on **2** is so difficult to understand that the possibility of kinetic hydride attack at iron or a metal carbonyl followed by rearrangement must be given serious consideration. For example, a reviewer suggested that hydride attack at iron accompanied by release of the alkene unit could give an intermediate acyl iron complex. Acyl to alkyl conversion followed by reductive elimination of carbon and hydrogen could then lead to **4**.

Experimental Section

General Data. ^1H NMR spectra were obtained on a Brucker WP200 or WP270 spectrometer. Decoupled ^{13}C NMR spectra from samples containing 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent were obtained on a JEOL FX 200 spectrometer (50.10 MHz) or a Brucker AM500 spectrometer (125 MHz). In cases where indicated, coupled ^{13}C NMR spectra were also obtained. Infrared spectra were measured on a Beckman 4230 infrared spectrometer. Mass spectra were determined on a Kratos MS-80. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard Schlenk techniques. Diethyl ether, THF, C_6H_6, C_6D_6, and hexane were distilled immediately prior to use from purple solutions of sodium and benzophenone. CH_2Cl_2 and acetone were dried over P_2O_5 and B_2O_3, respectively. CD_3CN was dried over CaH_2.

$(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHC(CH_3)C(CH_3)CO)^+PF_6^-$ (2). A 10-fold excess of 2-butyne (0.17 atm, 0.53 L, 24 °C, 3.7 mmol), dried over sodium, was vacuum transferred into a red suspension of **1** (182 mg, 0.38 mmol) in 8 mL of CH_2Cl_2 at −78 °C. The suspension was stirred for 30 min at ambient temperature, and solvent was evaporated under high vacuum. The brown residue was dissolved in 8 mL of acetone and filtered. Addition of 8 mL of diethyl ether to the acetone solution resulted in precipitation of a 74:26 ratio of two isomers of **2** (153 mg, 76%) as a dark brown solid. ^1H NMR (200 MHz, acetone-d_6, 23 °C): major isomer, δ 13.56 (s, μ-CH), 5.89 (s, C_5H_5), 5.36 (s, C_5H_5), 2.80 (s, CH_3), 1.78 (s, CH_3); minor isomer, δ 12.36 (s, μ-CH), 5.22 (s, C_5H_5), 5.02 (s, C_5H_5), 2.74 (s, CH_3), 1.71 (s, CH_3). ^{13}C NMR (50.1 MHz, CD_3CN, −30 °C): major isomer, δ 238.6, 226.6 (μ-CO, acyl CO), 205.7 (CO), 185.2 (d, J = 161 Hz, μ-CH), 93.6 (d, J = 187 Hz, C_5H_5), 91.2 (d, J = 183 Hz, C_5H_5), 124.4, 29.1 ($CH_3C{=}CCH_3$), 23.3 (q, J = 128 Hz, CH_3), 15.7 (q, J = 132 Hz, CH_3); minor isomer, δ 229.8, 228.1 (μ-CO, acyl CO), 205.3 (CO), 176.8 (d, J = 169 Hz, μ-CH), 90.6 (d, C_5H_5), 90.3 (d, C_5H_5), 34.8 ($CH_3C{=}CCH_3$), 22.3, 15.5 (CH_3), $CH_3C{=}CCH_3$ not observed. IR (Nujol): 2010 (s), 1867 (s), 1770 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{17}F_6Fe_2O_3P$: C, 40.19; H, 3.19; P, 5.76. Found: C, 40.05; H, 3.27; P, 5.82.

Kinetics of Reaction of 1 with 2-Butyne. On a high vacuum line, C_6H_6 (7 mm, 8.96 mL, 21 °C, 3.4 μmol, internal standard), 2-butyne (17 mm, 8.96 mL, 21 °C, 8.3 μmol), and CD_2Cl_2 (0.42 mL) were condensed into an NMR tube containing **1** (1 mg, 2.1 μmol). The tube was sealed under vacuum, agitated, centrifuged at −78 °C, and placed in a precooled (−55 ± 1 °C) 270-MHz NMR probe. The concentration of 1, [**1**] × 10^3 M (time in minutes) was found to be 4.90 (4.2), 4.19 (34.2), 3.78 (64.2), 3.75 (94.2), 3.28 (124.2), 3.02 (154.2), 2.85 (184.2), 2.53 (214.2), and 2.15 (244.2). Over the same time interval, the 2-butyne concentration dropped from 1.98 to 1.48 × 10^{-2} M. A plot of ln [**1**] vs. time yielded a straight line with slope $k_{obsd} = (5 \pm 1) \times 10^{-5}\ s^{-1}$. With an average [2-butyne] = 1.73 × 10^{-2} M, a second-order rate constant $k_2 = 3 \times 10^{-3}\ M^{-1}\ s^{-1}$ was calculated.

Saturation Transfer Measurement[5,6] of Rate of Conversion of *trans*-2 to *cis*-2. The experiment was performed at 265 ± 1 K by quickly saturating the magnetization of the δ 5.89 (C_5H_5) resonance of *cis*-**2** and monitoring the decay of the δ 5.02 (C_5H_5) resonance of *trans*-**2**. The δ 5.89 resonance was saturated with a 26-ms pulse at 2 mW followed by a variable-length pulse at 2 mW to maintain saturation. The decoupler was then gated off, and data were accumulated for 2.33 s. A 30-s relaxation delay was included between each scan. Magnetizations of the δ 5.02 resonance in arbitrary units (length of saturating pulse in seconds) were found to be 7.98 (0.0001), 7.73 (0.1), 7.05 (0.3), 5.97 (0.5), 5.27 (0.75), 4.57 (1.0), 3.62 (1.5), 2.28 (3.0), 1.75 (5.0), and 1.61 (10.0).

The data was analyzed in terms of eq 1, where $M(t)$ is the magnetization at time t, M_0 is the magnetization in the absence of a saturation pulse, $M_\infty = M_0\ (\tau_1/T_1)$ is the steady-state magnetization in the presence of a saturating pulse. τ is the average lifetime of a spin at the observation site, T_1 is the spin-lattice relaxation time of the observed magnetization, and $1/\tau_1 = 1/\tau + 1/T_1$.

$$M(t) = M_\infty + M_0(\tau_1/\tau)\exp(-t/\tau_1) \qquad (1)$$

The values of τ and τ_1 were obtained by an iterative nonlinear fitting routine of eq 1 where M_∞ was varied to generate the best fit. The final estimates were $\tau_1 = 1.3 \pm 0.4$ s and $\tau = 1.6 \pm 0.7$ s. The rate constant for *trans*-**2** → *cis*-**2** is $k = 0.6 \pm 0.2\ s^{-1}$.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}CHC(CH_3){=}CHCH_3)$ (4). Since **4** is readily converted to **5** in laboratory light, this entire procedure was run in the dark. Acetone (25 mL) was vacuum transferred onto solid **2** (300 mg, 0.56 mmol) and solid $NaBH_4$ (80 mg, 2.1 mmol). The resulting solution was stirred for 15 min at room temperature. Solvent was evaporated under high vacuum. The residue was dissolved in 20 mL of diethyl ether and filtered. The ether solution was passed through a 3-cm alumina column and evaporated under high vacuum to give **4** (143 mg, 65%) as a red powder: ^1H NMR (270 MHz, C_6D_6) δ 11.79 (s, μ-CH), 6.02 (q, J = 7.1 Hz, C=CH), 4.19 (s, 10 H, C_5H_5), 2.17 (s, CH_3), 1.82 (d, J = 7.1 Hz, CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, acetone-d_6, −30 °C) δ 273.4 (μ-CO), 214.5 (CO), 177.0 (μ-C), 158.6, 116.5 (C=C), 88.7 (C_5H_5), 19.9, 14.5 (CH_3); IR (CH_2Cl_2) 1988 (s), 1938 (sh), 1778 (s) cm^{-1}; HRMS, calcd for $C_{18}H_{18}Fe_2O_3$ 393.9949, found 393.9954. Anal. Calcd for $C_{18}H_{18}Fe_2O_3$: C, 54.86; H, 4.61. Found: C, 54.68; H, 4.50.

$(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHC(CH_3){=}CHCH_3)$ (5). A mixture of **2** (152 mg, 0.282 mmol) and $NaBH_4$ (40 mg, 1.056 mmol) in 20 mL of acetone was stirred for 45 min at ambient temperature. Solvent was evaporated under vacuum, and the residue was dissolved in diethyl ether (25 mL). The resulting red solution was filtered and photolyzed in a Rayonet photochemical reactor (maximum emission at 350 nm) for 40 min. Solvent was evaporated, and the residue was chromatographed (activity I alumina, diethyl ether). The material obtained from the green-brown first fraction was crystallized from ether–hexane at −30 °C to give **5** (23 mg, 22%) as a brown powder: ^1H NMR (270 MHz, C_6D_6) δ 11.42 (s, μ-CH), 4.26 (s, C_5H_5), 3.94 (s, C_5H_5), 1.81 (s, CH_3),

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[15] Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885–1888.

1.03 (d, *J* = 6.4 Hz, CH_3), −0.69 (q, *J* = 6.4 Hz, 1 H, C═CH); $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6) δ 270.4 (μ-CO), 217.8 (CO), 172.7 (μ-C), 97.0, 56.3 (C═C), 87.1, 84.0 (C_5H_5), 23.2, 18.4 (CH_3); IR (CH_2Cl_2) 1943 (s), 1766 (s) cm^{-1}; HRMS, calcd for $C_{17}H_{18}Fe_2O_2$ 366.0005, found 365.9995. Anal. Calcd for $C_{17}H_{18}Fe_2O_2$: C, 55.78; H, 4.97. Found: C, 55.40; H, 4.90.

$(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHC(C_6H_5)C(C_6H_5)CO)^+PF_6^-$ (6). A mixture of 1 (200 mg, 0.41 mmol) and diphenylacetylene (146 mg, 0.82 mmol) in 20 mL of CH_2Cl_2 was stirred at ambient temperature for 20 min. Solvent was evaporated under vacuum, and the residue was recrystallized twice by dissolving in 10 mL of acetone and precipitating by addition of 15 mL of hexane to give a 62:38 mixture of two isomers of **6** (221 mg, 81%) as an olive green powder: ^1H NMR (270 MHz, acetone-d_6) δ 13.75 (s, μ-CH, major isomer), 12.69 (s, μ-CH, minor isomer), 7.7–7.1 (m, C_6H_5), 6.14 (s, C_5H_5 major isomer), 5.56 (s, C_5H_5 major isomer), 5.43 (s, C_5H_5 minor isomer), 5.30 (s, C_5H_5 minor isomer), 2.08 (s, acetone of solvation); $^{13}C\{^1H\}$ NMR (50.1 MHz, CD_3NO_2, −15 °C) δ 231.6, 230.2, 222.4, 209.8, 209.2, 205.1 (CO), 184.9, 179.2 (μ-CH), 138.5, 138.1 (ipso), 132.6, 131.8, 131.2, 130.3, 129.8 (aryl), 94.5, 91.6, 91.1 (C_5H_5), 125.3, 124.7, 37.6, 32.5 (C═C), 31.0 (acetone of solvation); IR (Nujol) 2032 (s), 1920 (m), 1770 (m), 1712 (m, acetone solvate) cm^{-1}. Anal. Calcd for $C_{31}H_{27}F_6Fe_2PO_4$: C, 51.69; H, 3.79. Found: C, 51.74; H, 3.58.

$(C_5H_5)_2(CO)Fe_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^4\text{-}CHCHC(C_6H_5)CO)^+PF_6^-$ (7). Freshly distilled phenylacetylene (42 mg, 0.41 mmol) was added via syringe to 1 (100 mg, 0.21 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred 20 min at ambient temperature. The resulting red-brown solution was evaporated under high vacuum. The residue was recrystallized twice from acetone–hexane to give a 75:25 mixture of isomers of 7 (97 mg, 79%) as a brown powder: ^1H NMR (270 MHz, acetone-d_6) δ 13.74 (d, *J* = 7.5 Hz, μ-CH major isomer), 12.67 (d, *J* = 6.0 Hz, μ-CH minor isomer), 8.22 (d, *J* = 7.5 Hz, Fe_2CHC*H*═C major isomer), 8.10 (d, *J* = 6.0 Hz, Fe_2C-HC*H*═C minor isomer), 7.88 (m), 7.52 (m) (C_6H_5), 6.00 (s, C_5H_5 major isomer), 5.31 (s, C_5H_5 major isomer), 5.17 (s, C_5H_5 minor isomer), 5.16 (s, C_5H_5 minor isomer); ^{13}C NMR (50.1 MHz, CD_3NO_2, −10 °C) δ 237.7, 232.9, 230.4, 227.4, 205.6 (CO), 186.3 (d, *J* = 165 Hz, μ-CH major isomer), 178.9 (d, *J* = 169 Hz, μ-CH minor isomer), 131.5, 131.0, 129.7 (C_6H_5), 94.4 (d, *J* = 183 Hz, C_5H_5 major isomer), 91.8 (d, *J* = 183 Hz, C_5H_5 major isomer), 91.4 (d, *J* = 187 Hz, C_5H_5 minor isomer), 91.2 (d, *J* = 187 Hz, C_5H_5 minor isomer), 105.7 (d, *J* = 165 Hz, ═CH minor isomer), 104.4 (d, *J* = 165 Hz, ═CH major isomer), 37.0 (═CPh, minor isomer), 31.2 (═CPh, major isomer); IR (Nujol) 2030 (s), 1866 (s), 1788 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{17}F_6Fe_2O_3P$: C, 45.08; H, 2.93. Found: C, 44.98; H, 3.00.

Reaction of 1 with *tert*-Butylacetylene. A tenfold excess of *tert*-butylacetylene (0.20 atm, 0.53 L, 24 °C, 4.3 mmol) was vacuum transferred into a stirred red suspension 1 (209 mg, 0.43 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The mixture was stirred for 15 min at ambient temperature. Solvent was evaporated, and the residue was dissolved in 10 mL of acetone. Addition of 20 mL of hexane produced a dark brown precipitate (214 mg, 88%). ^1H NMR (270 MHz, acetone-d_6) showed that the precipitate was a 80:20 mixture of **9-PF$_6$** and **10-PF$_6$**. Peaks assigned to $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3){=}C(CH_3)_2{}^+PF_6$ (**9-PF$_6$**): δ 12.16 (d, *J* = 12.8 Hz, μ-C*H*═CH), 5.62 (s, 10 H, C_5H_5), 5.15 (d, *J* = 12.4 Hz, μ-CH═C*H*), 2.18 (s, CH_3), 1.94 (s, CH_3), 1.88 (s, CH_3). Peaks assigned to $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CHC(CH_3)_3)^+PF_6^-$ (**10-PF$_6$**): δ 12.00 (d, *J* = 3.7 Hz, μ-CH═C), 5.85 (s, C_5H_5), 5.60 (s, C_5H_5), 5.48 (d, *J* = 3.6 Hz, μ-CH═C═C*H*), 1.17 (s, *t*-Bu).

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH{=}C(CH_3)C(CH_3){=}CH_2)$ (11). NMe_3 (0.39 atm, 0.53 L, 24 °C, 8.6 mmol) was vacuum transferred into a CH_2Cl_2 solution (20 mL) containing a mixture of **9-PF$_6$** and **10-PF$_6$** (400 mg, 0.71 mmol) obtained from reaction of 1 with *tert*-butylacetylene. The reaction mixture was stirred for 20 min at ambient temperature and filtered to remove a white precipitate. The solution was evaporated, and the residue was purified by flash chromatography (silica gel, 1:1 hexane–CH_2Cl_2). Evaporation of the maroon second band gave **11** (117 mg, 39%) as a maroon powder: ^1H NMR (270 MHz, acetone-d_6) δ 12.11 (d, *J* = 13.0 Hz, μ-CH), 7.05 (d, *J* = 13.1 Hz, CH═C), 5.16 (d, *J* = 1.7 Hz, C═C*H*H), 4.98 (br s, C═CH*H*) 4.91 (s, 10 H, C_5H_5), 2.25 (s, CH_3) 1.87 (s, CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, acetone-d_6, −30 °C) δ 271.6 (μ-CO), 214.4 (CO), 156.9, 156.7, 145.3, 121.7, 112.0 (μ-C, C═CC═C), 88.2 (C_5H_5), 20.9, 13.5 (CH_3); IR (CH_2Cl_2) 1970 (s), 1936 (m), 1774 (s) cm^{-1}; HRMS, calcd for $C_{20}H_{20}O_3Fe_2$ 420.0105, found 420.0094. Anal. Calcd for $C_{20}H_{20}O_3Fe_2$: C, 57.18; H, 4.81. Found: C, 56.91; H, 4.88.

$[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CHC(CH_3){=}C(CH_3)_2)^+BF_4^-$ (9-BF$_4$). $HBF_4 \cdot OEt_2$ (33.5 μL, 0.27 mmol) was added to a CH_2Cl_2 (20 mL) solution of **11** (113 mg, 0.27 mmol) at 0 °C. The solution was concentrated to 3 mL, and 20 mL of hexane was vacuum transferred into the reaction flask. Solvent was decanted from a dark red-brown oil. When the oil was placed under high vacuum, a flocculant solid was produced. The solid was triturated by stirring in hexane for 16 h, isolated by filtration, washed with hexane, and dried under vacuum to give **9-BF$_4$** (95 mg, 69%) as a dark red-brown powder: ^1H NMR (270 MHz, acetone-d_6) δ 12.18 (d, *J* = 12.2 Hz, μ-CH), 5.62 (s, 10 H, C_5H_5), 5.14 (d, *J* = 12.2 Hz, ═CH), 2.17, 1.93, 1.87 (CH_3 singlets); ^{13}C NMR (50.1 MHz, acetone-d_6) δ 243.6 (μ-CO), 212.2 (CO), 167.3 (*J* = 156 Hz, μ-C), 144.6 (═*C*Me$_2$), 128.65 (Me*C*═), 102.1 (*J* = 156 Hz, ═CH), 90.9 (*J* = 184 Hz, C_5H_5), 23.2 (q, *J* = 125 Hz, CH_3), 21.3 (q, *J* = 125 Hz, CH_3), 14.6 (q, *J* = 125 Hz, CH_3); IR (CH_2Cl_2) 2030 (s), 2000 (w), 1860 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{21}BF_4Fe_2O_3$: C, 47.29; H, 4.18. Found: C, 46.93; H, 4.38.

$[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_2C(CH_3){=}C(CH_3)_2)$ (13). *tert*-Butylacetylene (0.33 atm, 0.53 L, 22 °C, 7.1 mmol) was added to 1 (311 mg, 0.64 mg) in 35 mL of CH_2Cl_2. Solvent was evaporated under vacuum, and $NEt_4{}^+HFe(CO)_4{}^-$[16] (350 mg, 1.17 mmol) was added to the solid product mixture in a glovebox. THF (30 mL) was vacuum transferred onto the mixture. The resulting solution was stirred 1 h, and solvent was evaporated. The residue was purified by flash chromatography (alumina, 1:1 CH_2Cl_2–hexane). Evaporation of the red-orange first band gave **13** (143 mg, 53%) as an orange-red powder: ^1H NMR (270 MHz, C_6D_6) δ 11.46 (t, *J* = 7.7 Hz, μ-CH), 4.19 (s, 10 H, C_5H_5), 4.13 (d, *J* = 7.8 Hz, CH_2), 2.02 (s, CH_3), 1.99 (s, CH_3), 1.81 (s, CH_3); $^{13}C\{^1H\}$ NMR (50.1 MHz, acetone-d_6, −30 °C) δ 273.7 (μ-CO), 214.3 (CO), 177.1 (μ-C), 132.7, 123.4 (C═C), 88.1 (C_5H_5), 61.0 (CH_2), 20.8, 20.5, 19.5 (CH_3); IR (CH_2Cl_2) 1970 (s), 1931 (m), 1774 (s) cm^{-1}; HRMS, calcd for $C_{20}H_{22}Fe_2O_3$ 422.0261, found 422.0266. Anal. Calcd for $C_{20}H_{22}Fe_2O_3$: C, 56.90; H, 5.26. Found: C, 56.88; H, 5.26.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHC{\equiv}CC(CH_3)_3)$ (12). A diethyl ether solution (1.5 mL) of $LiC{\equiv}CC(CH_3)_3$ (150 mg, 1.7 mmol) was slowly added to a mixture of 1 (503 mg, 1.07 mmol) and $CuIP(n\text{-}C_4H_9)_3$ (60 mg, 0.15 mmol) in 30 mL of CH_2Cl_2 at −78 °C. The resulting scarlet mixture was stirred 24 h at −78 °C. Solvent was evaporated under vacuum, and the residue was dissolved in 8 mL of CH_2Cl_2. The red CH_2Cl_2 solution was filtered and flash chromatographed (silica gel, 1:1 hexane–CH_2Cl_2). The first 3–5 mL of the first purple-red band [containing $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$] was discarded. Evaporation of solvent from the remainder of the first band and a closely following orange band afforded a dark red powder (88 mg, 20%) consisting of a 75:13:12 ratio of *cis,anti*-**12**:*trans*-**12**:*cis,syn*-**12**. ^1H NMR (270 MHz, acetone-d_6): *cis,anti*-**12**, δ 8.23 (s, μ-CH), 4.84 (s, C_5H_5), 1.39 (s, *t*-Bu); *trans*-**12**, δ 9.57 (s, μ-CH), 4.80 (s, C_5H_5) 4.75 (s, C_5H_5), 1.28 (s, *t*-Bu); *cis,syn*-**12**, δ 10.57 (s, μ-CH), 4.86 (s, C_5H_5), 1.13 (s, *t*-Bu). ^{13}C NMR (50.1 MHz, CD_2Cl_2, 0 °C): *cis,anti*-**12**, δ 271.8 (μ-CO), 212.5 (CO), 126.0 (d, *J* = 150 Hz, μ-CH), 113.3, 100.5 (C≡C), 90.3 (d, *J* = 180 Hz, C_5H_5), 32.0 (q, *J* = 125 Hz, CH_3), 29.2 (*C*(CH$_3$)$_3$); *trans*-**12**, δ 273.2 (μ-CO), 212.7 (CO), 130.1 (μ-CH), C≡C not observed, 91.7, 88.9 (C_5H_5), 31.5 (CH_3), *C*(CH$_3$)$_3$ not observed; *cis,syn*-**12**, δ 272.8 (μ-CO), 211.5 (CO), 129.6 (d, *J* = 147 Hz, μ-CH), 111.5, 101.9 (C≡C), 87.0 (d, *J* = 178 Hz, C_5H_5), 30.7 (q, *J* = 128 Hz, CH_3), 29.0 (*C*(CH$_3$)$_3$). IR (CH_2Cl_2): 1988 (s), 1952 (w), 1783 (m) cm^{-1}. HRMS: calcd for $C_{20}H_{20}Fe_2O_3$ 420.0110, found 420.0122. Anal. Calcd for $C_{20}H_{20}Fe_2O_3$: C, 57.18; H, 4.81. Found: C, 57.18; H, 5.01.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}C{=}CHC(CH_3)_3)^+BF_4^-$ (10-BF$_4$). $HBF_4 \cdot OEt_2$ (39 μL, 0.31 mmol) was added to a 20 mL of CH_2Cl_2 solution of **12** (135 mg, 0.32 mmol) at −78 °C. The scarlet solution was warmed to ambient temperature, filtered, and concentrated to 10 mL. A brown-red precipitate formed on addition of 20 mL of diethyl ether and was filtered, washed with ether (3 × 2 mL), and dried under vacuum to give **10-BF$_4$** (99 mg, 62%): ^1H NMR (270 MHz, acetone-d_6) δ 12.01 (d, *J* = 3.6 Hz, 1 H, μ-CH), 5.84 (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_5H_5), 5.47 (d,

J = 3.4 Hz, C=CH), 1.17 (s, 9 H, *t*-Bu); ^{13}C NMR (50.1 MHz, CD_3NO_2, 0 °C) δ 243.2 (μ-CO), 212.5, 207.4 (CO), 152.0 (C=*C*=C), 145.6 (d, J = 167 Hz), 127.3 (d, J = 161 Hz) (*C*=C=*C*), 93.0 (d, J = 183 Hz), 90.6 (d, J = 183 Hz) (C_5H_5), 37.6 (*C*(CH_3)$_3$), 30.0 (q, J = 121 Hz, CH_3); IR (CH_2Cl_2) 2042 (s), 2020 (w), 1866 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{21}BF_4Fe_2O_3$: C, 47.29; H, 4.18. Found: C, 46.95; H, 4.15.

X-ray Structure Determination of 2. Crystals for the diffraction study were grown by vapor diffusion of diethyl ether into an acetone solution of 2. A black, rectangular thin plate of dimensions 0.07 × 0.34 × 0.72 mm was mounted on a glass fiber and coated with epoxy. Collection of the diffraction data was carried out on a Syntex-Nicolet P1 diffractometer equipped with a graphite-monochromated Mo Kα source and a modified LT-1 low-temperature device.

Preliminary cell constants and an orientation matrix for a monoclinic (*b* unique) lattice were determined from 10 centered reflections found from a randomly oriented rotation photograph. An axial rotation photograph suggested the possibility of a superposition of a second lattice along the *a* axis. The final orientation matrix and cell constants were calculated from 15 centered high-angle reflections. As a check on the quality of data obtained from the crystal, a full hemisphere of reflections was collected in a shell from 3° > 2θ > 30°. Three standard reflections, examined after every 53 measurements, showed no signs of decay throughout the data collection. In this hemisphere 6 unique reflections out of a total of 766 unique data were rejected on the basis of discrepancy between equivalents; the merging R value for this shell was 0.042. These factors indicated that there was no problem arising from the twinned dimension. A second shell of data from 30° > 2θ > 45° was collected over a unique quadrant, using the same check reflections.

Data reduction, solution, and refinement of the structure were performed with the SHELXTL structure determination package (Nicolet XRD Corp., Madison, WI). Systematic absences of $\{h0l\}$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely define the space group to be $P2_1/c$. There were no violations of systematic absences. Absorption corrections were performed by using the method of Hope.[17]

Direct methods were used to locate the positions of the iron, phosphorus, and fluorine atoms. Subsequent difference Fourier maps revealed the location of the remaining non-hydrogen atoms. Attempts to refine all non-hydrogen atoms anisotropically resulted in some of the carbon atom thermal parameters becoming non-positive definite. This was attributed to the inadequacy of the absorption correction. Neither psi scan nor analytical absorption corrections corrected the problem. As a consequence, only the iron, phosphorus, and fluorine atoms were refined anisotropically. All hydrogen atoms were included as fixed contributions at riding, idealized locations with thermal parameters set at 1.2 times that of the bonded carbon atom.

Some disorder in the PF_6 counteranion was evident particularly from the large thermal ellipsoids of the fluorine atoms. However, difference Fourier maps failed to suggest a suitable disorder model. The final refinement converged at R = 0.083 and R_w = 0.090.

The final electron density difference map showed several peaks on the order of 1 e/Å^3. The positions of these peaks were not associated with the structure and did not define any reasonable solvent molecule. Refinement of the structure using only the low-angle data from 3° > 2θ > 30° did not reproduce these peaks, suggesting they did not arise from low Z scatterers.

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Registry No. 1, 82660-14-8; *cis*-2, 106161-95-9; *trans*-2, 106247-69-2; 4, 103691-92-5; 5, 106161-97-1; *cis*-6, 106161-99-3; *trans*-6, 106247-72-7; *cis*-7, 106161-93-7; *trans*-7, 106247-74-9; 9-PF_6, 106247-70-5; 9-BF_4, 106162-01-0; 10-PF_6, 106162-03-2; 11, 106162-04-3; *cis,anti*-12, 106162-05-4; *trans*-12, 106247-75-0; *cis,syn*-12, 106247-76-1; 13, 106162-06-5; $NEt_4{}^+HFe(CO)_4$, 25879-01-0; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; phenylacetylene, 536-74-3; *tert*-butylacetylene, 917-92-0.

Supplementary Material Available: Complete listings of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for 2 (6 pages); a listing of observed and calculated structure factors for 2 (12 pages). Ordering information is given on any current masthead page.

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Organometallic Chemistry of Carbon–Nitrogen Multiple Bonds. 5. Reactions of Vanadocene with Nitrilium Salts and the Crystal Structure of $\{V(\eta^5\text{-}C_5H_5)_2[\eta^2\text{-}C(C_6H_5)NCH_3]\}BF_4$

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Reactions of vanadocene with nitrilium salts $[C_6H_5C{\equiv}NCH_3]BF_4$ and $[CH_3C{\equiv}NCH_3]BF_4$ produce adducts that are characterized by small ^{51}V hyperfine coupling constants (42.1 and 42.9 G, respectively) and C=N stretching absorptions characteristic of iminoacyls. $\{V(\eta^5\text{-}C_5H_5)_2[\eta^2\text{-}C(C_6H_5)NCH_3]\}BF_4$ was isolated and characterized, by a single-crystal X-ray structure, as an η^2-iminoacyl complex. The dark maroon complex crystallized in the monoclinic space group Cc with a = 13.872 (4) Å, b = 13.930 (5) Å, c = 9.315 (4) Å, and β = 99.33 (3)°; ρ_{calcd} = 1.44 g cm^{-3} for Z = 4 and M_r 386.13; R = 0.040 and R_w = 0.049 for 1673 data. The V–C and V–N bond distances are 2.054 (4) and 2.030 (4) Å, respectively. The C–N distance is 1.245 (7) Å, which gives a C–V–N angle of 35.2 (2)°. These adducts react with excess nitrilium salt to produce species, which have not been isolated, that have vanadium hyperfine coupling constants >60 G.

Introduction

A number of investigations have shown that iminium salts, $[R_2C{=}NR'_2]X$, which contain an unsaturated, electrophilic cation, react readily with a variety of organometallic compounds to yield complexes that contain η^1- and η^2-$CR_2NR'_2$ moieties.[1] The more highly unsaturated ni-

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