Reactions of the Cationic Iron Vinylidene Compound [Fe(η-C₅H₅)(CO)(PPh₃)(C=CH₂)]⁺BF₄⁻ with O–H, N–H, S–H, Cl–H, and C≡C Bonds

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The cationic vinylidene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C=CH_2)^+BF_4^-$, 1, reacts with a variety of alcohols (ROH) to produce cationic alkoxycarbene compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OR)Me\}]^+BF_4^-$ (R = Me, Et, *i*-Pr, CH₂CH=CH₂). The reaction of 1 with H₂S or MeSH affords analogous carbene compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SR)Me\}]^+BF_4^-$ (R = H, Me). While reaction of 1 with benzylamine yields only the aminocarbene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHCH_2Ph)Me\}]^+BF_4^-$, the corresponding reactions with MeNH₂ or Me₂NH afford both the carbene complexes $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NR'R)\text{-}Me\}]^+BF_4^-$ (R = H, R' = Me; R = R' = Me) and the alkynyl complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C≡CH)]$; reaction of 1 with Me₃N affords only this latter product. Dry HCl also adds across the vinylidene double bond of 1 to yield the chloromethylcarbene complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Cl)Me\}]^+BF_4^-$. In tetrahydrofuran (THF) solution 1 reacts spontaneously to produce the μ-cyclobutenylidene complex $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(PPh_3)_2(\mu\text{-}C_4H_3)]^+BF_4^-$ as a 3:1 mixture of diastereoisomers, the meso form being dominant. In contrast, the related vinylidene complex $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C=CH_2)]^+BF_4^-$ reacts in THF to give only the *R,R:S,S* pair of enantiomers of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(C_6H_{11})_3\}_2(\mu\text{-}C_4H_3)]^+BF_4^-$.

Introduction

Previously, we have described a convenient synthetic procedure for the isolation of cationic vinylidene complexes of iron, $[Fe(\eta\text{-}C_5H_5)(CO)(L)(C=CR_2)]^+BF_4^-$ {L = PPh₃, R = H, Me; L = PMe₂Ph, P(C₆H₁₁)₃, R = H}, by the reaction of the appropriate acyl precursor $[Fe(\eta\text{-}C_5H_5)(CO)(L)\{C(O)CHR_2\}]$ with (CF₃SO₂)₂O in the presence of HBF₄·Et₂O.[2] A separate communication described the solution characterization of these molecules.[3] The α-carbon atom of the vinylidene ligand in $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C=CH_2)]^+BF_4^-$, 1, was shown to be extremely reactive toward pyridine and tertiary phosphine nucleophiles, affording the vinyl derivatives $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Y)=CH_2\}]^+BF_4^-$ (Y = pyridine, 4-methylpyridine, PPh₃, PMe₂Ph); the molecular structure of one such complex was also determined.[2] Other workers have described related cationic vinylidene compounds 2 and 3 [M = Fe, Ru, Os] containing

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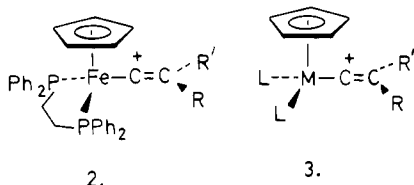
a variety of ligands L and L' and a number of different vinylidene substituents R and R'.[4–8] The only previously reported example of a cationic complex containing the parent, unsubstituted vinylidene ligand was 2 (R = R' = H).[4]

Classic methods for trapping unstable intermediate organic vinyl cations have involved reactions with alcohols or water.[9] While complexes 2 (R = R' = H, Me; R = Me,

R' = H) are reported to be unreactive toward water and alcohols,[4] as is the cationic vinylidene complex *trans*-$[Fe(dppe)_2Cl(C=CHPh)]^+$,[10] the corresponding compounds 3 (M = Fe, L = PPh₃, L' = CO, R = H, R' = Ph;[8] M = Ru, L' = PPh₃, L = PPh₃, CO, *t*-BuNC, PMe₃, P{OMe}₃, R = H, R' = Ph;[7] M = Ru, L = L' = PPh₃, R = H, R' = Me, CO₂Me)[7] have been shown to react with water and methanol to give respectively the neutral acyl compounds $[M(\eta\text{-}C_5H_5)LL'\{C(O)CHRR'\}]$ or the cationic alkoxycarbene compounds $[M(\eta\text{-}C_5H_5)LL'\{C(OMe)CHRR'\}]^+$. The rates of these reactions appear to be dependent upon both the steric and electronic properties of the ligands L and L';[7] sterically demanding ligands block the reactive α-carbon site while good electron-donor ligands serve to enhance the ability of the metal to stabilize the α-carbonium ion center and result in slower reactions.

This paper presents results which demonstrate that $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C=CH_2)]^+BF_4^-$, 1, is highly reactive toward addition of OH, NH, SH, ClH, and C≡C functionalities across the double bond of the vinylidene ligand.

Results and Discussion

Reactions With O–H Bonds. Compound 1 reacted rapidly with water, or in moist organic solvents, to give the acetyl complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$. Similarly 1 dissolved in alcohols, ROH, to give bright yellow solutions from which the cationic alkoxycarbene complexes 5–8 could be isolated in high yields. Compound 1 was
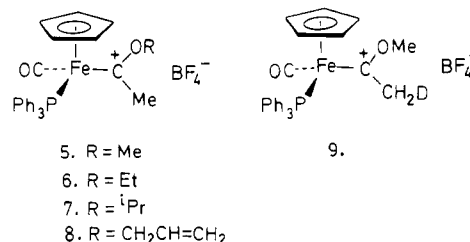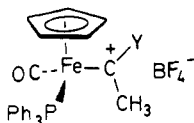
5. R = Me   9.
6. R = Et
7. R = *i*Pr
8. R = CH₂CH=CH₂

unreactive toward *t*-BuOH at 20 °C. An analogous reaction of 1 with CH₃OD afforded 9. The spectroscopic data

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Table I. IR, 1H NMR, and 19F NMR Data for Cationic Carbene Compounds of Iron

compd	ν_{CO},a cm^{-1}	$\delta(^1H)^b$ PPh$_3$	C$_5$H$_5$c	Me	Y	$\delta(^{19}F)^a$ (BF$_4^-$)
5	1985	7.57 (m)	4.89 (d, 1.5)	2.84 (s)	3.98 (s)	153.3 (s)
6	1983	7.54 (m)	4.88 (d, 1.5)	2.83 (s)	4.25 (m, CH$_2$) 1.40 (t, J = 7 Hz, Me)	153.6 (s)
7	1973	7.53 (m)	4.80 (d, 1.5)	2.95 (s)	3.40 (m, CHMe_2) 1.40 (d, J = 6 Hz, CHMe_2) 1.05 (d, J = 6 Hz, CHMe_2)	154.0 (s)
8	1977	7.55 (m)	4.88 (d, 1.3)	2.88 (s)	5.77 (m, CH=CH$_2$) 5.51 (m, CH=CH_2) 5.31 (m, CH=CH$_2$) 4.65 (d, J = 6 Hz, OCH$_2$)	154.0 (s)
9	1985	7.57 (m)	4.90 (d, 1.5)	2.83 (t)^e	3.98 (s)	153.3 (s)
10	1975	7.55 (m)	4.90 (d, 1.2)	2.60 (s)	4.32 (s, br)	f
11	1975	7.55 (m)	4.95 (d, 1.2)	2.61 (s)	3.19 (s)	154.0 (s)
12	1975 (3450)^g	7.50 (m)	4.82 (d, 1.3)	2.34 (s)	10.81 (s, br, NH) 4.67 (d, J = 5 Hz, CH$_2$) 7.50 (m, Ph)	153.6 (s)
13	1950 (3450)^g	7.60 (m)	4.77 (d, 1.3)	2.14 (s)	9.90 (s, br, NH) 2.98 (d, J = 5 Hz, Me)	153.9 (s)
14	1950	7.60 (m)	4.79 (d, 1.3)	2.37 (s)	3.34 (s, Me) 3.94 (s, Me)	153.8 (s)
16	1990	7.55 (m)	4.70 (s)	2.55 (s)		f

^{a} CH$_2$Cl$_2$ solution. ^{b} Ppm downfield from internal Me$_4$Si, CDCl$_3$ solution. ^{c} J_{PH} (Hz) in parentheses. ^{d} Ppm upfield from internal CFCl$_3$. ^{e} This resonance integrates to 2 protons, J_{HD} = 2 Hz. ^{f} Not recorded. ^{g} ν_{NH}.

for 5 and 6 were identical with those previously reported,[11] and the structures of 7–9 were established clearly by comparison of their IR and 1H NMR spectra (Table I) with those of 5 and 6. No iron analogues of 7 and 8 exist, although the closely related ruthenium compound [Ru(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O-i-Pr)CH$_2$Ph}]$^+$PF$_6^-$ has been reported;[7] while the 1H NMR signal for the isopropyl group of this latter compound could not be observed due to a solvent impurity,[7] the 1H NMR spectrum of 7 clearly shows the presence of two doublets corresponding to the diastereotopic methyl groups.

Compounds 5–9 arise by initial nucleophilic attack at the α-carbon of the vinylidene ligand by the alcohol oxygen atom, in a manner analogous to that already demonstrated for pyridine and tertiary phosphine nucleophiles.[2] Subsequent prototropic shifts afford the observed products, as shown by the formation of 9 from CH$_3$OD. When water is the nucleophile, this sequence would afford the unstable hydroxycarbene compound [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C-(OH)Me}]$^+$BF$_4^-$, which, as expected,[12] spontaneously deprotonates to give the acetyl product.

Reactions with S–H Bonds. In contrast, the reaction of 1 with liquid H$_2$S afforded an isolable sulfhydrylcarbene complex 10, and a similar reaction using liquid CH$_3$SH

10. R = H

11. R = Me

yielded the methylthiocarbene analogue 11. 1H NMR

spectroscopy (Table I) located the SH proton resonance of 10 at δ 4.32.[13] The 1H NMR resonances of the methyl(methylthio)carbene ligand of 11 were entirely compatible with those reported for the same ligand in [Ir(η-C$_5$H$_5$)I(PPh$_3$){C(SMe)Me}]$^+$I$^-$.[14] Compound 10 was quite unstable in solution; attempted deprotonation of the sulfhydryl group, using the hindered base NEt-i-Pr$_2$, produced a very unstable orange material which could only be characterized by its IR spectrum. The presence of strong bands at 1937 (ν_{CO}) and 1260 cm^{-1} ($\nu_{C=S}$) suggested that the neutral thioacyl complex [Fe(η-C$_5$H$_5$)(CO)-(PPh$_3$){C(S)Me}] might have been formed; no thioacyl compounds appear to have been reported in the literature, although a thioformyl compound of osmium has been characterized.[15]

Reactions with N–H Bonds. We have already established that 1 reacts cleanly with pyridine, or 4-methylpyridine, to yield vinyl compounds resulting from nucleophilic attack of the amine nitrogen atom at the vinylidene α-carbon atom.[2] Compound 1 dissolved slowly in benzylamine at room temperature to yield, on workup, the single yellow cationic methyl(benzylamino)carbene complex 12 in high yield. The IR and 1H NMR spectral
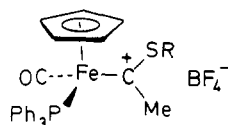
12. R = CH$_2$Ph; R′ = H

13. R = Me; R′ = H

14. R = R′ = Me

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Table II. IR and NMR Spectroscopic Data for Cationic Cyclobutenylidene Complexes

compd	ν_{CO},[b] cm⁻¹	nucleus	L	C₅H₅	α-C	CH	CH₂	CO
17	1954	¹H	7.40 (m)	4.51 (s)		7.80 (s)	3.20 (d, J = 14.4 Hz) 3.29 (d, J = 14.4 Hz)	
18	1954	¹H	7.40 (m)	4.65 (s)		7.80 (s)	3.30 (s)	
19	1954	¹H	1.59 (m)	4.91 (s)		8.32 (s)	3.72 (s)	
17		¹³C	127–132	87.8	304.0	286.0	21.6	209.9
18		¹³C	127–132	87.5	c	c	c	c
19		¹³C	28.5 (br)	85.8	330.6	290.0	24.9	218.0

[a] Ppm downfield from internal Me₄Si, CDCl₃ solution.   [b] CH₂Cl₂ solution.   [c] These resonances could not be observed for the minor isomer in solution.

properties of **12** agree well with those reported for the product of the reaction of [Fe(η-C₅H₅)(CO)(PPh₃){C-(OEt)Me}]⁺BF₄⁻ with benzylamine;[16] similar compounds [Fe(η-C₅H₅)(CO)(PPh₃){C(NRR′)Me}]⁺BF₄⁻ (R = R′ = H; R′ = H, R = (–)-CHMePh) have been obtained by an analogous route,[16,17] though secondary amines are reported to be unreactive.[17] Similarly **1** reacted smoothly with liquid MeNH₂ or Me₂NH to produce the corresponding compounds **13** and **14**; in these latter two reactions some deprotonation to produce [Fe(η-C₅H₅)(CO)(PPh₃)(C≡CH)], **15**, was also observed. This metal alkynyl complex was the sole product of the reaction of **1** with liquid Me₃N.[18]

The carbene compounds **12–14** clearly arise via nucleophilic attack at the vinylidene α-carbon by the amine, followed by proton transfer. Notably this is the exclusive mode of reaction for the weakly basic benzylamine (pK_a = 9.33),[19] which behaves like pyridine (pK_a = 5.25),[19] but the more basic amines MeNH₂ (pK_a = 10.66)[19] and Me₂NH (pK_a = 10.77)[19] act both as nucleophiles and bases. While Me₃N (pK_a = 9.81)[19] is a weaker base in aqueous solution than either MeNH₂ or Me₂NH, it is a stronger base in the absence of solvent,[20] and it is not surprising, therefore, that under these reaction conditions Me₃N acts exclusively as a base and cleanly deprotonates the vinylidene complex to give **15**. It has been noted that the more hindered amine, Et₂NH, will deprotonate [Fe(η-C₅H₅)(CO)-(PPh₃)(C=CHPh)]⁺BF₄⁻ to give the corresponding alkynyl iron complex.[8]

Two pieces of evidence point to the presence of considerable double-bond character between the nitrogen and α-carbon atoms of **12–14**. The value of ν_{CO} is significantly lower for these compounds than for the alkoxycarbene compounds **5–8** (Table I), indicating that the aminocarbene ligand is a weaker π acceptor than the alkoxycarbene ligand, due to increased heteroatom stabilization of the carbene carbon atom. The observation of two ¹H NMR resonances for the Me₂N group of **14** at 25 °C clearly substantiates this proposal.

Reaction with HCl. At –78 °C, **1** reacted swiftly with dry HCl in CH₂Cl₂ solution to give, on workup, an air- and moisture-sensitive brick-red solid formulated as the chloromethylcarbene complex **16**. The value of ν_{CO} for this
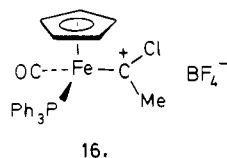
compound (Table I) is consistent with this formulation, but unfortunately samples of **16** prepared in this fashion could not be freed of paramagnetic impurities in order to allow NMR spectra to be recorded. Recrystallization attempts led invariably to further decomposition, and attempted chromatography on deactivated silica gel led to rapid hydrolysis to give [Fe(η-C₅H₅)(CO)(PPh₃){C(O)Me}]. To circumvent this problem, **16** was generated in CDCl₃ solution by adding one equivalent each of CF₃SO₃H and [Ph₃P=N=PPh₃]⁺Cl⁻ to **1**; the resultant red-purple solution exhibited an identical IR band at 1990 cm⁻¹ (see Table I). The ¹H NMR spectrum of this sample of **16** exhibited only PPh₃ resonances, a cyclopentadienyl peak at δ 4.70 and a methyl singlet at δ 2.55; the ¹³C{¹H} NMR spectrum exhibited a resonance at δ 344.50, characteristic of the α-carbon atom of such carbene complexes,[21] as well as a methyl peak at δ 13.40 and a cyclopentadienyl peak at δ 86.76. We feel that these data provide good evidence for the formulation of **16** as a chloromethylcarbene complex.

Formation of μ-1,3-Cyclobutenylidene Complexes. While **1** dissolved in dry CH₂Cl₂ or CDCl₃ without change and was insoluble in Et₂O,[2] it dissolved readily in dry THF to afford a bright orange solution which yielded deep orange crystals on workup. Although the crystals exhibited a single CO stretching band in the IR spectrum (Table II) together with bands characteristic of BF₄⁻, the ¹H NMR spectrum (60 MHz) was more complex and clearly indicated the presence of two isomeric species in solution. Two cyclopentadienyl resonances were observed (ratio 3:1), and the methylene region contained an AB quartet and a singlet, also in a 3:1 ratio. At 270 or 360 MHz the AB quartet simplified to an AX pattern with a coupling constant (14.4 Hz) characteristic of geminally coupled protons.[13b] A further singlet peak was observed at δ 7.80. A fast atom bombardment (FAB)[22] mass spectrum indicated that the molecular weight of the cationic portion of the molecule was 872.6.

These data are only compatible with the formation of a binuclear complex containing a cyclobutenylidene ligand, and the most reasonable conclusion appears to involve the formation of two diastereoisomeric pairs of enantiomers **17** and **18**. The major component must be the meso-

16.

17. L = PPh₃

18. L = PPh₃
19. L = P(C₆H₁₁)₃
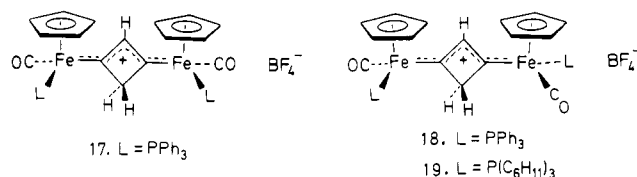
(16) Reger, D. L. Ph.D. Thesis, Massachusetts Institute of Technology, 1972.
(17) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237–9238.
(18) The deprotonation of **1** by *t*-BuO⁻ in *t*-BuOH has been described.[2]
(19) "CRC Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, OH, 1975.
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(21) The carbene carbon in the compound [Fe(η-C₅H₅)(CO)(PPh₃)-(CHPh)]⁺ resonates at δ 342: Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099–6101.
(22) A discussion of fast atom bombardment (FAB) mass spectrometry has appeared recently: Williams, D. H.; Bradley, C.; Bojesen, G.; Santikarn, S.; Taylor, L. C. E. *J. Am. Chem. Soc.* **1981**, *103*, 5700–5704.

compound 17, in which the methylene protons are symmetrically nonequivalent, and the minor component must be the *R,R:S,S* pair 18 in which the methylene protons are related by a twofold rotation axis. Surprisingly it was not possible to alter the 3:1 ratio of 17/18 either by repeated recrystallization or by chromatography on deactivated silica gel. A further curious observation was made when an analogue of 1, [Fe(η-C$_5$H$_5$)(CO){P(C$_6$H$_{11}$)$_3$}(C=CH$_2$)]$^+$-BF$_4^-$ was dissolved in THF. The ^{1}H NMR spectrum of the product (Table II) showed it to consist of a single isomer 19 which corresponds structurally to the minor isomer 18; only a singlet peak was observed for the methylene protons at 360 MHz. Supporting evidence was provided by ^{13}C NMR spectra (Table II) which clearly showed two cyclopentadienyl resonances for the mixture of 17 and 18 but only one for 19. A FAB mass spectrum of 19 confirmed the molecular weight of the cation as 908.6.

Similar cationic cyclobutenylidene complexes have been reported by two groups of workers,[8,23] from the protonation of [Fe(η-C$_5$H$_5$)(CO)$_2$(C≡CPh)] in the absence of nucleophiles. Formation of an intermediate cationic vinylidene complex [Fe(η-C$_5$H$_5$)(CO)$_2$(C=CHPh)]$^+$, followed by a cycloaddition reaction of this molecule with more acetylide, was proposed as a mechanism for this reaction.[8,23] It seems reasonable to suppose that partial deprotonation of 1 occurs in THF solution, to produce the alkynyl complex 15, which is then trapped in a cycloaddition reaction with 1, as shown below for the formation of the meso-compound 17. In agreement with this hypothesis, addition of 0.5 equiv of HBF$_4$·Et$_2$O to solutions of 15 afforded an identical

15. 20. 21.
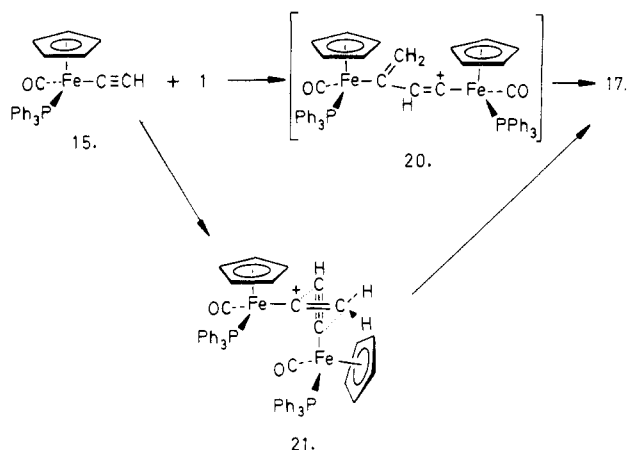
3:1 mixture of 17 and 18. It has been suggested that this mechanism may involve a stepwise cyclization via the intermediate 20,[8] although a concerted [$_\pi$2$_s$ + $_\pi$2$_a$] cycloaddition should also be feasible. Indeed, the vinyl cation would be a superb antarafacial component for such a cycloaddition, which should occur via the bisected transition state 21.[24] It is not clear where the origins of the preference for selective formation of the meso-diastereomer 17 lie or why an inversion of this preference occurs for the P(C$_6$H$_{11}$)$_3$ analogue of 1 to give 19. A possible explanation, which also accounts for our lack of success in separating 17 and 18, or even altering their ratio, would be that 17 and 18 were in equilibrium in solution. This would require a complete retrocycloaddition to regenerate 1 and 15 in solution and seems extremely implausible since the mixture of 17 and 18 can be chromatographed unchanged on water saturated silica gel, conditions under which imme-

diate hydrolysis of free 1 would occur. No traces of the expected product of hydrolysis, [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)-{C(O)Me}], or of 15, both of which can be chromatographed unchanged under these conditions, were ever detected. It seems likely, therefore, that the selectivity which occurs in cyclobutenylidene formation is kinetic rather than thermodynamic in origin.

Reaction with EtOCH=CH$_2$. In view of the ability of certain electrophilic carbene complexes to effect the cyclopropanation of electron rich olefins,[25] the reaction of 1 with ethyl vinyl ether was examined. No cyclopropanation was observed, but instead a surprisingly clean conversion of 1 to the ethoxymethylcarbene complex 6 was

22.
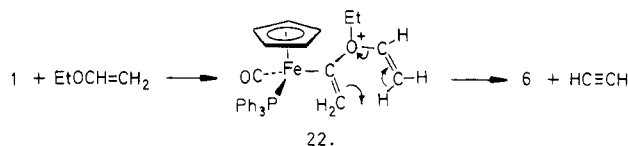
observed. A speculative mechanism for this transformation utilizes the demonstrated affinity of the α-carbon atom of 1 for oxygen nucleophiles to give 22, followed by an elimination reaction to give 6. No attempts were made to identify any organic byproduct(s).

Experimental Section

General Remarks. IR spectra were run on a Perkin-Elmer PE 257 instrument and calibrated against the 1601-cm^{-1} band of polystyrene. ^{1}H (60 MHz), ^{13}C (15 MHz), and ^{19}F (56 MHz) NMR spectra were run on a JEOL FX-60Q instrument; certain ^{1}H NMR spectra were run at 270 MHz on a Bruker HX-270 spectrometer or at 360 MHz on a Nicolet NT-360 spectrometer at the NSF-NMR Regional facilities at Yale University or Colorado State University, respectively. Fast atom bombardment cation mass spectra were obtained at the Middle Atlantic Mass Spectrometry Facility at the Johns Hopkins School of Medicine. Spectroscopic data are reported in Tables I and II or in the text.

Alcohols were obtained as spectrograde solvents and were used as received, with the exception of allyl alcohol which was distilled before use. Methylamine, dimethylamine, trimethylamine, H$_2$S, and methyl mercaptan were obtained from Matheson and were used as received. Benzylamine was dried over BaO before use. Organometallic reaction solvents were distilled from sodium benzophenone ketyl except for CH$_2$Cl$_2$ and CDCl$_3$ which were distilled from P$_4$O$_{10}$. All reactions were run under an atmosphere of dry nitrogen or on a vacuum line.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)(C=CH$_2$)]$^+$BF$_4^-$, 1, and [Fe(η-C$_5$H$_5$)-(CO){P(C$_6$H$_{11}$)$_3$}(C=CH$_2$)]$^+$BF$_4^-$ were prepared as previously described.[2]

Reaction of 1 with H$_2$O. A solution of 1 (0.10 g, 0.19 mmol) in CH$_2$Cl$_2$ (10 mL) was shaken vigorously with H$_2$O (5 mL). The organic layer was separated, dried (MgSO$_4$), filtered, and evaporated to afford [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O)Me}] as orange crystals (0.070 g, 80%). IR and ^{1}H NMR spectra were identical with literature data.[26]

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(OMe)Me}]$^+$BF$_4^-$ (5). The vinylidene compound 1 (0.10 g, 0.19 mmol) was dissolved in CH$_3$OH (20 mL). After 0.25 h the pale yellow solution was evaporated and the crude residue recrystallized from CH$_2$Cl$_2$/Et$_2$O to give 5 as yellow crystals (0.074 g, 70%; mp 164 °C). IR and ^{1}H NMR spectra were identical with literature data.[11]

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(OEt)Me}]$^+$BF$_4^-$ (6) was prepared in similar fashion from 1 (0.10 g, 0.19 mmol) and EtOH (20 mL), as yellow crystals (0.070 g, 65%; mp 108 °C dec). IR and ^{1}H NMR spectra were identical with literature data.[11]

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O-*i*-Pr)Me}]$^+$BF$_4^-$ (7) was similarly prepared from 1 (0.10 g, 0.19 mmol) and *i*-PrOH (15 mL),

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as yellow crystals (0.079 g, 72%; mp 173 °C). For IR and ^{1}H NMR data, see Table I. Anal. C, H.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(OCH$_2$CH=CH$_2$)Me}]$^+$BF$_4^-$ (8) was similarly prepared from 1 (0.10 g, 0.19 mmol) and allyl alcohol (15 mL), as dark yellow crystals (0.067 g, 61%; mp 130 °C). For IR and ^{1}H NMR data, see Table I. Anal. C, H.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(OMe)CH$_2$D}]$^+$BF$_4^-$ (9) was likewise prepared from 1 (0.10 g, 0.19 mmol) and CH$_3$OD (Aldrich, 15 mL), as pale yellow crystals (0.080 g, 75%; mp 108 °C). For IR and ^{1}H NMR data see Table I.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(SH)Me}]$^+$BF$_4^-$ (10). A Schlenck flask (100 mL) containing 1 (0.50 g, 0.95 mmol) was evacuated and cooled to -196 °C. Hydrogen sulfide was condensed on to solid 1 until the flask was about half-full. The flask was warmed to -78 °C to liquify the H$_2$S, and the reaction mixture was stirred for 1 h. Excess H$_2$S was removed under vacuum, and the flask was warmed to room temperature. The crude product was chromatographed on a 15 × 2 cm deactivated silica gel/Et$_2$O column. Et$_2$O eluted [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O)Me}] (0.050 g, 11%), and acetone eluted an orange band which yielded 10, after evaporation and recrystallization from CH$_2$Cl$_2$/Et$_2$O, as orange crystals (0.34 g, 65%; mp 104 °C). For IR and ^{1}H NMR data see Table I. Anal. C, H.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(SMe)Me}]$^+$BF$_4^-$ (11) was likewise prepared from 1 (0.50 g, 0.95 mmol) and MeSH (20 mL), by maintaining the reaction mixture at -24 °C using a CCl$_4$/N$_2$ (liquid) slush bath. Recrystallization of the crude product from acetone/Et$_2$O yielded 11 as yellow crystals (0.43 g, 79%; mp 141 °C dec). For IR and ^{1}H NMR data see Table I. Anal. C, H.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(NHCH$_2$Ph)Me}]$^+$BF$_4^-$ (12). Compound 1 (1.00 g, 1.91 mmol) was dissolved in benzylamine (20 mL) and stirred for 8 h. Excess benzylamine was removed under vacuum, and the crude residue was recrystallized from CH$_2$Cl$_2$/Et$_2$O (-30 °C) to give 12 as yellow crystals (0.89 g, 74%; mp 203 °C). For IR and ^{1}H NMR data, see Table I. Anal. C, H, N.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(NHMe)Me}]$^+$BF$_4^-$ (13). MeNH$_2$ (ca. 25 mL) was condensed on to 1 (1.00 g, 1.91 mmol) at -196 °C, and the reaction mixture was warmed to -24 °C (CCl$_4$/N$_2$ (liquid) slush bath) and stirred for 1 h. Excess amine was removed under vacuum, and the crude residue was chromatographed on a 15 × 2 cm deactivated silica gel/Et$_2$O column. Ether eluted [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O)Me}] (0.017 g, 2%) followed by [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)(C≡CH)],[2] 15 (0.092 g, 11%), and CH$_2$Cl$_2$ eluted a bright orange band, which on evaporation and recrystallization, afforded 13 as orange crystals (0.80 g, 75%; mp 137 °C). For IR and ^{1}H NMR data, see Table I. Anal. C, H, N.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(NMe$_2$)Me}]$^+$BF$_4^-$ (14) was prepared in a similar reaction using 1 (1.00 g, 1.91 mmol) and Me$_2$NH (25 mL). Chromatography as described above yielded [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O)Me}] (0.07 g, 8%), and 15 (0.11 g, 13%), eluting with Et$_2$O. Acetone eluted an orange band, which was evaporated and recrystallized from CH$_2$Cl$_2$/Et$_2$O to afford 14 as orange crystals (0.81 g, 77%; mp 176 °C). For IR and ^{1}H NMR data, see Table I. Anal. C, H, N.

Reaction of 1 with Me$_3$N. In a similar reaction, 1 (0.50 g, 0.95 mmol) and Me$_3$N (25 mL) were stirred at -116 °C (EtOH/N$_2$ (liquid) slush bath) for 2 h. Workup as described above yielded [Fe(η-C$_5$H$_5$)(CO)(PPh$_3$)(C≡CH)], 15[2] (0.34 g, 82%), after recrystallization from toluene/hexane.

[Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(Cl)Me}]$^+$BF$_4^-$ (16). A solution of 1 (1.15 g, 2.2 mmol) in CH$_2$Cl$_2$ (50 mL) was cooled to -78 °C and dry HCl gas was bubbled through the solution for 0.25 h. The mixture was stirred at -78 °C for 1 h, warmed to 25 °C, and stirred for 12 h. Removal of the solvent under vacuum and recrystallization of the residue from CH$_2$Cl$_2$/Et$_2$O afforded 16 as a brick-red solid (0.74 g, 60%; mp 85 °C dec). For IR data, see Table I. Satisfactory microanalysis results could not be obtained, and further recrystallizations led to further decomposition. Anal. Calcd for C$_{26}$H$_{23}$BClF$_4$FeOP: C, 55.71; H, 4.14; Cl, 6.32. Found: C, 55.17; H, 4.19; Cl, 5.22.

Alternatively, 16 was generated in a NMR tube by treating a solution of 1 (0.10 g, 0.19 mmol) in CDCl$_3$ (3 mL) with [Ph$_3$P=N=PPh$_3$]Cl (0.11 g, 0.19 mmol) followed by CF$_3$SO$_3$H (0.17 mL, 0.19 mmol). ^{1}H and ^{13}C NMR spectra of the resultant mixture are reported in Table I.

[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(PPh$_3$)$_2$(μ-C$_4$H$_3$)]$^+$BF$_4^-$ (17) and (18). Compound 1 (0.50 g, 0.95 mmol) was dissolved in dry THF (50 mL), and the orange solution was stirred for 4.5 h. Removal of the solvent under vacuum and chromatography of the residue on a 150 × 2 cm deactivated silica gel column with CH$_2$Cl$_2$, eluted a bright orange band. Evaporation, followed by recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded bright orange crystals (0.41 g, 89%; mp 165 °C dec), shown to consist of a 3:1 mixture of 17/18. For IR, ^{1}H NMR, ^{13}C NMR data, see Table II. Anal. C, H.

[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$(μ-C$_4$H$_3$)]$^+$BF$_4^-$ (19) was prepared similarly by stirring a solution of [Fe(η-C$_5$H$_5$)(CO){P(C$_6$H$_{11}$)$_3$}(C=CH$_2$)]$^+$BF$_4^-$ (0.86 g, 1.59 mmol) in THF (50 mL) for 12 h. Workup as above yielded 19 as red-orange crystals (0.65 g, 82%; mp 145 °C dec). For IR, ^{1}H NMR, ^{13}C NMR data, see Table II. Anal. C, H.

Reaction of 1 with EtOCH=CH$_2$. A suspension of 1 (1.15 g, 2.2 mmol) in Et$_2$O (20 mL) was treated with freshly distilled EtOCH=CH$_2$ (10 mL), and CH$_2$Cl$_2$ (15mL) was then added to help dissolve 1. The mixture was stirred for 8 h and then evaporated to dryness. Chromatography of the residue on a 150 × 2 cm deactivated silica gel column, eluting with a 1:1 acetone/CH$_2$Cl$_2$ mixture, afforded a single yellow band, which on evaporation yielded 6 (1.21 g; 96%), identified by its ^{1}H NMR spectrum.

Registry No. 1, 80642-55-3; 5, 32610-60-9; 6, 32611-17-9; 7, 80662-36-8; 8, 80662-38-0; 9, 80662-40-4; 10, 80662-42-6; 11, 80662-44-8; 12, 80662-46-0; 13, 80662-48-2; 14, 80662-30-2; 15, 80642-59-7; 16, 80662-32-4; 17, 80735-08-6; 18, 80662-34-6; 19, 80679-12-5; [Fe(η-C$_5$H$_5$)(CO){P(C$_6$H$_{11}$)$_3$}(C=CH$_2$)]$^+$BF$_4^-$, 80642-58-6; Fe(η-C$_5$H$_5$)(CO)(PPh$_3$){C(O)Me}, 12101-02-9.