Reactions of the Cationic Iron Vinylidene Compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$ with O–H, N–H, S–H, Cl–H, and C≡C Bonds

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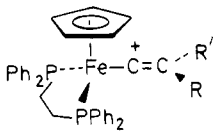
The cationic vinylidene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)^+BF_4^-$, 1, reacts with a variety of alcohols (ROH) to produce cationic alkoxycarbene compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OR)Me\}]^+BF_4^-$ (R = Me, Et, *i*-Pr, $CH_2CH{=}CH_2$). The reaction of 1 with H_2S or 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 $MeNH_2$ or Me_2NH afford both the carbene complexes $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NR'R)Me\}]^+BF_4^-$ (R = H, R′ = Me; R = R′ = Me) and the alkynyl complex $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$; reaction of 1 with Me_3N 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 = PPh_3, R = H, Me; L = PMe_2Ph, $P(C_6H_{11})_3$, R = H}, by the reaction of the appropriate acyl precursor $[Fe(\eta\text{-}C_5H_5)(CO)(L)\{C(O)CHR_2\}]$ with $(CF_3SO_2)_2O$ in the presence of $HBF_4\cdot Et_2O$.[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, PPh_3, PMe_2Ph); 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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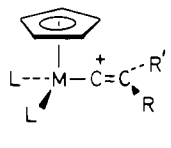


3.

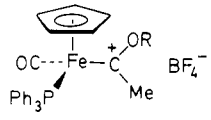
a variety of ligands L and L′ and a number of different vinylidene substituents R and R′.[4–8] The only previously reported example of a cationic complex containing the parent, unsubstituted vinylidene ligand was 2 (R = R′ = H).[4]

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 = PPh_3, L′ = CO, R = H, R′ = Ph;[8] M = Ru, L′ = PPh_3, L = PPh_3, CO, *t*-BuNC, PMe_3, $P\{OMe\}_3$, R = H, R′ = Ph;[7] M = Ru, L = L′ = PPh_3, R = H, R′ = Me, CO_2Me)[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.

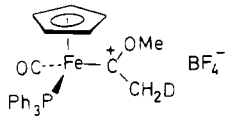
This paper presents results which demonstrate that $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$, 1, is highly reactive toward addition of OH, NH, SH, ClH, and C≡C functionalities across the double bond of the vinylidene ligand.

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
6. R = Et
7. R = ^{i}Pr
8. R = $CH_2CH{=}CH_2$



9.

unreactive toward *t*-BuOH at 20 °C. An analogous reaction of 1 with CH_3OD afforded 9. The spectroscopic data

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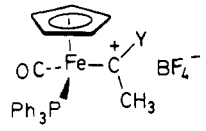
Table I. IR, ^{1}H NMR, and ^{19}F NMR Data for Cationic Carbene Compounds of Iron



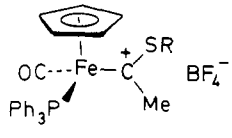
compd	ν_{CO},[a] cm^{-1}	$\delta(^1H)$[b] PPh$_3$	C_5H_5[c]	Me	Y	$\delta(^{19}F)$[a] (BF_4^-)
5	1985	7.57 (m)	4.89 (d, 1.5)	2.84 (s)	3.98 (s)	153.3 (s)
6	1983	7.54 (m)	4.88 (d, 1.5)	2.83 (s)	4.25 (m, CH_2) 1.40 (t, J = 7 Hz, Me)	153.6 (s)
7	1973	7.53 (m)	4.80 (d, 1.5)	2.95 (s)	3.40 (m, $CHMe_2$) 1.40 (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_2Cl_2 solution. [b] Ppm downfield from internal Me_4Si, $CDCl_3$ 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 ^{1}H NMR spectra (Table I) with those of **5** and **6**. No iron analogues of **7** and **8** exist, although the closely related ruthenium compound $[Ru(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O\text{-}i\text{-}Pr)CH_2Ph\}]^+PF_6^-$ has been reported;[7] while the ^{1}H NMR signal for the isopropyl group of this latter compound could not be observed due to a solvent impurity,[7] the ^{1}H 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_3OD. When water is the nucleophile, this sequence would afford the unstable hydroxycarbene compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OH)Me\}]^+BF_4^-$, 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_2S afforded an isolable sulfhydrylcarbene complex **10**, and a similar reaction using liquid CH_3SH



10. R=H
11. R=Me

yielded the methylthiocarbene analogue **11**. ^{1}H NMR spectroscopy (Table I) located the SH proton reasonance of **10** at δ 4.32.[13] The ^{1}H NMR resonances of the methyl(methylthio)carbene ligand of **11** were entirely compatible with those reported for the same ligand in $[Ir(\eta\text{-}C_5H_5)I(PPh_3)\{C(SMe)Me\}]^+I^-$.[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 $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(S)Me\}]$ 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 ^{1}H NMR spectral

12. R = CH_2Ph; 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	δ[a] L	C_5H_5	α-C	CH	CH_2	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		^{13}C	127-132	87.8	304.0	286.0	21.6	209.9
18		^{13}C	127-132	87.5	c	c	c	c
19		^{13}C	28.5 (br)	85.8	330.6	290.0	24.9	218.0

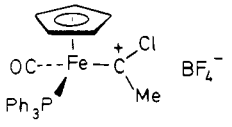
[a] Ppm downfield from internal Me_4Si, $CDCl_3$ solution. [b] CH_2Cl_2 solution. [c] These resonances could not be observed for the minor isomer in solution.

properties of **12** agree well with those reported for the product of the reaction of $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OEt)Me\}]^+BF_4^-$ with benzylamine;[16] similar compounds $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NRR')Me\}]^+BF_4^-$ (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 $MeNH_2$ or Me_2NH to produce the corresponding compounds **13** and **14**; in these latter two reactions some deprotonation to produce $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$, **15**, was also observed. This metal alkynyl complex was the sole product of the reaction of **1** with liquid Me_3N.[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 $MeNH_2$ (pK_a = 10.66)[19] and Me_2NH (pK_a = 10.77)[19] act both as nucleophiles and bases. While Me_3N (pK_a = 9.81)[19] is a weaker base in aqueous solution than either $MeNH_2$ or Me_2NH, it is a stronger base in the absence of solvent,[20] and it is not surprising, therefore, that under these reaction conditions Me_3N acts exclusively as a base and cleanly deprotonates the vinylidene complex to give **15**. It has been noted that the more hindered amine, Et_2NH, will deprotonate $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CHPh)]^+BF_4^-$ 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 Me_2N group of **14** at 25 °C clearly substantiates this proposal.

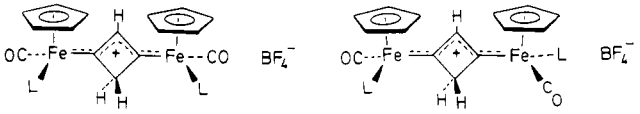
Reaction with HCl. At −78 °C, **1** reacted swiftly with dry HCl in CH_2Cl_2 solution to give, on workup, an air- and moisture-sensitive brick-red solid formulated as the chloromethylcarbene complex **16**. The value of ν_{CO} for this compound (Table I) is consistent with this formulation, but unfortunately 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 $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$. To circumvent this problem, **16** was generated in $CDCl_3$ solution by adding one equivalent each of CF_3SO_3H and $[Ph_3P{=}N{=}PPh_3]^+Cl^-$ 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 PPh_3 resonances, a cyclopentadienyl peak at δ 4.70 and a methyl singlet at δ 2.55; the $^{13}C\{^1H\}$ 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.



16.

Formation of μ-1,3-Cyclobutenylidene Complexes. While **1** dissolved in dry CH_2Cl_2 or $CDCl_3$ without change and was insoluble in Et_2O,[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 BF_4^-, 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-



17. L = PPh_3 18. L = PPh_3 19. L = $P(C_6H_{11})_3$

(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.
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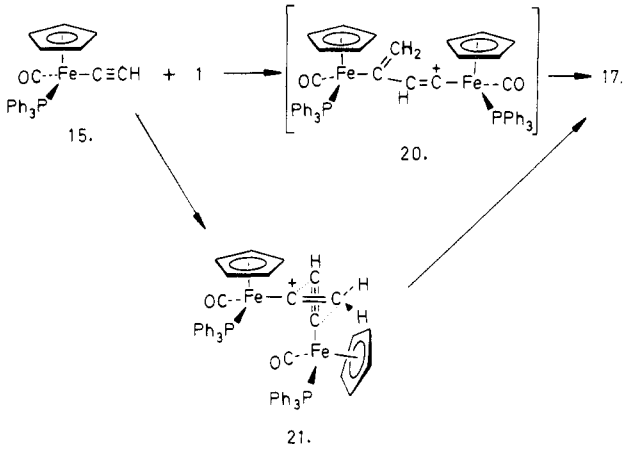
(21) The carbene carbon in the compound $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(CHPh)]^+$ resonates at δ 342: Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099–6101.
(22) A discussion of fast atom bombardment (FAB) mass spectrometry has appeared recently: Williams, D. H.; Bradley, C.; Bojesen, G.; Santikarn, S.; Taylor, L. C. E. *J. Am. Chem. Soc.* **1981**, *103*, 5700–5704.

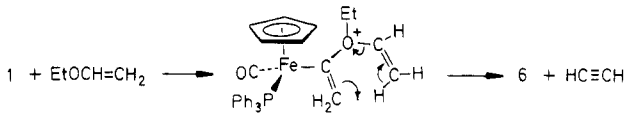
compound **17**, in which the methylene protons are symmetrically nonequivalent, and the minor component must be the *R,R*:*S,S* pair **18** in which the methylene protons are related by a twofold rotation axis. Surprisingly it was not possible to alter the 3:1 ratio of **17**/**18** either by repeated recrystallization or by chromatography on deactivated silica gel. A further curious observation was made when an analogue of **1**, $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ was dissolved in THF. The ^1H 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 $[Fe(\eta\text{-}C_5H_5)(CO)_2(C{\equiv}CPh)]$ in the absence of nucleophiles. Formation of an intermediate cationic vinylidene complex $[Fe(\eta\text{-}C_5H_5)(CO)_2(C{=}CHPh)]^+$, 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 $HBF_4{\cdot}Et_2O$ to solutions of **15** afforded an identical



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 $P(C_6H_{11})_3$ 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 immediate hydrolysis of free **1** would occur. No traces of the expected product of hydrolysis, $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$, 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. ^1H (60 MHz), ^{13}C (15 MHz), and ^{19}F (56 MHz) NMR spectra were run on a JEOL FX-60Q instrument; certain ^1H 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_2S, 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_2Cl_2 and $CDCl_3$ which were distilled from P_4O_{10}. All reactions were run under an atmosphere of dry nitrogen or on a vacuum line.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{=}CH_2)]^+BF_4^-$, **1**, and $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ were prepared as previously described.[2]

Reaction of 1 with H_2O. A solution of **1** (0.10 g, 0.19 mmol) in CH_2Cl_2 (10 mL) was shaken vigorously with H_2O (5 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and evaporated to afford $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ as orange crystals (0.070 g, 80%). IR and ^1H NMR spectra were identical with literature data.[26]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OMe)Me\}]^+BF_4^-$ (5). The vinylidene compound **1** (0.10 g, 0.19 mmol) was dissolved in CH_3OH (20 mL). After 0.25 h the pale yellow solution was evaporated and the crude residue recrystallized from CH_2Cl_2/Et_2O to give **5** as yellow crystals (0.074 g, 70%; mp 164 °C). IR and ^1H NMR spectra were identical with literature data.[11]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OEt)Me\}]^+BF_4^-$ (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 ^1H NMR spectra were identical with literature data.[11]

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O\text{-}i\text{-}Pr)Me\}]^+BF_4^-$ (7) was similarly prepared from **1** (0.10 g, 0.19 mmol) and *i*-PrOH (15 mL),

(23) Kolobova, N. Y.; Skripkin, V. V.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *169*, 293–300.
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(25) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203–1205.
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as yellow crystals (0.079 g, 72%; mp 173 °C). For IR and ^1H NMR data, see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OCH_2CH{=}CH_2)Me\}]^+BF_4^-$ (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 ^1H NMR data, see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(OMe)CH_2D\}]^+BF_4^-$ (9) was likewise prepared from 1 (0.10 g, 0.19 mmol) and CH_3OD (Aldrich, 15 mL), as pale yellow crystals (0.080 g, 75%; mp 108 °C). For IR and ^1H NMR data see Table I.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SH)Me\}]^+BF_4^-$ (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_2S, and the reaction mixture was stirred for 1 h. Excess H_2S 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_2O column. Et_2O eluted $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.050 g, 11%), and acetone eluted an orange band which yielded **10**, after evaporation and recrystallization from CH_2Cl_2/Et_2O, as orange crystals (0.34 g, 65%; mp 104 °C). For IR and ^1H NMR data see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(SMe)Me\}]^+BF_4^-$ (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_2O yielded **11** as yellow crystals (0.43 g, 79%; mp 141 °C dec). For IR and ^1H NMR data see Table I. Anal. C, H.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHCH_2Ph)Me\}]^+BF_4^-$ (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_2Cl_2/Et_2O (−30 °C) to give **12** as yellow crystals (0.89 g, 74%; mp 203 °C). For IR and ^1H NMR data, see Table I. Anal. C, H, N.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NHMe)Me\}]^+BF_4^-$ (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_2O column. Ether eluted $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.017 g, 2%) followed by $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$,[2] **15** (0.092 g, 11%), and CH_2Cl_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 ^1H NMR data, see Table I. Anal. C, H, N.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(NMe_2)Me\}]^+BF_4^-$ (14) was prepared in a similar reaction using 1 (1.00 g, 1.91 mmol) and Me_2NH (25 mL). Chromatography as described above yielded $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(O)Me\}]$ (0.07 g, 8%), and **15** (0.11 g, 13%), eluting with Et_2O. Acetone eluted an orange band, which was evaporated and recrystallized from CH_2Cl_2/Et_2O to afford **14** as orange crystals (0.81 g, 77%; mp 176 °C). For IR and ^1H NMR data, see Table I. Anal. C, H, N.

Reaction of 1 with Me_3N. In a similar reaction, 1 (0.50 g, 0.95 mmol) and Me_3N (25 mL) were stirred at −116 °C ($EtOH/N_2$ (liquid) slush bath) for 2 h. Workup as described above yielded $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(C{\equiv}CH)]$, **15**[2] (0.34 g, 82%), after recrystallization from toluene/hexane.

$[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{C(Cl)Me\}]^+BF_4^-$ (16). A solution of 1 (1.15 g, 2.2 mmol) in CH_2Cl_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_2Cl_2/Et_2O 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 $C_{26}H_{23}BClF_4FeOP$: 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 $[Ph_3P{=}N{=}PPh_3]Cl$ (0.11 g, 0.19 mmol) followed by CF_3SO_3H (0.17 mL, 0.19 mmol). ^1H and ^{13}C NMR spectra of the resultant mixture are reported in Table I.

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(PPh_3)_2(\mu\text{-}C_4H_3)]^+BF_4^-$ (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_2Cl_2, eluted a bright orange band. Evaporation, followed by recrystallization from CH_2Cl_2/Et_2O 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, ^1H NMR, ^{13}C NMR data, see Table II. Anal. C, H.

$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(C_6H_{11})_3\}_2(\mu\text{-}C_4H_3)]^+BF_4^-$ (19) was prepared similarly by stirring a solution of $[Fe(\eta\text{-}C_5H_5)(CO)\{P(C_6H_{11})_3\}(C{=}CH_2)]^+BF_4^-$ (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, ^1H 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_2O (20 mL) was treated with freshly distilled $EtOCH{=}CH_2$ (10 mL), and CH_2Cl_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_2Cl_2 mixture, afforded a single yellow band, which on evaporation yielded **6** (1.21 g; 96%), identified by its ^1H NMR spectrum.

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