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Chemistry of Dicarbonyl η^5-Cyclopentadienyliron Complexes. General Syntheses of Monosubstituted η^2-Olefin Complexes and of 1-Substituted η^1-Allyl Complexes. Conformational Effects on the Course of Deprotonation of (η^2-Olefin) Cations

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Abstract: Reaction of dicarbonyl η^5-cyclopentadienyl(η^1-allyl)iron with cationic electrophiles provides a general route to monosubstituted (η^2-olefin)iron complexes. Alternatively these may be obtained by an exchange reaction employing the olefin and dicarbonyl η^5-cyclopentadienyl(η^2-isobutylene)iron tetrafluoroborate. Deprotonation of the cationic olefin complexes provides a general route to 1-substituted η^1-allyliron complexes. The most stable conformation for the monosubstituted (η^2-olefin)iron cation is best represented by **17b**. The stereochemistry of the η^1-allyliron complexes derived by deprotonation of the complex cations can be accounted for in terms of preferred base abstraction of an allylic proton trans to the iron–olefin bond. Deprotonation of the allyl alcohol complex (**3p**) leads to the lactone (**26**) through a conformationally determined stereospecific intramolecular reaction. The ^{13}C NMR spectra of several (η^2-olefin)iron cations are recorded and shown to provide useful information relevant to their conformations. Deuteration of dicarbonyl η^5-cyclopentadienyl(η^1-cinnamyl)iron with deuteriotrifluoroacetic acid is shown to be nonstereospecific.

In order to examine the synthetic applications of $(3 + n)$ cycloaddition reactions[1] and of metal-assisted olefin condensations[2] employing dicarbonyl η^5-cyclopentadienyl-(η^1-allyl)iron complexes [hereafter designated as (η^1-allyl)Fp complexes], general methods for the preparation of these substances are required. Simple alkyl-substituted (η^1-allyl)Fp complexes have been prepared by metallation of the corresponding allyl halides or tosylates with the dicarbonyl η^5-cyclopentadienyl ferrate anion (Fp^-)[3] or through deprotonation of the dicarbonyl η^5-cyclopentadienyl(olefin)iron cation [Fp(olefin)$^+$].[1b] These latter complexes are in turn available either directly from the olefin by an exchange reaction with the Fp(isobutylene) cation[4] or through a reaction sequence involving the complex iron anion (Fp^-) and an epoxide.[5] These transformations are summarized below in Figure 1.

The present paper provides a general procedure for the introduction of functional groups at the terminal olefinic carbon atom of (η^1-allyl)Fp complexes, and a description of the chemistry of the intermediate Fp(olefin) cations, in particular their conformation and the stereochemistry of their deprotonation.

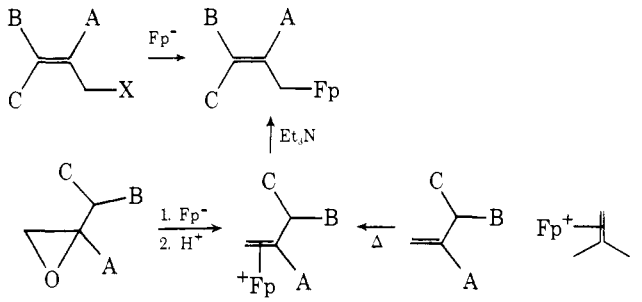
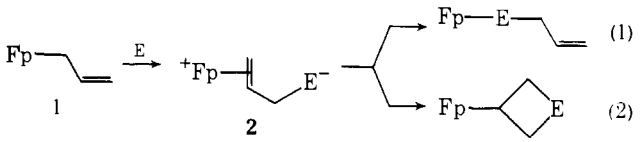


Figure 1.

Results and Discussion

Evidence for the formation of a dipolar intermediate (**2**) in the reactions of (η^1-allyl)Fp complexes with uncharged electrophiles has previously been summarized.[1d] These intermediates collapse by either anionic attack at the metal or on the activated olefin, affording "insertion" or cycloaddition products (eq 1 and 2).



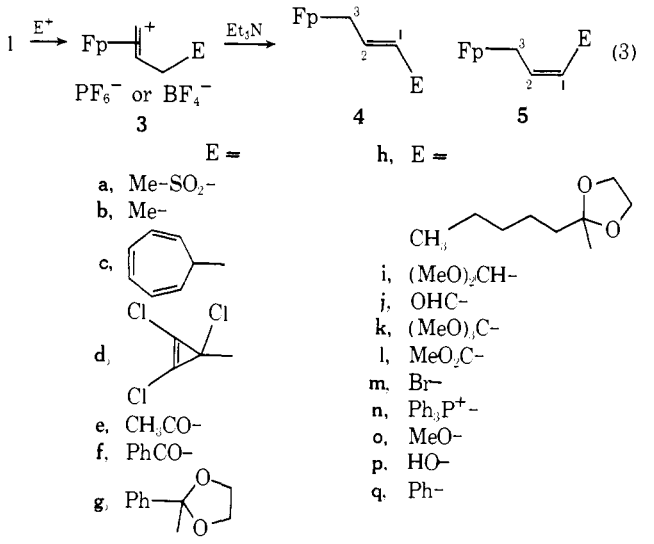
With cationic electrophiles, the intermediate (**2**, E instead of E^-) is incapable of further reaction and may readily be isolated. On deprotonation with triethylamine, the 1-substituted (η^1-allyl)Fp complex is obtained, generally in high yield (eq 3).[6] These substances, which are isolated as low-melting solids or oils, are readily characterized through their crystalline cycloaddition products with tetracyanoethylene (TCNE).

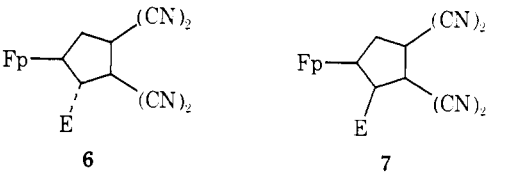
Sulfonylation. The reaction of (η^1-allyl)Fp complexes with sulfur dioxide generally affords "insertion" products[7] (eq 1). However, in the presence of a suitable additional electrophile, the intermediate (**2**) may be trapped. Thus, when the parent complex (**1**) is added to a suspension of trimethyloxonium tetrafluoroborate in liquid SO_2, the salt (**3a**) is isolated in high yield.[8] Deprotonation of **3a** proceeds readily at 0° to give the *trans*-1-methylsulfonylallyliron complex (**4a**) as the exclusive product in 90% yield. This was further characterized as its TCNE adduct **6a**. The formation of **3a** in the presence of oxonium salt suggests that **1** is converted rapidly and entirely to the dipolar ion **2** (E = SO_2) in liquid SO_2 solution since the oxonium salt alone may be shown to be sufficiently electrophilic to effect the alkylation of **1**.

Alkylation. When carried out in methylene chloride solution, the reaction of **1** with trimethyloxonium tetrafluoroborate gives the Fp(1-butenyl) cation (**3b**) in high yield. In contrast to **3a**, deprotonation of this cation gave a mixture of the *trans*- and *cis*-2-butenyl complexes (**4b** and **5b**) in a ratio of 3:2.

The reaction of tropylium tetrafluoroborate with **1** also proceeds rapidly at room temperature affording a quantitative yield of the salt (**3c**). Deprotonation at 0° gave, as with **3b**, a mixture of isomeric complexes **4c** and **5c**.[9] The adduct, obtained on treatment of this product with an equimolar amount of TCNE, is derived exclusively by a (3 + 2) cycloaddition reaction involving the metal-activated double bond, rather than the cycloheptatriene ring, since the adduct preserves the characteristic NMR absorption pattern of a cycloheptatriene ring and fails to exhibit cyclopropane proton absorption.[10]

Alkylation was also effected with the trichlorocyclopropenium ion,[11] but attempts to deprotonate the product (**3d**) led instead to regeneration of **1**.





Acylation. The introduction of an acyl function at C_1 in **1** may be accomplished by direct acylation at low temperatures employing acyl cations generated from acyl halides and silver hexafluoroantimonate.[12] The intermediate acylated cations (**3e,f**), formed with acetyl or benzoyl chloride, were not isolated but were deprotonated in situ by treatment with triethylamine. In each of these reactions, the product was exclusively the trans derivatives (**4e,f**).

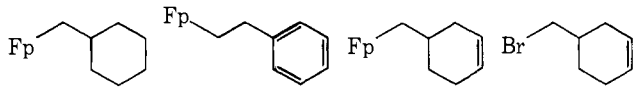
A more convenient procedure makes use of dialkoxycarbenium ions as electrophiles. These cations are readily available from orthoformates or 1,3-dioxolanes on treatment with trityl salts,[13] and their reactions with **1** take place rapidly at low temperatures to give the corresponding cations (**3**) as crystalline, air-stable substances, in high yield. Deprotonation is achieved rapidly at 0° to give essentially quantitative conversion to the 1-substituted allyl complex. In all of the cases examined (**3g–i**), deprotonation gave the trans isomer (**4g–i**) apparently as the exclusive product; none of the cis isomers could be detected in the NMR spectra of products of these reactions.

The hydrolytic stability of the protected acyl functions in these complexes varies considerably. Protonation of the activated double bond is apparently competitive with protonation of oxygen and may as a consequence retard hydrolysis of the ketal group. Complex **4g** resisted hydrolysis in a 10% aqueous dioxane solution of HCl at room temperature, while **4h** was converted with 5% HCl principally to the unconjugated demetallated ketone. Hydrolysis of **4i** to **4j** occurs rapidly and quantitatively in 1% HCl.

Carboxylation. Trimethoxycarbenium ion, prepared from trimethyl orthocarbonate and trityl cation, serves as a convenient electrophile for the introduction of a carboalkoxy function at C_1 in complex **1**. The cation (**3k**) is hydrolytically very sensitive and was converted directly to the ester (**4l**).

Bromination and Brominolysis. The cleavage of transition metal-carbon σ bonds by halogen or positive halogen re-

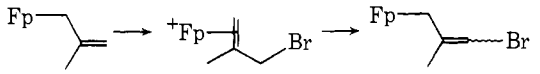
agents is well known.[14,15] The brominolysis of the Fe-C bond in (alkyl)Fp complexes is a very rapid reaction and may be achieved either with bromine,[15] pyridinium perbromide, or *N*-bromopyridinium bromide,[16] the latter reagent being preferred. The cleavage of the Fp-C bond in **8** and **9** at −78° with *N*-bromopyridinium bromide may be effected in high yield. Indeed, so rapid is the brominolysis reaction that it can be carried out selectively in the presence of an isolated center of unsaturation, as is illustrated by the conversion of **10** to **11**.



8 **9** **10** **11**

When the double bond is activated toward electrophilic attack by conjugation with the Fp-C bond, it becomes the preferred site of reaction. Even at −78°, the reaction of **1** with bromine is virtually instantaneous, and the cation (**3m**), isolated as the hexafluorophosphate salt, is obtained in high yield. In sharp contrast to preceding experience, deprotonation of this cation led *exclusively* to the *cis*-1-bromoallyliron complex (**5m**), as indicated by the vinyl proton coupling constant of 6.5 Hz. The TCNE adduct prepared from this complex is, not surprisingly, unstable and readily eliminates FpBr.

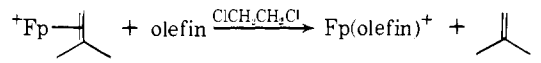
Bromination and deprotonation of the methallyliron complex (**12**) gave (1-bromo-2-methylallyl)Fp (**14**). Little if



12 **13** **14**

any of the isomeric 2-bromomethallyliron complex is formed in the deprotonation of the intermediate olefin complex (**13**), and the NMR spectrum of the product shows that it is a single stereoisomer, of as yet unknown stereochemistry.

Olefin Exchange Reaction. As an alternative to electrophilic substitution of preformed (η^1-allyl)Fp complexes, we undertook to explore the preparation of Fp(olefin) cations directly from the functionalized olefin by the exchange process shown below (eq 4).

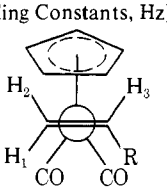


(4)

15

A number of simple mono- and dienes had previously been shown to enter successfully into this reaction.[4] The exchange reaction has been employed most successfully with monosubstituted olefins, although it is not confined to these, and a number of cycloalkene complexes including C-5, 6, 7, and 8 cycloalkenes,[1b,4] cyclohexa-1,3- and -1,4-dienes, cycloocta-1,5-diene, and norbornadiene[4] can be made by this method. The effectiveness of monosubstituted olefins as components in the exchange process is not surprising since efficient conversion to product complex depends on its thermodynamic stability, which is observed to decrease with increasing alkyl substitution of the olefin.[17] An instructive illustration of the importance of steric factors in the exchange reaction is provided by cyclopentene and cyclohexene which give 100 and 2% yields of Fp(olefin)$^+$ complexes, respectively, under identical conditions in the exchange reaction. Models show that a serious steric compression exists in the cyclohexene complex, involving an axial ring proton at C_4 of the cyclohexene ring with the Fp group. Comparable interactions are absent in the cyclopentene complex.

Table I. NMR Spectra of Monosubstituted Fp(olefin)$^+$ Complexes (Chemical Shifts, τ; Coupling Constants, Hz)



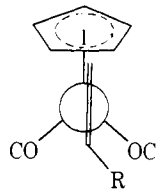
Complex	Cp	H_1 (J_{13})	H_2 (J_{23})
3b[a]	4.39	6.54 (15)	6.09 (8)
3c[a]	4.33	6.42 (15)	6.0 (8)
3g[a]	4.40	6.55 (14.5)	6.0 (9)
3h[a]	4.30	6.44 (15)	~5.93 (8)
3m[b]	4.22	6.32 (14)	5.98 (8)
3o[a]	4.32	6.44 (15)	5.96 (8)
3p[a]	4.32	6.36 (15)	5.97 (8)
3q[a]	4.31	6.35 (15)	6.02 (8)
24[c]	5.17	7.18 (11.5)	6.70 (7.5)

[a] Taken in nitromethane-d_3. [b] Taken in acetone-d_6. [c] Taken in $CDCl_3$.

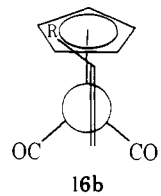
Of the three olefin complexes (**3n–p**) prepared in the exchange reaction, **3o** was alternatively prepared by metalation of 3-methoxypropene oxide with Fp$^-$ followed by treatment with acid.[5] Attempts to prepare an allyl cyanide olefin complex gave instead the nitrile coordinated cation $(FpN{\equiv}CCH_2CH{=}CH_2)^+$. Deprotonation of the methoxypropeneiron complex (**3o**), like **3m,** behaved exceptionally and gave exclusively the *cis*-1-methoxyallyliron complex (**5o**), as indicated by the vinyl proton coupling constant of 6 Hz. This was characterized as its TCNE and tosyl isocyanate adducts. Like the acetal complexes **4g,h,** the vinyl ether complex **5o** proved to be resistant to mild acid hydrolysis and was recovered in near quantitative yield after treatment with 3% aqueous HCl at reflux after 30 min. A discussion of the product formed in the deprotonation of **3p** is deferred to the section below.

Conformation of Monosubstituted Olefin Complexes. Four extreme conformations of these complexes may be considered (**16a,b** and **17a,b**). Of these, models[18,19] clearly indicate that, for conformations **16a,b,** in which the olefin axis is either in or near the Fp group symmetry plane, substantial steric interactions exist between ring protons or the carbonyl group and the olefin ligand.

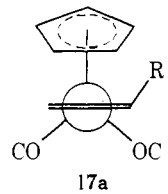
A clear distinction cannot be made on steric grounds between **17a** and **17b** since interactions subsist in each be-



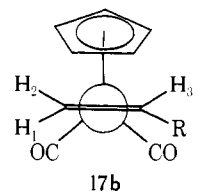
16a



16b



17a



17b

tween the olefin substituent and either ring protons or a carbonyl ligand. However, an examination of the NMR spectral data (Table I) for a series of these complexes provides grounds for concluding that a conformation close to the idealized form (**17b**) is favored. The close correspondence of terminal vinyl proton absorptions in these complexes suggests very similar conformational populations. For both

Table II. Carbonyl ^{13}C Resonance in Fp(olefin) Complexes (Chemical Shifts, ppm)[a]

Cation	CO		Δ
Fp—‖	209.60		
(3r)Fp—‖	209.21	210.96	1.75
(15)Fp—‖	210.83		
(3b)Fp—‖	208.88	210.76	1.88
(3m)Fp—‖—Br	207.27	209.27	2.00
(3o)Fp—‖—OMe	209.08	210.18	1.10

[a] From internal Me_4Si, taken in CD_3NO_2 solution. [b] Counterion BF_4^-. [c] Counterion PF_6^-.

3m and **3o,** ^{13}C NMR spectra provide evidence (vide infra) for significant interactions between the heteroatom and carbonyl ligands, and these can only be attained in **17b** or a conformation closely related to it.[20,21]

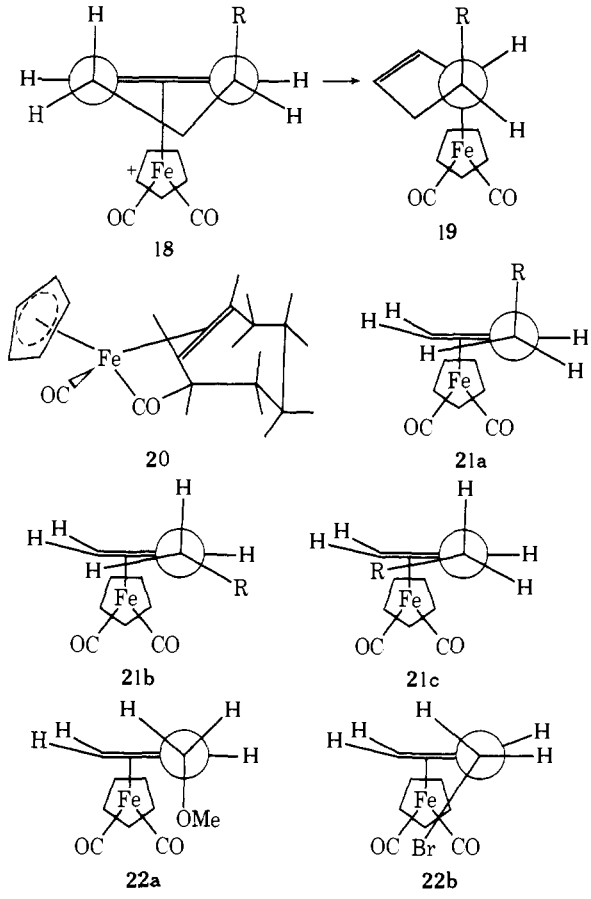
The relatively large chemical-shift differences between H_1 and H_2 (**17b**) may be due to anisotropy effects associated with cyclopentadienyl ring currents, but effects of the carbonyl ligands may also be significant.

Stereochemistry of Deprotonation. The ease with which deprotonation of Fp(olefin) cations may be achieved attests to the powerful acidifying effect which metal complexation has upon the allylic protons in these complexes. A quantitative measure of these acidities has not yet been made, but the fact that deprotonation is complete with triethylamine would require a pK_a of less than 10 for those cations.

The predominant or exclusive formation of (*trans*-allyl)Fp complexes (**4**) in the deprotonation of monosubstituted Fp(olefin) cations would appear to suggest that thermodynamic factors of product stability are determinant. However, a transition state for deprotonation lying closer to reactants than products seems more plausible in view of the pronounced acidity of the complex cations. Moreover, in the absence of special stabilizing factors, the exclusive formation of (*cis*-allyl)Fp complexes in the deprotonation of **3m** and **3o** is difficult to account for in terms of thermodynamic product control. Finally it can be shown that the *cis*-methoxy complex (**5o**) is not formed by isomerization of an initially generated trans isomer (**4o**) and must therefore be the kinetic product. The latter complex was prepared independently by metallation of *trans*-3-chloro-1-methoxy-1-propene,[22] with Fp^-. Treatment of **4o** with triethylammonium tetrafluoroborate in methylene chloride, under conditions identical with those employed to effect the deprotonation of **3o,** left it unchanged.

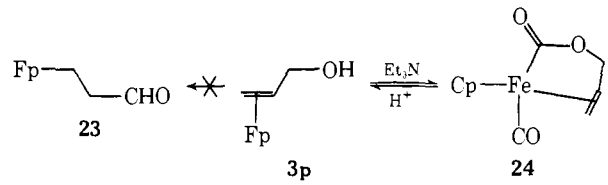
The results are better in accord with a process of kinetic deprotonation, in which conformational effects play a dominant role. The importance of these factors is to be seen in the stereospecific trans deprotonation of the cyclopentene complexes (**18** → **19**),[1b] and in the resistance to deprotonation of the Fp(cycloheptene) cation (**20**) which lacks allylic protons trans to the Fp-olefin bond.[1b,23] Thus, although conformation **21a** for monosubstituted olefin complexes may be favored on steric grounds, deprotonation would be expected to occur preferentially by way of **21b** or **21c.** Of these, the less crowded conformer **21b,** would yield *trans*-allyliron complexes (**4**) on deprotonation.

For cations such as **3o** and **3m,** models indicate that the methoxyl oxygen atom in the former may readily approach within bonding distance of one of the carbonyls (**22a**), while the longer C-Br bond in **3m** allows the halogen atom to interact with both ligands (**22b**).[24] Deprotonation through these conformations must give rise to the *cis*-allyliron complexes **5o** and **5m.**



The ^{13}C NMR data for a series of Fp(olefin) cations (Table II) provide evidence for such interactions. In chiral, monosubstituted olefin complexes, two carbonyl resonances are observed. For **3b** and **3r,** these absorptions are separated by almost 2 ppm. The lower field signal may be assigned to the carbonyl ligand proximate to the alkyl group (as in **17b**). Thus, carbonyl resonance in the ethylene complex lies close to the high-field signal observed in **3b** and **3r** while, in **15**[25] in which both carbonyls must be proximate to a methyl group, the signal lies near that of the low-field resonances in **3b** and **3r.** For the methoxypropylene complex (**3o**), the chemical-shift difference of carbonyl signals is significantly reduced, principally because of increased shielding of the low-field absorption, while for **3m,** greater shielding of *both* carbonyl groups compared with **3b** and **3r** is observed.

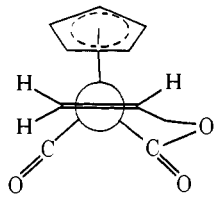
A dramatic illustration of the accessibility of the methoxyl oxygen to the ligand carbonyl center in **3o** is provided by the transformation of the closely related allyl alcohol complex (**3p**) on treatment with triethylamine. The product of this reaction is not the anticipated propionaldehyde complex (**23**), but the lactone (**24**), formed by intramolecular



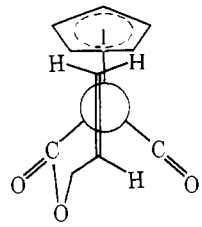
nucleophilic addition of the alcohol function to a carbonyl ligand. This transformation, which is reversible, is of further interest in view of the generally low order of reactivity

of carbonyl ligands in cationic cyclopentadienyliron carbonyl complexes.[26]

A further feature of this reaction deserves comment. The allyl alcohol complex (**3p**) like all of the other monosubstituted olefin complexes (**3**) is chiral, and its transformation to lactone creates a new asymmetric center at the metal atom. In principle a mixture of diastereomeric lactones might be anticipated. In fact only one is formed. Of the two possible diastereomers **25** and **26**, the latter may be excluded since the NMR spectrum of the lactone clearly shows that the terminal vinyl protons are in very different magnetic environments. Neglecting the anticipated shift of both of these protons to higher field, they each preserve the same relative chemical shifts as observed in the related cations (**3**). The high stereospecificity of the lactonization reaction is not surprising in view of the general preference for conformation **17b** in the cations (**3**) and of the further stabilization of this conformation in **3p** through the electrostatic interactions previously defined.

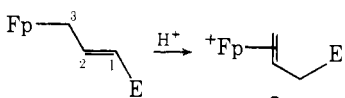


25



26

Stereochemistry of Protonation of Acyclic (η^1-allyl)Fp Complexes. The large difference in chemical shifts of methylene protons observed in many of the olefin complexes (**3**) prompted us to examine the stereochemistry of the reverse process (eq 5). The cinnamyl complex (**4q**) was chosen for these studies since the diastereotopic methylene proton absorptions are most clearly defined in the NMR spectrum of the corresponding cation (**3q**), although the lower field double doublet is partially obscured by the terminal methylene protons. When deuteration of **4q** was carried out with deuteriotrifluoroacetic acid, and the resulting cation was isolated as the hexafluorophosphate salt, the distribution of protium in the two diastereomeric positions of the product was found to be equivalent. Thus, in contrast to the protonation of (2-butynyl)Fp or to electrophilic attack by carbon electrophiles on (η^1-cycloalkenyl)Fp complexes,[1b] which give rise to products derived from trans electrophilic attack, protonation of acyclic (η^1-allyl)Fp complexes by CF_3COOH appears to be nonstereospecific. The formation of equal amounts of the diastereomerically deuterated cations (**3q**) requires that deuteration of **4q** proceed both cis and trans with respect to the Fp-C bond with equal facility. Further work is needed before the factors controlling the stereochemistry of electrophilic attack on unsaturated centers conjugated to metal-C σ bonds may be well defined.



4 3 (5)

Experimental Section

All operations were carried out in a nitrogen atmosphere. Solvents were dried, degassed, and stored under nitrogen and over molecular sieves. Ir spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. ^1H NMR spectra were determined on a Varian A-60 spectrometer (NIH GM-13183) and ^{13}C NMR spectra on a Bruker WH-90 at 22.62 MHz (NSF GU 3852, GP 37156). Mass spectra were obtained on an AEI MS-12 direct inlet spectrometer (NSF GP-3644). Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Reaction of 1 with Sulfur Dioxide in the Presence of Trimethyloxonium Tetrafluoroborate. Sulfur dioxide (15 ml) was distilled into a 100-ml flask on a high vacuum line. To this was added trimethyloxonium tetrafluoroborate[28] (1.48 g, 10 mmol). The solution was cooled to −20°, and 2.18 g (10 mmol) of **1** was added. Reaction was allowed to continue at −20° for 30 min. The solvent was allowed to evaporate in a stream of nitrogen, and the residue was triturated with acetone and filtered. Recrystallization from nitromethane afforded 3.0 g (80%) of the product (**3a**) as yellow crystals: ir (KBr) 2080, 2030 (CO), 1300, 1135 cm^{-1} (SO_2); NMR (CD_3NO_2, −10°) τ 4.15 (s, 5, Cp), 6.9 (s, 3, CH_3).

Anal. Calcd for $C_{11}H_{13}FeSO_4BF_4$: C, 34.37; H, 3.39; S, 8.33. Found: C, 34.25; H, 3.39; S, 8.15.

Deprotonation of 3a. Preparation of TCNE Adduct. Deprotonation of 384 mg (1 mmol) of **3a** was carried out with triethylamine for 15 min at 0°, and the reaction was worked up following the procedure for **3g**, to give 260 mg (**4a**) (90%); ir (neat film) 2010, 1960 (CO), 1300, 1125 cm^{-1} (SO_2); NMR ($CDCl_3$) τ 2.75 (dt, 1, J = 9.5, J' = 15 Hz, =CH), 3.95 (d, 1, J = 15, =CH), 5.20 (s, 5, Cp), 7.13 (s, 3, CH_3), 7.98 (d, 2, J = 10, CH_2).

Anal. Calcd for $C_{11}H_{12}FeO_4S$: C, 44.60; H, 4.05; S, 10.81. Found: C, 44.66; H, 4.15; S, 10.98.

The TCNE adduct (**6a**) was obtained employing the following general procedure. The complex was taken up in a small volume of methylene chloride, and a solution of an equivalent of TCNE in tetrahydrofuran was added to this. After 15 min at room temperature, solvent was removed, and the residue was recrystallized, generally from methylene chloride–hexane, 80% yield: dec 142°; ir (KBr) 2030, 1970 (CO), 1320, 1140 cm^{-1} (SO_2); NMR τ (CD_3NO_2) 4.90 (s, 5, Cp), 6.70 (s, 3, CH_3), 6.6–7.5 (m, 4, CH, CH_2).

Anal. Calcd for $C_{17}H_{12}FeN_4O_4S$: C, 48.11; H, 2.83; N, 13.21; S, 7.55. Found: C, 48.35; H, 3.00; N, 13.08; S, 7.53.

Reaction of 1 with Trimethyloxonium Tetrafluoroborate. A suspension of 1.85 g (12.5 mmol) of trimethyloxonium tetrafluoroborate[28] in 20 ml of methylene chloride was treated with 2.4 g (11 mmol) of **1** in 10 ml of methylene chloride. After stirring for 90 min, the solution was filtered through a short column of Celite, and the filtrate was diluted with ether. The yellow salt was collected and recrystallized from acetone–ether to give 3.0 g (85%) of product (**3b**): ir (KBr) 2080, 2040 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.39 (s, 5, Cp), 4.9 (m, 1, =CH) 6.09 (d, 1, J = 8 Hz, cis =CH_2), 6.54 (d, 1, J = 15 Hz, trans =CH_2), 7.6 (m, 2 H, CH_2), 8.84 (t, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{11}H_{13}FeO_2BF_4$: C, 41.25; H, 4.06. Found: C, 40.97; H, 4.23.

Deprotonation of 3b. Deprotonation of 640 mg of **3b** was carried out with triethylamine at 0° for 15 min following the procedure for **3g**. The product is an amber oil, 420 mg (91%): ir (neat film) 2000, 1940 cm^{-1} (CO); NMR (CS_2) τ 4.1–5.2 (m, 2, =CH), 5.35 (s, cis isomer Cp), 5.42 (s, trans isomer Cp), 8.0 (m, 2, CH_2), 8.47 (dm, 3, CH_3).

The trans isomer (**4b**) may be largely separated from the cis isomer by chromatography on a 5-ft neutral activity III alumina column, eluting with pentane. The NMR spectrum of the product is identical with that given below.

Preparation of 4b by Metallation of *trans*-2-Butenyl Benzenesulfonate. A solution of $NaCpFe(CO)_2$[29] in 200 ml of THF was prepared from 13.3 g (37.5 mmol) of dimer, and 15.9 g (75.0 mmol) of *trans*-2-butenyl benzenesulfonate, prepared from *trans*-2-butenyl alcohol, was added to this. The reaction was allowed to continue for 1 hr and was then worked up and the product chromatographed on neutral activity III alumina: NMR (CS_2) τ 4.6 (m, 2, =CH), 5.42 (s, 5, Cp), 7.92 (dm, 2, $J \sim 8$ Hz, CH_2), 8.45 (dm, 3, $J \sim 6$ Hz, CH_3).

TCNE Adduct of 4b. The adduct (**6b**), prepared in the usual manner, was recrystallized from methylene chloride–hexane and obtained in 77% yield: mp 149–151°; ir (KBr) 2020, 1960 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.90, 4.94 (2s, 5, Cp), 6.7–7.8 (m, 4, CH, CH_2), 8.48, 8.61 (2d, 3, J = 7 Hz, CH_3).

Reaction of 1 with Tropylium Tetrafluoroborate. Tropylium tetrafluoroborate (3.56 g, 20 mmol) was suspended in 50 ml of

methylene chloride, and 4.58 g (21 mmol) of **1** in 10 ml of methylene chloride was added to this. After 15 min, the solution was homogeneous. Solvent was then removed in vacuo, and the residue was taken up in 100 ml of ethanol and scratched. The crystalline product was collected, washed with ether, and recrystallized from acetone–ether to give 7.8 g (99%) of product (**3c**): ir (KBr) 2040, 2000 cm^{-1} (CO); NMR (CD_3NO_2) τ 3.28 (m, 2, $H_{3,4}$-cycloheptatriene), 3.7 (m, 2, $H_{2,5}$-cycloheptatriene), 4.33 (s, 5, Cp), 4.7 (m, 3, =CH, $H_{1,6}$-cycloheptatriene), 6.00 (d, 1, J = 8 Hz, cis =CH_2), 6.42 (d, 1, J = 15 Hz, trans =CH_2), 8.2 (m, 1, H_7-cycloheptatriene), 7.1 (m, 2, CH_2).

Anal. Calcd for $C_{17}H_{17}FeO_2BF_4$: C, 51.51; H, 4.29. Found: C, 51.58; H, 4.26.

Deprotonation of 3c. Deprotonation of 1.58 g (4 mmol) of **3c** was carried out with triethylamine at 0° for 15 min, and the product was isolated, following the procedure for **3g**, as an amber oil, 1.2 g (98%): ir (KBr) 2000, 1920 cm^{-1} (CO); NMR (CS_2) τ 3.4 (m, 2, $H_{3,4}$-cycloheptatriene), 4.0 (m, 2, $H_{2,5}$-cycloheptatriene), 4.3 (m, 2, $H_{1,6}$-cycloheptatriene), 4.9 (m, 2, =CH), 5.40, 5.47 (2s, 5, Cp), 7.7 (m, 1, CH), 7.88, 8.08 (2d, 2, J = 8 Hz, CH_2).

Anal. Calcd for $C_{17}H_{16}FeO_2$: C, 66.22; H, 5.19. Found: C, 66.43; H, 5.18.

TCNE Adduct of 4,5c. This was prepared in 69% yield following the standard procedure. The product crystallized slowly over a period of 24 hr: mp 143–144° dec; ir (KBr) 2040, 1970 cm^{-1} (CO); NMR (CD_3NO_2) τ 3.5 (m, 4, =CH), 4.97 (s, 5, Cp), 4.95 (m, 2, =CH) 6.7–8.1 (m, 5, CH, CH_2); mass spectrum (70 eV) m/e 436 (M^+).

Anal. Calcd for $C_{23}H_{16}FeN_4O_2$: C, 63.30; H, 3.67; N, 12.84. Found: C, 63.07; H, 3.55; N, 12.84.

Reaction of 1 with Trichlorocyclopropenium Hexachloroantimonate. Trichlorocyclopropenium hexachloroantimonate[11] (2.39 g, 5 mmol) and 1.09 g (5 mmol) of **1** were brought into reaction at room temperature in methylene chloride solution. An immediate precipitation of product took place. This was filtered and washed with methylene chloride–ether (1:1) to give 3.2 g (92%) of **3d**: ir (KBr) 2040, 2080 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.22 (Cp).

Anal. Calcd for $C_{13}H_{10}Cl_9FeO_2Sb$: C, 22.45; H, 1.44. Found: C, 22.41; H, 1.61.

Deprotonation of **3d** with diisopropylethylamine in nitromethane solution gave **1** as the only identifiable product (7%).

Acetylation of 1 with Acetyl Chloride. Preparation of 4e. Silver hexafluoroantimonate (2.2 g, 6.4 mmol) was dissolved in 15 ml of nitromethane at −30°, and acetyl chloride (0.5 g, 6.5 mmol) dissolved in 5 ml of nitromethane was added dropwise with stirring. After 15 min, Celite was added and the mixture rapidly filtered under N_2 into a solution of **1** (1.4 g, 6.4 mmol) in 10 ml of nitromethane at −30°. The reaction mixture was allowed to come to 0°, and triethylamine (0.7 g, 7.0 mmol) in 10 ml of nitromethane was added. After stirring an additional 15 min, the nitromethane was removed under reduced pressure and the residue extracted with ether. The ethereal solution was chromatographed rapidly on a neutral activity III alumina column. Elution with Skelly B gave some starting complex; continued elution with ether afforded the product as an orange oil. An analytical sample, orange crystals, mp 34.5–36°, was obtained by recrystallization from carbon disulfide at −45°: ir (CH_2Cl_2) 2010, 1950 (C≡O), 1625 cm^{-1} (C=O); NMR (CS_2) τ 3.0 (dt, 1, J = 15, J' = 9 Hz), 4.3 (d, 1, J = 15 Hz), 5.3 (s, 5, Cp), 7.95 (d, 2, J = 9 Hz, CH_2), 8.0 (s, 3, CH_3).

Anal. Calcd for $C_{12}H_{12}FeO_3$: C, 55.38; H, 4.62. Found: C, 54.99; H, 4.77.

TCNE Adduct of 4e. A solution of tetracyanoethylene (0.097 g, 0.75 mmol) in degassed benzene (8 ml) was added dropwise to a solution of the acetylallyl complex (0.19 g, 0.75 mmol) in benzene (3 ml). After standing for 2 hr, a yellow crystalline solid had precipitated. Petroleum ether (12 ml) was added to complete the precipitation. The product was collected by filtration and washed with several portions of petroleum ether to give 0.20 g (0.56 mmol, 70%). An analytical sample was obtained by slow evaporation of a methylene chloride–hexane solution with a nitrogen stream affording yellow needles (**6e**), mp 150–151° dec; ir (KBr) 2375 (CN), 2020, 1950 (C≡O), 1720 (C=O) cm^{-1}; NMR τ (CD_3NO_2) 4.9 (s, 5, Cp), 6.1–7.4 (m, 4, CH, CH_2), 7.45 (s, 3, CH_3).

Anal. Calcd for $C_{18}H_{12}N_4O_3Fe$: C, 55.67; H, 3.09; N, 14.43. Found: C, 55.11; H, 2.89; N, 14.37.

Benzoylation of 1 with Benzoyl Chloride. Isolation of 3f. The procedure above used in acetylation of **1** was carried out on 5.6 g (25.6 mmol) of **1**, employing 3.6 g (25.6 mmol) of benzoyl chloride and 8.8 g (25.6 mmol) of $AgSbF_6$ in nitromethane at −30°. The crude product after deprotonation with triethylamine was a red oil (2.5 g): NMR (CD_3NO_2) τ 2–2.8 (m, 6, Ph, CH=), 2.73 (d, 1, J = 15 Hz, CH=), 5.09 (s, 5, Cp), 7.75 (d, 2, J = 9 Hz, CH_2). This was taken up in 20 ml of methylene chloride and treated with 2.2 ml of hexafluorophosphoric acid in 4 ml of acetic anhydride. After pouring into ether and cooling, the red solid was filtered off and recrystallized from acetone–ether to give the product (**3f**) as a yellow solid: ir (KBr) 2050, 2080 (C≡O), 1681 (C=O) cm^{-1}; NMR (CD_3NO_2) τ 4.43 (Cp).

Anal. Calcd for $C_{17}H_{15}F_6FeO_3P$: C, 43.59; H, 3.21; Fe, 11.96. Found: C, 42.86; H, 3.16; Fe, 11.83.

Reaction of 1 with 2-Phenyl-1,3-dioxolenium Hexafluorophosphate. The above procedure was followed, utilizing 5.5 g (19 mmol) of carbenium ion[13] in 20 ml of methylene chloride and 4.58 g (21 mmol) of **1**. Reaction was continued at 0° for 30 min. Work-up as before and recrystallization of the product from acetone–ether gave 9.2 g (95%) of **3g**: ir (KBr) 2100, 2060 cm^{-1} (CO); NMR (CD_3NO_2) τ 2.6 (m, 5, Ar), 4.40 (s, 5, Cp), 5.2 (broad m, 1, =CH), 5.8–6.2 (m, 5, OCH_2, cis =CH_2), 6.55 (d, 1, J = 15 Hz, trans =CH_2), 6.88 (dd, 1, J = 14, J' = 3.5 Hz, CH_2), 8.13 (dd, 1, J = 14, J' = 10 Hz, CH_2).

Anal. Calcd for $C_{19}H_{19}FeO_4PF_6$: C, 44.52; H, 3.71. Found: C, 44.36; H, 3.90.

Deprotonation of 3g. Preparation of TCNE Adduct. A suspension of 512 mg (1 mmol) of **3g** in 10 ml of methylene chloride was cooled to 0°, and triethylamine (0.1 g, 1 mmol) was added. Reaction was continued at 0° for 30 min, solvent was then removed under reduced pressure, and the residue was extracted with ether. The extracts were concentrated and chromatographed on activity III neutral alumina with methylene chloride–ether (1:1) to give the crude product as an amber oil. Crystallization from hexane gave the product (**4g**) as yellow crystals: mp 51–53°, 330 mg (90%); ir (KBr) 2000, 1940 cm^{-1} (CO); NMR (CS_2) τ 2.75 (m, 5, Ar), 4.2 (dt, 1, J = 15, J' = 8 Hz, =CH), 4.68 (d, 1, J = 15 Hz, =CH), 5.47 (s, 5, Cp), 6.20 (m, 4, OCH_2), 8.05 (d, 2, J = 8 Hz, CH_2).

The above product (110 mg, 0.3 mmol) was taken up in 5 ml of methylene chloride and mixed at room temperature with a solution of TCNE (40 mg, 0.3 mmol) in 5 ml of THF. After 15 min, solvent was removed, and the residue was recrystallized from methylene chloride–hexane to give 100 mg (71%) of product (**6g**), mp 168–170° dec; ir (KBr) 2270 (CN), 2020, 1960 cm^{-1} (CO); NMR (CD_3NO_2) τ 2.35 (m, 5, Ar), 5.55 (s, 5, Cp), 5.65 (m, 4, OCH_2), 6–7.6 (m, 4, CH, CH_2).

Anal. Calcd for $C_{25}H_{18}FeN_4O_4$: C, 60.73; H, 3.64; N, 11.34. Found: C, 60.50; H, 3.65; N, 11.31.

Reaction of 1 with 2-*n*-Pentyl-1,3-dioxolenium Tetrafluoroborate. Triphenylmethyl tetrafluoroborate (6.60 g, 20 mmol) was dissolved in 50 ml of liquid SO_2, and hexanal ethylene glycol ketal (10 g, 69 mmol) was added. The solution was kept under reflux (−10°) for 2 hr, and solvent was then allowed to evaporate. The residue was recrystallized from methylene chloride–ether and collected in a Schlenk tube. The salt was dissolved in methylene chloride, and the solution was cooled to −20° before addition of 4.36 g (20 mmol) of **1**. Reaction was continued at this temperature for 20 min. The product was isolated as before and recrystallized from methylene chloride–ether to give 5.9 g (67%) of **3h**: ir (KBr) 2080, 2040 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.3 (s, 5, Cp), 5.1 (m, 1, =CH), 5.93 (d, 1, J = 8 Hz, cis =CH_2), 6.0 (s, 4, OCH_2), 6.44 (d, 1, J = 15 Hz, trans =CH_2), 7.13 (dd, 1, J = 13.5, J' = 3.5 Hz, allylic-CH_2), 7.8–9.1 (broad m, 12, allylic-CH_2, CH_2, CH_3).

Anal. Calcd for $C_{18}H_{25}FeO_4BF_4$: C, 48.21; H, 5.58. Found: C, 47.98; H, 5.62.

Deprotonation of 3h. Preparation of TCNE Adduct. A solution of 900 mg (2 mmol) of **3h** in 10 ml of methylene chloride was treated with 0.3 ml (2.0 mmol) of triethylamine. After 15 min, solvent was removed, the residue was extracted with ether, and the combined extracts were chromatographed on neutral activity III alumina with ether. The product, 600 mg (83%), was obtained as an amber oil: ir (neat film) 2010, 1940 cm^{-1}. The NMR spectrum indicated it to be an approximately 3:1 mixture of trans:cis isomers: NMR (CS_2) of principal component τ 4.05 (dt, 1, J = 15, J' = 8 Hz, =CH), 4.88 (d, 1, J = 15 Hz, =CH), 5.34 (s, 5, Cp), 6.26 (s, 4, OCH_2), 7.94 (d, 2, J = 8 Hz, CH_2Fp).

The complex (600 mg, 1.6 mmol) was converted to its TCNE adduct following the general procedure to give 580 mg (71%) of adduct: mp 138–139° dec; ir (KBr) 2030, 1970 cm^{-1} (CO); NMR ($CDCl_3$) τ 5.10 (s, 5, Cp), 5.88 (broad s, 4, OCH_2), 6.8–7.6 (m, 4, ring CH, CH_2), 7.8–9.1 (m, 11, CH_2, CH_3).

Anal. Calcd for $C_{24}H_{24}FeN_4O_4$: C, 59.02; H, 4.92; N, 11.48. Found: C, 58.84; H, 4.98; N, 11.27.

Hydrolysis of **4h** with 5% HCl at room temperature for 24 hr gave, after extraction with ether, a product which exhibited strong ir absorption at 1715 cm^{-1}.

Reaction of 1 with Dimethoxycarbenium Hexafluorophosphate. A suspension of dimethoxycarbenium hexafluorophosphate[13] (2.20 g, 10 mmol) in 40 ml of methylene chloride was cooled to −78°, and 2.40 g (11 mmol) of complex **1** was added. The mixture was allowed to warm to −20° and was kept at this temperature for 30 min. The resulting solution was then filtered through Celite, and the filtrate was diluted with 100 ml of ether. The yellow precipitate was collected, washed with ether, and recrystallized from methylene chloride–ether to give 3.4 g (78%) of complex **3i**; ir (KBr) 2090, 2053 cm^{-1} (CO); NMR (acetone-d_6) τ 4.12 (s, 5, Cp), 4.30 (m, 1, =CH), 5.45 (t, 1, CH), 5.80 (d, 1, J = 8 Hz, cis $=CH_2$), 6.30 (d, 1, J = 15 Hz, trans $=CH_2$), 6.65 (s, 6, OCH_3), 7.2 (m, 1, CH_2).

Anal. Calcd for $C_{13}H_{17}FeO_4PF_6$: C, 35.62; H, 3.88. Found: C, 35.37; H, 3.79.

Deprotonation of 3i. Preparation of TCNE Adduct. The procedure given above was followed employing 432 mg (1 mmol) of complex (**3i**). After 15 min of reaction at room temperature, solvent was removed, and the residue was extracted with methylene chloride–ether (1:9 v/v), and the extracts were filtered through Celite and concentrated to dryness to give 250 mg (84%) of **4i** as an amber oil: ir (neat film) 2020, 1950 cm^{-1} (CO); NMR (CS_2) τ 4.0 (dt, 1, J = 8, J' = 15 Hz, =CH), 4.85 (dd, 1, J = 15, J' = 5 Hz, =CH), 5.35 (s, 5, Cp), 5.3 (d, 1, MeOCH), 6.83 (s, 6, OCH_3), 7.95 (d, 2, J = 8 Hz, CH_2).

The above product was taken up in 5 ml of methylene chloride and converted to its TCNE adduct following the standard procedure to give 320 mg (88%) of adduct (**6i**): mp 135–137° dec; ir (KBr) 2040, 1990 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.92 (s, 5, Cp), 5.25 (d, 1, J = 3.5 Hz, MeOCH), 6.39, 6.41 (2s, 6, OCH_3), 6.6–7.8 (m, 4, CH, CH_2).

Anal. Calcd for $C_{19}H_{16}FeN_4O_4$: C, 54.29; H, 3.81; N, 13.33. Found: C, 54.07; H, 3.86; H, 13.18.

Hydrolysis of 4i, Conversion to 4j. A solution of 250 mg of **4i** in 10 ml of THF and 20 ml of 1% hydrochloric acid was shaken for 5 min and then extracted with methylene chloride. The combined extracts were washed to neutrality and dried, and solvent was removed. Chromatography on neutral activity III alumina with ether gave the product (**4j**) as an amber oil, 200 mg (95%): ir (neat film) 2010, 1950 (C≡O), 1653 (C=O), 1592 cm^{-1} (C=C); NMR (CS_2) τ 0.65 (d, 1, J = 7.5 Hz, CHO), 2.96 (dt, 1, J = 14.5, J' = 9.5 Hz, =CH), 4.23 (dd, 1, J = 14.5, J' = 7.5 Hz, =CH), 5.26 (s, 5, Cp), 7.88 (d, 2, J = 9.5 Hz).

Reaction of 1 with Trimethoxycarbenium Tetrafluoroborate. Deprotonation of 3l. Trimethoxycarbenium tetrafluoroborate[13] (1.88 g, 10 mmol) was dissolved in 20 ml of methylene chloride; the solution was cooled to 0°, and 2.40 g (11 mmol) of **1** was added. After stirring for 30 min, 50 ml of ether was added, and the orange precipitate was filtered off. An NMR spectrum showed it to be a mixture of Fp(propylene) and **3l** cations. The crude product was therefore taken up in 20 ml of methylene chloride, and 1.5 ml of triethylamine was added. After 15 min, solvent was removed, and the residue was extracted with ether. These were concentrated and chromatographed on neutral activity III alumina. Following elution of an initial band containing starting material (ether–hexane, 1:4), elution with ether–hexane (1:1) gave the product (**4l**) as an amber oil, 1.5 g (54%): ir (neat film) 2000, 1950 (C≡O), 1690 cm^{-1} (C=O); NMR (CS_2) τ 2.84 (dt, 1, J = 15, J' = 9 Hz, =CH), 4.55 (d, 1, J = 15 Hz, =CH), 5.30 (s, 5, Cp), 6.45 (s, 3, OCH_3), 8.0 (d, 2, J = 9 Hz, CH_2).

TCNE Adduct of 4l. A solution of 250 mg (0.9 mmol) of **4l** in 10 ml of methylene chloride was mixed with 128 mg (1 mmol) of TCNE in THF. After 15 min, the reaction was worked up as before and recrystallized from methylene chloride–hexane to give 300 mg (83%) of adduct (**6l**); mp 131–132°; ir (KBr) 2040, 1980 (C≡O), 1745 cm^{-1} (C=O); NMR ($CDCl_3$) τ 5.08 (s, 5, Cp), 6.1 (s, 3, OCH_3), 6.5–7.6 (m, 4, ring CH, CH_2).

Anal. Calcd for $C_{18}H_{12}FeN_4O_4$: C, 53.47; H, 2.97; N, 13.86. Found: C, 53.45; H, 3.07; N, 13.76.

Reaction of 1 with Bromine. A solution of 2.18 g (10 mmol) of **1** in 20 ml of methylene chloride was cooled to −78°, and bromine (1.9 g, 10.5 mmol) in 10 ml of methylene chloride was added to it. An immediate precipitation of the bromide salt was observed. After stirring an additional 15 min at −78°, 10 ml of acetone, followed by 2.44 g (11 mmol) of hexafluorophosphoric acid etherate, was added. A rapid stream of nitrogen was passed through the reaction mixture as it warmed to room temperature. Anhydrous ether (50 ml) was added to complete the precipitation, and the yellow salt (**3m**) (3.87 g, 87%) was collected. An analytical sample was obtained by dissolution in acetone at 0° and reprecipitation by addition of diethyl ether: ir (KBr) 2800, 2040 cm^{-1} (CO); NMR (acetone-d_6) τ 4.22 (s, 5, Cp), 5.8–6.6 (m, 4, $=CH_2$, CH_2), 4.85 (m, 1, =CH).

Anal. Calcd for $C_{10}H_{10}BrF_6FeO_2P$: C, 27.05; H, 2.25. Found: C, 26.89; H, 2.02.

Deprotonation of 3m. A solution of diisopropylethylamine (1.10 g, 7.7 mmol) in 5 ml of methylene chloride was added dropwise to the bromopropene salt (3.3 g, 7.5 mmol) suspended in 50 ml of methylene chloride at 0°. After stirring for 45 min at 0°, the solvent was removed under reduced pressure, and the residue was extracted with several small portions of petroleum ether. Concentration of the combined extracts afforded 1.78 g (80%) of the bromoallyl complex (**5m**) as an orange oil. Slow evaporation of a petroleum ether solution of the complex with a stream of nitrogen gave an analytical sample as orange crystals: mp 36–37°; ir (CH_2Cl_2) 2020, 1950 cm^{-1} (CO); NMR (CS_2) τ 3.7 (dt, 1, J = 9, J' = 6.5 Hz, =CH), 4.3 (d, 1, J = 6.5 Hz, =CH), 5.25 (s, 5, Cp), 8.0 (d, 2, J = 9 Hz, CH_2).

Anal. Calcd for $C_{10}H_9BrFeO_2$: C, 40.45; H, 3.06. Found: C, 40.28; H, 3.10.

Reaction of the above product with an equimolar amount of TCNE in methylene chloride–THF solution at 0° gave dicarbonyl η^5-cyclopentadienyliron bromide as the only isolable organometallic substance. An NMR spectrum (CD_3NO_2) of the product shows absorption at τ 4.86 (Cp of FpBr) as well as at 3.4 and 3.8 (2br m, 2) and at 6.3 (br s, 2), indicative of 1,1,2,2-tetracyanocyclopentene.

Preparation of (1-Bromo-2-methallyl)Fp (14). To a solution of 2.32 g (10 mmol) of (2-methallyl)Fp (**12**) in 35 ml of degassed CH_2Cl_2 at −78° was added a solution of bromine (1.60 g, 10 mmol) in 5 ml of CH_2Cl_2. After addition was complete, the mixture was allowed to stir for 15 min, and then 2.44 g (11 mmol) of $HBF_4 \cdot Et_2O$ was injected. The mixture was allowed to come to room temperature as a rapid stream of N_2 was passed through. Anhydrous ether (100 ml) was added to complete the precipitation. The product was collected at −50°, 3.1 g (80%). The yellow crystalline product was treated at 0° in CH_2Cl_2 solution with 1.1 g (8.4 mmol) of diisopropylethylamine in 5 ml of CH_2Cl_2. After 5 min, solvent was removed, and the residue was extracted with ether–petroleum ether (1:1). Concentration of the extracts left 2.10 g of dark orange oil: NMR (CS_2) τ 8.22 (d, 3, J = 1.3 Hz, Me), 7.93 (s, 2, CH_2), 5.23 (s, 5, Cp), 4.43 (q, 1, J = 1.3 Hz, =CH).

Brominolysis of Complex 8. The cyclohexylmethyl complex (0.55 g, 2.0 mmol) was dissolved in 10 ml of methylene chloride at −78°, and 0.48 g (2.0 mmol) of *N*-bromopyridinium bromide[16] was added to this. After 70 min, reaction was incomplete as indicated by an ir spectrum. An additional 0.48 g of brominating reagent was added. The solution was allowed to come to room temperature, solvent was removed, and the product was extracted with petroleum ether. The residue consisted of FpBr (0.5 g, 95%). The petroleum ether soluble fraction was chromatographed on activity II alumina to give 0.32 g of colorless oil, identified as cyclohexylmethyl bromide (79%) by VPC on DC 550.

Brominolysis of Complex 9. The same procedure as given above for the bromination of **8** was followed, except that complete consumption of **9** was achieved after 90 min of reaction at −78° with an equimolar amount of brominating reagent. At the end of this time, an ir spectrum of the reaction mixture showed complete conversion to FpBr. Work-up as before gave a 90% yield of FpBr. VPC analysis of the organic product identified it as β-phenethyl bromide (95%).

Brominolysis of Complex 10. The cyclohexenylmethyl complex (**10**) (0.71 g, 2.6 mmol) in 15 ml of methylene chloride was cooled to −78° and treated with 0.62 g (2.6 mmol) of *N*-bromopyridinium perbromide. Reaction was complete within 1 hr. Solvent was removed, and the product was extracted with petroleum ether. VPC analysis of product using chlorobenzene as internal standard on DC 550 indicated a 50% yield of product: NMR (CCl_4) τ 4.35 (m, 2, =CH), 6.7 (d, 2, J = 5 Hz, CH_2Br), 7.6-8.5 (m, 7, CH_2, CH).

Preparation of 3n by the Exchange Reaction. The complex **3n** was obtained following the procedure described below for **3o**. Recrystallization from acetonitrile-ether gave the complex (74%), mp 166.5-168° dec; ir (KBr) 2080, 2040 cm^{-1} (CO); NMR (CD_3NO_2) τ 2.17 (m, 15, Ar), 4.21 (s, 5, Cp), 4.8 (m, 1, =CH), 5.0-6.3 (m, 2, $=CH_2$), 6.6 (m, 2, CH_2).

Anal. Calcd for $C_{28}H_{25}FeO_2PB_2F_8$: C, 51.46; H, 3.85; P, 4.73. Found: C, 51.40; H, 3.95; P, 4.68.

Preparation of 3o by the Exchange Reaction. A solution of 960 mg (3.0 mmol) of the isobutylene salt (**15**) in 15 ml of 1,2-dichloroethane was heated to 70°, and a solution of 2.5 ml (30 mmol) of 3-methoxypropene in 5 ml of the same solvent was added by syringe, rapidly. The reaction was kept at 70° for 3 min and was then cooled to room temperature. Ether was added, and the crystalline product was collected and recrystallized from methylene chloride-ether, 710 mg (71%), dec 100°: ir (KBr) 2049, 2000 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.32 (s, 5, Cp), 4.7 (m, 1, =CH), 5.96 (d, 1, J = 8 Hz, cis $=CH_2$), 6.02 (d, 2, J = 4 Hz, CH_2), 6.44 (d, 2, J = 15 Hz, trans $=CH_2$), 6.65 (s, 3, OCH_3).

Anal. Calcd for $C_{11}H_{13}FeO_3BF_4$: C, 39.33; H, 3.91. Found: C, 39.35; H, 3.96.

Preparation of 3o from 1,2-Epoxy-3-methoxypropane. A solution containing 10.0 mmol of $NaCpFe(CO)_2$ in 20 ml of THF was prepared by reduction of $[CpFe(CO)_2]_2$.[31] The solution was cooled to 0°, and 0.87 g (10.0 mmol) of 1,2-epoxy-3-methoxypropane was added to it. After stirring at 0° for 45 min, 3.65 ml (20 mmol) of 48% aqueous HBF_4 in 5 ml of acetic anhydride was added dropwise. Precipitation was completed by addition of ether, and the product was collected and recrystallized from methylene chloride-ether to give 2.6 g (78%) of complex (**3o**), identical with the product above.

Deprotonation of 3o. Deprotonation of **3o** was carried out at 0°, employing an equivalent of triethylamine as previously described. The product (**5o**), mp 40.5-41.5°, was obtained in 97% yield: ir (neat film) 1996, 1941 (CO), 1660 cm^{-1} (C=C); NMR (CS_2) τ 4.38 (d, 1, J = 6 Hz, =CH), 5.32 (s, 5, Cp), 5.4 (m, 1, =CH), 6.53 (s, 3, OCH_3), 7.92 (d, 2, J = 9 Hz, CH_2).

Anal. Calcd for $C_{11}H_{12}FeO_3$: C, 53.27; H, 4.87. Found: C, 53.00; H, 4.84.

TCNE Adduct of 5o. The adduct was obtained following the usual procedure in 88% yield, mp 140° dec; ir (KBr) 2020, 1969 (CO), 2243 cm^{-1} (CN); NMR ($CDCl_3$) τ 5.08 (s, 5, Cp), 5.69 (s, 1, CHOMe), 6.28 (s, 3, OCH_3), 7.15 (m, 3, FpCH, CH_2).

Anal. Calcd for: $C_{17}H_{12}FeO_3N_4$: C, 54.29; H, 3.22; N, 14.95. Found: C, 54.36; H, 3.29; N, 14.73.

Tosyl Isocyanate Adduct of 5o. A freshly chromatographed sample of **3o** (0.36 g, 1.44 mmol) was taken up in 10 ml of methylene chloride and treated at 0° with 0.275 g (1.4 mmol) of tosyl isocyanate. The solution was stirred at room temperature for 1 hr, solvent was then removed, and the residue was triturated with hexane. The solid product so obtained was recrystallized twice from methylene chloride-hexane to give 0.52 g (83%) of adduct: mp 135-136°; ir (KBr) 2012, 1953 (C≡O), 1715 cm^{-1} (C=O); NMR τ 2.06, 2.66 (2d, 4, Ar), 5.16 (s, 5, Cp), 6.13 (dd, 2, CH_2), 6.72 (s, 3, OCH_3), 6.71 (d, 1, J = 5 Hz, CHOMe), 7.4 (m, 1, FpCH).

Anal. Calcd for $C_{19}H_{19}FeO_6NS$: C, 51.25; H, 4.32; N, 3.15; S, 7.20. Found: C, 50.99; H, 4.25; N, 3.24; S, 7.23.

Preparation of 3p by the Exchange Reaction. The exchange reaction was carried out as described previously for the preparation of **3o**, except that the molar ratio of isobutylene complex to allyl alcohol was 5:1, and the reaction was heated at 65-70° for 15 min. The product, obtained in 71% yield, was recrystallized from methylene chloride-ether: mp 150° dec; ir (KBr) 2080, 2040 cm^{-1} (CO); NMR (CD_3NO_2) τ 4.32 (s, 5, Cp), 4.3-5.0 (broad m, 2, =CH, OH), 5.6 (m, 2, CH_2), 5.97 (d, 1, J = 8 Hz, cis $=CH_2$), 6.36 (d, 1, J = 15 Hz, trans $=CH_2$).

Anal. Calcd for $C_{10}H_{11}FeO_3BF_4$: C, 37.27; H, 3.42. Found: C, 37.09; H, 3.40.

Deprotonation of 3p. Formation of Lactone 24. Deprotonation of 322 mg (1 mmol) of **3p** was carried out in nitromethane solution at 0° employing a 10% molar excess of triethylamine, and the work-up procedure was as given before. Chromatographic purification on alumina was carried through by elution with ether, then with methylene chloride. The product so obtained was recrystallized from methylene chloride-ether to give 157 mg (70%) of yellow needles: mp 125-126°; ir (KBr) 1985 (C≡O), 1650 cm^{-1} (C=O); NMR ($CDCl_3$) τ 4.8 (m, 1, =CH), 5.17 (s, 5, Cp), 5.63 (dd, 1, J = 10, J' = 6 Hz, CH_2O), 6.70 (d, 1, J = 7.5 Hz, cis $=CH_2$), 7.18 (d, 1, J = 11.5 Hz, trans $=CH_2$), 7.70 (t, 1, J = J' = 10 Hz, CH_2O).

Anal. Calcd for $C_{10}H_{10}FeO_3$: C, 51.28; H, 4.27. Found: C, 51.16; H, 4.25.

Attempted Preparation of an Fp(allyl cyanide) Olefin Complex. The exchange reaction with allyl cyanide was carried out following the procedure given for the preparation of **3o**. The product, an orange solid, was obtained in 43% yield: ir (CH_2Cl_2) 2070, 2025 (CO), 2285 cm^{-1} (CN); NMR (CD_3NO_2) τ 3.8-4.8 (m, 3, =CH, $=CH_2$), 4.49 (s, 5, Cp), 6.45 (m, 2, CH_2).

An NMR spectrum of allyl cyanide in CD_3NO_2 had: τ 3.8-4.8 (m, 3, =CH, $=CH_2$) and 6.85 (m, 2, CH_2).

Preparation of 4o. Crude *trans*-3-chloro-1-methoxy-1-propene, prepared from 2.7 g (38.4 mmol) of allenyl methyl ether,[22] was taken up in 5 ml of THF. A solution of 40 ml of sodium dicarbonylcyclopentadienylferrate (0.5 *M*, 20 mmol) was added to this at 0°. After 30 min at 0°, the reaction was warmed to room temperature for 10 min, and then solvent was removed in vacuo. Rapid filtration through alumina, using petroleum ether, followed by chromatography on alumina (40 g, activity III, neutral) yielded a 2:1 mixture of the *cis*- and *trans*-(methoxyallyl)Fp complexes (**5o** and **4o**), 2.5 g)50%). Separation of isomers was achieved on 95 g of alumina using 5% ether-95% petroleum ether to elute the cis isomer, and 10% ether-90% petroleum ether gave the trans isomer as a red oil: ir (CS_2) 1950, 2010 cm^{-1}; NMR (CS_2, 90 MHz) τ 3.85 (dt, 1, J = 12, J' = 1 Hz, =CH), 5.13 (dt, 1, J = 12, J' = 9.0 Hz, =CH), 5.41 (s, 5, Cp), 6.63 (s, 3, OCH_3), 7.89 (dd, 2, J = 9.0, J' = 1 Hz, CH_2).

Attempted Isomerization of 4o. To a 50-ml flask containing 10 ml of methylene chloride was added tetrafluoroboric acid-diethyl ether complex (190 mg, 1.17 mmol) followed by triethylamine (130 mg, 1.29 mmol). This was cooled to 0°, and **4o** (1.50 mmol) was added in 5 ml of methylene chloride. After 15 min at 0°, solvent was removed and the residue extracted with ether. After filtration through ether, starting material was recovered unchanged.

Preparation of (η^1-*trans*-Cinnamyl)Fp (4q). A solution of $NaFp$[31] in THF was cooled to −78° and treated with an equivalent of cinnamyl benzenesulfonate. After allowing the solution to come to room temperature, solvent was removed, and the residue was extracted repeatedly with ether, filtered, and concentrated. Chromatography on an activity III neutral alumina column (made up in ether) with petroleum ether gave the product as an amber oil: ir (CH_2Cl_2) 2010, 1960 cm^{-1} (CO); NMR (CS_2) τ 2.85 (m, 5, Ph), 3.53 (dt, 1, J = 15, J' = 7.5 Hz, =CH), 3.89 (d, 1, J = 15 Hz, =CH), 5.44 (s, 5, Cp), 7.75 (dd, 2, J = 7.5, J' = 1 Hz, CH_2).

Protonation of 4q. The cinnamyl complex (**4q**) (0.294 g, 1.00 mmol) was taken up in methylene chloride and treated with an equivalent of hexafluorophosphoric acid etherate at 0°. Ether was added, and the precipitated salt was collected and washed with ether to give 0.435 g (99%) of **3q**: mp 145° dec; ir (CH_2Cl_2) 2070, 2020 cm^{-1} (CO); NMR (CD_3NO_2) τ 2.65 (s, 5, Ph), 4.31 (s, 5, Cp), 4.4-5.1 (m, 1, =CH), 6.02 (d, 1, J = 8 Hz, cis $=CH_2$), 6.35 (d, 1, J = 15 Hz, trans $=CH_2$), 6.17 (dd, 1, J = 13.5, J' = 3.5 Hz, CH_2), 7.28 (dd, 1, J = 13.5, J' = 10 Hz, CH_2).

Deuteration of 4q. The cinnamyl complex (**4q**) (441 mg, 1.50 mmol) was added to 10 ml of deuteriotrifluoroacetic acid at room temperature. Reaction was allowed to continue for 30 min, and the solution was then added dropwise to a saturated aqueous solution of NH_4PF_6. The yellow salt was collected, washed with small portions of water, and then taken up in a minimum volume of acetone. Reprecipitation of the product with ether gave 590 mg (88%) of deuterio-**3q**. In a second experiment, a 92% yield of salt was obtained. Table III below summarizes the results of NMR integration of these products.

Table III

Expt No.	Integrations 5.9–6.6, τ	Integrations 7.0–7.6, τ	No. of integrations
1	2.51	0.57	12
2	2.49	0.46	1

^{13}C NMR Spectral Data. Fp(ethylene): δ 56.7 (t, J = 167 Hz, CH_2), 90.17 (d, J = 184 Hz, Cp), 209.60 (s, CO). Fp(propylene): δ 22.14 (q, CH_3), 55.80 (t, J = 167 Hz, $=CH_2$), 85.70 (d, J = 159 Hz, =CH), 89.97 (d, J = 185 Hz, Cp), 209.21, 210.96 (s, CO). **15**: δ 28.93 (q, J = 129 Hz, CH_3), 54.31 (t, J = 159.7 Hz, $=CH_2$), 89.91 (d, J = 180 Hz, Cp), 122.79 (s, CMe_2), 210.83 (s, CO). **3b**: δ 17.22 (q, CH_3), 30.62 (t, CH_2), 53.92 (t, $=CH_2$), 89.97 (d, Cp), 90.30 (d, =CH), 208.88, 210.76 (s, CO). **3m**: δ 34.37 (t, CH_2Br), 55.02 (t, $=CH_2$), 77.55 (d, =CH), 90.75 (d, Cp), 207.27, 209.27 (s, CO). **3o**: δ 50.94 (t, $=CH_2$), 58.77 (q, OCH_3), 71.53 (t, CH_2), 82.98 (d, =CH), 90.10 (d, Cp), 209.08, 210.18 (s, CO).

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