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MU-VINYLIDENE AND ETA('1)-1-CYCLOPROPENYLIRON COMPLEXES: CHEMISTRY AND SYNTHESIS VIA 1,1-DICHLOROCYCLOPROPANES

*The University of Oklahoma* PH.D. 1985

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THE UNIVERSITY OF OKLAHOMA

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# μ-VINYLIDENE AND $\eta^1$-1-CYCLOPROPENYLIRON COMPLEXES: CHEMISTRY AND SYNTHESIS VIA 1,1-DICHLOROCYCLOPROPANES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

DAVID JAMES HANLON

Norman, Oklahoma

1985

# μ-VINYLIDENE AND $\eta^1$-1-CYCLOPROPENYLIRON COMPLEXES: CHEMISTRY AND SYNTHESIS VIA 1,1-DICHLOROCYCLOPROPANES

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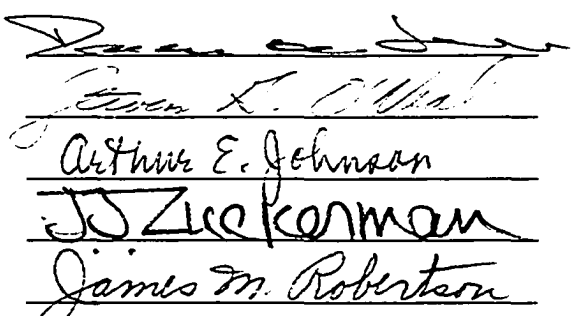

DISSERTATION COMMITTEE

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## ABSTRACT

The unusual conversion of a series of substituted 1,1-dichlorocyclopropenes into a series of substituted bridging vinylidene iron dimers via 1,3-bond cleavage of the cyclopropyl ring during the phase transfer catalyzed reaction of ($\mu$-CO) $\eta^5$-cyclopentadienyliron carbonyl dimer, $OH^-$, and the 1,1-dichlorocyclopropane was mechanistically investigated. Two probable intermediates, substituted 1-chlorocyclopropene substituted 1-($\eta^5$-cyclopentadienyl)(dicarbonyl)iron)-1-cyclopropenes were synthesized and characterized.

The reaction chemistry of the bridging vinylidene iron dimers was explored and the chemistry of the double bond proved to be the most fertile. The bridging vinylidene was converted to the bridging alkylidene by protonation followed by reduction.

The chemistry of the intermediate 1-($\eta^5$-cyclopentadienyl(dicarbonyl)iron)-1-cyclopropene was investigated. The reaction of the double bond has two competing processes, addition versus ring opening. The reaction with tetracyanoethylene forms a bicyclic addition

product resulting from the direct addition of tetracyanoethylene across the double bond. The reaction with $H^+$ is substitution dependent. The protonation of the unsubstituted 1-($\eta^5$-cyclopentadienyl)(dicarbonyl)iron-1-cyclopropene apparently forms the cyclopropyl carbene, while the substituted 1-($\eta^5$-cyclopentadienyl)dicarbonyliron-1-cyclopropene rearrange to form the cationic allene complex.

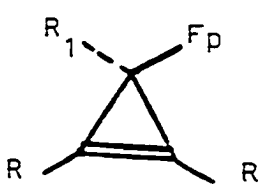
The removal of a hydride on C-3 of the 1-($\eta^5$-cyclopentadienyl)dicarbonyliron-1-cyclopropene forms the metalated-cyclopropenium salt. This cyclopropenium salt could then be reacted with a nucleophilic copper reagent to form new 1-$\eta^5$-cyclopentadienyl(dicarbonyl)iron-1-cyclopropene.

# CHAPTER 1

## $\eta^1$-1-Cyclopropenyliron Complexes: Chemistry and Synthesis via Substituted 1,1-Dichlorocyclopropanes

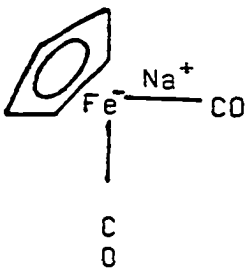
## INTRODUCTION

Organometallic compounds containing vinyl and substituted vinyl ligands are well established.[1-4] Examples of cyclopropyl and cyclopropenyl ligands are relatively rare. Rosenblum[5] reports the first cyclopropyl ligand in the iron complex dicarbonyl($\eta^5$-cyclopentadienyl)(cyclopropyl) iron [Fp-$C_3H_5$]. The cyclopropenyl complexes are reported in the $\eta^1$-complexed form by Gompper.[6,7]




| | | | |
|---|---|---|---|
| 1a | R=$R_1$=Ph | 1d | R=$R_1$=t-Bu |
| 1b | R=Ph,$R_1$=H | 1e | R=$R_1$=$Et_2N$ |
| 1c | R=t-Bu,$R_1$=Me | 1f | R=$R_1$=(i-Pr)$_2$N |

Complexes 1 are prepared by the reaction of NaFp 2 with cyclopropenium cations.[6,7] The cyclopropenium complex 3a is also reported as a product resulting from the reaction of 1b with a variety of reagents.



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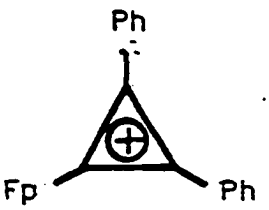
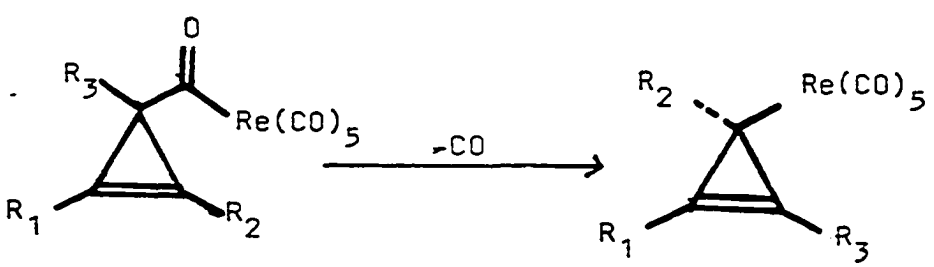


3a

3a

The Hughes[8-10] group reports the synthesis of two 3-$\eta^1$-cyclopropenylrhenium compounds 5a and 5b from the decarbonylation of 4a and 4b.



4 5

a $R_1$=t-Bu, $R_2$=$R_3$=H

b $R_1$=t-Bu, $R_2$=D, $R_3$=H

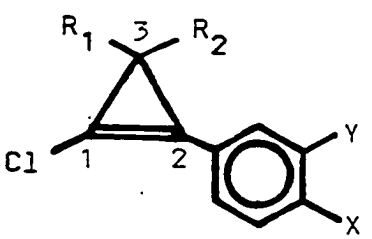
We report here the first example of a 1-metalated cyclopropene in the form of 1-Fp-2-arylcyclopropene. Chapter 2 describes the discovery of these new complexes. This chapter will deal with a discussion of the synthesis and explore some of the chemistry of these new complexes. By

analogy to the related σ-vinyl and σ-cyclopropyl analogs, reactions can involve simple addition to the π-bond or rearrangement via ring opening of the strained 3-membered ring, or both. It is the intent of the study to determine the scope and limitations of the metalated cyclopropene synthesis and define the reactions with organometallic and electrophilic reagents.

## RESULTS AND DISCUSSION

The syntheses of the substituted 1-Fp-cyclopropenes involves substituted 1,1-dichlorocyclopropanes as the organic starting materials. The substituted 1,1-dichlorocyclopropanes are converted into substituted 1-chlorocyclopropenes, 6, by a modification of the method reported by Weyerstahl.[11,12] The yields of 1-chlorocyclopropenes using this procedure are summarized in Table 1.

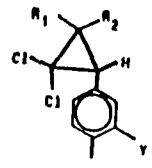
The $^{1}$H-NMR spectra of the substituted 1,1-dichlorocyclopropanes and substituted 1-chloropropenes are summarized in Tables 2 and 3.



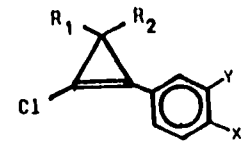

6

Carbon 3 in the substituted 1,1-dichlorocyclopropanes is in a diastereotopic environment due to the asymmetry at carbon 2. This is observed in the dimethyl and unsubstituted examples where the identical substituents absorbed at dif-

Table 1. The Reaction of Substituted 1,1-Dichlorocyclopropanes with Potassium t-Butoxide



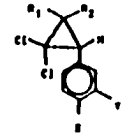
t-BuOK



| $R_1$ | $R_2$ | X | Y | mmole | mmole | Internal Standard | mmole | %* |
|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 5.51 | 8.2 | $CH_2Br_2$ | 2.42 | 44 |
| H | Me | H | H | 2.61 | 3.9 | $CH_2Br_2$ | 2.11 | 81 |
| Me | Me | H | H | 4.24 | 5.5 | $CH_2Br_2$ | 3.83 | 90 |
| H | H | Me | H | 2.60 | 3.9 | $CH_2Br_2$ | 1.51 | 58 |
| H | Me | Me | H | 1.97 | 3.0 | $CH_2Br_2$ | 1.58 | 80 |
| Me | Me | Me | H | 2.61 | 3.5 | Toluene | 1.85 | 71 |
| H | H | OMe | H | 1.93 | 2.9 | Mesitylene | 0.869 | 45 |
| H | Me | OMe | H | 1.97 | 2.7 | $CH_3NO_2$ | 1.73 | 88 |
| Me | Me | OMe | H | 2.12 | 3.5 | p-dioxane | 1.48 | 70 |
| Me | H | H | Cl | 1.43 | 2.1 | $CH_2Br_2$ | 1.00 | 70 |
| Me | Me | H | Cl | 2.14 | 3.2 | $CH_2Br_2$ | 1.95 | 91 |
| H | Ph | H | H | 2.47 | 3.5 | Toluene | 0.889 | 36 |

*All yields are based on an internal standard, performed at least in duplicate, and are ±10% based on the substituted 1,1-dichlorocyclopropane as determined by $^1$H-NMR spectra.

Table 2. $^1$H-NMR Spectra of Substituted 1,1-Dichlorocyclopropanes*Δ+



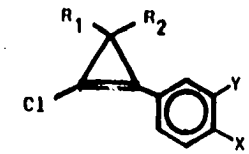
| | | | | | | | | | | $^nJ(^1H\text{-}X\text{-}Y\text{-}Z\text{-}^1H)$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | $R_2$ | $R_3$ | X | Y | $R_1$ | $R_2$ | $R_3$ | Ar | X | $J_{R_1R_2}$ Hz | $J_{R_1R_3}$ Hz | $J_{R_2R_3}$ Hz | $J_{1,2}$ Hz |
| H | H | H | H | H | 1,1.78(dd) | 1,1.90(dd) | 1,2.86(dd) | 5,7.27(s) | | 7 | 9 | 10 | |
| Me | H | H | H | H | 3,1.45(d) | 1,1.82(dq) | 1,2.31(d) | 5,7.18(s) | | 5.5 | | 7.5 | |
| Me | Me | H | H | H | 3,1.18(s) | 3,1.55(s) | 1,2.45(s) | 5,7.22(s) | | | | | |
| tBu | H | H | H | H | 1,2.76(d) | 9,1.21(s) | 1,2.76(d) | 5,7.28(s) | | | 10 $H_3$ | | |
| Ph | H | H | H | H | 2,3.25(s) | | | 10,7.37(s) | | | | | |
| H | H | H | Me | H | 2,2.50(d,d) | | 1,2.82(t) | 4,7.07(s) | 3,2.28(s) | 3 | 10 | | |
| Me | H | H | Me | H | 3,1.43(d) | 1,1.80(d,q) | 1,2.26(d) | 4,7.36(s) | 3,2.32(s) | 5 | | 4 | |
| Me | Me | H | Me | H | 3,1.20(s) | 3,1.57(s) | 1,2.33(s) | 4,7.47(s) | 3,2.37(s) | | | | |
| H | H | H | OMe | H | 2,1.80(dd) | | 1,2.83(5) | 4,6.82,7.30(AB) | 3,3.76(s) | 4 | 10 | | 8 |
| Me | H | H | OMe | H | 3,1.47(d) | 1,1.83(d,q) | 1,2.38(d) | 4,6.82,7.13(AB) | 3,3.87(s) | 6 | | 2 | 9 |
| Me | Mu | H | OMe | H | 3,1.08(s) | 3,1.50(s) | 1,2.37(s) | 4,6.82,7.30(AB) | 3,3.78(s) | | | | 9 |
| H | H | H | H | Cl | 2,1.90(dd) | | 1,2.58(dd) | 4,7.0-7.5(m) | | 4 | 7 | 4 | |
| Me | H | H | H | Cl | 3,1.50(d) | 1,90(d,q) | 1,2.47(d) | 4,7.1-7.5(m) | | 6 | | 4 | |
| Me | Me | H | H | Cl | 3,1.18(s) | 3,1.55(s) | 1,247(s) | 4,7.23(m) | | | | | |

*$^1$H-NMR spectra recorded in carbon tetrachloride are reported in δ relative to tetramethylsilane.

Δ$^1$H-NMR spectra are reported as number of protons, δ and splitting pattern.

+ The $^1$H-$^1$H coupling constants (J) are reported in Hertz.

Table 3. $^1$H-NMR Spectra of 1-Chlorocyclopropenes*Δ+




| No. | $R_1$ | $R_2$ | X | Y | $R_1$ | $R_2$ | Ar | X | $^nJ(^1H\text{-}X\text{-}Y\text{-}Z\text{-}^1H)$ $J_{R_1R_2}$ | $J_{1,2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 5g | H | H | H | H | 1,1.87(s) | | 10,7.0-7.6m | | | |
| 5c | Me | H | H | H | 3,1.33(d) | 1,2.43(q) | 5,7.0-7.6m | | 4 | |
| 6d | Me | Me | H | H | 6,1.42(s) | | 5,7.0-8.4m | | | |
| 5a | Ph | H | H | H | 1,3.40(s) | | 10.6.2-80 | | | |
| 5e | H | H | Me | H | 2,1.87(s) | | 4,7.37,7.13(AB) | 2.36(s) | | 8 |
| 5f | Me | H | Me | H | 3,1.33(d) | 1,1.87(q) | 4,7.11,7.36 | 2.36(s) | 4 | 7 |
| 5q | Me | Me | Me | H | 6,1.40(s) | | 4,7.08,7.25(AB) | 2.37(s) | | 6 |
| 5H | H | H | OMe | H | 2,1.80(s) | | 4,6.82,7.30(AB) | 3.75(s) | | 8 |
| 5i | Me | H | OMe | H | 3,1.30(d) | 1,2.40(q) | 4,6.77,7.30(AB) | 3.77(s) | | 10 |
| 5j | Me | Me | OMe | H | 3,1.40(s) | | 4,6.82,7.30(AB) | 3.78(s) | 4 | 9 |
| 5k | H | H | H | Cl | 2,191(s) | | 4,7.1-7.5(m) | | | |
| 5l | Me | Me | H | Cl | 6.1.40(s) | | 4,7.1-7.4(m) | | | |

*$^1$H-NMR spectra recorded in carbon tetrachloride and reported in δ relative to tetramethylsilane.

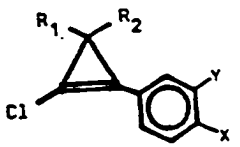
ΔThe $^1$H-NMR spectra are reported as number of protons, δ, and splitting pattern.

+The $^1$H-$^1$H coupling constants (J) are reported in Hertz.

ferent positions. The $^{1}$H-NMR spectrum is simplified when the substituted 1,1-dichlorocycloropane is converted to the substituted 1-chlorocyclopropene. The asymmetry at carbon 2 is removed along with the diastereotopic environment at carbon 3.

The carbon tetrachloride solution IR spectra of substituted 1-chlorocyclopropenes shows a band at 1805-1828 $cm^{-1}$ assigned to the double bond. The data is summarized in Table 4. The double bond absorption was shifted to lower frequency as substituents are added to carbon 3, indicating a weakening of the bond. The double bond band was shifted to higher frequency as the series phenyl, p-tolyl, p-anisol, to m-ClPh on carbon 3 is traversed, indicating an increase in the strength of the double bond. The lower frequency shift can be caused by two factors:
1. Donation of electron density into the double bond by the addition of alkyl groups to the cyclopropyl ring.
2. Steric strain introduced by the addition of alkyl substituents to the cyclopropyl ring. The higher-frequency shift caused by the aromatic substitution is found to correlate with the field effects which can be represented by the Taft values:[13] H, 0.0; Me, 0.05; OMe, 0.25; and M-Cl, 0.47. The larger the positive Taft value the more electron withdrawing the substituent and the larger the electron withdrawing capability of the aromatic group.[13]

Table 4. IR Spectra of 1-Chlorocyclopropenes*




| No. | X | Y | $R_1$ | $R_2$ | Double Bond $\upsilon$ $cm^{-1}$ |
|---|---|---|---|---|---|
| 6a | H | H | Ph | H | 1828 |
| 6b | H | H | H | H | 1826 |
| 6c | H | H | Me | H | 1817 |
| 6d | H | H | Me | Me | 1805 |
| 6e | Me | H | H | H | 1825 |
| 6f | Me | H | Me | H | 1818 |
| 6g | Me | H | Me | Me | 1812 |
| 6h | OMe | H | H | H | 1821 |
| 6i | OMe | H | Me | H | 1818 |
| 6j | OMe | H | Me | Me | 1817 |
| 6k | H | Cl | H | H | 1827 |
| 6l | H | Cl | Me | Me | 1820 |

*Recorded in carbon tetrachloride.

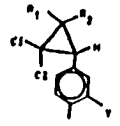
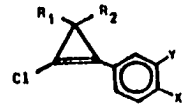
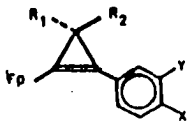
## Synthesis of 1-Fp-cyclopropenes

We report here the synthesis of a new class of compounds, substituted 1-Fp-cyclopropenes 7 by the reaction of $Na[CpFe(CO)_2]$, {NaFp}, with substituted 1-chlorocyclopropenes at room temperature in THF. The substituted 1-Fp-cyclopropenes were produced in yields ranging from 40 to 90% based on the substituted 1-chloropropenes and the results are summarized in Table 5.

The proton NMR spectral results in $CS_2$ of the 1-Fp-cyclopropenes are summarized in Table 6. The replacement of chlorine by iron on the cyclopropene ring results in an upfield shift of the signals of the substituents on carbon 3. This is a result of the donation of electron density from the orbitals in iron into the cyclopropene ring.

Infrared spectra are recorded in heptane and the results are summarized in Table 7. The double bond stretch is moved to lower frequency by 49-70 $cm^{-1}$ when chlorine is replaced by iron. This can be explained in terms of electron donation from iron into the C-C $\pi$-bond, therefor weakening it. The electron donation from iron to the C=C $\pi$-bond is also evidenced in the higher frequency shift of the iron-carbonyl bands. The carbonyl bands are found at 2034-2028 $cm^{-1}$ and 1982-1991 $cm^{-1}$. Typical Fp-alkyl carbonyls normally absorb at 2005 and 1960 $cm^{-1}$.[14] Removal

Table 5. The Reaction of Substituted 1-Chlorocyclopropenes with NaFp

| $R_1$ | $R_2$ | X | Y |  mmole | KOt mmole |  mmole%* | ml | NaFp[X] mmole | Internal Standard |  mmole%* | Mp[+] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 3.86 | 5.8 | 1.74,45 | 8 | 4.0 | Isolated | 1.24 71 | 58.5-60.0° |
| H | Me | H | H | 1.19 | 1.7 | 1.02,86 | 4 | 2.0 | Mesitylene | 0.809 79 | 70.5-72° |
| Me | Me | | H | 2.23 | 3.2 | 2.01,90 | 6 | 3.0 | Mesitylene | 1.40 70 | 100.5-101.5° |
| H | H | Me | H | 1.08 | 1.6 | 0.680,63 | 3 | 1.5 | p-dioxane | 0.56 82 | 54-56° |
| H | Me | Me | H | 1.20 | 1.8 | 1.06,88 | 3 | 1.5 | p-dioxane | 0.86 82 | 61.5-63.5° |
| Me | Me | Me | H | 1.15 | 1.8 | 0.920,80 | 4 | 2.0 | p-dioxane | | 120-122Δ |
| H | H | OMe | H | 1.14 | 1.6 | 0.422,37 | 3 | 6.5 | Mesitylene | 0.228 54 | Oil |
| H | Me | OMe | H | 2.24 | 3.4 | 1.97,88 | 8 | 4.0 | Mesitylene | 1.08 55 | 65.5-67.5° |
| Me | Me | OMe | H | 3.40 | 5.0 | 2.38,70 | 8 | 4.0 | Isolated | 1.01 43 | 85-87° |
| H | H | H | Cl | 2.28 | 3.5 | 2.05,90 | 6 | 3.0 | Isolated | 1.64 80 | Oil |
| Me | Me | H | Cl | 2.05 | 3.1 | 2.76,86 | 6 | 3.0 | Mesitylene | 1.64 93 | 80.0-82.0° |

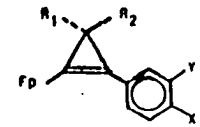
*All reported yields are based on an internal standard, performed in duplicate, and are ±10% as determined by $^1$H-NMR spectra.

Δ All reported yields of substituted 1-Fp-cyclopropenes are based on substituted 1-chlorocyclopropene.

+ The melting points reported are for the substituted 1-Fp-cyclopropenes.

X The NaFP solution in tetrahydrofuran was 0.5 M.

Table 6. The $^1$H-NMR Spectra of Substituted 1-Fp-cyclopropenes*Δ+




| No. | $R_1$ | $R_2$ | X | Y | $R_1$ | $R_2$ | Ar | X | Cp | $^nJ(^1H\text{-}X\text{-}Y\text{-}Z\text{-}^1H)$ $J_{R_1R_2}$ | $J_{1\text{-}2}$ Hz |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7b | H | H | H | H | 2,0.77(s) | | 5,6.7-7.3(m) | | 5,4.80(s) | | |
| 7c | Me | H | H | H | 3,1.07(d) | 1,1.35(q) | 5,6.9-7.3(m) | | 5,4.80(s) | 4 | |
| 7d | Me | Me | H | H | 6,1.16(s) | | 6.9-7.2(BS) | | 5,5.00(s) | | |
| 7e | tBu | H | H | H | 9,0.88(s) | 1,1.34(s) | 5,7.0-7.7(m) | | 5,4.93(s) | | |
| 7a | Ph | H | H | H | | 1,2.51(s) | 10,6.8-7.5(m) | | 5,4.82(s) | | |
| 7e | H | H | Me | H | 2,0.80(s) | | 6.8.7.4 | 3,2.27(s) | 5,4.83(s) | | |
| 7f | Me | H | Me | H | 3,1.07(d) | 1,1.33(q) | 6.8-7.4 | 3,2.27(s) | 5,4.80(s) | 4 | |
| 7g | Me | Me | Me | H | 6,1.17(s) | | 6.8-7.2(m) | 3,2.28(s) | 5,5.00(s) | | |
| 7h | H | H | OMe | H | 2,0.76(s) | | 4,6.67,7.17(AB) | 3,3.63(s) | 5,4.83(s) | | 8 |
| 7i | Me | H | OMe | H | 3,1.06(d) | 1,1.23(q) | 4,6.70,7.15(AB) | 3,3.70(s) | 5,4.93(s) | 4 | 8 |
| 7k | H | H | H | Cl | 6,1.20(s) | | 6.6-7.5 | 3,3.73(s) | 5,4.67(s) | | |
| 7l | Me | Me | H | Cl | 2,0.87(s) | | 4,6.9-7.5(m) | | 5,4.98(s) | | |
| | | | | | 4,1.12(s) | | 6.8-7.2 | | 5,4.93(s) | | |

*$^1$H-NMR spectra recorded in carbon tetrachloride are reported in relative to tetramethylsilane.

Δ$^1$H-NMR spectra are reported as number of protons, and splitting pattern.

+The $^1$H-$^1$H coupling constants (J) are reported in Hertz.

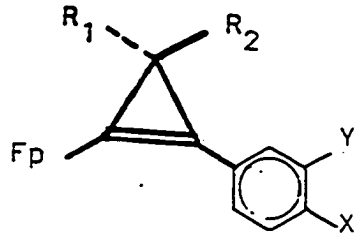
Table 7. IR Spectra of Fp-Cyclopropenes*

| No. | $R_1$ | $R_2$ | X | Y | $\nu$(XY), $cm^{-1}$ CO, $cm^{-1}$ | | C=C, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| 7a | Ph | H | H | H | 2030 | 1986 | 1730 |
| 7b | H | H | H | H | 2034 | 1988 | 1757 |
| 7c | Me | H | H | H | 2032 | 1985 | 1747 |
| 7d | Me | Me | H | H | 2030 | 1985 | 1733 |
| 7e | H | H | Me | H | 2031 | 1986 | 1756 |
| 7f | Me | H | Me | H | 2028 | 1985 | 1744 |
| 7g | Me | Me | Me | H | 2030 | 1986 | 1739 |
| 7h | H | H | OMe | H | 2031 | 1986 | 1761 |
| 7i | Me | H | OMe | H | 2030 | 1984 | 1722 |
| 7j | Me | Me | OMe | H | 2028 | 1982 | 1740 |
| 7k | H | H | H | Cl | 2031 | 1991 | 1754 |
| 7m | Me | Me | H | Cl | 2031 | 1987 | 1731 |

*IR spectra were recorded in heptane solution.

of electron density from iron decreases the backbonding to the carbonyls and increases the C≡O bond order.

The $^{13}$C-NMR spectra in $CDCl_3$ of 7 are summarized in Table 8. The assignment of carbons 4 and 5 is based on comparison to substituted aryl styrenes. $^{13}$C-NMR data for selected carbons in p-methylstyrene, m-Cl-styrene, and p-methoxystyrene are presented in Table 9.

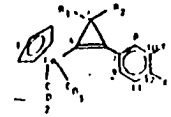



7

For meta-chlorostyrene, the 7 and 8 carbons are shifted upfield and downfield, respectively, when compared to styrene. If the same effect is observed in the cyclopropenes then the correct assignment would be C-5 at 130.52 and C-4 at 119.91 in 7b. Comparison of the other examples tends to support this assignment. Additional support for this assignment is obtained in the t-butylcyclopropene example where long-range coupling between C-5 and the aryl hydrogens is observed.

The coupling constant data are consistent with the assigned structures. The H-C coupling constants are in the range of 161.6-163.2 Hz (see Table 8) compared to 161 Hz for 8, 153 Hz for 8, 153 Hz for 9 endo-H, and 169 Hz for

Table 8. $^{13}$C-NMR Spectra of Substituted 1-Fp-Cyclopropenes*Δ



| $R_1$ | $R_2$ | X | Y | 1 | 2 and 3 | 4 | 5 | 6 | 7 | 8 and 9 | 10 and 11 | 12 | $R_1R_2$ | X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 86.19 | 214.19 | 119.91 | 130.52 | 11.64<br>t-163 | 133.41 | 128.43<br>d-159 | 126.89<br>d-159 | 135.42 | | |
| H | H | Me | H | 86.15 | 214.21 | 117.26 | 130.61 | 11.57<br>t-162.6 | 130.37 | 126.15<br>d-152 | 129.15<br>d-152 | 135.42 | | 21.16<br>q-125 |
| H | H | OMe | H | 86.15 | 214.34 | 117.90 | 130.01 | 11.55<br>t-162.8 | 126.49 | 128.12 | 114.50 | 158.07 | | 55.21 |
| H | H | H | Cl | 86.22 | 213.94 | 124.48 | 129.62 | 11.88<br>t-163.2 | 135.48 | 126.56 125.46<br>d-165 d-165 | 134.15 | 129.62 126.04<br>d-165 d-165 | 21.60<br>q-124 | |
| Me | H | H | H | 85.54 | 214.64<br>214.01 | 128.25 | 138.87 | 18.34<br>d-161.6 | 133.37 | 128.49<br>d-165 | 126.50<br>d-165 | 125.76<br>d-165 | 31,63<br>q-124 | |
| Me | H | Me | H | 85.55 | 214.71<br>214.07 | 126.58 | 138.82 | 18.30<br>d-161.6 | 130.55 | 126.51<br>d-157 | 129.24<br>d-157 | 135.45 | 21.15 | 21.30<br>q-125 |
| Me | H | OMe | H | 85.34 | 214.77<br>214.17 | 122.70 | 138.08 | 18.04<br>d-161.9 | 126.49 | 127.57<br>d-159 | 113.92<br>d-159 | 157.84 | 21.60<br>q-124 | 54.93<br>q-144 |
| Me | Me | H | H | 84.73 | 214.48 | 133.82 | 144.81 | 23.00 | 133.53 | 128.55 | 126.23 | 125.68 | 26.96<br>q-126 | |
| Me | Me | Me | H | 84.49 | 213.96 | 130.44 | 144.63 | 23.02 | 135.53 | 125.99 | 128.98 | 135.02 | 26.94 | 21.24 |
| Me | Me | OMe | H | 84.58 | 214.64 | 128.43 | 143.99 | 22.66 | 126.43 | 127.31<br>d-159 | 114.09<br>d-159 | 157.89 | 26.89<br>q-123 | 55.10<br>q-144 |
| Me | Me | H | Cl | 84.80 | 214.27 | 138.28 | 143.97 | 23.77 | 135.44 | 125.80 129.76<br>d-165 | 134.26 | 124.16 125.37<br>d-165 | 26.81<br>q-126 | |

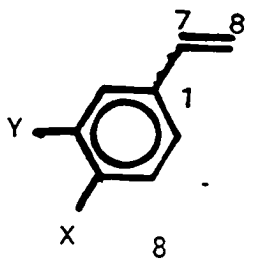
Table (continued)

| $R_1$ | $R_2$ | X | Y | 1 | 2 and 3 | 4 | 5 | 6 | 7 | 8 and 9 | 10 and 11 | 12 | $R_1R_2$ | X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ph | H | H | H | 85.67 | 213.82<br>214.04 | 129.10 | 149.96 | 29.07[131.45(s) 128.54 127.94 127.13 126.28*]<br>d-166[125.72 124.31 121.75(s)] | | | | | | |
| t-Bu | H | H | H | 85.97 | 214.12<br>215.14 | 125.19 | 139.50 | 37.16<br>d-152 | 133.84 | 126.58<br>d-159 | 128.38 | 125.70<br>d-161 | 34.20<br>29.68 | |

*$^{13}$C-NMR spectra recorded in $CDCl_3$ and reported in $\delta$ relative to tetramethylsilane.

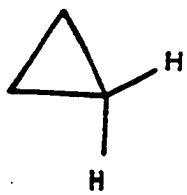
$^{\Delta 1}J_{H-^{13}C}$ coupling constants are reported in Hertz.

Table 9. $^{13}$C-NMR Spectra of Arylsubstituted Styrenes

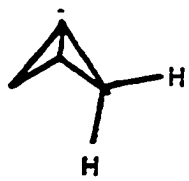



| X,Y | 1 | 7 | 8 | C-X |
|---|---|---|---|---|
| H,H | 136.10 | 135.50 | 112.00 | -- |
| Me,H | 136.50 | 136.30 | 112.80 | 136.50 |
| H,Cl | 137.50 | 133.40 | 113.80 | 133.40 |
| OMe,H | 130.10 | 135.30 | 110.20 | 158.70 |

for 9 exo-H.[15]

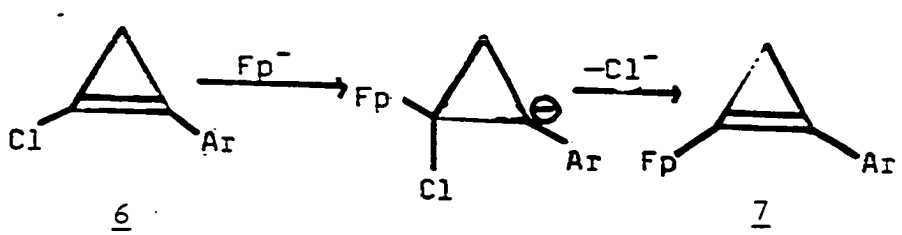



8




9

The procedure presented in this paper allows the synthesis of substituted 1-Fp-cyclopropenes in good yield from the reaction of NaFp and substituted 1-chlorocyclopenes. It is proposed that the nucleophilic $Fp^-$ attacks carbon 1 in an addition elimination mechanism outlined in Scheme 1.




6 7

Scheme 1. Addition/Elimination Mechanism

The yields vary with the ability of carbon 2 to stabilize the negative charge in the intermediate step. As expected the highest yields are observed with Ar=m-Cl phenyl due to its effective stabilization of the intermediate charge. The results are summarized in Table 5 (page 11).

## Limitations of the Synthesis of 1-Fp-1-Cyclopropenes

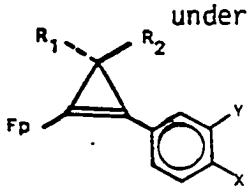
The method used in this research to prepare substituted 1-Fp-cyclopropenes has several limitations. The starting 1,1-dichlorocyclopropane must have an activating group at carbon 2 in addition to a hydrogen at carbon 2. Both of these conditions must be met before the 1-chlorocyclopropene can be prepared. An added limitation is the stability of the activating group to the potassium tertiary butoxide used in generating the 1-chlorocyclopropene. The substituted 1-chlorocyclopropenes are then reacted with NaFp to form substituted 1-Fp-1-cyclopropenes. The yields do not show clear patterns but it appears that in cases where the substituted 1-chlorocyclopropenes were formed in higher yields (perhaps due to greater stability) the yields of the substituted 1-Fp-cyclopropenes are higher.

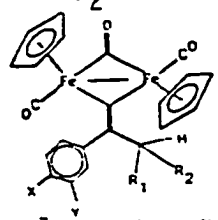
## Conversion of Fp-cyclopropenes to Bridging Vinylidene Iron Dimers

The conversion of 1-Fp-cyclopropenes to the bridging vinylidene iron dimers (BVD), by the reaction with $Fp_2$ and hydroxide under phase transfer catalysis, is unusual and interesting. The significance and mechanistic implications are discussed in Chapter 2. The yields for the conversion to the BVD are summarized in Table 10.

The conversion to the BVD occurs in good yield and represents a reasonable synthetic route a BVD. If other

Table 10. The Reaction of Substituted Fp-cyclopropene with $Fp_2$ under Phase Transfer Catalysis Conditions





| $R_1$ | $R_2$ | X | Y | mmole | $Fp_2$ mmole | Internal Standard | mmole | %* |
|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 0.84 | 1.12 | p-dioxane | 0.52 | 62 |
| Me | H | H | H | 0.76 | 1.05 | p-dioxane | 0.40 | 52 |
| Me | Me | H | H | 0.86 | 1.23 | p-dioxane | 0.48 | 56 |
| H | H | Me | H | 0.53 | 1.27 | p-dioxane | 0.39 | 74 |
| Me | H | Me | H | 0.84 | 1.16 | p-dioxane | 0.50 | 59 |
| Me | Me | Me | H | 0.28 | 0.43 | isolated | 0.20 | 70 |
| H | H | OMe | H | 0.42 | 0.86 | mesitylene | 0.29 | 70 |
| Me | H | OMe | H | 1.01 | 2.02 | mesitylene | 0.45 | 45 |
| Me | Me | OMe | H | 0.46 | 0.66 | mesitylene | 0.27 | 59 |
| Me | H | H | Cl | 0.70 | 1.03 | mesitylene | 0.10 | 14 |
| Me | Me | H | Cl | 0.74 | 1.49 | mesitylene | 0.50 | 68 |

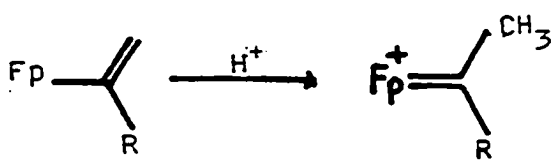
* All yields are based on an internal standard, performed at least in duplicate, and are ±10% based on the substituted 1-Fp-cyclopropene as determined by $^1$H-NMR spectra.

1-M-cyclopropenes (m=W,Mo) can be prepared, this would be a possible route to synthesis of mixed metal bridging vinylidene dimers.

## The Protonation of Substituted 1-Fp-cyclopropenes

The protonation of substituted 1-Fp-cyclopropenes at low temperature gave different products depending on the substitution on carbon 3.

The protonation of Fp-vinyl complexes 10 is a good method for the preparation of cationic Fp-alkylidene complexes.[3,4,16-18] The complexes are used as cyclopropanating agent when reacted with olefins.




10 11

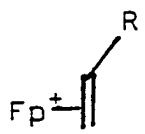
a R=H

b $R=CH_3$

c R=Ph

The formation of 12c is observed when $\eta^2$-Fp-styrene was protonated at -78° and then warmed to 25°C. Compound 11c is proposed as an intermediate even though no cyclopropana-

tion is observed in the presence of a large excess of alkene.[19] Cyclopropanation is observed with 11a and 11b, along with rearrangement to 12.[17,18]



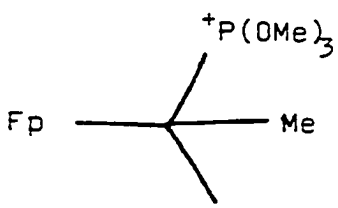
12

a R=H

b R=$CH_3$

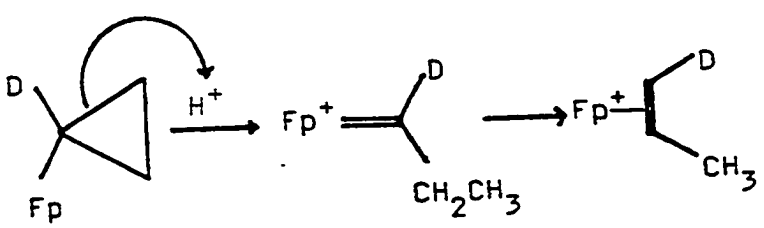
c R=Ph

The case for the alkylidene complex is further supported by its trapping with $P(OMe)_3$.[18]



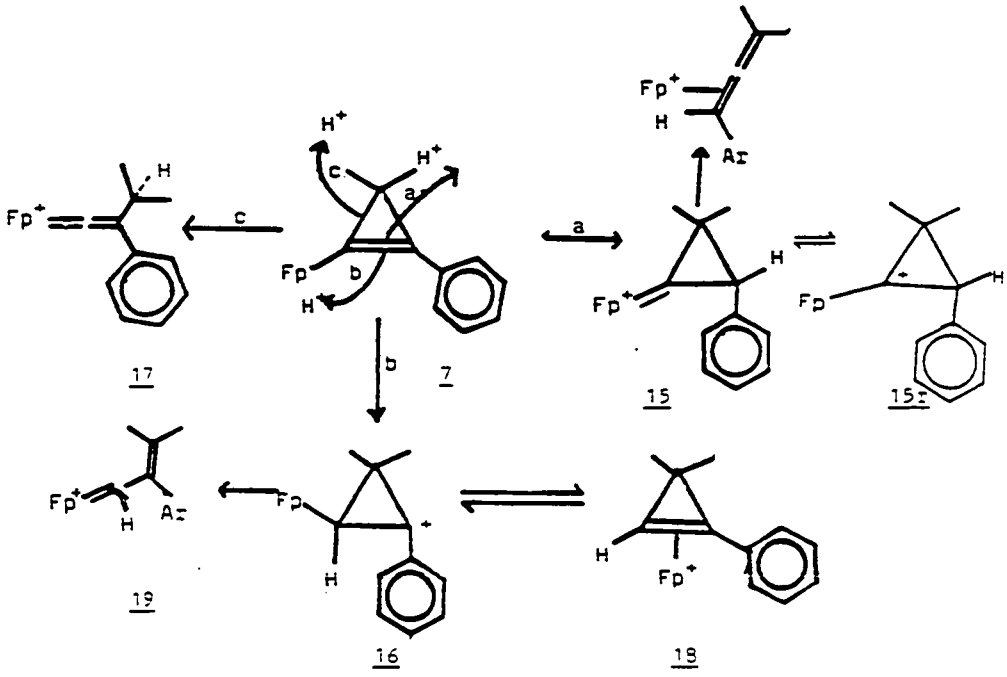
13

A similar result is obtained in the protonation of deuterated Fp-cyclopropane[14] where the $Fp^+$-alkylidene is shown to be an intermediate.[20]



14 11 12

Based on these precedents, the reaction of a proton with a 1-Fp-cyclopropene has three possible modes of attack as depicted in Scheme 2. The most probable site of electro-

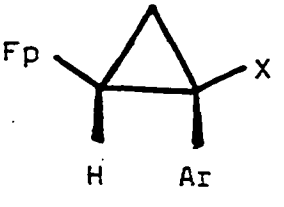



Scheme 2

Proposed Mechanism for the Protonation of 7b

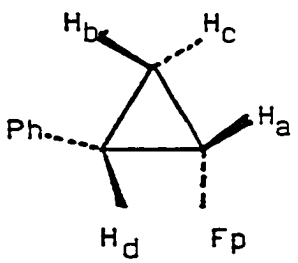
philic attack is the C-C π-bond. The proton could become attached to either of the two carbons (routes a or b) producing intermediates 15 and 16. Protonation of the C-C bond will yield intermediate 17 (via route c), a cationic vinylidene complex. A resonance form for 15 is a cyclopropyl cation, 15r. Such cations are known to rearrange rapidly to allyl cations. In this case, the allyl cation would be better stabilized as a Fp-$\eta^2$-allene olefin complex, 12. Although not formally a resonance form, structure 18 would be accessible through intermediate 16. Fp-$\eta^2$-alkene complexes are well known and rather stable but the strain in the ring may limit stability. Intermediate 16 can also open to form the vinylalkylidene 19. Intermediates like 17 are proposed from the reaction of electrophiles with Fp-acetylides, however, all were found to be very unstable.[21]

Protonation of 7b at -78°C in ether with $HBF_4 \cdot Me_2O$ yielded a solid that decomposes during isolation. The protonation is then performed with trifluoroacetic acid at 0°C in the presence of $NaCNBH_3$. A yellow organometallic was isolated that had a complex $^1$H-NMR (Table 11).




14

Table 11. $^1$H-NMR of Fp-cyclopropane*



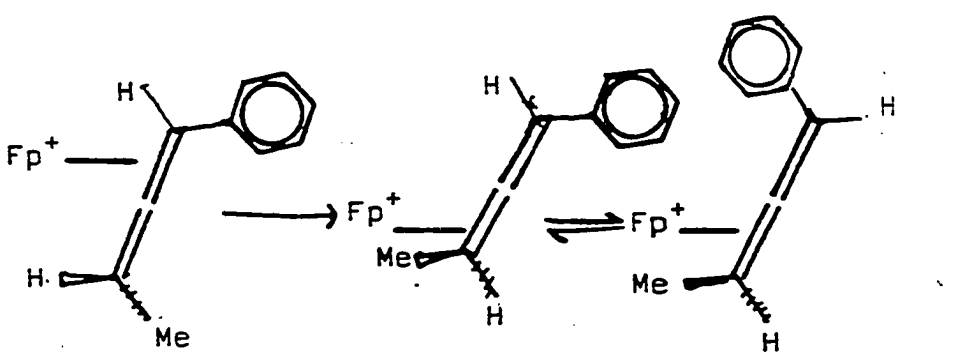

14

| | δ | $^n$J(A-B-C) |
|---|---|---|
| $H_a$ | .59 | $J_{ab}$=5 Hz, $J_{ac}$=5.5 Hz, $J_{ad}$=9 Hz |
| $H_{b,c}$ | 1.1 | $J_{bc}$=3.3 Hz, $J_{bd}$=8 Hz |
| $H_d$ | 2.1 - | $J_{cd}$=5.5 Hz |

*The proton NMR spectrum was recorded in $CS_2$ and is reported in δ relative to TMS.

The coupling constants most nearly fit the trans compound 14 (X=H) shown above. When the reaction was repeated using $D^+$, 14 (X=D) is formed as the signal at δ2.1 is reduced in intensity and the coupling pattern simplified. The $^{13}C$-NMR spectrum is consistent with structure 14 (X=H) (see Experimental Section).

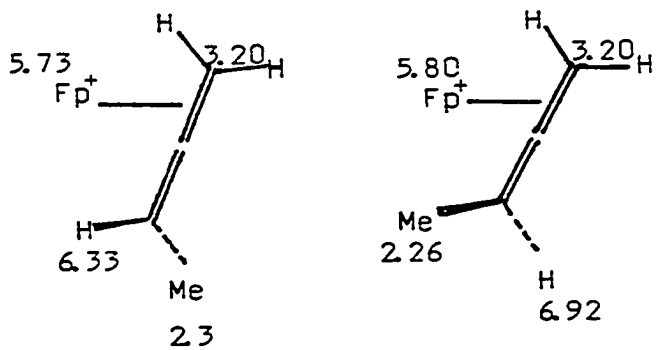
The protonation of 7c at low temperature in an NMR tube yields an $^1H$-NMR spectrum of a single compound that irreversibly isomerizes on warming to a mixture of two different products. The initially formed complex is tentatively assigned to 20a, which isomerizes to a mixture of 21a and 21b. The assignment of structures for 20a 21a, and 21b is based on comparison to the $^1H$-NMR data for 22




20 21a 21b

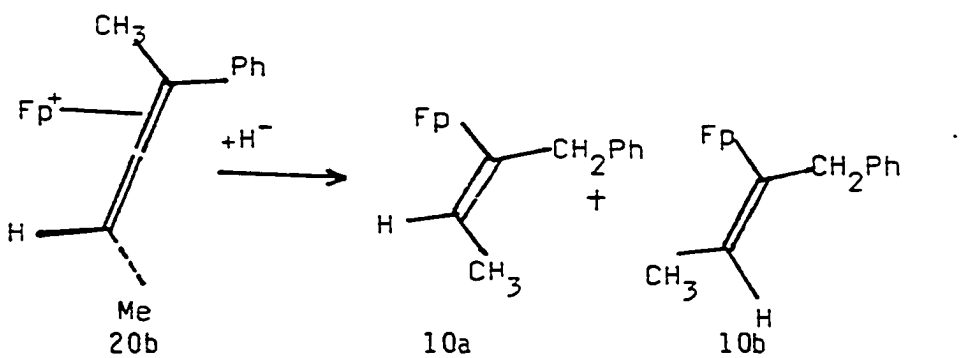
and 23 and the fact that 22 and 23 equilibrates at room temperature.[22] For 20a, the methyl is observed at 2.26 and it is coupled to a single proton at δ5.01 (J=Hz). The major product, 21, exhibits a methyl at δ2.10 and it is coupled to a single hydrogen at δ3.27 (J=6 Hz). Further

evidence for 20a is obtained through the protonation/reduction procedure described above for 1-Fp-2-phenylcyclopropene. Then 7c was protonated in the presence of $NaBH_3CN$, the




22 23

major product, produced in greater than 80% purity, is tentatively identified as $CH_3CH{=}C(Fp)CH_2Ph$. This product is most likely produced from hydride addition to 20b. Whether the Z- or E-olefinic isomer was obtained could not



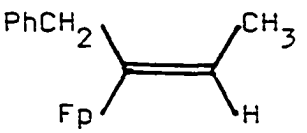

20b 10a 10b

be determined from the 60 mHz NMR data.

Protonation of 7a did not produce an isolable product, indicating the formation of a reactive intermediate. Even when protonation is done at low temperature in an NMR probe, only a multiplet of neutral Cp's was observed.

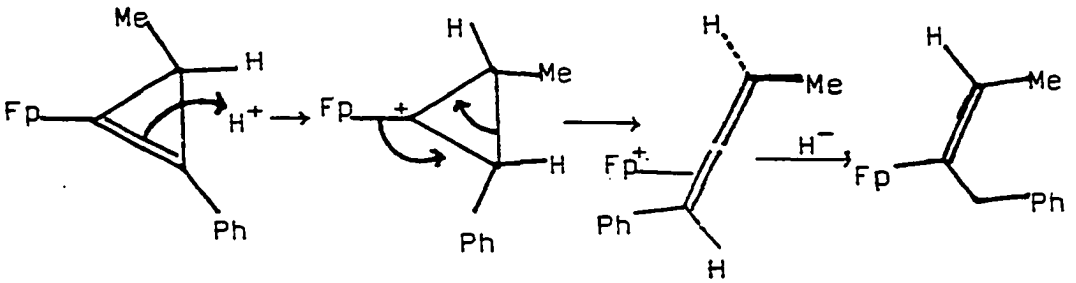
The protonation of 7c did produce an isolable product which is identified as a mixture of 21a and 21b. Low-temperature protonation in the NMR probe initially formed another allene complex 20a which isomerized to 21a and 21b on warming. The protonation of 7b must, therefore, go through intermediate 15 and then on to 20. The inability to observe a cationic product in the 7a protonation suggests that a reactive intermediate has been formed. Others have demonstrated that reactive $Fp^+=CR_2$ can be trapped with *in situ* nucleophiles.[17-19] We protonated 7a in the presence of sodium cyanoborohydride in an attempt to trap any reactive intermediates. When 7a is reacted with $CF_3CO_2H$ in the presence of $NaBH_3CN$, a 41% yield of 1-Fp-2-phenylcyclopropane is obtained. Such a reduction can occur via intermediates 15 and 16. Intermediate 15 is shown to be the true intermediate by using $D^+$ instead of $H^+$, producing 2-deuterio-1-Fp-2-phenylcyclopropane in 80% isotopic purity.

When 7b is subjected to the same *in situ* protonation followed by hydride trapping, a ring-opened product (10) is obtained. This is the expected product from



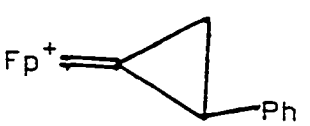

10a

hydride attack on structure 20a. Protonation appears to




7b 15r 20 10

be selective for the formation of intermediate 15 when Ar=Ph. The ring opening to form 11 is faster in 7b than in 7a. In the absence of hydride, 7a probably reacts with 15 to yield polymer faster than it opens to form 11. However, ring opening is faster for 7b than polymerization, or hydride attack, and 11 is produced. Methyl substituents have been shown to increase the rate of ring opening in cyclopropyl cations,[23] which is consistent with the results here. Although direct observation of 15a is not possible, the retention of the cyclopropane structure strongly implicates the cyclopropylidene complex as an intermediate in the protonation of 7a. This is the first evidence for a cyclopropylidene metal complex.

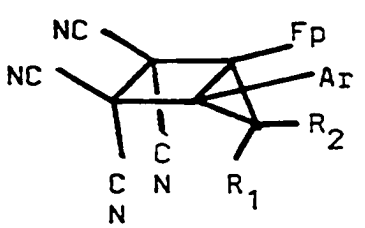



15

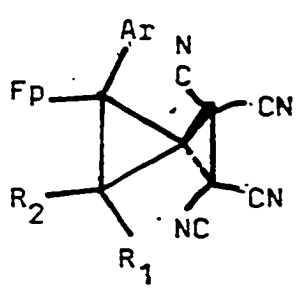
## Reaction of Substituted 1-Fp-cyclopropene with Tetracyanoethylene

The product of the reaction of substituted 1-Fp-cyclopropene with tetracyanoethylene (TCNE) has two rings with no double bonds. The proton NMR data are presented in Table 12 and IR data in Table 13.

The $^{1}$H-NMR spectrum of 24b shows two nonequivalent protons with one being δ0.87 ppm upfield relative to the other, with a coupling constant of 8 Hz, at δ1.33 and δ2.20. The IR data (Table 13) shows that the carbonyl stretches of the Fp group are relatively unaffected by the reaction: 2030 and 1985 $cm^{-1}$ in heptane for 7d compared to 2025 and 1983 $cm^{-1}$ in acetonitrile for 24d. There are two possible structures that are consistent with these data.



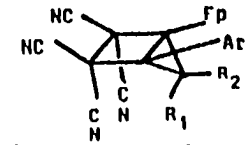

24




25

The $^{13}$C-NMR data of these compounds is summarized in Table 14. The first thing noted in the $^{13}$C-NMR spectrum of 24b is that there are four different cyano groups at δ110.99, δ112.55, δ113.42, and δ114.80. The assignment

Table 12. The $^1$H-NMR Spectra of the TCNE Adduct of Fp-cyclopropenes*$^{\Delta+}$




| No. | $R_1$ | $R_2$ | X | Y | $R_1$ | $R_2$ | Ar | X | Cp | $JR_1R_2$ Hz |
|---|---|---|---|---|---|---|---|---|---|---|
| 24b | H | H | H | H | 1,1.33(d) | 1,2.20(d) | 7.43 | | 5.38 | 8 |
| 24c | Me | H | H | H | 3,1.28(d) | 3,2.08(q) | 7.48 | | 5.47 | 6 hz |
| 24d | Me | Me | H | H | 3,1.00( ) | 3,2.09(s) | 7.45 | | 5.51 | |
| 24e | H | H | Me | H | | | | 3,2.33(s) | 5.40 | 7 |
| 24g | Me | Me | Me | H | 3,1.03(s) | 3,2.08(s) | 7.03-7.37 | 2.35(s) | 5.52 | |
| 24h | H | H | OMe | H | 1,1.50(d) | 1,2.11(d) | 6.6-7.6m | 3.83(s) | 5.37 | 8 hz |
| 24j | Me | Me | OMe | H | 3,1.01(s) | 3,2.08(s) | | 3,3.86(s) | 5.51 | |
| 24k | H | H | H | Cl | 1,1.62(s) | 1,2.20 | 7.4-7.6 | | 5.41 | 9 hz |

*$^1$H-NMR Spectra recorded in $d_6$-acetone relative to tetramethylsilane.

$^{\Delta}$The $^1$H-NMR spectra are reported as number of protons, δ and, splitting pattern.

$^+$TCNE is tetracyanoethylene.

Table 13. IR Spectra of the TCNE Adducts to Fp-cyclopropene*

| No. | $R_1$ | $R_2$ | X | Y | $\nu$ CO, $cm^{-1}$ | |
|---|---|---|---|---|---|---|
| 24b | H | H | H | H | 2030 | 1983 |
| 24c | Me | H | H | H | 2027 | 1980 |
| 24d | Me | Me | H | H | 2025 | 1978 |
| 24e | H | H | Me | H | 2030 | 1982 |
| 24g | Me | Me | Me | H | 2026 | 1977 |
| 24h | H | H | OMe | H | 2030 | 1981 |
| 24j | Me | Me | OMe | H | 2026 | 1978 |
| 24k | H | H | H | Cl | 2030 | 1982 |

*IR spectra were recorded in acetonitrile.

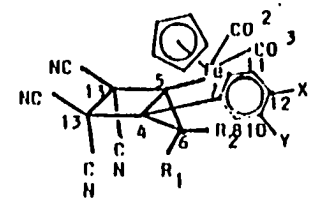


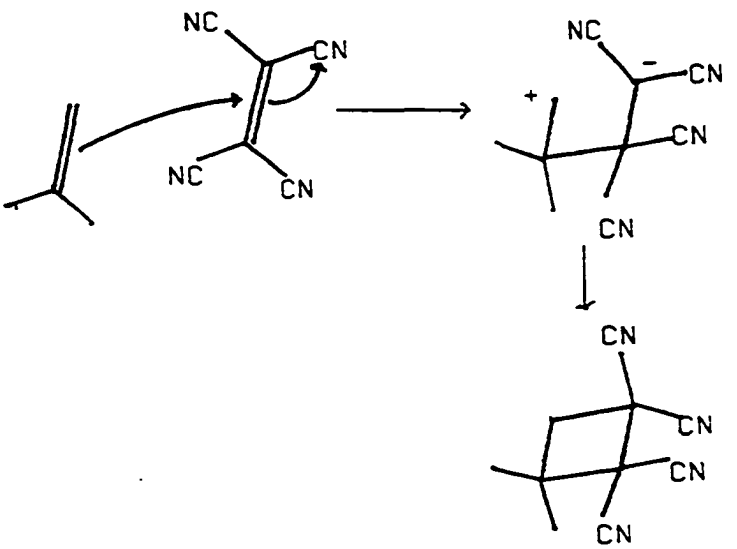

Table 14. $^{13}$C-NMR Spectra of the TCNE Adduct to Substituted Fp-cyclopropenes

| $R_1$ | $R_2$ | X | H | 1 | 2 & 3 | 4 | 5 | 6 | 7 | 8 & 9 | 10 & 11 | 12 | 13 | CN | CN | $R_1$ & $R_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 87.19 | 216.04<br>216.37 | 38.12 | 34.34 | 30.90 | 133.86 | 129.82 | 132.40 | 130.83 | 48.42<br>47.00 | 110.99<br>112.55 | 113.42<br>114.79 | | |
| Me | H | H | H | 87.33 | 216.04<br>215.05 | 40.87. | 40.10 | 30.81 | 132.14 | 120.98 | 132.14 | 130.69 | 47.51<br>48.39 | 111.28<br>112.44 | 112.84<br>115.15 | 16.46 | |
| Me | Me | H | H | 87.31 | 215.81<br>215.53 | 41.55 | 41.42 | 33.18 | 134.10 | 129.84 | 131.04 | 130.32 | 44.97<br>47.34 | 111.69<br>113.68 | 114.62<br>117.39 | 19.05<br>30.53 | |
| H | H | Me | H | 87.21 | 216.12<br>213.48 | 38.05 | 34.50 | 30.90 | 140.94 | 130.47 | 132.33 | 133.03 | 47.23<br>48.43 | 111.07<br>112.64 | 113.54<br>114.91 | 21.29 | |
| Me | Me | Me | H | 87.34 | 215.88 | 41.42 | 35.45 | 33.13 | 140.30 | 129.99 | 130.98 | 130.48 | 45.28<br>47.99 | 111.78<br>113.41 | 114.62<br>116.32 | 19.07<br>30.57 | 21.29 |
| H | H | OMe | H | 87.20 | 216.17<br>213.44 | 37.88 | 34.67 | 30.99 | 125.85 | 133.85 | 115.20 | 161.97 | 47.41<br>48.30 | 111.13<br>112.72 | 113.55<br>114.92 | 19.06 | 55.61 |
| Me | Me | OMe | H | 88.29 | 215.92 | 41.42 | 41.15 | 33.08 | 125.85 | 132.55 | 113.73 | 161.37 | 51.19<br>59.19 | 116.27<br>114.69 | 111.81<br>110.02 | 30.44 | 55.64 |
| H | H | H | Cl | 87.38 | 216.00<br>213.53 | 38.48 | 37.45 | 34.62 | 136.17 | 131.00 | 132.26 | 135.08 | 46.86<br>48.53 | 110.84<br>112.45 | 113.37<br>114.74 | | |

*$^{13}$C-NMR spectra recorded in $d_6$-acetone and reported in δ relative to tetramethylsilane.

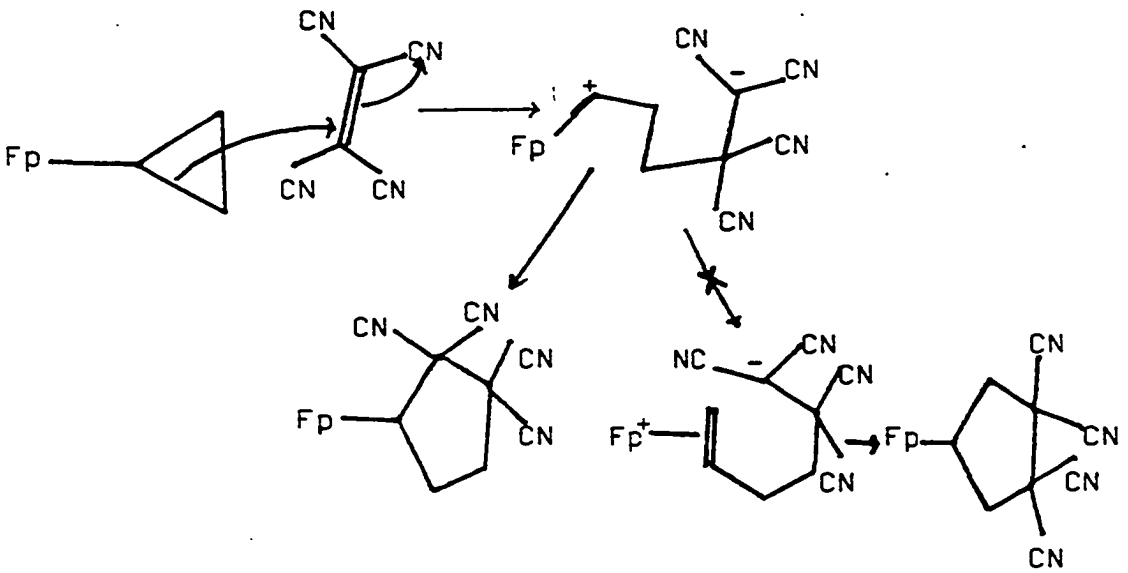
of carbons 4 and 5 is somewhat tentative and based on long-range coupling.

The protonation, hydride addition chemistry revealed a competition between ring opening and addition products. A reactant that has been used to investigate reactions of this type is tetracyanoethylene (TCNE). Tetracyanoethylene attacks as an electrophile but generates an internal nucleophilic site at the same time, thus allowing the trapping of intermediates (see Scheme 3).




Scheme 3. Proposed mechanism for TCNE addition to an alkene

The reaction of Fp-cyclopropane with TCNE reported by Rosenblum[5] is of some significance since ring closure is fast compared to rearrangement (see Scheme 4). In our system ring closure is also observed to be fast compared to rearrangement to a ring opened form (see Scheme 6). The aryl migration to form 25 is a possibility, however, this

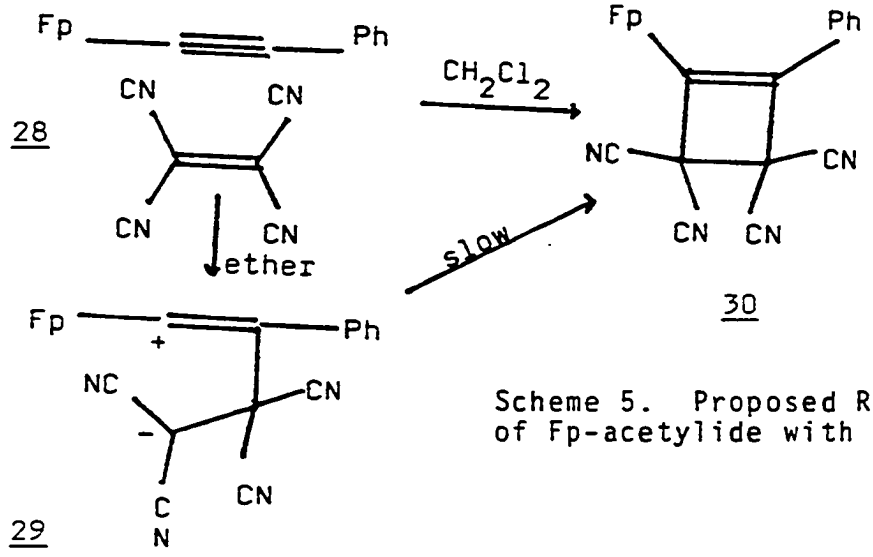


Scheme 4. Proposed Mechanism for the Reaction of Fp-cyclopropane with TCNE

type of rearrangement is not observed in the protonation studies and is, therefore, less likely than ring closure to form 24.

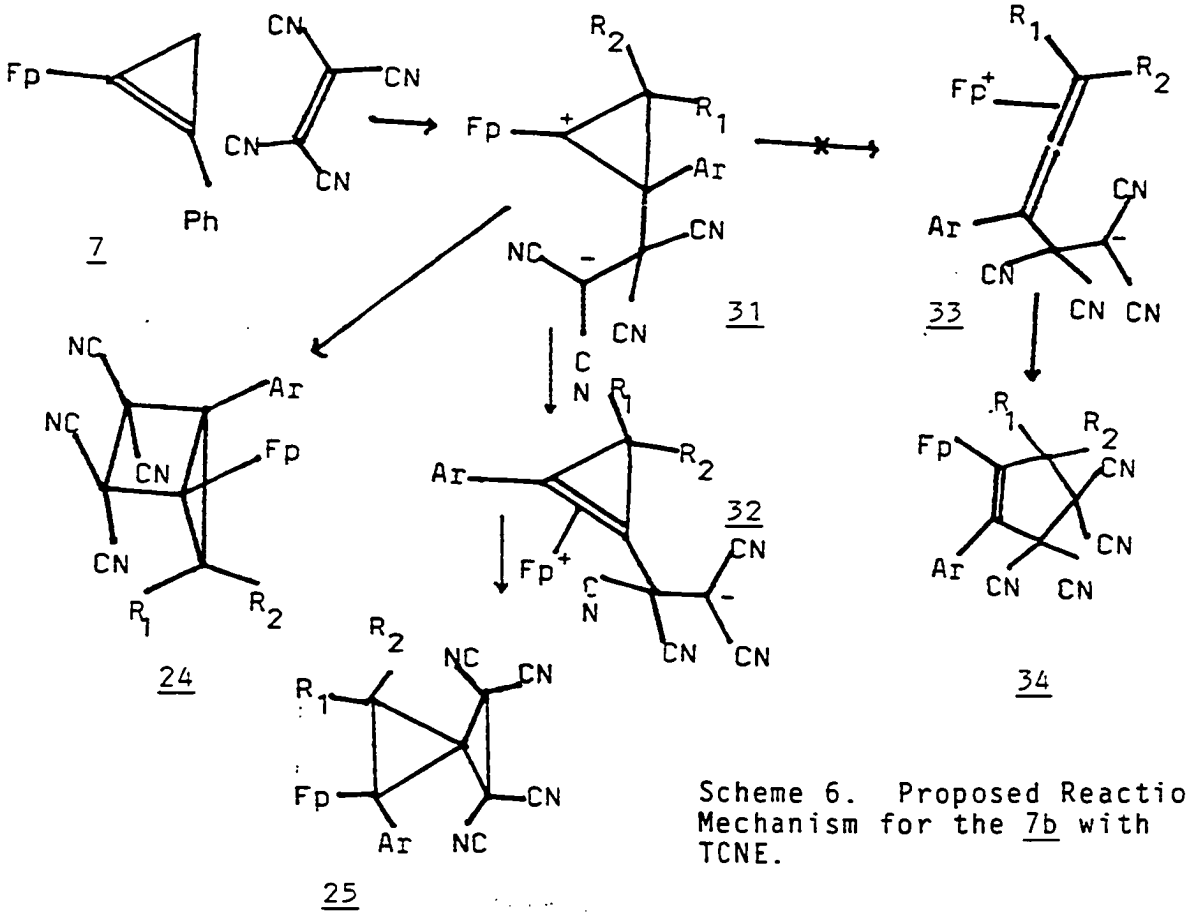
The chemical shift of the Cp in the proton NMR spectrum indicated a fair amount of positive charge on the iron. This was also observed in the CO stretches in the IR spectrum. A possible explanation would be the formation of a dipolar structure similar to that proposed by Davison and solar in reactions of Fp-acetylides with TCNE (see Scheme 5.

They base their assignment of 29 on the $^{1}$H-NMR resonance of the Cp at δ5.45 which is definitely in the cationic region for Cp. The material slowly isomerizes to yield 30. However, in our case the material in $CDCl_3$




Scheme 5. Proposed Reaction of Fp-acetylide with TCNE

has a Cp at δ5.13 but in $(CD_3)_2CO$ has a chemical shift

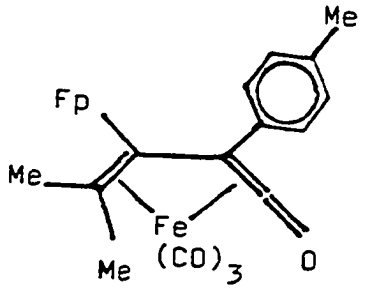



Scheme 6. Proposed Reaction Mechanism for the 7b with TCNE.

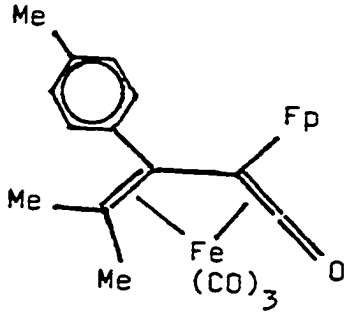
of δ5.43. Also, no large IR shift is observed in KBr *versus* acetonitrile for the CO's of *24b*. The $^{13}$C-NMR spectra also do not show a downfield signal in the region of δ300-350 ppm expected for a cationic alkylidene. The $^{1}$H chemical shift of the Cp is puzzling but can be due to some unusual electronic effect. The ultimate solution would be the crystal structure of the complexes.

## Reaction of $Fe_2(CO)_9$ with Substituted 1-Fp-cyclopropenes

Compound *7h* was reacted with $Fe_2(CO)_9$ to check for possible metal insertion into the Fp-substituted cyclopropene ring. Previous workers had demonstrated the insertion to be general for simple cyclopropenes.[16,25] Indeed, insertion was observed and the spectral data presented in Table 15 could be assigned to either of the structures presented for product *26* or *27*.

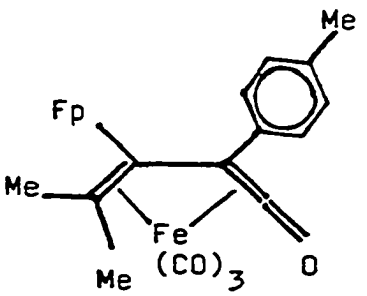



*26*

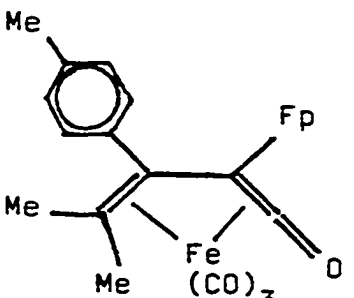



*27*

Table 15. Spectral data for 26 or 27.




26




27

$^{13}$C-NMR in $D_6$ Benzene*

| | | | |
|---|---|---|---|
| 1 | 85.91 | 8 | 59.80 |
| 2,3 | 215.01, 215.12 | 9,10 | 28.81,32.27 |
| 4 | 212.10 | 11 | 136.75 |
| 5 | 220.10 | 12,13 | 130/62 |
| 6 | -- | 14,15 | 131.70 |
| 7 | 75.02 | 16 | 138.18 |
| | | 17 | 21.20 |

$^{1}$H-NMR in $CS_2$ *

3H, 1.37(s)

3H, 1.57(s)

3H, 2.43(s)

5H, 4.57(s)

4H, 7.22(s)

IR Spectrum in Heptane

2050 $cm^{-1}$

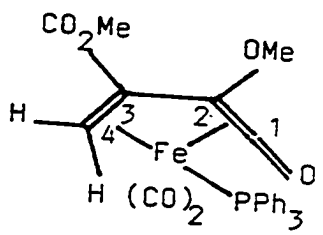
2026 $cm^{-1}$

1992 $cm^{-1}$

1982 $cm^{-1}$

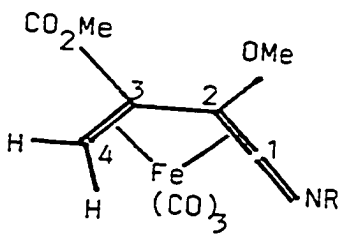
*NMR spectra are reported as $\delta$ relative to TMS.

The insertion of coordinatively unsaturated transiiion metals into cyclopropenes has been previously reported.[16,25,8] The reaction of 7g with $Fe_2(CO)_9$ produced a single compound that was identified as 26 by $^{13}C$ and $^1H$-NMR spectra (see Table 16). The initial assignment to structure 26 was based on comparison to similar complexes listed below.[26-28]

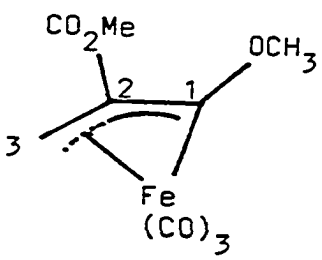



$^{13}C$ Data δ

1. 241.7
2. 103.5
3. 85.5
4. 24.4




1. 185.3
2. 112.1
3. 85.1
4. 30.2




1. 270.0
2. 52.4
3. 31.6

It is interesting to note that the ring opening by $Fe_2(CO)_9$ occurred at the same bond as observed in the preparation of the bridging vinylidene dimers (see Chapter 2).*

*An x-ray crystal structure of the reaction product of 7h with $Fe_2(CO)_9$ was recently completed[29] and is consistent with the proposed structure for 26.

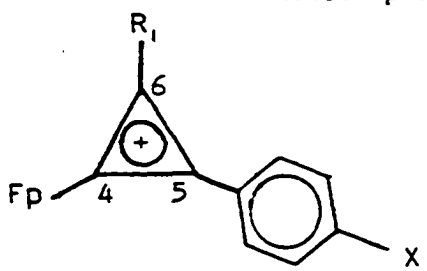
## Hydride Abstraction from Substituted 1-Fp-cyclopropenes

The reaction of substituted 1-Fp-cyclopropenes with a hydrogen on carbon 3 with triphenylcarbenium hexafluorophosphate produces the expected Fp-cyclopropenium salt. The $^{1}$H-NMR data is presented in Table 16. The proton-NMR spectrum of 3a matches the NMR spectrum of the previously prepared material.[6,7] This method allows the preparation of new metalated cyclopropenium salts containing a hydrogen on the ring. The $^{13}$C-NMR data is presented in Table 17.

The carbonyl peak in compound 3b was assigned to 210.91 because there is little change as the substituents varied. Carbon 6 was assigned to the peak at 182.87 because the peak is a doublet (J=242.3 Hz) in compound 3b. The other ring carbons (4 and 5) are assigned to 188.63 because 213.28 based on analogy to the Fp-cyclopropene where the Fp-carbon is observed at higher field.

The Fp-cyclopropenium salts are prepared from the reaction of a 1-Fp-1-cyclopropene containing at least 2 hydrogen on carbon 3 and triphenylcarbenium hexafluorophosphate. The fact that reaction occurs indicates the cyclopropenium cation is more stable than the triphenylcarbenium cation. The surprising factor in these compounds is relative chemical shift of the cyclopropenium carbons 4 and 5. It is expected that carbon 4 would be much further downfield than carbon 5 due to the ability of iron to stabilize a

Table 16. $^{1}$H-NMR Spectra of the Substituted Fp-cyclopropenium Salts$^{*\Delta+}$




| No. | $R_1$ | X | $R_1$ | Ar | X | Cp | $nJ(^{1}H\text{-}A\text{-}B\text{-}^{1}H)$ $J_{1,2}$ Hz |
|---|---|---|---|---|---|---|---|
| 3b | H | H | 1,11.61(s) | 7.6-8.5(m) | | 5,5.81(s) | |
| 3c | Me | H | 3,3.19(s) | 5,7.6-8.4(m) | | 5,5.75(s) | |
| 3f | Me | Me | 3,3.09(s) | 8.06,7.61(dq) | 2.53 | 5,5.62(s) | 8 |
| 3h | H | OMe | 1,11.39(s) | 8.29,7.35(dq) | 4.02 | 5,5.78(s) | 9 |
| 3i | Me | OMe | 3,3.14(s) | 8.18,7.31(dq) | 3.99 | 5,5.74(s) | 8 |
| 3a | Ph | H | | 7.7-8.7m | | 5.84 | |

$^{*1}$H-NMR spectra recorded in $d_6$-acetone relative to tetramethylsilane

$^{\Delta 1}$H-NMR spectra reported as a number of protons, and splitting pattern.

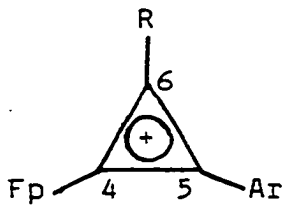
$^{+1}$H-$^{1}$H coupling constants (J) are reported in Hertz.

Table 17. $^{13}$C-NMR Spectra of the Substituted Fp-cyclopropenium Salts*



| No. | R | X | 1 | 2,3 | 4 | 5 | 6 | 7 | 8,9 | 10,11 | 12 | R | X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3b | H | H | 89.32 | 210.91 | 188.63 | 213.28 | 182.87 | 122.34 | 134.00 | 130.89 | 137.46 | | |
| 3c | Me | H | 88.70 | 211.47 | 191.55 | 208.52 | 186.72 | 123.02 | 133.63 | 131.02 | 136.88 | 13.25 | |
| 3a | Ph | H | 88.65 | 211.60 | 183.96 | 210.96 | 183.56 | 123.50 | 131.23 | 137.09 | | | |
| 3f | Me | Me | 88.87 | 211.98 | 190.61 | 209.90 | 186.12 | 120.68 | 134.01 | 132.13 | 149.62 | 13.29 | 22.10 |
| 3h | H | OMe | 89.51 | 211.05 | 186.55 | 209.00 | 179.99 | 114.90 | 136.72 | 116.14 | 167.66 | | 56.60 |
| 3i | Me | OMe | 88.59 | 211.73 | 188.63 | 203.81 | 184.65 | 115.33 | 136.34 | 116.49 | 166.81 | 12.99 | 56.51 |

*$^{13}$C-NMR recorded in $d_6$-acetone relative to tetramethylsilane.



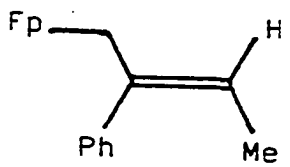

3

positive charge. However, the aryl group apparently stabilizes the positive charge to an equivalent degree. This method allows the preparation of a number of new cyclopropenium salts.

The presence of a positive charge in the molecule makes possible a nucleophilic addition to the ring. When compound 3b is reacted with $LiCu(Me)_2$ at -78°C a 45% yield of the substituted 1-Fp-cyclopropene resulting from addition to carbon 3 was obtained. The $LiCu(Me)_2$ is found to be more selective as $CH_3Li$ and $CH_3MgBr$ yields complex mixtures when reacted with 3b. The failure of the latter reactions may be due either to their enhanced ability to act as a base or to undergo electron-transfer reactions.

The procedure described here (hydride abstraction followed by nucleophilic addition) allows for the preparation of new substituted 1-Fp-cyclopropene complexes.

The reaction of sodium cyanoborohydride with 3c produced a 42% yield of a 1:1 mixture of 7c and a compound tentatively assigned as:



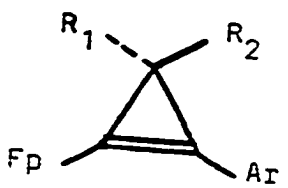

35

The reaction of 3b with sodium cyanoborohydride yields 42% of a 1:1 mixture of 7b and a compound that was not identified.

Reaction of Fp-cyanopropenium salts with nucleophiles produces 1-Fp-1-cyclopropenes. In this reaction, the nucleophile attacks carbon 6 forming the known substituted 1-Fp-1-cyclopropenes. The copper reagents are used since organolithium and organomagnesium compounds are basic enough to remove a proton and result in complex mixtures as observed by NMR spectroscopy and thin-layer chromatography. The use of organocopper reagents presents a possible route to a variety of new substituted 1-Fp-1-cyclopropenes.

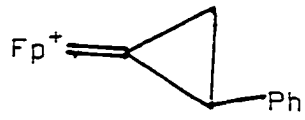
## SUMMARY

A series of new compounds, the substituted $\eta^1$-cyclopropenyl-cyclopentadienyl iron dicarbonyls 7 has been synthesized. The preparation is the simple addition/elimination reaction of NaFp with the substituted 1-chloro-cyclopropene to form the product 7.



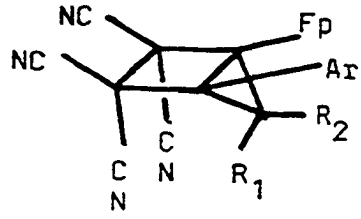

7

The reaction of 7 with various reactants was investigated. The protonation of 7 can take two different pathways depending on the substitution on carbon 3. The ring opens when carbon 3 has two methyl substituents. An interesting substituted 1-Fp-cyclopropane can be formed if carbon 3 is unsubstituted and protonation is followed by hydride addition. This is highly indicative of an intermediate like 15.




15

The reaction of 7 with the ambident reagent tetracyanoethylene yields a new compound 24. The inter-




24

esting result of this reaction is that no ring opened products are observed.

The hydride abstraction from the substituted 1-Fp-1-cyclopropenes with the trityl cation $(CPh_3)^+$ forms the expected substituted Fp-cyclopropenium cation. Compounds of this type are known and is another fact supporting the structure of the substituted 1-Fp-cyclopropenes.

The most interesting chemistry of the substituted 1-Fp-cyclopropenes is the competition for ring opening

versus stability of the substitute Fp-cyclopropyl cation. This area would be a fruitful area for further study in the substitution effect on the stabilities of intermediates in the protonation reaction.

## EXPERIMENTAL

### 1,1-Dichlorocyclopropanes

(2,2-Dichlorocyclopropyl)benzene is commercially available from Aldrich and a number of substituted 1,1-dichlorocyclopropanes are furnished by Professor E.H. Dehmlow: 1,1-dichloro-1-p-anisyl-3,3-dimethylcyclopropane, 1,1-dichloro-2-methyl-2-phenylcyclopropane, 1,1-dichloro-2-tolyl-3-methylcyclopropane, 1,1-dichloro-2-tolyl-3-methylcyclopropane, and 7,7-dichloroibicyclo[4.1.0] heptane. The method established by Makosza and Wawrzyniewicz[30] (improved by Dehmlow and Schonefield[31,32] and further refined by Magarian[33]) is used to generate the substituted 1,1-dichlorocyclopropanes from the olefins via dichlorocarbene. A number of the required olefins are commercially available: trans-anethole, 3-chlorostyrene, β-methylstyrene, 4-methylstyrene, trans-stilbene, and 4-vinylanisole. The remaining olefins are prepared by Marijke van der Helm or Ora Martin in a two-step synthesis: 1. The formation of a phosphonate ester via the Arbutzov reaction between 1 equivalent of m-chlorobenzylchloride or benzylchloride and triethylphosphite; 2. The modified Wittig reaction is carried out between the phosphonate ester and acetaldehyde or acetone

in dimethylformamide in the presence of sodium methoxide to produce 3-chloro-β,β-dimethylstyrene, trans-3-chloro-β-methylstyrene, and β,β-dimethylstyrene.

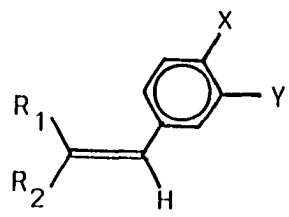
## General Procedure for 1,1-dichlorocyclopropane Preparation

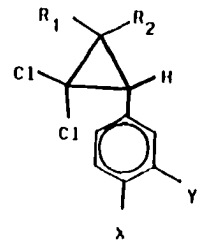
A 250 ml round bottom flask is charged with benzyltriethyammonium chloride (0.5 g, 2.2 mmol), chloroform (110 g) and the olefin (30-100 mmol), which was maintained at 0°C with rapid stirring as 50% $NaOH/H_2O$ (75 g) was added dropwise over a 1 h period. After addition is complete the reaction was allowed to warm to room temperature and left stirring overnight. The reaction mixture is added to a sparatory funnel containing ice water (200 g) and $CH_2Cl_2$ (75 mL). The layers are separated and the water layer washed with additional $CH_2Cl_2$ (2 x 75 mL) followed by drying of the combined $CH_2Cl_2$ layers with $MgSO_4$. Removal of solvent and distillation at reduced pressure using a microdistilling head or Kugelrohr apparatus yields the substituted 1,1-dichloropropanes (see Table 18).

## General Synthesis of Substituted 1-chloro-1-cyclopropenes

A modified version of the Weyerstahl method is used to generate the 1-chloro-1-cyclopropenes.[11,12] Solid t-BuOK (1.5 equiv) was added in three portions to a 100 mL round-bottom flask containing a 0°C stirring solution of

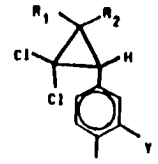
Table 18. Yields of 1,1-dichlorocyclopropanes

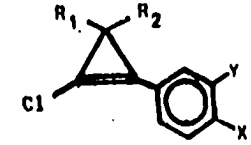



| $R_1$ | $R_2$ | X | Y | mmole | mmole % Yield | B.P. |
|---|---|---|---|---|---|---|
| Me | H | H | H | 92.23 | 85.77,93 | 110°@0.5 torr |
| Me | Me | H | H | 43.69 | 41.94,96 | 65°@0.2 torr |
| H | H | Me | H | 42.50 | 40.38,95 | 65°@0.3 torr |
| H | H | OMe | H | 37.30 | 32.82,88 | 95°@0.2 torr |
| Me | H | OMe | H | 66.66 | 56.66,85 | 91°@0.15 torr |
| H | H | H | Cl | 34.49 | 26.90,78 | 62°@0.1 torr |

Table 19. $^{1}$H-NMR Yields of 1-Chlorocyclopropenes





| $R_1$ | $R_2$ | X | Y | mmole | KOt mmole | Internal Standard | mmole | % Yield |
|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 5.51 | 8.2 | $CH_2BR_2$ | 2.42 | 44 |
| H | Me | H | H | 2.61 | 3.9 | $CH_2Br_2$ | 2.11 | 81 |
| Me | Me | H | H | 4.26 | 5.5 | $CH_2Br_2$ | 3.83 | 90 |
| H | H | Me | H | 2.60 | 3.9 | $CH_2Br_2$ | 1.51 | 58 |
| H | Me | Me | H | 1.97 | 3.0 | $CH_2Br_2$ | 1.58 | 80 |
| Me | Me | Me | H | 2.61 | 3.5 | Toluene | 1.85 | 71 |
| H | H | OMe | H | 93 | 2.9 | Mesitylene | 0.869 | 45 |
| H | Me | OMe | H | 1.97 | 2.7 | $CH_3NO_2$ | 1.73 | 88 |
| Me | Me | OMe | H | 2.12 | 3.5 | p-dioxane | 1.48 | 70 |
| Me | H | H | Cl | 1.43 | 2 1 | $CH_2Br_2$ | 1.00 | 70 |
| Me | Me | H | Cl | 2.14 | 3.2 | $CH_2Br_2$ | 1.95 | 91 |
| H | Ph | H | H | 2.47 | 3.5 | Toluene | 0.889 | 36 |

*All yields were performed at least in duplicate and are 10%.

the 1,1-dichlorocyclopropane (1 equivalent) in THF (15 mL). After 15 minutes a sample (1 mL) is removed from the reaction mixture and added to ice water (10 g) and ether (10 mL). The organic layer was separated and washed with a 5% $NH_4Cl/H_2O$ solution (10 mL), dried over $MgSO_4$ and the volume reduced to ~0.3 mL on a rotary evaporator at 25 torr. Carbon tetrachloride (10 mL) is added and the volume again reduced to ~0.3 mL. This procedure is repeated once more and the NMR and IR spectrum is obtained on the $CCl_4$ solution containing the 1-chlorocyclopropene. The yields are calculated by $^1$H-NMR spectra using an internal standard (see Table 19). The remaining 1-chlorocyclopropene solution in THF is then used in further reactions.

General Preparation of Substituted 1-Fp-cyclopropenes

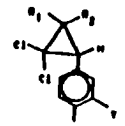
NaFp (0.5 M in THF, 1.5 equiv) is added via syringe to a 100 mL round-bottom flask containing a 0°C stirred solution of the 1-chlorocyclopropene (1 equiv) in THF (14 mL). The solution is then warmed to RT and stirred for 1 h. The solvent is removed at 0°C using a rotavap at 0.3 torr and the solid residue is chromatographed on a 15°C jacketed 4 x 8 cm activity III basic alumina column developed with 10% ether in hexane. A leading yellow-orange band followed by the dark red-brown band of $Fp_2$ are observed. The yellow-orange band is collected and the solvent removed as above. The residue is rechromatographed on a 15°C

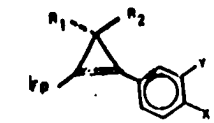
jacketed 2.5 x 25 cm activity III basic alumina column developed with 7% ether in hexane. Three highly colored bands are observed in most cases. A small leading yellow band is identified as 1-Fp-cyclopropene and the third band is a small amount of $Fp_2$ and the products are observed. The yields as determined by $^1$H-NMR spectroscopy are obtained on the product isolated after the second chromatography while the isolated yields are from the recrystallized product after two chromatographies, see Table 20). When the original reaction solution is not warmed to RT and stirred for 1 hour, it is very difficult to get a solid product. In addition, when the original Weyerstahl procedure is used [t-BuOK (1.5 equiv) in 10 mL THF is added slowly to a 15°C stirring solution of 1,1-dichlorocyclopropane (1 equiv) in THF (10 mL)] it is also difficult to obtain pure product. The analytical data are summarized in Table 21 and mass spectral data in Table 22.

## Conversion of 1-Fp-1-cyclopropene to the Bridging Vinylidene

After 1-Fp-1-cyclopropene (1 equiv), $Fp_2$ (1.5 equiv) and THF (15 mL) are added to a 100 mL round-bottom flask containing a mixture of 45% NaOH/$H_2O$ (11 g) and tetra-n-butylammonium hydrogen sulfate (150 mg, 0.4 mmol) the solution was stirred at RT until 7 is consumed as monitored by TLC. The work-up described in method A

Table 20. $^1$H-NMR Yields of Substituted 1-Fp-1-cyclopropenes





| $R_1$ | $R_2$ | X | Y | mmole | KOt mmole | mmole | % Yield | NaFp mL | NaFp mmole | Internal Standard | mmole | % Yield* | Mp $^oC$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | H | 3.86 | 5.8 | 1.74, | 45 | 8 | 4.0 | Isolated | 1.24, | 71 | 58.5-60.0 |
| H | Me | H | H | 1.19 | 1.7 | 1.02, | 86 | 4 | 2.0 | Mesitylene | 0.809, | 79 | 70.5-72 |
| Me | Me | | H | 2.23 | 3.2 | 2.01, | 90 | 6 | 3.0 | Mesitylene | 1.40, | 70 | 100.5-101.5 |
| H | H | Me | H | 1.08 | 1.6 | 0.680, | 63 | 3 | 1.5 | p-dioxane | 0.562, | 82 | 54.56 |
| H | Me | Me | H | 1.20 | 1.8 | 1.06, | 88 | 3 | 1.5 | p-dioxane | 0.876, | 82 | 61.5-63.5 |
| Me | Me | Me | H | 1.15 | 1.8 | 0.920, | 80 | 4 | 2.0 | P-dioxane | 0.422, | 51 | 120-122 |
| H | H | OMe | H | 1.14 | 1.6 | 0.422, | 37 | 3 | 1.5 | Mesitylene | 0.228, | 54 | oil |
| H | Me | OMe | H | 2.24 | 3.4 | 1.97, | 88 | 8 | 4.0 | Mesitylene | 1.08, | 55 | 65,5-67.5 |
| Me | Me | OMe | H | 3.40 | 5.0 | 2.38, | 70 | 8 | 4.0 | Isolated | 1.02, | 43 | 85-87 |
| H | H | H | Cl | 2.28 | 3.5 | 2.05, | 90 | 6 | 3.0 | Isolated | 1.64 | 80 | oil |
| Me | Me | H | Cl | 2.05 | 3.1 | 1.76, | 86 | 6 | 3.0 | Mesitylene | 1.64, | 93 | 80.0-82.0 |

*All yields are performed at least in duplicate and are 10% and based on 1-chlorocyclopropene as determined by $^1$H-NMR spectra.

Table 21. Analytical Data for Substituted 1-Fp-Cyclopropenes.

| | | | | Calc. | | Found | | High Resolution Mass Spectra | |
|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | $R_2$ | X | Y | %H | %C | %H | %C | Calc. | Found |
| H | H | H | H | | | | | 264.0254 | 264.0239 |
| Me | H | H | H | | | | | 278.0414 | 278.0414 |
| Me | Me | H | H | | | | | 292.0573 | 292.0554 |
| H | H | Me | H | 4.58 | 66.67 | 4.69 | 66.97 | | |
| Me | H | Me | H | | | | | 292.0573 | 292.0576 |
| Me | Me | Me | H | 5.43 | 68.29 | 5.48 | 68.44 | | |
| H | H | OMe | H | 4.38 | 63.34 | 4.03 | 63.79 | | |
| Me | H | OMe | H | 4.79 | 64.31 | 4.37 | 65.04 | | |
| Me | Me | OMe | H | 4.82 | 61.14 | 4.80 | 61.12 | | |
| H | H | H | Cl | 3.15 | 54.28 | 3.60 | 54.40 | | |
| Me | Me | H | Cl | | | | | 326.0182 | 437.0173 |

Table 22. Mass Spectral Data for the substituted 1-Fp-cyclopropenes.

| $R_1$ | $R_2$ | X | Y | $M^+$ | $M^+$-CO | $M^+$-2CO | $M^+$-2CO-Cp | $M^+$-Fp |
|---|---|---|---|---|---|---|---|---|
| H | H | H | H | (292,1.1) | (264.16.9) | (236,41.6) | (171,2.5) | (115,39.8) |
| Me | H | H | H | (306.1.1) | (278,81.4) | (250.1,68.4) | (185,12.7) | (129,23.9) |
| Me | Me | H | H | (320,.7) | (292,24.2) | (264,16.9) | (199.5.2) | (143,20.6) |
| H | H | Me | H | (306,.9) | (278,16.4) | (250,50.8) | (185,2.6) | (129,33.1) |
| Me | H | Me | H | (370,6.1) | (291.9,80.5) | (269,95.8) | (199,14.6) | (143,22.4) |
| Me | Me | Me | H | (334,.5) | (306,68.5) | (278,83.2) | (215,0) | (159,22.9) |
| Me | Me | OMe | H | (350,.3) | (322,38.5) | (294,43.4) | (229,22.4) | (173,100) |
| Me | H | OMe | H | (336,.8) | (308,73.1) | (280,96.2) | (217,13.1) | (161,0) |
| H | H | OMe | H | (322,.9) | (294,16.1) | (266,40.1) | (201,2.0) | (145,36.1) |
| H | H | H | Cl | (326,.8) | (298,15.8) | (270,47.3) | (305,2.7) | (149,41.7) |
| Me | Me | H | Cl | (354,0) | (326,47.3) | (298,18.8) | (233,5.9) | (177,15.7) |

*Mass spectral data reported as M/e abundance and % observed.

in the Experimental Section in Chapter 2 produced 41 in yields varying from 14 to 74%.

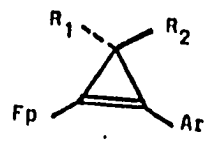
## Reaction of 1-Fp-1-cyclopropene with Tetracyanoethylene

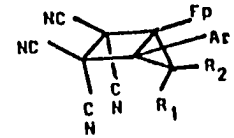
Solid tetracyanoethylene (TCNE) (0.9 equiv) is added to a 100 mL round-bottom flask containing a -78°C stirring mixture of 7 (1 equiv) is slowly added to precipi- After 1 h, hexane (50-60 mL) is slowly added to precipitate the solid product. The solid is removed by filtration, dissolved in $CH_2Cl_2$ and chromatographed on a 15°C jacketed 4 x 8 cm activity III neutral alumina column. Two bands were observed, a small leading orange band identified as 7 by $^1$H-NMR in $CS_2$ and a greenish band that was 95% pure tentatively assigned either structure 24 or 25 by $^1$H-NMR spectra. The yields are summarized in Table 23 and analytical data in Table 24.

## Reaction of 7h with $Fe_2(CO)_9$

7h (0.237 g, 0.71 mmol), $Fe_2(CO)_9$ (0.477 g, 1.31 mmol), and THF (25 mL) are added to a 100 mL round-bottom flask and stirred overnight. The solvent is removed on a rotary evaporator at 25 torr. The solid is chromatographed on a 4 x 12 cm silica gel column developed with ether/hexane. A single red band is isolated (0.152 g, 0.301 mmol, 42%). 136.1-137.3°C, Elemental analysis calculated 55.02%C,

Table 23. Yields of TCNE Adducts to 1-Fp-1-cyclopropene



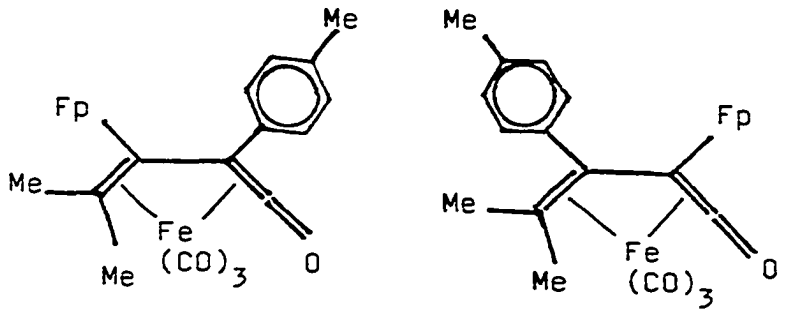




| Ar | $R_1$ | $R_2$ | mmole | TCNE mmole | mmole | Crude % Yield | % Purity[+] | Final % Yield[*] |
|---|---|---|---|---|---|---|---|---|
| Ph | H | H | 1.41 | 1.44 | 1.10 | 78 | 73 | 38 |
| Ph | H | Me | 1.92 | 2.00 | 1.40 | 73 | 74 | 29 |
| Ph | Me | Me | 1.20 | 1.23 | 0.78 | 65 | Good | 35 |
| tol | H | H | 1.79 | 1.72 | 1.15 | 67 | 88 | 40 |
| tol | Me | Me | 0.80 | 0.83 | 0.448 | 56 | Good | 40 |
| An | H | H | 1.54 | 1.52 | 1.29 | 85 | 60 | 40 |
| An | Me | Me | 0.71 | 0.70 | 0.49 | 70 | Good | 38 |
| mClPh | H | H | 0.74 | 0.092 | 0.49 | 68 | Good | 36 |

[+]%Purity was determined by $^1$H-NMR based on the Cp signals.

[*]Yields reported are isolated yields/

3.70%H, found 55.11%C and 3.72%H. Spectral data indicate one compound with 2 possible structures.




Hydride Abstraction from 1-Fp-cyclopropenes

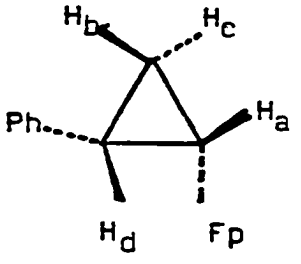
A -78°C solution of 7 (1 equiv) in $CH_2Cl_2$ (10 mL) is added via a cold syringe to a 100 mL round-bottom flask containing a -78°C stirring solution of $Ph_3C^+PF_6^-$ in $CH_2Cl_2$ (6 mL). After 1 hour the crude product is precipitated by the slow addition of ether (60 mL). The solid is removed by filtration and recrystallization from acetone and ether. The product is identified by IR, $^1$H-NMR (Table 16, page 41) and $^{13}$C-NMR (Table 17, page 42) to be the Fp-cyclopropenium salt (3). The physical and analytical data are summarized in Table 26.

Protonation of 1-Fp-2-phenyl-1-cyclopropene

Trifluoroacetic acid (75 mL, 0.98 mmol) is added via syringe to a 100 mL round-bottom flask containing a 0°C stirred solution of 7b (0.143 g, 0.49 mmol), NaCNBH (0.064 g, 1.03 mmol) and acetonitrile (6 mL). After analysis by TLC indicated all of 7b had been consumed the material

is worked up using the 1-Fp-cyclopropene procedure yields a material identified by IR, $^{1}$H-NMR and $^{13}$C-NMR as 1-Fp-2-phenyl-1-cyclopropane (0.056 g, 20 mmol, 41%).

A labeling study was conducted in which trifluoroacetic acid (0.105 mL, 1.36 mmol) in $D_2O$ (1 mL) is added via syringe to a 100 mL round-bottom flask containing a 0°C stirred solution of NaCNBH (0.088 g, 1.40 mmol), 7b (0.222 g, 0.76 mmol) and acetonitrile (6 mL). Work-up as before yielded the Fp-cyclopropane identified as 14b.



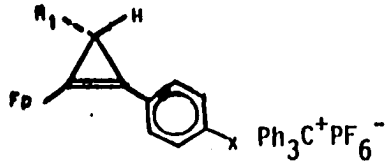

14b

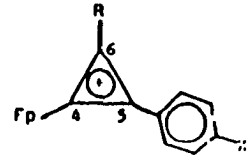
by NMR and mass spectroscopy where a parent ion peak was observed at 295 amu. It is not possible to determine the $D_0$, $D_1$, $D_2$, and $D_3$ ratios from the mass spectrum by simple means due to the isotope effect in the fragmentation. $^{1}$H-NMR spectral analysis indicates that 80% of the D is at position 2.

Protonation of 1-Fp-2-phenyl-3-methyl-1-cyclopropene

$HB_4$ $Me_2O$ (0.174 g, 1.30 mmol) is added via syringe to a 100 mL round-bottom flask containing a -78°C stirring solution of 7b (0.361 g, 1.18 mmol) and ether (15 mL). The solution is warmed slightly by removal from the dry

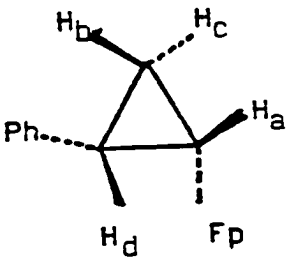
Table 24. Physical and Analytical Data for Fp-cyclopropenium Salts




| $R_1$ | X | | | | % Yield | MP°C | Elemental Analysis Calculated %H | %C | Found %H | %C |
|---|---|---|---|---|---|---|---|---|---|---|
| H | H | 2.12 | 2.08 | 0.38 | 18 | 170.0-173 dec | 2.55 | 44.07 | 2.56 | 44.09 |
| Me | H | 0.83 | 0.89 | 0.581 | 70 | 171.0-172.0 | 2.91 | 45.37 | 2.88 | 45.65 |
| Me | Me | 0.57 | 0.31 | 0.229 | 74 | 186.0-187.0 | 3.26 | 46.58 | 3.31 | 46.80 |
| H | OMe | 0.92 | 0.92 | 0.248 | 27 | 144-146 dec | 2.81 | 43.81 | 2.90 | 43.89 |
| Me | OMe | 1.70 | 1.53 | 0.995 | 65 | 172-172.5 | 3.15 | 45.03 | 3.25 | 45.26 |

Table 25. Data for Fp-cyclopropane*




$^{13}$C-NMR Data

| | | | |
|---|---|---|---|
| 1 | 85.21 | 7 | 129.19 |
| 2 | 216.94,216.68 | 8,9 | 127.61 |
| 3 | | 10,11 | 124.91 |
| 4 | 160.90 | 12 | 144.94 |
| 5 | 23.08 | | |
| 6 | 18.29 | | |

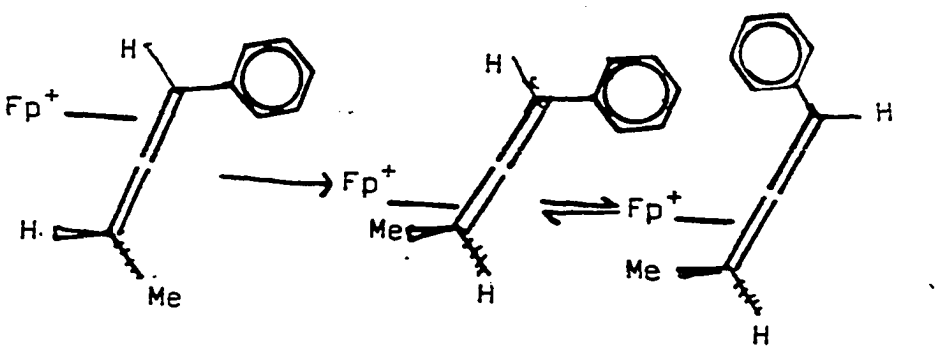
Elemental Analysis Calculated 4.79% H, 65.33% C, Experimental 5.03% H, 65.39% C.

Infrared spectrum in Heptane 1990.0, 1941.2 $cm^{-1}$ for CO stretches.

*$^{13}$C-NMR spectra recorded in $CDCL_3$ and reported in δ relative to tetramethylsilane.

ice/acetone bath and a yellow precipitate formes. The liquid is decanted and the yellow solid became a brown oil that was identified by $^1$H-NMR as two isomers.

7b (0.30 g, 0.10 mmol) in $CD_2Cl_2$ (0.3 mL) was filtered into a 5 mm NMR tube which was then colled to -78°C and fluorosulfonic acid (10 µL, 0.17 mmol) is added via syringe. The tube is then warmed to -50°C and $^1$H-NMR taken at 10° intervals up to -10° then chilled to -50°C and another spectrum taken. The $^1$H-NMR indicates that initially one compound is formed which then isomerizes into the mixture of 21a and 22b observed below.




20a 21a 21b

To a 100 mL flask is added 1-Fp-3-methyl-2-phenylcyclopropene (0.670 g, 2.2 mmol), $NaBH_3CN$ (0.275 g, 4.4 mmol) and 20 mL $CH_3CN$. The flask is cooled in an ice bath and $CF_3CO_2H$ (0.170 m , 2.2 mmol) added in 1 mL $CH_3CN$ over 1 minute. After 15 minutes the flask is left at RT for

20 minutes then the solvent is removed and the residue chromatographed on activity-IV alumina. A yellow-orange band is collected and the major product (>80%) is identified as $CH_3CH=C(Fp)CH_2Ph$. $^1$H-NMR ($CS_2$)$\delta$ : 7.10 (S,5H,Ph); 6.10 (q,1H,J=6.3 Hz); 5.32 (S,5H,Cp); 3.57 (S,2H.-$CH_2$-); 1.74 (d,3H,Me). The presence of 10-20% contaminants precluded obtaining an accurate elementalanalysis.

Reaction of 3 g with $LiCu(Me)_3$

3g (0.326 g. 0.748 mmol) in $CH_2Cl_2$ (6 mL) is added via syringe to a 100 mL round-bottom flask containing a -78°C stirring solution of $LiCu(Me)_2$ (1.0 mmol) in ether. When analysis by TLC indicates that the stirring material is consumed, the work-up as that of the 1-Fp-1-cyclopropene yielded 7b (0.096 g, 0.214 mmol, 42%) in 90% purity

The reaction is repeated with 3h (0.387 g, 0.86 mmol and $LiCu(Me)_2$ (1.0 mmol) with the work-up as before yielded 3c (0.129 g, 0.404 mmol, 47%) in 89% purity.

Reduction of 3g with $NaCNBH_3$

3h (0.292 g, 0.67 mmol) in $CH_3CN$ (5 mL) is added via syringe to a 100 mL round-bottom flask containing a 0°C stirred solution of $NaBH_3CN$ (0.062 g, 1.01 mmol) in $CH_3CN$ (6 mL). When analysis by TLC indicates all of the starting material is consumed the work-up yields 7c (0.013 g, 0.147 mmol, 22%) identified by $^1$H-NMR.

3h (3.3 g, 0.83 mmol) is reacted with $NaCNBH_3$ (0.142 g, 1.11 mmol) and worked up as before and yields 3d (0.063 g, 20 mmol, 24%) as identified by $^1H$-NMR.

## LITERATURE CITED


1. Brookhart, M.; Tucker, J.R.; Husk, G.R., J. Am. Chem. Soc., 1983, 105, 258.
2. Herrman, W.A., Adv. Organomet. Chem., 1982, 20, 159.
3. Kreamer, K.A.M.; Kuo, G.H.; O'Connor, E.J.; Helquist, P.; Kerber, R.C., J. Am. Chem. Soc., 1982, 104, 6119.
4. Bodnar, T.; Cutler, A.R., J. Organomet. Chem.,
5. Cutler, A.; Fish, R.; Giering, W.; Rosenblum, M., J. Am. Chem. Soc., 1972, 94, 4354.
6. Gompper, R.; Bartmann, E., Angew. Chem., Int. Ed. Engl., 1978, 17, 456.
7. Gompper, R.; Bartmann, E.; Nöth, H., Chem. Ber., 1979, 112, 218.
8. Desrosiers, P.J.; Hughes, R.P., J. Am. Chem. Soc., 1981, 103, 5593.
9. DeSimone, D.M.; Desrosiers, P.J.; Hughes, R.P., J. Am. Chem. Soc., 1982, 104, 4842.
10. Donaldson, W.A.; Hughes, R.P., J. Am. Chem. Soc., 1982, 104, 4846.
11. Henseling, K.-O.; Weyerstahl, P., Chem. Ber., 1975, 108, 2803.
12. Henseling, K.-O.; Quast, D.1.; Weyerstahl, P., Chem.

Ber., 1977, 110, 1027.

13. March, J., "Advanced Organic Chemistry," McGraw-Hill Book Company: New York, 1977, 253.
14. von Gustorf, E.A.K.; Grevels, F.-W.; Fischler, I., "The Organic Chemistry of Iron," Academic Press: New York, 1978.
15. Levy, B.C.; Wiberg, K.B.; Lampman, G.M.; Cuila, R.P.; Connor, D.S.; Schertler, P.; Lavanish, J., Tetrahedron, 1965, 21, 2749.
16. Newton, M.G.; Pantaleo, N.S.; King, R.B.; Chu, C.-K., J. Chem. Soc., Chem. Commun., 1979, 10.
17. Bodnar, T.; LaCroce, S.J.; Cutler, A.R.; Cutler, A.R., J. Am. Chem. Soc., 1980, 102, 3292.
18. Casey, C.P.; Miles, W.H.; Tukada, H.; O'Connor, J.M., J. Am. Chem. Soc., 1982, 104, 3761.
19. Kremer, K.A.M.; Helquist, P.; Kerber, R.C., J. Am. Chem. Soc., 1981, 103, 1862.
20. Cutlar, A.; Fish, R.W.; Giering, W.P.; Rosenblum, M., J. Am. Chem. Soc., 1972, 94, 4354.
21. Davison, A.; Selegue, J.P., J. Am. Chem. Soc., 1979, 101, 7232.
22. Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M., J. Am. Chem. Soc., 1977, 99, 2160.
23. Marvell, E.N., "Thermal Electrocyclic Reactions," Academic Press: New York, 1980, pp. 23-123.
24. Davison, A.; Solar, J.P., J. Organomet. Chem., 1979,

166, C13.

25. Dettlaf, G.; Behrens, U.; Weiss, E., Chem. Ber., 1978, 111, 3019.
26. Mitsudo, T.-A.; Sasaki, T.; Watanabe, Y.; Takegami, Y., J. Chem. Soc., Chem. Commun., 1978, 252.
27. Mitsudo, T.-A.; Watanabe, H.; Komiya, Y.; Watanabe, Y.; Takaegami, Y., J. Organomet. Chem., 1980, 190, C49.
28. Mitsudo, T.-A.; Watanabe, H.; Watanabe, Y.; Nitani, N.; Takegami, Y., J. Chem. Soc., Dalton Trans., 1979, 395.
29. Heeg, M.J.; Marten, D.F.; Bushman, D.R., personal communication.
30. Makoza, M.; Wawrzyniewicy, W., Tetrahedron Lett., 1969, 4659.
31. Dehmlow, E.V.; Schonefeld, J., Justus Liebigs Ann. Chem., 1971, 744, 42.
32. Dehmlow, E.B., Tetrahedron, 1972, 28, 175.
33. Magarian, R.A.; Benjamin, E.J., J. Pharm. Sci., 1975, 64, 1626.

# μ-Vinylidene- and $\eta^1$-Cyclopropenyliron Complexes: Chemistry and Synthesis via 1,1-Dichlorocyclopropanes

## Chapter 2

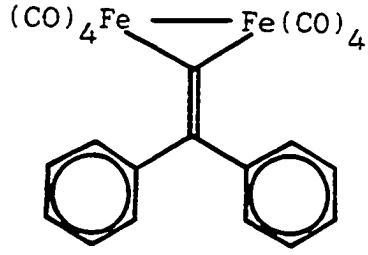
## μ-Vinylideneiron Complexes, Chemistry and Synthesis

### INTRODUCTION

Since the synthesis of ferrocene in 1951, the chemistry of organotransition-metal complexes has experienced remarkable growth stimulated by industrial research on homogeneous catalysis, by the inorganic chemist's interest in structural diversity, and by the organic and inorganic chemist's search for new synthetic methods. Organotransition-metal complexes are currently receiving intense study as models for reactions catalyzed by heterogeneous metal surfaces. Organotransition-metal complexes allow one to synthesize, isolate, and characterize possible intermediates in proposed reaction mechanisms. The results of these studies can then be applied to the heterogeneous system. Bridging alkylidene,[1-6] alkylidyne,[7-9] and vinylidene[10-32] transition-metal complexes

have recently received intense interest because they are related to proposed intermediates in various reactions catalyzed by transition-metal surfaces. The development of a rational synthesis of the bridging compounds is necessary for an understanding of the chemistry of these metal surfaces.

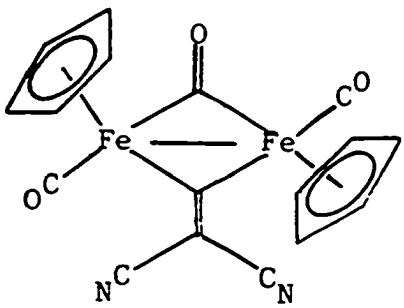
Bridging vinylidene are prepared by a variety of methods. The first reported bridging vinylidene was initially prepared by the photolysis of a mixture of diphenylketene and iron pentacarbonyl.[10] The structure of 40 is confirmed by x-ray crystallography.[11] Diphenylcarbene was initially proposed as an intermediate but was ruled out when di-iron nonacarbonyl reacted in the absence of U.V. light with diphenylketene to produce 40.



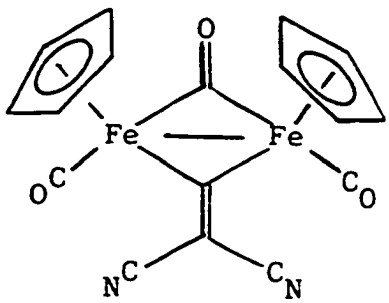

40

King[12,13] reports the synthesis of a pair of bridging vinylidenes 41n and 42n from the reaction of the nucleophilic dicarbonyl($\eta^5$-cyclopentadienyl)iron-($Fp^-$) with 1,1-dibromo-2,2-dicyanoethylene in yields of

2.5 and 0.5%, respectively. The structure of 42 is confirmed by x-ray crystallography.[14]

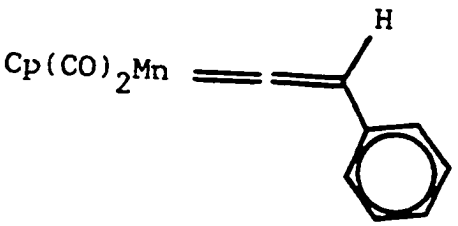


41n

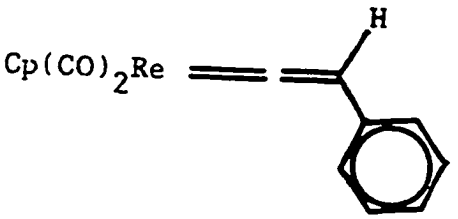


42n

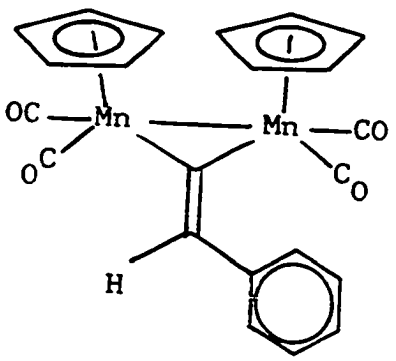
Several bridging vinylidenes are prepared via rearrangement of an alkyne. A Russian group reports the photolytic reaction of phenylacetylene and $CpMn(CO)_2THF$, (where THF is tetrahydrofuran and Cp is $\eta^5$-cyclopentadienyl) or $CpRe(CO)_3$ to produce the bridging vinylidenes 45a and 46a plus the monomeric vinylidenes 4a and 44a.[15-18] The structures of 43a, 45a, and 46a are confirmed by x-ray crystallography.[17,18] The monomeric vinylidene 43a can be converted into 45a by reaction with $CpMn(CO)_2 \cdot THF$ at 20°C. Likewise 44a can be converted into 46a by reaction with a methanolic KOH mixture. An unusual mixed metal bridging vinylidene can be prepared by reaction of 43a with $[CpRe(CO)_2]_2$ at 20°C to produce 47. Compound 47 can also be prepared by reaction of 43a with $CpMn(CO)_2 \cdot THF$ at 20°C.[19] The mixed metal bridging vinylidene slowly decomposes to yield 46a. This is the first report of



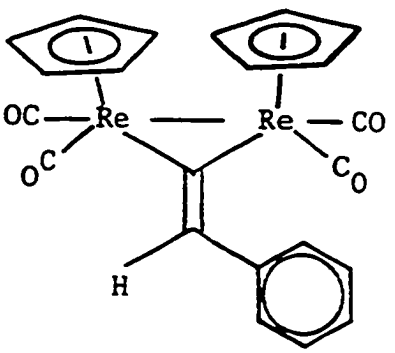

43a



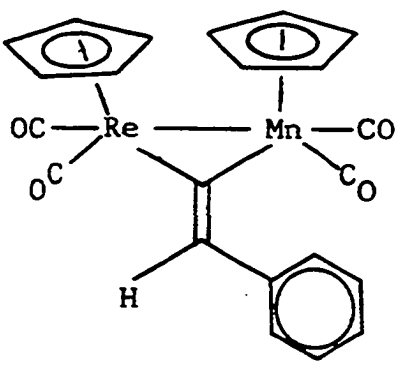

44a




45a



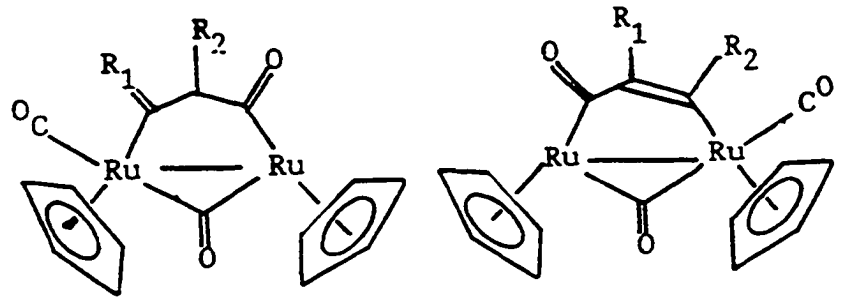

46a




47

a mixed metal bridging vinylidene.

Dyke and Knox report the photolytic reaction of $[CpRu(CO)_2]_2$ with acetylenes to yield complexes with the formulation $[Ru(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^3\text{-}C(O)C_2R_2]Cp_2]$.[48,20,21] They report the thermal conversion of 48a and 48b in toluene at 100°C to produce the bridging vinylidenes 49a, 49b, 50a, and 50b.

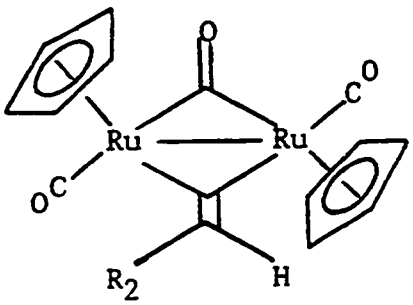


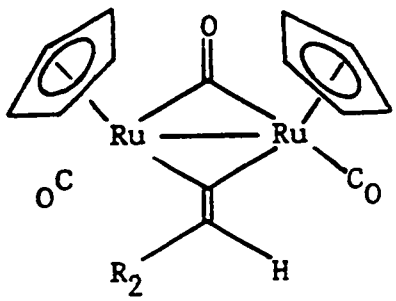

48a $R_1=R_2=H$

48b $R_1=H, R_2=Ph$

The yield of 49a and 50a is 35 and 30%, respectively. They report the isomers are separable by column chromatography but slowly convert in solution to give an equilibrium mixture. A similar isomerization occurs with 49b and 50b.

Cauton, et al., reports the synthesis of an unsubstituted bridging vinylidene 45b from the reaction of $CpMn(CO)_2(\eta^2\text{-}HC\equiv CH)$ with aqueous KOH in THF at reflux.





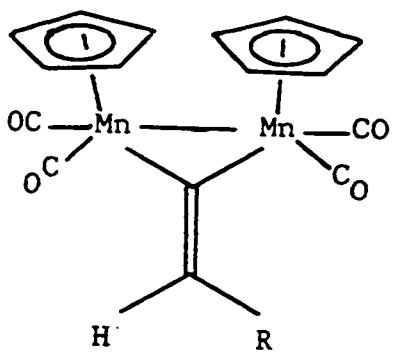
49a $R_2$=H

49b $R_2$=Ph

50a $R_2$=H

50b $R_2$=Ph

The analogous methyl substituted vinylidene 45c is prepared from the propyne complex.[22-24] The reaction



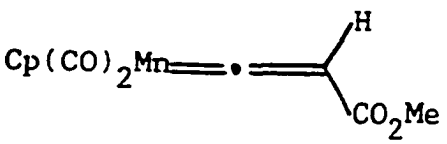
45b R=H

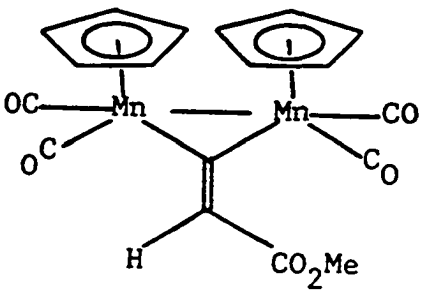
45c R=Me

is proposed to proceed through the monomeric vinylidene which reacts with the coordinatively unsaturated $[CpMn(CO)_2]$ yielding 45b and 45c.

Berke[24] reports the synthesis of a bridging vinyl-

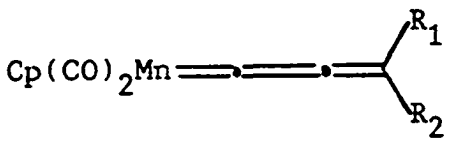
dene 45d from a monomeric vinylidene 43b in a reaction analogous to the conversion of 43a to 45a and 44a to 46a by reacting a coordinatively unsaturated metal species with a monomeric vinylidene complex. 43b is prepared from $CpMn(CO)_2(HC{\equiv}C\text{-}CO_2CH_3)$ by reaction with lithium diisopropylamide followed by addition of hydrochloric acid to form 45d.

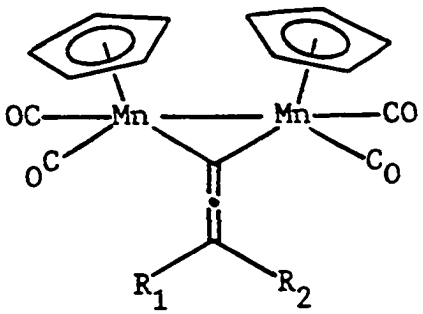



43b 45d

Berke[25] reports the synthesis of a bridging allenylidene 45c from the thermal reaction of the monomeric 43c.



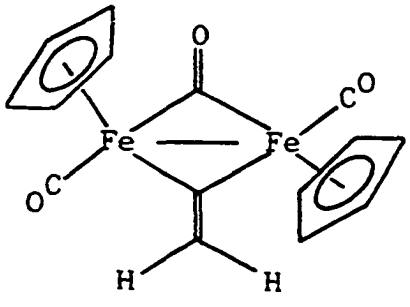




43c 45e

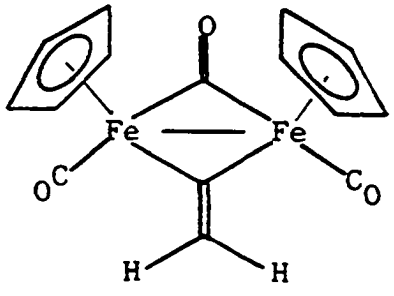
Compound 43c is prepared from $CpMn(CO)_2$ by treatment with 3 equivalents of alkyllithium followed by protonation

with hydrochloric acid. The reaction is proposed to proceed through the reaction of a coordinatively unsaturated manganese species attacking 43c to produce 45e. The conversion to 43c to 45e also occurs if $[CpMn(CO)_2 \cdot ether]_2$ is added to a solution of 43c thus implying the attack of coordinatively unsaturated metal on the metal-carbon multiple bond. This type of attack is becoming recognized as a good synthetic method to produce bridging alkylidenes and alkylidynes.

A different type of synthesis is reported by Stone, et al. in which a bridging carbonyl in $[CpFe(CO)_2]_2$, ($Fp_2$) is attacked by methyllithium followed by protonation with trifluoroacetic acid to produce 41b and 42b. Lu and




41o

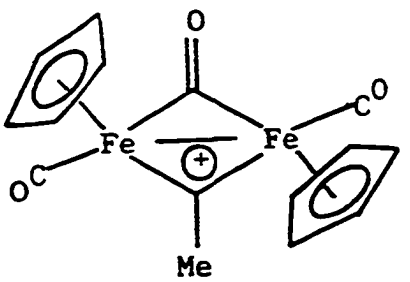



42o

Pettit, et al.[29] reports the synthesis of 41b and 42b from the hydrolysis of the briding carbyne 51.

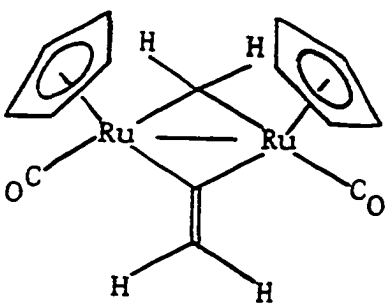
Rosenblum, et al.[9] reports the synthesis of bridging carbynes from the action of alkyl- and aryllithium reagents with $Fp_2$ followed by protonation with tetrafluoroboric

acid. The removal of a proton will then produce the bridging vinylidene.




51o

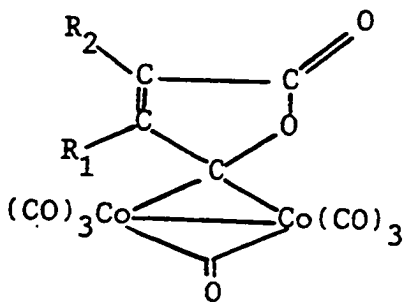
Knox, et al.,[30] reports the synthesis of a dimer containing a bridging vinylidene and a bridging methylidene from $(CpRuCO)_2(\mu\text{-}CH_2)(\mu\text{-}CO)$ by reaction with methyllithium followed by protonation with tetrafluoroboric acid followed by a water wash to produce 52.



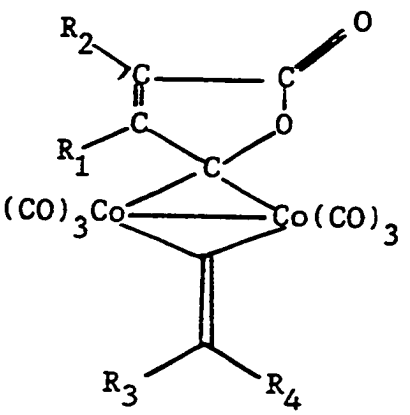

52

Another series of compounds containing alkylidene and vinylidene bridges in same molecule has been reported.[31] The reaction of $[Co(CO)_3]_2$-($\mu$-2,3-$R^1$,$R^2$-but-2-ene-4-olide-4-ylidene)($\mu$-CO), 53, with mono- or dihaloacetylenes forms

$[Co(CO)_3]_2(\mu\text{-}2,3\text{-}R^1_1,R^2\text{-but-2-en-4-olide-4-ylidene})(\mu\text{-}C{=}CR^3R^4)$, 54. The crystal structure for 54 has been determined.



53



54

$R_1$ = H

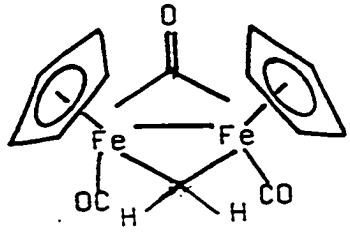
$R_2$ = n-pentyl

$R_3$ = I

$R_4$ = I

A different approach is reported by the Ziegler[32] group in which the iron dimer $Fp_2$ reacts with $(C_6H_6)_3P{=}CH_2$ in boiling THF p-dioxane to produce cis- and trans-$[CpFeCO]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, 55, (major) and $(CpFeCO)_2(\mu\text{-}C{=}CH_2)_2$, 42b, (minor). It is unclear whether the bridging vinylidene is produced from a Wittig-type reaction or from decomposition products.

Many bridging vinylidenes are prepared through the reaction of a coordinatively unsaturated metal species.




55

Gibson, et al.,[34,35] has demonstrated that phase-transfer catalysis* can produce $\eta^1$- and $\eta^3$-allyl metal complexes in the alkylation of metal carbonyls with allylic bromide. The presence of the $\eta^3$-allyl complexes implicate phase-transfer catalysis as a source of coordinative unsaturation at the transition metal center. Phase-transfer catalysis may then provide a route to the generation of bridging vinylidenes (BVD).

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*Phase-transfer catalysis concerns reactions between a substrate in an organic phase and a reagent present in another phase which is usually aqueous or solid. Reaction is achieved by means of a transfer agent; this agent is capable of solubilizing or extracting inorganic and organic ions, in the form of ion pairs, into organic media. Of the many possible phase transfer catalysts quaternary ammonium and phosphonium salts are the most widely used. Since the first publication in 1976 on organometallic phase-transfer catalysis the field has rapidly expanded.[33]

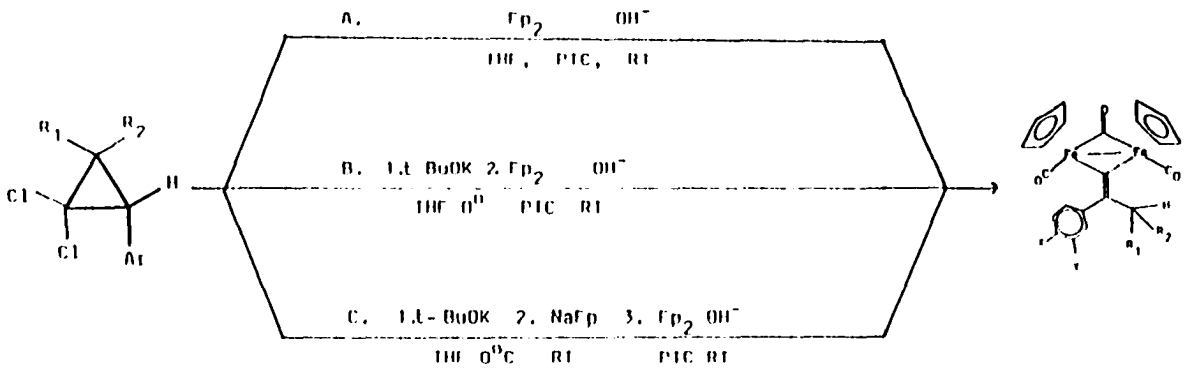



Figure 6. Reaction of 56 by Procedures A, B and C

## RESULTS AND DISCUSSION

1,1-Dichlorocyclopropanes can be converted to bridging vinylidene iron dimers by procedures A, B, and C as shown in Scheme 7. Procedure A was used initially involves the direct reaction of $(\mu\text{-CO})_2\text{-(CpFeCO)}_2$, [$Fp_2$] (2 equivalents) and 1,1-dichloro-2,3-diphenylcyclopropane (56d), under typical phase-transfer catalysis (PTC) conditions [10 g $NaOH/H_2O$ (45:55), THF, $n\text{-}Bu_4N^+HSO_4^-$]. A purple organometallic compound was isolated by column chromatography which isomerized to a red compound on standing.[36] The red compound was identified by x-ray crystallography as 42a, the cis-form of the benzylphenylvinylidene complex.[37] The structure of the purple compound

was then assigned to the trans-form, 41f, based on infrared stretching absorptions of the carbonyls and NMR spectral data. Procedure A was used to study other 1,1-dichlorocyclopropanes; however, separations are difficult due to the presence of organic contaminants. The mechanism of this unusual reaction is explored and two possible intermediates are identified (see later in this section). Procedures B and C utilizes these intremediates. Both were found to produce 41 incomparable yields to procedure A, but isolation of products was much easier. 1-Chlorocyclopropenes were shown to be intermediates in the reaction to form 41.

Procedure B relied on the fact that 1-chlorocyclopropenes are intermediates in Procedure A. Instead of using hydroxide as the base to perform the dehydrohalogenation, the Weyerstahl, et al.,[38,39] method of reacting the 1,1-dichlorocyclopropane with potassium t-butoxide (t-BuOK) in THF at 0°C is used. The crude 1-chlorocyclopropene produced in this is then reacted $Fp_2$ (1.5 equiv) under typical PTC conditions, producing the trans-vinylidene 41 as the major product.

For Procedure C, the generation of a 1-chlorocyclopropene is carried out as in Procedure B, but the 1-chlorocyclopropene (1 equivalent) is reacted with 2 equivalents of NaFP. A yellow organometallic compound is produced and identified as a substituted 1-Fp-cyclopropene in sub-

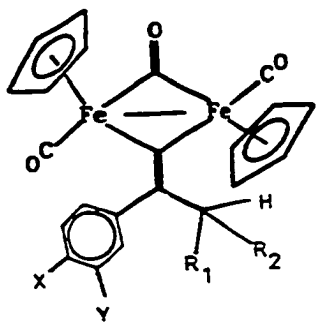
sequent experiments. The crude Fp-cyclopropene is then reacted with $Fp_2$ (1.5 equiv) under PTC to produce the trans-bridging vinylidene as the major product.

The workup and isolation procedures involve separation of the layers of the reaction solution and column chromatography of the organic layer on silica gel or alumina. Three major bands are collected, with the first yellow band containing ferrocene and unidentified organic compounds. The next major band contans the purple trans-vinylidene which was collected and chromatographed again in Procedures B and C to obtain analytical samples. The slowest moving band is usually $Fp_2$, however, in some cases the red cis-vinylidene could be detected but never completely separated from $Fp_2$.

The NMR yields for the production of 41 based on starting dichlorocyclopropane using Procedures A, B, and C are presented in Table 26. In all cases, an additional 5-10% yield of the cis-vinylidene is probably produced, but accurate yields for the cis-form could not be determined due to the separation problem with $Fp_2$.

The three procedures presented in this work using phase transfer catalysis allow the effective and selective formation of disubstituted bridging vinylidene iron dimers from substituted 1,1-dichloro-2-aryl-cyclopropanes; the results are summarized in Table 26. The orientation of the cyclopropane ring opening is 1,3-ring cleavage

Table 26. Synthesis of Bridging Vinylidenes




| $R_1$ | $R_2$ | X | Y | Procedure used | Product $(CpFeCO)_2(\mu\text{-}CO)$-$(\mu\text{-}C{=}CAr(Cr_1R_2R_3)$ | % Yield* |
|---|---|---|---|---|---|---|
| Ph | H | H | H | A | 41a | 17 |
| Ph | H | H | H | B | 41a | 17 |
| H | H | H | H | A | 41b | 28 |
| H | H | H | H | B | 41b | 24 |
| H | H | H | H | C | 41b | 24 |
| Me | H | H | H | B | 41c | 40 |
| Me | H | H | H | C | 41c | 45 |
| Me | Me | H | H | B | 41d | 39 |
| Me | Me | H | H | C | 41d | 31.6 |
| H | H | Me | H | B | 41e | 33 |
| H | H | Me | H | C | 41e | 35 |
| Me | H | Me | H | B | 41f | 66 |
| Me | H | Me | H | C | 41f | 37 |
| Me | Me | Me | H | B | 41g | 51 |
| Me | Me | Me | H | C | 41g | 43 |
| H | H | OMe | H | B | 41h | 27 |
| H | H | OMe | H | C | 41h | 14 |
| Me | H | OMe | H | B | 41i | 46 |
| Me | H | OMe | H | C | 41i | 31 |
| Me | Me | OMe | H | B | 41j | 61 |
| Me | Me | OMe | H | C | 41j | 40 |
| H | H | H | Cl | B | 41k | 7 |

Table 26 (continued)

| $R_1$ | $R_2$ | X | Y | Procedure used | Product $(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CAr(CR_1R_2R_3$ | % Yield* |
|---|---|---|---|---|---|---|
| H | H | H | Cl | C | 41k | 8 |
| Me | H | H | Cl | B | 41l | 14 |
| Me | H | H | Cl | C | 41l | 16 |
| Me | Me | H | Cl | B | 41m | 45 |
| Me | Me | H | Cl | C | 41m | 54 |

*% Yield is based on the substituted 1,1-dichlorocyclopropane performed at least in duplicate and is ±10%.

with all three procedures. The yields for the dimethyl-substituted cyclopropanes were better with procedures B and C. A possible explanation would be a steric effect making approach to the molecule more difficult.

The reaction of 56n and 56p illustrate two requirements for the reaction: A proton on carbon 2 and the aryl ring on carbon 2. Another limitation is the substituents must survive under PTC. It is shown that the reaction can occur with a variety of substituents on the aromatic ring plus a variety of substituents on carbon 3.

Comparison with Other Synthetic Methods

Only two other disubstituted iron bridging vinylidenes have been reported in the literature. The synthesis of 1 by the reaction of diphenylketene with nonacarbonyldiiron is of limited application due to the limited availability and stability of disubstituted ketenes. Also no yields are reported for this reaction. The synthesis of 42n by the reaction of 1,1-dibromo-2-2-dicyanoethylene with $Fp^-$ [12,13] is of limited synthetic usefulness due to low yield (3%) and the poor availability of 1,1-dibromo-2,2-disubstituted ethylenes. A third synthetic route does exist but has not been explored yet. The attack of an alkyl or aryllithium reagent on a metal dimer followed by protonation with trifluoroacetic acid is a potential path to disubstituted bridging vinylidenes.[28] A

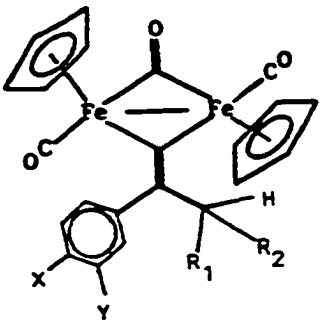
variation on this is the attack of the lithium reagent followed by treatment with a base to form the bridging vinylidene.[9] These two methods are potentially very useful and the yields are in the range of 40-70%. The only real problem that can be anticipated is the availability of the lithium reagents. The principal advantage to our synthesis is the reasonable yields and the ability to make a series of substituted examples.

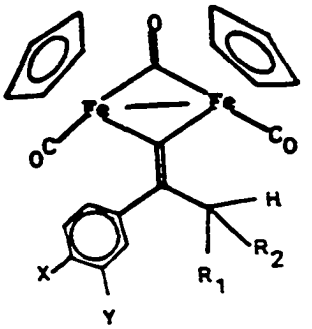
The trans-bridging vinylidene 41 produced by Procedures A, B, and C can be thermally isomerized to the cis-bridging vinylidenes 42 by heating to 80°C in toluene solution for 36 hours. The relative ratio of cis to trans was based on isolated materials since the NMR signals overlapped too closely for an NMR ratio determination. The results are summarized in Table 27.

There are no clear trends in the data. If a steric effect were dominating one would expect the isopropyl substituted bridging vinylidenes to favor the cis form more. There is a slight trend in this direction, but definite conclusions are difficult.

The nonequivalence of the Cp rings indicated there are no facile dynamic processes to equilibrate the rings. The crystal structure of 42a[37] showed the face of one phenyl ring pointing directly towards one Cp, explaining the large 0.5 ppm difference in the Cp resonances. This is a much larger difference in the Cp chemical shifts

Table 27. Conversion of trans-cis-Bridging Vinylidenes





| R | | X | Y | # | trans/cis | % Recovery* |
|---|---|---|---|---|---|---|
| H | H | H | H | 41b | 41 /42 1:4 | 78 |
| Me | H | H | H | 41c | 41 /42 1:5 | 82 |
| Me | Me | H | H | 41d | 41 /42 1:5 | 80 |
| H | H | Me | H | 41e | 41 /42 1:4 | 90 |
| Me | H | Me | H | 41f | 41 /42 1:5 | 88 |
| Me | Me | Me | H | 41g | 41 /42 1:5 | 88 |
| H | H | OMe | H | 41h | 41 /42 1:4 | 85 |
| Me | H | OMe | H | 41i | 41 /42 1:6 | 83 |
| Me | Me | OMe | H | 41j | 41 /42 1:6 | 81 |
| H | H | H | Cl | 41k | 41 /42 1:4 | 87 |
| Me | Me | H | Cl | 41m | 41 /42 1:6 | 83 |

*% Recovery is the amount of bridging vinylidene recovered compared to the starting amount of bridging vinylidene.

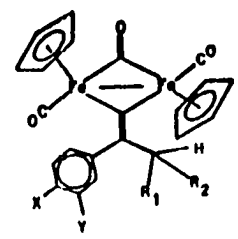
when compared to other reported selected bridging vinylidenes shown in Table 29. The chemical shift difference of the Cp's of 0.2 ppm observed in 45d can be attributed to a similar effect by the ester group. The signals for the other alkyl substituents are as expected for an asymmetric environment.

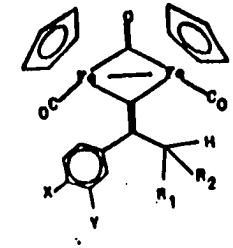
## $^{13}$C-NMR

The $^{13}$C-NMR spectra for the cis- and trans-bridging vinylidenes were obtained in $d_6$-benzene and are summarized in Table 30. Assignments were based on comparison to spectra of other similar compounds plus the trends observed in the new vinylidenes reported here. One difficult assignment was the pair of signals in the 260-270 ppm range. Both the bridging carbonyl and the bridging vinylidene carbons would be expected to absorb here, however, the assignments are readily made based on two points:

1. The chemical shift of the bridging carbonyl do not change significantly throughout the series (270.0±1.0 ppm). A larger change would be expected for the vinylidene carbon as it is closer to the site of structural changes.
2. The fully coupled spectrum showed long-range coupling for the vinylidene carbon and not for the carbonyl carbon. In all cases, long-range coupling between the hydrogens on the alkyl groups and the vinylidene carbons would be expected, and are observed. Other trends were noticed

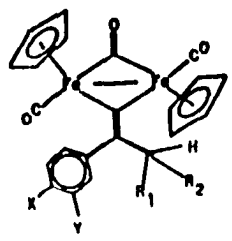
Table 28. Proton NMR Spectra of cis- and trans-Bridging Vinylidene Iron Dimers*

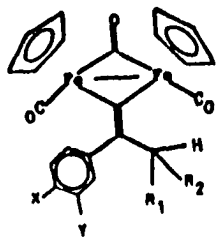




| Isomer | $R_1$ | $R_2$ | X | Y | | $R_1$ | | $R_2$ | | H | | Ar | | X | $Cp_1$ $Cp_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| t | H | H | H | H | 3 | 2.87(s) | | | | | | 6.8-7.3 | | | 4.23, 4.73 |
| c | H | H | H | H | | 2.83(s) | | | | | | 7.1-7.6 | | | 4.36, 4.85 |
| t | Me | H | H | H | 3 | 1.18(t) | 2 | 3.30(q) | | | | 7.06, 7.40 | | | 4.20, 4.77 |
| c | Me | H | H | H | 3 | 1.15(t) | 2 | 3.23(q) | | | | 7.2-7.6 | | | 4.37, 4.90 |
| t | Me | Me | H | H | 3 | 1.13(d) | 3 | 1.47(d) | | | | 3.60 | | | 4.10, 4.73 |
| t | H | H | Me | H | 3 | 2.87(s) | | | 3 | 1.3.9 | | 7.0-7.4 | 3 | 2.37(s) | 4.33, 4.88 |
| c | H | H | Me | H | 3 | 2.82(s) | | | | | | 7.03, 7.40 | 3 | 2.37(s) | 4.37, 4.83 |
| t | Me | H | Me | H | 3 | 1.02(t) | 2 | 3.28(q) | | | | 7.10, 7.36 | 3 | 2.37(s) | 4.10, 4.73 |
| c | Me | H | Me | H | 3 | 1.10(t) | 2 | 3.17(q) | | | | 7.13, 7.36 | 3 | 2.40(s) | 4.33, 4.90 |
| t | Me | Me | Me | H | 3 | 1.08(d) | 3 | 1.41(d) | 1 | 3.50-390 | | 7.0-7.3 | 3 | 2.40(s) | |
| c | Me | Me | Me | H | | | | | | | | | | | |
| t | H | H | OMe | H | 3 | 2.87(s) | | | | | | 6.7-7.5(AB) | 3 | 3.78(s) | 4.27, 4.77 |
| c | H | H | OMe | H | 3 | 2.82(s) | | | | | | 6.92,7.42(AB) | 3 | 3.85(s) | 4.42, 4.88 |
| t | Me | H | OMe | H | 3 | 1.20(t) | 2 | 3.23(q) | | | | 6.87, 7.40 | 3 | 3.73(s) | 4.20, 4.73 |
| c | Me | H | OMe | H | 3 | 1.12(t) | 2 | 3.18(q) | | | | 6.95, 7.37 | 3 | 3.90(s) | 4.37, 4.93 |

Table 28 (continued)

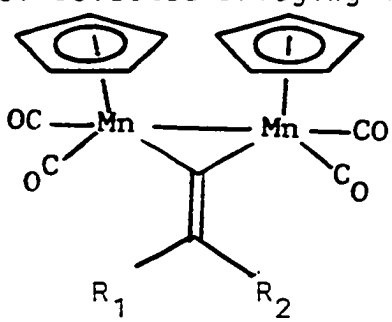




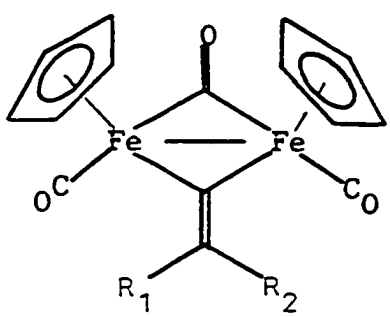
| Isomer | $R_1$ | $R_2$ | X | Y | | $R_1$ | | $R_2$ | | H | Ar | | X | $Cp_1$ $Cp_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| t | Me | Me | OMe | H | 3 | 1.08(d) | 3 | 1.42(d) | 1 | 3.2-3.8(m) | 6.73, 7.30 | 3 | 3.77(s) | |
| c | Me | Me | OMe | H | 3 | 1.05(d) | 3 | 1.35(d) | 1 | 3.5-3.9(m) | 6.92, 7.25 | 3 | 3.87(s) | 4.32, 4.85 |
| t | H | H | H | Cl | 3 | 2.87(s) | 3 | 1.35(d) | 1 | 3.5-3.9(m) | 6.9-7.5(m) | | | 4.28, 4.75 |
| c | H | H | H | Cl | 3 | 2.83(s) | | | | | 7.1-7.6(m) | | | 4.43, 4.86 |
| t | Me | H | H | Cl | 2 | 3.30(q) | | 1.20(t) | | | 6.8-7.5(m) | | | 4.23, 4.77 |
| t | Me | Me | H | Cl | 3 | 1.13(d) | 3 | 1.40(d) | | | 7.2-7.5 | | | 4.14, 4.75 |

*Proton NMR Spectra were recorded in deuterochloroform and reported as δ relative to TMS.

Table 29. $^{1}$H-NMR of Selected Bridging Vinylidenes*




| M | $R_1$ | $R_2$ | $Cp_1$ | $Cp_2$ | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|
| Mn | H | Ph | 4.72 | 4.79 | 8.46 | 7.0-8.3[19] |
| Mn | H | $CO_2Me$ | 4.04 | 4.22 | 7.2 | 3.62[24] |
| Mn | H | Me | 4.64 | 4.69 | 7.02 | 2.27,[22] |
| Mn | H | H | 4.10 | | 6.77[23] | |




| | M | $R_1$ | $R_2$ | Cp | $R_1$,$R_2$ |
|---|---|---|---|---|---|
| cis | Fe | H | H | 4.16 | 6.9[29] |
| cis | Fe | CN | CN | 5.03[12-14] | |
| cis | Ru | H | H | 5.2 | 6.27[20,21] |

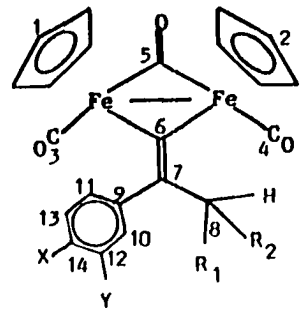
*$^{1}$H-NMR spectra data is from the literature and reported in δ relative to TMS.

in analyzing the $^{13}C$-NMR data, especially in comparing the cis and trans isomers. It should be noted that the factors that influence carbon chemical shifts in transition-metal complexes are complex, and observed trends are difficult to interpret. However, the reporting of trends can be useful in assigning spectra of new compounds and even in structure determination. Because of these concerns the following trends are described. All signals for the carbons directly attached to iron are either unchanged or shifted upfield in the cis-isomer relative to the trans. The average values for the upfield shifts in going from the trans- to the cis-isomers are: Terminal Co, 1.0 ppm; Cp, 2.5 ppm, μ-CO, 0.4 ppm; μ-C=C, 5.9 ppm. In addition, all except examples c and j also show an upfield shift for the other carbon of the vinylidene ligand when going from the trans- and cis-forms. Both the cis- and trans-isomers exhibit two different signals for the terminal carbonyls and the Cp rings. The differences between the carbon signals in the same molecule were found to be smaller in the cis isomer than the trans. The differences between the terminal CO's were 1.5 and 0.7 ppm which the Cp differences were 0.7 and 0.15 ppm for the trans- and cis-isomers, respectively.

IR Spectra

The cis- and trans-bridging vinylidenes exhibit

Table 30. $^{13}C$-NMR Spectra of cis- and trans-Bridging Vinylidene Iron Dimers*




| Compound # | $R_1$ | $R_2$ | X | Y | 1&2 | 3&4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41b | H | H | H | H | 89.98<br>90.62 | 212.80<br>214.25 | 271.06 | 270.72 | 147.74 | 28.43 | 146.67 | 125.61 | 128.16 | 129.04 | | |
| 42b | H | H | H | H | 87.50<br>87.68 | 212.20<br>212.88 | 270.08 | 264.26 | 148.80 | 29.41 | 145.81 | 125.67 | 128.58 | 129.10 | | |
| 41c | Me | H | H | H | 89.81<br>90.67 | 212.88<br>213.99 | 270.29 | 269.31 | 153.59 | 36.11<br>t-125 | 146.88 | 125.81<br>d-158 | 128.37<br>d-158 | 129.91 | 15.18<br>q-133 | |
| 42c | Me | H | H | H | 87.46<br>88.59 | 212.50<br>212.88 | 270.29 | 262.47 | 153.16 | 37.32 | 147.44 | 125.85 | 128.50 | 130.38 | 14.88 | |
| 41d | Me | Me | H | H | 89.90<br>90.62 | 212.92<br>213.69 | 270.89 | 266.36 | 157.86 | 41.68 | 145.72 | 125.98 | 128.47 | 131.53 | 22.87<br>24.41 | |
| 42d | Me | Me | H | H | 87.39<br>87.45 | 212.47<br>212.58 | 269.88 | 261.54 | 157.54 | 42.45 | 145.14 | 126.02 | 130.54 | 132.18 | 22.69<br>23.68 | |

Table 30 (continued)

| Compound | $R_1$ | $R_2$ | X | Y | 1&2 | 3&4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41e | H | H | Me | H | 90.03<br>90.71 | 212.80<br>214.29 | 270.55 | 66,67 | 146.80 | 28.47<br>q-117 | 145.17<br>d-158 | 127.69<br>d-158 | 129.05 | 134.95 | | 21.20 |
| 42e | H | H | Me | H | 87.72 | 212.87 | | | | | | | | | | |
| 41f | Me | H | Me | H | 89.86<br>90.75 | 212.97<br>214.08 | 270.63 | 263.92 | 153.36 | 36.12<br>t-123 | 144.10 | 129.10<br>d-158 | 129.82<br>d-158 | 134.99 | 15.18<br>q-125 | 21.16<br>q-125 |
| 42f | Me | H | Me | H | 87.46<br>87.62 | 212.54<br>212.96 | 270.50 | 261.30 | 153.03 | 37.32 | 144.53 | 128.48 | 130.25 | 134.92 | 14.91 | 21.24 |
| 41g | Me | Me | Me | H | 89.90<br>90.71 | 213.65<br>215.93 | 270.55 | 266.66 | 157.91 | 41.72 | 142.9 | 128.88 | 131.66 | 135.13 | 22.87<br>24.41 | 21.16 |
| 42g | Me | Me | Me | H | 87.40<br>87.53 | 212.65<br>212.79 | 270.59 | 261.31 | 157.31 | 41.95 | 142.13 | 128.87 | 132.03 | 135.16 | 19.91<br>23.28 | 21.41 |
| 41h | H | H | OMe | H | 89.98<br>90.71 | 212.80<br>214.29 | 270.21 | 267.21 | 146.37 | 38.51 | 140.63 | 130.17 | 113.58 | 158.42 | | 51.97 |
| 42h | H | H | OMe | H | 87.47<br>87.69 | 212.19<br>212.91 | 270.11 | 264.10 | 145.51 | 29.53 | 141.54 | 130.07 | 113.94 | 158.29 | | 54.92 |
| 41i | Me | H | OMe | H | 89.86 | 213.30 | 270.42 | 268.80 | 153.21 | 36.12 | 139.53 | 130.76 | 113.84 | 158.29 | 15.18 | 54.93 |
| 42i | Me | H | OMe | H | 87.48<br>87.62 | 212.58<br>213.05 | 270.38 | 262.72 | 152.69 | 35.84 | 139.95 | 132.28 | 113.28 | 158.17 | 14.93 | 54.87 |
| 41j | Me | Me | OMe | H | 89.90<br>90.67 | 212.93<br>213.65 | 270.51 | 266.96 | 157.53 | 41.68 | 138.33 | 132.60 | 113.58 | 158.42 | 22.91<br>24.37 | 54.85 |

Table 30 (continued)

| Compound | $R_1$ | $R_2$ | X | Y | 1&2 | 3&4 | 5 | 6 | 7 | 8 | 9 | 10 | 11,12 | 13 | 14 | $R_2$ | $R_2$ | X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 42j | Me | Me | OMe | H | 87.42<br>87.51 | 212.69<br>213.90 | 270.46 | 261.99 | 156.94 | 42.34 | 140.52 | | 133.02 | 113.54 | | 158.36 | 22.76<br>23.69 | 54.88 |
| 41k | H | H | H | Cl | 90.05<br>90.62 | 212.57<br>213.91 | 269.81 | 273.64 | 149.02 | 28.05 | 145.29 | 129.38 | 126.79 | 134.02 | 125.50 | 129.22 | | |
| 42k | H | H | H | Cl | 87.55<br>87.55 | 211.88<br>211.88 | 269.22 | 266.15 | 150.88 | 28.98 | 144.31 | 129.15 | 129.34 | 134.12 | 125.60 | 128.50 | | |
| 41l | Me | H | H | Cl | 89.92<br>90.66 | 212.72<br>213.77 | 269.74 | 271.76 | 152.35 | 35.81 | 148.46 | 129.91 | 127.52 | 134.27 | 125.74 | 129.77 | 15.03 | |
| 41m | Me | Me | H | Cl | 89.87<br>90.51 | 212.63<br>213.31 | 269.95 | 267.63 | 156.62 | 41.59 | 147.54 | 127.65 | 126.44 | 134.02 | 125.98 | 127.39 | 22.61<br>24.33 | |
| 42m | Me | Me | H | Cl | 87.36<br>87.36 | 212.33<br>214.59 | 268.96 | 262.03 | 156.16 | 42.39 | 146.94 | 132.08 | 130.35 | 133.81 | 125.46 | 128.50 | 22.51<br>23.55 | |

*C NMR recorded in $d_6$-Benzene relative to TMS.

normal CO stretches for compounds of this type.[12,13] In heptane solution the cis-isomer showed two strong terminal CO stretches at 2000 and 1965 $cm^{-1}$ while the trans had one strongly terminal CO band at 1973 $cm^{-1}$ and a weak shoulder at 1960 $cm^{-1}$. Both isomers had a bridging CO band at 1807 $cm^{-1}$ in heptane. The C=C stretch of the vinylidene was too weak to observe in heptane due to solubility problems, but could be observed around 1590 $cm^{-1}$ using a KBr disc. A summary of the data is presented in Table 31. The differences in the IR spectra were small and no clear trends were established.

In the reaction of 3,3-dimethyl-2-(m-chlorophenyl)-1-cyclopropene using Procedure B and C, a small darker purple band was isolated in addition to the normal bands observed in this type of reaction. This band was isolated and characterized by IR and $^{1}H$-NMR spectra, see Table 32. The structure was assigned the trans-bridging cyclopropylidene 57. The compound readily isomerized to the cis-configuration 58. The $^{13}C$-NMR of 57 was attempted at room temperature, but 57 isomerized to 58. The $^{13}C$-NMR spectrum of 58 is reported in Table 33.

This assignment is in agreement with the cis- and trans-bridging cyclopropylidene complexes (57b and 58b) prepared by Hoel.[47] The bridging carbon is observed at δ158.5 and the other cyclopropyl carbons at δ22.3 and 22.6. These are in agreement with the $^{13}C$-NMR spectrum

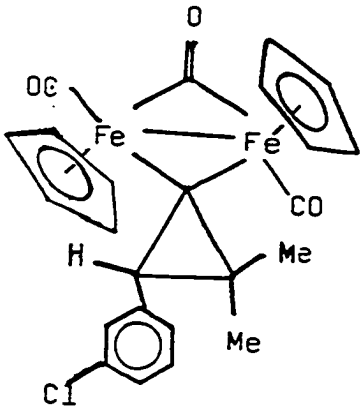
Table 31. IR Spectral Data for 41 and 42*

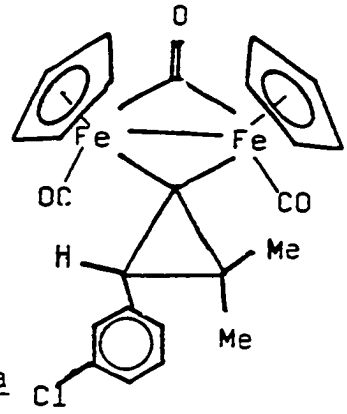
| $R_1$ | $R_2$ | X | Y | | $\nu$CO, $cm^{-1}$ | | $\nu$ C=C, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| Ph | H | H | H | 1975 | 1966 | 1809 | 1598 |
| Ph | H | H | H | 2000 | 1968 | 1809 | 1596 |
| H | H | H | H | 1976 | 1959 | 1808 | 1601 |
| H | H | H | H | 2000 | 1968 | 1808 | 1600 |
| Me | H | H | H | 1974 | 1959 | 1806 | 1591 |
| Me | H | H | H | 1999 | 1966 | 1806 | 1602 |
| Me | Me | H | H | 1973 | 1959 | 1805 | 1581 |
| Me | Me | H | H | 1999 | 1966 | 1805 | 1598 |
| H | H | Me | H | 1973 | 1958 | 1806 | 1592 |
| H | H | Me | H | 1966 | 1964 | 1806 | 1598 |
| Me | H | Me | H | 1972 | 1958 | 1805 | 1583 |
| Me | H | Me | H | 1999 | 1965 | 1805 | 1581 |
| Me | Me | Me | H | 1974 | 1960 | 1806 | 1584 |
| Me | Me | Me | H | 1999 | 1965 | 1805 | 1589 |
| H | H | OMe | H | 1972 | 1958 | 1806 | 1606 |
| H | H | OMe | H | 2000 | 1966 | 1806 | 1601 |
| Me | H | OMe | H | 1972 | 1957 | 1805 | 1603 |
| Me | H | OMe | H | 2000 | 1965 | 1806 | 1599 |
| Me | Me | OMe | H | 1972 | 1958 | 1804 | 1584 |
| Me | Me | OMe | H | 1999 | 1963 | 1805 | 1588 |
| H | H | H | Cl | 1972 | 1961 | 1808 | 1575 |

Table 31 (continued)

| $R_1$ | $R_2$ | X | Y | | CO, $cm^{-1}$ | | C=C, $Cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| H | H | H | Cl | 2000 | 1968 | 1809 | 1578 |
| Me | H | H | Cl | 1976 | 1962 | 1808 | 1580 |
| Me | Me | H | Cl | 1975 | 1960 | 1808 | 1589 |
| Me | Me | H | Cl | 1999 | 1961 | 1807 | 1597 |

*IR spectra recorded in heptane with the C=C stretches recorded in a KBr pellet.




58a

a $R_1=R_2=Me$ $R_3=$m-chlorophenyl

b $R_1=R_2=R_3=H$

observed for 58a. The crystal structure determination on 58b has been performed.[47] This structure is a cis-bridging cyclopropylidene iron dimer.[47]

Table 32. $^1$H-NMR* Spectra of 57 and 58

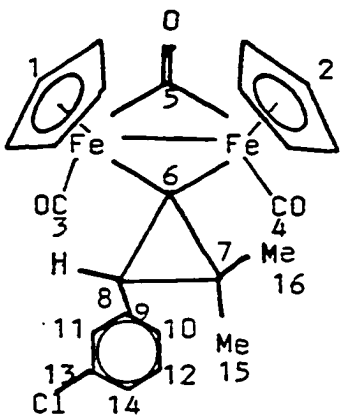
| | |
|---|---|
| trans | 7.4-7.7, Ar-H; 4.60, Cp; 4.20, Cp; 2.72, 1H(s); 1.90, $CH_3$(s); 1.41, $CH_3$(s) |
| cis | 7.4-7.7, Ar-H; 4.73, Cp; 4.49; Cp; 3.01, 1H(s); 1.84, $CH_3$(s); 1.74, $CH_3$(s) |

*NMR recorded in $CDCl_3$.

## Stability of 1,1-dichlorocyclopropanes to Phase-Transfer Conditions

The formation of the bridging vinylidenes from 1,1-dichlorocyclopropanes represents an unusual 2,3-opening of the cyclopropane ring. Most reactions that involve ring opening in 1,1-dichlorocyclopropanes result in cleavage of the 2,3-bond.[40] This fact suggested that the starting cyclopropane was not the key reactive species. To test for the stability of the 1,1-dichlorocyclopropane, Procedure A was

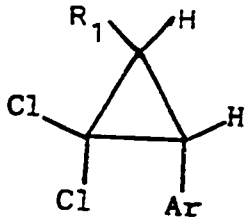
Table 33. $^{13}$C-NMR of 58*

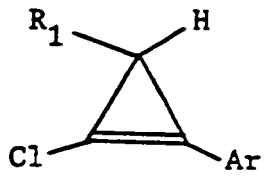



| Carbon # | δ | Carbon # | δ |
|---|---|---|---|
| 1,2 | 89.90, 92.60 | 10 | 129.81 |
| 3,4 | 212.41, 213.27 | 11 | 127.7 |
| 5 | 257.0 | 12 | 127.4 |
| 6 | 182.3 | 13 | 125.12 |
| 7 | 23.3 | 14 | 127.4 |
| 8 | 36.50 | 15 | 39.9 |
| 9 | 146.70 | 16 | 48.6 |

*$^{13}$C-NMR recorded in $d_6$-Benzene relative to TMS.

used with 56a and 56b but no $Fp_2$ was added. The starting cyclopropane rapidly disappeared under the phase-transfer conditions with hydroxide. The major monomeric product for 56a was identified as 1-chloro-1-phenylcyclopropene (6b) through comparison of spectral data previously reported by Weherstahl, et al.[38,39] The cyclopropene apparently formed through dehydrohalogenation mediated by hydroxide.




56a,b

a = $R_1$=Ph, Ar=Ph

b = $R_1$=H, Ar=Ph

6a,b

a $R_1$=Ph, Ar=Ph

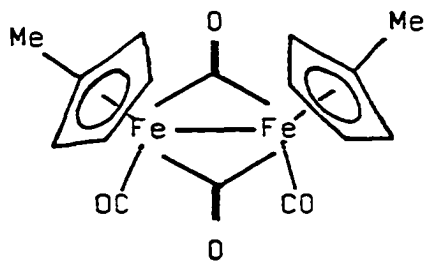
b $R_1$=H, Ar=Ph

The reaction was repeated except $Fp_2$ was added after all of the cyclopropane had disappeared. The bridging vinylidene formed rapidly and a comparable yield to that obtained in the direct reaction was obtained. In addition, Weyerstahl[38,39] had previously reported 1,3-bond cleavage in selected cases of 1-chlorocyclopropene reactions with alcohols. It was also observed that a hydrogen was required in C2 since 1,1-dichloro-2-methyl-2-phenylcyclopropane failed to yield a vinylidene dimer (see Table

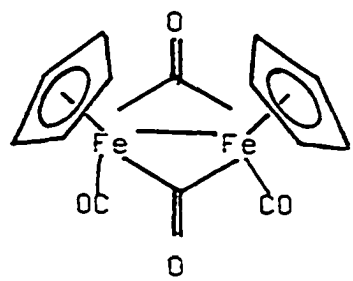
26). All of these facts strongly implicate the 1-chlorocyclopropene as a key intermediate in the vinylidene formation.

Crossover Between $Fp_2$ and $[(MeCP)Fe(CO)_2]_2$

The nature of the reactive iron species was explored to determine whether a metal dimer or monomer was involved. An equimolar mixture of $Fp_2$ and $[(MeCp)Fe(CO)_2]_2$ [MeCP = methylcyclopentadienyl] was subjected to PTC and




$(MeFP)_2$




$Fp_2$

the product mixture examined by mass spectroscopy (MS). Complete scrambling of the irons was indicated. A control demonstrated that crossover did not occur in the mass spectrometer. Although higher aggregates could be envisioned to explain the exchange, the most likely answer is a monomeric iron species as the key intermediate in

the crossover mechanism.

Reaction of Fp Anion with 1-chloro-2-phenylcyclopropene

Alper[41] had previously demonstrated that $Fp_2$ could be an apparent source of Fp anion under PTC. The direct reaction of Fp anion with the 1,1-dichlorocyclopropane had been previously shown to produce reduction products and no vinylidene complexes.[42] However, an earlier experiment reported here described how the starting cyclopropane was not stable under the reaction conditions and that the 1-chlorocyclopropene was rapidly produced. It was possible that the 1-chlorocyclopropane would react with Fp anion to produce the vinylidene complex directly. To test this possibility, 1.5 equivalents of Fp anion was reacted with 1-chloro-2-phenylcyclopropene (produced from t-BuOK and 1,1-dichloro-2-phenylcyclopropane in THF at 15°C) in THF. None of the bridging vinylidene complex could be detected, but a new organometallic was isolated and characterized by NMR, IR and MS as 1-Fp-2-phenylcyclopropene (7b). This represents a new class of compounds whose synthesis and chemistry was discussed in Chapter 1. When the Fp-cyclopropene was reacted with $Fp_2$ under PTC, the bridging vinylidene was produced in 74% yield.

Crossover in the Fp-cyclopropene

Several experiments were performed to determine if the 1-Fp-cyclopropene was a true intermediate in the

vinylidene production. A crossover experiment between 1-Fp-2-p-tolyl-dimethylcyclopropene (7a) and $[(MeCp)Fe(CO)_2]_2$ under PTC was performed to see if the iron on the cyclopropene would exchange. The mixture was chromatographed on an alumina column to remove the organic contaminants and analyzed by mass spectroscopy. Two vinylidene products were detected by peaks at M/e 354 and 368 and assigned to the product with 2 Cp rings and to the one with one Cp and the MeCp ring. The reaction with $[(MeCp)Fe(CO)_2]_2$ was much slower than the reaction with $Fp_2$ so the possibility existed that the unlabeled product was formed from $Fp_2$ produced in the decomposition of 7a. To check this possibility, the reaction was performed using MeFp-2-p-tolyl-3,3-dimethylcyclopropene [MeFp = $MeCpFe(CO)_2]_2$, and $Fp_2$; work up was as before. The only product detected was the one containing a single MeCp indicating no exchange of the iron group occurred once it was attached to the cyclopropene ring.

Attempted Isolation of 7 Under Phase Transfer Catalysis Conditions

Attempts were made to isolate the Fp-cyclopropenes under reaction conditions by adding a limiting amount of $Fp_2$ (1 equivalent) to 1-chloro-3,3-dimethyl-2-p-tolyl-cyclopropene (56g) (8 equiv) under PTC. Only the bridging vinylidene was detected. A competitive rate study was then performed where a limiting amount of $Fp_2$

was added to a mixture of 1-Fp-3,3-dimethyl-2-tolylcyclopropene (7g) and 1-chloro-3,3-dimethyl-2-phenylcyclopropene (56d) in one experiment and a mixture of 7d and 56g in another. The 7 reacted faster in both cases. Therefore, 7, if formed, would not be detected under the reaction conditions.

## Mechanism

The mechanism of the reaction of the 1,1-dichlorocyclopropanes with $Fp_2$ to form the vinylidene iron dimers was explored. A study of the mechanism was warranted because the reaction was unusual. In addition, a thorough study might provide an improved procedure to the important vinylidene metal dimers.

The observation that the aryl group and a proton on carbon 2 were necessary to produce the bridging vinylidene suggested that the 1,1-dichlorocyclopropane was reacting with the base under PTC. The stability of 56a and 56d (see Table 1) to PTC in the absence of $Fp_2$ was tested, and both underwent dehydrohalogenation to form the 1-chlorocyclopropene. Weherstahl, et al.,[38,39] had reported the production of 1-chlorocyclopropenes from 1,1-dichlorocyclopropanes by reaction with t-BuOK. He also reported seeing 1,3-ring-opened products in the reaction of 1-chlorocyclopropenes with alcohols. Procedure B is based on the fact that 1-chlorocyclopropenes generated via the

Weyerstahl procedure react with $Fp_2$ under PTC to produce the bridging vinylidene. These data and the requirement of the aryl group and proton on carbon 2 show that 1-chloro-cyclopropenes are intermediates in the conversion of 1,1-dichlorocyclopropanes to the bridging vinylidenes.

A crossover experiment between $Fp_2$ and $(MeFp)_2$ under PTC revealed complete scrambling of the two dimers. This was interpreted in terms of a monomeric intermediate.

Since $Fp^-$ is a possible species produced in the PTC reaction of $Fp_2$, $Fp^-$ was reacted with 1-chloro-2-phenylcyclopropene. The resulting organometallic was identified as 1-Fp-2-phenyl-1-cyclopropene. This yellow compound was then subjected to PTC in the presence of $Fp_2$ and the bridgeing vinylidene was produced. Reaction of 56g with excess $Fp^-$ in the presence of $H_2O$ or other proton sources did not produce the bridging vinylidene. In fact the only method to produce the bridging vinylidene from 56 is PTC and $Fp_2$. When $Fp^-$ and 56g are combined and subjected to PTC a very slow generation of the bridging vinylidene occurs; probably through the slow decomposition of $Fp^-$ to $Fp_2$, which then reacts.

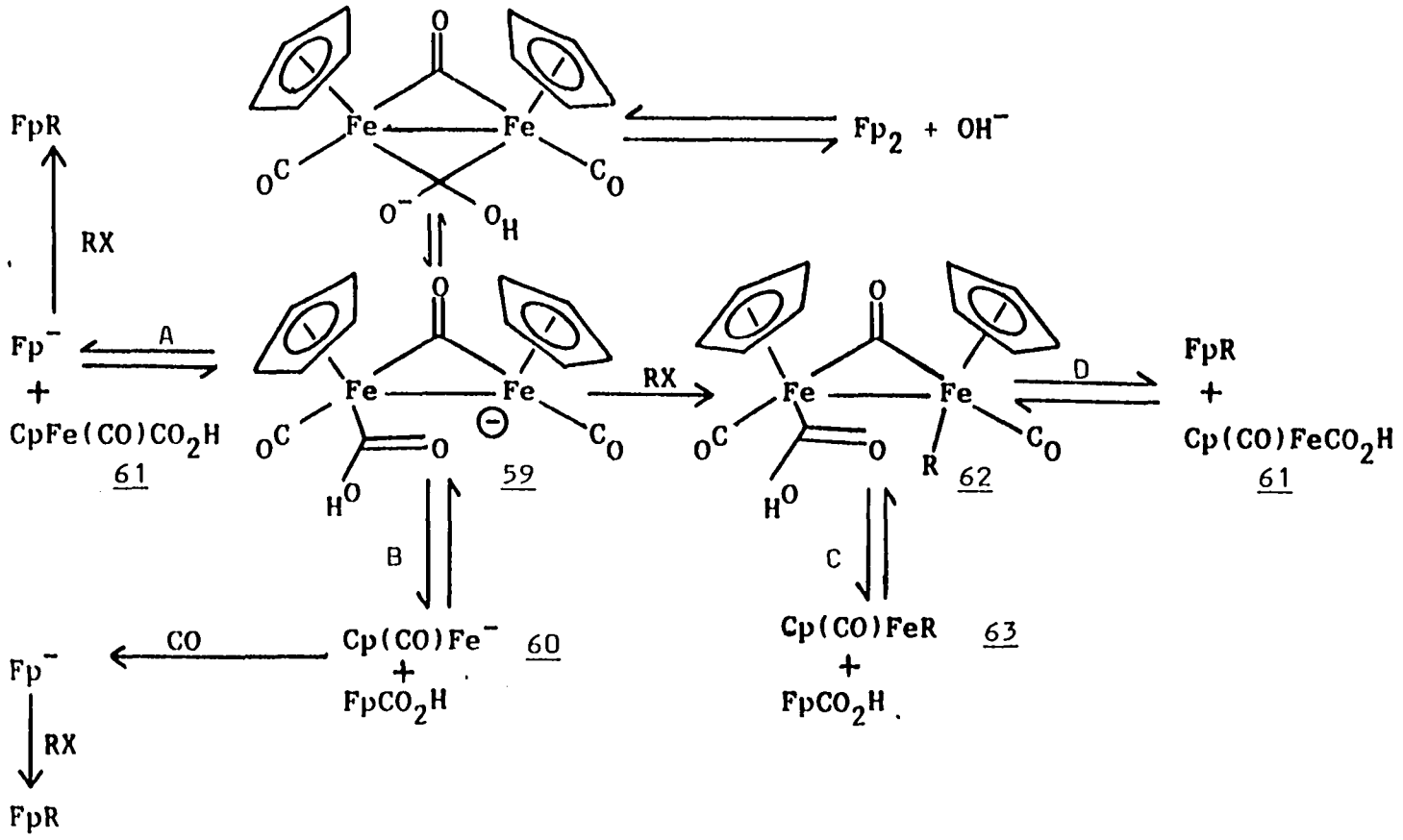
The question of whether the Fp group in the Fp-cyclopropene was one that appeared in the bridging vinylidene was investigated by a crossover experiment. Labeled MeFp-cyclopropene when reacted with $Fp_2$ produced only the monolabeled bridging vinylidene as shown by mass

spectrometry. This result ruled out the possibility that Fp-cyclopropenes could incorporate intact a reactive species derived from $Fp_2$.

The formation of 56 and its conversion to the bridging vinylidene do not prove it is an intermediate in the direct reaction to 1,1-dichlorocyclopropane with $Fp_2$ under PTC. Attempts to isolate the Fp-cyclopropene in reactions of a limiting amount of $Fp_2$ with a 1-chlorocyclopropene under PTC, yielded only the bridging vinylidene. The possibility that the Fp-cyclopropene reacted much faster than the 1-chlorocyclopropene was tested in a competitive rate study. The following sequence is deemed likely for $Fp_2$ reacting under PTC (see Scheme 8).

A mixture of 56g and 7d were combined and reacted with $Fp_2$ under PTC for 5 minutes and only 41i was formed, indicating only the reaction of 56g. The two substituents were reversed and 56d and 7g were reacted in a similar manner with the same results, only the Fp-cyclopropene reacted. This explains why no Fp-cyclopropene could be isolated under PTC. As fast as it is formed, it is preferentially converted to the bridging vinylidene.

This information does not prove that Fp-cyclopropenes are involved in the direct conversion of chlorocyclopropenes to bridging vinylidenes, but is highly suggestive. However, it does leave open the possibility of a dimeric species reacting directly with the 1-chloro-



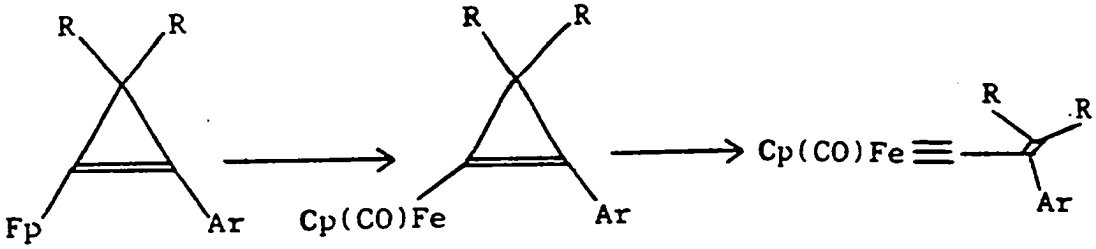

Scheme 8. Proposed Reaction Mechanism for PTC Reaction of $Fp_2$

cyclopropene.

The initial attack of the hydroxide on the bridging carbonyl (because of lower electron density) is similar to the attack of alkyl or aryllithium reagents on the bridging carbonyl of $(CpMCO)_2(\mu\text{-}CO)_2$.[9] The resulting hydroxycarbonyl species has been proposed in other phase-transfer reactions of hydroxide with transition-metal carbonyls.[43] Equilibria A and B are proposed based on the $Fp_2$ and $(MeFp)_2$ crossover study indicating substantial crossover. The monomeric intermediates similar to 59, 60, 61, 62, and 63 have been proposed by Gibson, et al.,[34,35] in her phase-transfer generation of $\sigma$ and $\pi$ allyls from transition metal-carbonyl halides, allyl bromide, and sodium hydroxide. When benzyl chloride was reacted with $Fp_2$ under PTC, $FpCH_2Ph$ was rapidly produced in 120-140% yield. When the reaction was carried out under a CO atmosphere the yield of $FpCH_2Ph$ was 180-195% (based on $Fp_2$).[44] These results indicate $Fp^-$ is produced under PTC and that could explain the observed reactivity toward cyclopropene metallation. When an allyl halide is used both $\sigma$ and $\pi$ complexes are formed and the ratio is not affected when a CO atmosphere is used.[44] This could be interpreted as the reaction proceeding through 62 via 59. Intermediates 62 could then partition between routes C and D to give the $\sigma$-allyl and $\pi$-allyl, respectively. If the $\pi$-allyl were formed from 60 or from the -allyl complex the addi-

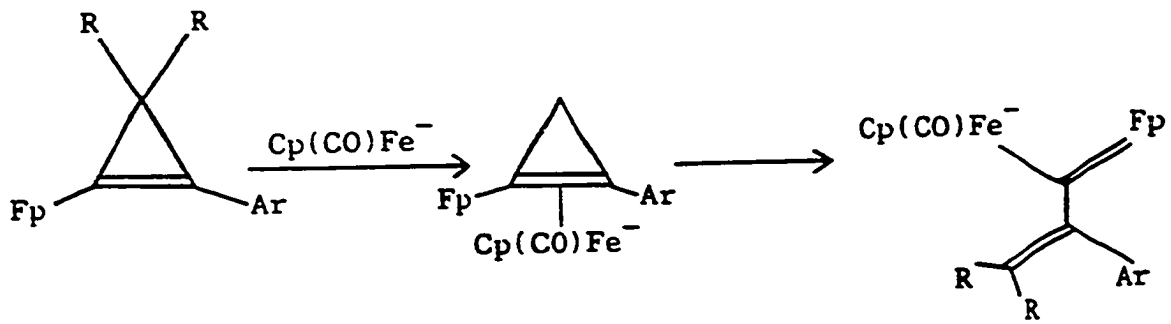
tion of CO should eliminate those pathways stopping π-allyl formation. Since this is not observed, intermediate 62 is implicated.

There is still the question of how 62 is converted to the bridging vinylidene. The phase-transfer conditions may be the source of coordinative unsaturation (implied from π-allyl formation) which could produce 54 and 65 via a cyclopropene/vinylcarbene rearrangement. Although



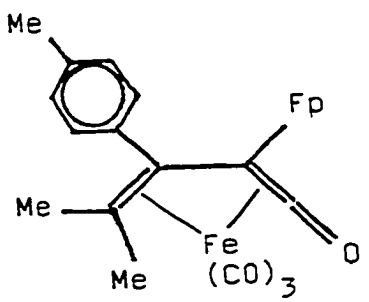

7 63 64

iron carbynes are not known, analogous tungsten and manganese carbynes are known.[45] This was deemed somewhat unlikely because no conversion of σ to π-allyls had been observed under these conditions. Another possible mechanism could be the insertion of coordinatively unsaturated iron into the cyclopropene ring:




7 65 66

The tendency for unsaturated metals to insert into cyclopropene bonds is well established. We have shown that $Fe_2(CO)_9$ will react with 7g to form 26. This




26

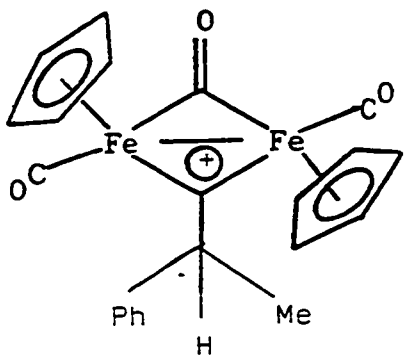
reaction is discussed in Chapter 1. The reaction has three possible mechanisms. 1. Reaction of a reactive dimeric intermediate that goes on to yield product. 2. Formation of 7 which then reacts with $OH^-$ to form a site of unsaturation followed by the cyclopropene to vinyl carbene rearrangement. This carbyne would then

react to give the product. 3. Formation of 7 which reacts with a coordinatively unsaturated metal species followed by reaction with $H_2O$ to produce the product. More investigation is needed to determine which mechanism is most likely.

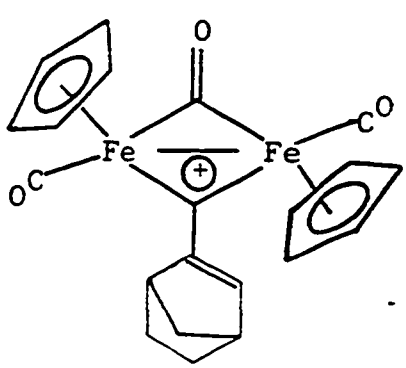
## Chemistry of the Bridging Vinylidenes

### Protonation of Bridging Vinylidenes

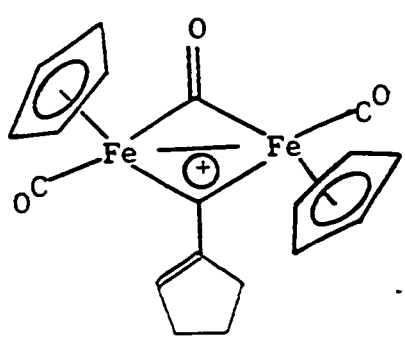
The protonation of 41d at -20°C yielded a compound that displayed a $^1$H-NMR spectrum with a methyl doublet at δ2.20, two Cp peaks at δ4.90 and 5.36, and a broad phenyl singlet at 7.5 and a multiplet at 6.02 in $CD_2Cl_2$ at 80 MHz. There are two probable structures as suggested by Knox,[20,21] the μ-vinyl or the μ-carbyne. The $^{12}$C-NMR at -10°C reveals a carbon at the low field value of 506 ppm. This value is consistent with a bridging carbyne structure 51b. This value is larger than that recorded for other bridging carbynes.[9,46] Rosenblum, et al., have reported bridging carbynes with chemical shifts of 432.65 and 448.27 ppm for 51c and 51d. Brookhart, et al.,[46] reports chemical shifts of 383.2 ppm for the monomeric cationic carbene complex 34. The larger chemical shift of 506 ppm could be due to the substitution on the carbyne carbon, but to-date no systematic system of predicting the effect of substituents on the chemical shift of the bridging carbyne carbon.




51b




51c



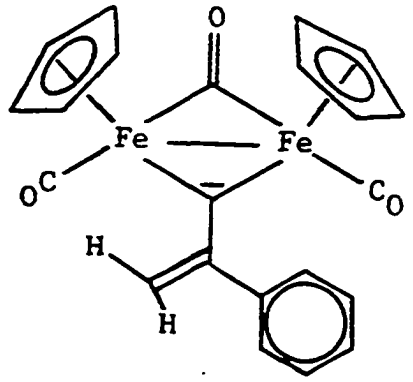

51d

The μ-carbyne 51b should be susceptible to reduction to form the bridging alkylidene. The μ-carbyne 51b in $CH_2Cl_2$ at -78°C was added to $NaCNBH_3$ in $CH_2Cl_2$ at -78°C. The resulting neutral purple compound was isolated by column chromatography. The purple compound readily isomerizes during purification to the red cis-compound. The $^1$H-NMR of the red cis compound is consistent with the bridging alkylidene complex.[36] The $^1$H-NMR spectrum assigned to the cis-alkylidene had a methyl doublet at δ1.87, J=6 Hz, a multiplet between δ3.3 and 4.1, a pair of Cp singlets at δ4.26 and 4.42, a broad phenyl multiplet at δ7.1-7.8, and a proton doublet at δ11.66, J=12 Hz. The IR spectrum is also consistent with the cis-structure CO stretches at 1984 vs. 1945, and 1793 $cm^{-1}$ The presence of two strong carbonyl stretches is indicative of the cis-configuration. The presence of a doublet at δ11.6 is very consistent with the bridging alkylidene structure. The bridging alkylidene reported by Knox also has a signal at δ11.6. The conversion of the bridging vinylidene to the bridging alkylidene is consistent with the known chemistry of the bridging compounds.

Attempted Deprotonation of 41b

Attempted deprotonation of 41b with a series of bases to form the anionic species 67. Anion 67 could be an intermediate in the bridging vinylidene synthesis,

and if stable, would react with alkylating agents to form new bridging vinylidenes. However, no evidence was found




67

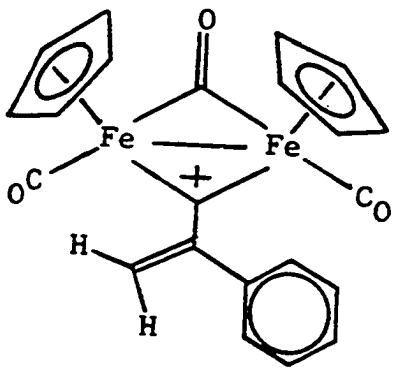
that 67 could be formed by the action of t-BuOK, methyllithium or t-butyllithium. This implies that the complex has a very low acidity.

Attempted Hydride Abstraction from 41b

Several attempts were made to prepare 51e by the reaction of $Ph_3C^+PF_6^-$ on 41b. The starting material apparently disappeared (by TLC) but the only isolable material was the starting material and its cis isomer. This indicates if 41b is formed, it is an extremely good hydride abstractor.

Oxidation of Ceric Ammonium Nitrate

Compound 41b was oxidized with 5 equiv of ceric ammonium nitrate. The resulting mixture was analyzed

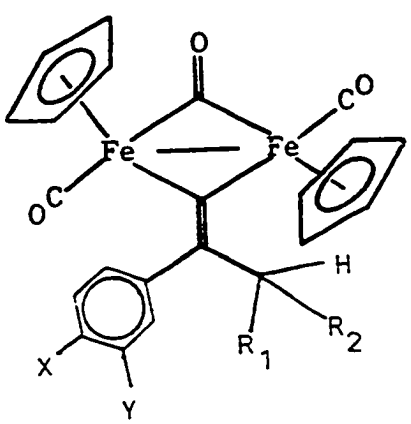


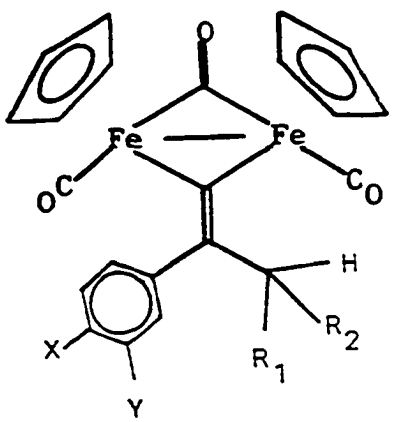

51e

by NMR and TLC but a very complex mixture of organic compounds was detected. No single compound could be isolated or characterized. Therefore, oxidation is not a clean method of removing the bridging organic group.

## SUMMARY

The importance of catalytic processes such as the Fischer-Tropsch synthesis has led to extensive research into the chemistries of bridging alkylidene, alkylidyne and vinylidene transition-metal complexes.[1-32] The focus of this research has been the synthesis and chemistry of a series of substituted bridging vinylidene iron complexes 41 and 42.




Bridging vinylidene transition-metal complexes are prepared in a variety of methods.[10-32] However, two main methods of synthesis are evident:

1. Reaction of a coordinatively unsaturated transition metal species with a monomeric vinylidene complex to form the bridging vinylidene.

2. Attack of an alkyl lithium reagent on a bridging carbonyl followed by protonation to form the bridging vinylidene complex. The limitations of these types of reactions are the availability of the necessary starting materials.

A new method of synthesizing bridging vinylidene iron dimers 41 and 42 has been developed. The new method begins with substituted 1,1-dichlorocyclopropanes. The substituted 1,1-dichlorocyclopropanes can then be reacted with a base to form the corresponding 1-chlorocyclopropene. The 1-chlorocyclopropene can then be converted to the bridging vinylidene iron dimer in two ways:

1. Reaction with $Fp_2$ under phase-transfer catalysis (see page 82).

2. Reaction with NaFp followed by reaction with $Fp_2$ under phase-transfer conditions.

No bridging vinylidene iron dimer could be formed unless phase-transfer catalysis was used.

The mechanism of this reaction was investigated and the following reaction mechanism is proposed.

1. $Fp^-$ is formed from the reaction of $OH^-$ on $Fp_2$.

2. The $Fp^-$ reacts with the substituted 1-chlorocyclopropene to form the substituted 1-Fp-1-cyclopropene.

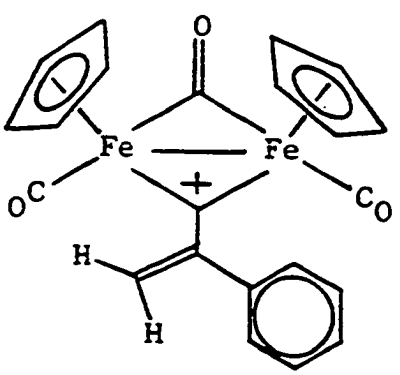
3. The reaction of $OH^-$ with $Fp_2$ can also produce a coordinatively unsaturated iron species which can attack the cyclopropene ring, inserting into the 1,3 bond on

cyclopropene ring.

4. Subsequent reaction to form the bridging vinylidene structure.

This proposed mechanism is reasonable based on the available data (see page 107). Other mechanisms are possible, but this is the one favored by the author.

The reaction of 41 with a variety of reagents was attempted. The chemistry of the double bond proved to be the most fruitful. The protonation forms the expected cationic intermediate. This species can then be reacted with hydride to form the bridging alkylidene complex.




51e

This new synthesis of a series of bridging vinylideneiron complexes allows one to investigate the effect of substitution on the bridging vinylidene moiety. This may then give a better understanding of the role of various factors in the reactions of bridging vinylidene iron dimers.

# EXPERIMENTAL

## General Methods

All reactions involving organometallic reagents were performed under a nitrogen atmosphere. The tetrahydrofuran (THF) was freshly distilled before use from sodium benzophenone dianion. Methylene chloride ($CH_2Cl_2$) was distilled from $P_2O_5$ and stored over molecular sieves. Hexane was distilled ACS grade. Chloroform (reagent grade) was passed through activity-I neutral alumina. All other solvents were used as received. Benzyltriethylammonium chloride (TEBA) and tetrabutylammonium hydrogen sulfate (TBAH) were used as received from Aldrich. The $[CpFe(CO)_2]_2$, ($Fp_2$) was purchased from Pressure Chemical Co. and recrystallized from $CH_2Cl_2$ and hexane. The $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2(MeFp)_2$ was used as received from Alpha Inorganics. Thin-layer chromatograph (TLC) was performed using Analtech silica and alumina plates. Column chromatography was performed using Sigma WB5 basic alumina, WN5 neutral alumina or E.M. Merck silica gel or equivalent. $^1$H-NMR were recorded on a Varian T60, EM360, XL100, or an IBM-NR80. Chemical shifts were reported in parts per million ($\delta$) downfield from the internal standard, tetra-

methylsilane (TMS). IR spectra were recorded using a Perkin Elmer 298. Routine mass spectra were recorded on a Hewlett Packard 5985 at 70 ev unless otherwise noted. High resolution mass spectra were performed by the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, Nebraska. Elemental Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points were obtained on a Kofler hotstage or a Thomas Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Spectral information is presented in the Results section.

1,1-Dichlorocyclopropanes

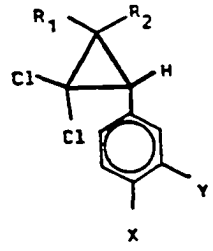
A detailed synthetic procedure is presented in Chapter 1.

Preparation of $[(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CR_2)]$

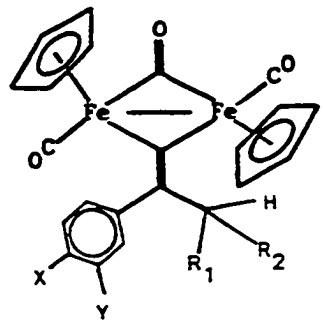
Procedure A. To a 100 ml round-bottom flask is added 45% $NaOH/H_2O$ (11 g), THF (15 ml), a 1,1-dichlorocyclopropane (1 equivalent), and $Fp_2$ (1.5 equivalents), followed by the addition of tetrabutylammonium hydrogen sulfate (TBAH) (0.1 g, .25 mmole). The solution is stirred at room temperature (RT) and monitored by TLC (silica gel developed with 25% ether/hexane). The product is detected by the presence of a purple band between the leading organic band the the trailing $Fp_2$ band. After most of the 1,1-dichlorocyclopropane has reacted, the

phases are separated by centrifugation. The aqueous layer is washed with ether (2 x 15 ml), the organic layers are combined, dried over $MgSO_4$, and the solvent removed at 25 torr. The residue is dissolved in $CH_2Cl_2$ diluted to a 1:2 mixture with hexane and applied to a 6 x 12 cm activity III basic alumina column. All columns are developed under a small positive nitrogen pressure with an ether in hexane mixture that gradually increased in ether content unless otherwise noted. There are three bands observed. The first, a small leading organic band with a very small overlapping yellow organometallic band is followed by the red-brown band of $Fp_2$. The purple band is collected and the solvent removed at 23 torr. The yield is calculated at this point by NMR using an internal standard. The crude material at this point contains, in addition to the bridging vinylidene, 20% $Fp_2$ and 35% extra organic material based on NMR integrals. The purple residue is then chromatographed on a 2.5 x 35 cm activity III basic alumina column using ether/hexane. The bands of this column are similar to the first except the purple band is much larger than the other two bands. The bridging vinylidene isolated is about 90% of the NMR yield with 15% extra phenyl peaks. Analytical samples are collected from materials prepared by Procedure B or C because the purity is better. The data is summarized in Table 34.

Table 34. Reaction of 17 by Procedure A




$Fp_2$



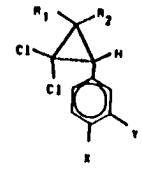

| $R_1$ | $R_2$ | mmole | mmole | Internal Standard | mmole | % Yield |
|---|---|---|---|---|---|---|
| Ph | H | 1.77 | 2.97 | p-dioxane | 0.50 | 28 |
| Ph | Ph | 1.50 | 2.1 | p-dioxane | 0.31 | 25 |

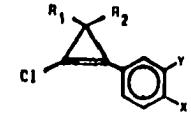
Procedure B. Potassium tertiary-butoxide (t-BuOK) (1.5 equivalent) is added to a 100 ml round-bottom flask containing a stirring 0° solution (0.25 mmole) of a 1,1-dichlorocyclopropane (1 equivalent) and THF (15 ml). After 15 minutes $Fp_2$ (1.5 equivalents), 45% $NaOH/H_2O$ (11 g), and TBAH (100 mg, .25 mmole). The solution is then stirred until most of the organic had disappeared by TLC (silica gel developed with 25% ether in hexane). The phases are separated by centrifugation, and the aqueous layer is washed with ether (2 x 15 ml). The organic layers are combined, dried over $MgSO_4$, and the solvent removed at 25 torr. The residue is purified as described in Procedure A. The first column looks just like the column in Procedure A. The purple band at this point contains in addition to the bridging vinylidene, 20% $Fp_2$ and 20% extra phenyl based on NMR integrals. The second column yields about 90% of the NMR yield in about 95% purity. Analytical samples are chromatographed as described in Procedure A and freshly recrystallized from ether in hexane prior to analysis. The data is summarized in Table 40.

Preparation of $Na^+[CpFe(CO)_2]^-$

Sodium (1.5 g, 0.75 mmole) is added in small parts to a stirring, flame-dried 250 ml amalgam flask (shown in Figure 3) containing mercury (15 ml). The Na/HG was allowed to cool to RT. THF (100 ml) and $Fp_2$ are added

Table 35. $^1$H-NMR Yields of 41 by Procedure B





| | Ar | $R_1$ | $R_2$ | mmole | $KOC(CH_3)_3$ | mmole | Internal Standard | mmole | % Yield |
|---|---|---|---|---|---|---|---|---|---|
| b | Ph | H | H | 1.71 | 2.6 mm | 2.84 | p-dioxane | 0.43 | 25 |
| c | Ph | Me | H | 2.43 | 3.6 mm | 3.26 | p-dioxane | 0.97 | 40 |
| d | Ph | Me | Me | 2.96 | 4.4 mm | 4.16 | p-dioxane | 0.86 | 33 |
| e | p tol | H | H | 2.60 | 3.9 mm | 3.15 | p-dioxane | 0.86 | 33 |
| f | p tol | Me | H | 1.97 | 3.0 mm | 2.91 | acetonitrile | 1.30 | 66 |
| g | p tol | Me | Me | 2.61 | 3.5 mm | 3.45 | toluene | 1.33 | 51 |
| h | an | H | H | 1.93 | 2.9 mm | 2.55 | mesitylene | 0.52 | 27 |
| i | an | Me | H | 1.77 | 2.7 mm | 1.68 | mesitylene | 0.81 | 46 |
| j | an | Me | Me | 2.07 | 3.5 mm | 3.12 | p-dioxane | 1.26 | 61 |
| k | m-clPh | H | H | 1.49 | 2.2 mm | 1.48 | mesitylene | 0.10 | 7 |
| l | m-clPh | Me | H | 2.95 | 4.4 mm | 4.39 | isolated | 0.43 | 14 |
| m | m-clPh | Me | Me | 2.14 | 3.2 mm | 1.41 | mesitylene | 0.96 | 45 |
| n | Ph | Ph | H | 2.36 | 3.5 mm | 2.41 | p-dioxane | 0.40 | 17 |

*The yields represent an average of a minimum of 2 runs and are 10%.

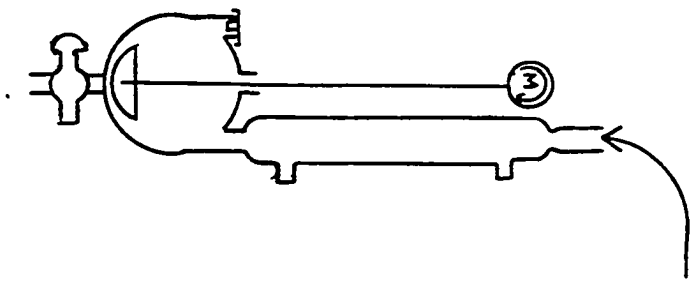
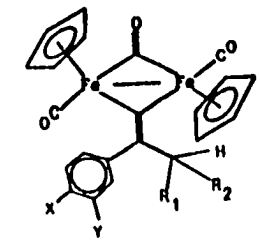



Figure 1. Mercury amalgam Apparatus

to the amalgam and vigorously stirred for 45 minutes. The stirring is stopped and the Na/Hg removed through the bottom stopcock. The 0.5 M NaFP solution is then transferred under $N_2$ via the bottom stopcock into a 125 m Erlenmeyer flask with a rubber septum. The solution is stored in a freezer.

Procedure C. The t-BuOK (1.5 equivalents) is added to a 100 mL round-bottom flask containing a stirring 0°C solution (0.25 mmol) of a 1,1-dichlorocyclopropane (1 equiv) and THF (15 mL). After 15 minutes NaFP in THF (0.5 mmol/1.5 equiv) is added via syringe and the solution is allowed to warm to RT and stirr for 1-1½ hours. $Fp_2$ (1 equiv), 45% NaOH/$H_2O$ (11 g) and TBAH (100 mg, .25 mmol) were added and stirred until the yellow organometallic disappeared by TLC (silica gel developed with 25% ether in hexane). The phases are separated by centrifugation and the aqueous layer washed with

Table 36. Reaction of 7 by Procedure C



| $R_1$ | $R_2$ | $R_3$ | $^{+-}KO\text{-}C(CH_3)_3$ mmole | NaFp mmole | $Fp_2$ mmole | Internal Standard | Yield mmole | % |
|---|---|---|---|---|---|---|---|---|
| Ph | H | H | 3.26 | 4.9 | 3.39 | isolated | 0.78 | 29 |
| Ph | Me | H | 2.38 | 3.5 | 4.24 | mesitylene | 1.07 | 45 |
| Ph | Me | Me | 1.27 | 1.95 | 1.82 | mesitylene | 0.40 | 31.6 |
| p-tol | H | H | 2.80 | 4.2 | 2.14 | p-dioxane | 0.98 | 35 |
| p-tol | Me | H | 2.40 | 3.6 | 2.85 | p-dioxane | 0.89 | 37 |
| p-tol | Me | Me | 2.31 | 3.5 | 2.88 | mesitylene | 0.99 | 43 |
| An | H | H | 2.19 | 3.3 | 2.29 | mesitylene | 0.31 | 14 |
| An | Me | H | 2.02 | 3.0 | 1.04 | mesitylene | 0.62 | 31 |
| An | Me | Me | 2.24 | 3.4 | 2.40 | mesitylene | 0.90 | 90 |
| m-ClPh | H | H | 1.43 | 2.1 | 1.16 | mesitylene | 0.11 | 8 |
| m-ClPh | Me | Me | 2.06 | 3.1 | 2.99 | mesitylene | 1.11 | 54 |

ether (1 x 15 ml). The organic layers are combined, dried over $MgSO_4$ and the solvent removed at 25 torr. The residue is chromatographed in the manner described in Procedure A.

The first column looks similar to the column seen in Procedure A. A leading organic band followed by a small yellow organometallic band is observed. The purple bridging vinylidene is eluted next followed by the red-brown dimer. The purple band at this point contained, in addition to the bridging vinylidene, 25% $Fp_2$ and 15% extra phenyl based on NMR integrals. The second column yielded about 85% of the NMR yield in 95% purity. The data are summarized in Table 36. The analytical and mass spectral data are summarized in Tables 37 and 38.

Conversion of Trans to Cis Bridging Vinylidene

The trans-bridging vinylidene 41 (0.1-0.5 g, 0.21-0.99 mmol) were placed as a solid in a 1 x 10 cm ampule equipped with a joint. Toluene (4-6 ml) was added, the solution is degassed by the freeze-thaw method on a vacuum line, sealed using an $O_2/CH_4$ flame, and placed in an 80°C temperature bath for 36 hours. The ampules were then opened and the solvent removed on a Büchi rotavap at 0.2 torr. The trans/cis mixture is chromatographed as described in Procedure A. Only 2 bands are present: the leading purple trans compound followed by the red cis compound.

Table 37. Analytical Data for 41 and 42.

| | $R_1$ | $R_2$ | X | Y | Calc M W (M 100) | Exp (M 100) | E.A. Calc %C | E.A. Calc %H | E.A. Found %C | E.A. Found %7 | M.P. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | H | H | H | H | | | 59.76 | 4.11 | 59.64 | 4.18 | 128.8-131.5 |
| 42 | H | H | H | H | | | 59.76 | 4.11 | 59.48 | 4.10 | 195.7-196.3 |
| 41 | Me | H | H | H | | | 60.56 | 4.42 | 60.26 | 4.43 | 133.0-134.0 |
| 42 | Me | H | H | H | | | 60.56 | 4.42 | 59.81 | 4.44 | 185.1-187.0 |
| 41 | Me | Me | H | H | | | 61.31 | 4.72 | 61.12 | 4.80 | 170.2-171.1 |
| 42 | Me | Me | H | H | 442.0356 | 442.0303 | | | | | 108.1-209.2 |
| 41 | H | H | Me | H | | | 60.56 | 4.42 | 60.59 | 4.46 | 140.1-141.0 |
| 42 | H | H | Me | H | 428.0051 | 428.0176 | | | | | 165.1-166.1 |
| 41 | Me | H | Me | H | | | 61.31 | 4.72 | 61.71 | 4.78 | 135.0-136.0 |
| 42 | Me | H | Me | | | | 61.31 | 4.72 | 60.75 | 4.75 | 156.0-157.0 |
| 41 | Me | Me | Me | H | | | 62.02 | 5.00 | 61.75 | 5.16 | 145.0-146.0 |
| 42 | Me | Me | Me | H | 456.1382 | 456.1476 | | | | | 165.0-166.0 |
| 41 | H | H | OMe | H | | | 58.20 | 4.27 | 58.55 | 4.60 | 146.0-147.1 |
| 42 | H | H | OMe | H | 444.0784 | 444.0884 | | | | | 184.0-185.1 |

Table 37 (continued)

| | $R_1$ | $R_2$ | X | Y | Calc M W (M 100) | Exp (M 100) | E.A. Calc %C | E.A. Calc %H | E.A. Found %C | E.A. Found %H | M.P. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | Me | H | OMe | H | | | 59.29 | 4.56 | 58.55 | 4.53 | 121.5-123.5 |
| 42 | Me | H | OMe | H | 458.1053 | 458.1143 | | | | | 162.5-164.0 |
| 41 | Me | Me | OMe | H | | | 60.03 | 4.84 | 60.16 | 4.90 | 134.0-135.0 |
| 42 | Me | Me | OMe | H | 472.1328 | 472.1299 | | | | | 200.0-203.0 |
| 41 | H | H | H | Cl | 445.5024 | 445.5122 | | | | | 133.9-134.1 |
| 42 | H | H | H | Cl | 445.5024 | 445.5127 | | | | | 167.0-168.0 |
| 41 | Me | H | H | Cl | 462.5291 | 462.5387 | | | | | oil |
| 41 | Me | Me | H | Cl | 476.5563 | 476.5668 | | | | | 137.0-138.0 |
| 42 | Me | Me | H | Cl | 476.5563 | 476.5633 | | | | | 222.9-224.8 |

Table 38. Mass Spectral Data for 41 and 42*

| | $R_1$ | $R_2$ | X | Y | $M^+$, % | $M-CO^+$, % | $M-2CO^+$, % | $M=3CO^+$, % |
|---|---|---|---|---|---|---|---|---|
| 41 | H | H | H | H | (442.10.2) | (414.15.7) | (386.27.0) | (358.89.7) |
| 42 | H | H | H | H | (492,11.5) | (414,19.6) | (386.22.1) | (358,73.1) |
| 41 | Me | H | H | H | (456,19.9) | (428,24.2) | (400,40.7) | (372,100) |
| 42 | Me | H | H | H | (456,2.2) | (428,3.3) | (400,5.0) | (372.100) |
| 41 | Me | Me | H | H | (470,2.4) | (442,5.3) | (414,5.3) | (386,45.8) |
| 42 | Me | Me | H | H | (470,2.5) | (442.5.3) | (414,4.4) | (386,31.4) |
| 41 | H | H | H | Cl | (476,4.6) | (448,8.9) | (420,12.1) | (392,47.9) |
| 42 | H | H | H | Cl | (476,16.4) | (448,25.5) | (420,30.0) | (392,100) |
| 41 | Me | H | H | Cl | (490,11.5) | (462,19.6) | (434,22.1) | (406,73) |
| 41 | Me | Me | H | Cl | (405,1.5) | (476,3.0) | (448,2.8) | (420,21.5) |
| 42 | Me | Me | H | Cl | (504,2.5) | (476,4.2) | (448,3.8) | (420,33.5) |
| 41 | H | H | Me | H | (456,7.0) | (428,10.1) | (400,15.9) | (372,64.8) |
| 42 | H | H | Me | H | (456,9.0) | (428,10.8) | (400,18.4) | (372,43.4) |
| 41 | Me | H | Me | H | (470,11.6) | (442,16.4) | (414,27.3) | (386,84.1) |
| 42 | Me | H | Me | H | (470,7.1) | (442,7.8) | (414,10.6) | (386,27.3) |
| 41 | Me | Me | Me | H | (484,24.7) | (456,34.6) | (428,35.5) | (400,100) |

Table 38 (continued)

| | $R_1$ | $R_2$ | X | Y | $M^+$, %) | $M-CO^+$, % | M-2CO , % | $M=3CO^+$, % |
|---|---|---|---|---|---|---|---|---|
| 42 | Me | Me | Me | H | (484,10.6) | (456,15.8) | (428,17.3) | (400,100) |
| 41 | H | H | OMe | H | (472,5.4) | (444,5.7) | (416,12.0) | (388,58.8) |
| 42 | H | H | OMe | H | (472,14.5) | (444,16.4) | (416,27.8) | (388,100) |
| 41 | Me | H | OMe | H | (486,6.0) | (458,9.5) | (430,17.1) | (402,64.8) |
| 42 | Me | H | OMe | H | (486,3.6) | (458,5.4) | (430,8.5) | (402,27.5) |
| 41 | Me | Me | OMe | H | (500,1.8) | (472,4.9) | (444,5.1) | (416,25.5) |
| 42 | Me | Me | OMe | H | (500,7.9) | (472.13.9) | (444,16.2) | (416,100) |

*Mass spectral data reported as M/e abundance and % observed.

The ratios reported are based on isolated materials. The purity of these compounds is very high. The results are summarized in Table 29.

## Mechanistic Experiments

### Stability of 1,1-dichlorocyclopropanes to Sodium Hydroxide Under Phase Transfer Catalysis

Trans-1,1-dichloro-2,3-diphenylcyclopropane (0.518 g, 1.79 mmol), TBAH (100 mg, 0.25 mmol), and THF (15 mL) were added to a 100 ml round-bottom flask containing a stirring 45% $NaOH/H_2O$ solution (11 g). After one hour a 2 ml sample was removed, the phases separated by centrifugation, the organic layer dried over $MgSO_4$, and the solvent removed at 25 torr. NMR indicates no starting material remaining. The major organic product is identified by NMR as 1-chloro-2,3-diphenylcyclopropene by comparison to the NMR spectra of 1-chlorocyclopropenes reported by Weyerstahl.[38,39] $Fp_2$ (1.00 g, 2.83 mmole) and tetrabutylammonium hydrogen sulfate (TBAH) 0.11 g, 0.25 mmol) are added to the remainder of the reaction mixture. The bridging vinylidene is immediately formed. After 1 hour thematerial is worked up using the procedure described in Procedure A yielding 115 g, 0.29 mmol, 15%) plus 40% extra phenyl by NMR integration.

1,1-Dichloro-2-phenylcyclopropane (0.422 g, 2.26 mmol) is reacted in a similar manner. The 2 ml fraction is removed, worked up, and analyzed by NMR the same way.

The product is identified as 1-chloro-2-phenylcyclopropene by comparing its NMR to the NMR Weyerstahl reported for 1-chloro-2-phenylcyclopropene.[38,39] $Fp_2$ (1.15 g, 3.26 mmol) and TBAH (0.100 g, 125 mmol) are added to the reaction mixture. The bridging vinylidene is immediately formed. The material is worked up using the procedure described in Procedure A yielding a 23% yield by NMR containing 40% extra phenyl.

Crossover Using $Fp_2$ and $(MeFP)_2$

$Fp_2$ (0.251 g, 171 mmol) and $(MeFp)_2$ (-.283 g, 0.74 mmol) are added to a 100 mL round-bottom flask containing a stirring mixture of 45% $NaOH/H_2O$ (11 g), THF (15 mL), and TBAH (0.100 g, 0.25 mmol). After 15 minutes the phases are separated by centrifugation, the organic layer dried over $MgSO_4$, and the solvent removed at 25 torr. The solid is analyzed by its mass spectrum. The masses of the parent ions of the three possible dimers $Fp_2$, (MeFp)Fp, and $(MeFp)_2$ at 354 (14.1%), 368 (11.3%), and 382 (17.1%) amu, respectively, indicated crossover has occurred.

A control experiment was run in which a mixture of $Fp_2$ (0.021 g, 0.060 mmol) and $(MeFP)_2$ (0.23 g, 0.059 mmol) are cocrystallized and the solid analyzed by mass spectroscopy. No crossover is observed; instead the two starting materials are observed by the detection of the parent peaks at 382 (8.8%) and 354 (13.2%). A small peak

at 368 (1.3%) is also observed but was considered insignificant when compared to crossover observed in the PTC experiment.

Rection of 1-chloro-2-phenylcyclopropene with NaFp

A solution of t-BuOK (0.29 g, 2.6 mmol) in THF (10 mL) is added over 5 minutes to a 100 mL round-bottom flask containing a stirred mixture of 1,1-dichloro-2-phenylcyclopropane (0.333 g, 1.78 mmol) in THF (5 mL) at 15°C. After 15 minutes the reaction is quenched by the addition of ether (15 mL) and ice water (20 g), the organic layer washed with 5% $NH_4Cl$ in $H_2O$ (15 mL), dried over $MgSO_4$, and the volume reduced to 10 mL at 25 torr. The solution is cooled to 0°C and NaFP in THF (4 ml x 0.5 m, 2 mmol) is added via syringe and stirred at 0°C and 0.5 torr. The solid was chromatographed on a 4 x 8 cm 15°C jacketed activity III basic alumina column developed with ether in hexane. The column has 3 bands; a leading band of an organic and organometallic, the major orange 1-Fp-2-phenylcyclopropene band followed by the red-brown $Fp_2$ band. The solvent is again removed at 0°C and 0.5 torr. The major fraction is rechromatographed on a 15°C jacketed 1.0 x 20 cm activity III basic alumina column to give 1-Fp-2-phenyl-1-cyclopropene (0.17 g, 0.57 mmol, 32%) as an oil.

General Synthesis of Fp-cyclopropenes

A detailed synthetic procedure is given in Chapter 1 (page 52.

Reaction of 1-Fp-2-tolyl-3,3-dimethylcyclopropene with $(MeFp)_2$ and Sodium Hydroxide Under Phase Transfer Catalysis

Fp-2-tolyl-3,3-dimethyl-1-cyclopropene (9.336 g, 1.01 mmol), $(MeFp)_2$ (0.588 g, 1.54 mmol), and THF (15 mL) are added to a 100 mL round-bottom flask containing a stirred solution of 45% $NaOH/H_2O$ (11 g) and TBAH. After 15 minutes, the phases are separated by centrifugaiton, the aqueous layer washed with ether (2 x 15 ml), the combined organic layers dried over $MgSO_4$, and the solvent removed at 25 torr. The solid residue is chromatographed on a 6 x 12 cm activity III basic alumina column to yield 3 fractions. The small leading yellow band is identified as the starting material by NMR. The major purple band is eluted next and identified as the bridging vinylidene by NMR. The mass spectrum at 12 ev revealed the parent ion peaks of two dimers $[CpFeCO]^-[MeCp)FeCO](\mu\text{-}CO)$-$[\mu\text{-}C{=}C(i\text{-}pr)(p\text{-}tol)]$ at 498 amu (23.7%) and $[CpFeCO)_2$-$(\mu\text{-}CO)[\mu\text{-}C{=}C(i\text{-}pr)(p\text{-}tol)]$ at 484 amu (10.4%).

Preparation of 1-$MeCpFe(CO)_2$-2-tolyl-3,3-dimethylcyclopropene

$(MeFP)_2$ (0.752 g, 1.97 mmol) and THF (10 mL) are added to a 50 mL round flask containing a stirred

1% Na/Hg amalgam (64 g). The excess amalgam is removed from the flask after 45 minutes. 56 g (0.635 g, 3.29 mmol) in THF (6 mL) is added via syringe and stirred at room temperature for one hour. The solvent is removed at 0°C and 0.5 torr and the resulting solid chromatographed on a 4 x 8 cm jacketed 15°C activity III basic alumina column using ether in hexane. There are two main bands; a large orange band with a small leading organic edge and the dimer band following. The removal of the solvent from the first band yielded an oil (0.860 g, 2.47 mmole, 75%). Elemental analysis: calculated: 66.95%C, 5.79%H; found: 66.15%C, 5.87%H; I.R. in heptane: CO stretches: 2024, 1977 and double bond stretch at 1736 $cm^{-1}$.

Reaction of 1-MeFP-2-p-tolyl-3,3-dimethylcyclopropane with $FP_2$ and Sodium Hydroxide Under Phase Transfer Catalysis

$Fp_2$ (1.12 g, 3.15 mmol), 1-MeFp-2-p-tolyl-3,3-dimethylcyclopropene (0.86 g, 2.47 mmol) and THF (15 mL) are added to a 100 m round-bottom flask containing a stirred solution of 45% $NaOH/H_2O$ (11 g) and TBAH. After 5 minutes the phases are separated by centrifuging the aqueous layer, washed with ether (2 x 15 ml), the organic layers combined and dried with $MgSO_4$, and the solvent removed on a rotary evaporator at 25 torr. The solid residue is chromatographed on a 6 x 12 cm activity III basic alumina column splitting the effluent into 3 fractions.

The first fraction is the starting material identified by NMR. The purple band contained only (μ-CO)[μ-C=C(i-pr)(p-tol)][COFeCp)][COFe(MeCp)] (0.38 g, 0.76 mmol, 31%) as identified by IR in heptane CO stretches 205, 1962, 1953 and C=C 1798. Elemental analysis calculated 62.68%C, 5.26%H, found: 62.74%C,5.26%H.

Attempted Isolation of Fp-cyclopropenes Under Phase Transfer Coitions

$Fp_2$ (0.103 g, 0.29 mmol) in THF (5 mL) is slowly added to a 100 mL round-bottom flask containing a stirred mixture of 566g (0.359 g, 1.88 mmol), THF (15 mL), 45% $NaOH/H_2O$ (11 g) and TBAH. The bridging vinylidene is formed immediately with no detectable amount of the Fp-cyclopropene by TLC (silica gel developed with 25% ether in hexane). After 5 minutes the phases are separated by centrifugation, the aqueous phase washed with ether (2 x 15 ml), the combined organic layers dried over $MgSO_4$, and the solvent is removed on a rotary evaporator at 25 torr.

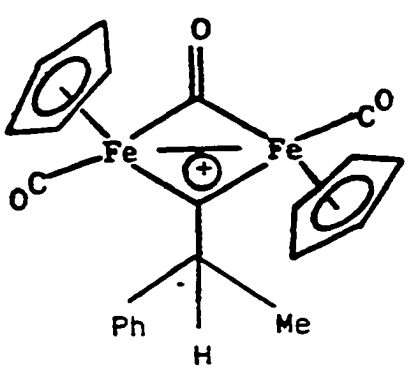
A competitive rate study was then conducted. $Fp_2$ (0.045 g, 0.12 mmol) in THF (5 mL) is slowly added to a 100 ml round-bottom flask containing 1-chloro-3,3-dimethyl-2-p-tolylcyclopropene (0.12 g, 0.62 mmol) 56g (0.067 g, 0.21 mmol), THF (10 mL), 10 g $NaOH/H_2O$ (45:55) and TBAH. The reaction is stirred 2 minutes and the

phases separated by centrifugation. The organic layer is dried over $MgSO_4$, and the solvent removed on a rotary evaporator. The oil residue is purified on an activity III basic alumina column. The NMR indicates only the product resulting from the reaction of the Fp-cyclopropene.

To check for a reactivity difference the reaction is repeated using 1-chloro-3,3-dimethyl-2-phenylcyclopropene (0.194 g, 1.09 mmole, 56g, 0.44 mmol) again indicated only the product resulting from the reaction 56g in 43% yield using p-dioxane as an internal standard.

Protonation of $[(\mu\text{-CO})(\mu\text{-CMePh})(COFeCp)_2]$

$[(\mu\text{-CO})(\mu\text{-CMePh})(COFeCp)_2]$ (0.030 g, 0.07 mmol) was dissolved in $CD_2Cl_2$ (0.4 ml) and filtered into an NMR tube. The solution is cooled to -78°C and fluorosulfuric acid (10 µl, 0.17 mmol) added via syringe. The $^1$H-NMR spectra was recorded at -50°C and at 10°C intervals up to 0°C. The $^{13}$C-NMR spectra is recorded at -10°C. The




51b

major product is identified as 51b as determined by comparison of $^{1}H$ and $^{13}C$-NMR data from other bridging cationic carbynes.

Synthesis of $[(\mu\text{-CO})(\mu\text{-CHCHPhMe})(COFeCP)_2]$

$HBF_4$ $Me_2O$ (0.175 g, 1.08 mmol) was added via syringe to a 100 ml round-bottom flask containing a stirring solution of $[(\mu\text{-CO})(\mu\text{-CHCHPhMe})(COFeCp)_2]$ (0.400 g, 0.90 mmol) in $CH_2Cl_2$ (10 mL) at -78°C. The cationic material was precipitated by the addition of hexane (30 ml). The hexane was decanted and the oil washed with more hexane (20 ml). The oil was then dissolved in $CH_2Cl_2$ (10 ml) at -78°C and added via a glass syringe cooled to -78°C to a stirring solution of $NaCNBH_3$ (0.102 g, 1.63 mmol) in $CH_2Cl_2$ (10 m ) at -78°C.

Thesolvent is removed on a rotary evaporator after most of the ionic material had reacted (detected by TLC). The solid is chromatographed on a jacketed 15°C silica gel column developed with ether/hexane to yield $[(\mu\text{-CO})(\mu\text{-CHCHPhMe})(COFeCP)_2]$ (0.188 g, 0.42 mmol, 47%); mp 215-216.0°C, H.R.M.S. calculated -1 CO, 416.0196; experimental, -1 CO, 415.0201.

Attempted Deprotonation of $[\mu\text{-Cp})(\mu\text{-C-CMePh})(COFeCP)_2]$

A base is added to a 100 ml round-bottom flask containing a stirred solution of $[(\mu\text{-CO})(\mu\text{-C=CMePh})(COFeCp)_2]$ at -78°C. The solution is allowed to warm to

room temperature and quenched with MeOD (0.5 ml). Examination by NMR revealed no deuterium incorporation. This data is summarized in Table 14.

Table 39.

| [(μ-CO)(μ-C=MePh)$(COFeCp)_2$] | Base | % Recovery |
|---|---|---|
| 0.35 mmole | KOt-Bu (0.7 mmole) | 87 |
| 0.33 mmole | MeLi (0.7 mmole) | 84 |
| 0.34 mmole | t-BuLi (1 mmole) | 83 |

Attempted Hydride Abstraction from trans-[(μ-CO)(μ-C=CMePh)$(COFeCP)_2$]

Trans-[μ-CO)(μ-C=CMePh)$(COFeCP)_2$] (0.22 g, 0.5 mmol in $CH_2Cl_2$ (6 mL) was added via syringe to a 100 ml round-bottom flask containing a stirred solution of $Ph_3C^+PF_6$ (0.48 mmol) in $CH_2Cl_2$ (6 mL) at -78°C. After warmed to room temperature, the reaction is analyzed by TLC (silica gel developed with 25% ether/hexane) which indicated all of the starting material has been consumed. Hexane is added to precipitate any cationic materials but no solid formed. The solvent is removed on a rotary evaporator at 25 torr and an NMR of the residue indicated only the starting material.

Oxidation of $[(\mu\text{-CO})(\mu\text{-C=CPhMe})(\text{COFeCp})_2]$ with Ceric Ammonium Nitrate

$[(\mu\text{-CO})(\mu\text{-CPhMe})(\text{COFeCp})_2]$ (0.68 mmol) in THF (5 ml) are added via syringe to a 100 ml round-bottom flask containing a stirred mixture of ceric ammonium nitrate in THF (5 ml) and MeOH (5 ml). The solution rapidly turned dark. The solvent is removed on a rotary evaporator at 25 torr and the resulting solid washed with ehter (2 x 24 ml). The ether layers are combined and the solvent removed on a rotary evaporator at 25 torr. The residue is chromatographed on a 2.5 x 15 cm silica gel column using ether in hexane. The resulting material showed no major components, only a mixture of a large number of different compounds.

## LITERATURE CITED


1. Theopold, K.H.; Bergman, R.G., J. Am. Chem. Soc., 1983, 105, 464.
2. Herrman, W.W., Adv. Organomet. Chem., 1982, 20, 159.
3. Herrman, W.A., Angew. Chem., 1982, 94, 118.
4. Brady, R.C., III; Pettit, R., J. Am. Chem. Soc., 1980, 102, 6181.
5. Osterloh, W.T.; Cornell, M.E.; Pettit, R., J. Am. Chem. Soc., 1982, 104, 3759.
6. Tebbe, F.N.; Parshall, G.W.; Reddy, G.S., J. Am. Chem. Soc., 1980, 102, 1752.
7. Herrman, W.A.; Plank, J.; Ziegler, M.L.; Balbach, B., J. Am. Chem. Soc., 1980, 102, 5906.
8. Herrman, W.A.; Plank, J.; Guggolz, E.; Ziegler, M.L., Angew. Chem. Int. Ed. Engl., 1980, 19, 651.
9. Nitay, M.; Priester, W.; Rosenblum, J., J. Am. Chem. Soc., 1978, 100, 3620.
10. Mills, O.S.; Redhouse, A.D., J. Chem. Soc. A, 1966, 444.
11. Mills, O.S.; Redhouse, A.D., J. Chem. Soc. A, 1968, 1282.
12. King, R.B.; Saran, M.S., J. Am. Chem. Soc., 1973, 95,

1811.

13. King, R.B.; Saran, M.S., J. Am. Chem. Soc., 1973, 95, 1784.

14. Kircher, R.M.; Ibers, J.A., J. Organomet. Chem., 1974, 82, 243.

15. Nesmeyanov, A.N.; Aleksandrov, G.G.; Antorova, A.B.; Anisimov, K.N.; Kolobova, N.E.; Struchkov, Yu.T., J. Organomet. Chem., 1976, 110, C36.

16. Andrianov, V.G.; Stuchkov, Yu.T.; Kolobova, N.E.; Antonova, A.B.; Obezyuk, N.S., J. Organomet. Chem., 1976, 122, C33.

17. Antonova, A.B.; Kolobova, N.E.; Petrovsky, P.V.; Lokshin, B.V.; Obezyuk, N.S., J. Organomet. Chem., 1977, 137, 55.

18. Kolobova, N.E.; Antonova, A.B.; Khitrova, O.M.; Antipin, M.Yu.; Struchkov, Yu.T., J. Organomet. Chem., 1977, 137, 69.

19. Sizoi, V.F.; Nekrasov, Yu.S.; Sikharev, Yu.N.; Kolobova, N.E.; Khitrova, O.M.; Obezyuk, N.S.; Antonova, A.B., J. Organomet. Chem., 1978, 162, 171.

20. Davies, D.L.; Dyke, A.F.; Endesfelder, A.; Knox, S.A.R.; Naish, P.J.; Orpen, A.G.; Plaas, D.; Gaylor, G.E., J. Organomet. Chem., 1980, 198, C43.

21. Dyke, A.F.; Knox, S.A.R.; Naish, P.J.; Orpen, A.G., J. Chem. Soc., Chem. Commun., 1980, 441.

22. Folting, K.; Huffman, J.C.; Lewis, L.N.; Caulton,

K.G., Inorg. Chem., 1979, 18, 3483.

23. Lewis, L.N.; Huffman, J.C.; Caulton, K.G., Inorg. Chem., 1980, 19, 1246.
24. Berke, H., Z. Naturforsch., Teil B, 1980, 35b, 86.
25. Berke, H., Chem. Ber., 1980, 113, 1370.
26. Chetcuti, M.H.; Chetcuti, P.A.M.; Jeffery, J.C.; Mills, R.M.; Mitrprachachon, P.; Pickering, S.J.; Stone, S.G.A.; Woodward, P., J. Chem. Soc. Dalton Trans., 1982, 699.
27. Brun, P.; Dawkins, G.M.; Green, M.; Mills, R.M.; Salaün, J.Y.; Stone, S.G.A.; Woodward, P., J. Chem. Soc., Chem. Commun.., 1981, 966.
28. Dawkins, G.M.; Green, M.; Jeffery, J.C.; Stone, S.G.A., J. Chem. Soc., Chem. Commun., 1980, 1120.
29. Lu, P.Y.; Pettit, R., personal communication.
30. Harris, P.J.; Howard, J.; Knox, S.A.; Phillips, R.; Stone, F.; Woodward, P., J. Chem. Soc., Dalton Trans., 1976, 377.
31. Horvath, J.T.; Palyi, G.; Marko, L., J. Chem. Soc., Chem. Commun., 1979, 1054.
32. Horswagen, R.; Alt, R.; Speth, D.; Ziegler, M.L., Angew. Chem., Int. Ed. Engl., 1981, 20, 1049.
33. Dehmlow, E.; Dehmlow, S., "Phase Transfer Catalysis," Verlag Chemie: Weinheim, 1980.
34. Gibson, D.H.; Hsu, W.L.; Ahmed, F.U., J. Organomet. Chem., 1981, 215, 379.

35. Gibson, D.H.; Ahmed, F.U.; Phillips, K.R., Organometallics, 1982, 1, 679.

36. Marten, D.F.; Dehmlow, E.V.; Hanlon, D.J.; Hossain, M.B.; van der Helm, D., J. Am. Chem. Soc., 1981, 103, 4940.

37. Hossain, M.B.; Hanlon, D.J.; Marten, D.F.; van der Helm, D., Acta Cryst., 1982, B38, 1457.

38. Henseling, K.-O.; Weyerstahl, P., Chem. Ber., 1975, 108, 2803.

39. Henseling, K.-O.; Quast, D.; Weyerstahl, P., Chem. Ber., 1977, 110, 1027.

40. Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M., J. Am. Chem. Soc., 1977, 99, 2160.

41. Alper, H.; Paik, H.-N., J. Am. Chem. Soc., 1978, 100, 508.

42. Marten, D.F.; Wilburn, S., unpublished data.

43. Darensborg, D.J.; Froelich, J.A., J. Am. Chem. Soc., 1978, 100, 338.

44. Marten, D.F., unpublished results.

45. Fischer, E.O.; Schubert, U., J. Organomet. Chem., 1975, 100, 59.

46. Brookhart, M.; Tucker, J.R.; Husk, G.R., J. Am. Chem. Soc., 1983, 105, 258.

47. Hoel, E.; Ansell, G.; Leta, S., Organometallics, 1984, 3, 1633.