

## COMPLEXES OF $\eta^5$ -CYCLOPENTADIENYLDICARBONYLIRON DERIVED FROM *cis*-3,4-DICHLOROCYCLOBUTENE

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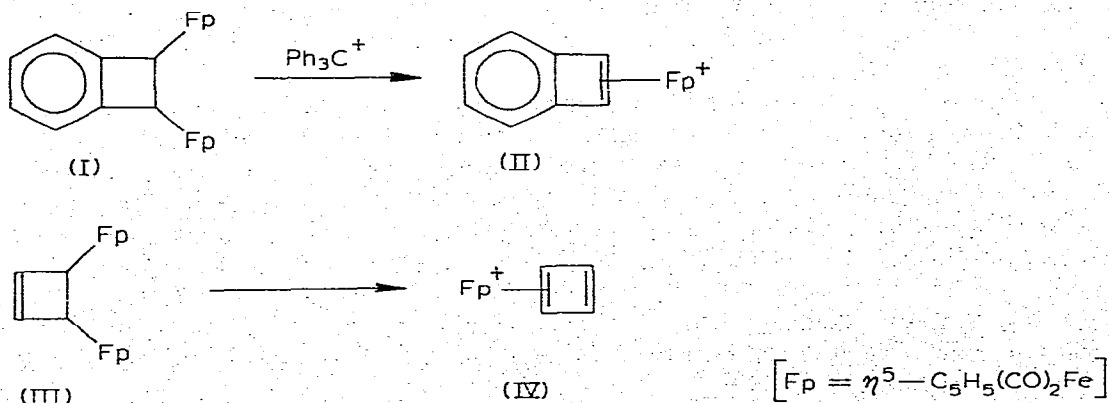
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### Summary

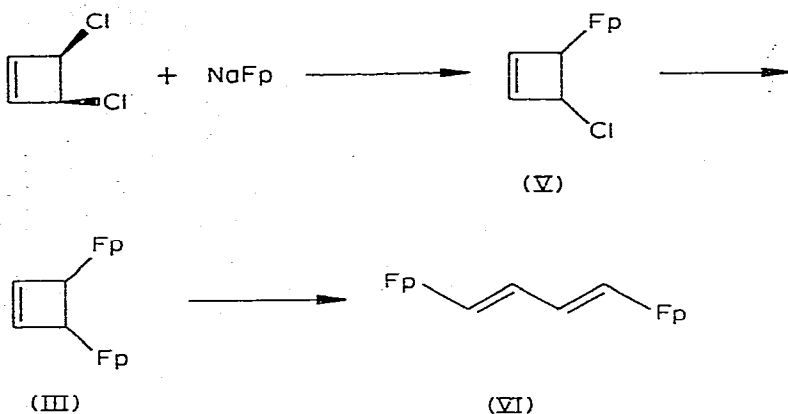
The metathesis between  $\text{Na}[\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}]$  ( $\text{NaFp}$ ) and *cis*-3,4-dichlorocyclobutene afforded *trans*- $\text{Fp}-\overline{\text{CHCH=CH-CHCl}}$  V and *trans*- $\text{Fp}\overline{\text{CHCH=CHCH}}\text{Fp}$  III. Both V and III underwent quantitative thermal isomerization to the *trans,trans*-butadienes,  $\text{FpCH=CH-CH=CHCl}$  VII and  $\text{FpCH=CH-CH=CHFp}$  VI, respectively. Complex V was hydrolyzed and isomerized on neutral alumina to the *trans*-butenal complex  $\text{FpCH}_2\text{CH=CHCHO}$ . Protonation of III gave  $\text{Fp}_2\text{C}_4\text{H}_5^+$ , which was converted by triethylamine to the cyclobutenyl complex,  $\text{Fp}\overline{\text{CH-CH=CH-CH}_2}$ . Treatment of VI with  $\text{I}_2$  or  $\text{HCl}$  in methylene chloride afforded  $\text{ICH=CH-CH=CHI}$  and  $\text{Fp}_2[\text{C}_4\text{H}_6]^{+2} \cdot 2\text{HCl}_2^-$ , respectively.

### Introduction

The successful preparation of a cationic  $\eta^2$ -benzocyclobutadiene complex II via the oxidative demetalation of the binuclear benzocyclobutadiene complex I [1] suggested that the parent  $\eta^2$ -cyclobutadiene complex IV might be generated in a similar manner provided the binuclear cyclobutadiene complex III could be



prepared. The metathesis between *cis*-3,4-dichlorocyclobutene and Na[Fp] ( $[\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}]$  (NaFp)) is known to afford the binuclear butadienylene complex [2-6] VI presumably by way of intermediates V and III.



With a view toward isolating complexes III and V, the reaction between *cis*-3,4-dichlorocyclobutene and NaFp was reinvestigated. Herein are reported the results of this investigation.

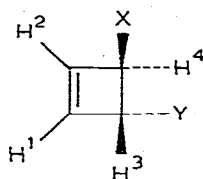
## Results and discussion

The products obtained from the reaction between NaFp and *cis*-3,4-dichlorocyclobutene are dependent upon the reaction temperature. Thus, without external cooling, the predominant product was the binuclear butadienylene complex VI admixed with lesser amounts of the mononuclear chlorobutadienyl complex VII. In contrast, the binuclear cyclobutadiene complex III was isolated in 28% yield when the reactants were mixed at  $-78^\circ\text{C}$  and immediately allowed to warm to  $0^\circ\text{C}$ . The chlorocyclobutenyl complex V, which was isolated in small amounts by the latter procedure, was obtained in reasonable yield (17%) when the reaction mixture was initially allowed to stand at  $-78^\circ\text{C}$  for 16 h.

Separation of III, V and VI was readily effected by taking advantage of the different solubility properties of each complex. Thus, V is soluble in petroleum ether, whereas III is sparingly soluble and VI is insoluble. Complex III was separated from VI by recrystallization of the mixture from carbon disulfide in which VI is only sparingly soluble.

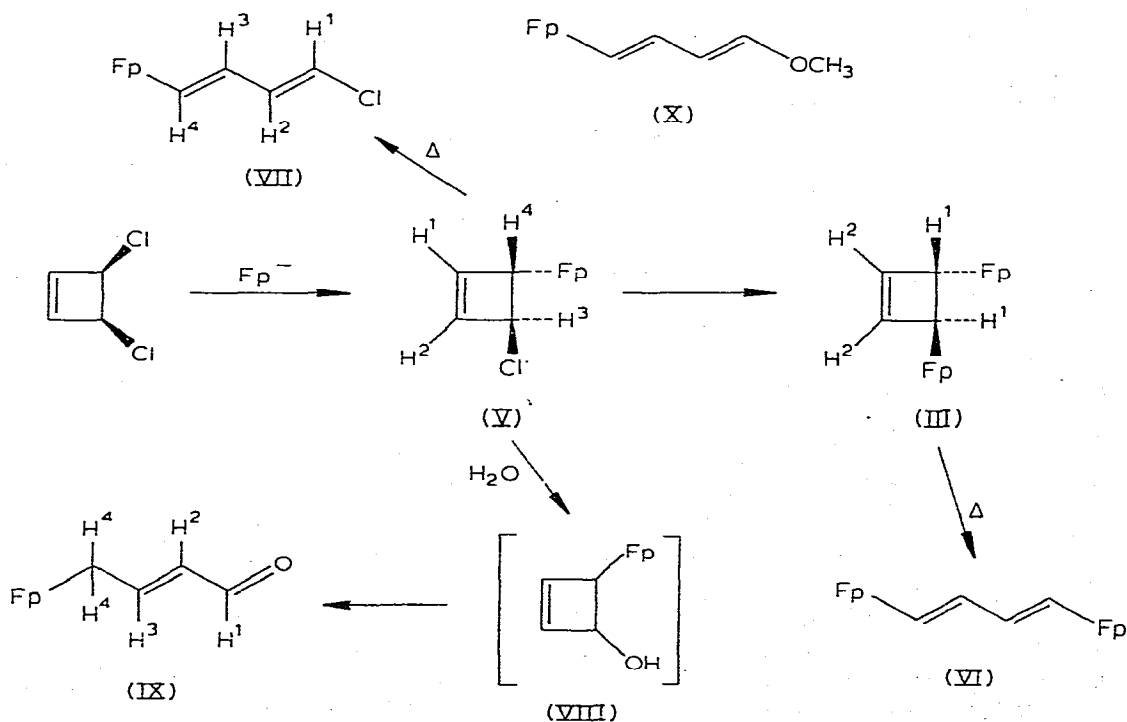
The identity of complex III was established by its PMR spectrum which exhibits a multiplet at  $\tau$  4.29, a singlet  $\tau$  5.38, and a multiplet at  $\tau$  6.33, which were assigned to the olefinic, cyclopentadienyl, and allylic protons, respectively. The observation of only two carbonyl stretching frequencies ( $1981, 1922\text{ cm}^{-1}$ ) in the IR spectrum of III supported the equivalence of the two iron groups. The *trans* stereochemistry of III was inferred by the quantitative thermal isomerization of III to VI, the structure of which has been determined by X-ray crystallography [3,4]. In the absence of special electronic effects due to the iron groups, the symmetry-allowed thermal conrotatory ring opening of III to VI requires a *trans*-substituted cyclobutene [7].

TABLE 1  
PMR DATA FOR *trans*-DISUBSTITUTED CYCLOBUTENES



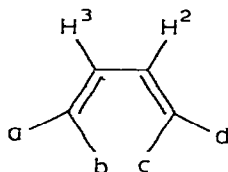
X	Y	H <sup>1</sup> ( $\tau$ )	H <sup>2</sup> ( $\tau$ )	H <sup>3</sup> ( $\tau$ )	H <sup>4</sup> ( $\tau$ )	Ref.
Cl	Cl	3.82	3.82	5.32	5.32	8
Fp	Fp	4.29	4.29	6.33	6.33	This work
Fp	Cl	3.72	4.37	5.59	6.17	This work

The assignment of the resonances of the PMR spectrum of V was based on a comparison of this spectrum with that of *trans*-3,4-dichlorocyclobutene [8] and complex III (Table 1). Thus, the resonances at  $\tau$  4.37 and  $\tau$  6.17 were assigned to the olefinic and allylic protons nearest to the Fp group whereas the resonances



at  $\tau$  3.75 and 5.59 were assigned to the olefinic and allylic protons nearest to the chlorine. The cyclopentadienyl resonance occurs at  $\tau$  5.18. The *trans*-stereochemistry of V was established by the observation of a small vicinal coupling ( $\sim 2$  Hz) between the allylic protons of the four-membered ring, and by the quantitative electrocyclic isomerization of V to the *trans,trans*-chlorobutadienyl com-

TABLE 2  
COUPLING CONSTANTS (Hz) FOR 1,4-DISUBSTITUTED 1,3-BUTADIENES

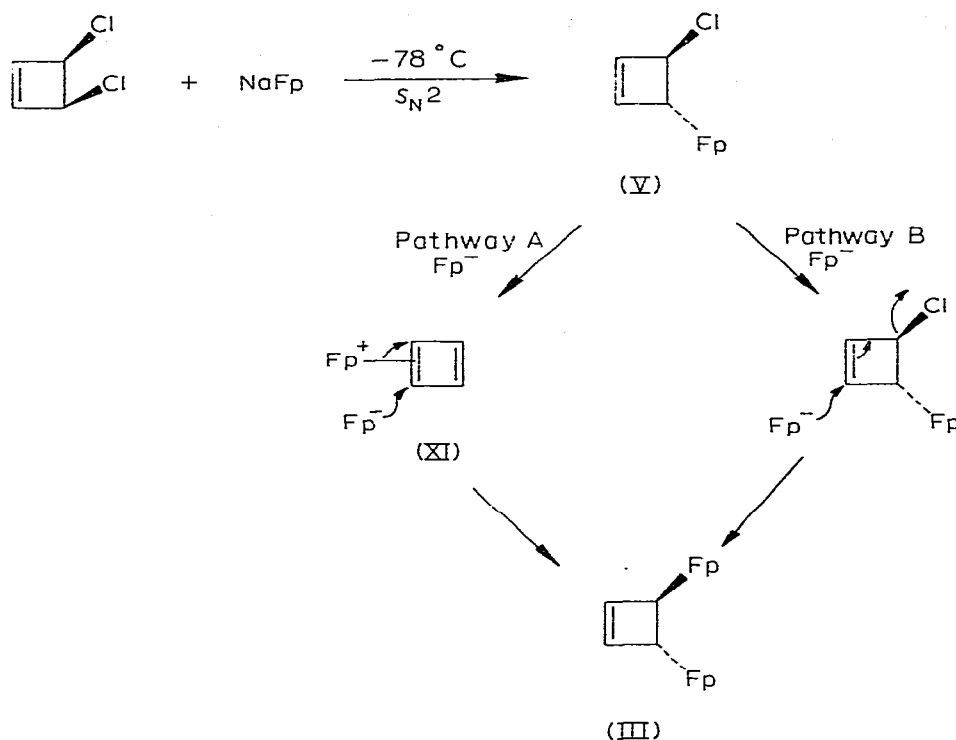


Source	Substituents				$J_{a,H^3}$	$J_{b,H^3}$	$J_{c,H^2}$	$J_{d,H^2}$	Ref.
	a	b	c	d					
—	Cl	Cl	—	7.28	—	—	7.28	10	
Cl	—	—	Cl	—	13.12	13.12	—	10	
—	Cl	—	Cl	7.28	—	13.34	—	10	
Fp	—	—	Cl	—	14.3	12.8	—	This work	
Fp	—	—	OCH <sub>3</sub>	—	14.3	13.5	—	9	
Fp	—	—	Fp	—	17	17	—	20	

plex VII. The assignment of the resonances of the PMR spectrum of VII was based on a comparison of this spectrum with that of the *trans,trans*-methoxybutadienyl complex X, the spectrum of which has been interpreted with the aid of the NMR shift reagent Eu(fod)<sub>3</sub> [9]. The *trans,trans*-stereochemistry of II was determined by comparison of the coupling constants of II with literature values for *trans,trans*-, *cis,trans*-, and *cis,cis*-1,4-dichlorobutadiene (Table 2) [10]. The carbonyl stretching frequencies (2000, 1938 cm<sup>-1</sup>) agree well with those of other neutral Fp-alkyl complexes.

The formation of V from *cis*-3,4-dichlorocyclobutene and NaFp probably occurs via an S<sub>N</sub>2 mechanism involving displacement of chloride by the potent nucleophile Fp<sup>-</sup> [11]. Two reasonable pathways exist for the transformation of V to III. Pathway A involves the ionization of V to the η<sup>2</sup>-cyclobutadiene complex XI, which is subsequently attacked by Fp<sup>-</sup> at the complexed double bond to give the *trans* binuclear complex III. The ionization of V to the η<sup>2</sup>-cyclobutadiene complex XI at -78°C is improbable considering the stability of V at room temperature, i.e. V fails to react with 1,3-diphenylisobenzofuran at room temperature, whereas XI reacts with dienes instantaneously at -78°C [9]. Furthermore, no products derived from complex XI (i.e., a *syn*-tricyclooctadiene complex or *syn*-tricyclooctadiene) were observed. An alternative mechanism, pathway B, involves attack by Fp<sup>-</sup> at the cyclobutene double bond in V and elimination of chloride via an S<sub>N</sub>2' mechanism. The S<sub>N</sub>2' mechanism has been shown to be the preferred pathway for the reaction between Fp<sup>-</sup> and allylic systems [12]. Thus, pathway B is a reasonable mechanism for the formation of complex III.

The η<sup>1</sup>-4-(3-chlorocyclobutenyl) complex V is the only example of an isolable 3-chloro-4-metallocyclobutene, and is also the first example of a stable β-chloroalkyl complex of iron. Since other potential β-chloroalkyl complexes exist only in the ionic form Fp[olefin]Cl<sup>-</sup> [13], the failure of the cyclobutenyl ligand in V to liberate Cl<sup>-</sup> indicates that formation of the cationic η<sup>2</sup>-cyclobutadiene complex XI is energetically unfavorable. The instability of XI relative to



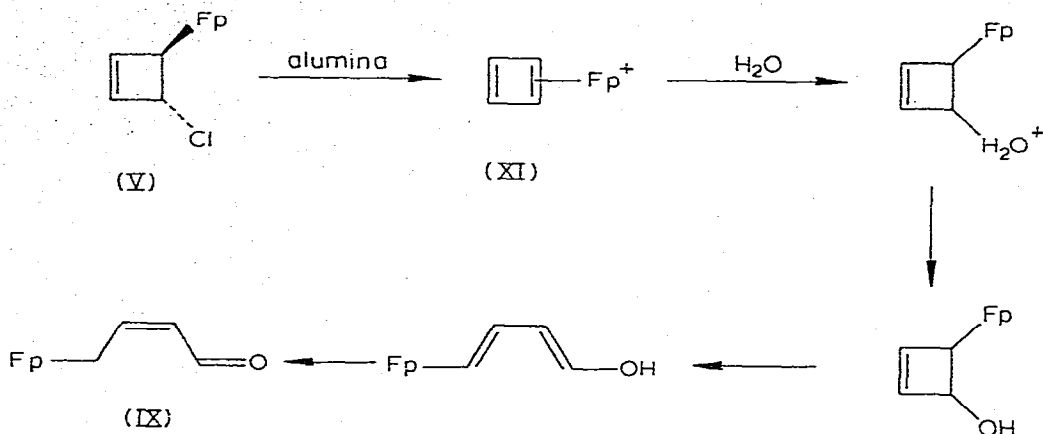
other cationic olefin complex cannot be attributed to a greater strain energy in XI as compared to V, since the strain energies of cyclobutene and cyclobutadiene are calculated to be approximately the same [14-16]. Therefore, the stability of V is interpreted as demonstrating that the  $\eta^2$ -cyclobutadiene ligand in XI is antiaromatic in the same sense as free cyclobutadiene.

Complexes III and VI, which are stable on activity I neutral alumina, may be less expeditiously separated by column chromatography. In contrast, V was quantitatively hydrolyzed and isomerized to the butenal complex IX when chromatographed. *cis*-3,4-Dichlorocyclobutene is stable under similar conditions. The PMR spectrum of IX exhibits a doublet at  $\tau$  0.71 assigned to the aldehydic proton, a singlet at  $\tau$  5.25 due to the cyclopentadienyl protons, a doublet at  $\tau$  7.85 assigned to the methylene protons adjacent to the iron group, and multiplets at  $\tau$  3.06 and  $\tau$  4.18 in the ratio of 1/5/2/1/1. Proton-proton decoupling was used to assign the multiplets at  $\tau$  4.18 and 3.06 to the H<sup>2</sup> and H<sup>3</sup> protons, respectively. The IR spectrum of IX shows carbonyl stretching absorptions at 2000 and 1940  $\text{cm}^{-1}$  (C=O) and at 1648  $\text{cm}^{-1}$  (CH=O). Recently, IX has been prepared independently [11].

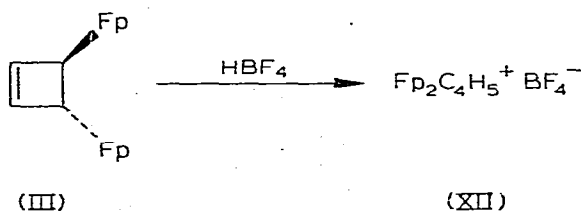
The formation of IX via the hydrolysis of V on alumina is interpreted as involving the intermediacy of the  $\eta^2$ -cyclobutadiene complex XI. Thus, alumina functions as a Lewis acid [18], abstracting the chloride from V to form XI. Water then adds to the complexed double bond of XIII. Electrocyclic ring-opening and tautomerization of the intermediate  $\beta$ -hydroxycyclobutenyl complex affords the butenal complex IX. An alternative mechanism involving direct nucleophilic displacement of the Cl group in V by water is argued against by the

observation that *cis*-3,4-dichlorocyclobutene is stable on alumina.

Protonation of complex III with fluoroboric acid in acetic anhydride afforded a cationic binuclear complex XII. The PMR spectrum of XII exhibits a



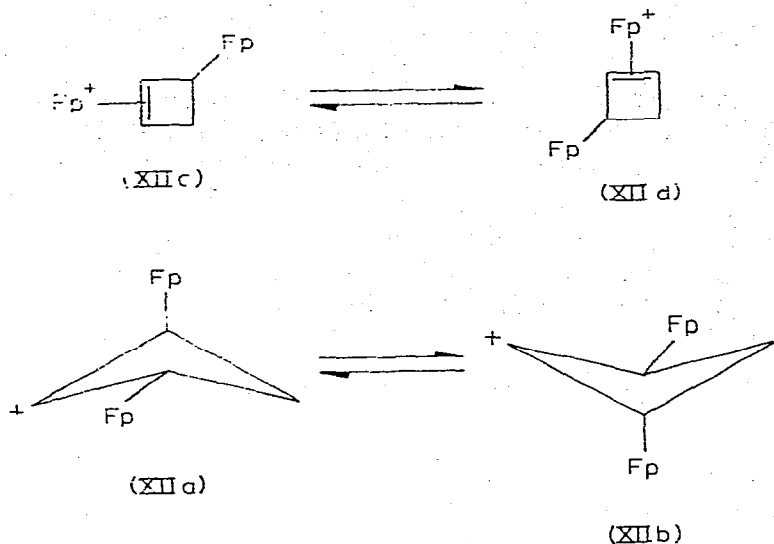
single sharp resonance of  $\tau$  4.75 for the two cyclopentadienyl rings in addition to multiplets centered at  $\tau$  3.57, 6.00, and 7.70 in the ratio of 1/2/2. The PMR spectra of XII were invariant between  $-85^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ . The IR spectrum of



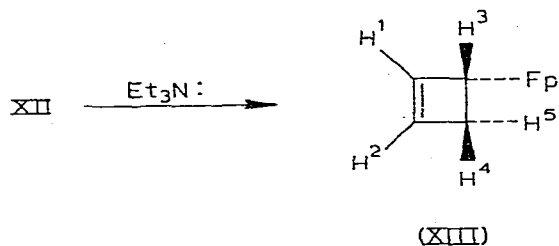
XII exhibits three carbonyl stretching bands (2050, 1998, 1935  $\text{cm}^{-1}$ ); the center band appears to be two overlapping bands. The intensity of the bands was unaltered by successive recrystallizations of XII or by changes in the technique (mull or solution) by which the IR spectra were obtained. Thus, on the IR time scale there were two nonequivalent iron groups. The IR and PMR data support a fluxional structure XIIc  $\rightleftharpoons$  XIIId. A carbenium ion structure, XIIa-XIIb, in which the pseudo-axial and pseudo-equatorial iron groups are equilibrated by puckering of the ring, would also account for these spectroscopic observations. However, the carbonyl stretching frequencies of XII are consistent with a neutral and a cationic iron group and, thereby, exclude XIIa and XIIb as a possible structure of XII.

Treatment of XII with triethylamine gave the known cyclobutenyl complex XIII [17], which was identified by comparison of the PMR spectrum of XIII with that of an authentic sample.

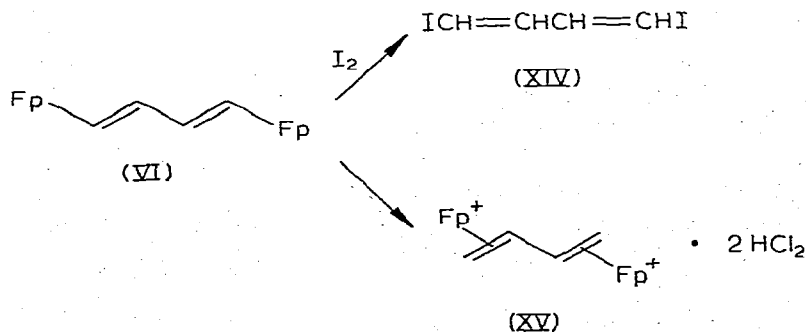
The PMR spectrum of the binuclear butadienylene complex VI exhibits, in addition to a cyclopentadienyl resonance, a sharp singlet resonance for the butadienylene protons when polar solvents such as acetone, tetrahydrofuran, or methylene chloride are used. At  $-65^{\circ}\text{C}$ , the C<sub>4</sub>H<sub>4</sub> resonance was observed to broaden in tetrahydrofuran. In aromatic solvents the expected AA'BB' pattern



was observed. The solution chemistry of VI is in accord with its formulation as a binuclear butadienylyne complex. Thus, treatment of II with iodine afforded 1,4-diiodobutadiene XIV. When treated with anhydrous hydrogen chloride, VI



was converted to the dicationic binuclear butadiene complex XV the structure of which was determined by IR spectroscopy and by its thermal decomposition to FpCl, butadiene, and hydrogen chloride. The PMR spectrum could not be obtained because of the lability of XV at low temperatures in liquid sulfur dioxide.



## Experimental

### General procedures

In general all reactions were carried out under a nitrogen atmosphere or in the vacuum line standard techniques. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

### Physical measurements

IR spectra were recorded on a Perkin—Elmer Model 180 Spectrophotometer. PMR spectra were obtained on a Jeol C-60 High Resolution Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an internal standard. Melting points are uncorrected.

### Preparation of *trans,trans*-1,4-bis( $\eta^5$ -cyclopentadienyldicarbonyliron)-1,3-butadiene (VI)

To a solution of NaFp (0.1 mol) in 250 ml of tetrahydrofuran was added rapidly 6.15 g (0.05 mol) of *cis*-3,4-dichlorocyclobutene [19] in 50 ml of tetrahydrofuran. The color of the reaction mixture darkened and the temperature rose from 24°C to 40°C. After the mixture had been cooled to 24°C, 100 ml of hexane was added and the resulting mixture was filtered through 5 cm of Celite. Rotary evaporation of the filtrate afforded a mixture of oil and crystals. The residue was dissolved in a minimum amount of tetrahydrofuran. An equal volume of pentane was added and the solution was placed in the refrigerator for several days. Large orange crystals developed which were collected by filtration yielding 13-15 g (60-70%) of the binuclear butadienylene complex VI. The latter is soluble in tetrahydrofuran, less so in methylene chloride, and *sym*-tetrachloroethane, very slightly soluble in acetone and benzene and virtually insoluble in all other common organic solvents. The PMR spectrum of VI, as determined on a saturated tetrahydrofuran solution, exhibited resonances at  $\tau$  3.76 (s, 2) and  $\tau$  5.05 (s, 5). In tetrahydrofuran at -65°C, the resonance at  $\tau$  3.76 was observed to broaden. No further change in the spectrum was observed between -65°C and -100°C, the temperature at which the solution solidified. The resonance at  $\tau$  3.76 was observed as a singlet in both methylene chloride and *sym*-tetrachloroethane. In benzene- $d_6$  the  $\tau$  3.76 resonance appeared as an AA'BB' multiplet.\* The IR spectrum (KBr) of VI showed bands at 3100 w, 2980 w, 2030 w, 2000 vs, 1950 vs, 1515 m, 1420 w, 1390 w, 1135 m, 990 m, 830 m, 595 s  $\text{cm}^{-1}$ . The IR spectrum of the carbonyl region, as determined on a saturated cyclohexane solution, showed two bands at 2016 and 1970  $\text{cm}^{-1}$ . (Found: C, 53.28; H, 3.46.  $\text{C}_{18}\text{H}_{14}\text{Fe}_2\text{O}_4$  calcd.: C, 53.3; H, 3.46%).

### The determination of the stoichiometry of the reaction between VI and hydrogen chloride and thermal decomposition of the resulting adduct XV

Methylene chloride, 5 ml, and 0.1059 g (0.262 mmol) of VI were placed in an ampule. The complex partially dissolved to form an orange solution. Hydrogen chloride, 2.25 mmol, was condensed into the ampule at -196°C. The ampule was closed to the vacuum line and allowed to warm to 24°C. The color of the mixture turned to a deep red and then rapidly to yellow concomitant with the precipitation of a yellow solid. After the precipitation of the yellow solid, the

\* The coupling constants have been determined [20].



ampule was cooled to  $-78^{\circ}\text{C}$  and the volatile components were distilled through a trap at  $-112^{\circ}\text{C}$  into a trap at  $-196^{\circ}\text{C}$  where residual hydrogen chloride was collected. The methylene chloride that collected in the  $-112^{\circ}\text{C}$  trap was redistilled in a similar manner until the vapor pressure at  $0^{\circ}\text{C}$  had become constant. Thus, 1.19 mmol of hydrogen chloride was collected. Remaining in the ampule was 0.1414 g of a yellow solid, a 98% yield based on the formation of this material as  $\text{FpC}_4\text{H}_6 \cdot 2\text{HCl}_2$ . The yellow solid was allowed to stand at  $24^{\circ}\text{C}$ , part of the time in the dark, for 7 days. At the end of this time the solid had become a deep red. The volatile products were distilled into a  $-196^{\circ}\text{C}$  trap where 0.700 mmol of product (a 92% yield based on formation of 2 mmol of hydrogen chloride per mmol of butadiene) was collected. The butadiene and hydrogen chloride were separated by repeated distillation through a  $-160^{\circ}\text{C}$  trap. The butadiene collected in the  $-160^{\circ}\text{C}$  trap was separated from a small amount of less volatile material by distillation through a  $-112^{\circ}\text{C}$  trap. Butadiene, 0.226 mmol, (87%) was recovered and identified by comparison of its IR spectrum to the published spectrum [21]. Hydrogen chloride, 0.412 mmol (79%), was recovered; v.p.  $-122^{\circ}\text{C}/122$  mm (lit.  $-111.8^{\circ}\text{C}/125$ ). In the ampule there remained 0.112 g (92%) of  $\text{FpCl}$ , m.p.  $85-87^{\circ}\text{C}$  (lit. [23]  $84-87^{\circ}\text{C}$ ).

*The reaction between VI and hydrogen chloride in methylene chloride. The characterization of the yellow solid XV*

Hydrogen chloride was bubbled through a suspension of VI, 1 g (2.46 mmol) in 20 ml of methylene chloride. Initially, the mixture became a deep red and the complex dissolved. Within a few minutes a yellow solid precipitated and the supernatant liquid became a very pale yellow. The mixture was filtered; the residue washed several times with methylene chloride, and then dried quickly by the passage of dry nitrogen over the solid. The yellow solid XV, 1 g, decomposed to a deep red solid within minutes at  $24^{\circ}\text{C}$ . The yellow solid decomposed immediately with the evolution of gas upon the addition of water. It was, however, stable indefinitely at  $-78^{\circ}\text{C}$ . The PMR spectrum of XV, determined on a liquid sulfur dioxide solution, initially exhibited resonances at  $\tau$  3.25, 4.05, 4.25, 4.70, 4.80, 4.96. The sample was rapidly decomposing as shown by the change in the intensities of the various resonances after several minutes. After 24 h the spectrum exhibited a broad resonance centered at  $\tau$  4.5, a singlet at  $\tau$  4.96 and another somewhat broader resonance centered at  $\tau$  7.67. The IR spectrum (KBr) of the yellow solid showed bands at 3500-3000 w, 3045, 2087 s, 2060 s, 1800-1600 m, 1500 vw, 1435 m, 1260 vw, 1250-900 w, 1148 vw, 1005 m,w, 880 m, 590 m, 553 m, 475 w, 390 w  $\text{cm}^{-1}$  (Found: C, 38.62; H, 4.51; Cl, 23.06.  $\text{C}_{13}\text{H}_{16}\text{Cl}_4\text{Fe}_2\text{O}_4$  calcd.: C, 39.15; H, 3.36; Cl, 25.76%.)

*The reaction between VI and iodine*

VI, 1 g (2.47 mmol), and 1.25 g (4.94 mmol) of iodine were added to 20 ml of tetrahydrofuran and allowed to stand at  $24^{\circ}\text{C}$  for 15 h. Rotary evaporation of the solution afforded a dark residue with a sarsaparilla-like odor. The residue was extracted with 10 ml of carbon tetrachloride and the extract was chromatographed on 40 g of neutral alumina using carbon tetrachloride as the eluent. A very pale yellow fraction was initially collected. Rotary evaporation of the solvent afforded 0.6 g of a virtually colorless oil, the PMR spectrum of which exhibited a multiplet resonance between  $\tau$  3.0 and 4.0. Thin layer chromato-

graphy showed the oil to be essentially one compound with a trace of two others. Two more crystallizations from hexane yielded analytically pure 1,4-diiodobutadiene XIV: mp. 87-88°C; PMR ( $\text{CCl}_4$ )  $\tau$  3.0-4.0 (m, AA'BB'); IR (KBr) 3040 m, 1150 m, 1390 m, 1150 m, 960 m, 710 w, 635 w; UV (EtOH), 2655 Å,  $\epsilon$   $2.74 \times 10^4$ , 2604 Å,  $\epsilon$   $2.86 \times 10^4$ , 2280 Å,  $\epsilon$   $6.57 \times 10^3$  (Found: C, 15.93; H, 1.22; I, 83.30. calcd.:  $\text{C}_4\text{H}_4\text{I}_2$  C, 15.72; H, 1.31; I, 83.10%.) XIV was unstable at room temperature and decomposed to a red oil over a period of several days.

*Preparation of trans-3,4-bis( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene III*

To a solution of 3.0 g (0.024 mol) of *cis*-3,4-dichlorocyclobutene in 10 ml of tetrahydrofuran at  $-78^\circ\text{C}$  was added a solution of NaFp (0.061 mol) in 100 ml of tetrahydrofuran. After 10 min the reaction mixture was allowed to warm to  $0^\circ\text{C}$  and was filtered through 5 cm of Celite, which was washed twice with 25 ml of tetrahydrofuran. The solvent was evaporated by passing a stream of nitrogen through the solution until crystals formed. The solution was stored at  $0^\circ\text{C}$  overnight. Large diamond-shaped crystals of VI 1.3 g (13%), were collected by filtration and washed with petroleum ether and  $\text{CS}_2$ . The filtrate was evaporated and cooled by passing nitrogen through the solution to yield 2.8 g (28%) of *trans*-3,4-bis( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene III. III was further characterized by its quantitative isomerization of VI (vide infra). III: PMR ( $\text{CS}_2$ )  $\tau$  4.29 (m, 2,  $\text{H}^2$ ), 5.38 (s, 10, Cp), 6.33 (m, 2,  $\text{H}^1$ ); IR (Nujol) 1981, 1922  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).

*Preparation of trans-3-chloro-4-( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene V*

To a solution of 5.0 g (0.04 mol) of *cis*-3,4-dichlorocyclobutene in 11 ml of tetrahydrofuran at  $-78^\circ\text{C}$  was added a solution of NaFp (0.04 mol) in 108 ml of tetrahydrofuran. The reaction mixture was allowed to stand for 16 h at  $-78^\circ\text{C}$  before warming to  $24^\circ\text{C}$ . After the tetrahydrofuran had been removed in vacuo from the reaction mixture, the resulting residue was extracted three times with 25 ml of petroleum ether and the extract was evaporated by passing a stream of nitrogen through the solution. The residue was taken up in petroleum ether and filtered. The chlorocyclobutenyl complex V (1.9 g, 17.8%) was collected by fractional crystallization of the petroleum ether filtrate at  $-78^\circ\text{C}$ . The residue was then extracted with  $\text{CS}_2$  to yield 2.7 g (16.4%) of the binuclear cyclobutadiene complex III. V: mp. 65-67°C; PMR ( $\text{CS}_2$ )  $\tau$  3.72 (m, 1,  $\text{H}^1$ ), 4.37 (m, 1,  $\text{H}^2$ ), 5.18 (s, 5, Cp), 5.59 (m, 1,  $\text{H}^3$ ), 6.17 (m, 1,  $\text{H}^4$ ); IR (Nujol) 2000, 1950  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ) (Found: Fe 21.35.  $\text{C}_{11}\text{H}_9\text{ClFeO}_2$  calcd.: Fe 21.11%.)

*Thermal isomerization of trans-3,4-bis( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene III to VI*

A solution of 0.512 g (1.26 mmol) of III and 50 ml of toluene was refluxed for 1 h, allowed to cool to  $24^\circ\text{C}$ , and rotary evaporated to yield 0.5089 g (99.2%) of VI, which was identified by comparison of its PMR spectrum to that of an authentic sample.

*Thermal isomerization of trans-3-Chloro-4-( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene V to VII*

A solution of 0.527 g (1.98 mol) of V and 50 ml of toluene was refluxed

for 1 h, allowed to cool to 24°C and rotary evaporated to yield 0.4790 (95.0%) of *trans,trans*-1-chloro-4-( $\eta^5$ -cyclopentadienyldicarbonyliron) butadiene VII: PMR (CS<sub>2</sub>)  $\tau$  2.98 (d, 1, H<sup>1</sup>,  $J_{1,2} = 14.3$  Hz), 3.81 (m, 2, H<sup>2</sup> and H<sup>3</sup>), 4.35 (d, 1, H<sup>4</sup>,  $J_{3,4} = 12.8$  Hz), 5.27 (s, 5, Cp); IR (neat) 2003, 1947 cm<sup>-1</sup> (C=O); mass spectrum (70 eV) parent peak at  $m/e$  264. (Found: C, 51.31; H, 4.62; Cl, 11.70. C<sub>11</sub>H<sub>9</sub>ClFeO<sub>2</sub> calcd.: C, 50.0; H, 3.4; Cl, 13.9%.)

*Reaction of trans-3-chloro-4-( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene V with alumina*

A benzene solution, 5 ml, of V (0.489 g, 1.85 mmol) was chromatographed on alumina (neutral, activity I, 3.5 × 4 cm). The column was eluted with benzene and then 5% methanol in benzene. Rotary evaporation of the yellow eluate afforded 0.342 g (75%) of the butenal complex, IX. The spectroscopic properties of IX are identical to those of an authentic sample [17]. Proton-proton decoupling was used to assign the multiplets at  $\tau$  3.06 and 4.18: PMR (CS<sub>2</sub>)  $\tau$  0.71 (d, 1, H<sup>1</sup>,  $J_{1,2} = 7.5$  Hz), 3.06 (m, 1, H<sup>3</sup>,  $J_{3,4} = 9$  Hz), 4.18 (m, 1, H<sup>2</sup>,  $J_{2,3} = 15$  Hz), 5.25 (s, 5, Cp) 7.85 (d, 2, H<sup>4</sup>); IR (neat) 2000, 1940 cm<sup>-1</sup> (C=O); 1648 cm<sup>-1</sup> (CH = 0).

*Protonation of trans-3,4-bis( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene III*

A cold solution of 1.5 ml of fluoroboric acid in 15 ml of acetic anhydride was added dropwise to 1.515 g (1.26 mmol) of III in a 125 ml erlenmeyer flask at -78°C. After the mixture had been warmed to 24°C, 20 ml of diethyl ether was added, and the resulting mixture was filtered to yield an unidentified yellow solid. After the addition of petroleum ether to the filtrate 0.1250 g (20.1%) of XII was collected by filtration as orange crystals. The PMR spectrum of XII in CD<sub>3</sub>COCD<sub>3</sub> was invariant between 24°C and -85°C. XII: PMR (CD<sub>3</sub>NO<sub>2</sub>)  $\tau$  3.57 (m, 1, H<sup>1</sup>), 4.75 (s, 10, Cp), 6.00 (m, 2, H<sup>2</sup> and H<sup>3</sup>), 7.70 (m, 2, H<sup>4</sup>); IR (Nujol) 2050, 1998, 1935 cm<sup>-1</sup> (C≡O). (Found: Fe, 22.30. C<sub>18</sub>H<sub>15</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>4</sub> calcd.: Fe 22.63%.)

*Reaction of XII with triethylamine.*

Triethylamine, 0.2 ml, was added to a 50 ml flask containing 0.117 g (0.236 mmol) of XII in 15 ml of methylene chloride at -78°C. The flask was stoppered and allowed to warm to 24°C. The solvent was evaporated by passing a stream of nitrogen through the solution. The residue was taken up in petroleum ether and filtered. The filtrate was evaporated to yield 0.0315 g (58%) 3-( $\eta^5$ -cyclopentadienyldicarbonyliron)cyclobutene XIII which was identified by comparison of its PMR spectrum with that of an authentic sample [17]: PMR (CS<sub>2</sub>)  $\tau$  3.69 (m, 1, H<sup>1</sup>,  $J_{1,2} = 2.3$  Hz), 4.23 (m, 1, H<sup>2</sup>), 5.25 (s, 5, Cp), 6.12 (m, 1, H<sup>3</sup>,  $J_{3,4} = 3.7$  Hz), 6.96 (m, 1, H<sup>4</sup>,  $J_{4,5} = 14.7$  Hz), 7.66 (m, 1, H<sup>5</sup>).

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