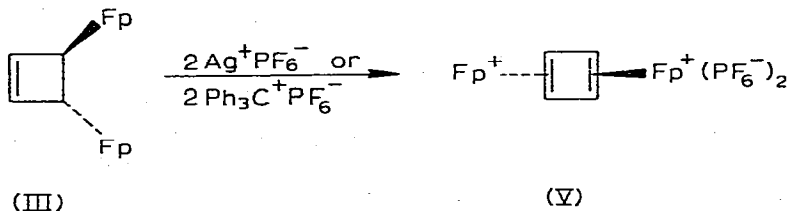


aration of II, the oxidative demetalation of the binuclear complex I by Ph_3C^+ , also was unusual and appeared to offer an entry into η^2 -cyclobutadiene complexes provided the binuclear complex III was available. With the preparation of III as our goal, we reinvestigated the reaction between *cis*-3,4-dichlorocyclobutene and NaFp [2] and found it to give not only III but also the novel 3-chlorocyclobutenyl complex IV. Herein we report the generation and characterization of the first η^2 -cyclobutadiene complexes*.

Results

When methylene chloride solutions of the binuclear cyclobutadiene complex III and trityl hexafluorophosphate or silver hexafluorophosphate were mixed at -78°C and warmed to 24°C , the binuclear cyclobutadiene complex V was formed in 56 or 35% yield respectively, as a bright yellow, methylene chloride-insoluble, air-stable solid. Complex V was further purified by recrystallization from nitromethane.



The structure of V was established by consideration of its spectroscopic and chemical properties. Thus, the equivalence of the two iron groups is indicated by the presence of a ten proton singlet resonance at τ 4.26 in the PMR spectrum of V, which occurs in a region characteristic of cationic complexes of the type $\text{Fp}[\text{alkene}]^+$, and by the observation of two metal carbonyl bands (2080 and 2040 cm^{-1}) in the IR spectrum of V (Table 1). The only additional resonance in the PMR spectrum of V is a four proton singlet at τ 4.53, which was assigned to the equivalent protons of the four-membered ring. The proton decoupled ^{13}C NMR spectrum of V exhibits three singlet resonances at 206.0, 92.8, and 74.8 ppm downfield from tetramethylsilane, which were assigned to the car-

TABLE 1
SPECTROSCOPIC DATA FOR $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}[\text{alkene}]^+$ COMPLEXES

Olefin	$\nu(\text{C}=\text{O})$ (cm^{-1})	$\eta^5\text{-C}_5\text{H}_5$ (τ , ppm)
$\text{CH}_2=\text{CH}_2^a$	2083, 2049	4.34 ^b
$\text{CH}_3\text{CD}=\text{CH}_2^c$	2089, 2055 ^d	4.40 ^b
$\text{PhCH}=\text{CH}_2^e$	2082, 2040 ^d	4.13 ^f
V	2085, 2040 ^d	4.26 ^g

^a Ref. 3. ^b SO_2 solution. ^c Ref. 7. ^d Nujol mull. ^e Ref. 4. ^f Acetone- d_6 solution. ^g Nitromethane- d_3 solution.

* Part of this work has appeared in preliminary communications [2b,c].

TABLE 2

THE ^{13}C NMR DATA (ppm downfield from tetramethylsilane) FOR $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}[\text{alkene}]^+$ COMPLEXES

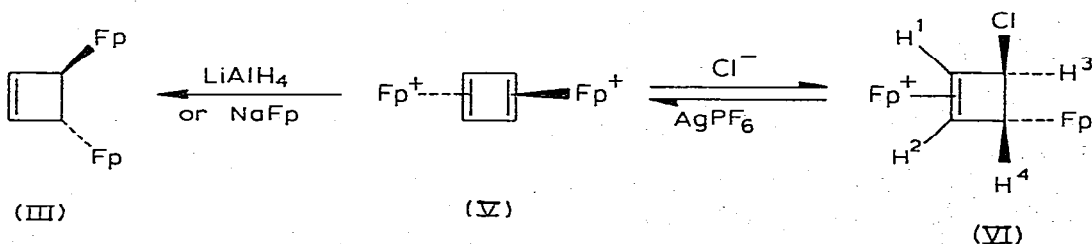
	$\text{Fp}^+ \begin{array}{ c } \hline \square \\ \hline \end{array} \text{Fp}^+$ (V)	$\text{Fp}^+(\text{CH}_2=\text{CH}_2)^{b,c}$	$\text{Fp}^+(\text{CH}_2=\text{CHPh})^{c,e}$	$\text{Fp}^+(\text{CH}_2=\text{CHCH}_3)^{b,e}$
C=O	206.0	209.5	209	—
C ₅ H ₅	92.8	90.1	90.4	91.3
C ₄ H ₄	74.8	—	—	—
CH ₂ =	—	56.8	48.7	58.0
=CH	—	—	85.6	88.8
Ph	—	—	128	—
CH ₃	—	—	—	24

^aCF₃CO₂D. ^bRef. 5. ^cCD₃NO₂. ^dRef. 6. ^eCDCl₃.

bonyl, cyclopentadienyl, and cyclobutadiene carbons, respectively. The ^{13}C chemical shifts compare well with the values reported for other $\text{Fp}[\text{alkene}]^+$ complexes (Table 2). The proton coupled ^{13}C NMR spectrum of V exhibited a singlet for the carbonyl groups; however, the resonances attributed to the cyclopentadienyl and cyclobutadiene ligands are both split into doublets (J 178 and 182 Hz, respectively).

In contrast to the LiAlH_4 reduction of the η^2 -benzocyclobutadiene complex II [2] and other $\text{Fp}[\text{alkene}]^+$ complexes [7], this reagent did not add hydride to V, but rather effected a two-electron reduction of V to III. Similarly, NaFp , which is known to liberate the olefin from $\text{Fp}[\text{olefin}]^+$ complexes (vide infra), also reduced V to III. When V was treated with NaFp in the presence of 1,3-diphenylisobenzofuran, the Diels–Alder adduct of cyclobutadiene and 1,3-diphenylisobenzofuran was not observed.

Although V is a dicationic complex, neither iron appears to be labile. Thus, treatment of V with benzyltriethylammonium chloride afforded the chloride addition product VI. Complex VI is stable in solution when kept below 20°C, but at higher temperatures decomposes to FpCl and other products (vide infra). Treatment of VI with silver hexafluorophosphate regenerated V in 58% yield. The structure of VI was established by consideration of its spectroscopic properties. The assignment of the resonances in the PMR spectrum of VI was

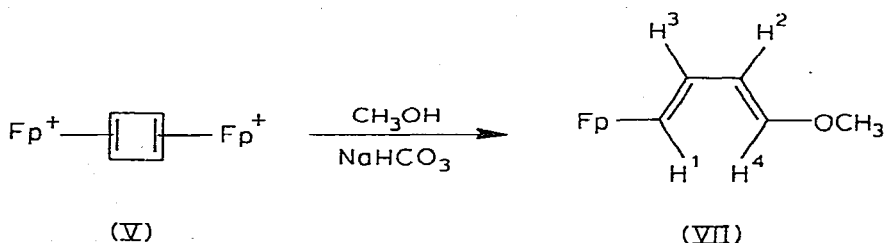


based on comparison with the spectrum of IV, assuming that complexation of the double bond in IV would have no effect on the sequence of the chemical shifts of the protons. The singlet resonances at τ 4.23 and 4.98 were assigned to

the cyclopentadienyl protons of the cation and neutral iron groups, respectively.

The narrow multiplets in the PMR spectrum of VI were assigned as follows: 3.20 (H(1)), 4.98 (H(2)), 5.46 (H(3)), and 6.57 (H(4)). The *trans*-stereochemistry was inferred from the narrow multiplets for H(3) and H(4) indicative of a small vicinal coupling ($J_{3,4} \sim 1$ Hz). The IR spectrum of VI shows two sets of carbonyl stretching absorptions; one at 2060 and 2025 and the other at 2000 and 1944 cm^{-1} in agreement with the values obtained for other Fp-alkyl complexes and Fp[alkene]⁺ complexes.

The methoxybutadienyl complex VII was obtained by reaction of V with a mixture of methanol and sodium bicarbonate. The *trans,trans*-stereochemistry was based on comparison of the coupling constants of the PMR spectrum of VII with the values for other 1,4-disubstituted 1,3-butadienes [8]. The NMR shift reagent Eu(fod)₃, was used to assign the protons of the PMR spectrum of VII.



The reaction between η^1 -4-(3-chlorocyclobutenyl)- η^5 -cyclopentadienyldicarbonyliron (IV) and silver hexafluorophosphate in the presence of dienes (cyclopentadiene and 1,3-diphenylisobenzofuran) was investigated. Although IV failed to react with cyclopentadiene in methylene chloride at 25°C over a 4 h period, a rapid reaction ensued when a methylene chloride solution of IV was added to a mixture of silver hexafluorophosphate and excess cyclopentadiene in methylene chloride at -78°C. A 58% yield of the cationic complex VIII of *syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene was obtained. The failure to observe a high field resonance ($\sim \tau$ 9.3) which is characteristic of Fp(norbornadiene)⁺ [9] and Fp(norbornylene)⁺ [10] complexes, in the PMR spectrum of VIII indicated that the iron was bonded to the double bond of the four-membered ring (Table 3).

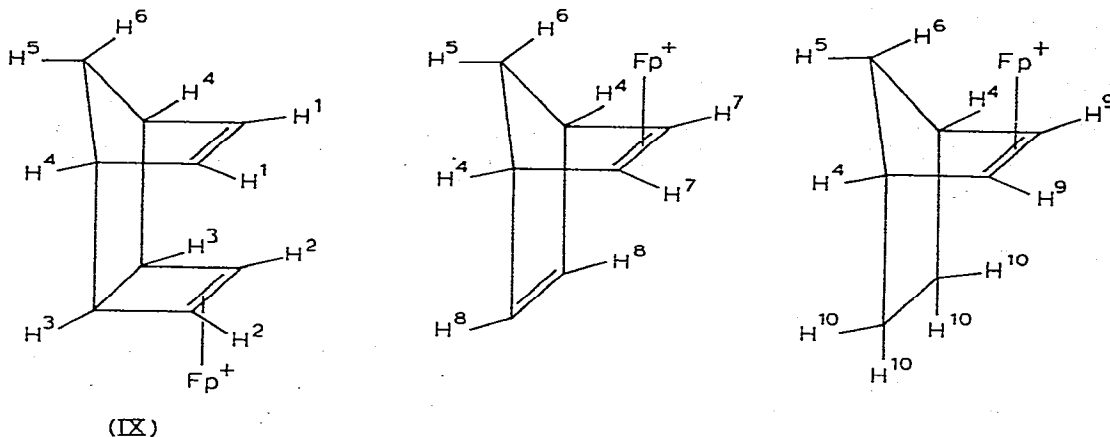
Complex VIII was further characterized by reductive demetalation of VIII with NaFp to afford *syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (IX). The PMR spectrum of IX was identical to an PMR spectrum of an authentic sample of IX prepared by the oxidative degradation of cyclobutadiene tricarbonyliron in the presence of cyclopentadiene [11].

Addition of IV to a mixture of silver hexafluorophosphate and 1,3-diphenylisobenzofuran gave a 2.5% yield of complex X, which upon treatment with NaFp afforded the known Diels-Alder adduct XI [12] of 1,3-diphenylisobenzofuran and cyclobutadiene. The low yield of X is probably due to the insolubility of 1,3-diphenylisobenzofuran in methylene chloride at -78°C.

When a methylene chloride solution of silver hexafluorophosphate was added slowly to a methylene chloride solution of IV at -78°C, the binuclear *syn*-tricyclooctadiene complex XII was obtained in 29% yield. The PMR spectrum of XII exhibits narrow multiplets at τ 4.21 and 7.05 and a singlet at τ 4.30 in a

TABLE 3

COMPARISON OF THE PMR DATA (τ , ppm) OF THE 3,4-*syn*-TRICYCLO[4.2.1.0^{2,5}]NONA-3,7-DIENE, NORBORNADIENE, AND NORBORNYLENE COMPLEXES OF $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}^+$



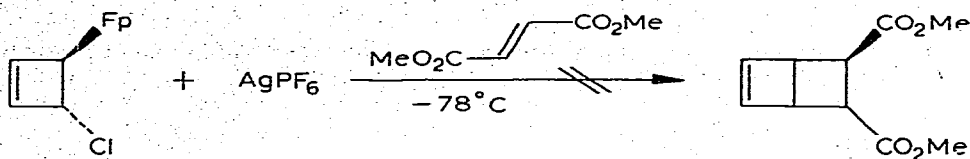
Cp	4.20	4.36	4.28
H(1)	3.60	—	—
H(2)	4.38	—	—
H(3)	7.01	—	—
H(4)	7.25	6.43	7.13
H(5)	8.09	8.16	8.18
H(6)	8.25	9.43	9.23
H(7)	—	3.98	—
H(8)	—	3.20	—
H(9)	—	—	6.84
H(10)	—	—	8.79

ratio of 4/4/10 which were assigned to the olefinic, allylic, and cyclopentadienyl protons, respectively. Decoupling of the multiplet at τ 7.05 caused the narrow multiplet at τ 4.21 to sharpen to a singlet, indicating that the protons at τ 7.05 and 4.21 are spin-spin coupled. The IR carbonyl stretching absorptions (2080, 2035 cm^{-1}) are in agreement with the values for other $\text{Fp}[\text{alkene}]^+$ complexes (Table 1). Treatment of XII with NaFp afforded the known *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (XIII) [12,13].

The slow addition of a benzene solution of IV to a stirred benzene/methylene chloride (1/1) solution of silver hexafluorophosphate afforded an unidentified gray-white solid which exhibited a sharp resonance at τ 6.07 in the NMR spectrum (CD_3NO_2).

When IV was treated with silver hexafluorophosphate in the presence of the electrophilic dienophile, dimethyl fumarate, no consumption of the dienophile was observed by comparison of the ratio of nitrobenzene (internal standard) to dimethyl fumarate in PMR spectra taken before and after the reaction (0.89/1.00 compared to 0.91/1.00).

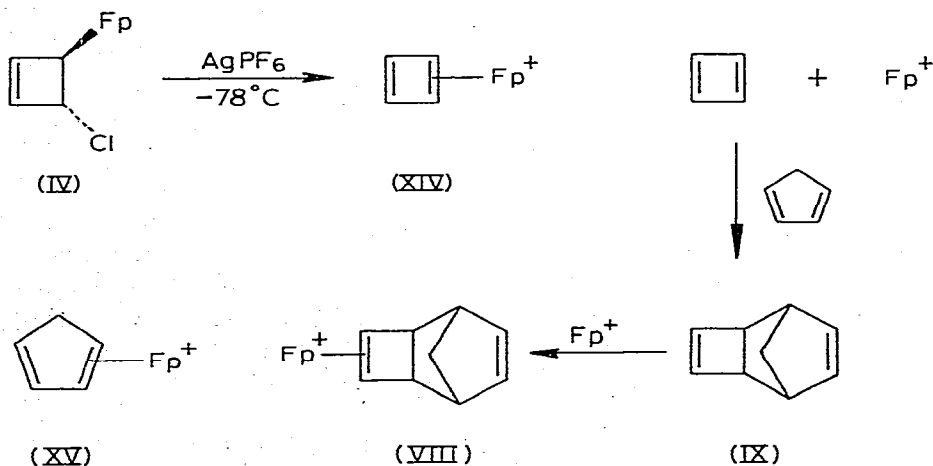
Decomposition of the binuclear complex VI in a methylene chloride solution of 1,3-diphenylisobenzofuran at 24°C overnight afforded the Diels-Alder adduct X. Subsequent reductive demetalation of X gave XI in 48% yield. Under similar



conditions, neither IV nor V reacted with 1,3-diphenylisobenzofuran. The olefin salt, $\text{Fp}[\text{CH}_2\text{CH}_2]^+\text{BF}_4^-$ failed to react with 1,3-diphenylisobenzofuran under these conditions.

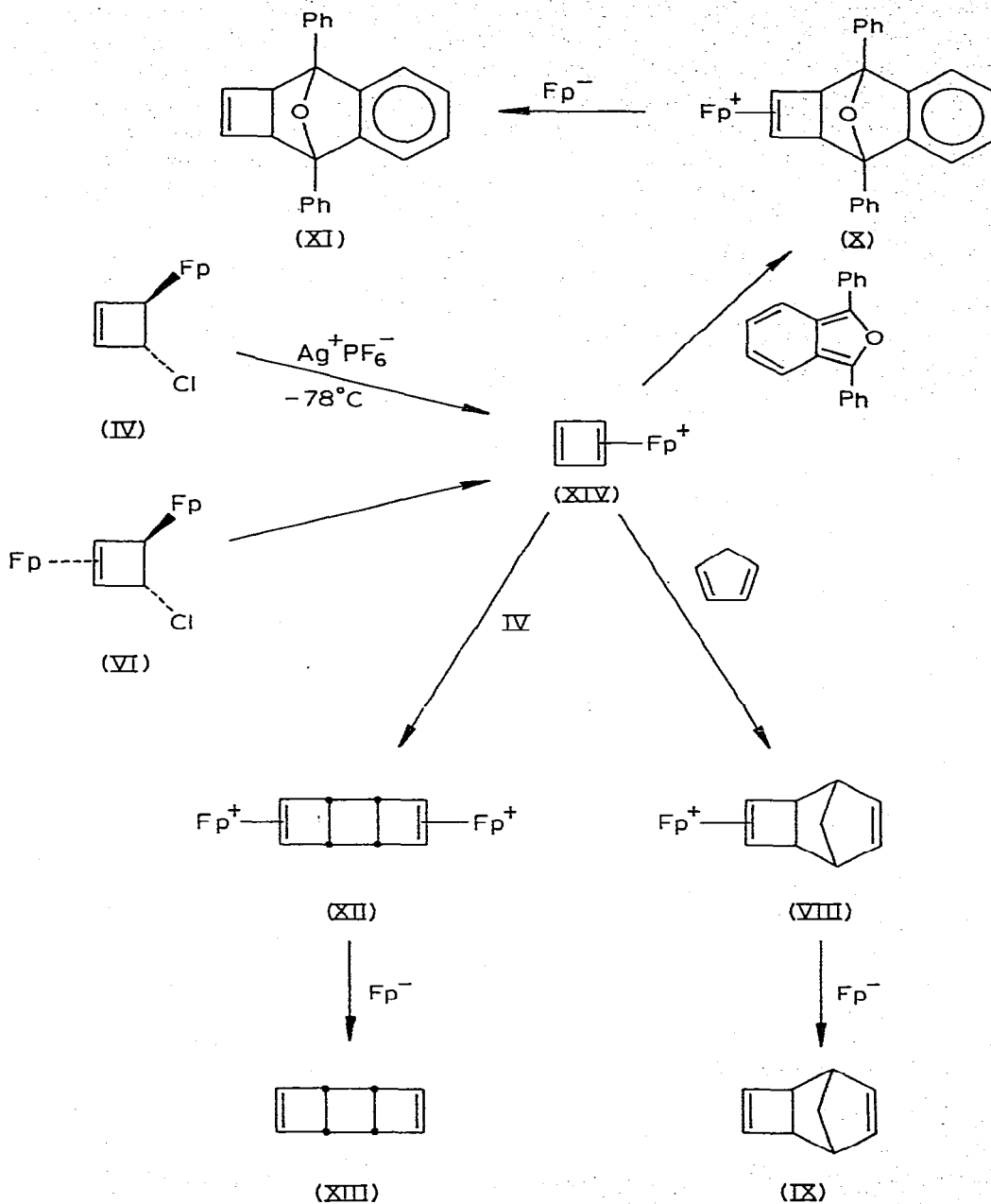
Discussion

The formation of the cycloadducts VIII, X, and XII is strong evidence in support of the intermediacy of a reactive η^2 -cyclobutadiene complex XIV, generated via β -chloride abstraction from complex IV (Scheme 1). An alternative mechanism for the formation of VIII, X, and XII involving the generation of free cyclobutadiene would require dissociation of XIV followed by cycloaddition to form the Diels-Alder adducts IX, XI, and XIII, and subsequent recomplexation of the adducts by Fp^+ , as shown below. This mechanism is untenable for several reasons. Displacement of the olefin ligand from $\text{Fp}[\text{olefin}]^+$ involves a rate-determining dissociative step with an activation energy of 16-25 kcal [14].



Cyclobutene ligands are relatively nonlabile and complex XII, although dicationic, failed to react with iodide over a period of several hours at 24°C. Cyclobutadiene should be a better donor ligand than cyclobutene derivatives and therefore, cyclobutadiene should form a less labile iron-olefin bond than XII. This assumption is reasonable since the ionization potentials of cyclobutadiene, cyclobutene, and Fp are 8.5 eV [15], 9.34 eV [16], and 7.7 eV [17], respectively. Since the smaller the energy difference between the interacting orbitals of the metal and the ligand the stronger the metal-ligand bond, Fp would be predicted to form a stronger bond with cyclobutadiene than with cyclobutene. Thus, it is unlikely that XIV would dissociate at -78°C. The generation of Fp^+

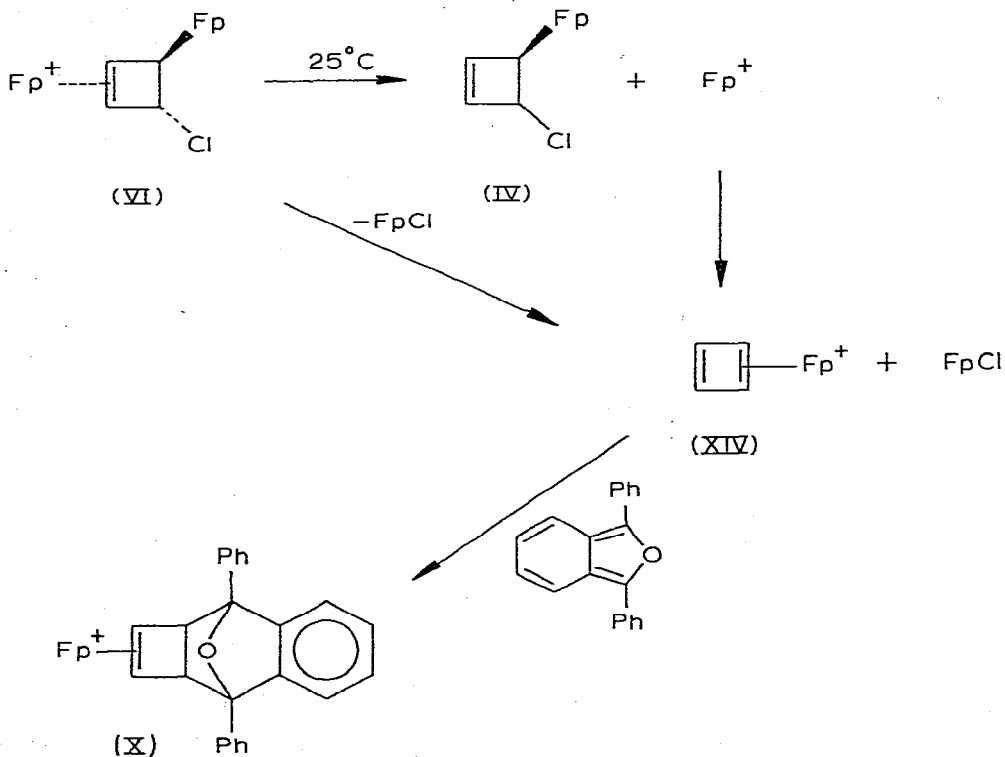
SCHEME 1.

Reactions of η^2 -cyclobutadiene- η^5 -cyclopentadienyldicarbonyliron hexafluorophosphate.

in the presence of cyclopentadiene would be expected to yield, in addition to VIII, the cyclopentadiene complex XV, which is not observed. In contrast to cyclobutadiene which reacts with electrophilic dienophiles to give Diels-Alder adducts [18-20] IV failed to yield a Diels-Alder adduct with dimethylfumarate when treated with silver hexafluorophosphate. Hence, it is reasonable to assume

that cyclobutadiene is not involved in the reactions of IV with silver hexafluorophosphate.

The thermal decomposition of the binuclear complex VI also generated XIV, which was trapped by 1,3-diphenylisobenzofuran as the Diels–Alder adduct X. The failure of both IV and V to react with 1,3-diphenylisobenzofuran under similar conditions argues against the intermediacy of these complexes in the formation of X. Also, the possibility that VI directly reacted with 1,3-diphenylisobenzofuran may be excluded by the observation that other olefin complexes, such as $\text{Fp}[\text{ethylene}]^+$, failed to react with 1,3-diphenylisobenzofuran. Thus, the only reasonable mechanism to account for the formation of XI from VI and 1,3-diphenylisobenzofuran involves the decomposition of VI via the stepwise or concerted elimination of FpCl , to form XIV, which then reacts with 1,3-diphenylisobenzofuran to afford XI. This mode of generation of XIV does not involve silver hexafluorophosphate and thereby militates against the involvement of a silver-complexed intermediate or a silver-catalyzed reaction in the formation of cyclo-adducts VIII, X, and XII from IV.

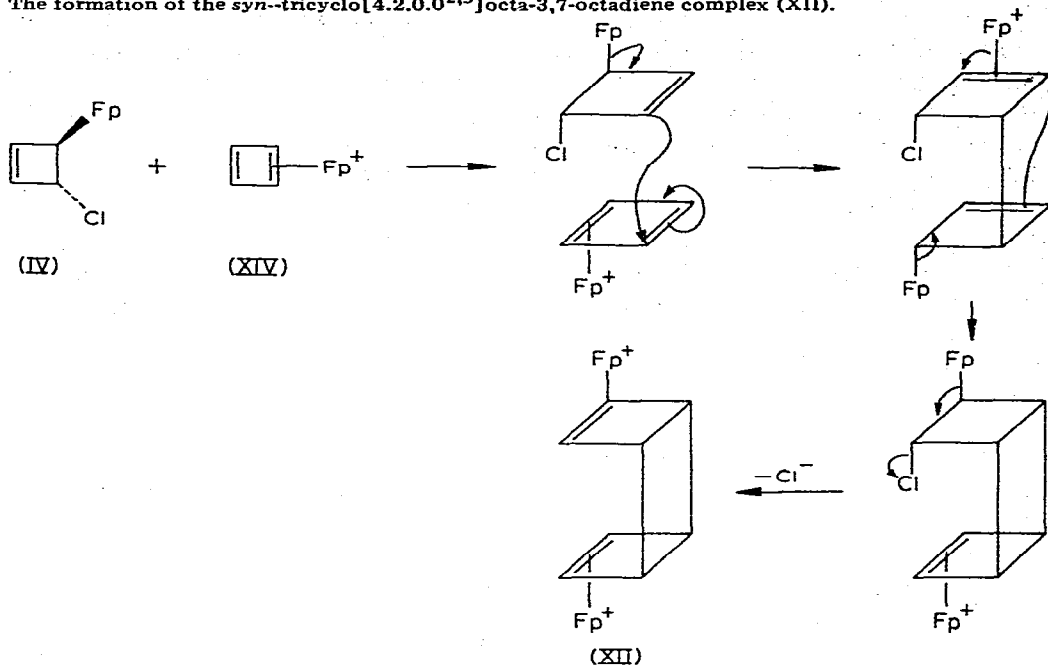


The formation of the *syn*-tricyclooctadiene complex XII could be accounted for by the dimerization of XIV, however there is reason to believe that this is not the case. Complex XII was only observed when a solution of silver hexafluorophosphate was added to a solution of IV. The inverse addition did not yield XII but rather gave an incompletely characterized substance. In both of these reactions, the maximum concentration of XIV should be similar and therefore XII should be observed in both instances if XIV were dimerizing. The fact

that XII is only observed in the first experiment strongly suggests that XIV is reacting, as it is formed, with IV. Therefore the formation of XII may be accounted for by a sequence of metal assisted additions involving XIV and IV as outlined in Scheme 2.

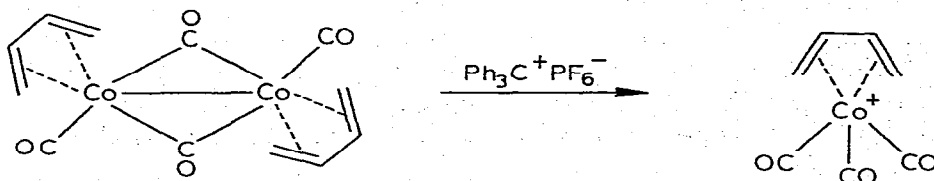
SCHEME 2.

The formation of the *syn*-tricyclo[4.2.0.0^{2,3}]octa-3,7-octadiene complex (XII).



trans-3,4-Bis(η^5 -cyclopentadienyldicarbonyliron)cyclobutadiene (III) is the first example of a cyclobutadiene ligand simultaneously bonded to two transition metal groups and possessing an uncoordinated double bond. In contrast to earlier suggestions [23], the cyclobutadiene ligand of III is not fluxional on the NMR time scale at 30°C. Although III is easily protonated [2] and oxidized, the cyclobutadiene ligand is remarkably unreactive to a variety of dienes and dienophiles [24].

Treatment of the binuclear complex III with trityl hexafluorophosphate effected a two-electron oxidation of III to generate the binuclear complex V. The failure of trityl to attack the uncoordinated double bond in III can be partially explained by considering the stereochemistry of III. The bulky *trans*-Fp groups are above and below the cyclobutadiene ring, thereby sterically hindering attack on the double bond or abstraction of an allylic hydrogen. There is precedent in the literature for trityl hexafluorophosphate acting as an oxidizing agent. For example, trityl hexafluorophosphate serves to oxidize dienedicarbonyl-cobalt dimers to dienetricarbonyl-cobalt cations [25].



The chemistry of V demonstrated that the integrity of the four-membered ring is maintained in V, and in conjunction with the iron analysis and the spectroscopic data, strongly supports the bridging cyclobutadiene structure. Lithium aluminum hydride effected a two-electron reduction of V to III. Similarly, treatment of V with NaFp gave III.

Except for its susceptibility to nucleophilic addition V exhibits remarkable kinetic stability especially when compared to the cationic mononuclear η^2 -cyclobutadiene complex XIV. There are probably two primary reasons for this stability. First, intermolecular reactions are inhibited by the large iron groups situated on both faces of the bridging cyclobutadiene ligand. Second, any cycloaddition reaction (i.e., Diels–Alder reactions) requires the decomplexation of one of the iron groups, a process that would probably add at least 20 kcal/mol to the activation energy of the reaction. On the other hand, in XIV one face of the cyclobutadiene ligand is unencumbered; thus the approach of another reactant is not inhibited. Also in the η^2 -cyclobutadiene ligand of XIV the intra- or inter-molecular utilization of the free double bond would not necessarily require the decomplexation of the metal.

Conclusions

(1) We have demonstrated that η^2 -cyclobutadiene complexes exist and in certain instances are isolable. As a corollary of the first point, η^2 -cyclobutadiene complexes should also be considered as possible reaction intermediates along with η^4 -cyclobutadiene complexes in certain catalytic and stoichiometric reactions. Our results certainly lend support to the postulation of bridging cyclobutadiene complexes in ligand transfer reactions. (2) Our results support the thesis that a reactive cyclobutadiene complex is not involved in formation of diene- η^2 -cyclobutadiene adducts generated during the oxidative degradation of cyclobutadienetricarbonyliron. There is, however, a good possibility that η^2 -cyclobutadiene complexes may be involved in the formation of cyclobutadiene-diene adducts. (3) The formation of *syn*-tricyclooctadiene can no longer be considered *prima facie* evidence for the intermediacy of cyclobutadiene in reactions involving transition metals. (4) It appears that η^2 -cyclobutadiene and probably η^4 -cyclobutadiene ligands retain the antiaromaticity of the free hydrocarbon. (5) The chemistry of η^2 -cyclobutadienoid complexes such as II, V and XIV will add a new and interesting facet to the area of metal-assisted addition and cycloaddition reactions [22].

Further chemical and structural investigations of these and related complexes are in progress.

Experimental

General procedures

Physical measurements. IR spectra were recorded on a Perkin–Elmer Model 180 Spectrophotometer, calibrated with polystyrene. The PMR spectra were obtained on a JEOL C-60 High Resolution Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an internal standard. The proton–proton decoupled PMR spectra were recorded on a Hitachi Perkin–Elmer R-24 High

Resolution Nuclear Magnetic Resonance Spectrometer.

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

Materials. Tetrahydrofuran and diethyl ether (Fisher Chemical Company) were stored over lithium aluminum hydride (Alfa Inorganics, Inc.) and distilled prior to use. Nitromethane (Fisher) was distilled from calcium carbonate. Petroleum ether (30-60°) was used as purchased from Fisher. All other solvents were reagent grade and used without further purification.

Dicyclopentadiene (Aldrich Chemical Co., Inc.), iron pentacarbonyl (GAF), silver hexafluorophosphate (Ozark Mahoning), 1,3-diphenylisobenzofuran (Aldrich), benzyltriethylammonium chloride (Aldrich), cyclooctatetraene (Columbia or Research Organic/Inorganic Chem. Corp.), dimethyl acetylene dicarboxylate (Columbia) and triphenylcarbinol (Columbia) were used as received. Lithium borohydride, lithium aluminum deuteride, sodium borohydride, lithium wire, fluoroboric acid, and hexafluorophosphic acid were used as purchased from Alfa. Chromatographic Grade, neutral, activity I alumina and Celite 545 were used as purchased from Fisher. Thick layer chromatographic plates (20 × 20 cm, 2 mm thickness) aluminum oxide (type T) F-255, were purchased from Brinkmann Instruments, Inc. Chlorine was obtained from Matheson Gas Products. Deuterated solvents (nitromethane- d_3 , chloroform- d_1 , and acetone- d_6) were purchased from Aldrich or Stohler Chemical Co.

Preparation of μ -(η^2_1 -1,2- η^2_2 -3,4-cyclobutadiene)bis(η^5 -cyclopentadienyl)dicarbonyliron)bis(hexafluorophosphate) (V)

To a 200 ml flask containing 100 ml of methylene chloride was added 11.8 g (0.030 mol) of trityl hexafluorophosphate. The flask was cooled to -78°C and 6.2 g (0.015 mol) of III [2] was added. Upon warming to room temperature under nitrogen, a solid formed which was collected by filtration and washed with methylene chloride. The solid was recrystallized by dissolving in nitromethane and adding methylene chloride to precipitate 1.04 g (50.4% based on III) of V, an air-stable yellow solid: PMR (CD_3NO_2) τ 4.26 (s, 10, Cp), 4.53 (s, 4, H); IR (Nujol) 2040, 2080 cm^{-1} ($\text{C}\equiv\text{O}$) (Found: Fe, 15.84. $\text{C}_{18}\text{C}_{14}\text{F}_{12}\text{Fe}_2\text{O}_4\text{P}_4$ calcd.: Fe, 16.05%.)

Preparation of V by the reaction between III and silver hexafluorophosphate

Methylene chloride, 20 ml and 0.623 g (2.46 mmol), of silver hexafluorophosphate were added to a 50 ml flask. The flask was cooled to -78°C and as 0.5 g (1.23 mmol) of III was added a noticeable reaction occurred. The black mixture was warmed to 24°C , filtered through Celite and the Celite was washed with methylene chloride. The filter flask was changed and the solid residue in the Celite was extracted with nitromethane. Diethyl ether was added to the nitromethane filtrate and a yellow precipitate was collected. The yellow solid was dissolved in nitromethane and methylene chloride was added to precipitate 0.3 g (35%) of V which had a PMR spectrum identical to that of V prepared by the reaction with trityl hexafluorophosphate.

Reaction between V and lithium aluminum hydride

As V, 0.281 g (0.405 mmol) was added to a 15 ml centrifuge tube contain-

ing lithium aluminum hydride 0.167 g (4.40 mmol) in 10 ml of tetrahydrofuran, a vigorous reaction occurred. The reaction mixture was filtered through alumina (1 × 2.5 cm) and washed with petroleum ether. The yellow eluate was rotary evaporated. A PMR spectrum of the residue 0.027 g (17%) in carbon disulfide was identical to that of an authentic sample of III.

Preparation of $\mu\text{-}\eta^1\text{-4-}\eta^2\text{-1,2-(3-chlorocyclobutenyl)bis}(\eta^5\text{-cyclopentadienyldi-carbonyliron) hexafluorophosphate (VI)$

To 5 ml of dry nitromethane in a 100 ml round bottom flask was added 0.3500 g (1.53 mmol), of benzyltriethylammonium chloride. The flask was cooled in an ice bath and 1.0043 g (1.44 mmol) of V was added. The reaction mixture was stirred magnetically for about 30 min, during which time all of the yellow solid had gone into solution. Diethyl ether was added until the solution became slightly cloudy and a yellow precipitate formed slowly. Filtration yielded a first crop of 0.1160 g of VI. The procedure was repeated to afford an additional 0.2848 g of VI for a total yield of 0.4008 g (47.6%). The low temperature PMR spectrum in CD_3COCD_3 showed no change in resonances down to -30°C ; PMR (CD_3COCD_3) τ 3.20 (m, 1, H(1)), 4.23 (s, 5, Cp(1)), 4.69 (s, 5, Cp(2)), 4.98 (m, 1, H(2)), 5.46 (m, 1, H(3)), 6.57 (m, 1, H(4)); IR (Nujol) 1944, 2000, 2025, 2060 cm^{-1} ($\text{C}\equiv\text{O}$). (Found: Fe, 18.89. $\text{C}_{18}\text{H}_{14}\text{ClF}_6\text{Fe}_2\text{O}_4\text{P}$ calcd.: Fe, 19.06%.)

Reaction between VI and silver hexafluorophosphate

To 7 ml of methylene chloride in a 15 ml centrifuge tube was added 0.05 g (0.197 mmol) of silver hexafluorophosphate. The tube was cooled in an ice bath and 0.059 g (0.102 mmol) of VI was added. The tube was stoppered and allowed to warm to room temperature. As the tube was shaken, the reaction mixture became cloudy and darkened. The reaction mixture was filtered through Celite in a fritted funnel and was washed twice with 5 ml of methylene chloride. The funnel then was fitted to a clean flask and the Celite was washed with nitromethane until the filtrate was lightly colored. As methylene chloride was added to the nitromethane filtrate a yellow solid precipitated. Filtration yielded 0.0411 g (58%) of V as a yellow solid, the PMR spectrum of which was identical to that of an authentic sample.

Reaction between V and NaFp

A 15 ml centrifuge tube containing 0.5 g (0.715 mmol) of V was cooled in an ethanol dry-ice bath. To this was added NaFp (1.49 mmol) in 2.7 ml of tetrahydrofuran. The reaction mixture was warmed to 24°C and centrifuged. The tetrahydrofuran solution was transferred to a clean centrifuge tube and the solvent was evaporated by passing nitrogen through the mixture. The PMR spectrum of the residues in carbon disulfide showed resonances attributed to $\text{FpCH}=\text{CH}-\text{CH}=\text{CHFp}$ (III) and Fp_2 by comparison to spectra of authentic samples.

Reaction between V and NaFp in the presence of 1,3-diphenylisobenzofuran

A 25 ml flask containing 0.2701 g (1.00 mmol) of 1,3-diphenylisobenzofuran, 0.4809 g (0.69 mmol) of V, and 5 ml of dry tetrahydrofuran was cooled to -78°C . A solution of 1.70 mmol of NaFp in 3 ml of tetrahydrofuran, was

slowly syringed into the flask. The reaction mixture was warmed to 24°C and the solvent was evaporated by passing nitrogen through the mixture. Benzene and a few drops of dimethyl acetylene dicarboxylate were added, the resulting solution was heated gently. The benzene solution was percolated through alumina (3 × 4 cm) and eluted with petroleum ether and benzene. A yellow fraction was collected and the solvent was rotary evaporated. An PMR spectrum of the residue in CS₂ showed resonances attributed to III and F_pCH=CHCH=CHF_p by comparison to spectra of authentic samples. No Diels–Alder adduct XII was detected in the PMR spectrum.

Reaction between V and methanol

Methanol, 25 ml, 0.3 g of sodium bicarbonate, and 0.5 g (0.715 mmol) of V were added to a 50 ml flask. After the mixture had been stirred for 15 h, the methanol was rotary evaporated and the residue was taken up in benzene and filtered through Celite. After rotary evaporation of the benzene, the resulting orange oil was chromatographed on alumina (1 × 9 cm) and eluted with petroleum ether. To further purify the yellow product, the yellow bands were rechromatographed on alumina (2.5 × 15 cm), eluting with petroleum ether. A bright yellow band was collected which after rotary evaporation yielded 0.03 g (16%) of *trans,trans*-3-methoxy-4-(η^5 -cyclopentadienyldicarbonyliron)butadiene (VII) as a gold solid: m.p. 61–63°C; PMR (CS₂) τ 2.25 (d, 1, H(1), $J_{1,3}$ 14.3 Hz), 3.12 (m, 1, H(2)), $J_{2,3}$ 9.8 Hz, $J_{2,4}$ 13.5 Hz), 3.68 (m, 1, H(3)), 4.88 (d, 1, H(4)), 5.17 (s, 5, Cp), 6.49 (s, 3, OCH₃); IR (Nujol) 2000, 1938 cm⁻¹ (C=O) (Found: C, 55.07; H, 4.37. C₁₂H₁₂O₃Fe calcd.: C, 55.4; H, 4.61%.

Assignment of protons of VII by use of an NMR shift reagent

PMR spectrum of VII (0.0259 g in 0.40 ml CS₂) was obtained relative to internal tetramethylsilane. The shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium (Eu(fod₃)) (Aldrich, Resolve-Al) was added to the sample in three portions and a PMR spectrum was obtained after each addition. The data are summarized in Table 4.

Reaction between *trans*-3-chloro-4-(η^5 -cyclopentadienyliron)cyclobutene (IV) and silver hexafluorophosphate in the presence of cyclopentadiene

Dichloroethane, 4 ml, was added to 0.8338 g (3.28 mmol) of silver hexafluorophosphate and 0.69 g (10.4 mmol) of cyclopentadiene in a 15 ml centrifuge tube. After the mixture had been cooled to -78°C, a solution of 0.7635 g (2.90 mmol) of IV in 2 ml of dichloroethane was added slowly. The reaction mixture was warmed to 24°C, filtered through Celite, and the Celite was washed

TABLE 4
PMR SPECTRUM OF COMPOUND VII (τ , ppm)

Eu(fod) ₃ (mg)	H(1)	H(2)	H(3)	H(4)	OCH ₃	Cp
0	2.25	3.12	3.68	4.88	6.49	5.21
12.2	2.03	0.83	3.05	2.80	4.15	5.23
14.7	1.99	0.27	2.94	2.45	3.76	5.23
18.0	1.97	-0.23	2.71	1.88	3.07	5.23

with methylene chloride until the filtrate was slightly colored. Diethyl ether was added to the methylene chloride filtrate and the resulting precipitate was collected by filtration. The crude solid was dissolved in acetone; diethyl ether was added to precipitate a yellow solid which upon filtration afforded 0.534 g (58%) of η^2 -3,4-*syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene- η^5 -cyclopentadienyldicarbonyl-iron hexafluorophosphate (VIII). PMR (CD₃COCD₃) τ 3.60 (m, 2, H(1)), 4.20 (s, 5, Cp), 4.38 (m, 2, H(2)), 7.01 (m, 2, H(3)), $J_{3,4}$ 3.8 Hz), 7.25 (m, 2, H(4)), 8.09 (m, 1, H(5)), 8.25 (m, 1, H(6)); IR (Nujol) 2065, 2015 cm⁻¹ (C=O). (Found: Fe, 12.70. C₁₆H₁₅F₆FeO₂ calcd.: Fe, 12.69%.)

Liberation of syn-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene from complex VIII

A solution of 0.56 mmol of NaF₅ in 1 ml of tetrahydrofuran was syringed into a 15 ml centrifuge tube containing 0.1708 g (0.39 mmol) of VIII. The reaction mixture turned red immediately. After addition of 3 ml of water, the product was extracted with carbon disulfide. The carbon disulfide extract then was extracted 3 times with 2 ml portions of water. The PMR spectrum of the carbon disulfide extract was identical to the spectrum of an authentic sample of *syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene as prepared below.

Preparation of syn-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene [11] via oxidation of cyclobutadieneiron tricarbonyl with ceric ammonium nitrate in the presence of cyclopentadiene

Cyclobutadieneiron tricarbonyl [26] (3.5 g, 0.018 mol) and cyclopentadiene (2.5 g, 0.038 mol) were added to 25 ml of methanol in a 100 ml flask. After the flask had been cooled to 0°C, 11 g (0.020 mol) of ceric ammonium nitrate was added slowly as the contents were stirred magnetically. The reaction flask was then stoppered with a rubber serum cap through which a syringe needle (No. 18) was inserted to relieve gas pressure. The reaction mixture was stirred magnetically for 2 h during which time the color of the mixture changed from yellow to dark orange-brown. Water (25 ml) was added to the flask and the contents were filtered through Celite and washed with diethyl ether until the filtrate was only slightly colored. The filtrate was extracted five times with 100 ml portions of water. The water extracts were then extracted twice with diethyl ether (50 ml). The diethyl ether extracts were combined, dried over sodium sulfate and filtered through magnesium sulfate. Rotary evaporation of the solvent afforded *syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (IX) [11]: PMR (CS₂) τ 4.11 (m, H(1), 2), 4.22 (m, H(2), 2), 7.05 (m, H(3), 2, $J_{3,4}$ 7.5 Hz), 8.50 (m, H(6), 1).

Reaction between IV and silver hexafluorophosphate in the presence of 1,3-diphenylisobenzofuran and liberation of the Diels-Alder adduct XI

To a 50 ml flask were added 1.0104 g (3.99 mmol) of silver hexafluorophosphate, 15 ml of 1,2-dichloroethane and 1.0450 g (3.87 mmol) of 1,3-diphenylisobenzofuran. The flask was cooled to -78°C and 1.0041 g (3.80 mmol) of IV was added. After warming to 24°C, the reaction mixture was filtered through 1 cm of Celite which was washed with methylene chloride. Addition of diethyl ether to the methylene chloride filtrate caused precipitation of an orange solid (0.0621 g, 2.5%) of the Diels-Alder complex X. The PMR spectrum was complicated and therefore, the adduct was identified by liberation of the

olefin from the metal complex. To a 50 ml flask containing 0.0631 g (0.096 mmol) of XI was added 2.82 mmol of NaFp in 0.5 ml of tetrahydrofuran. The residue resulting from the rotary evaporation of the tetrahydrofuran was taken up in benzene, centrifuged, and streaked across a thick layer chromatographic plate (alumina, 20 × 20 cm, 2 mm thickness). The plate was developed for 2.5 h in benzene. A band at 10 to 12 cm from the bottom edge was scraped off, stirring with 50 ml of benzene for 0.5 h. Solvent was removed to give 0.0103 g (33.3% based on X) of the Diels—Alder adduct XI, which was identified by comparison of its IR and PMR spectra to those of an authentic sample [12].

Reaction of trans-3-chloro-4-(η^5 -cyclopentadienyldicarbonyliron)cyclobutene (IV) with silver hexafluorophosphate

To a 15 ml centrifuge tube was added 0.4917 g (1.86 mmol) of IV and the tube was cooled to -78°C . A solution of 0.5048 g (1.99 mmol) of silver hexafluorophosphate in 4 ml of methylene chloride was added slowly to the tube. After warming to 24°C the reaction mixture was filtered through Celite which was washed with methylene chloride until the filtrate was slightly colored. The funnel was then fitted to a clean flask and the Celite was washed with nitromethane. Addition of diethyl ether to the nitromethane filtrate caused precipitation of a yellow solid. Filtration yielded 0.4026 g (29%) of η_1^2 -3,4- η_2^2 -7,8-syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-dienebis(η^5 -cyclopentadienyldicarbonyliron) bis-(hexafluorophosphate) (XII): PMR (CD_3NO_2): τ 4.21 (m, 4, H(1)), 4.30 (s, 10, Cp), 7.05 (m, 4, H(2)); IR (C=O) 2080, 2035 cm^{-1} . (Found: Fe, 15.13. $\text{C}_{22}\text{H}_{18}\text{F}_{12}\text{Fe}_2\text{O}_4\text{P}_2$ calcd.: Fe, 14.93%.)

Liberation of syn-tricyclo[4.2.0.0^{2,5}]octadiene from complex XII

A solution of 1.13 mmol of NaFp in 1 ml of tetrahydrofuran was syringed into a 15 ml centrifuge tube containing 0.279 g (0.372 mmol) of XII. The centrifuge tube was shaken vigorously as an exothermic reaction occurred and color of the mixture changed from yellow to red. After the addition of 3 ml of water, the product was extracted with carbon disulfide. The PMR spectrum of the carbon disulfide extract was identical to the PMR spectrum of an authentic sample of syn-tricyclo[4.2.0.0^{2,5}]octadiene [12,13].

Reaction of VI with 1,3-diphenylisobenzofuran and liberation of the Diels—Alder adduct XI

To a 10 ml round bottom flask were added 2 ml of 1,2-dichloroethane, 0.3161 g (1.169 mmol) of 1,3-diphenylisobenzofuran, and 0.25 g (0.427 mmol) of VI. The reaction mixture was stirred magnetically overnight and then filtered to give 0.0668 g of an unidentified green salt that was not further characterized. The solvent was evaporated by passing nitrogen through the filtrate. This residue was dissolved in methylene chloride and petroleum ether was added to precipitate a yellow solid. Filtration afforded 0.9493 g (54.2%) of the Diels—Alder complex X. The complex was placed in a 15 ml centrifuge tube and treated with 0.282 mmol of NaFp in 0.5 ml of tetrahydrofuran. After evaporation of the tetrahydrofuran by passing nitrogen through the solution, a PMR spectrum of the residue in carbon disulfide showed the presence of the Diels—Alder adduct

XI. The residue was taken up in 5 ml of benzene, centrifuged and chromatographed on alumina (20 × 20 cm, 2 mm thickness). After development in benzene for about 2.5 h, a band 1 cm to 8 cm from the bottom of the plate was scraped off and stirred with benzene for 0.5 h. Filtration and rotary evaporation of the filtrate yielded 0.0662 g (48.4% based on VI) of the Diels—Alder adduct XI which gave a PMR spectrum identical to that of an authentic sample.

Reaction of trans-3-chloro-4-(η^5 -cyclopentadienyldicarbonyliron) with 1,3-diphenylisobenzofuran

To a 10 ml flask were added 0.3229 g (1.19 mmol) of 1,3-diphenylisobenzofuran, 4 ml of 1,2-dichloroethane, and 0.1175 g (0.445 mmol) of IV. The reaction mixture was stirred magnetically overnight. The 1,2-dichloroethane was evaporated in a stream of nitrogen and 0.282 mmol of NaFp in 0.5 ml of tetrahydrofuran was added. The tetrahydrofuran was evaporated under a stream of nitrogen. A PMR spectrum of the residue in carbon disulfide showed no Diels—Alder complex X.

Reaction of V with 1,3-diphenylisobenzofuran

To a 15 ml centrifuge tube were added 0.0745 g (0.107 mmol) of V, 0.786 g (3.91 mmol) of 1,3-diphenylisobenzofuran, 0.5 ml of 1,2-dichloroethane, and 0.5 ml of nitromethane. After allowing the reaction to proceed overnight, the solvents were evaporated under a stream of nitrogen. A PMR spectrum of the residue in CD_3NO_2 showed the starting material, V, and no Diels—Alder complex X.

Reaction of η^2 -ethene- η^2 -cyclopentadienyldicarbonyliron tetrafluoroborate with 1,3-diphenylisobenzofuran

To a 15 ml centrifuge tube were added 0.0786 g (0.291 mmol) of 1,3-diphenylisobenzofuran, 0.5 ml of dichloroethane, 0.5 ml of nitromethane, and 0.0317 g (0.109 mmol) of η^2 -ethene- η^2 -cyclopentadienyldicarbonyliron tetrafluoroborate. After the reaction mixture had been stirred overnight, the solvents were evaporated by passing a stream of nitrogen through the solution. A PMR spectrum of the residue in CD_3NO_2 showed the presence of only the starting materials.

Reaction of trans-3-chloro-4-(η^5 -cyclopentadienyldicarbonyliron)cyclobutene with silver hexafluorophosphate in the presence of dimethyl fumarate

A stock solution was prepared from 0.6105 g (4.33 mmol) of dimethyl fumarate, 0.5194 g (2.05 mmol) of silver hexafluorophosphate, and 0.2635 g (2.14 mmol) of nitrobenzene in 4.0 ml of methylene chloride. A 3.0 ml aliquot of the stock solution was syringed into a centrifuge tube which was then cooled to $-78^\circ C$. A solution of 0.4987 g (1.88 mmol) of IV in 2.0 ml of methylene chloride was syringed slowly into the tube. After warming to room temperature the reaction mixture was centrifuged and a PMR spectrum was taken. The ^{13}C satellites of methylene chloride resonance interfered with the integration of the dimethyl fumarate resonance. Therefore, the solvent was evaporated and the PMR spectra were taken in 1,2-dichloroethane. The ratio of dimethyl fumarate/nitrobenzene in the stock solution was 0.89/1.00 compared to 0.91/1.00 in the solution after reaction, as determined by the integration of the PMR spectra.

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