Journal of Organometallic Chemistry, 107 (1976) 359—375

THE PREPARATION AND CHARACTERIZATION OF BENZOCYCLOBUTENYLIDENE-, NAPHTHO[*b*]CYCLOBUTENYLIDENE-, AND η^2-BENZOCYCLOBUTADIENE-η^5-CYCLOPENTADIENYLDICARBONYLIRON HEXAFLUOROPHOSPHATE

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(Received September 8th, 1975)

Summary

The preparation and characterization of the first isolable cationic mononuclear complexes bearing a η^2-cyclobutadienoid ligand or a carbene ligand lacking heteroatom stabilization are described. The reaction between 1-bromobenzocyclobutene and Na[η^5-$C_5H_5(CO)_2Fe$] (NaFp) afforded η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (III). Treatment of III with trityl hexafluorophosphate gave benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V). Naphtho[*b*]cyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (VI) was formed in an analogous manner. Both V and VI gave 1,1-disubstituted cyclobutenes when treated with nucleophilic reagents.

η^2-Benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate, (XIX), which was prepared by the oxidation of bis-1,2-(η^5-cyclopentadienyldicarbonyliron)benzocyclobutene by trityl hexafluorophosphate, afforded *trans*-1,2-disubstituted benzocyclobutenes when treated with nucleophilic reagents. The η^2-benzocyclobutadiene ligand of XIX was displaced by I^- and trapped as the Diels—Alder adduct by 1,3-diphenylisobenzofuran.

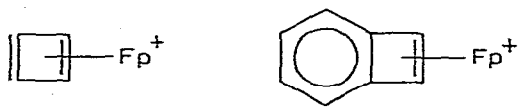
Introduction

The ancillary ligands of the alkyl, η^1-allyl, and cationic η^2-alkene complexes, FpR* and Fp(alkene)$^+$, respectively, are thermally nonlabile; hence the loss of carbon monoxide and subsequent *polyhapto* coordination of unsaturated ligands is unknown for Fp(alkene)$^+$ and extremely rare for FpR complexes. Because of the kinetic stability and ease of preparation of these two classes of complexes,

* Fp ≡ η^5-$C_5H_5(CO)_2Fe$.

the chemistry of these substances has been the subject of numerous studies. In particular, there is interest in FpR and Fp(alkene)$^+$ complexes as reagents in organic synthesis [1] and as model compounds in studies of the chemistry of the transition metal—carbon σ-bond [2].

The chemical and structural properties of the Fp group suggested that this group should also form complexes (I and II) which possess novel and heretofore



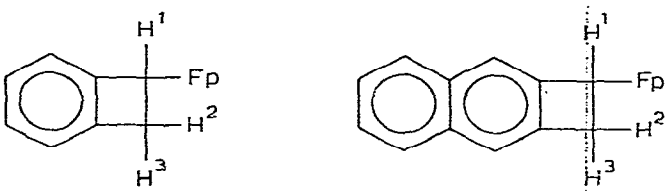
(I) (II)

unknown η^2-cyclobutadienoid ligands. Such ligands may be expected to manifest a reactivity different from that of the free hydrocarbon or the η^4-cyclobutadienoid ligand. Thus, complexes such as I and II may be useful reagents in organic synthesis. Furthermore, chemical and structural studies of η^2-cyclobutadienoid complexes may help to elucidate the role of reactive cyclobutadiene complexes in the oxidative degradation of η^4-cyclobutadiene complexes [3], ligand transfer reactions [4], the nickel carbonyl-promoted linear dimerization of benzocyclobutadiene [5], the transition metal-catalyzed dimerization, oligomerization and polymerization of alkynes [6], and the isomerization of metallacyclopentadienes to η^4-cyclobutadiene complexes [7] and the reverse of this latter process [8].

This paper describes the preparation of the first isolable cationic mononuclear η^2-benzocyclobutadiene complex (II) and the serendipitous preparation of the novel cationic carbene complexes, V and VI, both of which lack heteroatom or other special forms of stabilization.

Results

η^1-1-Benzocyclobutenyl- and η^1-1-naphtho[*b*]cyclobutenyl-η^5-cyclopentadienyldicarbonyliron (III and IV, respectively) were prepared by the metathesis between 1-bromobenzocyclobutene or 1-bromonaphthocyclobutene and NaFp*. Both III and IV were characterized by elemental analyses, and PMR and IR



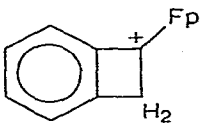
(III) (IV)

spectroscopy. In particular, the PMR spectra of III and IV compare well with those of model compounds. Thus, for III, the *trans*, *cis* and *geminal* relation-

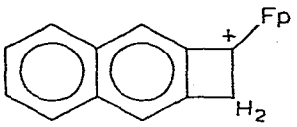
* During the course of this work, it was found that III is more conveniently prepared by the reduction of 1,2-dibromobenzocyclobutene by NaFp in the presence of cyclopentadiene [10].

ships of H^1—H^2, H^1—H^3 and H^2—H^3 respectively were established by the observation of $J(H^1, H^2)$ 2.1, $J(H^1, H^3)$ 4.9, $J(H^2, H^3)$ 13.5 Hz which are typical of the coupling constants of monosubstituted benzocyclobutenes [9].

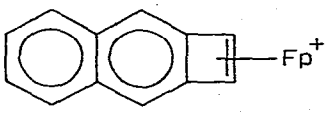
When either III or IV was added to a methylene chloride solution of trityl hexafluorophosphate, the cationic carbene complexes, V or VI, respectively, were formed. The spectroscopic properties of V are not sufficient to formulate the compound as a carbene complex (V) rather than a η^2-cyclobutadienoid complex II. The PMR spectrum of V exhibits singlet resonances at τ 5.35 and



(V)



(VI)

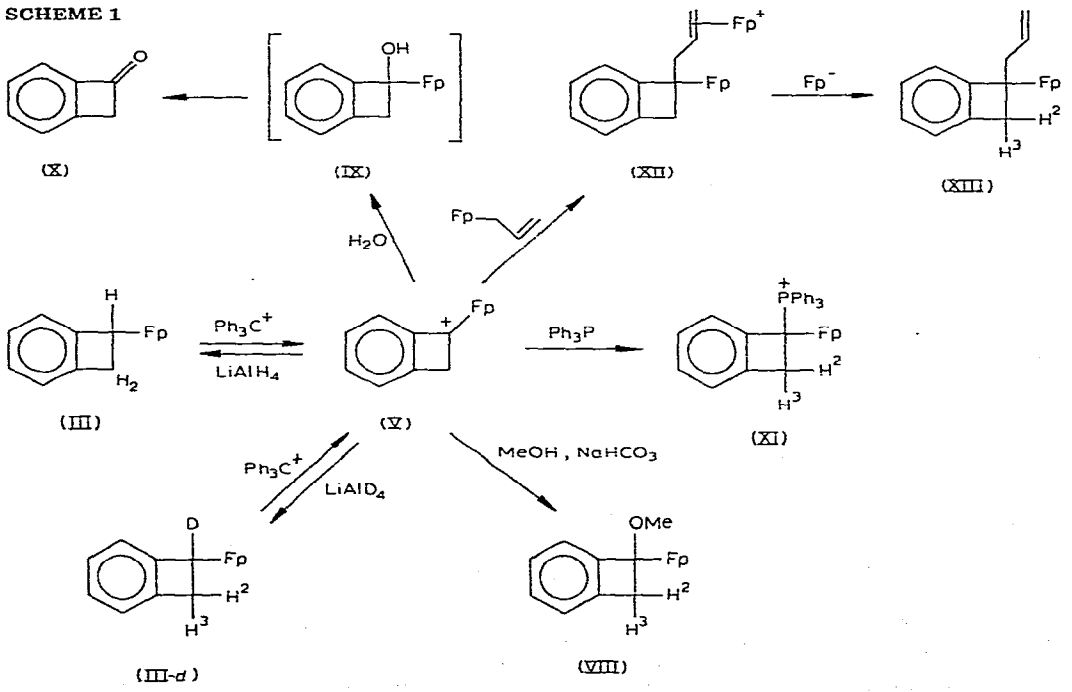


(VII)

4.10 with a relative intensity of 2 : 5. The four proton aromatic resonance observed at τ 2.17 is not of the $AA'BB'$ type and, therefore, appeared to be inconsistent with the formulation of V as a η^2-benzocyclobutadiene complex II which would have been expected to possess, on the average, a plane of symmetry. The chemical shift of the cyclopentadienyl resonance and the positions of the carbonyl stretching frequencies (2065 and 2020 cm^{-1}) of V compare with the values reported for other Fp(alkene)$^+$ complexes [11].

The formation of several 1,1-disubstituted benzocyclobutenes, when V was treated with nucleophilic reagents, allowed the unambiguous identification of V as a carbene complex (Scheme 1). Thus, reduction of V with lithium aluminum hydride afforded III whereas lithium aluminum deuteride gave III-*d*. The ob-

SCHEME 1



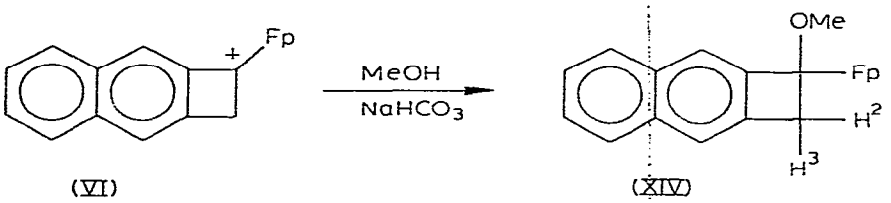
servation of a pair of doublets with $J(H^2, H^3)$ 14.7 in the PMR spectrum of III-*d* and the absence of a resonance at τ 5.95 indicated that the deuterium was attached to the ligating carbon of the benzocyclobutenyl ligand. Treatment of III-*d* with trityl hexafluorophosphate gave V without incorporation of deuterium.

The methoxy derivative, VIII, was prepared by treatment of V with a mixture of methanol and sodium bicarbonate. The observation of a pair of doublets, $J(H^2, H^3)$ 13.5 Hz, in the PMR spectrum of VIII supported its formulation as a 1,1-disubstituted benzocyclobutene. The hydroxy derivative, IX, which was prepared by the treatment of V with a mixture of methylene chloride and aqueous sodium bicarbonate, was unstable and decomposed during the work-up of the reaction mixture to benzocyclobutenone and Fp_2.

Triphenylphosphine added to the ligating carbon of the benzocyclobutenylidene ligand of V to afford the triphenylphosphonium salt XI. In the PMR spectrum of XI, the resonances attributed to both H^2 and H^3 were observed as a broad doublet at τ 6.05.

Alkylation of V by η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron gave the cationic binuclear complex XII which was characterized only by IR spectroscopy. Reductive demetalation of XII with NaFp afforded the neutral mononuclear complex XIII. In the PMR spectrum of XIII, the four-membered ring protons, H^2 and H^3, were observed as a multiplet centered at τ 7.36.

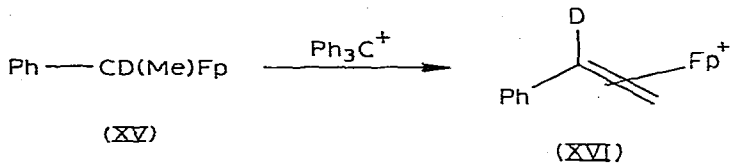
The PMR spectrum of the naphtho[*b*]cyclobutenylidene complex VI exhibits singlets at τ 5.14 and τ 4.01 with relative intensities of 2 : 5. The six proton aromatic resonance was observed as a multiplet centered at τ 2.02. As with V, the spectroscopic properties of VI cannot unambiguously identify VI as a carbene complex rather than a η^2-naphtho[*b*]cyclobutadiene complex VII. The structure of the methoxy adduct, XIV, formed by treatment of VI with a mitxure of methanol and sodium bicarbonate, supported the formulation of VI as a carbene complex. Thus, in the PMR spectrum of XIV the resonances of the four-membered ring protons were observed as a pair of doublets, $J(H^2, H^3)$ 15.0 Hz, indicative of *geminal* protons.



(VI) (XIV)

Complexes V and VI are indefinitely stable at 24°C when stored in the absence of moisture. In nucleophilic solvents, the decomposition of V was rapid; however, in nitromethane, sulfur dioxide or methylene chloride, V is indefinitely stable.

The 1-deuterio-1-phenylethyl complex XV was converted by trityl hexafluorophosphate to the styrene complex XVI. The absence of a multiplet centered at τ 3.69, which is observed in the PMR spectrum of Fp(styrene)$^+$ [12] indicated that the reaction had occurred with complete retention of deuterium in XVI



(XV) (XVI)

via β-hydride abstraction. The reaction between the benzyl complex, XVII, and trityl hexafluorophosphate afforded 1,1,1,2-tetraphenylethane.

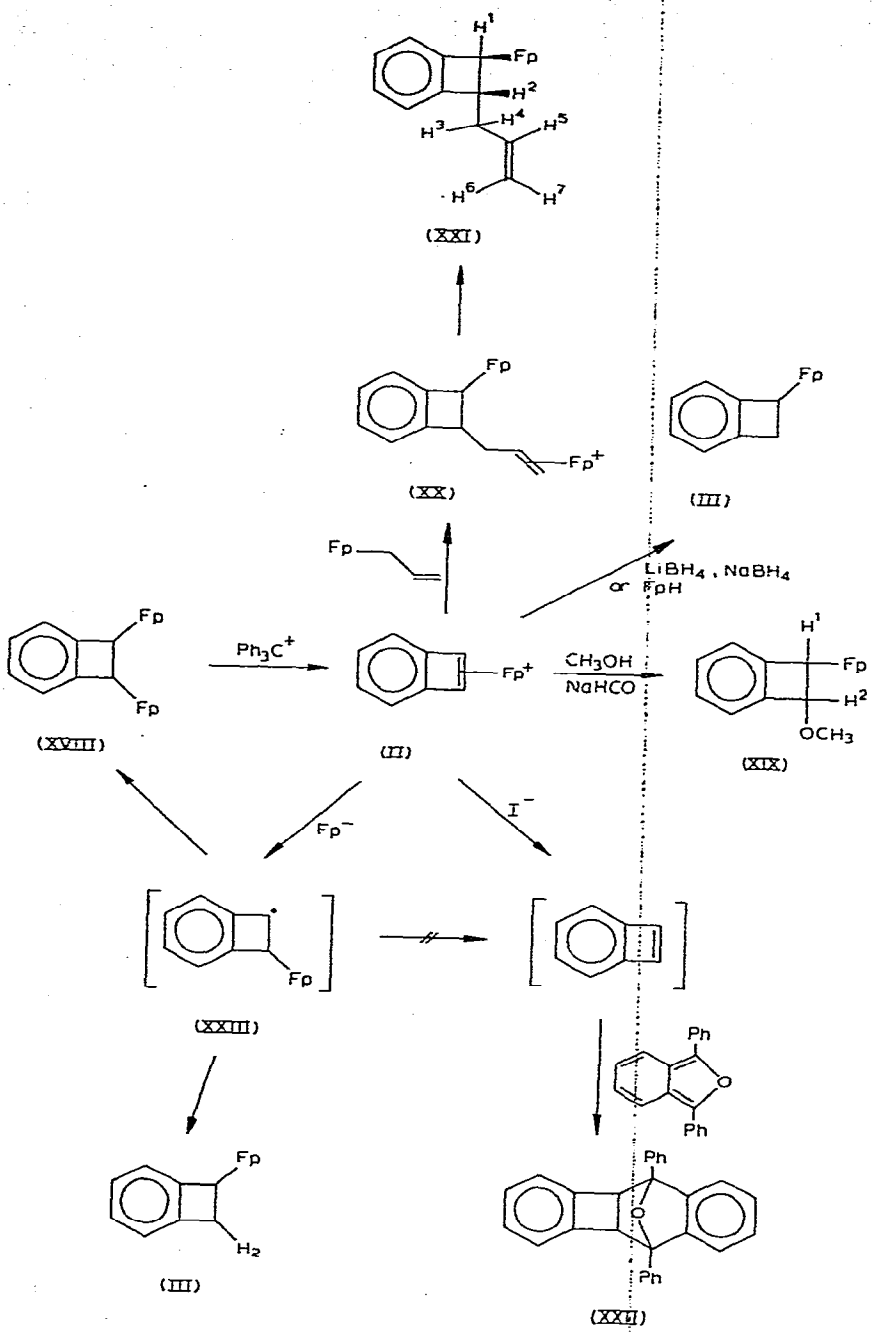
$$\underset{\text{(XVII)}}{FpCH_2Ph} \xrightarrow{Ph_3C^+} Ph_3CCH_2Ph$$

Oxidation of 1,2-bis(η^5-cyclopentadienyldicarbonyliron)benzocyclobutene (XVIII) [13] with trityl hexafluorophosphate at —78° C gave η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II). Although II is indefinitely stable under nitrogen at —18° C, it decomposed at 24°C; especially in the presence of moisture. Compound II is apparently unstable in solution and thus attempts to obtain a PMR spectrum of II have been unsuccessful. The carbonyl absorptions (2070 and 2035 cm^{-1}) of II are typical of the cationic alkene complexes [Fp(alkene)$^+$]. The overall IR spectrum of II is very similar to that of the related styrene complex $Fp(CH_2{=}CHPh)^+PF_6^-$. The iron analysis of II is consistent with the formulation of II as a mononuclear complex.

The identity of II was established by the characterization of *trans*-1,2-disubstituted benzocyclobutenes formed by the addition of nucleophilic reagents to II (Scheme 2). *trans*-1,2-Disubstituted benzocyclobutenes are readily characterized by a small coupling ($J \sim 2$ Hz) between the four-membered ring protons [9]. Thus, treatment of II with a mixture of sodium bicarbonate in methanol gave the *trans*-methoxy adduct XIX. The PMR spectrum of XIX exhibits, in addition to the resonances due to the aromatic, cyclopentadienyl and methoxy protons, two doublets at τ 5.59 and 6.00 (J 1.5 Hz) which were assigned to the four-membered ring protons. II was alkylated by a methylene chloride solution of η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron to yield the cationic binuclear complex XX which upon subsequent treatment with NaFp gave the neutral complex XXI. In the PMR spectrum of XXI, the resonance of H^1 of the four-membered ring is a well resolved doublet although the resonance assigned to H^2 is a multiplet because of coupling with the diastereotopic protons of the adjacent methylene group. The small coupling (1.8 Hz) between H^1 and H^2 confirmed the *trans* orientation of the iron and propenyl groups. Reduction of II with lithium borohydride, sodium borohydride, or FpH in tetrahydrofuran afforded III in 21, 45 or 40% yields, respectively. When II was reduced with NaFp in tetrahydrofuran, both III and XVIII were formed. When this reaction was carried out in the presence of 1,3-diphenylisobenzofuran, the Diels—Alder adduct XXII of benzocyclobutadiene and 1,3-diphenylisobenzofuran was not observed.

Treatment of II with a methylene chloride solution of tetra-n-butylammonium iodide in the presence of 1,3-diphenylisobenzofuran gave the Diels—Alder adduct XXII.

SCHEME 2



Discussion

In several respects, benzocyclobutadiene resembles cyclobutadiene [14]. First, both hydrocarbons are anti-aromatic, highly reactive, and unisolable com-

pounds. In addition, both hydrocarbons bond to transition metals as the η^4-cyclobutadienoid ligand [15]. Despite the similarities between benzocyclobutadiene and cyclobutadiene, it was anticipated that a η^2-benzocyclobutadiene complex would be more stable kinetically than the η^2-cyclobutadiene analog. This is reasonable since two carbon atoms of the four-membered ring of the η^2-benzocyclobutadiene ligand are incorporated into the aromatic nucleus and the other two carbon atoms are bound to the metal. Thus, reaction at any of the four carbon atoms of the four-membered ring would result in partial or complete decomplexation of the metal or destruction of the aromatic nucleus. Hence the probability of being able to prepare and isolate the η^2-benzocyclobutadiene complex II seemed high as compared to the probability of isolating I. Therefore, II was chosen as the initial target in our research program concerning η^2-cyclobutadienoid transition-metal complexes.

In principle, the preparation of II appeared to be straight forward. β-hydride abstraction from alkyl ligands of FpR by the trityl ion has afforded, in most instances, cationic η^2-alkene complexes [1]. It was anticipated that II could be prepared from the benzocyclobutenyl complex III via β-hydride abstraction. Surprisingly, when III was allowed to react with trityl hexafluorophosphate, the benzocyclobutenylidene complex V was formed in high yield. There can be no doubt that V was formed via α-hydride abstraction since the 1-deuteriobenzocyclobutenyl complex III-*d* also gave V without incorporation of deuterium when treated with trityl hexafluorophosphate.

The preference for α-hydride rather than β-hydride abstraction does not appear to be steric in nature since both the α- and *trans*-β-hydrogen are equally exposed to attack by the trityl ion. Since the strain energies of cyclobutene and cyclobutadiene are calculated to be very similar [16] it is unlikely that the strain energies of the benzocyclobutenylidene and η^2-benzocyclobutadiene ligands are very different. Thus, the difference in strain energies does not appear to be a viable explanation.

An alternative explanation of the unusual course of this reaction concerns the relative stabilities of the benzocyclobutenylidene and η^2-benzocyclobutadiene ligands. Since the structures of alkene ligands of electrophilic metals differ only slightly from the structures of the uncoordinated alkenes [17], the structure of the η^2-benzocyclobutadiene ligand of II probably resembles the structure of benzocyclobutadiene. Therefore, it is likely that the η^2-benzocyclobutadiene ligand retains the anti-aromaticity of the free hydrocarbon. The anti-aromaticity of the η^2-benzocyclobutadiene ligand is probably reflected in a relatively large activation energy for β-hydride abstraction from III. It is believed that V is the kinetic and thermodynamic product.

In order to further explore the possibility that the anti-aromaticity of benzocyclobutadiene was responsible for the unusual α-hydride abstraction from III, the reaction between the naphtho[*b*]cyclobutenyl complex IV and trityl hexafluorophosphate was investigated. Naphtho[*b*]cyclobutadiene is predicted to be nonaromatic rather than anti-aromatic [18]. Attesting to the veracity of these predictions is the existence of several stable substituted naphtho[*b*]cyclobutadienes [19]. Despite the greater stability of naphtho[*b*]cyclobutadiene, IV also underwent α-hydride abstraction to form the naphtho[*b*]cyclobutenylidene complex VI.

α-Hydride abstraction is without precedent. All comparable reactions follow different reaction pathways. For example, the 1-deuterio-1-phenylethyl complex XV was converted by trityl hexafluorophosphate to the corresponding cationic styrene complex XVI, with complete incorporation of deuterium. When β-hydrogens are absent, such as in the benzyl complex XVII, the trityl ion adds directly to the ligating carbon thereby displacing Fp^+. Apparently this latter reaction is sterically inhibited for III and IV.

In view of the high reactivity of $FpCH_2^+$ [20], it is remarkable that V and VI can even be isolated. When $FpCH_2^+$ is generated in the absence of trapping agents, $Fp(ethylene)^+$ is isolated as one of the major products [20]. The formation of $Fe(ethylene)^+$ is best envisioned as involving electrophilic attack of $FpCH_2^+$ on the parent methoxymethyl complex XXIV. Subsequent protonation of the

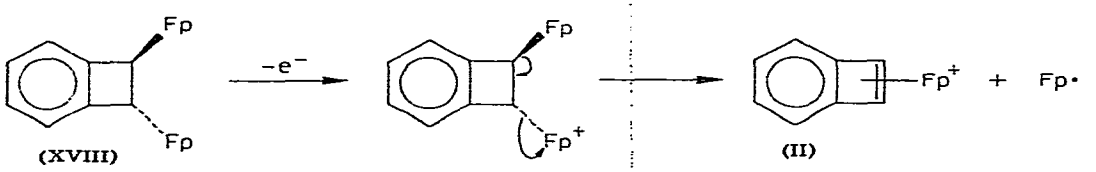
$$FpCH_2^+ + \underset{(XXIV)}{FpCH_2OMe} \rightarrow \underset{(XXV)}{FpCH_2{-}CH_2{-}OMe} \xrightarrow{H^+} Fp(CH_2CH_2)^+$$

resulting β-methoxyethyl complex XXV and loss of methanol yields $Fp(ethylene)^+$. For the same steric reasons that the trityl ion does not attack the ligating carbons of III or IV, neither V nor VI adds to the ligating carbons of cyclobutenyl ligands of III or IV.

The isopropylidene complex XXVI decomposes by a 1,2-β-hydride shift to form the isomeric η^2-propene XXVII [21]. Such a rearrangement of V or VI is unfavorable since the antiaromatic η^2-cyclobutadienoid ligands would be formed. Thus, the degradative pathways available to other cationic carbene complexes are excluded for V and VI.

(XXVI) (XXVII)

Alternative methods of preparation of II were considered. Replacement of the *trans*-β-hydrogen in III with a better leaving group (i.e. XIX) and subsequent treatment of this material with strong acid appeared to be a resaonable method of preparation of II. Since the preparation of XIX required a multistep synthesis, our attention turned to the neutral binuclear benzocyclobutadiene complex XVIII [13] that presumably possesses *trans*-Fp groups. It was reasoned that XVIII could be demetalated in a one or two electron process to yield II. It has been reported recently that Fp· may act as a good leaving group in the oxidative demetalation of Fp—alkyl complexes [22].

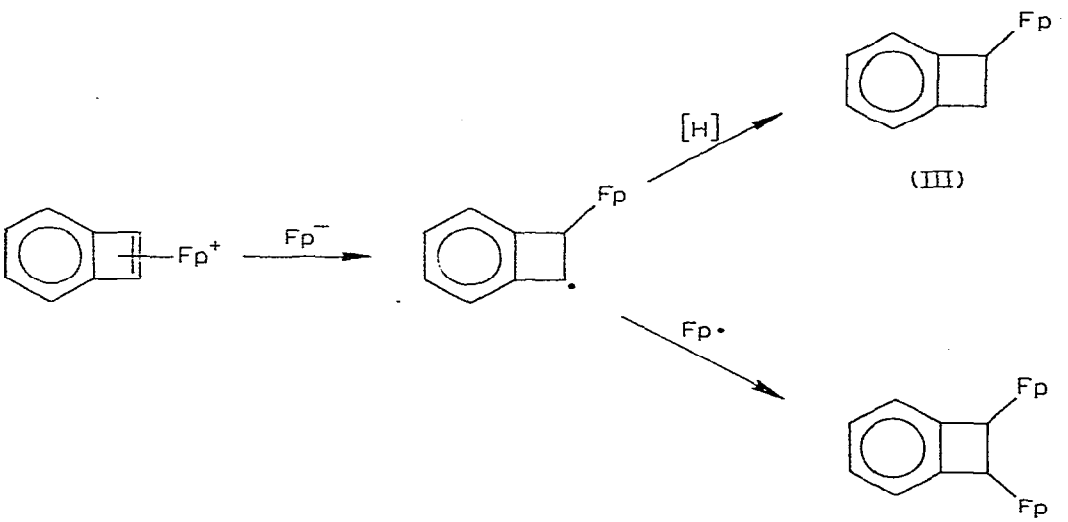


(XVIII) (II)

The preparation of II via the oxidation of XVIII with trityl hexafluorophosphate was successful. Thus, II precipitated from methylene chloride as it formed during the course of this reaction.

Our expectations about the reactivity of II are correct. Thus, in contrast to I [23], II is isolable, shows no tendency to react with its progenitor XVIII or to function as a dienophile. The chemistry of II is in accord with its formulation as a η^2-benzocyclobutadiene complex. Thus, II reacted with nucleophilic reagents to form *trans*-1,2-disubstituted benzocyclobutenes. The η^2-benzocyclobutadiene ligand, which is labile, was displaced by iodide and trapped by 1,3-diphenylisobenzofuran as the Diels—Alder adduct. These reactions are typical of Fp(alkene)$^+$ complexes [1].

The reduction of II by NaFp is unusual in that displacement of the benzocyclobutadiene ligand did not occur and that the complexes III and XVIII were formed. A reasonable explanation of these observations is that II is reduced to the benzocyclobutenyl radical XXVIII which either adds another Fp$^\bullet$ to form XVIII or abstracts a hydrogen to form III [10].



Experimental

Physical measurements

IR spectra were recorded on a Perkin—Elmer Model 180 Spectrophotometer, calibrated with polystyrene. The PMR spectra were obtained on a JOEL C-60 High Resolution Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an internal standard.

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

Materials

Tetrahydrofuran and diethyl ether were stored over lithium aluminum hydride and distilled prior to use. All other solvents were reagent grade and used without further purification. Dicyclopentadiene, tetra-n-butylammonium iodide

(Aldrich), iron pentacarbonyl (GAF), and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (Columbia), were used as received. Lithium borohydride, sodium borohydride, lithium aluminum deuteride, and chromatographic grade, neutral, activity I alumina were used as purchased from Alfa—Ventron. Thick layer chromatographic plates (20 × 20 cm, 2 mm thickness), aluminum oxide (type T) F-255, were purchased from Brinkmann Instruments, Inc. Deuterated solvents (nitromethane-d_3, and acetone-d_6) were used as purchased from Aldrich or Stohler Chemical Co.

Preparation of η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (III)

To a 500 ml flask containing a solution of NaFp (0.114 mol) in 100 ml of tetrahydrofuran was added 5 g (0.027 mol) of 1-bromobenzocyclobutene [24]. After the mixture had been stirred for 1 h, 100 ml of petroleum ether was added and the resulting mixture was filtered through Celite. The Celite was washed with petroleum ether until the filtrate was only lightly colored. Rotary evaporation of the filtrate gave a dark residue which was taken up in a minimum amount of petroleum ether. This solution was filtered through Celite, and the filtrate was chromatographed on alumina (4 × 40 cm). Elution with benzene—petroleum ether (1 : 10) and subsequent rotary evaporation of the bright yellow eluate afforded a brown oil which was crystallized from petroleum ether at —78°C to yield 3.8 g (50%) of η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (III); m.p. 66—68°C; PMR (CS_2) τ 3.18 (m, 4, Ar), 5.37 (s, 5, Cp), 5.95 (m, 1, $J_{1,2}$ = 2.1 Hz, $J_{1,3}$ = 4.9 Hz, H^1), 6.56 (m, 1, $J_{2,3}$ = 13.5 Hz, H^3), 7.31 (m, 1, H^2); IR (neat) 2003, 1942 cm^{-1} (C≡O). (Found: C, 64.03; H, 4.42. $C_{15}H_{12}FeO_2$ calcd.: C, 64.3; H, 4.28%.)

Preparation of η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V)

To a solution of trityl hexafluorophosphate, 12.5 g (0.032 mol), in 100 ml of methylene chloride in a 250 ml flask at —78°C was added 9.0 g (0.032 mol) of III. After the reaction mixture had been warmed to 24°C, the solvent was evaporated by bubbling a stream of nitrogen through the reaction mixture until crystals appeared. The first crop of orange-red crystals, 10.75 g, was collected by filtration and washed with a small amount of methylene chloride. Further evaporation and filtration yielded an additional 1.25 g of V for a total yield of 12.0 g (87.5%) of η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V); PMR (CD_3NO_2) τ 2.17 (m, 4, Ar), 4.10 (s, 5, Cp), 5.33 (s, 2, CH_2); IR (hexachlorobutadiene) 2065, 2020 cm^{-1} (C≡O). (Found: Fe, 13.12. $C_{15}H_{11}F_6FeO_2P$ calcd.: Fe, 13.16%.)

Reaction of η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V) with lithium aluminum hydride

Diethyl ether, 5 ml, 0.05 g (1.3 mol) of lithium aluminum hydride, and 0.5 g (1.2 mol) of V were added to a 50 ml flask. After the reaction mixture had been stirred for 1 h, the residue resulting from the rotary evaporation of the diethyl ether was taken up in petroleum ether and percolated through alumina (2 × 3 cm) eluting with petroleum ether and diethyl ether. A yellow eluate was collected and rotary evaporated to give 0.2 g (60%) of a yellow oil, which exhibited a PMR spectrum identical to that of an authentic sample of III.

Reaction of η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V) with lithium aluminum deuteride

Diethyl ether, 20 ml, 0.2 g (4.7 mmol) of lithium aluminum deuteride, and 2.0 g (4.7 mmol) of V were added to a 100 ml flask. The reaction mixture was stirred overnight during which time the color changed from orange-red to yellow. The residue resulting from the rotary evaporation of the solvent was extracted with petroleum ether, and the extracts were percolated through alumina (2 × 3 cm) eluting with petroleum ether and diethyl ether. Rotary evaporation of the yellow eluate gave 0.75 g (57%) of η^1-1-(1-deuteriobenzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (III-*d*); PMR (CS_2) τ 3.13 (m, 4, Ar), 5.37 (s, 5, Cp), 6.53 (d, 1, $J_{2,3}$ = 14.7 Hz, H^3), 7.28 (d, 1, H^2).

Reaction of η^1-1-(1-deuteriobenzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (III-d) with trityl hexafluorophosphate

To a 100 ml flask were added 20 ml of methylene chloride, 0.7 g (1.82 mmol) of trityl hexafluorophosphate, and 0.5 g (1.78 mmol) of III-*d*. After the reactants had been mixed, the solvent was evaporated under a stream of nitrogen until crystals appeared. The solid was collected by filtration and washed with methylene chloride to afford 0.65 g (86%) of V, the PMR spectrum of which was identical to the spectrum of V prepared previously and thereby showed no incorporation of deuterium.

Reaction of η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V) with methanol

To a 50 ml flask were added 25 ml of methanol, 0.3 g of sodium bicarbonate, and 1.035 g (2.42 mmol) of V. The flask was stoppered with a rubber serum cap through which a syringe needle had been inserted. After the mixture had been stirred overnight, the residue which resulted from the rotary evaporation of the mixture was extracted with petroleum ether and filtered. Rotary evaporation of the filtrate gave 0.586 g (79%) of η^1-1-(1-methoxybenzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (VIII) as yellow-orange crystals; m.p. 88.5—90°C; PMR (CS_2), τ 3.01 (m, 4, Ar), 5.25 (s, 5, Cp), 6.43 (d, 1, $J_{2,3}$ = 13.5 Hz, H^3), 6.78 (d, 1, H^2), 6.76 (s, 3, Me); IR (Nujol) 1989, 1916 cm^{-1} (C≡O). (Found: C, 61.83; H, 4.30. $C_{16}H_{14}FeO_3$ calcd.: C, 61.9; H, 4.52%.)

Reaction between η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V) and triphenylphosphine

A solution of 0.0852 g (0.325 mmol) of triphenylphosphine in methylene chloride was syringed slowly into a solution of 0.1049 g (0.248 mmol) of V in 10 ml of methylene chloride. The yellow solid that was precipitated by the addition of diethyl ether to the reaction mixture was collected by filtration and washed with diethyl ether to afford 0.140 g (83%) of η^1-1-(1-triphenylphosphoniumbenzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (XI); m.p. 195°C (dec.); PMR (CD_3NO_2), τ 2.55 (m, 19, Ar), 4.96 (s, 5, Cp), 6.05 (d, 2, J = 9.75 Hz, CH_2); IR (Nujol) 2014, 1967 cm^{-1} (C≡O). (Found: Fe, 8.43. $C_{33}H_{26}F_6FeO_2P_2$ calcd.: Fe, 8.14%.)

Reaction between η^1-1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V) and water

To a 50 ml flask were added 25 ml of methylene chloride, 1.0 ml of water, 0.3 g of sodium bicarbonate, and 1.04 g (2.47 mmol) of V. The flask was stoppered with a serum cap through which a syringe needle had been inserted. After the reaction mixture had been stirred overnight and then dried over $MgSO_4$, it was percolated through alumina (2 × 3 cm) eluting with methylene chloride. The residue which resulted from the rotary evaporation of the eluate was taken up in 5 ml of methylene chloride and transferred to a short-path distillation apparatus. Vacuum distillation (10^{-2} mmHg) of the residue gave 0.0935 g (32%) of benzocyclobutenone (X) as a yellow oil. The PMR spectrum of X showed a trace amount of ferrocene in the product; PMR (CCl_4), τ 2.67 (m 4, Ar), 6.07 (s, 2, H); IR (neat) 1785, 1765 cm^{-1} (C=O). (Lit. [25] IR (neat) 1785, 1764 cm^{-1} (C=O)).

Reaction between η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron and η^1-benzocyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (V)

To a 100 ml flask, were added 1.0 g (2.36 mmol) of V and 20 ml of methylene chloride. The flask was capped and 0.57 g (2.60 mmol) of η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron was added via syringe. This solution was refrigerated for 1 h at −18° C. Filtration of the resulting mixture afforded 0.610 g (43.1%) of the solid yellow binuclear complex XII; IR (Nujol) 2070, 2010, 1995, 1935 cm^{-1} (C≡O). XII was further characterized by its conversion to the mononuclear complex XIII.

Reaction between NaFp and XII

Into a 25 ml flask, equipped with a serum cap, was added 7 ml of a tetrahydrofuran solution of NaFp (3.5 mmol) and 0.610 g (0.953 mmol) of XII. Petroleum ether, 10 ml, was added to the mixture, and the mixture was filtered through 3 cm of Celite. The residue, resulting from the rotary evaporation of the filtrate, was dissolved in petroleum ether and chromatographed on alumina (2 × 25 cm). Elution with petroleum ether and benzene and subsequent rotary evaporation of the yellow eluate afforded η^1-1-[1-(2-propenyl)benzocyclobutenyl]-η^5-cyclopentadienyldicarbonyliron (XIII); m.p. 59—62° C; PMR (CS_2) τ 3.04 (m, 4, Ar), 4.35 (m, 1, =CH), 5.10 (m, 2, $=CH_2$), 5.31 (s, 5, Cp), 6.93 (d, 2, J = 4.5 Hz, CH_2); 7.36 (m, 2, CH_2); IR (neat) 1985, 1920 cm^{-1} (C≡O). (Found: Fe, 17.68. $C_{18}H_{16}FeO_2$ calcd.: Fe, 17.46%.)

Preparation of η^1-1-(2-deuterio-2-phenyl)ethyl-η^2-cyclopentadienyldicarbonyliron (XV)

(a). Preparation of 1-deuterio-1-phenylethanol. Diethyl ether (~30 ml) was vacuum distilled from $LiAlH_4$ into a 100 ml flask containing 1.0 g (0.024 mol) $LiAlD_4$. Into this solution was added 10 g (0.083 mol) of acetophenone over a 10 min period. After the mixture had been stirred for 3 h, 1 ml of water, 1 ml of 15% aqueous sodium hydroxide, and 3 ml of water were added sequentially. The mixture was filtered through magnesium sulfate which was subsequently washed with diethyl ether. After rotary evaporation of the filtrate, short-path

vacuum distillation (10^{-2} mmHg) of the residue yielded 9.4 g (91%) of 1-deuterio-1-phenylethanol; PMR (neat) τ 2.70 (m, 5, Ar), 4.93 (s, 1, OH), 8.58 (s, 3, CH_3).

(b). Preparation of 1-chloro-1-deuterio-1-phenylethane. To a 100 ml flask were added 9.4 g (0.076 mol) of 1-deuterio-1-phenylethanol, 18.2 g (0.153 mol) of thionyl chloride, and 50 ml of chloroform. The reaction mixture was refluxed and the excess thionyl chloride and chloroform were distilled out of the flask at about 62° C. The resulting brown residue was short-path distilled (10^{-2} mmHg) to yield 8 g (79%) of 1-chloro-1-deuterio-1-phenylethane as a pale yellow liquid; PMR (neat) τ 2.70 (m, 5, Ar), 8.42 (s, 3, Me).

(c). Preparation of η^1-1-(1-deuterio-1-phenylethyl)-η^5-cyclopentadienyldicarbonyliron (XV). Into a solution of NaFp (0.084 mol) in 100 ml of tetrahydrofuran at —78° C was added 8 g (0.06 mol) of 1-chloro-1-deuterio-1-phenylethane. The reaction mixture was warmed to 24° C and filtered through Celite. The residue, resulting from the rotary evaporation of the filtrate, was dissolved in petroleum ether and chromatographed on alumina (4 × 35 cm). Elution with petroleum ether and subsequent rotary evaporation of the yellow eluate afforded 7.1 g (44.3%) of η^1-1-(1-deuterio-1-phenylethyl)-η^5-cyclopentadienyldicarbonyliron (XIII) as dark brown crystals; PMR (CS_2) τ 3.00 (m, 5, Ar), 5.53 (s, 5, Cp), 8.40 (s, 3, CH_3).

Reaction between trityl tetrafluoroborate and η^1-benzyl-η^5-cyclopentadienyldicarbonyliron

A solution of 0.6913 g (2.10 mmol) of trityl tetrafluoroborate in 5.0 ml methylene chloride was added slowly to a 25 ml flask at 0° C containing a solution of 0.465 g (1.74 mmol) of η^1-benzyl-η^5-cyclopentadienyldicarbonyliron in 5.0 ml methylene chloride. The reaction flask was stoppered under N_2. After 18 h the reaction mixture was filtered through neutral alumina (2 × 3 cm) and eluted with petroleum ether. Rotary evaporation of the solvent yielded 0.5535 g of crude product which was shown to be ca. 75% 1,1,1,2-tetraphenylethane by its PMR spectrum. An analytically pure sample of 1,1,1,2-tetraphenylethane was obtained by recrystallization of the crude material from petroleum ether (60—90° C) and subsequent recrystallization from diethyl ether; m.p. 140—141° C (lit. 144° C); PMR (CS_2); τ 2.90 (s, 15, Ph), τ 3.34 (m, 5, Ph), τ 6.17 (s, 2, CH_2).

Reaction of η^1-1-(1-deuterio-1-phenylethyl)-η^5-cyclopentadienyldicarbonyliron (XV) with trityl hexafluorophosphate

To a solution of 2.66 g (6.85 mmol) of trityl hexafluorophosphate in 10 ml of 1,2-dichloroethane was added 1 g (3.53 mmol) of η^1-1-(1-deuterio-1-phenylethyl)-η^5-cyclopentadienyldicarbonyliron. After the reactants had been mixed, the solvent was evaporated by passing nitrogen through the solution until crystals appeared. Filtration of the reaction mixture afforded 0.82 g (54%) of η^2-1,2-(1-deuterio-1-phenylethene)-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (XVI); PMR (CD_3NO_2) τ 2.51 (m, 5, Ar), 4.33 (s, 5, Cp), 5.75 (m, 2, $=CH_2$).

Preparation of η^1-1-naphtho[b]cyclobutenyldicarbonyliron (IV)

Into a solution of 0.034 mol of NaFp in 100 ml of tetrahydrofuran, was added 3.0 g (0.012 mol) of 1-bromonaphtho[*b*]cyclobutene. After the mixture

had been stirred for 0.5 h, 100 ml of petroleum ether was added and the reaction mixture was filtered through Celite. The Celite was washed with petroleum ether until the filtrate was lightly colored. After rotary evaporation of the filtrate, the residue was dissolved in petroleum ether—benzene (3 : 2) and chromatographed on 400 g of alumina. Elution with petroleum ether—benzene (1 : 1) and subsequent rotary evaporation of the yellow eluate yielded 2.7 g (66.5%) of IV as a yellow oil. Crystallization of this oil from petroleum ether gave η^1-1-naphtho[*b*]cyclobutenyl-η^5-cyclopentadienyldicarbonyliron (IV); m.p. 157—158°C; PMR (CS_2) τ 2.63 (m, 6, Ar), 5.23 (s, 5, Cp), 5.78 (m, 1, $J_{1,3}$ = 6.0 Hz, $J_{1,2}$ = 3.75 Hz, H^1); 6.42 (m, 1, $J_{2,3}$ = 15.0 Hz, H^3); 7.19 (m, 1, H^2); IR (Nujol) 2000, 1925 cm^{-1} (C≡O). (Found: C, 69.25; H, 4.15. $C_{19}H_{14}FeO_2$ calcd.: C, 69.2%.)

Preparation of η^1-1-naphtho[b]cyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (VI)

A solution of V, 2.7 g (8.18 mmol), in 50 ml of methylene chloride was added to 3.2 g (8.25 mmol) of trityl hexafluorophosphate in 100 ml of methylene chloride in a 250 ml flask. After the addition, the solvent was evaporated by passing a stream of nitrogen through the solution until crystals appeared. Filtration of the mixture yielded 1.3 g (33.5%) of η^1-1-naphtho[*b*]cyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (VI); m.p. 161—163°C (dec.); PMR (CD_3NO_2) τ 2.02 (m, 6, Ar), 4.01 (s, 5, Cp), 5.14 (s, 2, CH_2); IR (Nujol) 2085, 2035 cm^{-1} (C≡O). (Found: Fe, 11.68. $C_{19}H_{13}F_6FeO_2P$ calcd.: Fe, 11.77%.)

Reaction of η^1-1-naphtho[b]cyclobutenylidene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (VI) with methanol

Methanol, 25 ml, 0.3 g of sodium bicarbonate and 1.0 g (2.11 mmol) of VI were added to a 50 ml flask. The flask was stoppered with a serum cap through which a syringe needle had been inserted. After the mixture had been stirred overnight, the residue resulting from the rotary evaporation of solvent was extracted with petroleum ether and the extracts filtered through Celite. The residue resulting from the rotary evaporation of the filtrate was dissolved in diethyl ether and chromatographed on alumina (3 × 5 cm). Elution with diethyl ether and subsequent rotary evaporation of the yellow eluate gave 0.45 g (59%) of η^1-1-(1-methoxynaphtho[*b*]cyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (XIV); m.p. 98—99°C; PMR (CS_2) τ 2.63 (m, 6, Ar), 5.29 (s, 5, Cp), 6.31 (d, 1, $J_{1,3}$ = 15.0 Hz, H^3), 6.63 (d, 1, H^2), 6.71 (s, 3, Me); IR (KBr) 1995, 1922 cm^{-1} (C≡O). (Found: Fe, 15.57. $C_{20}H_{16}O_3Fe$ calcd.: Fe, 15.51%.)

Preparation of η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II)

To a solution of trityl hexafluorophosphate 1.7 g (4.38 mmol) in 25 ml of methylene chloride at —78°C was added 2.0 g (4.37 mmol) of 1,2-bis(η^5-cyclopentadienyldicarbonyliron)benzocyclobutene (XVIII) [13]. As the reaction mixture warmed the solvent was evaporated by passing a stream of nitrogen through the reaction mixture until a red solid appeared. Filtration of the reaction mixture and washing the residue with methylene chloride gave 1.2 g (64.8%)

of η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II); IR (Nujol) 2070, 2035 cm^{-1} (C≡O). (Found: Fe, 13.34; $C_{15}H_{11}F_6FeO_2P$ calcd.: Fe, 13.16%.)

Reaction between η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) and methanol

To a 50 ml flask were added 25 ml of methanol, 0.3 g of sodium bicarbonate, and 0.5 g (1.18 mmol) of II. The flask was stoppered with a serum cap through which a syringe needle had been inserted. After the mixture had been stirred overnight, the residue resulting from the rotary evaporation of the mixture was extracted with petroleum ether and percolated through 2 cm of alumina. Rotary evaporation of the yellow eluate afforded 0.3 g (82%) of *trans*-η^1-2-(1-methoxybenzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron) (XIX), m.p. 86—88°C (dec.); PMR (CS_2) τ 2.96 (m, 4, Ar), 5.23 (s, 5, Cp), 5.59 (d, 1, $J_{1,2}$ = 1.5 Hz, H^1), 6.00 (d, 1, H^2), 6.61 (s, 3, Me); IR (Nujol) 1995, 1940 cm^{-1} (C≡O). (Found: C, 62.02; H, 4.80. $C_{16}H_{14}O_3Fe$ calcd.: C, 61.9; H, 4.52%.)

Reaction between η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) and η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron

To a 15 ml centrifuge tube, containing 0.518 g (1.22 mmol) of II in 5 ml of methylene chloride, was added 0.511 g (2.34 mmol) of η^1-1-(2-propenyl)-η^5-cyclopentadienyldicarbonyliron. After 0.25 h at 24°C, the reaction mixture was filtered and the residue washed with methylene chloride until the filtrate was slightly colored. The cationic complex, XX, which was precipitated by addition of diethyl ether to the filtrate, was collected by filtration. Crude XX was then treated with a solution of NaFp (1.20 mmol), in 3 ml of tetrahydrofuran. The solvent was evaporated entirely by passing a stream of nitrogen through the solution. The residue was extracted with petroleum ether and the resulting solution was percolated through alumina (3 × 4 cm) eluting with petroleum ether. Rotary evaporation of the yellow eluate afforded 0.347 g (88.9%) of η^1-*trans*-1-(2-propenyl)benzocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (XXI), as an orange oil; PMR (CS_2), 3.18 (m, 4, Ar), 4.18 (m, 1, $J_{5,6}$ = 4.5 Hz, H^5), 4.98 (m, 1, H^6), 5.26 (m, 1, $J_{5,7}$), 5.33 (s, 5, Cp), 6.38 (d, 1, $J_{1,2}$ = 1.8 Hz, H^1), 7.03 (m, 1, H^2), 7.68 (m, 2, H^3 and H^4); IR (neat) 1995, 1930 cm^{-1} (C≡O). (Found: Fe, 17.72. $C_{14}H_{16}FeO_2$ calcd.: Fe, 17.45%).

Reaction of η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) with lithium borohydride

To 20 ml of tetrahydrofuran in a 50 ml flask were added 0.5 g (1.8 mmol) of II and 0.03 g (1.36 mmol) of lithium borohydride. A vigorous reaction occurred as the lithium borohydride was added to the mixture. After several minutes the solvent was evaporated by passing a stream of nitrogen through the reaction mixture. The resulting residue was dissolved in benzene and chromatographed on alumina (2.5 × 15 cm). Elution with petroleum ether and subsequent rotary evaporation of the yellow eluate gave 0.7 g (21%) of a yellow oil, which exhibited a PMR spectrum identical to that of an authentic sample of III.

Reaction of η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) with sodium borohydride

To a centrifuge tube containing 5 ml of tetrahydrofuran were added 0.5 g (1.18 mmol) of II and 0.5 g (13.2 mmol) of sodium borohydride. After the mixture had been shaken for several minutes, it was chromatographed on alumina (2.5 × 15 cm) eluting with petroleum ether. Rotary evaporation of the yellow eluate gave 0.15 g (45%) of a yellow oil, which exhibited a PMR spectrum identical to that of an authentic sample of III.

Reaction between η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) and hydrido-η^5-cyclopentadienyldicarbonyliron

To a 50 ml flask were added 3 mmol of FpH (prepared by the reduction by sodium amalgam of 0.53 g of $[Cp(CO)_2Fe]_2$ in 5.3 ml of tetrahydrofuran and subsequent treatment of the resulting solution of NaFp with 0.48 g (3.5 mmol) of 2-bromo-2-methylpropane) and 0.5 g (1.12 mmol) of II. After the reaction mixture had been stirred for several minutes, petroleum ether, 30 ml, was added and the resulting mixture was filtered through Celite. After rotary evaporation of the filtrate, the residue was taken up in benzene and chromatographed on alumina (4 × 30 cm) eluting with petroleum ether to afford, after rotary evaporation of the yellow eluate, III, 0.126 g (40%). A second yellow eluate was shown by its PMR spectrum to be a mixture of XVII and unidentified organic material (0.016 g).

Liberation of benzocyclobutadiene from η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II)

To a solution of 1.0 g (2.7 mmol) of tetra-n-butylammonium iodide, and 0.64 g (2.36 mmol) of 1,3-diphenylisobenzofuran in 20 ml of methylene chloride at —78°C was added 1 g (2.36 mmol) of II. The flask was stoppered with a serum cap through which a syringe needle had been inserted. The reaction vessel was warmed to 24°C and was stirred for 2 h. After the rotary evaporation of the solvent, the residue was extracted with diethyl ether and the extracts were filtered. The residue, resulting from the rotary evaporation of the filtrate, was chromatographed on alumina (2.5 × 30 cm), eluting with ether—petroleum ether (1:3). Rotary evaporation of the yellow eluate afforded a yellow oil (0.49 g) the PMR spectrum of which showed the presence of 1,3-diphenylisobenzofuran and the Diels—Alder adduct XXII. This residue was dissolved in 5 ml of benzene, treated with a few drops of dimethylacetylenedicarboxylate, heated gently, and rotary evaporated. The resulting residue was taken up in benzene and chromatographed on alumina (2.5 × 15 cm) eluting with benzene. Rotary evaporation of the yellow elute afforded a yellow oil. Crystallization of this oil from petroleum ether afforded crystals of the Diels—Alder adducts, XXII, 0.209 (25%); m.p. 185—188°C. Subsequent recrystallization from hot methanol gave crystals of XXII, which were further characterized by comparison of the PMR spectrum of this sample with that of an authentic sample prepared by the method of Cava; m.p. 189—200°C (lit. [26] 200—202°C) PMR (CS_2) τ 2.94 (m, 18, Ar), 6.03 (s, 2, C_2H_2).

Reaction between η^2-1,2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (II) and NaFp

Into a 50 ml flask containing a solution of 5.1 mmol of NaFp in 9 ml of tetrahydrofuran at −78°C was added 1.00 g (2.35 mmol) of II. After the solution had been warmed to 24°C, petroleum ether was added and the resulting mixture was filtered through Celite. The residue resulting from the rotary evaporation of the filtrate was dissolved in benzene and chromatographed on alumina (4 × 45 cm). Elution with petroleum ether and subsequent rotary evaporation of the eluates afforded III, 0.104 g (16%), unidentified organic material, 0.14 g, and XVIII, 0.059 g; when the reaction between II and NaFp was carried out in the presence of 1,3-diphenylisobenzofuran, the Diels—Alder adduct XXII was not observed.

Acknowledgement

We gratefully acknowledge the generous support of the Research Corporation, the donors of the Petroleum Research Fund administered by the American Chemical Society, and the Graduate School of Boston University.

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