Journal of Organometallic Chemistry, 99 (1975) 269—279

THE REDUCTIVE METALATION OF 1,2-DIHALOBENZOCYCLOBUTENES BY $NaFe(CO)_2Cp$ AND $HFe(CO)_2Cp$

THOMAS BAUCH, ANDREA SANDERS, CHARLES V. MAGATTI, PAUL WATERMAN, DEBORAH JUDELSON and WARREN P. GIERING*

Department of Chemistry, Boston University, Boston, Massachusetts 02215 (U.S.A.)

(Received October 25th, 1974)

Summary

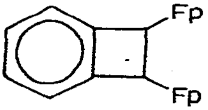
The reactions between *cis*- and *trans*-1,2-dibromo- or 1,2-diidobenzocyclobutene and $NaFe(CO)_2Cp$ (NaFp) were investigated. The mechanism of formation of 1,2-bis(cyclopentadienyldicarbonyliron)benzocyclobutene (I) and 1-(cyclopentadienyldicarbonyliron)benzocyclobutene (II) is thought to involve initial formation of benzocyclobutadiene, addition of a Fp radical to benzocyclobutadiene and subsequent addition of a second Fp radical to form I, or hydrogen abstraction from FpH to form II.

Introduction

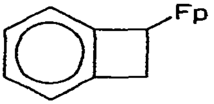
Because of the diverse roles played by alkyl and related complexes in catalytic, stoichiometric, and biological processes, considerable effort has been expended on developing and understanding the chemistry of alkyl—transition metal complexes. In particular, the mechanism and hence the stereochemistry of metalation processes have received attention [1-25].

The alkylation of organometallic anions [15-25] with alkyl halides generally occurs via an S_N2 process with inversion of configuration at the substrate carbon. However, Rosenblum [26] and subsequently Jensen [27] and coworkers suggested that the metalation of bromocyclopropanes may not involve an $S_N2(C)$ process. In particular, Jensen noted that metalation of organic substrates by organometallic anions may occur by five different mechanisms: (1) $S_N2(C)$ (backside), (2) $S_N2(C)$ (frontside), (3) metal—halogen exchange (four center), (4) transmetalation, and (5) electron transfer. Recently, a radical chain mechanism has been proposed for the alkylation of certain noble metal complexes [3].

We became actively interested in the mechanism of metalation reactions involving $NaFe(CO)_2Cp$(NaFp) when in the course of another study we had reason to prepare the known binuclear benzocyclobutadiene complex I by the metathesis of NaFp with *trans*-1,2-dibromobenzocyclobutene [28]. Surprisingly, when the literature preparation was repeated [29], we isolated significant although quite variable yields of the mononuclear benzocyclobutenyl complex II* which was unreported in the earlier work. Although the formation of I could be envisaged as occurring via S_N2(C) processes, the formation of II clearly



(I)



(II)

Fp ≡ $Cp(CO)_2Fe$

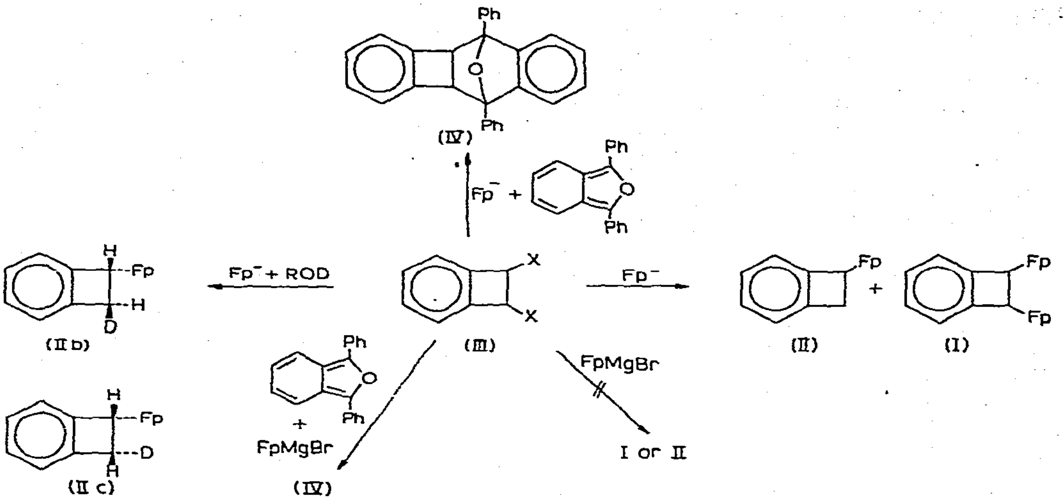
indicated that a more complex mechanism also was operative. Since the alkyl, allyl and related derivatives of $Cp(CO)_2Fe$ are of potential synthetic utility in organic chemistry [31], since NaFp is an important reagent for metalating organic substrates [32], and since II is the progenitor of an interesting class of cationic carbene complexes [30,33], the reaction between NaFp and 1,2-dihalobenzocyclobutenes has been studied in an attempt to delineate the pathway by which II is formed.

Results

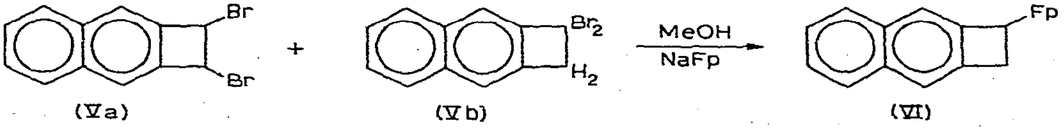
The reaction between NaFp and *trans*-1,2-dibromo-, *cis*-1,2-diiodo- or *trans*-1,2-diiodobenzocyclobutene (IIIa-IIIc) in tetrahydrofuran afforded the known binuclear benzocyclobutadiene complex [28] I and a 5-6% yield of the mononuclear complex II, in addition to a number of uncharacterized oligomers which appear to be of the type $(C_8H_6)_nFp_2$. When the reactions with IIIb and IIIc were carried out in the presence of 1,3-diphenylisobenzofuran, the Diels—Alder adduct IV [34] of benzocyclobutadiene and the isobenzofuran was isolated in 25% yield. In these experiments the yields of I and II were reduced to less than 2%. Treatment of IIIa with 0.025 mol of NaFp and 0.38 mol of t-Butanol, afforded II in 12% yield. When methanol was used instead of t-butanol, the yield of II was increased to 37%. Water, however, afforded less than a 1% yield of II. The major isolated product of the latter reaction was 1-bromobenzocyclobutene in 18% yield. The addition of a large excess of cyclopentadiene to the reaction mixture afforded yields of II as high as 51%. The addition of styrene to the methanol reaction mixture reduced the yield of II to 28%. In the presence of t-BuOD, CH_3OD or a limited amount of D_2O, the *trans* deuterated benzocyclobutenyl complex IIb was formed. The amount of *cis*-deuterated material (IIc) was less than 5%. The metathesis between NaFp and *trans*-1-bromo-2-deuterobenzocyclobutene afforded an equimolar mixture of IIb and IIc. The addition of a mixture of FpBr and IIIa to a solution of NaFp failed to increase the yield of II as compared to the yield of II in a control reaction.

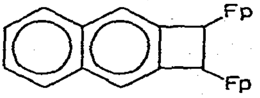
---

* The preparation and spectroscopic properties of II have been reported [30].



The reaction between FpMgBr and IIIa did not yield either I or II, although IIIa was completely consumed. In the presence of 1,3-diphenylisobenzofuran, IV was formed in 20% yield. The dibromonaphthocyclobutenes [35] V also were reductivily metalated to afford VI*. The binuclear naphthocyclobutadiene complex VII was not observed. Treatment of II with NaFp and Fp_2 did not afford I.




(VII)

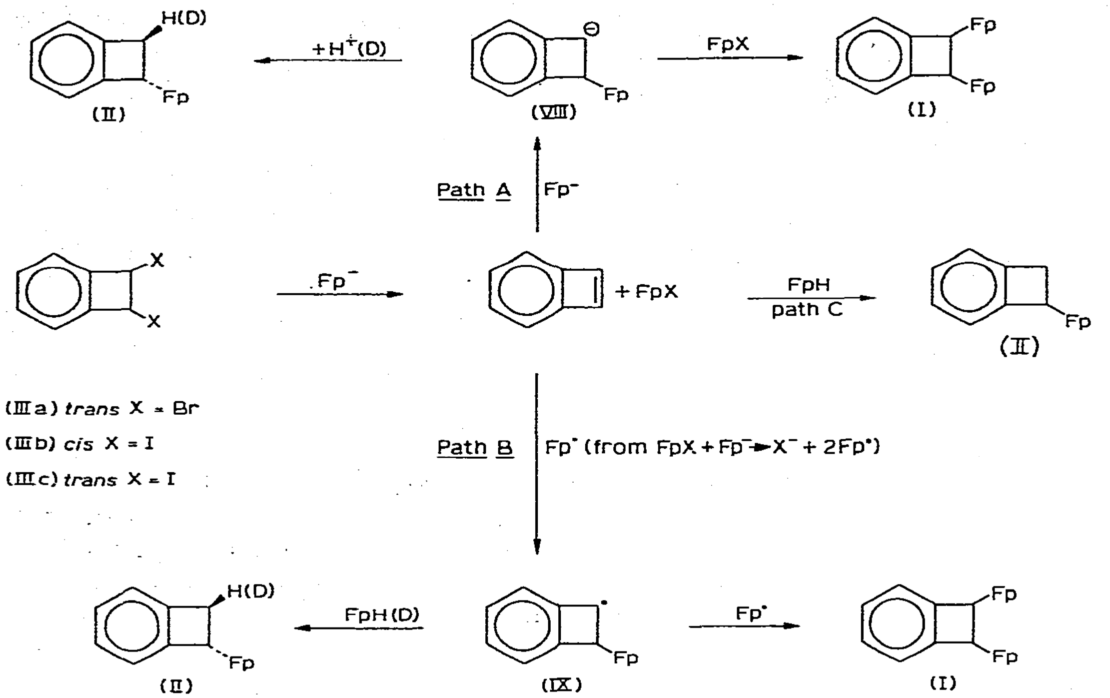
Discussion

There are five reasonable mechanisms by which I and II could be generated from 1,2-dihalobenzocyclobutenes. The first three mechanisms (Scheme 1) involve the initial formation of benzocyclobutadiene via an E2 dehalogenation of III by NaFp. In path A the Fp^- adds to benzocyclobutadiene to form the metallocarbanion VIII. This can subsequently abstract a proton from the solvent and form II or react with FpX (formed during the dehalogenation step) to give I. Path B differs from A only in that the organometallic species that attacks benzocyclobutadiene is the radical $Fp^\cdot$ (generated by reaction between Fp^- and FpX). The resultant benzocyclobutenyl radical IX may either abstract a hydrogen (most likely from traces of FpH, vide infra) and form II or add another $Fp^\cdot$ and form I. The third alternative for benzocyclobutadiene is some undefined

---

* An independent preparation of VI will be reported in another paper [30b].

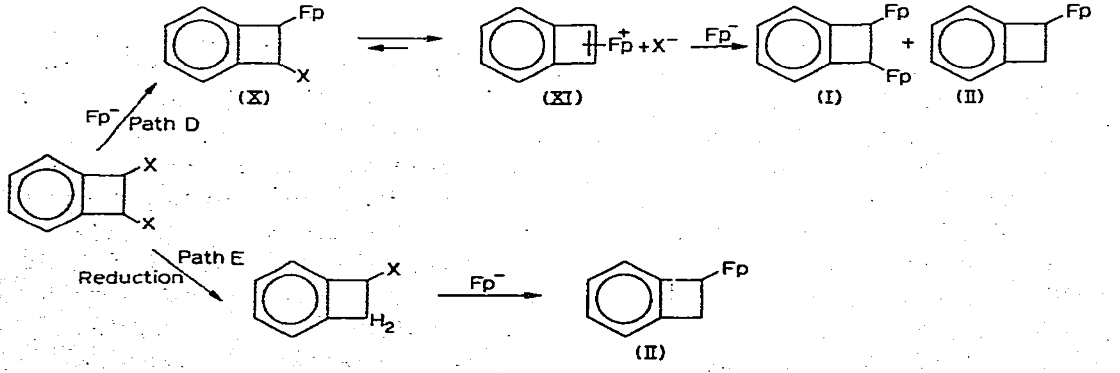
SCHEME 1



concerted addition reaction between FpH (vide infra) and benzocyclobutadiene (path C).

In another reaction pathway, D (Scheme 2), III is monometalated to yield X which would most likely immediately ionize to yield the η^2-benzocyclobutadiene complex XI. This is known to yield both I and II when reduced with NaFp [36]. Finally pathway E accounts for the formation of II by initial formation of a 1-halobenzocyclobutene and subsequent metalation with NaFp.

SCHEME 2



Based on the results at hand, the initial step in the reduction appears to be the generation of benzocyclobutadiene. Thus the formation of the Diels—Alder adduct IV and concomitant decrease in the yields of both I and II suggests that benzocyclobutadiene is the progenitor of both I and II. The fact that both *cis* and *trans* isomers IIIb and IIIc afford the same products is consistent with the intermediacy of benzocyclobutadiene. Also, the generation of benzocyclobutadiene and the failure to isolate I and II when FpMgBr is substituted for NaFp indicates that the dehalogenation is the reductive process of lowest activation energy. It is to be noted that $BrCH_2CHBr$ [37] and $BrCH_2{-}C{\equiv}C{-}CH_2Br$ [38] are quantitatively reduced by NaFp by an apparent E2 dehalogenation. The proclivity of NaFp to attack bromine is dramatically illustrated by the reduction of $BrCH_2SiMe_2Cl$ to form the disilapentane XII [39]. Thus, initial attack by NaFp on the iodo or bromo groups of III is quite reasonable.

$$\text{NaFp} + BrCH_2SiMe_2Cl \rightarrow \underset{\text{(XII)}}{BrCH_2SiMe_2CH_2SiMe_2Cl}$$

If the initial and key intermediate is benzocyclobutadiene, then pathway E may be eliminated as a viable possibility. Conclusive evidence militating against E is obtained by an examination of the stereochemistry of the metalation of *trans*-1-bromo-2-deuterobenzocyclobutene by NaFp. This compound, which is readily prepared by the reduction of IIIa by FpD*, yields an equimolar mixture of IIb and IIc rather than exclusively IIb as is observed in the reduction of IIIa with NaFp.

The benzocyclobutadiene ligand of XI is labile and in principle could be the source of benzocyclobutadiene [36]. However, it has been reported that the reduction of XI in the presence of 1,3-diphenylisobenzofuran failed to yield the Diels—Alder adduct IV, although both I and II were formed [36]. Thus pathway D also is eliminated.

The concerted pathway, C, also can be eliminated since this would give the *cis* product IIc rather than the observed *trans* product IIb.

The anionic pathway A and the radical pathway B remain as viable possibilities. The carbanion VIII should be reactive and be rather indiscriminate base. In contrast, the radical IX should be a rather discriminate hydrogen abstractor since IX is in essence a benzylic radical. An infrared spectrocopic examination of the solutions of NaFp containing t-BuOH, MeOH or H_2O shows that Fp^- (absorption (C≡O) at 1875 and 1780 cm^{-1}) is the major organometallic component of the solution whereas FpH (absorption (C≡O) at 2014 and 1960 cm^{-1}) is a minor component when t-BuOH is the addend. When MeOH is the addend there is a predominance of FpH and when H_2O is the addend there is quantitative conversion of Fp^- to FpH as evidenced by the complete dissappearance of the bands at 1875 and 1780 cm^{-1} (the pK_a of FpH appears to be slightly greater than that of MeOH). Since the reaction follows a different course when only FpH is present (i.e. the H_2O reaction), and since the yield of II increases as the concentration of FpH increases as long as Fp^- is present, it is necessary that both FpH and Fp^- are involved in the reduction. In the experiments with t-BuOH, MeOH and H_2O the total amount of readily available acidic protons is the same whether the proton source is the hydroxylic addend or FpH. Therefore, if the carbanion VIII

---

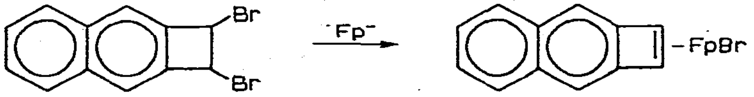
[*] This appears to be a free radical process. We will report on the reactivity of FpH in the very near future [40].

were formed, the yield of II should be the same regardless of the alcohol used. In actuality it is not and maximizes when cyclopentadiene is the addend. On the other hand, if the radical IX is involved and FpH is acting as a hydrogen donor then the yield of II will depend on the amount of FpH available. This is consonant with our observations.

There is additional evidence that militates against the intermediacy of the carbanion. The formation of I from VIII would require the metathesis of VIII with FpX. However, the yields of I and II are essentially uneffected when a mixture of FpBr and IIIa are added to a solution of NaFp. The probability of this metathesis also seems low since FpBr is generated in the presence of a large excess of Fp^-. FpBr is known to undergo a rapid one electron reduction with Fp^-; thus the lifetime of FpBr in the presence of Fp^- will be extremely short [41].

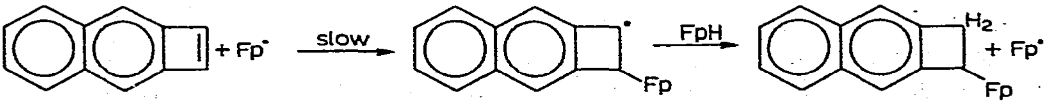
The reduction of FpBr by Fp^- will, however, generate a relatively high concentration of $Fp^\cdot$ radicals in the presence of the highly reactive benzocyclobutadiene. Apparantly the rate of addition of $Fp^\cdot$ to benzocyclobutene to form IX is sufficiently large so as to be able to compete with the facile dimerization of benzocyclobutadiene. IX then either adds an additional $Fp^\cdot$ to form I or abstracts a hydrogen from FpH to form II. It is quite likely that IX is also involved in the Fp^- reduction of the η^2-benzocyclobutadiene complex XI.

It is interesting that FpMgBr and other organometallic anions [28] fail to form the analogs I and II although IIIa is quantitatively reduced. There are two possible explanations of this phenomenon. First, the rate of formation of the requisite organometallic radicals may be slower than the rate of dimerization of benzocyclobutadiene. Second, the organometallic radicals other than $Fp^\cdot$ may not be sufficiently nucleophilic to compete with the dimerization of benzocyclobutadiene.



$$Fp^- + FpBr \longrightarrow 2Fp^\cdot + X^-$$

$$2Fp^\cdot \xrightarrow{\text{fast}} Fp_2$$



(XIII)

The failure of the dibromonaphthocyclobutene V to form the binuclear complex VI probably is a result of the diminished reactivity of naphthocyclobutadiene as compared to benzocyclobutadiene. Thus the rate of reaction between napthocyclobutadiene and $Fp^\cdot$ probably is slower than the rate of dimerization of the $Fp^\cdot$ radicals. Hence the probability of the naphthocyclobutenyl radical XIII reacting with Fp· is small. The concentration of Fp· may be large enough, however, to initiate a radical chain reaction involving Fp·, napthocyclobutadiene and FpH. This would account for the formation of VI.

Experimental

General procedures

In general, all reactions were carried out under a nitrogen atmosphere or in the vacuum line using standard techniques. Complexes I and II were routenily characterized by NMR spectroscopy. The NMR spectra of I and II have been reported elsewhere [28,29]. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Physical measurements

Infrared 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.

Materials

trans-1,2-Dibromo-, *trans*-1,2-diiodo- and *cis*-1,2-diiodo-benzocyclobutene were prepared according to published procedures [42]. 1,3-Diphenylisobenzofuran was purchased from Aldrich Chemical Company. Chromatographic Grade, neutral activity I alumina was used as purchased from Alfa—Ventron.

Reaction between NaCp(CO)$_2$Fe and trans-1,2-dibromobenzocyclobutene

To a 100 ml round flask containing 25.2 mmol of NaCpFe(CO)$_2$ (prepared from 4.46 g [Cp(CO)$_2$Fe]$_2$) in 44.6 ml of tetrahydrofuran at −78°C, was added dibromobenzocyclobutene (3.0 g, 11.4 mmol) in 15 ml of tetrahydrofuran. After warming to room temperature, petroluem ether (60 ml) was added and the solution filtered through Celite. The solvents were removed by rotary evaporation, the residue extracted with benzene and chromatographed on a 4 × 25 cm column of neutral activity I alumina. Sequential elution with petroleum ether and benzene afforded three bands: η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (0.19 g, 6.5% yield based on dibromobenzocyclobutene), 1,2-bis(cyclopentadienyldicarbonyliron)benzocyclobutene with unidentified organic material (0.39 g), and cyclopentadienyldicarbonyl iron dimer.

Reaction between cis- or trans-1,2-diiodobenzocyclobutene and NaCp(CO)$_2$Fe

cis-1,2-Diiodobenzocyclobutene, 1.006 g (2.71 mmol), was added to a 20 ml tetrahydrofuran solution of NaCp(CO)$_2$Fe (5.68 mmol) which was previously cooled to −78°C. After the mixture had warmed to 24°C, 50 ml of petroleum ether was added and the mixture was filtered twice through a 3 cm bed of Celite. The residue which resulted from rotary evaporation of the filtration was dissolved in a minimum amount of benzene and chromatographed on a 32 × 4 cm column of neutral activity I alumina made up in petroleum ether. Elution with 50/50 petroleum ether—benzene afforded, after evaporation of the eluates, ferrocene (0.32 g), II (0.036 g, 5% yield) and III (0.2018 g, 16%).

trans-1,2-Diiodobenzocyclobutene afforded ferrocene (0.155 g), II (0.0705 g, 9%) and III (0.159 g, 13%).

The reaction between trans-1,2-diiodobenzocyclobutene and NaCp(CO)$_2$Fe in the presence of 1,3-diphenylisobenzofuran

To a 100 ml round-bottom flask equipped with a nitrogen inlet tube, was added 40 ml of tetrahydrofuran, 1.32 g (3.70 mmol), of *trans*-diiodobenzocyclobutene, and 1.23 g (4.55 mmol) of 1.3-diphenylisobenzofuran. The bright yellow solution was cooled to —78°C and 14.8 mmol of NaCp(CO)$_2$Fe prepared from 2.62 g (7.4 mmol) of [CpFe(CO)$_2$]$_2$, in 26.2 ml of tetrahydrofuran was synringed into the flask under a stream of nitrogen. The reaction mixture was warmed to room temperature with magnetic stirring. After 45 min, 100 ml of petroleum (30-60°C) was added and the reaction mixture was filtered through Celite and washed with petroleum ether until the washings were colorless. The solvent was rotary evaporated and an NMR spectrum taken on the residue showed no binuclear or mononuclear benzocyclobutene. The residue was taken up in benzene and 2.0 ml of dimethyl acetylenedicarboxylate was added. The mixture was refluxed for 1 hour under nitrogen, filtered through 1 inch alumina (activity 1), and stripped of solvent on a rotary evaporator. The crude product was taken up in benzene and chromatographed through alumina (activity I, 4 × 35 cm column) and eluted with 60/40 petroleum ether—benzene.

The NMR spectra of the fractions collected indicated the presence primarily of the Diels—Alder adduct, a trace of the binuclear benzocyclobutene complex (I), and no detectable mononuclear benzocyclobutene complex (II). Thick-layer chromatography was used to purify the Diels—Alder adduct (0.334 g, 24.4%), which was identified by comparison of its NMR spectrum which that of an authentic sample prepared by the method of Cava [42b]. Similar results were obtained for *trans*-1,2-dibromo- and *cis*-1,2-diiodobenzocyclobutene. The substitution of BrMgFe(CO)$_2$Cp and NaFe(CO)$_2$Cp afforded a 20% yield of the Diels—Alder adduct.

Reaction between NaFe(CO)$_2$Cp and trans-1,2-dibromobenzocyclobutene in the presence of cyclopentadiene

To a 250 ml round bottom flask containing 25.2 mmol of NaFe(CO)$_2$Cp (prepared from 4.46 g [Cp(CO)$_2$Fe]$_2$ in 44.6 ml of tetrahydrofuran and freshly prepared cyclopentadiene (7.55 g, 114 mmol) at —78°C was added *trans*-1,2-dibromobenzocyclobutene (3.0 g, 11.4 mmol) in 15 ml of tetrahydrofuran. The flask was warmed to room temperature, petroleum ether (60 ml) was added and the reaction mixture was filtered through Celite. Following rotary evaporation of the solvents, the residue was extracted with benzene and chromatographed on a 4.5 × 46.5 cm column of neutral activity I alumina. Sequential elution with petroleum ether, benzene, and diethyl ether afforded four bands: ferrocene (0.12 g), η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (1.62 g, 51% yield based on the dibromobenzocyclobutene), I (0.17 g, 3% yield based on dibromobenzocyclobutene) and [Cp(CO)$_2$Fe]$_2$ dimer (1.97 g).

Reaction of NaCp(CO)$_2$Fe with II in the presence of [Cp(CO)$_2$Fe]$_2$

Into a 100 ml round bottom flask containing 5.8 mmol of NaCp(CO)$_2$Fe (prepared from 11.01 g of $[Cp(CO)_2Fe]_2$) and $[Cp(CO)_2Fe]_2$ 2 g (5.7 mmol) in 30 ml of tetrahydrofuran at —78°C was added η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (0.8 g, 2.9 mmol) in 5 ml of tetrahydrofuran. Upon warming to room temperature, petroleum ether (30 ml) was added and the mixture filtered through Celite. The solvents were removed by rotary evaporation and the residue was extracted with benzene. Chromatography on a 4 × 25 cm column of neutral activity I alumina (eluents petroleum ether and benzene) afforded two bands: η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (0.637 g, 80% recovery of the material) and cyclopentadienyldicarbonyliron dimer (1.80 g).

Preparation of trans 1-(η^5-cyclopentadienyldicarbonyliron)-2-deuterobenzocyclobutene (IIb) using D_2O

A 540 ml tetrahydrofuran solution of 0.32 mol $NaFe(CO)_2Cp$ was prepared from 54 g of $[Cp(CO)_2Fe]_2$. D_2O, 6 ml, was added and the resultant solution cooled to —78°C. 1,2-Dibromobenzocyclobutene (18 g, 0.1 mol) in 50 ml THF was added rapidly. Workup as previously described yielded IIb (2.98 g, 23%).

Reaction between trans-1-bromo-2-deutero-benzocyclobutene and $NaFe(CO)_2Cp$

To 1.5 mmol $NaFe(CO)_2Cp$ (prepared from 0.27 g of $[Cp(CO)_2Fe]_2$) in 2.7 ml of tetrahydrofuran at —78°C was added 1.25 mmol (0.2308 g) of *trans*-1-bromo-2-deuterobenzocyclobutene. The reaction mixture was allowed to warm to room temperature, stirred for several minutes and petroleum ether was added. This was filtered through Celite and the solvents removed by rotary evaporation. This residue was extracted with petroleum ether and percolated through one inch of neutral activity I alumina. Removal of the solvent afforded 0.238 g of yellow crystals. These were shown by NMR to be a 1/1 mixture of *cis*- and *trans*-1-cyclopentadienylcarbonyliron-2-deuterobenzocyclobutene. NMR (CS_2): τ 3.20 (m, 4, Ar), 5.45 (s, 5, Cp), 5.95 (d (br), 1), 6.60 (s (br), ½, CHD, *cis* to H), 7.34 (s (br), ½, CHD).

Reaction between $Cp(CO)_2FeMgBr$ and trans-1,2-dibromo benzocyclobutene

To a 250 ml round bottom flask containing 0.05 mol of $Cp(CO)_2FeMgBr$ (prepared from 8.85 g of $[Cp(CO)_2Fe]_2$ in 50 ml of tetrahydrofuran at —78°C) was added 3 g of 1,2-dibromobenzocyclobutene (0.0114 mol). The reaction mixture was allowed to warm to room temperature and the solvent removed by rotary evaporation. The residue was dissolved in benzene, filtered through Celite and the benzene removed by rotary evaporation. The solid was extracted with petroleum ether. The residue was shown by NMR to consist only of $[Cp(CO)_2Fe]_2$. The petroleum ether fraction was condensed by rotary evaporation to approximately 20 ml and chromatographed on a 4 × 45 cm column of activity I alumina Elution with petroleum ether and 50/50 petroleum ether—benzene afforded six bands. The first band consisted of 0.032 g ferrocene. The last five bands afforded 0.179 g of unidentified organic products. Neither I or II were observed during the course of this reaction.

Reaction of $NaCp(CO)_2Fe$ with 1,2-dibromobenzocyclobutene in the presence of $Cp(CO)_2FeBr$

To a 250 ml round bottomed flask containing 25.2 mmol of $NaCp(CO)_2Fe$

(prepared from 4.46 g of [Cp(CO)$_2$Fe]$_2$ in 45 ml of tetrahydrofuran at —78°C) was added a finely ground mixture of 1,2-dibromobenzocyclobutene (3 g, 11.4 mmol) and Cp(CO)$_2$FeBr (2.57 g, 10 mmol). The mixture was swirled, allowed to warm to room temperature, and the solvent was removed by rotary evaporation. The solid material was extracted with benzene and filtered through Celite. The solution was concentrated by rotary evaporation to a volume of approximately 10 ml and chromatographed on a 4 X 30 cm column of activity I neutral alumina. Elution with petroleum ether, gradually changing to benzene, afforded four bands. The first consisted of ferrocene (0.1673 g). The second was η^1-1-benzocyclobutenyl-η^5-cyclopentadienyldicarbonyliron (0.1989 g, 6.2% yield based on the dibromobenzocyclobutene). The third band was 1,2-bis(cyclopentadienyldicarbonyliron)benzocyclobutene (0.7068 g, 14% based on the dibromobenzocyclobutene).

Reaction between trans-1,2-dibromobenzocyclobutene and NaCp(CO)$_2$Fe in the presence of weak acids: methanol, t-butanol, water, and methanol with styrene

In a typical run, in a 250 ml round bottom flask were placed 25.2 mmol of NaCp(CO)$_2$Fe (prepared from 4.46 g of [Cp(CO)$_2$Fe]$_2$) in 44.6 g of tetrahydrofuran and 0.375 mol of the hydroxylic addend. This mixture was cooled to —78°C and 11.4 mmol (3 g) of 1,2-dibromobenzocyclobutene was added. The mixture was allowed to warm to room temperature , petroleum ether was added, and the reaction mixture was filtered through Celite. Following rotary evaporation of the solvent, the residue was extracted with 15 ml of benzene and chromatographed on a 4 X 35 cm column of neutral activity I alumina. The products were isolated by sequential elution with petroleum ether, 50/50 petroleum ether—benzene, and finally benzene.

In the presence of t-butanol, methanol or water, the yield of IIa was 12, 37 or <1%, respectively. In the water reaction, the major product was 1-bromobenzocyclobutene (18%). When styrene (4 g) was added to the methanol reaction, the yield of IIa was reduced to 28%.

Reaction between 1,1- and 1,2-dibromonaphthalocyclobutenes and NaCp(CO)$_2$Cp in the presence of methanol.

To a 100 ml tetrahydrofuran solution of NaCp(CO)$_2$Fe (0.10 mol, prepared from 17.7 g of [Cp(CO)$_2$Fe]$_2$) was added 5 ml of methanol. The mixture was cooled to —78°C and 8 g (0.025 mol) of a mixture of the dibromonaphthocyclobutenes in 20 ml of tetrahydrofuran was added. The mixture was warmed in room temperature, filtered through Celite. The residue that results from rotary evaporation of the filtrate was chromatographed on a 4 X 45 cm column of neutral activity I alumina. Elution with 50/50 petroleum ether—benzene afforded η^1-1-naphthocyclobutenylcyclopentadienyldicarbonyliron (VI) 3.8 g (44% based on starting bromide). VI was identified by comparison of its NMR spectrum to that of an authentic sample [30b].

Acknowledgement

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

References

1 R.G. Pearson and W.R. Muir, J. Amer. Chem. Soc., 92 (1970) 5519.
2 J.A. Labinger, R.J. Braus, D. Dolphin and J.A. Osborn, Chem. Commun., (1970) 612.
3 J.A. Labinger, A.V. Kramer and J.A. Osborn, J. Amer. Chem. Soc., 95 (1973) 7908 and refs. therein.
4 J.S. Bradley, D.E. Connor, D. Dolphin, J.A. Labinger and J.A. Osborn, J. Amer. Chem. Soc., 94 (1972) 4043.
5 F.R. Jensen and B. Knickel, J. Amer. Chem. Soc., 93 (1971) 6339.
6 S. Otsuka, A. Nakamura, T. Yoshida and M. Naruto, J. Amer. Chem. Soc., 95 (1973) 3180.
7 K.S.Y. Lau, R.W. Fries and J.K. Stille, J. Amer. Chem. Soc., 96 (1974) 4983.
8 P.W. Schneider, P.F. Phelan and J. Halpern, J. Amer. Chem. Soc., 77 (1969)
9 J. Halpern and J.P. Maher, J. Amer. Chem. Soc., 87 (1965) 5361.
10 J. Kwiatik and J.K. Seyles, J. Organometal. Chem., 3 (1965) 421.
11 C.E. Castro and W.C. Kray, J. Amer. Chem. Soc., 85 (1963) 2768.
12 C.H.W. Jones, R.G. Jones, P. Partington and R.M.G. Roberts, J. Organometal. Chem., 32 (1971) 201.
13 G.S. Koermer, M.L. Hall and T.G. Taylor, J. Amer. Chem. Soc., 94 (1972) 7205.
14 H.G. Kuivila, J.L. Considine and J.D. Kenedy, J. Amer. Chem. Soc., 94 (1972) 7206.
15 P.L. Bock, D.J. Boschetto, J.R. Rasmussen, J.P. Demers and G.M. Whitesides, J. Amer. Chem. Soc., 96 (1974) 2814.
16 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 93 (1971) 1529.
17 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 91 (1969) 4313.
18 J.P. Collman, S.R. Winter and D.R. Clark, J. Amer. Chem. Soc., 94 (1972) 1788.
19 K.M. Nicholas and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 4449.
20 R.W. Johnson and R.G. Pearson, Chem. Commun., (1970) 986.
21 D. Dodd and M.D. Johnson, Chem. Commun., (1971) 571,
22 G.N. Schrauzer and E. Deutsch, J. Amer. Chem. Soc., 91 (1969) 3341.
23 F.R. Jensen, V. Madan and D.H. Buchanan, J. Amer. Chem. Soc., 93 (1971) 5283.
24 F.R. Jensen, V. Madan and D.H. Buchanan, J. Amer. Chem. Soc., 92 (1970) 1414.
25 R.F. Heck, J. Amer. Chem. Soc., 85 (1963) 1460.
26 A. Cutler, R.W. Fish, W.P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 94 (1972) 4354.
27 F.R. Jensen and D.H. Buchanan, J. Chem. Soc. Chem. Commun., (1973) 153.
28 R.B. King, W.C. Zipperer and A. Efraty, J. Organometal. Chem., 38 (1972) 121.
29 A. Sanders, C.V. Magatti and W.P. Giering, J. Amer. Chem. Soc., 96 (1974) 1610.
30 a. A. Sanders, L. Cohen, W.P. Giering, D. Kenedy and C. Magatti, J. Amer. Chem. Soc., 95 (1973) 5430.
b. A. Sanders, C. Lorenc, C.V. Magatti, L. Cohen, D. Kenedy and W.P. Giering, submitted for publication.
31 M. Rosenblum, Accounts Chem. Res., 7 (1974) 122.
32 R.B. King, Accounts Chem. Res., 3 (1970) 417.
33 L. Cohen, W.P. Giering, D. Kenedy, C.V. Magatti and A. Sanders, J. Organometal. Chem., 65 (1974) C57.
34 M.P. Cava and R. Poheke, J. Org. Chem., 27 (1962) 1564.
35 a. M.P. Cava and A.F.C. Hsu, J. Amer. Chem. Soc., 94 (1972) 6441.
b. M.P. Cava and R.L. Shirley, J. Amer. Chem. Soc., 82 (1960) 654.
36 A. Sanders, T. Bauch and W.P. Giering, submitted for publication.
37 W.P. Giering, unpublished results.
38 T. Bauch and W.P. Giering, submitted for publication.
39 C. Windus, S. Sujishi and W.P. Giering, J. Organometal. Chem., in press.
40 T. Bauch, P. Waterman, E. Chou and W.P. Giering, work in progress.
41 R.E. Dessy and P.M. Weissman, J. Amer. Chem. Soc., 88 (1966) 5124.
42 a. F.R. Jensen and W.E. Coleman, J. Org. Chem., 23 (1958) 869.
b. G. Fraenkel, Y. Asahi, M.J. Mitchell and M.P. Cava, Tetrahedron, 20 (1964) 1179.