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ADDITION REACTIONS TO CYCLOPOLYOLEFIN TRANSITION METAL π COMPLEXES *

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Summary

The non-coordinated double bonds of (η^4-1,2,3,4-cycloheptatriene)Fe(CO)$_3$ and (η^4-1,2,5,6-cyclooctatetraene)Co(η^5-C$_5$H$_5$) add methylene generated from the Simmons-Smith reaction to yield (η^4-2,3,4,5-bicyclo[5.1.0]octa-2,4-diene)-Fe(CO)$_3$ and (η^4-2,3,7,8-tricyclo[7.1.0.0^{4,6}]deca-2,7-diene)Co(η^5-C$_5$H$_5$). An analogous reaction of (η^4-1,2,3,4-cyclooctatetraene)Fe(CO)$_3$ yields (η^4-6,7,8,9-tricyclo[8.1.0.0^{3,5}]undeca-6,8-diene)Fe(CO)$_3$, a product of the addition of three equivalents of methylene in which a cyclopropyl ring opening is proposed to occur. Dichlorocarbene, generated from $C_6H_5HgCCl_2Br$, would not react in a similar fashion. A $BH_3 \cdot$ THF solution would react with these starting materials but unusual products were produced.

Introduction

The coordination of an alkene or polyalkene molecule to a transition metal substantially perturbs the organic ligand. For example, in the X-ray crystal structure of η^4-1,2,3,4-cyclooctatetraeneiron tricarbonyl [1] the two non-coordinated double bonds have a normal butadiene type structure whereas the C—C bond distances of the coordinated diene fragment are all essentially equal and lengthened considerably from a normal C—C double bond length. One can take chemical advantage of these changes to alter the reactivity of coordinated alkene and alkyne molecules. For example, compounds of the general formula (diene)Fe(CO)$_3$ are inert to Br$_2$ and H$_2$ under conditions in which the free diene would react [2]. Use of metal coordination to specific functional groups in polyfunctional molecules should thus lead to reactions in which the metal acts as a blocking or directing reagent [3]. This idea has been used, for example, in

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* No reprints available.

the protection of the alkyne group in reactions with other functionality for substituted alkyne-cobalt complexes of the general formula $(RCCR')Co_2(CO)_6$ [4]. Also, the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ group has been used to protect specific double bonds from electrophilic addition reactions [5]. A variety of electrophiles have been reacted with cyclic polyalkenes coordinated to a transition metal [6]. In many of these reactions rearranged products are observed as in the simple protonation [7] and tetracyanoethylene addition reaction [8] with η^4-1,2,3,4-cyclooctatetraeneiron tricarbonyl.

It was decided to use the coordination of some but not all of the double bonds in cyclopolyolefins to direct the location of addition reactions of carbenes to alkenes to form cyclopropane derivatives. One report of an unsuccessful reaction of this type had been briefly reported [6b] but in light of the other successful work in this area this project was initiated. We have shown that methylene, generated from the Simmons-Smith reaction [9] will add to free double bonds in cycloalkene metal complexes. Reactions with dihalocarbene were unsuccessful and the reaction of these molecules with $BH_3 \cdot THF$ lead to unexpected products. A preliminary report of this work has appeared [10].

Experimental

General data

All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Carbon-13 NMR spectra were recorded with ^1H decoupling using CS_2 as the solvent and internal standard. Chemical shifts are reported in ppm vs. TMS assigning the CS_2 resonance to be at 192.8 ppm. $(\eta^4\text{-}1,2,3,4\text{-}C_8H_8)Fe(CO)_3$ [11] and $(\eta^4\text{-}1,2,3,4\text{-}C_7H_8)Fe(CO)_3$ [12] were prepared by literature methods. $(\eta^4\text{-}1,2,5,6\text{-}C_8H_8)Co(\eta^5\text{-}C_5H_5)$ was prepared by mixing $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and cyclooctatetraene in refluxing hydrocarbon solvent (boiling range 110°—120°C) for 18 hours. Purification using column chromatography yielded unreacted $(\eta^5\text{-}C_5H_5)Co(CO)_2$, which was recycled, and $(\eta^4\text{-}1,2,5,6\text{-}C_8H_8)Co(\eta^5\text{-}C_5H_5)$. Total conversion after two reactions was 52%. Seyferth reagent was purchased from Ventron Corporation or prepared by literature methods [13]. Zinc—copper couple was prepared by the method of LeGoff [14a] or of Shank and Shechter [14b]. No differences in reactivity were noted. Borane in THF solution was purchased from Ventron Corporation. CD_2I_2 was prepared by a literature method [15].

Simmons-Smith reactions

With $(\eta^4\text{-}1,2,3,4\text{-}C_7H_8)Fe(CO)_3$. To a 100 ml three neck flask fitted with a reflux condenser and a pressure equalizing dropping funnel was added zinc—copper couple (3.8 g) and one crystal of I_2. After evacuating the system and refilling with N_2, CH_2I_2 (3.47 ml, 11.6 g, 43 mmol) and ether (20 ml) were added to the flask and $(\eta^4\text{-}1,2,3,4\text{-}C_7H_8)Fe(CO)_3$ (1.5 ml, 2.0 g, 8.6 mmol) and ether (20 ml) were added to the dropping funnel. The solution in the flask was heated to reflux. Within 0.5 h, the purple color of I_2 was replaced by a grey color. The solution of $(\eta^4\text{-}1,2,3,4\text{-}C_7H_8)Fe(CO)_3$ was added to the refluxing mixture, and the resulting mixture allowed to reflux an additional 18 hours. At the end of this time, the solution was allowed to cool, reduced in volume by evaporation, and chromatographed on a column prepared from 75% Woelm, 25% Alcoa alumina with hexane. Elution with hexane yielded a yellow band which was collected to afford yellow crystals (0.40 g. 23%) upon evaporation of the solvent. The IR and ^{1}H NMR spectra of this complex match the literature values for (bicyclo[5.1.0]octadiene)Fe(CO)$_3$ [7a]. The ^{13}C NMR spectrum is identical to that measured by us on an authentic sample: δ(C) 211.5 (CO); 88.5, 85.8 (C_3, C_4); 64.2, 62.1 (C_2, C_5); 24.6 (C_6); 18.9 (C_8); 15.4, 14.8 (C_1, C_7).

(η^4-1,2,3,4-C_7H_8)Fe(CO)$_3$ and CD_2I_2 were allowed to react under conditions similar to those described above to yield (8,8-dideuteriobicyclo[5.1.0]octadiene)Fe(CO)$_3$. The ^{13}C NMR spectrum of this material is the same as that presented above except that the resonance at 18.9 was not observed.

With (η^4-1,2,3,4-C_8H_8)Fe(CO)$_3$. A reaction of (η^4-1,2,3,4-C_8H_8)Fe(CO)$_3$ (2.0 g, 8.2 mmol) and CH_2I_2 (6.6 ml, 22 g, 82 mmol) was carried out as described above. Purification by chromatography yielded a yellow solid shown to be η^4-6,7,8,9-bicyclo[8.1.0.0^{3,5}]undecadieneiron tricarbonyl (0.98 g, 42%) (Found: C, 58.60, H, 5.07. $C_{14}H_{14}O_3Fe$ calcd: C, 58.77; H, 4.90.) High resolution mass spectrum: calcd for $C_{14}H_{14}O_3Fe^+$, 286.0291; Found: 286.0300. IR spectrum (cm^{-1} in hexane): ν(CO) 2035, 1970, and 1960. ^{13}C NMR spectrum: δ(C) 211.4, 91.9, 66.0, 29.5, 24.8, 19.1, and 18.6; for assignments see the Results and discussion section. ^{1}H NMR (δ in C_6D_6): 4.67 (2, doublet of triplets, inner olefin protons), 3.56 (2, doublet of triplets, outer olefin protons), 2.01 (1, broad doublet, ring methylene *exo*), 1.47, 0.85 (2,4, multiplets, protons on C_1, C_3, C_5, C_{10} and cyclopropyl methylene *exo*), 0.46 (1, multiplet, ring methylene *endo*) and −0.11 (2, multiplet cyclopropyl methyl *endo*).

(η^4-1,2,3,4-C_8H_8)Fe(CO)$_3$ and CD_2I_2 were allowed to react under the conditions described above, yielding a yellow solid. Mass spectrum: 292 (molecular ion). ^{1}H NMR (δ in CS_2, from external TMS): 5.35 (2, multiplet, inner diene), 3.78 (2, multiplet, outer diene), 1.30 (4, second order AB pattern, bridgehead). ^{2}H NMR (proton decoupled, δ in CS_2 measured from external acetone-d_6): 3.01, 1.98, 1.39, and 1.00, relative intensity 1 : 2 : 1 : 2. ^{13}C NMR: 211.4, 91.1, 65.9, 24.5 and 18.1. See Results and discussion section for assignments of the ^{13}C and ^{2}H spectra.

With (η^4-1,2,5,6-C_8H_8)Co(η^5-C_5H_5). A reaction of (η^4-1,2,5,6-C_8H_8)Co(η^5-C_5H_5) (2.0 g, 8.8 mmol) and CH_2I_2 (7.1 ml, 23.5 g, 88 mmol) was carried out as described above. Purification by column chromatography yields yellow crystals of η^4-2,3,7,8-tricyclo[7.1.0.0^{4,6}]deca-2,7-dienecobalt (η^5-cyclopentadienyl) (0.43 g, 19%). High resolution mass spectrum: calc for $C_{15}H_{17}Co^+$, 256.0662; found, 256,0632. ^{13}C NMR spectrum: δ(C) 83.92, 65.58, 21.34, and 12.58; for assignment see Results and discussion section. ^{1}H NMR (δ in CS_2): 4.38 (5, singlet, cyclopentadienyl protons), 3.50 (4, singlet, olefinic protons), 1.2 (2, multiplet, *exo* methylene protons), 0.69 (4, doublet, bridgehead protons) and 0.06 (2, singlet, *endo* methylene protons).

Hydroboration reactions

Reaction of $BH_3 \cdot THF$ with (η^4-1,2,3,4-C_8H_8)Fe(CO)$_3$. To a solution of (η^4-1,2,3,4-C_8H_8)Fe(CO)$_3$ (2 g, 8.2 mmol) in ether (15 ml) was added via pressure equalizing dropping funnel $BH_3 \cdot THF$ (0.93 *M* in ether, 8.8 ml, 8.2

mmol). This mixture was stirred for two hours, after which time ethylene glycol was added dropwise to consume unreacted $BH_3 \cdot THF$. This mixture can be treated with glacial acetic acid (20 ml) or a basic solution of H_2O_2, or this step omitted, obtaining the same product in each case. The mixture was filtered, obtaining a crude solid which was dissolved in benzene and this solution chromatographed on 25% Woelm, 75% Alcoa alumina. Elution with benzene yields a yellow solution, which, upon evaporation of solvent, yields a yellow solid whose IR and ^1H NMR spectra are identical with those reported for (η^4-1,2,3,4: η^4-5,6,7,8-C_8H_8)$Fe_2(CO)_6$ (0.59 g, 38%) [11]. ^{13}C NMR: δ(C) 93.4 (inner diene carbons), 57.4 (outer diene carbons) (CO resonance was not observed due to saturation because of the experimental conditions used).

Reaction of (η^4-1,2,3,4-C_7H_8)$Fe(CO)_3$ with $BH_3 \cdot THF$. To a solution of (η^4-1,2,3,4-C_7H_8)$Fe(CO)_3$ (2.5 ml, 3.4 g, 14 mmol) in THF (20 ml) was added via pressure-equalizing dropping funnel $BH_3 \cdot THF$ (7.5 ml of 0.93 *M* solution, 7.0 mmol) and the resulting solution stirred for one hour. At the end of this time, a yellow solid had formed. Ethylene glycol was added dropwise to consume unreacted $BH_3 \cdot THF$. Filtration of the solution yielded a crude yellow solid which could be recrystallized from hot hexane to yield yellow crystals (1.5 g). The same product is obtained if the reaction mixture is treated with glacial acetic acid or with an alkaline H_2O_2 solution prior to filtration. This material is believed to be η^4-1,2,3,4 : η^4-7,8,9,10-cyclododeca-1,3,7,9-tetraenediiron hexacarbonyl (Found: C, 49.07; H, 3.68; Fe, 25.23; O (by difference), 22.02. $C_{18}H_{16}O_6Fe_2$ calcd: C, 49.09; H, 3.64; Fe, 25.45; O, 21.82.) ^1H NMR (δ in C_6H_6): 5.20 (4, quartet, inner diene protons), 3.05 (4, multiplet, outer diene protons), 1.98 (8, triplet, methylene protons). ^{13}C NMR: δ(C) 211.5 (CO), 89.5 (inner diene carbons), 61.0 (outer diene carbons), 29.4 (CH_2). IR (cm^{-1} in benzene): ν(CO) 2060 (Sharp), 1930 (Broad).

Oxidative cleavage of ligands from products

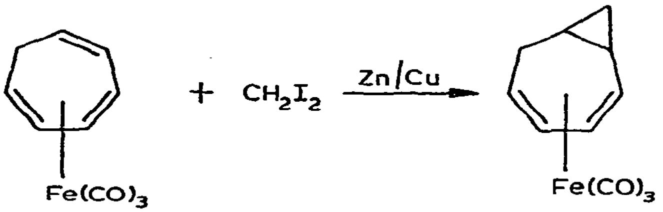
Tricyclo[8.1.0.0^{3,5}]undecadiene. To a solution of tricyclo[9.1.0.0^{3,5}]undecadieneiron tricarbonyl (0.2 g, 0.7 mmol) in MeOH (10 ml) maintained at 0° C was added dropwise via pressure-equalizing dropping funnel a solution of $Ce(NH_4)_2(NO_3)_6$ (1.15 g, 2.1 mmol) in MeOH (20 ml). The resulting mixture was kept at 0° C and stirred for one hour, upon which the mixture was poured into a separatory funnel containing CH_2Cl_2 and ice water. The organic layer was collected, dried over $MgSO_4$, and the solvent evaporated at 0° C; yielding a small amount of yellow liquid. ^{13}C NMR recorded in MeOH: δ(C) 131.7, 127.8 (C_6, C_7, C_8, C_9); 29.7 (C_2); 18.8, 16.5, 14.4 (cyclopropyl carbons).

Tricyclo[7.1.0.0^{4,6}]decadiene. To $C_{10}H_{12}Co(\eta^5$-$C_5H_5)$ (0.55 g, 2.2 mmol) dissolved in MeOH (100 ml) was added $Ce(NH_4)_2(NO_3)_6$ (2.5 g, 4.5 mmol) and the resulting mixture stirred thirty minutes. The mixture was then poured into a separatory funnel with water and ether, the organic layer collected, dried over $MgSO_4$, and the solvent removed. ^{13}C NMR: δ(C) 133.9 (olefinic), 18.3 (bridgehead), 13.5 (methylene). Mass spectrum: 132 (parent ion), 118 (parent ion minus one methylene), 104 (parent ion minus two methylenes).

Results and discussion

Carbene addition reactions

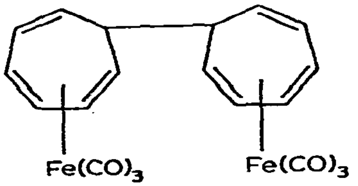
That methylene can be added to the non-coordinated double bonds of cyclopolyolefin metal complexes is shown by equation 1.



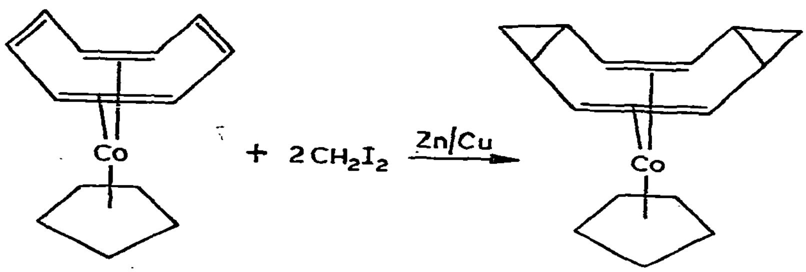
(1)

(I)

The product of the reaction, I, is a known complex in which the stereochemistry of the cyclopropyl ring is known to be *trans* or *anti* to the metal. Thus, the methylene addition takes place specifically on the less sterically hindered face of the ring as expected. A reaction similar to that shown in equation 1 has been reported to yield the binuclear compound pictured below [6b]. We have not observed this product in our reaction. As definitive assignment of the cyclopropyl ring methylene carbon atom in the $^{13}C\ \{^1H\}$ NMR spectrum was desired, 8,8′-dideutero-I was prepared using CD_2I_2 in reaction 1. The resonance at 18.9 ppm in the spectrum of I was absent in the spectrum of the dideutero compound and is assigned to the cyclopropyl methylene carbon atom. A CD_2 carbon atom would be expected to show as a quintet slightly shifted from its original position and was simply not observed in the spectrum of this relatively dilute sample.



A similar reaction of $(\eta^4\text{-1,2,5,6-}C_8H_8)Co(\eta^5\text{-}C_5H_5)$ with excess Simmons-Smith reagent yields II as shown in equation 2

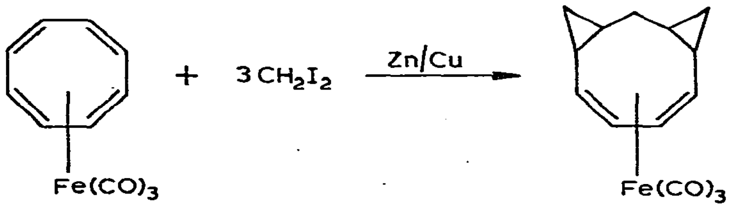


(2)

(II)

In this reaction, the tub configuration of the C_8H_8 ring in the starting material blocks reaction at the *anti* side of the ring and thus the expected stereochemistry of II is for both cyclopropyl rings to be *syn* to the metal. The $^{13}C\ \{^1H\}$ NMR spectrum of II shows only three resonances for the $C_{10}H_{12}$ ring assigned to the four coordinated olefinic carbon atoms (65.58 ppm), the four bridgehead methine carbon atoms (12.58 ppm) and a third of ca. half the intensity of the previous two assigned to the two methylene carbon atoms (21.34 ppm) in addition to the resonance for the η^5-C_5H_5 carbon atoms (83.92 ppm). Thus, only a completely symmetrical isomer is produced, believed to have the *syn* configuration.

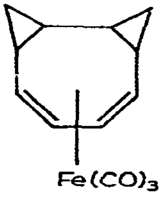
Unexpectedly, a similar reaction of excess Simmons-Smith reagent with (η^4-1,2,3,4-C_8H_8)$Fe(CO)_3$ yields III as shown in equation 3.



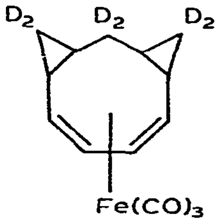
(3)

(III)

The expected product, IV, is not observed. The molecular formula is supported by both elemental analysis and high resolution mass spectroscopy.



(IV)



(V)

The molecular structure was elucidated using the ^1H, $^2H\ \{^1H\}$ and $^{13}C\ \{^1H\}$ NMR spectra of III and V prepared as in reaction 3 using CD_2I_2. The $^{13}C\ \{^1H\}$ spectra of III and V are shown in Fig. 1 with the appropriate assignments. As with I, deuterium substituted carbon atoms disappear into the base line due to carbon—deuterium coupling. Support for the assignments is that the cyclopropyl methylene groups resonate at 19.1 ppm, very close to that for the analogous methylene group in I. The spectra clearly show that the cyclopropyl groups are on the same side of the ring, presumably *anti* to the metal similar to the known structure of I. Although the ^1H NMR of III is complex, the ^1H NMR spectrum of V (Fig. 2) shows the expected resonances for the coordinated diene hydrogen atoms and the four resonances of a second order AB pattern centered at δ 1.30 as expected for the remaining four hydrogen atoms in V. The $^2H\ \{^1H\}$ NMR spectrum of V is shown in Fig. 3. The less intense reso-

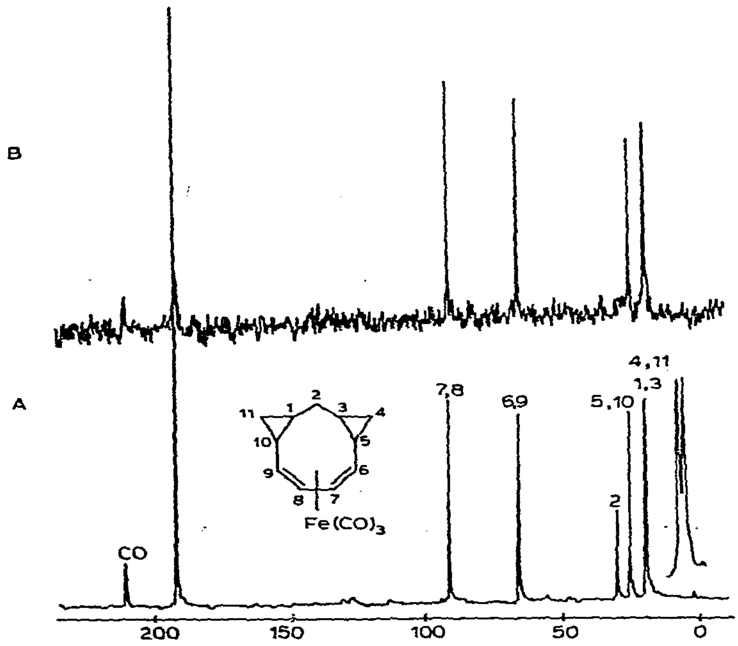


Fig. 1. Proton decoupled ^{13}C NMR spectra. A. Compound III with peak assignments and proposed structure. Insert at right is an expansion of the resonances assigned to carbons 1, 3, 4 and 11. B. The d^6 analog of III, deuterated at positions 2, 4, and 11. The resonance at 193 in both is from the CS_2 solvent.

nances at 3.01 and 1.39 ppm are assigned to the ^2H atoms of the unique methylene group and those at 1.98 and 1.0 to the cyclopropyl methylene ^2H atoms. Following Aumann, the more deshielded resonance of cyclopropyl methylene groups is *exo* with respect to the ring [16]. The analysis of the complex ^1H NMR of III follows these assignments (see Experimental).

Scheme 1 shows a reasonable mechanism for the formation of III. The first equivalent of methylene adds to transform the ligand into bicyclo[6.1.0]nona-

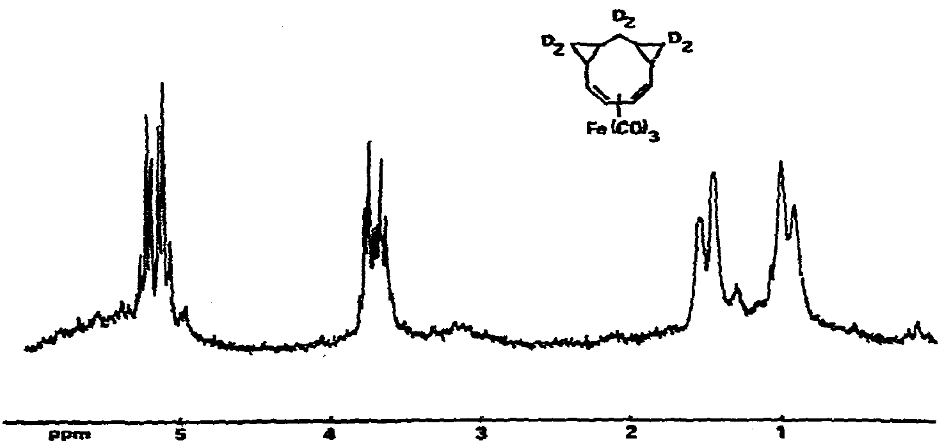


Fig. 2. Proton NMR of V in CS_2. For assignments see Results and discussion section.

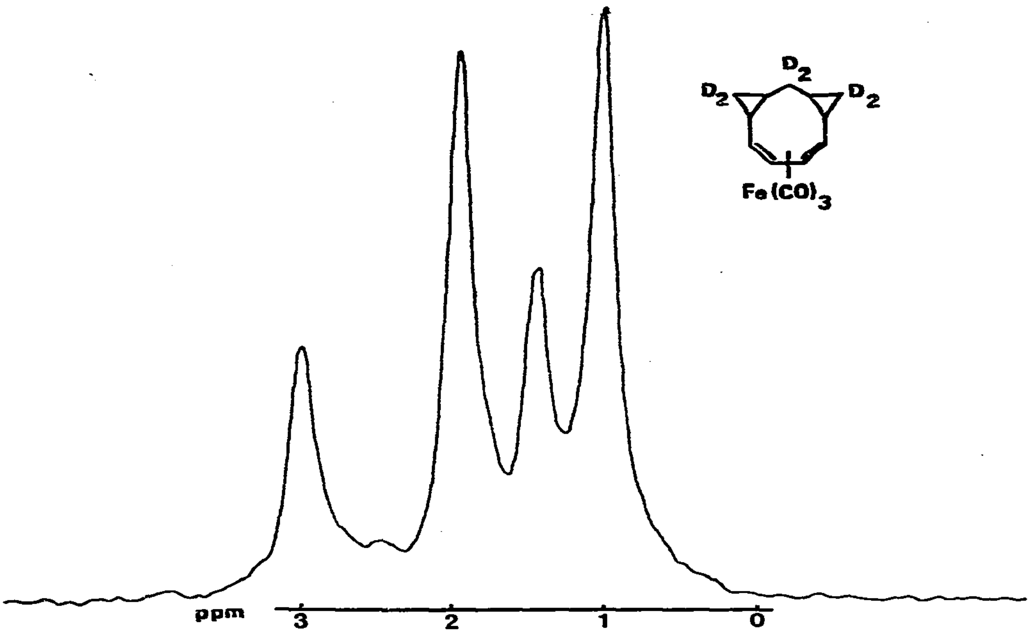
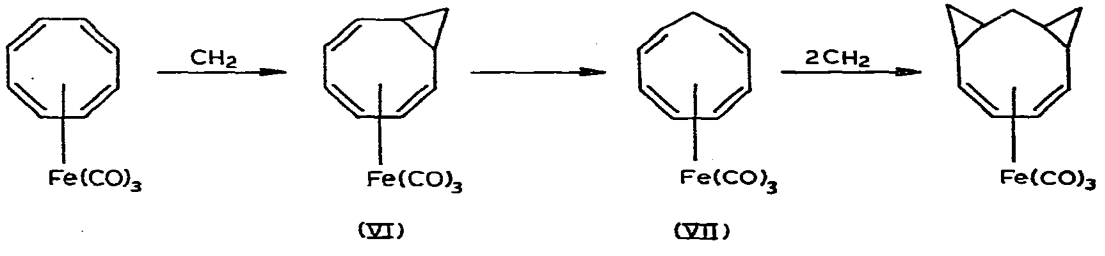
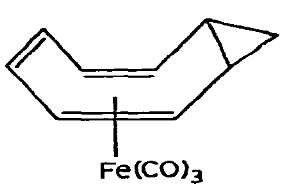


Fig. 3. Deuterium NMR of V in CS_2. For assignments see Results and discussion section.

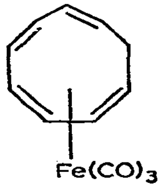
triene which undergoes ring opening and a 1,2 iron shift to yield VII faster than it adds a second equivalent of methylene to form the expected product IV. This ring opening is known to occur for the free organic molecule at 90° C [17] or when photolyzed at low temperature [18], followed by collapse to dihydroindene. The intermediate VI is proposed to be the *anti* isomer in accordance with earlier arguments. An isomer, VIII, has been prepared, along with other products in the reaction of bicyclo[6.1.0]nonatriene with iron carbonyls [19]. As double bonds adjacent to the cyclopropyl ring are coordinated to the metal, this isomer is not expected to rearrange readily as does VI. In this same reaction of bicyclo[6.1.0]nonatriene, IX, an isomer of VII as well as small amounts of VII have been reported [19,20]. These results are not in conflict with the proposed exclusive formation of VII in Scheme 1 because isomerization in these reactions is believed to take place before the final coordination of the Fe$(CO)_3$ fragment.

SCHEME 1





(VIII)



(IX)

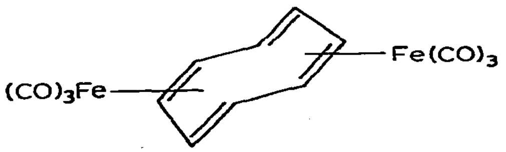
Once the ring opening occurs, two more equivalents of methylene can add to the free double bonds of VII to yield the observed product. These additions must be more rapid than the first because when the amount of Simmons-Smith reagent was limited in the reaction, only a lower yield of III was obtained along with starting material. Note that this proposed scheme fits the deuteration study. Also, this study eliminate more complicated rearrangements involving hydrogen shifts.

Small amounts of the free polycyclic ligands from II and III were isolated by oxidative cleavage reactions with Ce^{4+} and were identified by ^{13}C NMR. As with the *trans* isomer of II [21], both of these compounds are stable to rearrangement when heated at ca. 80°C for 8 h.

The Seyferth reagent, $C_6H_5HgCCl_2Br$, is known to deliver CCl_2 under mild conditions [22]. Heating this reagent in benzene with each of the three starting materials outlined above for the Simmons-Smith reactions did not lead to the isolation of the expected dihalocarbene addition products. Although the starting materials were consumed, no iron or cobalt containing species were identified. A very recent publication has demonstrated that CCl_2 generated from $CHCl_3$ and base can be added to the non-coordinated bond of (η^4-1,2,3,4-cycloheptratriene)$Fe(CO)_3$ [23] and also to some similar acyclic systems.

Hydroboration reactions

The reaction of (η^4-1,2,3,4-C_8H_8)$Fe(CO)_3$ with commercially available $BH_3 \cdot$ THF solution followed by a variety of standard work-up conditions yields the known complex X [1,11]. Even more unexpected was the product of an analogous reaction with (η^4-1,2,3,4-C_7H_8)$Fe(CO)_3$ believed to be XI from a total analysis and ^1H and ^{13}C $\{^1H\}$ data. Comparison with an authentic sample proves that it is not (1,3-cyclohexadiene) $Fe(CO)_3$. How such a molecule would form in the reaction is not clear. Unfortunately, crystals of suitable quality for an X-ray crystal structure could not be obtained. Finally, (η^4-1,2,5,6-C_8H_8)Co-(η^5-C_5H_5) formed an insoluble material when mixed with $BH_3 \cdot$ THF. It should be noted that (η^4-1,2,3,4-hepta-1,3,5-triene)$Fe(CO)_3$ reacts with BH_3 generated in situ from BF_3/$NaBH_4$ at the non-coordinated double bond to yield after oxidative work-up the expected alcohol product [24].



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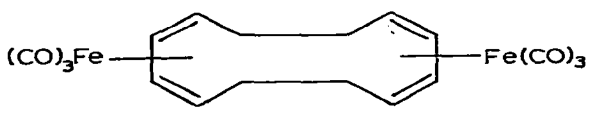

(XI)

Acknowledgement

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