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METAL VAPOR SYNTHESIS OF (η^5-CYCLOPENTADIENYL)(η^5-CYCLOHEXADIENYL)IRON

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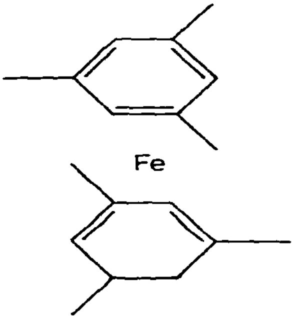
Summary

The cocondensation of iron atoms and benzene onto a liquid nitrogen cooled surface gives a reactive intermediate which, when reacted with cyclopentadiene, gives Fe(η^5-C_5H_5)(η^5-C_6H_7). An isotopic labelling study indicates that the hydrogen transfer from cyclopentadiene to coordinated benzene occurs *exo* with respect to the metal and is intermolecular in nature.

Introduction

A variety of (η^6-arene)(η^4-diene)iron complexes have been prepared by metal vapor syntheses. Though many of the syntheses were by design [1—3], several were fortuitous [2,3]. For example, the cocondensation of iron atoms with mesitylene gave I. Formation of the coproduct, bimesityl, indicates that the two additional hydrogen atoms in the diene of I were abstracted from two separate molecules of mesitylene. In another reaction [3,4] cocondensation of



(I)

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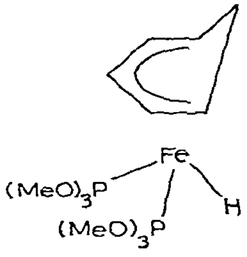
[*] Contribution No. 2702.

cyclohexadiene and iron atoms gives (η^6-benzene)(η^4-cyclohexadiene)iron(II) and extensive disproportionation of the cyclohexadiene to cyclohexene and benzene. These reactions and others indicate that iron atoms can readily transfer hydrogen atoms between unsaturated organic molecules.

An appealing mechanism for this hydrogen atom transfer involves a metal hydride intermediate formed by *endo* hydrogen atom transfer. Such a transfer has been proposed previously [3b]. The discovery of III in a mixture of products formed by the cocondensation of iron atoms with cyclohexadiene and trimethyl phosphite fits nicely with this mechanism. Additional support comes from the stereospecific hydrogen atom transfer observed in the mass spectroscopic fragmentation of (η^5-cyclopentadienyl)(η^5-cyclohexadienyl)iron (IV) [5] and (cyclohexadiene)tricarbonyliron (V) [6]. Both these species transfer an *endo*-hydrogen atom from the ring to the metal giving an arene hydride and a dienyl hydride, respectively.



(III)

The preparation of IV from the (cyclopentadienyl)(benzene)iron cation is a well-known reaction [5,7]. The product was originally formulated as the zerovalent species, (η^6-benzene)(η^5-cyclopentadiene)iron(VI) [7a] but more detailed spectroscopic characterization led to the correct structural assignment [7b]. Skell has previously mentioned the synthesis of IV by metal vapor techniques [8a], and a detailed report will be published [8b].

Results

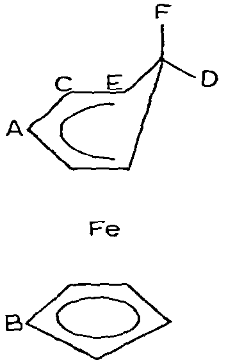
The reaction of iron atoms with benzene on a liquid nitrogen cooled surface gives a highly reactive mixture [9] which decomposes to bulk metal and benzene upon warming to room temperature. When the mixture is reacted with cyclopentadiene at −120°C, two products are isolated: IV and a small quantity of ferrocene [8]. Although the procedure gives (η^6-arene)(η^4-diene)iron species for other dienes [1], no such product is observed in this reaction. The 220 MHz ^{1}H NMR spectrum and assignment given in Table 1 are consistent with the literature [5b].

When the reaction is run with benzene-d_6 and cyclopentadiene-h_6, the ^{1}H NMF spectrum consists of two lines: a singlet at 4.31 and a broad singlet at 1.69 ppm. Under high amplitude, a small peak is observed at 2.04 ppm, but the relative intensity indicates this to be a very minor isomer component of the mixture.

A second isotopic experiment using benzene-h_6 and a 1/1 mixture of cyclopentadiene-d_6 [10] and -h_6 gives a mixture of four major isotopic products

TABLE 1

^1H NMR OF $Fe(\eta^5-C_5H_5)(\eta^5-C_6H_7)$ AT 220 MHz (C_6D_6 TMS)



Assignment	ppm	Integration	Pattern (Couplings in Hz)
A	5.8	1	Trip. of Trip., $J_{AC} = 5$, $J_{AE} = 1$
B	4.31	5	Singlet
C	4.28	2	Obscured by B
D	2.47	1	Doub. of Trip. of Mult. $J_{DF} = 12$, $J_{DE} = 6.5$, $J_{CB} > 1$
E	2.04	2	Trip. of Trip., $J_{EA} = J_{EF} = 1$, $J_{EC} = J_{ED} = 6.5$
F	1.69	1	Doub. of Mult., $J_{FD} = 12$.

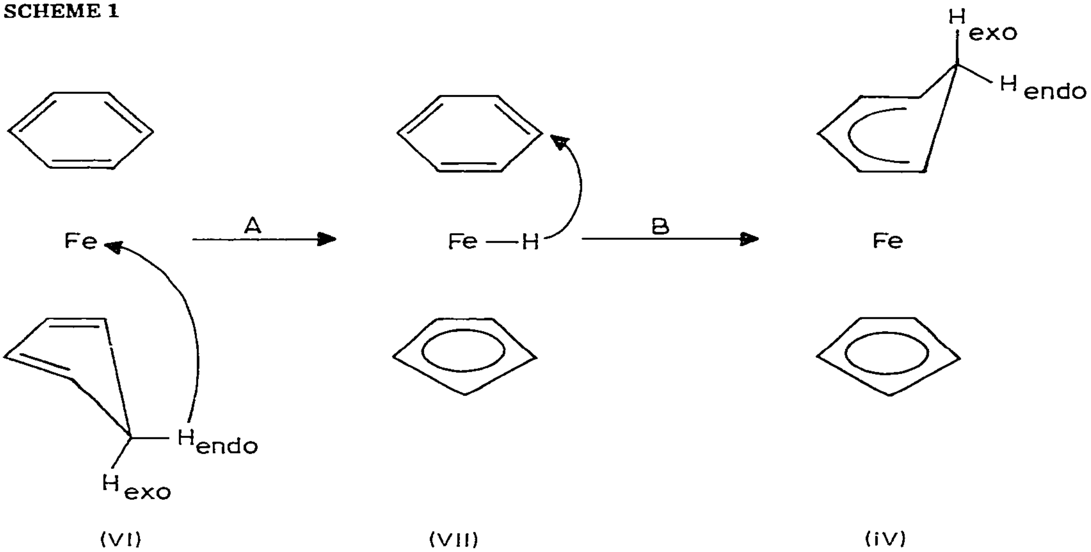
with compositions $FeC_{11}H_{12}$, $FeC_{11}H_{11}D$, $FeC_{11}H_7D_5$, and $C_{11}H_6D_6$ as determined by mass spectrometry.

Discussion

The cocondensation of iron atoms with benzene gives a "solvated" iron(0) species involving one [11] or two [9] molecules of benzene. Reaction of this unstable intermediate with dienes is known to give Fe(arene)(diene) complexes as isolable species [1—3,9]. Additionally, reaction of bis(hexamethylbenzene)-iron with dienes is known to give (hexamethylbenzene)(diene)iron complexes [12a]. (η^6-Hexamethylbenzene)(η^4-cyclopentadiene)iron is also known [12b]. Therefore, reaction with cyclopentadiene would conceivably give VI, which, in two steps involving *endo* hydrogen transfer (Scheme 1), would isomerize to the observed product IV. Step A gives a product related to III [4] if the benzene is η^4-coordinated to maintain an 18-electron system [13]. The *endo* transfer in Step B has been demonstrated in some η^4-diene complexes [14] but it should be pointed out that protonation of η^4-triene systems occurs *exo* [15].

The isotopic labelling experiment with benzene-d_6 was carried out to confirm the proposed mechanism. The assignment of the ^1H NMR spectrum is well established [5] and, as expected, the labelled complex gave only two resonances. It was with some surprise that we discovered the only resonance other than that of the cyclopentadienyl group was that of the *exo* hydrogen atom. The same product is obtained by the reaction of $NaBH_4$ with $[Fe(C_5H_5)(C_6D_6)][BF_4]$, a reaction known to give an *exo* product [5,7]. Thus, the mechanism proposed in Scheme 1 must be ruled out. Hoffmann [16] has shown previously that this mechanism was unlikely because there is an antibonding interaction between the iron and the *endo* hydrogen atoms.

SCHEME 1



The second labelling experiment involving cyclopentadiene-d_6 gave four isotopic isomers of IV. Had the reaction given two isomers, $FeC_{11}H_{12}$ and $FeC_{11}H_6D_6$, the reaction would have to be intramolecular in nature. The observation of four isomers necessitates an intermolecular reaction in which the *exo* hydrogen atom on one molecule comes from either free cyclopentadiene or cyclopentadiene associated with another molecule of complex.

Conclusions

Though it is possible to rule out the mechanism for the formation of IV proposed in Scheme 1, it is not possible to define an alternative mechanism. It is clear that to give a stereospecific product, the benzene ligand must be coordinated to iron at the time of hydrogen addition. Though plausible, it is not certain that the cyclopentadiene ligand must be coordinated as shown in VI prior to hydrogen loss. Hydride (H^-) transfer from free cyclopentadiene is unlikely. Free cyclopentadiene can act as a protonic (H^+) acid ($pK_a = 15$) and it is known that zerovalent iron complexes can be very basic. Also, hydrogen atom ($H^\cdot$) transfer from free cyclopentadiene cannot be discounted. Assuming cyclopentadiene coordination to iron at the time of hydrogen transfer, this study does not allow differentiation between loss of the *exo* or *endo* hydrogen atoms (as $H^\cdot$ or H^-).

Experimental

The cyclopentadiene-d_6 was generated from TlC_5D_5 [10]. All other reactants were commercially available. The design of the metal atom evaporator and experimental conditions have been detailed elsewhere [4]. All other manipulations were carried out in the nitrogen atmosphere of a Vacuum Atmospheres drybox. ^{1}H NMR spectra were recorded on a Varian HR-220 spectrometer and mass spectra were obtained on a Du Pont-491 spectrometer by electron impact.

Preparation of $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)$ (IV). The evaporator flask was immersed in liquid nitrogen and methylcyclohexane (20 ml) was condensed onto the walls of the flask. Iron (~10 g), benzene (100 ml), and methylcyclohexane (150 ml) were cocondensed over a period of 2 h. Freshly cracked cyclopentadiene (50 ml) was then condensed into the flask, followed by more methylcyclohexane. The entire mixture was allowed to melt and slide to the bottom of the flask where it was stirred as it warmed slowly to room temperature over 2 h. The mixture was filtered through Celite® to remove metallic iron. Excess ligand and solvent were removed under reduced pressure, leaving a mixture of ferrocene and IV. The ferrocene and some IV were removed by sublimation and the product was finally recrystallized from pentane. Yield 4.1 g. ^{1}H NMR; See Table 1. Mass spectrum in agreement with ref. 5.

Preparation of isotopically labelled IV. These reactions were carried out similarly, but on a lower scale. Iron (5 g), benzene-d_6 (50 ml) and cyclopentadiene (40 ml) were used to prepare $Fe(C_5H_5)(C_6HD_6)$. ^{1}H NMR: 4.31 C_5H_5 (5, S); 1.68 *exo*-CH_2 (1, S); 2.04 (observed as a trace impurity, no integration. As an alternative method, $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6HD_6)$ was prepared by appropriate modification of the literature method [7]. Iron (10 g), benzene (100 ml), cyclopentadiene (10 ml), and cyclopentadiene-d_6 (10 ml, ~95% enriched) were used in the final experiment. No attempt was made to remove the various contaminating ferrocenes prior to the mass spectral measurement.

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