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REACTIONS OF COORDINATED ARENES: SYNTHESES OF SUBSTITUTED (η^5-CYCLOHEXADIENYL) (η^5-CYCLOPENTADIENYL)IRON(II), AND (η^6-ARENE) (η^4-CYCLOHEXADIENE)IRON(0) COMPLEXES

LOREN K. BEARD, Jr., MICHAEL P. SILVON, and PHILIP S. SKELL

The Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

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Summary

The complexes obtained from the co-deposition of iron atoms with arenes react with cyclopentadiene to give the substituted (η^5-cyclohexadienyl)-(η^5-cyclopentadienyl)iron(II) complexes, and with hydrogen to give the (η^6-arene)(η^4-cyclohexadiene)iron(0) complexes. The latter reaction was used to demonstrate that the complex obtained in the case of toluene is not a 1 : 1 adduct.

Introduction

The high vacuum, low temperature co-condensation of the first row Group VIII metals with toluene is a convenient route to synthetically useful, labile complexes of iron, cobalt, and nickel in their zero oxidation state. While their low thermal stability has made difficult the precise characterization of the structures of these complexes, these same properties have made them especially good starting materials for syntheses of a variety of organometallics. The decomposition temperatures of the complexes vary, from: —30°C for iron, —50°C for cobalt, to —85°C for nickel. Solutions kept at —120°C are stable for extended periods. They can be made by employing a 1 : 1 mixture of toluene and pentane as the condensation medium.

An early report of the benzene/iron complex [1] reported it was explosive. Although we have not experienced explosions, caution is advisable. The benzene complexes are not as stable as the toluene complexes. The use of more highly substituted arenes (xylenes, mesitylene), leads to more stable complexes The bis(η^6-hexamethylbenzene)-iron(0), and -cobalt(0) complexes have been prepared, and are stable at room temperature [2]. In this paper, we report the results of our studies of the iron/arene systems, and their reactions with cyclopentadiene, and hydrogen.

Results and discussion

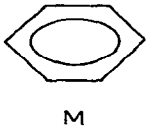
Properties of the iron/arene complexes

Attempts to isolate a sample of the pure iron/toluene complex from toluene solutions were unsuccessful. Concentration by high-vacuum removal of toluene at −78° C, and crystallization from toluene/butane solutions at −120° C both led to an increased rate of decomposition of the complex as the removal of excess toluene progressed. Thus, while the composition is unambiguously that of a bis-arene complex when the ligand is hexamethylbenzene, conclusive evidence of the composition is not available for the more labile complexes such as that with toluene.

Infrared studies directed toward definition of the structures of these complexes have led to conflicting conclusions. Spectra recorded in our laboratory show that chromium and iron react with toluene during co-deposition at −196° C to make, initially, the same products as are present after warming to −80° C, the known bis(η^6-toluene)chromium(0) [3] in the case of chromium. There is no change in the spectrum on cycling the temperature from −196° C to −80° C and back. On the other hand, cobalt and nickel produce bands for at least two materials at −196° C, some of them disappearing when the matrices are warmed to −90°C [18].

Efner, Tevault, Fox, and Smardzewski [4] also have studied the matrix IR spectra of arene complexes of chromium, iron, cobalt, and nickel. Since they observed only bis(η^6-arene)chromium(0) bands, despite the high-dilution conditions (Ar/arene ratios of 200/1) employed in their 10 K depositions, it must follow that they had extensive migration of metal atoms and arenes in their system to account for a termolecular product formation, and the absence of any other bands attributable to a mono-arene chromium. The bands they observed for iron, cobalt, and nickel are the same as those we observed in benzene matrices which had not been warmed, containing both the labile, and more stable species.

When they co-deposited chromium with an equimolar mixture of C_6H_6 and C_6D_6, they observed bands attributable to the mixed sandwich, (η^6-C_6H_6)-(η^6-C_6D_6)chromium(0), but did not observe similar bands in the spectra of the iron, cobalt, and nickel analogs, under the same conditions. Caution should be used in interpreting these results since these are not high quality spectra, and bands for mixed complexes could be weak if the ligands are not strongly bound. They also observed a first order dependence on toluene of the rate of complex formation, although details of this experiment were not given. For these reasons, they proposed for the iron, cobalt, and nickel complexes mono-arene structures. We are not aware of any precedent for such structures, nor would they be expected to have a long lifetime in the liquid phase, at −120° C, as we observe. In addition, mono-arene structures would lead one to predict a stability sequence in which the nickel complex would be most stable, which is opposite of that which we observe. These considerations, coupled with the results (below) of the hydrogenation experiment done in a mixture of protio-



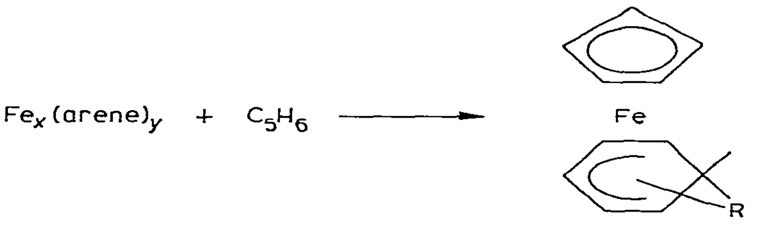
(Ia, M = Fe, 14e^-;
Ib, M = Co, 15e^-;
Ic, M = Ni, 16e^-)

and deuterio-toluene make the mono-arene structure untenable, and suggest that alternative interpretations are indicated for the Efner et al. spectra.

Several reactions of the iron/toluene complex have been reported. Most of these have involved simple displacement of the arene ring(s) by 2- or 4-electron donors. We reported the synthesis of (η^4-butadiene)(η^6-toluene)iron(0), and (η^6-toluene)bis(trifluorophosphine)iron(0) by treatment of the iron/toluene matrix with the appropriate displacing ligand [5]. Ittel prepared (η^6-toluene)-bis(trimethyl phosphite)iron(0) by the same route [6]. We have found that reaction with trimethylphosphine leads to complete displacement of toluene, and recovery of the known "tetrakis(trimethylphosphine)iron" complex [7—9] in which the iron atom has inserted into a C—H bond. While Weber and Brintzinger [10] obtained a good yield of dicarbonyl(η^6-hexamethylbenzene)-iron(0) from the reaction of bis(η^6-hexamethylbenzene)iron(0) with CO, we were unable to prepare the toluene analog by the same means. Instead, when the iron/toluene complex was treated with CO (—78 C, 1 atm), we obtained salts of iron carbonyl anions which reacted with concentrated sulfuric acid to give $Fe_3(CO)_{12}$, and $Fe_5C(CO)_{15}$ [11,12].

Reactions with cyclopentadiene

In 1975, we reported that the reaction of the iron/benzene complex with cyclopentadiene gives (η^5-cyclopentadienyl)(η^5-cyclohexadienyl)iron(II), rather than the arene-diene complex [13]. This reaction differs from the above reactions in that it involves a reaction of one of the aromatic ligands. This reaction is general for alkyl-substituted arenes. Thus, IIa—IId have been prepared by this route. Typically, iron atoms were co-condensed with the arene and a low-melt-



(IIa, R = H;
IIb, R = CH_3;
IIc, R = $(CH_3)_2$;
IId, R = $C(CH_3)_3$)

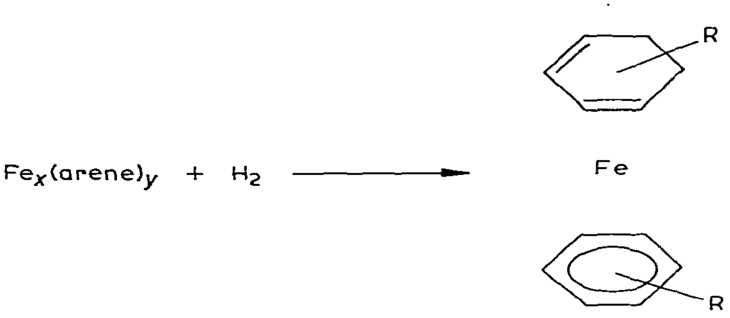
ing co-solvent (pentane, methylcyclohexane), at —196° C. After the co-condensation reaction, cyclopentadiene was distilled into the reactor, and the mixture was allowed to react, usually for one hour at —78° C. A color change was observed on melting the matrix, and on warmup a red-orange solution was obtained. This solution was filtered to remove unreacted metal, and the excess of solvent and ligands were removed in vacuo. The complexes are relatively pure at this stage, but can be further purified by sublimation. The benzene analog, IIa, is volatile below room temperature, and the removal of contaminating ferrocene can be difficult.

The reaction presumably proceeds through an arenecyclopentadieneiron intermediate, which undergoes a subsequent hydrogen atom transfer. We saw no evidence for this intermediate in the NMR spectrum of a sample of IIb which had not been warmed above —30° C. Ittel has reported evidence that the transfer is an intermolecular process [14]. The NMR and mass spectra of these complexes are consistent with those reported in the literature, in those cases where the complexes have been reported previously (IIa, and IIb) [15]. The presence of two singlets in the methyl region of the NMR spectrum of the toluene analog, IIb, indicated that at least two isomers are present, but the complexity of the spectrum prevented a determination of the relative amounts of these isomers. The chemical shift of the cyclopentadienyl protons is near δ 4.0 ppm, very similar to the value for ferrocene. The mass spectra of complexes of this type have been studied in detail, and in each case, a large $P - 1$ peak was observed [15b, c].

The cyclopentadiene reaction was used to demonstrate that the iron/toluene complex exchanges toluene for other arenes slowly in solution at —78° C. Iron atoms were co-condensed with toluene, and the product was stirred in an equimolar mixture of toluene and *m*-xylene for 24 hours. The resultant mixture was treated with cyclopentadiene to give an approximately equimolar mixture of IIb, and IIc. We have not observed arene exchange in complexes such as II, even when they were stored in arene solvents at room temperature for days.

Reactions with hydrogen

In 1975, Timms [16] found that the reaction of iron atoms with mesitylene leads to the recovery of (η^6-mesitylene)(η^4-trimethylcyclohexadiene)iron(0) as the only product. When toluene solutions of the iron/toluene complex were allowed to stand at —78° C for several hours, or days, small yields of isomers of (η^4-methylcyclohexadiene)(η^6-toluene)iron(0) were obtained. Weber and Brintzinger [11] also have reported that when bis(η^6-hexamethylbenzene)iron(0) decomposes in benzene solution, (η^4-cyclohexadiene)(η^6-hexamethylbenzene)-iron(0) is formed in small yield. This yield can be increased by the introduction of hydrogen gas during the reaction. Good yields of similar complexes can be obtained by stirring the iron/arene complexes in a hydrogen atmosphere at low temperature. In this way, we have prepared IIIa—IIId. In a typical reaction, the co-condensation was carried out in a co-solvent, and the mixture was warmed to —78° C (—96° C for the benzene complex), and stirred in one atmosphere of hydrogen for six to twenty-four hours. The solution was warmed, filtered, and the excess arene was removed by pumping. The yellow, air-sensitive solids could be purified by sublimination. The complexes decomposed if



(IIIa, R = H;
IIIb, R = CH_3;
IIIc, R = $C(CH_3)_3$;
IIId, R = $(CH_3)_3$)

left in solution over finely divided iron metal for long periods. The NMR spectrum of the benzene analog, IIIa, was as reported in the literature [17]. The spectrum of the toluene complex, IIIb, was similar, with the addition of peaks in the methyl region which are attributed to the methyl groups on the isomeric methylcyclohexadienes, and on the toluene ring. We made use of the hydrogenation reaction to show that the iron/toluene complex is not a monoareneiron species. Diene formation in this reaction must be an iron-mediated process. If the Efner et al. structure (Ia) were correct, then $Fe(C_7H_{10})$ must be the primary product obtained in the presence of hydrogen, and the addition of C_7H_8 must occur in a subsequent step. This hypothesis can be subjected to test by first preparing the protio-iron/toluene complex in protio-toluene, and then adding deuterio-toluene to the medium before the addition of hydrogen. A medium consisting of equimolar amounts of C_7H_8 and C_7D_8 should produce an equimolar mixture of $Fe(C_7H_{10})(C_7H_8)$ and $Fe(C_7H_{10})(C_7D_8)$.

On the other hand, if the complex is bis(η^6-toluene)iron(0), or some other material which contains at least two toluene moieties in the starting material (e.g., an allyl-hydride type molecule such as that proposed by Weber and Brintzinger as the intermediate in the decomposition of bis(η^6-hexamethylbenzene)iron(0)), and the two protio-toluenes present initially are incorporated into the arenediene complex, without exchange, then the expected product would be free of deuterium. (This would be true even if the exchange described above is somewhat faster than the hydrogenation, if the reaction is stopped at very low conversion.)

We cocondensed 500 mg of iron with 15 ml of toluene. To this protio-toluene complex in toluene solution, 15 ml of toluene-d_8, and 50 ml of pentane were added. The solutions then was stirred under one atmosphere of hydrogen. After two hours, a sample was taken, and the arenediene complex was analyzed by mass spectrometry. The mass spectral data showed peaks at m/e = 242, and 250, corresponding to the d_0, and d_8 complexes respectively. The ratio of the areas of the peaks, 242 : 250, was 100 : 1, showing that the mixture was almost completely free of deuterium. This result cannot be explained if the complex has a structure such as Ia. This result is consistent with formulation of the complex as bis(η^6-toluene)iron(0), but does not rule out other structures, such as oligomers, or structures in which the iron atom has inserted into one toluene molecule. It should be noted that although the conversion at two hours is low, the yield of arenediene complex is much higher than that obtained spontaneously.

Experimental

The metal atom evaporator is described elsewhere [17]. All ligands were commercially obtained, and dried before use. All iron complexes were handled using standard Schlenk techniques. All of the complexes are sensitive to air, and many will decompose if left in solution in contact with bulk iron. NMR samples were sealed under vacuum, and recorded on a Varian A-60, or EM-360 spectrometer. Mass spectra were recorded on an AEI MS902 mass spectrometer.

The preparation of (η^5-methylcyclohexadienyl)(η^5-cyclopentadienyl)iron(II)

Iron atoms (500 mg, 8.9 mmol) were codeposited with thirty ml of toluene over thirty minutes. The mixture was warmed to —78° C, and 3 ml of cyclopentadiene was distilled into the reactor. This mixture was warmed to room temperature, filtered, and the excess of toluene and cyclopentadiene was removed by pumping. This left a volatile red oil. NMR spectroscopy showed that this oil was a mixture of three isomers of (η^5-methylcyclohexadienyl)(η^5-cyclopentadienyl)iron(II), and ferrocene. Ferrocene could be removed by fractional sublimation, but the three isomers were inseparable. The NMR and mass spectral data are given in Table 1.

The preparation of (η^5-cyclohexadienyl)(η^5-cyclopentadienyl)iron (II)

Iron atoms (430 mg, 7.7 mmol) were co-deposited with 30 ml of a 15% solution of benzene in hexane. The mixture was warmed to —78 C, and 3 ml of cyclopentadiene was distilled into the reactor. The mixture was stirred for one hour at this temperature, and then slowly warmed to room temperature. Benzene and hexane were removed by pumping, and the residue was sublimed to give 360 mg (23%) of a red solid. NMR and mass spectral data were in agreement with the literature (See Table 1).

The reaction of the iron/toluene complex with m-xylene

Iron atoms (760 mg, 13.6 mmol) were co-deposited with 30 ml of toluene over 30 min. The mixture was warmed to —78° C, and 30 ml of *m*-xylene were distilled into the reactor. The mixture was stirred for 24 hours at this temperature, and then 5 ml of cyclopentadiene were distilled in. The mixture then was warmed to room temperature over one hour. Excess cyclopentadiene and arenes were removed by pumping, and the residue was dissolved in pentane, filtered, and the pentane was removed by pumping to yield a red oil. The mass spectrum showed that the red oil is a mixture of (η^5-cyclopentadienyl)(η^5-dimethylcyclohexadienyl)iron(II), and (η^5-cyclopentadienyl)(η^5-methylcyclohexadienyl)iron(II), and ferrocene (See Table 1).

The preparation of (η^5-t-butylcyclohexadienyl)(η^5-cyclopentadienyl)iron(II)

Iron atoms (500 mg, 8.9 mmol) were co-deposited with 20 ml of t-butylbenzene over one hour. Fifty ml of hexane were distilled into the reactor, and the mixture was warmed to —78° C. Three ml of cyclopentadiene were distilled in, and the reaction mixture was stirred at —78° C for one hour, and then slowly warmed to room temperature. The solution was filtered, and the excess of reactants was removed by pumping. The product was a red solid, (182 mg, 8%) whose mass spectrum is consistent with formulation as (η^5-t-butylcyclohexadienyl)(η^5-cyclopentadienyl)iron(II) (See Table 1).

TABLE 1

SPECTRA DATA

Compound	Mass Spec. m/e (rel. int., %)	NMR			Ref.
		Multiplicity	δ (ppm)	Rel. int.	
IIa	200(60)	Mult.	5.9	1	
	199(55)	Sing.	4.0	12 ^{a}	
	186(100) ^{b}	Mult.	1.9—2.6	5	15
	134(30)	Mult.	1.4—1.7	5	
IIb	214(80)	Mult.	6.1	1	
	213(75)	Sing.	4.0	10 ^{a}	
	186(100) ^{b}	Sing.	3.4	11	
	148(40	Sing.	1.5		15b
		Sing.	1.3		
		Mult.	1.5—2.5		
IIc + IIb	228(40)				
	227(35)				
	214(40)				
	213(35)				
	186(100) ^{b}				
IId	256(80)				
	255(75)				
	190(50)				
	186(100) ^{b}				
IIIa	214(100)	Sing.	4.9	6	
	134(75)	Mult.	4.6	2	
		Mult.	2.5	2	17
		Mult.	1.5	4	
IIIb	93(100)	Sing.	4.8	6	
	242(80)	Mult.	4.6—5.0		
	148(60)	Mult.	4.5	2	
		Mult.	3.4	2	
		Sing.	2.0	4	
		Sing.	1.9	2	
		Mult.	1.6	4	
		Sing.	1.4	1.5	
IIIc	274(100)	Sing.	4.2	3	
	164(75)	Sing.	3.6	1	
		Sing.	1.8	9	
		Sing.	1.8	3	
		Sing.	1.4	1	
		Sing.	0.9	3	
		Sing.	0.8	3	
IIId	326(100)				
	190(75)				

^{a} Includes ferrocene impurity. ^{b} Ferrocene.

The preparation of (η^4-methylcyclohexadiene)(η^6-toluene)iron(0)

Iron atoms (460 mg, 8.2 mmol) were co-deposited with 40 ml of toluene. The solution was stirred at —78° C under one atmosphere of hydrogen for 24 hours. The reaction mixture was filtered to remove unreacted iron, and the excess toluene was removed by pumping. The residue was sublimed to give 800 mg (40%) of (η^4-methylcyclohexadiene)(η^6-toluene)iron(0) isomers. The NMR and mass spectral data are given in Table 1.

This complex also is formed slowly and spontaneously when toluene solutions of the iron/toluene complex are allowed to stand at —78° C for several hours, or days. The yield was low, but larger than the amount of diene contaminant present in the starting toluene.

The preparation of (η^6-t-butylbenzene)(η^4-t-butylcyclohexadiene)iron(0)

Iron atoms (1.1 g, 19 mmol) were co-deposited with 25 ml of t-butylbenzene over one hour. Forty ml of hexane were distilled into the reactor to wash down the solid product. The mixture was then warmed to —78° C, and stirred under one atmosphere of hydrogen for six hours. The mixture was warmed, filtered, and the excess of t-butylbenzene was removed by pumping to give 300 mg (5%) of a yellow solid. The mass spectral data are given in Table 1.

The preparation of (η^6-benzene)(η^4-cyclohexadiene)iron(0)

The walls of the reactor vessel were cooled to 77 K, and coated with 30 ml of methylcyclohexane. Then, iron atoms (1.2 g) were co-deposited with 30 ml of a 50/50 mixture of benzene and methylcyclohexane, over 30 minutes. After the co-deposition reaction, an additional 30 ml of methylcyclohexane was distilled in. The reactor was warmed to —96° C, and the solution was stirred under one atmosphere of hydrogen for six hours. The solution was then warmed to room temperature, filtered, and the excess of benzene and methylcyclohexane was removed by pumping. The yield was 220 mg (5%) of a yellow solid. Spectral data are given in Table 1.

The preparation of (η^6-mesitylene)(η^4-trimethylcyclohexadiene)iron(0)

The reactor vessel was cooled to 77 K, and the walls were coated with 30 ml of methylcyclohexane. Iron atoms (900 mg) were co-deposited with 30 ml of mesitylene. An additional 30 ml of methylcyclohexane was distilled in. The mixture was warmed to —78° C, and stirred under one atmosphere of hydrogen for 18 hours. The solution was warmed, filtered, and the excess of mesitylene and methylcyclohexane was removed by pumping. The yield was 1.1 g (23%) of orange powder. The NMR and mass spectral data are given in Table 1.

The reaction of the iron/toluene complex with hydrogen in the presence of deuterio-toluene

Iron atoms (500 mg) were co-deposited with 15 ml of toluene over thirty minutes. The reactor was warmed to —78° C, and 15 ml of toluene-d_8 was distilled in. This mixture was siphoned to a cold flask (—78° C), and stirred under one atmosphere of hydrogen. Samples were taken after one half-hour, and after two hours. The samples were worked up as described above. The mass spectrum of the two-hour sample showed a peak at m/e = 242 ($FeC_{14}H_{18}$), and a peak at

$m/e = 250$ ($FeC_{14}H_{10}D_8$), which had an intensity about 1/100 of that of the peak at 242. Both peaks showed a clear iron isotope pattern.

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