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# IRON BENZENE REACTIONS: A MATRIX ISOLATION MÖSSBAUER INVESTIGATION

STEWART F. PARKER * and CHARLES H.F. PEDEN **

*Department of Chemistry, University of California at Santa Barbara, Santa Barbara, CA, 93106 (U.S.A.)*

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## Summary

The products of the cocondensation of iron atoms with benzene, at both 7 and 77 K, have been investigated by Mössbauer spectroscopy. On the basis of a benzene concentration study, it is concluded that iron forms two mononuclear bis-benzene complexes. By comparison of the Mössbauer parameters of these complexes to known systems, the two products are assigned to the 20 electron complex $Fe(\eta^6\text{-}C_6H_6)_2$ and the 18 electron complex $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$. An $Fe(C_6H_6)$ product is also formed at low benzene concentrations.

## Introduction

There is extensive chemistry of metal complexes that contain intact arenes coordinated in an $\eta^6$ manner [1]. Many examples of both $M(\eta^6\text{-arene})(\text{ligand})_x$ and $M(\eta^6\text{-arene})_2$ complexes are known. (There are no known examples of mononuclear transition metal complexes containing more than two $\eta^6$-arene ligands.) The most studied of the bis-arene complexes is $Cr(C_6H_6)_2$ and its derivatives [2]. For many of the alkyl-substituted derivatives, the most efficient method of synthesis is the cocondensation of chromium atoms with the arene at 77 K [3].

Mono-arene complexes, M(arene), of the Group IB metal atoms formed at 77 K have been recently reported [4]. These are $\eta^6$, 17 electron complexes. Interestingly, the copper complex is destabilized by substitution on the benzene ring by both electron-donating and -withdrawing groups, the substitution having little effect on the Ag and Au complexes. More recently, Ozin et al. [5] have synthesized both mono- and di-$\eta^6$-phenylvanadium complexes (11 and 17 electron complexes, respec-

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* Present address: School of Chemical Sciences, University of East Anglia, Norwich, NR4 7JJ (Great Britain).

** Present address: Surface Science Division 1134, Sandia National Laboratories, Albuquerque, NM, 87185 (U.S.A.).

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tively) by varying the benzene concentration in argon matrices at 12 K.

The cocondensation of iron atoms with arenes has been investigated by a number of workers. The first report was the 77 K macroscale cocondensation of iron with benzene [6]. This gave a complex, $Fe(C_6H_6)_x$, that was reported to decompose explosively at $-30\,^\circ C$.

A matrix isolation study [7] of Cr, Fe, Co, and Ni using both $Ar/C_6H_6$ (0.5–4%) mixtures at 10 K and pure $C_6H_6$ at 77 K has been reported. On the basis of a ligand concentration study and the use of mixed isotopes ($C_6H_6/C_6D_6$), it was concluded that mono-arene complexes, $M(C_6H_6)$ where M = Fe, Co, Ni, were the only mononuclear products. In contrast to this, the researchers were unable to isolate the M = Cr mono-arene complex, obtaining only the bis-arene complex. This suggests that in the case of Cr, either the mono-arene complex is very weakly bound or that there was sufficient migration in the fluid layer [8] that occurs before solidification of the matrix to allow for further reaction to the bis-arene complex. However, as has been previously noted [9,10], the absence of an infrared spectrum for a mixed $C_6H_6/C_6D_6$ complex in the mixed isotope studies does not conclusively prove that $x = 1$ in the complexes, $M(C_6H_6)_x$. It could be explained by weak vibrational coupling between the two rings.

On the basis of the products recovered from the reaction of iron/toluene solutions with deuterium gas, Skell and coworkers [9,10] concluded that the species obtained was a ditolueneiron complex. They also stated that infrared studies showed that the complex formed by cocondensation at 77 K and that in solution at 200 K were the same.

UV-vis studies [11] of MCH/toluene (10%) (MCH = methylcyclohexane) cocondensed with iron show unequivocally that at least two products are present. Deposition at 150 K in a rotary solution reactor gave three bands at 300, 355 and 436 nm. Preparation of a solid matrix at 77 K using the same mixture shows the presence of the first complex, and a second product with bands at 310, 340 and 378 nm. This latter product converts to the first on melting of the matrix at 150 K. The band of the first product at 436 nm was assigned to a metal-to-ligand charge transfer band from the iron to diene $\pi^\star$ levels. For this reason, the product was tentatively identified as ($\eta^6$-toluene)($\eta^4$-toluene)iron. No definite conclusion was reached for the less stable second product. Possibilities named were $\eta^6$-tolueneiron, di-$\eta^6$-tolueneiron or di-$\eta^4$-tolueneiron.

Infrared studies [12] of the products remaining after cocondensation of iron with arene (toluene, mesitylene and durene) followed by evaporation of the matrix led to the conclusion that the products were di-$\eta^6$-areneirons, based on the similarity of the spectra of the iron products to those of the corresponding chromium complexes.

Thus, in spite of a considerable amount of work using several approaches, the nature of the products of iron-arene cocondensations have not been unambiguously characterized. It was felt by the authors that the unique specificity of $^{57}$Fe Mössbauer spectroscopy might allow this to be accomplished.

## Results and discussion

The cocondensation of low concentrations of iron with benzene at 7 K results in the formation of three products, **A**, **B** and **C**, shown in the decomposed contributions in Fig. 1a. The use of higher concentrations of iron at 7 K results in an additional product, **D**. Warming these matrices to 77 K results in the loss of the original products and the formation of new ones. Whilst the original products are readily reproducible, the new products vary from one experiment to another.

Cocondensation at 77 K (Fig. 1b) reproducibly results in the formation of **A** and **B**, together with another product, **E**. However, the ratio of the products, **A**/**B**, is different at 77 K from that at 7 K (**A**/**B** = 1/1 at 7 K, **A**/**B** = 1/3 at 77 K). The observation that the spectra are dominated by **A** and **B** at both 7 and 77 K strongly suggests that the two products contain only one iron atom.

The pure benzene spectra give no information on the ligand stoichiometry of the complexes. For this reason, lower concentrations of benzene in the noble gases were examined. The cocondensation of iron with Kr/$C_6H_6$ (5%) at 7 K, shows the presence of **A**, **B** and another product, **F**. The use of still lower concentrations of benzene results in spectra that contain only **F** and unreacted iron atoms. $Fe_1$. This persists down to benzene concentrations so low that only unreacted $Fe_1$ and $Fe_2$ are obtained. Further, **F** is obtained when the only other product is $Fe_1$. This is very good evidence that **F** contains only one iron atom and one coordinated benzene molecule; thus, **F** is assigned to $Fe(C_6H_6)$.

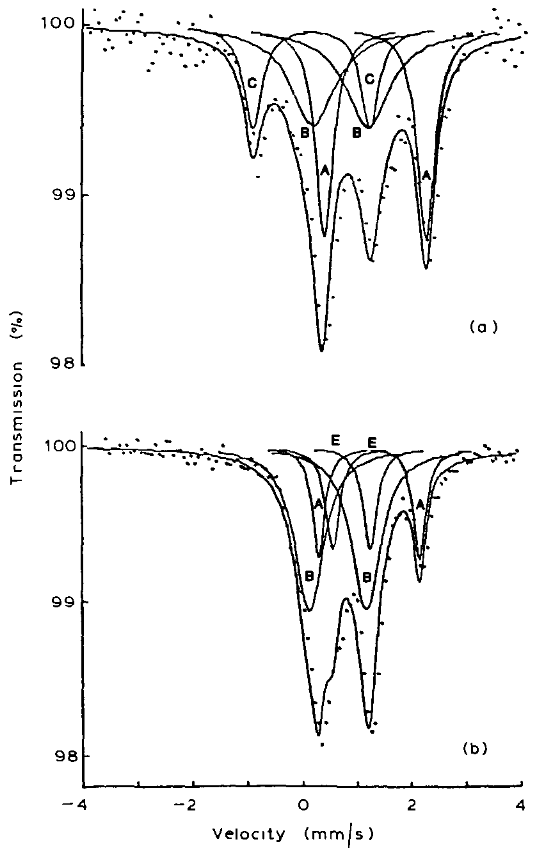

Fig. 1. Mössbauer spectrum of $C_6H_6$/Fe condensed at (a) 7 K, [Fe] = 0.6% and (b) 77 K, [Fe] = 0.7%, in two different experiments.

The absence of both **A** and **B** at very low benzene concentrations where $Fe_1$ and $Fe(C_6H_6)$ are the only products, shows that both **A** and **B** must contain two benzene molecules. The dominance of **B** over **A** at 77 K suggests that there is a larger activation energy for the formation of **B** and/or that **B** is the thermodynamically more stable product.

The isomer shift ($\delta$) and quadrupole splitting ($\Delta$) of **A** are similar to those recently reported [13] for the 20 electron complex $Fe(\eta^6\text{-HMB})_2$ (HMB = hexamethylbenzene). For this reason, **A** is assigned to $Fe(\eta^6\text{-}C_6H_6)_2$, with the usual sandwich structure. To our knowledge, the isomer shift of **A**, +1.23 mm/s, is the most positive isomer shift ever reported for an iron(0) complex.

The more stable transition metal complexes usually conform to the 18 electron rule [2]. The 20 electron complex, **A**, can achieve this in several ways. Loss of two metal valence electrons would give the known complex, $Fe(\eta^6\text{-}C_6H_6)_2^{2+}$. The formation of this at 7 K by direct reaction would appear unlikely, especially in the absence of any reasonable counterion. Furthermore, Mössbauer parameters of $Fe(\eta^6\text{-mesitylene})_2(BPh_4)_2$ [14] and $Fe(\eta^6\text{-HMB})_2(PF_6)_2$ [13] are known; both sets of parameters are very similar to each other ($\delta = +0.59$, $\Delta = 1.95$ mm/s and $\delta = +0.56$, $\Delta = 2$ mm/s, respectively) and very different from those of both **A** and **B**. A second way to achieve an 18 electron complex would be for one of the coordinated benzene ligands to distort, such that it is coordinated as an $\eta^4$-diene. We assign **B** to this product, $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$, with the structure shown in Fig. 2.

The product **B**, $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$, is an example of an unusual, but not unprecedented type of complex. Iron forms a number of complexes of the type ($\eta^6$-arene)($\eta^4$-diene)iron [15,16]. The congener of iron in the second row of the transition metals, ruthenium, forms the very similar complexes, $Ru(C_6H_6)_2$ and $Ru(HMB)_2$ [17]. Proton NMR [18] and an X-ray structure determination [19], respectively, have shown that in both of these complexes, the coordination is of the form ($\eta^6$-arene)($\eta^4$-arene)ruthenium. In particular, the benzene complex of Ru is an exact analog of the structure proposed for **B**.

The complex $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ is known [20]. This should be a very close model for the proposed structure of product **B**. Accordingly, the complex was prepared by the literature method [20], and the Mössbauer spectrum recorded. As is typical of organometallic compounds, this gave a weak spectrum at room temperature. Excellent spectra were obtained at 77 and 7 K. The similarity of the Mössbauer

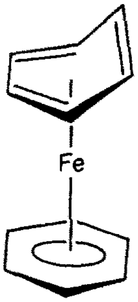

Fig. 2. Proposed structure of product **B**.

TABLE 1

MOSSBAUER PARAMETERS[a] OF $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$

| $T$(K) | $\delta$ | $\Delta$ |
|---|---|---|
| 7 | +0.51 | 0.94 |
| 77 | +0.49 | 0.92 |
| 298 | +0.46 | 0.85 |

[a] Isomer shifts ($\delta$) and quadrupole splittings ($\Delta$) are in mm/s.

parameters of $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ (see Table 1) to those of **B** is good evidence for correctness of the assignment.

UV-vis studies [11] of the two products obtained in a cocondensation of iron with MCH/toluene(10%) at 77 and 150 K have concluded that the more stable product was ($\eta^6$-toluene)($\eta^4$-toluene)iron. This lends further support to our proposed structure for **B** since it is clearly the dominant product in our studies at the higher deposition temperature of 77 K. However, we note that the UV-vis spectrum of ($\eta^6$-toluene)($\eta^4$-toluene)iron (300, 355 and 436 nm) differs from that of $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ (258 ($g = 17{,}300$ $M^{-1}$ cm$^{-1}$, structured), 378(sh) and 410(sh) nm in n-hexane). The reason for this discrepancy is not clear to us.

The identities of the products, **C**, **D** and **E**, are less certain. The most reasonable assignment is to the reaction products of iron multimers with benzene, $Fe_y(C_6H_6)_z$ ($y \geqslant 2$, $z \geqslant 1$). In view of the many possible modes of bonding of benzene to metal clusters and surfaces [1], no attempt has been made to further characterize these products. The Mössbauer parameters for all the products obtained are given in Table 2.

## Experimental

Detailed descriptions of the matrix isolation Mössbauer apparatus and procedures have been previously published [21,22]. Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using a $^{57}$Co in Rh source, and are computer fit to a sum of quadrupole doublets. The pairs of peaks were constrained to have equal amplitudes and full widths at half maximum with Lorentzian line shapes. The standard statistical tests $X^2$ and MISFIT were used as quantitative

TABLE 2

MÖSSBAUER PARAMETERS[a] FOR THE SPECIES OBSERVED IN THE IRON-BENZENE SYSTEM

| Species | $T$(K) | $\delta$ | $\Delta$ | Assignment |
|---|---|---|---|---|
| **A** | 7 | +1.22 | 1.84 | $Fe(\eta^6\text{-}C_6H_6)_2$ |
| **B** | 7 | +0.64 | 1.04 | $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$ |
| **C** | 7 | +0.10 | 2.10 | $Fe_n(C_6H_6)_m$ ($n \geqslant 2, m \geqslant 1$) |
| **D** | 7 | −0.14 | 3.77 | $Fe_p(C_6H_6)_q$ ($p \geqslant 2, q \geqslant 1$) |
| **E** | 77 | +0.88 | 0.68 | $Fe_r(C_6H_6)_s$ ($r \geqslant 2, s \geqslant 1$) |
| **F** | 7 | +0.45 | 1.20 | $Fe(C_6H_6)$ |

[a] Isomer shifts ($\delta$) and quadrupole splittings ($\Delta$) are in mm/s.

measures of the quality of the fit. All isomer shifts are reported relative to α-Fe metal at room temperature.

Benzene (Mallinckrodt) was dried over $CaH_2$ and distilled under vacuum. It was subjected to several freeze-pump-thaw degas cycles immediately prior to use. It should be noted that omission of either or both of the first two steps had no effect on the resulting spectra. ($\eta^6$-benzene)($\eta^4$-1,2,3,4-cyclohexa-1,3-diene)iron, [Fe($\eta^6$-$C_6H_6$)($\eta^4$-$C_6H_8$)] was prepared by the method of Fischer and Müller [20]. Infrared, $^1$H NMR and mass spectral data were in agreement with literature values [15,20].

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## References

1 E.L. Muetterties, J.R. Bleeke, E.J. Wucherer and T.A. Albright, Chem. Rev., 82 (1982) 499, and ref. therein.
2 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., Wiley-Interscience, New York, 1974, p. 744.
3 K.J. Klabunde, Chemistry of Free Atoms and Particles, Academic Press, New York, 1980.
4 A.J. Buck, B. Mile and J.A. Howard, J. Am. Chem. Soc., 105 (1983) 3381.
5 M.P. Andrews, H.X. Huber, S.M. Mattar, D.F. McIntosh and G.A. Ozin, J. Am. Chem. Soc., 105 (1983) 6170.
6 P.L. Timms, J. Chem. Soc. Chem. Comm., (1969) 1033.
7 H.F. Efner, D.E. Tevault, W.B. Fox and R.R. Smardzewski, J. Organomet. Chem., 146 (1978) 45.
8 J.E. Hulse and M. Moskovits, J. Chem. Soc. Faraday Trans. II, (1977) 471.
9 L.K. Beard, Jr., M.P. Silvon and P.S. Skell, J. Organomet. Chem., 209 (1981) 245.
10 A.L. Shobert, Ph.D. thesis, Pennsylvania State University, 1982.
11 G.A. Ozin, C.G. Francis, H.X. Huber, M. Andrews and L. Nazar, J. Am. Chem. Soc., 103 (1981) 2453.
12 T.S. Kurtikyan and V.T. Aleksanyan, Isv. Akad. Nauk. SSSR, Ser. Khim., 27 (1978) 2298.
13 P. Michaud, J.-P. Mariot, F. Varret and D. Astruc, J. Chem. Soc. Chem. Comm., (1982) 1383.
14 R.A. Stukan, N.A. Vol'kenau, A.N. Nesmeyanov and V.I. Gol'danskii, Isv. Akad. Nauk. SSSR, Ser. Khim., 8 (1966) 1472, quoted in W.N. Morrison, E.Y. Ho and D.N. Hendrickson, Inorg. Chem., 14 (1975) 500.
15 S.D. Ittel and C.A. Tolman, Organometallics, 1 (1982) 1432.
16 E.A.K. von Gustorf, F.-W. Grevels and I. Fischler (Eds.), The Organic Chemistry of Iron, Academic Press, New York, 1978.
17 E.O. Fischer and C. Elschenbroich, Chem. Ber., 103 (1970) 162.
18 P.L. Timms and R.B. King, J. Chem. Soc. Chem. Comm., (1978) 898.
19 G. Huttner and S. Lange, Acta Crystallogr. Sect. B, (1972) B25.
20 E.O. Fischer and J. Müller, Z. Naturforsch., 176 (1962) 776.
21 T.K. McNab and P.H. Barrett, in I.J. Gruverman (Ed.), Mössbauer Effect Methodology, Vol. 7, Plenum Press, New York, 1979, p. 59.
22 S.F. Parker, Ph.D. thesis, University of California at Santa Barbara, 1983.