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# ARENE LIGAND EXCHANGE IN ARENE CYCLOPENTADIENYLIRON COMPLEXES

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## SUMMARY

It has been found that electroneutral arenecyclopentadienyl π-complexes of iron, $AreneFeC_5H_5$ (Arene=$C_6H_6$, $C_{10}H_8$), in the presence of donor solvents exchange their arene ligands for π-cyclopentadienyl ligand, other arenes, CO or $P(OPh)_3$.

These reactions lead accordingly to ferrocene, to some new arenecyclopentadienyliron π-complexes and to the dimers of the type $[C_5H_5FeL_2]_2$, where L=CO, $P(OPh)_3$.

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In an earlier communication we reported the reduction of benzenecyclopentadienyliron tetrafluoroborate[1] to the respective electroneutral π-complex, $C_6H_6FeC_5H_5$, which was the first uncharged arenecyclopentadienyliron complex to be reported. It is a dark-green crystalline solid which can be stored only in an inert atmosphere. Its reactivity differs sharply from that of the initial benzenecyclopentadienyliron cation. Thus, the novel π-complex exchanges its arene ring for other ligands under extraordinarily mild conditions. When $C_6H_6FeC_5H_5$ is heated to 40° in tetrahydrofuran the dark-green reaction mixture gradually becomes orange-yellow in colour and a dark precipitate is formed.

$$2\,C_6H_6FeC_5H_5 \xrightarrow[\approx 40^\circ]{\text{THF}} (C_5H_5)_2Fe + 2\,C_6H_6 + [Fe] \qquad (1)$$

The products of this reaction are ferrocene (51%) and benzene, as has been demonstrated by GLC. The precipitate formed also contains inorganic iron.

Ferrocene can also be formed from THF solutions of $C_6H_6FeC_5H_5$ at room temperature but in this case the process is very slow. In acetonitrile, benzenecyclopentadienyliron is converted to ferrocene within minutes even at 20°. The reaction rate is slow in dimethoxyethane, close to zero in ether, and zero in light petroleum. In other words, the reaction is favoured by solvents which are reasonably strong electron donors. From this we have assumed that the solvent molecules participate in the reaction by displacing the arene ligand and stabilizing the intermediate fragment (probably $C_5H_5Fe$). Stabilisations of this kind are well known[2].

Reaction (1) may be carried out without isolating the unstable electroneutral benzenecyclopentadienyliron intermediate:

$$[\mathrm{AreneFeC_5H_5}]\mathrm{BF_4} + \mathrm{Na/Hg} \xrightarrow{\mathrm{THF}} [\mathrm{AreneFeC_5H_5}] \xrightarrow{\mathrm{THF}}$$

$$(\mathrm{C_5H_5})_2\mathrm{Fe} + \mathrm{Arene} + [\mathrm{Fe}]$$

$$(\mathrm{Arene} = \mathrm{C_6H_6}, \mathrm{C_{10}H_8})$$

The final reaction mixture is coloured due to the formation of the $\mathrm{AreneFeC_5H_5}$, being green when the arene is benzene and dark violet when it is naphthalene. Indeed, even when isolated the uncharged naphthalene cyclopentadienyliron is dark violet in colour.

Earlier[3,4] we found that arenecyclopentadienyliron cations are converted into ferrocene by the action of reducing agents. This results may be explained in terms of reaction (1):

$$2\,[\mathrm{AreneFeC_5H_5}]\mathrm{BF_4} \xrightarrow[\mathrm{THF}]{\mathrm{Red.}} (\mathrm{C_5H_5})_2\mathrm{Fe} + 2\,\mathrm{Arene} + [\mathrm{Fe}]$$

$$(\mathrm{Red.} = \mathrm{Na}, \mathrm{C_2H_5ONa/C_2H_5OH}, \mathrm{NaNH_2/NH_3}, \mathrm{RNa}, \mathrm{RLi}, \mathrm{RMgX}, [\mathrm{C_{10}H_8}]^-\mathrm{Na}^+)$$

In fact, benzene abstraction and ferrocene formation are associated with the electroneutral $\pi$-complex formed via cation reduction, rather than with the initial cation.

The benzene in $\mathrm{C_6H_6FeC_5H_5}$ may be replaced by another arene. Thus, benzenecyclopentadienyliron on heating with an excess of naphthalene in an ether/THF mixture produces (after having been oxidised with atmospheric oxygen in the presence of $\mathrm{NaBF_4}$) naphthalenecyclopentadienyliron tetrafluoroborate.

$$\begin{tikzcd}[column sep=large] \mathrm{C_6H_6FeC_5H_5} + \mathrm{C_{10}H_8} \arrow[r, "\mathrm{THF/Et_2O}", "30-40^\circ"'] & {[\mathrm{C_{10}H_8FeC_5H_5}] + (\mathrm{C_5H_5})_2\mathrm{Fe} + \mathrm{C_6H_6}} \arrow[d, "\mathrm{NaBF_4}"', "\mathrm{O_2}"] \\ & {[\mathrm{C_{10}H_8FeC_5H_5}]\mathrm{BF_4}} \end{tikzcd} \qquad (2)$$

The yield of $[\mathrm{C_{10}H_8FeC_5H_5}]\mathrm{BF_4}$ is low (ca. 6%) and also ferrocene (43%) is invariably formed. The yield of ferrocene increases, while that of $[\mathrm{C_{10}H_8FeC_5H_5}]\mathrm{BF_4}$ falls, with an increase in the reaction time. This is quite reasonable since not only does the initial $\mathrm{C_6H_6FeC_5H_5}$ generate ferrocene, but the compound $\mathrm{C_{10}H_8FeC_5H_5}$ which is formed does so as well*. Reaction (2) does not proceed in ether.

Other ligand exchanges have been carried out through the use of a simpler technique not involving isolation of the electroneutral $\pi$-complex (*cf.* short communication[5]).

$$[\mathrm{AreneFeC_5H_5}]\mathrm{BF_4} \xrightarrow[\mathrm{THF}]{\mathrm{Na/Hg}} [\mathrm{AreneFeC_5H_5}] \xrightarrow[\mathrm{THF}]{\mathrm{Arene'}}$$

$$\begin{tikzcd} \longrightarrow [\mathrm{Arene'FeC_5H_5}] \arrow[d, "\mathrm{NaBF_4}"', "\mathrm{O_2}"] + (\mathrm{C_5H_5})_2\mathrm{Fe} + \mathrm{Arene} \\ {[\mathrm{Arene'FeC_5H_5}]\mathrm{BF_4}} \end{tikzcd}$$

$$(1)\ \mathrm{Arene} = \mathrm{C_{10}H_8}, \mathrm{Arene'} = \mathrm{C_6H_6};\ (2)\ \mathrm{Arene} = \mathrm{C_{10}H_8}, \mathrm{Arene'} = 1,3,5\text{-}(\mathrm{CH_3})_3\mathrm{C_6H_3}$$

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* Electroneutral $\mathrm{C_{10}H_8FeC_5H_5}$ is a dark-violet, extremely unstable compound. Its synthesis will be reported elsewhere.

The arene ligand is expelled from the benzenecyclopentadienyliron complex in a different fashion when two-electron donors such as CO or phosphites are used. $C_6H_6FeC_5H_5$ could, in fact be expected to exchange its benzene moiety for three CO groups giving rise to $C_5H_5Fe(CO)_3$ {or $[C_5H_5Fe(CO)_3]^+BF_4^-$ after oxidation}. The latter compound has been described[6] and is quite stable. However, the reaction actually proceeds via another route giving rise to the cyclopentadienyldicarbonyliron dimer, $[C_5H_5Fe(CO)_2]_2$, (10%) as the main product with ferrocene (ca. 5%) as the by-product: probably the formation of the 19-electron $C_5H_5Fe(CO)_3$ complex is less favourable than dimer formation.

The reaction with triphenylphosphite proceeds in exactly the same way.

$$C_6H_6FeC_5H_5+L \xrightarrow[\approx 20^\circ]{\text{THF}} [C_5H_5FeL_2]_2+(C_5H_5)_2Fe+C_6H_6$$

$(L=CO, (PhO)_3P)$

Other exchanges have been carried out using a simplified technique.

$$[\text{Arene}FeC_5H_5]BF_4 \xrightarrow[\text{THF}]{\text{Na/Hg}} [\text{Arene}FeC_5H_5] \xrightarrow[\text{THF}]{L} [C_5H_5FeL_2]_2$$

(1) Arene $= C_6H_6$, $L = CO$;
(2) Arene $= C_{10}H_8$, $L = CO$;
(3) Arene $= C_{10}H_8$, $L = (PhO)_3P$

The results obtained demonstrate that the arene ligand in the electroneutral benzenecyclopentadienyliron complex is bonded to the metal to a much weaker degree than in the $[C_6H_6FeC_5H_5]^+$ cation. In $C_6H_6FeC_5H_5$, the iron is formally a 19-electron atom; such violations of Sidgewick's rule are known for various $\pi$-complexes, with arene derivatives of transition metals being included among these. Such compounds are, as a rule, thermally unstable, being readily oxidised and hydrolysed. This behaviour has been explained by assuming that the "extra" electrons occupy antibonding orbitals of the $\pi$-complexes[8]. This explanation agrees well with the decreased arene–metal bonding observed in this work.

## EXPERIMENTAL

Benzenecyclopentadienyliron must be used in a thoroughly purified dry argon atmosphere, and the solvents used must be saturated with argon.

### *Benzenecyclopentadienyliron*

A suspension of $[C_6H_6FeC_5H_5]BF_4$ (1 g, 3.5 mmole) in 100 ml of THF was added to 1% sodium amalgam. The mixture was stirred at room temperature until a green colour appeared, then cooled to $-5^\circ$ and stirred for a further 2 h. After this, the mixture was cooled down to $-40^\circ$, left until the unreacted initial compound had sedimented and filtered under argon. The resulting dark-green $C_6H_6FeC_5H_5$ solution was stable for several days at solid $CO_2$ temperature, but decomposed rapidly at room temperature. From this solution either (a) the benzenecyclopentadienyliron complex was isolated or (b) its concentration was determined and the solution used for subsequent reactions. The latter procedure was found to be the best from a synthetic point of view since the electroneutral benzenecyclopentadienyliron was found to be extremely readily oxidised or decomposed by heat.

(a) The solution of $C_6H_6FeC_5H_5$ in THF was distilled under reduced pressure (−20°/4 mmHg) to remove the solvent. The residue was dissolved in ligroin, the solution was filtered into a weighed flask and the solvent carefully removed at −30° *in vacuo*. This procedure yielded 0.24 g (35%) of benzenecyclopentadienyliron.

(b) The dissolved $C_6H_6FeC_5H_5$ was oxidized to give $[C_6H_6FeC_5H_5]^+$, the oxidant using being $(C_6H_5)_3CCl$[1]:

$$C_6H_6FeC_5H_5 + (C_6H_5)_3CCl \rightarrow [C_6H_6FeC_5H_5]Cl + (C_6H_5)_3^{\cdot}$$

An aliquot of the filtered benzenecyclopentadienyliron solution was titrated with a solution of triphenylchloromethane in THF until the green colour had vanished. The $C_6H_6FeC_5H_5$ content was calculated from the amount of $(C_6H_5)_3CCl$ consumed. As a check, in some experiments the $[C_6H_6FeC_5H_5]^+$ formed was precipitated as the tetrafluoroborate. The yield was compared with that calculated from the titration data. The difference was never more than 3–4%.

### *Conversion of $C_6H_5FeC_5H_5$ into ferrocene*

(a) Benzenecyclopentadienyliron (0.2 g, 1 mmole) dissolved in THF was stirred at 30–40° for 2 h. The green colour was gradually transformed to yellowish-brown while a dark coloured precipitate was formed. Ether and water were added and the layers were separated. The organic layer gave ferrocene, 0.046 g (51% yield, m.p. 172–173°).

(b) Benzenecyclopentadienyliron (0.2 g, 1 mmole) dissolved in 100 ml of THF was treated with 25 ml of acetonitrile at room temperature. The mixture instantaneously become reddish-yellow in colour, and a brown precipitate was formed. After several minutes, water and ether were added and the layers separated. The organic layer gave ferrocene, 0.051 g (57% yield, m.p. 173°).

### *Conversion of $C_{10}H_8FeC_5H_5$ into ferrocene*

A suspension of naphthalenecyclopentadienyliron tetrafluoroborate (0.5 g, 1.5 mmole) in 50 ml of THF was added to 1% sodium amalgam [obtained from Na (0.35 g, 15 mmole) and Hg (3.4 ml)] with vigorous stirring at room temperature. The mixture became dark violet in 3–5 min. It was then cooled to −30° and stirred for a further 4 h. During this period, the colour intensified and latter within ca. 2 h became darker, the mixture finally assuming a dark brown colour. This mixture was decomposed with water and extracted with ether. The organic layer gave ferrocene (0.08 g, 60% yield), m.p. 171–173°, after purification by conversion into $[(C_5H_5)_2Fe]^+$ by the action of $FeCl_3$ followed by reduction with ascorbic acid. The water layer gave the initial $[C_{10}H_8FeC_5H_5]BF_4$ (0.06 g, 12%) identified by TLC on $Al_2O_3$ using dichloroethane/ethanol, 100/16 v/v, as the eluant. The same method was used to separate ferrocene (yield 38%) from $[C_6H_6FeC_5H_5]BF_4$ without the isolation of the $C_6H_6FeC_5H_5$ intermediate.

### *Exchange of the benzene ligand for naphthalene in $C_6H_6FeC_5H_5$*

Naphthalene (1.92 g, 15 mmole) was added to $C_6H_6FeC_5H_5$ (0.33 g, 1.64 mmole) dissolved in 100 ml of THF. The mixture was stirred at 35–40° for 2 h. It was then cooled to 0°, treated with 50 ml of a solution of $NaBF_4$ in water and shaken in air for some time. The layers were separated, the organic layer giving ferrocene (0.07 g, 43% yield), m.p. 172–173°. The orange-coloured water layer was neutralised with HCl and then evaporated. The dry residue was extracted with dichloroethane to give a mixture of $[C_{10}H_8FeC_5H_5]BF_4$ and $[C_6H_6FeC_5H_5]BF_4$. The mixture was separated by TLC on $Al_2O_3$ using dichloroethane/ethanol, 100/16 v/v as the eluant, to give $[C_{10}H_8FeC_5H_5]BF_4$ (ca. 6% yield), m.p. 131–133° (dec.). The IR spectrum was identical with the spectrum of the authentic sample.

### *The substitution of other arenes for naphthalene in $C_{10}H_8FeC_5H_5$*

(*a*) *Reaction with benzene.* A suspension of $[C_{10}H_8FeC_5H_5]BF_4$ (0.3 g, 0.8 mmole) in a mixture of 40 ml of THF and 3 ml of benzene was added to sodium amalgam obtained from Na (0.3 g, 12 mmole) and Hg (2 ml). The reaction mixture was stirred at — 15° for 5 h. The mixture became dark violet in colour and then turned black. It was worked up as described above. From the water layer, a mixture of $[C_{10}H_8FeC_5H_5]BF_4$ and $[C_6H_6FeC_5H_5]BF_4$ was obtained. The latter compound was isolated by means of TLC on $Al_2O_3$ using dichloroethane/ethanol, 100/16 v/v as the eluant (0.01 g, 6.4% yield). The compound was identified chromatographically and through its UV spectrum ($\lambda_{max}$ 239 nm for both the synthesised and the reference samples). The ether layer gave ferrocene, 0.045 g (55% yield).

(*b*) *Reaction with mesitylene.* A suspension of $[C_{10}H_8FeC_5H_5]BF_4$ (0.5 g, 1.5 mmole) in 80 ml of THF plus 2 ml of mesitylene was added to sodium amalgam obtained from Na (0.35 g, 13 mmole) and Hg (2.5 ml). The mixture was stirred at −25° for 5 h, then worked up as previously described. A mixture of $[(CH_3)_3C_6H_3FeC_5H_5]BF_4$ and $[C_{10}H_8FeC_5H_5]BF_4$ obtained from the water layer was pyrolysed (300°, 1 h), and the products extracted with heptane and analysed by GLC. Mesitylene, naphthalene and ferrocene were identified. The mesitylene/naphthalene ratio, 1/3.5, corresponds to the composition of the initial mixture of π-complex tetrafluoroborates. Ferrocene was formed through their thermal disproportionation. The ether layer also gave ferrocene, 0.045 g (34% yield).

### *Exchange of benzene for CO groups in $C_6H_6FeC_5H_5$*

(a) Carbon monoxide was bubbled through a solution of benzenecyclopentadienyliron (0.35 g, 1.75 mmole) in 100 ml of THF at room temperature for 1 h. The dark green solution became red-violet in colour. The solvent was evaporated and chromatography on $Al_2O_3$ showed that the residue contained $[C_5H_5Fe(CO)_2]_2$ and $(C_5H_5)_2Fe$. The mixture was separated on thin layers of $Al_2O_3$ using benzene/ligroin, 1/1 v/v as the eluant, to give $[C_5H_5Fe(CO)_2]_2$, 0.21 g (70% yield), m.p. 193–195°. A mixture of the compound with the authentic sample[9] had m.p. 192–195°. The IR spectrum (1760, 1940, 1965 $cm^{-1}$) agrees with the structure (*cf.* also ref. 9). In addition ferrocene (0.007 g, ca. 5% yield) was identified chromatographically.

(b) A suspension of benzenecyclopentadienyliron tetrafluoroborate (0.5 g, 1.7 mmole) in 50 ml of THF was added to sodium amalgam [obtained from Na (0.35 g, 13 mmole) and Hg (2.5 ml)] at room temperature. Within 10 min. the yellow solution became bright green in colour. Carbon monoxide was bubbled through the reaction mixture at −10° for 5 h. The mixture was then decomposed with water and treated with ether. The ether layer gave ferrocene (0.01 g, 7.6% yield), m.p. 171–173°, and $[C_5H_5Fe(CO)_2]_2$ (0.5 g, 15% yield), m.p. 192–194°. A mixture of the compound with the authentic sample had m.p. 192–195°, and the IR spectrum was identical to that reported[9].

The water layer gave the initial $[C_6H_6FeC_5H_5]BF_4$, (0.06 g, 12% of the initial amount used).

### *Exchange of $(C_6H_5O)_3P$ for benzene in $C_6H_6FeC_5H_5$*

Triphenylphosphite (2.14 g, 7 mmole) was added to benzenecyclopentadienyliron (0.2 g, 1 mmole) dissolved in 100 ml of THF and the mixture was stirred at room temperature for 2 h. The dark green solution became dark blue and then yellowish brown in colour. Some decomposition could be observed. After stirring for a further 2 h, the solution was treated with 30 ml of water and 100 ml of ether. The layers were separated and the organic layer was dried over $MgSO_4$ and the solvent evaporated. Chromatography on $Al_2O_3$ showed that the residue contained $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$ and ferrocene. The mixture was separated on thin layers of $Al_2O_3$ using ligroin/benzene, 3/1 v/v as the eluant, to give the dimer $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$ (0.088 g, 27% yield), m.p. 130–132° (lit.[10] m.p. 132–133°). A mixture of the compound with the authentic sample had m.p. 130–132°. The IR spectrum (1180, 1200, 1225 $cm^{-1}$) was identical with that reported[10].

### *Substitution of other ligands for naphthalene in $C_{10}H_8FeC_5H_5$*

(*a*) *Reaction with carbon monoxide.* A suspension of $[C_{10}H_8FeC_5H_5]BF_4$ (0.5 g, 1.5 mmole) in 150 ml of THF was added to sodium amalgam [Na (0.35 g, 13 mmole) and Hg (3.4 ml)] with vigorous stirring at room temperature. Immediately after the violet colour had appeared the reaction mixture was cooled down to −25° and CO was bubbled through it for 4½ h. The mixture was treated in the usual way (see above). The water layer gave 0.06 g (12%) of the starting material. The organic layer (analysed by chromatography on $Al_2O_3$) contained $[C_5H_5Fe(CO)_2]_2$ and ferrocene. The mixture was separated as described above for exchange with CO groups, to give ferrocene (0.01 g, 7.6% yield), m.p. 170–172° and $[C_5H_5Fe(CO)_2]_2$, (0.08 g, 30.7% yield), m.p. 193–195°. A mixture of the compound with the authentic sample had m.p. 192–195°, and the IR spectrum was identical to that reported in the literature[9].

(*b*) *Reaction with triphenyl phosphite.* A suspension of $[C_{10}H_8FeC_5H_5]BF_4$ (0.5 g, 1.5 mmole) in 80 ml of THF was added to sodium amalgam [Na (0.35 g, 13 mmole) and Hg (2.5 ml)] at room temperature with stirring. Within 2–3 min, the mixture became violet in colour. It was treated with triphenyl phosphite (0.93 g, 3 mmole) and stirred at −10 to −15° for 4 h. It was then worked up in the usual way. No unreacted starting material was found in the water layer. The organic layer, worked up as described above for exchange with $(C_6H_5O)_3P$ groups, gave ferrocene (0.03 g, 22% yield), m.p. 170–172°, and $\{C_5H_5Fe[P(OC_6H_5)_3]_2\}_2$, (0.03 g, 27.2% yield), m.p. 131–133°. A mixture of the compound with the authentic sample had m.p. 130–132°, and the IR spectrum (1180, 1200, 1225 $cm^{-1}$) corresponded to that reported[10]. (Found: C, 66.65; H, 4.74; P, 8.33. $C_{41}H_{35}FeO_6P_2$ calcd.: C, 66.36; H, 4.69; P, 8.23%.)

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