σ-Cyclopentadienyliron Derivatives as Intermediates in the Formation of Ferricenium Chloride and Ferrocene[1a,b]

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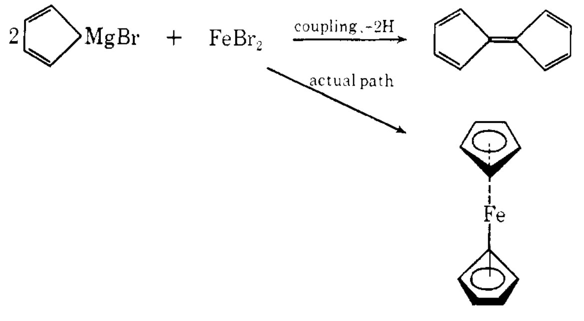
Abstract: Di-σ-cyclopentadienyliron chloride monotetrahydrofuranate (**2**) was prepared from the reaction of sodium cyclopentadienide and iron(III) chloride in a 2:1 molar ratio at −80° in tetrahydrofuran (THF). This compound (**2**) is stable either as a yellow solid at −80° or in THF solution at room temperature. Above −50° or upon the addition of organic solvents, such as ether or *n*-pentane, **2** rearranges to a blue solid, ferricenium chloride. Tris-σ-cyclopentadienyliron (**3**) was not isolated from the reaction of sodium cyclopentadienide and iron(III) chloride in a 3:1 molar ratio in THF. However, studies on periodic hydrolysis of each reaction mixture (2:1 or 3:1) at −80° and room temperature establish that **3** is an intermediate in the formation of ferrocene (**1**).

Ferrocene (**1**) was first prepared from the reaction of cyclopentadienylmagnesium bromide with iron halides in diethyl ether by Kealy and Pauson in 1951.[2] In spite of the numerous investigations on **1** and related compounds,[3] to date no mechanism for the formation of **1** has been reported. Kealy and Pauson originally intended to prepare fulvalene *via* an aryl coupling reaction.[4]



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Since that time, considerable light has been shed on the mechanism of the coupling reaction, which was actually first observed in the formation of biphenyl from the reaction of phenylmagnesium halide and chromium(III) chloride.[4] With the characterization of Hein's complexes, *i.e.*, arene-π-chromium complexes, and with the isolation of an intermediate, tris-σ-phenylchromium tristetrahydrofuranate, from the reaction between phenylmagnesium bromide and chromium(III) chloride,[5,6] came the realization that the coupling reaction involved the formation and homolytic cleavage of metal–carbon σ bonds.[7-9]

In our studies on the course of the reaction of sodium cyclopentadienide and iron(III) chloride in 2:1 and 3:1 molar ratios, we found that di-σ-cyclopentadienyliron chloride monotetrahydrofuranate (**2**), which can be isolated, rearranges to ferricenium chloride, and that tris-σ-cyclopentadienyliron (**3**) appears to be an intermediate in the formation of **1**.

A pale yellow solid was isolated from the reaction of sodium cyclopentadienide and iron(III) chloride in a 2:1 molar ratio conducted in THF at −80° over a 6-month period. The solid, which is stable below −50° and in THF solution at room temperature, was characterized as di-σ-cyclopentadienyliron chloride monotetrahydrofuranate (**2**) by chemical and spectral analyses.

σ bonding between the cyclopentadienyl carbon and iron atoms was assigned from the following evidence. The infrared spectrum of **2** in THF shows a strong absorption at 1620 cm^{-1} characteristic of the conjugated double bonds in the σ-bonded cyclopentadienyl ring.[10] Weak absorptions in the C–H stretching region at 2880 cm^{-1} and an absorption at 3080 cm^{-1} compared well with the values of known σ-bonded cyclopentadienyl metal compounds.[10,11] Compound **2** was hydrolyzed at −50° with a methanol–hydrochloric acid mixture, producing iron(III) chloride and polymeric cyclopentadiene (without H_2 evolution). This polymeric material has a very similar infrared spectrum to polymeric material formed by the low-temperature polymerization of cyclopentadiene by iron(III) chloride. An organic group σ bonded to a transition metal generally produces the protonated analog without gas evolution upon hydrolysis.[12] In this case, the hydrolysis of **2** produced cyclopentadiene which could have been readily polymerized by the iron(III) chloride also formed. The polymerization of cyclopentadiene by iron(III) chloride has been documented.[13] Experiments showed that

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[1] (a) Supported by Air Force Office of Scientific Research Grant No. AF-AFOSR 824-67; (b) presented in part at the Third International Symposium on Organometallic Chemistry, Munich, West Germany, 1967; (c) address correspondence to this author at Chemistry Department, Texas A & M University, College Station, Texas 77843.

[2] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[3] Many review articles and monographs have been published on the chemistry of ferrocene and related compounds. Some of these are: (a) P. L. Pauson, *Quart. Rev.* (London), **9**, 391 (1955); (b) in "Non-Benzenoid Aromatic Compounds," D. Ginzberg, Ed., Interscience Publishers, New York, N. Y., 1958, p 107; (c) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1959); (d) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959); (e) M. Rosenblum, "Chemistry of Iron Group Metallocenes," Part I, John Wiley and Sons, Inc., New York, N. Y., 1965.

[4] G. M. Bennett and E. E. Turner, *J. Chem. Soc.*, 1054 (1914).

[5] H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **79**, 3062 (1957).

[6] H H. Zeiss and W. Herwig, *ibid.*, **81**, 4798 (1959).

[7] M. Tsutsui, *Ann. N. Y. Acad. Sci.*, **93**, 33 (1961).

[8] P. Kasai, M. Tsutsui, and J. Ariyoshi, unpublished results.

[9] Such arrangements are referred to as σ–π rearrangements. A review article on this topic is M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Agnew. Chem.*, in press.

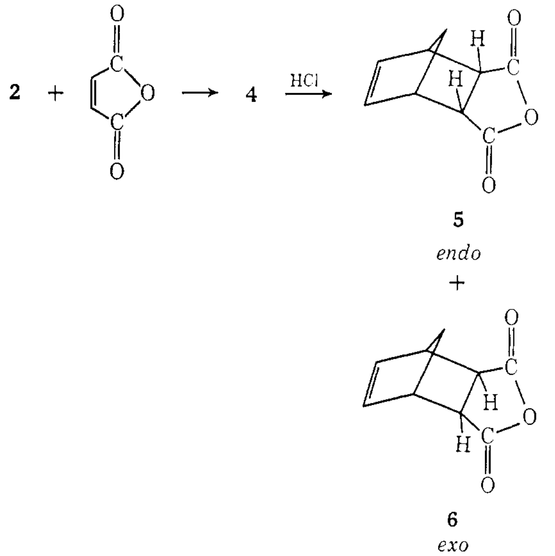
[10] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 106 (1956).

[11] T. S. Piper and G. Wilkinson, *Chem. Ind.* (London), 1296 (1955).

[12] B. F. Hallum and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

π-cyclopentadienyliron compounds such as ferricenium chloride and **1** gave no reaction with these hydrolyzing agents under similar conditions. This result indicates that **2** is not π-bonded, but rather a σ-bonded cyclopentadienyl compound.

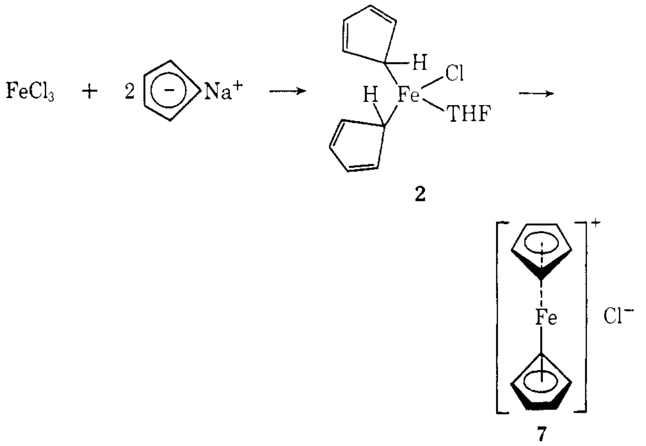
Further evidence for σ bonding comes from the reaction of **2** with maleic anhydride; a brick-red solid (**4**) was isolated from the reaction mixture. Compound **4** was not characterized, but its ir spectrum shows the presence of the anhydride grouping and ignition shows that a metal is present. After hydrolysis of **4** with concentrated hydrochloric acid, *endo*- and *exo*-bicyclo[2.2.1]-hept-5-ene 2,3-anhydrides (**5**, **6**) were separated from the reaction mixture.



π-Cyclopentadienylmetal complexes also react with maleic anhydride (probably as Lewis acids); however, attack on the cyclopentadienyl ring does not occur since the π complex is regenerated on treatment with acid.[14] The reaction of maleic anhydride with a cyclopentadienyl metal compound, which does not regenerate a π complex upon treatment with acid, is considered sufficient evidence to signify a σ-bonded ring without further characterization.[15]

No signal was observable in nmr measurements of **2** in THF because of the interference of strong paramagnetic resonance. From the chemical shifts of THF, however, the iron appears to be spin-free d^5.[16,17]

Upon warming **2** above −50° or upon the addition of organic solvents such as methylene chloride, ether, or *n*-pentane at −80°, the yellow solid rearranges almost immediately to a deep blue solid which was subsequently characterized as the ferricenium cation **7**.[18]



The mass spectrum obtained is consistent with the fragmentation pattern expected for **2** with peaks corresponding to σ-dicyclopentadienyliron, σ-monocyclopentadienyliron, cyclopentadiene ion, and THF; *m/e* at 186, 121, 72, 66, and 56. Because of the thermal instability of **2**, only analyses for iron and chlorine were obtained. *Anal.* Found: Fe, 20.0; Cl, 11.4. Elemental analysis thus verifies the designation of a monotetrahydrofuranate (*Anal.* Calcd for $(C_5H_5)_2FeClC_4H_8O$: Fe, 19.0; Cl, 12.1), rather than the unsolvated or ditetrahydrofuranate (*Anal.* Calcd for $(C_5H_5)_2FeCl$: Fe, 25.2; Cl, 16.0. Calcd for $(C_5H_5)_2FeCl \cdot 2C_4H_8O$: Fe, 15.27; Cl, 9.69).

The reaction of sodium cyclopentadienide and iron(III) chloride in a 2:1 molar ratio at −80° in THF was studied in detail for about 6 months; see Table I. Periodically, samples were withdrawn and a portion was hydrolyzed at −80° while the remaining portion was both raised to room temperature and hydrolyzed within 3 min.[19] As is shown, **1** is formed only during the room-temperature hydrolysis, indicating the probable transformation of its precursor **3**, which is stable at −80° and does not rearrange to **1** at this temperature. Furthermore, the amount of **1** decreases as the reaction time increases, indicating some change in the intermediate as the reaction proceeds. These data are interpreted as showing that, in the early stages of reaction, there is an equilibrium of mono-, di-, and tri-σ-cyclopentadienyliron tetrahydrofuranates. In spite of the fact that the addition of sodium cyclopentadienide is slow and controlled, some **3**, the precursor to **1**, is formed because of the limited solubility of iron(III) chloride in THF at −80°. **3** was later shown to produce **1**.

Table I. Reaction of Sodium Cyclopentadienide and Iron(III) Chloride in a 2:1 Molar Ratio in THF at −80°

Reaction time, days	% **1**[a] by hydrolysis at −80°	Room temp
3.5	Trace	20
7	Trace	18
12	Trace	7
147	Trace	Trace

[a] Determined from % iron(III) chloride consumed.

As the reaction proceeds, **3** plus the excess iron(III) chloride and **3** plus mono-σ-cyclopentadienyliron dichloride probably undergo redistribution reactions to give **2**. The redistribution of **3** is consistent with the

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(13) P. J. Wilson and J. H. Wells, *Chem. Rev.*, **34**, 1 (1944).

(14) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

(15) T. S. Piper and G. Wilkinson, *ibid.*, **2**, 32 (1956); W. Strohmeir and R. M. Lemmon, *Z. Naturforsch.*, **14a**, 109 (1959).

(16) Due to experimental difficulties in determining the amount of **2** in solution, this measurement could only be approximate.

(17) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); H. P. Fritz and K. E. Schwarzhans, *J. Organometal Chem.* (Amsterdam), **1**, 208 (1964).

(18) **7** was characterized spectrally by comparison with a compound prepared in these laboratories and with the reported spectra: A. N. Nesmeyanov, L. P. Yur'eva, R. B. Materikova, and B. Ya. Getnarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 731 (1965); I. J. Spilners, *J. Organometal. Chem.* (Amsterdam), **11**, 381 (1968).

(19) In a 3-min period of reaction between sodium cyclopentadienide and iron(III) chloride (2:1 or 3:1) at room temperature, no **1** was isolated.

decrease in the amount of **1** isolated. The reaction is completed after approximately 6 months, at which time the maximum amount of **2** was isolated.

Among the three probable σ intermediates, mono-, **2**, and **3**, **3** is the most probable precursor of **1** because **2** rearranges to the ferricenium cation and not to **1**; and by analogy the mono σ species is not expected to rearrange to **1**.

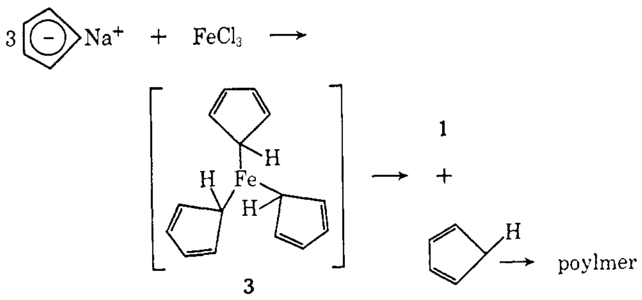
A similar reaction was conducted using sodium cyclopentadienide and iron(III) chloride (3:1) at −80° for 6 months. The results of this experiment can be found in Table II. Again, during all periods of reaction, only a trace of **1** was obtained after each hydrolysis at −80°, consistent with the formation of a stable intermediate, predicted to be **3**. However, hydrolysis at room temperature gave increasing yields of **1** to a maximum of 70–80% at the end of 6 months. This indicates that there must be a redistribution reaction similar to the redistribution discussed for the 2:1 reaction, but in this case, a 3:1 molar ratio gives all **3**.

Table II. Reaction of Sodium Cyclopentadienide and Iron(III) Chloride (3:1) in THF at −80°

	% **1**[a] by hydrolysis at	
Reaction time, days	+80°	Room Temp
1.5	Trace	5
15	Trace	22
92	Trace	30
140	Trace	60
200	Trace	70

[a] Determined from % iron(III) chloride consumed.

During attempts to isolate **3**, **1** and the polymeric cyclopentadienyl compound were found to be the major products when the temperature of the reaction mixture was raised to −60°. This result indicates that **3** is converted to **1** at this temperature, which was critical. Because of thermal instability, attempts to isolate **3** from the reaction mixture were unsuccessful. Furthermore, attempts to introduce strongly stabilizing ligands such as triphenylphosphine, ethylphenylphosphine, and pyridine were unsuccessful and resulted in the formation of **1** in each case. A plausible path for the formation of **1** follows.



The predicted formation of a cyclopentadienyl radical is further substantiated by the isolation of polymeric cyclopentadiene which always accompanies the preparation of **1**. The exact nature of cleavage between the iron atom and the σ-cyclopentadienyl carbon in **2** is being investigated by the use of epr.

Experimental Section

Reagents and Instruments. Reactions were carried out and products purified under a prepurified, Linde super dry, nitrogen atmosphere. Reagent grade solvents and chemicals were used throughout. THF was stored over potassium hydroxide and distilled from sodium. Benzene, *n*-hexane, and *n*-pentane were distilled from sodium, ether from lithium aluminum hydride, and dichloromethane from magnesium sulfate. Cyclopentadiene was obtained by distilling dicyclopentadiene and collecting the distillate at 0°. Iron(III) chloride, both anhydrous and hexahydrated, was dried by refluxing with thionyl chloride, distilling off excess thionyl chloride, and heating the black solid at 60° and 0.1 mm for 24 hr. Triphenylphosphine and maleic anhydride were used without further purification other than drying at 0.1 mm for 1 hr with nitrogen flushing. Diethylphenylphosphine was prepared according to Meisenheimer.[20] Sodium cyclopentadienide was prepared by the reaction of sodium with cyclopentadiene in THF.[21]

Iron was determined volumetrically by the standard procedure of reduction to iron(II) and estimation with standard dichromate solution.[22a] Complete decomposition of the analysis sample was achieved by heating the compound at 100° with an excess of aqua regia. Chloride was determined volumetrically according to the Volhard method.[22b] To ensure complete ionization of chloride ion, the sample was heated at 100° for 8 hr with concentrated nitric acid (halogen free) and excess standard silver nitrate.

The infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Ultraviolet spectra were recorded with a Bausch and Lomb Spectronic 505 or a Cary Model 15 spectrophotometer. Nmr spectra were determined with a Varian A-60 spectrometer with a variable-temperature probe. Mass spectra were measured with a Consolidated Electrodynamics Corp. mass spectrophotometer, Type 21-103C. Gas chromatographic analyses were conducted on an F and M Model 810-19 gas chromatograph using flame ionization detection. The analyses were made on a 6-ft stainless steel column of SE30 rubber (5%) on 80–100 mesh Chromosorb G.

Di-σ-cyclopentadienyliron Chloride Monotetrahydrofuranate (2). Sodium cyclopentadienide in THF (54.2 ml, 0.018 mole) was added dropwise, over a 4-hr period, to a stirred suspension of iron(III) chloride (1.46 g, 0.009 mole) in THF at −80°. Stirring was continued at −80° for about 6 months. The reaction mixture was centrifuged to remove sodium chloride, the centrifugate was evaporated to one-fifth the original volume, and *n*-pentane (50 ml) was added. This mixture was centrifuged and cooled to −80°, the pentane decanted off, and THF (50 ml) added. The dark brown solid remaining undissolved (polymer-like organic material) was centrifuged off and the THF solution evaporated to dryness at about 0.5 mm, the last stages of the evaporation being carried out at −50°. Repeated washings with a *n*-pentane–THF (10:1) solution (until the washings appeared pale yellow) gave **2**: ir spectrum 3080 (m), 2880 (w), 2810 (w), 1710 (m), 1620 (m), 1400 (m), 1370 (w), 1360 (w), 1190 (m, br), 1000 (s), 815 (s), 760 (sh), 655 (m, br) cm^{-1}; uv spectrum λ_{max}^{THF} 313 mμ. *Anal.* Calcd for $(C_5H_5)_2FeClC_4H_8O$: Fe, 19.0; Cl, 12.1. Found: Fe, 20.0; Cl, 11.4. The mass spectrum showed abundant fragment ions at 186, 121, 72, 66, and 56.

Reaction of Di-σ-cyclopentadienyliron Chloride (2) with Maleic Anhydride. Maleic anhydride, dried at 0.1 mm for 1 hr, in THF was added to a solution of **2** in THF, the reaction mixture turning red. After centrifuging, the solution was evaporated to dryness giving a brick-red, ether-insoluble solid (**4**) which was well washed with ether to remove excess maleic anhydride. After centrifuging, all further manipulations were carried out in the atmosphere: ir spectrum 3350 (s, br), 2950 (m), 1750 (s), 1740 (sh), 1610 (s), 1430 (s) cm^{-1}. Ir determinations were made in THF solution in 0.2-mm cells. Ignition leaves an inorganic residue.

4 was hydrolyzed by warm concentrated hydrochloric acid. Sublimation of the ether extract gave two crystalline materials melting at 164.5 and 143°, respectively. These compounds were identified as *endo*-bicyclo[2.2.1]hept-5-ene 2,3-anhydride (**5**) and

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(20) J. Meisenheimer, H. Glawe, H. Greeske, A. Schorning, and E. Vieweg, *Ann.*, **449**, 227 (1926).

(21) M. Shlosser, *Angew Chem.*, **76**, 258 (1964), and references therein.

(22) J. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, The Macmillan Co., New York, N. Y., 1952; (a) pp 567–572; (b) p 545.

the *exo* isomer (6) by glpc and by comparison of their ir spectra with those of authentic samples.[23,24]

endo-**Bicyclo[2.2.1]hept-5-ene 2,3-anhydride (5)** was prepared by the addition of cyclopentadiene to a solution of maleic anhydrida in ether, mp 164–165°.[23]

The *exo* **isomer 6** was prepared by the thermal rearrangement of the *endo*-anhydride **5** at 190°:[24] mp 144–145°, lit.[24] 140–142°

Tris-σ-cyclopentadienyliron (3). Sodium cyclopentadienide (216 ml of 1.15 *M*, 0.245 mole) was added dropwise over a period of 4 hr to a stirred mixture of iron(III) chloride (13.41 g, 0.083 mole) in THF (60 ml) at −80°. The reaction mixture was then stirred at −80° for about 6 months. Attempts to isolate **3** were unsuccessful. When the temperature was raised above −60°, **1** was obtained in over 70% yield as well as iron(III) chloride and the polymeric material.

Attempted Preparation of Tris-σ-cyclopentadienyliron Chloride Diethylphenylphosphine. Trisdiethylphenylphosphine–iron(III) trichloride was prepared *in situ* by the addition of diethylphenylphosphine (3.33 g, 0.02 mole) in benzene (50 ml) to iron(III) chloride (1.09 g, 0.0067 mole) at room temperature. The mixture was stirred for 15 hr until a clear solution resulted. This benzene solution was added slowly to a stirred sodium cyclopentadienide solution in THF (16 ml. 0.021 mole) at −30°, the color changing immediately to orange-yellow. The temperature was allowed to rise slowly, and stirring was continued at room temperature for 15 hr. The solution was concentrated to 10 ml and on cooling to 0° yellow-orange crystals separated out. These were shown to be **1** from their ir spectrum.

Attempted Preparation of Tris-σ-cyclopentadienyliron Tristriphenylphosphine. A solution of triphenylphosphine (7.86 g, 0.03 mole) in THF (75 ml) was added to iron(III) chloride (1.62 g, 0.01 mole). The suspension obtained was cooled to −80° and sodium cyclopentadienide in THF (22.5 ml, 0.03 mole) was added with vigorous stirring for 18 hr at room temperature. The solution was concentrated and *n*-hexane (100 ml) was added, but no crystals formed even on cooling. The solution was evaporated to dryness and washed well with water leaving a yellow solid which was characterized by its ir spectrum to be a mixture of **1** and triphenylphosphine.

Acknowledgment. We thank M. Haya and E. Manda for their experimental assistance.

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(23) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(24) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951);