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SYNTHESIS AND DEPROTONATION OF η^6-ARENE-η^5-CYCLOPENTADIENYLIRON(II) COMPLEXES BEARING NH_2, OH OR SH SUBSTITUENTS

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Summary

η^6-Aniline-η^5-cyclopentadienyliron(II) cation has been prepared by the reaction of ferrocene, aniline, and $AlCl_3$. η^6-Phenol-η^5-cyclopentadienyliron(II) and η^6-thiophenol-η^5-cyclopentadienyliron(II) cations have been made by nucleophilic displacement of Cl^- from η^6-chlorobenzene-η^5-cyclopentadienyliron(II) cation using OH^- or SH^-. Deprotonation of these cations with appropriate bases gives neutral cyclohexadienyl complexes with exocyclic C=N, C=O, or C=S bonds.

Introduction

Evidence of increased acidity of alpha protons in bis(η^6-arene)iron(II) cations [1] stimulated additional work which led to isolation of neutral cyclohexadienyliron(II) complexes formed by deprotonating η^6-arene-η^5-cyclopentadienyliron(II) cations (arene = fluorene, triphenylmethane, carbazole, diphenylamine) [2]. The fluorene derivative was also extensively studied by Johnson and Treichel [3,4] who concluded that the compound has considerable charge separation.

Recent reports from several laboratories have described the isolation and characterization of several cyclohexadienylmetal complexes with exocyclic double bonds to C, N, or O in which a metal other than iron is involved. η^5-Fluorenylmanganese tricarbonyl [3,5], (1—5-η^5-6-phenyliminocyclohexadienyl)manganese tricarbonyl [6], (1—5-η^5-cyclohexadien-6-onyl)bis(triphenylphosphine)ruthenium(II) hydride [7], η^3-allyl-(1—5-η^5-cyclohexadien-6-onyl)chromium dicarbonyl [8], and (1—5-η^5-cyclohexadien-6-onyl-η^5-pentamethylcyclopentadienylrhodium(III) cation [9] have been described.

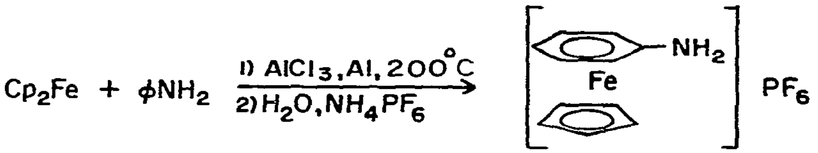
Such species are of interest not only as unusual metal complexes, but also because of the potential they offer for modifying the reaction chemistry of arenes. With this in mind, we chose to synthesize the simplest examples of cyclohexadienyliron complexes with exocyclic C=N, C=O, and C=S bonds.

Results and discussion

Synthesis of arene salts

η^6-Aniline-η^5-cyclopentadienyliron(II) cation I has previously been prepared from η^6-chlorobenzene-η^5-cyclopentadienyliron(II) cation II by nucleophilic displacement of Cl^- using NH_3 in an autoclave [10] or potassium phthalimide with a subsequent, ethanolic hydrazine work-up [11]. Nesmeyanov, Vol'kenau, and Bolesova reported that the aniline complex could not be prepared by the reaction of ferrocene, aniline, and $AlCl_3$ [12], a procedure they had found useful for many other arenes including chlorobenzene.

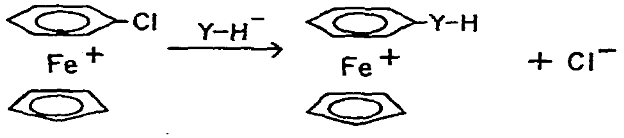
In our hands, the reaction of ferrocene, aniline, and $AlCl_3$ has proved to be an excellent synthetic approach to $[I]PF_6$. A successful reaction is facilitated by use of excess $AlCl_3$ (mole ratio, ferrocene/$AlCl_3 \simeq 1/4$) to offset that lost by coordination to the amine function of aniline and by use of elevated temperatures (ca. 190—200° C). This procedure gave the desired salt in 37% yield compared to an overall yield of 24% for the previously described, two-step procedure starting with chlorobenzene.



([I]PF6)

Neither η^6-phenol-η^5-cyclopentadienyliron(II) cation III nor η^6-thiophenol-η^5-cyclopentadienyliron(II) cation IV has previously been reported. Nesmeyanov and co-workers found that the phenol complex could not be made by reaction of phenol, ferrocene, and $AlCl_3$, and their attempts to synthesize it from II using NaOH or Na_2CO_3 in water led to extensive decomposition [11].

We now report that III may be readily prepared from the chlorobenzene complex by reaction with excess NaOH in 50% aqueous acetone. Following evaporation of the acetone under vacuum, filtration, and acidification of the filtrate with concentrated hydrochloric acid, it was necessary to extract the product with CH_2Cl_2 because of its appreciable solubility in aqueous acid. The hexafluorophosphate salt, $[III]PF_6$, which was prepared in 36% yield, could be purified by chromatography on alumina with subsequent recrystallization from acetone/ether or CH_2Cl_2/ether.



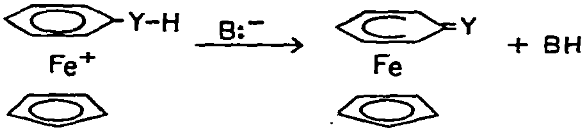
(II Y = O or S)

The analogous reaction of II with excess NaSH occurred rapidly in acetonitrile. After chromatography of the product under nitrogen on an alumina column and acidification with concentrated aqueous HCl, a 50% yield of the thiophenol complex, [IV]PF_6, was obtained. In this synthesis, as in the synthesis of [III]PF_6, an intermediate cyclohexadienyl complex is produced which requires acidification to generate the cation.

Attempted synthesis of the phenol complex III by reaction of HI with η^6-anisole-η^5-cyclopentadienyliron(II) cation was unsuccessful.

Cyclohexadienyl complexes

Deprotonation of [I]PF_6, [III]PF_6, and [IV]PF_6 is easily effected. In the case of the phenol and thiophenol complexes it is more convenient to react the chlorobenzene complex, [II]PF_6, with excess NaOH or NaSH and isolate the neutral complex directly rather than first isolating the intermediate salt.

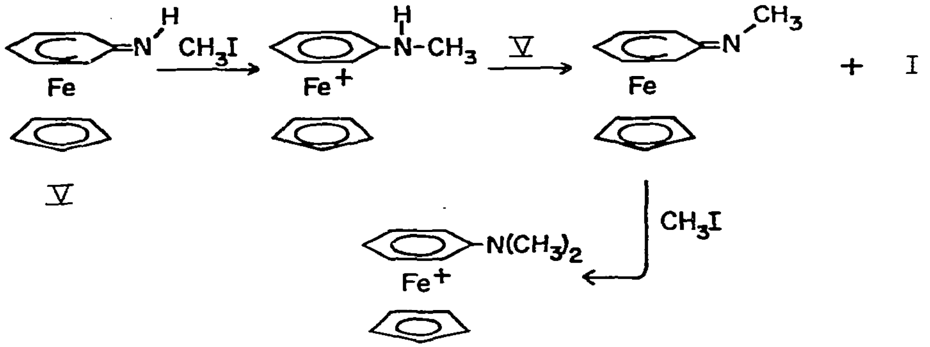


Cation	Y	Compound
I	NH	V
III	O	VI
IV	S	VII

The aniline derivative V is most conveniently prepared using [I]PF_6 and $NaNH_2$ in CH_2Cl_2 (79% yield). Deprotonation of I could also be effected with $NaCH_2CN$ in acetonitrile, but product purification was more difficult. When deprotonation was attempted with $NaNH_2$ in either liquid NH_3 or tetrahydrofuran, the deep red color of V appeared but changed to black after a few minutes. The decomposition products were not identified. V was also susceptible to decomposition when allowed to stand in acetone and was rather air-sensitive. Presumably because of its instability, elemental analyses of V were unsatisfactory. Pure samples were obtained as indicated by NMR spectra and the molecular formula was verified by high resolution mass spectrometry. The structure assignment is also supported by deuteration and methylation experiments.

The reaction of V with CH_3COOD regenerated cation I the NMR spectrum of which showed a relative area of one for nitrogen bound protons. In a control experiment, the treatment of undeuterated [I]PF_6 with CH_3COOD produced a solution the NMR of which showed a relative area of two for nitrogen bound protons. A pronounced downfield shift of the N—H absorption from δ 5.7 for [I]PF_6 in acetone-d_6 to δ 9.4 in acetone-d_6 containing CH_3COOD suggests that a π-coordinated anilinium ion exists in acidic media. From these results, one may conclude that exchange of D for N—H protons in I does not occur appreciably in short time periods (<30 min), that one proton was removed from nitrogen in the deprotonation experiment, and that no irreversible structural change follows deprotonation.

The reaction of V with excess CH_3I gave an orange oil which subsequently was converted to a crystalline hexafluorophosphate. The elemental analysis and NMR spectrum showed it to be η^6-*N*,*N*-dimethylaniline-η^5-cyclopentadienyliron(II) hexafluorophosphate. Unlike the reaction with CH_3COOD, which is believed to quench V immediately, the reaction with CH_3I is apparently slow enough that after monomethylation of a part of V, proton transfer may occur from the newly formed cation to V, thus creating I. The *N*-methylimino intermediate may then be methylated a second time to give the previously unreported *N*,*N*-dimethylaniline complex.



Methylation of VI and VII with CH_3I proceeds without the complication of proton transfer to yield the known π-anisole cation and the previously unknown π-thioanisole cation, respectively. The behavior of VI contrasts with that of η^3-allyl-(1—5-η^5-cyclohexadien-6-onyl)chromium dicarbonyl which Trahanovsky and Hall found to be unreactive to CH_3I [8]. We also found $[I]PF_6$, $[III]PF_6$, and $[IV]PF_6$ to be unreactive to CH_3I.

The infrared spectrum of VI exhibits a moderately strong absorption at 1661 cm^{-1} in support of a C=O structure. This absorption is 30—64 cm^{-1} higher in frequency than similar peaks observed in other laboratories for analogous complexes of ruthenium [7], chromium [8], and rhodium [9] suggesting a somewhat higher bond order for the carbonyl group in our compound. A strong absorption at 1082 cm^{-1} in the infrared spectrum of VII is indicative of a C=S function. The infrared spectrum of V does not allow unequivocal assignment of a C=N structure because the absorptions found at 1631 and 1551 cm^{-1} also appear in the spectrum of $[I]PF_6$.

The similarity in NMR spectra exhibited by V and VI infers similar structures. In CD_3CN, the cyclohexadienyl protons of V appear as multiplets in the ranges δ 5.30—5.63(3) and δ 4.83—5.05(2) while in acetone-d_6 the cyclohexadienyl protons of VI appear as multiplets in the ranges δ 5.33—5.63(3) and δ 4.67—4.97(2). In contrast, the arene protons of the precursors, $[I]PF_6$ and $[III]PF_6$ appear at δ 5.80—6.38 (m, 5) and δ 6.28 (s, 5), respectively, in acetone-d_6.

The high resolution mass spectrum of V included small peaks corresponding to the particles $C_{20}H_{20}Fe_2^+$ and $C_{15}H_{15}Fe_2^+$. These intriguing ions presumably result from thermal decomposition.

Experimental

All reactions were performed under nitrogen. The neutral complexes were purified and stored under nitrogen. Decomposition temperatures were determined using evacuated sealed capillaries. Carbon and hydrogen analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., or Atlantic Microlab, Inc., Atlanta, Ga. Iron analyses were determined using a Perkin—Elmer Model 290 B atomic absorption spectrophotometer. Infrared spectra were obtained on a Beckman IR-10 instrument. Mass spectra were recorded using an AEI MS-30 spectrometer with 70 eV ionizing energy.

Proton NMR spectra were measured with a Varian A-60-A or Jeol PMX-60 spectrometer. Chemical shifts are expressed in delta (δ) units relative to internal tetramethylsilane.

η^6-Chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate (dec. 224—228°C) was prepared in 28% yield by a modification of the method reported by Nesmeyanov et al. [12] for the corresponding tetrafluoroborate. No aluminum powder was used, and ascorbic acid was added during the work-up to reduce ferricinium ion prior to the precipitation step.

Sodium hydrogen sulfide was prepared by the Inorganic Syntheses procedure [13].

η^6-Aniline-η^5-cyclopentadienyliron(II) hexafluorophosphate, [I]PF_6

Ferrocene (34.27 g, 0.184 mol), aniline (30.26 g, 0.163 mol), aluminum chloride powder (94.0 g, 0.707 mol), aluminum powder (15.04 g, 0.557 mol) and decalin (140 ml) were stirred under nitrogen at 200°C for 5 h.

The dark mixture was then cooled to 0°C and solvolyzed with 10% aqueous methanol (200 ml). Following filtration, the orange aqueous layer was separated from an orange organic layer and washed with diethyl ether (2 × 30 ml). The aqueous layer was then treated with sufficient NH_4PF_6 (10.0 g, 0.0629 mol) in water to give complete precipitation. The yellow-orange product was washed with water and diethyl ether, dried, and then reprecipitated from acetone/diethyl ether to give 21.58 g (36.9%) of an orange powder, dec. 242°C (lit. [11] dec. 250°C).

NMR (acetone-d_6): cyclopentadienyl, δ 4.98 (s, 5); coordinated arene, 5.80—6.38 (m, 5); NH_2, 5.57—5.80 (b, s, 2).

IR (KBr): 3499s, 3401s, 3248w, 3135w, 3096w, 1634s, 1554s, 1472s, 1421s, 1389s, 1305s, 1162s, 845vs (br), 740s, 556s, 475s, 461s cm^{-1}.

η^6-Phenol-η^5-cyclopentadienyliron(II) hexafluorophosphate, [III]PF_6

η^6-Chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate (4.54 g, 0.0120 mol), sodium hydroxide (5.00 g, 0.125 mol), and 50% aqueous acetone (80 ml) were stirred under nitrogen. An orange aqueous layer and a deep brown organic layer were observed. After 36 h the acetone was distilled under vacuum. The residual slurry was filtered to separate an orange solution from a yellow solid (starting material) which was washed with water. Acidification of the filtrate with concentrated hydrochloric acid produced a color change from orange to yellow and a small amount of yellow precipitate. The mixture was then extracted with CH_2Cl_2 (5 × 40 ml). The solvent was removed from the

CH_2Cl_2 extracts producing a brown residue. Recrystallization of the residue from acetone/diethyl ether gave golden needles (2.24 g).

Further purification was achieved by chromatographing an acetone solution of the product on alumina. A yellow band eluted with acetone was discarded. An orange band eluted with 30% aqueous acetone was collected and acidified with concentrated hydrochloric acid. After evaporation of the solvent at 45° C under vacuum, the residue was reprecipitated from CH_2Cl_2/diethyl ether as a fine yellow powder, dec. 204—206° C, weighing 1.65 g (36.3%). Found: C, 36.95; H, 3.15; Fe, 15.55. $C_{11}H_{11}OFePF_6$ calcd.: C, 36.70; H, 3.08; Fe, 15.51%.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 5.12 (s, 5); coordinated arene, 6.28 (s, br, 5); OH, 9.05 (s, br, 1).

IR (KBr): 3495s (br), 3121s (br), 1548s, 1518m, 1469m, 1444s, 1420m, 1276m, 1218m (br), 833vs (br), 551s, 523m, 476s, 452m cm^{-1}.

η^6-Thiophenol-η^5-cyclopentadienyliron(II) hexafluorophosphate, [IV]PF_6

η^6-Chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate (2.32 g, 6.12 mmol), sodium hydrogen sulfide (2.16 g, 38.6 mmol), and acetonitrile (20 ml) immediately formed a deep red solution when stirred under nitrogen in a Schlenk tube. After 20 min the solution was filtered to separate a blue-green residue which was washed with acetonitrile (4 × 30 ml). Evaporation of the solvent from the filtrate and washings under vacuum left a deep-red solid. The product was dissolved in acetone and chromatographed on alumina under nitrogen. A small, yellow band eluted with acetone was discarded. An orange band was eluted with 30% aqueous acetone. Acidification of this solution with concentrated hydrochloric acid produced a color change from red-orange to yellow. Excess NH_4PF_6 was added and the solvent was removed in vacuo. The residue was recrystallized under nitrogen from acetone/diethyl ether and CH_2Cl_2/diethyl ether to give 1.16 g (50.4%) of an olive-green product, dec. 236—238° C. Found: C, 35.25; H, 2.96; Fe, 14.41. $C_{11}H_{11}SFePF_6$ calcd.: C, 35.13; H, 2.95; Fe, 14.85%.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 5.20 (s, 5); coordinated arene, 6.28—6.78 (m,5); SH 3.6—3.92 (s, br, 1).

IR (KBr): 3124m, 2584w, 1625w, 1505w, 1451m, 1421s, 1408m, 1385m, 1099m, 1011w, 835vs (br), 703w, 552s, 503m, 467s (br) cm^{-1}.

(1—5-η^5-6-Iminocyclohexadienyl)-η^5-cyclopentadienyliron(II), V

Reaction in CH_2Cl_2. η^6-Aniline-η^5-cyclopentadienyliron(II) hexafluorophosphate (1.05 g, 2.92 mmol), sodium amide (1.34 g, 34.4 mmol), and CH_2Cl_2 (90 ml) produced a deep red color when stirred under nitrogen. After 1.75 h the solution was filtered and taken to dryness under vacuum. The residue was recrystallized from CH_2Cl_2/diethyl ether and gave 0.49 g (79%) of a red solid, dec. 140—146° C.

^1H NMR (acetonitrile-d_3): cyclopentadienyl, δ 4.53 (s, 5); cyclohexadienyl, 5.30—5.63 (m, 3), 4.83—5.05 (m, 2); NH, not observed.

IR (KBr): 3458m, 3400m, 3100m, 1631m, 1551s, 1469s, 1419m, 1342m, 1149w, 1005w, 838s (br), 661m, 557s, 472m (br) cm^{-1}.

Mass spectrum, 80° C probe temperature (*m/e*, rel. int.): 372, 0.1; 307, >0.1; 213, 4.5; 186, 35.7; 121, 28.8; 93, 100; 92, 12.1; 66, 89.6; 65, 50.5; 56, 16.3. Exact mass calcd. for $^{12}C_{20}{}^{1}H_{20}{}^{56}Fe_2$, 372.02620; found, 372.02633. Exact mass calcd. for $^{12}C_{15}{}^{1}H_{15}{}^{56}Fe_2$, 306.9871; found, 306.9894. Parent peak exact mass calcd. for $^{12}C_{11}{}^{1}H_{11}{}^{14}N^{56}Fe$, 213.02390; found, 213.02352.

Reaction in CH_3CN. Small pieces of sodium (0.90 g, 39 mmol) were slowly added to acetonitrile (80 ml) under nitrogen. After 10 min, gas evolution ceased and a pale yellow solution and white solid were observed. Addition of η^6-aniline-η^5-cyclopentadienyliron(II) hexafluorophosphate (2.53 g, 7.07 mmol) led to a deep red solution which was stirred for 3 h. It was then filtered and reduced in volume to 10 ml under vacuum. Addition of diethyl ether (300 ml) gave a red-orange precipitate which was identical with the compound prepared in CH_2Cl_2.

(1—5-η^5-Cyclohexadien-6-onyl)-η^5-cyclopentadienyliron(II), VI

Addition of 50% aqueous acetone (120 ml) to a flask containing η^6-chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate (5.41 g, 0.0135 mol) and potassium hydroxide (4.18 g, 0.0745 mol) gave a yellow-brown solution which gradually turned orange-brown. After the mixture had been stirred 18 h under nitrogen, the acetone was evaporated under vacuum. The remaining aqueous mixture was rapidly filtered in air and then taken to dryness under vacuum at room temperature. The brown residue was extracted with CH_2Cl_2 (2 × 100 ml). Evaporation of the CH_2Cl_2 extract solutions gave a solid which was subsequently reprecipitated from CH_2Cl_2/diethyl ether to yield an orange powder, dec. 112—114° C, weighing 2.39 g (82.7%). Found: Fe, 26.6. $C_{11}H_{10}FeO$ calcd.: Fe, 26.1%.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 4.57 (s,5), cyclohexadienyl, 4.67—4.97 (m,2), 5.33—5.63 (m,3).

IR (KBr): 3060w, 1661m, 1535s (br), 1471s, 1417m, 1387m, 1346s, 1142m, 1112m, 1047w, 1005m, 841s, 689s, 542s, 476s cm^{-1}.

Mass spectrum, 110° C probe temperature (*m/e*, rel. int.): 214, 36.2; 186, 49.4; 121, 36.3; 94, 100; 66, 24.3; 65, 28.7; 56, 19.3; 51, 85. Parent peak exact mass calcd. for $^{12}C_{11}{}^{1}H_{10}{}^{56}Fe^{16}O$, 214.00800; found, 214.00791.

(1—5-η^5-Cyclohexadien-6-thionyl)-η^5-cyclopentadienyliron(II), VII

η^6-Chlorobenzene-η^5-cyclopentadienyliron(II) hexafluorophosphate (7.07 g, 18.7 mmol), sodium hydrogen sulfide (4.19 g, 74.8 mmol), and acetonitrile (70 ml) were stirred under nitrogen. After 20 min the deep red solution was filtered to remove a blue-green residue which was washed with acetonitrile (10 × 20 ml). The combined filtrates were reduced in volume to approximately 150 ml, and 100 g of alumina was added. Following evaporation of the remaining solvent under vacuum, the alumina was added to a 5 × 40 cm chromatographic column of alumina previously filled under nitrogen.

A small yellow band eluted with acetone was discarded. A red-orange band was eluted with 20% aqueous acetone. After removal of the solvent from this fraction under vacuum with final heating to 45° C, the residue was recrystallized from CH_2Cl_2/diethyl ether to give 2.38 g (55%) of a red-orange solid which darkens at 125—128° C and decomposes at 183° C. Found: Fe, 24.0. $C_{11}H_{10}FeS$ calcd.: Fe, 24.3%.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 5.02 (s, 5); cyclohexadienyl, 6.00—6.37 (s, br, 3), 6.37—6.84 (s, br, 2).

^1H NMR (chloroform-d): cyclopentadienyl, δ 4.70 (s, 5); cyclohexadienyl, 5.37—6.00 (s, br, 3), 6.00—6.34 (s, br, 2).

IR (KBr): 3025w, 1628w, 1487s, 1418s, 1399m, 1383m, 1082s, 842s, 711m, 641m, 463s cm^{-1}.

Mass spectrum, 100° C probe temperature (m/e, rel. int.): 230, 3.5; 186 ($C_{12}H_{10}S$), 85.1; 186 ($C_{10}H_{10}Fe$), 100; 185 ($C_{12}H_9S$), 56.0; 184 ($C_{12}H_8S$), 36.1; 154, 20.5; 152, 10.0; 121, 31.4; 110, 15.9; 77, 14.2; 66, 52.1; 65, 31.5. Parent peak exact mass calcd. for $^{12}C_{11}{}^1H_{10}{}^{56}Fe^{32}S$, 229.98520; found 229.98663.

Methylation of (1—5-η^5-6-iminocyclohexadienyl)-η^5-cyclopentadienyliron(II), V

A solution of V was prepared from [I]PF_6 (1.05 g, 2.92 mmol), and sodium amide (1.49 g, 38.2 mmol) in CH_2Cl_2 (100 ml) as described previously. After 1.75 h, the solution was filtered to remove $NaNH_2$ and excess CH_3I (1.5 ml) was added. A small amount of yellow precipitate and a slow change in solution color from red to yellow were observed. Removal of the solvent under vacuum gave an orange oil which could not be crystallized. Treatment with 0.1 *M* aqueous $AgNO_3$ gave a yellow solution which was filtered to remove silver iodide. Addition of ammonium hexafluorophosphate (0.50 g, 3.1 mmol) to the filtrate gave a yellow-orange precipitate. The precipitate was extracted with CH_2Cl_2 and reprecipitated by addition of pentane to give 0.38 g (33% based on Fe, 66% based on mechanism shown) of a brown solid. The product was purified by chromatography on a dry-packed 1 × 20 cm silica gel column. A yellow band eluted with CH_2Cl_2 produced orange needles when the solvent was removed. Recrystallization from CH_2Cl_2-pentane gave a flocculant orange solid, m.p. 153—156° C, which was identified as η^6-*N*,*N*-dimethylaniline-η^5-cyclopentadienyliron(II) hexafluorophosphate. Found: C, 40.23; H, 4.11; Fe, 14.7. $C_{13}H_{16}FeNPF_6$ calcd.: C, 40.31; H, 4.13; Fe, 14.5%.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 5.11 (s, 5); coordinated arene, 6.08—6.37 (m, 3), 5.83—6.08 (m, 2); methyl, 3.21 (s, 6).

IR (KBr): 3126m, 2925w, 1564s, 1493w, 1447m, 1431m, 1367m, 1235m, 1193m, 1005w, 830s (br), 656m, 556s, 475m, 463m cm^{-1}.

Methylation of (1—5-η^5-cyclohexadien-6-onyl)-η^5-cyclopentadienyliron(II), VI

The filtrate left after recrystallization of a sample of VI from CH_2Cl_2/diethyl ether was treated with excess CH_3I (1 ml). The red solution, which was stirred 1 h under nitrogen, slowly changed to a cloudy orange. After removal of the solvent under vacuum, the orange residue was recrystallized from $CHCl_3$/diethyl ether to give η^6-anisole-η^5-cyclopentadienyliron(II) iodide, dec. 143—146° C. Its identity was confirmed by comparison of its NMR spectrum with that of an authentic sample of the corresponding hexafluorophosphate which had been prepared by the method of Nesmeyanov et al. [11].

^1H NMR (chloroform-d): cyclopentadienyl, δ 5.25 (s, 5); coordinated arene, 6.50 (s, 5); methyl, 4.08 (s, 3).

Methylation of (1—5-η^5-cyclohexadien-6-thionyl)-η^5-cyclopentadienyliron(II), VII

Methyl iodide (0.8 ml, 8.4 mmol) was added to a filtered solution of VII (0.51 g, 2.2 mmol) in chloroform (15 ml). The red solution slowly turned orange as it was stirred under nitrogen. After 30 min, diethyl ether (80 ml) was added and produced an orange oil which slowly crystallized. After filtration and drying under vacuum, 0.58 g (71%) of a yellow-orange solid was produced, dec. 119—122°C. It was identified as η^6-thioanisole-η^5-cyclopentadienyliron(II) iodide. Found: C, 38.65; H, 3.42; Fe, 15.2. $C_{12}H_{13}FeSI$ calcd.: C, 38.75; H, 3.52; Fe, 15.0%.

^1H NMR (chloroform-*d*): cyclopentadienyl, δ 5.28 (s, 5); coordinated arene, 6.65 (s, 5); methyl, 2.81 (s, 3).

IR (KBr): 3073m, 3035m, 1630w, 1503m, 1444s, 1418s, 1387m, 1159m, 1146w, 1089s, 1006m, 979w, 854s, 689m, 500m, 469s (br) cm^{-1}.

Deuteration experiments

η^6-Aniline-η^5-cyclopentadienyl(II) hexafluorophosphate, [I]PF_6. [I]PF_6 (ca. 0.05 g) was dissolved in acetone-d_6 (0.50 ml) and filtered into an NMR tube. Acetic acid-*d* (0.2 ml) was added to the solution and the ^1H NMR spectrum was obtained.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 4.85 (s, 5, br); coordinated arene, 5.85 (s, 5, br); N—H, 9.40 (s, 2, br).

(1—5-η^5-6-Iminocyclohexadienyl)-η^5-cyclopentadienyliron(II), V. V (ca. 0.10 g) was dissolved in acetone-d_6 (0.50 ml) and filtered into an NMR tube. Acetic aicd-*d* (0.2 ml) was added and produced an immediate color change from red to orange. The ^1H NMR spectrum was then obtained.

^1H NMR (acetone-d_6): cyclopentadienyl, δ 4.85 (s, 5, br); coordinated arene, 5.85 (s, 5, br); N—H, 9.90 (s, 1, br).

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