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π-CYCLOHEXADIENYLIRON COMPLEXES BEARING EXOCYCLIC DOUBLE BONDS

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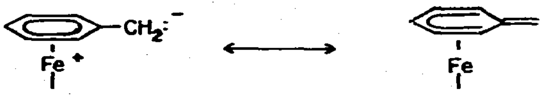
Summary

Sodium amide and sodium bis(trimethylsilyl)amide abstract α protons from certain π-arene-π-cyclopentadienyliron(II) cations to produce neutral π-cyclohexadienyl complexes bearing exocyclic C=C or C=N bonds. Also reported are the first examples of π-arene-π-cyclopentadienyliron(II) cations of aromatic amines synthesized by direct reaction of the amine, ferrocene and $AlCl_3$.

Introduction

Previous work in this laboratory has shown that bis(π-arene)iron(II) cations undergo addition of carbon and hydrogen nucleophiles [1]. It has also been shown that iron-coordinated methyl substituted arenes undergo proton exchange reactions when treated with nitrogen or oxygen bases [2]. Partial structure I, for which two resonance forms may be written, is presumably an intermediate in the latter processes.



(Ia) (Ib)

In order to find support for this hypothesis we have studied the behavior of certain π-arene-π-cyclopentadienyliron(II) salts in the presence of nitrogen bases.

Results and discussion

π-Arene salts

Several previously unreported π-arene-π-cyclopentadienyliron(II) salts were synthesized in moderate yields (Table 1) by heating an arene, ferrocene, $AlCl_3$,

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TABLE 1

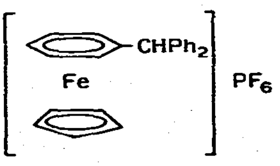
ARENE SALTS

Compound	Arene	Time (h)	Temp. (°C)	Yield (%)	Dec. temp. (°C)
II	Diphenylamine	3.5	150—180	6	180—181 (m.p.)
III	Carbazole	4	140—150	43	204—206
IV	Benzimidazole	3	140—155	25	166—169
V	Triphenylmethane	5	140—150	26	215—220 [a]
VII	Triphenylmethane				223—228 [b]
VI	Fluorene	4	155	34	163—165

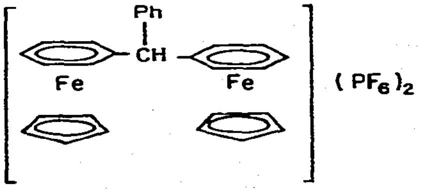
[a] As a hemi-hydrate. [b] As a hydrate.

and Al powder in decalin. The hexafluorophosphate complexes prepared were those of diphenylamine (II), carbazole (III), benzimidazole (IV), and triphenylmethane (V) as well as the previously reported fluorene complex VI [3]. π-Co-ordination of an aromatic amine by direct reaction with ferrocene has not been described, presumably because of the reported failure of aniline to undergo such a reaction [3].

The reaction of triphenylmethane with ferrocene produced not only V but also small amounts of VII. V could be separated from VII by extraction with CH_2Cl_2. From NMR and microanalytical data it was determined that V was isolated as a hemi-hydrate despite prolonged drying at 56°C in vacuo. The NMR of VII showed that it was isolated as a hydrate free from proton-containing impurities but satisfactory microanalytical data could not be obtained. The other complexes also retained water but could be dried completely by prolonged evacuation at 56°C.



(V)



(VII)

The ^1H NMR spectra are reported in Table 2. The N—H absorption appears as a broad singlet at low field for compounds II (τ 2.13 ppm) and III (τ —0.38 ppm) but is not detectable in the spectrum of IV. The cyclopentadienyl protons appear in the range τ 4.9 to 5.4 ppm. The coordinated arene protons are generally in the range τ 3.0—4.0 ppm and the uncoordinated arene protons are generally in the range τ 2.2—3.0 ppm.

The mass spectra of the salts show small peaks for the parent cation in every case except VII. The spectrum of VII does have a peak at *m/e* 365 corresponding to the fragment produced by loss of one CpFe group. Peaks representing cations derived from Cp_2Fe, CpFe, and the parent arene are prominent in each spectrum.

π-Cyclohexadienyl compounds

VI reacted with sodium bis(trimethylsilyl)amide in ether or benzene to give a deep green product VIII identified by its ^1H NMR spectrum. Since our isolation

TABLE 2

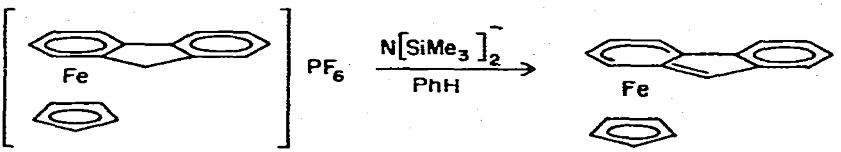
^1H NMR SPECTRA OF ARENE SALTS

Position, τ(ppm, multiplicity, rel. area) [a]

Compound	Cp	π-arene	Uncoord. arene	Other
II	5.05(s,5)	3.65—4.15(m,5)	2.38—2.98(m,5)	N—H, 2.13(broad s,1)
III	5.38(s,5)	3.58—3.93(m,2)	1.50—1.72(m,1) 2.22—2.93(m,5) [b]	N—H, —0.38(broad s,1)
IV	5.21 (s,5)	3.72—3.88(m,2) 2.52—2.68(m,2)		C—H, 1.03(broad, 1) N—H, not observed
V	4.88(s,5)	3.37—3.75(m,5)	2.60(s,10)	C—H, 4.08(s,1) H_2O, 7.25(s,1)
VII	4.92(s,10)	3.41(s,10) [c]	2.27—2.45(m,5)	C—H, 3.96 (s,1) H_2O, 7.23(s,2)
VI	5.15(s,5)	3.37—3.65(m,2)	2.18—2.62(m,3)	*endo*-C—H, 5.50(d,1) *J* 23 Hz)
		2.62—3.07(m,2)	1.67—2.00(m,1)	*exo*-C—H, 5.77(d,1, *J* 23 Hz) H_2O, 7.18(broad s,2)

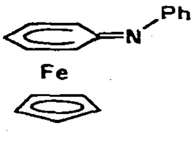
[a] In acetone-d_6. TMS internal. [b] Overlapping multiplets of coordinated (2) and uncoordinated (3) arene protons. [c] Broad(3.35—3.47) with evidence of poorly resolved fine structure. In CH_3CN peaks appeared at τ 2.55(s,5), 3.63—3.97(m,10), 4.45(s,1), 5.20(s,10) ppm.

of VIII a related synthesis has been reported by Johnson and Treichel [4,5] *.



(VI) (VIII)

The analogous reactions of II, III and V with $NaNH_2$ in NH_3 gave IX, X and XI, respectively. Each of the products was air and water sensitive and was isolated in 85—90% yield (Table 3). VI also undergoes deprotonation when treated with $NaNH_2$ in NH_3 but additional chemistry intervenes which will be described in another paper. Previously, Russian workers have reported that $NaNH_2$ promotes degradation of π-arene-π-cyclopentadienyliron(II) cations [6], an observation not characteristic of our compounds.



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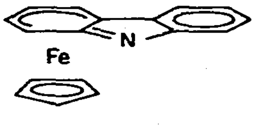
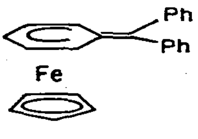


(X)



(XI)

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* Preliminary accounts of portions of this work were presented at the Meeting-in-Miniature of the Florida Section, American Chemical Society, Orlando, Florida, May 8, 1975, and the Southeastern Regional Meeting, American Chemical Society, Gatlinburg, Tennessee, October 27, 1976.

TABLE 3

CYCLOHEXADIENYL COMPLEXES

Compound	Formula	M.p. (°C)	Yield (%)	Color	Iron analysis (Found)(calcd.) (%)
VIII	$C_{18}H_{14}Fe$	105—107	43	Deep green	19.8 (19.5)
IX	$C_{17}H_{15}NFe$	122—124	85	Red	19.3 (19.3)
X	$C_{17}H_{13}NFe$	176—178	90	Red	19.8 (19.4)
XI	$C_{24}H_{20}Fe$	115—117	90	Red-brown	15.2 (15.4)

In the ^{1}H NMR spectra of the neutral compounds (Table 4) the Cp absorptions are shifted upfield by 0.4—0.8 ppm relative to the starting salts. The uncoordinated arene protons are shifted slightly upfield relative to the salts and the π-coordinated ring protons are shifted upfield ~0.6—2.1 ppm relative to the salts. The absorption patterns of the π-cyclohexadienyl ring protons resemble those of other π-cyclohexadienyl complexes which have been described [7]. The peak positions are intermediate between those of complexes in which the negative charge must be placed in the coordinated ring and those of π-arene complexes, a result consistent with the additional charge delocalization allowed by the exocyclic double bond. Pauson and Segal reported the deprotonation of π-(diphenylamine)manganese tricarbonyl cation to produce the analog of IX but did not describe the NMR spectrum [8].

No rearrangement of VIII to the isomeric dibenzoferrocene structure occurred when it was heated either in the solid state or in solution. The NMR spectrum of a solution of XI in tetrachloroethylene was unchanged when the solution was warmed from 40 to 100°C indicating that the potential propellor-like shift of phenyl groups across the iron atom does not occur.

The mass spectra of the cyclohexadienyl complexes each give the expected

TABLE 4

^{1}H NMR SPECTRA OF CYCLOHEXADIENYL COMPLEXES

Position, τ(ppm, multiplicity, rel. area) [a]

Compound	Cp	π-Cyclohexadienyl	Uncoord. arene	Other
VIII	5.98(s,5)	4.28—4.73(m,2) 3.43—3.62(m,1) 2.87—3.25(m,2) [b]	2.32—2.87(m,2) 1.67—1.92(m,1)	vinyl C—H 4.25(s,1)
IX	5.42(s,5)	5.18—under 5.42 peak(m,2) 4.45—4.83(m,2) 4.17—4.43(m,1)	3.00—3.28(m,3) 2.58—2.95(m,2)	
X	5.87(s,5)	4.18—4.50(m,2) 2.82—3.07(m,2)	3.07—3.35(m,1) 2.20—2.73(m,2) 1.73—1.93(m,1)	
XI	5.45(s,5)	5.62—5.88(m,2) 4.89—5.18(m,2) 3.75—4.06(m,1)	2.54—3.12(m,10)	

[a] In acetone-d_6, TMS internal. [b] Overlapping multiplets of coordinated (1) and uncoordinated (1) ring protons.

parent peak as well as the expected peaks corresponding to Cp_2Fe^+, $CpFe^+$ and the arene fragment. XI alone gave a very prominent parent peak (93% of the base peak) and also was unique in providing a significant peak at *m/e* 298 corresponding to loss of the cyclopentadienyl group to give $C_{19}H_{15}Fe$. These observations suggest that the bond between the cyclohexadienyl ring and the iron atom is especially strong in this compound and that it more closely approximates in its π electron distribution partial structure Ib than any of the other compounds. This conclusion is also supported by the fact that the NMR of XI has π-cyclohexadienyl proton absorptions at significantly higher field than any of the others.

Each of the cyclohexadienyl complexes reacted with dilute aqueous HCl to regenerate the starting cations.

The extent of which the canonical forms Ia and Ib contribute to the structure of a given molecule is expected to be a function of the molecular geometry and, in particular, the greater the extent to which carbon 6 and the exocyclic carbon deviate from the plane of the remaining carbon atoms, the smaller the expected contribution of form Ia. The work of Johnson and Treichel [5] suggests that form Ia is particularly important in the case of VIII while our work suggests that form Ib is particularly important in the case of XI.

The successful isolation and characterization of these compounds makes it increasingly probable that intermediates with partial structure I are also involved in the reactions of bis(arene)iron(II) cations with nitrogen and oxygen bases.

Experimental

All reactions were performed under dry nitrogen. The neutral complexes were purified and stored under nitrogen. Melting or decomposition temperatures were determined using evacuated sealed capillaries and are uncorrected. Carbon, hydrogen, and nitrogen analyses were done by PCR, Inc., Gainesville, Florida, and iron analyses were determined using a Perkin—Elmer Model 290B atomic absorption spectrophotometer. Proton NMR spectra were measured with a Varian A60-A instrument. Infrared spectra were measured on a Beckman IR-11 spectrophotometer. Mass spectra were recorded using an AEI MS-30 spectrometer with 70 eV ionizing energy.

Synthesis of arene salts

The procedure described below for the synthesis of the carbazole salt is similar to those used for each of the other salts. Variations in reaction time, temperature, and yield are given in Table 1.

Synthesis of III

Ferrocene (5.23 g, 0.028 mol), carbazole (9.56 g, 0.057 mol), aluminum chloride powder (7.70 g, 0.058 mol), and aluminum powder (2.19 g, 0.081 mol) were stirred in decalin (50 ml) at 140—150°C for 4 h. The mixture was cooled with an ice bath and solvolyzed with 15% aqueous methanol. After filtration and separation of layers, the orange-brown water layer was washed with ether. It was then treated with sufficient NH_4PF_6 (2.35 g, 0.014 mol) in water to give complete precipitation. After recrystallization from CH_2Cl_2/ether, the product was bronze-colored and weighed 5.21 g (43%).

III. Anal. Found: C, 47.15; H, 3.63; N, 3.23; Fe, 12.9. $C_{17}H_{14}NFePF_6$ calcd.: C, 47.14, H, 3.26; N, 3.23; Fe, 12.9%. IR(KBr): 3417 s, 3097 m, 1627 s, 1567 s, 1498 s, 1443 s, 1376 s, 1331 s, 1249 s, 838 s, 759 s cm^{-1}.

II. Anal. Found: C, 47.16; H, 3.88; N, 3.16; Fe, 12.2. $C_{17}H_{16}NFePF_6$ calcd.: C, 46.92; H, 3.71; N, 3.22; Fe, 12.8%. IR(KBr): 3389 s, 3117 w, 1548 s, 1469 m, 1386 s, 839 s(br), 557 s, 467 m cm^{-1}.

IV. Anal. Found: C, 37.97; H, 3.14; N, 8.09; Fe, 14.3. $C_{12}H_{11}N_2FePF_6$ calcd.: C, 37.53; H, 2.89; N, 7.29; Fe, 14.5%. IR(KBr): 3135 s, 1444 s, 1425 s, 1403 s, 1300 s, 1255 s, 957 s, 840 s(br), 645 s, 559 s, 468 s cm^{-1}.

V. Anal. Found: C, 55.62; H, 4.68. $C_{24}H_{21}FePF_6 \cdot 1/2H_2O$ calcd.: C, 55.52; H, 4.27%. IR(KBr): 3124 m, 3039 w, 2929 w, 1600 m, 1498 s, 1456 s, 1425 s, 840 s, (br), 755 s, 717 s, 705 s, 614 m, 560 s cm^{-1}.

Synthesis of cyclohexadienyl complexes

The syntheses of IX and XI were similar to the synthesis of X except that ether was used for their extraction. IX was recrystallized from benzene/pentane and XI was recrystallized from ether/pentane at −78°C.

X. Ammonia (90 ml) was distilled into a Schlenk tube previously charged with III (0.89 g, 0.0020 mol) and $NaNH_2$ (0.84 g, 0.021 mol). The red solution which formed immediately was stirred 3 h. After evaporation of the ammonia, the bright red residue was extracted with benzene (4 × 90 ml). The extract was filtered and evaporated to dryness to give X (0.70 g, 90%).

The product was recrystallized from CH_2Cl_2/ether, benzene/ether, or acetone/ether,

IR(KBr): 1613 m, 1544 m, 1477 m, 1434 s, 1389 s, 1330 s, 1287 m, 1234 s, 1007 m, 844 s, 757 s, 559 m, 482 s cm^{-1}.

Mass spectrum, 200°C probe temperature (*m*/*e*, rel. int.): 287, 0.1; 186, 17.9; 168, 13.4; 167, 100; 166, 22.4; 139, 11.1; 121, 8.9; 107, 13.1; 83.5, 11.4. Parent peak exact mass found, 287.0373. $^{12}C_{17}\,^{1}H_{13}\,^{14}N^{56}Fe$ calcd. 287.0396.

IX. IR(KBr): 3066 m, 1596 m, 1562 s, 1494 s, 1475 s, 1421 m, 1386 s, 1217 m, 814 m, 764 m, 717 m, 667 m, 498 m, 484 m, 466 m cm^{-1}.

Mass spectrum, no heat (*m*/*e*, rel. int.): 289, 1.4; 186, 31.5; 169, 100; 168, 55.9; 167, 37.3; 121, 15.0. Parent peak exact mass found, 289.0552. $^{12}C_{17}\,^{1}H_{15}\,^{14}N^{56}Fe$ calcd. 289.0552.

XI. IR(KBr): 3058 m, 1588 s, 1423 s, 1270 s, 837 s, 758 s, 697 s, 598 s, 468 m, 303 s cm^{-1}.

Mass spectrum, 130°C probe temperature (*m*/*e*, rel. int.): 364, 93.0; 298, 23.3; 243, 60.4; 186, 21.5; 165, 100; 121, 39.5. Parent peak exact mass found, 364.0920. $^{12}C_{24}\,^{1}H_{20}\,^{56}Fe$ calcd. 364.0910.

VIII. Ether (70 ml) was added to a Schlenk tube previously charged with VI (0.98 g, 0.0023 mol) and $Na[N(SiMe_3)_2]$ (1.29 g, 0.0071 mol). The blue-green solution which formed immediately was stirred for 1.5 h and then filtered. The residue was washed with ether until little colored material was extracted. Removal of the ether under reduced pressure followed by prolonged evacuation gave VIII as a dark green residue weighing 0.27 g (43%) which was recrystallized from ether at −78°C.

IR(KBr): 1602 s, 1532 s, 1470 s, 1428 s, 1386 s, 1338 s, 1226 s, 1005 m, 835 s, 752 s, 472 s cm^{-1}.

Mass spectrum, 140°C probe temperature (*m/e*, rel. int.): 286, 1; 186, 69.8; 165, 100; 166, 49.7; 121, 33.3. Parent peak exact mass found, 286.0435. $^{12}C_{18}$ $^{1}H_{14}$ ^{56}Fe calcd. 286. 0.444.

Acknowledgements

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