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THE SYTHESIS AND STRUCTURE DETERMINATION OF BIS(1,3-DIMETHYLINDENYL)IRON(III) HEXAFLUOROPHOSPHATE

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Summary

The title compound is formed by the oxidation of bis(1,3-dimethylindenyl)iron by either HCl or $AgPF_6$. It crystallizes in the triclinic space group $P\bar{1}$, with two formula units per unit cell with lattice dimensions: a = 9.2586(16) Å, b = 13.2849(22) Å, c = 8.5681(16) Å, α = 98.062(14)°, β = 91.311(14)°, γ = 83.950(13)°. The observed density is 1.559(2) g cm^{-3}, in accord with the density calculated from these data (1.559 g cm^{-3}). Diffraction data were collected by automated diffractometer methods, and the crystal and molecular structure determined using conventional methods and refined by full matrix isotropic—anisotropic least squares analysis of 2136 independent counter data to give a final unweighted R value of 4.38%. The structure consists of discrete cationic and anionic units. In the cation the metal is coordinated to the five-membered rings of each indenyl ligand and is slightly displaced away from the six-membered ring. It has roughly a staggered configuration with six-membered rings assuming positions differing by 93.5° rotation of one ring. The iron to ring centroid distance is 1.716 Å, slightly greater than the analogous distance in the 1,1'-dimethylferrocenium cation.

Introduction

In the preceding paper [1] we described the characterization of a species arising from protonation of diindenyliron by various acids. This complex has a structure wherein the proton has added in a stereospecific manner to the C(1) carbon of the indenyl ligand, concurrent with migration of the metal coordination from the five- to the six-membered ring.

In attempting to extend this reaction to other indenylmetal species, we investigated the reaction of bis(1,3-dimethylindenyl)iron with HCl. The only reaction product obtained is a bis(1,3-dimethylindenyl)iron(III) complex, which was isolated as the hexafluorophosphate salt, and whose structural characterization by X-ray diffraction techniques is described herein.

Experimental

A. Syntheses

All synthetic work was performed using standard methods of exclusion of oxygen. Proton magnetic resonance spectra were obtained using a Varian A60A instrument, infrared spectra were obtained with a Beckman IR-10, and mass spectra were run on an AEI MS-109 double focusing mass spectrometer. Analyses were performed by the Galbraith Laboratory, Knoxville, Tenn.

Synthesis of bis(1,3-dimethylindenyl)iron. 1,3-Dimethylindene [2] (104 mmol) in 100 ml tetrahydrofuran was converted to 1,3-dimethylindenyllithium using one equivalent of n-butyllithium in hexane at 0°C. After stirring at ambient temperature for 1 h this solution was added to a suspension of $FeCl_2$ (from $FeCl_3$ + Fe metal) [3] in 120 ml tetrahydrofuran. The mixture was stirred for 1 h at room temperature and then heated at reflux for 80 min. Following solvent removal, the crude reaction products were transferred to a Soxhlet apparatus and extracted with pentane for 48 h. The extract was chilled to —78°, and filtered giving 9.2 g product (55%). The product could be further purified by sublimation at 85-95°/0.1 mm, m.p. 103-104°C. Mass spectrometric peak match confirmed the molecular formula (Found: 342.10708. $^{56}Fe^{12}C_{22}{}^{1}H_{22}$ calcd.: 342.10693.).

PMR spectrum. δ 1.94s (int. 12, four CH_3 groups); δ 3.42s (int. 2, CH on carbons 2 and 2'); δ 6.89s (int. 8, CH in six-membered rings).

Infrared spectrum (CCl_4). 3050m, 2980m, 2960m, 2910s, 2860m, 1440m, 1360s, 1315m, 1071s, 1028m, 951w, 720m.

Preparation of bis(1,3-dimethylindenyl)iron(III) hexafluorophosphate. Bis(1,3-dimethylindenyl)iron (0.896 g, 2.62 mmol) was placed in a flask connected to a standard vacuum line and evacuated. Approximately 30 ml of toluene was distilled into the flask, followed by 3.0 mmol of HCl (measured by volume). The flask was sealed and the reaction was allowed to proceed, with stirring, for 17 h, during which time a solid precipitated. Upon reopening the reaction flask, no non-condensible gas (H_2) was noted. Solvent was removed, leaving a brown residue. This was removed from the vacuum system, under nitrogen, and 0.75 g of NH_4PF_6 in 50 ml of acetone was added. Filtration was followed by addition of the acetone solution to ether which resulted in precipitation of a red-brown solid. This was purified further by crystallization from CH_2Cl_2—ether, yielding 0.21 g of product (17%); m.p. 225° (dec.). (Found: C, 54.4; H, 4.8; Fe, 10.7. $C_{22}H_{22}FePF_6$ calcd.: C, 54.1; H, 4.8; Fe, 11.4%.)

Infrared spectrum (Nujol mull). 1598s, 1022w, 899w, 830s, 776m, 747m, 736w.

Preparation of bis(1,3-dimethylindenyl)iron(III) hexafluorophosphate was accomplished in much better yield by the oxidation of bis(1,3-dimethylindenyl)iron with $AgPF_6$ in acetone. Silver metal precipitated and was filtered; the isolation of the product was carried out in the manner described above (80% yield).

B. Structure determination

Single crystal X-ray data. Well formed, dark red, needle-like crystals were grown by allowing slow vapor diffusion of ethyl ether into a dichloromethane solution of the compound. One of these crystals was trimmed to an approximate parallelepiped with dimensions 0.26 × 0.18 × 0.32 mm, and mounted in a capillary tube under argon. The crystal was placed on a Syntex $P\bar{1}$ four-circle computer controlled diffractometer equipped with a graphite monochromator, and 15 diffraction maxima were automatically centered in 2θ, χ, and ω. Mo-K_α (λ = 0.7107 Å) radiation was used throughout the alignment and data collection procedures. The preliminary Syntex routines [4] indicated a triclinic lattice with dimensions of: a = 9.2586(16) Å, b = 13.2849(22) Å, c = 8.5681(16) Å, α = 98.063(14)°, β = 91.311(14)°, γ = 83.950(13)°, unit cell volume 1307.61(31) Å^3. The space group was assumed to be $P\bar{1}$. With Z = 2 the calculated density is 1.559 g cm^{-3}. The density observed by flotation in carbon tetrachloride—hexane was 1.559 ± 0.002 g cm^{-3}. The triclinic Laue symmetry and associated lattice constants were verified by partial rotation photographic projections along each of the three reciprocal axes.

Intensity data were collected using the $\theta - 2\theta$ scan technique with variable scan speeds from 2 to 24°/min, which in the Syntex procedure is determined as a function of peak intensity. Stationary crystal—stationary counter backgrounds were counted for a total of 2/3 of the time used for the scan count. Two standard peaks were monitored every 50 reflections during the entire data collecting process and showed no significant deviation in intensity (± 2.5%). A total of 2871 reflections distributed through the four octants hkl, $h\bar{k}l$, $\bar{h}\bar{k}l$, and $\bar{h}kl$ for which $2.0° \leqslant 2\theta < 45.0°$ were collected. These data were then corrected in the usual manner for Lorentz and polarization effects and used to calculate structure factor amplitudes $|F_o| = (I/\mathrm{Lp})^{1/2}$, where Lp is the Lorentz-polarization factor, and the estimated standard deviations were $\sigma(F) = \sigma(I)/(2F_o\mathrm{Lp})$. An instrument instability factor was set equal to 0.003 (I^2) and introduced into $\sigma(I)$ to avoid overweighting of the strong reflections in subsequent least-squares refinement. The data were merged to give 2136 independent observations for which $I > 2.0\sigma(I)$. The effects of absorption (μ = 8.88 cm^{-1}) were ignored. The variation between the minimum and maximum transmission factors was 0.79 to 0.87.

Solution and refinement of structure. The solution of the structure, requiring location of one of the two formula units in the unit cell, was done by the heavy atom method. An initial three dimensional Patterson map* located the iron and phosphorus atoms. Fourier synthesis, phased on the iron atom, located all the carbon and fluorine atoms in the structure. Full matrix isotropic least-squares refinement converged to the discrepancy values $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ = 9.82% and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100$ = 13.67%, with $w_i = 1/\sigma(F_o)^2$. Attempts at this stage to locate the hydrogen atoms by difference Fourier techniques were unsuccessful. Hence ideal coordinates with C—H distance set to 1.0 Å (B_{iso} = 8.0 Å^2) were included as fixed atom contributions in further anisotropic refinement. The methyl hydrogens were included as half-weighted in two orientations about the C—CH$_3$ bond. After several cycles of block-diagonal refinement in which the parameters were placed ten atoms per block, a difference map revealed all hydrogen atom positions. These C—H distances were again renormalized to 1.0 Å and the final refinement series

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* All crystallographic computer programs used in the structural determination and least-squares refinement were written by one of us (J.C.C.). Plots were made using ORTEP (C.K. Johnson) [8].

converged at R_1 = 4.38 and R_2 = 5.65%. A final cycle, varying *xyz* only for all non-hydrogen atoms, indicated complete convergence of the block diagonal results with the greatest shift for any parameter 0.18σ. No attempt was made to refine the hydrogen parameters. The final data to parameter ratio was 7.5/1. The standard deviation in an observation of unit weight was 1.50.

TABLE I. FINAL ATOM POSITIONAL PARAMETERS FOR $[Fe(C_{11}H_{11})_2]PF_6$ ($\times 10^4$)

Atom	*x*	*y*	*z*
P	−2564(1)	2548(1)	−827(1)
F(1)	−2827(5)	3545(3)	−1559(6)
F(2)	−3020(5)	3087(4)	827(5)
F(3)	−4161(4)	2308(4)	−1143(5)
F(4)	−2074(5)	1979(3)	−2476(4)
F(5)	−960(4)	2761(4)	−478(5)
F(6)	−2264(5)	1525(4)	−102(6)
Fe	1828.5(6)	2374.5(4)	4460.5(7)
C(1)	2438(5)	3567(3)	3372(5)
C(2)	997(5)	3383(3)	2961(5)
C(3)	126(5)	3506(3)	4327(5)
C(8)	2466(5)	3887(3)	5046(5)
C(9)	1023(5)	3862(3)	5640(5)
C(10)	3699(6)	3536(4)	2288(7)
C(11)	−1459(5)	3379(4)	4404(6)
C(4)	743(5)	4119(3)	7266(6)
C(5)	1849(6)	4382(4)	8244(6)
C(6)	3286(6)	4374(4)	7696(7)
C(7)	3601(5)	4123(3)	6139(6)
C(1')	1311(5)	923(3)	3550(5)
C(2')	987(5)	1133(3)	5181(5)
C(3')	2273(5)	1340(3)	6051(5)
C(8')	2860(5)	918(3)	3407(5)
C(9')	3461(4)	1182(3)	4937(5)
C(11')	2418(6)	1594(4)	7801(5)
C(10')	271(6)	658(4)	2206(6)
C(4')	4941(5)	1326(3)	5129(6)
C(5')	5776(6)	1191(4)	3816(8)
C(6')	5194(6)	927(4)	2297(7)
C(7')	3751(6)	784(3)	2060(5)
H(2)	639	3196	1862
H(4)	−256	4095	7678
H(5)	1659	4590	9396
H(6)	4066	4555	8477
H(7)	4617	4103	5744
H(2')	4	1135	5647
H(4')	5355	1534	6206
H(5')	6835	1267	3924
H(6')	5854	842	1375
H(7')	3341	588	982
H(11A)	−2070	4024	4278
H(11B)	−1668	3168	5457
H(11C)	−1710	2819	3566
H(10A)	3734	4206	1906
H(10B)	3611	2989	1371
H(10C)	4624	3355	2865
H(11'A)	2604	955	8308
H(11'B)	1502	1992	8240
H(11'C)	3235	2024	8062
H(10'A)	187	−90	2031
H(10'B)	611	885	1236
H(10'C)	−709	1036	2481

TABLE 2

ANISOTROPIC THERMAL PARAMETERS[a] (X 10^4)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	106(2)	92(1)	132(2)	−15(1)	1(2)	8(1)
F(1)	366(10)	149(4)	596(16)	56(5)	124(10)	166(7)
F(2)	324(9)	246(6)	252(8)	−100(6)	94(7)	−105(6)
F(3)	149(5)	235(5)	288(8)	−64(4)	−29(5)	−8(5)
F(4)	310(8)	193(5)	206(7)	8(5)	92(6)	−34(5)
F(5)	157(6)	310(7)	371(10)	−116(6)	−33(6)	74(7)
F(6)	305(9)	175(5)	474(13)	20(5)	77(8)	162(6)
Fe	102.0(9)	37.4(4)	110.0(10)	−6.4(4)	−1.4(7)	11.1(4)
C(1)	152(8)	42(3)	158(8)	−11(4)	17(6)	25(4)
C(2)	158(8)	50(3)	138(8)	−6(4)	−21(6)	32(4)
C(3)	120(7)	40(3)	176(9)	3(3)	−5(6)	26(4)
C(8)	121(7)	37(3)	177(9)	−20(3)	−14(6)	18(4)
C(9)	128(7)	34(3)	152(8)	0(3)	−9(6)	11(4)
C(10)	210(10)	81(4)	229(11)	−24(5)	75(9)	41(5)
C(11)	116(7)	69(4)	240(11)	−6(4)	−35(7)	31(5)
C(4)	168(8)	48(3)	161(9)	−1(4)	9(7)	8(4)
C(5)	228(11)	60(4)	163(10)	−6(5)	−17(8)	−5(5)
C(6)	200(10)	57(4)	232(12)	−25(5)	−56(9)	0(5)
C(7)	128(8)	55(3)	232(11)	−17(4)	−12(7)	16(5)
C(1')	119(7)	43(3)	140(8)	−13(3)	−16(6)	11(4)
C(2')	117(7)	43(3)	141(8)	−7(3)	6(6)	22(4)
C(3')	129(7)	39(3)	117(7)	0(3)	4(6)	20(3)
C(8')	119(7)	41(3)	116(7)	−10(3)	1(5)	6(3)
C(9')	95(6)	42(3)	136(7)	−2(3)	−1(5)	14(3)
C(11')	175(8)	70(4)	116(8)	1(4)	−5(6)	16(4)
C(10')	174(9)	65(4)	181(9)	−24(4)	−70(7)	1(4)
C(4')	115(7)	53(3)	214(10)	−2(4)	−18(7)	6(4)
C(5')	126(8)	64(4)	310(15)	−4(4)	53(9)	2(6)
C(6')	197(11)	71(4)	224(12)	4(5)	99(9)	16(5)
C(7')	186(9)	58(3)	134(8)	−5(4)	34(7)	−1(4)

[a] Anisotropic temperature factors of the form exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$ were used for these atoms.

All least-squares refinements were based on the minimization of $\Sigma w_i \| F_o\ | F_c \|^2$. Included in the refinements were corrections for anomalous dispersion for Fe, P, F, and C from Cromer et al. [5]. The atomic scattering factors used for all non-hydrogen atoms were those compiled by Cromer et al. [6], while those used for hydrogen atoms were from Stewart et al. [7]. A listing of the calculated and observed structure factor amplitudes is available*. The positional parameters for all atoms are given in Table 1. Anisotropic thermal parameters are given in Table 2. Interatomic bonding distances and bond angles, with estimated standard deviations calculated from the full variance-covariance matrix of the last cycle are presented in Tables 3 and 4. Equations of least-squares planes are listed in Table 5. Selected intermolecular non-bonding distances are listed in Table 6.

(continued on p. 222)

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* A table of structure factors has been deposited as NAPS Document No. 02520, with ASIS/NAPS, c/o Microfiche Publications, 440 Park Ave. So., New York, New York 10016. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 3. INTERATOMIC DISTANCES (Å) FOR $[\mathrm{Fe(C_{11}H_{11})_2}]\mathrm{PF_6}$

Fe—C(1)	2.079(4)	Fe—C(1')	2.076(4)
Fe—C(2)	2.063(4)	Fe—C(2')	2.070(4)
Fe—C(3)	2.073(4)	Fe—C(3')	2.072(4)
Fe—C(8)	2.142(4)	Fe—C(8')	2.151(4)
Fe—C(9)	2.156(4)	Fe—C(9')	2.147(4)
C(1)—C(2)	1.409(6)	C(1')—C(2')	1.420(6)
C(2)—C(3)	1.417(6)	C(2')—C(3')	1.421(6)
C(3)—C(9)	1.439(6)	C(3')—C(9')	1.452(6)
C(8)—C(9)	1.446(6)	C(8')—C(9')	1.424(6)
C(1)—C(8)	1.438(6)	C(1')—C(8')	1.441(6)
C(1)—C(10)	1.503(7)	C(1')—C(10')	1.511(6)
C(3)—C(11)	1.499(6)	C(3')—C(11')	1.496(6)
C(9)—C(4)	1.411(6)	C(9')—C(4')	1.406(6)
C(4)—C(5)	1.352(7)	C(4')—C(5')	1.360(8)
C(5)—C(6)	1.420(8)	C(5')—C(6')	1.409(8)
C(6)—C(7)	1.360(7)	C(6')—C(7')	1.376(8)
C(8)—C(7)	1.422(6)	C(8')—C(7')	1.414(6)
P—F(1)	1.537(4)		
P—F(2)	1.542(4)		
P—F(3)	1.555(4)		
P—F(4)	1.559(4)		
P—F(5)	1.555(4)		
P—F(6)	1.569(4)		

TABLE 4. INTRAMOLECULAR BOND ANGLES (°) FOR $[\mathrm{Fe(C_{11}H_{11})_2}]\mathrm{PF_6}$

C(2)—C(1)—C(8)	107.0(4)	C(2')—C(1')—C(8')	107.1(4)
C(2)—C(1)—C(10)	127.8(4)	C(2')—C(1')—C(10')	127.3(4)
C(8)—C(1)—C(10)	125.1(4)	C(8')—C(1')—C(10')	125.5(4)
C(1)—C(2)—C(3)	110.5(4)	C(1')—C(2')—C(3')	109.5(4)
C(2)—C(3)—C(9)	106.9(4)	C(2')—C(3')—C(9')	107.2(4)
C(2)—C(3)—C(11)	127.4(4)	C(2')—C(3')—C(11')	127.0(4)
C(9)—C(3)—C(11)	125.5(4)	C(9')—C(3')—C(11')	125.6(4)
C(1)—C(8)—C(9)	108.0(4)	C(1')—C(8')—C(9')	108.6(3)
C(1)—C(8)—C(7)	133.1(4)	C(1')—C(8')—C(7')	130.8(4)
C(9)—C(8)—C(7)	118.7(4)	C(9')—C(8')—C(7')	120.3(4)
C(3)—C(9)—C(8)	107.5(4)	C(3')—C(9')—C(8')	107.4(4)
C(3)—C(9)—C(4)	132.3(4)	C(3')—C(9')—C(4')	131.7(4)
C(8)—C(9)—C(4)	120.2(4)	C(8')—C(9')—C(4')	120.6(4)
C(9)—C(4)—C(5)	118.6(5)	C(9')—C(4')—C(5')	117.9(5)
C(4)—C(5)—C(6)	122.2(5)	C(4')—C(5')—C(6')	121.9(5)
C(5)—C(6)—C(7)	120.9(5)	C(5')—C(6')—C(7')	121.9(5)
C(8)—C(7)—C(6)	119.3(5)	C(8')—C(7')—C(6')	117.3(4)
F(1)—P—F(2)	92.8(3)		
F(1)—P—F(3)	92.2(3)		
F(1)—P—F(4)	88.8(3)		
F(1)—P—F(5)	89.6(3)		
F(1)—P—F(6)	178.7(3)		
F(2)—P—F(3)	88.8(2)		
F(2)—P—F(4)	178.3(3)		
F(2)—P—F(5)	90.8(2)		
F(2)—P—F(6)	88.2(3)		
F(3)—P—F(4)	91.9(2)		
F(3)—P—F(5)	178.2(3)		
F(3)—P—F(6)	88.7(3)		
F(4)—P—F(5)	88.5(2)		
F(4)—P—F(6)	90.2(3)		
F(5)—P—F(6)	89.6(3)		

TABLE 5

LEAST-SQUARES PLANES

Atom	Deviation from plane (Å)	Atom	Deviation from plane (Å)
(a) Plane containing C(1), C(2), C(3), C(8), C(9), C(4), C(5), C(6), C(7) $-0.1116X + 0.9851Y - 0.1312Z - 3.5661 = 0^a$			
C(1)	0.0056	C(5)	0.0135
C(2)	0.0106	C(6)	−0.0211
C(3)	−0.0490	C(7)	−0.0251
C(8)	0.0357	C(10)	0.0808
C(9)	0.0187	C(11)	−0.0668
C(4)	0.0111		
(b) Plane containing C(1'), C(2'), C(3'), C(8'), C(9'), C(4'), C(5'), C(6'), C(7') $-0.0743X + 0.9926Y - 0.0963Z - 0.3705 = 0$			
C(1')	0.0370	C(5')	0.0257
C(2')	0.0091	C(6')	0.0235
C(3')	0.0184	C(7')	−0.0160
C(7')	−0.0474	C(10')	0.0292
C(9')	−0.0493	C(11')	−0.0089
C(4')	−0.0010		
(c) Plane containing C(1), C(2), C(3), C(8), C(9) $-0.1358X + 0.9810Y - 0.1388Z - 3.4831 = 0$			
C(1)	−0.0161	C(4)	0.0009
C(2)	.0251	C(5)	−0.0292
C(3)	−0.0237	C(6)	−0.0929
C(8)	0.0012	C(7)	−0.0931
C(9)	0.0135	C(10)	0.0370
		C(11)	−0.0053
(d) Plane containing C(1'), C(2'), C(3'), C(8'), C(9') $-0.0401X + 0.9937Y - 0.1042Z - 0.4049 = 0$			
C(1')	0.0231	C(4')	0.0903
C(2')	−0.0261	C(5')	0.1525
C(3')	0.0186	C(6')	0.1417
C(8')	−0.0114	C(7')	0.0575
C(9')	−0.0042	C(10')	−0.0092
		C(11')	−0.0158

[a] The equation of each least-squares plane is expressed in orthogonal coordinates (X, Y, Z) which are related to the triclinic cell coordinates (x, y, z) by the transformation: $X = x\sin\gamma + 2\cos\phi$, $Y = y + z\cos\alpha + x\cos\gamma$, and $Z = z\cos\rho$ where $\cos\phi = (\cos\beta - \cos\gamma\cos\alpha/\sin\gamma$ and $\cos\rho = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}\sin\gamma$. In this transformation X lies in the xy plane, Y coincides with y and Z is perpendicular to the xy plane.

TABLE 6

SELECTED INTERMOLECULAR NON-BONDING DISTANCES (Å)

F(2) ··C(10)*A*[a]	3.276(7)
F(5)· C(4)*B*	3 346(7)
F(6) ·C(10')	3.257(7)
C(9') · C(5')*C*	3.466(7)

[a] Symmetry operation codes: *A*, −1 + *x*, *y*, *z*; *B*, *x*, *y*, −1 + *z* and *C*, 1 − *x*, −*y*, 1 − *z*.

Description of the structure

The structure of bis(1,3-dimethylindenyl)iron(III) hexafluorophosphate consists of discrete cations and anions at substantial non-bonding distances; the nearest (non-bonding) approach of the cation and anion is indicated in the various fluorine to carbon distances of about 3.3 Å.

Two views of the structure of the bis(1,3-dimethylindenyl)iron(III) cation are given in Figs. 1 and 2. The iron atom can be seen to be coordinated to the five-membered ring of each indenyl ligand. The iron—ring centroid distance is 1.716 Å, and the centroid—iron—centroid angle is 177.7°. This metal—centroid distance is comparable to the value of 1.695(1) Å found in 1,1-dimethylferricenium triiodide [9]. The value found in diindenyliron is 1.71 Å [10], but disorder in the crystal limits the accuracy of this measurement.

The axial view of this cation clearly shows the staggered configuration of the two five-membered rings. Trotter and MacDonald [11] have used the mean angle subtended at the iron atom by pairs of almost superimposed atoms when a ferrocene system is projected on the mean plane of the two rings as a measure of the eclipsedness of the ring systems. For an exactly eclipsed system this angle is 0°, and for a completely staggered system, the angle is 36°. In the bis(1,3-dimethylindenyl)iron cation, this angle is 21.7°. It is interesting that the analogous angle in the 1,1'-dimethylferricenium ion is 2.2°, and the coordinated rings in this species are thus approximately eclipsed. It may reasonably be argued that the staggered configuration observed in our complex results from the minimization of non-bonding interactions of the various ring substituents including the fused six-membered rings.

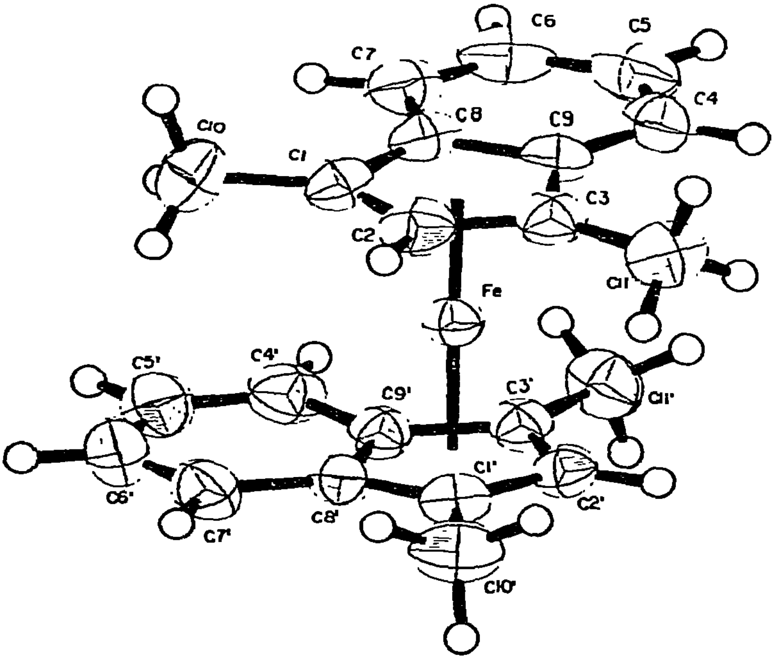

Fig. 1. View of the bis(1,3-dimethylindenyl)iron(III) cation, showing the labeling of the atoms.

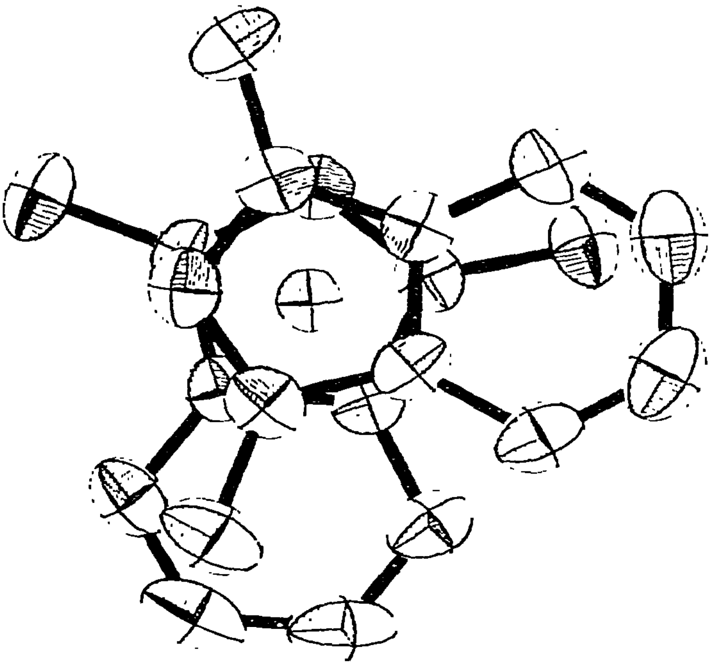

Fig. 2. Axial view of the bis(1,3-dimethylindenyl)iron(III) cation with hydrogen atoms omitted for clarity.

The angle formed by the intersection of the two planes determined by the metal atom and the centroids of the five- and six-membered rings is 93.5°.

The carbon frameworks of both indenyl ligands deviate only slightly from planarity. The maximum deviation of any carbon atom from the least-squares plane is 0.049 Å. Among the carbons in the coordinated five-membered ring the deviation is even less, to a maximum of 0.026 Å. However, methyl groups do deviate markedly from this plane. On one ligand the methyl groups are 0.081 and 0.067 Å out of the plane, inclined away from the metal atom. On the other ligand one methyl group is inclined away from the metal (0.037 Å out of the plane of the ring); the other is inclined slightly toward the metal. These positions seem to be a function of the intramolecular repulsions of substituent groups on the two ligands. The axial view of this species (Fig. 2) clearly portrays the relative orientation of these groups.

Examination of the iron—carbon distances show that C(8) and C(9), and C(8') and C(9') in the second ring, are about 0.08 Å farther from the metal than are the remaining carbon atoms in the five-membered rings (C(1), C(2), C(3); C(1'), C(2'), C(3')). This slight displacement of the metal away from the six-membered ring presumably reflects electronic factors and not steric factors, however, since C(4), C(5), C(6), and C(7) are on the iron side of the cyclopentadienyl plane in both ligands.

Discussion

The crystal and molecular structure of this compound offered no particular surprises. Coordination of the five-membered rings of the indenyl ligands to iron was observed, with bond distances and angles having the expected values. The relative orientations of the two 1,3-dimethylindenyl rings are noteworthy. These appear to be required in order to minimize inter-ring repulsions.

The synthesis of this compound merits some further comment. We noted earlier [1] that protonation of the unsubstituted analog, diindenyliron, gave a relatively low yield of the ring protonated h^5-indenyl-h^6-indeneiron(III) cation, along with substantial decomposition. A mechanism of formation of the metal complex was suggested which involved initial protonation of the metal followed by transfer of the proton to an *endo* position on the ring. Once formed, this final product was stable. To rationalize the substantial decomposition accompanying this (assumed) process, two possibilities were suggested. One is that the initial protonated metal species is oxidized, perhaps by oxygen in the system. It is known that protonated ferrocenes are extremely sensitive to oxygen [12]; yet extraordinary precautions to exclude oxygen here appeared to effect little change in the system, which argues against this idea. Alternatively, the proton itself might serve as an oxidizing agent, and H_2 might then be evolved; or, the hydrogen might hydrogenate free indene present due to decomposition. Inherent in this suggestion is the requirement that the diindenyliron(III) cation be unstable; otherwise its presence would have been noted.

Attempted protonation of bis(1,3-dimethylindenyl)iron(II) using gaseous HCl in toluene failed to give a ring-protonated complex analogous to the complex obtained with diindenyliron. Instead, from this reaction, the only metal complex that could be isolated was the product of one-electron oxidation, the bis(1,3-dimethylindenyl)iron(III) cation which was isolated as the hexafluorophosphate salt in 17% yield. The most reasonable explanation for the formation of this complex is that protonation of the metal occurs, but that subsequent transfer of the metal-bound hydrogen atom to the indenyl ring is either very slow, or perhaps thermodynamically unfavorable. If this is so, it is likely that in subsequent workup oxidation (by oxygen) occurs to give the observed cation. It is appropriate to note that no hydrogen gas was evolved in this reaction, as might have been anticipated if the oxidizing agent was H^+.

Following the characterization of the product of reaction with HCl as the one-electron oxidized species, the use of other possible oxidizing agents was investigated. The oxidation of bis(1,3-dimethylindenyl)iron was quite easy to accomplish [13]. A mild oxidizing agent such as $AgPF_6$ produced a nearly quantitative yield of the oxidized product.

Although electrochemical data [13] suggested that the ease of oxidation of diindenyliron and bis(1,3-dimethylindenyl)iron was comparable, treatment of the former with $AgPF_6$ gave no stable iron complex. Instead, decomposition was noted with the resultant metal product being an iron oxide. No starting material was recovered. Although this is rather indirect evidence, it nonetheless supports the tentative hypothesis offered earlier concerning the oxidative degradation of a protonated diindenyliron.

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References

1 P.M. Treichel and J.W. Johnson, J. Organometal. Chem., 88 (1975) 207.
2 L. Ohlsson and I. Wallmarch, Acta Chem. Scand., 20 (1966) 750.
3 R.B. King, Organometallic Syntheses, Academic Press, New York, 1964, p.73.
4 R.A. Sparks et al., Operations Manual, Syntex P1̄ Diffractometer, Syntex Analytical Instruments, Cupertino, California, 1970.
5 D.T. Cromer and D. Libermann, J. Chem. Phys., 53 (1970) 1891.
6 D.T. Cromer and J.B. Mann, Acta Crystallogr., A24 (1968) 321.
7 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
8 C.K. Johnson, ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustations, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1964.
9 J.W. Bats, J.J. DeBoer and D. Bright, Inorg. Chim. Acta, 5 (1971) 605.
10 J. Trotter, Acta Crystallogr., 11 (1958) 355.
11 J. Trotter and A.C. MacDonald, Acta Crystallogr., 21 (1966) 359.
12 T.E. Bitterwolf and A.C. Ling, J. Organometal. Chem., 40 (1972) C29.
13 P.M. Treichel, J.W. Johnson and K.P. Wagner, J. Organometal. Chem., 88 (1975) 227.