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Conformational variability in π-complexes of hexaethylbenzene. Crystal and molecular structure of $[(C_6Et_6)(C_5H_5)Fe]BPh_4$

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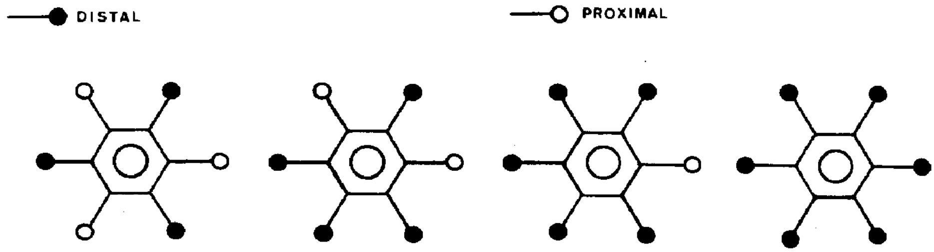
Abstract

[(Hexaethylbenzene)Fe(C_5H_5)][BPh_4], [$1BPh_4$], crystallizes in the monoclinic space group, $P2_1/c$, with a 15.7288(23), b 15.4411(14), c 16.3356(20)Å, β 107.972(10)° and D_{calc} 1.208 g cm^{-3} for $Z = 4$. Least-squares refinement gave a conventional R value of 0.047 for 2881 independent observed reflections. The structure reveals that the complexed hexaethylbenzene moiety in **1** adopts a conformation such that five ethyl groups point away from the iron atom (distal) and only one is directed towards the iron atom (proximal). This observation contrasts with an earlier crystallographic study conducted ($1PF_6$), in which the hexaethylbenzene ligand was shown to adopt a four distal/two proximal conformation. In other ways the cations in $1BPh_4$ and $1PF_6$ are almost identical, thereby suggesting that even subtle packing effects may influence the conformation adopted by sterically crowded ligands such as hexaethylbenzene.

Introduction

It has been demonstrated by several groups [1–5] that complexation of bulky arene molecules to transition metal moieties may result in restricted motion of the arene ring or its substituents. In such a context hexaethylbenzene (HEB) has been extensively studied [2,3] and complexed HEB has been observed to adopt one (or more) of the conformations A–D in the solid state. Thus far attention has focussed



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primarily upon HEB complexed to the tripodal or "piano-stool" metal moieties $Cr(CO)_2L$ and in a series of elegant studies by Mislow [2] it was demonstrated that steric effects influence the conformational preference of the HEB ligand. Therefore for L = CO [2a,b], CS [2e,3b,c], $C_4H_2O_3$ [2f], PMe_3 [2d], PEt_3 [2c] and PPh_3 [2a,b] a gradual trend from **A**, the favoured conformation for uncomplexed HEB to **D**, the least favoured conformation for uncomplexed HEB, was observed in the solid state (distal = away from metal; proximal = towards metal).

The isolectronic cation $[(HEB)(C_5H_5)Fe]^+$ (**1**) has also been a subject of investigation as it represents a readily accessible "full sandwich" analogue of the aforementioned chromium "half-sandwich" complexes and it exhibits very interesting redox chemistry [6]. An earlier crystallographic study [3a] indicates that **1**PF_6 adopts conformation **B** in the solid state (i.e. four distal methyl groups) thereby making **1** the only crystallographically characterized species that exclusively adopts this conformation in the solid state [7]. As part of our general interest in cationic transition metal arene complexes [8] we have had cause to isolate **1** as its tetraphenylborate salt, **1**BPh_4. We have undertaken X-ray structural characterization of this salt in order to determine if packing effects (i.e. use of a very bulky counter ion) may influence conformation of the cation. In this contribution we report the results of our structural investigation of **1**BPh_4, which reveal that in this instance **1** exclusively adopts conformation **C** in the solid state [7,9].

Results and discussion

Final fractional coordinates are displayed in Table 1 and important bond distances and angles are presented in Table 2. Perspective and overhead ORTEP [10] views of **1** (Fig. 1) reveal that the conformation adopted by the HEB ligand corresponds not to type **B**, as was seen for its PF_6^- salt, but to type **C** (five distal methyl groups, one proximal). The HEB in **1**BPh_4 is therefore the first complexed HEB to exclusively adopt such a conformation [7,9] in the solid state. The conformation of the C_5 ring relative to the C_6 ring is the one that would be expected according to the steric requirements of the proximal methyl of the C_6 ring (i.e. type 1 as defined by ref. 3a). Approximate C_s symmetry is therefore held by the cation. Surprisingly, there are very few X-ray structural comparisons available for areneiron(II) complexes. Bond distances and angles within the cation are as would be expected close to those seen for **1**PF_6. Steric strain manifests itself via slight tilting of the C_5 and C_6 rings. Least squares planes calculations show that the dihedral angles between the two ring planes is 5.4°, however, planarity remains within 0.02 Å in both rings and the dihedral angles between the $C_{ring}–CH_2–CH_3$ planes are within 5 of 90°. The Fe–C bond distances exhibit the expected trend as the Fe–Cp distances show a range of 2.033(5) to 2.066(5) Å (average 2.050 Å vs. average 2.054 Å for PF_6) and the areneiron distances range from 2.083(4) to 2.126(4) Å (average 2.100 Å vs. average 2.109 Å for **1**PF_6 and average 2.130 Å for $[Fe(mesitylene)_2][PF_6]_2$ [11]). For both rings the longest Fe–C distances, as expected, correspond to the location of the proximal ethyl group.

There are no unusual interionic contacts that might account for the conformation adopted by **1**BPh_4. We must therefore conclude that the energy difference between conformations B and C of **1** is small enough to be influenced by even subtle packing effects in the solid state. Our observation therefore supports the assertion that at

Table 1

Atomic parameters x, y, z and B_{iso}, esd's refer to the last digit printed

	x	y	z	B_{iso} [a]
Fe(1)	0.76929(4)	0.25956(4)	0.45928(4)	2.20(3)
C(11)	0.6500(3)	0.2653(4)	0.3637(3)	4.7(3)
C(12)	0.6894(4)	0.1854(4)	0.3633(3)	5.1(3)
C(13)	0.7723(4)	0.1991(3)	0.3482(3)	4.5(3)
C(14)	0.7825(3)	0.2884(3)	0.3403(3)	3.9(3)
C(15)	0.7068(4)	0.3290(3)	0.3496(3)	4.1(3)
C(21)	0.7604(3)	0.3393(3)	0.5598(3)	2.14(22)
C(211)	0.7063(3)	0.4210(3)	0.5551(3)	3.8(3)
C(212)	0.7157(4)	0.4590(4)	0.6447(4)	5.8(4)
C(22)	0.8478(3)	0.3459(3)	0.5541(3)	2.06(22)
C(221)	0.8893(3)	0.4349(3)	0.5523(3)	3.0(3)
C(222)	0.8764(4)	0.4746(3)	0.4636(3)	4.2(3)
C(23)	0.8983(3)	0.2706(3)	0.5507(3)	2.14(21)
C(231)	0.9914(3)	0.2797(3)	0.5427(3)	3.3(3)
C(232)	1.0621(3)	0.2899(4)	0.6302(4)	4.9(3)
C(24)	0.8605(3)	0.1868(3)	0.5540(3)	2.74(24)
C(241)	0.9106(4)	0.1054(3)	0.5406(4)	6.2(4)
C(242)	0.9798(5)	0.0749(5)	0.6184(5)	9.3(5)
C(25)	0.7745(3)	0.1795(3)	0.5642(3)	2.74(24)
C(251)	0.7340(4)	0.0907(3)	0.5693(3)	4.4(3)
C(252)	0.7619(4)	0.0571(4)	0.6601(4)	6.3(4)
C(26)	0.7237(3)	0.2560(3)	0.5662(3)	2.53(22)
C(261)	0.6286(3)	0.2484(4)	0.5710(3)	4.2(3)
C(262)	0.6246(4)	0.2397(5)	0.6610(4)	6.7(4)
B(1)	0.8034(4)	0.2844(3)	1.0060(3)	2.5(3)
C(31)	0.8485(3)	0.1947(3)	1.0574(3)	2.36(22)
C(32)	0.8237(3)	0.1644(3)	1.1262(3)	3.3(3)
C(33)	0.8584(3)	0.0896(3)	1.1716(3)	3.6(3)
C(34)	0.9220(3)	0.0429(3)	1.1500(3)	3.9(3)
C(35)	0.9490(3)	0.0697(3)	1.0821(4)	4.0(3)
C(36)	0.9126(3)	0.1443(3)	1.0373(3)	3.3(3)
C(41)	0.8572(3)	0.3162(3)	0.9389(3)	2.54(22)
C(42)	0.9084(3)	0.3905(3)	0.9475(3)	3.2(3)
C(43)	0.9510(3)	0.4144(3)	0.8880(3)	4.5(3)
C(44)	0.9426(4)	0.3657(4)	0.8173(3)	4.9(3)
C(45)	0.8919(4)	0.2915(4)	0.8043(3)	4.8(3)
C(46)	0.8505(3)	0.2682(3)	0.8646(3)	3.9(3)
C(51)	0.7009(3)	0.2655(3)	0.9453(3)	2.42(23)
C(52)	0.6478(3)	0.3332(3)	0.9004(3)	3.5(3)
C(53)	0.5633(3)	0.3210(3)	0.8432(3)	3.9(3)
C(54)	0.5267(3)	0.2385(3)	0.8286(3)	3.25(24)
C(55)	0.5772(3)	0.1711(3)	0.8720(3)	3.5(3)
C(56)	0.6613(3)	0.1845(3)	0.9293(3)	2.77(24)
C(61)	0.8061(3)	0.3562(3)	1.0805(3)	2.56(23)
C(62)	0.7311(3)	0.3900(3)	1.0973(3)	3.3(3)
C(63)	0.7363(4)	0.4477(3)	1.1631(3)	3.9(3)
C(64)	0.8165(4)	0.4760(3)	1.2163(3)	4.2(3)
C(65)	0.8937(4)	0.4437(3)	1.2035(3)	4.0(3)
C(66)	0.8871(3)	0.3848(3)	1.1376(3)	3.32(25)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 2

Important Bond Distances (Å) and Angles (°) for 1BPh$_4$.

(i) cation distances			
Fe(1)–C(11)	2.039(5)	C(21)–C(22)	1.410(6)
Fe(1)–C(12)	2.033(5)	C(21)–C(26)	1.427(6)
Fe(1)–C(13)	2.054(5)	C(211)–C(212)	1.542(7)
Fe(1)–C(14)	2.066(5)	C(22)–C(221)	1.525(6)
Fe(1)–C(15)	2.059(5)	C(22)–C(23)	1.418(6)
Fe(1)–C(21)	2.092(4)	C(221)–C(222)	1.530(7)
Fe(1)–C(22)	2.126(4)	C(23)–C(231)	1.516(6)
Fe(1)–C(23)	2.122(4)	C(23)–C(24)	1.432(6)
Fe(1)–C(24)	2.084(4)	C(231)–C(232)	1.524(7)
Fe(1)–C(25)	2.093(4)	C(24)–C(241)	1.535(7)
Fe(1)–C(26)	2.083(4)	C(24)–C(25)	1.417(7)
C(11)–C(12)	1.381(8)	C(241)–C(242)	1.472(9)
C(11)–C(15)	1.394(8)	C(25)–C(251)	1.526(6)
C(12)–C(13)	1.416(9)	C(25)–C(26)	1.432(6)
C(13)–C(14)	1.400(7)	C(251)–C(252)	1.503(8)
C(14)–C(15)	1.393(8)	C(26)–C(261)	1.526(6)
C(21)–C(211)	1.510(6)	C(261)–C(262)	1.498(7)
(ii) anion distances			
B(1)–C(31)	1.660(7)	B(1)–C(51)	1.637(7)
B(1)–C(41)	1.653(7)	B(1)–C(61)	1.636(7)
(iii) cation angles			
C(11)–C(12)–C(13)	107.8(5)	C(23)–C(24)–C(25)	119.9(4)
C(12)–C(11)–C(15)	108.6(5)	C(241)–C(24)–C(25)	120.2(4)
C(12)–C(13)–C(14)	107.5(5)	C(24)–C(241)–C(242)	114.5(5)
C(13)–C(14)–C(15)	107.8(5)	C(24)–C(25)–C(251)	120.5(4)
C(11)–C(15)–C(14)	108.3(5)	C(24)–C(25)–C(26)	119.8(4)
C(211)–C(21)–C(22)	118.9(4)	C(251)–C(25)–C(26)	119.6(4)
C(211)–C(21)–C(26)	121.5(4)	C(25)–C(251)–C(252)	111.4(4)
C(22)–C(21)–C(26)	119.6(4)	C(21)–C(26)–C(25)	120.0(4)
C(21)–C(211)–C(212)	112.4(4)	C(21)–C(26)–C(261)	119.9(4)
C(21)–C(22)–C(221)	119.8(4)	C(25)–C(26)–C(261)	120.0(4)
C(21)–C(22)–C(23)	120.9(4)	C(26)–C(261)–C(262)	113.4(4)
C(221)–C(22)–C(23)	119.3(4)	C(32)–C(31)–C(36)	114.2(4)
C(22)–C(221)–C(222)	116.5(4)	C(31)–C(32)–C(33)	123.6(5)
C(22)–C(23)–C(231)	119.6(4)	C(32)–C(33)–C(34)	120.0(4)
C(22)–C(23)–C(24)	119.7(4)	C(33)–C(34)–C(35)	119.0(4)
C(231)–C(23)–C(24)	120.7(4)	C(34)–C(35)–C(36)	119.8(5)
C(23)–C(231)–C(232)	112.0(4)	C(31)–C(36)–C(35)	123.4(4)
C(23)–C(24)–C(241)	119.8(4)		

140 K **1** exists as three coexisting stereoisomers (**B**, **C** and **D**) [2e]. It is relevant in this context that calculations have determined energy differences of only 3.48 or 2.20 kcal/mol between these conformations in uncomplexed hexaethylbenzene [2a]. The room temperature solution NMR spectra of **1**BPh$_4$ further support small energy differences between conformations as they are indicative of rapid interconversion of the ethyl groups, an observation consistent with earlier reports on **1**PF$_6$ [2e,3a].

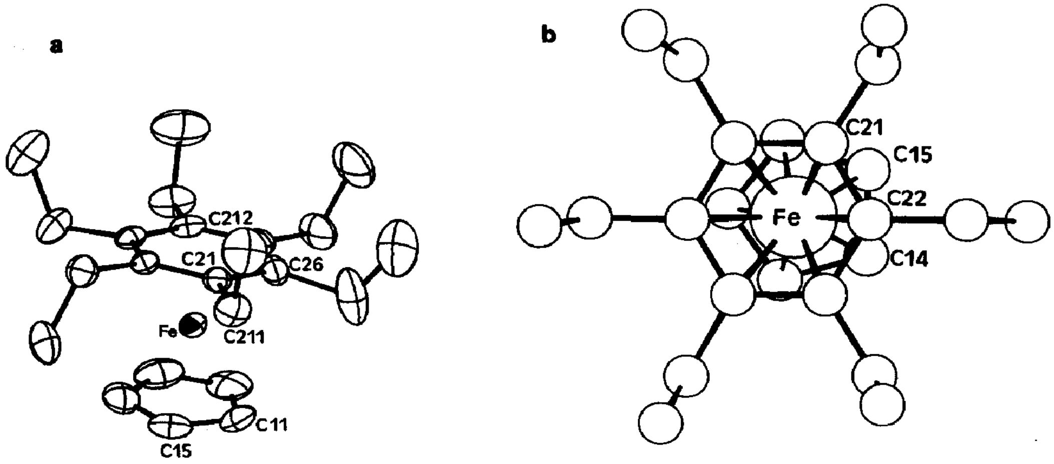

Fig. 1. (a) perspective and (b) overhead views of the $[(C_6Et_6)Fe(C_5H_5)]^+$ cation in $[(C_6Et_6)Fe(C_5H_5)]$-$[BPh_4]$.

Experimental

Synthesis. **1** was prepared by mixing ferrocene (Aldrich, 1.40 g, 0.00753 mol), aluminium chloride (Johnson–Matthey–Aesar, 4.0 g, 0.030 mol), aluminium powder (Fisher, 0.20 g, 0.0074 mol) and hexaethylbenzene (Eastman Kodak, 2.45 g, 0.00994

Table 3

Crystallographic data collection and structure refinement parameters for $[(C_6Et_6)Fe(C_5H_5)]BPh_4$

Formula	$FeC_{47}H_{55}B$
Formula Wt.	686.4
Radiation	Mo-K_α
Crystal System	Monoclinic
Space Group	$P2_1/n$
a, Å	15.7288(23)
b, Å	15.4411(14)
c, Å	16.3356(20)
β, °	107.972(10)
V, Å^3	3773.9
Z	4
D_{calc}, g cm^{-3}	1.208
μ, cm^{-1}	6.4
Crystal dimensions, mm	0.40×0.30×0.30
Scan type	θ–2θ
2θ range, °	4–45
Reflections measured	4923
Reflections observed [a]	2881
Parameters refined	442
Ratio data/parameter	6.5
R	0.047
R_w	0.050
GOF	1.295

[a] $I > 2.5\sigma(I)$

mol) in decahydronaphthalene at 100 °C for 18 h under N_2. Hydrolysis, filtration and addition of an excess of aqueous $NaBPh_4$ (Aldrich) to the aqueous phase precipitated **1**BPh_4. After drying 2.79 g (0.00406 mol, 53.9%) of yellow powdered **1**BPh_4 was isolated and confirmed pure by NMR: ^1H (60 MHz, acetone-d_6): δ 7.26m, 6.72m (BPh_4); 4.77s (C_5H_5); 3.02q (CCH_2CH_3); 1.36t (CCH_2CH_3). ^{13}C (91 MHz, acetone-d_6): δ 137.0d, 125.9d, 122.1d (BPh_4); 105.3s (CCH_2CH_3); 78.5d (C_5H_5); 23.8t (CCH_2CH_3); 16.3q (CCH_2CH_3) and analysis (found: C, 82.09; H, 8.04. $FeC_{47}H_{55}B$ calcd.: C, 82.24; H, 8.08%.

Crystals suitable for X-ray analysis were grown via slow evaporation of an acetone solution of 1BPh_4.

X-ray crystallography. An orange, air stable crystal of **1**BPh_4 was mounted and sealed in a thin-walled glass capillary and placed on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions from 25 reflections with 2θ angles in the range 30.00–35.00 ° are listed along with other pertinent data collection parameters in Table 3. The structure was solved via heavy-atom methods and refined using the NRC VAX Crystal Structure System [12] locally adapted for a Wicat Systems S-1260 computer. Refinement converged at $R = 0.047$ with all non-hydrogen atoms refined with anisotropic thermal parameters and hydrogen atoms placed in calculated positions (C–H 0.96 Å). Careful examination of a difference Fourier map at this stage showed no evidence of disorder for any of the ethyl groups.

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References and notes

1 (a) R.K. Pomeroy and D.J. Harrison, J. Chem. Soc., Chem. Commun., (1980) 661; (b) X. Hu, J. Duchowski and R.K. Pomeroy, ibid., (1988) 362.

2 (a) G. Hunter, D.J. Iverson, K. Mislow and J.F. Blount, J. Am. Chem. Soc., 102 (1980) 5942; (b) D.J. Iverson, G. Hunter, J.F. Blount, J.R. Damewood and K. Mislow, ibid., 103 (1981) 6073; (c) G. Hunter, J.F. Blount, J.R. Damewood, D.J. Iverson and K. Mislow, Organometallics, 1 (1982) 448; (d) J.F. Blount, G. Hunter and K. Mislow, J. Chem. Soc., Chem. Commun., (1984) 170; (e) G. Hunter and K. Mislow, ibid., (1984) 172; (f) G. Hunter, T.J.R. Weakly, K. Mislow and M.G. Wong, J. Chem. Soc., Dalton Trans., (1986) 577.

3 (a) J.R. Hamon, J.Y. Saillard, A. Le Beuze, M.J. McGlinchley, and D. Astruc, J. Am. Chem. Soc., 104 (1982) 7549; (b) M.J. McGlinchley, J.L. Fletcher, B.G. Sayer, P. Bougeard, R. Faggiani, C.J.L. Lock, A.D. Bain, C. Rodger, E.P. Kundig, D. Astruc, J.R. Hamon, P. Le Maux, S. Top and G. Jaouen, J. Chem. Soc., Chem. Commun., (1983) 634; (c) M.J. McGlinchley, P. Bougeard, B.G. Sayer, R. Hofer and C.J.L. Lock, ibid., (1984) 789.

4 E.M. Campi, B.M.K. Gatehouse, W.R. Jackson, I.D. Rae and M.G. Wong, J. Chem. Soc., Chem. Commun., (1984) 175.

5 U. Zenneck, Ch. Elschenenbroich and R. Mockel, J. Organomet. Chem., 219 (1981), 177.

6 D. Astruc, Acc. Chem. Res., 19 (1986) 377.

7 (HEB)Cr$(CO)_2(PMe_3)$ adopts conformations **B** and **C** in the solid state (approximate ratio 4/1). See ref. 2d for details.

8 M.V. Gaudet, A.W. Hanson, P.S. White and M.J. Zaworotko, Organometallics, in press.

9 (HEB)Cr(CO)$_2$PEt$_3$ adopts type **C** conformation in equal population with conformation **D** in the solid state (ref. 2c); (HEB)Cr(CO)$_2$PPh$_3$ adopts conformation **C** in approximately one third of molecules in the solid state, the remainder adopt conformation **D** (ref. 2d).

10 C.K. Johnson, ORTEP; Report ORNL-3794, revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

11 T.S. Cameron, A. Linden, C. Sturge and M.J. Zaworotko, unpublished results.

12 E.J. Gabe, F.L. Lee and Y. Le Page in G.M. Sheldrick, C. Kruger and R. Goddard (Eds.), Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases, Clarendon Press, Oxford; p. 167–174, 1985.