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Crystal structure of Fe(η^6-$C_5H_5BCMe_3$)$_2$, a "problem structure"

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Abstract

The complex Fe(η^6-$C_5H_5BCMe_3$)$_2$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$(C_i^1; No. 2) with unit cell dimensions of *a* 8.770(1) Å, *b* 8.878(1) Å, *c* 11.991(1) Å, α 107.56(1)°, β 90.85(1)°, γ 90.13(1)°, *V* 890.0(2) Å^3 and $Z = 2$. A full sphere of data was collected on a four-circle diffractometer. The structure was solved and refined to *R* 7.93% for all 3155 independent reflections and *R* 4.98% for those 2002 data with $|F_0| > 6\sigma|F_0|$. The molecules lie on crystallographic inversion centers at 0, 0, 0 and 1/2, 0, 1/2; the crystallographic asymmetric unit therefore consists of two independent half molecules. The molecule centered at 0, 0, 0 (molecule "A") is ordered and well-defined; that centered on 1/2, 0, 1/2 (molecule "B") is probably disordered, as indicated by larger "thermal parameters" and a greater range of apparent interatomic distances. Discussion emphasizes the geometry of molecule A, which has precise C_i symmetry with Fe(1A)–B(1A) 2.297(4) Å and Fe(1A)–C(ring) distances ranging from 2.057(6) Å to 2.138(4) Å.

1. Introduction

Complexes of the formal $C_5H_5BR^-$ anion were reported by Herberich and Greiss in 1972 [1]. Thus, the cobalt complexes Co(C_5H_5BR)$_2$ and Co(C_5H_5)(C_5H_5BR) were formed by ring expansion of the C_5H_5 rings in Co(C_5H_5)$_2$ by use of the organoboron dihalides RBX_2 ($R = C_6H_5$, X = Cl, Br; $R = CH_3$, X = Br). This and the later extensive work of Herberich and his coworkers have been summarized in a review article [2].

A second entry into this field was made when Ashe and coworkers utilized the techniques developed in their previous synthesis of the "1-phenylborabenzene" anion $C_5H_5BPh^-$ [3] to prepare a variety of bis(1-substituted-"borabenzene") iron complexes [4], including the complex Fe(η^6-$C_5H_5BCMe_3$)$_2$ used in the current study.

It should be noted that the nomenclature for compounds based on C_5H_5B and the $C_5H_5BH^-$ ion has undergone some changes [2]. Thus, the unknown parent compound C_5H_5B has been termed borabenzene, borinane, borinine and borine. The $C_5H_5BH^-$ anion is now known as boratabenzene, but was originally termed borinate [1] or the borabenzene anion [3,4].

2. Experimental details

Crystals of Fe(η^6-$C_5H_5BCMe_3$)$_2$ were provided to M.R.C. by Professor A.J. Ashe, III in 1974. Attempts to solve the structure at that time were fruitless because of the mistaken assumption that the crystal was monoclinic. (Interaxial angles are, in fact, 107.56°, 90.85° and 90.13°, see below). The remaining crystals were stored, mislaid for about 17 years and were rediscovered recently. No visible decomposition had occurred and a second crystallographic study was undertaken. The composition of the material was also checked by ^1H NMR (in $CDCl_3$); the pattern described for the complex in ref. 4 was observed.

The following structural study gives rise to some obvious problems. We emphasize that complete structural analyses (with a full sphere of diffraction data) were performed on two different crystals, yielding equivalent results. We provide details of the better such study (in terms of slightly lower *R*-factors).

A red crystal of approximate dimensions 0.4 × 0.3 × 0.3 mm was sealed into a thin-walled capillary and was aligned on an upgraded Syntex P2$_1$/Siemens R3

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diffractometer. A complete shell of data ($\pm h$, $\pm k$, $\pm l$) was collected for the range $2\theta = 5.0–50.0°$. Details of data collection and refinement are provided in Table 1.

TABLE 1. Experimental data for X-ray diffraction study of $Fe(\eta^6\text{-}C_5H_5BCMe_3)_2$

Crystal data	
Empirical formula	$C_{18}H_{28}B_2Fe$
Color; habit	red crystal
Crystal size (mm)	$0.4 \times 0.3 \times 0.3$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.770(1)$ Å $b = 8.878(1)$ Å $c = 11.991(1)$ Å $\alpha = 107.56(1)°$ $\beta = 90.85(1)°$ $\gamma = 90.13(1)°$
Volume	890.0(2) Å^3
Z	2
Formula weight	321.9
Density (calc.)	1.201 Mg m^{-3}
Absorption coefficient	0.836 mm^{-1}
$F(000)$	344
Data collection	
Diffractometer	Siemens R3
Radiation	Mo Kα ($\lambda = 0.717073$ Å)
Temperature (K)	295
Monochromator	Highly oriented graphite crystal
2θ range	5.0 to 50.0°
Scan type	$2\theta - \theta$
Scan speed	Constant; 2.00° min^{-1} in ω
Scan range (ω)	0.50° plus Kα-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$ $-14 \le l \le 14$
Reflections collected	6310
Independent reflections	3155 ($R_{int} = 0.94\%$)
Reflections $> 6\sigma$	2002
Solution and refinement	
System	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement method	Full-Matrix Least-Squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Hydrogen atoms	Riding model, refined isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.009F^2$
Number of parameters refined	205
Final R indices (all data)	$R = 7.93\%$, $wR = 7.56\%$
R indices (6σ data)	$R = 4.98\%$, $wR = 5.51\%$
Goodness of fit	1.54
Largest and mean Δ/σ	0.001, 0.000
Data to parameter Ratio	15.4:1
Largest difference peak	0.67 e Å^{-3}
Largest difference hole	-0.50 e Å^{-3}

The crystal belongs to the triclinic system, but the angles β and γ are close to 90°, with $\beta = 90.85(1)°$ and $\gamma = 90.13(1)°$. A further observation is that data with $h + l = 2n + 1$ are systematically weak – *i.e.*, the unit cell is pseudo-B-centered. Possible space groups are the non-centrosymmetric triclinic space group $P1$ (No. 1) or the centrosymmetric triclinic space group $P\bar{1}$ (No. 2). We chose the latter on the basis of (a) statistical distribution of E-values [5], (b) the far greater probability of a synthetic triclinic crystal with $Z = 2$ belonging to the centrosymmetric space group $P\bar{1}$, rather than to the noncentrosymmetric space group $P1$ [6] and (c) the extraordinarily small probability of a centrosymmetric molecule crystallizing in the two different chiral forms of a enantiometrically pure non-centrosymmetric crystal (D- and L-hands of the polar space group $P1$) [7]. The 6310 data were merged to 3155 independent reflections, with the excellent merging factor of $R_{int} = 0.94\%$.

The structure was solved by direct methods using the Siemens SHELX PLUS system. The appearance of iron atoms at 0, 0, 0 and 1/2, 0, 1/2 explained the pseudo-B-centering condition. Refinement converged with R 7.93% and wR 7.56% for all 3155 unique data and R 4.98% and wR 5.51% for those 2002 data with $|F_0| > 6\sigma|F_0|$. Hydrogen atoms were placed in calculated positions with $d(\text{C–H}) = 0.96$ Å [8]. Residual features on a final difference-Fourier map were in the range $-0.50 \rightarrow +0.67$ e$^-$ Å^{-3}. The structure thus appeared to be both correct and complete. However, there are some indications of a disorder problem (see Discussion).

Final atomic coordinates are collected in Table 2. Anisotropic displacement coefficients are provided in Table 3.

3. Discussion

The crystallographic asymmetric unit is composed of two independent half-molecules. Molecule "A" is centered on Fe(1A) at the inversion center at 0, 0, 0; molecule "B" is centered on Fe(1B) at the inversion center at 1/2, 0, 1/2. Packing of the molecules in the unit cell is illustrated in Figs. 1 and 2. Interatomic distances and angles are collected in Tables 4 and 5.

As shown in Fig. 3, molecule A is well-behaved, with normal looking atomic vibration ellipsoids and with normal and internally consistent bond lengths (*vide infra*). In contrast to this, molecule B has inappropriately shaped "vibration ellipsoids" (see Fig. 4), which clearly indicate some effect other than true vibration; bond lengths involving the η^6-C_5B ring are also systematically in error.

We will continue by discussing, in order, the dimensions within the ordered molecule A and the nature of the disorder in molecule B.

TABLE 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for $Fe(\eta^6\text{-}C_5H_5BCMe_3)_2$

	x	y	z	U_{eq} [a]
Molecule A				
Fe(1A)	0	0	0	43(1)
B(1A)	−1649(5)	1933(5)	988(4)	49(2)
C(2A)	41(5)	2327(5)	1212(4)	60(2)
C(3A)	1057(6)	1328(7)	1552(4)	76(2)
C(4A)	584(7)	−115(7)	1658(4)	79(2)
C(5A)	−892(7)	−656(7)	1363(4)	81(2)
C(6A)	−1997(5)	293(5)	1028(4)	61(2)
C(11A)	−2874(5)	3112(5)	695(3)	55(1)
C(12A)	−2152(8)	4242(9)	144(8)	151(5)
C(13A)	−3527(10)	4034(10)	1837(6)	177(5)
C(14A)	−4118(8)	2261(8)	−87(7)	150(4)
H(2AA)	427	3284	1102	95(18)
H(3AA)	2101	1650	1731	103(19)
H(4AA)	1304	−757	1917	83(16)
H(5AA)	−1158	−1688	1403	98(17)
H(6AA)	−3005	−135	825	96(17)
H(12A)	−2916	4920	−23	222(15)
H(12B)	−1382	4872	653	222(15)
H(12C)	−1696	3633	−573	222(15)
H(13A)	−4270	4756	1703	222(15)
H(13B)	−4004	3336	2203	222(15)
H(13C)	−2724	4616	2337	222(15)
H(14A)	−4815	3010	−241	222(15)
H(14B)	−3708	1615	−811	222(15)
H(14C)	−4647	1604	289	222(15)
Molecule B				
Fe(1B)	5000	0	5000	45(1)
B(1B)	6960(6)	1647(7)	5866(4)	65(2)
C(2B)	7332(8)	−31(8)	5430(10)	166(6)
C(3B)	6331(17)	−1395(11)	5617(14)	261(10)
C(4B)	5380(21)	−608(15)	6427(9)	220(11)
C(5B)	4621(16)	600(19)	6718(7)	257(10)
C(6B)	5534(10)	1855(11)	6506(5)	181(5)
C(11B)	7979(5)	3023(5)	5667(3)	55(2)
C(12B)	9273(8)	3380(9)	6587(5)	121(3)
C(13B)	7128(8)	4474(7)	5742(9)	174(6)
C(14B)	8767(8)	2539(9)	4482(5)	126(4)
H(2BA)	8214	−429	4972	387(48)
H(3BA)	6639	−2481	5357	350(48)
H(4BA)	4825	−1484	6539	364(47)
H(5BA)	3696	787	7156	705(47)
H(6BA)	5143	2907	6808	300(47)
H(12D)	9909	4212	6492	220(15)
H(12E)	8847	3699	7355	220(15)
H(12F)	9871	2446	6489	220(15)
H(13D)	7808	5252	5614	220(15)
H(13E)	6322	4256	5164	220(15)
H(13F)	6702	4866	6508	220(15)
H(14D)	9364	3409	4404	220(15)
H(14E)	9420	1654	4428	220(15)
H(14F)	8007	2251	3869	220(15)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.1. Molecule A

This molecule is ordered and has precise C_i symmetry — the atoms in the η^6-C_5B ring are therefore eclipsed although the two B–CMe_3 moieties are in a relative *trans*-(1,4′) juxtaposition (see Fig. 5).

Distances from the iron atom to the η^6-ligand show the following trends. The Fe(1A)–B(1A) distance of 2.297(4) Å is the longest; those carbon atoms adjacent to boron are associated with the next longest distances, with Fe(1A)–C(2A) = 2.138(4) Å and Fe(1A)–C(6A) = 2.128(5) Å; the remaining three distances are the shortest with values of, cyclically, Fe(1A)–C(3A) = 2.081(4) Å, Fe(1A)–C(4A) = 2.078(5) Å and Fe(1A)–C(5A) = 2.057(6). Distances within the η^6-C_5B ring include the boron–carbon distances of B(1A)–C(2A) = 1.523(6) Å and B(1A)–C(6A) = 1.501(7) Å (average B–C = 1.512 Å) and carbon–carbon distances of C(2A)–C(3A) = 1.399(8) Å, C(3A)–C(4A) = 1.388(9) Å, C(4A)–C(5A) = 1.383(9) Å and C(5A)–C(6A) = 1.417(8) Å (average C–C = 1.397 Å).

The exocyclic boron–(tertiary butyl) distance, B(1A)–C(11A) = 1.609(7) Å, is some 0.10 Å longer than the intraring B–C distances, confirming the multiple bond character of the latter.

Angles within the η^6-C_5B ring are essentially regular except for a contraction at boron associated with the longer B–C bonds. Thus, the angle C(6A)–B(1A)–C(2A) is 111.3(4)°; angles *ortho* to this are B(1A)–C(2A)–C(3A) 122.3(4)° and B(1A)–C(6A)–C(5A) 122.5(4)° (average = 122.4°); angles at the *meta* position are C(2A)–C(3A)–C(4A) 121.4(5)° and C(6A)–C(5A)–C(4A) 121.1(5)° (average = 121.3(5)°; the angle at the *para* position is C(3A)–C(4A)–C(5A) 120.8(6)°.

Although, to the best of our knowledge, no bis(boratabenzene)iron complexes have been studied, similar patterns of M–C(B) distances and intraring angles have been observed in such species as *cis*-$[(\eta^6\text{-}C_5H_5BMe)Fe(CO)(\mu\text{-}CO)]_2$ [9], $Co(\eta^6\text{-}C_5H_5BMe)_2$ [10], $Co(\eta^6\text{-}C_5H_5BOMe)_2$ [2,10], $(\eta^6\text{-}C_5H_5BPh)Co(CO)_2$ [11], $(\eta^6\text{-}C_5H_5BPh)Mn(CO)_3$ [9] and $(\eta^6\text{-}C_5H_5BMe)V(CO)_4$ [12].

3.2. Molecule B

This molecule is associated with anomalous vibration ellipsoids (specifically those for atoms C(2B), C(3B), C(5B) and C(6B) and, possibly, C(4B)—see Fig. 4). Note that the iron atom, Fe(1B), and the B–CMe_3 moiety show no unusual effects. As may be seen in Table 3, the largest U_{ii} values for atoms C(2B) → C(6B) are far greater (by a *factor* of ×3.1 to ×5.7) than for atoms C(2A) → C(6A); no such differences are found for other atoms. Possible explanations include the following.

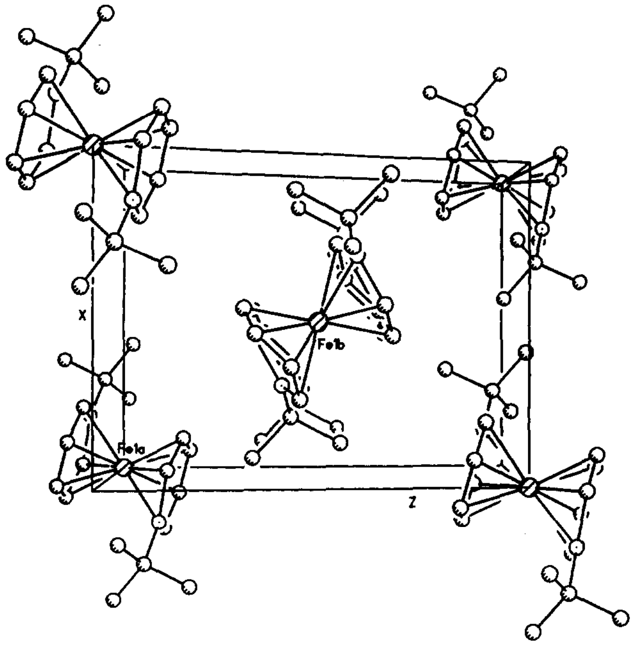

Fig. 1. Packing of molecules viewed down *b* and showing the pseudo-B-centering.

(1) Crystal twinning. This would be unusual for such a low crystal class as triclinic, but not impossible since *a* and *b* are approximately equal and γ is close to 90°. We did, however, carry out complete structural analyses on two different well-formed crystals.

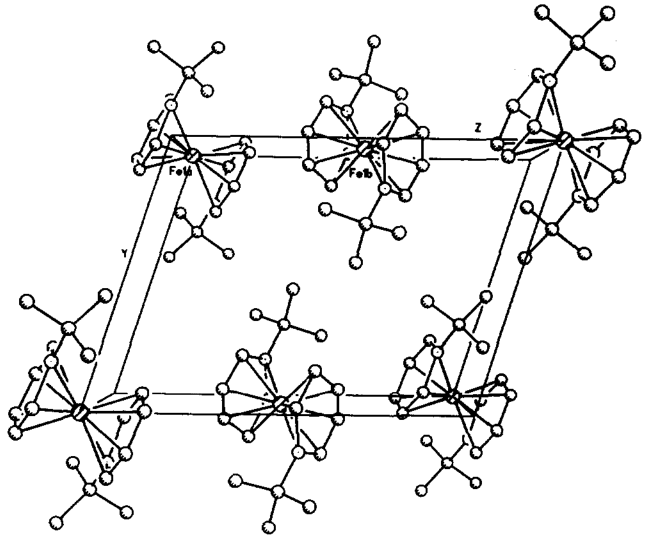

Fig. 2. Packing of molecules viewed down *a*.

(2) Misidentification of crystal class and/or space group. The misidentification of crystal *class* is now unlikely, since we had previously misidentified this complex as belonging to the higher monoclinic system – see Experimental details. Misidentification of the space group in the triclinic system is unlikely. That molecule situated at the inversion center at 0, 0, 0 (molecule A) is well behaved and clearly has true C_i symmetry. That centered at 1/2, 0, 1/2 (molecule B) is less well behaved. It is extraordinarily unlikely that the

TABLE 3. Anisotropic displacement coefficients ($Å^2 \times 10^3$) [a] for $Fe(\eta^6\text{-}C_5H_5BCMe_3)_2$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1A)	49(1)	46(1)	34(1)	11(1)	4(1)	12(1)
B(1A)	57(3)	54(3)	35(2)	17(2)	13(2)	12(2)
C(2A)	63(3)	50(2)	55(2)	8(2)	−8(2)	−2(2)
C(3A)	69(3)	96(4)	47(3)	23(3)	−17(2)	−4(3)
C(4A)	105(4)	95(4)	37(2)	42(3)	8(2)	19(2)
C(5A)	109(4)	86(4)	64(3)	31(3)	43(3)	46(3)
C(6A)	65(3)	65(3)	59(3)	8(2)	21(2)	24(2)
C(11A)	55(2)	59(2)	50(2)	16(2)	5(2)	17(2)
C(12A)	116(5)	141(6)	256(10)	43(5)	33(6)	151(7)
C(13A)	239(10)	212(9)	82(4)	186(8)	50(5)	42(5)
C(14A)	105(5)	107(5)	206(8)	31(4)	−82(5)	3(5)
Fe(1B)	52(1)	46(1)	42(1)	−8(1)	−6(1)	20(1)
B(1B)	77(3)	76(3)	47(3)	−30(3)	−25(2)	28(2)
C(2B)	84(4)	79(4)	362(13)	−28(3)	−93(6)	114(6)
C(3B)	314(18)	85(6)	391(22)	−4(8)	−263(18)	93(10)
C(4B)	408(26)	199(14)	102(8)	−140(14)	−144(12)	128(10)
C(5B)	263(15)	401(22)	48(4)	−220(15)	48(6)	−22(8)
C(6B)	185(8)	204(9)	88(5)	−146(7)	74(5)	−59(5)
C(11B)	55(2)	57(2)	55(2)	−13(2)	−4(2)	20(2)
C(12B)	132(6)	149(6)	99(4)	−84(5)	−47(4)	64(4)
C(13B)	102(5)	70(4)	367(14)	3(4)	10(7)	90(6)
C(14B)	115(5)	162(7)	89(4)	−61(5)	25(4)	20(4)

[a] The anisotropic displacement exponent takes the form: $-2\pi^2 (h^2a^{*2}U_{11} + \ldots + 2hka{\star}b{\star}U_{12})$

TABLE 4. Bond distances (Å)

Molecule A (ordered)		Molecule B (disordered)	
Fe(1A)–B(1A)	2.297(4)	Fe(1B)–B(1B)	2.278(5)
Fe(1A)–C(2A)	2.138(4)	Fe(1B)–C(2B)	2.104(7)
Fe(1A)–C(3A)	2.081(4)	Fe(1B)–C(3B)	1.995(15)
Fe(1A)–C(4A)	2.078(5)	Fe(1B)–C(4B)	1.968(13)
Fe(1A)–C(5A)	2.057(6)	Fe(1B)–C(5B)	1.999(9)
Fe(1A)–C(6A)	2.128(5)	Fe(1B)–C(6B)	2.091(7)
C(2A)–C(3A)	1.399(8)	C(2B)–C(3B)	1.566(16)
C(3A)–C(4A)	1.388(9)	C(3B)–C(4B)	1.321(20)
C(4A)–C(5A)	1.383(9)	C(4B)–C(5B)	1.224(21)
C(5A)–C(6A)	1.417(8)	C(5B)–C(6B)	1.456(19)
C(6A)–B(1A)	1.501(7)	C(6B)–B(1B)	1.460(10)
B(1A)–C(2A)	1.523(6)	B(1B)–C(2B)	1.462(8)
B(1A)–C(11A)	1.609(7)	B(1B)–C(11B)	1.589(7)
C(11A)–C(12A)	1.502(11)	C(11B)–C(12B)	1.534(8)
C(11A)–C(13A)	1.490(8)	C(11B)–C(13B)	1.470(8)
C(11A)–C(14A)	1.477(8)	C(11B)–C(14B)	1.531(7)

true space group is $P1$ with only minor deviations from $P\bar{1}$. (At the suggestion of a referee we have carried out refinement in space group $P1$. The results were unsatisfactory. Bond distances in molecule B became even worse, bond distances in molecule A deteriorated badly and "η-refinement" produced a value of $\eta = +0.04(6)$. Clearly *P1* is not the correct space group.)

(3) An artifact of crystal decomposition. Frankly, we are not too familiar with this problem (nor, we suspect, is anyone else). However, the classic example is that of $[IrO_2(Ph_2PCH_2PPh_2)_2][PF_6]$ originally studied by McGinnety *et al.* [13] and reexamined by Laing *et al.* [14]. Here it was established that crystal decomposition had led to mutually inconsistent Ir–ligand distances and an anomalously long O–O bond. This seems not be relevant to the present case, since the crystals appeared to be of excellent quality (despite their age) and only one *site* is affected.

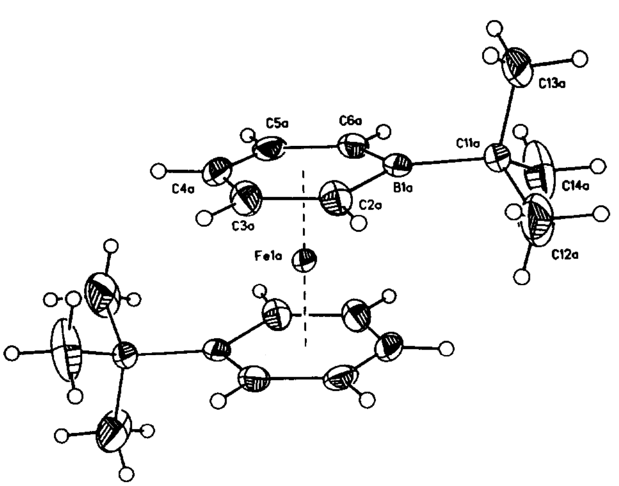

Fig. 3. Labeling of atoms and atomic vibration ellipsoids for the ordered molecule A.

(4) Co-crystallization of two different molecular species. This seems improbable since (i) the complex is well characterized, (ii) only one *site* is affected and (iii) the overall shape of molecule B is essentially the same as that of molecule A. The only chemically accessible

TABLE 5. Interatomic angle (deg)

Molecule A (ordered)		Molecule B (disordered)	
B(1A)–Fe(1A)–C(2A)	40.0(2)	B(1B)–Fe(1B)–C(2B)	38.7(2)
C(2A)–Fe(1A)–C(3A)	38.7(2)	C(2B)–Fe(1B)–C(3B)	44.8(5)
C(3A)–Fe(1A)–C(4A)	39.0(2)	C(3B)–Fe(1B)-C(4B)	38.9(6)
C(4A)–Fe(1A)–C(5A)	39.1(2)	C(4B)–Fe(1B)–C(5B)	35.9(6)
C(5A)–Fe(1A)–C(6A)	39.5(2)	C(5B)–Fe(1B)–C(6B)	41.6(5)
C(6A)–Fe(1A)–B(1A)	39.4(2)	C(6B)–Fe(1B)–B(1B)	38.7(3)
B(1A)–C(2A)–C(3A)	122.3(4)	B(1B)–C(2B)–C(3B)	124.6(8)
C(2A)–C(3A)–C(4A)	121.4(5)	C(2B)–C(3B)–C(4B)	101.9(9)
C(3A)–C(4A)–C(5A)	120.8(6)	C(3B)–C(4B)–C(5B)	141.9(14)
C(4A)–C(5A)–C(6A)	121.1(5)	C(4B)–C(5B)–C(6B)	107.4(13)
C(5A)–C(6A)–B(1A)	122.5(4)	C(5B)–C(6B)-B(1B)	125.9(9)
C(6A)–B(1A)–C(2A)	111.3(4)	C(6B)–B(1B)–C(2B)	109.9(6)
C(2A)–B(1A)–C(11A)	123.6(4)	C(2B)–B(1B)–C(11B)	124.3(5)
C(6A)–B(1A)–C(11A)	125.0(4)	C(6B)–B(1B)–C(11B)	125.8(5)
B(1A)–C(11A)–C(12A)	112.2(4)	B(1B)–C(11B)–C(12B)	107.7(5)
B(1A)–C(11A)–C(13A)	106.2(5)	B(1B)–C(11B)–C(13B)	113.7(4)
B(1A)–C(11A)–C(14A)	112.5(4)	B(1B)–C(11B)–C(14B)	112.9(4)
C(12A)–C(11A)–C(13A)	108.6(5)	C(12B)–C(11B)–C(13B)	109.9(5)
C(12A)–C(11A)–C(14A)	108.2(5)	C(12B)–C(11B)–C(14B)	105.5(4)
C(13A)–C(11A)–C(15A)	109.1(5)	C(13B)–C(11B)–C(15B)	106.8(1)

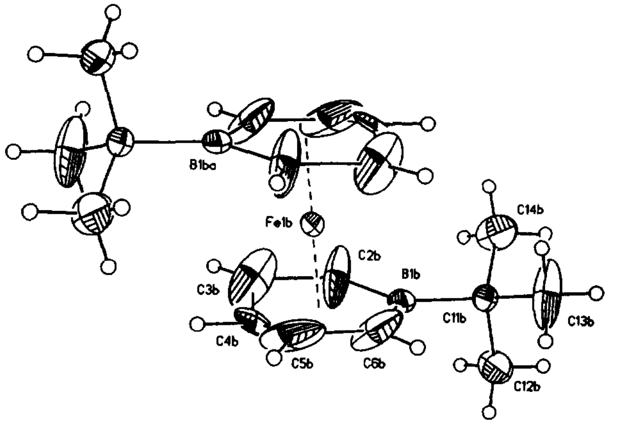

Fig. 4. Labeling of atoms and "atomic vibration ellipsoids" for the disordered molecule B.

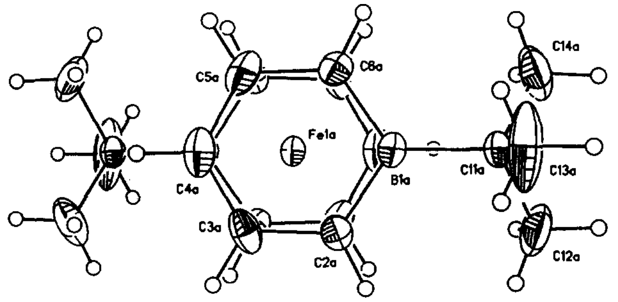

Fig. 5. The eclipsed configuration of molecule A.

species would appear to be $Fe(\eta^5\text{-}C_5H_5BCMe_3)(\eta^5\text{-}C_5H_5)$, but this would leave large voids in the crystal (there is also no ^1H NMR evidence for this species – see Experimental details).

(5) Disorder of molecules at site B. There could be two (or more) sites of equivalent energy for molecule B. The location of the iron atom is secure at 1/2, 0, 1/2 and the peripheral $B\text{-}CMe_3$ groups appear to be firmly locked into position with B–C and C–Me distances in good agreement with those of molecule A. The proposed disorder would involve either a static or (less likely) dynamic rotation of C_5B moieties about the $B\text{-}CMe_3$ bond with concomitant slippage on the surface of the iron atom. The observed Fe(1B)–C(nB) distances, which are shorter than the Fe(1A)–C(NB) distances by 0.034 Å ($n = 2$), 0.086Å ($n = 3$), 0.110 Å ($n = 4$), 0.058 Å ($n = 5$) and 0.037 Å ($n = 6$) are then the artificial results of averaging two or more sets of atomic locations. This similarly explains the anomalous range of C–C(ring) "distances" (1.224–1.566 Å) in molecule B.

(6) Existence of a possible superlattice. This was checked on photographs; no evidence for such a superlattice was found.

Overall, we prefer explanation (5), although (1) is not impossible. In either case there are two or more orientations for molecule B at the defined site.

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