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THE PREPARATION AND STRUCTURE OF μ-IODOBIS(h^5-CYCLOPENTADIENYLDICARBONYLIRON) FLUOROBORATE*

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SUMMARY

The identity and structure of a compound which arises frequently in the generation of $(h^5\text{-}C_5H_5)Fe(CO)_2^+$ ion from $(h^5\text{-}C_5H_5)Fe(CO)_2I$ and $AgBF_4$ have been determined. The substance was shown to be $\{[h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}BF_4$, a compound already known from the work of Fischer and Moser. It consists of a BF_4^- anion and a cation formed by two $(h^5\text{-}C_5H_5)Fe(CO)_2$ groups, having the expected shape and dimensions, united by a bridging iodine atom. The Fe–I bonds have an average length of 2.588 Å and the Fe–I–Fe angle is 110.8(1)°. The Fe–Fe distance of 4.26 Å is consistent with the expectation that there should be no metal–metal bond. Presumably the large Fe–I–Fe angle results from a compromise between the tendency of I to maximize *p* character in its bonding orbitals and the necessity of minimizing non-bonded contact between the $(h^5\text{-}C_5H_5)Fe(CO)_2$ groups. Crystallographic data are: space group, *P2/a*; unit cell dimensions, $a = 15.605(2)$ Å, $b = 9.607(2)$ Å, $c = 12.373(2)$ Å, $\beta = 104.86(1)°$, $V = 1792.9(6)$ Å^3; $d_{calc} = 2.10$ g/cm^3 for $Z = 4$; $d_{obs} = 2.08 \pm 0.02$ g/cm^3. Refinement using 1595 independent reflections with $F_o^2 > 3\sigma(F_o^2)$ was terminated at residuals of $R_1 = 0.076$ and $R_2 = 0.114$.

INTRODUCTION

In the course of investigations of the reactions of the transient species $(h^5\text{-}C_5H_5)Fe(CO)_2^+$, which was normally generated by the action of $AgBF_4$ on $(h^5\text{-}C_5H_5)Fe(CO)_2I$, an unidentified and unwanted product was frequently obtained. This substance often came to hand, without any special effort, in the form of air-stable, well-formed crystals, eminently suitable for X-ray study. The decision was therefore made to identify the substance definitively by this method, without making any deliberate effort to identify it on the basis of other data.

The compound was found to be $\{[h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}BF_4$, a formulation

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fully consistent with all analytical and spectroscopic evidence. It was then also possible to prepare it deliberately and in good yields, and to show that it is identical with the substance prepared earlier by Fischer and Moser[1] using $BF_3 \cdot OEt_2$ to deiodinate $(h^5\text{-}C_5H_5)Fe(CO)_2I$.

It is to be stressed that the crystallographic study reported here was intentionally terminated at a stage of refinement short of that which is presumably attainable. The purpose of the work was to obtain an unequivocal identification of the compound and a description of its structure sufficiently accurate for all ordinary chemical purposes. The observed and calculated structure factors are being made available so that further refinement can be carried out by anyone desiring to do so.

EXPERIMENTAL

Preparation and characterization

Our method of preparation employs silver ion as the deiodinating agent. A solution of $(h^5\text{-}C_5H_5)Fe(CO)_2I$ (1.0 g, 3.3 mmol) in 60 ml of dry benzene was added slowly to a suspension of $AgBF_4$ (0.3 g, 1.5 mmol) in 150 ml of dry benzene. A red-brown precipitate began to form immediately. The mixture was stirred for 2 h and then allowed to stand until a clear supernatant layer had formed. This was removed with a syringe and discarded. The product was extracted from the solid residue with 80 ml of dry, degassed CH_2Cl_2. The yield, after recrystallization from CH_2Cl_2/benzene, was 0.75 g, 74%. All operations were carried out under nitrogen.

The substance was shown to be $\{[(h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}BF_4$, identical to the substance obtained by Fischer and Moser[1] by its properties: m.p. 137–138° dec. (Found: C, 29.7; H, 2.09. $C_{14}H_{10}BF_4Fe_2IO_4$ calcd.: C, 29.62; H, 1.78%.) NMR in acetone-d^6, singlet at τ 4.44; ν(CO) (CH_2Cl_2 solution), 2064, 2050, 2017 cm^{-1}.

X-Ray data

Crystallization from benzene/methylene chloride at 0° produced large multifaceted crystals. From these a reddish-black crystal of dimensions 0.48 × 0.38 × 0.20 mm was selected and glued to a glass fiber. Data were collected at a temperature of $22 \pm 2°$ on a Syntex P$\bar{1}$ automated diffractometer using Mo-K_α radiation monochromatized with a graphite crystal. The following crystal data were obtained: monoclinic system, systematic absences of $h = 2n+1$ for $h0l$ indicating space group $P2/a$ (a non-standard setting for $C_{2h}^4 - P2/c$), $s = 15.605(2)$ Å, $b = 9.607(2)$ Å, $c = 12.373(2)$ Å, $\beta = 104.86(1)°$, $V = 1792.9(6)$ Å^3, $d_{calc} = 2.10$ g/cm^3 for $Z = 4$ and mol.wt. $= 567.64$; $d_{obs} = 2.08 \pm 0.02$ g/cm^3 (by flotation). The cell constants and orientation matrix used in data collection were obtained from least-squares refinement of the setting angles for fifteen carefully centered reflections with $25° < 2\theta < 40°$. Using the θ–2θ scan technique with variable scan rates ranging from 2.0 to 24.0°/min and a scan range from 2θ(Mo–K_{α_1}) $-0.9°$ to 2θ(Mo–K_{α_2})$+0.9°$, 1904 reflections up to $2\theta_{max} = 40°$ were collected. The intensities of four standard reflections that were remeasured every 100 reflections showed no significant variation. Lorentz and polarization corrections were applied to the data. No absorption correction (μ 34.56 cm^{-1}) or extinction correction was made.

*Structural determination and refinement**

All but three of the top 28 peaks in a three-dimensional Patterson map could be interpreted in terms of three heavy atoms in the asymmetric unit. By varying scattering factor tables in several least-squares refinements, the atoms were identified

TABLE 1, POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a] ANISOTROPICALLY REFINED ATOMS[b]

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	0.0965(1)	0.0823(2)	0.2992(2)	28(1)	105(3)	73(2)	−2(1)	21(1)	8(2)
Fe(2)	−0.0809(1)	0.4158(2)	0.1731(2)	29(1)	99(3)	72(2)	0(1)	18(1)	−7(2)
I	0.5724(6)	0.27871(10)	0.15251(8)	33.2(8)	114.4(21)	72.6(12)	5.1(6)	27.4(6)	11.6(8)

ISOTROPICALLY REFINED ATOMS

Atom	*x*	*y*	*z*	$B(Å^2)$
F(1,1)	−0.192(1)	0.354(2)	0.470(1)	12.5(5)
F(1,2)	−0.292(1)	0.509(2)	0.410(2)	15.5(6)
F(2,1)	0.178(1)	−0.048(2)	−0.017(2)	10.5(5)
F(2,2)	0.253(1)	0.109(2)	0.094(2)	13.3(5)
B(1)	−1/4	0.439(3)	1/2	4.4(6)
B(2)	1/4	0.047(3)	0	3.9(5)
O(1,1)	0.046(1)	0.248(1)	0.469(1)	6.2(3)
O(1,2)	0.282(1)	0.155(1)	0.362(1)	7.0(3)
O(2,1)	−0.166(1)	0.370(1)	−0.062(1)	5.7(3)
O(2,2)	−0.162(1)	0.182(1)	0.257(1)	5.8(3)
C(1,1)	0.069(1)	0.183(2)	0.401(1)	4.1(3)
C(1,2)	0.209(1)	0.127(2)	0.337(1)	4.8(4)
C(1,3)	0.099(2)	−0.084(2)	0.191(2)	7.6(4)
C(1,4)	0.006(1)	−0.050(2)	0.188(2)	7.6(5)
C(1,5)	−0.001(1)	−0.062(2)	0.302(1)	5.7(4)
C(1,6)	0.077(1)	−0.110(2)	0.369(2)	6.4(5)
C(1,7)	0.138(1)	−0.124(2)	−0.308(2)	6.5(4)
C(2,1)	−0.132(1)	0.387(1)	0.031(1)	4.0(3)
C(2,2)	−0.128(1)	0.276(2)	0.221(1)	3.8(3)
C(2,3)	−0.118(2)	0.617(3)	0.156(2)	6.7(6)
C(2,4)	−0.030(1)	0.610(2)	0.178(2)	6.4(5)
C(2,5)	0.002(1)	0.552(2)	0.285(2)	7.1(5)
C(2,6)	−0.076(2)	0.520(3)	0.322(2)	6.2(6)
C(2,7)	−0.150(2)	0.565(2)	0.241(2)	7.8(6)

[a] Numbers in parenthesis are estimated standard deviations in the least significant digits in this and all other tables. [b] x, y, and z are fractional coordinates. The form of the thermal ellipsoid is $\exp[-10^{-4}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

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* The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; JIMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; and LIST, a data listing program by Snyder.

as two iron atoms bridged by an iodine atom. Subsequent difference Fourier syntheses revealed the remainder of the structure: two cyclopentadienyl rings, four carbonyl groups and two independent tetrafluoroborate anions. No attempt was made to locate hydrogen atoms, nor to include their ideal positions as fixed contributions to the structure factors.

Only the 1595 independent reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares refinements. Here $\sigma(F_o^2)$ in the standard deviation of the observed intensity and is calculated as previously described[2] using 0.05 for the parameter p. The function minimized in least-squares refinements is $\Sigma w(|F_o|-|F_c|)^2$, where the weight w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from International Tables[3]; anomalous dispersion effects[4] were included for Fe, I, and F.

After the last cycle of least-squares refinement the discrepancy indices are $R_1 = \Sigma(||F_o|-|F_c||/\Sigma|F_o| = 0.076$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.114$. In this cycle the iron and iodine atoms were refined anisotropically and all other atoms were refined with isotropic temperature factors; the final parameters are given in Table 1. The observed and calculated structure factors are available*.

A final difference Fourier synthesis showed residual electron density (1.4e/Å^3) concentrated in the plane of cyclopentadienyl ring and around the fluorine atoms. There is no evidence of disorder in the BF_4^- anions.

Because the original intention was merely to identify the compound and since we have no use for more precise dimensions of $\{[(h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}^+$ we did not continue refinement of the structure.

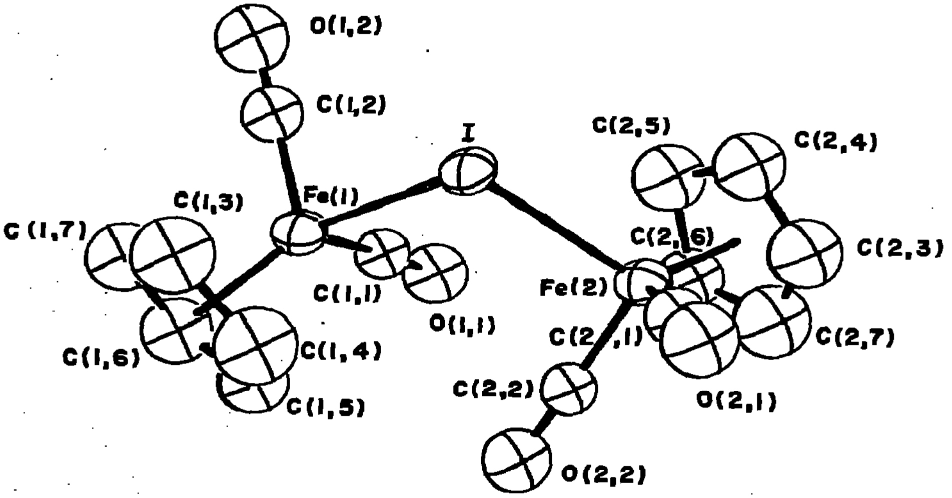

Fig. 1. A view of the $\{[h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}^+$ ion showing 50% probability ellipsoids and the atomic numbering scheme.

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* The table of structure factors has been deposited as NAPS Document No. 02154, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

RESULTS

The crystal structure consists of well-separated $\{[(h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}^+$ cations and BF_4^- anions. Two $(h^5\text{-}C_5H_5)Fe(CO)_2$ units are bridged by an I atom as depicted in Fig. 1. The numbering scheme and 50% probability thermal ellipsoids are shown in the ORTEP drawing. There are two crystallographically independent

TABLE 2

BOND DISTANCES (Å)

Fe(1)–I	2.581(2)	Fe(2)–I	2.595(2)
Fe(1)–C(1,1)	1.72(2)	Fe(2)–C(2,1)	1.75(2)
Fe(1)–C(1,2)	1.74(2)	Fe(2)–C(2,2)	1.71(2)
Fe(1)–C(1,3)	2.10(2)	Fe(2)–C(2,3)	2.01(2)
Fe(1)–C(1,4)	2.12(2)	Fe(2)–C(2,4)	2.02(2)
Fe(1)–C(1,5)	2.07(2)	Fe(2)–C(2,5)	2.09(2)
Fe(1)–C(1,6)	2.10(2)	Fe(2)–C(2,6)	2.09(2)
Fe(1)–C(1,7)	2.08(2)	Fe(2)–C(2,7)	2.09(2)
C(1,1)–O(1,1)	1.19(2)	C(2,1)–O(2,1)	1.15(2)
C(1,2)–O(1,2)	1.15(2)	C(2,2)–O(2,2)	1.19(2)
C(1,3)–C(1,4)	1.48(3)	C(2,3)–C(2,4)	1.32(3)
C(1,3)–C(1,7)	1.47(3)	C(2,3)–C(2,7)	1.37(3)
C(1,4)–C(1,5)	1.45(3)	C(2,4)–C(2,5)	1.41(3)
C(1,5)–C(1,6)	1.37(3)	C(2,5)–C(2,6)	1.44(3)
C(1,6)–C(1,7)	1.37(3)	C(2,6)–C(2,7)	1.39(3)
B(1)–F(1,1)	1.34(2)	B(2)–F(2,1)	1.42(2)
B(1)–F(1,2)	1.32(2)	B(2)–F(2,2)	1.29(2)

TABLE 3

BOND ANGLES (Deg.)

Fe(1)–I–Fe(2)	110.8(1)		
C(1,1)–Fe(1)–C(1,2)	94.9(8)	C(2,1)–Fe(2)–C(2,2)	95.8(7)
C(1,1)–Fe(1)–I	92.5(5)	C(2,1)–Fe(2)–I	90.0(6)
C(1,2)–Fe(1)–I	92.6(6)	C(2,2)–Fe(2)–I	94.5(6)
Cent(1)–Fe(1)–C(1,1)[a]	124.1	Cent(2)–Fe(2)–C(2,1)	124.1
Cent(1)–Fe(1)–C(1,2)	121.2	Cent(2)–Fe(2)–C(2,2)	121.3
Cent(1)–Fe(1)–I	123.2	Cent(2)–Fe(2)–I	123.1
Fe(1)–C(1,1)–O(1,1)	176(1)	Fe(2)–C(2,1)–O(2,1)	179(1)
Fe(1)–C(1,2)–O(1,2)	179(2)	Fe(2)–C(2,2)–O(2,2)	177(2)
C(1,7)–C(1,3)–C(1,4)	103(2)	C(2,7)–C(2,3)–C(2,4)	113(2)
C(1,3)–C(1,4)–C(1,5)	107(2)	C(2,3)–C(2,4)–C(2,5)	108(2)
C(1,4)–C(1,5)–C(1,6)	109(2)	C(2,4)–C(2,5)–(2,6)	105(2)
C(1,5)–C(1,6)–C(1,7)	109(2)	C(2,5)–C(2,6)–C(2,7)	108(2)
C(1,6)–C(1,7)–C(1,3)	111(2)	C(2,6)–C(2,7)–C(2,3)	105(2)
F(1,1)–B(1,1)–F(1,2)	108(1)	F(2,1)–B(2)–F(2,2)	106(1)

[a] Cent ( ) refers to the centroid of the cyclopentadienyl ring on the corresponding iron atom.

BF_4^- anions in the unit cell; each B atom lies on a crystallographic two-fold axis. Selected bond distances and angles are given in Tables 2 and 3, respectively.

DISCUSSION

The compound we have investigated, $\{[(h^5\text{-}C_5H_5)Fe(CO)_2]_2I\}BF_4$, was first prepared and characterized, except as to its detailed structure by Fischer and Moser[1] prior to 1965. It is, moreover, only one of a class of compounds[1,5-8] of general formula $\{[(h^5\text{-}C_5H_5)Fe(CO)_2X\}Y$, where X = Cl, Br, I and Y = BF_4, $AlCl_4$ or PF_6. In addition to the previously reported methods of preparation, we find that reaction of $(h^5\text{-}C_5H_5)Fe(CO)_2I$ with $AgBF_4$ in 2/1 mole ratio is also a suitable preparative reaction.

The $(h^5\text{-}C_5H_5)Fe(CO)_2$ moieties (not crystallographically equivalent) each have dimensions which are typical of those found in a number of other cases, including several molecules with bridging groups, such as $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2GeCl_2$[9], $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$[10], $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2Sn(h^1\text{-}C_5H_5)_2$[11] and $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2SO_2$[12].

The central Fe–I–Fe grouping and rotational configuration of the cation are the features of greatest interest. It appears that the overall structure of the cation is largely determined by intramolecular non-bonded repulsions. Both the transoid relationship of the two $(h^5\text{-}C_5H_5)Fe(CO)_2$ groups and the large angle at the iodine atom can thus be understood.

Presumably the tendency of the bridging iodine atoms would be to form bonds at or near an angle of 90° so as to optimize the employment of its *p* orbitals. When the attached groups are not particularly bulky, this is observed, as in the case of the diphenyl iodonium ion[13] where the C–I–C angle is 92°. The steric demands of the $(h^5\text{-}C_5H_5)Fe(CO)_2$ groups widen this to 110.8(1)°. It would be interesting to see if the corresponding angles are not even larger for the Cl- and Br-bridged analogs.

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