above and also the randomization was done within regions of sin θ, without any use of tables of random numbers. In practice it would be advisable to test the correlation first and make sure that the value of k is as close to zero as possible, which can be expected to lead to better results. The agreement between C_A and ϱ is also seen in Table 1 to be fairly satisfactory.

Table 1. *Observed values of* k, C_A *and* ϱ

Crystal	k	C_A*	ϱ†
Ephedrine HCl			
Non-centric	0·209	0·691	0·628
Centric	0·240	0·677	0·550
α-Rhamnose monohydrate:			
Non-centric	0·220	0·783	0·715
Centric	0·165	0·610	0·629

* Theoretically $C_A=\varrho$ when $k=0$.

† Theoretical value of ϱ is 0·637 for centric and 0·785 for non-centric cases.

The theoretical values of R' and R'' for the two cases are given in Table 2, which also contains the observed values with the test data. The agreement is satisfactory except in one case, namely the acentric projection of ephedrine hydrochloride. The observed value (0·538) for this case is rather closer to the centric than to the acentric one. This may be attributed to the statistical fluctuation and the rather imperfect randomization.

Table 2. *Theoretical and observed values of the functions* R' *and* R''

	R'		R''	
	Centric	Acentric	Centric	Acentric
Theoretical	0·559	0·429	0·727	0·614
L-Ephedrine hydrochloride	0·596	0·484	0·699	0·610
α-Rhamnose monohydrate	0·561	0·538	0·708	0·660

Lastly, it appears that the functions R' and R'' may also find useful application in crystal structure refinement. For instance, one may calculate their values between the observed and calculated structure factors (or intensities). If the proposed model is completely wrong and has no relation to the correct structure, the values of R' and R'' are to be expected to be the theoretical ones calculated above. Use of this function for regular structure refinement seems to be an interesting possibility. These aspects are under detailed study and will be reported later.

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References

Kenney, J. F. & Keeping, E. S. (1954). *Mathematics of Statistics*, Part I. New York: Van Nostrand.

McGeachin, H. McD. & Beevers, C. A. (1957). *Acta Cryst.* **10**, 227.

Phillips, D. C. (1954). *Acta Cryst.* **7**, 159.

Srinivasan, R. & Chandrasekharan, R. (1966). *Indian J. Pure Appl. Phys.* **4**, 178.

Srinivasan, R. & Subramanian, E. (1964). *Acta Cryst.* **17**, 67.

Srinivasan, R., Subramanian, E. & Ramachandran, G.N. (1964). *Acta Cryst.* **17**, 1010.

Weatherburn, C. E. (1961). *A First Course in Mathematical Statistics*. London: Cambridge Univ. Press.

Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1966). **21**, 652

The Crystal and Molecular Structure of Tricarbonyltetrakis(trifluoromethyl)cyclopentadienone-iron

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Tricarbonyltetrakis(trifluoromethyl)cyclopentadienone-iron crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions $a=9\cdot300$, $b=11\cdot696$, $c=16\cdot537$ Å, $\beta=119\cdot3^\circ$, $Z=4$. A three-dimensional Fourier synthesis and least-squares analysis of 968 independent reflexions has reduced the discrepancy index to 0·083. The non-planarity of the substituted cyclopentadienone ligand shows that in a simple valence-bond description of the molecular structure, the formation of localized σ and π bonds between the metal ion and cyclic ligand contributes substantially to the bonding, a conclusion supported by the observed carbon–carbon bond lengths (average e.s.d. 0·034 Å) and bond angles (mean e.s.d. 2°). The three carbonyl groups are not arranged with strict C_{3v} symmetry and a comparison is made with the structures of similar transition metal complexes and interpreted in the light of molecular-orbital theory. Atomic and molecular vibrations and the arrangement of the molecules in the crystal are also discussed.

Introduction

The preparation and characterization of a number of fluorocarbon complexes of transition metal ions have been reported by Boston, Sharp & Wilkinson (1960, 1962), Boston, Grim & Wilkinson (1963) and Dickson & Wilkinson (1964). The reaction of hexafluorobut-2-yne with pentacarbonyliron (Boston *et al.*, 1962) yields a single product which, on the basis of infrared studies, may be formulated as tricarbonyltetrakis(trifluoromethyl)cyclopentadienone-iron. High resolution ^{19}F nuclear magnetic resonance studies indicate two distinct environments for the fluorine atoms, and this was taken to indicate that the bonding between the metal ion and cyclic ligand was asymmetric. The present analysis allows a detailed discussion of the nature of the metal–ligand bond and comparison with related structures.

Experimental

Yellow-orange plate-like crystals were obtained by slow crystallization from chloroform; they show a slight tendency to decomposition and therefore all X-ray data were obtained from crystals protected by a thin coating of Formvar. The crystals are monoclinic, the unit-cell parameters determined from an analysis of high-angle precession data being $a = 9{\cdot}300 \pm 0{\cdot}004$, $b = 11{\cdot}696 \pm 0{\cdot}006$, $c = 16{\cdot}537 \pm 0{\cdot}010$ Å, and $\beta = 119{\cdot}3 \pm 0{\cdot}1^\circ$.

The observed density, measured by flotation in Rohrbach's solution, is $2{\cdot}064 \pm 0{\cdot}012$ g.cm^{-3} and is in good agreement with the value of $2{\cdot}072$ g.cm^{-3} calculated on the basis of four molecules of $(CF_3)_4C_5OFe(CO)_3$ in the unit cell. Intensities of the reflexions $h0l$, $h1l$, $h2l$, $h3l$, $h4l$ and $h5l$ were measured from non-integrated equi-inclination Weissenberg photographs (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) while those of the $0kl$, $1kl$, $2kl$, $3kl$ and $hk0$ reflexions were estimated from non-integrated precession photographs. The systematic absences $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$ unambiguously define the space group as $P2_1/c$ (C_{2h}^5, no. 14) and imply that the four molecules of $(CF_3)_4C_5OFe(CO)_3$ all occupy general positions in the unit cell.

All reflexion intensities were estimated by the usual visual method of comparison with a standard strip, using multiple-exposure film techniques; the usual formulae for diffraction by a mosaic crystal were used to derive relative values of $|F_{\text{obs}}|^2$. No corrections for absorption were made, the crystals used being approximately spherical ($\pm 20\%$) with dimensions averaging 0·20 mm.

The determination and refinement of positional and thermal parameters

The calculation of the three Patterson syntheses $P(0vw)$, $P(u0w)$ and $P(uv0)$ suggested preliminary coordinates for the iron atom of $x = 0{\cdot}15$, $y = 0{\cdot}25$, $z = 0{\cdot}10$, a least-squares refinement of this position giving reliability indices $R(0kl) = 0{\cdot}52$, $R(h0l) = 0{\cdot}56$ and $R(hk0) = 0{\cdot}39$; the corresponding two-dimensional electron-density syntheses could not be interpreted. A three-dimensional Patterson synthesis based on 968 independent reflexions confirmed that the y coordinate of the heavy atom was approximately 0·25 although some ambiguity regarding the choice of the x and z coordinates was apparent as a result of the overlap of two inversion peaks, each of unit weight, and indistinguishable from a Harker peak of double weight also lying at $Y = \frac{1}{2}$ in vector space. The calculation of a gradient-sharpened Patterson function (Jacobsen, Wunderlich & Lipscomb, 1961) resolved one peak to give approximate iron coordinates of $x = 0{\cdot}159$, $y = 0{\cdot}237$, $z = 0{\cdot}219$; the wrong choice of z coordinate from the two-dimensional data corresponds to the accumulation of light-atom vectors in the corresponding Patterson syntheses.

A comparison of the observed and calculated structure factors based on the new iron position showed the reliability index for the complete three-dimensional data to be 0·46 which was reduced to 0·43 in one cycle of least-squares refinement of positional and isotropic thermal parameters; the iron-phased three-dimensional Fourier synthesis immediately showed the positions of twenty-seven of the remaining twenty-eight atoms in the crystallographic asymmetric unit, the last carbon atom being positioned by the usual bond length and bond angle criteria.

Block-diagonal least-squares analysis of the three positional and isotropic vibrational parameters for each atom was begun at this point and converged the discrepancy index to 0·161 after eight cycles of refinement. Calculated structure factor amplitudes were based on the atomic scattering factors listed in *International Tables for X-ray Crystallography*; no dispersion corrections were applied to the atomic scattering factors of iron. This unit weights refinement analysis was continued by the refinement of anisotropic temperature factors when convergence was completed in nine cycles to a reliability index of 0·104. A comparison of the observed and calculated structure factors revealed no systematic errors other than six low-order reflexions apparently suffering from extinction; omission of these reflexions followed by three further cycles of least-squares refinement reduced R from 0·099 to 0·094. The intramolecular bond lengths at this point were still far from satisfactory, a result which may be attributed to the large apparent motions of the trifluoromethyl groups and to the inadequacy of representation of the atomic vibrations by the conventional ellipsoids of vibration. The importance of the weighting scheme in the least-squares analysis was therefore investigated at this point.

With weights proportional to the inverse of the observed structure-factor amplitude, nine cycles of least-squares refinement produced convergence, as judged by a final maximum positional shift of $\sigma/4$, at a reliability index of 0·090. The average difference in positional parameters of the carbon atoms between the unit weights and F^{-1} refinement analyses was 0·034 Å, the maximum being 0·049 Å. Finally weights defined by the equation

$$\omega = \frac{1}{1 + \left(\frac{|F_{\text{obs}}| - b}{a}\right)^2}$$

were adopted. With $a = 7$, and $b = 5$, this scheme uses weights which vary continuously between approximately 0·5 for the smallest observed structure factor amplitude to $\sim 0{\cdot}2$ for the largest observed value, passing through a maximum of unity at about $k\,|F_{\rm obs}| = 53$. With this weighting scheme, convergence was reasonably rapid in so far as four cycles of least squares reduced R to 0·083. 'Final' shifts were now smaller than those obtained with 'unit' and 'reciprocal' weights, being all less than $\frac{1}{6}\,\sigma$ and in general less than $0{\cdot}1\,\sigma$.

Atomic positional and vibrational parameters are listed in Tables 1 and 2 respectively, observed and calculated structure factors being recorded in Table 3. The composite electron density in the molecule is shown in Fig. 1; the electron density in the planes containing the fluorine atoms of the individual fluoromethyl groups is shown in Fig. 2.

Table 1. *Atomic coordinates and their estimated standard deviations*

	x	y	z	σ_x	σ_y	σ_z
Fe	0·15752	0·23754	0·21798	0·0028 Å	0·0026 Å	0·0026 Å
C(1)	0·0011	0·2367	0·2540	0·0220	0·0253	0·0209
C(2)	0·1006	0·1056	0·1539	0·0229	0·0181	0·0206
C(3)	0·3064	0·1618	0·3170	0·0214	0·0205	0·0215
C(4)	0·0797	0·4361	0·1914	0·0234	0·0179	0·0207
C(5)	0·2478	0·3996	0·2557	0·0204	0·0183	0·0188
C(6)	0·3156	0·3445	0·2096	0·0242	0·0190	0·0182
C(7)	0·1884	0·3188	0·1208	0·0256	0·0172	0·0214
C(8)	0·0362	0·3587	0·1100	0·0202	0·0175	0·0180
C(9)	0·3290	0·4534	0·3514	0·0224	0·0235	0·0238
C(10)	0·5007	0·3324	0·2409	0·0208	0·0326	0·0305
C(11)	0·2095	0·2685	0·0421	0·0305	0·0258	0·0230
C(12)	−0·1348	0·3402	0·0304	0·0243	0·0230	0·0209
O(1)	−0·0997	0·2515	0·2718	0·0160	0·0155	0·0149
O(2)	0·0632	0·0209	0·1147	0·0192	0·0150	0·0168
O(3)	0·4057	0·1149	0·3822	0·0165	0·0170	0·0161
O(4)	−0·0147	0·5017	0·1991	0·0162	0·0141	0·0157
F(1)	0·2330	0·4596	0·3843	0·0185	0·0180	0·0154
F(2)	0·3925	0·5515	0·3558	0·0208	0·0141	0·0166
F(3)	0·4489	0·3856	0·4106	0·0181	0·0155	0·0154
F(4)	0·5817	0·4132	0·2899	0·0184	0·0266	0·0313
F(5)	0·5281	0·3491	0·1715	0·0220	0·0292	0·0282
F(6)	0·5680	0·2465	0·2747	0·0141	0·0234	0·0272
F(7)	0·0677	0·2144	−0·0210	0·0234	0·0199	0·0160
F(8)	0·2374	0·3384	−0·0027	0·0269	0·0163	0·0196
F(9)	0·3073	0·1803	0·0684	0·0194	0·0166	0·0141
F(10)	−0·1772	0·2411	0·0027	0·0176	0·0159	0·0151
F(11)	−0·2409	0·3820	0·0542	0·0141	0·0196	0·0167
F(12)	−0·1553	0·4060	−0·0421	0·0166	0·0157	0·0132

Table 2. *Atomic vibrational parameters* (× 10⁴) *and their estimated standard deviations*

	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Fe	188 (3)	80 (2)	51 (1)	4 (4)	99 (3)	6 (9)
C(1)	291 (36)	231 (27)	80 (10)	26 (34)	172 (33)	284 (69)
C(2)	315 (42)	79 (17)	81 (11)	41 (24)	150 (37)	42 (50)
C(3)	242 (37)	127 (19)	98 (12)	45 (27)	197 (38)	−15 (53)
C(4)	405 (46)	74 (16)	93 (12)	−78 (24)	302 (42)	−110 (52)
C(5)	203 (32)	92 (17)	63 (10)	2 (22)	21 (29)	−79 (48)
C(6)	418 (48)	98 (17)	40 (8)	50 (22)	91 (34)	−43 (56)
C(7)	522 (58)	44 (14)	103 (13)	34 (23)	366 (49)	14 (52)
C(8)	212 (34)	89 (17)	56 (9)	39 (22)	42 (30)	62 (47)
C(9)	201 (36)	216 (29)	103 (14)	−39 (33)	137 (38)	−55 (60)
C(10)	43 (27)	451 (45)	188 (19)	178 (51)	206 (38)	17 (60)
C(11)	603 (64)	206 (29)	83 (12)	−31 (35)	170 (47)	272 (84)
C(12)	316 (45)	172 (24)	58 (10)	19 (28)	−9 (35)	−37 (62)
O(1)	433 (31)	148 (14)	121 (9)	−8 (23)	258 (29)	−2 (49)
O(2)	510 (41)	151 (16)	121 (11)	−36 (21)	201 (35)	−115 (45)
O(3)	338 (31)	257 (21)	112 (10)	140 (24)	182 (30)	121 (46)
O(4)	350 (31)	129 (13)	119 (9)	−31 (20)	225 (30)	38 (37)
F(1)	615 (40)	411 (27)	115 (9)	−201 (26)	297 (32)	−306 (54)
F(2)	899 (54)	197 (16)	149 (11)	−158 (22)	324 (40)	−548 (52)
F(3)	584 (40)	246 (18)	121 (9)	5 (23)	−16 (31)	−10 (47)
F(4)	303 (33)	671 (45)	509 (31)	−624 (63)	433 (55)	−679 (69)
F(5)	645 (51)	808 (51)	411 (26)	510 (62)	866 (66)	393 (86)
F(6)	188 (24)	533 (33)	467 (26)	605 (53)	327 (43)	337 (58)
F(7)	1020 (61)	457 (32)	114 (9)	−159 (29)	401 (40)	115 (71)
F(8)	1746 (93)	233 (18)	238 (15)	108 (28)	1196 (69)	163 (71)
F(9)	836 (47)	329 (20)	103 (8)	76 (21)	421 (35)	561 (54)
F(10)	581 (36)	218 (16)	138 (10)	−80 (24)	−131 (30)	−225 (52)
F(11)	230 (25)	482 (30)	161 (11)	−114 (31)	41 (27)	93 (49)
F(12)	520 (34)	286 (19)	82 (7)	111 (21)	0 (26)	−43 (46)

Table 3. *Observed and calculated structure factor amplitudes*

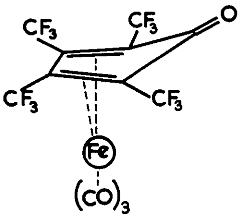
[illegible]

The molecular structure

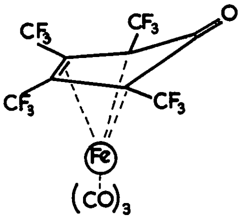
Observed bond lengths and bond angles, uncorrected for librational effects, together with their estimated standard deviations are listed in Tables 4 and 5 respectively and correspond to the numbering of atoms shown in Fig. 3, which represents the projection of the molecule along **c**.

The cyclopentadienone ligand

Relevant molecular dimensions of the coordinated cyclopentadienone ligand are summarized in Fig. 4. As in the structure of π-cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienone-cobalt (Gerloch & Mason, 1964) the bonding of the transition metal ion to the cyclopentadienone is such as to stabilize a non-planar conformation of this ligand, which is bent about the line C(5)–C(8) by 20·1°. In valence bond terms, this non-planarity is accounted for by the proposal that in addition to the usual π-bonded structure (I), some contribution to the bonding is made by the localized σ–π bond structure (II); the structure can then be discussed as involving the bonding of the metal to the substituted butadiene fragment of the cyclic ligand consisting of atoms C(5), C(6), C(7) and C(8), which are rigorously coplanar (maximum deviation from the mean plane is less than one-thirtieth of the mean positional standard deviation of the separate atoms; Table 6). In this extreme model of the bonding the ketonic group is not directly involved in the metal–ligand bond although in the case of the cyclopentadienone structures this assumption is less valid than, say, in π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium (Churchill & Mason, 1963, 1966), where there is a much larger deviation from planarity of the cyclic ligand. While the valence bond scheme is conceptually useful, it suffers from the disadvantage that it does not allow a detailed discussion of the bond lengths in the cyclic ligand. It is also open to the misunderstanding that the formulations (I) and (II) imply a 'fundamental difference in the electronic structures' (Schrauzer, 1965).



(I)



(II)

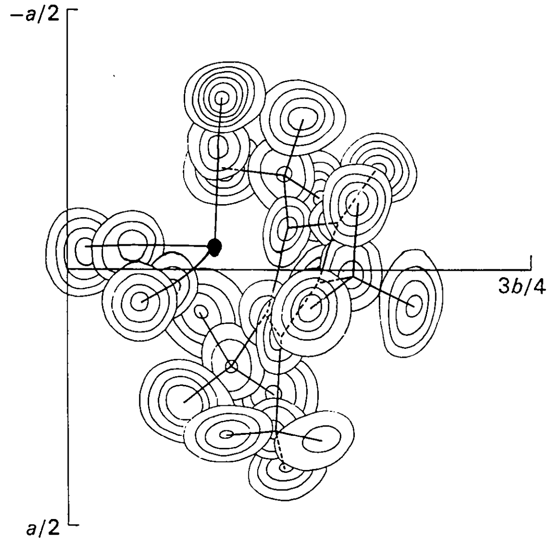


Fig. 1. The molecular electron density. Contours are drawn at every 1 e.Å^{-3}.

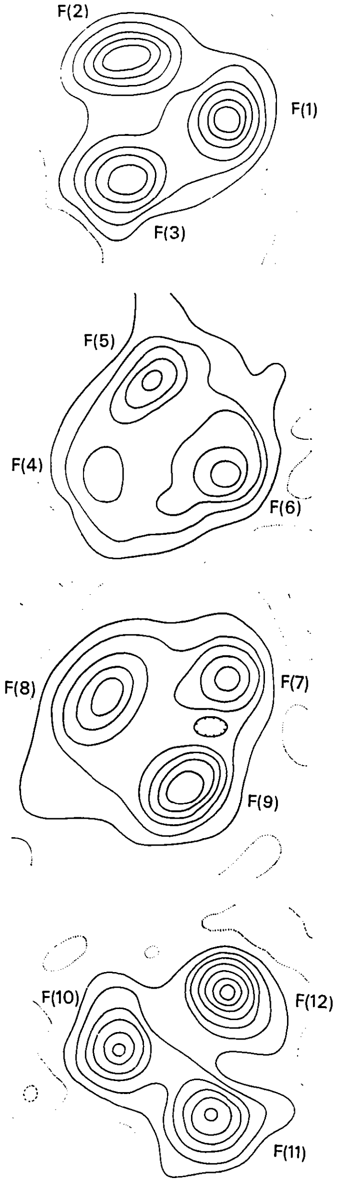


Fig. 2. The electron density in the mean plane containing the fluorine atoms of each trifluoromethyl group. Contours are drawn at every 1 e.Å^{-3}.

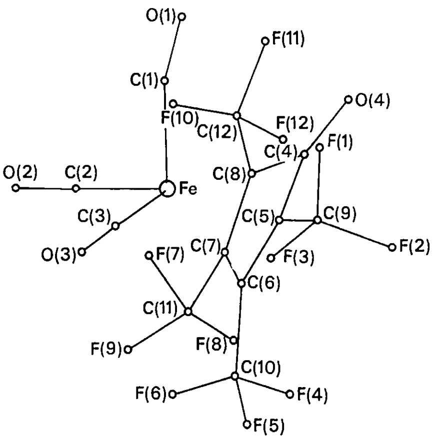


Fig. 3. Numbering of atoms.

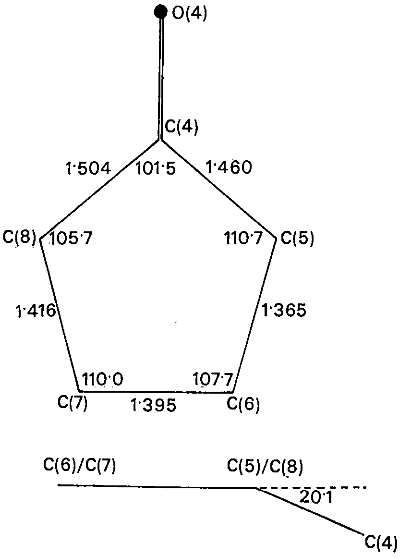


Fig. 4. The geometry of the cyclopentadienone ligand.

Table 5. *Bond angles and their standard deviations*

Atoms	Angle	e.s.d.
C(1)–Fe —C(2)	97·8°	1·1°
C(1)–Fe —C(3)	94·7	1·1
C(2)–Fe —C(3)	89·3	1·1
Fe —C(1)—O(1)	170·3	2·2
Fe —C(2)—O(2)	178·3	1·6
Fe —C(3)—O(3)	178·3	2·1
C(5)–C(4)—C(8)	101·5	1·7
C(4)–C(5)—C(6)	110·7	2·2
C(5)–C(6)—C(7)	107·7	2·4
C(6)–C(7)—C(8)	110·0	1·8
C(7)–C(8)—C(4)	105·7	2·2
C(5)–C(4)—O(4)	132·6	2·4
C(8)–C(4)—O(4)	125·5	2·7
C(4)–C(5)—C(9)	116·6	1·7
C(6)–C(5)—C(9)	130·4	2·4
C(5)–C(6)—C(10)	126·9	2·5
C(7)–C(6)—C(10)	124·4	1·9
C(6)–C(7)—C(11)	125·7	2·5
C(8)–C(7)—C(11)	123·9	2·8
C(7)–C(8)—C(12)	128·8	1·9
C(4)–C(8)—C(12)	125·2	1·8
C(5)–C(9)—F(1)	112·4	2·4
C(5)–C(9)—F(2)	114·4	2·0
C(5)–C(9)—F(3)	109·3	1·8
F(1)–C(9)—F(2)	109·3	1·9
F(1)–C(9)—F(3)	103·5	2·1
F(2)–C(9)—F(3)	107·3	2·5
C(6)–C(10)–F(4)	111·9	2·2
C(6)–C(10)–F(5)	110·9	2·9
C(6)–C(10)–F(6)	119·1	2·3
F(4)–C(10)–F(5)	98·3	2·6
F(4)–C(10)–F(6)	109·4	3·5
F(5)–C(10)–F(6)	105·1	2·4
C(7)–C(11)–F(7)	110·5	2·3
C(7)–C(11)–F(8)	114·6	2·1
C(7)–C(11)–F(9)	112·5	2·4
F(7)–C(11)–F(8)	104·9	2·8
F(7)–C(11)–F(9)	98·2	2·2
F(8)–C(11)–F(9)	114·5	2·4
C(8)–C(12)–F(10)	117·9	2·3
C(8)–C(12)–F(11)	108·1	2·0
C(8)–C(12)–F(12)	108·9	1·9
F(10)–C(12)–F(11)	107·9	2·1
F(10)–C(12)–F(12)	108·8	2·1
F(11)–C(12)–F(12)	104·5	2·1

Table 4. *Intramolecular bond lengths and their standard deviations*

Bond	Length	e.s.d.	Bond	Length	e.s.d.
Fe —C(1)	1·822 Å	0·019 Å	C(5)—C(9)	1·517 Å	0·037 Å
Fe —C(2)	1·798	0·021	C(6)—C(10)	1·543	0·038
Fe —C(3)	1·779	0·028	C(7)—C(11)	1·525	0·030
			C(8)—C(12)	1·503	0·041
Fe —C(4)	2·408	0·019			
Fe —C(5)	2·043	0·020	C(9)—F(1)	1·256	0·024
Fe —C(6)	1·986	0·022	C(9)—F(2)	1·276	0·028
Fe —C(7)	2·006	0·019	C(9)—F(3)	1·327	0·036
Fe —C(8)	2·121	0·022			
			C(10)–F(4)	1·233	0·046
C(1)–O(1)	1·125	0·024	C(10)–F(5)	1·306	0·037
C(2)–O(2)	1·141	0·027	C(10)–F(6)	1·171	0·042
C(3)–O(3)	1·158	0·035			
			C(11)–F(7)	1·371	0·045
C(4)–C(5)	1·460	0·040	C(11)–F(8)	1·215	0·029
C(5)–C(6)	1·365	0·024	C(11)–F(9)	1·301	0·036
C(6)–C(7)	1·395	0·042			
C(7)–C(8)	1·416	0·033	C(12)–F(10)	1·238	0·029
C(8)–C(4)	1·504	0·030	C(12)–F(11)	1·322	0·025
			C(12)–F(12)	1·357	0·027
C(4)–O(4)	1·218	0·025			

The molecular orbital theory of bonding in 'π' complexes of transition metal ions can be summarized by the wave equation

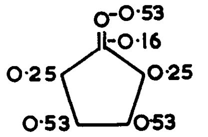
$$\Psi(M,L)=c_1\psi_1(M^-,L^+)+c_2\psi_2(M^+,L^-)$$

in which the coefficients c_1 and c_2 specify the relative importance of the forward- and back-donation processes respectively. Following our earlier remarks, we can consider the interaction of the metal orbitals with the four $p\pi$ orbitals of the butadiene fragment of the cyclic ligand; if these latter are labelled A to D, they form the basis for molecular orbitals of symmetries $2A_2$ and $2B_1$ of the form

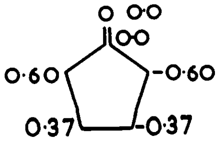
		Energy
$a_2(1)=\frac{1}{\sqrt{1+\lambda^2}}$	$\{A+D+\lambda(B+C)\}$	$\alpha+1{\cdot}6\beta$
$a_2(2)=\frac{1}{\sqrt{1+\lambda^2}}$	$\{\lambda(A+D)-(B+C)\}$	$\alpha-0{\cdot}6\beta$
$b_1(1)=\frac{1}{\sqrt{1+\mu^2}}$	$\{(A-D)+\mu(B-C)\}$	$\alpha+0{\cdot}6\beta$
$b_1(2)=\frac{1}{\sqrt{1+\mu^2}}$	$\{\mu(A-D)-(B-C)\}$	$\alpha-1{\cdot}6\beta$

where we have neglected overlap. In the π-bonded structure, the bonding molecular orbitals span A_2 and B_1 with the ligand contribution arising from $a_2(1)$ and $b_1(1)$. By contrast the σ–π-bonded structure (II) has bonding molecular orbitals which span $2A_2+B_1$ since it now explicitly includes the back donation process using the ligand orbital $a_2(2)$ (the coefficient c_2 in the wave equation is now non-zero). For cyclopentadienone, the atomic orbital coefficients and energy levels of the higher lying filled and lower lying unfilled molecular orbitals, calculated by the simple Hückel procedure, are given below.

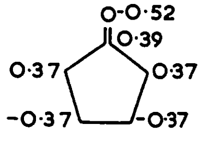
Energy



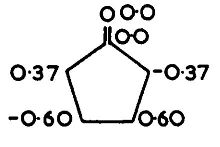
$\alpha+1{\cdot}4\beta$ (doubly filled)



$\alpha+0{\cdot}6\beta$ (doubly filled)



$\alpha-0{\cdot}03\beta$ (unfilled)



$\alpha-1{\cdot}7\beta$ (unfilled)

The forward donation bonding process principally involves the interaction of

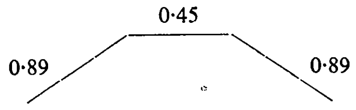
(1) the molecular orbital of energy $\alpha+1{\cdot}4\beta$ with a d_{z^2} or d_{z^2}/s hybrid metal orbital. The overlap of the ligand and metal orbitals will be enhanced if the ketonic group is bent out of plane, the main feature observed in the present structure, and

(2) the molecular orbital of energy $\alpha+0{\cdot}6\beta$ with a metal d_{xz} or suitable hybrid orbital. The ketonic group, being situated at the node of the ligand molecular orbitals, plays no part in this particular interaction.

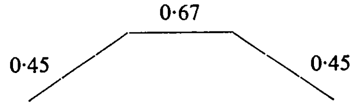
Back donation from filled metal orbitals largely proceeds to the very low lying antibonding ligand orbital of energy $\alpha-0{\cdot}03\beta$. The metal–ligand overlap will be increased if the oxygen *alone* is now non-coplanar with the five-membered ring.

The major source of the distortion from planarity of the cyclic ligand in the structures of π-cyclopentadienyltetrakis (trifluoromethyl) cyclopentadienonecobalt (Gerloch & Mason, 1964) and tricarbonyltetrakis-(trifluoromethyl)cyclopentadienone-iron thus originates from the interaction described under (1) above.

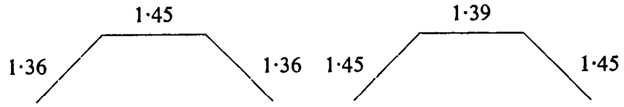
The observed bond lengths illustrate the need for invoking back-donation. In the ground state of butadiene, the Hückel bond orders for the carbon–carbon bonds are:



while in the first excited state, they are:



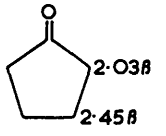
These bond orders correspond approximately to the bond lengths shown below:

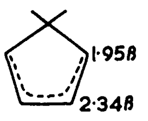


Ground state

Excited state

The donation of electrons from the filled molecular orbitals on the ligand to the unfilled metal orbitals serves to decrease the average bond order although forward donation alone will retain the alternation pattern of short-long-short. In the butadiene fragment of the coordinated cyclopentadienone ligand of the present structure, the mean bond lengths averaged over chemically equivalent bonds are 1·39, 1·40 and 1·39 Å, and this pattern can only be explained *via* a back-donation mechanism. It should be noted that an essential difference between the structures of π-$C_5H_5CoC_4(CF_3)_4CO$ and $C_4(CF_3)_4COFe(CO)_3$ is that the ligands *trans* to the cyclopentadienone ligand differ considerably in their π-bonding characteristics. Less back-donation to the cyclopentadienone ligand must take place in the iron-tricarbonyl complex than in the cobalt-cyclopentadienyl derivative. With the relatively weak π-accepting cyclopentadienyl anion, the charge localization in the cyclopentadienone ligand should be greater. Such a situation exists, for example, in the structure of π-cyclopentadienyl-1-phenylcyclopentadienylcobalt (Churchill & Mason, 1964*a*); all the available accurate data have been summarized by Churchill & Mason (1966*b*). A comparison of electron localization energies (a measure of the energy required to localize an additional electron at a formal sp^2 carbon) in cyclopentadienone and cyclopentadiene is instructive:





The localization energy is least at the atoms at which bending of the cyclic ligands takes place and is smallest for the cyclopentadiene ligand which shows the greatest deviation from planarity (Kettle & Mason, 1966*a*).

The carbonyl ligands

The three carbonyl groups while completing a pseudo-octahedral arrangement around the metal ion are not arranged according to strict C_{3v} symmetry. The (O)C–Fe–C(O) bond angles are 89, 95 and 98°, a pattern of distortion which is identical with that found in a large number of other tricarbonyl complexes in which there is a lack of cylindrical symmetry in the bonding electron distribution around the metal (*e.g.* Churchill & Mason, 1964*b*; Dickens & Lipscomb, 1962; Mills & Robinson, 1963). As such the angular distortion in these complexes is analogous to the bond length distortions observed in several π-cyclopentadienyl complexes, (Bennett, Churchill, Gerloch & Mason, 1964).

The mean planes defining the butadiene- and carbonyl-carbon atoms respectively are oriented at 6·6° with respect to one another rather than being strictly parallel; this feature is also found in the other complexes mentioned earlier. A possible theoretical explanation for these deviations has been put forward recently by Kettle & Mason (1966*b*).

The trifluoromethyl groups

Table 6 shows that the carbon atoms of the trifluoromethyl groups are not strictly coplanar with the butadiene moiety of the cyclopentadienone ligand; a representation of the orientations of the four CF_3 groups about the mean plane of the butadiene residue is shown in Fig. 5. Three trifluoromethyl groups, corresponding to C(9), C(10), and C(11), have taken up an arrangement which involves two F···F contacts of approximately 2·8 Å between neighbouring groups [the van der Waals diameter of fluorine is 2·70 Å (Pauling, 1960)] and together with O(4) form an interlocked system. The remaining $C(12)F_3$ group is associated with very short F(7)–F(10) and O(4)–F(11) contacts, the associated steric strain being partially relieved by the displacement of C(12) below the butadiene plane. Relief of this intramolecular overcrowding by the moving away of O(4) is apparently prevented by short intermolecular contacts to this atom.

Table 6. *The orientation of the butadiene fragment*

Direction cosines of mean plane referred to	
a	−0·34613
b	−0·87819
$c \sin \beta$	0·33011

	Mean deviation from plane	e.s.d.
C(5)	0·0004 Å	0·019 Å
C(6)	−0·0007	0·021
C(7)	0·0007	0·022
C(8)	−0·0004	0·019
Fe	1·670	0·003
C(1)	2·45	0·02
C(2)	2·72	0·02
C(3)	2·72	0·02
C(4)	−0·32	0·02
C(9)	−0·09	0·02
C(10)	−0·24	0·03
C(11)	−0·14	0·03
C(12)	0·14	0·02
O(1)	2·76	0·02
O(2)	3·42	0·02
O(3)	3·37	0·02
O(4)	−0·63	0·02

The observed variation in the carbon–fluorine bond lengths represents the most unsatisfactory feature in the present structural determination and is similar to those observed in the structures of π-cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienone cobalt (Gerloch & Mason, 1964) and π-cyclopentadienylhexakis-(trifluoromethyl)benzenerhodium (Churchill & Mason, 1963, 1966*a*). The variation is apparently significant judged by the positional standard deviations but in fact seems to be associated with errors in the positional parameters of all carbons of the trifluoromethyl groups. Thus the distance between the fluorine atoms and the ring carbon atom to which the CF_3 group is attached is constant (2·33 ± 0·03 Å) so that the fluorine atoms seem to have been adequately positioned by the least-squares refinement procedure. The treatment of the fluorine vibrations by the usual ellipsoid representation

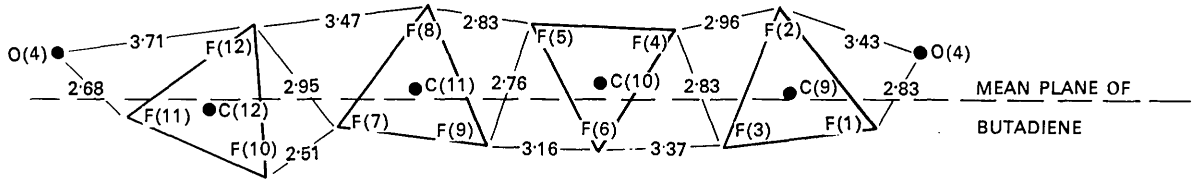


Fig. 5. The arrangement of the trifluoromethyl groups around the cyclic ligand.

together with the omission from the least-squares matrix of important cross-terms has undoubtedly led to a solution of the present structure in which the carbon coordinates of the fluoromethyl groups are systematically in error, in addition to the usual under-estimation of standard deviations.

Crystal packing and atomic thermal motions

The crystal structure viewed along the *a* and *b* crystal axes is shown in Figs. 6 & 7 respectively, the shortest (< 3·5 Å) intermolecular contacts being listed in Table 7.

The magnitudes and directions (referred to the orthogonal axes *a*, *b* and *c'* of the crystal) of the principal axes of the atomic vibration ellipsoids are given in Table 8. The values given for the fluorine atoms can be analysed in terms of librations about the respective carbon–carbon bonds, the mean librational angles for the groups associated with C(9), C(10), C(11) and C(12) being 16·4, 27·6, 19·0 and 15·3°. In view of the comments made earlier on the refinement process, these values have to be treated with some caution although they appear to be correlated with the environment of the various trifluoromethyl groups. The group F(4)–F(5)–F(6) has fewer significant intermolecular contacts than any other group while the groups F(1)–F(2)–F(3) and F(10)–F(11)–F(12) are relatively locked in position by the oxygen atom, O(4). Some coupling together of the librational motions of the CF_3 groups around the ring must be assumed because the intramolecular non-bonded F···F distances are, as was mentioned earlier, close to the van der Waals diameter of fluorine. The calculated librational amplitudes correlate qualitatively with the electron densities of the fluorine atoms in each of the trifluoromethyl groups (Fig. 2).

We are grateful to Professor G. Wilkinson for providing us with a sample of the complex and to Mrs J. Dollimore, Mr O. S. Mills and Dr J. S. Rollett and Dr R. Sparks for copies of their Mercury computer programs. One of us (N.A.B.) acknowledges the award of a Research Fellowship of the University of Sheffield.

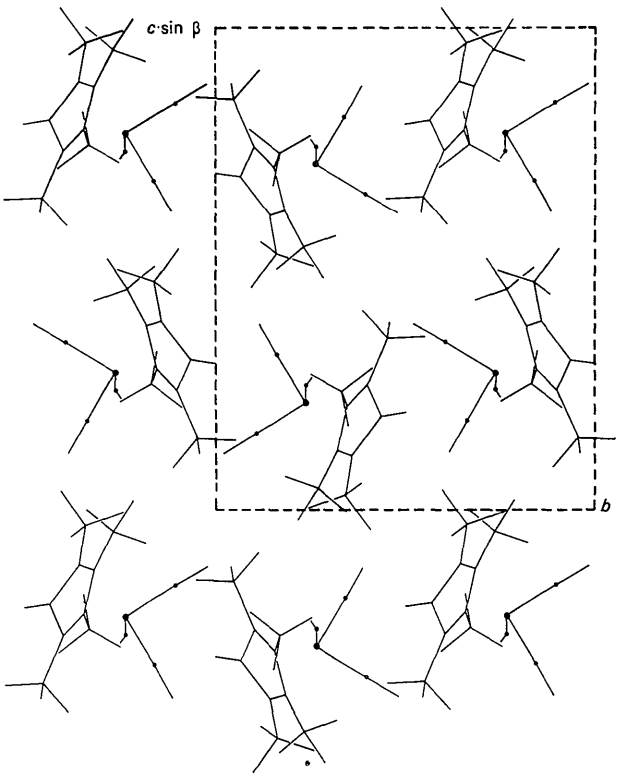


Fig 6. The crystal structure projected on to (100).

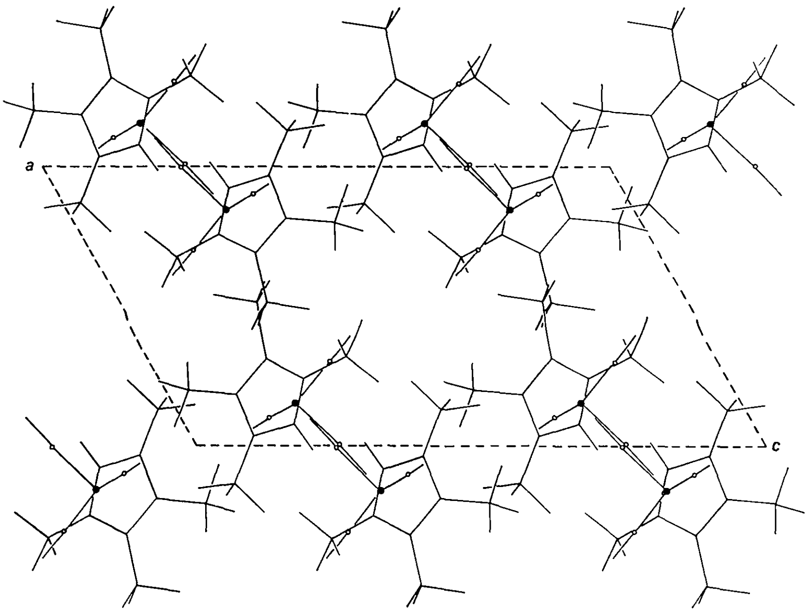


Fig. 7. The crystal structure projected onto (010).

Table 7. *Interatomic non-bonded distances less than* 3·5 Å

Atoms	Symmetry	Distance	Atoms	Symmetry	Distance
C(1)–O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	2·84 Å	O(3) –O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·46 Å
C(2)–O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·15	F(5)	$(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·37
F(1)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·32	F(8)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·05
F(4)	$(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·46	F(11)	$(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·12
C(3)–O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·20	O(4)—F(8)	$(-x, 1-y, -z)$	3·43
F(8)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·34	F(1)—F(7)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·36
C(4)–F(12)	$(-x, 1-y, -z)$	3·42	F(9)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·22
C(7)–F(12)	$(-x, 1-y, -z)$	3·43	F(2)—F(3)	$(1-x, 1-y, 1-z)$	3·47
C(8)–F(12)	$(-x, 1-y, -z)$	3·36	F(6)	$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·28
O(1)–O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·07	F(9)	$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	2·87
F(2)	$(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·42	F(3)—F(10)	$(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·38
F(5)	$(x-1, y, z)$	3·23	F(6)—F(10)	$(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·33
F(6)	$(x-1, y, z)$	3·12	F(12)	$(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·37
F(7)	$(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·02	F(8)—F(11)	$(-x, 1-y, -z)$	3·38
O(2)–O(2)	$(-x, -y, -z)$	3·41	F(12)	$(-x, 1-y, -z)$	3·26
O(4)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·33	F(12)–F(12)	$(-x, 1-y, -z)$	3·34
F(1)	$(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	2·85			
F(4)	$(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3·14			
F(7)	$(-x, -y, -z)$	3·10			

Table 8. *Atomic vibration axes* (*length and direction cosines relative to a,b,c′*)

Atom	Major axis		Medium axis		Minor axis	
	Length	Direction cosines	Length	Direction cosines	Length	Direction cosines
Fe	0·209 Å	0·9022 0·1886 0·3880	0·197 Å	0·3062 −0·9135 −0·2679	0·189 Å	−0·3039 −0·3605 0·8819
	Major axis		Medium axis		Minor axis	
C(1)	0·38	(0·525, 0·841, 0·132)	0·24	(−0·014, −0·146, 0·989)	0·18	(0·851, −0·521, −0·064)
C(2)	0·28	(0·967, 0·102, 0·234)	0·25	(−0·255, 0·422, 0·870)	0·18	(−0·009, −0·901, 0·434)
C(3)	0·28	(−0·001, −0·534, −0·845)	0·24	(0·590, −0·683, 0·431)	0·19	(0·807, 0·499, −0·316)
C(4)	0·33	(0·622, −0·303, 0·722)	0·20	(0·718, 0·589, −0·371)	0·14	(0·313, −0·749, −0·584)
C(5)	0·29	(0·850, −0·335, −0·407)	0·21	(−0·009, 0·763, −0·647)	0·17	(−0·527, −0·553, −0·645)
C(6)	0·34	(0·972, −0·237, 0·010)	0·23	(−0·193, −0·817, −0·543)	0·14	(−0·137, −0·526, 0·839)
C(7)	0·35	(0·744, 0·040, 0·667)	0·20	(−0·610, 0·451, 0·652)	0·13	(−0·275, −0·892, 0·359)
C(8)	0·27	(0·935, 0·060, −0·350)	0·23	(0·162, 0·806, 0·570)	0·16	(−0·316, 0·589, −0·744)
C(9)	0·33	(−0·031. 0·948, −0·318)	0·28	(0·399, −0·280, −0·873)	0·21	(0·916, 0·154, 0·369)
C(10)	0·47	(0·150, −0·746, −0·649)	0·35	(0·035, 0·660, −0·751)	0·01	(−0·988, −0·089, −0·125)
C(11)	0·44	(0·855, 0·518, 0·015)	0·27	(0·399, −0·678, 0·618)	0·23	(−0·330, 0·522, 0·786)
C(12)	0·35	(0·899, −0·317, −0·302)	0·28	(0·316, 0·947, −0·053)	0·19	(−0·303, 0·048, −0·952)
O(1)	0·32	(0·734, −0·051, 0·677)	0·28	(−0·664, −0·265, 0·699)	0·27	(0·144, −0·963, −0·228)
O(2)	0·36	(0·969, −0·248, 0·018)	0·31	(0·118, 0·394, −0·911)	0·25	(−0·219, −0·885, −0·411)
O(3)	0·38	(−0·032, 0·846, 0·532)	0·28	(0·994, 0·083, −0·071)	0·24	(−0·104, 0·526, −0·844)
O(4)	0·30	(−0·036, −0·322, 0·946)	0·29	(0·868, 0·459, 0·189)	0·23	(−0·495, 0·828, 0·263)
F(1)	0·48	(0·314, −0·865, 0·392)	0·35	(0·936, 0·351, 0·023)	0·24	(0·158, −0·360, −0·920)
F(2)	0·52	(0·864, −0·454, 0·215)	0·35	(0·392, 0·341, −0·854)	0·19	(−0·314, −0·823, −0·473)
F(3)	0·48	(0·936, −0·033, −0·351)	0·34	(0·036, 0·999, 0·001)	0·26	(−0·351, 0·014, −0·936)
F(4)	0·74	(0·145, 0·624, −0·768)	0·47	(0·544, −0·699, −0·465)	0·17	(0·826, 0·351, 0·441)
F(5)	0·71	(−0·028, −0·796, −0·605)	0·44	(0·242, −0·592, 0·769)	0·23	(0·970, 0·125, −0·209)

Table 8 (*cont.*)

Atom	Major axis		Medium axis		Minor axis	
	Length	Direction cosines	Length	Direction cosines	Length	Direction cosines
Fe	0·209 Å	0·9022 0·1886 0·3880	0·197 Å	0·3062 −0·9135 −0·2679	0·189 Å	−0·3039 −0·3605 0·8819

Atom	Major axis	Medium axis	Minor axis
F(6)	0·72 (0·253, −0·575, −0·778)	0·37 (0·414, 0·792, −0·450)	0·17 (−0·874, 0·208, −0·438)
F(7)	0·52 (0·757, 0·653, 0·027)	0·46 (0·569, −0·679, 0·465)	0·22 (0·321, −0·337, −0·885)
F(8)	0·64 (0·784, 0·101, 0·613)	0·33 (0·203, −0·974, −0·099)	0·17 (0·587, 0·202, −0·784)
F(9)	0·52 (0·717, 0·637, 0·284)	0·29 (0·382, −0·699, 0·605)	0·20 (−0·584, 0·325, 0·744)
F(10)	0·53 (0·905, −0·088, −0·415)	0·35 (−0·129, 0·875, −0·467)	0·20 (−0·404, −0·476, −0·781)
F(11)	0·51 (0·315, 0·887, −0·339)	0·37 (−0·540, 0·461, 0·705)	0·22 (−0·781, 0·039, −0·623)
F(12)	0·45 (0·819, −0·489, −0·301)	0·35 (−0·545, −0·826, −0·141)	0·21 (−0·180, 0·279, −0·943)

References

Bennett, M. J., Churchill, M. R., Gerloch, M. & Mason, R. (1964). *Nature, Lond.* **201**, 1318.

Boston, J. L., Grim, S. O. & Wilkinson, G. (1963). *J. Chem. Soc.* p. 3468.

Boston, J. L., Sharp, D. W. A. & Wilkinson, G. (1960). *Chem. and Ind.* p. 1358.

Boston, J. L., Sharp, D. W. A. & Wilkinson, G. (1962). *J. Chem. Soc.* p. 3488.

Churchill, M. R. & Mason, R. (1963). *Proc. Chem. Soc.* p. 365.

Churchill, M. R. & Mason, R. (1964*a*). *Proc. Roy. Soc.* A**279**, 191.

Churchill, M. R. & Mason, R. (1964*b*). *Proc. Chem. Soc.* p. 226.

Churchill, M. R. & Mason, R. (1966*a*). *Proc. Roy. Soc.* A, **292**, 61.

Churchill, M. R. & Mason, R. (1966*b*). *Advances in Organometallic Chemistry.* In the press.

Dickens, B. & Lipscomb, W. N. (1962). *J. Chem. Phys.* **37**, 2084.

Dickson, R. S. & Wilkinson, G. (1964). *J. Chem. Soc.* p. 2699.

Gerloch, M. & Mason, R. (1964). *Proc. Roy. Soc.* A,**279,** 170.

Jacobsen, R. A., Wunderlich, J. A. & Lipscomb, W. N. (1961). *Acta Cryst.* **14**, 598.

Kettle, S. F. A. & Mason, R. (1966*a*). *J. Organometallic Chem.* **5**, 97.

Kettle, S. F. A. & Mason, R. (1966*b*). *J. Organometallic Chem.* In the press.

Mills, O. S. & Robinson, G. (1963). *Acta Cryst.* **16**, 758.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Oxford Univ. Press.

Schrauzer, G. N. (1965). *Inorg. Chem.* **4**, 264.