Conglomerate crystallization in organometallic compounds V [☆]. The crystal and molecular structure

$$of\ \Big(\ \underset{\rule{3cm}{0.4pt}}{C_5H_4-CH_2-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-Fe}(CO)\Big)_2$$
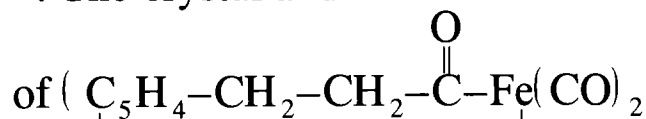
Ivan Bernal [a],[*], Heinz Vogt [b]

[a] Chemistry Department, University of Houston, Houston, TX 77204-5641, USA
[b] Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Abstract

The compound crystallizes in the enantiomorphic space group $P2_12_12_1$ with cell constants of $a = 6.883(2)$, $b = 11.123(2)$ and $c = 11.941(2)$ Å, $V = 914.21$ Å^3 and d(calc; $z = 4$ mol (unit cell)$^{-1}$) $= 1.765$ g cm^{-3}. Data were collected over the range of $4° \leqslant 2\theta \leqslant 50°$, corrected for Lorentz–polarization and absorption effects, which produced a total of 2312 reflections; of these, 1314 were unique and had intensities above background (e.g. $I \geqslant 3\sigma(I)$) and were used in the solution and refinement of the structure.

The structure was solved by Patterson methods and the phasing from the heavy atom produced all the other non-hydrogen atoms in a difference map. The Cp ring was refined as a rigid body and the hydrogen atoms were added at idealized positions (C–H, 0.95 Å). Refinement converged and the correct enantiomorph was selected by testing suitable Bijvoet pairs. The final refinement of the structure, using the correct enantiomorph gave discrepancy indices of $R(F) = 0.0288$ and $R_W(F) = 0.0250$.

The novelty of this study is the fact that the molecule is chiral owing, exclusively, to the non-planarity of the ring fragment defined by the $(C_5H_4-CH_2-C(=O)-Fe$ portion of the molecule, of which the $C-C(H_2)-C(=O)-Fe$ is helical. For the sample used in this study, the torsional angle of this fragment $(C(1)-C(10)-C(9)-C(8))$ is $\delta(+38.9°)$.

Keywords: Iron; X-ray structure; Conglomerate crystallization

1. Introduction

The compound was unexpectedly obtained during an attempt to prepare a bridged ($-CH_2-CH_2-$) ferrocene. Its crystal structure demonstrated the interesting and initially unexpected result that the compound crystallizes as a conglomerate; however, although not noted in studies of related species, there are a variety of related Cp–Fe compounds which display the same conglomerate crystallization behavior.

2. Experimental details

2.1. Synthesis

Compound I was prepared by reacting $C_5H_4(CH_2)_2$ with $Fe_2(CO)_9$ as described earlier [2].

2.2. Crystallography

Data were collected with an Enraf–Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification [3] of the SDP-PLUS software package [4]. The crystal chosen was centered with data in the $22° \leqslant 2\Theta \leqslant 36°$ range and examination of the cell constants, absences and Niggli matrix [5] unambiguously showed it to crystallize in space group $P2_12_12_1$. Details of data collection and data processing for I are summarized in Table 1. The intensity data

---

[☆] Dedicated to Professor Henri Brunner on the occasion of his 60th birthday. For parts I–IV see Refs. [1a]–[1d] respectively.

[*] Corresponding author.

Table 1

Summary of data collection and processing parameters

Space group	$P2_12_12_1$
Cell constants	
a (Å)	6.883(2)
b (Å)	11.123(2)
c (Å)	11.941(2)
Cell volume V (Å^3)	914.21
Molecular formula	$C_{10}H_8O_3Fe$
Molecular weight (g mol^{-1})	243.02
Density (Calc. $z = 4$ mol cell^{-1}) (g cm^{-3})	1.765
Radiation employed	Mo Kα ($\lambda = 0.71073$ Å)
Absorption coefficient μ (cm^{-1})	12.38 cm^{-1}
Relative transmission coefficients	0.8642–0.9985
Data collection range $2\theta(°)$	4–50
Scan width $\Delta\theta$	$1.0 + 0.35 \tan \theta$
Maximum scan time (s)	240
Scan speed range (° min^{-1})	0.38–5.03
Total number of data collected	2312
Number of data used in refinement [a]	1314
Total number of variables	101 [b]
$R = \Sigma \|F_o\| - \|F_c\| / \Sigma \|F_o\|$	0.0288
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma \|F_o\|^2]^{1/2}$	0.0250
Weights used w	$[\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 998 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry-related standards or did not meet the criterion that $I \geqslant 3s(I)$.

[b] The Cp ring was refined as a rigid body; see discussion for this point.

Table 2

Determination of the absolute configuration via the Bijvoet test

Indices			$I(+++)$ [a]	$I(---)$	Observed ratio [b]	Calculated ratio [c]	Result
5	3	1	5292	5677	0.97	1.063	Invert
3	2	1	4185	5121	0.90	1.095	Invert
2	2	1	12756	13818	0.96	1.061	Invert
1	2	1	4284	3782	1.06	0.938	Invert
3	1	1	27726	29052	0.98	1.037	Invert
1	2	2	4716	4468	1.03	0.964	Invert
2	5	3	5254	4683	1.06	0.931	Invert
3	4	3	12232	10424	1.06	0.953	Invert
1	3	3	17857	16974	1.03	0.976	Invert
1	2	4	20087	21587	0.96	1.047	Invert
2	2	4	5093	4649	1.05	0.960	Invert
4	3	4	7871	8708	0.95	1.026	Invert
1	3	4	3883	3515	1.05	0.944	Invert
1	4	4	17990	18777	0.98	1.021	Invert
1	6	4	4774	4395	1.04	0.966	Invert
3	6	5	3248	3521	0.96	1.050	Invert
3	2	5	25792	24134	1.03	0.954	Invert
1	2	6	11153	12054	0.96	1.053	Invert
1	3	6	3041	3302	0.96	1.092	Invert

[a] $I(+++)$ and $I(---)$ are the measured intensities for reflections of indices h, k, l and $-h, -k, -l$ respectively.

[b] Since we were comparing experimental values with calculated values of $F(h, k, l)$ and of $F(-h, -k, -l)$, the fourth column gives the square root of the ratio of the values in the second and third columns.

[c] Note that the values listed in the fourth column are almost exactly the inverse of those in the fifth column, for a total of 19 independent measurements.

were corrected for absorption using empirical curves derived from φ scans [3,4] of suitable reflections. The scattering curves were taken from the compilation of Cromer and Waber [6].

The structure was solved from the Patterson map using iron as the heavy atom. After refinement of the scale factor and the positional parameters of the Fe, a difference Fourier map produced all the non-hydrogen atoms. The absolute configuration of the molecule was determined from comparison of a suitable set of Bijvoet pairs whose values are listed in Table 2. Hydrogen atoms of were added at idealized positions (C–H, 0.95 Å). Treating the Cp ring atoms as a rigid body and adding the hydrogen atoms as fixed contributions ($B = 5.0$ Å^2) resulted in refinement of the overall structure to final $R(F)$ and $R_w(F)$ factors listed in Table 1. Atomic coordinates are listed in Table 3; bond lengths, angles and torsional angles are listed in Table 4. Anisotropic thermal paramenters and structure factor tables have been deposited as supplementary material.

3. Results

The stereochemistry of the molecule is shown in Fig. 1 which displays the labelling system used in the

Table 3

Atomic coordinates

Atom	x/a	y/b	z/c
Fe	0.12488(7)	−0.52242(4)	−0.44574(4)
O(6)	0.4046(4)	−0.6190(2)	−0.2883(2)
O(7)	0.4243(4)	−0.4207(3)	−0.5886(2)
O(8)	0.2514(4)	−0.3129(3)	−0.3236(3)
C(6)	0.2928(5)	−0.5838(3)	−0.3498(3)
C(7)	0.3061(5)	−0.4589(3)	−0.5321(3)
C(8)	0.1189(6)	−0.3782(3)	−0.3489(3)
C(9)	−0.0852(5)	−0.3562(4)	−0.2984(3)
C(10)	−0.2426(6)	−0.3863(4)	−0.3836(3)
C(1)	−0.178(0)	−0.497(0)	−0.446(0) [a]
C(2)	−0.129(0)	−0.610(0)	−0.395(0)
C(3)	−0.038(0)	−0.682(0)	−0.478(3)
C(4)	−0.025(0)	−0.613(0)	−0.578(0)
C(5)	−0.108(0)	−0.499(0)	−0.557(0)
H(2)	−0.159(0)	−0.637(3)	−0.310(0)
H(3)	0.013(0)	−0.773(0)	−0.468(0)
H(4)	0.037(0)	−0.643(0)	−0.657(0)
H(5)	−0.120(0)	−0.426(0)	−0.616(0)
H(9A)	−0.098(1)	−0.263(0)	−0.274(0)
H(9B)	−0.104(1)	−0.412(0)	−0.225(0)
H(10A)	−0.261(1)	−0.312(0)	−0.441(0)
H(10B)	−0.378(1)	−0.404(3)	−0.341(0)
CPC [b]	−0.095	−0.580	−0.491

[a] The Cp atoms were refined as a rigid body. See text.

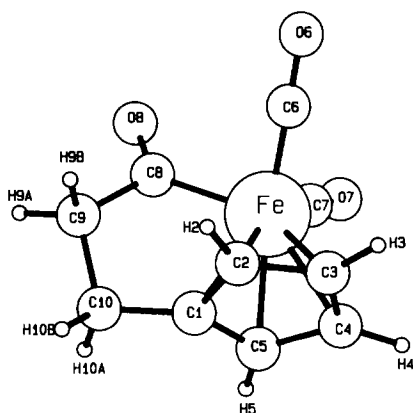[b] CPC, centroid of the cyclopentadienyl ring.

Fig. 1. A view of the molecule showing the numbering system used in labeling the atoms. Note the helical nature of the $Cp(C)-CH_2-CH_2-CO-$ fragment attached to the iron atom.

crystallographic study whose coordinates are presented in Table 3. As may be observed in Fig. 1, the acyl-containing ring is not planar, as is obvious from the position of C(9) with respect to the other atoms of the ring, the value of the C(8)–C(9)–C(10)–C(1) torsional angle being 38.9°. This result is quite interesting since this conformational dissymmetry is the only feature of the molecule which carries chiral information. The two Fe–C–O fragments are essentially linear, their angular values being 177.3(2)° and 178.4(2)°. As expected, the

angular value of the Fe–C(8)–O(8) fragment is (128.3(2)°), nearly that of a trigonal central carbon atom. Other features of the molecule are non-remarkable and agree with values of related molecules available in the literature.

For example, a closely related compund reported by Churchill and Wang [7] differs only by the fusion of a butadiene fragment onto what is the CH_2-CH_2- fragment of the acyl ligand. They found the $Fe(CO)_2$ portion of their molecule to have Fe–C distances of 1.753(3) and 1.762(4) Å. Ours are 1.765(2) and 1.766(2) Å. The Fe–C(=O)–Fe–C and C=O distances are 1.9596(30) and 1.206(4) Å, while ours are 1.978(2) and 1.204(2) Å respectively, and the Fe–Cp portion of the molecule is basically identical; however, this comparison is not so valid since we used a rigid-body refinement which idealizes the Cp ring. Despite this minor caveat, the compounds differ little in their basic stereochemistry, having closely related distances and angles except for the torsional angle at the acyl fragment. The torsional angle of theirs is only 7.6° while ours is nearly 40°. This, apparently, has a profound effect in the crystallization pathway selected by the two molecules since theirs crystallizes as a racemate ($P2_1/c$) while ours crystallizes as a conglomerate in the enantiomorphic space group $P2_12_12_1$.

The packing diagram of our compound is shown in Fig. 2 (an *a* projection), which shows the molecules

Table 4
Bond lengths (Å), angles (°) and torsional angles (°)

Bond lengths			
Fe...C(1)	2.102(1)	Fe...C(6)	1.765(2)
Fe...C(2)	2.087(1)	Fe...C(7)	1.766(2)
Fe...C(3)	2.135(1)	Fe...C(8)	1.978(2)
Fe...C(4)	2.140(1)	Fe...Cp [a]	1.731(1)
Fe...C(5)	2.095(1)	C(8)...C(9)	1.548(2)
C(6)...O(6)	1.134(2)	C(9)...C(10)	1.524(2)
C(7)...O(7)	1.139(2)	C(10)...C(1)	1.502(2)
C(8)...O(8)	1.204(2)		

Bond angles			
Fe–C(6)–O(6)	177.3(2)	C(8)–C(9)–C(10)	110.5(1)
Fe–C(7)–O(7)	178.4(2)	C(9)–C(10)–C(1)	107.3(1)
Fe–C(8)–O(8)	128.3(2)	C(9)–C(8)–O(8)	119.6(2)
C(6)–Fe–C(7)	94.1(1)	Fe–C(8)–C(9)	112.0(1)
C(6)–Fe–C(8)	87.0(1)	C(7)–Fe–C(8)	91.8(1)

Selected torsional angles			
C(1)–Cp–Fe–C(6)	114.48	C(4)–Cp–Fe–C(7)	32.49
C(1)–Cp–Fe–C(7)	− 110.05	C(4)–Cp–Fe–C(8)	147.44
C(1)–Cp–Fe–C(8)	3.91	C(5)–Cp–Fe–C(6)	− 174.11
C(2)–Cp–Fe–C(6)	41.43	C(5)–Cp–Fe–C(7)	− 39.64
C(2)–Cp–Fe–C(7)	176.20	C(5)–Cp–Fe–C(8)	75.31
C(2)–Cp–Fe–C(8)	− 68.64	Fe–C(8)–C(9)–C(10)	− 39.97
C(3)–Cp–Fe–C(6)	− 30.01	Cp–Fe–C(6)–O(6)	− 172.13
C(3)–Cp–Fe–C(7)	104.46	Cp–Fe–C(7)–O(7)	− 77.42
C(3)–Cp–Fe–C(8)	− 140.58	Cp–Fe–C(8)–O(8)	− 166.79
C(4)–Cp–Fe–C(6)	− 101.98	Cp–Fe–C(8)–C(9)	16.32

[a] Cp is the center of the Cp ring. Also, the C–C distances of the rigid CP ring were fixed at 1.42 Å and their C–H distances at 1.08 Å.
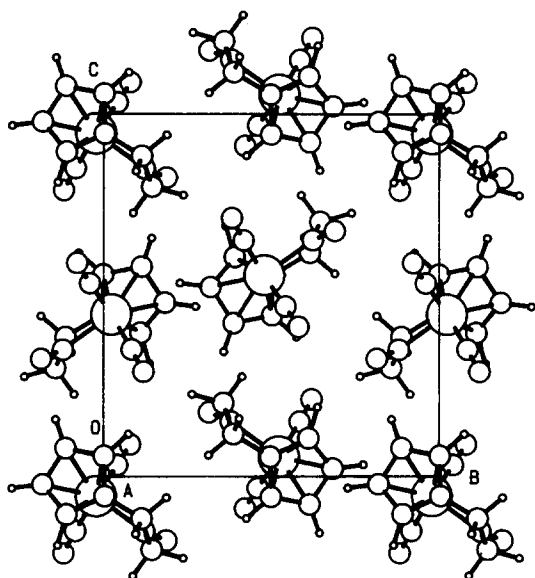
Fig. 2. The packing of the molecules in the unit cell. This is an *a* projection selected because it illustrates the helical strings formed by the molecules as the pack in the b and c directions. This packing phenomenon is best illustrated by following the orientation of the Cp rings as one moves to successive molecules along either of those directions.

arrayed in strings running along the *b* and *c* axes of the crystal. The molecules interact with one another along the *c* direction in a rather interesting fashion which is clarified by Fig. 3. This latter figure depicts only the molecules in the central row of the unit cell shown in Fig. 2 and shows the hydrogen contact between the acyl (C=O) oxygen and hydrogen on the Cp ring (O(8) · · · H(4), 2.514 Å) of the molecule directly above.
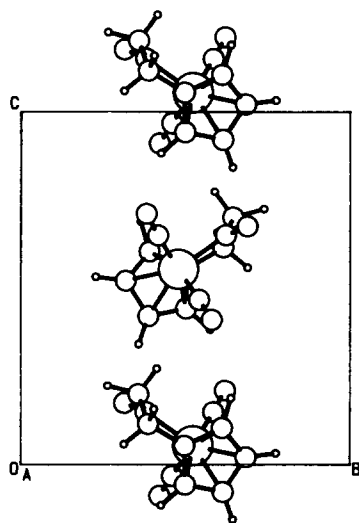

Fig. 3. A magnified view of one of the strings running along the c axis of the crystal. The spiraling arrangement of the Cp rings or of the acyl fragments, as one progresses from bottom to top, is rather evident. We know of no example of conglomerate crystallization in which such a spiraling effect is not present; this statement is true for organic, organometallic and coordination compounds.

This interaction is repeated infinitely along the *c* direction and causes the formation of spiraling strings in which the spiral twist is best illustrated by observing the positioning of the acyl ring along a given string. In this particular case, the central row clearly shows that the sense of the spiral is right handed as one moves from bottom to top. Thus, not only are molecules of a given crystal of the same chirality (their acyl rings are all δ or λ at the O=C–CH_2–CH_2–C(Cp) fragment) but also, in fact, there is a far more subtle source of chirality in the solid state, and that is the infinite spiral nature of the strings formed by the hydrogen-bonded interaction mentioned above.

4. Discussion

In the past, we have observed conglomerate crystallization in four other cases of organometallic compounds [1]. However, their nature was so disparate that we could not offer any sensible reason why they may have crystallize thus. The first example [1a] was a dinuclear cobalt compound of composition Cp_2Co_2-$(CO_2)_2$(μ-CH_2) which was one of the earliest examples of an (*m*-methylidine) dinuclear organometallic. In that paper, as in the subsequent papers [1], we refrained from speculation about the origin of the crystallization phenomenon but pointed out that the Co centers were homochiral (*RR* or *SS*, depending on the crystal chosen). The second example [1b] was [1-(diethylamino)-2-diphenylphosphino)ethane]Mo(CO)$_4$ whose Mo atom is a chiral center. In the third example, (C_5H_5)Mo(CO)$_2$(2-benzoylpyridine-1-phenylethylimine) there are two correlated chiral centers: the Mo atom and the aliphatic carbon of the imine fragment. The fourth case of conglomerate crystallization is a ferrocene whose Cp rings are linked by a [–CH_2–S–(CH_2)$_2$–O–(CH_2)$_2$–O–(CH_2)$_2$–S–CH_2–] bridge but the compound has no chiral centers. Interestingly, in the same paper [1d], we reported the structure of a related ferrocene whose terminal –CH_2– are methylated, thus making them chiral centers. The structure recorded shows the compounds to crystallize in the polar but not enantiomorphic space group *Fdd2* and that, for a given molecule, the two centers are homochiral (*RR* or *SS*). These data describe interesting facts concerning the crystallization path selected by a few organometallics studied in our laboratory; however, the diversity of their compositions and structures makes it difficult to provide anything other than facts.

The discovery that our compound crystallizes as a conglomerate provided an unexpected opportunity to provide a hint as to the requirements for an organometallic molecule such as ours to select such a crystallization pathway, as opposed to the far more common racemic pathway. This was possible by the

fortunate coincidence that Churchill and Wang [7] studied the structure of a compund which is a derivative of ours, namely one in which the chiral $O=C-CH_2-CH_2-C(Cp)$ fragment of ours has butadiene fused to it, producing cyclohexadiene.

The resulting cyclobutadiene ring has the following characteristics: (a) the two chiral methylene carbon atoms are an *R,S* pair giving rise to a mesomeric species; (b) the torsional angle at the ethylene fragment is only 7.6°, making the barrier to inversion extremely low and thus resulting in a fragment nearly devoid of dissymmetry; (c) the presence of the bulkier cyclobutadiene ring reduces the chances that the acyl oxygen interacts as strongly with the hydrogen atoms of the Cp ring of an adjacent molecule as in our case, thus eliminating the chance of spiral string formation. Interestingly, this appears to be the source of the difference between the crystallization behaviors of these closely related pair of molecules. If correct, we have begun to understand some of the factors affecting the selection of crystallization pathway in such molecules, and observations such as the above leave as the only alternative that the crystallization pathway is a conformationally driven phenomenon. Additional evidence that these factors are important are the following observations taken from the existing literature on CpFe compounds.

Churchill and Lin [8] reported the stereochemistry of bis(pentalenyl)iron which crystallizes in the enantiomorphic space group $P2_12_12_1$. Angelakos, et al. [9] determined the structure of a siloxane-bridged [n]ferrocenophane belonging also to the space group $P2_12_12_1$. In both cases the bridges are dissymmetric; in the former there is a twisted H–C–C–H fragment resembling the stereochemistry of hydrogen peroxyde while in the latter the ferrocene–Si(1)–O–Si(2)–ferrocene fragment is twisted in a fashion similar with that observed here. Thus, in none of the three compounds is there an asymmetric center but, in all three, the sole source of dissymmetry is in the bridge from the Cp ring to some other anchoring point.

Green et al. [10] determined the structure of tricarbonyl(isoprene)iron-hexafluoropropene (space group, $P2_12_12_1$) and found it to have a $(OC)_2Fe-C$ fragment somewhat related to ours; however, the molecule bears no Cp ring. Yet, it crystallizes as a conglomerate and may provide useful information concerning factors playing a role in the selection of crystallization pathway. Hillman et al. [11] reported that (μ^2-oxo)-bis-(tris-(μ^2-trimethylene)-ferrocene crystallizes in space group $P2_1$. The latter contains a peroxo bridge linking the two ferrocenes through a pair of methylenic fragments of the (μ^2-trimethylene) linkages, which renders the compound chiral since the –CH–O–O–CH–fragment is helical.

Finally, Fryzuk et al. [12] reported recently the structure of a CpZr compound having a Cp with a phosphine substituent which forms a Zr–P bond, giving rise to a

conformationally dissymmetric ring of composition Cp(C)–Si–C–P–Zr. This compound also crystallizes as a conglomerate in space group $P2_12_12_1$.

In conclusion, it appears that (a) ferrocene and ferrocene-like molecules attached to dissymmetric fragments have a noticeable tendency to form conglomerates and (b) destroying the dissymmetry (compare our compound and that of Churchill and coworkers) appears to influence the outcome and give rise to racemates. How general these preliminary suggestions are remains to be seen as more data appear in the literature. However, at least it provides a working suggestion to be tested by interested researchers. In the recent past, as noted above, examples of organometallics crystallizing as conglomerates belonged to such a broad classes of compounds as to render it an impossible task to find some common ground for analysis. Now, we have at least a clue as to what to look for in specific classes of compounds.

Acknowledgments

References and notes

[1] We have previously observed conglomerate crystallization in organometallics of various types: (a) M. Creswick, I. Bernal, W.A. Herrmann and I. Steffl, *Chem. Ber., 113* (1980) 1377; (b) G.R. Dobson, I. Bernal, G.M. Reisner, C.B. Dobson and S.E. Mansour, *J. Am. Chem. Soc., 107* (1985) 525; (c) I. Bernal, W.H. Ries, H. Brunner and D.K. Rastogi, *J. Organomet. Chem., 290* (1985) 353; (d) I. Bernal, G.M. Reisner, R.A. Bartsch, R.A. Holwerda and B.P. Czech, *Organometallics, 7* (1988) 253.

[2] P. Eilbracht, *Chem. Ber., 109* (1976) 1429.

[3] TEXRAY-230 is a 1985 modification of the SDP-PLUS [4] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77386, USA, for use with their automation of the CAD-4 diffractometer. Version of 1985.

[4] SDP-PLUS is the Enraf–Nonius Corporation X-ray diffraction data processing programs distributed by B.A. Frenz & Associates, 209 University Dr. East, College Station, TX 77840, USA. Version of 1985.

[5] R.B. Roof, A theoretical extension of the reduced cell concept in crystallography, *Rep. LA-4038*, 1969 (Los Alamos Scientific Laboratory).

[6] D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1975, Tables 2.2.8 and 2.3.1 respectively for the scattering factor curves and the anomalous dispersion values.

[7] M.R. Churchill and L.W.-Y. Wang, *Inorg. Chem., 14* (1975) 1680.

[8] M.R. Churchill and K.-K.G. Lin, *Inorg. Chem., 12* (19XX) 2274.

[9] C. Angelakos, D.B. Zamble, D.A. Foucher, A.J. Lough and I. Manners, *Inorg. Chem., 33* (1994) 1711.

[10] M. Green, B. Lewis, J.J. Daly and F. Sanz, *J. Chem. Soc., Dalton Trans.*, (1975) 1118.

[11] M. Hillman, B. Gordon, N. Dudek, R. Fajer, E. Fujita, J. Gaffney, P. Jones, A.J. Weiss and S. Takagi, *J. Organomet. Chem., 194* (1980) 229.

[12] M.D. Fryzuk, S.H. Mao, P.B. Duval and S.J. Rettig, *Polyhedron, 14* (1995) 11.