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MOLECULAR AND CRYSTAL STRUCTURE OF BIS(1,3-CYCLOHEXADIENE)MONOCARBONYLIRON

CARL KRÜGER AND YI-HUNG TSAY

Max-Planck-Institut für Kohlenforschung, 433 Mülheim (Ruhr), Lembkestraße 5 (Germany)

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SUMMARY

The crystal and the molecular structure of bis(1,3-cyclohexadiene)monocarbonyliron, $(C_6H_8)_2FeCO$, have been elucidated from three-dimensional X-ray diffraction data by Patterson and Fourier methods. The crystals used were orthorhombic, space group $P2_12_12_1$, with $a=17.089\pm0.005$, $b=8.495\pm0.004$ and $c=7.545\pm0.004$ Å, $Z=4$. Least-squares refinement of all positional and anisotropic thermal parameters using 1697 non-zero reflections resulted in a final R-value of 3.3%. The two 1,3-cyclohexadiene entities are bonded to the Fe in the same fashion as in related butadiene compounds.

The rings are arranged around the central atom with the saturated part pointing towards the carbonyl group. Although the diene entities are planar, a torsional angle of 3° remains in the strained ring systems. Both rings differ slightly in geometry as well as in their bonding to the iron atom.

EXPERIMENTAL

Bis(1,3-cyclohexadiene)monocarbonyliron, obtained from the photochemical reaction between pentacarbonyliron and 1,3-cyclohexadiene as described by Koerner von Gustorf *et al.*[1]*, crystallizes from pentane in orange-red needles.

Preliminary Weissenberg and precession photographs indicated orthorhombic symmetry, the space group being $P2_12_12_1$ ($h00=2n$, $0k0=2n$, $00l=2n$). Accurate cell dimensions, obtained by a least-squares treatment of the 2θ-values of 40 general high order reflections, measured on a diffractometer, are given in Table 1.

TABLE 1

CRYSTAL DATA OF $(C_6H_8)_2FeCO$

Space group $P2_12_12_1$
$a=17.089\pm0.005$ Å
$b=8.495\pm0.004$ Å
$c=7.545\pm0.004$ Å
d(calcd.) = $1.48\ g\cdot cm^{-3}$
$Z=4$

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* We are grateful to Dr. E. Koerner von Gustorf for supplying suitable crystals of the compound.

A complete set of intensity data of one octant was collected from a single crystal of the dimensions 0.43 × 0.35 × 0.93 mm, mounted along {001} on a Siemens–Hoppe computer-operated diffractometer. The data collecting procedure is described in detail elsewhere[2]. 1967 unique reflections were measured by a θ–2θ-scan technique, using Zr-filtered Mo-radiation ($\lambda=0.71069$). The intensities of 44 reflections were below the statistical noise of the detector and treated subsequently as unobserved.

TABLE 2

FINAL ATOMIC AND THERMAL PARAMETERS (× 10^4)

Atom	x	y	z	Atom	x	y	z
Fe	1268	1538	496	H_2	860	4574	440
C_1	1465	3309	2264	H_{3a}	1876	4712	−1500
C_2	1349	4033	642	H_{3b}	2174	5591	117
C_3	2045	4587	−423	H_{4a}	2849	3060	−1528
C_4	2711	3382	−353	H_{4b}	3113	3772	196
C_5	2488	1964	750	H_5	2811	1236	749
C_6	2083	2173	2333	H_6	2145	1441	3410
C_7	868	−270	2021	H_7	1112	−126	3059
C_8	1178	−951	478	H_8	1736	−1614	513
C_9	623	−1435	−991	H_{9a}	437	−2548	−636
C_{10}	−13	−231	−1277	H_{9b}	1003	−1578	−1929
C_{11}	67	1144	−12	H_{10a}	−21	100	−2406
C_{12}	272	849	1749	H_{10b}	−500	−528	−1205
C_{13}	1403	1592	−1797	H_{11}	−236	1983	−275
O	1494	1648	−3290	H_{12}	76	1396	2693
H_1	1090	3208	3178				

$\exp-(h^2\cdot u_{11}+\ldots k\cdot l\cdot u_{23})$

Atom	$u_{1,1}$	$u_{2,2}$	$u_{3,3}$	$u_{1,2}$	$u_{2,3}$	$u_{1,3}$
Fe	349	302	279	−9	13	19
C_1	658	504	447	−139	−146	108
C_2	524	348	628	7	−87	137
C_3	658	389	657	−87	60	163
C_4	457	595	658	−116	1	132
C_5	387	484	667	11	10	−49
C_6	558	582	440	−172	21	−135
C_7	751	467	432	−207	123	19
C_8	657	340	592	−24	83	−53
C_9	881	443	586	−222	−101	30
C_{10}	626	780	634	−251	14	−160
C_{11}	391	546	777	−46	16	−22
C_{12}	520	586	545	−178	−39	169
C_{13}	505	399	355	34	24	37
O	1083	798	361	106	17	134

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The position of the iron atom was determined from a three-dimensional Patterson map. One subsequent difference Fourier-synthesis revealed the two six-membered carbon rings and the carbonyl group. This model was refined isotropically for 5 cycles of block-diagonal least-squares by minimizing the quantity $[\Sigma w(|F_o|-|F_c|)^2]$. The conventional R-value dropped from 27 % to 16.6 %. The atomic scattering factors for neutral Fe, C, and O were taken from the tabulation of Cromer[3] while the values due to McWheeny[4] were used for hydrogen atoms. Ten more cycles of weighted anisotropical refinement of parameters decreased the R-factor to 6.6 %. At this stage, all sixteen hydrogen atoms were located at proper positions in a Difference-Fourier map. Five additional cycles of refinement of all positional parameters and temperature factors (anisotropic for non-hydrogen atoms, isotropic for hydrogen atoms) reduced the discrepancy factor to a final value of 3.3 %, including unobserved data. The final atomic and thermal parameters are listed in Table 2*.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A perspective drawing of the molecule $(C_6H_8)_2FeCo$ is shown in Fig. 1. Bond lengths and bond angles, together with their standard deviations, are listed in Table 3 and Fig. 2. The central iron atom is five-coordinated, with one carbonyl and the two butadiene groups of the 1,3-cyclohexadiene-moiety as ligands. They approximate to a tetragonal pyramid with the carbonyl carbon (C_{13}) located at the vertex, and four π-bonds towards the olefin forming the base. This arrangement corresponds with a d^2sp^2-hypridisation of the iron atom, which is, although less

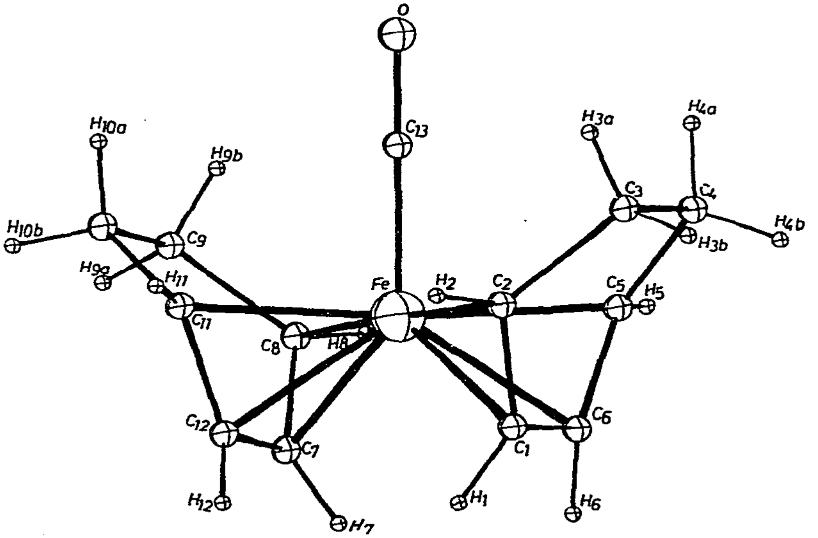

Fig. 1

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* A list of the structure factors may be obtained from the authors on request.

TABLE 3

BOND LENGTHS AND ANGLES OF THE HEAVY ATOMS

Bond lengths (Å) and standard deviations (× 10^4)		Bond angles (°) and standard deviations (× 10^2)	
Fe–C_1	2.0380(43)	C_1–Fe–C_{13}	127.36(18)
Fe–C_2	2.1266(34)	C_1–Fe–C_6	41.15(17)
Fe–C_5	2.1235(34)	C_2–Fe–C_{13}	90.90(19)
Fe–C_6	2.0366(40)	C_5–Fe–C_{13}	87.45(17)
Fe–C_7	2.0368(43)	C_5–Fe–C_6	39.01(17)
Fe–C_{11}	2.1147(35)	C_6–Fe–C_{13}	125.24(16)
Fe–C_{12}	2.0329(41)	C_7–Fe–C_{13}	128.57(18)
Fe–C_{13}	1.7472(33)	C_7–Fe–C_{12}	40.47(18)
Fe–C_8	2.1195(34)	C_{11}–Fe–C_{13}	87.22(17)
		C_{11}–Fe–C_{12}	39.28(18)
		C_{12}–Fe–C_{13}	125.29(16)
		C_1–Fe–C_2	38.75(18)
		C_1–Fe–C_8	138.84(18)
		C_8–Fe–C_{13}	91.67(18)
		C_8–Fe–C_{11}	76.73
		C_1–Fe–C_7	104.07(17)
		C_1–Fe–C_{12}	92.70(17)
		C_1–Fe–C_{11}	113.31(18)
		C_2–Fe–C_8	177.42(18)
		C_2–Fe–C_5	76.22
		C_2–Fe–C_7	138.09(17)
		C_2–Fe–C_{12}	108.49(17)
		C_2–Fe–C_{11}	103.25(16)
		C_5–Fe–C_8	104.00(16)
		C_5–Fe–C_7	114.06(18)
		C_5–Fe–C_{12}	146.03(18)
		C_5–Fe–C_{11}	174.64(19)
		C_6–Fe–C_8	108.58(17)
		C_6–Fe–C_7	92.62(17)
		C_6–Fe–C_{11}	146.00(18)
		C_6–Fe–C_{12}	109.47(17)
C_1–C_2	1.3843(62)	C_1–C_2–C_3	119.65(36)
C_2–C_3	1.5117(60)	C_2–C_3–C_4	111.03(33)
C_3–C_4	1.5303(57)	C_3–C_4–C_5	111.36(32)
C_4–C_5	1.5137(61)	C_4–C_5–C_6	119.70(37)
C_5–C_6	1.3913(60)	C_5–C_6–C_1	114.92(36)
C_6–C_1	1.4319(60)	C_6–C_1–C_2	115.96(36)
C_7–C_8	1.4038(61)	C_7–C_8–C_9	118.84(38)
C_8–C_9	1.5157(66)	C_8–C_9–C_{10}	111.78(38)
C_9–C_{10}	1.5092(73)	C_9–C_{10}–C_{11}	111.55(38)
C_{10}–C_{11}	1.5152(74)	C_{10}–C_{11}–C_{12}	118.90(42)
C_{11}–C_{12}	1.3962(66)	C_{11}–C_{12}–C_7	116.21(38)
C_{12}–C_7	1.4077(62)	C_{12}–C_7–C_8	115.47(38)
C_{13}–O	1.1381(45)	O–C_{13}–Fe	179.08(39)

common, energetically equivalent[5] to the regular dsp^3-hybridisation. The Fe atom is 0.032 Å displaced from the best plane (see Table 3) through the atoms C_2, C_5, C_8, and C_{11}. The Fe–C_{13} (carbonyl), the C_{13}–oxygen distances as well as the angle Fe–C–O, 179.1°, compare very well with those found in other carbonyl iron complexes[7].

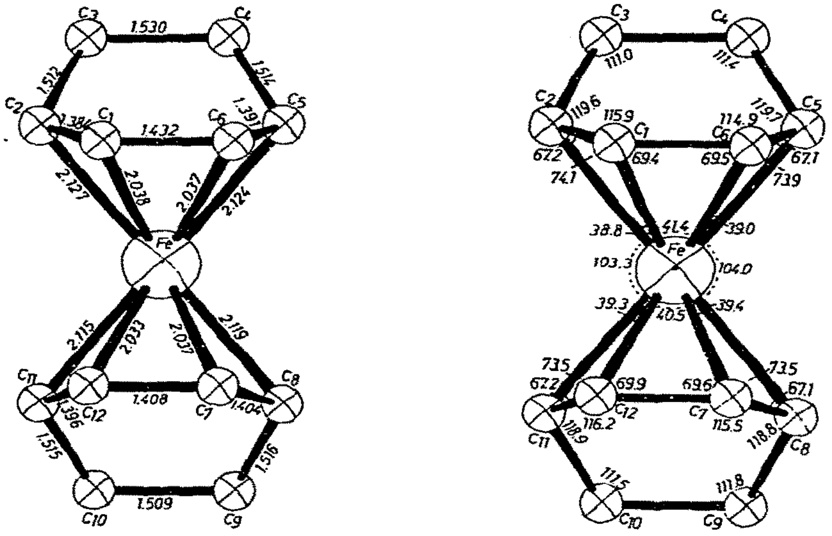


Fig. 2. Bond lengths and angles within the cyclohexadiene rings as viewed down the axis Fe–C–O.

All carbon atoms "bonded" to iron may be classified into two groups: four [Fe–C_n (where $n=2$, 5, 8, 11) with bond lengths in the range of 2.115 to 2.127 Å; while the remaining four Fe–C_n (where $n=1$, 6, 7, 12) bonds are essentially equal, ranging from 2.033 to 2.038 Å].

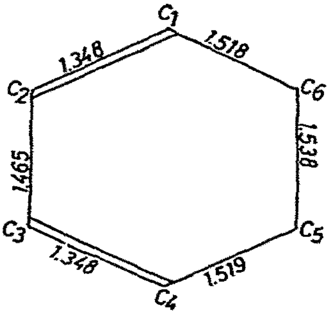
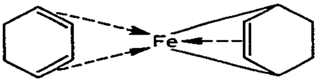


Fig. 3

The two complexed 1,3-cyclohexadiene-ligands in the asymmetric unit differ slightly in molecular dimensions as well as in their conformation from the free molecule, as studied by electron diffraction[6] (see Fig. 3). As in similar compounds[7], the delocalisation of electrons within the butadiene entity tends to make the bond lengths equal. Bonds C_1–C_6 and C_7–C_{12} are shortened from 1.468 Å in free 1,3-cyclohexadiene to 1.432 and 1.408 Å respectively. Correspondingly, the formerly double bonds C_2–C_3, C_4–C_5, C_8–C_9, and C_{10}–C_{11} are lengthened by about 0.05 Å each. However, there still seems to be a remarkable difference between both types of bonds, at least in one of the two rings.

An interesting feature is the behaviour of the bond angles at the C-atoms mentioned. Whereas in the isolated ring system they show the typical values for sp^3 (110.7°) and sp^2 (120.1°) hybridisation, in other known complexed butadiene systems the angles average to about 120° (sp^2). However, in our example this total equalisation is prevented by an obviously strong ring tension. Thus we observe slightly different bond angles at the terminal (119°) and at the central carbon atoms (116°) (see Fig. 2). The torsional angle of the free 1,3-cyclohexadiene (18.3°) is reduced to 3°. This residual small value causes the chirality of the molecule. The two butadiene entities are, however, planar within the limits of error [maximal deviations from the best planes are 0.001 Å (C_7) and 0.002 Å (C_1)]. The overall picture is consistent with the assumption of a slight asymmetry in bonding towards the extreme formulation given below:



The shortening along bond C_7–C_{12} causes, with keeping hybridisation of the remaining C atoms constant and the bonded butadiene planar, a slight decrease (outside the limit of error) of the opposite single bond C_9–C_{10}.

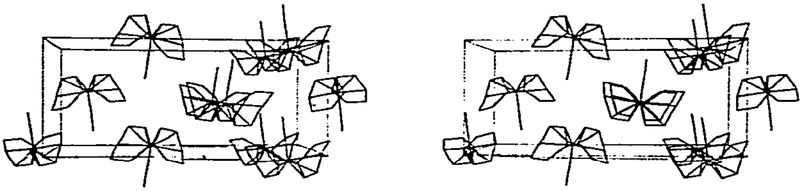


Fig. 4. Stereodiagram of the unit cell. The *a* axis is horizontal, the *c* axis vertical to the viewer.

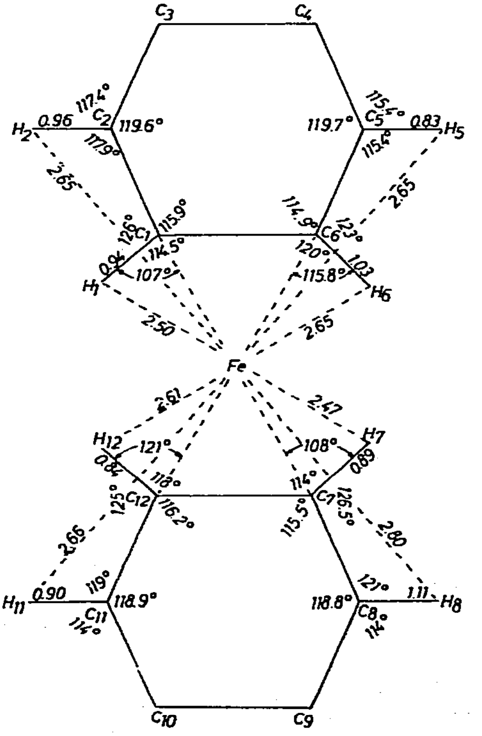


Fig. 5. Bond lengths and bond angles for some of the hydrogen atoms.

It seems difficult to explain the observed asymmetry of the molecule, especially as similar compounds show exact mirror symmetry[8,9]. One explanation might be the exterior asymmetric influence of packing forces in the molecule. Indeed the carbonyl group is pointing exactly towards the ring system in question (see packing diagramm, Fig. 4). This assumption is supported by the NMR spectrum of the compound. It is reported to show equivalent hydrogens in the slow time averaging scale of the NMR at various temperatures, thus indicating, if one does not assume *m*-symmetry of the molecule in solution, at least a rapid interchange between the two bonding schemes.

TABLE 4

BOND LENGTHS AND ANGLES OF THE HYDROGEN ATOMS

Bond lengths (Å) and standard deviations (× 10^3)		Bond angles (°) and standard deviations (× 10)	
H_1-C_1	0.945(49)	$H_1-C_1-C_2$	126.2(29)
		$H_1-C_1-C_6$	114.5(30)
H_2-C_2	0.959(50)	$H_2-C_2-C_1$	117.9(33)
		$H_2-C_2-C_3$	117.4(32)
H_6-C_6	1.037(55)	$H_6-C_6-C_1$	120.6(29)
		$H_6-C_6-C_5$	123.4(29)
H_5-C_5	0.829(52)	$H_5-C_5-C_4$	115.4(37)
		$H_5-C_5-C_6$	115.4(31)
$H_{4a}-C_4$	0.970(54)	$H_{4a}-C_4-C_5$	109.4(31)
		$H_{4a}-C_4-C_2$	124.7(31)
$H_{4b}-C_4$	0.864(48)	$H_{4b}-C_4-C_3$	110.3(36)
		$H_{4b}-C_4-C_5$	104.0(37)
		$H_{4b}-C_4-H_{4a}$	111.1(46)
$H_{3a}-C_3$	0.861(56)	$H_{3a}-C_3-C_2$	105.9(32)
		$H_{3a}-C_3-C_4$	110.8(35)
$H_{3b}-C_3$	0.962(55)	$H_{3b}-C_3-C_2$	104.1(31)
		$H_{3b}-C_3-C_4$	113.9(29)
		$H_{3b}-C_3-H_{3a}$	110.5(50)
H_7-C_7	0.895(49)	$H_7-C_7-C_8$	126.5(31)
		$H_7-C_7-C_{12}$	114.7(33)
H_8-C_8	1.110(48)	$H_8-C_8-C_7$	121.0(27)
		$H_8-C_8-C_9$	114.5(26)
$H_{10a}-C_{10}$	0.904(57)	$H_{10a}-C_{10}-C_9$	112.9(34)
		$H_{10a}-C_{10}-C_{11}$	110.2(37)
$H_{10b}-C_{10}$	0.876(50)	$H_{10b}-C_{10}-C_9$	119.4(37)
		$H_{10b}-C_{10}-C_{11}$	104.5(35)
		$H_{10b}-C_{10}-H_{10a}$	97.1(46)
$_{9a}-C_9$	1.018(54)	$H_{9a}-C_9-C_8$	105.0(28)
		$H_{9a}-C_9-C_{10}$	114.7(28)
$H_{9b}-C_9$	0.975(50)	$H_{9b}-C_9-C_8$	98.9(29)
		$H_{9b}-C_9-C_{10}$	117.0(31)
		$H_{9b}-C_9-H_{9a}$	107.6(43)
$H_{11}-C_{11}$	0.902(51)	$H_{11}-C_{11}-C_{10}$	114.6(33)
		$H_{11}-C_{11}-C_{12}$	119.7(33)
$H_{12}-C_{12}$	0.897(55)	$H_{12}-C_{12}-C_{11}$	125.5(35)
		$H_{12}-C_{12}-C_7$	118.0(34)

TABLE 5

SHORT INTERMOLECULAR DISTANCES

Atoms	Distance (Å)	Lattice point	to	Lattice point
C_{10}–O	3.678	000		$0\bar{1}\bar{1}$
C_5–O	3.601	000		000
C_1–C_{12}	3.744	000		000
C_2–C_{12}	3.731			
C_1–O	3.639	000		001
C_6–O	3.481			
C_3–C_6	3.558	000		$01\bar{1}$
C_1–C_3	3.566	000		010
C_1–C_4	3.621			

TABLE 6

SHORT INTRAMOLECULAR CONTACTS

Atoms	Distance (Å)
C_{13}–C_2	2.773
C_{13}–C_5	2.689
C_{13}–C_8	2.786
C_{13}–C_{11}	2.676

TABLE 7

BEST PLANES AND DISTANCES FROM THESE PLANES

(I) $6.3096x+3.8065y+6.1426z-2.7786=0$

C_2	-0.0012	C_3	0.0021
C_4	-0.0021	C_5	0.0012

(II) $2.2952x+0.1664y-7.4752z+0.0304=0$

C_2	0.0733	C_5	-0.0729
C_8	0.0729	C_{11}	-0.0732

(III) $10.9639x+6.1257y+1.9686z-4.0750=0$

C_1	-0.0025	C_2	0.0014
C_5	-0.0014	C_6	0.0025

(IV) $11.7494x+6.1546y-0.3409z-0.7833=0$

C_7	-0.0010	C_8	0.0005
C_{11}	-0.0006	C_{12}	0.0010

(V) $9.8306x+4.0298y-5.0264z-0.5332=0$

C_8	0.0007	C_9	-0.0013
C_{10}	0.0013	C_{11}	-0.0007

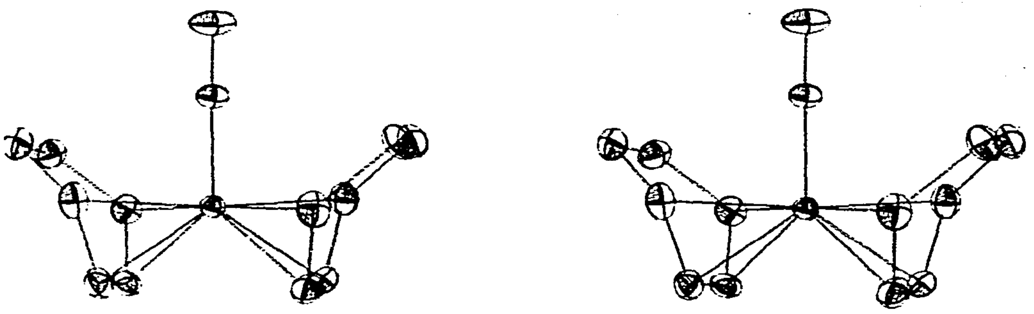


Fig. 6

All hydrogens could be found on a difference map. After refinement of their positions and isotropic temperature factors the final distances and angles of those at the diene-group are shown in Fig. 5 (distances ±0.05 Å, angles ±2°). It seems to be worthwhile to note a difference in bonding angles towards the iron of H_1 (H_7) and H_6 (H_{12}). This effect resembles the effect of the molecular distortion mentioned above. Bond distances and angles are given in Table 4. Their fractional coordinates are listed in Table 2.

INTRA- AND INTERMOLECULAR CONTACTS

Intermolecular contacts are given in Table 5. Within the molecule some non-bonded distances to the C atom of the carbonyl group suggest some interactions. They are listed in Table 6.

REFERENCES

1 E. Koerner von Gustorf *et al.*, *Angew. Chem.*, 83 (1971) 249.
2 C. Krüger, *J. Organometal. Chem.*, 22 (1970) 697.
3 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18 (1965) 104.
4 J. McWheeny, *International Tables for X-Ray Crystallography*, 1962.
5 R. S. Berry, M. Tamres, C. J. Ballhausen and H. Johansen, *Acta Chem. Scand.*, 22 (1968) 231.
6 H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, 91 (1969) 10; M. Traetteberg, *Acta Chem. Scand.*, 22 (1968) 2305.
7 O. S. Mills and G. Robinson, *Acta Crystallogr.*, 16 (1963) 758.
M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, 301 (1967) 433.
R. Eiss, *Inorg. Chem.*, 9 (1970) 1650.
8 G. N. Schrauzer, *Inorg. Chem.*, 4 (1965) 264.
9 R. E. Davis, G. L. Cupper and H. D. Simpson, *American Crystallographic Association, Summer Meeting August 1970, Abstract N4*, Ottawa.