

Structural Studies of Organometallic Compounds.

I. The Crystal and Molecular Structures of ($\beta,\alpha,1,6$ -tetrahapto:2,3,4,5-tetrahapto-3, α -Dimethylstyrene)bis(tricarbonyliron) and 4,5,6,7-tetrahapto-[(2,3,9,8-tetrahapto-1,1',1''-Tricarbonyl-1-ferraindene)tricarbonyliron($Fe-Fe$)]tricarbonyliron

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The structures of the title compounds have been determined. 3, α -Dimethylstyrenebis(tricarbonyliron) is monoclinic, $a = 9.297$ (3), $b = 7.010$ (10), $c = 13.078$ (3) Å, $\beta = 93.1$ (2)°, space group $P2_1$, $Z = 2$. Intensities of 2653 reflexions were measured on a four-circle diffractometer (graphite-monochromated Mo $K\alpha$); the structure refined to $R = 0.042$ and the absolute configuration was determined. The molecule consists of two planar (isoprene)tricarbonyliron groups, which intersect at an angle of 34.3°. The two $Fe(CO)_3$ groups are *trans* to one another; that interacting with the ring extends from the outer convex surface of the organic ligand while that interacting with the extra-ring double bond extends from the inner concave surface. 1,1,1-Tricarbonylferraindenebis(tricarbonyliron) is orthorhombic, $a = 12.818$ (3), $b = 14.220$ (3), $c = 10.120$ (10) Å, space group $P2_12_12_1$, $Z = 4$. Intensities of 2269 reflexions were measured on a two-circle (Stoe Weissenberg) diffractometer (graphite-monochromated Mo $K\alpha$); the structure refined to $R = 0.083$; the absolute configuration was not determined. The two $Fe(CO)_3$ groups interacting with *cis*-butadiene groups have a disposition similar to that found in 3, α -dimethylstyrenebis(tricarbonyliron); in addition the iron atom of the $Fe(CO)_3$ interacting with the ferracyclopentadiene ring forms a single bond with the Fe atom of this ring. The $Fe_2(CO)_6(Fe-Fe)$ moiety thus formed has dimensions similar to those found in analogous molecules. The dimensions of fifteen (*cis*-butadiene)tricarbonyliron moieties in twelve different organometallic compounds are compared [only results with $\sigma(C-C) < \sim 0.005$ Å are considered]. The (*cis*-butadiene)tricarbonyliron has remarkably concordant dimensions but significant environmental effects are discernible. Histograms of some bond-length and bond-angle distributions are presented.

1. Introduction

Stable compounds are formed by interaction between the *cis*-butadiene moiety of many organic ligands and the tricarbonyliron moiety; the parent compound of the series, (*cis*-butadiene)tricarbonyliron, was prepared first by Reihlen, Gruhl, Hessling & Pfrengle (1930) and later studied chemically (Hallam & Pauson, 1958) and crystallographically (Mills & Robinson, 1963). Since then the crystal structures of over forty analogous compounds have been determined. We report here the structure of 3, α -dimethylstyrenebis(tricarbonyliron)[†] [prepared by a photochemical route by Victor, Ben-Shoshan & Sarel (1970a, 1970b, 1972)], in which the eight π electrons of the ligand interact with two separate tricarbonyliron groups, and of 1,1,1-tricarbonylferraindenebis(tricarbonyliron)[†] (Victor, Ben-Shoshan & Sarel, 1971) which differs from the

known 1,1,1-tricarbonylphenylferraindene(tricarbonyliron) (Degrève, Meunier-Piret, Van Meerssche & Piret, 1967) by an additional interaction of a tricarbonyliron group with a *cis*-butadiene moiety (and absence of the phenyl substituent from the ferraindene ring). This second molecule, therefore, has three chemically different tricarbonyliron groups, and provides a convenient comparison of their geometries.

The structural results have been reported (Herbstein & Reisner, 1972, 1975).

2. Experimental

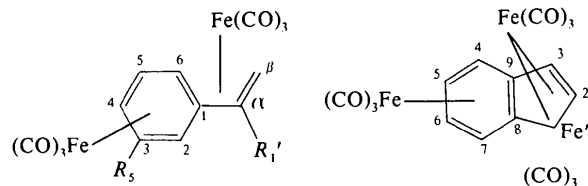
Crystallographic results for various tricarbonyliron compounds of substituted styrenes (Victor, Ben-Shoshan & Sarel, 1972) are summarized in Table 1. Intensity measurements for the two crystals studied in detail were first made in this laboratory on a Stoe Weissenberg semi-automatic diffractometer and used for the solution of the structures by Patterson and Fourier techniques. More accurate intensity measurements on 3, α -dimethylstyrenebis(tricarbonyliron) were later made at Caltech on a four-circle diffractometer. Details of the experimental techniques used to solve

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[†] Systematic names, following Cotton (1968), are given in the title; chemical numbering is in the caption to Table 1 and crystallographic numbering in Figs. 3 and 7.

Table 1. Crystallographic results

Numbers in parentheses here and throughout this paper are estimated standard deviations in the least significant digit. Cell dimensions were determined by standard and back-reflexion methods (Herbstein, 1963) and densities by flotation. Numbering for R_1 , R_5 follows Victor *et al.* (1972).



- (I) $R_1' = \text{CH}_3$; $R_5 = \text{H}$
 (II) $R_1' = \text{C}_6\text{H}_5$; $R_5 = \text{H}$
 (III) $R_1' = R_5 = \text{CH}_3$

Compound I

α -Methylstyrenebis(tricarbonyliron), $\text{C}_{15}\text{H}_{10}\text{O}_6\text{Fe}_2$

Red needles, elongated along [001]

Orthorhombic

Space group $P2_12_12_1$

$a = 18.20 \text{ \AA}$

$b = 12.18$

$c = 7.04$

$V = 1561 \text{ \AA}^3$

[Compound 10b of Victor *et al.* (1972)]

FW 397.93
 m.p. 131°C
 $Z = 4$
 $D_m = 1.66 \text{ g cm}^{-3}$
 $D_c = 1.70$

Compound II

α -Phenylstyrenebis(tricarbonyliron), $\text{C}_{20}\text{H}_{12}\text{O}_6\text{Fe}_2$

Red prisms

Orthorhombic

Space group $Pc2_1n$ or $Pcmm$

$a = 12.00 \text{ \AA}$

$b = 8.94$

$c = 18.30$

$V = 1963 \text{ \AA}^3$

[Compound 10n of Victor *et al.* (1972)]

FW 460.00
 m.p. 115°C
 $Z = 4$
 $D_m = 1.58 \text{ g cm}^{-3}$
 $D_c = 1.57$

Compound III

3, α -Dimethylstyrenebis(tricarbonyliron), $\text{C}_{16}\text{H}_{12}\text{O}_6\text{Fe}_2$

Red needles, elongated along [010]

Monoclinic

Space group $P2_1$

$a = 9.297 (3) \text{ \AA}$

$b = 7.010 (10)$

$c = 13.078 (3)$

$\beta = 93.1 (2)^\circ$

$V = 851.07 (1) \text{ \AA}^3$

[Compound 10d II of Victor *et al.* (1972)]

FW 411.98
 m.p. 116°C
 $Z = 2$
 $D_m = 1.60 \text{ g cm}^{-3}$
 $D_c = 1.63$
 $\mu(\text{Mo } K\alpha) = 17.75 \text{ cm}^{-1}$
 $\lambda(\text{Fe } K\alpha_1) = 1.93998 \text{ \AA}$
 $\lambda(\text{Fe } K\alpha_2) = 1.93604$

Compound IV

1,1,1-Tricarbonylferraindenebis(tricarbonyliron), $\text{C}_{17}\text{H}_6\text{O}_9\text{Fe}_3$

Red needles, elongated along [001]

Orthorhombic

Space group $P2_12_12_1$

$a = 12.818 (3) \text{ \AA}$

$b = 14.220 (3)$

$c = 10.120 (10)$

$V = 1844.6 (2) \text{ \AA}^3$

[Compound IV of Victor *et al.* (1971)].

FW 521.78
 m.p. 126°C
 $Z = 4$
 $D_m = 1.84 \text{ g cm}^{-3}$
 $D_c = 1.879$
 $\mu(\text{Mo } K\alpha) = 23.92 \text{ cm}^{-1}$

Table 2. Details of experimental techniques used in the solution and refinement of 3, α -dimethylstyrenebis(tricarbonyliron) (III) and 1,1,1-tricarbonylferraindenebis(tricarbonyliron) (IV)

	(III)	(IV)
Diffractionmeter	Four-circle (GE Datex automated)	Two-circle (Stoe Weissenberg)
Radiation	Mo $K\alpha$ (graphite monochromator)	Mo $K\alpha$ (graphite monochromator)
Scan mode	$\theta-2\theta$, $1^\circ (2\theta) \text{ min}^{-1}$, 30 s background at scan extremities	$\theta-2\theta$, $1^\circ (2\theta) \text{ min}^{-1}$, 20 s background at scan extremities
Crystal size and shape	Needle, elongated along [101], $0.7 \times 0.19 \times 0.16 \text{ mm}$, showing {100}, {101}, {103} and {010}	Needle, $0.6 \times 0.25 \text{ mm}$ diameter, mounted about [001]
Number of independent non-zero reflexions	2653 ($2\theta < 60^\circ$)	2269
Number of reflexions used in last refinement stage	2652	2237
Behaviour of standards	No significant variation	
Absorption correction	Applied	Not applied ($\mu R < 0.25$)
Atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974)	
Refinement method	Full-matrix on F^2 (CRYM)	Block-diagonal on F (ORFLS)
Parameters refined:		
Non-hydrogen atoms	Coordinates and anisotropic temperature factors	
	240 parameters	290 parameters
Hydrogen atoms	Coordinates and isotropic temperature factors	Not included
	40 parameters	
Scale factors	1	10
Extinction correction	Not applied	
Number of reflexions/parameter	9.4	7.6
Absolute configuration	Determined	Not determined
R	0.042	0.083
Goodness of fit	1.4	0.64
Estimated standard deviations		
$\sigma(\text{Fe}-\text{Fe})$	0.0007 \AA	0.0018 \AA
$\sigma(\text{Fe}-\text{C})$	0.004	0.014
$\sigma(\text{C}-\text{C})$	0.005	0.020
$\sigma(\text{C}-\text{O})$	0.005	0.020
$\sigma(\text{C}-\text{H})$	0.04	—
$\sigma(\text{C}-\text{Fe}-\text{C})$	0.17°	0.6°
$\sigma(\text{Fe}-\text{C}-\text{O})$	0.33	1.3
$\sigma(\text{C}-\text{C}-\text{C})$	0.34	1.5
$\sigma(\text{C}-\text{C}-\text{H})$	1.9	—

and refine the two structures are given in Table 2. The final parameters are given in Tables 3 and 4.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32660 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. 3, α -Dimethylstyrenebis(tricarbonyliron)

Fractional coordinates of Fe are $\times 10^5$, of C and O $\times 10^4$, and of H $\times 10^3$; for numbering of atoms see Fig. 3. The absolute configuration of the molecule was determined experimentally. Estimated standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)*	34887 (4)	35595 (10)	17658 (3)
Fe(2)*	-5251 (5)	0*	26483 (3)
C(3)	-1608 (6)	-460 (6)	3702 (3)
C(4)	-1326 (4)	-1608 (10)	1719 (3)
C(5)	939 (4)	-1343 (7)	3203 (3)
C(6)	2262 (4)	5230 (7)	1110 (3)
C(7)	4663 (4)	5245 (9)	2452 (3)
C(8)	4724 (3)	3310 (6)	775 (3)
C(9)	-1877 (3)	2287 (7)	2157 (3)
C(10)	-712 (3)	2991 (5)	2814 (3)
C(11)	682 (3)	2565 (5)	2470 (2)
C(12)	792 (3)	1458 (6)	1561 (2)
C(13)	2294 (4)	1030 (5)	1328 (2)
C(14)	3373 (3)	726 (5)	2117 (3)
C(15)	3275 (3)	1812 (5)	3011 (2)
C(16)	2081 (3)	3108 (5)	2995 (2)
C(17)	-948 (4)	4036 (6)	3783 (3)
C(18)	4324 (4)	1633 (7)	3930 (3)
O(19)	-2301 (3)	-776 (5)	4378 (2)
O(20)	5469 (3)	3111 (5)	117 (2)
O(21)	1844 (3)	-2243 (4)	3586 (2)
O(22)	1478 (3)	6274 (5)	707 (2)
O(23)	-1849 (4)	-2623 (6)	1142 (2)
O(24)	5382 (3)	6306 (6)	2898 (3)
H(25)	206 (3)	399 (5)	354 (2)
H(26)	20 (3)	171 (5)	101 (2)
H(27)	235 (3)	49 (5)	72 (2)
H(28)	416 (4)	9 (6)	202 (2)
H(29)	521 (4)	118 (6)	370 (3)
H(30)	396 (4)	99 (6)	441 (3)
H(31)	449 (4)	283 (6)	420 (3)
H(32)	-179 (3)	363 (6)	415 (2)
H(33)	-90 (3)	531 (7)	362 (3)
H(34)	-33 (4)	389 (7)	429 (2)
H(35)	-189 (3)	248 (6)	140 (2)
H(36)	-275 (3)	235 (5)	241 (2)

* Fe(2) has arbitrarily been assigned the coordinate $y = 0$.

3. Results

3.1. 3, α -Dimethylstyrenebis(tricarbonyliron)

3.1.1. *The crystal structure.* The crystal structure (Fig. 1) is that of a typical molecular crystal and the intermolecular distances are not reported.

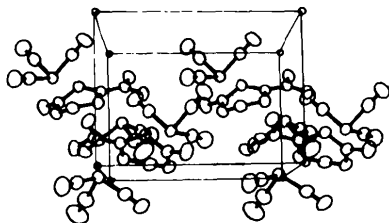


Table 4. 1,1,1-Tricarbonylferraindenebis(tricarbonyliron)

Fractional coordinates are $\times 10^4$ for non-hydrogen atoms; for numbering of atoms see Fig. 7. Estimated standard deviations are in parentheses. The H atoms could not be found from difference maps and calculated coordinates ($\times 10^2$) which were not refined are given; H atoms were not included in the structure factor calculations. The absolute configuration was not determined.

	<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)	2521 (1)	2977 (1)	-133 (2)
Fe(2)	2283 (1)	1311 (1)	629 (2)
Fe(3)	3653 (1)	2875 (1)	4355 (2)
C(4)	2368 (8)	3069 (8)	2015 (14)
C(5)	1377 (8)	3094 (8)	1436 (13)
C(6)	1228 (8)	2307 (7)	574 (13)
C(7)	2974 (7)	2286 (7)	1727 (12)
C(8)	3957 (9)	2269 (8)	2431 (13)
C(9)	4506 (9)	3134 (9)	2669 (13)
C(10)	3893 (11)	3895 (7)	2992 (15)
C(11)	2791 (9)	3750 (10)	2960 (16)
C(12)	3485 (12)	3932 (11)	-139 (20)
C(13)	1741 (10)	3465 (9)	-1431 (17)
C(14)	3228 (10)	2211 (8)	-1168 (15)
C(15)	3474 (11)	620 (8)	587 (14)
C(16)	1625 (11)	639 (10)	-572 (16)
C(17)	1618 (13)	742 (11)	2008 (19)
C(18)	2586 (13)	2139 (10)	4884 (17)
C(19)	4640 (11)	2190 (12)	5125 (16)
C(20)	3628 (12)	3726 (11)	5690 (18)
O(21)	4066 (11)	4500 (9)	-156 (20)
O(22)	3736 (11)	1835 (9)	-1972 (15)
O(23)	1326 (11)	3741 (8)	-2352 (15)
O(24)	4270 (9)	249 (8)	583 (12)
O(25)	1244 (9)	181 (9)	-1421 (15)
O(26)	1188 (13)	429 (11)	2835 (15)
O(27)	1939 (10)	1684 (11)	5256 (17)
O(28)	5284 (11)	1710 (12)	5596 (15)
O(29)	3654 (13)	4258 (11)	6547 (17)
H(30)	8	36	16
H(31)	6	23	0
H(32)	42	17	27
H(33)	53	32	26
H(34)	42	45	32
H(35)	23	41	36

3.1.2. *The molecular structure.* An overall view of the molecular structure is given in Fig. 2 and dimensions in Figs. 3 and 4. The organic ligand consists of two essentially planar portions: C(9), C(10), C(11), C(12), C(13) and C(16), and C(13), C(14), C(15) and C(16) [Table 5; planes and interplanar angles were calculated by the methods of Schomaker, Waser,

Fig. 1. ORTEP (Johnson, 1965) stereoview of the 3, α -dimethylstyrenebis(tricarbonyliron) crystal structure. The thermal ellipsoids are drawn at the 50% probability level. H atoms have not been included. The reference molecule (*i.e.* the molecule for which atomic coordinates are listed in Table 3) is at the lower left-hand side of the diagram.

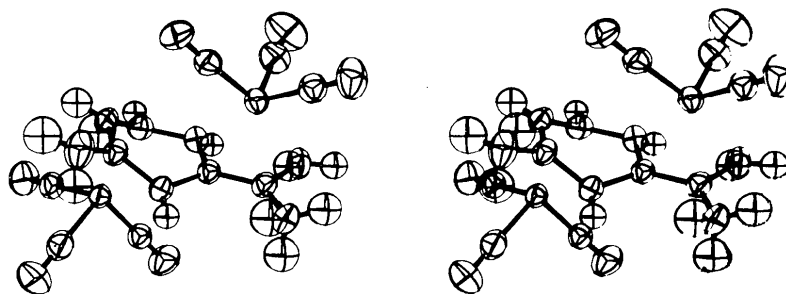


Fig. 2. ORTEP stereoview of 3,α-dimethylstyrenebis(tricarbonyliron). The thermal ellipsoids are drawn at the 50% probability level.

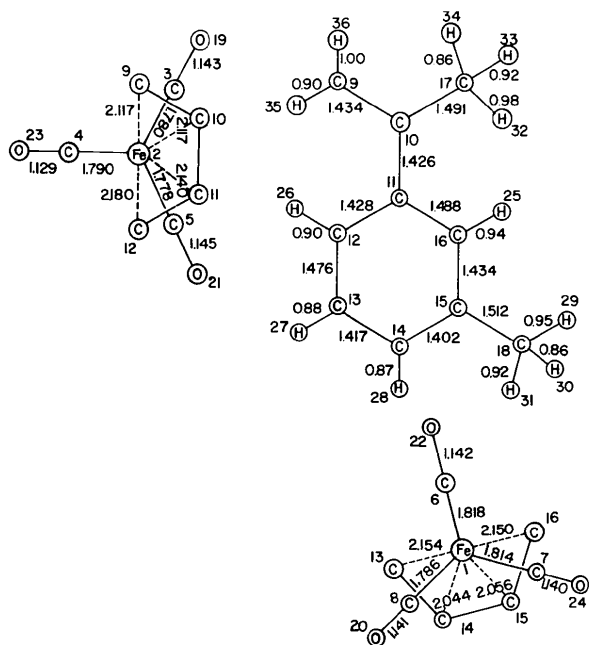


Fig. 3. 3,α-Dimethylstyrenebis(tricarbonyliron): numbering of atoms and interatomic distances (Å). E.s.d.'s are given in Table 2. In this diagram the atoms of plane 1 (Table 5) are taken to be in (or near) the plane of the page; atoms with positive deviations from plane 1 (in the sense of Table 5) are shown below the page and those with negative deviations above the page. Fe(1)–Fe(2) = 4.685 Å.

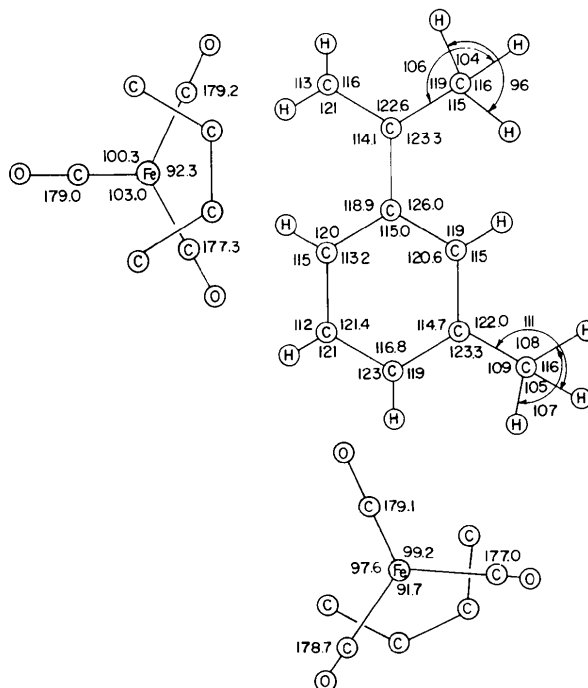


Fig. 4. 3,α-Dimethylstyrenebis(tricarbonyliron): bond angles (°). E.s.d.'s are given in Table 2.

Marsh & Bergman (1959) and Waser, Marsh & Cordes (1973)]. The six-membered 'benzene' ring is boat-shaped; thus the shape of the 3,α-dimethylstyrene moiety in this compound differs from its presumably planar shape in the free state. As a first approximation the molecule can be described as composed of two essentially non-interacting (*cis*-isoprene)tricarbonyliron units; in accordance with this the distances C(12)–C(13) and C(11)–C(16) are those expected for single bonds between sp^2 C atoms. The planes through these two units intersect in the line through C(13) and C(16) at an angle of 34.3° ; the two tricarbonyliron units have a *trans* arrangement, with Fe(1)(CO)₃ on the outer, convex side of the dimethylstyrene moiety while Fe(2)(CO)₃ is on the inner, concave side.

The molecular dimensions and conformation of the Fe(CO)₃ groups with respect to the *cis*-butadiene groups with which they interact are in good agreement with those reported for analogous structures (see Appendix I).

It is convenient to describe the geometry of the (*cis*-butadiene)tricarbonyliron group in terms of the pseudo-octahedral model (Johnson & Paul, 1970) (see also Appendix I §A3 and Fig. 15). Here the central plane of the pseudo-octahedron contains the two outer C of the butadiene and the two C atoms of the equivalent carbonyl groups.* The Fe atom is approximately in the centre of this plane and the unique carbonyl group* extends below it. The opposite vertex of the octahedron

* Equivalent and unique carbonyl groups are shown in Figs. 10 and 15.

is not occupied in molecules with isolated (butadiene)-tricarbonyliron groups but the *cis*-butadiene group, off to one side (Fig. 15), acts as the sixth ligand. We are

Table 5. Deviations (in Å) of atoms from various planes in 3,α-dimethylstyrenebis(tricarbonyliron)

Asterisked atoms were given zero weight in the calculation of the best planes; the signs of the deviations from planarity are defined with respect to the crystal axes (see legend to Fig. 3).

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(9)	-0.001				0.003
C(10)	-0.020				
C(11)	-0.017		-0.002		
C(12)	-0.019		0.002		-0.003
C(13)	0.020	-0.001	0.365*	0.038	
C(16)	0.003	0.001	0.387*	-0.037	
C(17)	0.106*				
H(35)	-0.65*				
H(36)	-0.17*				
H(26)	-0.54*				
H(27)	-0.10	0.10*			
H(25)	0.13*	0.13*			
Fe(2)	1.653*	-2.778*			-0.270*
C(15)	0.731*	-0.002	0.002		
C(14)	0.735*	0.002	-0.002		
C(18)		-0.024*			
H(28)		0.17*			
Fe(1)	-1.187*	1.669*		-0.224*	
C(7)				0.038	
C(8)				0.039	
C(3)					-0.003
C(5)					0.003

Equations of best planes expressed in the form $AX + BY + CZ + D = 0$, where X, Y, Z are atomic coordinates (in Å) with respect to the crystal axes, and D is the origin-to-plane distance (in Å)

Plane	Plane through carbon atoms	Coefficients in plane equations			
		A	B	C	D
1	9, 10, 11, 12, 13, 16	-0.0323	-0.8374	0.5466	-0.255
2	13, 14, 15, 16	0.5867	0.7100	-0.4204	-1.036
3	11, 12, 14, 15	0.3255	0.8110	-0.5028	-0.042
4	13, 16, 7, 8	0.5761	-0.6559	0.4561	-1.509
5	9, 12, 3, 5	0.3519	0.6906	0.6121	-2.218

interested in the deviations of Fe and C atoms from the central plane, and the angle ω between the vectors Fe—C(unique carbonyl), and Fe—mid-point (M) of the inner C—C bond of the butadiene.

In (III) (see Table 1) the central planes of the pseudo-octahedra of the two independent (butadiene)-tricarbonyliron groups are planes 4 and 5 of Table 5; the values of ω are 136.6 and 134.4° respectively. Both the deviations from planarity and the values of ω agree well with other results summarized in Appendix I.

3.2. 1,1,1-Tricarbonylferraindenebis(tricarbonyliron)

3.2.1. *The crystal structure.* The crystal structure (Fig. 5) is that of a typical molecular crystal and intermolecular distances are not reported.

3.2.2. *The molecular structure.* An overall view of the molecular structure is given in Fig. 6 and dimensions are in Figs. 7 and 8. The organic ligand consists of two essentially planar portions: C(8), C(9), C(10) and C(11), and C(6), C(5), C(4), C(7), C(8) and C(11) (Table 6). The six-membered ring is boat-shaped, as in (III), and thus the organic moiety is no longer planar, as would be expected for the hypothetical free molecule. As a first approximation the molecule can be described as consisting of two essentially non-interacting portions, a (*cis*-butadiene)tricarbonyliron portion and a (1,1,1-tricarbonylferracyclopentadiene)tricarbonyliron (Fe—Fe) portion. The two portions have C(8) and C(11) in common and their planes intersect at an angle of 32.5°. The distances C(4)—C(11) and C(7)—C(8) correspond, within limits of error, to values expected for single bonds between sp^2 C atoms; although they are both slightly shorter (by $1-2\sigma$) than the values found in (III), the differences are not considered significant.

The two tricarbonyliron units interacting with *cis*-butadiene portions of the molecule, *i.e.* Fe(1)(CO)₃ and Fe(3)(CO)₃, have a *trans* arrangement, with

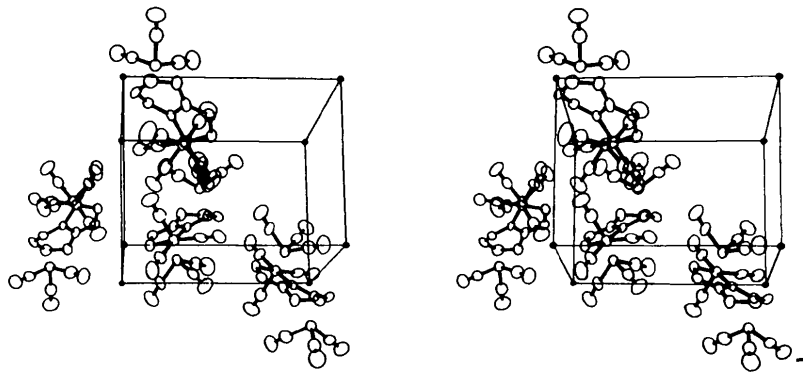


Fig. 5. ORTEP stereoview of the 1,1,1-tricarbonylferraindenebis(tricarbonyliron) crystal structure. The thermal ellipsoids are drawn at the 50% probability level. H atoms have not been included. The reference molecule (*i.e.* the molecule for which atomic coordinates are listed in Table 4) is at the lower left-hand corner of the unit cell.

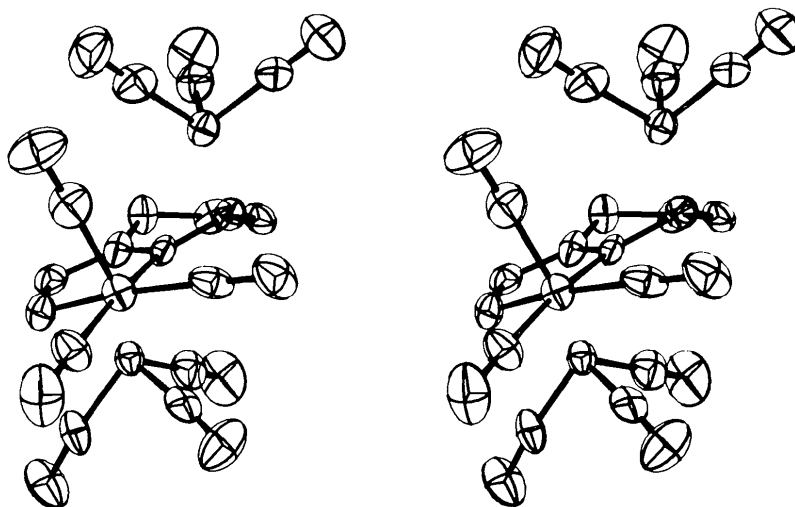


Fig. 6. ORTEP stereoview of 1,1,1-tricarbonylferraindenebis(tricarbonyliron). The thermal ellipsoids are drawn at the 50% probability level. Positions of the H atoms were not determined in this structure analysis.

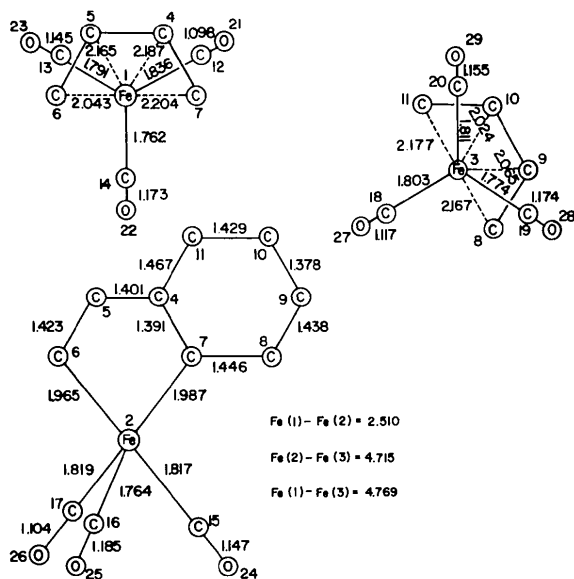


Fig. 7. 1,1,1-Tricarbonylferraindenebis(tricarbonyliron): numbering of atoms and interatomic distances (Å). E.s.d.'s are given in Table 2. In this figure the atoms of plane 1 (Table 6) are taken to be in or near the plane of the page; atoms with positive deviations from plane 1 (in the sense of Table 6) are shown below the page and those with negative deviations above the page. Note that C(17)—O(26) is the unique carbonyl bonded to Fe(2).

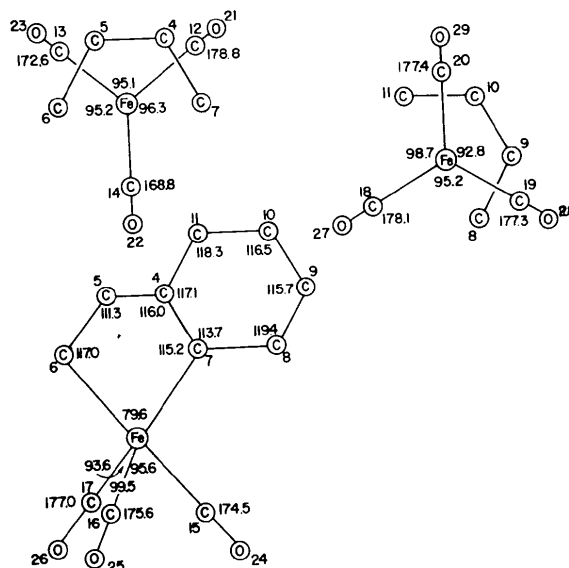


Fig. 8. 1,1,1-Tricarbonylferraindenebis(tricarbonyliron): bond angles ($^{\circ}$). E.s.d.'s are given in Table 2.

Fe(1)(CO)₃, on the inner, concave side of the organic moiety and Fe(2)(CO)₃, on the outer, convex side. Thus there is the same disposition of these two tricarbonyliron moieties with respect to the ligand in both (III) and (IV).

The two tricarbonyliron groups interacting with *cis*-butadiene moieties [*i.e.* Fe(1)(CO)₃ and Fe(3)(CO)₃] can be described as above, although the clear-cut distinction between ϵ_1 , ϵ_2 and δ that was found for

isolated (butadiene)tricarbonyliron units (see Appendix I) has disappeared for the second of these groups, perhaps because of the formation of the Fe—Fe single bond. The three carbonyl groups bonded to Fe(2), the Fe atom of the ferracyclopentadiene ring, may also be divided into a pair of equivalent carbonyls [C(15)—O(24), C(16)—O(25)] and a unique carbonyl [C(17)—O(26)]. The pseudo-octahedral model can be applied to this Fe atom — the central plane is formed as before by the two C of the equivalent carbonyls, and the two outer C atoms of the butadiene, which is now part of the ferracyclopentadiene ring. The central plane is plane 6 of Table 6, with Fe(2) displaced 0.16 Å in the direction

Table 6. Deviations (in Å) of atoms from various planes in 1,1,1-tricarbonylferraindenebis(tricarbonyliron)

Asterisked atoms were given zero weight in the calculation of the best planes; note that the signs of the deviations from the various planes are defined with respect to the crystal axes (and see the legend to Fig. 7).

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
C(11)	-0.001	-0.011	-0.047	-0.355*		
C(8)	-0.020	0.011	0.048	-0.405*		
C(7)	0.016			-0.013	-0.138	-0.010
C(6)	0.002				0.158	0.010
C(5)	-0.026					
C(4)	0.029			0.013		
Fe(2)	-0.188*					-0.162*
Fe(1)	1.705*				-0.295*	
C(10)	0.662*	0.021		-0.013		
C(9)	0.696*	-0.020		0.013		
Fe(3)	-1.240*	1.697*	-0.269*			
C(20)			0.048			
C(19)			-0.049			
C(12)					0.129	
C(13)					-0.149	
C(15)						0.010
C(16)						-0.010
C(17)						-1.982*

Equations of best planes expressed in the form $AX + BY + CZ + D = 0$, where X, Y, Z are atomic coordinates (in Å) with respect to the crystal axes and D is the origin-to-plane distance (in Å)

Plane	Plane through carbon atoms	Coefficients in plane equations			
		A	B	C	D
1	11, 8, 7, 5, 6, 4	0.4110	0.4976	-0.7639	-1.832
2	11, 10, 9, 8	0.0376	-0.2336	0.9716	-1.815
3	20, 19, 11, 8	0.7767	0.5732	-0.2610	-5.099
4	10, 9, 7, 4	0.2011	0.3969	-0.8955	-0.504
5	13, 12, 7, 6	-0.4226	0.6981	-0.5780	-1.807
6	6, 7, 15, 16	0.4039	0.7803	-0.7803	-1.738

of the unique carbonyl. The coordination site M of the isolated (butadiene)tricarbonyliron groups is here occupied by Fe(1) [$\omega' = \angle C(17)-Fe(2)-Fe(1) = 135.3^\circ$]; the Fe-Fe single bond takes the place of the interaction of Fe(1) with the π electrons of the butadiene. The opposite vertex of the pseudo-octahedron is occupied remotely by C(14) of the unique carbonyl group bonded to Fe(1), with $d[C(14)-Fe(2)] = 2.53 \text{ \AA}$, $\angle C(17)-Fe(2)-C(14) = 175.5^\circ$ and $\angle Fe(1)-C(14)-O(22) = 168.8^\circ$. The coordination about Fe(2) is shown in Fig. 6 and more directly in Fig. 7 of Hock & Mills (1961) and Fig. 1 of Riley & Davis (1975). Plane 5 of Table 6 shows that the central C atoms about Fe(1) deviate from planarity considerably more than is usual for isolated (butadiene)tricarbonyliron groups (Table 7) and rather more than other (tricarbonylferracyclopentadiene)tricarbonyliron(Fe-Fe) moieties (Table 9).

4. Discussion

4.1. Gross changes in ligand geometry as a consequence of interaction with the tricarbonyliron group

The ligands studied here, 3, α -dimethylstyrene and the hypothetical tricarbonylferraindene, are presumably planar in the free state but undergo the same sort of gross geometrical change on formation of their tricarbonyliron compounds that has been found for such ligands as cyclooctatetraene (Bastiansen, Hedberg & Hedberg, 1957; Dickens & Lipscomb, 1962), tropone (Cruickshank, Filippini & Mills, 1972; Dodge, 1964) and azepine (Paul, Johnson, Paquette, Barrett & Haluska, 1968; Woodhouse, Sim & Sime, 1974). (The first of each of these pairs of references refers to the geometry of the free ligand, and the second to the structure of a tricarbonyliron derivative; a complete documentation has not been attempted.) The angles between the planar *cis*-butadiene units in the six-membered rings are 34.3 and 32.5° respectively, somewhat smaller than those (range $36.3-39.9^\circ$) found in (1,3-cyclohexadiene)tricarbonyliron-type compounds (Cotton & Troup, 1974b).

4.2. The dimensions of the structural fragments

The two molecules may be considered to be made up of separate structural fragments with only small mutual interactions. Thus 3, α -dimethylstyrenebis(tricarbonyliron) consists of two (*cis*-isoprene)tricarbonyliron fragments while 1,1,1-tricarbonylferraindenebis(tricarbonyliron) consists of a (*cis*-butadiene)tricarbonyliron fragment and a (1,1,1-tricarbonylferracyclopentadiene)tricarbonyliron(Fe-Fe) fragment.

The geometry of the (*cis*-butadiene)tricarbonyliron fragment is remarkably constant (see Appendix I for a detailed discussion) but there are distinct environmental effects and the three (*cis*-butadiene)tricarbonyliron fragments studied (Figs. 3, 4, 7, 8) have dimensions that differ significantly among themselves. We do not attempt to explain these environmental effects. Bonding in $Fe(CO)_3$ (ligand) complexes has been discussed by Elian & Hoffmann (1975) and Elian, Chen, Mingos & Hoffmann (1976).

The geometry of the (tricarbonylferracyclopentadiene)tricarbonyliron(Fe-Fe) fragment appears to show more variation than that of the isolated (butadiene)tricarbonyliron fragment but there are not yet enough accurate results to demonstrate this unequivocally. One influence is the degree of interaction between the Fe atom of the five-membered ring and C(14) of the unique carbonyl group of the second $Fe(CO)_3$ portion of the structural fragment. In (IV) this interaction is present but weak, as is shown by the value of $d[Fe(2)-C(14)] = 2.53 \text{ \AA}$, and the deviation of $\angle Fe(1)-C(14)-O(22) (= 169^\circ)$ from 180° . Cotton (1976) has called such carbonyl groups, bonded

unsymmetrically to two Fe atoms, semibridging carbonyl groups. The tabulated results for six molecules containing (1,1,1-tricarbonylferracyclopentadiene)tricarbonyliron (*Fe-Fe*) moieties (Riley & Davis, 1975) show only minor differences from the geometry found here, as do two* sets of results not included in that tabulation [Degrève *et al.* (1967); present results. Prince (1976) has reported concordant results for tetraphenylferrole- $\text{Fe}(\text{CO})_3$, the compound studied by Riley & Davis (1975)]. The existence of a single bond between the two Fe atoms leads to a slight shift (by a few hundredths of an ångström) of the Fe atom with respect to the *cis*-butadiene moiety to which it is bonded; the details of this shift vary somewhat erratically from molecule to molecule.

The ferracyclopentadiene ring is not planar as Fe(2) deviates by 0.16 Å from the plane of the four C atoms, and furthermore is on the *opposite* side of the ferracyclopentadiene plane to Fe(1). This is apparently a general phenomenon for molecules of this type (Table 9) (Barnett & Davis, 1970). Five-membered FeC_4 rings are planar when the Fe atom is not bonded to another Fe atom (Herbstein & Kafory, 1977). In (IV) the coordination of the ligands about Fe(2) does fit the pseudo-octahedral model and thus the coordination about Fe at the tricarbonylferracyclopentadiene end of the *Fe-Fe* single bond is similar to that at the *cis*-butadiene end, even though the two Fe atoms are formally in different oxidation states.

On this basis we can present a description of the geometry of the (tricarbonylferracyclopentadiene)tricarbonyliron fragment in (IV) which emphasizes the similarity of the ligand arrangements about the two Fe atoms, and which also applies to the six molecules discussed by Riley & Davis (1975) and to that studied by Degrève *et al.* (1967). A stereoscopic view of this fragment is shown in Fig. 9. The central planes of the two pseudo-octahedra (planes 5 and 6 of Table 6) are hinged at C(6), C(7), the two outer C atoms of the butadiene group, with an angle of 128° between them. Fe(2) (of the ring) has seven ligands: three carbonyls in standard positions, two σ -bonded C atoms of the ring,

the semibridging carbonyl remotely at the vertex of the pseudo-octahedron opposite to the unique carbonyl, and Fe(1), off to one side. Fe(1) also has seven ligands: three carbonyls in standard positions, the two outer C atoms of the butadiene group and, off to one side and roughly symmetrically above and below the central plane of the Fe(1) pseudo-octahedron, Fe(2) and the inner bond of the butadiene. The arrangements about the two Fe atoms thus have many points of similarity but are not identical. The overall conformation of the fragment can be rationalized in terms of two interactions: (1) the interaction of Fe(1)(CO)₃ with the *cis*-butadiene portion of the ferracyclopentadiene ring and, in particular, the preference for the eclipsed mutual arrangement always found in isolated (*cis*-butadiene)tricarbonyliron groups, and (2) the interaction of Fe(2) with the semibridging carbonyl group. In the fragments considered here both these requirements are satisfied simultaneously but there are other, formally identical fragments where different conformations are adopted, as Thorn & Hoffman (1977) have pointed out in their analysis of bonding in $M_2(\text{CO})_6$ (ligand) complexes. Cotton (1976) has emphasized the role of the semibridging carbonyl group in equalizing the charge on the two Fe atoms, in accordance with the requirements of Pauling's electroneutrality rule.

Both molecules studied by us are chiral and crystallize in chiral space groups; hence, spontaneous resolution has occurred on crystallization. This happens fairly often; *e.g.* three of the eight (tricarbonylferracyclopentadiene)tricarbonyliron (*Fe-Fe*)-type molecules noted above are resolved spontaneously on crystallization (Chin & Bau, 1973; Riley & Davis, 1975; Prince, 1976; this work).

We are grateful to Professor S. Sarel and colleagues (Hebrew University, Jerusalem) for crystals, to Drs R. E. Marsh, S. Samson and F. Fronczek (Caltech) for their help with intensity measurements, to Dr D. Rabinovich and Dr Z. Shakked (Weizmann Institute) for extracting information from the Cambridge Data File, to Professor Michael Cais for helpful discussions and to the Israel Commission for Basic Research for financial support. Most of the calculations were made with the *CRYM* set of programs (Duchamp, Trus & Westphal, 1969).

* The formally similar molecule $[\text{C}_{18}\text{H}_{18}\text{O}_2]\text{Fe}_2(\text{CO})_6$ (Jeffreys & Willis, 1972) has been excluded from this comparison because the geometry reported for it differs (Thorn & Hoffmann, 1977) from that found for the other seven molecules.

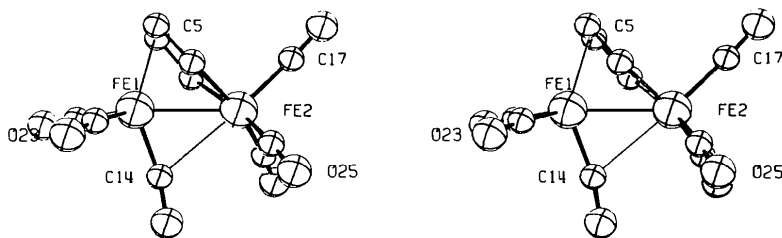


Fig. 9. ORTEP stereoview of the (tricarbonylferracyclopentadiene)tricarbonyliron fragment, viewed so as to emphasize the pseudo-octahedra about Fe(1) and Fe(2). The atom numbering refers to (IV) (but only part of this molecule is included in the diagram).

Table 7. Bond lengths etc. (Å) in $(CO)_3Fe-cis-butadiene$ moieties in various organometallic complexes

Organic ligand	$d[Fe-C(butadiene)]$					$d[Fe-C(carbonyl)]$					$d(C-O)$			Deviations* from plane of four C atoms of <i>cis-butadiene</i> moiety			Pseudo-octahedral model (Fig. 15) R.m.s. deviation from planarity, of two C atoms of equivalent CO groups and two outer C atoms of <i>cis-butadiene</i>	Deviation of Fe from this plane (towards unique CO)
	outer C	inner C	equivalent CO	unique CO	equivalent CO	unique CO	equivalent CO	unique CO	equivalent CO	unique CO	equivalent CO	unique CO	equivalent CO	unique CO	equivalent CO	unique CO		
1	1.412 (3)	1.417 (3)	1.411 (4)	2.139 (2)	2.132 (2)	1.783 (2)	1.783 (2)	1.788 (3)	1.788 (3)	1.147 (3)	1.154 (3)	1.144 (3)	C	H	O	-1.753	0.022	0.252
2	1.424 (5)	1.421 (5)	1.405 (5)	2.116 (3)	2.100 (3)	1.780 (3)	1.788 (4)	1.774 (3)	1.774 (3)	1.142 (4)	1.142 (4)	1.142 (4)	C	H	O	-1.843	0.051	0.241
3	1.431 (5)	1.431 (5)	1.406 (5)	2.096 (4)	2.151 (4)	1.799 (4)	1.807 (4)	1.805 (4)	1.805 (4)	1.136 (5)	1.134 (6)	1.125 (5)	C	H	H	-1.588	0.023	0.257
3-Formyl-N-ethoxycarbonylazepine ⁽ⁱⁱⁱ⁾																		
4	1.404 (7)	1.401 (8)	1.386 (7)	2.114 (6)	2.116 (6)	1.784 (7)	1.781 (6)	1.770 (6)	1.770 (6)	1.144 (7)	1.148 (6)	1.140 (6)	H	H	H	-1.648	0.006	0.238
5	1.424 (4)	1.427 (4)	1.399 (4)	2.103 (3)	2.125 (3)	1.798 (3)	1.788 (3)	1.793 (3)	1.793 (3)	1.127 (5)	1.135 (5)	1.136 (4)	H	H	H	-1.641	0.053	0.293
6	1.415 (4)	1.416 (3)	1.392 (3)	2.114 (2)	2.115 (2)	1.784 (3)	1.787 (3)	1.787 (3)	1.787 (3)	1.128 (5)	1.123 (5)	1.130 (4)	H	H	H	-1.641	0.053	0.290
7	1.412 (3)	1.422 (3)	1.401 (3)	2.105 (5)	2.108 (5)	1.784 (5)	1.797 (5)	1.791 (5)	1.791 (5)	1.135 (7)	1.141 (7)	1.127 (7)	H	H	H	-1.643	0.030	0.278
8	1.407 (4)	1.417 (3)	1.407 (3)	2.156 (2)	2.117 (2)	1.781 (2)	1.788 (2)	1.786 (2)	1.786 (2)	1.140 (3)	1.139 (3)	1.136 (3)	C	H	H	-1.625	0.013	0.250
9	1.413 (3)	1.426 (3)	1.401 (3)	2.156 (2)	2.138 (2)	1.786 (2)	1.783 (2)	1.778 (2)	1.778 (2)	1.137 (3)	1.136 (3)	1.145 (3)	H	H	H	-1.591	0.038	0.256
10	1.417 (5)	1.434 (5)	1.402 (5)	2.154 (4)	2.150 (4)	1.814 (4)	1.786 (4)	1.818 (4)	1.818 (4)	1.140 (5)	1.141 (5)	1.142 (5)	H	H	H	-1.669	0.038	0.224
11	1.428 (5)	1.434 (5)	1.426 (5)	2.117 (4)	2.180 (4)	1.778 (4)	1.780 (4)	1.790 (4)	1.790 (4)	1.145 (5)	1.143 (5)	1.129 (5)	H	H	H	-1.653	0.003	0.273
12	1.435 (4)	1.418 (4)	1.415 (4)	2.112 (3)	2.128 (3)	1.789 (4)	1.791 (4)	1.790 (4)	1.790 (4)	1.137 (4)	1.144 (4)	1.139 (4)	H	H	H	-1.646	0.015	0.226
13	1.429 (4)	1.428 (4)	1.387 (5)	2.098 (3)	2.097 (3)	1.799 (4)	1.789 (3)	1.772 (3)	1.772 (3)	1.125 (5)	1.133 (4)	1.145 (4)	H	H	H	-1.627	0.045	0.261
14	1.403 (6)	1.412 (6)	1.412 (6)	2.131 (4)	2.116 (4)	1.788 (4)	1.788 (4)	1.783 (4)	1.783 (4)	1.147 (6)	1.136 (5)	1.148 (6)	C	H	H	-1.615	0.048	0.244
15	1.394 (7)	1.415 (6)	1.416 (7)	2.139 (5)	2.127 (4)	1.793 (5)	1.792 (5)	1.793 (5)	1.793 (5)	1.141 (5)	1.133 (5)	1.136 (5)	H	H	H	-1.619	0.042	0.230

References: (i) Cotton, Davy, Frenz, Hardscastle & Troup (1973); no H positions given. (ii) Ireland, Brown, Stanford & McKenzie (1974). (iii) Woodhouse, Sim & Sime (1974). (iv) Cotton & Troup (1974b). (v) G. I. Birnbaum (1972); two non-equivalent moieties. (vi) K. B. Birnbaum (1972). (vii) Immirzi (1974). (viii) Present work; see Table 5 and Figs. 3 and 4; two non-equivalent moieties. (ix) Cotton & Troup (1974a). (x) Churchill & Chang (1975). (xi) Riley & Davis (1975); two molecules in the asymmetric unit, measurements at -32°C .

* The signs of these deviations conform to the usage of Immirzi (1974), i.e. deviation from the plane of the *cis-butadiene* group towards the Fe atom is taken as negative. Positions of non-hydrogen *anti*-substituents are often determined by other stereochemical considerations (e.g. these atoms may be part of a ring) and therefore only H substituents have been included in the *anti* column.

APPENDIX I

Statistical survey of the dimensions of the *cis*-butadiene(tricarbonyliron) moiety in various structures

The structures of some forty molecules (ions) containing isolated *cis*-butadiene(tricarbonyliron) moieties have been reported but only twelve structures, comprising fifteen individual *cis*-butadiene-Fe(CO)₃ groups, have $\sigma(\text{C}-\text{C}) < \sim 0.005 \text{ \AA}$. The histograms of measured values of bond lengths and angles are derived from the selected values included in Table 7, except for Fig. 12, where the overall population (not tabulated here) has been added; the fairly wide scatter of the overall population is the reason for its exclusion from the other diagrams. Bond angles (Table 8) are more reliable than lengths, because the latter are affected by molecular thermal motion (Domenicano, Vaciago & Coulson, 1975); results reported by the original authors are seldom corrected for thermal motion, and we have not attempted such a correction. 'Isolated' in the present context means that the Fe and carbonyl groups do not interact directly with other Fe and carbonyl groups in the same molecule. We have not included fluorinated ligands in the survey. Similar surveys have been made; in particular the dimensions of the *cis*-butadiene-Fe(CO)₃ moiety have been reviewed by Cotton, Day, Frenz, Hardcastle & Troup

(1973) and those of the 1,3-cyclohexadiene-Fe(CO)₃ moiety by Cotton & Troup (1974*b*).

Individual geometrical features of the moiety are discussed in terms of the description given in Fig. 10; the moiety as a whole is discussed in terms of a pseudo-octahedral model (Fig. 15).

A1. The tricarbonyliron group

The eclipsed conformation (Fig. 10) has been found in all the compounds whose structures have been reported. The three carbonyls of a particular tricarbonyliron moiety may be divided into two groups: two *equivalent* (to a first approximation) carbonyls similarly disposed towards the *cis*-butadiene moiety [*e.g.* C(5)O(21) and C(3)O(19); C(8)O(20) and C(7)O(24)] and one *unique* carbonyl whose projection points away from the *cis*-butadiene moiety [C(4)O(23); C(6)O(22)]. The three carbonyls are not arranged with C_{3v} symmetry as δ , the angle between Fe-C vectors to the two equivalent carbonyls, is always smaller than ϵ_1 , ϵ_2 , the angles between Fe-C vectors to equivalent and unique groups (Fig. 10). For the compounds included in Table 7, the respective ranges and means are δ : 89–94, 92.0 (1.6)°; ϵ_1 , ϵ_2 : 95–103, 100.0 (2.3)°. The distributions are rather broad, with no definite peaks discernible, although the separate distributions for δ

Table 8. Bond and other angles (°) for the organometallic complexes of Table 7

Organic ligand	<i>cis</i> -Butadiene group				Fe(CO) ₃ group			CO groups				ω
	α_1	α_2	β_1	β_2	equivalent	unique	δ	φ_1	φ_2	φ_3		
Tricyclo[6.3.0.0 ^{2,7}]undeca-3,5-diene	115.9 (2)	115.2 (2)	120.5 (2)	120.3 (2)	102.8 (1)	102.4 (1)	90.5 (1)	178.7 (2)	178.2 (5)	177.0 (4)	132.8	
3-Methoxy-1-methyl-5-(2-oxocyclohexyl)cyclohexadiene	115.0 (3)	115.0 (3)	118.3 (3)	120.5 (2)	100.2 (2)	100.2 (2)	94.4 (1)	175.9 (3)	177.3 (3)	179.1 (3)	132.8	
3-Formyl- <i>N</i> -ethoxycarbonylazepine	119.1 (3)	119.1 (3)	125.0 (3)	125.8 (3)	99.8 (2)	100.3 (3)	93.4 (2)	179.3 (4)	178.0 (4)	176.9 (4)	136.7	
Tricyclo[6.2.0.0 ^{2,7}]deca-3,5-diene	116.0 (5)	114.8 (6)	120.6 (5)	121.9 (6)	100.7 (2)	101.1 (3)	92.6 (2)	178.4 (5)	179.5 (5)	176.8 (6)	133.9	
12-Oxa[4.4.3]propella-2,4,7,9-tetraene (unsymmetrical)	114.2 (2)	114.5 (2)	117.7 (2)	117.8 (2)	95.7 (1)	96.2 (1)	92.5 (1)	177.1 (3)	178.7 (3)	172.8 (3)	147.6	
12-Oxa[4.4.3]propella-2,4,7,9-tetraene (symmetrical)	114.1 (3)	114.9 (3)	118.0 (3)	119.0 (3)	97.8 (2)	97.5 (2)	92.4 (2)	178.9 (3)	178.8 (3)	177.1 (3)	142.6	
2-[(<i>m</i> -Nitrophenyl)amino]- <i>trans,trans</i> -3,5-heptadiene	119.5 (1)	117.1 (1)	118.8 (3)	117.9 (3)	101.8 (2)	101.5 (2)	89.9 (2)	178.6 (3)	179.0 (3)	177.6 (3)	133.2	
2-Phenylamino- <i>cis,trans</i> -3,5-heptadiene	121.1 (3)	121.5 (3)	119.2 (3)	116.7 (3)	98.1 (2)	100.9 (2)	90.3 (2)	177.3 (3)	177.2 (3)	179.3 (3)	137.8	
3 α -Dimethylstyrene	116.8 (3)	114.7 (3)	121.4 (3)	120.6 (3)	99.2 (2)	97.6 (2)	91.7 (2)	178.7 (3)	177.0 (3)	179.1 (3)	136.6	
	114.1 (3)	118.9 (3)	121.0 (2)	120.0 (2)	103.0 (2)	100.3 (2)	92.3 (2)	179.2 (3)	177.3 (3)	179.0 (3)	134.3	
3,3'-Bis(bicyclo[4.2.0]octa-2,4-diene)	112.8 (3)	117.0 (3)			100.7 (1)	100.1 (2)	93.0 (2)	179.0 (3)	178.9 (3)	177.9 (3)		
[C ₅ H ₄ C ₆ H ₆ CO]Fe ₂ (CO) ₅	115.5 (3)	114.6 (3)			101.8 (2)	99.8 (2)	92.8 (2)	179.1 (4)	176.9 (3)	177.4 (3)	136.9	
<i>trans,trans</i> -3,5-Heptadien-2-ol	118.5 (4)	117.6 (4)	121.0 (2)	121.0 (2)	100.3 (2)	103.9 (2)	90.2 (2)	178.8 (4)	178.5 (4)	177.4 (4)	132.2	
	119.3 (4)	117.4 (4)	121.0 (2)	119.0 (2)	101.3 (2)	103.1 (2)	89.3 (2)	177.9 (4)	178.5 (3)	177.4 (4)	130.6	

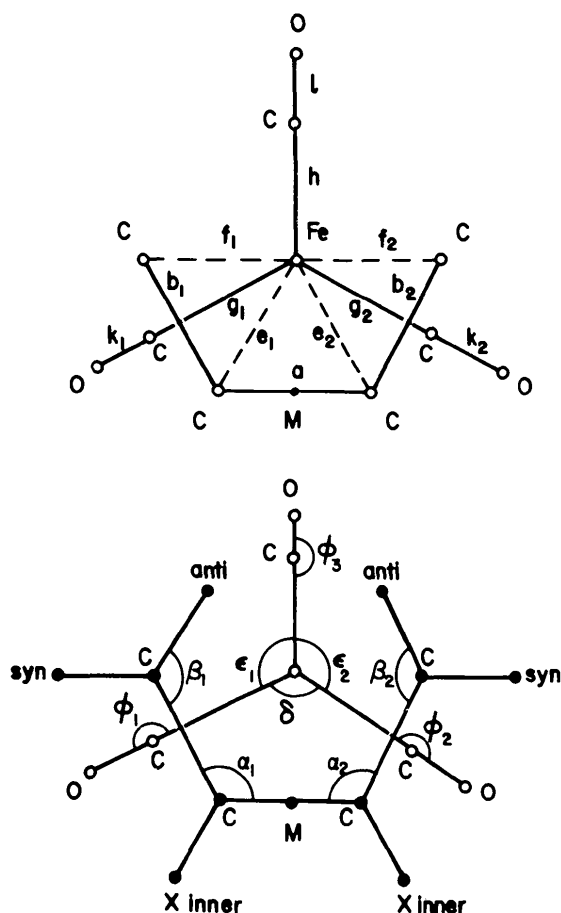


Fig. 10. Definitions of the dimensions in the *cis*-butadiene-tricarbonyliron moiety; we have used the symbols of Cotton & Troup (1974*b*) while the convention of siting the $\text{Fe}(\text{CO})_3$ group below the *cis*-butadiene conforms to the usage of Immirzi (1974; his Fig. 1). The *equivalent* CO groups have bond lengths g_1 , g_2 , k_1 , k_2 , and the *unique* CO group bond lengths are h , l .

and ϵ do not overlap. The $\text{Fe}-\text{C}-\text{O}$ angle has a mean value of $177.9(1.2)^\circ$, significantly different from 180° .*

The $\text{Fe}-\text{C}$ and $\text{C}-\text{O}$ distances have rather sharp histograms (Fig. 11) with mean values of $1.789(10)$ and $1.138(7)$ Å respectively. These values, despite their precision, are likely to suffer from systematic error because thermal motion has not been taken into account. While it would be of interest to study whether there is any correlation between $d(\text{Fe}-\text{C})$ and $d(\text{C}-\text{O})$, the spread of values ($\sim 2\sigma$ about the respective means) is too small to allow this to be done reliably and we have resisted the temptation to present a correlation diagram.

No dimensional differences are apparent between equivalent and unique carbonyl groups.

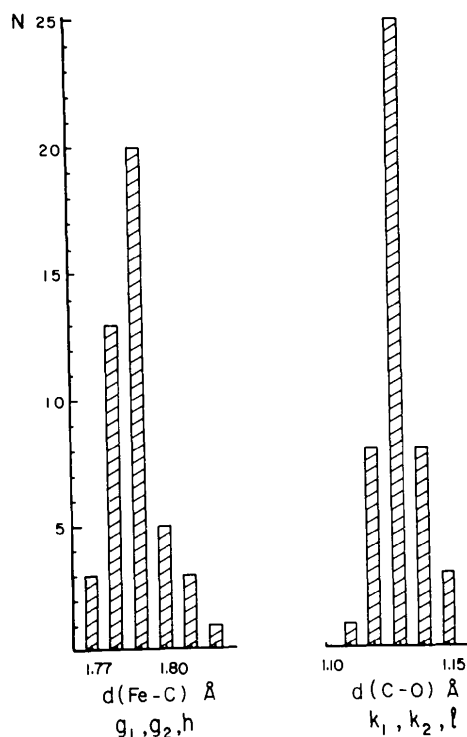


Fig. 11. Histograms of $\text{Fe}-\text{C}$ and $\text{C}-\text{O}$ distances found for the $\text{Fe}(\text{CO})_3$ moiety. There are 45 distances for each histogram; distinction between equivalent and unique carbonyl groups has not been made because it is not justified by the data.

A2. The *cis*-butadiene group

The bond lengths of outer and inner bonds give two overlapping distributions (Fig. 12); outer bonds have a mean length of $1.419(10)$ Å and a range of 1.394 – 1.434 Å, while the corresponding values for inner bonds are $1.404(11)$ Å and 1.386 – 1.426 Å respectively. The difference of 0.015 Å between the mean lengths of outer and inner bonds is slightly smaller than the value of 0.021 Å given by Cotton *et al.* (1973). The correlation diagram (Fig. 13) suggests that a linear relation such as $d(\text{outer}) = d(\text{inner}) + 0.016$ Å may apply, but there is considerable scatter and a clear decision was not possible because of the complications introduced by environmental effects.

The $\angle \text{C}-\text{C}-\text{C}$ inner angles (α_1, α_2) of the butadiene group and the $\angle \text{X}-\text{C}-\text{C}$ outer angles (β_1, β_2) give two broad and overlapping distributions. These values cannot be expected to be particularly illuminating as they will be influenced by the stereochemical requirements of the rest of the molecule, of which the *cis*-butadiene group is only a part.

Immirzi (1974) has pointed out that the substituents on outer C atoms of the *cis*-butadiene group can be designated *syn* and *anti* respectively (Fig. 10) and has shown that *anti* substituents are twisted away from the Fe atom and that *syn* substituents and the substituents on the inner C atoms are twisted towards the Fe atom.

* The distribution is not Gaussian.

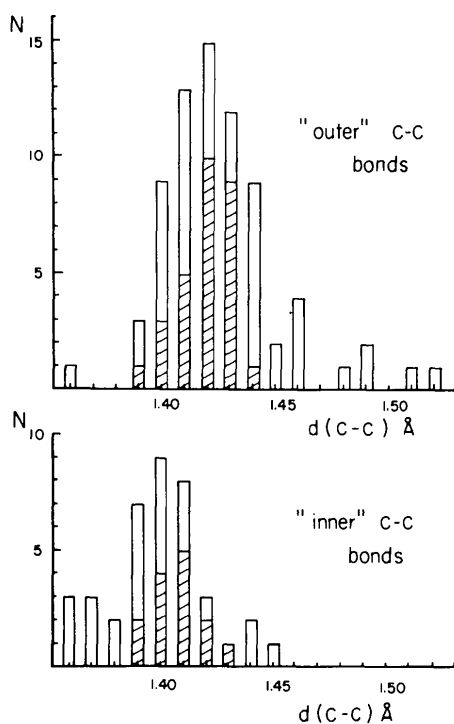


Fig. 12. Histograms of outer and inner C—C lengths in the *cis*-butadiene moiety. The distribution for all available results (not tabulated in the paper) is shown by the open-bar histogram while the selected population (listed in Table 7) is shown by the hatched-bar histogram.

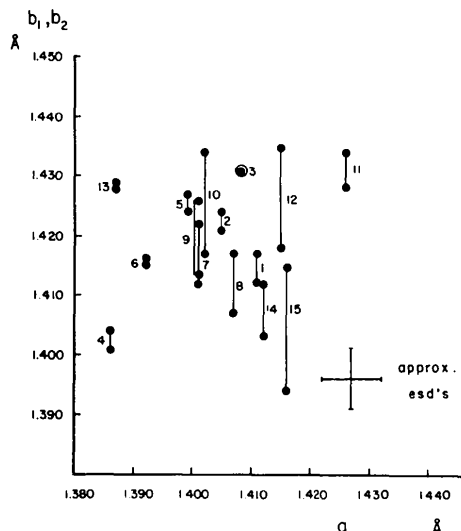


Fig. 13. A diagram showing the correlation between the outer and inner C—C lengths in the *cis*-butadiene moiety. The two separate values of $d(\text{outer})$ corresponding to each $d(\text{inner})$ are joined. The numbers refer to Table 7.

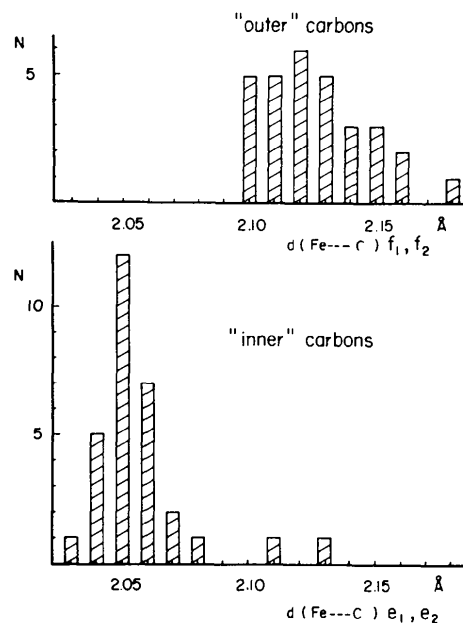


Fig. 14. Histograms of distance from Fe to outer and inner C atoms of the butadiene group.

This is a general phenomenon, as the results summarized in Table 7 show; Churchill (1965) has pointed out that these twists lead to an enhancement of the overlap of filled d orbitals of the Fe atom and π acceptor orbitals of the butadiene ligand.

A3. The *cis*-butadiene(tricarbonyliron) moiety as a whole

The distributions of distances from the Fe atom to the inner and outer C atoms of the *cis*-butadiene unit hardly overlap (Fig. 14). The values depend on the distance of the Fe atom from the plane of the butadiene group (which is about 1.64 Å if the outliers in Table 7 are disregarded) and the projected position of the Fe atom on this plane. The Fe—C distances (range 2.04–2.20 Å) are rather similar to those found for the σ -bonded Fe to C when the Fe is approximately octahedrally coordinated $\{d[\text{Fe}-\text{C}(sp^2)] \sim 2.04, d[\text{Fe}-\text{C}(sp^3)] \sim 2.14 \text{ \AA}\}$ [see Herbstein & Kaftory (1977) for summary].

The pseudo-octahedral model of the *cis*-butadiene(tricarbonyliron) moiety shown in Fig. 15 is convenient for discussion but its choice here does not bear any direct chemical implications.* The four C atoms (two from the equivalent carbonyl groups and the two outer atoms of the butadiene) lie close to a plane (Table 7), with small but significant deviations for some ligands. The Fe atom is always 0.2–0.3 Å below this plane, *i.e.*

* Cotton *et al.* (1973) have preferred a tetragonal-pyramidal model. The geometrical differences are not very large, as comparison of their Fig. 3 with our Fig. 15 shows.

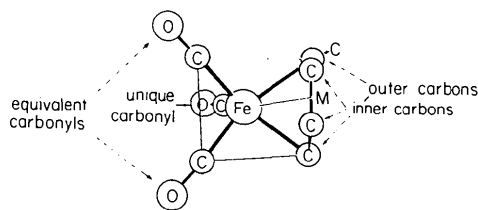


Fig. 15. The pseudo-octahedral model of the *cis*-butadiene-(tricarbonyliron) group.

it and the unique carbonyl group are displaced below this plane. The values of ω (the angle C—Fe—M, where C is the atom of the unique carbonyl group and M is the mid-point of the inner C—C bond of the butadiene) range from 132.8–147.6°. The distribution of ω values is rather featureless.

APPENDIX II

Application of the pseudo-octahedral model to (tricarbonylferracyclopentadiene)-tricarbonyliron(Fe—Fe) fragments

The results available for molecules of this general type are not accurate enough to permit the detailed

comparison performed in Appendix I. However, it is possible to analyse the geometrical arrangements about the two Fe atoms in terms of the pseudo-octahedral model. The results are given in Table 9, where it will be seen that the two Fe atoms have similar but not identical ligand arrangements.

The small differences of detail between the intra- and extra-ring Fe recur with remarkable consistency, e.g. Fe^{II} deviates from the central plane of its pseudo-octahedron by 0.15–0.17 Å, whereas Fe⁰ deviates by 0.25–0.30 Å. The distinction between ϵ and δ for C—Fe—C angles in Appendix I ($\epsilon > \delta$) no longer holds consistently for the present group of compounds. A consistent geometrical pattern is, however, found for the semibridging carbonyl group.

Note added in proof:—The accurate results reported for 1,4-diphenylbutadienetricarbonyliron: $\frac{1}{2}$ (1,4-diphenylbutadiene) (de Cian, L'Huillier & Weiss, 1973a), 1-ethoxycarbonyl-(1*H*)-1,2-diazepinetricarbonyliron (de Cian, L'Huillier & Weiss, 1973b) and tricarbonyl[η^4 -1(1*H*),2(2*H*)-diazepinium]iron trifluoroacetate (Carty, Taylor & Jablonski, 1976) are concordant with the discussion in Appendix I.

Singh (1965) has used histograms of C—N—C bond angles to aid in the location of H atoms in certain heterocyclic molecules; selected (e.s.d.'s < 1°) and overall populations were used.

Table 9. Structural details for some organometallic complexes containing the (tricarbonylferracyclopentadiene)-tricarbonyliron(Fe—Fe) fragment (application of the pseudo-octahedral model)

Definitions of symbols:

$\langle \Delta^2 \rangle^{1/2}$ is the r.m.s. deviation of the C atoms from the plane of the central ring of the pseudo-octahedron. Subscript 1 refers to the ring Fe atom and subscript 2 to the extra-ring Fe atom.

$\Delta(\text{Fe})$ is the deviation of the Fe atom from this mean plane (towards the unique carbonyl group)

ω^1 is the angle $C_u\text{—Fe}^{\text{II}}\text{—Fe}^0$, where C_u is the atom of the unique carbonyl bonded to Fe^{II} (the Fe atom of the ferracyclopentadiene ring) and Fe⁰ is the extra-ring Fe atom.

$\epsilon_1, \epsilon_2, \delta$ are defined in Fig. 10. Note that ϵ_1 and ϵ_2 have been arbitrarily ordered such that $\epsilon_1 > \epsilon_2$.

φ is the angle $C_u\text{—Fe}^{\text{II}}\text{—C}'_u$, where C'_u is the atom of the unique carbonyl bonded to Fe⁰.

ω is the angle $C_u\text{—Fe}^{\text{II}}\text{—M}$, where M is the mid-point of the inner bond of the butadiene group of the ferracyclopentadiene ring.

Compound	(CO) ₃ Fe ^{II} of ferracyclopentadiene ring								(CO) ₃ Fe ⁰ interacting with ring					Semibridging carbonyl		References	
	$d(\text{Fe}^{\text{II}}\text{—Fe}^0)$ (Å)	$\langle \Delta_1^2 \rangle^{1/2}$ (Å)	$\Delta_{\text{Fe}^{\text{II}}}$ (Å)	ω^1 (°)	ϵ_1 (°)	ϵ_2 (°)	δ (°)	φ (Å)	$\langle \Delta_2^2 \rangle^{1/2}$ (Å)	Δ_{Fe^0} (°)	ω (°)	ϵ_1 (°)	ϵ_2 (°)	δ (°)	$d(\text{Fe}^{\text{II}}\text{—C}'_u\text{—O})$ (Å)		$\text{C}'_u\text{—O}$ (°)
[C ₈ H ₆ O ₂] Fe ₂ (CO) ₆	2.493 (2)	0.012 (2)	0.17 (0.6)	135 (0.6)	99 (0.4)	96 (0.4)	92 (0.4)	175 (0.6)	0.028	0.28	144 (0.6)	96 (0.6)	96 (0.4)	98 (0.4)	2.48 (1)	168 (0.6)	(a)
[C ₆ H ₃ Cl ₂] Fe ₂ (CO) ₆	2.520 (3)	0.035 (3)	0.15 (4)	134.9 (4)	98.9 (5)	94.3 (5)	90.9 (5)	174.8 (6)	0.066	0.27	142.9 (6)	97.0 (6)	94.6 (6)	92.2 (6)	2.47 (1)	165 (0.6)	(b)
[C ₆ H ₃ H ₄] Fe ₂ (CO) ₆	2.505 (1)	0.038 (1)	0.15 (4)	132.6 (4)	97.5 (6)	95.8 (6)	91.2 (6)	175.3 (4)	0.072	0.25	139.7 (4)	98.0 (6)	95.7 (6)	88.8 (6)	2.37 (1)	165.5 (4)	(c)
[C ₈ H ₆] Fe ₂ (CO) ₆	2.510 (2)	0.010 (2)	0.16 (4)	135.3 (4)	99.5 (6)	93.6 (6)	95.6 (6)	175.5 (6)	0.144	0.30	142.5 (6)	96.3 (6)	95.2 (6)	95.1 (6)	2.53 (1)	168.8 (6)	(d)

References: (a) Hock & Mills (1961). (b) Degreè *et al.* (1967). (c) Riley & Davis (1975); Prince (1976). (d) Present work.

References

- BARNETT, B. L. & DAVIS, R. E. (1970). Amer. Cryst. Assoc. Meeting, New Orleans, Abstract H2.
- BASTIANSEN, O., HEDBERG, L. & HEDBERG, K. (1957). *J. Chem. Phys.* **27**, 1311–1317.
- BIRNBAUM, G. I. (1972). *J. Amer. Chem. Soc.* **94**, 2455–2459.
- BIRNBAUM, K. B. (1972). *Acta Cryst.* **B28**, 161–168.
- CARTY, A. J., TAYLOR, N. J. & JABLONSKI, C. R. (1976). *Inorg. Chem.* **15**, 1169–1174.
- CHIN, H. B. & BAU, R. (1973). *J. Amer. Chem. Soc.* **95**, 5068–5070.
- CHURCHILL, M. R. (1965). *J. Organomet. Chem.* **4**, 258–260.
- CHURCHILL, M. R. & CHANG, S. W.-Y. (1975). *Inorg. Chem.* **14**, 1680–1685.
- CIAN, A. DE, L'HUILLIER, P. M. & WEISS, R. (1973a). *Bull. Soc. Chim. Fr.* pp. 451–457.
- CIAN, A. DE, L'HUILLIER, P. M. & WEISS, R. (1973b). *Bull. Soc. Chim. Fr.* pp. 457–463.
- COTTON, F. A. (1968). *J. Amer. Chem. Soc.* **90**, 6230–6232.
- COTTON, F. A. (1976). *Progr. Inorg. Chem.* **21**, 1–28.
- COTTON, F. A., DAY, V. W., FRENZ, B. A., HARDCASTLE, K. I. & TROUP, J. M. (1973). *J. Amer. Chem. Soc.* **95**, 4522–4528.
- COTTON, F. A. & TROUP, J. M. (1974a). *J. Organomet. Chem.* **77**, 83–89.
- COTTON, F. A. & TROUP, J. M. (1974b). *J. Organomet. Chem.* **77**, 369–379.
- CRUICKSHANK, D. W. J., FILIPPINI, G. & MILLS, O. S. (1972). *Chem. Commun.* pp. 101–102.
- DEGRÈVE, Y., MEUNIER-PIRET, J., VAN MEERSSCHE, M. & PIRET, P. (1967). *Acta Cryst.* **23**, 119–126.
- DICKENS, B. & LIPSCOMB, W. N. (1962). *J. Chem. Phys.* **37**, 2084–2093.
- DODGE, R. P. (1964). *J. Amer. Chem. Soc.* **86**, 5429–5431.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
- DUCHAMP, D. J., TRUS, B. L. & WESTPHAL, J. (1969). Unpublished results.
- ELIAN, M., CHEN, M. M. L., MINGOS, D. M. P. & HOFFMANN, R. (1976). *Inorg. Chem.* **15**, 1148–1154.
- ELIAN, M. & HOFFMANN, R. (1975). *Inorg. Chem.* **14**, 1058–1076.
- HALLAM, B. F. & PAUSON, P. L. (1958). *J. Chem. Soc.* pp. 642–645.
- HERBSTEIN, F. H. (1963). *Acta Cryst.* **16**, 255–263.
- HERBSTEIN, F. H. & KAFTORY, M. (1977). *Acta Cryst.* **B33**, 3318–3321.
- HERBSTEIN, F. H. & REISNER, M. G. (1972). *Chem. Commun.* p. 1077.
- HERBSTEIN, F. H. & REISNER, M. G. (1975). 25th IUPAC Conf., Jerusalem.
- HOCK, A. A. & MILLS, O. S. (1961). *Acta Cryst.* **14**, 139–148.
- IMMIRZI, A. (1974). *J. Organomet. Chem.* **76**, 65–71.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Tables 2.2A and 2.3.1. Birmingham: Kynoch Press.
- IRELAND, R. E., BROWN, G. G., STANFORD, R. H. & MCKENZIE, T. C. (1974). *J. Org. Chem.* **39**, 51–59.
- JEFFREYS, J. A. D. & WILLIS, C. M. (1972). *J. Chem. Soc. Dalton*, pp. 2169–2173.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- JOHNSON, S. M. & PAUL, I. C. (1970). *J. Chem. Soc. (B)*, pp. 1783–1789.
- MILLS, O. S. & ROBINSON, G. (1963). *Acta Cryst.* **16**, 758–761.
- PAUL, I. C., JOHNSON, S. M., PAQUETTE, L. A., BARRETT, L. H. & HALUSKA, R. J. (1968). *J. Amer. Chem. Soc.* **90**, 5023–5024.
- PRINCE, S. R. (1976). *Cryst. Struct. Commun.* **5**, 451–458.
- REIHLEN, H., GRUHL, A., HESSLING, G. v. & PFRENGLE, O. (1930). *Liebigs Ann.* **482**, 161–182.
- RILEY, P. E. & DAVIS, R. E. (1975). *Acta Cryst.* **B31**, 2928–2930.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.
- SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.
- THORN, D. L. & HOFFMANN, R. (1977). To be published.
- VICTOR, R., BEN-SHOSHAN, R. & SAREL, S. (1970a). *Chem. Commun.* pp. 1680–1681.
- VICTOR, R., BEN-SHOSHAN, R. & SAREL, S. (1970b). *Tetrahedron Lett.* pp. 4257–4260.
- VICTOR, R., BEN-SHOSHAN, R. & SAREL, S. (1971). *Chem. Commun.* pp. 1241–1242.
- VICTOR, R., BEN-SHOSHAN, R. & SAREL, S. (1972). *J. Org. Chem.* **37**, 1930–1937.
- WASER, J., MARSH, R. E. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2703–2708.
- WOODHOUSE, D. I., SIM, G. A. & SIME, J. G. (1974). *J. Chem. Soc. Dalton*, pp. 1331–1335.