

S = 1.084

1651 reflections

108 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$ 

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = -0.03 (4)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$$

	x	y	z	$U_{eq}$
Co	0.15360 (4)	0.15360 (4)	0	0.0273 (2)
Cl	0.15326 (11)	-0.01694 (9)	-0.04214 (10)	0.0430 (3)
N1	0.1274 (3)	0.1889 (3)	-0.1462 (3)	0.0357 (9)
C1	0.0346 (4)	0.1432 (5)	-0.2021 (4)	0.0510 (14)
C2	-0.0334 (5)	0.2343 (5)	-0.2286 (6)	0.075 (2)
C3	0.0399 (4)	0.3235 (4)	-0.2439 (5)	0.0609 (18)
C4	0.1237 (4)	0.3054 (4)	-0.1616 (4)	0.0437 (14)
C5	0.0990 (4)	0.3553 (4)	-0.0621 (4)	0.0408 (13)
N2	0.1596 (3)	0.3043 (3)	0.0218 (3)	0.0291 (8)
C6	0.2695 (3)	0.3394 (4)	0.0311 (4)	0.0342 (11)
Cl1	0.15839 (12)	0.62661 (10)	0.01879 (10)	0.0530 (4)
O1W	-0.2676 (4)	-0.0525 (3)	0.0208 (4)	0.0742 (13)
O2W	-0.0834 (4)	-0.0834 (4)	0	0.139 (4)

Table 2. Selected geometric parameters (Å, °)

Co—N2	1.959 (3)	C2—C3	1.497 (8)
Co—N1 <sup>i</sup>	1.988 (4)	C3—C4	1.538 (7)
Co—Cl	2.2596 (12)	C4—C5	1.482 (7)
N1—C4	1.511 (6)	C5—N2	1.495 (6)
N1—Cl	1.515 (6)	N2—C6	1.488 (5)
Cl—C2	1.501 (8)	C6—C6 <sup>i</sup>	1.508 (9)
N2—Co—N2 <sup>i</sup>	86.8 (2)	N1—Co—Cl <sup>i</sup>	93.95 (12)
N2—Co—N1 <sup>i</sup>	91.12 (16)	N2—Co—Cl	173.91 (12)
N2—Co—N1	85.44 (15)	N2 <sup>i</sup> —Co—Cl	90.26 (11)
N2 <sup>i</sup> —Co—N1	91.12 (16)	N1—Co—Cl	89.30 (12)
N1 <sup>i</sup> —Co—N1	175.3 (2)	Cl <sup>i</sup> —Co—Cl	93.18 (7)
N2—Co—Cl <sup>i</sup>	90.26 (11)		

Symmetry code: (i) y, x, -z.

All H atoms of the ligand were placed at calculated positions [ $U(H) = 1.2U_{eq}(\text{attached atom})$ ]. The H atoms of the water molecule were located from the difference Fourier map and refined at fixed positions with  $U(H) = 1.2U_{eq}(O)$ . The oxonium H atoms were not located in the difference Fourier map and were not placed. The final difference Fourier map contained two peaks with heights of  $0.34 \text{ e } \text{Å}^{-3}$  around O2W, but these were not appropriate positions for H atoms.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1391). Services for accessing these data are described at the back of the journal.

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## A new polymorph of a carbonyliron complex from tetraphenylhexapentaene: bis( $\mu_3, \eta^2, \sigma^2$ -diphenylallenylidene)octa-carbonyltriiron

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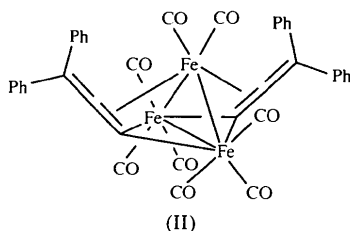
### Abstract

The crystal structure of a new polymorphic form of octa-carbonyl-1- $\kappa^3C, 2\kappa^3C, 3\kappa^2C$ -bis[ $\mu_3$ -3,3-diphenylallenylidene-1:2- $\kappa^2C^1$ :3(1,2- $\eta^2$ )]-triangulo-triiron(0)(3 Fe—Fe), [Fe<sub>3</sub>(C<sub>15</sub>H<sub>10</sub>)<sub>2</sub>(CO)<sub>8</sub>], has been determined. Reaction of tetraphenylhexapentaene with iron dodecacarbonyl leads to the title complex composed of an Fe<sub>3</sub>(CO)<sub>8</sub> central core bridging two C<sub>3</sub>Ph<sub>2</sub> ligands. The molecule adopts a synclinal conformation of the carbonyl groups in two Fe(CO)<sub>3</sub> groups of the Fe<sub>3</sub> triangle, in contrast to the synperiplanar conformation observed previously.

### Comment

The title compound was first obtained in a pure crystalline form by Zimniak & Jasiobędzki (1975). The same compound was synthesized later according to a sim-

ilar procedure in a reaction of a cumulene with iron dodecacarbonyl, and its structure was determined and described as a crystalline triclinic polymorphic  $\alpha$ -form, (I), in space group  $P\bar{1}$  [ $a = 12.436(2)$ ,  $b = 14.988(2)$ ,  $c = 10.105(1)$  Å,  $\alpha = 108.14(1)$ ,  $\beta = 106.66(1)$  and  $\gamma = 97.26(1)^\circ$  (Iyoda *et al.*, 1992); the solvent used for recrystallization was not indicated]. In contrast, recrystallization of the title complex (Zimniak & Jasiobędzki, 1975) from *n*-hexane led to the new monoclinic  $\beta$ -form, (II), in space group  $P2_1/c$ . The present X-ray crystal structure study was carried out to compare the geometries of molecules in both polymorphic forms. The reaction of the arene-substituted hexapentene system ( $\text{Ar}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CAr}_2$ ) with iron dodecacarbonyl produced the complex, which contains an  $\text{Fe}_3(\text{CO})_8$  central core bridging two equivalent  $\text{C}=\text{C}=\text{Ph}_2$  ligands. Similar symmetric incorporation was observed for azines (Bright & Mills, 1967; Zimniak & Zachara, 1997).



The molecular structure of (II) is shown in Fig. 1. The general folding of the molecule and observed bond lengths are in agreement with literature data (Iyoda *et al.*, 1992; Gervasio *et al.*, 1981). The central core consists of a three-membered  $\text{Fe1—Fe2—Fe3}$  ring that includes an  $\text{Fe}(\text{CO})_2$  and two chemically equivalent  $\text{Fe}(\text{CO})_3$  groups. The Fe atoms form an almost equilateral triangle. The Fe2 and Fe3 atoms are coordinated by atoms C1 and C4, forming  $\sigma$  bonds, whereas Fe1 is symmetrically  $\eta^2$ -coordinated by two double bonds ( $\text{C1}=\text{C2}$  and  $\text{C4}=\text{C5}$ ) relative to the plane defined by the central  $\text{Fe1—Fe2—Fe3}$  ring. The major distinction between the molecular structures of (I) and (II) is in the different conformations of the carbonyl groups bonded to the Fe2 and Fe3 atoms. In (II), the carbonyls at Fe2 and Fe3 are synclinal, with an average torsion angle of  $56.9^\circ$ , whereas in (I), a synperiplanar conformation was observed, with a corresponding angle of  $9.4^\circ$  (Fig. 2).

This difference is the reason for the significant alteration in appropriate bond lengths and angles in (I) and (II). In both structures, the central core shows an approximate  $C_3$  symmetry; however, in (II), the symmetry plane passes through all three Fe atoms, whereas in (I), an idealized symmetry plane is perpendicular to the central  $\text{Fe1}'\text{—Fe2}'\text{—Fe3}'$  ring and passes through atoms  $\text{Fe1}'$ ,  $\text{C1}'$ ,  $\text{C2}'$ ,  $\text{C4}'$  and  $\text{C5}'$  [the relevant atoms in (I) are denoted by primes]. As a result of this, the

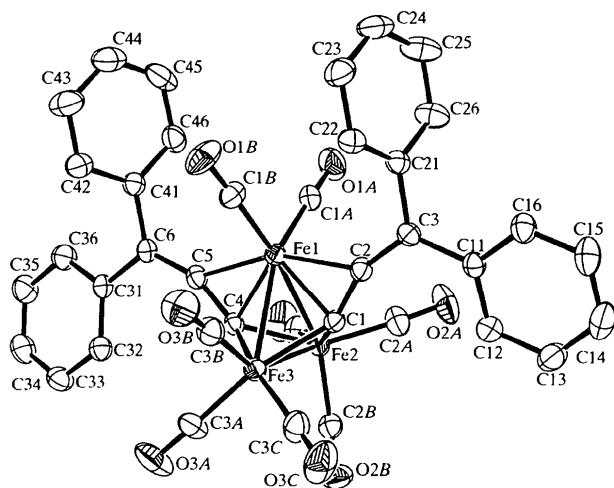


Fig. 1. ORTEP (Burnett & Johnson, 1996) plot of molecule (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

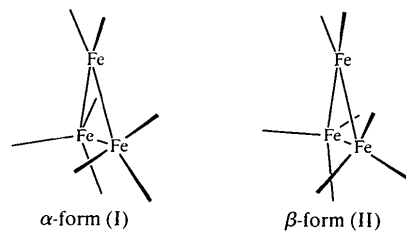


Fig. 2. Schematic presentation of the central core conformations adopted by the molecules in polymorphic forms (I) and (II).

carbonyl groups  $\text{C1B—O1B}$  and  $\text{C1A—O1A}$  at the Fe1 atom, situated on the symmetry plane mentioned, are crowded out by carbonyl  $\text{C3B—O3B}$  bonded to atom Fe3. This interaction is the reason for an elongation of the  $\text{Fe3—Fe1}$  bond [ $2.5437(5)$  Å] compared with the  $\text{Fe1—Fe2}$  and  $\text{Fe2—Fe3}$  bonds of  $2.5266(6)$  and  $2.5271(6)$  Å, respectively. The symmetry of the steric repulsions in (II) gives rise to the symmetry of the bonding of the allenyldiene ligands with the central core. In contrast, in (I), the asymmetric dislocation of the carbonyl groups at atoms  $\text{Fe2}'$  and  $\text{Fe3}'$  with respect to the ligands, and repulsions between carbonyl groups and atoms  $\text{C1}'$  and  $\text{C2}'$  result in different bonding forces for both ligands with the central core. This is manifested in a remarkable extension of the bonds  $\text{C1}'\text{—Fe1}'$  and  $\text{C2}'\text{—Fe1}'$  [ $1.989(3)$  and  $2.157(4)$  Å, respectively], and a shortening of  $\text{C4}'\text{—Fe1}'$  and  $\text{C5}'\text{—Fe1}'$  [ $1.901(3)$  and  $2.099(4)$  Å, respectively] compared with the corresponding bonds in (II) [ $\text{C1—Fe1}$   $1.947(2)$ ,  $\text{C2—Fe1}$   $2.139(2)$ ,  $\text{C4—Fe1}$   $1.939(2)$  and  $\text{C5—Fe1}$   $2.127(2)$  Å]. Thus, in (I), no deformation of the  $\text{Fe1}'\text{—Fe2}'\text{—Fe3}'$  ring was observed, and all bond lengths are almost equal. Furthermore, minor discrepancies in the terminal regions of molecules (I) and (II) were noted, espe-

cially in the twisting of the phenyl rings towards the plane of the central Fe<sub>3</sub> ring. In (II), this twisting is larger than in (I) and is 13.8 (1) and 24.8 (1)° for the least-squares planes of rings C21–C26 and C41–C46, respectively, whereas in (I), the corresponding values are 4.1 (2) and 9.8 (2)°. There are no short contact distances in the crystal lattice of (II) and thus no special intermolecular interactions occur.

We conclude that the title compound occurs as two favourable conformers, which differ in the mutual orientation of the Fe(CO)<sub>3</sub> groups in the central core. The structures of these conformers are expressed as two distinct polymorphic forms.

## Experimental

The preparation of the title compound was performed according to the procedure described previously by Zimniak & Jasiobędzki (1975), followed by recrystallization from *n*-hexane at ambient temperature [m.p. 443–448 K (decomposition)].

### Crystal data

[Fe<sub>3</sub>(C<sub>15</sub>H<sub>10</sub>)<sub>2</sub>(CO)<sub>8</sub>]

*M<sub>r</sub>* = 772.09

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 17.174 (3) Å

*b* = 8.9483 (16) Å

*c* = 22.132 (4) Å

β = 99.313 (13)°

*V* = 3356.4 (10) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.528 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.75–17.30°

μ = 1.332 mm<sup>-1</sup>

*T* = 293 (2) K

Prismatic

0.30 × 0.25 × 0.15 mm

Dark red

### Data collection

Siemens *P3* diffractometer

Profile data from ω–2θ scans

Absorption correction:

ψ scan (*XEMP*; Siemens, 1990)

*T<sub>min</sub>* = 0.633, *T<sub>max</sub>* = 0.819

6040 measured reflections

5841 independent reflections

4932 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.022

θ<sub>max</sub> = 25°

*h* = 0 → 20

*k* = 0 → 10

*l* = –26 → 26

2 standard reflections

every 70 reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.029

*wR*(*F*<sup>2</sup>) = 0.074

*S* = 1.033

5841 reflections

463 parameters

Only H-atom *U*'s refined

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0412*P*)<sup>2</sup> + 0.9826*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.255 e Å<sup>-3</sup>

Δρ<sub>min</sub> = –0.233 e Å<sup>-3</sup>

Extinction correction:

*SHELXL97*

Extinction coefficient:

0.0077 (3)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Fe1—Fe2	2.5266 (6)	Fe1—C1B	1.821 (3)
Fe1—Fe3	2.5437 (5)	Fe2—C2A	1.809 (3)
Fe2—Fe3	2.5271 (6)	Fe2—C2B	1.807 (3)
Fe1—C1	1.947 (2)	Fe2—C2C	1.802 (3)
Fe1—C4	1.939 (2)	Fe3—C3A	1.820 (3)
Fe1—C2	2.139 (2)	Fe3—C3B	1.767 (3)
Fe1—C5	2.127 (2)	Fe3—C3C	1.821 (3)
Fe2—C1	1.960 (2)	C1—C2	1.341 (3)
Fe2—C4	1.945 (2)	C2—C3	1.331 (3)
Fe3—C1	1.946 (2)	C4—C5	1.336 (3)
Fe3—C4	1.954 (2)	C5—C6	1.338 (3)
Fe1—C1A	1.780 (3)		
Fe2—Fe1—Fe3	59.789 (15)	Fe1—C1—Fe2	80.58 (8)
Fe1—Fe2—Fe3	60.440 (13)	Fe3—C1—Fe2	80.65 (8)
Fe1—Fe3—Fe2	59.770 (17)	C2—C1—Fe3	134.81 (16)
C1—Fe1—C4	83.02 (9)	C5—C4—Fe3	133.34 (17)
C2—Fe1—C5	158.91 (8)	C2—C1—Fe2	134.40 (18)
C1A—Fe1—C1B	94.64 (12)	C5—C4—Fe2	135.86 (17)
C1A—Fe1—Fe2	93.85 (8)	C1—C2—C3	156.2 (2)
C1B—Fe1—Fe3	111.83 (9)	C4—C5—C6	156.2 (2)
C1A—Fe1—Fe2—C2A	44.69 (12)	C2A—Fe2—Fe3—C3B	78.26 (19)
C1A—Fe1—Fe2—C2C	–53.64 (12)	C2B—Fe2—Fe3—C3C	49.39 (13)
C1B—Fe1—Fe3—C3B	–4.44 (12)	C2C—Fe2—Fe3—C3A	42.93 (16)

The data were corrected for Lorentz and polarization effects. The phase problem was solved by direct methods using *SHELXS86* (Sheldrick, 1990). All H atoms were located from the difference Fourier map and were positioned in geometrically idealized positions with isotropic displacement parameters.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991a). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991b). Program(s) used to solve structure: *SHELXS86*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL97* and *PARST96* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1302). Services for accessing these data are described at the back of the journal.

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