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## (2*S*)-(+)-Dicarbonyl( $\eta^4$ -2,6,6-trimethylcyclohepta-2,4-dienone)(triphenylphosphine-*P*)-iron

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### Abstract

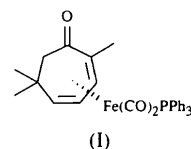
The title compound, [Fe(C<sub>10</sub>H<sub>14</sub>O)(C<sub>18</sub>H<sub>15</sub>P)(CO)<sub>2</sub>], is the first crystalline and enantiomerically pure iron complex with eucarvone as an organic ligand. The absolute configuration could be determined as 2*S*.

### Comment

Chiral carbonyl iron complexes of prochiral 1,3-dienes are valuable tools in stereoselective organic synthesis (Grée, 1989). It is necessary therefore to determine

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the absolute configuration of these complexes. Various methods are used to obtain optically pure or enantiomerically enriched complexes (Grée, 1989; Knölker & Hermann, 1996; Kane-Maguire, Pyne, Siu, Skelton & White, 1996; Maywald & Eilbracht, 1996). For the eucarvone (2,6,6-trimethyl-2,4-cycloheptadien-1-one) complex, the best preparative method, with up to 64% e.e., is kinetic resolution of the tricarbonyliron complex with various sparteine *N*-oxides as a chiral auxiliary (Petrowitsch & Eilbracht, 1997). The phosphine complex can be separated to its pure enantiomers by chiral HPLC. Correlation of the CD spectra of these samples with those of tricarbonyl(cycloheptadienone)iron (Sotokawa *et al.*, 1987) leads to the absolute configuration of the title compound, (I), as shown in Fig. 1 (Petrowitsch & Eilbracht, 1997).



This absolute configuration is confirmed by X-ray anomalous diffraction. The geometry of the organic ligand in the title compound, (I), is similar to the corresponding unsubstituted fragment in the crystal structure of tricarbonyl(2,3-dihydrotropone)iron (Sotokawa *et al.*, 1987). The replacement of the H atoms at C7 by bulkier methyl groups does not significantly influence the geometry of the seven-membered ring as a visual comparison [fractional coordinates or torsion angles are not given by Sotokawa *et al.* (1987)] of the two

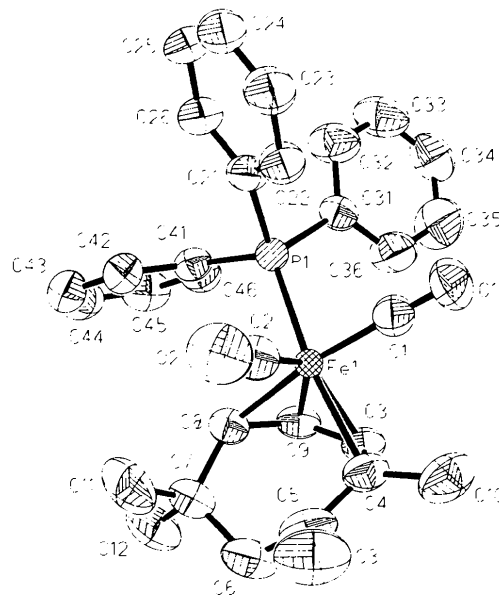


Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

rings shows. There is no structure for the eucarvone ligand in the Cambridge Structural Database. Two short intermolecular C—H...O contacts [C...O 3.229 (4), 3.320 (4) Å; H...O 2.494 (4), 2.415 (4) Å; C—H...O 136.1 (3), 164.4 (3)°] indicate hydrogen bonds.

## Experimental

A racemic mixture of the title compound (I) was prepared by stirring a solution of 1.0 equivalents of rac. eucarvone tricarbonyliron complex, 1.1 equivalents of triphenylphosphine and 1.0 equivalents of trimethylamine *N*-oxide in ethanol under argon for 30 min at room temperature. After evaporation, the residue is chromatographed on silica gel with petroleum/diethyl ether (10:1) to separate rac. (I) from traces of starting material and triphenylphosphane. The racemate was separated to its pure enantiomers by HPLC using a chiral stationary phase (CSP) with *n*-heptane/THF as eluent. The CSP was prepared from optically active *N*-methacryloyl-*L*-leucine-2,5-dimethylpentylamide by covalently bonding to modified silica gel under the conditions of radical polymerization (Arlt, Bömer, Grosser & Lange, 1991). Crystallization from dichloromethane/*n*-hexane at 263 K gave suitable crystals (m.p. 449 K).

### Crystal data

[Fe(C<sub>10</sub>H<sub>14</sub>O)-  
(C<sub>18</sub>H<sub>15</sub>P)(CO)<sub>2</sub>]

$M_r = 524.35$

Orthorhombic

$P2_12_12_1$

$a = 10.497 (2) \text{ \AA}$

$b = 13.332 (3) \text{ \AA}$

$c = 19.369 (4) \text{ \AA}$

$V = 2710.6 (10) \text{ \AA}^3$

$Z = 4$

$D_x = 1.285 \text{ Mg m}^{-3}$

$D_m$  not determined

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 94 916 reflections

$\theta = 4.64\text{--}25.65^\circ$

$\mu = 0.643 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Fragment

$0.45 \times 0.32 \times 0.26 \text{ mm}$

Orange

### Data collection

Nonius Kappa CCD diffractometer

360 frames via  $\omega$ -rotation

( $\Delta\omega = 1^\circ$ ) and two times  
3 s per frame

Absorption correction: none

94 916 measured reflections

5101 independent reflections

3044 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\text{max}} = 25.65^\circ$

$h = -12 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -23 \rightarrow 23$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.050$

$S = 0.825$

5101 reflections

338 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.001$

$\Delta\rho_{\text{max}} = 0.153 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.186 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Absolute configuration:

Flack (1983)

Flack parameter = 0.011 (13)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Fe1—C9	2.052 (2)	C4—C5	1.460 (4)
Fe1—C3	2.069 (2)	C4—C10	1.524 (4)
Fe1—C8	2.127 (2)	C5—C6	1.506 (4)
Fe1—C4	2.149 (3)	C6—C7	1.522 (4)
Fe1—P1	2.2484 (9)	C7—C8	1.513 (4)
O3—C5	1.229 (3)	C7—C11	1.523 (4)
C3—C9	1.393 (3)	C7—C12	1.552 (4)
C3—C4	1.422 (4)	C8—C9	1.417 (3)
C9—C3—C4	121.9 (3)	C8—C7—C6	111.4 (3)
C3—C4—C5	123.0 (3)	C8—C7—C11	111.5 (2)
C3—C4—C10	117.9 (3)	C6—C7—C11	111.5 (3)
C5—C4—C10	113.0 (3)	C8—C7—C12	106.0 (2)
O3—C5—C4	120.5 (3)	C6—C7—C12	108.1 (3)
O3—C5—C6	120.3 (3)	C11—C7—C12	107.9 (3)
C4—C5—C6	119.0 (3)	C9—C8—C7	124.5 (2)
C5—C6—C7	112.7 (2)	C3—C9—C8	120.8 (2)
C9—C3—C4—C5	44.6 (4)	C6—C7—C8—C9	31.8 (4)
C3—C4—C5—C6	3.3 (4)	C4—C3—C9—C8	-1.8 (3)
C4—C5—C6—C7	-71.9 (4)	C7—C8—C9—C3	-62.6 (3)
C5—C6—C7—C8	50.0 (4)		

The data collection covered the whole sphere of reciprocal space. The crystal-to-detector distance was 2.6 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. The structure was solved by direct methods (*SHELXS86*; Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (*SHELXL93*; Sheldrick, 1993). All H atoms were placed geometrically and refined with a riding model including free rotation about C<sub>methyl</sub>—C bonds, and with  $U_{\text{iso}}$  constrained to be  $1.5U_{\text{eq}}$  of the carrier atom.

Data collection: Nonius Kappa CCD software. Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93* and *PARST95* (Nardelli, 1995).

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