

to play a particular role or appears to be affected by a bond of the ionic type. The distances are longer than the sum of the ionic radii of K and O (2.66 Å). Owing to coordination to the potassium ion, the local environment is modified with respect to that found about the water molecule occupying this site in other monomeric structures. Four different cyclodextrin molecules participate in the coordination, two O atoms belong to one cyclodextrin unit translated along the *b* axis [O(24) and O(34)]; two others belong to symmetry-related cyclodextrin units ( $-x, \frac{1}{2} + y, -z$ ) [O(27) and  $(1 - x, \frac{1}{2} + y, -z)$  O(35)]. The potassium ions trapped in the cyclodextrin double layers form an infinite zigzag chain with an angle of 123° along the *b* axis (Fig. 1), the K—K distance being 6.02 Å.

This structure confirms the versatility of the basic monomer  $\beta$ -cyclodextrin hydrate structure which here is shown capable of accepting a potassium ion without significant changes in the lattice; this is also the case for a range of hydrate structures and simple monosubstituted  $\beta$ -cyclodextrin derivatives now under investigation.

This research was partly supported by the MRT and Rhône Poulenc.

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*Acta Cryst.* (1991). **C47**, 1833–1835

## Structure of 1,1,1,2,2,2-Hexacarbonyl- $\{\mu$ -3-[1( $\eta^6$ )-2-methylphenyl]-2( $\eta^4$ )-1-oxo-1-phenyl-2-propene}-chromiumiron

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(Received 10 November 1990; accepted 20 February 1991)

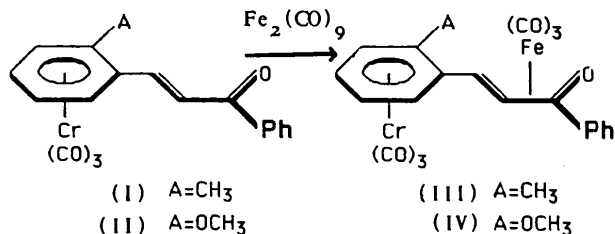
**Abstract.**  $[\text{CrFe}(\text{CO})_6(\text{C}_{16}\text{H}_{14})]$ ,  $M_r = 498.19$ , triclinic,  $P\bar{1}$ ,  $a = 9.719$  (1),  $b = 11.143$  (2),  $c = 11.860$  (3) Å,  $\alpha = 100.76$  (15),  $\beta = 113.7$  (16),  $\gamma = 107.98$  (15)°,  $V = 1045$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.58$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 11.4$  cm<sup>-1</sup>,  $T = 293$  K,  $F(000) = 504$ ,  $R = 0.027$  for 3361 reflections with  $F_o^2$

$\geq 3\sigma(F_o^2)$ . The relative configuration of the title complex obtained by reaction of 1-phenyl-3-( $\eta^6$ -*o*-methylphenyl)tricarbonylchromiumprop-2-en-1-one with nonacarbonyliron is unambiguously (*RS*, *SR*).

**Introduction.** Selective reactions of chiral *ortho*-substituted arene–chromium–tricarbonyl complexes have been reported (Davies & Goodfellow, 1989;

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Solladie-Cavallo, Quazzotti, Colonna & Manfredi, 1989; Brocard, Mahmoud, Pelinski & Maciejewski, 1989; Lebibi, Pelinski, Maciejewski & Brocard, 1990). The metallocenic chiral center of arena-chromium-tricarbonyl complexes is used for the induction of benzylic carbon. On the other hand, the chiral benzylic alcohol can be used to control the configuration of the metallocenic center (Uemura, Minami & Hayashi, 1988; Brocard, Pelinski, Lebibi, Mahmoudi & Maciejewski, 1989). In a recent communication (Mahmoudi, Lamiot, Baert, Maciejewski & Brocard, 1990), we reported a new metallocenic induction on formation of a new chiral center. The reaction of 1-phenyl-3-( $\eta^6$ -*o*-methylphenyl)tricarbonylchromiumprop-2-en-1-one (I) or 1-phenyl-3-( $\eta^6$ -*o*-methoxyphenyl)tricarbonylchromiumprop-2-en-1-one (II) with Fe<sub>2</sub>(CO)<sub>9</sub> provided the  $\eta^4$ - $\alpha,\beta$ -unsaturated ketone-Fe(CO)<sub>3</sub> complexes (III) and (IV) (see scheme). HPLC (high-performance liquid chromatography) analysis and 400 MHz <sup>1</sup>H NMR spectroscopy indicated that only one diastereoisomer was obtained. NMR study did not allow us to assign the relative configuration of these new complexes. We turned to single-crystal X-ray analysis of the methyl complex (III) for an indisputable stereochemical assignment.



**Experimental.** Red-brown crystals of the complex (I) were obtained by cooling ethanol solution. Crystal of dimensions 0.3 × 0.6 × 0.4 mm mounted on an Enraf-Nonius CAD-4 diffractometer, Mo K $\alpha$  (graphite-monochromatized) radiation.  $\omega$ -2 $\theta$  scan. Unit cell determined from least-squares analysis of 25 reflections with  $20 \leq \theta \leq 27^\circ$ . Total of 3675 independent reflections with  $\sin \theta / \lambda \leq 0.595 \text{ \AA}^{-1}$  measured in the range  $-11 \leq h \leq 11$ ,  $-13 \leq k \leq 13$ ,  $l \leq 14$  from which 3361 reflections satisfied  $I \geq 3\sigma(I)$ . The intensities of four reference reflections ( $\bar{1}05$ ,  $\bar{5}32$ ,  $\bar{4}3\bar{1}$ ,  $1\bar{1}\bar{5}$ ) measured every 7200 s of X-ray exposure time showed no significant variation. Lorentz-polarization corrections applied but absorption and extinction ignored. Structure solved from interpretation of Patterson map (SHELXS86; Sheldrick, 1986); full-matrix least-squares refinement of 280 parameters based on  $F$  (SHELX76; Sheldrick, 1976), with anisotropic thermal parameters applied to all non-H atoms. Phenyl H atoms were inserted at calculated positions; the methyl group was treated as a rigid

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^2$ ) with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Fe	2500 (1)	2318 (1)	2725 (1)	66 (1)
Cr	-2300 (1)	3930 (1)	1640 (1)	69 (1)
C10'	-3650 (4)	2204 (3)	1342 (3)	87 (4)
O10'	-4495 (4)	1138 (3)	1191 (3)	127 (4)
C20'	-2044 (4)	4345 (3)	3290 (3)	81 (4)
O20'	-1957 (4)	4587 (3)	4312 (3)	123 (4)
C30'	-4135 (4)	4279 (4)	1192 (3)	109 (5)
O30'	-5303 (3)	4467 (3)	970 (3)	193 (5)
C10''	3617 (4)	4081 (4)	3168 (3)	78 (4)
O10''	4530 (3)	5214 (3)	3476 (3)	104 (4)
C20''	2277 (4)	1807 (4)	1086 (3)	81 (4)
O20''	2077 (4)	1485 (3)	53 (2)	112 (4)
C30''	4408 (4)	2233 (4)	3812 (4)	97 (5)
O30''	5572 (3)	2174 (3)	4504 (3)	152 (5)
O1	1124 (3)	492 (2)	2636 (2)	78 (3)
C2	1263 (4)	1351 (3)	3633 (3)	70 (4)
C3	829 (4)	2414 (3)	3349 (3)	74 (4)
C4	111 (3)	2297 (3)	2002 (3)	68 (3)
C5	-298 (3)	3371 (3)	1584 (3)	66 (3)
C6	-1512 (4)	3069 (3)	244 (3)	75 (4)
C7	-1979 (4)	4080 (3)	-97 (3)	96 (4)
C8	-1255 (4)	5393 (3)	834 (3)	108 (5)
C9	-35 (4)	5709 (3)	2120 (3)	85 (4)
C10	419 (4)	4700 (3)	2490 (3)	67 (4)
C11	-2287 (4)	1698 (3)	-801 (3)	78 (4)
C12	1862 (4)	1210 (3)	4941 (3)	78 (4)
C13	2305 (5)	164 (4)	5119 (4)	139 (6)
C14	2825 (6)	2 (5)	6328 (4)	180 (8)
C15	2908 (5)	855 (4)	7365 (4)	123 (6)
C16	2487 (6)	1894 (4)	7206 (4)	141 (7)
C17	1949 (5)	2070 (4)	5999 (4)	133 (6)

CH<sub>3</sub> unit with its original orientation taken from the strongest H-atom peak on a difference Fourier synthesis. No H-atom coordinates were refined. Final  $R = 0.027$ , unit weights,  $S = 3.80$  and  $(\Delta/\sigma)_{\max} = 0.03$ . The largest peaks in a final difference map were 0.31 and  $-0.32 \text{ e \AA}^{-3}$ . Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) for Fe and Cr, given in *SHELX76* for C and O, and from Stewart, Davidson & Simpson (1965) for H atoms. All calculations performed on a Micro-VAX II.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,\* interatomic distances and bond angles are listed in Table 2. The relative configuration of the molecules is shown in Fig. 1.

The relative configuration is identified as (*RS,SR*) and assuming that the diastereoselectivity is determined in the interaction between the *ortho* group with the unsaturated ketone and the Cr(CO)<sub>3</sub>

\* Lists of structure factors, anisotropic thermal parameters, <sup>1</sup>H NMR chemical shifts and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54016 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Fe—C10''	1.775 (4)	O1—C2	1.304 (4)
Fe—C20''	1.822 (3)	C2—C3	1.427 (5)
Fe—C30''	1.829 (4)	C3—C4	1.423 (4)
Fe—O1	2.017 (2)	C3—C12	1.481 (4)
Fe—C2	2.108 (4)	C4—C5	1.482 (5)
Fe—C3	2.060 (4)	C5—C6	1.441 (4)
Fe—C4	2.118 (4)	C5—C10	1.414 (5)
Cr—C10'	1.834 (3)	C6—C7	1.406 (5)
Cr—C20'	1.818 (3)	C6—C11	1.506 (5)
Cr—C30'	1.832 (3)	C7—C8	1.411 (5)
Cr—C5	2.239 (2)	C8—C9	1.395 (5)
Cr—C6	2.265 (2)	C9—C10	1.410 (4)
Cr—C7	2.233 (2)	C12—C13	1.385 (6)
Cr—C8	2.223 (2)	C12—C17	1.384 (6)
Cr—C9	2.231 (2)	C13—C14	1.383 (6)
Cr—C10	2.207 (2)	C14—C15	1.364 (7)
C10'—O10'	1.147 (5)	C15—C16	1.362 (7)
C20'—O20'	1.153 (5)	C16—C17	1.389 (6)
C30'—O30'	1.153 (5)		
C10''—O10''	1.137 (5)		
C20''—O20''	1.126 (4)		
C30''—O30''	1.130 (5)		
C10''—Fe—C20''	97.0 (2)	O1—C2—C3	114.5 (3)
C10''—Fe—C30''	90.1 (2)	O1—C2—C12	121.0 (3)
C20''—Fe—C30''	105.2 (2)	C3—C2—C12	124.5 (3)
O1—Fe—C2	36.8 (1)	C2—C3—C4	116.1 (3)
C2—Fe—C3	40.0 (1)	C3—C4—C5	121.7 (3)
C3—Fe—C4	39.8 (1)	C4—C5—C6	120.5 (3)
C10'—Cr—C20'	86.1 (2)	C4—C5—C10	121.5 (3)
C10'—Cr—C30'	86.9 (2)	C6—C5—C10	118.0 (3)
C20'—Cr—C30'	85.2 (2)	C2—C7—C8	121.5 (3)
C5—Cr—C6	37.3 (1)	C7—C8—C9	119.8 (3)
C6—Cr—C7	36.4 (1)	C8—C9—C10	119.6 (3)
C7—Cr—C8	36.5 (1)	C5—C10—C9	122.0 (3)
C8—Cr—C9	36.5 (1)	C2—C12—C13	119.8 (3)
C9—Cr—C10	37.0 (1)	C2—C12—C17	122.1 (3)
C5—Cr—C10	37.1 (1)	C13—C12—C17	118.1 (4)
Fe—C10''—O10''	178.5 (5)	C12—C13—C14	120.2 (4)
Fe—C20''—O20''	177.3 (3)	C13—C14—C15	121.3 (5)
Fe—C30''—O30''	178.3 (4)	C14—C15—C16	119.1 (5)
Cr—C10'—O10'	177.9 (3)	C15—C16—C17	120.6 (5)
Cr—C20'—O20'	176.9 (3)	C16—C17—C12	120.6 (4)
Cr—C30'—O30'	175.6 (4)		

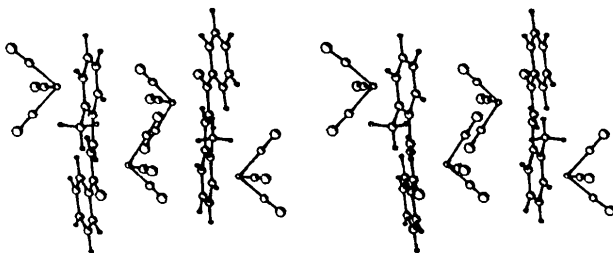


Fig. 1. Stereoscopic view of the molecule (PLUTO; Motherwell &amp; Clegg, 1978).

moiety with  $\text{Fe}_2(\text{CO})_9$ , the *m*-methoxy isomer of (II) was treated with  $\text{Fe}_2(\text{CO})_9$ . We obtained a mixture (1/1) of the two diastereoisomers which verified the proposed explanation.

As observed in the structure of tricarbonyl-[1-6- $\eta$ -(2-ethylanisol)]chromium (Baert, Lamiot, Lebibi & Brocard, 1988) or in the structure of (2,2-dimethyl-7-methoxy-1-tetralol)chromium (Uemura,

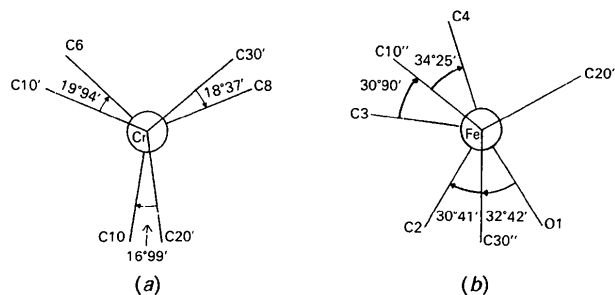


Fig. 2. Newman projections: (a) along the direction from the Cr atom to the center of the ring; (b) along the direction perpendicular to the O1—C2—C3—C4 mean plane.

Nishikawa, Take, Ohmishi, Hirotsu, Higuchi & Hayashi, 1983), the Cr—C(arene) distances are in the range 2.207–2.265 Å, with maxima observed for the substituted atoms C(5) (2.239 Å) and C(6) (2.265 Å). In this way, the configuration of the tricarbonyl chromium group with respect to the methylphenyl ring is roughly eclipsed (see Fig. 2) with the carbonyl groups located near the C(6), C(8) and C(10) atoms. The Fe—C (or Fe—O) distances are in good agreement with those observed in the literature (Alcock, Danks, Richards & Thomas, 1989).

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