and two isomers of [Ru{C≡C(CN)₂CPh≡C(CN)₂}{P(OMe)₃}₂(Cp)] [2·231 (1) to 2·238 (2) Å; Bruce, Cifuentes, Snow & Tiekink, 1989]. This slight lengthening may be due to effective competition for π-backbonding electron density by the carbonyl ligand in (I).

The Ru—Cl bond distance of 1·880 (6) Å in (I) falls within the range of Ru—CO distances of 1·869 (2) Å for [Ru(CO)(PPh₃)₂(Cp)][BPh₄] (II; Wisner, Bartczak & Ibers, 1985), 1·890 (2) Å for [Ru(CO)(PPh₃)₂(Cp)][Co(CO)₄] (III; Doyle & Van Engen, 1985) and 1·863 (3) Å for [Ru(CO)-(PPh₃)₂(η^5-indenyl)][ClO₄].CH₂Cl₂ (IV; Oro, Ciriano, Campo, Foces-Foces & Cano, 1985). Similarly, the C—O bond distance for (I), 1·115 (6) Å, does not differ significantly from the values of 1·144 (3), 1·135 (3) and 1·145 (4) Å found respectively in structures (II)–(IV). This is not surprising, as metal–carbon and carbon–oxygen distances in metal carbonyl compounds are notoriously insensitive to changes in ancillary ligands. The carbonyl stretching frequencies in the infrared spectra are better indicators of electron density available for backbonding at ruthenium, being 2022, 1987, 1978 and 1970 cm⁻¹ for compounds (I)–(IV), respectively.

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Structure of (+)-(3*S*,4*R*,5*R*,1'*R*,2'*S*,5'*R*)-Tetracarbonyl{(3,4-η^2)-5-[5'-methyl-2'-(1-methylethyl)cyclohexyloxy]-2(5*H*)-furanone}iron

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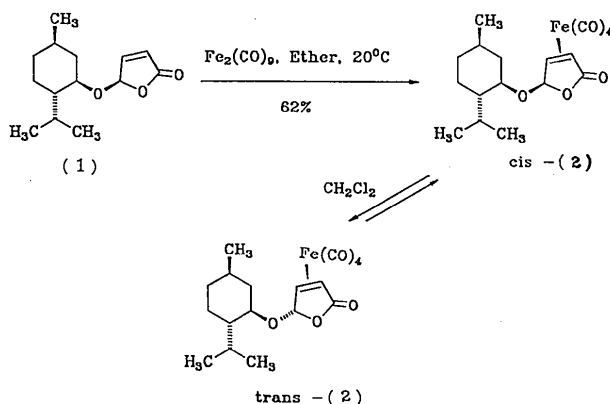**Abstract.** $C_{18}H_{22}FeO_7$, $M_r = 406·2$, orthorhombic, $P2_12_12_1$, $a = 6·4633$ (3), $b = 10·7995$ (7), $c = 28·056$ (1) Å, $V = 1958·3$ Å³, $Z = 4$, $D_x = 1·38$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 8·00$ cm⁻¹, $F(000) = 848$, $T = 293$ K, $R = 0·030$ for 3655 observed reflections, crystals obtained from hexane.

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A striking feature of the molecular structure is an unusual 'anti-steric' *cis* orientation of the menthyloxy- and the Fe(CO)$_4$ ligands. The experimental results have been supplemented by the results of quantum chemical *ab initio* calculations.

Introduction. In connection with studies directed towards the use of diastereo- and enantiomerically pure transition-metal complexes in asymmetric synthesis we have discovered an iron compound with unusual 'anti-steric' configuration.

Experimental. Reaction of iron enneacarbonyl with the easily available $(-)$-5-menthyloxy-2(5H)-furanone (1) (Feringa & de Lange, 1988) in ether yields 62% of enantiomerically pure $(+)$-(3S,4R,5R,1$'R$,2$'S$,5$'R$)-Tetracarbonyl{(3,4-η^2)-5-[5'-methyl-2'-(1-methylethyl)cyclohexyloxy]-2(5H)-furanone}iron (2). The product [m.p. = 368–371 K (decomp.); $[\alpha]_D^{20°C} = +24\cdot1°$ ($c = 0\cdot92$, ether)], which epimerizes rapidly in CH$_2$Cl$_2$ solution, is obtained in the form of pale yellow needles.

Crystal size: $0\cdot36 \times 0\cdot43 \times 0\cdot43$ mm. Data collection on an Enraf–Nonius CAD-4 diffractometer by a coupled $\Omega/2\theta$ scan technique, where the time to measure the background was half that spent measuring the peak. The intensity of a reflection and its e.s.d. were calculated from $I = [\text{INT} - 2(\text{BGL} + \text{BGR})]$ and $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{1/2}$, where INT, BGL, and BGR are the peak intensity, and left and right background. The horizontal detector aperture and the ω scan range varied as $1\cdot9 + 1\cdot05\tan\theta$ mm and $0\cdot7 + 0\cdot35\tan\theta°$, respectively. Data were corrected for Lorentz and polarization effects. Graphite-monochromated Mo $K\alpha$ radiation, 25 reflections in the range $10\cdot32 \leq \theta \leq 16\cdot14°$ for determination of cell constants, no absorption correction, for intensity measurement $(\sin\theta/\lambda)_{\text{max}} = 0\cdot65$ Å^{-1}, $h\ 0 \rightarrow \pm8$, $k\ 0 \rightarrow 13$, $l\ 0 \rightarrow 36$, total number of reflections 4772, merged according to point group 222 to give 3655 reflections with $I \geq 2\cdot0[\sigma(I)]$. Three stand-

ard reflections, no decomposition or movement of the crystal detected during measurement.

The structure has been solved by means of the heavy-atom method. Thermal parameters for Fe, C, and O have been refined anisotropically. The positions of the H atoms could partly be located in a difference map and have partly been calculated; however, all turned out to be stable under isotropic refinement ($U_H = 0\cdot05$ Å^2). Full-matrix least-squares refinement of a total number of 324 parameters resulted in $R = 0\cdot030$, $wR = 0\cdot030$, where the quantity minimized was $\Sigma w(\Delta F)^2$ with $w = [\sigma^2(F_o)]^{-1}$ and $\Delta F = |F_o| - |F_c|$.

Error of fit $S = 1\cdot64$, an enantiopol parameter of $0\cdot02$ (Flack, 1983) gave the absolute configuration, final residual electron density $\rho = 0\cdot35$ e Å^{-3}, and final average shift over e.s.d. $0\cdot35$. Real and imaginary parts of the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Besides some locally written routines, the following programs were used: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965) for data reduction, *SHELX*76 (Sheldrick, 1976) for Fourier calculations, *GFMLX*, a highly modified version of *ORFLS* (Busing, Martin & Levy, 1962) by F. Hirshfeld (blocking options and subsidiary parameters), P. Coppens, L. Leiserowitz, D. Rabinovich, D. Brauer & H. Flack (enantiopol refinement) for full-matrix least-squares refinement, *XANADU* (Roberts & Sheldrick, 1975) for calculations of best planes, torsion angles and idealized H-atom positions, *ORTEP* (Johnson, 1965) and *SCHAKAL* (Keller, 1986) for molecular drawings, *GAUSSIAN*86 (Frisch, Binkley, Schlegel, Raghavachari, Melius, Martin, Stewart, Bobrowicz, Rohlfing, Kahn, DeFrees, Seeger, Whiteside, Fox, Fleuder & Pople, 1984) for the quantum chemical calculations. The results of the X-ray structure analysis are summarized in Tables 1 and 2, which give the final atomic coordinates and selected interatomic distances and angles. Fig. 1 shows the molecular structure, and Fig. 2 the packing of the molecules in the unit cell.*

Discussion. Compound (2) is a typical [Fe(CO)$_4(\eta^2$-olefin)] complex in that the species might be derived from an iron pentacarbonyl molecule in which one of the equatorial carbonyl groups has been replaced by the C=C segment of the ligand. The plane defined by the axial carbonyl groups and the iron atom is essentially orthogonal to the equatorial plane. The

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Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with standard deviations in parentheses*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0·7365 (1)	1·0067 (1)	0·9644 (1)	0·041 (1)
O1	0·5529 (3)	0·7577 (2)	0·9631 (1)	0·094 (2)
O2	0·3513 (3)	1·1185 (2)	1·0007 (1)	0·087 (2)
O3	1·1348 (3)	0·8918 (2)	0·9387 (1)	0·073 (1)
O4	0·9392 (3)	1·0666 (2)	1·0553 (1)	0·085 (1)
O5	0·9724 (3)	1·0663 (2)	0·8599 (1)	0·061 (1)
O6	1·1320 (3)	1·2143 (2)	0·9024 (1)	0·083 (1)
O7	0·7626 (3)	0·8907 (1)	0·8537 (1)	0·047 (1)
C1	0·6209 (4)	0·8547 (2)	0·9642 (1)	0·058 (1)
C2	0·4992 (4)	1·0770 (3)	0·9868 (1)	0·056 (2)
C3	0·9802 (4)	0·9367 (2)	0·9459 (1)	0·049 (1)
C4	0·8611 (4)	1·0438 (2)	1·0207 (1)	0·058 (2)
C5	0·9774 (4)	1·1551 (2)	0·8951 (1)	0·058 (2)
C6	0·7749 (4)	1·1588 (2)	0·9187 (1)	0·049 (1)
C7	0·6469 (4)	1·0696 (2)	0·8973 (1)	0·045 (1)
C8	0·7615 (4)	1·0183 (2)	0·8550 (1)	0·048 (1)
C9	0·8191 (4)	0·8343 (2)	0·8082 (1)	0·045 (1)
C10	0·8273 (4)	0·6944 (2)	0·8177 (1)	0·046 (1)
C11	0·8650 (5)	0·6270 (3)	0·7699 (1)	0·063 (2)
C12	0·7029 (5)	0·6580 (2)	0·7331 (1)	0·062 (1)
C13	0·6945 (4)	0·7960 (2)	0·7231 (1)	0·057 (2)
C14	0·6649 (5)	0·8668 (2)	0·7696 (1)	0·053 (2)
C15	0·5292 (7)	0·8297 (4)	0·6871 (1)	0·079 (2)
C16	0·9756 (4)	0·6579 (2)	0·8582 (1)	0·058 (2)
C17	0·9403 (7)	0·5236 (3)	0·8739 (2)	0·086 (3)
C18	1·2006 (6)	0·6811 (5)	0·8467 (2)	0·092 (3)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *with standard deviations in parentheses*

Fe—C1	1·804 (3)	O7—C9	1·462 (3)
Fe—C2	1·824 (3)	C5—C6	1·467 (4)
Fe—C3	1·823 (2)	C6—C7	1·405 (3)
Fe—C4	1·819 (3)	C7—C8	1·504 (3)
Fe—C6	2·100 (2)	C9—C10	1·535 (3)
Fe—C7	2·085 (2)	C9—C14	1·513 (4)
O1—C1	1·137 (3)	C10—C11	1·546 (4)
O2—C2	1·126 (3)	C10—C16	1·540 (4)
O3—C3	1·129 (3)	C11—C12	1·508 (4)
O4—C4	1·123 (3)	C12—C13	1·518 (4)
O5—C5	1·377 (3)	C13—C14	1·525 (4)
O5—C8	1·465 (3)	C13—C15	1·515 (5)
O6—C5	1·204 (3)	C16—C17	1·533 (4)
O7—C8	1·379 (2)	C16—C18	1·511 (5)

C7—C6—Fe	69·8 (1)	C7—Fe—C6	39·2 (1)
C5—C6—Fe	111·1 (2)	C7—Fe—C4	146·8 (1)
C8—C7—C6	107·4 (2)	C7—Fe—C3	96·8 (1)
C8—C7—Fe	117·1 (2)	C7—Fe—C2	86·7 (1)
C6—C7—Fe	71·0 (1)	C7—Fe—C1	100·3 (1)
C7—C8—O7	113·2 (2)	C6—Fe—C4	107·8 (1)
C7—C8—O5	104·7 (2)	C6—Fe—C3	92·8 (1)
O7—C8—O5	110·6 (2)	C6—Fe—C2	89·1 (1)
C14—C9—C10	112·1 (2)	C6—Fe—C1	139·4 (1)
C14—C9—O7	111·3 (2)	C4—Fe—C3	87·5 (1)
C10—C9—O7	105·5 (2)	C4—Fe—C2	88·9 (1)
C16—C10—C11	115·0 (2)	C4—Fe—C1	112·8 (1)
C16—C10—C9	113·7 (2)	C3—Fe—C2	176·3 (1)
C11—C10—C9	108·6 (2)	C3—Fe—C1	88·8 (1)
C12—C11—C10	112·3 (2)	C2—Fe—C1	91·8 (1)
C13—C12—C11	111·7 (2)	C8—O5—C5	109·6 (2)
C15—C13—C14	111·2 (2)	C9—O7—C8	116·2 (2)
C15—C13—C12	112·6 (3)	O1—C1—Fe	177·8 (2)
C14—C13—C12	109·8 (2)	O2—C2—Fe	178·9 (3)
C13—C14—C9	114·4 (2)	O3—C3—Fe	173·7 (2)
C18—C16—C17	111·2 (3)	O4—C4—Fe	179·6 (2)
C18—C16—C10	113·5 (3)	C6—C5—O6	130·5 (2)
C17—C16—C10	111·2 (3)	C6—C5—O5	108·7 (2)
		O6—C5—O5	120·8 (2)
		C7—C6—C5	108·3 (2)

C=C moiety lies virtually in the equatorial plane and the deviations of its termini from the least-squares plane defined by the atoms C1, C4, Fe, C6, and C7 are 0·051 (C6) and 0·058 Å (C7), respectively. The five-membered ring is also close to planarity, the mean deviation from its least-squares plane being only 0·042 Å. The planes defined by C1, C4, Fe, C6, and C7 on the one and C7, C6, C5, O5, and C8 on the other hand enclose an angle of 107·9°, reflecting the steric demands of the 'olefin' ligand. Interestingly, the axial Fe—C3—O3 segment is distinctly bent [173·7 (2)°], while all other Fe—CO units are almost linear. This structural feature might indicate a specific interaction between the Fe—C3—O3 section and certain elements of the 'alkene' part (see below). As is usually found, the axial Fe—CO bonds are somewhat longer than their equatorial counterparts; however, the difference is not so marked as, *e.g.* 0·23 Å in the case of acrylonitrile(tetracarbonyl)iron (Luxmoore & Truter, 1962). With an average value of 2·093 (2) Å the bonds between the C atoms of the C=C bond and the metal atom are not only close to the value obtained for the acrylonitrile complex, but also to those found for tetracarbonyl(fumaric acid)-iron (Corradini, Pedone & Sirigu, 1966; Pedone & Sirigu, 1967; Pedone & Sirigu, 1968). However, they are slightly shorter than in (1,5-cyclooctadiene)bis-
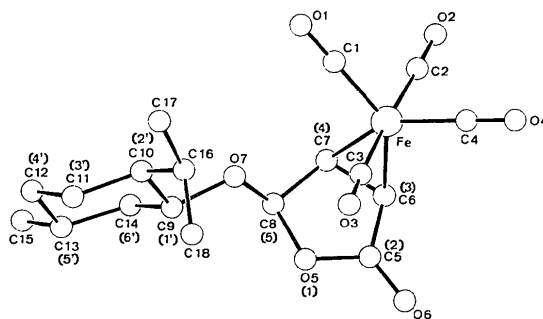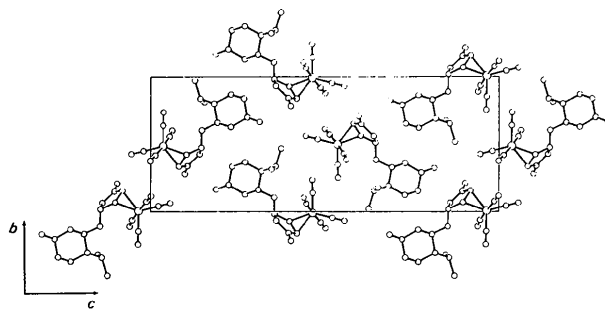

Fig. 1. View of a single molecule. The numbers in parentheses correspond to the IUPAC nomenclature.

Fig. 2. Packing of the molecules in the unit cell. View of the structure normal to the *cb* plane.

$C_{18}H_{22}FeO_7$

(tetracarbonyl)iron [2·147 (6) Å] (Krüger, 1970). At 1·405 (3) Å the length of the C=C bond in (2) is very close to that in the acrylonitrile and 1,5-cyclooctadiene compounds. Since no X-ray data for the uncomplexed furanone ligand are available, we judged the influence of complexation on the geometry of the ligand by comparison of the structural parameters of the complexed unit with the results of a quantum chemical *ab initio* calculation for a model compound in which the menthyl group had been replaced by an H atom, assuming that the influence of the remote menthyl substituent on the geometry of the five-membered ring is negligible. The calculation has been performed with the 6-31G* basis set (Hariharan & Pople, 1973) and thus the geometry optimized regarding the total energy of the molecule (final value: $E_{tot} = -378·37893$ a.u.) might be considered quite reliable. For the C=C double bond length we obtained a value of 1·315 Å. Comparison between experimentally determined C=C bond distances and the corresponding computational results obtained with the same basis set reveals that the former value might be about 0·02 Å too short (Hehre, Radom, v. Ragué Schleyer & Pople, 1986). Applying this empirical correction to our computational bond length we end up with an elongation of the double bond upon complexation of approximately 0·07 Å. This value is quite similar to the one determined for the acrylonitrile complex (0·06 Å) (Luxmoore & Truter, 1962). This lengthening of the olefinic double bond upon complexation is a common feature of η^2-alkene complexes and might be understood in terms of the Dewar–Chatt–Duncanson model (Dewar, 1951; Chatt & Duncanson, 1953), in which σ donation from an occupied olefinic π MO into an empty metal orbital is synergically supplemented by back donation from a filled metal orbital into an unoccupied π^* MO of the olefin.

Somewhat unexpected is the 'anti steric' *cis* orientation of the menthyloxy- and the tetracarbonyliron fragments, since reactions of the double bond in butenolide (1) normally occur on the less hindered face, leading to *trans* products (Ferringa & De Lange, 1988; Hoffmann, Scharf & Runsink, 1989). The reason for the unusual orientation of the ligands in the crystal might be sought either in intrinsic molecular properties of the two possible isomers, *i.e.* a lower total energy of the *cis* compared with the *trans* isomer, or in kinetic effects as a facilitation of the *cis* versus the *trans* approach by parts of the menthyloxy substituents. However, another possibility would be that the reaction initially leads to an equilibrium mixture of both the *cis* and the *trans* isomer of (2), but that under the conditions of the experiment the solubility of the *cis* species is lower, resulting in a constant removal of this isomer from the solution.

Exploratory calculations by means of the extended Hückel theory indicate that the 'anti steric' configuration of the complex might be due to intrinsic molecular properties. This problem is currently being scrutinized by further quantum chemical calculations, and a full account of this theoretical work will be given elsewhere.

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