

Cl1—Ru—P1	83.04 (3)	Ru—P2—C13	116.3 (1)
Cl1—Ru—P2	93.28 (3)	Ru—P2—C19	119.82 (9)
P1—Ru—P2	83.48 (2)	Ru—P2—C31	109.73 (8)
Ru—P1—C1	120.81 (9)	P1—C30—C31	107.1 (2)
Ru—P1—C7	117.42 (9)	P2—C31—C30	108.7 (2)
Ru—P1—C30	108.33 (8)		

Both crystals were mounted in random orientations on glass fibers. Rotation photographs were used to locate reflections for subsequent indexing. Axial photographs confirmed the axial lengths for both unit cells and $2/m$ Laue diffraction symmetry. The reflection conditions $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) resulted in the space-group assignment as $P2_1/c$. Data for both compounds included a number of redundant data at low angle as a measure of the precision and quality of the data sets. Both structures were solved *via* direct methods which resulted in the Ru-atom position and the positions of a small group of atoms including Cl and P. The structures were completed by running full-matrix least-squares cycles on the partial model with isotropic displacement parameters followed by difference Fourier syntheses.

Large positive residuals [greater than $1.0 \text{ e } \text{Å}^{-3}$ for (A) and greater than $3.0 \text{ e } \text{Å}^{-3}$ for (B)] remained in the difference Fourier maps for both structures after the assignment of all non-H atoms in the compounds. Examination of these residuals revealed the presence of a chloroform molecule in the asymmetric unit of both structures. Disorder of the chloroform molecule in the structure of (A) required modeling with two sets of Cl atoms with fractional site occupancies. The sums of the occupancies for corresponding Cl atoms ranged from 0.958 to 1.054. Simultaneous refinement of both sets of Cl atoms was ill-behaved, so one set of Cl atoms was refined with strongly damped shifts while the parameters for the other set were fixed. The roles of both sets of Cl atoms were alternated until the refinement converged.

All non-H atoms were refined with anisotropic displacement parameters. H atoms were located in the difference Fourier maps but were placed at idealized positions; each assigned an isotropic displacement parameter 30% larger than the isotropic displacement parameter of the C atom to which it is bonded. The only exception to this procedure was for H28 on the disordered chloroform molecule in the structure of (A). This single H atom was located in difference Fourier maps and its position and isotropic displacement parameter refined assuming full occupancy. No other residual Fourier peak could be assigned to a second H atom of the disordered molecule. H-atom positions were updated throughout the final cycles of refinement. Examination of strong, low-angle reflections revealed no systematic extinction effects.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *MULTAN11/82* (Main *et al.*, 1982); program(s) used to refine structures: *MolEN*; molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and H28 for (A), and bond distances and angles involving non-H atoms for (B) have been deposited with the IUCr (Reference: BK1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricarbonyl(η^5 -2,4-dimethylpentadienyl)-iron Tetrafluoroborate

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Abstract

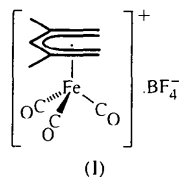
The title compound, [Fe(C₇H₁₁)(CO)₃]BF₄, has been found to have the expected piano-stool geometry, except that the unique carbonyl ligand is tilted towards the

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dienyl ligand by about 25° relative to the other carbonyl ligands. As in the case of the $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_{11})]^+$ cation, a large difference appears to exist between the internal C—C—C bond angles [129.1(7) *versus* 122.1(6)°] of the open dienyl ligand.

Comment

An earlier structural study of $[\text{Co}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})]\text{BF}_4$, where 2,4-C₇H₁₁ is 2,4-dimethylpentadienyl (Ernst, Ma, Sergeson, Zahn & Ziegler, 1987), revealed that the central C—C—C bond angle of the 2,4-C₇H₁₁ ligand was unusually large relative to the average of the interior angles about the methylated C-atom positions, *i.e.* 131.0(13) *versus* 118.2(10)°. It was not clear, however, whether this difference is due to the net charge of the complex or to the relatively high oxidation state (+3) of the Co center. In an effort to distinguish between these two possibilities, we have undertaken the structure determination of $[\text{Fe}(2,4\text{-C}_7\text{H}_{11})(\text{CO})_3]\text{BF}_4$, (I).



The structure of (I) is shown in Fig. 1. The C(5)—C(6)—C(7) angle of 129.1(7)° is significantly larger than the adjacent angles about the C(5) and C(7) atoms, which average 122.1(6)°. While the magnitude of the difference is greater than the norm (Ernst, 1984), the statistical uncertainties are significant enough that a definite conclusion can not be reached. The rather large $J^{13\text{C}}\text{—H}$ value of 187 Hz for the central C atom (*cf.* 180 Hz for the terminal CH₂ groups and 134 Hz for the CH₃ groups) is in agreement with the relatively high *s*-orbital contribution for that atom. Furthermore, it should be noted that in related systems, replacement of a carbonyl ligand by more strongly donating ligands leads to smaller differences: *cf.* $[\text{Ru}(2,4\text{-C}_7\text{H}_{11})(\text{CO})_2(\text{PEt}_3)]^+$ [127.6(6) *versus* 121.4(3)°] and $[\text{Ru}(2,4\text{-C}_7\text{H}_{11})(\text{CO})(\text{PEt}_3)_2]^+$ [124.8(11) *versus* 124.1(19)°] (Newbound, Stahl, Ziegler & Ernst, 1990). Thus, there could be a real dependence of the difference in angles on the electron density present in the complex.

Several other parameters are also worthy of mention. The methyl groups are tilted below the plane of the pentadienyl ligand [C(4)—C(8)] by an average of 8.7(5)° (the sine of the tilt angle being the ratio of the deviation below the plane to the C—CH₃ bond length). Such a value is reasonable compared with values found in related complexes, as are the relative tilts of the carbonyl ligands below the Fe atom. These tilts can be defined

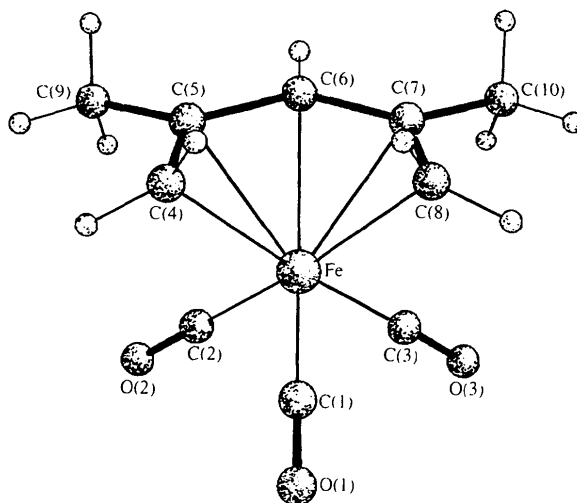


Fig. 1. The structure of the $[(\eta^5\text{-}2,4\text{-dimethylpentadienyl})\text{Fe}(\text{CO})_3]^+$ cation, including H-atom positions.

by the ratio of the deviation of the carbonyl C atoms below the Fe-atom location to the Fe—CO bond length, according to which a much smaller tilt is observed for the unique carbonyl ligand [C(1)—O(1)] relative to the average of the other two [15.2(7) *versus* 40.2(8)°]. This leads to a noticeably small 'trans' C(1)—Fe—C(6) angle of 147.9(3)°. Finally, the Fe—C bond lengths are longest for the terminal C atoms [average 2.177(6) Å], intermediate for the formally uncharged C atoms in the 2 and 4 positions [C(5) and C(7); average 2.145(6) Å], and shortest for the central C atom [2.109(7) Å]. A similar trend was observed for $[\text{Co}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})]^+$, with *M*—C bond lengths shorter by *ca* 0.1 Å.

Four similar structures have been reported. A related neutral compound has been reported by Ma, Weber, Ziegler & Ernst (1987), containing an I atom in place of one carbonyl group. The neutral dicarbonyl dimer has been reported by Gedridge, Patton, Ernst & Ma (1987). Lumini, Cox, Roulet & Schenk (1992) reported a neutral ruthenium analog, with an I atom in place of one carbonyl group, and Gatilov, Bokii & Siruchkov (1975) have reported an analog containing the heptamethylcyclohexadienyl ligand.

Experimental

Yellow crystals, grown from nitromethane/ether solution, were obtained from the reaction of either $[\text{Fe}(\eta^4\text{-}2,4\text{-dimethylpentadiene})(\text{CO})_3]$ or $[(\eta^4:\eta^4\text{-}2,4,7,9\text{-tetramethyl-}1,3,7,9\text{-decatetraene})\text{Fe}_2(\text{CO})_6]$ with $\text{C}(\text{C}_6\text{H}_5)_3\text{BF}_4^-$ (1 and 2 equivalents, respectively) in CH_2Cl_2 (Ma, Weber, Ziegler & Ernst, 1986).

Crystal data

$[\text{Fe}(\text{C}_7\text{H}_{11})(\text{CO})_3]\text{BF}_4$
 $M_r = 321.85$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic
 $P2_1/c$
 $a = 11.095$ (3) Å
 $b = 10.098$ (3) Å
 $c = 11.607$ (4) Å
 $\beta = 91.34$ (3)°
 $V = 1300.2$ (7) Å³
 $Z = 4$
 $D_x = 1.64$ Mg m⁻³
 D_m not measured

Cell parameters from 25 reflections
 $\theta = 20-25^\circ$
 $\mu = 1.204$ mm⁻¹
 $T = 295$ K
 Block
 $0.30 \times 0.30 \times 0.30$ mm
 Yellow

C(4)—C(5)	1.407 (11)	C(5)—C(6)	1.427 (13)
C(6)—C(7)	1.375 (13)	C(7)—C(8)	1.415 (11)
C(5)—C(9)	1.500 (13)	C(7)—C(10)	1.516 (13)
C(1)—Fe—C(2)	97.6 (4)	C(2)—Fe—C(6)	105.3 (3)
C(2)—Fe—C(3)	88.6 (4)	C(4)—Fe—C(6)	70.3 (3)
C(2)—Fe—C(4)	95.4 (4)	C(1)—Fe—C(8)	86.6 (4)
C(1)—Fe—C(6)	147.9 (3)	C(3)—Fe—C(8)	93.9 (4)
C(3)—Fe—C(6)	105.7 (4)	C(4)—C(5)—C(6)	121.2 (8)
C(2)—Fe—C(8)	174.9 (4)	C(4)—C(5)—C(9)	120.8 (8)
C(4)—Fe—C(8)	82.0 (3)	C(6)—C(5)—C(9)	117.6 (7)
C(6)—Fe—C(8)	69.7 (3)	C(5)—C(6)—C(7)	129.1 (7)
C(1)—Fe—C(3)	96.9 (4)	C(6)—C(7)—C(8)	122.9 (8)
C(1)—Fe—C(4)	85.6 (4)	C(6)—C(7)—C(10)	117.4 (7)
C(3)—Fe—C(4)	175.1 (4)	C(8)—C(7)—C(10)	119.4 (8)

Data collection

Nicolet R3m diffractometer
 ω scans
 Absorption correction: none
 2606 measured reflections
 2544 independent reflections
 1435 observed reflections
 $[F_o > 5\sigma(F_o)]$
 $R_{int} = 0.015$

$\theta_{max} = 25^\circ$
 $h = -14 \rightarrow 14$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 14$
 3 standard reflections monitored every 197 reflections
 intensity decay: <1%

Refinement

Refinement on F^2
 $R = 0.0742$
 $wR = 0.0773$
 $S = 1.60$
 1436 reflections
 101 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o) + 0.0010F_o^2]$

$(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.71$ e Å⁻³
 $\Delta\rho_{min} = -0.59$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Direct-methods (*SOLV* in *SHELXTL*; Sheldrick, 1985) structure solution and least-squares refinement were performed with all non-H atoms anisotropic and all H atoms calculated, with C—H = 0.96 Å and $U = 1.2U$ of the attached C atom. The H-atom positions for the terminal CH₂ groups were calculated by assuming *sp*³ hybridization of the terminal C atoms (*cf.* Ernst, 1984). *SHELXTL* programs were used for all computations. As a result of β being close to 90°, the unit cell appeared pseudo-orthorhombic. Use of *TRACER* (Lawton & Jacobson, 1965) and a check of reflections having odd indices for a cell whose axes were all doubled failed to indicate any higher symmetry. High displacement parameters were found for F(2), F(3) and F(4), apparently due to rotational disorder about the B—F(1) bond. The highest peaks in the difference Fourier map, however, were associated with the Fe atom, while peaks due to the F atoms were much less significant. As a result, no attempt was made to model the disorder more accurately. The somewhat high value of the *R* factor may, in part, reflect this disorder and the resulting lower rigidity of the lattice in general.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Fe	0.2478 (1)	0.4884 (1)	0.7085 (1)	0.041 (1)
C(1)	0.2465 (9)	0.6277 (8)	0.6111 (7)	0.056 (3)
C(2)	0.3578 (10)	0.3884 (9)	0.6347 (7)	0.063 (4)
C(3)	0.1288 (10)	0.3937 (9)	0.6350 (8)	0.061 (3)
O(1)	0.2458 (8)	0.7159 (6)	0.5523 (6)	0.084 (3)
O(2)	0.4257 (8)	0.3283 (8)	0.5880 (6)	0.095 (3)
O(3)	0.0565 (8)	0.3377 (8)	0.5880 (6)	0.088 (3)
C(4)	0.3798 (8)	0.6013 (7)	0.8091 (7)	0.051 (3)
C(5)	0.3678 (8)	0.4738 (8)	0.8563 (6)	0.050 (3)
C(6)	0.2522 (8)	0.4201 (7)	0.8803 (6)	0.044 (3)
C(7)	0.1399 (9)	0.4732 (8)	0.8582 (6)	0.050 (3)
C(8)	0.1224 (8)	0.6016 (8)	0.8117 (7)	0.051 (3)
C(9)	0.4748 (9)	0.3837 (9)	0.8691 (8)	0.060 (3)
C(10)	0.0319 (9)	0.3833 (9)	0.8732 (8)	0.061 (3)
F(1)	0.7508 (6)	0.4033 (5)	0.7181 (6)	0.097 (3)
F(2)	0.7615 (12)	0.6027 (9)	0.7931 (8)	0.184 (7)
F(3)	0.8336 (11)	0.5699 (10)	0.6292 (10)	0.185 (6)
F(4)	0.6454 (10)	0.5705 (11)	0.6527 (11)	0.184 (6)
B	0.7505 (13)	0.5337 (10)	0.6976 (11)	0.065 (4)

Table 2. Selected geometric parameters (Å, °)

Fe—C(1)	1.805 (8)	Fe—C(2)	1.815 (10)
Fe—C(3)	1.825 (10)	Fe—C(4)	2.174 (8)
Fe—C(5)	2.152 (8)	Fe—C(6)	2.109 (7)
Fe—C(7)	2.138 (8)	Fe—C(8)	2.180 (9)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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