Absorption correction:
ψ scans (*XEMP*; Siemens, 1990)
$T_{\min} = 0.155$, $T_{\max} = 0.277$
2322 measured reflections
1181 independent reflections
986 observed reflections [$I > 2\sigma(I)$]

$h = -23 \rightarrow 23$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 147 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)[F^2 > 2\sigma(F^2)] = 0.0268$
$wR(F^2) = 0.0618$
$S(F^2) = 1.045$
1181 reflections
73 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.289$ e Å^{-3}
$\Delta\rho_{\min} = -1.218$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

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

	x	y	z	U_{eq}
Au	0.64124 (2)	1/2	0.33587 (4)	0.02612 (14)
Cl1	0.71731 (12)	1/2	0.1453 (2)	0.0263 (5)
P	0.56968 (12)	1/2	0.5249 (3)	0.0213 (5)
F	0.4928 (2)	0.2067 (5)	0.6240 (4)	0.0357 (10)
C1	1/2	0.3227 (13)	1/2	0.027 (2)
C2	0.6049 (5)	1/2	0.7267 (10)	0.028 (2)
C3	0.5530 (5)	1/2	0.8509 (11)	0.037 (3)
C4	0.6491 (4)	0.3237 (11)	0.7393 (8)	0.035 (2)
C5	0.8315 (6)	1/2	0.8319 (11)	0.041 (3)
Cl2	0.8308 (2)	1/2	0.6264 (3)	0.0460 (7)
Cl3	0.9133 (2)	1/2	0.9152 (4)	0.0637 (9)

Table 4. *Selected geometric parameters (Å, °) for (2)*

Au—P	2.212 (2)	F—C1	1.360 (6)
Au—Cl1	2.284 (2)	C2—C3	1.522 (12)
P—C2	1.846 (9)	C2—C4	1.532 (9)
P—C1	1.883 (6)		
P—Au—Cl1	178.55 (10)	F—C1—P	114.7 (2)
C2—P—C1	111.0 (2)	P—C1—P^{i}	96.1 (4)
C1—P—C1^{i}	83.9 (4)	C3—C2—C4	111.0 (5)
C2—P—Au	117.3 (3)	C4^{iii}—C2—C4	109.5 (8)
C1—P—Au	114.53 (12)	C3—C2—P	114.6 (7)
F^{ii}—C1—F	105.6 (7)	C4—C2—P	105.2 (4)
F^{ii}—C1—P	113.0 (2)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, 1-z$; (iii) $x, 1-y, z$.

H atoms were refined using a riding model or rigid methyl groups. Similarity restraints (278 in total) were employed for the U components of neighbouring light atoms of complex (1). The largest features of residual electron density (*ca* 2 e Å^{-3}) were located near the CF$_2$ groups (possibly indicating slight disorder) in (1) and in the solvent region in (2).

For both compounds, data collection: *P*3 (Nicolet, 1987); cell refinement: *P*3; data reduction: *XSCANS* (Siemens, 1994*a*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*93.

Crystals were kindly provided by Dr K. Ruhnau and Professor M. Fild of this Institute. We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BS1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Cotton, F. A., Darensbourg, D. J. & Kolthammer, B. W. S. (1981). *Inorg. Chem.* **20**, 4440–4444.

Fild, M., Jones, P. G., Ruhnau, K. & Thöne, C. (1994). *Z. Naturforsch. Teil B*, **49**, 1361–1367.

Jones, P. G. (1996). *Acta Cryst.* C**52**, 1919–1921.

Jones, P. G. & Bembenek, E. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 397–401.

Nicolet XRD Corporation (1987). *Nicolet P3 Data Collection Operators Manual.* Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, California 95014, USA.

Pickardt, J., Rosch, L. & Schumann, H. (1976). *Z. Anorg. Allg. Chem.* **426**, 66–76.

Ruhnau, K. (1992). PhD thesis, Technical University of Braunschweig, Germany

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1990). *XEMP. Empirical Absorption Correction Program.* Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*a*). *XSCANS Users Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Tetrafluoroborate Salt of Tricarbonyl(2-methoxy-η^5-cyclohexadienyl)iron(II)

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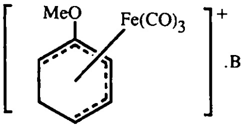
Abstract

The structure of tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron(1+) tetrafluoroborate, [Fe-

$(C_7H_9O)(CO)_3]BF_4$, is reported. Although the tetrafluoroborate salt crystallizes in a different space group to the previously reported hexafluorophosphate salt, the cations are isostructural.

Comment

The reactivity of cyclohexadienyl cation–metal complexes with nucleophiles has been widely studied (Birch *et al.*, 1981; Pearson, 1981). A mixture of the isomers tricarbonyl[(1,2,3,4-η)-1-methoxy-1,3-cyclohexadiene]iron(0) and tricarbonyl[(1,2,3,4-η)-2-methoxy-1,3-cyclohexadiene]iron(0) undergoes hydride abstraction with triphenylmethyl tetrafluoroborate, forming the corresponding dienyl isomers tricarbonyl[(1,2,3,4,5-η)-1-methoxy-2,4-cyclohexadien-1-yl]iron(II) and tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron(II) cations (Birch & Chamberlain, 1988). The 1-methoxy isomer is readily hydrolyzed by water to form tricarbonyl[(2,3,4,5-η)-2,4-cyclohexadien-1-one]iron(0). The 2-methoxy isomer can be recovered by precipitation from the aqueous solution. We recovered the cyclohexadienone complex by extracting with diethyl ether (Birch & Chamberlain, 1988) and crystals of the title complex, (I), were isolated from the aqueous solution.



(I)

The structure of the hexafluorophosphate salt of the title complex has been reported previously (Eisenstein, Butler & Pearson, 1984). The two salts crystallize in different space groups (monoclinic and triclinic). There is no statistically significant change in the solid-state structure on changing the cation. Among the Fe—C(dienyl) distances, Fe—C1 and Fe—C2 are significantly longer than Fe—C5 and Fe—C6.

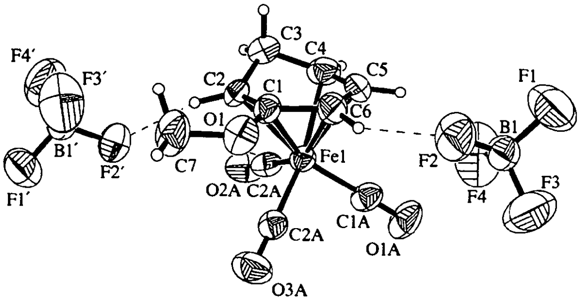


Fig. 1. The molecular structure of $[Fe(C_7H_9O)(CO)_3]BF_4$ showing the atom-numbering scheme and the hydrogen-bonding interactions between one cation and two anions. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Following the hydrolysis of a mixture of tricarbonyl[(1,2,3,4,5-η)-1-methoxy-2,4-cyclohexadien-1-yl]iron tetrafluoroborate and tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron tetrafluoroborate, the cyclohexadienone complex was extracted with diethyl ether (Birch & Chamberlain, 1988). Crystals were obtained from the aqueous layer which was allowed to sit open to the atmosphere in the dark for 10 d.

Crystal data

$[Fe(C_7H_9O)(CO)_3]BF_4$
$M_r = 335.83$
Monoclinic
$P2_1/n$
$a = 9.3811\ (11)$ Å
$b = 13.2775\ (12)$ Å
$c = 10.4870\ (10)$ Å
$\beta = 98.177\ (9)°$
$V = 1293.0\ (2)$ Å^3
$Z = 4$
$D_x = 1.725$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 11.95–12.50°$
$\mu = 1.223$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.42 × 0.30 × 0.24 mm
Orange

Data collection

Siemens $P4$ diffractometer
ω–2θ scans
Absorption correction: none
2852 measured reflections
2205 independent reflections
1459 observed reflections $[I > 2\sigma(I)]$
$R_{\text{int}} = 0.033$

$\theta_{\text{max}} = 25°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.067$
$wR(F^2) = 0.150$
$S = 1.08$
2140 reflections
181 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 6.5923P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.03$
$\Delta\rho_{\text{max}} = 0.69$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.55$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
Fe1	0.64400 (10)	0.66823 (7)	0.35034 (9)	0.0379 (3)
C1*A*	0.5033 (8)	0.6336 (6)	0.4456 (7)	0.052 (2)
C2*A*	0.6877 (8)	0.7881 (6)	0.4288 (7)	0.048 (2)
C3*A*	0.7745 (8)	0.5932 (6)	0.4533 (6)	0.045 (2)
O1*A*	0.4155 (6)	0.6126 (5)	0.5040 (6)	0.078 (2)
O2*A*	0.7155 (7)	0.8632 (4)	0.4764 (5)	0.071 (2)
O3*A*	0.8589 (6)	0.5466 (5)	0.5152 (5)	0.073 (2)
C1	0.7444 (7)	0.6112 (5)	0.1885 (6)	0.042 (2)
C2	0.7719 (7)	0.7145 (5)	0.2013 (6)	0.042 (2)
C3	0.6574 (8)	0.7866 (6)	0.1438 (7)	0.053 (2)
C4	0.5233 (8)	0.7494 (6)	0.1915 (7)	0.058 (2)
C5	0.4915 (8)	0.6488 (7)	0.1858 (7)	0.061 (2)
C6	0.6005 (8)	0.5760 (6)	0.1853 (6)	0.050 (2)

O1	0.8455 (5)	0.5395 (4)	0.1983 (5)	0.0544 (13)
C7	0.9908 (8)	0.5693 (7)	0.1927 (9)	0.079 (3)
B1	0.3250 (3)	0.3528 (3)	0.1959 (3)	0.055 (2)
F1	0.2085 (4)	0.3438 (4)	0.1061 (4)	0.114 (2)
F2	0.4454 (3)	0.3430 (4)	0.1412 (4)	0.086 (2)
F3	0.3215 (5)	0.2811 (4)	0.2858 (4)	0.126 (2)
F4	0.3236 (5)	0.4436 (3)	0.2524 (5)	0.129 (2)

Table 2. *Selected geometric parameters (Å, °)*

Fe1—C3*A*	1.812 (8)	C1—C2	1.399 (9)
Fe1—C2*A*	1.812 (8)	C1—C6	1.425 (9)
Fe1—C1*A*	1.824 (8)	C2—C3	1.500 (9)
Fe1—C5	2.095 (7)	C3—C4	1.502 (10)
Fe1—C6	2.112 (7)	C4—C5	1.367 (11)
Fe1—C4	2.163 (7)	C5—C6	1.408 (10)
Fe1—C2	2.189 (6)	O1—C7	1.429 (8)
Fe1—C1	2.191 (6)	B1—F1	1.343 (2)
C1*A*—O1*A*	1.129 (8)	B1—F2	1.343 (2)
C2*A*—O2*A*	1.129 (8)	B1—F3	1.344 (2)
C3*A*—O3*A*	1.133 (8)	B1—F4	1.344 (2)
C1—O1	1.336 (8)		
C3*A*—Fe1—C2*A*	97.0 (3)	O2*A*—C2*A*—Fe1	179.2 (6)
C3*A*—Fe1—C1*A*	90.9 (3)	O3*A*—C3*A*—Fe1	178.0 (6)
C2*A*—Fe1—C1*A*	96.2 (3)	O1—C1—C2	124.9 (6)
C3*A*—Fe1—C5	138.4 (3)	O1—C1—C6	115.3 (6)
C2*A*—Fe1—C5	124.5 (3)	C2—C1—C6	119.0 (7)
C1*A*—Fe1—C5	87.6 (3)	O1—C1—Fe1	124.4 (5)
C3*A*—Fe1—C6	101.8 (3)	C2—C1—Fe1	71.3 (4)
C2*A*—Fe1—C6	152.4 (3)	C6—C1—Fe1	67.7 (4)
C1*A*—Fe1—C6	103.4 (3)	C1—C2—C3	118.4 (6)
C5—Fe1—C6	39.1 (3)	C1—C2—Fe1	71.4 (4)
C3*A*—Fe1—C4	165.5 (3)	C3—C2—Fe1	91.9 (4)
C2*A*—Fe1—C4	88.4 (3)	C4—C3—C2	103.9 (6)
C1*A*—Fe1—C4	101.9 (3)	C5—C4—C3	119.7 (7)
C5—Fe1—C4	37.4 (3)	C5—C4—Fe1	68.6 (4)
C6—Fe1—C4	68.8 (3)	C3—C4—Fe1	92.8 (5)
C3*A*—Fe1—C2	100.8 (3)	C4—C5—C6	121.1 (7)
C2*A*—Fe1—C2	88.0 (3)	C4—C5—Fe1	74.0 (5)
C1*A*—Fe1—C2	167.0 (3)	C6—C5—Fe1	71.1 (4)
C5—Fe1—C2	80.0 (3)	C5—C6—C1	117.5 (7)
C6—Fe1—C2	68.9 (3)	C5—C6—Fe1	69.8 (4)
C4—Fe1—C2	65.8 (3)	C1—C6—Fe1	73.7 (4)
C3*A*—Fe1—C1	86.7 (3)	C1—O1—C7	118.1 (6)
C2*A*—Fe1—C1	124.1 (3)	F1—B1—F2	110.0 (2)
C1*A*—Fe1—C1	139.6 (3)	F1—B1—F3	109.3 (2)
C5—Fe1—C1	68.8 (3)	F2—B1—F3	109.7 (2)
C6—Fe1—C1	38.6 (2)	F1—B1—F4	109.3 (2)
C4—Fe1—C1	79.1 (3)	F2—B1—F4	109.7 (2)
C2—Fe1—C1	37.3 (2)	F3—B1—F4	108.8 (2)
O1*A*—C1*A*—Fe1	179.5 (7)		

The geometry of the BF_4 anion was restrained to tetrahedral symmetry, with B—F 1.342 (2) and F—F 2.192 (3) Å. Orientational disorder of the BF_4 anion, evident from excess electron-density maps, required either acceptance of a highly non-realistic molecular geometry or the above restraint. No model involving split molecular positions was obvious and the remaining excess electron density is probably responsible for the relatively high agreement indices. No absorption correction was attempted due to degradation of the crystal after data collection.

Data collection: *XSCANS*2.0 (Siemens, 1992). Cell refinement: *XSCANS*2.0. Data reduction: *XSCANS*2.0. Program(s) used to solve structure: *XS* (Siemens, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *INSIGHT*II (Biosym/MSI, 1995). Software used to prepare material for publication: *SHELXTL*.

This work was supported by Nebraska NSF–EPSCoR (OSR-9255225) and the University of Nebraska–Lincoln Research Council.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1242). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Biosym/MSI (1995). *INSIGHT*II. Release 95.0. Biosym Technologies, San Diego, California, USA.

Birch, A. J. & Chamberlain, K. B. (1988). *Org. Synth.* **6**, 996–1000.

Birch, A. J., Ratnayake, B. M., Chamberlain, K., Chauncy, B., Dahler, P., Day, A. I., Jenkins, I. D., Kelly, L. F., Khor, T.-C., Kretschmer, G., Liepa, A. J., Narsula, A. S., Raverty, W. D., Rizzardo, E., Sell, S., Stephenson, G. R., Thompson, D. J. & Williamson, D. H. (1981). *Tetrahedron*, **37**, Suppl. No. 1, 289–302.

Eisenstein, O., Butler, W. M. & Pearson, A. J. (1984). *Organometallics*, **3**, 1150–1157.

Pearson, A. J. (1981). *Transition Met. Chem.* **6**, 67–78.

Sheldrick, G. M. (1994). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1992). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XS. Program for X-ray Structure Solution.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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A Dinuclear Molybdenum Complex: [{MoClO(pyridine)$_2$}$_2$(μ-S)$_2$].2C_5H_5N

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Abstract

In the title dinuclear molybdenum–chloro–oxo–sulfido–pyridine complex, di-μ-sulfido-bis[chloro(oxo)bis(pyridine-*N*)molybdenum](*Mo—Mo*) bis(pyridine) solvate, $[Mo_2Cl_2(O)_2(S)_2(C_5H_5N)_4].2C_5H_5N$, the two Mo atoms are each coordinated by one chloro, one oxo and two pyridine ligands, and are bridged by two μ-S ligands. The distance between the Mo atoms is 2.837 (1) Å, suggesting the existence of an Mo—Mo single bond.

Comment

Excision reactions of non-molecular compounds to extract dinuclear or cluster cores as molecular complexes have been extensively studied, especially with group 6 metal halides/chalcogenides (Lee & Holm,

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