

## Structure of *cis*-Dichlorobis[(2-methylecyclopropylmethoxy)diphenylphosphine]platinum(II) Chloroform Solvate, $[\text{PtCl}_2(\text{C}_{17}\text{H}_{19}\text{OP})_2]\cdot\text{CHCl}_3$

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**Abstract.**  $M_r = 926.0$ , monoclinic,  $P2_1/c$ ,  $a = 11.628$  (4),  $b = 18.274$  (8),  $c = 17.266$  (6) Å,  $\beta = 93.63$  (2)°,  $U = 3662$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.68$  g cm<sup>-3</sup>,  $\lambda = 0.7093$  Å,  $\mu(\text{Mo } K\alpha) = 43.6$  cm<sup>-1</sup>,  $F(000)$  (with anomalous dispersion) = 1826,  $T = 118$  K,  $R(F^2) = 0.082$ ,  $R_w(F^2) = 0.111$  for 4749 unique data including those with  $F_o^2 \leq 0$  and 407 variables,  $R(F) = 0.053$ ,  $R_w(F) = 0.056$  for 4156 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The structure contains a square-planar Pt<sup>II</sup> center coordinated by *cis*-chloro *cis*-phosphorus ligands. The Pt–Cl distances are 2.358 (2) and 2.369 (2) Å while the Pt–P distances are 2.222 (2) and 2.224 (3) Å. There is substantial tetrahedral distortion of the geometry about the Pt<sup>II</sup> center with deviations of atoms from the best, weighted Cl<sub>2</sub>PtP<sub>2</sub> plane being Cl(1), 0.143 (2); Cl(2), –0.131 (2); P(1), 0.119 (2); P(2), –0.153 (2); and Pt, –0.025 (2) Å.

**Introduction.** The title compound was prepared in connection with an ongoing study of the interactions with transition-metal systems of chelated cyclopropanes (Youngs & Ibers, 1983*a,b*; Youngs, Mahood, Simms, Swepston, Ibers, Shang, Huang & Lu, 1983).

**Experimental.** A mixture of pyridine (4.72 g) and HO–CH<sub>2</sub>–CH–CH<sub>2</sub>–CH–CH<sub>3</sub> (5.15 g) was added to (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCl (13.1 g) in diethyl ether at 273 K, allowed to warm to room temperature over a 12 h period, and then refluxed for 2 h. Distillation gave the final product, *i.e.* (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P–O–CH<sub>2</sub>–CH–CH<sub>2</sub>–CH–CH<sub>3</sub>. The latter compound (0.30 g) was added to *cis*-PtCl<sub>2</sub>(PhCN)<sub>2</sub> (0.23 g) in a toluene–CH<sub>2</sub>Cl<sub>2</sub> mixture and the solution was stirred for 12 h. The solvents were removed under vacuum and ethanol was added. Filtration gave a yellow filtrate and a white precipitate. The colorless crystals suitable for X-ray analysis were obtained from a toluene, diethyl ether, and chloroform mixture.

Two prismatic crystals displaying faces of the {100} and {011} forms, 0.31 and 0.36 mm long, of cross-sections 0.26 × 0.33 mm and 0.22 × 0.32 mm, calculated volumes 0.0267 and 0.0258 mm<sup>3</sup> respectively;

crystals mounted roughly along [100]; Picker FACS-1 (for procedures see, *e.g.*, Waters & Ibers, 1977); quoted cell dimensions and estimated standard deviations derived from least-squares analysis of setting angles for 18 well centered reflections with  $28^\circ \leq 2\theta \leq 30^\circ$  for both crystals and averaged; intensities of six standard reflections (821; 479; 040; 2,4,11; 200; and 002) did not vary significantly during data collection; absorption correction (de Meulenaer & Tompa, 1965); transmission factor ranged from 0.258 to 0.380 and from 0.287 to 0.421, respectively; max.  $h,k,l$  –13 to 13, 19 and 18; 5199 reflections measured to  $(\sin \theta) \lambda^{-1} = 0.54$  Å<sup>-1</sup>; 3984 unique reflections having  $F_o^2 > 3\sigma(F_o^2)$ ; application of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares [ $\sum w(\Delta F^2)^2$  minimized] combined with difference electron density syntheses; H atoms from a difference electron density map and idealized (C–H = 0.95 Å, tetrahedral or trigonal angles) with thermal parameters 1.0 Å<sup>2</sup> greater than the equivalent  $B$  of the atom to which it is attached and held fixed during subsequent refinement; initial refinement on  $F$  having  $F_o^2 > 3\sigma(F_o^2)$ ; final refinements on  $F_o^2$  including  $F_o^2 \leq 0$ ;  $w = 1/\sigma^2(F^2)$ ; max. positional parameter  $\Delta/\sigma$  0.367 for  $x$  of P(2) excluding chains with cyclopropyl rings which display possible disorder; max. and min. height on final difference electron density synthesis: 2.2 (1) and –2.3 (1) e Å<sup>-3</sup>, 0.58 Å from Pt atom; programs: *ORFFE* (Busing, Martin & Levy, 1964), *ORTEPII* (Johnson, 1976), see also Waters & Ibers (1977); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The molecular structures and labeling are shown in Fig. 1. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table I.‡ Bond distances and angles are given in Table

‡ Lists of structure amplitudes, anisotropic thermal parameters, bond lengths and bond angles within the phenyl rings, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39433 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2 and Table 3 contains a comparison of bond lengths and angles within the  $\text{Cl}_2\text{-Pt-P}_2$  group as found in the literature.

Table 1. Positional parameters and equivalent  $B$  values for the non-hydrogen atoms

Estimated standard deviations of the least significant figures are given in parentheses.  $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$ .

	$x$	$y$	$z$	$B_{\text{eq}}(\text{\AA}^2)$
Pt	0.19161 (3)	0.42651 (2)	0.30666 (2)	1.7
Cl(1)	0.3282 (2)	0.5228 (1)	0.3117 (1)	2.6
Cl(2)	0.0460 (2)	0.5156 (1)	0.2865 (1)	2.4
Cl(3)	0.7716 (3)	0.1981 (2)	0.3799 (2)	5.4
Cl(4)	0.7909 (4)	0.0456 (2)	0.4189 (2)	8.4
Cl(5)	0.5751 (4)	0.1059 (2)	0.3627 (4)	10.9
P(1)	0.0530 (2)	0.3443 (1)	0.3183 (1)	1.8
P(2)	0.3386 (2)	0.3484 (1)	0.3119 (1)	2.1
O(1)	0.0887 (5)	0.2658 (3)	0.3538 (3)	2.1
O(2)	0.3129 (5)	0.2634 (3)	0.2948 (3)	2.2
C(1)	0.1379 (9)	0.2562 (5)	0.4321 (5)	3.1
C(2)	0.177 (1)	0.1792 (7)	0.4408 (7)	6.3
C(3)	0.105 (1)	0.1216 (8)	0.4525 (7)	6.6
C(4)	0.195 (1)	0.1459 (6)	0.5152 (6)	3.9
C(5)	0.131 (1)	0.0471 (7)	0.4135 (7)	5.4
C(6)	0.2674 (8)	0.2422 (5)	0.2169 (6)	2.7
C(7)	0.237 (1)	0.1624 (7)	0.2184 (7)	5.5
C(8)	0.311 (1)	0.1063 (8)	0.2067 (8)	6.3
C(9)	0.226 (1)	0.1237 (6)	0.1411 (6)	4.0
C(10)	0.313 (1)	0.0344 (7)	0.2453 (7)	5.2
C(11)	0.9471 (7)	0.3777 (5)	0.3828 (5)	2.0
C(12)	0.9855 (8)	0.4051 (5)	0.4544 (5)	2.4
C(13)	0.9084 (9)	0.4253 (5)	0.5077 (5)	2.8
C(14)	0.7913 (8)	0.4193 (5)	0.4894 (5)	2.7
C(15)	0.7535 (8)	0.3934 (5)	0.4182 (6)	2.9
C(16)	0.8304 (8)	0.3723 (5)	0.3641 (5)	2.7
C(17)	0.9770 (7)	0.3134 (4)	0.2299 (5)	1.8
C(18)	0.9555 (7)	0.3618 (5)	0.1685 (5)	1.9
C(19)	0.9003 (7)	0.3367 (5)	0.0995 (5)	2.3
C(20)	0.8676 (8)	0.2649 (6)	0.0913 (5)	2.8
C(21)	0.8864 (8)	0.2165 (5)	0.1523 (5)	2.6
C(22)	0.9442 (7)	0.2407 (5)	0.2209 (5)	2.3
C(23)	0.4447 (7)	0.3683 (5)	0.2411 (5)	2.2
C(24)	0.5503 (8)	0.3341 (5)	0.2481 (5)	3.0
C(25)	0.6269 (8)	0.3408 (6)	0.1907 (6)	3.3
C(26)	0.5984 (9)	0.3835 (6)	0.1271 (6)	3.2
C(27)	0.4939 (9)	0.4167 (5)	0.1196 (6)	3.2
C(28)	0.4156 (7)	0.4107 (5)	0.1762 (5)	2.4
C(29)	0.4151 (7)	0.3399 (5)	0.4068 (5)	2.1
C(30)	0.4208 (7)	0.4005 (5)	0.4560 (5)	2.5
C(31)	0.4787 (8)	0.3954 (6)	0.5288 (5)	2.8
C(32)	0.5319 (8)	0.3309 (6)	0.5508 (5)	3.2
C(33)	0.5267 (9)	0.2709 (6)	0.5016 (6)	3.6
C(34)	0.4664 (8)	0.2753 (5)	0.4300 (6)	3.0
C(35)	0.725 (1)	0.1107 (6)	0.3577 (7)	4.6

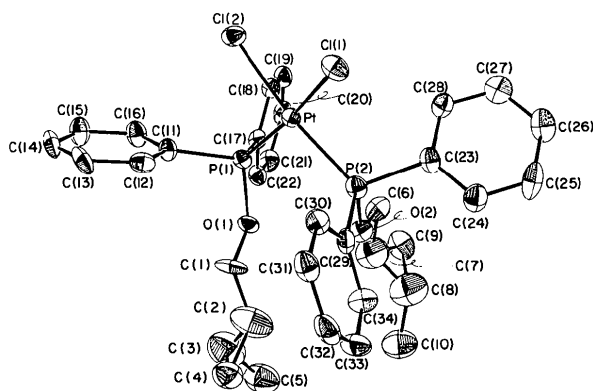


Fig. 1. The molecular structure and atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

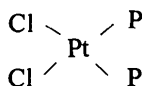
Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for the central part of the molecule excluding the phenyl rings

Pt—P(1)	2.222 (2)	Pt—P(2)	2.224 (3)
Pt—Cl(1)	2.369 (2)	Pt—Cl(2)	2.358 (2)
P(1)—O(1)	1.604 (6)	P(2)—O(2)	1.605 (6)
P(1)—C(11)	1.818 (8)	P(2)—C(23)	1.828 (8)
P(1)—C(17)	1.805 (9)	P(2)—C(29)	1.82 (1)
O(1)—C(1)	1.44 (1)	O(2)—C(6)	1.47 (1)
C(1)—C(2)	1.48 (2)	C(6)—C(7)	1.50 (2)
C(2)—C(3)	1.37 (2)	C(7)—C(8)	1.36 (2)
C(2)—C(4)	1.43 (2)	C(7)—C(9)	1.51 (2)
C(3)—C(4)	1.52 (2)	C(8)—C(9)	1.49 (2)
C(3)—C(5)	1.56 (2)	C(8)—C(10)	1.47 (2)
C(35)*—Cl(3)	1.72 (1)	C(35)—Cl(4)	1.74 (1)
C(35)—Cl(5)	1.75 (1)		
P(1)—Pt—P(2)	97.00 (9)	Cl(1)—Pt—Cl(2)	88.05 (9)
P(1)—Pt—Cl(1)	171.03 (8)	P(2)—Pt—Cl(2)	172.55 (8)
P(2)—Pt—Cl(1)	87.94 (9)	P(1)—Pt—Cl(2)	87.82 (9)
Pt—P(1)—O(1)	103.7 (2)	Pt—P(2)—O(2)	118.7 (2)
Pt—P(1)—C(11)	110.6 (3)	Pt—P(2)—C(23)	113.2 (3)
Pt—P(1)—C(17)	117.0 (3)	Pt—P(2)—C(29)	115.0 (3)
P(1)—O(1)—C(1)	123.0 (6)	P(2)—O(2)—C(6)	118.5 (5)
O(1)—C(1)—C(2)	108.1 (9)	O(2)—C(6)—C(7)	108.2 (9)
C(1)—C(2)—C(3)	124 (1)	C(6)—C(7)—C(8)	126 (1)
C(1)—C(2)—C(4)	122 (1)	C(6)—C(7)—C(9)	117 (1)
C(3)—C(2)—C(4)	66.2 (9)	C(8)—C(7)—C(9)	62.2 (9)
C(2)—C(3)—C(4)	58.8 (9)	C(7)—C(8)—C(9)	63.9 (9)
C(3)—C(4)—C(2)	55.1 (8)	C(8)—C(9)—C(7)	53.9 (8)
C(2)—C(3)—C(5)	118 (1)	C(7)—C(8)—C(10)	127 (1)
C(4)—C(3)—C(5)	115 (1)	C(9)—C(8)—C(10)	122 (1)
C(11)—P(1)—C(11)	108.0 (4)	C(23)—P(2)—C(29)	107.8 (4)
O(1)—P(1)—C(11)	103.6 (4)	O(2)—P(2)—C(23)	101.3 (4)
O(1)—P(1)—C(17)	98.3 (4)	O(2)—P(2)—C(29)	99.1 (4)
P(1)—C(11)—C(12)	118.5 (7)	P(2)—C(23)—C(24)	119.2 (7)
P(1)—C(11)—C(16)	121.8 (7)	P(2)—C(23)—C(28)	120.7 (7)
P(1)—C(17)—C(18)	120.0 (7)	P(2)—C(29)—C(30)	118.8 (7)
P(1)—C(17)—C(22)	120.7 (7)	P(2)—C(29)—C(34)	121.0 (7)

\* The atoms C(35), Cl(3), Cl(4), and Cl(5) belong to the  $\text{CHCl}_3$  molecule.

The molecular structure contains a square-planar  $\text{Pt}^{\text{II}}$  center that shows a substantial tetrahedral distortion, evident both from the deviations of atoms from the  $\text{Cl}_2\text{PtP}_2$  plane and from the *trans*-P—Pt—Cl angles of  $171.03 (8)$  and  $172.55 (8)^\circ$ . The deviations of atoms from the best weighted least-squares plane defined by atoms Cl(1), Cl(2), P(1), P(2) are  $0.143 (2)$ ,  $-0.131 (2)$ ,  $0.119 (2)$ , and  $-0.153 (2) \text{\AA}$ , respectively, and  $-0.025 (2) \text{\AA}$  for the Pt atom. There are three angles around the Pt atom that are smaller than the idealized  $90^\circ$ :  $\text{P(1)—Pt—Cl(2)} = 87.82 (9)$ ,  $\text{Cl(1)—Pt—Cl(2)} = 88.05 (9)$ , and  $\text{Cl(1)—Pt—P(2)} = 87.94 (9)^\circ$ . The mutually *cis* P atoms subtend a rather large angle of  $97.00 (9)^\circ$ . These deformations arise from the steric interactions between bulky phosphine ligands and have been frequently observed in other structures that contain the *cis*- $\text{PtCl}_2\text{P}_2$  entity (Table 3). It has been noted previously (Russell, Tucker & Wilson, 1976; Hitchcock, Jacobson & Pidcock, 1977) that in complexes of the *cis*- $[\text{PtCl}_2\text{L}(\text{PR}_3)]$  type, the Pt—P bond length shows a significant variation with  $L$ . The variation with  $L$  of the Pt—Cl bond lengths is smaller and in the opposite sense from the Pt—P bond lengths. The Pt—P and Pt—Cl bond lengths found in the present structure fit this correlation very well (Hitchcock, Jacobson & Pidcock, 1977, Fig. 2), in spite of the fact that the same groups are connected to both P atoms.

Table 3. Bond lengths (Å) and angles (°) within the



entity in some published structures

Compound	Pt—Cl	Pt—P	Cl—Pt—Cl	P—Pt—P	<i>trans</i> -Cl—Pt—P	<i>cis</i> -Cl—Pt—P	Reference	
<i>cis</i> -PtCl <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub>	orthorhombic	2.350 (1)	av. 2.249 (2)	87.54 (7)	99.43 (6)	av. 171.02 (7)	av. 86.73 (7)	(a)
	monoclinic	{ 2.359 (1) 2.345 (1)	av. 2.245 (1)	88.46 (4)	98.11 (3)	169.30 (3) 173.09 (4)	90.77 (4) 83.43 (4)	
<i>cis</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> [P(OPh) <sub>3</sub> ]		2.350 (2)	2.182 (2) 2.269 (1)	87.4 (1)	97.9 (1)	172.3 (1) 171.6 (1)	88.6 (1) 86.7 (1)	(b)
						174.5 (4)	91.3 (3)	(c)
<i>cis</i> -PtCl <sub>2</sub> [P(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>		av. 2.376 (9)	2.248 (7)	87.7 (3)	96.2 (4)	171.1 (4)	85.1 (4)	(c)
								(d)
<i>cis</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> (PF <sub>3</sub> )		2.357 (3) 2.305 (3)	2.272 (3) 2.141 (3)	89.4 (1)	101.3 (1)	175.6 (1) 172.4 (1)	83.1 (1) 86.2 (1)	(d)
								(e)
<i>cis</i> -PtCl <sub>2</sub> [2,11-bis(Ph <sub>2</sub> PCH <sub>3</sub> )-benzo[ <i>c</i> ]phenanthrene} chloroform solvate		2.335 (3) 2.358 (3)	2.199 (2) 2.256 (3)	88.7 (1)	96.6 (1)	173.4 (1) 177.9 (1)	85.2 (1) 89.6 (1)	(e)
								(f)
<i>cis</i> -PtCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> (mesityl)(Ph <sub>2</sub> methyleneP) chloroform solvate		2.353 (3)	2.255 (3)	87.1 (1)	104.8 (1)	170.8 (1) 170.4 (1)	83.7 (1) 84.4 (1)	(f)
								This work

References: (a) Kin-Chee, McLaughlin, McPartlin & Robertson (1982); (b) Caldwell, Manojlović-Muir & Muir (1977); (c) Messmer, Amma & Ibers (1967); (d) Hitchcock, Jacobson & Pidcock (1977); (e) Bracher, Grove, Venanzi, Bachechi, Mura & Zambonelli (1980); (f) Kroto, Nixon, Taylor, Frew & Muir (1982).

Examination of the external dimensions of the coordination figure shows it to be a twisted rectangle rather than a square. The respective distances are: Cl(1)···Cl(2) = 2.285 (4), P(1)···P(2) = 3.330 (3), P(1)···Cl(2) = 3.178 (3) and P(2)···Cl(1) = 3.190 (4) Å. The appropriate angles at P(1), P(2), Cl(1), and Cl(2) are 89.24 (8), 89.13 (9), 89.84 (8), and 90.16 (8)°, respectively. The portions of the molecule containing methylcyclopropane rings exhibit some apparent disorder, even though the data were collected at 118 K. This disorder affects bond lengths and angles within the cyclopropane rings. However, no useful model for such disorder was found from difference electron density syntheses. Owing to this disorder, the mean cyclopropane C—C distance, 1.44 (2) Å, is foreshortened, being smaller than the normal length in saturated hydrocarbons: 1.537 (5) Å (Sutton, 1965) and 1.510 (5) Å found from an electron diffraction study of cyclopropane (Bastiansen, Fritsch & Hedberg, 1964). The average angle is exactly 60° for both cyclopropane rings and the bond lengths opposite the smallest angles are the shortest ones. A similar arrangement was observed for *trans*-2,*trans*-3-dimethylcyclopropanecarboxylic acid (Luhan & McPhail, 1972). The remaining bond lengths and angles have typical values. There is a well defined molecule of chloroform present in the crystal structure. The closest contact between Pt complex and solvent is Cl(3)···C(16) = 3.3 Å.

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*Acta Cryst.* (1984). **C40**, 1567–1570

**Bis( $\mu$ -ethylthio-*S*)-bis[carbonyl( $\eta^5$ -cyclopentadienyl)iron](Fe–Fe) Chlorate,  
C<sub>16</sub>H<sub>20</sub>Fe<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>·ClO<sub>3</sub><sup>-</sup>**

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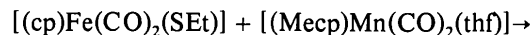
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**Abstract.**  $M_r = 503.6$ , tetragonal,  $P4_32_12$ ,  $a = 9.180(5)$ ,  $c = 24.156(5)$  Å,  $V = 2036(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.70(5)$ ,  $D_x = 1.643(5)$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 1.056$  mm<sup>-1</sup>,  $F(000) = 1028$ ,  $T = 295$  K, final  $R = 0.078$  for 862 observed reflections. The Fe–Fe distance of 2.957(4) Å corresponds to an overall one-electron interaction; S–Fe = 2.240(4) Å. Both the cation and the chlorate anion exhibit crystallographic twofold symmetry; this symmetry imposes disorder on the latter.

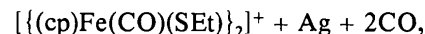
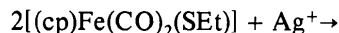
**Introduction.** We are currently attempting to synthesize the mixed-metal complex [(cp)Fe(CO)<sub>2</sub>( $\mu$ -SEt)(CO)<sub>2</sub>Mn(Mecp)]<sup>+</sup> (cp =  $\eta^5$ -cyclopentadienyl, Mecp =  $\eta^5$ -methylcyclopentadienyl). This complex is a hybrid of the known cations [{"(cp)Fe(CO)<sub>2</sub>]<sub>2</sub>( $\mu$ -SEt)]<sup>+</sup> (English, Nassimbeni & Haines, 1978) and [{"(Mecp)Mn(CO)<sub>2</sub>]<sub>2</sub>( $\mu$ -SEt)]<sup>+</sup> (Burckett-St. Laurent, Caira, English, Haines & Nassimbeni, 1977); the latter compound has an Mn–Mn bond while there is no Fe–Fe interaction in the former. The degree of interaction between Fe and Mn in the hybrid would therefore be of interest. However, in the course of an attempt to prepare this compound by reacting [(cp)Fe(CO)<sub>2</sub>(SEt)] (Ahmad, Bruce & Knox, 1966) with [(Mecp)Mn(CO)<sub>2</sub>(thf)] (thf = tetrahydrofuran) (Strohmeier, von Hobe, Schönauer & Laporte, 1962), the title complex was obtained when AgClO<sub>4</sub> was added to the reaction mixture. The complex was initially characterized as the perchlorate salt; however, as a referee has pointed out, the model used for the anion in the X-ray structure analysis was incompatible with ClO<sub>4</sub><sup>-</sup> and closer investigation of difference maps of the electron density round Cl confirmed the presence of ClO<sub>3</sub><sup>-</sup>. The

mechanism whereby ClO<sub>4</sub><sup>-</sup> is reduced to ClO<sub>3</sub><sup>-</sup> in this particular reaction is not clear: however, thf is susceptible to oxidation at the  $\alpha$ -carbon position (Robertson, 1948) and perchloric acid is of course a powerful oxidizing agent. As the thf was not dried before use, it seems likely that this oxidation, with corresponding reduction of ClO<sub>4</sub><sup>-</sup> to ClO<sub>3</sub><sup>-</sup>, was the source of ClO<sub>3</sub><sup>-</sup>. <sup>1</sup>H NMR spectra of thf solutions of AgClO<sub>4</sub> support this hypothesis.

With hindsight it would seem that the reaction



is in fact in equilibrium and in the presence of Ag<sup>+</sup> and excess thf the competing reaction



which has not been hitherto reported, results in the formation of the title compound. While the structure of the methylthio analogue of this compound as the tetrafluoroborate salt has been communicated (Connelly & Dahl, 1970), a subsequent full report on the crystallographic analysis has not appeared. An X-ray analysis was therefore carried out on [{"(cp)Fe(CO)(SEt)]<sub>2</sub>]ClO<sub>3</sub>, which could be obtained in suitable crystalline form.

**Experimental.** When an excess of AgClO<sub>4</sub> (1.0 g, 4.8 mmol) was added to a thf solution of [(cp)Fe(CO)<sub>2</sub>(SEt)] (0.3 g, 1.3 mmol) and [(Mecp)Mn(CO)<sub>2</sub>(thf)] formed *in situ* by UV irradiation of a thf solution of [(Mecp)Mn(CO)<sub>3</sub>] (0.3 g, 1.4 mmol), the