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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIPHENYLPHOSPHONIODITHIO-  
 CARBOXYLATO-SS'-CARBONYLBIS (TRIPHENYLPHOSPHINE) IRIDIUM (I)  
 TETRAFLUOROBORATE,  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ .

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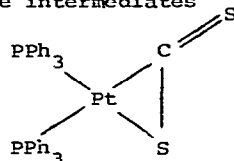
Summary

Crystal and molecular structures of the title compound have been determined from a three-dimensional X-ray analysis using diffractometer data. The crystals are monoclinic, space group  $P2_1/c$ , with  $Z = 4$  in a unit cell of dimensions  $a = 10.5876(9)$ ,  $b = 31.518(10)$ ,  $c = 16.2164(5)$  Å,  $\beta = 92.521(1)^\circ$ . The observed and calculated densities are 1.38 and 1.374 g cm<sup>-3</sup> respectively. The crystals decompose under X-rays, and three crystals were required to complete data collection. The structure was solved and refined by conventional methods to final residuals  $R$  and  $R_w$  of 0.087 and 0.107 respectively.

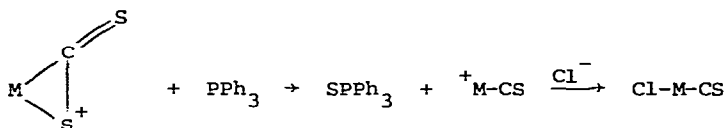
The crystals contain monomeric cations, and  $\text{BF}_4^-$  anions. The iridium atom is in a distorted trigonal bipyramidal environment consisting of the two sulphur atoms (one axial, one equatorial) of a bidentate triphenylphosphoniodithiocarboxylate ligand, two triphenylphosphine groups (equatorial) and the carbonyl ligand (axial). The non-equivalent Ir-S distances are 2.377 and 2.307(5) Å, the Ir-P distances are 2.334, 2.331(5) Å. Within the zwitterion, the C-S distances are 1.66 and 1.70(2) Å, while P-C is 1.78(2) Å. The condensation of  $\text{PPh}_3$  and  $\text{CS}_2$  to form the  $\text{PH}_3\text{P}^+-\text{CS}_2^-$  zwitterion is in contrast to that predicted previously.

## Introduction

During the preparation of the first thiocarbonyl complexes it was observed that the formation of *trans*-RhCl(CS)(PPh<sub>3</sub>)<sub>2</sub> by the interaction of *trans*-RhCl(PPh<sub>3</sub>)<sub>3</sub> and CS<sub>2</sub> in methanol containing excess triphenylphosphine proceeded via a green cationic intermediate [1]. A similar reaction with *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> proceeds via a deep blue solution from which the cation [Rh(CO)(π-CS<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> can be isolated [2]. These intermediates were proposed to be "π-bonded" CS<sub>2</sub> compounds of the type



whose structure had been verified by an X-ray structure determination [3]. In the presence of polar solvents, e.g. methanol, the intermediate is then attacked by triphenylphosphine to form the thiocarbonyl.



These reactions were subsequently studied in greater detail using the more stable iridium species. When IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> was treated as above, a dark violet solution resulted and the addition of sodium tetraphenylborate led to the formation of dark violet crystals which analysed as [Ir(CO)(CS<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>[BPh<sub>4</sub>]<sup>-</sup>. This was again formulated as an octahedral species with a π-bonded CS<sub>2</sub> ligand. However, when attempts were made to alkylate this species to form the dithioester compound which should react with acids in an alternative route to the thiocarbonyl complexes, they were unsuccessful [4]. It was also found that the violet species was only formed in the presence of excess PPh<sub>3</sub>, and that in the i.r. spectrum  $\nu_{(\text{CO})}$ , found at 1980 cm<sup>-1</sup>, was lower than for the parent cation, found at 1995 cm<sup>-1</sup>. These properties appear to be inconsistent with the formulation of a π-CS<sub>2</sub> species and, to resolve the ambiguity, crystals of composition [Ir(CS<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> were subjected to an X-ray structure determination. We now describe details of the refined crystal structure.

## Experimental

The crystals were supplied by Mr K.G. Town and Dr W.R. Roper of the University of Auckland. Preliminary oscillation and Weissenberg photography showed that they belonged to the monoclinic system with systematic absences ( $0k0$   $k = 2n + 1$ ;  $h0l$   $l = 2n + 1$ ) characteristic of space group  $P2_1/c$ . Accurate unit cell parameters were obtained from a least-squares refinement of the setting angles of twelve high-theta reflections using a Hilger and Watts four-circle automatic diffractometer [5]. Details of unit cell parameters and intensity data collection procedures are summarised in Table 1. It was found that the count rates declined steadily with time of irradiation, and it was necessary to use three separate crystals to complete data collection. The crystals were replaced when the counts for three standard reflections had declined to nearly 50% of their initial intensities. After scaling and averaging, the data were corrected for Lorentz and polarisation factors, and for absorption [6]. The observed data criterion was  $I > 3\sigma(I)$   $\{\sigma(I) = [T + t^2B + (pI)^2]^{1/2}$ ,  $T =$  integrated peak count,  $B =$  average background count,  $t =$  ratio of scan to background times,  $p$  was initially assigned as 0.04, but later in the refinement it was increased to 0.06 in an effort to render more uniform the weighting of the reflections [7].

## Structure determination and refinement

The structure was solved by means of Patterson and electron density maps [8]. Atomic scattering factors and dispersion corrections were from standard listings [9]. Refinement employed the full least-squares matrix and minimised the function  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w = 4|F_o|^2 / (\sigma^2(F_o)^2)$ . Residuals quoted are  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$  and  $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$ . Initial refinement used isotropic thermal parameters and rigid groups for the phenyl rings, but the temperature factors of atoms near the coordination sphere were later relaxed to allow for anisotropic motion, and the phenyl ring carbon atoms were refined individually. The residuals  $R$  and  $R_w$  were then 0.096 and

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTION FOR  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ .

Compound: Triphenylphosphoniodithiocarboxylato-SS'-carbonylbis(triphenylphosphine)-  
iridium(I) tetrafluoroborate

Formula:  $\text{C}_{56}\text{H}_{45}\text{OP}_3\text{S}_2\text{Ir}\cdot\text{BF}_4$  Molecular weight: 1118.62

Crystal habit: Needles with diamond-shaped cross-section.

$a = 10.5876(9) \text{ \AA}$

$b = 31.5180(10) \text{ \AA}$

$c = 16.2164(5) \text{ \AA}$

$\beta = 92.521(4)^\circ$

$V = 5406.17 \text{ \AA}^3$

$Z = 4$

$\rho_c = 1.374 \text{ g cm}^{-3}$

$\rho_o = 1.38 \text{ g cm}^{-3}$  (by flotation  
in aqueous KCl/KI)

Space group:  $C_{2h}^5 P2_1/c$  (No. 14)

Dimensions: Crystal 1 0.20 x 0.20 x 0.40 mm Mosaic spread: 0.32°

Crystal 2 0.14 x 0.14 x 0.21 mm 0.28°

Crystal 3 0.12 x 0.12 x 0.20 mm 0.30°

Crystal faces: Crystal 1 (-1 0 0, 0 1 1, 0 1 -1, 0 -1 -1, 0 -1 1, 2 1 -1)

Crystals 2 & 3 (-1 0 0, 0 1 1, 0 1 -1, 0 -1 -1, 0 -1 1, 1 -2 0)

X-radiation:  $\text{CuK}\alpha$ ,  $\lambda = 1.5418$

$\mu = 68.82 \text{ cm}^{-1}$

Collimators: Primary: 0.7 mm

Secondary: 5.0 mm

Take-off angle: 4°

Temperature: 291 K

Scan speed: 0.02°/second using  $2\theta/\omega$  scan.

Scan range: Symmetric scan of 2° in  $2\theta$

Background: 15 s stationary count at each end of scan range

Standard reflections: 3 standards remeasured after every 200 reflections

Observed data criterion: 4648 unique reflections with  $I > 3\sigma(I)$

0.127 respectively. However, the model contained a very distorted  $\text{BF}_4^-$  anion, and attempts were made to relocate these atoms. A 'difference' map revealed four poorly-defined and generally diffuse peaks. The fluorine atoms were placed in positions which best fitted these peaks whilst maintaining a reasonable tetrahedral geometry. The boron atom was positioned from a subsequent difference map. Although the geometry of the anion was somewhat improved by this relocation, it was nevertheless still distorted, and remained so even after further refinement. As no better description of the anion could be found, these atom positions were fixed for the final refinement. In the final cycle three scale factors (one for the data from each crystal used) were refined separately. The final values for  $R$  and  $R_w$  were 0.087 and 0.107 respectively.

Final atomic positions are listed in Table 2. The atomic numbering scheme is outlined in Fig. 1. Tables of thermal parameters and observed and calculated structure factors are available on request from the authors (G.R.C.).

(Continued on p. 270)

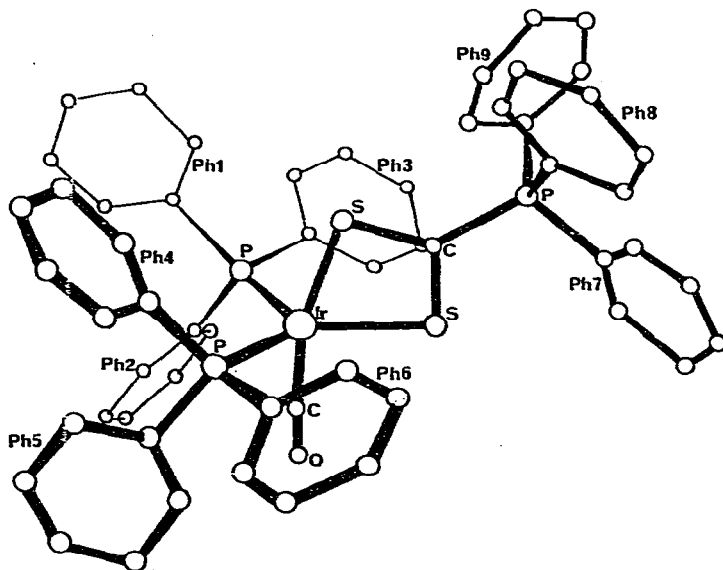


Fig. 1. A general view of  $[\text{Ir}(\text{S}_2\text{CPhPh}_3)(\text{CO})(\text{PPh}_3)_2]^+$  with the labelling of the phenyl rings.

TABLE 2

ATOMIC POSITIONS FOR  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ 

Atom	$x/a$	$y/b$	$z/c$
Ir	0.0866(1)	0.0932(0)	0.3425(0)
S(1)	0.1693(5)	0.1633(1)	0.3489(3)
S(2)	-0.0439(5)	0.1334(1)	0.4218(3)
P(1)	0.2656(5)	0.0609(1)	0.4036(3)
P(2)	0.0724(5)	0.0895(1)	0.1989(3)
P(3)	0.0265(6)	0.2235(1)	0.4661(3)
C(1)	-0.007(2)	0.0440(6)	0.3563(11)
C(2)	0.052(2)	0.1759(5)	0.4085(9)
O(1)	-0.064(2)	0.0152(4)	0.3707(9)
B	0.543(6)	0.338(2)	0.316(3)
F(1)	0.611(2)	0.2763(6)	0.3109(11)
F(2)	0.599(2)	0.3474(6)	0.2596(13)
F(3)	0.616(2)	0.3212(6)	0.4042(11)
F(4)	0.442(2)	0.3200(6)	0.3371(11)
Phenyl Groups			
Ph1			
C(11)	0.281(2)	0.0716(5)	0.5154(10)
C(12)	0.174(2)	0.0730(6)	0.5605(11)
C(13)	0.178(2)	0.0786(6)	0.6457(11)
C(14)	0.298(3)	0.0863(7)	0.6834(14)
C(15)	0.410(3)	0.0849(7)	0.6404(13)
C(16)	0.401(2)	0.0784(6)	0.5532(12)
Ph2			
C(21)	0.253(2)	0.0030(5)	0.3997(10)
C(22)	0.268(2)	-0.0208(6)	0.4703(11)
C(23)	0.259(3)	-0.0662(8)	0.4671(15)
C(24)	0.226(3)	-0.0842(8)	0.3881(16)
C(25)	0.218(2)	-0.0614(7)	0.3183(14)
C(26)	0.230(2)	-0.0155(6)	0.3261(12)
Ph3			
C(31)	0.429(2)	0.0718(6)	0.3681(10)
C(32)	0.496(2)	0.0402(7)	0.3380(12)
C(33)	0.614(3)	0.0485(9)	0.3052(15)

TABLE 2 continued..

C(34)	0.653 (3)	0.0895 (8)	0.3035 (14)
C(35)	0.590 (3)	0.1215 (8)	0.3379 (14)
C(36)	0.469 (3)	0.1129 (7)	0.3703 (13)
Ph4			
C(41)	0.198 (2)	0.1092 (6)	0.1375 (11)
C(42)	0.319 (3)	0.1083 (8)	0.1724 (15)
C(43)	0.432 (3)	0.1207 (10)	0.1261 (16)
C(44)	0.398 (3)	0.1325 (9)	0.0374 (18)
C(45)	0.276 (3)	0.1349 (8)	0.0101 (14)
C(46)	0.182 (2)	0.1210 (6)	0.0569 (11)
Ph5			
C(51)	0.047 (2)	0.0368 (6)	0.1555 (11)
C(52)	0.141 (2)	0.0168 (7)	0.1162 (12)
C(53)	0.119 (3)	-0.0289 (8)	0.0891 (15)
C(54)	0.008 (3)	-0.0452 (8)	0.1021 (15)
C(55)	-0.092 (3)	-0.0287 (8)	0.1399 (15)
C(56)	-0.600 (3)	0.0155 (8)	0.1705 (14)
Ph6			
C(61)	-0.064 (2)	0.1205 (6)	0.1565 (11)
C(62)	-0.140 (2)	0.1067 (7)	0.0896 (12)
C(63)	-0.232 (3)	0.1309 (8)	0.0527 (14)
C(64)	-0.259 (3)	0.1715 (8)	0.0945 (15)
C(65)	-0.190 (3)	0.1857 (8)	0.1623 (14)
C(66)	-0.090 (2)	0.1589 (7)	0.1939 (12)
Ph7			
C(71)	-0.123 (2)	0.2154 (6)	0.5181 (11)
C(72)	-0.224 (3)	0.2182 (8)	0.4684 (15)
C(73)	-0.352 (3)	0.2097 (8)	0.5161 (16)
C(74)	-0.340 (3)	0.2049 (8)	0.5956 (16)
C(75)	-0.215 (3)	0.2044 (9)	0.6432 (17)
C(76)	-0.116 (2)	0.2099 (6)	0.5985 (12)
Ph8			
C(81)	0.026 (2)	0.2694 (5)	0.4017 (9)
C(82)	0.129 (2)	0.2789 (7)	0.3576 (12)
C(83)	0.136 (2)	0.3157 (7)	0.3082 (12)
C(84)	0.032 (3)	0.3430 (8)	0.3068 (15)

TABLE 2 continued..

C(85)	-0.071(3)	0.3351(9)	0.3525(17)
C(86)	-0.083(3)	0.2974(8)	0.4013(14)
Ph9			
C(91)	0.154(2)	0.2295(6)	0.5439(11)
C(92)	0.162(2)	0.2681(7)	0.5834(13)
C(93)	0.252(3)	0.2718(8)	0.6490(14)
C(94)	0.337(2)	0.2405(7)	0.6723(12)
C(95)	0.314(3)	0.2020(7)	0.6296(13)
C(96)	0.234(2)	0.1962(7)	0.5641(13)

## Description of the crystal structure

The crystals consist of monomeric ions. The overall geometry is shown in Fig. 1, whilst Fig. 2 gives the geometry of the coordination sphere about the iridium atom. The thermal ellipsoids represent 50% probability boundaries. The molecular packing is seen in the stereoscopic diagrams of Fig. 3.

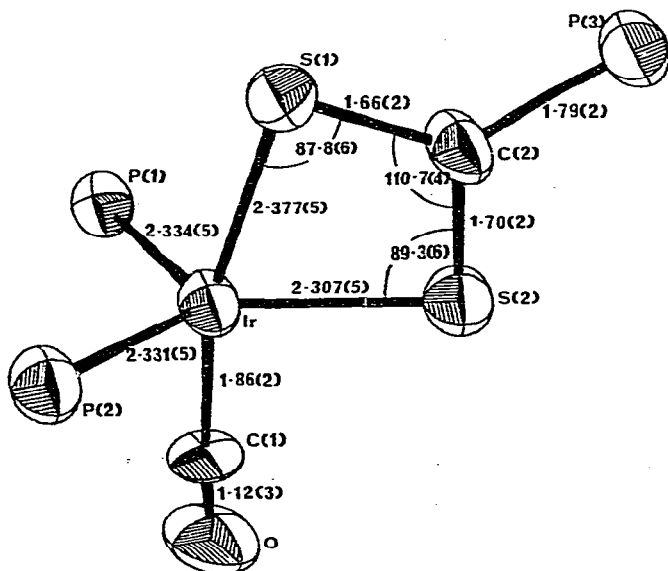


Fig. 2. The coordination geometry of  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]^+$ . The atoms are drawn as 50% probability ellipsoids.



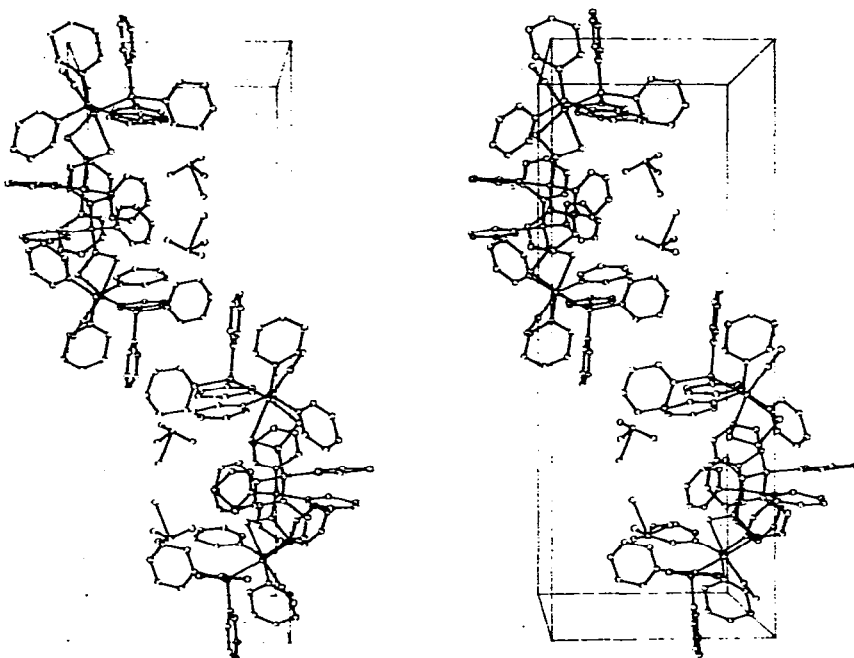


Fig. 3. A stereoscopic view of the molecular packing of  $[\text{Ir}(\text{S}_2\text{CPPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ .

The crystals were analysed as  $[\text{Ir}(\text{CS}_2)(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$  and had previously been formulated as an octahedral species containing a  $\pi$ -bonded  $\text{CS}_2$  ligand [2]. However, the configuration about the iridium atom is found to be that of a distorted trigonal bipyramid with *cis* phosphine ligands in the equatorial plane, the carbonyl ligand in one axial site and the remaining two sites, one equatorial and one axial, spanned by a bidentate sulphur bound triphenyl phosphine-carbon disulphide zwitterion ligand. The bidentate nature of the zwitterion introduces considerable distortion into the coordination geometry. It has a coordination angle of  $72.2(2)$  and consequently the angle between the two axial ligands, ideally  $180^\circ$ , is reduced to  $165.3(6)$ .

The Ir-S distances,  $2.377$  and  $2.307(5)$ , are not equivalent and the difference can be attributed to the differing axial and equatorial arrangements of the two bonds. It is also possible that the lengthening of Ir-S(1)

TABLE 3

INTERATOMIC DISTANCES (Å) FOR  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ 


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Ir - S(1)	2.377(5)	C(1) - O(1)	1.12(2)
Ir - S(2)	2.307(5)	C(2) - S(1)	1.66(2)
Ir - P(1)	2.334(5)	C(2) - S(2)	1.70(2)
Ir - P(2)	2.331(5)	C(2) - P(3)	1.79(2)
Ir - C(1)	1.86(2)		
P(1) - C(11)	1.84(2)	P(2) - C(61)	1.85(2)
P(1) - C(21)	1.83(2)	P(3) - C(71)	1.84(2)
P(1) - C(31)	1.88(2)	P(3) - C(81)	1.78(2)
P(2) - C(41)	1.81(2)	P(3) - C(91)	1.82(2)
P(2) - C(51)	1.82(2)		

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TABLE 4

INTERATOMIC ANGLES (°) FOR  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$ 

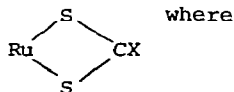

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S(1) - Ir - S(2)	72.2(2)	C(1) - Ir - P(2)	93.8(6)
P(1) - Ir - P(2)	114.7(3)	S(1) - Ir - P(1)	95.5(2)
C(1) - Ir - S(2)	93.2(6)	P(3) - C(2) - S(2)	119.5(4)
C(1) - Ir - S(1)	165.3(6)	S(1) - C(2) - P(3)	129.4(4)
P(2) - Ir - S(2)	124.8(3)	Ir - C(1) - O(1)	174.7(8)
P(2) - Ir - S(1)	95.6(2)		
Ir - P(1) - C(11)	111.8(6)	Ir - P(2) - C(61)	111.1(6)
Ir - P(1) - C(21)	111.2(5)	C(2) - P(3) - C(71)	105.8(8)
Ir - P(1) - C(31)	122.2(6)	C(2) - P(3) - C(81)	111.7(8)
Ir - P(2) - C(41)	121.0(6)	C(2) - P(3) - C(91)	109.0(8)
Ir - P(2) - C(51)	115.7(6)		

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can be attributed to the *trans* influence of the carbonyl ligand in the other axial site. There are few other Ir-S distances with which these can be compared. The shortest distance reported is 2.229(7) for the Ir(III) complex  $\text{IrCl}_2(\text{C}_{15}\text{H}_{13}\text{O})(\text{CH}_3)_2\text{SO}_2$  [10]. For Ir(I) complexes the Ir-S distances vary from 2.389(5) and 2.422(4) in  $[\text{IrS}_2((\text{PPh}_2)\text{CH}_2\text{CH}_2(\text{PPh}_2))_2]^+$  [11] to 2.49(1) in  $\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$  [12]. The distances for the coordinated zwitterion are therefore the shortest to be measured for Ir(I) complexes although the Ir-S(2) distance is not significantly different from the shorter of the Ir-S distances found in  $[\text{IrS}_2((\text{PPh}_2)\text{CH}_2\text{CH}_2(\text{PPh}_2))_2]^+$ .

The C-S distances in the zwitterion, 1.66 and 1.70(2), are equivalent and are consistent with C-X distances reported for dithiocarboxamide ligands, e.g.



X	S-C (average)	Ref.
N-(isopropyl) <sub>2</sub>	1.69(2)	[13]
N-(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	1.72(1)	[14]
H	1.68(1)	[15]

The distances imply a bond order of *ca.* 1.5 between the carbon and sulphur atoms. The C-S and C-P distances in the ligand can be compared with those found in the uncoordinated  $\text{Et}_3\text{P}^+\text{CS}_2^-$  molecule formed by the action of  $\text{CS}_2$  on triphenylphosphine [16]. There the C-S distances are 1.68 and 1.71(3) compared with 1.66 and 1.70(2) in the ligand, and the P-C distance is 1.79(2) compared with 1.78(2) in the ligand. However, the S-C-S angles are not comparable as coordination causes a decrease from 127(1)° to 110.7(3)°. This latter value is equivalent to the angle at the carbon atom in the coordinated dithiocarboxamide  $\text{S}_2\text{CN}(\text{isopropyl})_2$  (111.1(1)) [13].

The zwitterion ligand is not planar. The carbon atom is displaced + 0.03 Å and the phosphorus atom + 0.27 Å from the plane containing the iridium and sulphur atoms.

The Ir-CO distance, 1.86(2), is within the range of distances found in other iridium complexes. The small deviation from linearity of the Ir-C-O bonds is probably the result of the packing of the ions in the crystal as there are several close inter-molecular contacts involving the carbonyl ligand (Table 5).

The Ir-P distances, 2.334 and 2.331(5), are equivalent and lie in the range 2.248 - 2.452 typical of Ir-P distances found in an extensive survey of iridium triphenylphosphine complexes [17]. The angle subtended at iridium by these two phosphorus atoms, 114.7(3)°, is indicative, by its deviation from 120°, of the asymmetry in the equatorial plane of the molecule. Distances and angles involving the phenyl rings are included in the supplementary data.

The large isotropic temperature parameters for the tetrafluoroborate atoms indicate considerable disorder in the anion, and the atomic positions will be only approximate. This is reflected in the variation in the bond lengths (1.15 - 2.08) and the deviation in the angles from ideal tetrahedral geometry. Although alternative models were sought, more ideal representation of the anion did not improve the refinement of the molecule.

The results of this structural investigation are consistent with the i.r. spectrum and reactivity of the compound discussed in the introduction.

TABLE 5

INTERMOLECULAR APPROACHES  $< 3.5 \text{ \AA}$  FOR  $[\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BF}_4$

O(1) - C(12) <sup>2</sup>	3.229	F(1) - C(75) <sup>3</sup>	3.404
O(1) - C(13) <sup>2</sup>	3.194	F(2) - C(74) <sup>3</sup>	3.220
O(1) - C(22) <sup>2</sup>	3.440	F(2) - C(75) <sup>3</sup>	3.232
C(65) - C(75) <sup>3</sup>	3.486	F(3) - C(63) <sup>3</sup>	3.215
		F(3) - C(64) <sup>3</sup>	3.315
Atom transformations	2) $\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
	3) $- x$	$- y$	$- z$

It is probable that the other complexes of iridium and rhodium prepared in a similar manner [2] should now be reformulated as containing  $\text{Ph}_3\text{P}^+-\text{CS}_2^-$  ligands.

## References

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