

C17	-0.1270 (3)	0.2469 (4)	0.3827 (8)	0.049 (2)
C18	-0.1589 (4)	0.2270 (5)	0.4605 (8)	0.056 (2)
C19	-0.2074 (3)	0.1807 (5)	0.4105 (8)	0.055 (2)
C20	-0.2240 (3)	0.1543 (5)	0.2866 (7)	0.051 (2)
C21	-0.1924 (3)	0.1743 (4)	0.2084 (7)	0.0448 (14)
C22†	0	0.6100 (12)	1/4	0.052 (9)
Cl†	0.0529 (4)	0.6777 (12)	0.2375 (11)	0.139 (7)

† Site occupancy = 0.25.

Table 2. Selected geometric parameters (Å, °)

W—C1	2.005 (7)	W—P	2.489 (2)
W—C2	2.039 (8)		
C1 <sup>1</sup> —W—C1	85.4 (5)	C2—W—P	88.7 (2)
C1 <sup>1</sup> —W—C2	173.5 (3)	C2 <sup>1</sup> —W—P	88.3 (2)
C1—W—C2	91.7 (3)	C1 <sup>1</sup> —W—P <sup>1</sup>	97.3 (2)
C1 <sup>1</sup> —W—C2 <sup>1</sup>	91.7 (3)	C1—W—P <sup>1</sup>	86.0 (2)
C1—W—C2 <sup>1</sup>	173.5 (3)	C2—W—P <sup>1</sup>	88.3 (2)
C2—W—C2 <sup>1</sup>	91.8 (4)	C2 <sup>1</sup> —W—P <sup>1</sup>	88.7 (2)
C1 <sup>1</sup> —W—P	86.0 (2)	P—W—P <sup>1</sup>	175.57 (7)
C1—W—P	97.3 (2)		

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The final structural model used anisotropic displacement parameters for the non-H atoms, except for the C atom of the solvent molecule. H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to  $1.5U_{eq}$  of their carrier atoms. Refinement of the site-occupation factor of the CH<sub>2</sub>Cl<sub>2</sub> molecule indicated a 25% occupancy of the respective positions. The high degree of anisotropy observed for the Cl atom suggests unresolved disorder. The highest peaks in the final difference map were located near the W and Cl atoms.

Data collection: P3/V (Siemens, 1989). Cell refinement: P3/V. Data reduction: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL93.

This work was supported by the Fonds der Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1228). Services for accessing these data are described at the back of the journal.

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## Carbonylchloro[2-(diphenylphosphino)-thiophenolato-*P,S*]hydrido(triphenylphosphine-*P*)iridium(III)–Dichloromethane Solvate (4/1)

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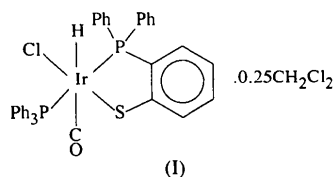
(Received 16 December 1996; accepted 4 April 1997)

### Abstract

In the title complex, [IrH(Cl)(C<sub>18</sub>H<sub>14</sub>PS)(C<sub>18</sub>H<sub>15</sub>P)(CO)].·0.25CH<sub>2</sub>Cl<sub>2</sub>, the two P donors, the chloro and thiolato functions, and the carbonyl and hydride ligands are bonded in mutually *trans* positions. The five-membered chelate ring has an envelope conformation with the metal atom deviating from the plane defined by the P and S donors and the two bridging phenylene C atoms.

### Comment

The title compound, (I), resulted from oxidative addition of hydrogen chloride to the iridium(I) complex [Ir(CO){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}{η<sup>2</sup>-P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>S-2}] (Dahlenburg, Herbst & Kühnlein, 1997). The present X-ray study was undertaken in order to confirm the stereochemistry of the product so obtained, since the hydride coordination *cis* or *trans* to S, Cl or CO could not be established unequivocally on the basis of IR and NMR data alone.



This structure determination proves that the hydride is bonded *trans* with respect to the CO, thiolato and chloro ligands, with the two P donors also occupying mutually *trans* sites in the pseudo-octahedral coordination sphere. The angle of 9.7 (4)° between the normals to the planes defined by P1, Ir and S, and P1, C2, C3 and S, indicates an envelope conformation of the five-membered chelate ring. As expected, the Ir—P bond within the metallacycle, 2.313 (2) Å, is slightly shorter than the distance between the central metal atom and the P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> ligand, 2.357 (3) Å. Both Ir—P bond lengths are similar to those in related metallacyclic (triphenylphosphane)iridium(III) complexes, *e.g.* *mer*-[IrH(Br){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>{η<sup>2</sup>-P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-2}] displaying

Ir—P distances of 2.341(6) and 2.309(6) Å for its *trans*-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P—Ir—(η<sup>2</sup>-P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-2) fragment (Von Deuten & Dahlenburg, 1980). The metal-to-ligand distances observed for both the Ir—S and Ir—Cl bonds, 2.357(3) and 2.431(3) Å, respectively, also compare favourably with those of other representative iridium(III) complexes for which Ir—S and Ir—Cl distances have been reported in the ranges 2.33–2.40 and 2.39–2.46 Å, respectively; see, Khare & Eisenberg (1972), Raston & White (1976), and Zizelman & Stryker (1989).

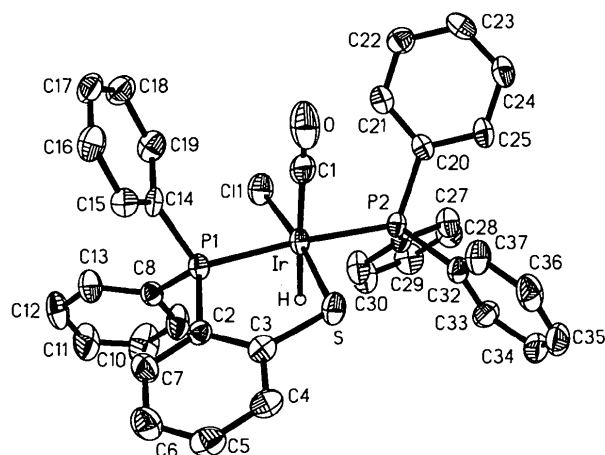


Fig. 1. Structure of the title complex with displacement ellipsoids drawn at the 30% probability level. H atoms except the hydro ligand and solvent molecules have been omitted.

## Experimental

Complex (I) was prepared as described previously (Dahlenburg, Herbst & Kühnlein, 1997). Single crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/pentane (found: C 54.1, H 3.9%; C<sub>37.25</sub>H<sub>30.50</sub>Cl<sub>1.50</sub>IrOP<sub>2</sub>S requires C 53.68, H 3.60%).

### Crystal data

[IrH(Cl)(C<sub>18</sub>H<sub>14</sub>PS)-  
(C<sub>18</sub>H<sub>15</sub>P)(CO)]·  
0.25CH<sub>2</sub>Cl<sub>2</sub>

*M<sub>r</sub>* = 833.49

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 13.869 (1) Å

*b* = 12.606 (2) Å

*c* = 19.699 (5) Å

β = 96.94 (1)°

*V* = 3418.8 (11) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.619 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

### Data collection

Enraf–Nonius CAD-4  
diffractometer

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 25  
reflections

θ = 10–16°

μ = 4.206 mm<sup>-1</sup>

*T* = 293 (2) K

Column

0.4 × 0.4 × 0.2 mm

Pale yellow

5010 reflections with  
*I* > 2σ(*I*)

ω/2θ scans

Absorption correction:

empirical *via* ψ scans

(North, Phillips &

Mathews, 1968)

*T<sub>min</sub>* = 0.531, *T<sub>max</sub>* = 0.992

6897 measured reflections

6693 independent reflections

*R<sub>int</sub>* = 0.020

θ<sub>max</sub> = 25.97°

*h* = -17 → 16

*k* = 0 → 15

*l* = 0 → 24

3 standard reflections

frequency: 60 min

intensity decay: <2%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.056

*wR*(*F*<sup>2</sup>) = 0.167

*S* = 1.068

6620 reflections

405 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.09*P*)<sup>2</sup>

+ 12.69*P*] with

*P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = -0.011

Δρ<sub>max</sub> = 1.932 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -1.941 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ir—Cl1	1.904 (10)	Ir—P2	2.357 (2)
Ir—P1	2.313 (2)	Ir—Cl11	2.431 (3)
Ir—S	2.357 (3)	Ir—H	1.59 (3)
Cl1—Ir—P1	92.6 (4)	S—Ir—Cl11	173.11 (10)
Cl1—Ir—S	90.3 (4)	P2—Ir—Cl11	89.87 (9)
P1—Ir—S	86.23 (8)	Cl1—Ir—H	176 (4)
Cl1—Ir—P2	92.9 (4)	P1—Ir—H	89 (4)
P1—Ir—P2	174.43 (8)	S—Ir—H	87 (4)
S—Ir—P2	93.88 (8)	P2—Ir—H	85 (4)
Cl1—Ir—Cl11	95.3 (4)	Cl11—Ir—H	88 (4)
P1—Ir—Cl11	89.48 (9)	O—C1—Ir	178.7 (12)

All non-H atoms were located by direct methods and subsequent difference Fourier syntheses and least-squares refinement. Careful inspection of the final Δ*F* map revealed the approximate position of the hydride ligand which was refined with an Ir—H distance restraint of 1.60(3) Å. Weak distance restraints with effective standard deviations of 0.015 Å were also imposed on the C=O and Ir—CO bonds in order to prevent these from refining to geometrically unreasonable lengths; this may be due to libration or an (unidentified) disorder phenomenon. Non-H atoms were refined anisotropically, except for the C atom of the solvent molecule. The carbon-bonded H atoms were included in geometrically idealized positions employing a riding model, with isotropic displacement parameters set to 1.5 times the *U<sub>eq</sub>* or *U<sub>iso</sub>* of their carrier atoms. The solvent molecule was found to display disorder about a center of symmetry of the monoclinic unit cell (Wyckoff position 2*c*). Refinement of the site-occupation factor indicated a 25% occupancy, in agreement with the results derived from elemental analysis. The largest features in the final difference map were located at distances less than 0.8 Å from the Ir atom.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1994). Cell refinement: *CAD-4-PC Software*. Data reduction: *MOLLEN* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1186). Services for accessing these data are described at the back of the journal.

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## Bis(1,1,1,5,5,5-hexafluoroacetylacetonato-O,O')bis(2,2,6,6-tetramethylpiperidinyl-1-oxy-O)cobalt(II)†

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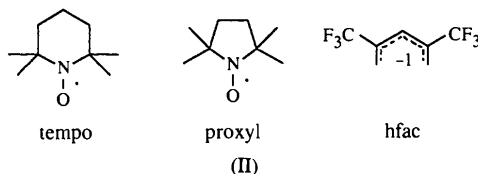
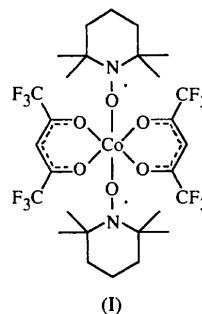
## Abstract

The structure of [Co(C<sub>5</sub>HF<sub>6</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>9</sub>H<sub>18</sub>NO)<sub>2</sub>], measured at 173 K, is isostructural with the analogous manganese derivative at 295 K previously reported. The main differences are that in the title compound the nitroxyl O atom is disordered over two positions in a 9:1 ratio, and the M—O—N angle (where M is the metal) is about 20° more acute than reported for the manganese derivative.

† Alternative name: bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-O,O')bis(2,2,6,6-tetramethyl-1-piperidyl 1-oxide-O)cobalt(II).

## Comment

Adducts of nitroxyl free radicals (and closely related nitronyl nitroxides) with metal complexes containing the 1,1,1,5,5,5-hexafluoroacetylacetonato anion (hfac) have been of interest for their unusual magnetic and structural properties (Caneschi, Gatteschi & Rey, 1991; Porter, Dickman & Doedens, 1986). Reaction of M(hfac)<sub>2</sub> complexes with nitroxyls such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) or 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl), where M = Mn (Dickman, Porter & Doedens, 1986), Co, Ni (Porter, Dickman, & Doedens, 1988), Cu (Dickman & Doedens, 1981) or V=O (Drago, Kuechler & Kroege, 1979), results in mono- or bis-nitroxyl adducts which exhibit antiferromagnetic coupling between unpaired electrons on the metal and the radical. Previous structural studies of the isostructural compounds M(hfac)<sub>2</sub>(proxyl)<sub>2</sub> (M = Mn, Co, Ni) and Mn(hfac)<sub>2</sub>(tempo)<sub>2</sub>, (II), revealed a large difference in the M—O—N angle for the tempo derivative compared with the proxyl adducts (Dickman *et al.*, 1986; Porter *et al.*, 1988). The more acute angle observed for the proxyl derivatives was attributed to the smaller steric hindrance of the nitroxyl O atom by the five-membered ring methyl groups compared with the piperidinyl methyl groups.



The title compound, (I), had been prepared previously but was found to be relatively unstable at room temperature and no structural analysis was performed at the time (Dickman, 1984). The facile decomposition of the cobalt derivative was assumed to be due to the smaller ionic radius of cobalt compared with manganese, resulting in more unfavorable steric interaction between the tempo radical and Co(hfac)<sub>2</sub> moieties. The present structural analysis of (I) was performed at low temperature in order to investigate the basis of the relative instability of the cobalt derivative and the reproducibility of a larger M—O—N angle in six-coordinate tempo complexes.