trans-Carbonylchloridobis(ferrocenyl-diphenylphosphane-κP)rhodium(I) dichloromethane monosolvate and trans-carbonylchloridobis(ferrocenyl-diphenylphosphane-κP)iridium(I) dichloromethane monosolvate

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The isomorphous crystal structures of the title compounds, $[Fe_2M(C_5H_5)_2(C_{17}H_{14}P)Cl(CO)]\cdot CH_2Cl_2$ or trans-$[MCl(CO)(PPh_2Fc)_2]\cdot CH_2Cl_2$ (M = Rh or Ir, and Fc is ferrocenyl), are reported. The data collection for M = Rh was performed at 293 (2) K, while the M = Ir data were collected at 160 (2) K. The compounds crystallize with two independent half-molecules in the asymmetric unit, both occupying inversion centres, and are accompanied by a single dichloromethane molecule on a general position. Due to the symmetry, there is 0.50/0.50 disorder present in the chloride and carbonyl positions. One molecule in each structure also has a second type of disorder in the chloride and carbonyl positions, which was refined over another two positions of equal distribution. The steric impact of the bulky PPh$_2$Fc ligands was evaluated using the Tolman cone-angle model, resulting in an average value of 172° for the four molecules in both structures.

Comment

As part of our general interest in phosphane ligands containing ferrocene, a systematic study has been conducted on the PPh$_2$Fc ligand (Fc is ferrocenyl; Otto & Roodt, 1997; Otto *et al.*, 1998, 2000; Otto, 2001*a*; Steyl *et al.*, 2001). In addition, the rhodium Vaska systems are often used for ligand-evaluation purposes, as stable crystalline complexes are obtained containing both the CO group and the P atom as suitable handles for spectroscopic studies (Roodt *et al.*, 2003). Even though the Rh Vaska analogue containing the PPh$_2$Fc ligand was published previously (Otto & Roodt, 2004), we

additionally obtained crystals of the isomorphous Rh^I and Ir^I complexes containing a dichloromethane solvent molecule, namely trans-carbonylchloridobis(ferrocenyldiphenylphosphane-κP)rhodium(I) dichloromethane monosolvate, (I), and trans-carbonylchloridobis(ferrocenyldiphenylphosphane-κP)-iridium(I) dichloromethane monosolvate, (II), the crystal structures of which are reported herein.

(I) M = Rh
(II) M = Ir
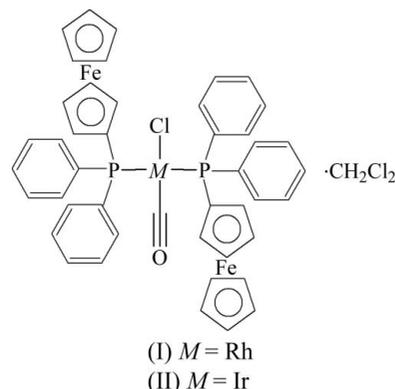
The title coordination complexes crystallize with two independent molecules in the asymmetric unit, with each crystallographically independent molecule straddling an inversion centre (at the Rh and Ir metal centre), resulting in a 0.50/0.50 statistical disorder in the chloride and carbonyl groups. Each pair of half-molecules is accompanied by a single dichloromethane solvent molecule located on a general position. Molecule 1 of each structure additionally suffers from a second disorder in the chloride and carbonyl positions, which has been refined with an equal distribution over two sites (see Fig. 1 and the *Refinement* section for further details).

Each of these coordination complexes exhibits a distorted square-planar geometry, with the bulky PPh$_2$Fc ligands in a *trans* orientation, as expected (Figs. 1 and 2). Due to the disorder in the chloride and carbonyl positions, the bond distances associated with these ligands could only be obtained with less than the desirable level of accuracy and additional restraints were required to maintain comparable lengths for identical bonds (Table 1). The bond distances and angles within the PPh$_2$Fc ligands are within normal ranges, with typically a shorter P—C bond to the ferrocenyl group than those to the Ph groups. The two cyclopentadienyl rings within the ferrocenyl group also display the expected eclipsed conformation typical for monosubstitution. The orientations of the ferrocenyl groups differ by 7.3 (2) and 7.3 (3)° between molecules 1 and 2 for (I) and (II), respectively, as shown by the relevant torsion angles (Table 1).

Isomorphism is not uncommon in molecules containing large ligands that can dominate the packing mode in the crystal structure. Especially in square-planar complexes, large ligands *trans* to each other can render insignificant any small variations in the linear coordination core of the molecule. In this regard, we have reported the extensive isomorphism observed in a series of complexes, trans-$[MRY(EPh_3)_2]$, where M = Pt or Pd, RY = Cl$_2$ or MeCl and E = P or As (Otto, 2001*b*).
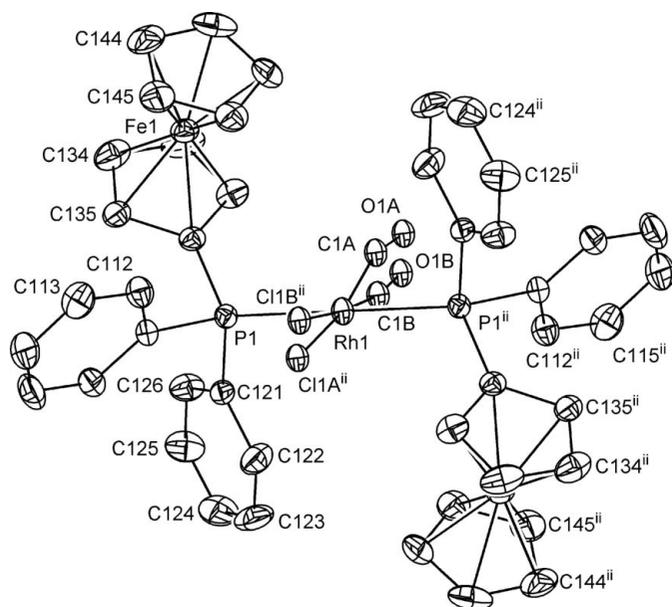
metal-organic compounds

Figure 1
The structure of molecule 1 of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the statistical disorder in the chloride and carbonyl positions have been omitted for clarity; the random disorder in the chloride and carbonyl positions is indicated. Molecule 2 is numbered accordingly, with the first digit referring to the number of the molecule and the second and third digits to the atom in the molecule. [Symmetry code: (ii) $-x$, $-y + 2$, $-z + 2$.]
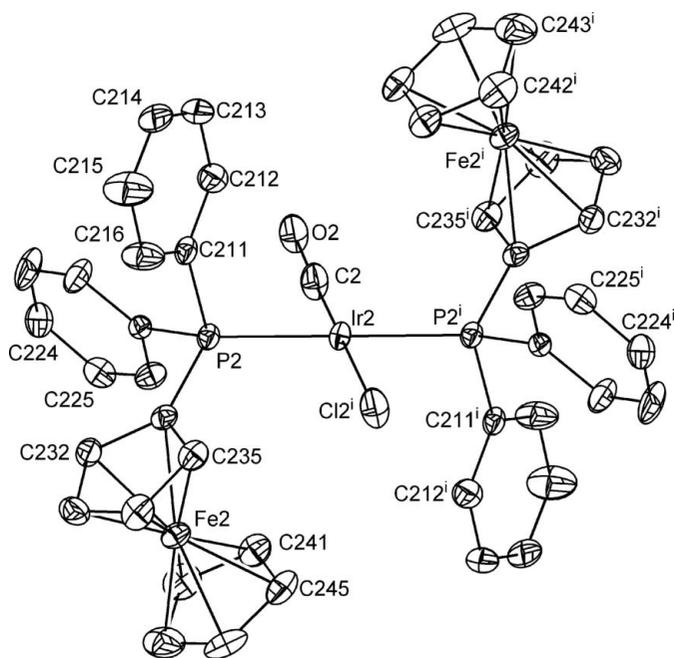

Figure 2
The structure of molecule 2 of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the statistical disorder in the chloride and carbonyl positions have been omitted for clarity. Molecule 1 is numbered accordingly, with the first digit referring to the number of the molecule and the second and third digits to the atom in the molecule. [Symmetry code: (ii) $-x + 1$, $-y + 1$, $-z + 1$.]

Discovering that the Rh and Ir Vaska complexes containing the bulky PPh_2Fc ligand are isomorphous should thus not be unexpected when they are crystallized from the same solvent. The extent to which the PPh_2Fc ligands dominate the packing results in the two structures being very similar, with major differences limited to slight variations in bond distances and angles of the chloride and carbonyl ligands (Table 1). The major differences in some of the 'inner core' geometric parameters include $C1A—M1—Cl1A = 165.4\,(6)°$ in (I) and $171.8\,(9)°$ in (II), and $O2—C2—M2 = 157.7\,(15)°$ in (I) and $174.8\,(17)°$ in (II).

The average $M—P$ bond distances are within the expected ranges at $2.3352\,(13)$ and $2.3280\,(19)$ Å for (I) and (II), respectively, as is the case for the average $M—Cl$ bond distances of $2.380\,(4)$ and $2.354\,(5)$ Å, respectively (see Table 2 for comparative data from the literature). In all complexes listed in Table 2, both the $M—P$ and $M—Cl$ bond distances are slightly longer for Rh than for Ir.

Describing the steric demand of phosphane ligands has been the topic of many studies and a variety of models have been developed (Bunten *et al.*, 2002). In practice, the Tolman cone angle (Tolman, 1977) is still the most commonly used model, due to its simplicity and ease of calculation. Applying this model (using an $M—P$ bond distance of 2.28 Å) to the data here results in values of 171 and 172° for molecules 1 and 2 of (I), respectively, and 172° for both molecules of (II). The Tolman model has been further developed (Otto, 2001*c*) into the concept of the 'effective cone angle', where the crystallographically determined $M—P$ bond length is used in the

calculations. Using this model results in values of 169 and 170° for (I), and 171 and 170° for (II). The steric demand of the PPh_2Fc ligand was previously shown to be very dependent on the orientation of the Fc group (Otto *et al.*, 2000). It is, however, clear from the current data that the 7.3 (2) and 7.3 (3)° difference in orientation for the Rh and Ir complexes, respectively, does not result in a significant altering of the steric impact experienced in the two molecules.

Experimental

Compound (I)

Crystal data

[Fe₂Rh(C₅H₅)₂(C₁₇H₁₄P)Cl(CO)]·CH₂Cl₂
$M_r = 991.68$
Triclinic, $P\bar{1}$
$a = 9.4520 (19)$ Å
$b = 12.989 (3)$ Å
$c = 18.067 (4)$ Å
$\alpha = 108.05 (3)°$

$\beta = 96.38 (3)°$
$\gamma = 95.21 (3)°$
$V = 2077.4 (9)$ Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.39$ mm⁻¹
$T = 293$ K
$0.30 \times 0.15 \times 0.05$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1998)
$T_{min} = 0.700$, $T_{max} = 0.894$

18195 measured reflections
10001 independent reflections
5920 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.131$
$S = 0.93$
10001 reflections
518 parameters

58 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 1.27$ e Å⁻³
$\Delta\rho_{min} = -1.42$ e Å⁻³

Compound (II)

Crystal data

[Fe₂Ir(C₅H₅)₂(C₁₇H₁₄P)Cl(CO)]·CH₂Cl₂
$M_r = 1080.97$
Triclinic, $P\bar{1}$
$a = 9.436 (5)$ Å
$b = 12.978 (5)$ Å
$c = 18.091 (5)$ Å
$\alpha = 107.903 (5)°$

$\beta = 96.269 (5)°$
$\gamma = 95.225 (5)°$
$V = 2077.3 (15)$ Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 4.19$ mm⁻¹
$T = 160$ K
$0.24 \times 0.05 \times 0.04$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1998)
$T_{min} = 0.433$, $T_{max} = 0.850$

18144 measured reflections
9994 independent reflections
5972 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.106$
$S = 0.91$
9994 reflections
518 parameters

58 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 1.44$ e Å⁻³
$\Delta\rho_{min} = -1.32$ e Å⁻³

Table 1
Selected geometric parameters (Å, °) for (I) and (II).

	(I), M = Rh	(II), M = Ir
$M1-C1A$	1.798 (14)	1.767 (18)
$M1-C1B$	1.756 (14)	1.736 (17)
$M1-Cl1A$	2.364 (4)	2.345 (5)
$M1-Cl1B$	2.390 (4)	2.354 (4)
$M1-P1$	2.3345 (12)	2.3290 (18)
$C1A-O1A$	1.112 (16)	1.244 (19)
$C1B-O1B$	1.243 (16)	1.235 (19)
$P1-C111$	1.826 (5)	1.824 (7)
$P1-C121$	1.824 (4)	1.845 (6)
$P1-C131$	1.805 (5)	1.806 (7)
$M2-C2$	1.682 (12)	1.626 (15)
$M2-Cl2$	2.385 (3)	2.362 (3)
$M2-P2$	2.3358 (13)	2.3270 (19)
$C2-O2$	1.242 (14)	1.283 (17)
$P2-C211$	1.831 (5)	1.830 (7)
$P2-C221$	1.819 (5)	1.828 (6)
$P2-C231$	1.806 (5)	1.807 (7)
$C1A-M1-C1B$	24.1 (8)	20.7 (11)
$Cl1A-M1-Cl1B$	17.49 (13)	25.8 (9)
$C1A^i-M1-Cl1A$	165.4 (6)	171.8 (9)
$C1B^i-M1-Cl1B$	171.5 (7)	173.1 (10)
$C1A^i-M1-P1$	88.5 (5)	88.9 (9)
$C1B-M1-P1$	88.6 (6)	89.9 (9)
$O1A-C1A-M1$	165.9 (18)	163 (2)
$O1B-C1B-M1$	175.1 (17)	173 (2)
$C2-M2-Cl2^{ii}$	176.2 (6)	176.3 (7)
$C2-M2-P2$	89.1 (4)	87.3 (6)
$O2-C2-M2$	157.7 (15)	174.8 (17)
$M1-P1-C131-C141$	−50.1 (2)	−49.5 (3)
$M2-P2-C231-C241$	−42.8 (2)	−42.2 (3)

Symmetry codes: (i) $-x, -y + 2, -z + 2$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2
Comparative X-ray data (Å) for *trans*-[$MCl(CO)(P)_2$] complexes.

M	P	$M-P$	$M-Cl$	Reference
Rh	PPh₃	2.322 (1)	2.382 (1)	(a)
	P(ρ-Tol)₃	2.3325 (11)	2.347 (2)	(b)
	PBz₃	2.3160 (16)	2.3654 (15)	(c)
	PCy₃	2.3508 (3)	2.3880 (13)	(d)
	PPh₂Fc	2.3346 (9)	2.3670 (18)	(e)
	PPh₂Fc	2.3345 (12)	2.377 (4)	(f)
		2.3358 (13)	2.385 (3)	(f)
Ir	PPh₃	2.3133 (24)	2.306 (8)	(g)
	P(ρ-Tol)₃	2.331 (2)	2.364 (2)	(h)
	PCy₃	2.3486 (8)	2.374 (3)	(i)
	PPh₂Fc	2.3290 (18)	2.350 (5)	(f)
		2.3270 (19)	2.362 (3)	(f)

References: (a) Dunbar & Haefner (1992); (b) Otto *et al.* (1999); (c) Muller *et al.* (2002); (d) Wilson *et al.* (2002); (e) Otto & Roodt (2004); (f) this work (average $M-Cl$ value reported for molecule 1); (g) Blake *et al.* (1991); (h) Churchill *et al.* (1987); (i) Grobbelaar *et al.* (2009). Note: Cy is cyclohexyl.

The Cl—M—CO portions of the two structures showed different behaviour for the two independent molecules in the unit cell. In each case, one unit (labelled Rh1 or Ir1) had large thermal vibrations associated with the chloride and carbonyl ligands. These ligands, already disordered in a 50:50 ratio due to the inversion centre, was further split over an additional two positions and refined with independent occupancies summing to 0.50. As the values obtained from the refinement were very similar [for Rh, (I): $A = 0.242 (3)$ and $B = 0.258 (3)$; for Ir, (II): $A = 0.235 (4)$ and $B = 0.265 (4)$], the values were subsequently fixed at a 0.25 occupancy for each in the final refinement cycles. Several bonding and ellipsoid restraints were applied to ensure that the refinement remained stable.

All H atoms were placed in geometrically idealized positions, with C—H = 0.93 Å for CH (aryl) and 0.97 Å for CH₂, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH₂. The maximum residual electron density for both structures is located within 0.4 Å of atom Cl4, associated with the dichloromethane solvent molecule, while the minimum residual electron density for both structures is situated within 0.1 Å of atom Cl1B.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008);

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molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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