Dicarbonyldichloridobis(Trimethylphosphane)Iron(Ii)–Carbonyldichloridotris(Trimethylphosphane)Iron(Ii)–Tetrahydrofuran (1/1/2)

Nigam Rath
University of Missouri–St. Louis

Meghan Stouffer
University of Washington

Matthew Janssen
University of Washington

John Bleeke
University of Washington

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Dicarboxyldichloridobis(trimethylphosphane)iron(II)—carbonyldichlorotris(trimethylphosphane)iron(II)—tetrahydrofuran (1/2)

Nigam P. Rath, a* Meghan Stouffer, b Matthew K. Janssen b and John R. Bleekeb

aDepartment of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri–St Louis, 1 University Boulevard, St Louis, MO 63121-4400, USA, and bDepartment of Chemistry, Washington University, One Brookings Drive, St Louis, MO 63130-4899, USA.

Correspondence e-mail: rathn@umsl.edu

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; disorder in solvent or counterion; R factor = 0.034; wR factor = 0.081; data-to-parameter ratio = 22.5.

The asymmetric unit of the title crystal, [FeCl2(C3H9P)3(CO)]·[FeCl2(C3H9P)2(CO)2]·2C4H8O, contains half molecules of the two closely related FeII complexes lying on mirror planes and a tetrahydrofuran solvent molecule, one C atom of which is disordered over two sets of sites with site occupancy factors 0.633 (9) and 0.367 (9). In both FeII complex molecules, a distorted octahedral coordination geometry has been observed around the Fe atoms. Weak intermolecular C—H···O interactions are observed in the crystal structure.

Related literature

For the synthetic background, see: Harris et al. (1978). For the crystal structure of a related complex, see: Venturi et al. (2004).

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
Tmin = 0.800, Tmax = 0.895
4904 reflections
218 parameters

Table 1

Hydrogen-bond geometry (Å, °).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C42—H42B···O1S 0.98 | 2.53 | 3.422 (3) | 151 |
| C43—H43C···O1 0.98 | 2.58 | 3.510 (3) | 158 |
| C43—H43A···O1b 0.98 | 2.43 | 3.392 (3) | 167 |

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

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae et al., 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2394).

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Dicarbonyldichloridobis(trimethylphosphane)iron(II)–carbonyldichloridotris(tri-methylphosphane)iron(II)–tetrahydrofuran (1/1/2)

Nigam P. Rath, Meghan Stouffer, Matthew K. Janssen and John R. Bleeke

S1. Comment
An interesting cocrystallization has occurred from a reaction of CO with Cl₂Fe(PMe₃)₂, resulting in compound (I), C₈H₁₈Cl₂FeO₂P₂, from the addition of two equivalents of CO to Cl₂Fe(PMe₃)₂ and compound (II), C₁₀H₂₇Cl₂FeOP₃, probably from the addition of one equivalent of CO, followed by the rapid addition of one equivalent of free PMe₃, which is present in the reaction solution. In this paper, we report the crystal structure of the two compounds, (I) and (II) which have been cocrystallized along with a molecule of tetrahydrofuran solvate per molecule of complex (Fig. 1).

The asymmetric unit of the title crystal contains half molecules of the two compounds, (I) and (II), lying on mirror planes and a molecule of tetrahydrofuran solvate, C₄H₈O; a carbon atom of the solvent molecule is disordered over two sites C₄S and C₄S’ with site occupancy factors 0.633 (9) and 0.367 (9). In compound (I), the PMe₃ ligands occupying axial positions, are trans with respect to each other with an angle of 175.20 (4)° and the CO and Cl are trans with respect to each other at equatorial positions. In compound (II), the trans PMe₃ ligands are located at 166.41 (4)° to each other; the 3rd PMe₃ is trans to a Cl. The octahedral coordination is completed with the 2nd Cl being trans to a CO ligand. In both compounds, the ligands around Fe lie in slightly distorted octahedral coordination geometry. An overlay plot of the two molecules drawn by Mercury (Macrae et al., 2008) shows the close similarity of the two molecules (Fig. 2).

There are weak intermolecular interactions of the type C–H···O which are observed between both the carbonyl O atoms of (I) and a methyl hydrogen atom of (II). The O of the solvent THF also has weak interactions with a methyl hydrogen atoms of (II) (Table 1).

S2. Experimental
FeCl₂ (0.21 g, 1.62 x 10⁻³ mol) and PMe₃ (0.40 ml, 3.86 x 10⁻³) were stirred in 20 ml of THF for 10 min, producing a clear gray solution of Cl₂Fe(PMe₃)₂ (Harris et al., 1978) in the presence of excess PMe₃. Carbon monoxide was then bubbled through the solution until the color changed to an intense orange. The THF solvent was removed under vacuum and the resulting powder was extracted with pentane. After filtration through Celite, the pentane was removed under vacuum. The product was dissolved in a 1:2 mixture of THF and pentane and cooled to 243 K, causing orange crystals to form overnight.

S3. Refinement
H atoms bonded to the C atoms located on the mirror planes were located in a difference map and refined using a riding model. Other H atoms were calculated with idealized geometries with C–H = 0.98 and 0.99 Å for methyl and methylene type H-atoms, respectively, and refined using a riding model with Uiso(H) = 1.2 (1.5 for methyl groups) times Ueq(C). A molecule of THF was located in the asymmetric unit wherein C4 was disordered with partial occupancy factors 0.633 (9) and 0.367 (9).
Figure 1
The molecular structure of (I) and (II) with atom labels and 50% probability displacement ellipsoids for non-H atoms. Disordered atoms in the solvent are omitted for clarity. Symmetry codes represented by A in atomic labels: for (I) = x, 0.5 - y, z and for (II) = x, 1.5 - y, z.
Figure 2
Overlay plot of the two molecules.
Figure 3
A unit cell packing plot of the title crystal; H atoms have been omitted for clarity.

Dicarbonyldichloridobis(trimethylphosphane)iron(II)– carbonyldichloridotris(trimethylphosphane)iron(II)– tetrahydrofuran (1/1/2)

Crystal data

\[
\begin{align*}
[\text{FeCl}_2\text{(C}_3\text{H}_9\text{P})_3\text{(CO)}]\cdot[\text{FeCl}_2\text{(C}_3\text{H}_9\text{P})_2\text{(CO)}_2]\cdot2\text{C}_4\text{H}_8\text{O} \\
M_r &= 862.10 \\
\text{Orthorhombic, } \text{Pnma} \\
a &= 10.8391 (9) \text{ Å} \\
b &= 16.9670 (12) \text{ Å} \\
c &= 22.2871 (18) \text{ Å} \\
V &= 4098.8 (6) \text{ Å}^3 \\
Z &= 4 \\
F(000) &= 1808
\end{align*}
\]

\[
D_e = 1.397 \text{ Mg m}^{-3} \\
\text{Mo } K\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å} \\
\text{Cell parameters from 9975 reflections} \\
\theta = 2.6–27.4^\circ \\
\mu = 1.20 \text{ mm}^{-1} \\
T = 100 \text{ K} \\
\text{Plate, light yellow} \\
0.20 \times 0.12 \times 0.10 \text{ mm}
\]

Data collection

\[
\begin{align*}
\text{Bruker APEXII CCD} \\
\text{diffractometer} \\
\text{Radiation source: fine-focus sealed tube} \\
\text{Graphite monochromator} \\
\text{Detector resolution: 8.3333 pixels mm}^{-1} \\
\varphi \text{ and } \omega \text{ scans} \\
\text{(SADABS; Bruker, 2008)} \\
T_{\text{min}} = 0.800, T_{\text{max}} = 0.895
\end{align*}
\]

144514 measured reflections
4904 independent reflections
3939 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{\text{max}} = 27.6^\circ, \theta_{\text{min}} = 1.5^\circ$
$h = -14 \rightarrow 14$
$k = -21 \rightarrow 22$
$l = -29 \rightarrow 29$
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.081$
$S = 1.06$
4904 reflections
218 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 5.017P]$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$\Delta \rho_{\text{max}} = 0.68 \text{ e} \text{ Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.70 \text{ e} \text{ Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors (gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger. SHELX restraints used:

delu o2 c2

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{Å}^2$)

|      | $x$    | $y$    | $z$         | $U_{11}$/$U_{eq}$ | Occ. (<1) |
|------|--------|--------|-------------|-------------------|-----------|
| Fe1  | 0.74441(4) | 0.2500 | 0.609986(19) | 0.01347(10)      |           |
| Cl1  | 0.64447(5) | 0.14941(3) | 0.66198(2) | 0.02064(12)      |           |
| P1   | 0.89145(8) | 0.2500 | 0.68214(4)  | 0.01903(18)      |           |
| P2   | 0.58528(8) | 0.2500 | 0.54398(4)  | 0.01575(17)      |           |
| O1   | 0.86416(17) | 0.37737(10) | 0.54685(8) | 0.0268(4)        |           |
| C1   | 0.8188(2)  | 0.32598(13) | 0.57122(10) | 0.0180(5)        |           |
| C11  | 0.9949(3)  | 0.33405(17) | 0.68026(13) | 0.0353(7)        |           |
| H11A | 0.9465    | 0.3828  | 0.6812      | 0.053*           |           |
| H11B | 1.0441    | 0.3324  | 0.6434      | 0.053*           |           |
| H11C | 1.0498    | 0.3323  | 0.7152      | 0.053*           |           |
| C12  | 0.8343(4)  | 0.2500 | 0.75831(15) | 0.0277(8)        |           |
| H12A | 0.7861    | 0.2036  | 0.7650      | 0.042*           |           |
| H12B | 0.9084    | 0.2500  | 0.7829      | 0.042*           |           |
| C21  | 0.5823(2)  | 0.33398(15) | 0.49372(12) | 0.0258(5)        |           |
| H21A | 0.5116    | 0.3294  | 0.4665      | 0.039*           |           |
| H21B | 0.6587    | 0.3354  | 0.4703      | 0.039*           |           |
| H21C | 0.5749    | 0.3826  | 0.5172      | 0.039*           |           |
| C22  | 0.4336(3)  | 0.2500 | 0.57645(16) | 0.0263(8)        |           |
| H22A | 0.3697    | 0.2500  | 0.5460      | 0.039*           |           |
| H22B | 0.4224    | 0.2044  | 0.6013      | 0.039*           |           |
| Fe2  | 0.39182(4) | 0.7500 | 0.91114(2)  | 0.01534(11)      |           |
| Cl2  | 0.17671(7) | 0.7500 | 0.90064(4)  | 0.02288(17)      |           |
| Cl3  | 0.38648(9) | 0.7500 | 1.01832(4)  | 0.0306(2)        |           |
P3  0.43591 (8)  0.7500  0.81372 (4)  0.01842 (18)
P4  0.36847 (6)  0.61635 (3)  0.91539 (3)  0.01807 (13)
O2  0.6473 (3)  0.7500  0.92770 (12)  0.0318 (6)
C2  0.5567 (5)  0.7500  0.92171 (15)  0.0287 (9)
C31 0.3099 (3)  0.7500  0.76165 (16)  0.0280 (8)
H31A 0.3440  0.7500  0.7207  0.042*
H31B 0.2601  0.7974  0.7654  0.042*
C32  0.5302 (2)  0.66852 (14)  0.81642 (11)  0.0229 (5)
H32A  0.4848  0.6189  0.7912  0.034*
H32B  0.6071  0.6661  0.8095  0.034*
H32C  0.5493  0.6767  0.7439  0.034*
C41  0.2881 (3)  0.58171 (15)  0.98174 (11)  0.0291 (6)
H41A  0.2086  0.6088  0.9851  0.044*
H41B  0.3381  0.5929  1.0174  0.044*
H41C  0.2743  0.5248  0.9786  0.044*
C42  0.2761 (2)  0.56933 (14)  0.85754 (11)  0.0247 (5)
H42A  0.2698  0.5128  0.8659  0.037*
H42B  0.3152  0.5772  0.8184  0.037*
H42C  0.1933  0.5926  0.8572  0.037*
C43  0.5079 (2)  0.55672 (14)  0.91735 (11)  0.0240 (5)
H43A  0.5573  0.5712  0.9525  0.036*
H43B  0.5560  0.5659  0.8808  0.036*
H43C  0.4855  0.5009  0.9198  0.036*
C1S  0.7599 (3)  0.48598 (17)  0.79495 (13)  0.0420 (7)
H1S1  0.7804  0.4575  0.7575  0.050*
H1S2  0.6691  0.4908  0.7978  0.050*
C2S  0.8096 (3)  0.44219 (17)  0.84835 (14)  0.0413 (7)
H2S1  0.7417  0.4181  0.8717  0.050*
H2S2  0.8672  0.4001  0.8355  0.050*
C3S  0.8759 (3)  0.50294 (18)  0.88488 (13)  0.0400 (7)
H3S1  0.8205  0.5280  0.9146  0.048*  0.633 (9)
H3S2  0.9481  0.4801  0.9059  0.048*  0.633 (9)
C4S  0.9139 (6)  0.5590 (4)  0.8379 (3)  0.0371 (13)  0.633 (9)
H4S1  0.9280  0.6118  0.8555  0.044*  0.633 (9)
H4S2  0.9912  0.5411  0.8186  0.044*  0.633 (9)
O1S  0.8150 (2)  0.56183 (12)  0.79471 (9)  0.0454 (6)
H3S3  0.9638  0.4884  0.8897  0.048*  0.367 (9)
H3S4  0.8382  0.5075  0.9252  0.048*  0.367 (9)
C4S'  0.8641 (11)  0.5827 (7)  0.8499 (5)  0.0371 (13)  0.367 (9)
H4S3  0.8085  0.6195  0.8713  0.044*  0.367 (9)
H4S4  0.9457  0.6080  0.8450  0.044*  0.367 (9)

**Atomic displacement parameters (Å²)**

|          | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|----------|------------|------------|------------|------------|------------|------------|
| Fe1      | 0.0166 (2) | 0.0124 (2) | 0.0114 (2) | 0.000      | −0.00049 (17) | 0.000      |
| Cl1      | 0.0240 (3) | 0.0195 (3) | 0.0184 (3) | −0.0034 (2) | 0.0011 (2) | 0.0051 (2) |
| P1       | 0.0192 (4) | 0.0221 (4) | 0.0157 (4) | 0.000      | −0.0032 (3) | 0.000      |

*Acta Cryst.* (2011). *E67*, m462  sup-6
|   | U11  | U22  | U33  | U12  | U13  | U23  |
|---|------|------|------|------|------|------|
| P2 | 0.0188 (4) | 0.0154 (4) | 0.0130 (4) | 0.000 | −0.0015 (3) | 0.000 |
| O1 | 0.0345 (10) | 0.0197 (9) | 0.0262 (9) | −0.0062 (7) | 0.0047 (8) | 0.0025 (7) |
| C1 | 0.0199 (11) | 0.0182 (11) | 0.0159 (11) | 0.0019 (9) | −0.0024 (9) | −0.0033 (9) |
| C11 | 0.0331 (15) | 0.0431 (16) | 0.0295 (14) | −0.0166 (12) | −0.0103 (12) | 0.0045 (12) |
| C12 | 0.032 (2) | 0.036 (2) | 0.0151 (17) | 0.000 | −0.0034 (15) | 0.000 |
| C21 | 0.0278 (13) | 0.0243 (13) | 0.0253 (13) | 0.0000 (10) | −0.0057 (10) | 0.0076 (10) |
| C22 | 0.0202 (17) | 0.035 (2) | 0.0233 (18) | 0.000 | −0.0009 (14) | 0.000 |
| Fe2 | 0.0170 (2) | 0.0139 (2) | 0.0151 (2) | 0.000 | 0.0190 (18) | 0.000 |
| C12 | 0.0173 (4) | 0.0231 (4) | 0.0282 (4) | 0.000 | 0.019 (3) | 0.000 |
| C13 | 0.0299 (5) | 0.0303 (5) | 0.0314 (5) | 0.000 | 0.0294 (4) | 0.000 |
| P3 | 0.0199 (4) | 0.0185 (4) | 0.0168 (4) | 0.000 | −0.012 (3) | 0.000 |
| P4 | 0.0214 (3) | 0.0147 (3) | 0.0181 (3) | −0.0008 (2) | 0.0026 (2) | 0.0005 (2) |
| O2 | 0.0430 (17) | 0.0244 (14) | 0.0281 (15) | 0.000 | 0.0089 (13) | 0.000 |
| C2 | 0.066 (3) | 0.0088 (15) | 0.0116 (16) | 0.000 | 0.014 (18) | 0.000 |
| C31 | 0.0295 (19) | 0.0314 (19) | 0.0231 (18) | 0.000 | −0.0049 (15) | 0.000 |
| C32 | 0.0262 (12) | 0.0209 (12) | 0.0216 (12) | 0.0000 (9) | 0.0044 (10) | −0.0014 (9) |
| C41 | 0.0387 (15) | 0.0201 (12) | 0.0284 (13) | −0.0003 (11) | 0.0112 (12) | 0.0053 (10) |
| C42 | 0.0257 (13) | 0.0197 (12) | 0.0287 (13) | −0.0063 (10) | −0.0027 (10) | −0.0017 (10) |
| C43 | 0.0267 (13) | 0.0182 (12) | 0.0272 (13) | 0.0027 (10) | −0.0013 (10) | −0.0005 (10) |
| C1S | 0.066 (2) | 0.0282 (15) | 0.0321 (15) | −0.0039 (14) | −0.0086 (15) | −0.0017 (12) |
| C2S | 0.055 (2) | 0.0303 (15) | 0.0383 (17) | −0.0008 (14) | −0.0094 (15) | 0.0058 (13) |
| C3S | 0.0549 (19) | 0.0383 (17) | 0.0269 (14) | −0.0017 (14) | −0.0064 (14) | 0.0052 (12) |
| C4S | 0.040 (4) | 0.042 (3) | 0.029 (3) | −0.013 (2) | −0.008 (2) | 0.005 (2) |
| O1S | 0.0659 (15) | 0.0324 (11) | 0.0378 (12) | −0.0139 (10) | −0.0191 (11) | 0.0110 (9) |
| O1S' | 0.0549 (19) | 0.0383 (17) | 0.0269 (14) | −0.0017 (14) | −0.0064 (14) | 0.0052 (12) |
| C4S' | 0.040 (4) | 0.042 (3) | 0.029 (3) | −0.013 (2) | −0.008 (2) | 0.005 (2) |

**Geometric parameters (Å, °)**

|     |        |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|--------|
| Fe1—Cl1 | 1.749 (2) | P4—C42 | 1.817 (2) |    |
| Fe1—Cl | 1.749 (2) | P4—C43 | 1.819 (2) |    |
| Fe1—P1 | 2.2641 (10) | O2—C2 | 0.991 (5) |    |
| Fe1—P2 | 2.2670 (9) | C31—H31A | 0.9837 |    |
| Fe1—Cl1 | 2.3300 (6) | C32—H32A | 0.9800 |    |
| P1—C12 | 1.807 (4) | C32—H32B | 0.9800 |    |
| P1—Cl1 | 1.814 (3) | C32—H32C | 0.9800 |    |
| P1—Cl1i | 1.814 (3) | C41—H41A | 0.9800 |    |
| P2—C22 | 1.796 (4) | C41—H41B | 0.9800 |    |
| P2—C21 | 1.813 (2) | C41—H41C | 0.9800 |    |
| P2—C21i | 1.813 (2) | C42—H42A | 0.9800 |    |
| O1—C1 | 1.139 (3) | C42—H42B | 0.9800 |    |
| Cl1—H11A | 0.9800 | C43—H43A | 0.9800 |    |
| Cl1—H11B | 0.9800 | C43—H43B | 0.9800 |    |
| Cl1—H11C | 0.9800 | C43—H43C | 0.9800 |    |
| Cl2—H12A | 0.9565 | C1S—O1S | 1.419 (3) |    |
| Cl2—H12B | 0.9731 |    |    |    |    |    |
C21—H21A 0.9800 C1S—C2S 1.503 (4)
C21—H21B 0.9800 C1S—H1S1 0.9899
C21—H21C 0.9800 C1S—H1S2 0.986
C22—H22A 0.9693 C2S—C3S 1.497 (4)
C22—H22B 0.9597 C2S—H2S1 0.9895
Fe2—C2 1.803 (5) C2S—H2S2 0.9908
Fe2—P3 2.2232 (10) C3S—C4S 1.472 (6)
Fe2—P4 2.2837 (6) C3S—H3S1 0.9900
P3—C31 1.792 (4) C3S—H3S2 0.9900
P3—C32 1.823 (2) C4S—C4S′ 0.9900
P3—C32″ 1.823 (2) C4S′—H4S3 0.9900
P4—C41 1.814 (2)

C1—Fe1—C1 94.97 (15) C31—P3—Fe2 117.95 (13)
C1—Fe1—P1 91.50 (8) C32—P3—Fe2 116.50 (8)
C1—Fe1—P1 91.50 (8) C41—P4—C42 99.88 (13)
P1—Fe1—P2 91.74 (8) C41—P4—C43 101.48 (12)
P1—Fe1—P2 91.74 (8) C42—P4—Fe2 114.12 (9)
P1—Fe1—Cl1i 179.6 (8) P3—C31—H31A 108.3
P1—Fe1—Cl1 94.74 (12) P3—C31—H31B 111.6
P2—Fe1—Cl1 88.51 (2) P3—C32—H32A 109.5
P2—Fe1—Cl1 88.22 (2) P3—C32—H32B 109.5
P4—C41—P4—Fe2 114.12 (9)
P4—C41—H41A 109.5
P4—C41—H41B 109.5
P4—C41—H41C 109.5

O1—C1—Fe1 177.4 (2) H41A—C41—H41B 109.5
C21—P2—C2 103.45 (11) H41A—C41—H41C 109.5
C21—P2—C2i 103.45 (11) H42A—C42—H42B 109.5
C21—P2—C2i 103.45 (11) H42A—C42—H42C 109.5
C22—P2—Fe1 115.78 (12) H41B—C41—H41C 109.5
C21—P2—Fe1 114.50 (9) P4—C42—H42A 109.5
C21—P2—Fe1 114.50 (9) P4—C42—H42B 109.5
O1—C1—Fe1 177.4 (2) P1—C11—H11A 109.5
P1—C11—H11A 109.5 P1—C11—H11B 109.5
P1—C11—H11B 109.5 H11A—C11—H11B 109.5
P1—C11—H11C 109.5 P1—C11—H11C 109.5
| Bond/Angle | Value (°) | Bond/Angle | Value (°) |
|-----------|----------|-----------|----------|
| H11A—C11—H11C | 109.5 | P4—C43—H43B | 109.5 |
| H11B—C11—H11C | 109.5 | H43A—C43—H43B | 109.5 |
| P1—C12—H12A | 109.5 | P4—C43—H43C | 109.5 |
| P1—C12—H12B | 104.3 | H43A—C43—H43C | 109.5 |
| H12A—C12—H12B | 111.3 | H43B—C43—H43C | 109.5 |
| P2—C21—H21A | 109.5 | O1S—C1S—C2S | 107.5 (2) |
| P2—C21—H21B | 109.5 | O1S—C1S—H1S1 | 110.2 |
| H21A—C21—H21B | 109.5 | C2S—C1S—H1S1 | 110.2 |
| P2—C21—H21C | 109.5 | O1S—C1S—H1S2 | 110.1 |
| H21A—C21—H21C | 109.5 | C2S—C1S—H1S2 | 110.3 |
| H21B—C21—H21C | 109.5 | H1S1—C1S—H1S2 | 108.5 |
| P2—C22—H22A | 111.9 | C3S—C2S—C1S | 105.2 (2) |
| P2—C22—H22B | 110.4 | C3S—C2S—H2S1 | 110.8 |
| H22A—C22—H22B | 108.2 | C1S—C2S—H2S1 | 110.7 |
| C2—Fe2—P3 | 85.09 (11) | C3S—C2S—H2S2 | 110.5 |
| C2—Fe2—P4ii | 96.00 (2) | C1S—C2S—H2S2 | 110.7 |
| P3—Fe2—P4ii | 93.689 (19) | C4S—C3S—H3S1 | 101.1 (3) |
| C2—Fe2—P4 | 96.00 (2) | C4S—C3S—H3S1 | 111.6 |
| P3—Fe2—P4 | 93.687 (19) | C2S—C3S—H3S1 | 111.6 |
| P4ii—Fe2—P4 | 166.40 (4) | C4S—C3S—H3S2 | 111.6 |
| C2—Fe2—Cl2 | 178.23 (11) | C2S—C3S—H3S2 | 111.6 |
| P3—Fe2—Cl2 | 96.68 (4) | C3S—C2S—C1S | 109.4 |
| P4ii—Fe2—Cl2 | 83.905 (19) | H3S1—C3S—H3S2 | 109.4 |
| P4—Fe2—Cl2 | 83.906 (19) | O1S—C4S—C3S | 106.8 (4) |
| C2—Fe2—Cl3 | 83.88 (11) | O1S—C4S—H4S1 | 110.4 |
| P3—Fe2—Cl3 | 168.98 (4) | C3S—C4S—H4S1 | 110.4 |
| P4ii—Fe2—Cl3 | 87.469 (19) | H4S1—C4S—H4S2 | 108.6 |
| C2—Fe2—Cl3 | 87.471 (19) | C3S—C4S—H4S2 | 110.4 |
| C31—P3—C32 | 102.17 (11) | C3S—O1S—C4S | 106.3 (3) |
| C31—P3—C32ii | 102.17 (11) | H4S3—C4S—H4S4 | 108.9 |
| C32—P3—C32ii | 98.60 (16) | H3S1—C3S—H3S2 | 109.4 |

**Bond/Angle**

- C1—Fe1—P1—C12: -132.49 (7)  
- C1—Fe1—P1—C12: 132.49 (7)  
- C1—Fe1—P1—C12: 47.118 (16)  
- C1—Fe1—P1—C12: -47.117 (16)  
- C1—Fe1—P1—C11: 107.43 (14)  
- C1—Fe1—P1—C11: 12.42 (14)  
- C1—Fe1—P1—C11: -72.95 (12)  
- C1—Fe1—P1—C11: -167.19 (12)  
- C1—Fe1—P1—C11: -12.42 (14)  
- C1—Fe1—P1—C11: -107.43 (14)  
- C1—Fe1—P1—C11: 167.19 (12)  
- C1—Fe1—P1—C11: 72.96 (12)  
- C1—Fe1—P1—C11: 132.49 (7)  
- C1—Fe1—P2—C22: -132.49 (7)  
- C1—Fe1—P2—C22: -47.128 (16)  
- C1—Fe1—P2—C22: -12.42 (14)  
- C1—Fe1—P2—C22: -107.43 (14)  
- C1—Fe1—P2—C22: 167.19 (12)  
- C1—Fe1—P2—C22: 72.96 (12)  
- C1—Fe1—P2—C22: 132.49 (7)  
- C1—Fe1—P2—C22: 27.52 (11)  
- C1—Fe1—P2—C22: -132.18 (15)  
- C1—Fe1—P2—C22: -37.81 (10)  
- C1—Fe1—P2—C22: -122.09 (9)  
- C1—Fe1—P2—C22: -57.91 (9)  
- C1—Fe1—P2—C22: -153.62 (10)  
- C1—Fe1—P2—C22: -163.46 (11)  
- C1—Fe1—P2—C22: -67.12 (11)  
- C1—Fe1—P2—C22: -80.71 (11)  
- C1—Fe1—P2—C22: -96.68 (4)  
- C1—Fe1—P2—C22: -47.128 (16)  

*Acta Cryst. (2011). E67, m462*
| Bond                  | Distance (Å) | Angle (°) | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|--------------|-----------|
| C1—Fe1—P2—C22        | 47.126 (16)  |           | P3—Fe2—P4—C42 | -46.74 (10) |
| C1—Fe1—P2—C21        | -107.25 (12) |           | P4—Fe2—P4—C42 | 76.00 (19)  |
| C1—Fe1—P2—C21i       | -12.23 (12)  |           | C2—Fe2—P4—C43 | 49.60 (10)  |
| C11—Fe1—P2—C21       | 73.13 (10)   | C13—Fe2—P4—C42 | 144.24 (10) |
| C11—Fe1—P2—C21i      | 167.38 (10)  | C2—Fe2—P4—C43 | -7.49 (15)  |
| C11—Fe1—P2—C21i      | 12.23 (12)   | P3—Fe2—P4—C43 | 77.96 (10)  |
| C1—Fe1—P2—C21i       | 107.25 (12)  | P4—Fe2—P4—C43 | -159.30 (17)|
| C11—Fe1—P2—C21i      | -167.39 (10) | C2—Fe2—P4—C43 | 174.30 (10)|
| C11—Fe1—P2—C21       | -73.14 (10)  | C13—Fe2—P4—C43 | -91.06 (10) |
| C2—Fe2—P3—C31        | 180.0        | O1S—C1S—C2S—C3S | 11.0 (4)   |
| P4—Fe2—P3—C31        | -84.29 (2)   | C1S—C2S—C3S—C4S | -28.5 (4)  |
| P4—Fe2—P3—C31        | 84.29 (2)    | C2S—C3S—C4S—O1S | 36.8 (5)   |
| C12—Fe2—P3—C31       | 0.0          | C2S—C1S—O1S—C4S | 11.8 (4)   |
| C13—Fe2—P3—C31       | 180.000 (1)  | C3S—C4S—O1S—C1S | -31.1 (6)  |
| C2—Fe2—P3—C32        | 57.91 (9)    |           |              |           |

Symmetry codes: (i) x, −y+1/2, z; (ii) x, −y+3/2, z.

### Hydrogen-bond geometry (Å, °)

|                   | D—H | H····A | D····A | D—H····A |
|-------------------|-----|-------|-------|---------|
| C42—H42···O15iii | 0.98 | 2.53  | 3.422 (3) | 151     |
| C43—H43c···O1iii | 0.98 | 2.58  | 3.510 (3) | 158     |
| C43—H43c···O1iv  | 0.98 | 2.43  | 3.392 (3) | 167     |

Symmetry codes: (iii) x=1/2, y, −z+3/2; (iv) −x+3/2, −y+1, z+1/2.