Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[1L-3,4-Bis-*O*-(diphenylphosphino)-1,2,5,6-tetra-*O*-methyl-*chiro*-inositol-κ^2P,P'][η^4-(*Z*,*Z*)-cycloocta-1,5-diene]-rhodium(I) tetrafluoridoborate chloroform solvate

Graeme J. Gainsford,* Cees Lensink and Andrew F. Falshaw

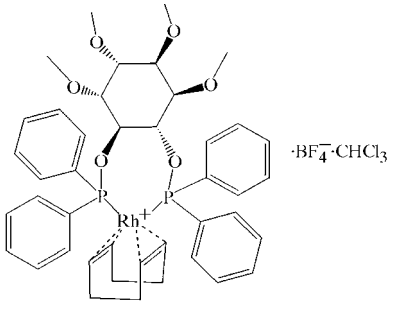
Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

Received 7 May 2007
Accepted 29 May 2007
Online 23 June 2007

The title compound, $[Rh(C_8H_{12})(C_{34}H_{38}O_6P_2)]BF_4\cdot CHCl_3$, a novel asymmetric hydrogenation catalyst, crystallizes with two independent almost identical cations and anions. Cell-packing interactions are provided by nonclassical hydrogen bonding between phenyl and chloroform H atoms and fluoro and chloro donors of the BF_4^- anion and the chloroform solvent molecule.

Comment

This study is part of a programme aimed at developing new catalysts for the asymmetric hydrogenation of alkenes based on carbohydrate precursor molecules (Gainsford *et al.*, 2000; Falshaw *et al.*, 1999, 2007). Only a few structures of catalysts related to the title compound, (I), have been reported [in the following, refcodes in the Cambridge Structural Database (CSD; Version 5.28, updated January 2007; Allen, 2002) are given in capitals]. A preliminary report of this study was given by Gainsford *et al.* (2005).



(I)

The asymmetric unit contains two independent Rh^I complexes containing the novel ligand CANDYPHOS (CP), BF_4^- anions and chloroform solvent molecules. Both chloroform molecules show some disorder, which was modelled using two full Cl atoms and two linked positions (approximately 0.5 occupancy each) for the remaining H and Cl atoms. The CP ligands were confirmed to have absolute carbon configurations of *SSRRRR* (C21–C26 and C31–C36). The independent $[Rh^I(CP)(COD)]^+$ cations (COD is cycloocta-1,5-diene; one is shown in Fig. 1 and selected geometric parameters are given in Table 1) are essentially identical with a close superposition overlap of the final models possible (Fig. 2). The r.m.s. fit of coordinates was 0.223 Å, with bond and angle r.m.s. values of 0.023 Å and 1.43° (Spek, 2003). Minor orientational differences of the phenyl rings are seen; for example, the O1—P1—C111—C112 and O3—P3—C311—C312 torsion angles are −117.6 (7) and −112.6 (7)°, respectively.

The seven-membered chelate rings are in the δ-twist-chair conformation (Kadyrov *et al.*, 1999; Anconi *et al.*, 2006). The P-aryl ring conformations are somewhat similar to those reported in QAHZEF (Aghmiz *et al.*, 2004), with $\alpha(f)$, $\beta(r)$, α' and β' angles [as defined by Seebach *et al.* (1992) and RajanBabu *et al.* (1997)] of 15.3 (2) and 16.2 (2), 66.5 (3) and 65.4 (3), 55.0 (3) and 51.5 (3), and 50.0 (3) and 54.1 (3)°, respectively (calculated using *PLATON*; Spek, 2003). There seems some disparity between reported values in these two reference papers and the deposited coordinates in the CSD, but it is also clear that there is a considerable variation observed in such Rh complexes, with angles ranging from 11.2 (QAHZEF) to 75.0° (NIJMUO; RajanBabu *et al.*, 1997). The *chiro*-inositol rings are closest to chair conformations, with atoms C22 and C32 at the foot and atoms C25 and C35 at the head positions; the displacement Q and θ values (Cremer & Pople, 1975) for the C21–C26 and C31–C36 rings are 0.569 (8) and 0.577 (8) Å, and 11.2 (8) and 9.5 (8)°, respectively.

The Rh—P bonds range from 2.255 (2) to 2.2719 (18) Å, within the ranges noted in the closely-related structures ZATSAO {phenyl[2,3-bis(*O*-diphenylphosphino)-β-D-gluco-

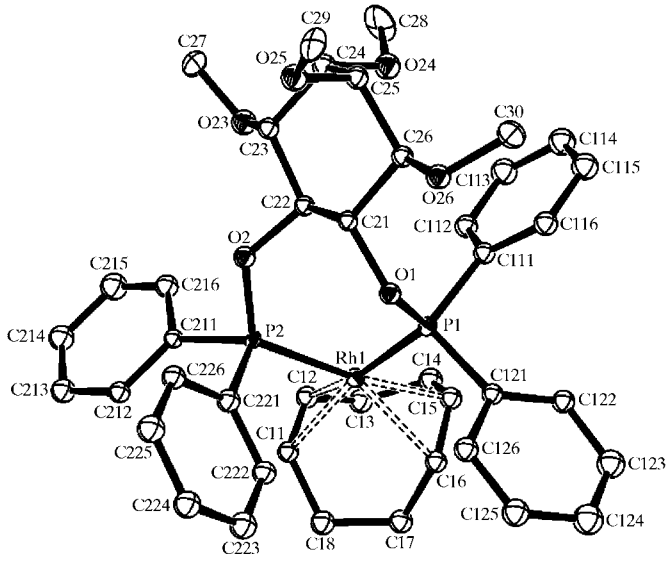


Figure 1
An *ORTEP-3* view (Farrugia, 1997) of the molecular structure of (I), with displacement ellipsoids shown at the 30% probability level. H atoms have been excluded for clarity.

 © 2007 International Union of Crystallography

pyranoside][η^4-(*Z*,*Z*)-cycloocta-1,5-diene]rhodium(I) tetrafluoroborate; 2.250 and 2.275 Å; Kempe *et al.*, 1995}, NIJMUO ((1*S*,2*S*)-(η^2,η^2-cycloocta-1,5-diene){1,2-bis[(diphenylphosphino)oxy]cyclohexane}rhodium(I) hexafluorantimonate benzene solvate; 2.250 and 2.238 Å) and QAHZEF {[η^4-(*Z*,*Z*)-cycloocta-1,5-diene][3,4-bis-*O*-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-L-iditol]rhodium(I) tetrafluoroborate dichloromethane solvate; 2.288–2.311 Å}. The P—O distances here [average 1.617 (4) Å] are self-consistent and within the range noted in these papers (1.610–1.642 Å).

The Rh–cyclo-1,5-diene bond-distance ranges [2.227 (8)–2.293 (10) Å] are within those observed previously, *viz.* 2.238–2.317 Å (QOPKEL; Kempe *et al.*, 2001) and 2.219–2.305 Å (POTGEK; Kempe *et al.*, 1998). The COD rings have twisted boat conformations (Bats *et al.*, 2004), and are skewed with regard to the RhP_2 plane, similar to the configuration observed in, for example, CACNAW (Holz *et al.*, 2001). A CSD survey of related (*L*)Rh(COD)$^+$ compounds, where *L* is a bis(phosphine) ligand linked into a seven-membered ring by four atoms (17 hits), shows that the COD-coordinated C atoms are always asymmetrically placed with respect to the RhP_2 plane [with bond mid-points from 0.06 to 0.60 Å out of the plane (PUHPAJ; Borns *et al.*, 1998)]. In our case, the mid-point of one C═C set is coplanar [the out-of-RhP_2-plane values are 0.015 (8) and 0.033 (8) Å], while the other set is 0.355 (8) and 0.248 (8) Å from the plane. These values are very similar to those in the bis(phosphine) complex BEDPIJ (Anderson & Pignolet, 1981) and in one of the two cations in QAHZEF; the COD atomic disorder found in this latter study suggests that other close intramolecular interactions may be the cause for the COD rotational skewness observed both here and in related compounds (*e.g.* CACNAW).

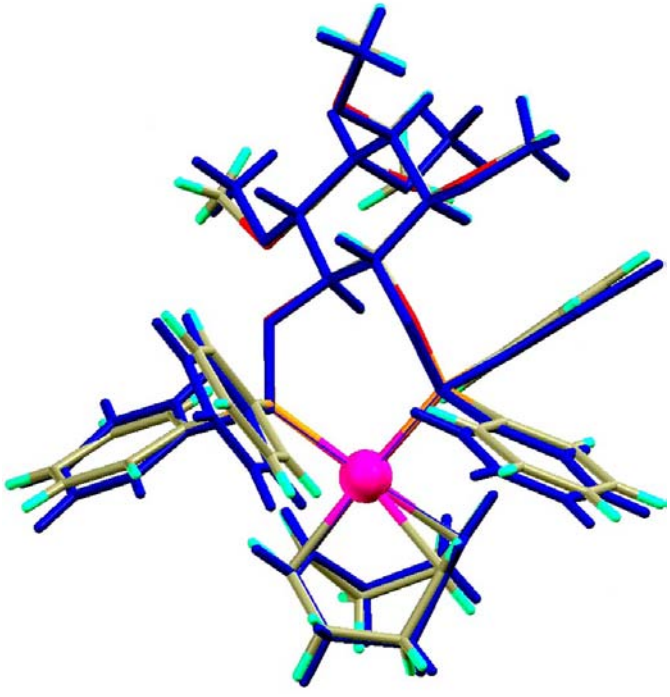


Figure 2
A *Mercury* (Bruno *et al.*, 2002) view of the superimposed independent cations in (I).

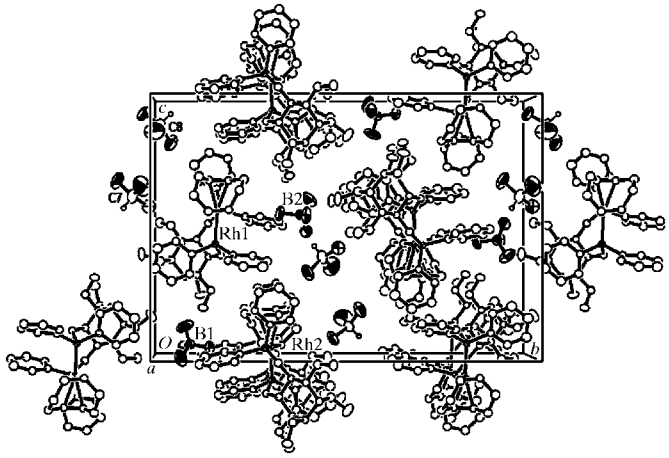


Figure 3
An *ORTEP-3* (Farrugia, 1997) packing view down the *a* axis, with displacement ellipsoids shown at the 50% probability level. Key asymmetric atoms are labelled; only the chloroform H atoms and the major conformation of the chloroform molecules are shown for clarity.

The crystalline packing (Fig. 3) is stabilized by weak but significant hydrogen-bonding interactions between the cations and the chloroform molecules and fluoroborate anions (Table 2). The H124···Cl71 interaction, involving the *trans*-to-P phenyl H atom, has been noted in several compounds [*e.g.* H···Cl = 2.76 Å and C—H···Cl = 161° in a ruthenium–triphenylphosphine complex (VAKFAP; Snelgrove *et al.*, 2003)]. Interactions between chloroform solvent molecules and tetrafluoroborate anions similar to those reported here have also been observed [*e.g.* in LUBTAD (Moores *et al.*, 2002), with H···F = 2.34 Å and C—H···F = 171°]. Significant interactions of phenyl H atoms in the *meta* position with fluoroborate anions (H113, H115, H313 and H315) have been noted in at least ten CSD structures since 2003. The parameters observed in a copper(I) salt (AVEXUU; Fournier *et al.*, 2004) and a ruthenium(I) salt (EWOJAB; Keisham *et al.*, 2004) are H···F distances of 2.38 and 2.37 Å, and C—H···F angles of 169 and 153°, respectively. Finally, there are at least three attractive C—H···π interactions (the last three entries of Table 2) and a close contact between methoxy atom O33 and chloroform atom Cl8*A* at ($-x+1$, $y+\frac{1}{2}$, $-z+1$) [2.930 (9) Å]. Fig. 2 does not show these intermolecular interactions but visually confirms that the estimated potential solvent volume of 166 Å^3 (Spek, 2003) is not localized in the lattice.

Experimental

A solution of 1L-3,4-bis-*O*-(diphenylphosphino)-1,2,5,6-tetra-*O*-methyl-*chiro*-inositol (122 mg, 0.20 mmol) in tetrahydrofuran (5 ml) was added dropwise to a solution of $(RhCODCl)_2$ (49 mg, 0.10 mmol) in tetrahydrofuran (5 ml). The reaction mixture was stirred at room temperature for 17 h. $AgBF_4$ (0.039 g, 0.2 mmol) was added and the reaction mixture stirred for 2 h. Filtration and removal of the solvent yielded an orange solid. Crystallization from $CHCl_3$/pentane yielded

the pure title compound as a $CHCl_3$ solvate (yield: 0.078 g, 76%). ^{31}P NMR ($CDCl_3$): δ 134.8 (J_{Rh-P} = 178 Hz). Analysis calculated for $C_{43}H_{51}BCl_3F_4O_6P_2Rh$: C 50.54, H 5.03%; found: C 50.44, H 5.00%.

Crystal data

$[Rh(C_8H_{12})(C_{34}H_{38}O_6P_2)]BF_4\cdot CHCl_3$	β = 91.596 (7)°
M_r = 1021.85	V = 4518.0 (16) Å^3
Monoclinic, $P2_1$	Z = 4
a = 9.3231 (17) Å	Mo $K\alpha$ radiation
b = 26.611 (6) Å	μ = 0.69 mm^{-1}
c = 18.218 (4) Å	T = 158 (2) K
	0.9 × 0.4 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer	19306 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	15833 independent reflections
T_{min} = 0.785, T_{max} = 0.973	13832 reflections with $I > 2\sigma(I)$
	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064	H-atom parameters constrained
$wR(F^2)$ = 0.150	$\Delta\rho_{max}$ = 0.83 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −1.48 e Å^{-3}
15833 reflections	Absolute structure: Flack (1983), 6332 Friedel pairs
645 parameters	Flack parameter: 0.05 (3)
1 restraint	

Table 1
Selected geometric parameters (Å, °).

Rh1—C12	2.227 (8)	Rh1—C16	2.291 (9)
Rh1—C11	2.256 (8)	P1—O1	1.613 (5)
Rh1—P2	2.257 (2)	P1—C111	1.816 (8)
Rh1—C15	2.259 (9)	P2—C211	1.795 (7)
Rh1—P1	2.272 (2)		
C12—Rh1—C11	35.1 (3)	C45—Rh2—C46	33.9 (3)
Rh1—P1—O1—C21	−78.0 (5)	Rh2—P3—O3—C31	−77.7 (5)
Rh1—P2—O2—C22	−14.7 (6)	Rh2—P4—O4—C32	−9.0 (6)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centres of phenyl rings C321–C326, C121–C126 and C411–C416, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7A···F23^{i}	1.03	2.39	3.402 (17)	166
C8—H8A···F12^{ii}	1.03	2.29	3.148 (16)	139
C8—H8A···F14^{ii}	1.03	2.34	3.262 (14)	149
C113—H113···F23^{i}	0.95	2.45	3.258 (12)	142
C115—H115···F11	0.95	2.38	3.210 (12)	146
C124—H124···Cl71^{iii}	0.95	2.83	3.726 (12)	158
C313—H313···F12^{iv}	0.95	2.55	3.482 (13)	167
C315—H315···F24^{v}	0.95	2.53	3.426 (13)	158
C423—H423···F12^{vi}	0.95	2.40	3.296 (14)	157
C18—H18A···Cg1^{vii}	0.99	2.77	3.607 (10)	142
C48—H48A···Cg2^{vi}	0.99	2.71	3.600 (8)	150
C47—H47B···Cg3^{vi}	0.99	2.82	3.693 (10)	147

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+1$; (ii) $x, y, z+1$; (iii) $-x+2, y+\frac{1}{2}, -z+1$; (iv) $-x+1, y+\frac{1}{2}, -z$; (v) $x-1, y, z-1$; (vi) $x-1, y, z$; (vii) $x+1, y, z+1$.

The disorder of the chloroform atoms was modelled using two-position linked atoms for one H and one Cl atom in each of the two molecules; H atoms were positioned (C—H = 1.03 Å) and fixed in the final refinement cycles with one common U_{iso} value. Identical anisotropic displacement parameters were used for disordered chloroform atoms Cl8A and Cl8B, with identical isotropic parameters for Cl7A and Cl7B. The final major occupancies for the linked atoms were 0.564 (10) and 0.534 (6) for the C7 and C8 molecules, respectively. All other C-bound H atoms were constrained to their expected geometries (C—H = 0.95–1.00 Å) and were refined with U_{iso}(H) values of 1.2 or 1.5 times U_{eq} of their parent C atom. Only selected non-H atoms were refined with anisotropic displacement parameters in order to maintain a reasonable data/parameter ratio. There is a strong suggestion of the presence of a minor crystal fragment contributing to some of the data. The worst fit data (the top 35 reflections) have $F_o >> F_c$; removal of data for which $F_o > 1.5F_c$ (830 data with R around 20%) improved agreement R_1 (0.064 to 0.055) but with only insignificant changes in the model. Given no definitive experimental evidence for this, the full collected data results are presented here.

Data collection: *SMART* (Siemens, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Siemens, 2001) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

The authors thank Professor Ward T. Robinson and Dr J. Wikaira of the University of Canterbury for their assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3095). Services for accessing these data are described at the back of the journal.

References

Aghmiz, M., Aghmiz, A., Diaz, Y., Masdeu-Bulto, A., Claver, C. & Castillon, S. J. (2004). *J. Org. Chem.* **69**, 7502–7510.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Anconi, C. P. A., Nascimento, C. S., Dos Santos, H. F. & De Almeida, W. B. (2006). *Chem. Phys. Lett.* **418**, 458–466.
Anderson, M. P. & Pignolet, L. H. (1981). *Inorg. Chem.* **20**, 4101–4107.
Bats, J. W., Rivas Nass, A. & Hashmi, A. S. K. (2004). *Acta Cryst.* E**60**, m85–m87.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Borns, S., Kadyrov, R., Heller, D., Baumann, W., Spannenberg, A., Kempe, R., Holz, J. & Borner, A. (1998). *Eur. J. Inorg. Chem.* pp. 1291–1295.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Falshaw, A., Gainsford, G. J. & Lensink, C. (1999). *Acta Cryst.* C**55**, 1353–1355.
Falshaw, A., Gainsford, G. J., Lensink, C., Slade, A. T. & Wright, L. J. (2007). *Polyhedron*, **26**, 329–337.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fournier, E., Sicard, S., Decken, A. & Harvey, P. D. (2004). *Inorg. Chem.* **43**, 1491–1501.
Gainsford, G. J., Falshaw, A., Lensink, C. & White, S. (2005). Book of Abstracts, MS80.298.5(C102), XXth Congress of the International Union of Crystallography, Florence, Italy.
Gainsford, G. J., Lensink, C., Hart, J. B. & Falshaw, A. (2000). *Acta Cryst.* C**56**, 1396–1398.
Holz, J., Sturmer, R., Schmidt, U., Drexler, H. J., Heller, D., Krimmer, H. P. & Borner, A. (2001). *Eur. J. Org. Chem.* pp. 4615–4624.
Kadyrov, R., Borner, A. & Selke, R. (1999). *Eur. J. Inorg. Chem.* pp. 705–711.

Keisham, S. S., Mozharivskyj, Y. A., Carroll, P. J. & Kollipara, M. R. (2004). *J. Organomet. Chem.* **689**, 1249–1256.
Kempe, R., Schwarze, M. & Selke, R. (1995). *Z. Kristallogr.* **210**, 555–556.
Kempe, R., Spannenberg, A. & Heller, D. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 633–635.
Kempe, R., Spannenberg, A., Heller, D., Kadyrov, R. & Fehring, V. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 157–160.
Moores, A., Mezailles, N., Maigrot, N., Ricard, L., le Mathey, F. & Floch, P. L. (2002). *Eur. J. Inorg. Chem.* pp. 2034–2039.
RajanBabu, T. V., Ayers, T. A., Halloday, G. A., You, K. K. & Calabrese, J. C. (1997). *J. Org. Chem.* **62**, 6012–6028.
Seebach, D., Plattner, D. A., Beck, A. K., Wang, Y. M., Humziker, D. & Petter, W. (1992). *Helv. Chim. Acta*, **75**, 2171–2209.
Sheldrick, G. M. (1996). *SADABS.* Version 2.03. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Siemens (2001). *SMART* (Version 5.045) and *SAINT-Plus* (Version 6.22). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Snelgrove, J. L., Conrad, J. C., Yap, G. P. A. & Fogg, D. E. (2003). *Inorg. Chim. Acta*, **345**, 268–278.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.