Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

syn-Tri-μ-chlorido-bis{[(*R*,*R*)/(*S*,*S*)-2,2′-bis(diphenylphosphino)-1,1′-biphenyl]-hydridoiridium(III)} tetrafluorido-borate dichloromethane disolvate

Lutz Dahlenburg,* Frank W. Heinemann, Dagmar Kramer and Ralf Menzel

Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-91058 Erlangen, Germany
Correspondence e-mail: lutz.dahlenburg@chemie.uni-erlangen.de

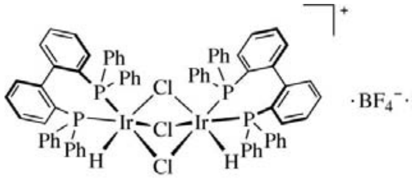
Received 22 January 2008
Accepted 11 February 2008
Online 23 February 2008

In the structure of the title compound, $[Ir_2Cl_3H_2(C_{36}H_{28}P_2)_2]$-$BF_4 \cdot 2CH_2Cl_2$, the bimetallic cation features a confacial bioctahedral structure that is held together by three bridging chloride ions and is very close to C_2 symmetric. The hydrides are in a *syn* orientation (*trans* to the same halide bridge), and the chelating bis(phosphine) atropisomers display a racemic (*R*,*R*)/(*S*,*S*) configuration. Because of the high *trans*-bond-weakening influence of the hydride ligands, the Ir—Cl bonds *trans* to Ir—H [2.5262 (7) and 2.5365 (7) Å] are significantly longer than those opposite the Ir—P linkages [2.4287 (7)–2.4672 (8) Å]. The Ir—P distances vary between 2.2464 (9) and 2.2565 (8) Å. This study illustrates the usefulness of sterically demanding biaryl-based P_2 ligands in the synthesis of halide-bridged Ir_2 complexes, which are valuable precursors of versatile catalysts for homogeneous C═O hydrogenation.

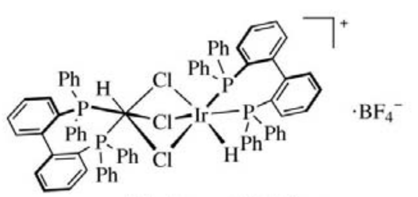
Comment

Recently, we reported on the oxidative addition of hydrogen chloride (HCl) to several bis(phosphine)-coordinated (cyclooctadiene)iridium(I) complexes, namely $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})(L_2)]BF_4$, with L_2 = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-binap)], (2*S*,4*S*)-2,4-bis(diphenylphosphino)-pentane [(*S*,*S*)-bdpp], and (1*S*,2*S*)-bis(diphenylphosphino)-cyclopentane [(*S*,*S*)-bdpcp]. Whereas reactions between HCl and $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})$\{(*S*,*S*)-bdpp\}]$BF_4$ or $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})$\{(*S*,*S*)-bdpcp\}]$BF_4$ yielded the usual mononuclear adducts, similar treatment of $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})$\{(*R*)-binap\}]$BF_4$ furnished the triply chloride-bridged diiridium complex $[Ir_2(\mu\text{-}Cl)_3H_2$\{(*R*)-binap\}$_2]BF_4$. We proposed that the action of HCl on the (*R*)-binap-containing precursor also produces a mononuclear iridium(III) complex as a first intermediate, where the greater bulkiness of the two 'Ph_2P-naphthyl' building blocks of the binap ligand compared with that of the two 'Ph_2P-alkyl' halves of the bdpp and bdpcp chelate phosphines facilitates the decoordination of the diene ligand through steric pressure. Bridge-closing combination of the remaining [IrClH\{(*R*)-binap\}]$^+$ fragments would then lead to $[Ir_2(\mu\text{-}Cl)_2H_2$\{(*R*)-binap\}$_2]^{2+}$, which stabilizes to $[Ir_2(\mu\text{-}Cl)_3H_2$\{(*R*)-binap\}$_2]^+$ by the addition of an extra chloride ion provided by the excess of HCl (Dahlenburg *et al.*, 2007). We expected that the formation of triply halide-bridged diiridium complexes $[Ir_2(\mu\text{-}X)_3H_2(L_2)]^+$ from hydrogen halides (H*X*) and iridium(I) $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})(L_2)]^+$ cations bearing sterically congested bis(phosphines) similar to, or different from, the binap ligand could be a general reaction. Hence, we set out to prepare additional members of this family of compounds because previous work had shown that opening of the chloride bridges of $[Ir_2(\mu\text{-}Cl)_3H_2$\{(*R*)-binap\}$_2]BF_4$ by various N,N-nucleophiles presents a useful method of synthesis for the otherwise involved mixed-ligand bis(chelates) [IrClH\{(*R*)-binap\}(1,2-diamine)]BF_4, which are of interest as (pre)catalysts for the enantioselective hydrogenation of ketones (Dahlenburg *et al.*, 2007).

In this context, we came across the reaction between HCl and $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})$(*rac*-biphep)]$BF_4$, where *rac*-biphep is racemic 2,2′-bis(diphenylphosphino)-1,1′-biphenyl, a binap-like chelate ligand which, because of its chiral flexibility, cannot be obtained as resolved enantiomers but can adopt stereochemically robust atropisomeric conformations in metal complexes bearing enantiopure coligands (Becker *et al.*, 2001; Korenaga *et al.*, 2001; Mikami *et al.*, 2001, 2002, 2004, 2005*a*,*b*). As anticipated, bimetallic $[Ir_2(\mu\text{-}Cl)_3H_2(\text{biphep})_2]BF_4$ was isolated from the reaction solution. ^1H and $^{31}P\{^1H\}$ NMR spectroscopic analysis proved the presence, in a 1:1 molar ratio, of two diastereomers, (I) and (II) (see scheme), differing only in the relative disposition of the hydride ligands and the pairwise configuration of the axially chiral bis(phosphine) chelates, which is *syn* or *anti* (*trans* to the same or to two different bridging chlorides) with regard to the orientation of the two Ir—H bonds, and (*R*,*R*)/(*S*,*S*) or (*R*,*S*) with regard to the chirality of the pair of possible biphep atropisomers. The racemic *syn* form, with the two biphep ligands in an (*R*,*R*) or (*S*,*S*) configuration, could be separated as the title addition compound by crystallizing the isomeric mixture from CH_2Cl_2–diethyl ether and this structure, (I), is presented here.



(I), the (*R*,*R*) enantiomer



(II), the *anti*-(*R*,*S*) form

doi:10.1107/S0108270108004198

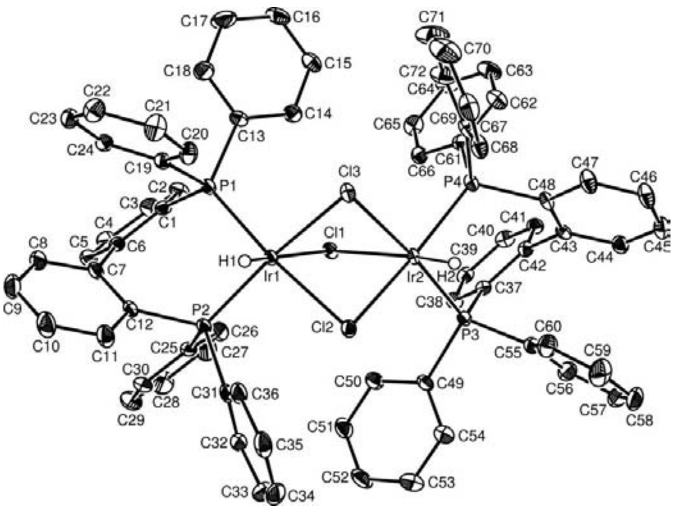


Figure 1
The structure of the bimetallic cation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms attached to C atoms have been omitted for clarity.

The molecular structure of the title (*R*,*R*) enantiomeric cation of the title compound is shown in Fig. 1. While a few structural studies of biphep complexes of Ru, Rh, Pd and Pt have been reported in recent years (Becker *et al.*, 2001; Doherty *et al.*, 2005; Korenaga *et al.*, 2001; Mikami *et al.*, 2001, 2002, 2004, 2005*a*,*b*; Osawara *et al.*, 2000), the title compound appears to be the first crystallographically characterized example with iridium as the central metal (Cambridge Structural Database, Version 5.28; Allen, 2002).

The geometry of the bimetallic cation can be described as triply chloride-bridged confacial bioctahedral, with two *syn*-aligned Ir—H bonds *trans* to the same halide bridge. The overall structure of the cationic component is virtually C_2 symmetric, with the twofold rotation axis passing through the mid-points of the Ir$\cdots$Ir vector and the Cl1 ligand *trans* to both hydrides.

The pairwise shared coordination planes spanned by one metal centre and two bridging chloride ligands are inclined to each other at angles between 120.81 (5) and 127.01 (5)°, with the interplanar angles of the three Ir(μ-Cl)Ir bridges varying from 118.20 (2) to 121.61 (2)°. All of these parameters compare favourably with those determined previously for the related binap complex $[Ir_2(\mu\text{-}Cl)_3H_2\{(R)\text{-binap}\}_2]BF_4$ (Dahlenburg *et al.*, 2007). The greater chiral flexibility of the biphep system compared with that of the binap ligand is mirrored by the angles between the normals to the two pairs of benzene planes in the biphenyl units, which are 61.0 (1) and 65.7 (1)°, and thus clearly fall below the range of 68–81° spanned by the corresponding dihedral angles between the naphthyl planes in $[Ir_2(\mu\text{-}Cl)_3H_2\{(R)\text{-binap}\}_2]BF_4$ (Dahlenburg *et al.*, 2007) and $[Ir_2(\mu\text{-}Cl)H_2(\mu\text{-}OCH_3)_2\{(R)\text{-binap}\}_2]Cl$ (Tani *et al.*, 1998*a*,*b*).

As a result of the high *trans*-bond-weakening influence of the hydride ligands, the Ir—Cl bonds *trans* to Ir—H are much longer than those opposite Ir—P (Table 1) and are amongst the longest Ir^{III}—μ-Cl distances reported to date (Dahlenburg *et al.*, 2007). The Ir—P bond lengths and the obtuse P—Ir—P angles agree well with the corresponding distances and valence angles of structurally characterized iridium complexes of the binap ligand (Dahlenburg *et al.*, 2007; Dorta *et al.*, 1997; Tani *et al.*,1998*a*,*b*; Yamagata *et al.*, 1997, 2006).

Experimental

A solution of dry HCl in diethyl ether was added dropwise to a tetrahydrofuran solution (30 ml) of $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})(rac\text{-biphep})]BF_4$ (142 mg, 0.16 mmol), which was obtained from $[Ir_2(\mu\text{-}Cl)_2(\eta^4\text{-}1,5\text{-}C_8H_{12})_2]$ and the phosphine in the presence of $AgBF_4$, similar to the procedure described previously for the preparation of $[Ir(\eta^4\text{-}1,5\text{-}C_8H_{12})\{(R)\text{-binap}\}]BF_4$ and related complex salts (Dahlenburg *et al.*, 2007). The dark-red mixture gradually became pale yellow and the addition of HCl was stopped when no further alteration of the colour was discernible. After stirring for an additional 30 min and concentration of the solution to ~1 ml, the product was precipitated by adding diethyl ether (50 ml), collected, washed with 3 × 2 ml of the same solvent and dried under vacuum. The yield was 120 mg (95%) of colourless $[Ir_2(\mu\text{-}Cl)_3H_2(\text{biphep})_2]BF_4$ as a 1:1 molar mixture of the *syn*-(*R*,*R*)/(*S*,*S*) diastereomer and the *anti*-(*R*,*S*) form, (II). Elemental analysis found: C 53.74, H 3.85%; calculated for $C_{72}H_{58}BCl_3F_4Ir_2P_4$. Spectroscopic analysis for the *syn*-(*R*,*R*)/(*S*,*S*) diastereomer: ^{1}H NMR (CDCl$_3$): δ −23.04 (*dd*, $^2J_{P,H}$ = 15.61, $^2J_{P',H}$ = 21.67 Hz, 2 × IrH); $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ −1.67, −7.52 (both *d*, $^2J_{P,P'}$ = 20.0 Hz, 1P each). Spectroscopic analysis for the *anti*-(*R*,*S*) form: ^{1}H NMR (CDCl$_3$): δ −22.47 (*dd*, $^2J_{P,H}$ = 16.07, $^2J_{P',H}$ = 22.01 Hz, 1 × IrH), −22.73 (*dd*, $^2J_{P,H}$ = 16.66, $^2J_{P',H}$ = 21.43 Hz, 1 × IrH); $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 0.00, −1.96, −4.14, −7.43 (all *d*, $^2J_{P,P'}$ = 18.0 Hz each, all 1P). Slow diffusion of diethyl ether into a saturated solution of the isomeric mixture in CH$_2$Cl$_2$ resulted in the deposition of single crystals of the title addition compound, (I).

Crystal data

$[Ir_2Cl_3H_2(C_{36}H_{28}P_2)_2]BF_4\cdot 2CH_2Cl_2$
M_r = 1794.48
Triclinic, $P\overline{1}$
a = 13.6578 (14) Å
b = 14.7640 (6) Å
c = 18.5300 (11) Å
α = 68.701 (3)°
β = 86.357 (6)°
γ = 86.228 (5)°
V = 3470.5 (4) Å^3
Z = 2
Mo *Kα* radiation
μ = 4.25 mm^{-1}
T = 150 (2) K
0.17 × 0.14 × 0.14 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.463, T_{max} = 0.550
85276 measured reflections
16517 independent reflections
13333 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.052
S = 1.03
16517 reflections
835 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 2.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.07 e Å^{-3}

H atoms attached to C atoms were positioned geometrically, with C—H = 0.95–0.99 Å, and were refined using appropriate riding models, with $U_{iso}(H) = 1.2U_{eq}(C)$. The positions of the two hydride ligands were derived from a final ΔF map; during refinement, their U_{iso} values were fixed at $1.5U_{eq}(Ir)$.

Table 1
Selected geometric parameters (Å, °).

Ir1—P1	2.2518 (8)	Ir2—P3	2.2464 (9)
Ir1—P2	2.2565 (8)	Ir2—P4	2.2526 (8)
Ir1—Cl3	2.4287 (7)	Ir2—Cl2	2.4374 (7)
Ir1—Cl2	2.4672 (8)	Ir2—Cl3	2.4563 (8)
Ir1—Cl1	2.5262 (7)	Ir2—Cl1	2.5365 (7)
Ir1—H1	1.44 (3)	Ir2—H2	1.44 (3)
P1—Ir1—P2	92.35 (3)	P4—Ir2—Cl2	167.55 (3)
P1—Ir1—Cl3	95.11 (3)	P3—Ir2—Cl3	174.60 (3)
P2—Ir1—Cl3	167.70 (3)	P4—Ir2—Cl3	91.50 (3)
P1—Ir1—Cl2	174.05 (3)	Cl2—Ir2—Cl3	79.33 (3)
P2—Ir1—Cl2	93.52 (3)	P3—Ir2—Cl1	97.83 (3)
Cl3—Ir1—Cl2	79.29 (3)	P4—Ir2—Cl1	107.55 (3)
P1—Ir1—Cl1	98.28 (3)	Cl2—Ir2—Cl1	79.27 (2)
P2—Ir1—Cl1	108.34 (3)	Cl3—Ir2—Cl1	79.53 (3)
Cl3—Ir1—Cl1	80.26 (2)	P3—Ir2—H2	88.1 (13)
Cl2—Ir1—Cl1	78.91 (2)	P4—Ir2—H2	81.1 (13)
P1—Ir1—H1	88.2 (14)	Cl2—Ir2—H2	91.1 (13)
P2—Ir1—H1	79.3 (13)	Cl3—Ir2—H2	93.7 (13)
Cl3—Ir1—H1	91.2 (13)	Cl1—Ir2—H2	169.1 (13)
Cl2—Ir1—H1	93.8 (13)	Ir1—Cl1—Ir2	82.56 (2)
Cl1—Ir1—H1	169.6 (13)	Ir2—Cl2—Ir1	85.85 (2)
P3—Ir2—P4	93.80 (3)	Ir1—Cl3—Ir2	86.28 (2)
P3—Ir2—Cl2	95.58 (3)		

Data collection: *COLLECT* (Bruker, 2002); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Version 1.9.2; Westrip, 2008).

Support of this work by the Deutsche Forschungsgemeinschaft (Bonn, SFB 583) is gratefully acknowledged. The authors are also indebted to Mr P. Bakatselos for his skilful assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3123). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Becker, J. J., White, P. S. & Gagné, M. R. (2001). *J. Am. Chem. Soc.* **123**, 9478–9479.

Bruker (2002). *COLLECT*, *SADABS* (Version 2.06) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.

Dahlenburg, L., Menzel, R. & Heinemann, F. W. (2007). *Eur. J. Inorg. Chem.* pp. 4364–4374.

Doherty, S., Knight, J. G., Rath, R. K., Clegg, W., Harrington, R. W., Newman, C. R., Campbell, R. & Amin, H. (2005). *Organometallics*, **24**, 2633–2644.

Dorta, R., Egli, P., Zürcher, F. & Togni, A. (1997). *J. Am. Chem. Soc.* **119**, 10857–10858.

Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Korenaga, T., Aikawa, K., Terada, M., Kawauchi, S. & Mikami, K. (2001). *Adv. Synth. Catal.* **343**, 284–288.

Mikami, K., Aikawa, K. & Korenaga, T. (2001). *Org. Lett.* **3**, 243–245.

Mikami, K., Aikawa, K., Yusa, Y. & Hatano, M. (2002). *Org. Lett.* **4**, 91–94.

Mikami, K., Kakuno, H. & Aikawa, K. (2005*a*). *Angew. Chem.* **117**, 7423–7426.

Mikami, K., Kakuno, H. & Aikawa, K. (2005*b*). *Angew. Chem. Int. Ed.* **44**, 7257–7460.

Mikami, K., Kataoka, S., Yusa, Y. & Aikawa, K. (2004). *Org. Lett.* **6**, 3699–3701.

Osawara, M., Yoshida, K. & Hayashi, T. (2000). *Organometallics*, **19**, 1567–1571.

Tani, K., Iseki, A. & Yamagata, T. (1998*a*). *Angew. Chem.* **110**, 3590–3592.

Tani, K., Iseki, A. & Yamagata, T. (1998*b*). *Angew. Chem. Int. Ed.* **37**, 3381–3383.

Westrip, S. P. (2008). *publCIF*. In preparation.

Yamagata, T., Iseki, A. & Tani, K. (1997). *Chem. Lett.* **12**, 1215–1216.

Yamagata, T., Tadaoka, H., Nagata, M., Hirao, T., Kataoka, Y., Ratovelomanana-Vidal, V., Genet, J. P. & Mashima, K. (2006). *Organometallics*, **25**, 2505–2513.