metal-organic compounds

An optically pure P–alkene-ligated Ir^I complex

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The asymmetric unit of (P)-chloridobis[(S)-(+)-5-(3,5-dioxa-4-phosphacyclohepta[2,1-a:3,4-a′]dinaphthalen-4-yl)dibenz[b,f]-azepine]iridium(I)–benzene–pentane (1/1/1), [IrCl(C$_{34}$H$_{22}$N-O$_2$P)$_2$]·C$_6$H$_6$·C$_5$H$_{12}$, contains two formula units. The two symmetry-independent molecules of the Ir complex have similar conformations and approximate C_2 symmetry, with small deviations arising from slightly different puckering of the seven-membered dioxaphosphacycloheptadiene rings. The Ir atoms have trigonal–bipyramidal coordination geometry, with the P atoms in axial positions. The steric strain of the bidentate coordination of the P–alkene ligand through its P and alkene C atoms causes the N atom to have pyramidal geometry, compared with the trigonal–planar geometry observed in the free ligand. The coordination also results in an *anti* conformation of the binaphthyl and alkene groups within the P–alkene ligand.

Comment

Chiral P–alkene ligands are attracting growing interest in the field of enantioselective catalysis (Defieber *et al.*, 2008). For example, the alkene-phosphoramidite (S)-(+)-N-(3,5-dioxa-4-phosphacyclohepta[2,1-a:3,4-a′]dinaphthalen-4-yl)dibenz[b,f]-azepine, (1) (Briceño & Dorta, 2007; Mariz *et al.*, 2008), was used as a ligand in the Ir-catalyzed enantioselective formation of allylic amines from allylic alcohols (70% ee) (Defieber *et al.*, 2007) and for the Rh-catalyzed conjugate addition (CA) of arylboronic acids to enones with up to 99% ee (Drinkel *et al.*, 2010). In the latter case, the fully characterized monomeric Rh precatalysts, (2), of composition [RhCl(κ^1-P–alkene)(κ^2-P–alkene)] bearing two equivalents of P–alkene ligand (1), displayed exclusive *cis* coordination of the P atoms and a square-planar coordination environment. Roggen & Carreira (2010) recently described the crystal structure of a similar monomeric Ir–iodide complex of composition [IrI(P–alkene)$_2$] bearing, in a *trans* arrangement, the achiral variant of P–alkene ligand (1), *i.e.* featuring the 2,2′-biphenol motif instead of the chiral auxiliary (S)-binaphthol. This complex is

a competent catalyst for the stereospecific substitution of chiral allylic alcohols with sulfamic acid to afford optically active allylic amines with enantiospecificities >98%. Breher *et al.* (2004) described a crystal structure of a related achiral [IrCl(P–alkene)$_2$] complex also displaying *trans* or axial positioning of the P atoms in the trigonal–bipyramidal coordination environment. We note that the aforementioned pentacoordinate Ir complexes are *per se* chiral, possessing stereogenic Ir centres, but obviously without the use of enantiodiscriminating auxiliaries they are obtained as racemates. Here, we disclose the crystal structure of such a complex that is optically pure. The enantiomerically pure ligand (S)-(1) was used to synthesize the title complex, (3), and to our surprise its formation was perfectly diastereospecific based on NMR spectroscopy [possible diastereomers are (M,S,S) and (P,S,S); see also the pair of enantiomers of (3) depicted in the scheme]. Single-crystal X-ray analysis then allowed us to determine the absolute configuration at Ir, which is (P).
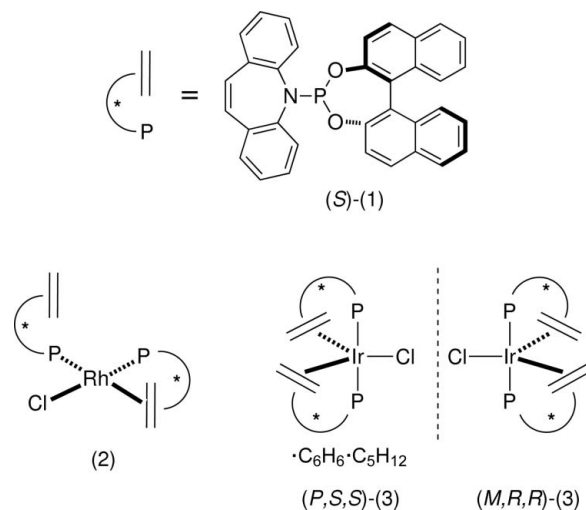
The asymmetric unit of (3) contains two molecules of the Ir complex, two of benzene and two of pentane. The two independent molecules of the Ir complex have largely similar conformations (Fig. 1), with the largest differences being in the orientations of the binaphthyl rings as a result of different puckering of the seven-membered dioxaphosphacyclohepta-diene rings. The Cremer & Pople (1975) puckering parameters for the seven-membered rings are listed in Table 2 and show that the total puckering amplitude, Q, is somewhat different for the two seven-membered rings in each independent Ir complex molecule, but that the pattern is similar across the two molecules. An overlay of the two molecules is shown in Fig. 2, which demonstrates that small variations in the ring puckering have a significant effect on the positions of the atoms at the remote ends of the naphthyl rings. The molecules are approximately C_2 symmetric about the Ir—Cl axis, although the different ring puckering in the two seven-membered rings diminishes the exactness of the fit to C_2 symmetry. In contrast, the corresponding Ir complex with
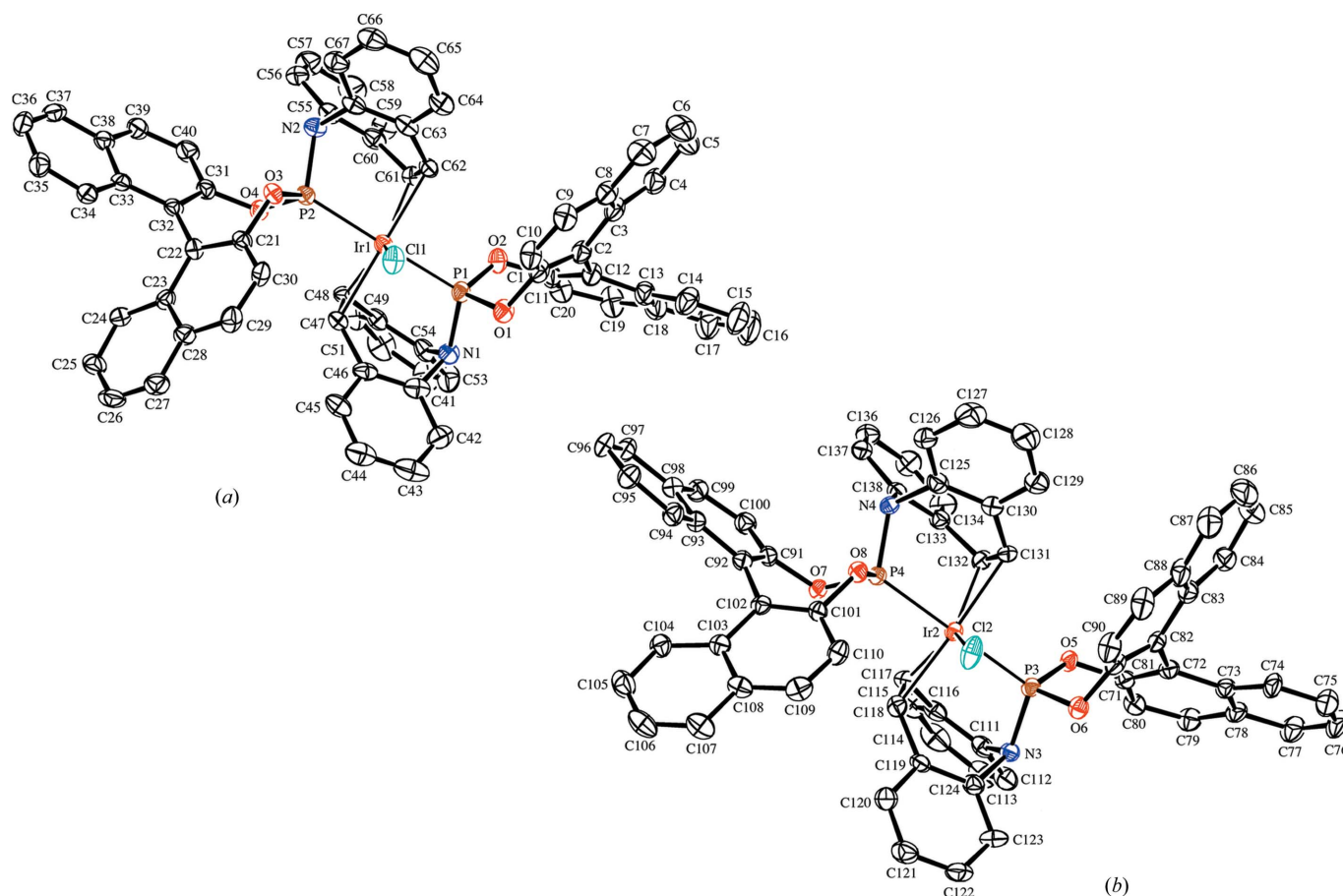
Figure 1
View of (*a*) molecule *A* and (*b*) molecule *B* of the Ir complex of (3), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

biphenyl groups in the P–alkene ligands has crystallographic C_2 symmetry (Roggen & Carreira, 2010).

The coordination environment in the Ir complex of (3) can be considered as trigonal bipyramidal, with the P atoms in axial positions, and the equatorial positions occupied by the Cl atom and the two alkene functions, each of which may be regarded as occupying a single site in the formal equatorial trigonal plane. This arrangement parallels the architecture reported by Roggen & Carreira (2010). In each of the independent molecules, the Ir atom lies well within the plane defined by the Cl atom and the four alkene C atoms. The maximum deviations of these six atoms from the mean plane are 0.028 (4) Å for atom C48 in molecule *A* and 0.081 (5) Å for atom C118 in molecule *B*. The P—Ir—*X* bond angles, where *X* is any equatorial atom, lie in the narrow range 85.66 (12)–94.16 (12)°. Taking the bisector, *Y*, of each alkene C—Ir—C angle as the effective 'bond' position of the alkene group gives Cl—Ir—*Y* angles in the range 109.85 (12)–112.70 (13)° and *Y*—Ir—*Y* angles of 139.31 (17) and 136.10 (17)°. These angles are closer to those required for a trigonal–bipyramidal coordination geometry than those expected for a square-planar arrangement with the Cl atom at the apex, thus indicating that the former is a more suitable description of the coordination geometry of the Ir atoms in (3).

The alkene C—C bond lengths [1.447 (6)–1.453 (6) Å] compare well with those in the complexes reported by Breher *et al.* (2004) and Roggen & Carreira (2010), and are significantly longer than those of the coordinated alkene in Rh complex (2) [1.405 (9) Å; Drinkel *et al.*, 2010] and the alkene
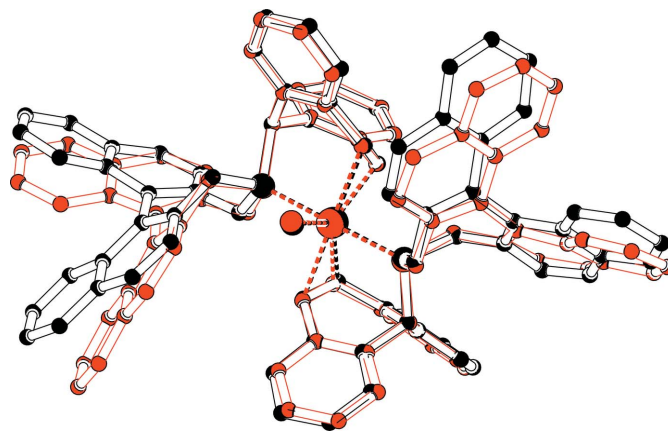

Figure 2
Overlay of the two independent complex molecules of (3), generated by matching the positions of the Ir, P, Cl and N atoms. H atoms have been omitted for clarity. Molecule *B* is shown in black.

function in the free ligand, (1) [1.34 (2) Å; Mariz *et al.*, 2008], which suggests a relatively high π-basicity of Ir^I (Dewar, 1951; Chatt & Duncanson, 1953). The Ir—P [mean 2.274 (2) Å] and Ir—Cl [mean 2.4453 (15) Å] distances (Table 1), are consistent with those reported by Roggen & Carreira (2010) and collated by Orpen *et al.* (2006). The dihedral angles between the planes of the naphthalene systems within the binaphthyl units, which are in the range 56.24 (17)–64.62 (13)° across the four independent binaphthyl groups, are similar to those found in the free ligand (53.2°; Mariz *et al.*, 2008) and in (2) (*ca* 52°; Drinkel *et al.*, 2010).

The four independent N atoms in the P–alkene ligands of (3) have distinctly pyramidal geometry, with the sum of the bond angles about the N atoms in the range 335.6 (5)–337.0 (5)°. In contrast, the corresponding N atom in the free ligand, (1), has a trigonal–planar geometry, subtending a bond-angle sum of 360 (1)° (Mariz *et al.*, 2008). The pyramidalization of the ligand N atom in (3) is similar to that observed in the bidentate ligand of the Rh complex, (2) (Drinkel *et al.*, 2010), and may be a consequence of steric strain introduced by the bidentate coordination to the Ir atom through the P and alkene C atoms, which effectively creates six-membered boat-shaped chelate rings. The bite angles of the four independent ligands in the structure, P—Ir—Y, where Y is the bisector of each allyl C—Ir—C angle, are in the range 86.51 (13)–87.90 (13)°. When viewed along the P—Ir bond, the P—N bond closely eclipses the Ir—Y vector. Drinkel *et al.* (2010) discussed the torsion angle Y···N—P···Z, where Z is the mid-point of the bond joining the two naphthyl units in the binaphthyl group. This torsion angle for the bidentate P–alkene ligand of (2) is approximately 180°, which indicates an *anti* conformation of the binaphthyl and alkene groups, whereas *syn* conformations are found in the free ligand and in the monodentate ligand of (2). The absolute values of the corresponding torsion angles for (3) are in the range 170.8 (2)–179.1 (2)° and also indicate an *anti* conformation for the bidentate ligands, which is consistent with the previous observations.

The packing of the molecules is fairly unremarkable, with one of each of the independent benzene and pentane solvent molecules lying in narrow channels running parallel to the [010] direction. The remaining solvent molecules occupy interstices between the complex molecules. There are no π–π interactions, with the shortest distance between the centres of gravity of any aromatic rings being approximately 4.0 Å. The shortest contacts of C—H···π and C—H···O types are also considered to be too long to be indicative of significant attractive interactions.

The use of complex (3) as an enantioselective catalyst for organic transformations is currently being investigated, and results will be published in due course.

Experimental

The title iridium complex, (3), was prepared by adding dropwise a solution of (*S*)-(1) (1.325 g, 2.610 mmol) in benzene (10.3 g) to a vigorously stirred slurry of [IrCl(coe)$_2$]$_2$ (coe is cyclooctene; 0.585 g,

0.652 mmol) in benzene (3.6 g). The resulting deep-red solution was stirred for 2 d at 353 K and gradually turned a brighter red. Evaporation of the volatiles followed by washing with pentane and drying *in vacuo* afforded a beige powder (yield 1.350 g, 74%). Diffraction quality colourless monocrystals were obtained by layering a solution of (3) (50 mg, containing *ca* 2 equivalents of cocrystallized benzene) in CDCl$_3$ (0.6 ml) in an NMR tube with pentane (1.2 ml).

Crystal data

[IrCl(C$_{34}$H$_{22}$NO$_2$P)$_2$]·C$_6$H$_6$·C$_5$H$_{12}$	$V = 6298.19$ (8) Å^3
$M_r = 1392.97$	$Z = 4$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 22.2716$ (1) Å	$\mu = 2.27$ mm^{-1}
$b = 12.6944$ (1) Å	$T = 160$ K
$c = 23.6689$ (2) Å	$0.28 \times 0.12 \times 0.10$ mm
$\beta = 109.7487$ (4)°	

Data collection

Nonius KappaCCD area-detector diffractometer	99162 measured reflections
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	21763 independent reflections
$T_{min} = 0.536$, $T_{max} = 0.649$	20907 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{max} = 1.36$ e Å^{-3}
$wR(F^2) = 0.068$	$\Delta\rho_{min} = -1.06$ e Å^{-3}
$S = 1.05$	Absolute structure: Flack & Bernardinelli (1999, 2000), with 10122 Friedel pairs
21762 reflections	
1610 parameters	Flack parameter: −0.018 (3)
90 restraints	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ir1—P1	2.2756 (12)	Ir2—P3	2.2790 (11)
Ir1—P2	2.2676 (11)	Ir2—P4	2.2717 (11)
Ir1—Cl1	2.4512 (11)	Ir2—Cl2	2.4394 (11)
Ir1—C47	2.184 (4)	Ir2—C117	2.187 (4)
Ir1—C48	2.189 (4)	Ir2—C118	2.192 (4)
Ir1—C61	2.189 (5)	Ir2—C131	2.185 (4)
Ir1—C62	2.185 (4)	Ir2—C132	2.187 (4)
C47—C48	1.452 (6)	C117—C118	1.453 (6)
C61—C62	1.447 (6)	C131—C132	1.449 (6)
P1—Ir1—P2	175.06 (4)	P3—Ir2—P4	179.35 (4)
P1—Ir1—Cl1	91.85 (4)	P3—Ir2—Cl2	89.45 (4)
P2—Ir1—Cl1	93.08 (4)	P4—Ir2—Cl2	89.91 (4)
C47—Ir1—P1	87.93 (12)	C117—Ir2—P3	86.33 (12)
C48—Ir1—P1	85.86 (12)	C118—Ir2—P3	89.74 (12)
C61—Ir1—P1	90.91 (12)	C131—Ir2—P3	91.57 (12)
C62—Ir1—P1	91.81 (12)	C132—Ir2—P3	92.96 (12)
C47—Ir1—P2	92.35 (12)	C117—Ir2—P4	94.16 (12)
C48—Ir1—P2	91.26 (12)	C118—Ir2—P4	90.38 (12)
C61—Ir1—P2	85.66 (12)	C131—Ir2—P4	88.37 (12)
C62—Ir1—P2	87.74 (12)	C132—Ir2—P4	87.40 (12)

The asymmetric unit of (3) contains two molecules of the Ir complex, two of benzene and two of pentane. The atomic coordinates were tested carefully for a relationship from a higher-symmetry space group using the program *PLATON* (Spek, 2009), but none could be found. The solvent molecules may be slightly disordered. A disordered model was not developed, but the bond lengths and angles in the two benzene solvent molecules were restrained to be similar and the C—C distances were restrained to a target value of 1.395 (5) Å.

Similarly, the bond lengths and angles in the two pentane solvent molecules were restrained to be similar and the C—C distances were restrained to a target value of 1.520 (4) Å. Neighbouring atoms within one benzene and one pentane molecule were restrained to have similar atomic displacement parameters. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å for the aromatic H atoms and 1.00 Å for the alkene H atoms, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The determined absolute configuration established by the structure determination agreed with that expected from the synthesis [(S)-binaphthyl groups].

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *DIRDIF94* (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Table 2
Puckering parameters (Cremer & Pople, 1975) for the seven-membered dioxaphosphacycloheptadiene rings of (3).

Ring	Total puckering amplitude, Q (Å)	φ_2 (°)	φ_3 (°)
Molecule A			
P1/O1/O2/C11/C12/C2/C1	1.008 (4)	126.6 (3)	16.4 (4)
P2/O3/O4/C21/C22/C32/C31	1.459 (3)	296.1 (3)	234.59 (18)
Molecule B			
P3/O5/O6/C81/C82/C72/C71	0.998 (4)	135.5 (3)	21.2 (5)
P4/O7/O8/C91/C92/C102/C101	1.418 (3)	298.3 (3)	234.01 (17)

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