Bis[1,2-bis(diphenylphosphino)ethane-$\kappa^2 P,P'$]difluoridoruthenium(II) trichloromethane disolvate

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In the crystal structure of the title compound, [RuF$_2$-(C$_{26}$H$_{24}$P$_2$)$_2$]·2CHCl$_3$, the Ru atom lies on a centre of symmetry with a *trans* arrangement of the F atoms. A H···F contact (2.249 Å) suggests weak intramolecular hydrogen bonding. The solvent molecules exhibit hydrogen bonding with the F atoms (H···F = 1.91 Å).

Comment

Synthetic strategies into ruthenium–fluoride complexes, especially those ligated by bidentate phosphanes, often employ toxic thallium-based metathesis reagents (Barthazy *et al.*, 2000), such that alternative routes into ruthenium–fluoride complexes are, therefore, desirable. Previous work has shown that the fluorine bridges in [RuF$_2$(CO)$_3$]$_4$ are amenable to cleavage by a variety of Lewis bases, affording a facile route into ruthenium–fluoride complexes ligated by monodentate phosphanes (Coleman *et al.*, 1997). However, questions regarding how changes in ligand denticity may influence this reaction protocol remain unanswered.

The reaction between [RuF$_2$(CO)$_3$]$_4$ and bis(diphenylphosphino)ethane (dppe) was facile at room temperature, as evidenced by vigorous evolution of carbon monoxide. Multiple recrystallizations from chloroform/dichloromethane and hexane solutions afforded the product [RuF$_2$(dppe)$_2$]·2CHCl$_3$, (I) (Fig. 1). The coordination geometry can best be described as octahedral, with the Ru atom on a centre of symmetry and the phenyl rings of the ligand backbone adopting a staggered conformation with respect to each other. Although this could be rationalized on steric grounds, the conformation may also be affected by weak secondary bonding interactions between the metal-bound F atoms and the neighbouring aryl rings. Indeed, the H26···F1 nonbonded contact (2.249 Å) suggests weak intramolecular hydrogen bonding, as has been previously observed in the related complex [RuF$_2$(dppp)$_2$] [dppp is 1,3-bis(diphenylphosphino)propane; Barthazy *et al.*, 2000]. It is noteworthy that two chloroform molecules cocrystallize within the unit cell, and

these engage in hydrogen-bonding interactions with the axial F atoms; the distance from atom C27 to atom F1 [2.905 (5) Å] and the H27···F1 hydrogen-bond length (1.91 Å) suggest a fairly strong interaction.
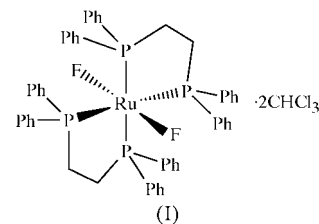
The Ru—P bond lengths (Table 1) in (I) are in good agreement with those previously reported for the related complex [RuF$_2$(dppp)$_2$] [2.310 (2) Å]. Intriguingly, the Ru—F bond length in (I) is substantially longer than that observed in [RuF$_2$(dppp)$_2$] [2.065 (3) Å]. The participation of the metal-bound F atoms in hydrogen-bonding interactions with the two chloroform molecules may be responsible for this.

Compound (I) represents a rare example of an octahedral fluoride complex ligated only by phosphorus donors. Furthermore, given the ability of fluorine to act as a strong π donor, the adoption of an F-*trans*-F (not F-*trans*-P) configuration in (I) is somewhat surprising, since the π-acceptor capability of alkyl and aryl phosphanes is well established (Orpen & Connelly, 1985, 1990). Indeed, the stereochemistry observed in (I) is in direct contrast to that reported for the related complex [RuF$_2$(dppp)$_2$], which assumes an F-*trans*-P
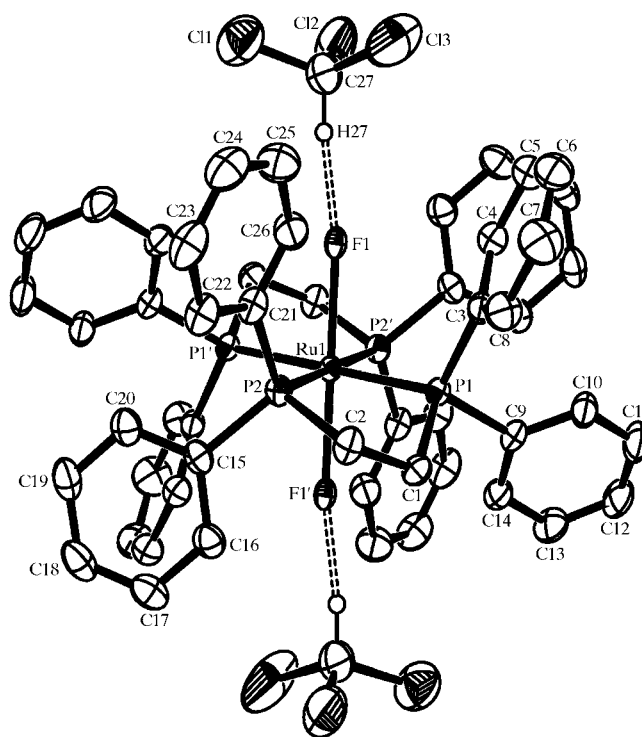

Figure 1
An *ORTEP-3* (Farrugia, 1997) representation of (I), showing 50% probability displacement ellipsoids. H atoms of the ligand have been omitted for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry code: (') −x + 1, −y, −z.]

metal-organic compounds

configuration. It is possible that this is associated with the geometrical restrictions imposed by the chelation constraints of the two-C-atom bridge in dppe [in (I)] when compared with the three-C-atom bridge of dppp {in [RuF$_2$(dppp)$_2$]}. However, this trend is not mirrored in chlorine chemistry; both *trans*-[RuCl$_2$(dppe)$_2$] (Polam & Porter, 1993) and *cis*-[RuCl$_2$(depe)$_2$] [depe is 1,2-bis(diethylphosphino)ethane; Winter *et al.*, 2000] employ a phosphane with a two-C-atom bridge. It is noteworthy that the related complex [RuF(FHF)(dmpe)$_2$] [dmpe is 1,2-bis(dimethylphosphino)ethane] also adopts an F-*trans*-P configuration (Kirkham *et al.*, 2001).

Experimental

For the preparation of (I), a Schlenk tube was charged with [RuF$_2$(CO)$_3$]$_4$ (250 mg, 0.280 mmol) and 1,2-bis(diphenylphosphino)ethane (1.114 g, 2.800 mmol). Dichloromethane (40 ml) was transferred on to the solids *via* a cannula, and the solution was stirred under a partial vacuum for 12 h. All volatiles were removed *in vacuo*. Recrystallization from a chloroform/dichloromethane/hexane solution afforded (I) as an air- and moisture-sensitive yellow powder in 8% yield. *m/z* (FAB+): 897 ([$M - 2F$]$^+$, 100%), 499 ([$M - 2F - $ dppe]$^+$, 46%). ^{1}H NMR (CDCl$_3$): δ 7.80–7.20 (*m*, 40H, Ar-CH), 2.60–1.90 (*m*, 8H, CH$_2$). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −318.2 (*q*, $^2J_{PF}$ = 19 Hz, RuF). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.8 (*br s*, RuP). ν_{max} (cm^{-1}, solid): 2919 (*br*), 1479 (*s*), 1435 (*s*), 1094 (*s*), 741 (*br*), 691 (*br*).

Crystal data

[RuF$_2$(C$_{26}$H$_{24}$P$_2$)$_2$]·2CHCl$_3$	V = 2604.0 (3) Å^3
M_r = 1174.59	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 11.3274 (8) Å	μ = 0.78 mm^{-1}
b = 17.8090 (12) Å	T = 150 (2) K
c = 12.9556 (9) Å	$0.18 \times 0.12 \times 0.11$ mm
β = 94.8850 (10)°	

Data collection

Bruker SMART CCD area-detector diffractometer	22716 measured reflections
	6177 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	5249 reflections with $I > 2\sigma(I)$
T_{min} = 0.873, T_{max} = 0.918	R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052	329 parameters
$wR(F^2)$ = 0.145	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 1.86 e Å^{-3}
6177 reflections	$\Delta\rho_{min}$ = −1.60 e Å^{-3}

All H atoms were refined using a riding model, using the default *SHELXL97* parameters (Sheldrick, 1997), and with isotropic displacement parameters of 1.2 times the U_{iso} value of the bonded C atom. The displacement parameters of atoms Ru1 and F1 were

Table 1
Selected geometric parameters (Å, °).

Ru1—F1	2.1729 (18)	P1—C1	1.835 (3)
Ru1—P1	2.3356 (8)	P2—C2	1.865 (3)
Ru1—P2	2.3510 (8)	C1—C2	1.519 (4)
F1—Ru1—P1	95.64 (5)	C1—P1—Ru1	104.53 (11)
P1—Ru1—P2	81.88 (3)	C2—P2—Ru1	108.80 (11)

restrained using the *SHELXL97* commands DELU 0.005 and SIMU. The largest residual electron-density peak in the final difference Fourier map was located 0.35 Å from atom Cl3.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Barthazy, P., Stoop, R. M., Wörle, M., Togni, A. & Mezzetti, A. (2000). *Organometallics*, **19**, 2844–2852.
Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Coleman, K. S., Fawcett, J., Holloway, J. H., Hope, E. G. & Russell, D. R. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3557–3562.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kirkham, M. S., Mahon, M. F. & Whittlesey, M. K. (2001). *Chem. Commun.* pp. 813–814.
Orpen, A. G. & Connelly, N. G. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1310–1311.
Orpen, A. G. & Connelly, N. G. (1990). *Organometallics*, **9**, 1206–1210.
Polam, J. R. & Porter, L. C. (1993). *J. Coord. Chem.* **29**, 109–119.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Winter, R. F., Brunner, B. M. & Scheiring, T. (2000). *Inorg. Chim. Acta*, **310**, 21–26.