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#### Key indicators

Single-crystal X-ray study  
 T = 180 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$   
 Disorder in main residue  
 R factor = 0.041  
 wR factor = 0.075  
 Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## $(\eta^3\text{-Allyl})[(R)\text{-}(+)\text{-}2,2'\text{-bis(diphenylphosphino)-}1,1'\text{-binaphthyl}]$ palladium(II) trifluoromethane-sulfonate dichloromethane solvate

The crystal structure of the title compound,  $[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_{44}\text{H}_{32}\text{P}_2)](\text{CF}_3\text{SO}_3) \cdot \text{CH}_2\text{Cl}_2$ , has been determined at 180 (2) K in the non-centrosymmetric space group  $P2_12_12_1$ . The structure contains only one crystallographically unique Pd metal centre, exhibiting a pseudo-square-planar geometry, and is formed by cationic layers intercalated by trifluoromethane-sulfonate anions and dichloromethane molecules.

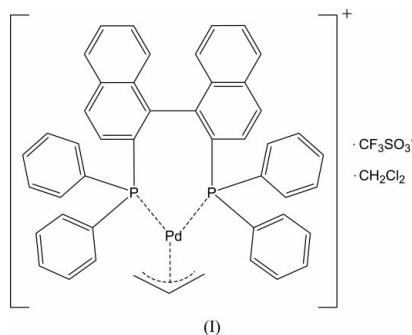
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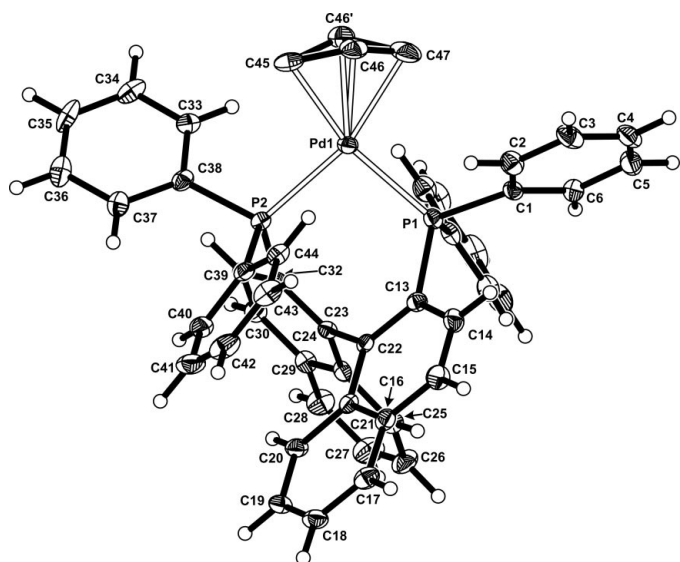
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#### Comment

As part of our research devoted to the syntheses and structural characterization of novel chiral catalysts with direct applications in asymmetric hydrogenation processes, we have synthesized the title compound, (I), using a similar experimental procedure to that described for  $[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_9\text{H}_{18}\text{N}_2)]\text{CF}_3\text{SO}_3$  (Jones *et al.*, 2003), but using (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*R*-BINAP) as the chiral ligand.



BINAP, a conformationally flexible atropisometric diphosphine, is a very interesting ligand since, apart from being able to coordinate to several transition metal centres (Ozawa & Hayashi, 1992; Ikariya *et al.*, 1985), it also affords potent catalytic complexes due to the high steric hindrance around the cation. The addition of *R*-BINAP to the intermediate  $[\text{Pd}(\eta^3\text{-allyl})(\text{THF})_2]^+$  cation displaces the coordinated solvent molecules (THF), forming a seven-membered chelate ring and leading to the formation of  $[\text{Pd}(\eta^3\text{-allyl})(\text{R}-\text{BINAP})]^+$  (Fig. 1). The  $\eta^3$ -allyl appears disordered over two different positions with occupancy factors of approximately 50% for each. In accordance with what has been observed for related complexes, the Pd metal centre shows a pseudo-square-planar geometry and the Pd—C and Pd—P bond distances are within the expected range of values (see Fig. 1 and Table 1) (Jones *et al.*, 2003; Bruno *et al.*, 2002; Sauthier *et al.*, 2000; Albinati *et al.*, 1991). Individual  $[\text{Pd}(\eta^3\text{-allyl})(\text{R}-\text{BINAP})]^+$  complexes close pack along the **b** direction, leading to the formation of layers which alternate in an *ABAB*... fashion (two layers per *b*-axis



**Figure 1**  
A view of the complex cation present in the title compound, showing the labelling scheme for all non-H atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. The trifluoromethanesulfonate anion, the dichloromethane molecule and all the H atoms of the  $\eta^3$ -allyl ligand have been omitted for clarity. Labels for C31, C32, and also for the C7–C12 aromatic ring have been omitted because the atoms are eclipsed.

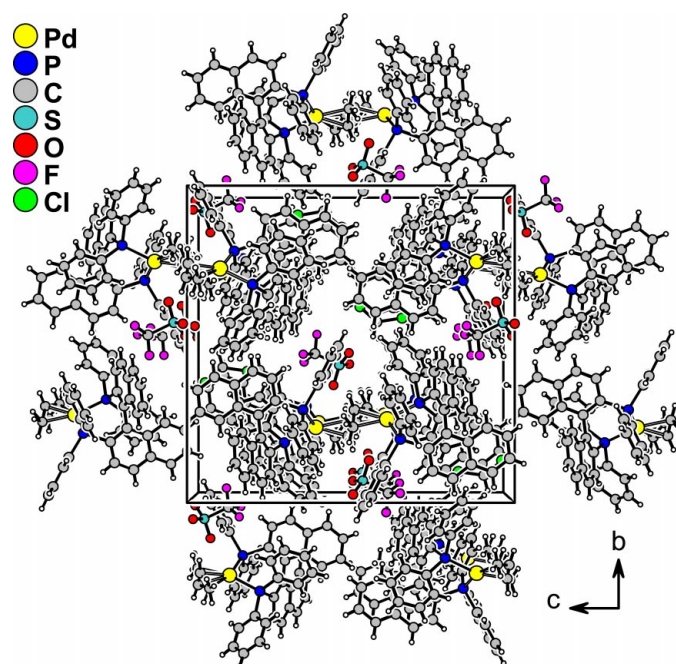
repeat) (Fig. 2). Within the layers, small zigzag void spaces are occupied by the trifluoromethanesulfonate anions and dichloromethane molecules (Fig. 2).

## Experimental

All chemicals were purchased from Aldrich and used without further purification. Solvents were dried and degassed using appropriate methods. Standard Schlenk line techniques were also employed.  $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}_2]$  (35 mg, 0.096 mmol) was dissolved in tetrahydrofuran (THF, 10 ml), followed by the addition of  $\text{AgCF}_3\text{SO}_3$  (53 mg, 0.21 mmol). The resulting solution was stirred at ambient temperature, after which it was filtered to remove AgCl. *(R)*-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (129 mg, 0.20 mmol) was added to the filtrate and the solution was stirred for 30 min. The addition of *ca* 20 ml of hexane led to precipitation of the title compound, which was filtered off and washed with hexane ( $2 \times ca$  20 ml) and diethylether ( $2 \times ca$  20 ml). The compound was then dried *in vacuo* to form a white powder (165 mg, 90% yield). Crystals suitable for X-ray diffraction analysis were obtained using recrystallization methods from a  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{MeOH}$  solution.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 3.10 (*m*,  $\text{CH}_2$ , 2H), 4.10 (*m*,  $\text{CH}_2$ , 2H), 5.92 (*m*, CH, 1H), 6.40–7.80 (*m*, Ph, 32H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 65.9 ( $\text{CH}_2$ , allyl); 123.5 (CH, allyl); 126–133 (Ph).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 22.2 (*d*,  $J = 50$  Hz); 23.3 (*d*,  $J = 50$  Hz).

### Crystal data

$[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_{44}\text{H}_{32}\text{P}_2)](\text{CF}_3\text{SO}_3) \cdot \text{CH}_2\text{Cl}_2$   
 $M_r = 1004.10$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 11.1814$  (3) Å  
 $b = 19.7359$  (4) Å  
 $c = 20.3672$  (4) Å  
 $V = 4494.53$  (18) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.484$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 19214 reflections  
 $\theta = 1.0$ – $25.0^\circ$   
 $\mu = 0.70$  mm<sup>-1</sup>  
 $T = 180$  (2) K  
 Block, colourless  
 $0.12 \times 0.10 \times 0.07$  mm



**Figure 2**  
Perspective view along the **a** direction of (I). Cationic  $[\text{Pd}(\eta^3\text{-allyl})(R\text{-BINAP})]_n^+$  layers alternate in the **b** direction in an *ABAB*... fashion, and are intercalated by the trifluoromethanesulfonate anions and dichloromethane molecules.

### Data collection

Nonius KappaCCD diffractometer  
 Thin-slice  $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)  
 $T_{\min} = 0.898$ ,  $T_{\max} = 0.961$   
 29207 measured reflections  
 7894 independent reflections  
 6903 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.064$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -11 \rightarrow 13$   
 $k = -23 \rightarrow 23$   
 $l = -24 \rightarrow 24$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.075$   
 $S = 1.05$   
 7894 reflections  
 560 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 4.6523P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.42$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 3491 Friedel reflections  
 Flack parameter =  $-0.03$  (2)

**Table 1**

Selected geometric parameters (Å, °).

Pd1–C46'	2.141 (10)	Pd1–C46	2.177 (9)
Pd1–C45	2.164 (4)	Pd1–P2	2.3000 (11)
Pd1–C47	2.176 (5)	Pd1–P1	2.3023 (11)
C46'–Pd1–C45	35.2 (4)	C47–Pd1–P2	163.61 (15)
C46'–Pd1–C47	35.3 (3)	C46–Pd1–P2	131.9 (3)
C45–Pd1–C47	66.9 (2)	C46'–Pd1–P1	134.1 (3)
C46'–Pd1–C46	24.7 (3)	C45–Pd1–P1	164.35 (14)
C45–Pd1–C46	35.7 (3)	C47–Pd1–P1	99.90 (16)
C47–Pd1–C46	35.4 (3)	C46–Pd1–P1	128.9 (3)
C46'–Pd1–P2	128.4 (3)	P2–Pd1–P1	95.97 (4)
C45–Pd1–P2	97.97 (14)		

All H atoms were placed at calculated positions and allowed to ride during subsequent refinement, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The

allyl ligand was found to be disordered: the middle C atom has been modelled with variable occupancy factors over two different positions, C46 and C46', and found to have occupancy factors of 52 (2) and 48 (2)%, respectively.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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## References

- Albinati, A., Kunz, R., Ammann, C. & Pregosin, P. S. (1991). *Organometallics*, **10**, 1800–1806.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Blessing, R. H. (1995). *Acta Cryst. A* **51**, 33–58.
- Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, G., Lanza, S., Nicolo, F., Tresoldi, G. & Rosace, G. (2002). *Acta Cryst. C* **58**, m316–m318.
- Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
- Ikariya, T., Ishii, Y., Kawano, H., Arai, T., Saburi, M., Yoshikawa, S. & Akutagawa, S. (1985). *Chem. Commun.* pp. 922–924.
- Jones, M. D., Almeida Paz, F. A., Davies, J. E. & Johnson, B. F. G. (2003). *Acta Cryst. E* **59**, m105–m107.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Ozawa, F. & Hayashi, T. (1992). *J. Organomet. Chem.* **428**, 267–277.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sauthier, M., Fornies-Camer, J., Touper, L. & Reau, R. (2000). *Organometallics*, **19**, 553–562.