

$(\eta^3\text{-Allyl})[(S)\text{-}(+)\text{-}(2\text{-pyrrolidinylmethyl})\text{-pyrrolidine}]$ palladium(II) trifluoromethanesulfonate

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The title compound, $[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_9\text{H}_{18}\text{N}_2)]\text{CF}_3\text{SO}_3$, crystallizes in the non-centrosymmetric space group $P2_12_12_1$ and contains only one crystallographically unique Pd metal centre, showing a pseudo-square-planar geometry. $(S)\text{-}(+)\text{-}(2\text{-Pyrrolidinylmethyl})\text{pyrrolidine}$ (pmp, $\text{C}_9\text{H}_{18}\text{N}_2$) acts as an N,N' -bidentate chelating ligand, leading to the formation of the chiral $[\text{Pd}(\eta^3\text{-allyl})(\text{pmp})]^+$ complex cation, which is hydrogen bonded to the trifluoromethanesulfonate anion.

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Key indicators

Single-crystal X-ray study

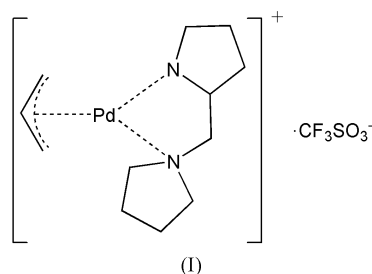
 $T = 180\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$ R factor = 0.032 wR factor = 0.069

Data-to-parameter ratio = 18.9

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

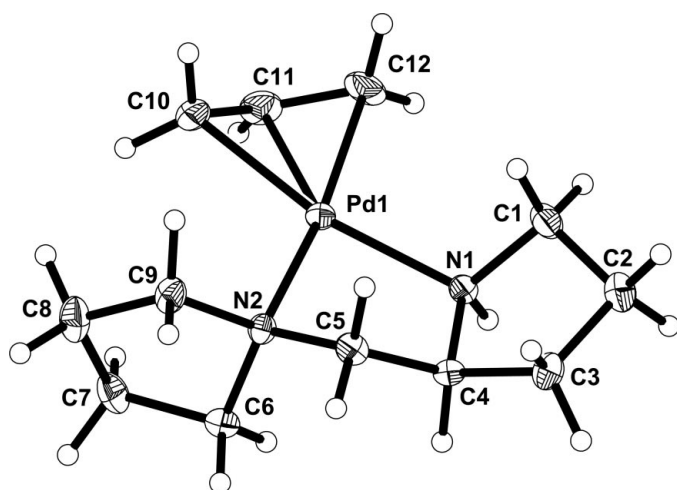
Comment

We have been focusing our research on the use of amines which can lead to the synthesis of chiral catalysts, with direct applications in asymmetric hydrogenation processes (Jones *et al.*, 2003; Raynor *et al.*, 2000). The title compound, (I), can be readily synthesized from the reaction between $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}_2]$ and AgCF_3SO_3 in tetrahydrofuran (THF), forming the $[\text{Pd}(\eta^3\text{-allyl})(\text{THF})_2]^+$ cation. The addition of the chiral $(S)\text{-}(+)\text{-}(2\text{-pyrrolidinylmethyl})\text{pyrrolidine}$ (pmp) displaces the coordinated solvent molecules, forming a five-membered chelate ring and thus generating the desired complex, $[\text{Pd}(\eta^3\text{-allyl})(\text{pmp})]^+$ (Fig. 1), which shows a pseudo-square-planar geometry for the Pd metal centre (Table 1) (Sauthier *et al.*, 2000). The Pd—C and Pd—N bond distances are consistent with those found in related complexes (see Table 1) (Bruno *et al.*, 2002; Albinati *et al.*, 1991). A classical $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond links the complex cation to the trifluoromethanesulfonate anion (Figs. 2 and 3, and Table 2).

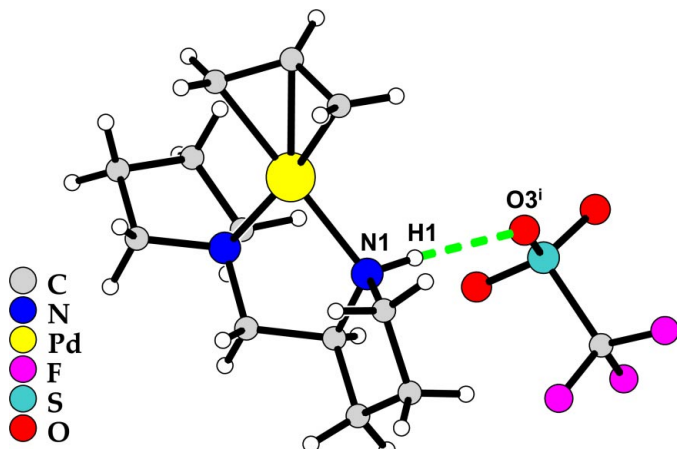


Experimental

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. $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}_2]$ (100 mg, 0.27 mmol) was dissolved in THF (10 ml), followed by the addition of AgCF_3SO_3 (140 mg, 0.54 mmol). The resulting solution was stirred at ambient temperature for 1 h, after which it was filtered in order to remove AgCl . $(S)\text{-}(+)\text{-}(2\text{-Pyrrolidinylmethyl})\text{pyrrolidine}$ (0.09 ml, 0.54 mmol) was added to the filtrate and the solution was stirred for another hour. The addition of


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. The trifluoromethanesulfonate anion has been omitted for clarity.


Figure 2

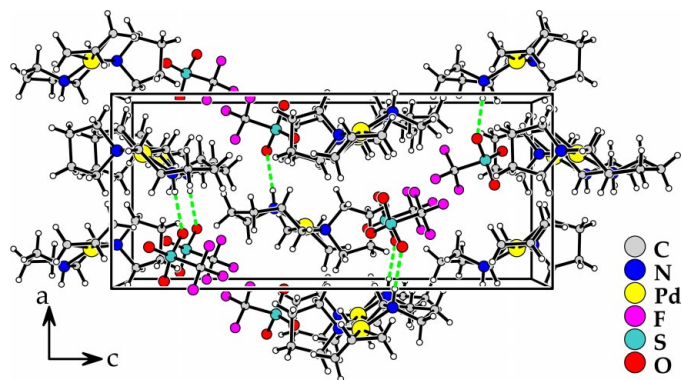
View in detail of the N—H...O hydrogen bond between the trifluoromethanesulfonate anion and the complex cation (green dashed line). For hydrogen-bond details and symmetry code, see Table 2.

ca 20 ml of hexane led to the precipitation of the title compound, which was washed with hexane ($3 \times$ ca 20 ml) and diethyl ether ($2 \times$ ca 20 ml). The compound was then dried *in vacuo* to form an off-white powder (175 mg, 72% yield). Crystals suitable for X-ray diffraction analysis were obtained using recrystallization methods from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ solution. Elemental composition, calculated (using single-crystal data): C 34.67%, H 5.11%, N 6.22%; found: C 34.67%, H 5.10%, N 6.21%. $M^+ = 301 \text{ g mol}^{-1}$.

Crystal data

$[\text{Pd}(\text{C}_3\text{H}_5)(\text{C}_9\text{H}_{18}\text{N}_2)]\text{CF}_3\text{SO}_3$
 $M_r = 450.79$
 Orthorhombic, $P2_12_12_1$
 $a = 9.1222(2) \text{ \AA}$
 $b = 9.1647(2) \text{ \AA}$
 $c = 20.6053(6) \text{ \AA}$
 $V = 1722.65(7) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.738 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 8414 reflections
 $\theta = 1.0\text{--}27.5^\circ$
 $\mu = 1.24 \text{ mm}^{-1}$
 $T = 180(2) \text{ K}$
 Block, yellow
 $0.16 \times 0.12 \times 0.10 \text{ mm}$


Figure 3

Perspective view along the b direction of (I). Hydrogen bonds between the trifluoromethanesulfonate anion and the complex cation (see Table 2) are drawn as green dashed lines.

Data collection

Nonius KappaCCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.826$, $T_{\max} = 0.886$
 11560 measured reflections
 3927 independent reflections

3488 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\max} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -10 \rightarrow 11$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.069$
 $S = 1.03$
 3927 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.41 \text{ e \AA}^{-3}$
 Absolute structure: (Flack, 1983),
 1664 Friedel pairs
 Flack parameter = $-0.10(3)$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Pd1—C12	2.098 (3)	Pd1—C10	2.124 (4)
Pd1—N1	2.111 (3)	Pd1—N2	2.139 (3)
Pd1—C11	2.120 (4)		
C12—Pd1—N1	102.83 (14)	C11—Pd1—C10	37.87 (15)
C12—Pd1—C11	38.44 (15)	C12—Pd1—N2	171.11 (18)
N1—Pd1—C11	137.96 (14)	N1—Pd1—N2	82.66 (10)
C12—Pd1—C10	69.04 (16)	C11—Pd1—N2	138.19 (13)
N1—Pd1—C10	168.51 (14)	C10—Pd1—N2	104.46 (13)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1—H1 \cdots O3 ⁱ	0.93	2.09	3.017 (4)	176

Symmetry code: (i) $x - 1, y, z$.

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

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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