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trans-Bromido[4,5-difluoro-2-(trifluoromethylsulfonyloxy)phenyl-κC^1]bis(triphenylphosphine-κP)palladium(II)

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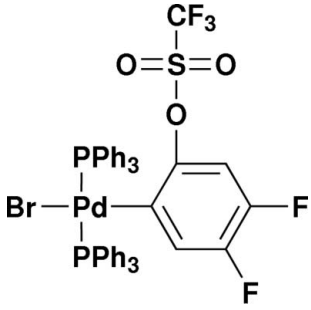
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; R factor = 0.030; wR factor = 0.032; data-to-parameter ratio = 11.7.

The title compound, *trans*-[PdBr($C_7H_2F_5O_3S$)($C_{18}H_{15}P$)$_2$], was obtained in quantitative yield by oxidative addition of the electrophile 1-bromo-3,4-difluoro-2-(trifluoromethylsulfonyloxy)benzene to Pd(PPh_3)$_4$ in toluene, and was recrystallized from a mixture of tetrahydrofuran and pentane. The structure was resolved by single-crystal X-ray diffraction and turned out to be one of the few known examples among complexes of general formula *trans*-[(PAr_3)$_2$Pd(X)Ar′] that exhibit double π–π stacking intramolecular interactions (three aromatic rings are piled above each other).

Related literature

For the role of phosphines in Suzuki cross-coupling, see: Espino *et al.* (2007). For the Cambridge Structural Database, see: Allen (2002); Fletcher *et al.* (1996). For related literature, see: Espino *et al.* (2007); Flemming *et al.* (1998); Gniewek *et al.* (2006); Hartwig *et al.* (1996); Hwang *et al.* (2005); Janiak (2000); Sundermeier *et al.* (2003); Prince (1982); Watkin (1994).



Experimental

Crystal data

[PdBr($C_7H_2F_5O_3S$)($C_{18}H_{15}P$)$_2$]
M_r = 972.03
Monoclinic, $P2_1/n$
a = 14.4320 (2) Å
b = 14.3157 (3) Å
c = 19.5504 (3) Å
β = 103.0167 (9)°
V = 3935.41 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.69 mm^{-1}
T = 150 K
0.12 × 0.08 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.87, T_{max} = 0.87
29420 measured reflections
9258 independent reflections
5917 reflections with $I > 3\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.032
S = 1.10
5917 reflections
505 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—Br1	2.4892 (4)	Pd1—P1	2.3315 (8)
Pd1—C1	2.013 (3)	Pd1—P2	2.3377 (8)
Br1—Pd1—C1	177.59 (9)	Br1—Pd1—P2	90.60 (2)
Br1—Pd1—P1	89.26 (2)	C1—Pd1—P2	90.68 (8)
C1—Pd1—P1	89.68 (8)	P1—Pd1—P2	173.75 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C21—H211···Br1	1.00	2.80	3.522 (3)	129
C27—H271···O3	1.00	2.56	3.495 (4)	156
C33—H331···Br1	1.00	2.78	3.581 (3)	137

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2391).

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supplementary materials

Acta Cryst. (2007). E**63**, m2047-m2048 [**doi:10.1107/S1600536807031492**]

trans-Bromido[4,5-difluoro-2-(trifluoromethylsulfonyloxy)phenyl-κC^1]bis(triphenylphosphine-κP)palladium(II)

G. Espino, J. M. Brown and A. R. Cowley

Comment

The title compound was prepared in the course of a recently reported work about the role of phosphines in Suzuki cross-coupling (Espino *et al.*, 2007).

The coordination geometry of the Pd atom in the title compound, (1) (Fig. 1), closely approximates to planarity; the deviation of the metal atom from the best-plane of four coordinated atoms is 0.044 (3) Å. The Pd1/Br1/C1/P1/P2 plane makes an angle of 73.7 (1)° with that of the coordinated phenyl ring. The PPh_3 ligands are in *trans* disposition, so it seems that isomerization of the *cis* isomer takes place after oxidative addition, since otherwise, the former disposition would be the most reasonable after the addition (see Fig.1). Furthermore, a weak intramolecular hydrogen bond between O3 and C27 is observed, which conditions the orientation of the trifluoromethanesulfonate group (see Table 2).

The Pd—C bond length (Table 1) is virtually identical to that reported for [PdBr(Ph)(PPh_3)$_2$] (2.012 (4) Å; Sundermeier *et al.*, 2003) and [PdBr(*p*-$C_6H_4CF_3$)(PPh_3)$_2$] (1.995 (6) Å; Flemming *et al.*, 1998). The Pd—Br bond length is significantly shorter than that observed for [PdBr(Ph)(PPh_3)$_2$] (2.532 (1) Å) and [PdBr(*p*-$C_6H_4CF_3$)(PPh_3)$_2$] (2.5244 (9) Å). Moreover, the two Pd—P bond lengths (Table 1) are very similar to each other, and are also very close to those found in [PdBr(Ph)(PPh_3)$_2$] and [PdBr(*p*-$C_6H_4CF_3$)(PPh_3)$_2$], which range between 2.322 (2) Å and 2.346 (2) Å.

Two intramolecular π–π stacking interactions are observed between the Pd-σ-coordinated aryl ligand and two phenyl groups of two different PPh_3 ligands (see Fig.2). As a consequence, the molecule adopts a sandwich type conformation which is observed in just a few of other similar complexes of general formula [(PAr_3)$_2$Pd(*X*)Ar'], while in most of these derivatives (Fletcher *et al.*, 1996), according to our CSD search, the stacking (alignment) of three aryl rings is far from the ideal geometry.

Distances between centroids of the Pd-bonded aryl ring and each of the two phenyl rings are *Cg*1···*Cg*2 = 3.587 (5) Å and *Cg*1···*Cg*3 = 3.671 (5) Å, where *Cg*1, *Cg*2 and *Cg*3, respectively, are the centroids of the C1—C6 (A), C8—C13 (B) and C38—C43 (C) rings. The dihedral angles between the rings are: A/B = 16.99 (17)° and A/C = 18.92 (16)° (see Fig. 2). The angles formed between the centroid-centroid vectors (*Cg*1—*Cg*2 and *Cg*1—*Cg*3) and normal to the Pd-coordinated aryl ring are 21.9° and 20.8° respectively, meaning that according to the literature these parameters are into the range accepted for these type of interactions (Janiak, 2000).

Moreover, C(Ph)—P—Pd—C(σ-Ar) torsion angles, C1—Pd1—P1—C8 and C1—Pd1—P2—C38, are 1.98 (14) and 6.89 (14)°, respectively, close to zero. According to the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002), the number of similar compounds which show both of these torsion angles under 8° is very limited and up to now, restricted to a couple of cases: [(PPh_3)$_2$Pd(F)Ph] (1.95° and 4.41°; Flemming *et al.*, 1998) and [(PPh_3)$_2$Pd(Cl)Ph] (7.99° and 5.90°;

Hwang *et al.*, 2005). Two other complexes exhibit values around 10° are [$(PPh_3)_2Pd(I)(C_6H_4I)$] (9.07° and 9.11°; Gniewek *et al.*, 2006) and [$(PPh(o\text{-}C_6H_4CH_3)_2)_2Pd(Br)(p\text{-Tol})$] (10.84° and 10.80°; Hartwig *et al.*, 1996).

In line with this, the Newman-type projections along the P1—P2 axis show an almost eclipsed conformation for both phosphine ligands, with a mean torsion angle for the C^i—P—P—C^i groups of 7.9° (see Fig. 3).

The weak π-π interactions could play a role in the stabilization of the *trans* isomer *versus* the *cis* isomer, along with the lower steric hindrance attributed to the first, and the *trans* effect, so explaining the isomerization process.

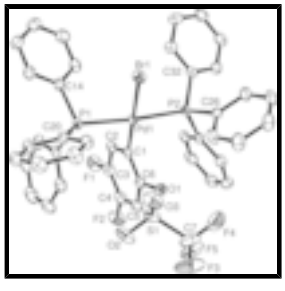
Experimental

The title compound was synthesized under a nitrogen atmosphere by reacting $Pd(PPh_3)_4$ (0.1 g, 0.043 mmol), toluene (2 ml) and 3,4-difluoro-2-trifluoromethanesulfonyloxybromobenzene (0.03 g, 0.087 mmol) in a Schlenk tube (see scheme 2). The mixture was refluxed for *ca* 24 h. The original suspension of $Pd(PPh_3)_4$ in toluene became a solution after a couple of hours, but reflux was maintained overnight to ensure the completion of the reaction. The solvent was removed and the white solid residue was washed with pentane (3 × 8 ml) in order to eliminate the leaving PPh_3. Finally, the product was dried under vacuum, (0.069 gr, 0.071 mmol, 82%). The white solid turned out to be soluble in $CDCl_3$ and toluene but insoluble in pentane. $^{19}F\{^1H\}$-NMR (377 MHz): −75.24 p.p.m. (s, 3 F, *CF3*); −138.88 p.p.m. (d, $^3J_{FF}$ = 20.6 Hz, 1 F, *C—F*); −142.93 p.p.m. (d, $^3J_{FF}$ = 20.6 Hz, 1 F, *C—F*). $^{31}P\{^1H\}$-NMR (162 MHz): 24.06 p.p.m. (s, 2P). ^1H-NMR (400 MHz): 6.48 p.p.m. (t, J=9.67, 9.67 Hz, 1H); 6.06 p.p.m. (dd, J=6.31, 10.83 Hz, 1H). $^{13}C\{^1H\}$-NMR (126 MHz): 149.24 (d, J=11.86 Hz); 147.24 (d, J=11.93 Hz); 145.97 (d, J=19.37 Hz); 134.83 (t, J=6.24, 6.24 Hz); 132.18 (d, J=9.96 Hz); 132.10 (*s*); 130.55 (t, J=24.05, 24.05 Hz); 130.42 (s, 1 C); 128.59 (d, J=12.14 Hz); 128.09 (t, J=5.17, Hz); 125.35 (*s*); 124.54 (d, J=15.84 Hz); 119.51 (*s*); 116.97 (*s*); 108.54 (d, J=20.68 Hz). MS: $[M–Br+K]^+$=930; $[M–Br]^+$=891. Analysis calculated for $C_{43}H_{32}BrF_5O_3P_2PdS$: C 53.13, H 3.32, S 3.30%; found: C 53.30, H 3.55, S 3.47%.

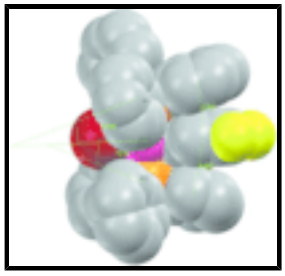
Refinement

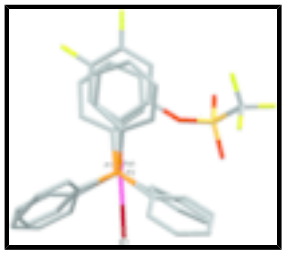
The H atoms were all located in a difference map, but were repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry, with C—H distances of 1.00 Å, and with $U_{iso}(H)$ = 1.2–1.5 times U_{eq} of the parent C atom, after which the positions were refined with riding constraints.

Figures



Scheme 1. The chemical diagram of the title compound.
Scheme 2. Synthetic procedure.
Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
Fig. 2. A spacefill representation of π–π stacking interactions between the aryl ligand and two phenyl groups belonging to two different PPh_3 ligands, showing distances (Å) between centroids and interplane angles (°).
Fig. 3. A Newman-type projection along the P1–P2 axis, showing the eclipsed conformation for both PPh_3 ligands.
Fig. 4. The reaction scheme for the formation of (1).





trans-Bromido[4,5-difluoro-2-(trifluoromethylsulfonyloxy)phenyl- κC^1]bis(triphenylphosphine-κ*P*)palladium(II)

Crystal data

$[PdBr(C_7H_2F_5O_3S)(C_{18}H_{15}P)_2]$	F_{000} = 1944
M_r = 972.03	D_x = 1.640 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 29420 reflections
a = 14.4320 (2) Å	θ = 5–28°
b = 14.3157 (3) Å	μ = 1.69 mm^{-1}
c = 19.5504 (3) Å	T = 150 K
β = 103.0167 (9)°	Block, pale yellow
V = 3935.41 (12) Å^3	0.12 × 0.08 × 0.08 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	5917 reflections with $I > 3.0\sigma(I)$
Monochromator: graphite	R_{int} = 0.047
T = 150 K	θ_{max} = 27.5°
ω scans	θ_{min} = 5.1°
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −18→18
T_{min} = 0.87, T_{max} = 0.87	k = −18→18
29420 measured reflections	l = −24→25
9258 independent reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = [1-(F_o-F_c)^2/36\sigma^2(F)]^2/ [0.323T_0(x) + 0.164E-01T_1(x) + 0.115T_2(x)]$ where T_i are Chebychev polynomials and x = F_c/F_{max} (Watkin, 1994; *P*rince, 1982)
$wR(F^2) = 0.032$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.10$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
5917 reflections	$\Delta\rho_{min} = -0.69$ e Å^{-3}
505 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.329188 (16)	0.324809 (16)	0.601732 (12)	0.0171
Br1	0.34657 (2)	0.25546 (2)	0.720712 (17)	0.0263
C1	0.3092 (2)	0.3810 (2)	0.50513 (16)	0.0211
C2	0.3638 (2)	0.4559 (2)	0.48901 (17)	0.0236
C3	0.3449 (2)	0.4939 (2)	0.42243 (18)	0.0275
C4	0.2725 (3)	0.4591 (3)	0.37014 (17)	0.0307
C5	0.2185 (2)	0.3853 (3)	0.38228 (18)	0.0292
C6	0.2389 (2)	0.3490 (2)	0.45023 (16)	0.0223
F1	0.39784 (16)	0.56600 (15)	0.40802 (12)	0.0400
F2	0.25560 (16)	0.49941 (18)	0.30544 (11)	0.0440
O1	0.18666 (16)	0.26748 (16)	0.46369 (12)	0.0273
S1	0.07900 (6)	0.26758 (7)	0.46216 (5)	0.0326
O2	0.03476 (19)	0.3504 (2)	0.43190 (16)	0.0479
O3	0.0657 (2)	0.2320 (2)	0.52674 (15)	0.0472
C7	0.0455 (3)	0.1723 (4)	0.3980 (2)	0.0506
F3	−0.0461 (2)	0.1579 (3)	0.38763 (17)	0.0851
F4	0.0915 (2)	0.0951 (2)	0.42243 (16)	0.0699
F5	0.0676 (2)	0.1954 (2)	0.33823 (13)	0.0643
P1	0.26893 (5)	0.46045 (5)	0.64151 (4)	0.0186
C8	0.2361 (2)	0.5534 (2)	0.57685 (17)	0.0224
C9	0.1532 (2)	0.5402 (2)	0.52444 (18)	0.0277
C10	0.1291 (3)	0.6030 (3)	0.46960 (19)	0.0381
C11	0.1871 (3)	0.6800 (3)	0.4666 (2)	0.0432
C12	0.2677 (3)	0.6936 (3)	0.5184 (2)	0.0410
C13	0.2925 (3)	0.6312 (2)	0.57362 (18)	0.0299
C14	0.3633 (2)	0.5113 (2)	0.70937 (16)	0.0214
C15	0.4573 (2)	0.4921 (2)	0.70651 (18)	0.0265
C16	0.5327 (2)	0.5294 (3)	0.7558 (2)	0.0327

C17	0.5145 (3)	0.5856 (3)	0.80912 (18)	0.0323
C18	0.4220 (3)	0.6051 (3)	0.81227 (18)	0.0313
C19	0.3462 (2)	0.5684 (2)	0.76294 (18)	0.0289
C20	0.1609 (2)	0.4516 (2)	0.67506 (15)	0.0205
C21	0.1219 (2)	0.3642 (2)	0.68444 (18)	0.0262
C22	0.0368 (2)	0.3604 (3)	0.7063 (2)	0.0324
C23	−0.0085 (2)	0.4412 (3)	0.71997 (19)	0.0322
C24	0.0308 (2)	0.5272 (2)	0.71130 (17)	0.0284
C25	0.1149 (2)	0.5329 (2)	0.68816 (17)	0.0242
P2	0.40604 (5)	0.19609 (5)	0.56595 (4)	0.0187
C26	0.3561 (2)	0.0843 (2)	0.58363 (15)	0.0213
C27	0.2581 (2)	0.0795 (2)	0.5773 (2)	0.0294
C28	0.2150 (3)	−0.0047 (3)	0.5866 (2)	0.0364
C29	0.2686 (3)	−0.0843 (2)	0.6040 (2)	0.0344
C30	0.3662 (3)	−0.0799 (2)	0.6113 (2)	0.0355
C31	0.4099 (2)	0.0037 (2)	0.60090 (19)	0.0284
C32	0.5332 (2)	0.1896 (2)	0.60660 (16)	0.0215
C33	0.5688 (2)	0.2357 (2)	0.66937 (17)	0.0259
C34	0.6651 (2)	0.2283 (3)	0.70215 (18)	0.0325
C35	0.7246 (2)	0.1736 (3)	0.6724 (2)	0.0325
C36	0.6900 (2)	0.1285 (2)	0.6093 (2)	0.0315
C37	0.5944 (2)	0.1359 (2)	0.57637 (18)	0.0267
C38	0.4036 (2)	0.1914 (2)	0.47197 (16)	0.0210
C39	0.4543 (2)	0.2595 (2)	0.44329 (17)	0.0249
C40	0.4446 (2)	0.2662 (3)	0.37136 (18)	0.0301
C41	0.3848 (3)	0.2034 (3)	0.32734 (18)	0.0326
C42	0.3373 (3)	0.1350 (3)	0.35490 (17)	0.0317
C43	0.3459 (2)	0.1290 (2)	0.42744 (17)	0.0275
H21	0.4168	0.4817	0.5262	0.0290*
H51	0.1670	0.3586	0.3444	0.0352*
H91	0.1113	0.4852	0.5267	0.0343*
H101	0.0701	0.5932	0.4321	0.0459*
H111	0.1700	0.7254	0.4269	0.0534*
H121	0.3089	0.7491	0.5162	0.0512*
H131	0.3511	0.6422	0.6112	0.0371*
H151	0.4704	0.4509	0.6685	0.0328*
H161	0.5997	0.5159	0.7528	0.0393*
H171	0.5685	0.6120	0.8453	0.0381*
H181	0.4093	0.6460	0.8506	0.0373*
H191	0.2795	0.5831	0.7658	0.0350*
H211	0.1548	0.3055	0.6755	0.0319*
H221	0.0078	0.2983	0.7123	0.0405*
H231	−0.0695	0.4374	0.7361	0.0404*
H241	−0.0015	0.5856	0.7217	0.0348*
H251	0.1423	0.5954	0.6809	0.0295*
H271	0.2185	0.1371	0.5660	0.0360*
H281	0.1444	−0.0076	0.5806	0.0451*
H291	0.2374	−0.1447	0.6113	0.0426*
H301	0.4055	−0.1375	0.6241	0.0421*

H311	0.4804	0.0058	0.6059	0.0341*
H331	0.5254	0.2744	0.6912	0.0314*
H341	0.6909	0.2624	0.7470	0.0378*
H351	0.7931	0.1667	0.6967	0.0382*
H361	0.7337	0.0905	0.5873	0.0381*
H371	0.5692	0.1028	0.5309	0.0324*
H391	0.4977	0.3033	0.4752	0.0301*
H401	0.4798	0.3153	0.3511	0.0377*
H411	0.3767	0.2084	0.2753	0.0397*
H421	0.2964	0.0894	0.3230	0.0371*
H431	0.3104	0.0797	0.4472	0.0328*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01936 (11)	0.01532 (10)	0.01728 (11)	0.00154 (9)	0.00543 (8)	0.00046 (9)
Br1	0.03054 (17)	0.02712 (16)	0.02220 (15)	0.00269 (13)	0.00787 (13)	0.00649 (13)
C1	0.0205 (15)	0.0175 (14)	0.0274 (16)	0.0036 (12)	0.0100 (12)	−0.0031 (12)
C2	0.0220 (15)	0.0234 (16)	0.0270 (16)	0.0047 (12)	0.0092 (13)	0.0001 (13)
C3	0.0279 (17)	0.0274 (17)	0.0322 (18)	0.0032 (13)	0.0170 (15)	0.0060 (14)
C4	0.0370 (19)	0.0377 (19)	0.0207 (16)	0.0141 (16)	0.0133 (14)	0.0110 (14)
C5	0.0302 (18)	0.0332 (18)	0.0247 (16)	0.0079 (15)	0.0070 (14)	0.0007 (14)
C6	0.0244 (15)	0.0216 (15)	0.0212 (15)	0.0040 (12)	0.0056 (12)	0.0022 (12)
F1	0.0416 (12)	0.0365 (12)	0.0470 (13)	−0.0025 (10)	0.0209 (10)	0.0164 (10)
F2	0.0467 (13)	0.0616 (15)	0.0256 (11)	0.0122 (11)	0.0122 (10)	0.0203 (10)
O1	0.0242 (12)	0.0246 (12)	0.0315 (12)	−0.0043 (9)	0.0029 (10)	0.0002 (10)
S1	0.0241 (4)	0.0417 (5)	0.0318 (5)	0.0032 (4)	0.0063 (3)	0.0100 (4)
O2	0.0287 (14)	0.0540 (18)	0.0621 (19)	0.0158 (12)	0.0126 (13)	0.0246 (15)
O3	0.0430 (16)	0.064 (2)	0.0386 (15)	0.0112 (14)	0.0178 (13)	0.0201 (14)
C7	0.044 (2)	0.061 (3)	0.039 (2)	−0.025 (2)	−0.0057 (18)	0.004 (2)
F3	0.0478 (16)	0.121 (3)	0.074 (2)	−0.0506 (18)	−0.0132 (14)	0.0256 (19)
F4	0.087 (2)	0.0438 (16)	0.0671 (18)	−0.0166 (15)	−0.0074 (16)	−0.0074 (14)
F5	0.0681 (18)	0.088 (2)	0.0324 (12)	−0.0339 (16)	0.0027 (12)	−0.0090 (13)
P1	0.0206 (4)	0.0165 (4)	0.0200 (4)	0.0019 (3)	0.0071 (3)	−0.0007 (3)
C8	0.0263 (16)	0.0185 (15)	0.0247 (16)	0.0056 (12)	0.0104 (13)	−0.0007 (12)
C9	0.0311 (17)	0.0266 (17)	0.0280 (17)	0.0053 (14)	0.0120 (14)	0.0028 (14)
C10	0.042 (2)	0.042 (2)	0.0309 (19)	0.0152 (18)	0.0095 (16)	0.0100 (17)
C11	0.063 (3)	0.036 (2)	0.035 (2)	0.019 (2)	0.0195 (19)	0.0153 (17)
C12	0.062 (3)	0.0226 (18)	0.044 (2)	0.0010 (17)	0.023 (2)	0.0078 (16)
C13	0.043 (2)	0.0191 (16)	0.0310 (18)	−0.0010 (14)	0.0146 (16)	0.0012 (13)
C14	0.0255 (16)	0.0173 (14)	0.0215 (15)	−0.0001 (12)	0.0058 (12)	−0.0005 (12)
C15	0.0242 (16)	0.0246 (16)	0.0332 (18)	0.0015 (13)	0.0122 (14)	−0.0003 (14)
C16	0.0212 (16)	0.037 (2)	0.040 (2)	−0.0009 (14)	0.0073 (14)	−0.0012 (16)
C17	0.0334 (19)	0.0314 (18)	0.0306 (18)	−0.0083 (15)	0.0038 (15)	−0.0033 (15)
C18	0.0356 (19)	0.0298 (18)	0.0278 (17)	−0.0022 (15)	0.0058 (14)	−0.0079 (14)
C19	0.0289 (17)	0.0286 (17)	0.0299 (17)	0.0033 (14)	0.0081 (14)	−0.0065 (14)
C20	0.0227 (15)	0.0221 (15)	0.0178 (14)	0.0007 (12)	0.0068 (12)	−0.0006 (12)
C21	0.0249 (16)	0.0254 (16)	0.0295 (17)	0.0021 (13)	0.0088 (14)	0.0007 (13)

C22	0.0282 (18)	0.0302 (18)	0.043 (2)	0.0004 (14)	0.0165 (16)	0.0047 (16)
C23	0.0264 (17)	0.040 (2)	0.0343 (19)	0.0024 (15)	0.0157 (15)	0.0051 (16)
C24	0.0289 (17)	0.0321 (18)	0.0260 (17)	0.0069 (14)	0.0104 (14)	0.0017 (14)
C25	0.0247 (16)	0.0235 (16)	0.0256 (16)	0.0020 (13)	0.0081 (13)	−0.0001 (13)
P2	0.0200 (4)	0.0173 (4)	0.0187 (4)	0.0021 (3)	0.0038 (3)	−0.0009 (3)
C26	0.0268 (16)	0.0194 (14)	0.0177 (14)	0.0002 (12)	0.0048 (12)	−0.0009 (12)
C27	0.0254 (17)	0.0216 (16)	0.043 (2)	0.0033 (13)	0.0112 (15)	0.0040 (15)
C28	0.0315 (19)	0.0263 (18)	0.055 (2)	−0.0045 (15)	0.0174 (18)	−0.0019 (17)
C29	0.040 (2)	0.0210 (16)	0.045 (2)	−0.0044 (15)	0.0168 (17)	−0.0013 (15)
C30	0.040 (2)	0.0188 (16)	0.046 (2)	0.0048 (15)	0.0068 (17)	0.0014 (15)
C31	0.0283 (17)	0.0222 (16)	0.0348 (18)	0.0037 (13)	0.0070 (14)	−0.0004 (14)
C32	0.0198 (14)	0.0228 (15)	0.0212 (15)	0.0026 (12)	0.0033 (12)	0.0040 (12)
C33	0.0231 (16)	0.0287 (17)	0.0268 (16)	−0.0005 (13)	0.0074 (13)	0.0010 (14)
C34	0.0256 (17)	0.043 (2)	0.0256 (17)	−0.0035 (15)	−0.0005 (13)	−0.0023 (15)
C35	0.0199 (15)	0.0355 (18)	0.0400 (19)	0.0024 (15)	0.0022 (14)	0.0024 (17)
C36	0.0264 (17)	0.0271 (18)	0.042 (2)	0.0055 (14)	0.0093 (15)	0.0031 (15)
C37	0.0276 (17)	0.0246 (16)	0.0288 (17)	0.0015 (13)	0.0080 (14)	−0.0030 (13)
C38	0.0208 (14)	0.0196 (15)	0.0230 (15)	0.0044 (12)	0.0059 (12)	−0.0027 (12)
C39	0.0226 (16)	0.0250 (16)	0.0277 (16)	0.0059 (13)	0.0071 (13)	0.0012 (13)
C40	0.0285 (17)	0.0353 (19)	0.0304 (18)	0.0109 (15)	0.0146 (14)	0.0086 (15)
C41	0.0330 (19)	0.044 (2)	0.0227 (17)	0.0158 (16)	0.0094 (14)	0.0010 (15)
C42	0.0348 (19)	0.0369 (19)	0.0211 (16)	0.0065 (15)	0.0012 (14)	−0.0069 (14)
C43	0.0306 (18)	0.0245 (17)	0.0269 (17)	0.0054 (13)	0.0050 (14)	−0.0003 (13)

Geometric parameters (Å, °)

Pd1—Br1	2.4892 (4)	C20—C21	1.401 (4)
Pd1—C1	2.013 (3)	C20—C25	1.392 (4)
Pd1—P1	2.3315 (8)	C21—C22	1.389 (5)
Pd1—P2	2.3377 (8)	C21—H211	1.00
C1—C2	1.407 (4)	C22—C23	1.385 (5)
C1—C6	1.379 (4)	C22—H221	1.00
C2—C3	1.380 (5)	C23—C24	1.382 (5)
C2—H21	1.00	C23—H231	1.00
C3—C4	1.379 (5)	C24—C25	1.390 (4)
C3—F1	1.351 (4)	C24—H241	1.00
C4—C5	1.365 (5)	C25—H251	1.00
C4—F2	1.361 (4)	P2—C26	1.819 (3)
C5—C6	1.395 (4)	P2—C32	1.831 (3)
C5—H51	1.00	P2—C38	1.831 (3)
C6—O1	1.445 (4)	C26—C27	1.395 (5)
O1—S1	1.547 (2)	C26—C31	1.390 (4)
S1—O2	1.412 (3)	C27—C28	1.386 (5)
S1—O3	1.414 (3)	C27—H271	1.00
S1—C7	1.842 (5)	C28—C29	1.377 (5)
C7—F3	1.307 (5)	C28—H281	1.00
C7—F4	1.322 (6)	C29—C30	1.384 (5)
C7—F5	1.322 (5)	C29—H291	1.00
P1—C8	1.823 (3)	C30—C31	1.389 (5)

P1—C14	1.825 (3)	C30—H301	1.00
P1—C20	1.827 (3)	C31—H311	1.00
C8—C9	1.402 (5)	C32—C33	1.386 (5)
C8—C13	1.390 (5)	C32—C37	1.397 (4)
C9—C10	1.382 (5)	C33—C34	1.398 (5)
C9—H91	1.00	C33—H331	1.00
C10—C11	1.394 (6)	C34—C35	1.383 (5)
C10—H101	1.00	C34—H341	1.00
C11—C12	1.372 (6)	C35—C36	1.384 (5)
C11—H111	1.00	C35—H351	1.00
C12—C13	1.385 (5)	C36—C37	1.389 (5)
C12—H121	1.00	C36—H361	1.00
C13—H131	1.00	C37—H371	1.00
C14—C15	1.397 (4)	C38—C39	1.407 (4)
C14—C19	1.394 (4)	C38—C43	1.387 (5)
C15—C16	1.388 (5)	C39—C40	1.385 (5)
C15—H151	1.00	C39—H391	1.00
C16—C17	1.389 (5)	C40—C41	1.400 (5)
C16—H161	1.00	C40—H401	1.00
C17—C18	1.380 (5)	C41—C42	1.373 (5)
C17—H171	1.00	C41—H411	1.00
C18—C19	1.387 (5)	C42—C43	1.398 (5)
C18—H181	1.00	C42—H421	1.00
C19—H191	1.00	C43—H431	1.00
Br1—Pd1—C1	177.59 (9)	P1—C20—C21	120.6 (2)
Br1—Pd1—P1	89.26 (2)	P1—C20—C25	119.3 (2)
C1—Pd1—P1	89.68 (8)	C21—C20—C25	120.0 (3)
Br1—Pd1—P2	90.60 (2)	C20—C21—C22	119.0 (3)
C1—Pd1—P2	90.68 (8)	C20—C21—H211	120.5
P1—Pd1—P2	173.75 (3)	C22—C21—H211	120.5
Pd1—C1—C2	123.0 (2)	C21—C22—C23	121.0 (3)
Pd1—C1—C6	121.5 (2)	C21—C22—H221	119.5
C2—C1—C6	115.5 (3)	C23—C22—H221	119.5
C1—C2—C3	120.6 (3)	C22—C23—C24	119.8 (3)
C1—C2—H21	119.7	C22—C23—H231	120.1
C3—C2—H21	119.7	C24—C23—H231	120.1
C2—C3—C4	120.8 (3)	C23—C24—C25	120.3 (3)
C2—C3—F1	119.8 (3)	C23—C24—H241	119.8
C4—C3—F1	119.4 (3)	C25—C24—H241	119.8
C3—C4—C5	121.1 (3)	C20—C25—C24	119.9 (3)
C3—C4—F2	118.9 (3)	C20—C25—H251	120.1
C5—C4—F2	120.0 (3)	C24—C25—H251	120.1
C4—C5—C6	116.6 (3)	Pd1—P2—C26	113.67 (10)
C4—C5—H51	121.7	Pd1—P2—C32	114.03 (10)
C6—C5—H51	121.7	C26—P2—C32	105.88 (14)
C5—C6—C1	125.3 (3)	Pd1—P2—C38	115.21 (10)
C5—C6—O1	117.9 (3)	C26—P2—C38	103.88 (14)
C1—C6—O1	116.7 (3)	C32—P2—C38	102.96 (14)
C6—O1—S1	124.0 (2)	P2—C26—C27	117.7 (2)

O1—S1—O2	111.48 (15)	P2—C26—C31	123.6 (2)
O1—S1—O3	108.66 (15)	C27—C26—C31	118.7 (3)
O2—S1—O3	122.49 (18)	C26—C27—C28	120.5 (3)
O1—S1—C7	96.96 (18)	C26—C27—H271	119.7
O2—S1—C7	108.2 (2)	C28—C27—H271	119.7
O3—S1—C7	105.9 (2)	C27—C28—C29	120.5 (3)
S1—C7—F3	108.9 (4)	C27—C28—H281	119.7
S1—C7—F4	109.9 (3)	C29—C28—H281	119.7
F3—C7—F4	109.4 (4)	C28—C29—C30	119.3 (3)
S1—C7—F5	109.8 (3)	C28—C29—H291	120.3
F3—C7—F5	109.8 (3)	C30—C29—H291	120.3
F4—C7—F5	109.0 (4)	C29—C30—C31	120.6 (3)
Pd1—P1—C8	115.78 (10)	C29—C30—H301	119.7
Pd1—P1—C14	107.51 (10)	C31—C30—H301	119.7
C8—P1—C14	104.37 (14)	C26—C31—C30	120.2 (3)
Pd1—P1—C20	118.35 (10)	C26—C31—H311	119.9
C8—P1—C20	100.94 (14)	C30—C31—H311	119.9
C14—P1—C20	108.91 (14)	P2—C32—C33	119.7 (2)
P1—C8—C9	117.0 (2)	P2—C32—C37	120.7 (2)
P1—C8—C13	123.6 (3)	C33—C32—C37	119.6 (3)
C9—C8—C13	119.1 (3)	C32—C33—C34	120.1 (3)
C8—C9—C10	120.2 (3)	C32—C33—H331	120.0
C8—C9—H91	119.9	C34—C33—H331	120.0
C10—C9—H91	119.9	C33—C34—C35	119.9 (3)
C9—C10—C11	119.9 (4)	C33—C34—H341	120.0
C9—C10—H101	120.1	C35—C34—H341	120.0
C11—C10—H101	120.1	C34—C35—C36	120.3 (3)
C10—C11—C12	119.9 (3)	C34—C35—H351	119.8
C10—C11—H111	120.0	C36—C35—H351	119.8
C12—C11—H111	120.0	C35—C36—C37	119.9 (3)
C11—C12—C13	120.7 (4)	C35—C36—H361	120.0
C11—C12—H121	119.6	C37—C36—H361	120.0
C13—C12—H121	119.6	C32—C37—C36	120.2 (3)
C8—C13—C12	120.1 (3)	C32—C37—H371	119.9
C8—C13—H131	120.0	C36—C37—H371	119.9
C12—C13—H131	120.0	P2—C38—C39	118.7 (2)
P1—C14—C15	117.7 (2)	P2—C38—C43	121.7 (2)
P1—C14—C19	123.4 (2)	C39—C38—C43	119.2 (3)
C15—C14—C19	118.9 (3)	C38—C39—C40	120.7 (3)
C14—C15—C16	120.9 (3)	C38—C39—H391	119.7
C14—C15—H151	119.5	C40—C39—H391	119.7
C16—C15—H151	119.5	C39—C40—C41	119.1 (3)
C15—C16—C17	119.5 (3)	C39—C40—H401	120.4
C15—C16—H161	120.2	C41—C40—H401	120.4
C17—C16—H161	120.2	C40—C41—C42	120.7 (3)
C16—C17—C18	120.0 (3)	C40—C41—H411	119.7
C16—C17—H171	120.0	C42—C41—H411	119.7
C18—C17—H171	120.0	C41—C42—C43	120.3 (3)
C17—C18—C19	120.8 (3)	C41—C42—H421	119.9

C17—C18—H181	119.6	C43—C42—H421	119.9
C19—C18—H181	119.6	C42—C43—C38	120.0 (3)
C14—C19—C18	119.9 (3)	C42—C43—H431	120.0
C14—C19—H191	120.0	C38—C43—H431	120.0
C18—C19—H191	120.0		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C21—H211···Br1	1.00	2.80	3.522 (3)	129
C27—H271···O3	1.00	2.56	3.495 (4)	156
C33—H331···Br1	1.00	2.78	3.581 (3)	137

Fig. 1

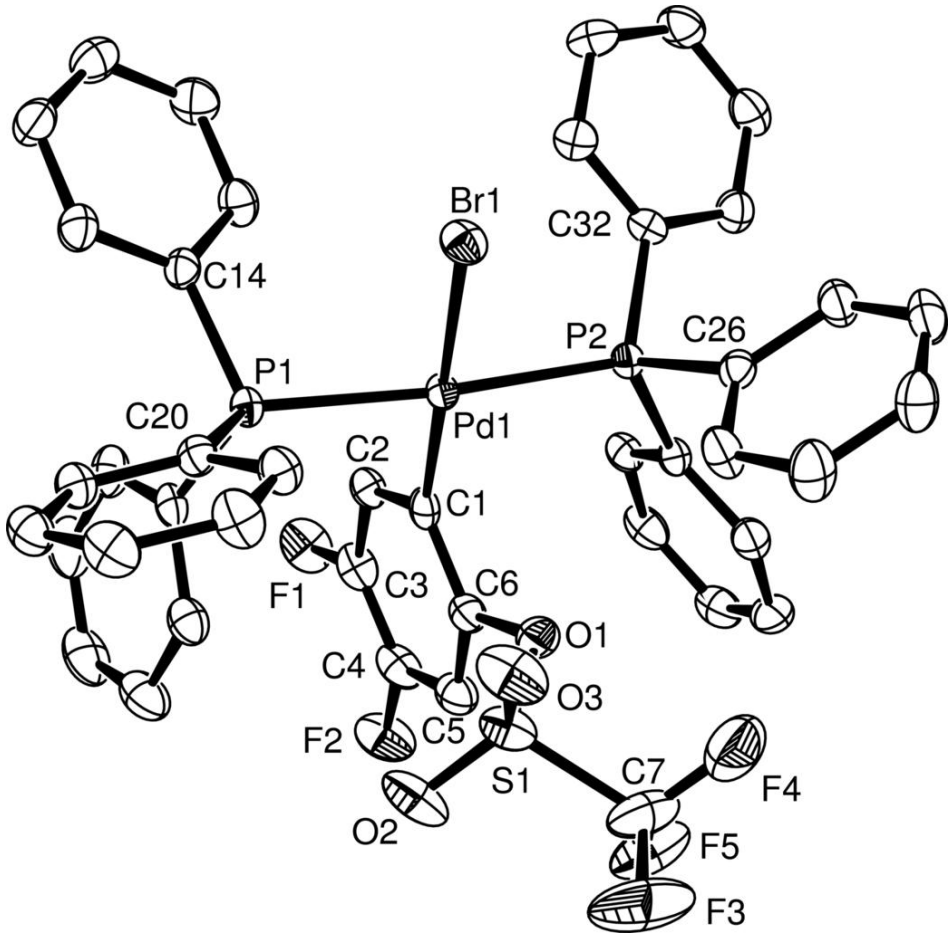

Br1
C32
C14
P2
C26
P1
C20
Pd1
C2
C1
F1
C3
C6
O1
C4
O3
F2
C5
S1
C7
F4
O2
F5
F3

Fig. 2

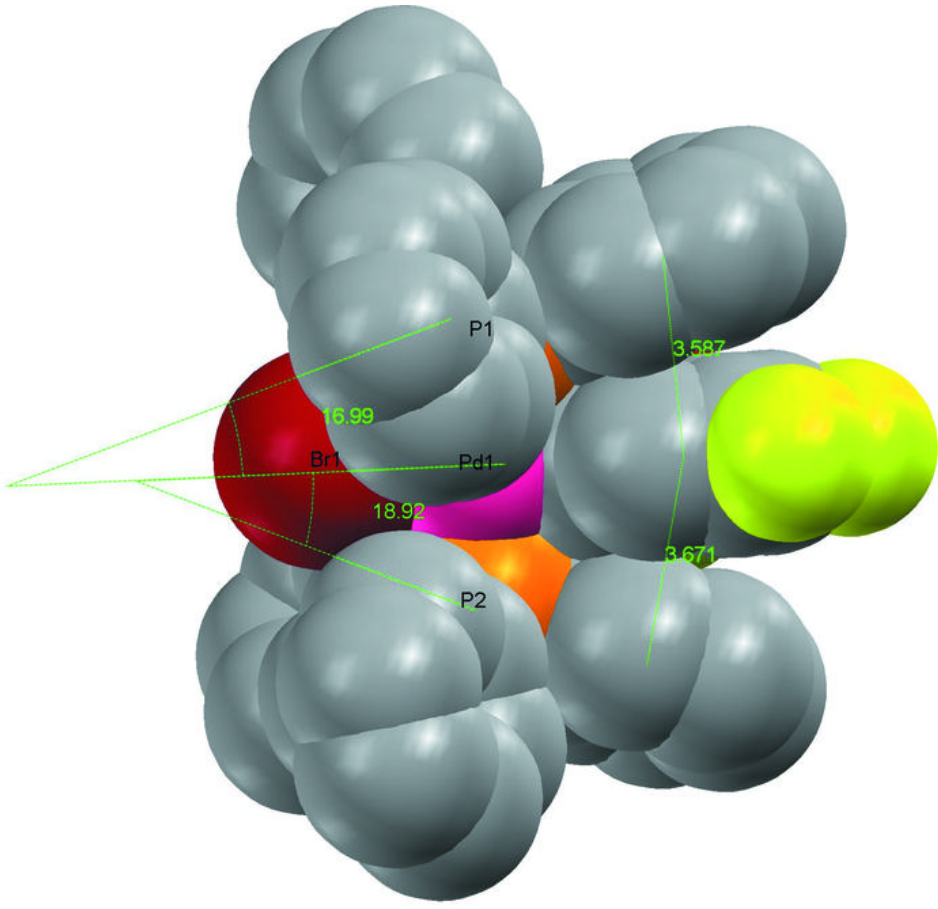


Fig. 3

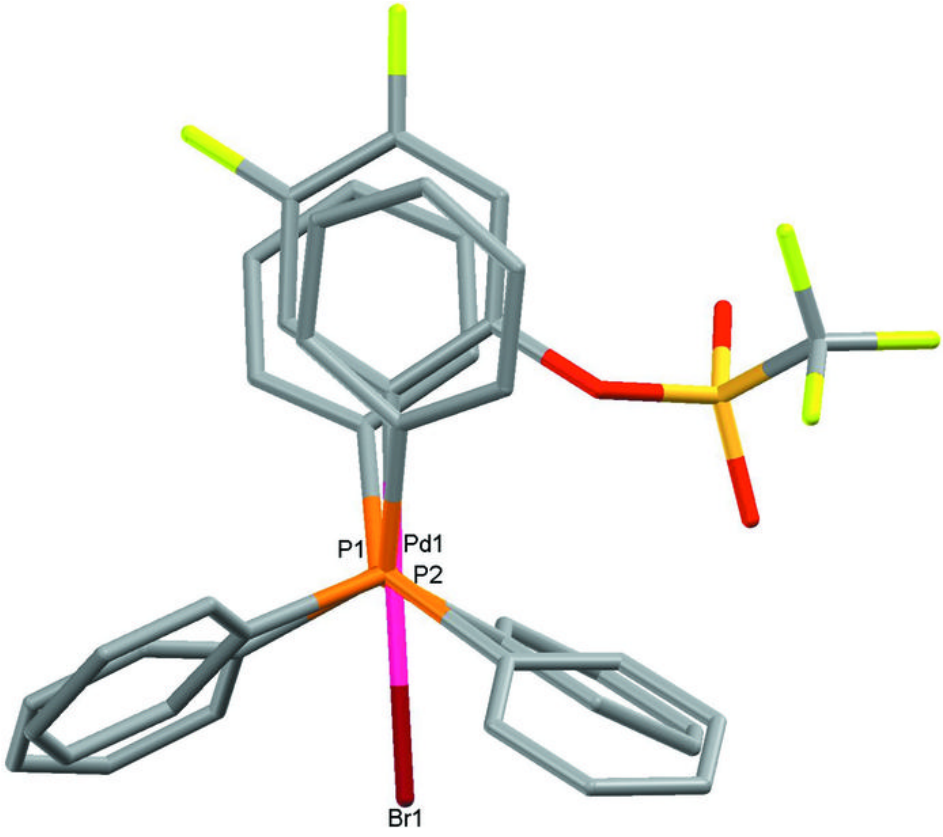
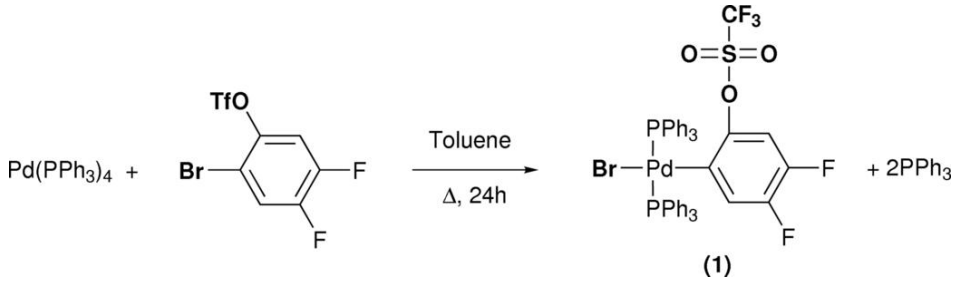


Fig. 4


Pd(PPh3)4 +
TfO
Br
F
F
Toluene
Δ, 24h
CF3
O=S=O
O
PPh3
Br
Pd
PPh3
F
F
+ 2PPh3

(1)