$S = 1.2$
1191 reflections
79 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0065F^2]$

Atomic scattering factors from *SHELX*76 (Sheldrick, 1976); *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	3/4	1/4	1/2	0.0360 (4)
Cl(1)	0.6820 (2)	0.4682 (3)	0.3745 (2)	0.059 (1)
Cl(2)	0.8315 (2)	0.4726 (3)	0.6177 (2)	0.0497 (9)
Br	0.4478 (1)	0.7017 (2)	0.35312 (8)	0.0735 (6)
C(2)	0.6605 (8)	0.720 (1)	0.6263 (9)	0.058 (4)
N(1)	0.6012 (7)	0.788 (1)	0.6583 (7)	0.055 (4)
C(5)	0.5170 (9)	0.798 (2)	0.5731 (8)	0.058 (5)
C(4)	0.5292 (8)	0.731 (1)	0.4899 (7)	0.049 (4)
N(3)	0.6174 (6)	0.686 (1)	0.5244 (6)	0.051 (3)

Table 2. *Selected geometric parameters* (Å, °)

Pd—Cl(1)	2.309 (3)	N(3)—C(2)	1.33 (1)
Pd—Cl(2)	2.323 (3)	N(3)—C(4)	1.36 (2)
Br—C(4)	1.839 (9)	C(4)—C(5)	1.37 (2)
N(1)—C(2)	1.33 (2)	N(3)···Cl(1)	3.19 (1)
N(1)—C(5)	1.40 (1)	N(1)···Cl(2^i)	3.19 (1)
Cl(1)—Pd—Cl(2)	89.8 (1)	Br—C(4)—N(3)	122 (1)
C(2)—N(1)—C(5)	109 (1)	Br—C(4)—C(5)	130 (1)
C(2)—N(3)—C(4)	110 (1)	N(3)—C(4)—C(5)	108 (1)
N(1)—C(2)—N(3)	108 (1)	N(1)—C(5)—C(4)	105 (1)

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The Pd atom was first located from a Patterson map using *SHELXS*86 (Sheldrick, 1985) and then a difference Fourier map revealed the other atoms (*SHELX*76; Sheldrick, 1976). The relatively large R and R_{int} values are a result of the quality of the crystal and its decay.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 1222–1225

Triethylammonium Hydrogen Dichlorotris(diphenylphosphinito-*P*)rhodium(III)–Tetrahydrofuran (1/1)

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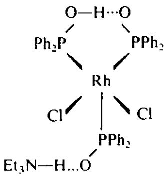
Abstract

The title complex, triethylammonium dichlorobis{hydrogen bis[oxodiphenylphosphato(1−)-*P*]}[oxodiphenylphosphato(1−)-*P*]rhodium(III)–tetrahydrofuran (1/1), $[C_6H_{16}N][RhCl_2(C_{12}H_{10}OP)\{(C_{12}H_{10}OP)_2H\}].C_4H_8O$, has square-pyramidal geometry which is unusual for rhodium(III) complexes. It occurs as an ion pair with the Et_3NH^+ ion hydrogen bonded to the O atom [2.631 (23) Å] of the unique apical Ph_2PO ligand. The basal Ph_2PO ligands are connected by an O···O hydrogen bond [2.411 (23) Å].

Comment

During the course of studies on the coordination chemistry of mixed anhydrides of acrylic and diphenylphosphinous acids $Ph_2PO_2CCR{=\!=}CR'R''$ (Borowski *et al.*, 1990; Iraqi *et al.*, 1991), we discovered that under some circumstances, *e.g.* reaction with $[RhCl(PPh_3)_3]$ (Irvine, Cole-Hamilton, Barnes & Hodgson, 1989; Irvine, Glidewell, Cole-Hamilton, Barnes & Howie, 1991), $Ph_2PO_2CCH{=\!=}CH_2$ was transformed into coordinated Ph_2POPPh_2. Since, in solution $Ph_2PO_2CCH{=\!=}CH_2$ slowly converts to $Ph_2PP(O)Ph_2$, we studied the reaction of $[RhCl(PPh_3)_3]$ with $Ph_2PP(O)Ph_2$ (Irvine, 1990). The major product was $[RhCl(PPh_3)(Ph_2PPOPh_2)]$, with the title compound (I) as a minor product.



(I)

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The title molecule is shown in Fig. 1. Being a d^6 metal ion, almost all complexes of Rh^{III} are octahedral. However, the Rh atom in structure (I) has five-coordinate square-pyramidal geometry consisting of two *cis* Cl atoms, the atoms P1 and P2 from two Ph_2PO ligands in the basal plane and the atom P3 of the remaining apical Ph_2PO ligand. The Rh atom lies 0.327 (3) Å above the basal plane. The empty sixth coordination site is blocked to some extent by the axial phenyl groups (C1–C6 and C31–C36) of the basal Ph_2PO groups. There is no evidence of direct interaction of the C or H atoms of these rings with Rh. The two basal Ph_2PO ligands are hydrogen bonded to give a ring consisting of Rh, P2, O1, H, O3 and P4. The O1···O3 distance of 2.411 (23) Å can be compared with 2.382 Å in $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ (Irvine, Preston, Barnes & Cole-Hamilton, 1991) and probably indicates strong symmetrical hydrogen bonding. The dimensions in the ring are comparable with those in other compounds of this type (Irvine, Preston, Barnes & Cole-Hamilton, 1991; Duncan, Stephenson, Walkinshaw, Heddon & Roundhill, 1984). In $[RhMeI_2(PPh_3)_2]$ (Troughton & Skapski, 1968) and $[RhCl_2(NO)(PPh_3)_2]$ (Goldberg, Kubiac, Meyer & Eisenberg, 1975), which are also square-pyramidal Rh^{III} complexes, the Rh—P distances are rather longer than those of (I), but the Rh—Cl distances of the latter are very similar to those of (I).

The atom O2 from the apical Ph_2PO ligand forms a hydrogen bond *via* H41 to N41 of the Et_3NH^+ cation; the O2···N41 distance is 2.593 (25) Å. We are not aware of any other complexes in which an interaction of this kind has been structurally characterized although aluminium phosphates in which Et_3NH^+ is bonded to framework O atoms are known (Huo *et al.*, 1992). Among the ethyl groups, C43 and C45 are equatorial but the adjacent P2 atom with its bulky phenyl groups forces C47 to be axial with respect to the N—H direction. The presence of Et_3NH^+ in the crystal was unexpected. It was probably derived from triethylamine used in the preparation of $Ph_2PP(O)Ph_2$ by the reaction of Ph_2PCl with water.

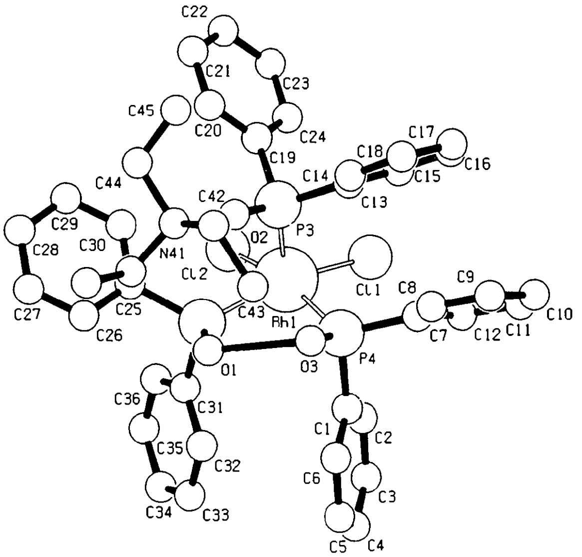

Fig. 1. Square pyramidal $[RhCl_2\{(Ph_2PO)_2H\}Ph_2PO]$, showing the O1···O3 hydrogen bond.

The tetrahydrofuran molecule occupies a lattice site and is not involved in coordination or hydrogen bonding.

Reactions of $Ph_2PP(O)Ph_2$ with other transition elements have been shown to give Ph_2POPPh_2 complexed in either a unidentate or bidentate manner (Wang, Prasad, Gabe & Bradley, 1982; Irvine, Cole-Hamilton, Barnes & Hodgson, 1989; Irvine, Glidewell, Cole-Hamilton, Barnes & Howie, 1991; Irvine, Preston, Barnes & Cole-Hamilton, 1991), but fragmentation to Ph_2PO does not appear to have been reported. We have, however, observed the formation of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CHRPPh_3)]$ from reactions involving $Ph_2PO_2CCH{=}CHR$ (R = H, Me) and $[RuCl_2(PPh_3)_4]$, although we do not believe that Ph_2POPPh_2, either free or complexed, is an intermediate (Irvine, Preston, Barnes & Cole-Hamilton, 1991).

Experimental

Crystals of (I) were grown from tetrahydrofuran solution at 270 K over several days using the last fraction obtained from fractional crystallization of a solution obtained from the reaction of $[RhCl(PPh_3)_3]$ with $Ph_2PP(O)Ph_2$ under reflux.

Crystal data

$[C_6H_{16}N][RhCl_2(C_{12}H_{10}OP)\text{-}\{(C_{12}H_{10}OP)_2H\}].C_4H_8O$
$M_r = 928.44$
Monoclinic
$P2_1/n$
$a = 14.886\ (6)$ Å
$b = 20.676\ (10)$ Å
$c = 15.239\ (6)$ Å
$\beta = 103.88\ (3)°$
$V = 4553.3\ (34)$ Å^3
$Z = 4$
$D_x = 1.354$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12–15°$
$\mu = 0.639$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.6 × 0.4 × 0.2 mm
Yellow

Data collection

Nicolet $P3$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.85$, $T_{\max} = 0.99$
8650 measured reflections
8069 independent reflections
2196 observed reflections $[F > 5\sigma(F)]$

$R_{\text{int}} = 0.0943$
$\theta_{\max} = 25.04°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 24$
$l = -18 \rightarrow 17$
2 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0683$
$wR(F^2) = 0.1546$
$S = 1.051$
2196 reflections
443 parameters
Riding phenyl H atoms assigned a common refined isotropic displacement parameter

Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.100P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.057$
$\Delta\rho_{\max} = 0.737$ e Å^{-3} (1.28 Å from Rh)
$\Delta\rho_{\min} = -0.457$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh1	0.69830 (12)	0.09445 (7)	0.88893 (11)	0.0277 (5)
P2	0.6140 (4)	0.0807 (3)	0.7444 (3)	0.033 (2)
P3	0.7934 (4)	0.1627 (3)	0.8416 (4)	0.0308 (14)
P4	0.6056 (4)	0.1796 (3)	0.9057 (3)	0.0304 (14)
Cl1	0.7574 (4)	0.0831 (3)	1.0487 (3)	0.048 (2)
Cl2	0.7595 (4)	−0.0112 (2)	0.8764 (3)	0.044 (2)
O1	0.5568 (9)	0.1404 (6)	0.7034 (8)	0.047 (4)
O2	0.7611 (9)	0.1871 (6)	0.7460 (8)	0.039 (4)
O3	0.5749 (9)	0.2214 (6)	0.8201 (7)	0.034 (4)
C1	0.5011 (9)	0.1429 (7)	0.9268 (9)	0.036 (5)
C2	0.5039 (9)	0.0930 (7)	0.9886 (8)	0.039 (5)
C3	0.4220 (12)	0.0666 (6)	1.0012 (9)	0.059 (7)
C4	0.3374 (9)	0.0900 (9)	0.9520 (11)	0.055 (7)
C5	0.3346 (9)	0.1399 (9)	0.8902 (10)	0.061 (7)
C6	0.4164 (13)	0.1663 (6)	0.8776 (8)	0.057 (7)
C7	0.6363 (10)	0.2363 (7)	0.9997 (9)	0.047 (6)
C8	0.6373 (10)	0.3014 (8)	0.9768 (9)	0.061 (7)
C9	0.6558 (11)	0.3481 (6)	1.0443 (14)	0.074 (8)
C10	0.6735 (11)	0.3298 (8)	1.1346 (12)	0.074 (9)
C11	0.6726 (11)	0.2648 (10)	1.1574 (8)	0.077 (9)
C12	0.6540 (11)	0.2180 (6)	1.0899 (10)	0.060 (7)
C13	0.8268 (9)	0.2324 (5)	0.9160 (8)	0.031 (5)
C14	0.8213 (10)	0.2926 (7)	0.8745 (7)	0.054 (7)
C15	0.8484 (10)	0.3478 (5)	0.9263 (11)	0.064 (7)
C16	0.8810 (10)	0.3427 (6)	1.0194 (11)	0.053 (6)
C17	0.8865 (10)	0.2824 (7)	1.0609 (7)	0.049 (7)
C18	0.8594 (9)	0.2273 (5)	1.0091 (8)	0.042 (6)
C19	0.9025 (7)	0.1186 (6)	0.8548 (10)	0.029 (5)
C20	0.9410 (12)	0.1201 (7)	0.7803 (8)	0.068 (8)
C21	1.0271 (12)	0.0922 (9)	0.7855 (11)	0.072 (8)
C22	1.0746 (8)	0.0628 (7)	0.8652 (14)	0.074 (9)
C23	1.0361 (10)	0.0614 (7)	0.9397 (11)	0.072 (8)
C24	0.9500 (10)	0.0893 (7)	0.9345 (8)	0.047 (6)
C25	0.6644 (9)	0.0502 (6)	0.6539 (8)	0.023 (5)
C26	0.6041 (8)	0.0473 (6)	0.5688 (10)	0.049 (6)
C27	0.6366 (11)	0.0290 (7)	0.4942 (7)	0.054 (7)
C28	0.7294 (12)	0.0135 (7)	0.5048 (9)	0.070 (8)
C29	0.7898 (8)	0.0164 (7)	0.5898 (11)	0.068 (8)
C30	0.7572 (9)	0.0347 (7)	0.6644 (8)	0.051 (7)
C31	0.5257 (10)	0.0190 (8)	0.7465 (9)	0.057 (7)
C32	0.4361 (12)	0.0372 (7)	0.7476 (9)	0.051 (7)
C33	0.3701 (9)	−0.0097 (11)	0.7507 (10)	0.086 (10)
C34	0.3937 (14)	−0.0749 (9)	0.7526 (10)	0.098 (12)
C35	0.4833 (16)	−0.0930 (7)	0.7515 (10)	0.090 (10)
C36	0.5493 (10)	−0.0461 (10)	0.7484 (9)	0.068 (8)
N41	1.2150 (16)	0.2493 (10)	1.0922 (13)	0.076 (8)
C42	1.2019 (27)	0.1793 (14)	1.1055 (20)	0.123 (15)
C43	1.1146 (17)	0.1683 (12)	1.1503 (22)	0.096 (12)
C44	1.3018 (22)	0.2620 (19)	1.0531 (19)	0.110 (12)
C45	1.3845 (21)	0.2322 (16)	1.1094 (19)	0.096 (10)
C46	1.1399 (19)	0.2874 (11)	1.0354 (18)	0.077 (9)
C47	1.1032 (20)	0.2590 (14)	0.9344 (18)	0.094 (10)
C51	0.4428 (43)	0.4160 (20)	0.7845 (31)	0.179 (23)
C52	0.4537 (46)	0.4402 (30)	0.8910 (45)	0.233 (36)
C53	0.3883 (48)	0.4169 (48)	0.8779 (57)	0.342 (63)
C54	0.3607 (36)	0.3471 (24)	0.8628 (37)	0.166 (24)
O55	0.3975 (35)	0.3557 (21)	0.7849 (29)	0.274 (23)

Table 2. *Selected geometric parameters* (Å, °)

Rh1—P3	2.237 (6)	P3—C19	1.830 (11)
Rh1—P2	2.276 (6)	P4—O3	1.542 (12)
Rh1—P4	2.288 (6)	P4—C7	1.822 (12)
Rh1—Cl2	2.392 (5)	P4—C1	1.828 (12)
Rh1—Cl1	2.394 (5)	N41—C42	1.48 (3)
P2—O1	1.544 (13)	N41—C46	1.47 (3)
P2—C25	1.833 (11)	N41—C44	1.57 (3)
P2—C31	1.838 (12)	C42—C43	1.62 (4)
P3—O2	1.508 (12)	C44—C45	1.46 (4)
P3—C13	1.826 (11)	C46—C47	1.61 (3)
P3—Rh1—P2	90.6 (2)	O2—P3—C19	110.0 (8)
P3—Rh1—P4	89.8 (2)	C13—P3—C19	102.9 (6)
P2—Rh1—P4	89.8 (2)	O2—P3—Rh1	116.3 (6)
P3—Rh1—Cl2	105.5 (2)	C13—P3—Rh1	113.4 (5)
P2—Rh1—Cl2	86.6 (2)	C19—P3—Rh1	105.3 (5)
P4—Rh1—Cl2	164.3 (2)	O3—P4—C7	105.7 (7)
P3—Rh1—Cl1	106.4 (2)	O3—P4—C1	106.8 (7)
P2—Rh1—Cl1	162.7 (2)	C7—P4—C1	101.1 (7)
P4—Rh1—Cl1	92.6 (2)	O3—P4—Rh1	113.7 (5)
Cl2—Rh1—Cl1	86.4 (2)	C7—P4—Rh1	122.6 (5)
O1—P2—C25	104.9 (7)	C1—P4—Rh1	105.2 (5)
O1—P2—C31	103.6 (8)	C42—N41—C46	119.9 (22)
C25—P2—C31	101.4 (7)	C42—N41—C44	111.3 (26)
O1—P2—Rh1	114.5 (5)	C46—N41—C44	105.4 (23)
C25—P2—Rh1	122.8 (5)	N41—C42—C43	109.9 (25)
C31—P2—Rh1	107.5 (5)	C45—C44—N41	111.2 (25)
O2—P3—C13	108.1 (7)	N41—C46—C47	113.7 (19)
Rh1—P2—O1—O3	−4.4 (9)	O3—O1—P2—C31	112.3 (7)
P2—O1—O3—P4	−21.0 (10)	O3—O1—P2—C25	−141.8 (7)
O1—O3—P4—Rh1	35.6 (7)	O1—O3—P4—C1	−80.0 (7)
O3—P4—Rh1—P2	−37.0 (6)	O1—O3—P4—C7	172.9 (7)
P4—Rh1—P2—O1	19.6 (6)		

The crystals did not diffract strongly and the dataset contained many weak reflections [$F < 5\sigma(F)$] which were found to be particularly unreliable and which were eliminated from the refinement. After location of the Rh and Cl atoms from a Patterson synthesis, all the remaining non-H atoms were found on difference maps. Because of the limited dataset the phenyl rings were treated as rigid groups in the refinement. No attempt was made to include the H atom lying between O1 and O3 and all other H atoms were placed in calculated positions. The lattice tetrahydrofuran molecule is clearly disordered with very unsatisfactory interatomic distances. No attempt has been made to resolve the disorder because of the lack of interest in a solvent molecule given the limited dataset. Data collection and cell refinement were performed using the diffractometer software. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976) with final cycles using *SHELXL* (Sheldrick, 1994); final refinement was on F^2 using only data with $F > 5\sigma(F)$ as used in the earlier refinement in *SHELX*76. Molecular graphics: *PLUTON* (Spek, 1992). Software used to prepare material for publication: *SHELXL*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: LI1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Bis[3-sulfido-1,3-bis(2-thienyl)-prop-2-enone-*O*,*S*]palladium(II)

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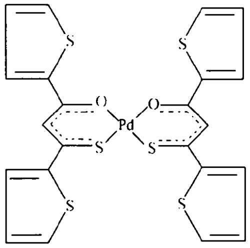
Abstract

Bis[3-sulfido-1,3-bis(2-thienyl)prop-2-enone-*O*,*S*]-palladium(II), $[Pd(C_{11}H_7OS_3)_2]$, exists as the *cis* isomer with the O donor atom of one ligand opposite the S donor atom of the other. The mean Pd—O and Pd—S distances are 2.014 (14) and 2.231 (5) Å, respectively. Although the mean *cis* angles around Pd deviate markedly from 90°, its environment is almost exactly planar. In each independent molecule one of the four thiophene rings is disordered by rotation about its bond to the chelate ring. The result is that while three of the thiophene rings are always *endo*, the fourth is *exo* in 50% of the molecules. In neither conformation are there any significant intermolecular Pd···S contacts.

Comment

We recently reported the analogous 1:2 Pd^{II} and Cu^{II} complexes of the related ligand 3-hydroxy-1,3-bis(2-thienyl)prop-2-enone: in the Cu complex the orientation of one of the thiophene rings was determined by a specific pattern of Cu···S intermolecular contacts (Baxter, Blake, Gould, Heath & Stephenson, 1993). To our knowledge only three Pd^{II} complexes with mixed *O*,*S* donor chelates have been structurally characterized: bis(monothiodibenzoylmethanate)palladium (Shkol'nikova, Yutal, Shugam & Knyazeva, 1973) and bis(2,2,6,6-tetramethylhept-4-ene-5-thiol-3-onato)palladium (Pope & Boeyens, 1976) occur as *cis* isomers while bis(1,1-diethyl-3-benzoylthioureato)palladium (Fitzl, Beyer, Sieler, Richter, Kaiser & Hoyer, 1977) is the only known example of the *trans* form.



(I)

For the present compound, (I), the crystal studied was composed exclusively of the *cis* form, with two very similar independent molecules in the asymmetric unit. The mean Pd—O and Pd—S distances are 2.014 (14) and 2.231 (5) Å, respectively; the average *cis* angles are 81.5 (3)° for O—Pd—O, 86.7 (1)° for S—Pd—S and 95.9 (2)° for O—Pd—S, the last of these corresponding to the bite angle of the chelate ligand. Although these angles around Pd differ appreciably from 90°, their sum (360.0°) indicates near-planarity. Bond lengths and angles have values close to those found for the other two *cis* complexes. In each independent molecule one of the four thiophene rings is disordered by rotation about its bond to the chelate ring, with the result that while three thiophene rings are always *endo*, the fourth is *exo* in 50% of the molecules. In neither their *endo* or *exo* conformation do the S atoms of the thiophene rings participate in any close Pd···S intermolecular contacts.

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