C43′	−0.0564 (5)	0.5772 (10)	0.3381 (5)	0.053 (4)
C44′	−0.0280 (2)	0.4831 (4)	0.3736 (2)	0.058 (4)
C61′†	0.0455 (2)	0.6421 (4)	0.0682 (2)	0.089 (15)
S61′†	0.0971 (2)	0.6876 (4)	0.0169 (2)	0.060 (3)
C62′†	−0.0189 (2)	0.6660 (4)	0.0444 (2)	0.028 (7)
C63′†	−0.0256 (2)	0.7219 (4)	−0.0166 (2)	0.078 (17)
C64′†	0.0320 (2)	0.7394 (4)	−0.0366 (2)	0.077 (11)
C71′†	0.0512 (2)	0.6252 (4)	0.0626 (2)	0.005 (6)
S71′†	−0.0328 (2)	0.6410 (4)	0.0432 (2)	0.061 (3)
C72′†	0.0829 (2)	0.7045 (4)	0.0197 (2)	0.109 (17)
C73′†	0.0386 (2)	0.7642 (4)	−0.0209 (2)	0.052 (8)
C74′†	−0.0246 (2)	0.7430 (4)	−0.0165 (2)	0.051 (14)

† Site occupancy = 0.5.

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

Pd1—O1	1.997 (8)	Pd1′—O1′	2.028 (8)
Pd1—O2	2.024 (8)	Pd1′—O2′	2.008 (8)
Pd1—S1	2.237 (4)	Pd1′—S1′	2.225 (4)
Pd1—S2	2.233 (4)	Pd1′—S2′	2.229 (3)
S1—C3	1.724 (11)	S1′—C1′	1.726 (12)
S2—C6	1.716 (12)	S2′—C6′	1.689 (12)
O1—C1	1.257 (12)	O1′—C3′	1.283 (12)
O2—C4	1.273 (13)	O2′—C4′	1.263 (12)
C1—C2	1.420 (14)	C1′—C2′	1.382 (14)
C1—C11	1.483 (14)	C1′—C11′	1.469 (14)
C2—C3	1.372 (13)	C2′—C3′	1.374 (14)
C3—C31	1.475 (13)	C3′—C31′	1.483 (15)
C4—C5	1.398 (14)	C4′—C5′	1.440 (15)
C4—C41	1.472 (14)	C4′—C41′	1.462 (14)
C5—C6	1.391 (14)	C5′—C6′	1.360 (14)
C6—C71	1.470 (12)	C6′—C71′	1.494 (11)
C6—C61	1.531 (12)	C6′—C61′	1.541 (12)
O1—Pd1—O2	80.7 (3)	O2′—Pd1′—O1′	82.2 (3)
O1—Pd1—S2	176.9 (2)	O2′—Pd1′—S1′	178.0 (3)
O2—Pd1—S2	96.2 (2)	O1′—Pd1′—S1′	95.8 (3)
O1—Pd1—S1	95.9 (2)	O2′—Pd1′—S2′	95.8 (2)
O2—Pd1—S1	176.2 (3)	O1′—Pd1′—S2′	177.1 (3)
S2—Pd1—S1	87.22 (13)	S1′—Pd1′—S2′	86.13 (13)
C3—S1—Pd1	109.5 (4)	C1′—S1′—Pd1′	109.9 (5)
C6—S2—Pd1	109.0 (4)	C6′—S2′—Pd1′	108.7 (4)
C1—O1—Pd1	131.0 (7)	C3′—O1′—Pd1′	130.0 (8)
C4—O2—Pd1	129.8 (7)	C4′—O2′—Pd1′	132.6 (8)
O1—C1—C2	127.7 (11)	C2′—C1′—C11′	123.3 (11)
O1—C1—C11	115.5 (10)	C2′—C1′—S1′	125.3 (10)
C2—C1—C11	116.9 (10)	C11′—C1′—S1′	111.3 (9)
C3—C2—C1	128.2 (11)	C3′—C2′—C1′	132.0 (12)
C2—C3—C31	117.7 (10)	O1′—C3′—C2′	126.1 (12)
C2—C3—S1	127.4 (9)	O1′—C3′—C31′	113.1 (11)
C31—C3—S1	114.9 (8)	C2′—C3′—C31′	120.7 (11)
O2—C4—C5	127.0 (11)	O2′—C4′—C5′	123.8 (11)
O2—C4—C41	115.1 (10)	O2′—C4′—C41′	117.8 (11)
C5—C4—C41	117.9 (11)	C5′—C4′—C41′	118.5 (11)
C6—C5—C4	128.9 (12)	C6′—C5′—C4′	129.4 (11)
C5—C6—C71	120.3 (10)	C5′—C6′—C71′	120.1 (10)
C5—C6—C61	116.3 (10)	C5′—C6′—C61′	111.7 (10)
C5—C6—S2	127.8 (10)	C5′—C6′—S2′	129.1 (10)
C71—C6—S2	111.7 (7)	C71′—C6′—S2′	110.9 (7)
C61—C6—S2	115.6 (7)	C61′—C6′—S2′	119.0 (7)
C12—C11—C1	132.5 (10)	C12′—C11′—C1′	128.2 (10)
C12—C11—S11	111.8 (7)	C12′—C11′—S11′	112.9 (7)
C1—C11—S11	115.6 (8)	C1′—C11′—S11′	119.0 (9)
C32—C31—C3	127.7 (8)	C32′—C31′—C3′	129.3 (10)
C3—C31—S31	120.3 (8)	C3′—C31′—S31′	118.2 (9)
C42—C41—C4	128.2 (10)	C42′—C41′—C4′	131.0 (10)
C4—C41—S41	118.5 (8)	C4′—C41′—S41′	116.1 (8)
C62—C61—C6	130.5 (5)	C62′—C61′—C6′	131.2 (4)
C6—C61—S61	117.7 (5)	C6′—C61′—S61′	114.4 (4)
C72—C71—C6	129.4 (5)	C72′—C71′—C6′	133.3 (4)
C6—C71—S71	118.1 (5)	C6′—C71′—S71′	117.5 (5)

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1989). Software used to prepare material for publication: local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichloro(1-trimethylsilyl-1,5-cyclooctadiene)-palladium(II)

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Abstract

There are two independent molecules of $[PdCl_2(C_{11}H_{20}Si)]$ in the asymmetric unit. The coordination geometry about Pd^{II} is square planar. The structure exhibits positional disorder. The silyl substitution at the vinylic position is found to cause a lengthening of the metal–olefin bond.

Comment

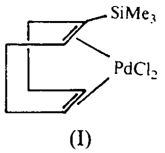
A substituent on a C═C double bond modifies the available π-electronic charge and affects olefin–

π-metal coordination (Ittel & Ibers, 1976). An Si moiety at a vinylic position is known to bring about major changes in the properties of the double bond (Weber, 1983; Bassindale & Taylor, 1989; Panek, 1991) by the donor–acceptor interaction of the silicon orbitals (Goirdan, 1983). The influence of Si is also observed in π-transition-metal complexes where it causes strengthening (Fitch, Flores & George, 1971; Fitch, Chan & Froehlich, 1978; Fitch & Osterloh, 1981) or weakening (Fitch & Herbold, 1970) of the metal–olefin coordination bond relative to its unsilylated analogue. The reactivity of the Si—C bond in a vinylsilane is modified by complexation with a transition metal and it is speculated in this connection that a direct Si—*M* π interaction may occur (Haiduc & Popa, 1977).

In addition to electronic effects, steric factors (Hwu & Wang, 1989) are also important when the bulky trimethylsilyl (tms) group is present at the α position of the coordinating double bond.

1-Trimethylsilyl-1,5-cyclooctadiene (tms-cod) is an ideal chelating ligand for direct comparison of the coordinating characteristics of an α-silylated C=C bond with those of the unsilylated double bond within tms-cod itself, as well as with those of the coordinated double bonds of the simple 1,5-cyclooctadiene (cod). Molecular and crystal structures of cod complexes of Pd with different anionic ligands have been determined in order to understand the nature of the bonding and conformational features of the ligands (Rettig, Wing & Weiger, 1981; Albeniz, Espinet, Jeannin, Lesvisalles & Mann, 1990). Spectral data of several complexes of tms-cod that we reported recently (Bandodakar & Nagendrappa, 1992) have revealed certain structural features which are indicative of the formation of a relatively weaker bond by the silylated double bond.

With a view to obtain detailed information on the comparative bonding characteristics of silylated and unsilylated double bonds, as well as on the conformation of cod as modified by the tms group and other structural parameters, we have carried out a single-crystal X-ray analysis of the tms-cod-$PdCl_2$ complex, (I); the results are reported here.



(I)

The positional parameters for all the non-H atoms, including those for the minority position (starred) of the two molecules, are recorded in Table 1. The coordination geometry about Pd is square planar. There are no differences between the molecules *A* and *B* with regard to the conformations of the tms-cod rings; each has a C_2 twist-boat conformation, as does cod both in gaseous phase and in most of its metal complexes (Rettig, Wing & Weiger, 1981). An *ORTEP*II (Johnson, 1976) drawing of one of the molecules, *A*, with atom-numbering scheme, is shown in Fig. 1.

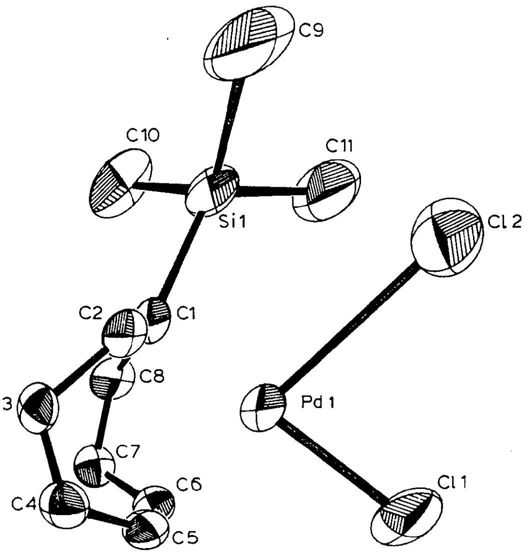


Fig. 1. *ORTEP*II plot (Johnson, 1976) of molecule *A* of tms-cod-$PdCl_2$. Displacement ellipsoids are shown at the 50% probability level.

There are two independent molecules in the asymmetric unit, both of which exhibit positional disorder. The structure was refined with partial occupancy factors of 0.9 (major) and 0.1 (minor) assigned to the disordered atoms. The major and minor atoms were found to be related by mirror symmetry with the mirror at $y = \frac{1}{4}$ passing through the atoms C(1), C(6) and Si. Fig. 2 (viewed down the *x* axis) displays this relation for molecule *A*. The positions corresponding to the minority atoms produce extremely short contacts with those of the majority atoms. We believe that the observed disorder is more likely to be static than dynamic, as such large-scale conformational motion would be prohibitive in the lattice. However, further study at low temperature is warranted to confirm this tentative conclusion.

One of the objectives of studying the diolefin–metal complexes is to obtain information on how the changes in geometric arrangement of the coordinated olefin can affect the metal–olefin bond strength. The latter is also influenced by the electronic and steric contributions from a vinylic substituent. A primary parameter that reflects the degree of this olefin–π-metal interaction is bond distance. Table 3 lists the distances between the metal atom and the mid-

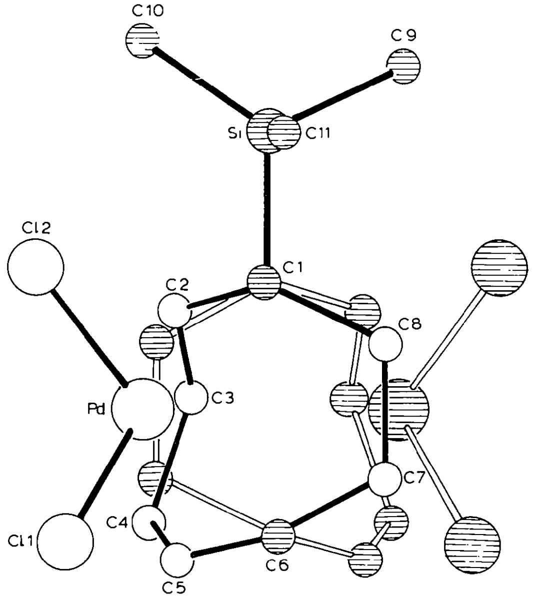


Fig. 2. *PLUTO* diagram (Motherwell & Clegg, 1978) of molecule *A* (viewed down the *x* axis) displaying the relation between the disordered atoms. The mirror plane passes through the Si, C1 and C6 atoms. The open and shaded spheres represent positions corresponding to majority and minority atoms, respectively.

points of the C=C bonds in tms-cod with those of the cod-Pd^{II} complex. This distance in the tms-cod-Pd^{II} complex corresponding to the silyl-substituted double bond is about 0.05 Å longer than the distance involving the unsilylated double bond. The latter compares well with the distance between the metal and the double-bond midpoint [2.09 (1) Å] in the cod-Pd^{II} complex. In other words, the silyl moiety causes lengthening of the metal–olefin bond. Therefore, steric factors seems to be playing a more important role than electronic. That there is less interaction between C(1) and Pd is also reflected in the ^{13}C NMR spectrum (Bandodakar & Nagendrappa, 1992) of the Pd^{II} complex which shows practically no change in the chemical shift of C(1).

The Si$\cdots$Pd distance [3.56 (1) Å in molecule *A* and 3.58 (1) Å in molecule *B*] indicates that there is no interaction between the two atoms in the complex as speculated for π-olefin complexes (Haiduc & Popa, 1977). The C=C bond distance in the complex compared to that in the free olefine is also a measure of the metal–olefin bond strength. The C(1)=C(2) bond distance is not significantly different from that in vinyl silanes, but the C(5)=C(6) bond distance is considerably lengthened.

Experimental

Crystal data

$[PdCl_2(C_{11}H_{20}Si)]$
$M_r = 357.5$
Monoclinic
$P2_1/a$
$a = 12.536$ (1) Å
$b = 12.867$ (2) Å
$c = 17.759$ (2) Å
$\beta = 93.01$ (1)°
$V = 2860.7$ (3) Å^3
$Z = 8$
$D_x = 1.659$ Mg m^{-3}
$D_m = 1.657$ Mg m^{-3}
D_m measured by flotation in aqueous KI solution

Mo $K\alpha$ radiation
$\lambda = 0.71079$ Å
Cell parameters from 25 reflections
$\theta = 9.0$–$15.0°$
$\mu = 166$ mm^{-1}
$T = 293$ K
Rectangular
0.275 × 0.275 × 0.025 mm
Colourless
Crystal source: chloroform–ethanol (1:1) mixture

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4958 measured reflections
4284 independent reflections
4275 observed reflections [$I > 1.5\sigma(I)$]

$R_{int} = 0.04$
$\theta_{max} = 25°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity variation: 2%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.044$
$S = 0.89$
4275 reflections
457 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(|F_o|) + 0.0033|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.08$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Pd*A*	0.4965 (1)	0.1368 (1)	0.1539 (1)	0.0282 (1)
Cl(1A)	0.6170 (1)	0.0688 (1)	0.0722 (1)	0.0453 (1)
Cl(2*A*)	0.5745 (1)	0.0397 (1)	0.2501 (1)	0.0511 (1)
SiA	0.4803 (1)	0.2497 (1)	0.3358 (1)	0.0371 (1)
C(1*A*)	0.4183 (3)	0.2468 (3)	0.2348 (2)	0.0313 (1)
C(2*A*)	0.3469 (4)	0.1678 (4)	0.2122 (3)	0.0341 (1)
C(3*A*)	0.2541 (4)	0.1805 (4)	0.1555 (3)	0.0416 (2)
C(4*A*)	0.2781 (4)	0.1441 (4)	0.0762 (3)	0.0433 (2)
C(5*A*)	0.3909 (4)	0.1680 (4)	0.0547 (3)	0.0376 (2)
C(6*A*)	0.4470 (3)	0.2559 (3)	0.0714 (2)	0.0377 (1)
C(7*A*)	0.4027 (4)	0.3516 (4)	0.1085 (3)	0.0445 (2)
C(8*A*)	0.4214 (5)	0.3514 (4)	0.1964 (3)	0.0438 (2)
C(9*A*)	0.4224 (6)	0.3695 (4)	0.3761 (4)	0.0690 (2)
C(10*A*)	0.4341 (5)	0.1363 (4)	0.3910 (3)	0.0596 (2)
C(11*A*)	0.6301 (4)	0.2644 (4)	0.3407 (3)	0.0547 (2)
Pd*B*	0.7799	0.1517 (1)	0.8034 (1)	0.0310 (1)
Cl(1*B*)	0.8440 (1)	0.0367 (1)	0.7181 (1)	0.0590 (1)
Cl(2*B*)	0.9033 (1)	0.0880 (1)	0.8938 (1)	0.0531 (1)
SiB	0.7494 (1)	0.2439 (1)	0.6133 (1)	0.0404 (1)
C(1*B*)	0.6968 (3)	0.2511 (3)	0.7125 (2)	0.0313 (1)
C(2*B*)	0.6256 (4)	0.1804 (3)	0.7389 (3)	0.0328 (1)
C(3*B*)	0.5398 (3)	0.2047 (4)	0.7935 (3)	0.0397 (2)
C(4*B*)	0.5706 (4)	0.1767 (4)	0.8745 (3)	0.0425 (2)
C(5*B*)	0.6856 (4)	0.2018 (4)	0.8968 (3)	0.0398 (2)
C(6*B*)	0.7423 (4)	0.2870 (4)	0.8733 (3)	0.0396 (1)
C(7*B*)	0.6958 (4)	0.3750 (4)	0.8282 (3)	0.0440 (2)
C(8*B*)	0.7010 (4)	0.3624 (4)	0.7427 (3)	0.0395 (2)
C(9*B*)	0.8961 (4)	0.2578 (5)	0.6127 (3)	0.0653 (2)

C(10B)	0.6892 (6)	0.3583 (5)	0.5621 (3)	0.0666 (2)
C(11B)	0.7001 (5)	0.1256 (5)	0.5628 (3)	0.0664 (2)
Pd1*	0.4959	0.3635	0.1555	0.0266
Cl(1A)*	0.6168	0.4301	0.0723	0.0432
Cl(2A)*	0.5747	0.4576	0.2523	0.0467
C(2A)*	0.3483	0.3341	0.2135	0.0585
C(3A)*	0.2522	0.3200	0.1543	0.0316
C(4A)*	0.2797	0.3575	0.0748	0.0358
C(5A)*	0.3915	0.3337	0.0536	0.0577
C(7A)*	0.4048	0.1474	0.1072	0.0618
C(8A)*	0.4234	0.1475	0.1962	0.0354
Pd2*	0.7805	0.3475	0.8041	0.0289
Cl(2B)*	0.9042	0.4087	0.8976	0.0445
Cl(1B)*	0.8464	0.4586	0.7163	0.0566
C(2B)*	0.6249	0.3214	0.7374	0.0519
C(3B)*	0.5369	0.2951	0.7929	0.0032
C(4B)*	0.5710	0.3234	0.8760	0.0558
C(5B)*	0.6866	0.2930	0.8979	0.0361
C(6B)*	0.7405	0.2238	0.8745	0.0177
C(7B)*	0.6974	0.1245	0.8280	0.0619
C(8B)*	0.7017	0.1374	0.7420	0.0394

* Minor occupancy factor = 0.1. Major and minor are related by mirror symmetry with the mirror plane at $y = \frac{1}{4}$ passing through C(1), C(6) and Si.

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

PdA—Cl(1A)	2.320 (1)	PdB—Cl(1B)	2.293 (2)
PdA—Cl(2A)	2.294 (2)	PdB—Cl(2B)	2.320 (2)
PdA—C(1A)	2.275 (4)	PdB—C(1B)	2.269 (4)
PdA—C(2A)	2.225 (5)	PdB—C(2B)	2.227 (5)
PdA—C(5A)	2.185 (5)	PdB—C(5B)	2.184 (5)
PdA—C(6A)	2.187 (4)	PdB—C(6B)	2.204 (5)
SiA—C(1A)	1.917 (4)	SiB—C(1B)	1.915 (4)
SiA—C(9A)	1.863 (6)	SiB—C(9B)	1.848 (5)
SiA—C(10A)	1.867 (6)	SiB—C(10B)	1.868 (7)
SiA—C(11A)	1.885 (5)	SiB—C(11B)	1.856 (6)
C(1A)—C(2A)	1.399 (6)	C(1B)—C(2B)	1.374 (6)
C(1A)—C(8A)	1.510 (6)	C(1B)—C(8B)	1.529 (6)
C(2A)—C(3A)	1.507 (7)	C(2B)—C(3B)	1.518 (7)
C(3A)—C(4A)	1.529 (7)	C(3B)—C(4B)	1.513 (7)
C(4A)—C(5A)	1.515 (7)	C(4B)—C(5B)	1.510 (7)
C(5A)—C(6A)	1.356 (6)	C(5B)—C(6B)	1.383 (7)
C(6A)—C(7A)	1.516 (6)	C(6B)—C(7B)	1.488 (7)
C(7A)—C(8A)	1.566 (8)	C(7B)—C(8B)	1.532 (8)
Cl(1A)—PdA—Cl(2A)	89.7 (1)	Cl(1B)—PdB—Cl(2B)	89.1 (1)
Cl(1A)—PdA—C(1A)	161.0 (1)	Cl(1B)—PdB—C(1B)	93.3 (1)
Cl(1A)—PdA—C(2A)	162.0 (1)	Cl(1B)—PdB—C(2B)	95.3 (1)
Cl(1A)—PdA—C(5A)	87.2 (1)	Cl(1B)—PdB—C(5B)	156.2 (1)
Cl(1A)—PdA—C(6A)	90.9 (1)	C(10B)—SiB—C11B	107.2 (3)
Cl(2A)—PdA—C(1A)	92.8 (1)	PdB—C(1B)—SiB	117.4 (2)
Cl(2A)—PdA—C(2A)	95.0 (1)	PdB—C(1B)—C(2B)	70.5 (3)
Cl(2A)—PdA—C(5A)	156.5 (1)	PdB—C(1B)—C(8B)	105.8 (3)
Cl(2A)—PdA—C(6A)	167.3 (1)	Cl(1B)—PdB—C(6B)	167.1 (1)
C(1A)—PdA—C(2A)	36.2 (2)	Cl(2B)—PdB—C(1B)	162.9 (1)
C(1A)—PdA—C(5A)	97.6 (2)	Cl(2B)—PdB—C(2B)	160.8 (1)
C(1A)—PdA—C(6A)	82.6 (1)	Cl(2B)—PdB—C(5B)	86.9 (1)
C(2A)—PdA—C(5A)	81.5 (2)	Cl(2B)—PdB—C(6B)	92.5 (1)
C(2A)—PdA—C(6A)	88.3 (2)	C(1B)—PdB—C(2B)	35.6 (2)
C(5A)—PdA—C(6A)	36.1 (2)	C(1B)—PdB—C(5B)	97.3 (2)
C(1A)—SiA—C(9A)	103.2 (2)	C(1B)—PdB—C(6B)	81.5 (2)
C(1A)—SiA—C(10A)	110.8 (2)	C(2B)—PdB—C(5B)	81.5 (2)
C(1A)—SiA—C(11A)	113.5 (2)	C(2B)—PdB—C(6B)	87.3 (2)
C(9A)—SiA—C(10A)	107.9 (3)	C(5B)—PdB—C(6B)	36.7 (2)
C(9A)—SiA—C(11A)	107.9 (3)	C(1B)—SiB—C(9B)	113.0 (2)
C(10A)—SiA—C(11A)	113.0 (2)	C(1B)—SiB—C(10B)	105.1 (2)
PdA—C(1A)—SiA	115.8 (2)	C(1B)—SiB—C(11B)	111.2 (2)
PdA—C(1A)—C(2A)	70.0 (3)	C(9B)—SiB—C(10B)	107.3 (3)
PdA—C(1A)—C(8A)	104.3 (3)	C(9B)—SiB—C(11B)	112.5 (3)
SiA—C(1A)—C(2A)	120.3 (3)	SiB—C(1B)—C(2B)	122.9 (3)
SiA—C(1A)—C(8A)	112.7 (3)	SiB—C(1B)—C(8B)	111.1 (3)
C(2A)—C(1A)—C(8A)	123.3 (4)	C(2B)—C(1B)—C(8B)	120.8 (4)
PdA—C(2A)—C(1A)	73.8 (3)	PdB—C(2B)—C(1B)	73.9 (3)
PdA—C(2A)—C(3A)	110.4 (3)	PdB—C(2B)—C(3B)	109.3 (3)
C(1A)—C(2A)—C(3A)	124.9 (4)	C(1B)—C(2B)—C(3B)	125.2 (4)
C(2A)—C(3A)—C(4A)	113.6 (4)	C(2B)—C(3B)—C(4B)	113.8 (4)
C(3A)—C(4A)—C(5A)	113.7 (4)	C(3B)—C(4B)—C(5B)	113.0 (4)
PdA—C(5A)—C(4A)	107.1 (3)	PdB—C(5B)—C(4B)	106.6 (3)
PdA—C(5A)—C(6A)	72.0 (3)	PdB—C(5B)—C(6B)	72.4 (3)
C(4A)—C(5A)—C(6A)	126.4 (4)	C(4B)—C(5B)—C(6B)	126.1 (5)
PdA—C(6A)—C(5A)	71.8 (3)	PdB—C(6B)—C(5B)	70.9 (3)
PdA—C(6A)—C(7A)	112.1 (3)	PdB—C(6B)—C(7B)	112.8 (3)
C(5A)—C(6A)—C(7A)	125.1 (4)	C(5B)—C(6B)—C(7B)	124.9 (5)
C(6A)—C(7A)—C(8A)	113.1 (4)	C(6B)—C(7B)—C(8B)	114.7 (4)
C(1A)—C(8A)—C(7A)	116.5 (4)	C(1B)—C(8B)—C(7B)	116.4 (4)
C(1A)—C(2A)—C(3A)—C(4A)	97.7 (6)		
C(2A)—C(3A)—C(4A)—C(5A)	−37.0 (6)		
C(3A)—C(4A)—C(5A)—C(6A)	−39.4 (7)		
C(4A)—C(5A)—C(6A)—C(7A)	−6.3 (7)		
C(5A)—C(6A)—C(7A)—C(8A)	93.2 (5)		
C(6A)—C(7A)—C(8A)—C(1A)	−33.9 (6)		
C(2A)—C(1A)—C(8A)—C(7A)	−37.9 (6)		
C(1B)—C(2B)—C(3B)—C(4B)	−99.2 (5)		
C(2B)—C(3B)—C(4B)—C(5B)	40.6 (6)		
C(3B)—C(4B)—C(5B)—C(6B)	36.3 (7)		
C(4B)—C(5B)—C(6B)—C(7B)	7.0 (8)		
C(5B)—C(6B)—C(7B)—C(8B)	−92.2 (6)		
C(6B)—C(7B)—C(8B)—C(1B)	30.4 (6)		
C(2B)—C(1B)—C(8B)—C(7B)	43.3 (6)		

Table 3. *Selected distances* (Å) *and angles* (°) *in the coordination polyhedra*

	tms-cod-$PdCl_2$		
	A	*B*	cod-$PdCl_2$
Pd–olefin-midpoint distance	2.14 (1) 2.07 (1)	2.14 (1) 2.04 (1)	2.09 (1) 2.09 (1)
Olefin-midpoint–Pd–olefin-midpoint angle	87.2 (3)	86.6 (3)	86.3 (2)
Cl—Pd—Cl angle	89.7 (1)	89.1 (1)	90.31 (5)

Program used to solve structure: *SHELXS86* (Sheldrick, 1985). Program used to refine structure: *SHELX76* (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving minor occupancy positions and a stereoview of the packing in the crystal lattice have been deposited with the IUCr (Reference: AB1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclopentadienyl(thioacetamide-*S*)-bis(triphenylphosphine-*P*)ruthenium(II) Tetrafluoroborate

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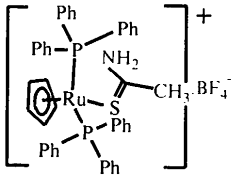
Abstract

The title compound $[\mathrm{Ru}(C_5H_5)(C_2H_5NS)(C_{18}H_{15}P)_2]BF_4$ crystallizes in the space group $P2_1/c$. The Ru atom has pseudotetrahedral coordination geometry formed by the cyclopentadienyl centroid, the two PPh_3 ligands and the S atom of the neutral thioacetamide molecule. The Ru—S and C=S distances are 2.3820 (13) and 1.671 (5) Å, respectively, and the Ru—S=C angle is 116.3 (2)°. The Ru atom is at a distance of 0.405 (9) Å from the plane formed by the atoms of the thioacetamide group.

Comment

Structural parameters of transition-metal sulfides are of interest because these complexes are employed in model studies of desulfurization catalysts. The structure determination of the title compound (1) was undertaken in order to compare the structural parameters of the small S=C*R*$_2$ ligand with those of previously reported complexes, namely, two complexes of dithiooxamide, a bridging Ru′–dtoxa–Ru′ unit (I) and a chelating dtoxa–Ru′ complex (II), where Ru′ is $\mathrm{CpRu(PPh_3)_2^+}$ and dtoxa is $NH_2C(S)C(S)NH_2$ (Draganjac, Minick & Cordes, 1993), an Ru complex of thiobenzaldehyde (III) (Schenk, Stur & Dombrowski, 1992) and an Ru′ complex of 1-propanethiol (IV) (Amarasekera & Rauchfuss, 1989). The small thioacetamide molecule as a fourth unit in a tetrahedral complex with three other large ligands might be considered to show Ru—S parameters which are very nearly free of any steric perturbations.



(1)

The Ru—S distance [2.3820 (13) Å] in the title complex is comparable to both the average Ru—S distance involving the bridging unit of (I) and the Ru—S distance involving the mercapto unit of (IV) [2.372 (6) and

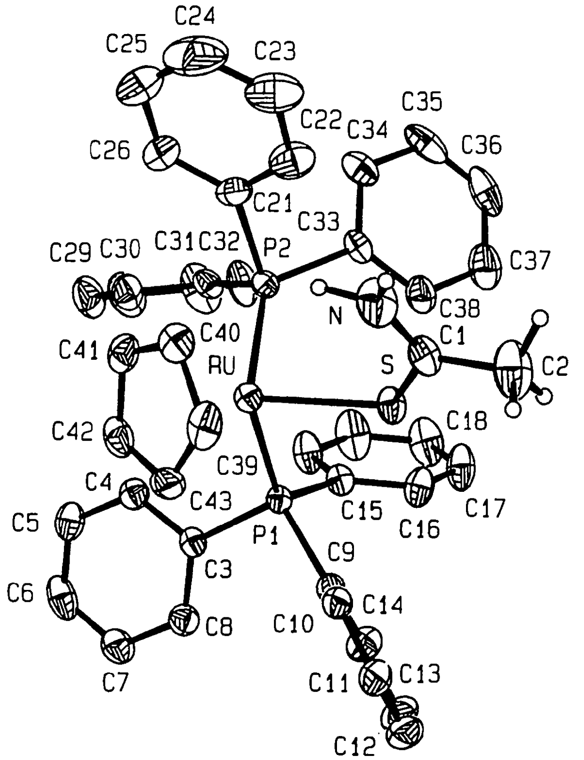


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the cation with 30% probability ellipsoids showing the numbering scheme. H atoms have been omitted for clarity.

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