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THE MOLECULAR STRUCTURE OF CHLOROTHIOMETHOXYMETHYLTRIPHENYLPHOSPHINEPALLADIUM(II) AT —160 AND 20°C

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Summary

The molecular structure of [$PdCl(CH_2SCH_3)(PPh_3)$] has been determined from three-dimensional X-ray diffraction data collected at both —160 and 20°C. The crystal belongs to the monoclinic system, space group $P2_1/c$, with four formula units in a cell of dimensions: *a* 11.398(2), *b* 9.788(1), *c* 17.267(2) Å and *β* 95.38(1)° at —160°C; *a* 11.454(3), *b* 9.880(2), *c* 17.459(2) Å and *β* 95.84(1)° at 20°C. The structure was solved by the conventional heavy atom method, and refined by the least-squares procedure to $R = 0.049$ (—160°C) and 0.068 (20°C) for observed reflections. No essential difference is observed between molecular structures at —160 and 20°C. The geometry around the palladium atom is square-planar. The CH_2SCH_3 group, bonded to the palladium atom through Pd—C and Pd—S bonds, forms a metallocyclic three-membered ring [Pd—C(1) 2.042(6), Pd—S 2.371(1), S—C(1) 1.756(6) and S—C(2) 1.807(7) Å, Pd—C(1)—S 76.9(2), Pd—C(1)—H 113(3) and 122(4)°, S—C(1)—H 115(3) and 112(4) and H—C(1)—H 113(5)° at —160°C].

Introduction

Among many studies of the metal—sulfur bonds, the preparation and the molecular structure of a molybdenum complex involving a thiomethoxymethyl (CH_2SCH_3) group have been reported [1,2]. It has been shown hitherto that two limiting modes are possible in the bonding of the CH_2SCH_3 group to the metal atom. One involves a carbon—sulfur double bond π-bonded to the metal atom. The CH_2SCH_3 group must be more stable in the form of the positively charged methylenemethylsulfonium ion and behaves as a two-electron ligand. The other type is the formation of a three-membered metal—carbon—sulfur ring containing the metal—carbon σ-bond and the donation of the sulfur to the metal atom. The CH_2SCH_3 group functions as a neutral three-electron ligand. In addition to these types, a third mode which has only the metal—carbon σ-bond also is possible. In order to make detailed discussions of the bonding scheme of the CH_2SCH_3 group to the metal atom, the determination of the precise molecular structure, including the locations of the methylene hydrogen atoms is indispensable.

Very recently, novel palladium complexes containing a CH_2SCH_3 group have been prepared by Okawara and his coworkers of Osaka University [3,4].

$$\begin{tikzcd} Pd(PPh_3)_4 + ClCH_2SCH_3 \arrow[r] & {[PdCl(CH_2SCH_3)(PPh_3)_2]} \arrow[d, shift right, "\text{recrystallization }(-Ph_3P)"'] \\ & {[PdCl(CH_2SCH_3)(PPh_3)]} \arrow[u, shift right, "(+Ph_3P)"'] \end{tikzcd}$$

In order to obtain information about how the CH_2SCH_3 group is bonded to the palladium atom, a series of X-ray crystal structure analyses of CH_2SCH_3-containing palladium complexes have been carried out. This paper describes the precise determination of the molecular structure of chlorothiomethoxymethyltriphenylphosphinepalladium(II) $[PdCl(CH_2SCH_3)(PPh_3)]$ at −160°C. The molecular structure at room temperature (20°C) also has been determined and is compared with the low temperature structure.

Experimental

Yellow prismatic crystals of $[PdCl(CH_2SCH_3)(PPh_3)]$ were kindly supplied by Professor R. Okawara and his coworkers. Preliminary oscillation and Weissenberg photographs showed the crystal to be monoclinic, and the systematic absences of reflections, $0k0$ with k odd and $h0l$ with l odd, determined the space group as $P2_1/c$. Unit-cell parameters were determined accurately by a least-squares fit of high order reflections. Crystal data are shown in Table 1.

Measurements of unit-cell parameters and integrated intensities were made on a Rigaku automated, four-circle, single-crystal diffractometer. A crystal with approximate dimensions 0.2 × 0.2 × 0.2 mm was used for the intensity measure-

TABLE 1

CRYSTAL DATA

$C_{20}H_{20}ClPPdS$, mol. wt. 465.28, $F(000)$ = 936
Monoclinic, Space group $P2_1/c$

	−160°C	20°C
a (Å)	11.398(2)	11.454(3)
b (Å)	9.788(1)	9.880(2)
c (Å)	17.267(2)	17.459(2)
β (°)	95.38(1)	95.84(1)
U (Å^3)	1917.9(5)	1965.5(7)
μ(Mo-K_α) (cm^{-1})	12.7	12.1
D_c (g cm^{-3})	1.612	1.573
D_m [a] (g cm^{-3})		1.57
Z	4	4

[a] By flotation in carbon tetrachloride/n-hexane at 25°C.

ment. The required low temperature was attained by the gas flow method using liquid nitrogen. Totals of 4183 (at —160°C) and 4308 (at 20°C) reflections with 2θ less than 54° were collected by the θ—2θ scan technique using graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å). The scan width was $\Delta\theta = (1.0 + 0.35 \tan\theta)°$ and the scan speed was 4° min^{-1}. The background intensities were measured for 5 st at both ends of a scan. 684 (at —160°C) and 1099 (at 20°C) reflections were considered as unobserved. Three standard reflections (062, 40$\bar{8}$ and 800) were measured at regular intervals to monitor crystal stability and orientation. No intensity decrease was observed during the experiment. Corrections for the usual Lorentz and polarization effects were carried out, while no correction for absorption and extinction was made $[(\mu R)_{max} = 0.2]$.

Structure solution and refinement

The structure was solved by the conventional heavy atom method using the intensity data obtained at —160°C. The coordinates of the palladium and phosphorus atoms were determined from a three-dimensional Patterson map. The locations of all the remaining non-hydrogen atoms were determined from the subsequent Fourier map based on these atomic positions.

The refinements of the structures at low and room temperatures were carried out in parallel with each other by the block-diagonal least-squares procedure using the HBLS-V program [5]: the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Several cycles of isotropic refinement reduced the R indices ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) to 0.067 (at —160°C) and 0.098 (at 20°C) for non-zero reflections. No abnormal thermal factors were observed. A few more cycles of anisotropic refinements reduced the R values to 0.057 and 0.075. At this stage, all hydrogen atoms for both low and room temperature structures were found reasonably from difference Fourier maps, parameters of which were refined isotropically in the subsequent refinements. The final R indices are 0.049 and 0.068 for non-zero (0.074 and 0.123 for all) reflections at —160 and 20°C, respectively. The weighting scheme used was $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$ for $|F_o| > 0$ and $w = c$ for $|F_o| = 0$, where σ_{cs} is the value obtained from the counting statistics and values of a, b and c used at the final refinements are 0.0749, 0.0002 and 0.0233 (at —160°C) and 0.1065, —0.0003 and 0.0249 (at 20°C). The final weighted R indices ($R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$) are 0.061 and 0.075. The atomic scattering factors used were taken from those of Stewart et al. [6] for hydrogen atoms and those of Hanson et al. [7] for non-hydrogen atoms.

The final atomic positional and thermal parameters at —160 and 20°C are listed in Tables 2 and 3. A table of observed and calculated structure factors is available *.

(continued on p. 58)

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* The table of structure factors has been deposited as NAPS Document No. 03050 (44 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting \$ for photocopies or \$ for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

FINAL ATOMIC PARAMETERS OF NON-HYDROGEN ATOMS

Positional parameters in fraction of cell edges and anisotropic thermal parameters in the form of $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl\}$. Estimated standard deviations in parentheses (a) −160°C, (b) 20°C.

(a)

ATOM	X	Y	Z	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
PD	.17497(3)	-.00811(4)	.03909(2)	.00264(2)	.00353(3)	.001134(11)	-.00037(5)	.00052(3)	-.00026(3)
CL	.17651(11)	-.09190(13)	.16996(7)	.00377(10)	.00377(12)	.00124 (4)	-.00042(18)	.00078(10)	.00086(11)
S	.07963(12)	-.15675(14)	-.05533(8)	.00308(10)	.00454(13)	.00157 (4)	-.0011 (2)	.00022(10)	-.00148(13)
P	.27864(11)	.10732(13)	.06347(7)	.00222(9)	.00287(12)	.00074 (4)	-.00007(17)	.00036(9)	-.00007(11)
C(1)	.1393 (5)	.0017 (6)	-.0789 (3)	.0047 (4)	.0052 (6)	.00106 (16)	-.0017 (9)	.0000 (4)	-.0008 (5)
C(2)	.1890 (6)	-.2790 (7)	-.0800 (4)	.0068 (6)	.0065 (7)	.0025 (2)	.0037 (10)	.0022 (6)	-.0017 (6)
C(11)	.3249 (5)	.2762 (5)	-.0214 (3)	.0039 (4)	.0033 (5)	.00091 (15)	.0006 (7)	.0011 (4)	.0001 (4)
C(12)	.4427 (5)	.2996 (6)	-.0328 (3)	.0037 (4)	.0064 (6)	.00143 (18)	-.0023 (8)	.0002 (4)	-.0002 (5)
C(13)	.4727 (5)	.3650 (6)	-.1001 (3)	.0051 (5)	.0070 (7)	.00141 (18)	-.0036 (9)	.0018 (5)	.0007 (6)
C(14)	.3852 (5)	.4095 (6)	-.1555 (3)	.0064 (5)	.0044 (6)	.00128 (18)	-.0030 (9)	.0014 (5)	.0005 (5)
C(15)	.2671 (5)	.3876 (6)	-.1451 (3)	.0055 (5)	.0047 (6)	.00129 (17)	.0001 (9)	.0002 (5)	.0001 (5)
C(16)	.2364 (5)	.3205 (6)	-.0790 (3)	.0041 (4)	.0046 (5)	.00132 (17)	.0007 (8)	.0008 (4)	-.0004 (5)
C(21)	.4150 (4)	.1553 (5)	.1241 (3)	.0029 (4)	.0043 (5)	.00085 (15)	-.0015 (7)	.0008 (4)	.0002 (5)
C(22)	.4713 (5)	.2568 (5)	.1707 (3)	.0032 (4)	.0047 (5)	.00121 (16)	-.0004 (8)	-.0000 (4)	.0005 (5)
C(23)	.5763 (5)	.2298 (6)	.2162 (3)	.0039 (4)	.0059 (6)	.00134 (17)	-.0007 (8)	-.0003 (4)	-.0010 (5)
C(24)	.6254 (5)	.0997 (6)	.2148 (3)	.0027 (4)	.0080 (7)	.00120 (17)	.0005 (8)	.0002 (4)	.0014 (5)
C(25)	.5694 (4)	-.0031 (6)	.1684 (3)	.0028 (4)	.0050 (5)	.00182 (18)	.0021 (8)	.0017 (4)	.0010 (5)
C(26)	.4650 (5)	.0259 (5)	.1237 (3)	.0036 (4)	.0040 (5)	.00125 (16)	-.0002 (7)	.0001 (4)	.0007 (5)
C(31)	.2019 (4)	.3189 (5)	.1139 (3)	.0027 (4)	.0037 (5)	.00124 (16)	.0013 (7)	-.0004 (4)	-.0011 (5)
C(32)	.1966 (5)	.4553 (6)	.0922 (3)	.0052 (5)	.0045 (6)	.00151 (18)	-.0007 (8)	.0007 (5)	-.0005 (5)
C(33)	.1311 (6)	.5501 (6)	.1301 (3)	.0059 (5)	.0042 (6)	.0019 (2)	.0022 (9)	-.0013 (5)	-.0014 (5)
C(34)	.0717 (5)	.5078 (6)	.1917 (3)	.0037 (4)	.0057 (6)	.0022 (2)	.0057 (9)	-.0009 (4)	-.0036 (6)
C(35)	.0773 (5)	.3718 (7)	.2159 (3)	.0035 (4)	.0097 (8)	.00130 (18)	-.0010 (9)	.0008 (4)	-.0026 (6)
C(36)	.1418 (4)	.2786 (5)	.1772 (3)	.0031 (4)	.0042 (5)	.00138 (17)	-.0009 (7)	.0004 (4)	-.0008 (5)

(b)

ATOM	X	Y	Z	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
PD	.17496(5)	-.00893(6)	.04059(3)	.00592(4)	.00789(5)	.002745(18)	-.00114(9)	.00120(4)	-.00070(6)
CL	.1754 (2)	-.0940 (2)	.16917(12)	.0105 (2)	.0098 (2)	.00310 (7)	-.0019 (4)	.0019 (2)	.0018 (2)
S	.0858 (2)	-.1596 (2)	-.05282(14)	.0083 (2)	.0120 (3)	.00418 (9)	-.0049 (4)	.0005 (2)	-.0049 (3)
P	.27588(16)	.18644(19)	.06468(10)	.00533(14)	.0067 (2)	.00201 (6)	-.0034 (3)	.00031(15)	-.00018(17)
C(1)	.1417 (7)	-.0046 (9)	-.0765 (5)	.0085 (7)	.0122 (11)	.0032 (3)	-.0028 (16)	-.0011 (7)	-.0034 (10)
C(2)	.1996 (12)	-.2777 (12)	-.0718 (7)	.0203 (17)	.0153 (16)	.0064 (6)	.001 (3)	.0063 (16)	-.0066 (16)
C(11)	.3192 (7)	.2743 (7)	-.0191 (4)	.0079 (7)	.0074 (8)	.0025 (3)	-.0017 (12)	.0009 (7)	-.0003 (7)
C(12)	.4337 (8)	.2989 (10)	-.0306 (4)	.0088 (8)	.0152 (12)	.0024 (3)	-.0013 (16)	.0016 (7)	.0010 (10)
C(13)	.4630 (9)	.3647 (11)	-.0971 (5)	.0116 (10)	.0183 (15)	.0042 (4)	-.010 (2)	.0062 (10)	.0014 (13)
C(14)	.3774 (9)	.4059 (10)	-.1510 (5)	.0145 (11)	.0133 (12)	.0028 (3)	-.002 (2)	.0057 (9)	.0019 (10)
C(15)	.2637 (9)	.3840 (9)	-.1408 (5)	.0137 (10)	.0093 (10)	.0025 (3)	.0031 (16)	-.0019 (9)	.0013 (9)
C(16)	.2329 (7)	.3172 (9)	-.0762 (5)	.0091 (8)	.0113 (10)	.0028 (3)	-.0001 (15)	-.0003 (8)	.0029 (9)
C(21)	.4116 (6)	.1566 (7)	.1246 (4)	.0047 (5)	.0086 (8)	.0021 (2)	-.0016 (11)	.0004 (6)	.0001 (7)
C(22)	.4668 (7)	.2573 (9)	.1714 (5)	.0072 (7)	.0106 (10)	.0032 (3)	-.0000 (14)	-.0006 (7)	-.0010 (9)
C(23)	.5712 (7)	.2303 (10)	.2171 (5)	.0062 (7)	.0157 (13)	.0038 (3)	.0049 (15)	-.0009 (8)	-.0022 (11)
C(24)	.6221 (7)	.1062 (10)	.2158 (5)	.0055 (7)	.0185 (14)	.0032 (3)	.0003 (16)	.0001 (7)	.0020 (11)
C(25)	.5691 (7)	.0154 (9)	.1697 (5)	.0076 (7)	.0121 (11)	.0044 (4)	.0090 (16)	.0021 (8)	.0024 (11)
C(26)	.4640 (7)	.0394 (8)	.1242 (5)	.0061 (6)	.0085 (9)	.0037 (3)	.0037 (12)	-.0001 (7)	.0012 (8)
C(31)	.1997 (6)	.3150 (7)	.1156 (4)	.0060 (6)	.0075 (9)	.0025 (2)	-.0004 (11)	-.0007 (6)	-.0011 (7)
C(32)	.1939 (8)	.4469 (9)	.0950 (5)	.0102 (9)	.0092 (10)	.0044 (4)	.0013 (15)	.0037 (9)	-.0010 (10)
C(33)	.1317 (9)	.5401 (10)	.1347 (6)	.0132 (11)	.0105 (11)	.0050 (4)	.0021 (18)	-.0009 (11)	.0004 (11)
C(34)	.0729 (7)	.4987 (10)	.1950 (5)	.0073 (7)	.0167 (14)	.0049 (4)	.0052 (18)	.0005 (8)	-.0089 (13)
C(35)	.0797 (8)	.3641 (10)	.2166 (5)	.0097 (9)	.0159 (14)	.0039 (4)	-.0032 (18)	.0036 (9)	-.0054 (12)
C(36)	.1415 (8)	.2758 (8)	.1765 (5)	.0099 (8)	.0081 (9)	.0035 (3)	.0013 (14)	.0026 (8)	-.0018 (9)

TABLE 3

FINAL ATOMIC PARAMETERS OF HYDROGEN ATOMS

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp\{-B(\sin\theta/\lambda)^2\}$

Atom	*X*	*Y*	*Z*	*B*
(a) —160°C				
H(12)	0.504(5)	0.274(6)	0.005(3)	1.1(10)
H(13)	0.555(5)	0.386(6)	—0.108(3)	1.9(12)
H(14)	0.400(6)	0.459(7)	—0.198(4)	2.6(14)
H(15)	0.203(6)	0.422(7)	—0.186(4)	3.1(15)
H(16)	0.159(5)	0.296(6)	—0.071(3)	1.1(11)
H(22)	0.439(5)	0.354(6)	0.166(3)	1.2(11)
H(23)	0.611(5)	0.288(6)	0.244(3)	1.5(12)
H(24)	0.699(5)	0.085(6)	0.247(3)	1.5(11)
H(25)	0.614(5)	—0.092(6)	0.165(3)	2.0(12)
H(26)	0.418(7)	—0.044(8)	0.094(5)	4.8(19)
H(32)	0.239(5)	0.484(6)	0.062(3)	2.0(13)
H(33)	0.132(6)	0.628(7)	0.119(4)	3.1(15)
H(34)	0.032(5)	0.564(6)	0.212(3)	1.9(12)
H(35)	0.035(5)	0.341(6)	0.262(3)	1.4(11)
H(36)	0.135(5)	0.191(6)	0.192(4)	2.3(13)
H(1A)	0.081(5)	0.072(6)	—0.095(3)	1.2(11)
H(1B)	0.203(6)	—0.008(7)	—0.115(4)	3.1(15)
H(2A)	0.254(6)	—0.243(8)	—0.068(4)	4.1(17)
H(2B)	0.183(7)	—0.295(8)	—0.133(5)	5.2(20)
H(2C)	0.159(6)	—0.368(8)	—0.059(4)	4.3(18)
(b) 20°C				
H(12)	0.491(5)	0.264(6)	0.008(4)	2.2(13)
H(13)	0.541(8)	0.390(10)	—0.095(6)	7.9(27)
H(14)	0.397(5)	0.450(7)	—0.197(4)	2.6(14)
H(15)	0.211(6)	0.415(8)	—0.171(4)	4.1(18)
H(16)	0.155(6)	0.297(8)	—0.067(4)	4.0(18)
H(22)	0.425(6)	0.340(7)	0.167(4)	3.6(17)
H(23)	0.609(6)	0.286(8)	0.239(4)	4.3(18)
H(24)	0.693(6)	0.091(7)	0.244(4)	2.8(15)
H(25)	0.595(7)	—0.073(8)	0.165(4)	4.6(19)
H(26)	0.422(6)	—0.044(7)	0.098(4)	3.5(17)
H(32)	0.238(6)	0.479(7)	0.061(4)	2.7(15)
H(33)	0.133(7)	0.624(8)	0.122(5)	5.1(20)
H(34)	0.035(7)	0.548(9)	0.213(5)	5.3(21)
H(35)	0.041(6)	0.338(8)	0.249(4)	4.2(18)
H(36)	0.148(7)	0.193(8)	0.189(4)	4.9(20)
H(1A)	0.084(7)	0.059(8)	—0.090(5)	5.0(20)
H(1B)	0.212(10)	0.014(12)	—0.086(7)	10.5(36)
H(2A)	0.259(8)	—0.251(10)	—0.040(5)	6.9(25)
H(2B)	0.198(7)	—0.306(8)	—0.114(4)	4.5(19)
H(2C)	0.159(11)	—0.365(14)	—0.043(8)	13.2(43)

Results and discussion

Figure 1 shows a perspective view of the molecule with atomic numbering. Figure 2 represents ORTEP drawings of the molecule with thermal ellipsoids enclosing 50% probability levels at —160 and 20°C. Bond lengths and bond angles, along with their estimated standard deviations, are given in Tables 4 and 5.

No essential difference is observed in molecular structures at —160 and 20°C

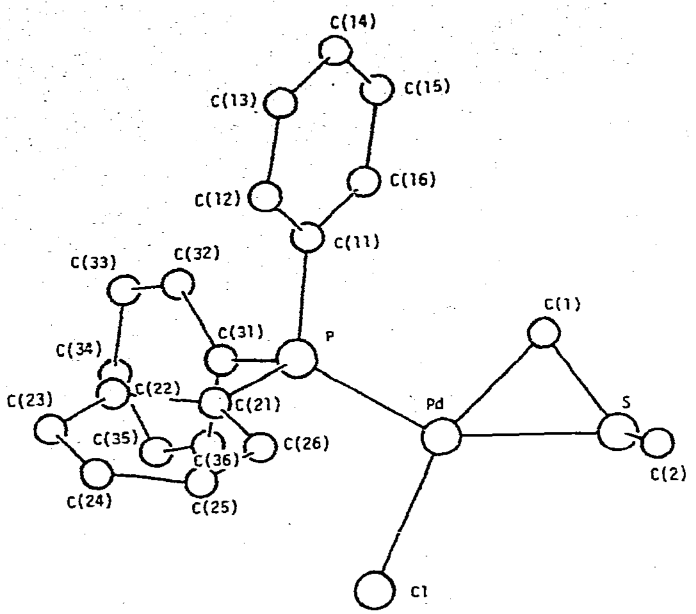
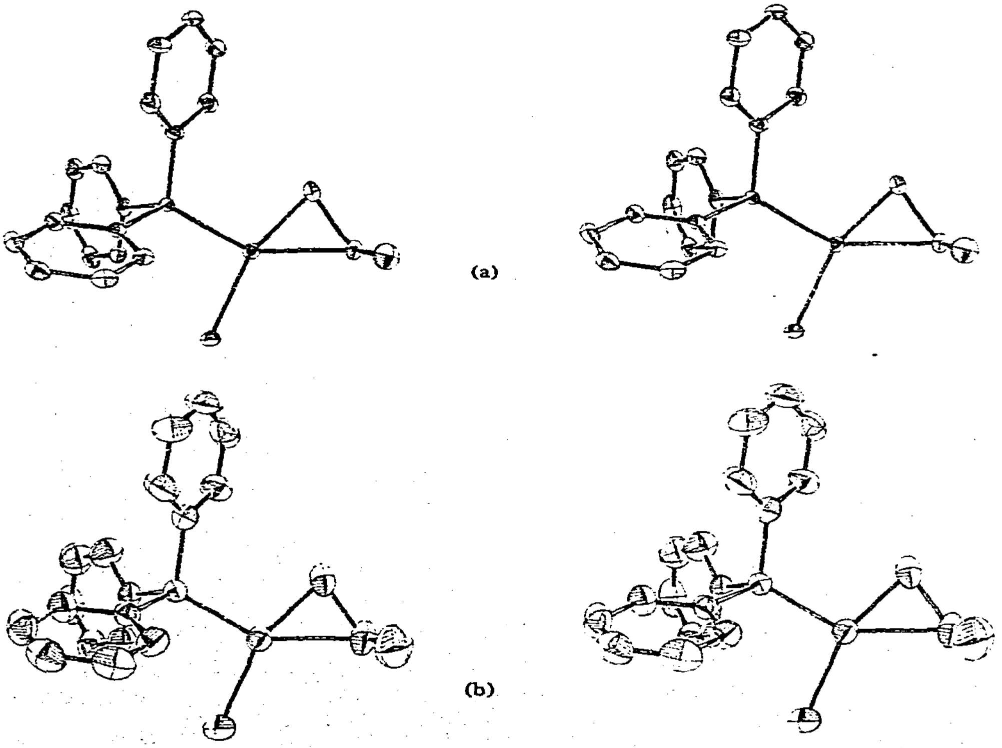


Fig. 1. A perspective view of the molecule and the numbering system of the atoms. Hydrogen atoms are omitted.


(a)

(b)

Fig. 2. ORTEP drawings of the molecule. The thermal ellipsoids correspond to 50% probability level. Hydrogen atoms are omitted for clarity. (a) —160°C, (b) 20°C.

TABLE 4

BOND LENGTHS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bonds involving non-hydrogen atoms			(b) Bonds involving hydrogen atoms		
Length (Å)	−160°C	20°C	Length (Å)	−160°C	20°C
Pd—Cl	2.402(1)	2.397(2)	C(1)—H(1A)	0.98(6)	0.92(8)
Pd—S	2.371(1)	2.362(3)	C(1)—H(1B)	1.01(7)	0.85(12)
Pd—P	2.267(1)	2.267(2)	C(2)—H(2A)	0.82(8)	0.88(10)
Pd—C(1)	2.042(6)	2.042(9)	C(2)—H(2B)	0.92(8)	0.79(8)
S—C(1)	1.756(6)	1.726(9)	C(2)—H(2C)	1.02(8)	1.13(14)
S—C(2)	1.807(7)	1.806(14)	C(12)—H(12)	0.95(6)	0.97(6)
P—C(11)	1.825(5)	1.814(8)	C(13)—H(13)	0.98(6)	0.92(10)
P—C(21)	1.818(5)	1.808(7)	C(14)—H(14)	0.91(7)	0.95(7)
P—C(31)	1.824(5)	1.823(7)	C(15)—H(15)	1.02(7)	0.81(8)
C(11)—C(12)	1.394(8)	1.368(12)	C(16)—H(16)	0.94(5)	0.94(8)
C(12)—C(13)	1.396(8)	1.400(15)	C(22)—H(22)	1.02(6)	0.95(7)
C(13)—C(14)	1.386(9)	1.351(15)	C(23)—H(23)	0.83(6)	0.78(8)
C(14)—C(15)	1.391(9)	1.350(14)	C(24)—H(24)	0.97(6)	0.92(7)
C(15)—C(16)	1.390(8)	1.383(13)	C(25)—H(25)	1.01(6)	0.84(8)
C(16)—C(11)	1.416(8)	1.396(12)	C(26)—H(26)	0.98(8)	0.96(7)
C(21)—C(22)	1.397(7)	1.397(11)	C(32)—H(32)	0.80(6)	0.87(7)
C(22)—C(23)	1.394(8)	1.393(13)	C(33)—H(33)	0.79(7)	0.86(8)
C(23)—C(24)	1.393(8)	1.359(14)	C(34)—H(34)	0.82(6)	0.74(9)
C(24)—C(25)	1.402(8)	1.381(14)	C(35)—H(35)	1.02(6)	0.80(8)
C(25)—C(26)	1.387(8)	1.395(12)	C(36)—H(36)	0.90(6)	0.85(8)
C(26)—C(21)	1.389(7)	1.384(11)			
C(31)—C(32)	1.386(8)	1.352(12)			
C(32)—C(33)	1.392(9)	1.393(14)			
C(33)—C(34)	1.377(9)	1.369(15)			
C(34)—C(35)	1.395(9)	1.382(14)			
C(35)—C(36)	1.383(8)	1.360(13)			
C(36)—C(31)	1.401(7)	1.368(11)			

except for the thermal ellipsoids. At −160°C the estimated standard deviations of bond lengths and bond angles are very small, e.s.d.'s of C—C bond lengths in phenyl groups lying between 0.007 and 0.009 Å. The description of the molecular structure and the discussion will be made mainly on the low temperature structure.

Figure 3 shows the coordination geometry around the palladium atom with selected bond lengths and bond angles. The remarkable feature of the molecular structure is that a Pd—C(1)—S three-membered ring is formed, the CH_2SCH_3 group being attached to the palladium atom according to the second type of bonding mentioned above. The geometry around the palladium atom is square-planar. The equation of the least-squares plane formed by Pd, Cl, S, P and C(1) atoms, and the deviations of atoms from the plane are given in Table 6. The maximum deviation is 0.04 Å.

In the CH_2SCH_3 group, the observed bond length of S—C(1) (1.756(6) Å) is slightly shorter than that of S—C(2) (1.807(7) Å). The estimated S—C single and double bond lengths have been reported as 1.82 and 1.61 Å, respectively [8]. The S—C(1) bond length in the present complex is not significantly different from that of the S—C single bond. The geometry around the C(1) atom approximately coincides with that of the sp^3 carbon, bond angles around it

TABLE 5

BOND ANGLES INVOLVING NON-HYDROGEN ATOMS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Angle (°)	−160°C	20°C
Cl—Pd—S	113.56(5)	112.66(9)
Cl—Pd—P	98.95(5)	99.92(8)
S—Pd—C(1)	46.15(16)	45.4(3)
P—Pd—C(1)	101.37(16)	102.0(3)
Pd—S—C(1)	56.98(19)	57.4(3)
Pd—S—C(2)	106.7(2)	105.3(5)
C(1)—S—C(2)	103.8(3)	103.7(5)
Pd—C(1)—S	76.9(2)	77.1(4)
Pd—P—C(11)	115.98(17)	115.7(3)
Pd—P—C(21)	111.35(17)	111.1(3)
Pd—P—C(31)	114.81(17)	115.1(2)
C(11)—P—C(21)	104.4(2)	104.8(3)
C(11)—P—C(31)	103.5(2)	104.1(3)
C(21)—P—C(31)	105.6(2)	104.9(3)
P—C(11)—C(12)	123.1(4)	123.3(6)
P—C(11)—C(16)	118.0(4)	119.3(6)
C(16)—C(11)—C(12)	118.9(5)	117.4(8)
C(11)—C(12)—C(13)	120.5(5)	121.2(9)
C(12)—C(13)—C(14)	120.1(6)	119.9(10)
C(13)—C(14)—C(15)	120.3(6)	120.1(10)
C(14)—C(15)—C(16)	120.0(6)	120.9(9)
C(15)—C(16)—C(11)	120.2(5)	120.4(8)
P—C(21)—C(22)	122.1(4)	122.2(6)
P—C(21)—C(26)	118.9(4)	119.5(6)
C(26)—C(21)—C(22)	119.1(5)	118.3(7)
C(21)—C(22)—C(23)	120.9(5)	120.6(8)
C(22)—C(23)—C(24)	119.3(5)	120.5(9)
C(23)—C(24)—C(25)	120.3(5)	119.8(9)
C(24)—C(25)—C(26)	119.5(5)	120.4(9)
C(25)—C(26)—C(21)	121.0(5)	120.4(8)
P—C(31)—C(32)	124.2(4)	123.7(6)
P—C(31)—C(36)	117.7(4)	118.5(6)
C(36)—C(31)—C(32)	118.0(5)	117.7(8)
C(31)—C(32)—C(33)	121.8(5)	121.2(9)
C(32)—C(33)—C(34)	119.2(6)	120.2(10)
C(33)—C(34)—C(35)	120.4(6)	118.6(10)
C(34)—C(35)—C(36)	119.7(6)	119.7(9)
C(35)—C(36)—C(31)	120.9(5)	122.6(8)

being Pd—C(1)—H(1A) 113(3), Pd—C(1)—H(1B) 122(4), S—C(1)—H(1A) 115(3), S—C(1)—H(1B) 112(4) and H(1A)—C(1)—H(1B) 113(5)°; however, Pd—C(1)—S 76.9(2)°. Thus, the S—C(1) bond is a single bond but may have a partial double bond character. The S—C(2) bond length (1.807(7) Å) is approximately equal to the expected S—C single bond length. The bond angle of C(1)—S—C(2) is 103.8(3)° and the methyl carbon C(2) is located 1.775 Å away from the coordination plane. Similar features as above are observed in the molybdenum complex $[Mo(\pi\text{-}C_5H_5)(CO)_2(CH_2SCH_3)]$ [2] (e.g. S—C(1) 1.78(1), S—C(2) 1.82(1) Å, and C(1)—S—C(2) 105.0(5)°).

The Pd—C(1) bond length (2.042(6) Å) is within the usual range of the Pd^{II}—C(sp^3) σ bond [9]. The Pd^{II}—S distances in palladium complexes whose

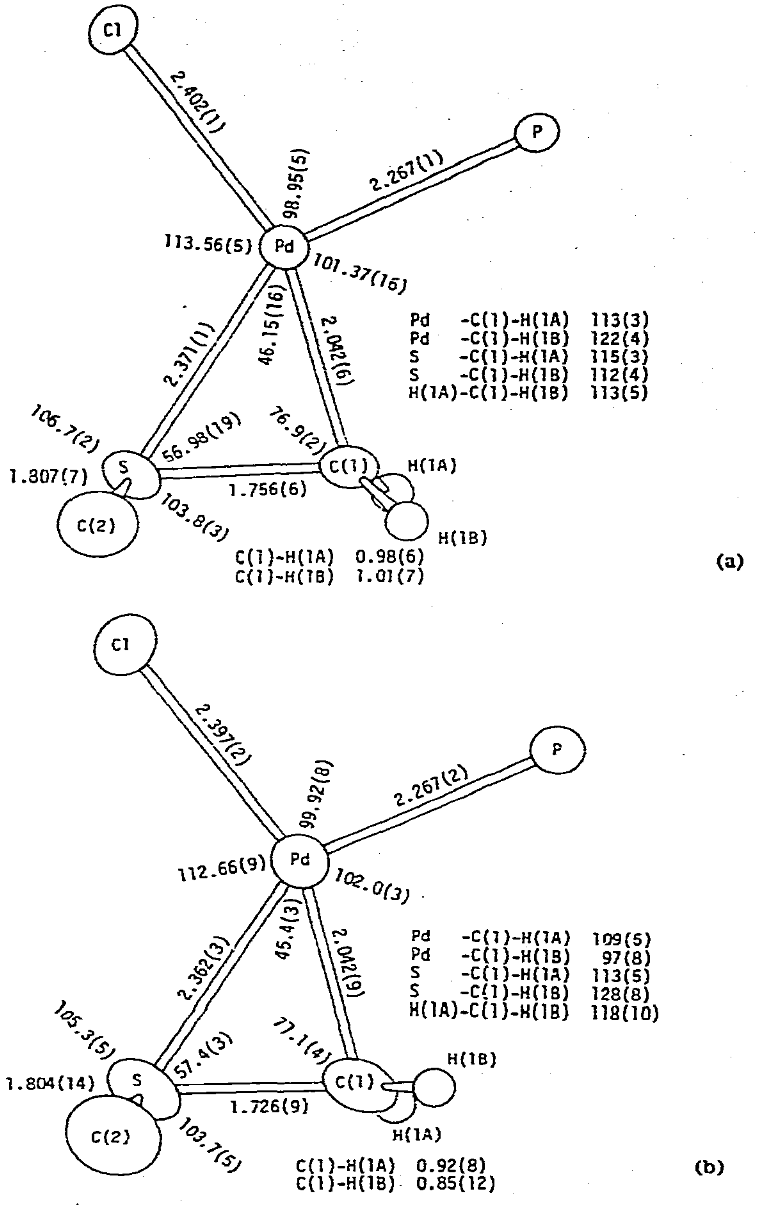


Fig. 3. The coordination geometry around the palladium atom. (a) —160°C, (b) 20°C.

molecular structures have been determined hitherto by the X-ray diffraction method, fall in the range between 2.23 and 2.45 Å *. Among these, the Pd—S bond lengths of complexes which have the same type of coordination of the

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* This information has been obtained from the XDC data base of the TOOL-IR System at the Computer Center of the University of Tokyo which is based on the data base at Cambridge Crystallographic Data Center [10,11].

TABLE 6

LEAST-SQAURES PLANES

The equation of the plane is of the form: $AX + BY + CZ + D = 0.0$, where X, Y and Z are measured in Å units; $X = ax + cz \cos\beta$, $Y = by$ and $Z = cz \sin\beta$.

Square-planar plane of Pd through Pd, Cl, S, P and C(1)

(a) −160°C

$-0.87151X + 0.47992Y + 0.10074Z + 1.66402 = 0.0$

(b) 20°C

$-0.88209X + 0.46440Y + 0.07906Z + 1.71412 = 0.0$

Deviations of atoms from the plane (Å)

	−160°C	20°C
Pd	+0.011	+0.025
Cl	+0.013	+0.009
S	−0.037	−0.040
P	−0.025	−0.028
C(1)	+0.040	+0.037

sulfur atom as that in the present complexes are listed in Table 7. The Pd—S bond length in the present complex (2.371(1) Å) is considered to be a normal Pd—S length; however, it is slightly longer than those in Table 7 which lie between 2.23 and 2.31 Å. This may be partly due to the strain caused by the formation of the three-membered ring.

As shown in Table 4(a), all tne bond lengths at 20°C are merely shorter than those at −160°C. This is considered mainly due to the larger thermal vibration of molecules at 20°C. Therefore, this fact shows the importance of the diffraction work at low temperature in order to obtain precise structural data.

The crystal structure viewed along the b axis is given in Fig. 4. All intermolecular atomic contacts are considered to be at the usual Van der Waals contacts.

All computations were carried out on a NEAC 2200—700 computer at Osaka

TABLE 7

Pd—S BOND LENGTHS OF PALLADIUM COMPLEXES WHICH HAVE THE SAME COORDINATION OF THE SULFUR ATOM AS THAT IN THE PRESENT COMPLEX

Pd complex	Length (Å)	Reference
$Pd(Cl)_2NH_2CH(COOH)CH_2SCH_3$	2.230(4) 2.261(4)	12
$Pd(C_{10}H_{22}N_2OS_2) \cdot (NO_3)_2$	2.261(1) 2.267(1)	13
$Pd(Cl)_2(C_{18}H_{36}N_2O_4S_2)$	2.264(1) 2.265(1)	14
$Pd(Cl)_2NH_2CH(COOH)CH_2CH_2SCH_3$	2.265(4)	15
$Pd(C_{34}H_{28}S_4)$	2.292(3) 2.308(2)	16
$Pd_2(Br)_4(CH_3SCH_3)_2$	2.30(2)	17

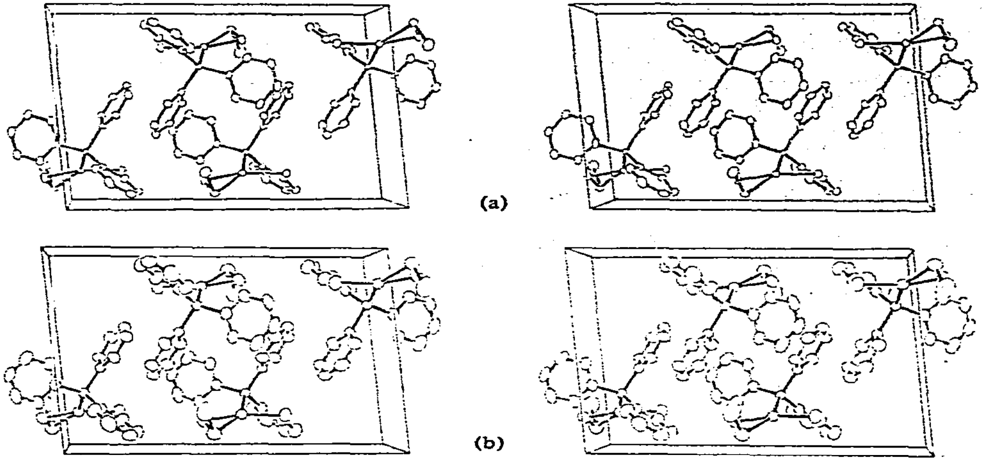

Fig. 4. The crystal structure in a unit cell as viewed down the b axis. Atoms are represented by thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for clarity. (a) —160°C, (b) 20°C.

University. Figures 2, 3 and 4 were drawn on a NUMERICON 7000 system at Osaka University with the local version of ORTEP-II [18].

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