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STUDIES ON STRUCTURAL CHEMISTRY OF PALLADIUM COMPLEXES CONTAINING METAL-SULPHUR BONDS

(金属ーイオウ結合を有するパラジウム錯体の
構造化学に関する研究)

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CONTENTS

INTRODUCTION

X-ray crystallography has been widely applied to the study on organometallic chemistry and has made a great contribution to elucidate the structure and bonding of organometallic compounds. For instance, it was one of the most dramatic discoveries at the early stage of the history of organometallic chemistry that the X-ray diffraction studies determined the structure of ferrocene(Eiland & Pepinsky, 1952; Fischer & Pfab, 1952; Dunitz & Orgel, 1953; Dunitz, Orgel & Rich, 1956). Since then, a variety of organometallic compounds containing many different ligands have been investigated by many crystallographers.

Among the organometallic compounds containing the group VIII transition metals, organopalladium complexes have also been widely investigated hitherto from the viewpoints of both synthetic and structural chemistry. The palladium atom has been bound with various organic ligands(groups) to form mainly square-planar coordination geometry in palladium(II) complexes. On the other hand, the sulphur atom, which is included as a hetero atom in organic ligands(groups), fulfills a wide variety of functions in metal complexes. One reason why the sulphur atom is bonded to the metal atom in many different manners is that it is able to take several coordination numbers. It is very interesting to investigate the coordination behaviour of the sulphur atom in various organic ligands(groups) to the metal atom and to understand the nature of the palladium-sulphur bond.

It is a very serious problem to elucidate the bonding behaviour in organometallic compounds that the precision of the structure obtained from the X-ray analysis is enough high to make exact discussion or not. It is inevitable for the X-ray crystal structure analyses of organometallic compounds that the ambiguity remains for the locations of lighter atoms because organometallic compounds always contain the metal atoms which have much larger scattering power of X-ray than the other lighter atoms such as carbon atoms. Therefore, it was usually difficult that the results from the X-ray structure determination had high precision enough to make the detailed discussion of the structures in organometallic compounds. In order to raise the precision of the structure analyses, one of the direct and efficient techniques is the intensity data collection at lower temperatures such as liquid nitrogen temperature. The low temperature measurements enable to reduce the thermal vibration of the molecule and it is expected that the locations of atoms, including the lighter atoms, are determined with high precision enough to make the detailed discussion and that the reliable positions of even hydrogen atoms are also determined.

The present study is concerned with the molecular structures of several palladium complexes in which the metal atom is bound to the sulphur-containing ligands(groups), determined by the X-ray crystal structure analyses in order to make clear the coordination behaviour of these ligands(groups) to the palladium atom. As mentioned above, the precise molecular structure is indispensable to make the detailed discussion of the bonding. Then, most of the crystal structure analyses presented here have been carried out at liquid nitrogen temperature to obtain the precise structural data.

Chapter 1 deals with the molecular structures of five palladium complexes containing the methylthiomethyl or phenylthiomethyl group.

Chapter 2 deals with the molecular structures of two palladium complexes containing the thia-allyl or thioamidomethyl group.

CHAPTER 1

Molecular Structures of Palladium Complexes Containing Methylthiomethyl or Phenylthiomethyl Group

1.1 Introduction

In this chapter, molecular structures of palladium complexes containing methylthiomethyl(CH_2SCH_3) or phenylthiomethyl ($CH_2SC_6H_5$) group are described, and the coordination behaviour of these groups to the metal atom is discussed. It is of particular interest that three limiting coordination modes are possible in the bonding of the $CH_2SR(R=CH_3, C_6H_5)$ group to the metal atom(King & Bisnette, 1965; Rodulfo de Gil & Dahl, 1969). These coordination modes in case of the CH_2SCH_3 group are shown in Fig. 1-1. One of these modes is the formation of a three-membered metal-carbon-sulphur ring containing the metal-carbon σ-bond and the donation of the sulphur to the metal atom(type a). The CH_2SCH_3 group functions as a bidentate ligand. The another type involves a carbon-sulphur double bond π-bonded to the metal atom(type b). The CH_2SCH_3 group must be more stable in the form of the positively charged methylenemethylsulphonium ion and

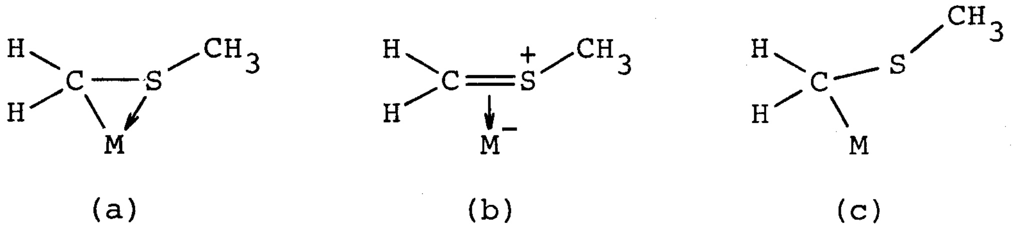

Fig. 1-1. Possible coordination modes in the bonding of the CH_2SCH_3 group to the metal atom.

behaves as a monodentate, two-electron ligand. The other type which has only the metal-carbon σ-bond also is possible(type c). Until now, only a molybdenum complex involving a methylthiomethyl group has been prepared by King & Bisnette(1965), and the structure of the complex has been determined by Rodulfo de Gil & Dahl(1969). From the viewpoint of structural chemistry, it is interesting to reveal the coordination behaviour of these group to the metal atom in group VIII transition metal complexes such as palladium.

Recently, novel palladium complexes containing the CH_2SCH_3 or $CH_2SC_6H_5$ group have been prepared by Okawara and his co-workers of this University(Yoshida, Matsumura & Okawara, 1975; Yoshida, Kurosawa & Okawara, 1976; Yoshida, 1977; Miki, Yoshida, Kai, Yasuoka & Kasai, 1977). The outline of the reactions is summarized in Scheme 1-1. The complex I was obtained from the

Scheme 1-1.

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

$$\mathrm{(I)} + X^+Y^- \longrightarrow \mathrm{[Pd(CH_2SCH_3)(PPh_3)_2]^+Y^-\,(III)} + \mathrm{XCl}$$

X^+Y^-: (a) NH_4PF_6
(b) $AgClO_4$
(c) NH_4BF_4
(d) CH_3OSO_2F
(e) $AgNO_3$

$$\mathrm{PdCl_2(C_6H_5CN)_2} + \mathrm{LiCH_2SC_6H_5} \longrightarrow \mathrm{[Pd(CH_2SC_6H_5)_2]_4\,(IV)}$$

reaction between a zero-valent palladium complex, tetrakis(triphenylphosphine)palladium(0) and chloromethylmethylsulphide. Repeated recrystallization of the complex I removed one of the triphenylphosphine ligands set free to give the complex II. The chlorine atom in the complex I was able to be exchanged by various kinds of counter anions, and then some cationic complexes(III) were isolated. On the other hand, a stable dialkyl tetrameric palladium complex containing phenylthiomethyl groups(IV) was prepared from the reaction of dichlorodibenzonitrilepalladium(II) with lithiummethylphenylsulphide.

A series of the X-ray crystal structure analyses of the following complexes have been carried out to obtain information about how the CH_2SR groups are bonded to the palladium atom:

(I) $[PdCl(CH_2SCH_3)(PPh_3)_2]$
(II) $[PdCl(CH_2SCH_3)(PPh_3)]$
(IIIa) $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$
(IIIb) $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4$
(IV) $[Pd(CH_2SC_6H_5)_2]_4$

In order to make detailed discussion of the bonding scheme of the CH_2SR groups to the metal atom, the determination of precise molecular structures including the locations of the methylene hydrogen atoms is indispensable. All the structure determinations in this chapter have been made at liquid nitrogen temperature.

1.2 Experimental

Crystals used in this study were kindly supplied by Prof. R. Okawara and his co-workers. All the crystals were stable in air and at room temperatures, except for those of $[Pd(CH_2SC_6H_5)_2]_4$(IV), which are unstable at room temperature and decomposed after *ca.* 12h at 25°C. Preliminary oscillation and Weissenberg photographs taken at room temperature with Cu-$K\alpha$ radiation showed all the crystals belong to the monoclinic system. The systematic absences of reflexions determined the space group of each crystal as $P2_1/c$ or $P2_1/n$(C^5_{2h}, No. 14). No photographic works of IV, however, were carried out because of the instability of the crystals. The determination of preliminary crystallographic data of IV was also made on a diffractometer. The observed density of crystals was measured by flotation in carbon tetrachloride/*n*-hexane at 25°C. Crystal data are summarized in Table 1-1. Accurate cell dimensions at both -160 and 20°C(or 18°C) were determined by a least-squares fit of 2θ values of 20 ∿ 25 strong reflexions. The crystal setting was established by the Rigaku soft-ware system for a FACOM U-200-controlled diffractometer based on the method of Busing & Levy(1967).

Intensity data were collected at liquid nitrogen temperature(-160°C) on a Rigaku diffractometer using Mo-$K\alpha$ radiation (λ=0.71069 Å). The required low temperature was attained by the gas flow method using liquid nitrogen. Intensity data collection at room temperature(20°C) were also made for the crystal of $[PdCl(CH_2SCH_3)(PPh_3)]$(II) in order to compare the structure at room temperature with that at low temperature.

Experimental conditions for five kinds of crystals are tabulated in Table 1-2. Throughout the data collection, three or four standard reflexions were measured at regular intervals to monitor crystal stability and orientation. No intensity decrease was observed during experiments in each crystal. Corrections for usual Lorentz and polarization effects were carried out, while neither absorption nor extinction corrections were applied.

Although the repeated recrystallization of crystals of the cationic complexes III were carried out carefully to obtain good crystals, most of crystals were generally unsuitable to the X-ray diffraction study. In spite of relatively small crystals, intensity data collection was barely possible for $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa) and $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4$(IIIb). Crystals of $[Pd(CH_2SCH_3)(PPh_3)_2]SO_3F$(IIId) were too small to make intensity data collection. The complex IIIe, $[Pd(CH_2SCH_3)\cdot(PPh_3)_2]NO_3$, did not crystallize. Crystals of $[Pd(CH_2SCH_3)\cdot(PPh_3)_2]BF_4$(IIIc) obtained from recrystallization were comparatively large enough to collect intensities. As shown in Fig. 1-2, however, oscillation and Weissenberg photographs of IIIc showed abnormal features, that is, many diffuse spots near the normal Bragg reflexions. If all the diffuse spots were neglected, those showed the monoclinic symmetry with approximate dimensions: a=18.0, b=18.4, c=12.3 Å, β=107° and U=3896 $Å^3$. The systematic absences of reflexions ($h+k=2n+1$) determined the lattice type as the C-centred lattice. Possible space groups are $C2$, Cm and $C2/m$. These diffuse spots may be due to the disordered structure in the crystal packing. Therefore, the further investigation of IIIc was abandoned.

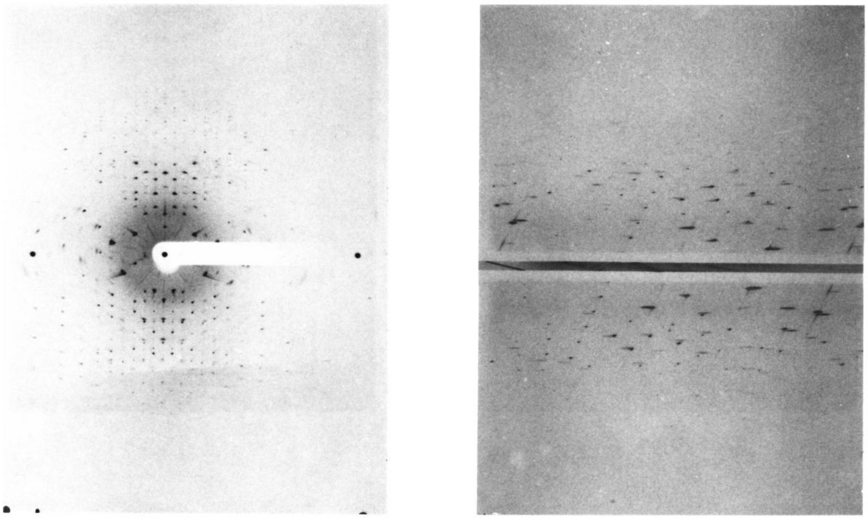

Fig. 1-2. Oscillation(left) and Weissenberg(right) photographs of $[Pd(CH_2SCH_3)(PPh_3)_2]BF_4$(IIIc)

Table 1-1. Crystal data

$[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I)

$C_{38}H_{35}ClP_2PdS\cdot CH_2Cl_2$, F.W. 812.51, $F(000)=1651$

Monoclinic, Space group $P2_1/n$, $Z=4$

	[-160°C]	[20°C]
a (Å)	14.973(3)	15.139(3)
b (Å)	15.333(3)	15.463(3)
c (Å)	17.377(3)	17.693(3)
β (°)	115.77(1)	115.47(1)
U (Å^3)	3592.7(13)	3739.3(13)
μ(Mo-$K\alpha$)(cm^{-1})	9.02	8.67
Dc (g cm^{-3})	1.503	1.444
Dm (g cm^{-3})		1.44

$[PdCl(CH_2SCH_3)(PPh_3)]$(II)

$C_{20}H_{20}ClPPdS$, F.W. 465.28, $F(000)=936$

Monoclinic, Space group $P2_1/c$, $Z=4$

	[-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-$K\alpha$)(cm^{-1})	12.7	12.4
Dc (g cm^{-3})	1.612	1.573
Dm (g cm^{-3})		1.57

Table 1-2. (continued)

$[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (IIIa)

$C_{38}H_{35}P_2PdS \cdot PF_6$, F.W. 837.10, $F(000)=1696$

Monoclinic, Space group $P2_1/c$, $Z=4$

	[-160°C]	[20°C]
a (Å)	11.535(2)	11.650(2)
b (Å)	17.990(4)	18.198(5)
c (Å)	17.754(2)	17.956(3)
β (°)	101.07(1)	101.24(2)
U ($Å^3$)	3615.5(11)	3733.7(15)
μ(Mo-Kα) (cm^{-1})	7.55	7.31
Dc (g cm^{-3})	1.538	1.489
Dm (g cm^{-3})		1.49

$[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (IIIb)

$C_{38}H_{35}P_2PdS \cdot ClO_4 \cdot 0.25CH_2Cl_2$, F.W. 812.8, $F(000)=1658$

Monoclinic, Space group $P2_1/n$, $Z=4$

	[-160°C]	[20°C]
a (Å)	11.496(5)	11.526(4)
b (Å)	20.872(9)	21.110(8)
c (Å)	15.056(6)	15.328(5)
β (°)	94.77(4)	94.42(4)
U ($Å^3$)	3600(3)	3718(3)
μ(Mo-Kα) (cm^{-1})	8.03	7.78
Dc (g cm^{-3})	1.499	1.452
Dm (g cm^{-3})		1.44

$[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ (IV)

$C_{56}H_{56}Pd_4S_8 \cdot CH_2Cl_2$, F.W. 1496.1, $F(000)=2984$

Monoclinic, Space group $P2_1/n$, $Z=4$

	[-160°C]	[18°C]
a (Å)	16.302(3)	16.605(4)
b (Å)	19.394(4)	19.529(5)
c (Å)	18.552(3)	18.675(4)
β (°)	91.28(2)	91.32(2)
U ($Å^3$)	5864(2)	6054(2)
μ(Mo-Kα) (cm^{-1})	15.8	15.3
Dc (g cm^{-3})	1.695	1.641

Table 1-2. Experimental conditions for intensity data collection

Complex	[I]	[II]	[IIIa]	[IIIb]	[IV]
Crystal					
colour	light yellow	yellow	colourless	colourless	orange-yellow
shape	prisms	prisms	needles	prisms	plates
size(mm)	0.3×0.3×0.35	0.2×0.2×0.2	0.1×0.1×0.25	0.25×0.3×0.35	0.25×0.3×0.05
X-ray					
source	Mo-$K\alpha$ (40KV, 25mA)	Mo-$K\alpha$ (40KV, 25mA)	Mo-$K\alpha$ (40KV, 25mA)	Mo-$K\alpha$ (40KV, 30mA)	Mo-$K\alpha$ (40KV, 25mA)
monochromator	graphite	graphite	graphite	Zr-filter	graphite
Scan					
mode	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
speed(°min^{-1})	4	4	4	4	4
range(a and b) [$\Delta\theta=(a+b\tan\theta)°$]	1.0, 0.35	1.0, 0.35	1.25, 0.35	1.25, 0.35	1.0, 0.35
background(sec)	5	5	5	5	5
2θmax(°)	54	54	54	54	40
Standard reflexions	800, 80$\bar{4}$, 612, 742	062, 40$\bar{8}$, 800	600, 019, 219	800, 0,10,0, 008, 555	060, 30$\bar{5}$, 61$\bar{3}$, 90$\bar{7}$
Temperature(°C)	-160	-160 & 20	-160	-160	-160
Number of reflexions					
measured	7832	4183 4308	7899	7907	5516
unobserved(zero)	700	684 1099	3322	2064	1153
non-zero	7132	3499 3209	4577	5843	4363

1.3 Structure Solution and Refinement

The structures were solved by the conventional heavy atom method. The refinements of structures were carried out by the block-diagonal least-squares procedure using the *HBLS-V* programme(Ashida, 1979); the function minimized being $\sum w(|Fo|-|Fc|)^2$. The R and R_w(weighted R) indices are defined by $R=\sum||Fo|-|Fc||/\sum|Fo|$ and $R_w=\{\sum w(|Fo|-|Fc|)^2/\sum w|Fo|^2\}^{1/2}$, respectively. The atomic scattering factors for non-hydrogen atoms were taken from those of Hanson, Herman, Lea & Skillman (1964) for I and II, and *International Tables for X-ray Crystallography*(1974) for IIIa, IIIb and IV, respectively. For hydrogen atoms, the scattering factors given by Stewart, Davidson & Simpson(1965) were used.

All computations were carried out on following computers: NEAC 2200-700, ACOS 800 and ACOS 900 computers at Computation Center, Osaka University, a FACOM 230-60 computer at Data Processing Center, Kyoto University and an ACOS 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University.

$[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2(I)$

For the structure solution and through early stages of the refinement, a limited data set(3878 reflexions, $2\theta\leq 42°$) was used to save computer time. A three-dimensional Patterson map easily gave the approximate coordinates of the palladium atom. The remaining non-hydrogen atoms, including those of the solvent molecule(CH_2Cl_2), were located from successive Fourier maps based on the atomic position of palladium.

A few cycles of isotropic refinement converged with R=0.077 for non-zero reflexions. Several subsequent cycles of anisotropic refinement reduced the R index to 0.052 for observed reflexions. At this stage, a differnce Fourier map was calculated, from which all the hydrogen atoms were reasonably located. Several more cycles of refinement were carried out anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. The R index converged to 0.031 for non-zero reflexions of the limited data set. Subsequently the remaining 3956 reflexions were added, and further refinement was carried out for the total of 7832 reflexions. The final R indices are 0.035 and 0.043 for 7132 non-zero and for all 7832 reflexions, respectively. The weighting scheme used was $w=(\sigma_{cs}^2+a|Fo|+b|Fo|^2)^{-1}$ for $|Fo|>0$, and $w=c$ for $|Fo|=0$, where σ_{cs} is the standard deviation obtained from the counting statistics and the values of a, b and c used in the final refinement are 0.0633, 0.0007 and 0.0603, respectively. The final weighted R index(R_w) is 0.054 for all reflexions. The final atomic positional and thermal parameters are listed in Tables 1-3 and 1-4.

$[PdCl(CH_2SCH_3)(PPh_3)]$ (*II*)

The structure was solved 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. Several cycles of isotropic refinement reduced the R indices to 0.067 (at -160°C) and 0.098(at 20°C) for non-zero reflexions. No abnormal thermal factors were observed. A few 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) reflexions at -160 and 20°C, respectively. The weighting scheme used was $w=(\sigma_{cs}^2+a|Fo|+b|Fo|^2)^{-1}$ for $|Fo|>0$ and $w=c$ for $|Fo|=0$, where σ_{cs} is the value obtained from the counting statistics and the 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) are 0.061(at -160°C) and 0.075(at 20°C) for all reflexions, respectively. The final atomic positional and thermal parameters at -160 and 20°C are listed in Tables 1-5 and 1-6.

$[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$*(IIIa)*

For the structure solution and the refinements, 3906 reflexions($Fo>3\sigma(Fo)$) were used. The approximate coordinates of the palladium atom were determined from a three-dimensional Patterson map. All non-hydrogen atoms were located reasonably by the subsequent Fourier synthesis.

Several cycles of isotropic refinement for non-hydrogen atoms reduced the *R* value to 0.17. The isotropic temperature factors of the fluorine atoms in the PF_6 anion showed relatively large values(maximum B=11.2 $Å^2$). The further anisotropic refinement did not go on straightforwards, some abnormal temperature factors being observed. Therefore, the subsequent refinement was carried out step by step using small damping factors for shifts of the parameters. In the Fourier map at this stage, a relatively high peak(*ca.* 80% of the height of the C(1) atom) was found near the location of the sulphur atom. This peak, which was distant 1.12 and 2.37 Å from the sulphur and palladium atoms respectively, might be assigned as the disordered fragment of the sulphur atom. However, if so, the geometry of the coordination plane around the palladium atom was far from the square-planar coordination. Then, this peak was ignored and was not included from the refinement. The final *R* and *Rw* factors are 0.141 and 0.159 for 3906 reflexions, respectively. The unit weights were employed throughout all stages of refinement.
The final atomic positional and thermal parameters are presented in Table 1-7.

$[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ *(IIIb)*

For the structure solution and the refinements, 4595 reflexions($Fo > 3\sigma(Fo)$, 2θ up to 50°) were employed. A three-dimensional Patterson map easily gave the location of the palladium atom. The subsequent Fourier map base on this atomic position determined all the locations of non-hydrogen atoms in the $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation.

A few cycles of isotropic refinement including 42 atoms in the cation converged the *R* value to 0.14. At this satge, a difference Fourier map was calculated, from which coordinates of the Cl atom of the ClO_4 anion were determined. However, the electron densities around the atomic position of Cl were relatively low and very broad. Only a location of one of four O atoms in the ClO_4 anion was found from the difference Fourier maps, while remaining three O atoms were not located. These Cl and O atoms indicated the abnormally large temperature factors in the further refinements. In addition,three peaks were found on the Fourier map, which were interpreted as those of the CH_2Cl_2 molecule. Several more cycles of refinement were carried out anisotropically for Pd, S, P and C atoms in the cationic complex and isotropically for Cl, O and C atoms in the ClO_4 anion and the CH_2Cl_2 molecule. However, the temperature factors of Cl and C atoms in the CH_2Cl_2 molecule were exceptionally large. The calculated density for formula weight assuming that one molecule of CH_2Cl_2 is included in an asymmetric unit of the unit cell[1.566 g cm^{-3}] is much larger than the observed value of 1.44 g cm^{-3}. These facts imply a lower occupancy of the CH_2Cl_2 molecule than unity. The occupancy factor for the CH_2Cl_2 molecule was estimated as 1/4, which gives the calculated density of 1.452 g cm^{-3} and a good fit with the observed value. The coordinates of only a C atom of CH_2Cl_2 were fixed in the further refinements. The final R and R_w values are 0.102 and 0.117 for 4595 reflexions, respectively. The unit weights were employed throughout each step of refinement. The final atomic positional and thermal parameters are listed in Table 1-8.

$[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ (IV)

A three-dimensional Patterson function revealed the positions of four palladium atoms. In the Fourier map based on these atomic positions, 10 additional high peaks were found. Among these, 8 peaks were considered as being due to the sulphur atoms, and the remaining two peaks were deduced to be those due to the chlorine atoms of the CH_2Cl_2 molecule of solvation. The remaining carbon atoms were located in the subsequent difference Fourier map.

Through the early stages of the refinement, 4175 reflexions ($2\theta \leqq 36.4°$) were used to save computer time. A few cycles of isotropic refinement using unit weight converged the R value to 0.094 for 3407 observed reflexions. Several cycles of refinement for the Pd, Cl and S atoms anisotropically and for the C atoms isotropically were carried out using the weighting scheme: $w=(\sigma_{cs}^2+a|Fo|+b|Fo|^2)^{-1}$ for $|Fo|>0$, and $w=c$ for $|Fo|=0$, where σ_{cs} is the value obtained from the counting statistics and a, b and c are constants adjusted in the refinement. The R and R_w indices converged to 0.084 for non-zero(0.121 for all) reflexions and 0.115 for all reflexions, respectively. Further refinement including anisotropic carbon atoms was not successful, abnormal thermal parameters of several carbon atoms being observed. Therefore, an anisotropic refinement for carbon atoms was abandoned. At this stage, the remaining 1341 reflexions were added. After a few cycles of refinement the R index converged finally to 0.089 for 4363 non-zero(0.136 for all 5516) reflexions. The final weighted R index(R_w) is 0.120 for all reflexions and the weighting parameters, a, b and c used in the final refinement are 0.1120, 0.0018 and 0.0446, respectively. The final atomic positional and thermal parameters are listed in Table 1-9.

Table 1-3. Final atomic parameters for non-hydrogen atoms of $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I)

Positional parameters in fraction of cell edges and 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.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD	.47809(2)	.40375(2)	.71944(2)	.00167(1)	.00113(1)	.00126(1)	-.00025(2)	.00130(2)	-.00019(2)
CL(1)	.52674(5)	.53789(4)	.79909(4)	.00255(4)	.00113(2)	.00147(2)	-.00041(5)	.00118(5)	-.00059(4)
S	.49846(6)	.21688(5)	.76990(5)	.00334(4)	.00132(3)	.00151(3)	-.00041(5)	.00169(6)	.00019(4)
P(1)	.31757(5)	.41103(4)	.71095(4)	.00157(3)	.00114(3)	.00111(2)	-.00015(5)	.00132(5)	-.00001(4)
P(2)	.63063(5)	.39872(4)	.71292(4)	.00142(3)	.00106(3)	.00105(2)	-.00003(4)	.00101(5)	.00017(4)
C(1)	.45010(20)	.27834(17)	.67222(17)	.00193(14)	.00113(10)	.00156(10)	-.00049(19)	.0015 (2)	-.00039(17)
C(2)	.4813 (3)	.1058 (2)	.7295 (2)	.0064 (3)	.00126(13)	.00313(16)	-.0002 (3)	.0034 (3)	.0004 (2)
C(11)	.2469 (2)	.50624(19)	.65186(18)	.00277(16)	.00152(11)	.00134(10)	.0006 (2)	.0019 (2)	-.00002(17)
C(12)	.1440 (3)	.5122 (2)	.6244 (2)	.00329(18)	.00275(15)	.00372(16)	.0015 (3)	.0044 (3)	.0020 (3)
C(13)	.0918 (3)	.5864 (2)	.5831 (3)	.0037 (2)	.00309(16)	.00372(17)	.0031 (3)	.0040 (3)	.0025 (3)
C(14)	.1414 (3)	.6557 (2)	.5669 (2)	.0050 (2)	.00227(14)	.00216(13)	.0027 (3)	.0023 (3)	.0010 (2)
C(15)	.2416 (3)	.6496 (2)	.5911 (2)	.0045 (2)	.00228(14)	.00284(15)	-.0004 (3)	.0015 (3)	.0020 (2)
C(16)	.2949 (2)	.5755 (2)	.6328 (2)	.00309(17)	.00241(13)	.00198(12)	.0000 (2)	.0012 (2)	.0012 (2)
C(21)	.3130 (2)	.41575(17)	.81440(17)	.00196(14)	.00126(10)	.00135(10)	-.00035(19)	.0019 (2)	-.00025(16)
C(22)	.4004 (2)	.4171 (2)	.88901(20)	.00183(15)	.00312(14)	.00179(12)	.0004 (2)	.0018 (2)	.0008 (2)
C(23)	.3966 (2)	.4215 (2)	.96850(19)	.00232(16)	.00368(16)	.00128(11)	.0001 (3)	.0012 (2)	.0000 (2)
C(24)	.3074 (2)	.4255 (2)	.97322(19)	.00307(17)	.00238(13)	.00176(12)	.0000 (2)	.0028 (2)	-.0005 (2)
C(25)	.2197 (2)	.4237 (3)	.8982 (2)	.00249(17)	.00492(19)	.00210(13)	-.0004 (3)	.0027 (3)	-.0005 (3)
C(26)	.2231 (2)	.4183 (3)	.8194 (2)	.00195(16)	.00483(19)	.00169(12)	-.0005 (3)	.0015 (2)	-.0006 (2)
C(31)	.23611(20)	.31987(18)	.65772(17)	.00160(13)	.00149(11)	.00157(10)	-.00006(19)	.00150(20)	-.00011(17)
C(32)	.2405 (2)	.2434 (2)	.70344(20)	.00271(16)	.00186(12)	.00206(12)	-.0006 (2)	.0017 (2)	.00058(20)
C(33)	.1920 (3)	.1683 (2)	.6611 (2)	.00331(18)	.00161(12)	.00368(16)	-.0010 (2)	.0031 (3)	.0004 (2)
C(34)	.1387 (2)	.1683 (2)	.5724 (2)	.00290(17)	.00224(14)	.00340(15)	-.0021 (2)	.0025 (3)	-.0022 (2)
C(35)	.1315 (2)	.2440 (2)	.5270 (2)	.00245(16)	.00320(15)	.00199(12)	-.0011 (3)	.0017 (2)	-.0017 (2)
C(36)	.1802 (2)	.3194 (2)	.56900(18)	.00203(14)	.00227(13)	.00152(11)	-.0005 (2)	.0013 (2)	-.00020(19)
C(41)	.6483 (2)	.48472(18)	.64788(17)	.00233(14)	.00159(11)	.00123(10)	-.0005 (2)	.0015 (2)	.00027(17)
C(42)	.7208 (2)	.4770 (2)	.61784(20)	.00291(16)	.00190(12)	.00224(12)	.0000 (2)	.0029 (2)	.00075(20)
C(43)	.7369 (3)	.5437 (2)	.5716 (2)	.00385(19)	.00276(15)	.00287(14)	-.0002 (3)	.0044 (3)	.0010 (2)
C(44)	.6807 (3)	.6198 (2)	.5542 (2)	.00388(20)	.00256(14)	.00264(14)	-.0002 (3)	.0030 (3)	.0021 (2)
C(45)	.6093 (2)	.6279 (2)	.5840 (2)	.00323(18)	.00201(13)	.00255(13)	.0009 (2)	.0020 (3)	.0017 (2)
C(46)	.5916 (2)	.56100(20)	.63017(19)	.00209(15)	.00178(12)	.00216(12)	.0007 (2)	.0016 (2)	.00132(19)
C(51)	.7370 (2)	.40504(17)	.81775(18)	.00171(13)	.00113(10)	.00141(10)	.00034(18)	.00068(20)	-.00007(16)
C(52)	.7232 (2)	.3869 (2)	.89072(19)	.00233(15)	.00224(12)	.00166(11)	-.0002 (2)	.0019 (2)	.00061(19)
C(53)	.8038 (2)	.3833 (2)	.97084(19)	.00266(16)	.00241(13)	.00144(11)	.0003 (2)	.0012 (2)	.00028(20)
C(54)	.8988 (2)	.3986 (2)	.97913(20)	.00229(16)	.00216(13)	.00172(12)	.0011 (2)	.0001 (2)	-.00008(19)
C(55)	.9131 (2)	.4175 (2)	.9073 (2)	.00182(15)	.00233(13)	.00256(13)	.0002 (2)	.0013 (2)	-.0004 (2)
C(56)	.8330 (2)	.4205 (2)	.82681(20)	.00211(15)	.00198(12)	.00208(12)	.0004 (2)	.0017 (2)	.00056(20)
C(61)	.65873(20)	.29995(18)	.66887(18)	.00180(13)	.00154(11)	.00165(10)	-.00011(19)	.0021 (2)	-.00033(17)
C(62)	.7028 (2)	.2293 (2)	.72178(19)	.00334(17)	.00184(12)	.00165(11)	.0009 (2)	.0016 (2)	-.00003(19)
C(63)	.7136 (3)	.1499 (2)	.6875 (2)	.00370(19)	.00197(13)	.00273(14)	.0011 (3)	.0016 (3)	-.0005 (2)
C(64)	.6806 (2)	.1411 (2)	.6002 (2)	.00312(17)	.00202(13)	.00312(14)	-.0009 (2)	.0040 (3)	-.0017 (2)
C(65)	.6370 (3)	.2115 (2)	.5470 (2)	.00398(19)	.00249(14)	.00193(12)	-.0017 (3)	.0032 (3)	-.0014 (2)
C(66)	.6254 (2)	.2904 (2)	.58083(19)	.00295(16)	.00200(12)	.00175(11)	-.0005 (2)	.0018 (2)	-.00031(19)
CL(1S)	.01002(10)	.25798(7)	.80760(7)	.00945(9)	.00268(4)	.00261(4)	-.00058(10)	.00290(10)	-.00024(6)
CL(2S)	-.04724(7)	.35913(7)	.65288(7)	.00397(5)	.00344(4)	.00388(4)	.00016(7)	.00258(8)	.00239(7)
C(S)	-.0362 (4)	.2542 (3)	.6977 (3)	.0099 (4)	.00205(16)	.00316(17)	-.0007 (4)	.0047 (4)	-.0005 (3)

Table 1-4. Final atomic parameters for hydrogen atoms of $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I)

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

Atom	x	y	z	B
H(12)	.108(3)	.460(3)	.634(3)	3.8(10)
H(13)	.016(3)	.586(3)	.564(3)	4.2(11)
H(14)	.105(3)	.709(3)	.541(3)	4.0(10)
H(15)	.279(3)	.695(3)	.580(3)	3.2(9)
H(16)	.362(3)	.568(3)	.647(3)	4.3(11)
H(22)	.471(3)	.416(2)	.889(2)	2.0(7)
H(23)	.459(4)	.425(3)	1.023(3)	5.0(12)
H(24)	.306(3)	.430(2)	1.029(2)	2.2(7)
H(25)	.152(3)	.422(3)	.899(3)	3.6(10)
H(26)	.156(3)	.415(3)	.767(3)	4.2(11)
H(32)	.280(3)	.244(3)	.768(3)	3.2(9)
H(33)	.195(3)	.113(3)	.692(3)	3.5(9)
H(34)	.104(3)	.112(3)	.544(3)	3.2(9)
H(35)	.094(3)	.247(3)	.463(3)	4.4(11)
H(36)	.178(3)	.377(3)	.536(2)	2.4(8)
H(42)	.763(3)	.423(2)	.629(2)	2.3(8)
H(43)	.791(3)	.539(3)	.551(2)	2.9(8)
H(44)	.691(3)	.666(3)	.518(3)	4.4(11)
H(45)	.568(3)	.680(3)	.570(3)	3.2(9)
H(46)	.541(3)	.570(2)	.648(2)	2.3(8)
H(52)	.656(3)	.373(3)	.885(3)	3.2(9)
H(53)	.790(3)	.371(3)	1.022(2)	2.8(8)
H(54)	.962(3)	.395(2)	1.037(2)	2.5(8)
H(55)	.980(3)	.427(3)	.910(3)	4.1(10)
H(56)	.848(3)	.434(3)	.776(3)	3.8(10)
H(62)	.732(3)	.235(3)	.789(3)	3.4(9)
H(63)	.748(4)	.097(3)	.725(3)	4.2(11)
H(64)	.692(3)	.085(2)	.576(3)	2.5(8)
H(65)	.612(3)	.203(3)	.485(3)	3.5(9)
H(66)	.588(3)	.345(3)	.537(3)	3.0(8)
H(1A)	.380(2)	.270(2)	.642(2)	1.6(7)
H(1B)	.487(3)	.263(2)	.639(2)	2.4(8)
H(2A)	.401(3)	.102(3)	.695(3)	4.2(11)
H(2B)	.528(4)	.098(3)	.697(3)	5.2(13)
H(2C)	.503(3)	.071(3)	.780(3)	4.3(11)
H(1S)	-.097(5)	.221(4)	.666(4)	8.9(18)
H(2S)	.008(6)	.223(6)	.652(5)	12.4(25)

Table 1-5. Final atomic parameters for non-hydrogen atoms of [PdCl(CH$_2$SCH$_3$)(PPh$_3$)](II)

Positional parameters in fraction of cell edges and 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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{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)	.18732(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)

Table 1-5. (continued)

(b) 20°C

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{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)	-.0004(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)	.0054(9)	.1697(5)	.0076(7)	.0121(11)	.0044(4)	.0090(16)	.0021(8)	.0024(11)
C(26)	.4640(7)	.0304(8)	.1242(5)	.0061(6)	.0085(9)	.0037(3)	.0007(12)	-.0001(7)	.0012(8)
C(31)	.1997(6)	.3150(7)	.1156(4)	.0060(6)	.0075(8)	.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 1-6. Final atomic parameters for hydrogen atoms of $[PdCl(CH_2SCH_3)(PPh_3)](II)$.

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

(a) -160°C

Atom	x	y	z	B
H(12)	.504(5)	.274(6)	.005(3)	1.1(10)
H(13)	.555(5)	.386(6)	-.108(3)	1.9(12)
H(14)	.400(6)	.459(7)	-.198(4)	2.6(14)
H(15)	.203(6)	.422(7)	-.186(4)	3.1(15)
H(16)	.159(5)	.296(6)	-.071(3)	1.1(11)
H(22)	.439(5)	.354(6)	.166(3)	1.2(11)
H(23)	.611(5)	.288(6)	.244(3)	1.5(12)
H(24)	.699(5)	.085(6)	.247(3)	1.5(11)
H(25)	.614(5)	-.092(6)	.165(3)	2.0(12)
H(26)	.418(7)	-.044(8)	.094(5)	4.8(19)
H(32)	.239(5)	.484(6)	.062(3)	2.0(13)
H(33)	.132(6)	.628(7)	.119(4)	3.1(15)
H(34)	.032(5)	.564(6)	.212(3)	1.9(12)
H(35)	.035(5)	.341(6)	.262(3)	1.4(11)
H(36)	.135(5)	.191(6)	.192(4)	2.3(13)
H(1A)	.081(5)	.072(6)	-.095(3)	1.2(11)
H(1B)	.203(6)	-.008(7)	-.115(4)	3.1(15)
H(2A)	.254(6)	-.243(8)	-.068(4)	4.1(17)
H(2B)	.183(7)	-.295(8)	-.133(5)	5.2(20)
H(2C)	.159(6)	-.368(8)	-.059(4)	4.3(18)

(b) 20°C

Atom	x	y	z	B
H(12)	.491(5)	.264(6)	.008(4)	2.2(13)
H(13)	.541(8)	.390(10)	-.095(6)	7.9(27)
H(14)	.397(5)	.450(7)	-.197(4)	2.6(14)
H(15)	.211(6)	.415(8)	-.171(4)	4.1(18)
H(16)	.155(6)	.297(8)	-.067(4)	4.0(18)
H(22)	.425(6)	.340(7)	.167(4)	3.6(17)
H(23)	.609(6)	.286(8)	.239(4)	4.3(18)
H(24)	.693(6)	.091(7)	.244(4)	2.8(15)
H(25)	.595(7)	-.073(8)	.165(4)	4.6(19)
H(26)	.422(6)	-.044(7)	.098(4)	3.5(17)
H(32)	.238(6)	.479(7)	.061(4)	2.7(15)
H(33)	.133(7)	.624(8)	.122(5)	5.1(20)
H(34)	.035(7)	.548(9)	.213(5)	5.3(21)
H(35)	.041(6)	.338(8)	.249(4)	4.2(18)
H(36)	.148(7)	.193(8)	.189(4)	4.9(20)
H(1A)	.084(7)	.059(8)	-.090(5)	5.0(20)
H(1B)	.212(10)	.014(12)	-.086(7)	10.5(36)
H(2A)	.259(8)	-.251(10)	-.040(5)	6.9(25)
H(2B)	.198(7)	-.306(8)	-.114(4)	4.5(19)
H(2C)	.159(11)	-.365(14)	-.043(8)	13.2(43)

Table 1-7. Final atomic parameters of [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$]PF$_6$(IIIa)

Positional parameters in fraction of cell edges and 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.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD	0.67007(14)	0.02532(11)	0.22058(9)	0.00315(10)	0.00246(6)	0.00098(4)	-0.00153(16)	0.00053(10)	-0.00056(11)
S	0.4737(6)	0.0431(5)	0.1540(4)	0.0055(6)	0.0039(4)	0.0022(3)	-0.0002(7)	0.0012(6)	-0.0005(5)
P(1)	0.8027(5)	0.0113(3)	0.1363(3)	0.0030(4)	0.00079(16)	0.00124(15)	0.0002(4)	0.0005(4)	0.0001(3)
P(2)	0.7904(5)	0.0270(4)	0.3379(3)	0.0032(4)	0.00143(17)	0.00102(15)	-0.0013(5)	0.0006(4)	0.0008(3)
C(1)	0.509(3)	0.0299(19)	0.2547(16)	0.007(3)	0.0038(12)	0.0028(10)	-0.001(4)	0.002(3)	-0.000(2)
C(2)	0.422(3)	-0.0465(16)	0.1216(17)	0.009(3)	0.0025(11)	0.0037(12)	0.001(3)	0.003(3)	0.0010(17)
C(11)	0.9603(18)	0.0021(13)	0.1724(12)	0.0034(16)	0.0019(8)	0.0014(7)	0.0010(17)	0.0005(16)	0.0001(11)
C(12)	1.034(3)	0.0647(15)	0.1936(15)	0.007(3)	0.0019(9)	0.0025(9)	0.000(3)	0.002(3)	-0.0003(15)
C(13)	1.153(3)	0.057(3)	0.2267(16)	0.007(3)	0.0073(19)	0.0020(9)	-0.004(4)	0.004(3)	-0.002(3)
C(14)	1.201(2)	-0.0149(18)	0.2377(14)	0.0042(19)	0.0044(13)	0.0022(9)	0.002(3)	0.0012(19)	0.0006(18)
C(15)	1.133(3)	-0.0780(18)	0.2190(14)	0.006(3)	0.0042(13)	0.0016(8)	-0.001(3)	0.002(3)	-0.0009(17)
C(16)	1.0122(17)	-0.0656(14)	0.1866(11)	0.0016(14)	0.0028(9)	0.0012(7)	0.0022(18)	-0.0007(15)	0.0011(12)
C(21)	0.7993(17)	0.0861(11)	0.0662(10)	0.0027(15)	0.0010(7)	0.0008(6)	0.0011(15)	0.0008(15)	0.0005(10)
C(22)	0.890(3)	0.0965(14)	0.0257(14)	0.006(3)	0.0021(9)	0.0021(8)	0.001(3)	0.004(3)	0.0012(14)
C(23)	0.880(3)	0.1543(16)	-0.0267(14)	0.012(4)	0.0027(10)	0.0018(9)	-0.004(3)	0.005(3)	-0.0017(15)
C(24)	0.782(4)	0.203(3)	-0.038(2)	0.009(4)	0.0050(16)	0.0043(14)	-0.002(4)	0.001(4)	0.004(3)
C(25)	0.698(3)	0.2005(15)	0.0086(16)	0.007(3)	0.0017(9)	0.0033(11)	0.000(3)	0.002(3)	0.0013(15)
C(26)	0.707(2)	0.1384(16)	0.0649(17)	0.0017(16)	0.0034(11)	0.0042(12)	-0.001(3)	-0.002(3)	0.0013(19)
C(31)	0.762(2)	-0.0702(14)	0.0806(13)	0.0040(18)	0.0018(8)	0.0023(8)	-0.0006(19)	0.0018(19)	-0.0003(13)
C(32)	0.791(3)	-0.0808(16)	0.0060(14)	0.007(3)	0.0027(10)	0.0024(9)	-0.001(3)	0.005(3)	-0.0011(16)
C(33)	0.753(3)	-0.1461(16)	-0.0366(15)	0.013(4)	0.0023(10)	0.0018(9)	-0.003(3)	-0.002(3)	-0.0011(15)
C(34)	0.690(3)	-0.2019(14)	-0.0044(15)	0.006(3)	0.0014(8)	0.0033(10)	0.003(3)	-0.003(3)	-0.0024(15)
C(35)	0.659(3)	-0.1909(18)	0.067(2)	0.004(3)	0.0033(12)	0.0060(16)	0.002(3)	-0.005(3)	0.000(3)
C(36)	0.698(3)	-0.1252(16)	0.1053(16)	0.005(3)	0.0029(11)	0.0030(10)	0.003(3)	-0.001(3)	0.0005(17)
C(41)	0.7210(15)	0.0348(10)	0.4227(10)	0.0021(13)	0.0004(6)	0.0013(6)	-0.0006(15)	0.0004(14)	-0.0005(10)
C(42)	0.6496(19)	0.0966(12)	0.4276(12)	0.0042(18)	0.0014(8)	0.0019(8)	-0.0019(18)	0.0033(19)	-0.0000(12)
C(43)	0.599(3)	0.1029(15)	0.4932(16)	0.008(3)	0.0021(10)	0.0031(11)	-0.004(3)	0.004(3)	-0.0026(16)
C(44)	0.621(3)	0.0489(16)	0.5508(13)	0.006(3)	0.0039(12)	0.0015(8)	-0.001(3)	0.003(2)	-0.0011(15)
C(45)	0.687(2)	-0.0107(14)	0.5444(13)	0.0049(19)	0.0022(9)	0.0021(8)	-0.002(3)	0.0002(19)	-0.0004(14)
C(46)	0.7395(19)	-0.0183(13)	0.4816(12)	0.0050(18)	0.0012(7)	0.0018(7)	0.0003(19)	0.0008(17)	0.0003(13)
C(51)	0.889(3)	0.1070(12)	0.3525(13)	0.005(2)	0.0011(7)	0.0019(8)	-0.0001(19)	0.0011(19)	-0.0004(12)
C(52)	0.9790(19)	0.1157(13)	0.4191(13)	0.0042(18)	0.0015(8)	0.0017(8)	-0.0016(18)	-0.0012(18)	0.0020(12)
C(53)	1.055(2)	0.1755(13)	0.4251(13)	0.0047(18)	0.0011(7)	0.0024(8)	-0.0006(18)	0.001(2)	-0.0008(12)
C(54)	1.042(3)	0.2272(13)	0.3686(15)	0.006(3)	0.0011(8)	0.0033(10)	0.000(3)	0.001(3)	-0.0008(14)
C(55)	0.954(3)	0.2195(13)	0.3025(12)	0.006(2)	0.0020(9)	0.0011(7)	-0.005(3)	-0.0007(18)	-0.0003(12)
C(56)	0.877(3)	0.1587(14)	0.2950(12)	0.007(3)	0.0019(9)	0.0009(7)	-0.000(3)	-0.0002(18)	0.0009(12)

Table 1-7. (continued)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(61)	0.8805(19)	-0.0566(12)	0.3545(11)	0.0042(17)	0.0014(7)	0.0010(6)	-0.0002(18)	0.0008(16)	-0.0004(11)
C(62)	1.000(3)	-0.0585(12)	0.3761(12)	0.008(3)	0.0011(7)	0.0008(6)	0.004(2)	-0.0001(19)	-0.0003(11)
C(63)	1.063(3)	-0.1269(14)	0.3881(12)	0.007(3)	0.0023(9)	0.0006(6)	0.002(3)	0.0029(19)	0.0006(12)
C(64)	0.999(3)	-0.1986(13)	0.3739(12)	0.007(3)	0.0014(8)	0.0011(7)	0.001(2)	0.0035(19)	-0.0006(12)
C(65)	0.877(3)	-0.1935(14)	0.3518(13)	0.007(3)	0.0019(9)	0.0013(7)	0.002(3)	-0.004(2)	0.0002(13)
C(66)	0.817(3)	-0.1225(17)	0.3369(14)	0.005(3)	0.0039(12)	0.0019(9)	0.002(3)	0.001(3)	0.0017(16)
P(3)	0.5228(7)	0.2723(4)	0.2220(4)	0.0067(7)	0.0020(3)	0.0026(3)	0.0010(6)	-0.0004(6)	-0.0016(4)
F(1)	0.4013(16)	0.2265(11)	0.2079(12)	0.0083(18)	0.0044(9)	0.0063(10)	-0.0002(19)	0.003(3)	0.0011(15)
F(2)	0.454(3)	0.336(2)	0.246(2)	0.019(4)	0.012(2)	0.014(3)	0.020(5)	-0.018(5)	-0.018(4)
F(3)	0.639(2)	0.3163(13)	0.2365(15)	0.014(3)	0.0054(11)	0.0081(13)	-0.011(3)	0.001(3)	-0.0023(19)
F(4)	0.583(3)	0.2017(15)	0.207(3)	0.012(3)	0.0059(12)	0.018(3)	0.006(3)	-0.003(5)	-0.014(3)
F(5)	0.493(3)	0.293(3)	0.1375(13)	0.025(5)	0.016(3)	0.0031(9)	-0.023(6)	-0.004(3)	0.006(3)
F(6)	0.549(3)	0.249(3)	0.3079(13)	0.021(4)	0.014(3)	0.0038(9)	0.002(5)	-0.004(3)	0.003(3)

Table 1-8. Final atomic parameters of $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (IIIb).

(a) 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.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD	0.04915(9)	0.13720(5)	0.17868(7)	0.00550(8)	0.00125(2)	0.00238(4)	-0.00079(8)	0.00058(9)	0.00062(6)
S	0.0116(6)	0.1166(3)	0.0287(4)	0.0133(6)	0.00370(17)	0.0042(3)	-0.0021(5)	0.0012(6)	0.0008(4)
P(1)	0.0635(3)	0.24730(16)	0.1976(3)	0.0026(3)	0.00112(8)	0.00259(15)	0.0002(3)	0.0011(3)	0.00106(17)
P(2)	0.0470(3)	0.09187(15)	0.3175(3)	0.0026(3)	0.00099(7)	0.00263(15)	-0.0003(3)	0.0013(3)	0.00100(17)
C(1)	0.0133(12)	0.0517(6)	0.0945(9)	0.0061(12)	0.0003(3)	0.0033(7)	-0.0009(9)	-0.0003(14)	-0.0001(7)
C(2)	-0.145(3)	0.1380(16)	0.0090(16)	0.013(3)	0.0071(12)	0.0069(14)	-0.001(3)	-0.002(3)	0.000(3)
C(11)	-0.0487(11)	0.2778(7)	0.2647(9)	0.0039(10)	0.0021(4)	0.0025(7)	0.0008(10)	0.0028(13)	0.0021(8)
C(12)	-0.1645(12)	0.2541(8)	0.2405(11)	0.0027(10)	0.0022(4)	0.0055(9)	0.0014(11)	0.0021(15)	0.0046(10)
C(13)	-0.2558(13)	0.2746(10)	0.2911(13)	0.0039(12)	0.0040(7)	0.0074(12)	0.0040(14)	0.0049(19)	0.0070(14)
C(14)	-0.2320(15)	0.3146(11)	0.3623(12)	0.0077(16)	0.0045(7)	0.0050(10)	0.0049(17)	0.006(2)	0.0047(14)
C(15)	-0.1190(16)	0.3373(10)	0.3864(12)	0.0086(16)	0.0041(7)	0.0043(9)	0.0047(17)	0.006(2)	0.0014(12)
C(16)	-0.0253(14)	0.3176(9)	0.3382(11)	0.0075(15)	0.0027(5)	0.0043(9)	0.0046(14)	0.0057(18)	0.0013(10)
C(21)	0.2024(10)	0.2823(6)	0.2391(8)	0.0031(9)	0.0011(3)	0.0025(6)	-0.0001(9)	0.0021(12)	0.0006(7)
C(22)	0.2981(11)	0.2424(7)	0.2590(9)	0.0032(10)	0.0016(4)	0.0030(7)	0.0004(10)	0.0027(13)	0.0011(8)
C(23)	0.4068(12)	0.2683(8)	0.2850(10)	0.0034(10)	0.0024(5)	0.0032(7)	0.0012(11)	0.0013(13)	0.0033(9)
C(24)	0.4196(13)	0.3344(8)	0.2908(10)	0.0048(12)	0.0027(5)	0.0035(8)	-0.0015(12)	0.0006(15)	0.0014(10)
C(25)	0.3255(12)	0.3745(7)	0.2717(10)	0.0042(11)	0.0018(4)	0.0041(8)	-0.0007(11)	0.0006(14)	0.0001(9)
C(26)	0.2145(12)	0.3485(7)	0.2455(9)	0.0046(11)	0.0016(4)	0.0034(7)	0.0002(10)	0.0015(14)	0.0006(8)
C(31)	0.0371(10)	0.2898(6)	0.0913(9)	0.0025(9)	0.0013(4)	0.0030(7)	-0.0003(9)	0.0002(12)	0.0003(7)
C(32)	0.1283(12)	0.2868(7)	0.0336(9)	0.0045(11)	0.0015(4)	0.0030(7)	-0.0012(10)	0.0007(13)	0.0007(8)
C(33)	0.1167(12)	0.3197(7)	-0.0484(9)	0.0049(11)	0.0015(4)	0.0027(7)	-0.0003(10)	-0.0006(13)	-0.0002(8)
C(34)	0.0152(12)	0.3532(6)	-0.0742(9)	0.0056(11)	0.0008(3)	0.0029(6)	-0.0011(9)	-0.0008(13)	0.0003(7)
C(35)	-0.0743(11)	0.3556(7)	-0.0179(9)	0.0036(10)	0.0013(4)	0.0040(7)	-0.0006(10)	-0.0032(13)	-0.0004(8)
C(36)	-0.0650(11)	0.3247(6)	0.0660(9)	0.0039(10)	0.0007(3)	0.0032(7)	-0.0004(9)	-0.0004(13)	-0.0000(7)
C(41)	0.1782(10)	0.0470(6)	0.3522(9)	0.0028(9)	0.0007(3)	0.0032(7)	-0.0003(8)	0.0016(12)	0.0001(7)
C(42)	0.2668(11)	0.0424(6)	0.2909(9)	0.0029(10)	0.0010(3)	0.0035(7)	-0.0015(9)	0.0029(12)	-0.0012(7)
C(43)	0.3702(11)	0.0079(7)	0.3183(9)	0.0028(10)	0.0015(4)	0.0038(7)	0.0001(9)	0.0014(13)	-0.0015(8)
C(44)	0.3847(12)	-0.0205(7)	0.4013(10)	0.0043(11)	0.0012(4)	0.0040(7)	0.0015(10)	-0.0012(14)	-0.0011(8)
C(45)	0.2974(11)	-0.0162(6)	0.4608(9)	0.0041(10)	0.0008(3)	0.0036(7)	-0.0002(9)	0.0001(13)	0.0006(7)
C(46)	0.1956(11)	0.0176(7)	0.4342(9)	0.0041(10)	0.0013(4)	0.0028(6)	-0.0001(9)	0.0009(13)	0.0012(7)
C(51)	0.0327(11)	0.1422(6)	0.4149(9)	0.0044(10)	0.0009(3)	0.0030(6)	0.0007(9)	0.0009(12)	0.0010(7)
C(52)	0.1176(11)	0.1876(7)	0.4365(9)	0.0043(10)	0.0013(4)	0.0028(7)	-0.0007(10)	0.0009(13)	0.0004(7)
C(53)	0.1115(14)	0.2267(7)	0.5105(9)	0.0076(14)	0.0017(4)	0.0026(7)	0.0014(12)	0.0016(15)	0.0006(8)
C(54)	0.0178(13)	0.2190(7)	0.5655(9)	0.0072(13)	0.0018(4)	0.0025(7)	0.0023(12)	0.0003(15)	0.0002(8)
C(55)	-0.0669(12)	0.1728(7)	0.5452(9)	0.0038(11)	0.0021(4)	0.0029(7)	0.0010(11)	0.0001(13)	0.0000(8)
C(56)	-0.0621(11)	0.1329(7)	0.4688(9)	0.0028(9)	0.0017(4)	0.0036(7)	0.0006(10)	0.0013(12)	0.0014(9)
C(61)	-0.0753(11)	0.0359(6)	0.3152(8)	0.0038(10)	0.0013(3)	0.0022(6)	-0.0010(9)	0.0016(12)	0.0006(7)
C(62)	-0.1868(12)	0.0603(8)	0.2881(11)	0.0037(11)	0.0020(4)	0.0047(9)	-0.0006(11)	0.0003(15)	0.0023(9)
C(63)	-0.2836(12)	0.0197(8)	0.2816(11)	0.0043(12)	0.0022(5)	0.0046(9)	-0.0016(11)	-0.0016(15)	0.0016(10)
C(64)	-0.2677(12)	-0.0464(7)	0.2998(10)	0.0042(11)	0.0016(4)	0.0041(8)	-0.0031(10)	0.0010(14)	0.0004(9)
C(65)	-0.1563(12)	-0.0696(7)	0.3275(10)	0.0050(12)	0.0014(4)	0.0040(8)	-0.0015(10)	-0.0002(15)	0.0003(8)
C(66)	-0.0603(12)	-0.0293(6)	0.3350(9)	0.0055(11)	0.0009(3)	0.0025(6)	-0.0010(10)	0.0017(13)	-0.0003(7)

Table 1-8. (continued)

(b) Positional parameters in fraction of cell edges and isotropic thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

Atom	x	y	z	B
CL(1)	0.5065(15)	0.1197(9)	0.1529(11)	20.7(6)
O(1)	0.579(3)	0.1116(14)	0.0822(19)	18.5(10)
CL(1S)	0.240(3)	0.0348(16)	-0.025(3)	9.1(8)
CL(2S)	0.378(3)	-0.0351(15)	0.092(2)	8.5(7)
C(S)	0.380	0.013 (0)	0.003	9.(3)

Table 1-9. Final atomic parameters of $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ (IV)

(a) 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.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD(1)	.16800(9)	.22963(8)	.21040(8)	.00175(7)	.00094(5)	.00086(5)	-.00004(9)	.00085(9)	.00010(8)
PD(2)	.22687(9)	.08501(8)	.13267(8)	.00174(7)	.00082(5)	.00093(5)	-.00016(9)	.00053(9)	-.00006(8)
PD(3)	.45218(9)	.11498(8)	.21992(8)	.00168(7)	.00083(5)	.00089(5)	-.00007(9)	.00058(9)	-.00007(8)
PD(4)	.40930(9)	.28021(8)	.23964(8)	.00174(7)	.00081(5)	.00089(5)	.00004(9)	.00072(9)	.00009(8)
S(1A)	.2547 (3)	.2355 (3)	.3166 (3)	.0015 (2)	.00068(15)	.00071(16)	.0004 (3)	.0010 (3)	.0001 (3)
S(1B)	.1110 (3)	.1253 (3)	.2573 (3)	.0017 (2)	.00100(17)	.00141(18)	-.0004 (3)	.0013 (3)	.0003 (3)
S(2A)	.3523 (3)	.1131 (3)	.0739 (3)	.0018 (2)	.00105(16)	.00085(17)	.0006 (3)	.0012 (3)	.0001 (3)
S(2B)	.1634 (3)	.1735 (3)	.0595 (3)	.0016 (2)	.00082(16)	.00081(16)	.0006 (3)	.0005 (3)	.0001 (3)
S(3A)	.3372 (3)	.0532 (3)	.2654 (3)	.0012 (2)	.00076(16)	.00102(17)	-.0002 (3)	.0005 (3)	-.0000 (3)
S(3B)	.4692 (3)	.1644 (2)	.3384 (3)	.0011 (2)	.00053(15)	.00088(16)	.0002 (3)	.0009 (3)	.0005 (3)
S(4A)	.3166 (3)	.2956 (3)	.1387 (3)	.0015 (2)	.00066(15)	.00077(16)	.0003 (3)	.0008 (3)	-.0000 (3)
S(4B)	.5151 (3)	.2511 (3)	.1579 (3)	.0016 (2)	.00098(16)	.00092(17)	-.0002 (3)	.0013 (3)	-.0000 (3)
CL(1S)	.8602 (6)	.2868 (6)	-.0086 (5)	.0059 (5)	.0067 (4)	.0038 (3)	-.0040 (7)	.0006 (6)	-.0012 (6)
CL(2S)	.8480 (6)	.2004 (7)	.1160 (5)	.0062 (5)	.0094 (6)	.0047 (4)	.0052 (9)	.0006 (7)	.0005 (8)

Table 1-9. (continued)

(b) Positional parameters in fraction of cell edges and isotropic thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

Atom	x	y	z	B
C(S)	.797 (2)	.2350(20)	.047 (2)	7.6(9)
C(1A)	.2136(12)	.3196(10)	.1688(10)	1.5(4)
C(1B)	.0937(12)	.2189(11)	.1176(11)	1.8(4)
C(2A)	.2813(11)	.0078(9)	.1923(9)	.8(4)
C(2B)	.1174(12)	.0630(10)	.1827(10)	1.4(4)
C(3A)	.4405(11)	.0744(10)	.1205(10)	1.2(4)
C(3B)	.5522(11)	.1682(10)	.1858(10)	1.1(4)
C(4A)	.3236(11)	.3075(10)	.3128(10)	1.2(4)
C(4B)	.4868(12)	.2569(11)	.3257(11)	1.7(4)
C(1A1)	.1799(11)	.2607(10)	.3812(10)	1.1(4)
C(1A2)	.1492(12)	.2100(10)	.4263(11)	1.6(4)
C(1A3)	.0889(12)	.2288(11)	.4763(11)	1.7(4)
C(1A4)	.0570(13)	.2919(11)	.4795(11)	2.1(4)
C(1A5)	.0887(13)	.3464(11)	.4336(12)	2.4(4)
C(1A6)	.1491(12)	.3272(10)	.3836(11)	1.7(4)
C(1B1)	.0007(13)	.1396(11)	.2701(11)	1.9(4)
C(1B2)	-.0537(14)	.0918(12)	.2511(12)	2.9(5)
C(1B3)	-.1366(16)	.1032(14)	.2661(14)	3.8(6)
C(1B4)	-.1604(14)	.1616(12)	.3010(12)	2.9(5)
C(1B5)	-.1036(14)	.2108(12)	.3220(12)	2.8(5)
C(1B6)	-.0196(13)	.2008(11)	.3065(11)	2.3(4)
C(2A1)	.3463(13)	.0671(11)	-.0122(12)	2.4(4)
C(2A2)	.3800(15)	.0973(12)	-.0699(13)	3.1(5)
C(2A3)	.3738(17)	.0596(14)	-.1410(14)	4.2(6)
C(2A4)	.3374(16)	-.0037(14)	-.1412(14)	4.3(6)
C(2A5)	.3041(15)	-.0336(13)	-.0790(13)	3.4(5)
C(2A6)	.3069(14)	.0013(12)	-.0129(12)	2.9(5)
C(2B1)	.1017(13)	.1317(11)	-.0102(11)	1.9(4)
C(2B2)	.1423(14)	.1225(12)	-.0741(12)	2.9(5)
C(2B3)	.0996(16)	.0955(13)	-.1337(14)	3.8(6)
C(2B4)	.0149(17)	.0735(14)	-.1253(14)	4.3(6)
C(2B5)	-.0252(14)	.0866(12)	-.0591(13)	3.1(5)
C(2B6)	.0214(13)	.1146(11)	-.0007(12)	2.3(4)
C(3A1)	.3955(11)	-.0135(10)	.3125(10)	1.3(4)
C(3A2)	.3971(13)	-.0120(11)	.3881(11)	2.1(4)
C(3A3)	.4479(15)	-.0597(13)	.4274(13)	3.4(5)
C(3A4)	.4917(15)	-.1082(12)	.3896(13)	3.0(5)
C(3A5)	.4900(13)	-.1113(11)	.3130(11)	2.3(4)
C(3A6)	.4385(12)	-.0636(11)	.2728(11)	1.7(4)
C(3B1)	.5648(11)	.1335(9)	.3791(10)	.9(4)
C(3B2)	.6096(11)	.1776(10)	.4220(10)	1.2(4)
C(3B3)	.6821(12)	.1540(11)	.4574(11)	1.8(4)
C(3B4)	.7051(13)	.0825(11)	.4481(11)	1.9(4)
C(3B5)	.6572(12)	.0426(11)	.4025(11)	1.9(4)
C(3B6)	.5862(12)	.0660(10)	.3657(10)	1.5(4)
C(4A1)	.3496(13)	.3703(11)	.0958(11)	1.9(4)
C(4A2)	.3907(12)	.3649(10)	.0278(10)	1.4(4)
C(4A3)	.4180(13)	.4203(11)	-.0098(11)	2.1(4)
C(4A4)	.4019(14)	.4878(12)	.0159(12)	2.7(5)
C(4A5)	.3628(14)	.4971(12)	.0843(12)	2.7(5)
C(4A6)	.3358(12)	.4383(10)	.1203(11)	1.7(4)
C(4B1)	.5970(11)	.3101(10)	.1712(10)	1.1(4)
C(4B2)	.6741(15)	.2934(13)	.1960(14)	3.7(5)
C(4B3)	.7365(17)	.3426(15)	.2072(15)	4.7(6)
C(4B4)	.7169(16)	.4130(13)	.1914(14)	3.8(6)
C(4B5)	.6438(16)	.4304(14)	.1652(14)	3.8(6)
C(4B6)	.5813(14)	.3798(12)	.1568(12)	2.8(5)

1.4 Results and Discussion

$[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2(I)$

Figure 1-3 shows a perspective view of the molecule with atomic numbering. An *ORTEP* plot(Johnson, 1976) of the complex and solvent molecules with thermal ellipsoids at 50% probability level is presented in Fig. 1-4. Bond lengths and bond angles along with their estimated standard deviations are given in Tables 1-10 and 1-11.

The present X-ray structure determination has been carried out with high precision. The estimated standard deviations of bond lengths and bond angles are very small, those of C-C bond lengths in phenyl groups lying between 0.004 and 0.006 Å.

Figure 1-5 shows the coordination geometry around the palladium atom with selected bond lengths and bond angles. The remarkable feature of the molecular structure is that no donation of the sulphur atom to the metal atom is observed in the CH_2SCH_3 group. This group is bonded to the palladium atom only through the Pd-C σ-bond according to the type c of the bonding mode shown in Fig. 1-1. The palladium atom is four-coordinate and is surrounded in an approximately planar fashion by two *trans* phosphorus atoms of the triphenylphosphine ligands, the Cl atom and a σ-bonded C atom of the CH_2SCH_3 group. The equations of the least-squares planes including the palladium atom and atomic deviations from the planes are given in Table 1-12. The deviations of the Cl, C and two P atoms from the square-planar plane are relatively large[maximum 0.18 Å]. As a gross approximation, the geometry around the palladium atom may be distorted tetrahedrally[Cl(1)-Pd-C(1)=169.73(9) and

P(1)-Pd-P(2)=174.19(3)°], which is connected with an interaction between sulphur and metal atoms mentioned below. The CH_2SCH_3 group is located almost perpendicular to the coordination plane, the dihedral angle between the C(1), S and C(2) plane and the coordination plane being 90.7°.

In the CH_2SCH_3 group, the observed bond length of S-C(1) [1.796(3) Å] is slightly shorter than that of S-C(2)[1.817(5) Å]. Taking the estimated S-C single bond length[1.82 Å](Abrahams, 1956) into consideration, both are considered to be S-C single bonds. Although the C(1) atom is the sp^3 carbon[Pd-C(1)-H(1A) =109(2), Pd-C(1)-H(1B)=113(2), S-C(1)-H(1A)=110(2), S-C(1)-H(1B) =109(2) and H(1A)-C(1)-H(1B)=114(3)°], the Pd-C(1)-S angle of 100.64(14)° is smaller than the expected value for the sp^3 carbon. The non-bonded Pd···S distance is 2.973(1) Å. These Pd-C(1)-S angle and Pd···S distance might imply that the sulphur atom slightly interacts with the metal atom, in spite of the absence of the Pd-S coordination bond. The C(1)-S-C(2) angle of 101.28(18)° is also slightly smaller than the expected value.

The Pd-C(1) bond length[2.061(3) Å] is a normal value for a Pd(II)-C(sp^3) σ-bond. Among the palladium complexes whose molecular structures have been determined by the X-ray diffraction method, the Pd-Cl distances in which the chlorine atom is located at the terminal position fall in the range between 2.24 and 2.45 Å*. Therefore, the Pd-Cl bond length in the present complex I [2.408(1) Å] is normal. Table 1-13* presents Pd-P bond lengths in all complexes hitherto reported in which the phosphorus atoms of two trialkylphophine ligands are mutually *trans*. The Pd-P bond lengths in the present complex I [2.346(1) and 2.337(1) Å] are fairly similar to each other and are relatively long among those in Table 1-13.

The crystal structure viewed along the b axis is given in Fig. 1-6. No abnormally short intermolecular contacts are observed, the shortest contact between non-hydrogen atoms being 3.319(6) Å[Cl(1)(x,y,z)···C(S)(1/2-x,1/2+y,3/2-z)].

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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 transcribed from the data base at the Cambridge Crystallographic Data Centre(Yamamoto, Negishi, Ushimaru, Tozawa, Okabe & Fujiwara, 1975; Shimanouchi & Yamamoto, 1976).

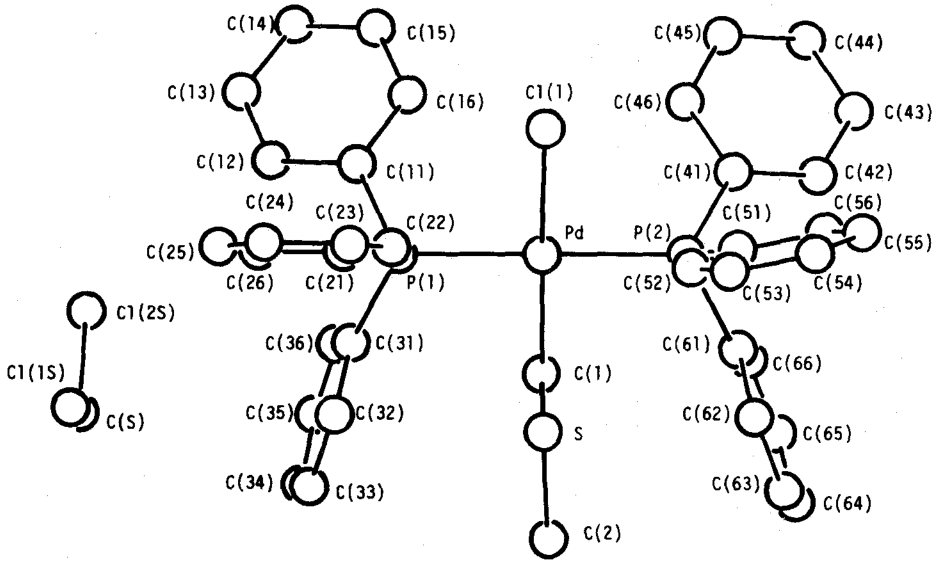

Fig. 1-3. A prespective view of the molecule and the numbering system of the atoms of [PdCl(CH_2SCH_3)(PPh_3)$_2$]·CH_2Cl_2(I). Hydrogen atoms are omitted for clarity.

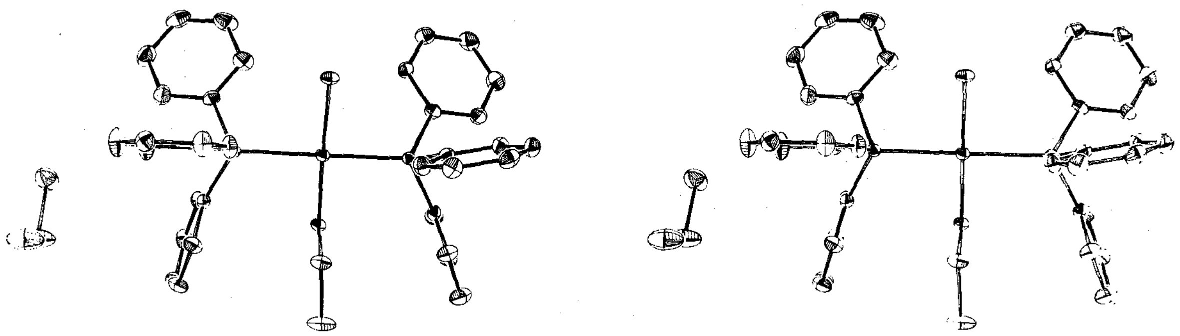

Fig. 1-4. *ORTEP* drawings of the complex and solvent molecules of [PdCl(CH_2SCH_3)(PPh_3)$_2$]·CH_2Cl_2(I)(stereoscopic drawings). The thermal ellipsoids correspond to 50% probability level. Hydrogen atoms are omitted for clarity.

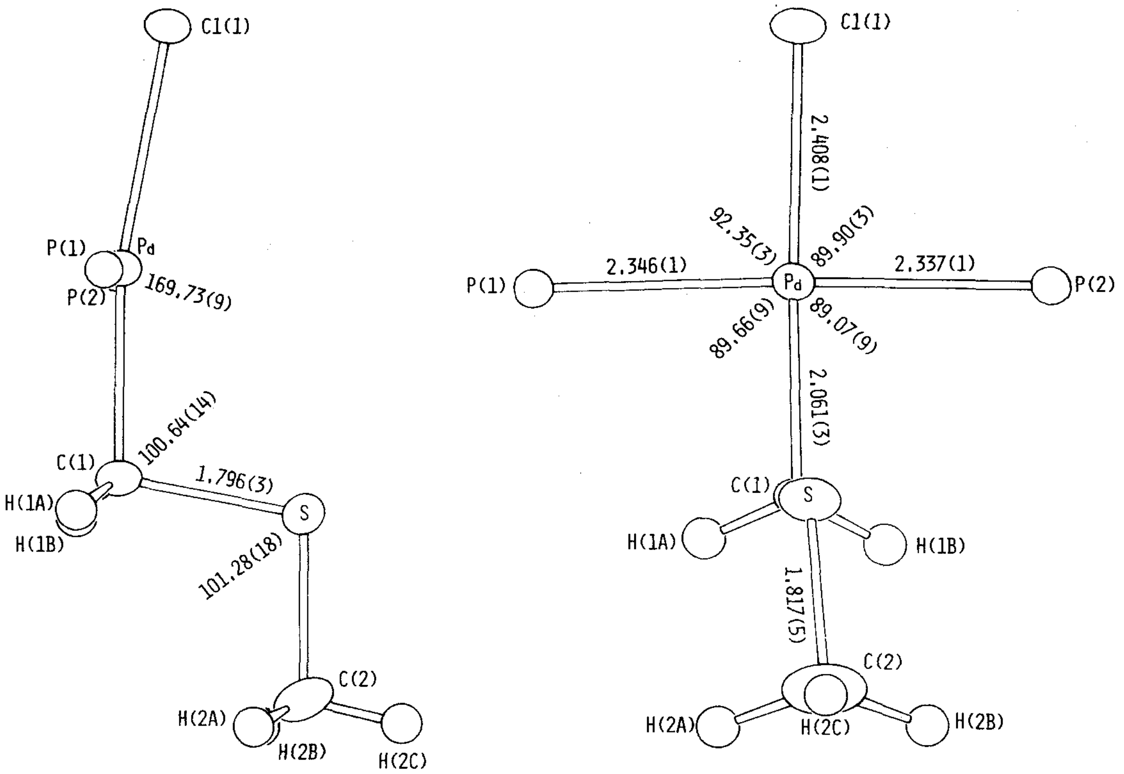

Fig. 1-5. The coordination geometry around the palladium atom in $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I).

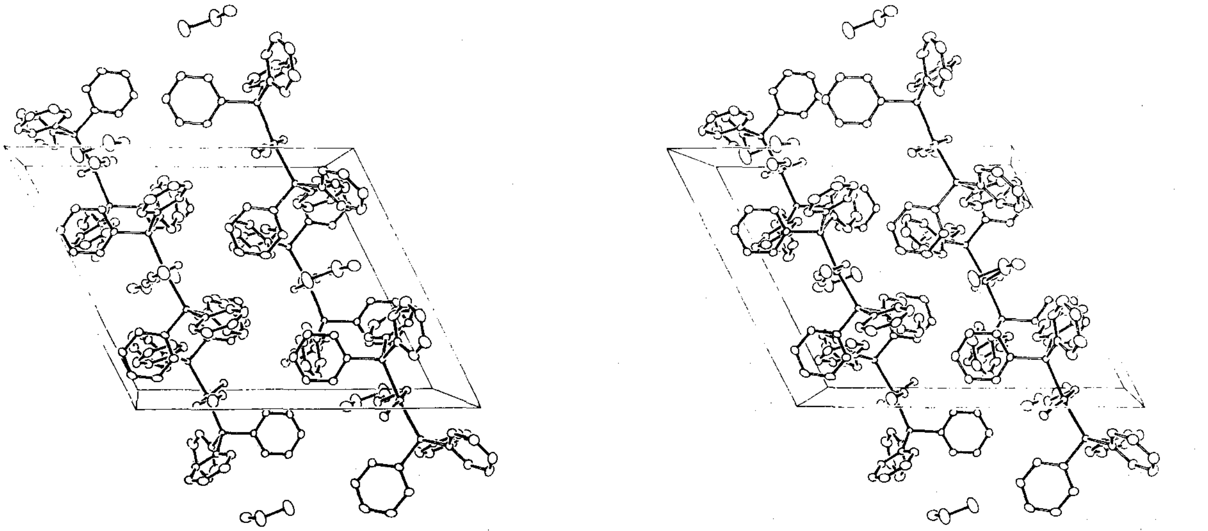

Fig. 1-6. The crystal structure of $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I) as viewed down the b axis(stereoscopic drawings). Atoms are represented by thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for clarity.

Table 1-10. Bond lengths in [PdCl(CH$_2$SCH$_3$)(PPh$_3$)$_2$]·CH$_2$Cl$_2$(I). Estimated standard deviations in parentheses.

(a) Bonds involving non-hydrogen atoms

Length(Å)		Length(Å)	
Pd-Cl(1)	2.408(1)	Pd···S	2.973(1)*
Pd-P(1)	2.346(1)	Pd-P(2)	2.337(1)
Pd-C(1)	2.061(3)		
S-C(1)	1.796(3)	S-C(2)	1.817(5)
P(1)-C(11)	1.833(3)	P(2)-C(41)	1.829(3)
P(1)-C(21)	1.830(3)	P(2)-C(51)	1.828(3)
P(1)-C(31)	1.821(3)	P(2)-C(61)	1.827(3)
C(11)-C(12)	1.403(5)	C(41)-C(42)	1.400(5)
C(12)-C(13)	1.390(6)	C(42)-C(43)	1.385(5)
C(13)-C(14)	1.393(6)	C(43)-C(44)	1.392(6)
C(14)-C(15)	1.374(6)	C(44)-C(45)	1.382(5)
C(15)-C(16)	1.395(6)	C(45)-C(46)	1.397(5)
C(16)-C(11)	1.401(5)	C(46)-C(41)	1.398(5)
C(21)-C(22)	1.385(5)	C(51)-C(52)	1.399(5)
C(22)-C(23)	1.409(5)	C(52)-C(53)	1.392(5)
C(23)-C(24)	1.375(5)	C(53)-C(54)	1.387(5)
C(24)-C(25)	1.391(5)	C(54)-C(55)	1.385(5)
C(25)-C(26)	1.396(6)	C(55)-C(56)	1.392(5)
C(26)-C(21)	1.386(5)	C(56)-C(51)	1.396(5)
C(31)-C(32)	1.401(5)	C(61)-C(62)	1.389(5)
C(32)-C(33)	1.390(5)	C(62)-C(63)	1.395(5)
C(33)-C(34)	1.394(6)	C(63)-C(64)	1.382(5)
C(34)-C(35)	1.382(5)	C(64)-C(65)	1.387(5)
C(35)-C(36)	1.393(5)	C(65)-C(66)	1.388(5)
C(36)-C(31)	1.398(4)	C(66)-C(61)	1.395(5)
Cl(1S)-C(S)	1.727(6)	Cl(2S)-C(S)	1.763(6)

* Non-bonded distance.

Table 1-10. (continued)

(b) Bonds involving hydrogen atoms

Length(Å)		Length(Å)	
C(1)-H(1A)	0.96(4)	C(1)-H(1B)	0.98(4)
C(2)-H(2A)	1.09(5)		
C(2)-H(2B)	1.08(6)		
C(2)-H(2C)	0.97(5)		
C(12)-H(12)	1.02(5)	C(42)-H(42)	1.01(4)
C(13)-H(13)	1.04(5)	C(43)-H(43)	1.02(4)
C(14)-H(14)	0.98(5)	C(44)-H(44)	1.00(5)
C(15)-H(15)	0.97(5)	C(45)-H(45)	0.98(5)
C(16)-H(16)	0.94(5)	C(46)-H(46)	0.94(4)
C(22)-H(22)	1.05(4)	C(52)-H(52)	1.00(5)
C(23)-H(23)	1.01(6)	C(53)-H(53)	1.01(4)
C(24)-H(24)	0.98(4)	C(54)-H(54)	1.04(4)
C(25)-H(25)	1.03(5)	C(55)-H(55)	1.00(5)
C(26)-H(26)	1.02(5)	C(56)-H(56)	1.03(5)
C(32)-H(32)	1.02(5)	C(62)-H(62)	1.05(5)
C(33)-H(33)	0.99(5)	C(63)-H(63)	1.02(5)
C(34)-H(34)	1.03(5)	C(64)-H(64)	1.01(4)
C(35)-H(35)	1.01(5)	C(65)-H(65)	0.98(5)
C(36)-H(36)	1.05(4)	C(66)-H(66)	1.11(4)
C(S)-H(1S)	0.97(8)	C(S)-H(1B)	1.32(9)

Table 1-11. Bond angles involving non-hydrogen atoms in $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I). Estimated standard deviations in parentheses.

Angle(°)		Angle(°)	
Cl(1)-Pd-P(1)	92.35(3)	Cl(1)-Pd-P(2)	89.90(3)
P(1)-Pd-C(1)	89.66(9)	P(2)-Pd-C(1)	89.07(9)
Cl(1)-Pd-C(1)	169.73(9)	P(1)-Pd-P(2)	174.19(3)
Pd-C(1)-S	100.64(14)	C(1)-S-C(2)	101.28(18)

Table 1-11. (continued)

Angle(°)		Angle(°)	
Pd-P(1)-C(11)	113.53(11)	Pd-P(2)-C(41)	114.38(10)
Pd-P(1)-C(21)	114.52(10)	Pd-P(2)-C(51)	113.36(10)
Pd-P(1)-C(31)	115.92(10)	Pd-P(2)-C(61)	117.11(10)
C(11)-P(1)-C(21)	105.05(14)	C(41)-P(2)-C(51)	106.27(14)
C(11)-P(1)-C(31)	103.34(14)	C(41)-P(2)-C(61)	102.55(14)
C(21)-P(1)-C(31)	103.09(14)	C(51)-P(2)-C(61)	101.65(14)
P(1)-C(11)-C(12)	121.6(3)	P(2)-C(41)-C(42)	120.9(2)
P(1)-C(11)-C(16)	120.4(3)	P(2)-C(41)-C(46)	120.2(2)
C(16)-C(11)-C(12)	118.0(3)	C(46)-C(41)-C(42)	118.9(3)
C(11)-C(12)-C(13)	121.1(4)	C(41)-C(42)-C(43)	120.9(3)
C(12)-C(13)-C(14)	119.9(4)	C(42)-C(43)-C(44)	120.3(4)
C(13)-C(14)-C(15)	119.6(4)	C(43)-C(44)-C(45)	119.2(4)
C(14)-C(15)-C(16)	121.1(4)	C(44)-C(45)-C(46)	121.3(3)
C(15)-C(16)-C(11)	120.2(3)	C(45)-C(46)-C(41)	119.5(3)
P(1)-C(21)-C(22)	119.8(2)	P(2)-C(51)-C(52)	119.0(2)
P(1)-C(21)-C(26)	120.9(3)	P(2)-C(51)-C(56)	122.0(2)
C(26)-C(21)-C(22)	119.3(3)	C(56)-C(51)-C(52)	118.8(3)
C(21)-C(22)-C(23)	119.6(3)	C(51)-C(52)-C(53)	120.6(3)
C(22)-C(23)-C(24)	121.0(3)	C(52)-C(53)-C(54)	120.1(3)
C(23)-C(24)-C(25)	119.2(3)	C(53)-C(54)-C(55)	119.7(3)
C(24)-C(25)-C(26)	120.0(4)	C(54)-C(55)-C(56)	120.6(3)
C(25)-C(26)-C(21)	120.9(4)	C(55)-C(56)-C(51)	120.2(3)
P(1)-C(31)-C(32)	119.9(2)	P(2)-C(61)-C(62)	120.0(2)
P(1)-C(31)-C(36)	120.8(2)	P(2)-C(61)-C(66)	120.6(2)
C(36)-C(31)-C(32)	118.6(3)	C(66)-C(61)-C(62)	119.0(3)
C(31)-C(32)-C(33)	120.6(3)	C(61)-C(62)-C(63)	120.6(3)
C(32)-C(33)-C(34)	120.1(4)	C(62)-C(63)-C(64)	120.1(4)
C(33)-C(34)-C(35)	119.8(4)	C(63)-C(64)-C(65)	119.7(4)
C(34)-C(35)-C(36)	120.3(3)	C(64)-C(65)-C(66)	120.4(3)
C(35)-C(36)-C(31)	120.5(3)	C(65)-C(66)-C(61)	120.3(3)
Cl(1S)-C(S)-Cl(2S)	111.9(3)		

Table 1-12. Least-squares planes in $[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$(I).

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 $Z = cz\sin\beta$.

(a) Coordination plane of Pd through Pd, Cl(1), P(1), P(2) and C(1)

$$0.023X + 0.440Y - 0.898Z + 7.380 = 0.0$$

(b) Plane defined by Pd, Cl(1), C(1), S and C(2)

$$-1.000X + 0.023Y + 0.013Z + 1.455 = 0.0$$

Deviations of atoms from the plane(Å)

	Plane a	Plane b
Pd	+0.036	+0.023
Cl(1)	-0.175	-0.040
P(1)	+0.151	+2.362*
P(2)	+0.148	-2.313*
C(1)	-0.148	+0.031
S	-1.935*	+0.043
C(2)	-2.116*	-0.052

The dihedral angle between the planes a and b is 91.4°.

* Not included in the least-squares calculation.

Table 1-13. Pd-P bond lengths of palladium complexes in which the phosphorus atoms of two trialkylphosphine ligands are mutually *trans*.

Pd complex	Length(Å)	Reference
$\mathrm{PdHCl(PEt_3)_2}$	2.308(4)[a]	Schneider & Shearer(1973)
$\mathrm{PdCl(Azb)(PEt_3)_2}$[c]	2.309(9)[b]	Weaver(1970)
$\mathrm{PdCl_2(PMe_2Men)_2}$[d]	2.310(5)	Kan, Miki, Kai, Yasuoka & Kasai(1978)
$\mathrm{Pd(SCN)_2\{P(OPh)_3\}_2}$	2.312(1)	Jacobson, Wong, Chieh & Carty(1974)
$\mathrm{PdCl(Dtt)(PPh_3)_2}$[e]	2.325(3)[a]	Bonbieri, Immirzi & Toniolo(1975)
$\mathrm{PdCl(COCOOMe)(PPh_3)_2}$	2.325(7)[a]	Fayos, Dobrzynsky, Angelici & Clardy(1973)
$\mathrm{Pd(SCN)_2\{PPh_2(C{=}CBu\text{-}}t\mathrm{)\}_2}$	2.326(3)	Beran, Carty, Chieh & Patel(1973)
$\mathrm{PdI_2(PMe_2Ph)_2}$(orthorhombic form)	2.330(8)[a]	Bailey & Mason(1968)
$\mathrm{PdI_2(PPh_3)_2}$	2.331(2)	Debaerdemaeker, Kutoglu, Schmid & Weber(1973)
$\mathrm{PdI_2(PMe_2Ph)_2}$(monoclinic form)	2.333(7)	Bailey & Mason(1968)
$\mathrm{PdCl(CH_2SCH_3)(PPh_3)_2}$	2.342(1)[a]	this work(the complex I)
$\mathrm{PdBr\{C_4(COOMe)_4H\}(PPh_3)_2}$	2.35[a]	Roe, Bailey, Moseley & Maitlis(1972)
$\mathrm{PdCl_2(PMe_2neoMen)_2}$[d]	2.353(5)[a]	Kan, Miki, Kai, Yasuoka & Kasai(1978)

a Averaged value of two Pd-P bonds.

b Averaged value of four(crystallographically independent) Pd-P bonds.

c Azb = 2-(phenylazo)phenyl

d Men = menthyl, neoMen = neomenthyl.

e Dtt = 1, 3-di-*p*-tolyltriazenido

[PdCl(CH_2SCH_3)(PPh_3)](II)

Figure 1-7 shows a perspective view of the molecule with atomic numbering. Figire 1-8 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 1-14 and 1-15.

No essential difference is observed in molecular structures at -160 and 20°C 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 1-9 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 type a of the bonding mode presented in Fig. 1-1. 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 1-16. 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 (Abrahams, 1956).

The S-C(1) bond length in this 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 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 $[Mo(C_5H_5)(CO)_2 \cdot (CH_2SCH_3)]$(Rodulfo de Gil & Dahl, 1969)[*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. The Pd(II)-S distances in palladium complexes whose molecular structures have been determined hitherto by the X-ray diffraction method, fall in the range between 2.24 and 2.47 Å*. Among these, the Pd-S bond lengths of complexes which have the same type of coordination of the sulphur atom as that in this complex are listed in Table 1-17. The Pd-S bond length in this complex[2.371(1) Å] is considered to be a normal Pd-S length; however, it is slightly

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* This information has been obtained from the XDC data base of the TOOL-IR sytem at the Computer Center of the University of Tokyo which is based on the data base at the Cambridge Crystallographic Data Centre(Yamamoto, Negishi, Ushimaru, Tozawa, Okabe & Fujiwara, 1975; Shimanouchi & Yamamoto, 1976).

longer than those in Table 1-17 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 1-14(a), all the 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. 1-10. All intermolecular atomic contacts are considered to be at the usual van der Waals contacts.

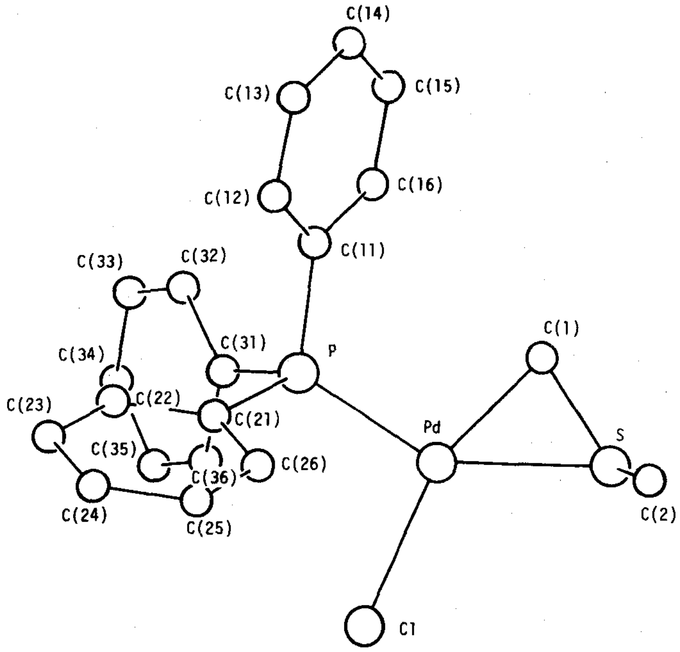

Fig. 1-7. A perspective view of the molecule and the numbering system of the atoms of [PdCl(CH_2SCH_3)(PPh_3)](II). Hydrogen atoms are omitted for clarity.

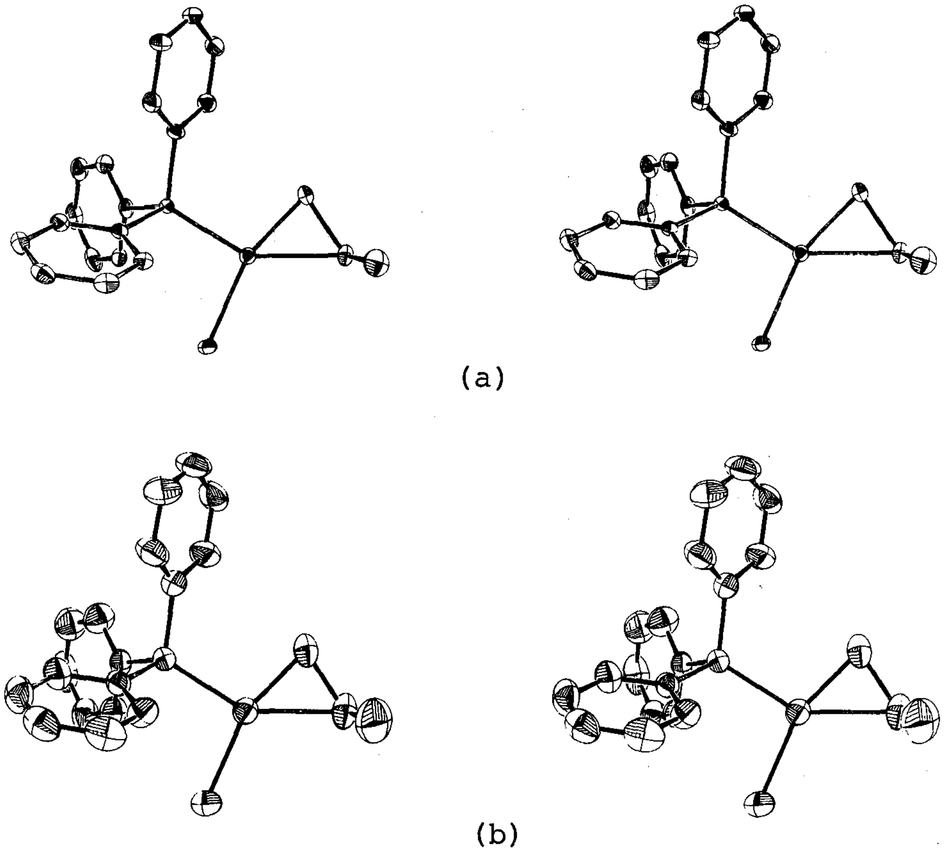

Fig. 1-8. *ORTEP* drawings of the molecule of [PdCl(CH_2SCH_3)·(PPh_3)](II)(stereoscopic drawings). The thermal ellipsoids correspond to 50% probability level. Hydrogen atoms are omitted for clarity. (a) -160°C, (b) 20°C.

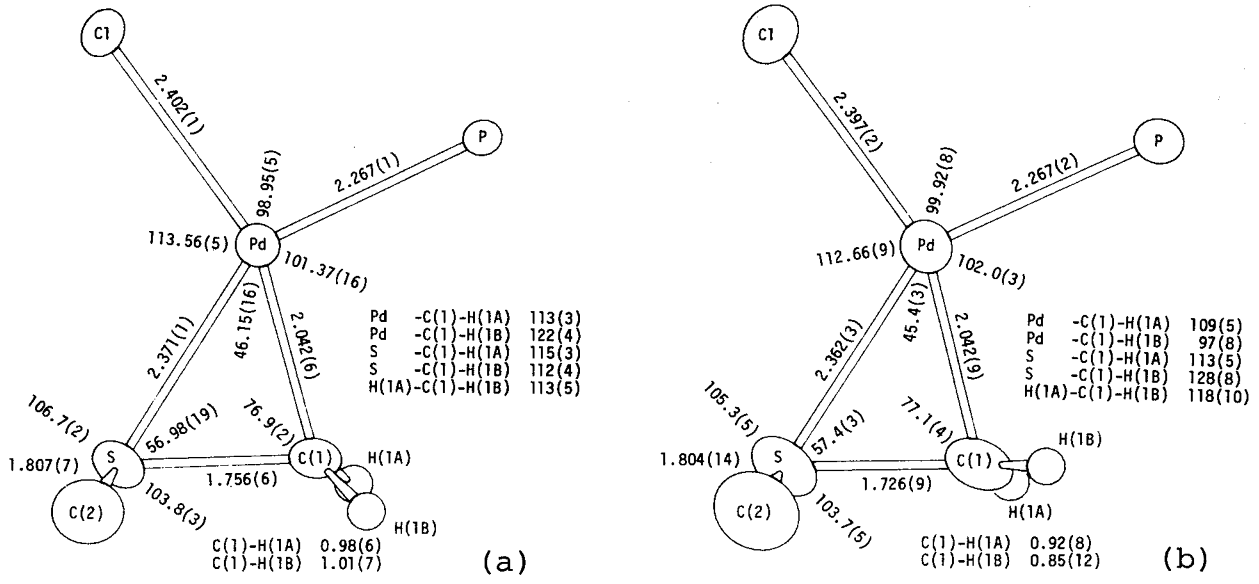

Fig. 1-9. The coordination geometry around the palladium atom in [PdCl(CH_2SCH_3)(PPh_3)](II). (a) -160°C, (b) 20°C.

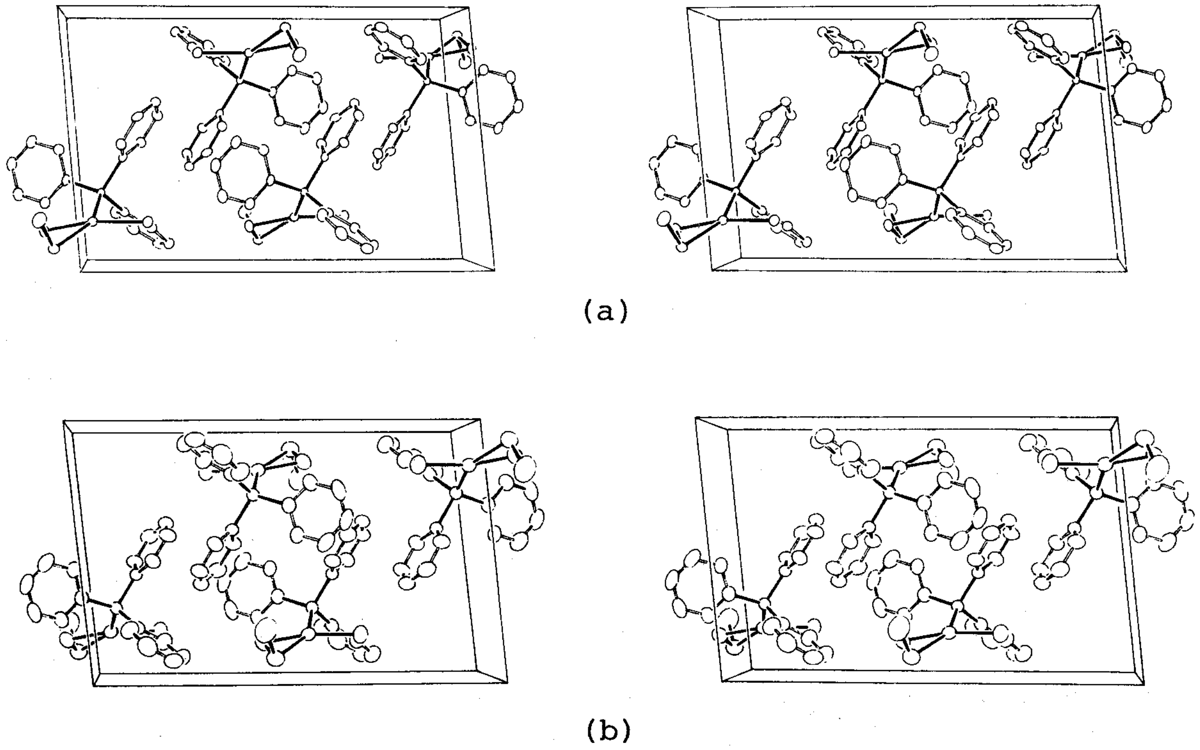

Fig. 1-10. The crystal structure of [PdCl(CH_2SCH_3)(PPh_3)](II) as viewed down the b axis(stereoscopic drawing). Atoms are represented by thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for clarity. (a) -160°C, (b) 20°C.

Table 1-14. Bond lengths in [PdCl(CH_2SCH_3)(PPh_3)](II). Estimated standard deviations in parentheses.

(a) Bonds involving non-hydrogen atoms

Length(Å)	[-160°C]	[20°C]
Pd-Cl	2.402(1)	2.397(2)
Pd-S	2.371(1)	2.362(3)
Pd-P	2.267(1)	2.267(2)
Pd-C(1)	2.042(6)	2.042(9)
S-C(1)	1.756(6)	1.726(9)
S-C(2)	1.807(7)	1.806(14)
P-C(11)	1.825(5)	1.814(8)
P-C(21)	1.818(5)	1.808(7)
P-C(31)	1.824(5)	1.823(7)
C(11)-C(12)	1.394(8)	1.368(12)
C(12)-C(13)	1.396(8)	1.400(15)
C(13)-C(14)	1.386(9)	1.351(15)
C(14)-C(15)	1.391(9)	1.350(14)
C(15)-C(16)	1.390(8)	1.383(13)
C(16)-C(11)	1.416(8)	1.396(12)
C(21)-C(22)	1.397(7)	1.397(11)
C(22)-C(23)	1.394(8)	1.393(13)
C(23)-C(24)	1.393(8)	1.359(14)
C(24)-C(25)	1.402(8)	1.381(14)
C(25)-C(26)	1.387(8)	1.395(12)
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)

Table 1-14. (continued)

(b) Bonds involving non-hydrogen atoms

Length(Å)	[-160°C]	[20°C]
C(1)-H(1A)	0.98(6)	0.92(8)
C(1)-H(1B)	1.01(7)	0.85(12)
C(2)-H(2A)	0.82(8)	0.88(10)
C(2)-H(2B)	0.92(8)	0.79(8)
C(2)-H(2C)	1.02(8)	1.13(14)
C(12)-H(12)	0.95(6)	0.97(6)
C(13)-H(13)	0.98(6)	0.92(10)
C(14)-H(14)	0.91(7)	0.95(7)
C(15)-H(15)	1.02(7)	0.81(8)
C(16)-H(16)	0.94(5)	0.94(8)
C(22)-H(22)	1.02(6)	0.95(7)
C(23)-H(23)	0.83(6)	0.78(8)
C(24)-H(24)	0.97(6)	0.92(7)
C(25)-H(25)	1.01(6)	0.84(8)
C(26)-H(26)	0.98(8)	0.96(7)
C(32)-H(32)	0.80(6)	0.87(7)
C(33)-H(33)	0.79(7)	0.86(8)
C(34)-H(34)	0.82(6)	0.74(9)
C(35)-H(35)	1.02(6)	0.80(8)
C(36)-H(36)	0.90(6)	0.85(8)

Table 1-15. Bond angles involving non-hydrogen atoms in [PdCl(CH$_2$SCH$_3$)(PPh$_3$)](II). Estimate standard deviations in parentheses.

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)

Table 1-15. (continued)

Angle(°)	[-160°C]	[20°C]
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(8)	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)

Table 1-16. Least-squares planes in $[PdCl(CH_2SCH_3)(PPh_3)]$ (I).

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 $Z = cz\sin\beta$.

Coordination plane of Pd through Pd, Cl, S, P and C(1)

(a) -160°C

$$-0.8715X + 0.4799Y + 0.1007Z + 1.6640 = 0.0$$

(b) 20°C

$$-0.8821X + 0.4644Y + 0.0791Z + 1.7141 = 0.0$$

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
C(2)	-1.775*	-1.788*

* Not included in the least-squares calculation.

Table 1-17. Pd-S bond lengths of palladium complexes which have the same coordination of the sulphur atom as that in [PdCl$(CH_2SCH_3)(PPh_3)$](II)

Pd complex	Length(Å)	Reference
$PdCl_2NH_2CH(COOH)CH_2SCH_3$	2.230(4) 2.261(4)	Battaglia, Corradi, Palmieri, Nardelli & Tani(1973)
$Pd(C_{10}H_{22}N_2OS_2)(NO_3)_2$	2.261(4) 2.267(1)	Louis, Pelissard & Weiss(1974)
$PdCl_2(C_{18}H_{36}N_2O_4S_2)_2$	2.264(1) 2.265(1)	Louis, Thierry & Weiss(1974)
$PdCl_2NH_2CH(COOH)CH_2CH_2SCH_3$	2.265(4)	Warren, McConnell & Stephenson(1970)
$Pd(C_{34}H_{28}S_4)$	2.292(3) 2.308(2)	Clark, Waters & Whittle(1973)
$Pd_2Br_4(CH_3SCH_3)_2$	2.30(2)	Sales, Stokes & Woodward(1968)

$[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa)

Figure 1-11 shows an *ORTEP* drawing(Johnson, 1976) of the $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation. Atoms are represented by thermal ellipsoids enclosing 30% probability levels. Bond lengths and bond angles are listed in Tables 1-18 and 1-19.

Two crystallographically difficult problems arise in the present structure analysis. One is abnormally large thermal vibration of the PF_6 anion. Figure 1-12 gives the electron density distribution on planes which contain the phosphorus and four fluorine atoms of the PF_6 anion. Six fluorine atoms, especially F(2), F(4), F(5) and F(6) atoms, show low peak heights and broadening in electron density distribution due to the large thermal motion. In fact, the ^{19}F NMR study of this crystal suggested that the PF_6 anions are rapidly reorienting about the octahedral axes at random, or nearly so, even at liquid nitrogen temperature*. The other problem is the possibility of the disordered structure in the CH_2SCH_3 group. As mentioned before, a relatively high peak remained near the location of the sulphur atom in the electron density map. However, this could not be surely assigned as a disordered fragment of the sulphur atom considering the chemical geometry around the palladium atom.

Figure 1-13 shows the coordination geometry around the palladium atom along with selected bond lengths and bond angles. The geometry around the palladium atom is essentially considered

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* The observed second moment is only 2.3 G^2 between 77 and 300K, which is ascribable to interionic magnetic interactions (Kiriyama & Furukawa, 1978).

as square-planar. The equations of the coordination planes and atomic deviations from the planes are presented in Table 1-20. The dihedral angles between planes concerning the coordination geometry around the palladium atom are shown in Table 1-21. The coordination of the CH_2SCH_3 group to the palladium atom is considered as the type a of bonding shown in Fig. 1-1, which is similar to the complex II. The planarity of the coordination plane is not so high, the maximum deviation from the least-squares plane being 0.17 Å. The C(1) and S atoms in the CH_2SCH_3 group are located at the opposite side, 0.13 and 0.20 Å away, of the plane defined by the Pd, P(1) and P(2) atoms, respectively(Table 1-20). Figure 1-14 shows the perspective view of this coordination geometry. The S-C(1) and S-C(2) bond lengths[1.77(4) and 1.78(4) Å] are close to that of the S-C single bond[1.82 Å](Abrahams, 1956), which are comparable with those found in II[S-C(1)=1.756(6) and S-C(2)=1.807(7) Å]. The Pd-C(1) bond length of 2.06(4) Å is also close to that found in II[2.042(6) Å], which is considered to be a normal value for the Pd(II)-C(sp^3) σ-bond. The Pd-S bond length of 2.367(8) Å is similar to that found in II[2.371(1) Å].

Two Pd-P bond lengths are 2.350(5) and 3.271(6) Å. The difference in these is partly due to the difference of *trans*-influence between the carbon and sulphur atoms.

The crystal structure projected along the a* axis is given in Fig. 1-15. All intermolecular atomic contacts are considered to be at the van der Waals contacts, the shortest atomic contact being 3.22(4) Å[C(15)(x,y,z)...F(3)(2-x,-1/2+y,1/2-z)].

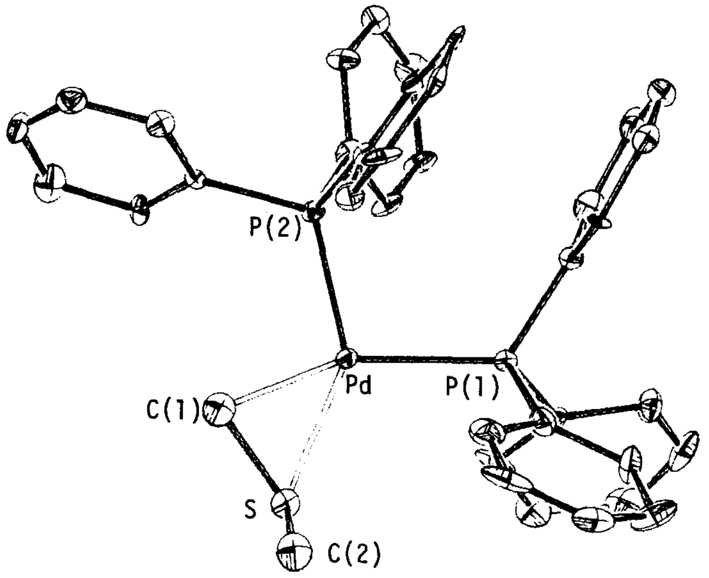
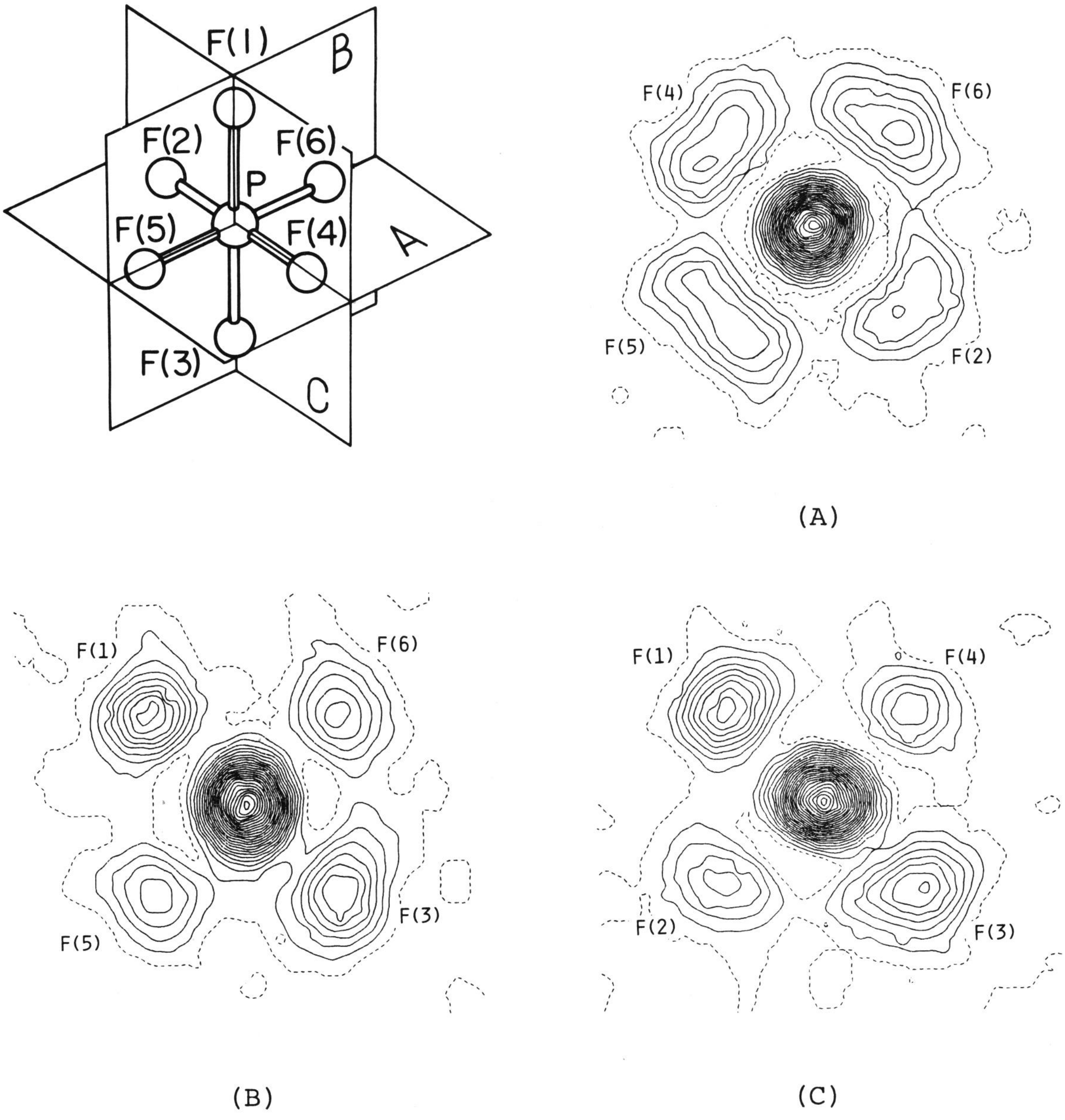


Fig. 1-11. An *ORTEP* drawing of $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa). The thermal ellipsoids correspond to 30% probability levels. The atomic numberings for the phenyl groups are omitted.



(A)

(B)

(C)

Fig. 1-12. Electron density distribution on three planes of the octahedral PF_6 anion in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (IIIa). The contours are drawn at the interval of 1.0 e/Å^3. Zero contours are shown as broken lines while negative contours are omitted.

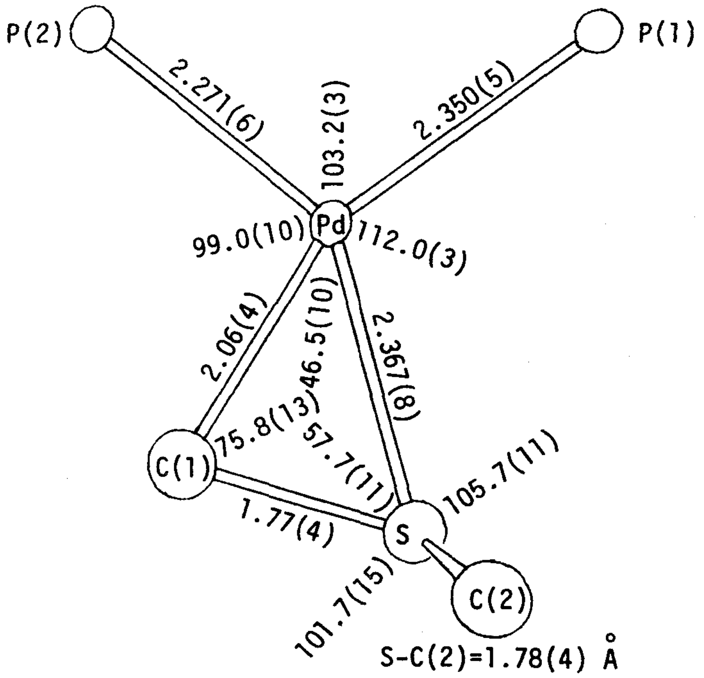


Fig. 1-13. The coordination geometry around the palladium atom in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa).

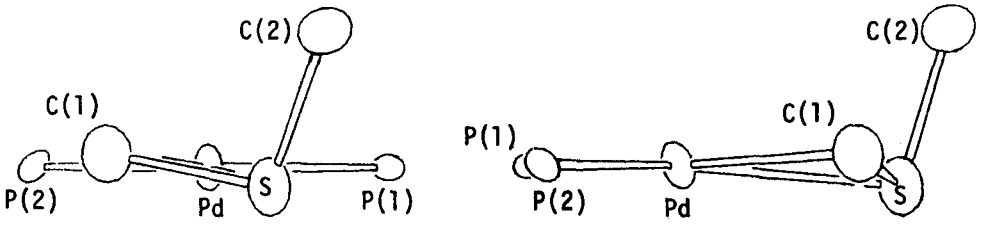


Fig. 1-14. Perspective views of the coordination plane in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa).

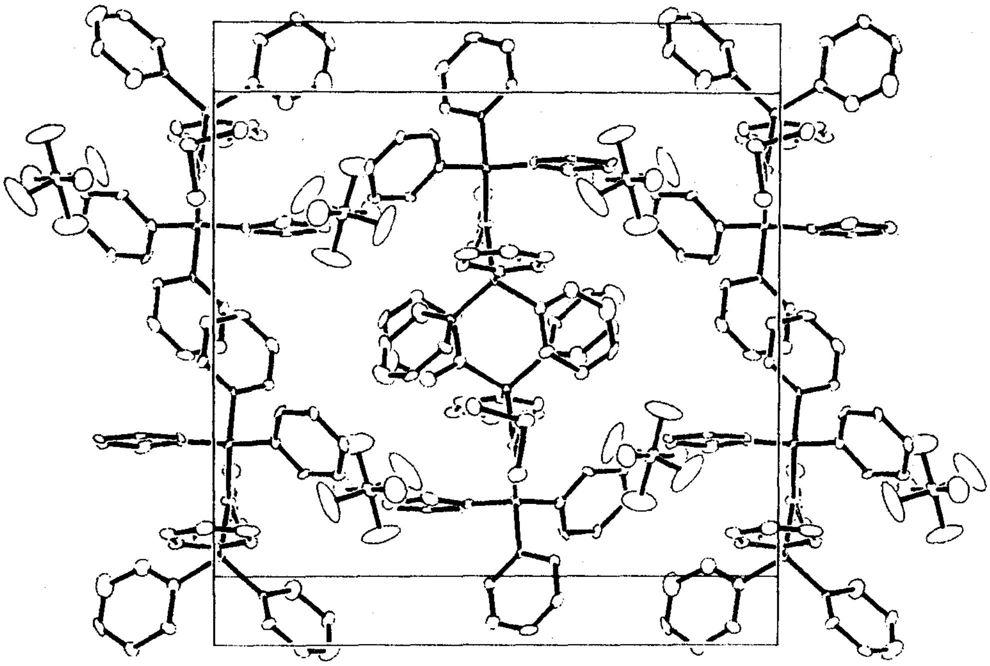


Fig. 1-15. The crystal structure of $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (IIIa) projected along the a* axis. Atoms are represented by thermal ellipsoids at 30% probability levels.

Table 1-18. Bond lengths in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa). Estimated standard deviations in parentheses.

Length(Å)		Length(Å)	
Pd-P(1)	2.350(5)	Pd-P(2)	2.271(6)
Pd-S	2.367(8)	Pd-C(1)	2.06(4)
S-C(1)	1.77(4)	S-C(2)	1.78(4)
P(1)-C(11)	1.82(3)	P(2)-C(41)	1.84(2)
P(1)-C(21)	1.83(2)	P(2)-C(51)	1.82(3)
P(1)-C(31)	1.78(3)	P(2)-C(61)	1.82(3)
C(11)-C(12)	1.42(4)	C(41)-C(42)	1.40(3)
C(12)-C(13)	1.39(5)	C(42)-C(43)	1.40(4)
C(13)-C(14)	1.41(5)	C(43)-C(44)	1.40(4)
C(14)-C(15)	1.38(5)	C(44)-C(45)	1.33(4)
C(15)-C(16)	1.42(4)	C(45)-C(46)	1.37(4)
C(16)-C(11)	1.36(4)	C(46)-C(41)	1.40(3)
C(21)-C(22)	1.39(4)	C(51)-C(52)	1.43(4)
C(22)-C(23)	1.39(4)	C(52)-C(53)	1.38(4)
C(23)-C(24)	1.41(5)	C(53)-C(54)	1.36(4)
C(24)-C(25)	1.39(5)	C(54)-C(55)	1.40(4)
C(25)-C(26)	1.49(4)	C(55)-C(56)	1.40(4)
C(26)-C(21)	1.42(4)	C(56)-C(51)	1.37(4)
C(31)-C(32)	1.44(4)	C(61)-C(62)	1.36(4)
C(32)-C(33)	1.42(5)	C(62)-C(63)	1.43(4)
C(33)-C(34)	1.42(5)	C(63)-C(64)	1.48(4)
C(34)-C(35)	1.39(5)	C(64)-C(65)	1.39(4)
C(35)-C(36)	1.40(5)	C(65)-C(66)	1.45(4)
C(36)-C(31)	1.36(4)	C(66)-C(61)	1.40(4)
P(3)-F(1)	1.60(3)	P(3)-F(2)	1.50(4)
P(3)-F(3)	1.53(3)	P(3)-F(4)	1.50(4)
P(3)-F(5)	1.52(4)	P(3)-F(6)	1.56(4)

Table 1-19. Bond angles in $[Pd(CH_2SCH_2)(PPh_3)_2]PF_6$(IIIa). Estimated standard deviations in parentheses.

Angle(°)		Angle(°)	
P(1)-Pd-P(2)	103.2(3)	P(2)-Pd-C(1)	99.0(10)
P(1)-Pd-S	112.0(3)	C(1)-Pd-S	46.5(10)
Pd-S-C(1)	57.7(11)	Pd-S-C(2)	105.7(11)
C(1)-S-C(2)	101.7(15)	Pd-C(1)-S	75.8(13)
Pd-P(1)-C(11)	121.0(8)	Pd-P(2)-P(41)	117.7(7)
Pd-P(1)-C(21)	115.0(7)	Pd-P(2)-P(51)	113.3(8)
Pd-P(1)-C(31)	107.7(8)	Pd-P(2)-P(61)	111.5(8)
C(11)-P(1)-C(21)	101.3(10)	C(41)-P(2)-C(51)	100.4(10)
C(11)-P(1)-C(31)	105.3(11)	C(41)-P(2)-C(61)	104.8(10)
C(21)-P(1)-C(31)	105.1(10)	C(51)-P(2)-C(61)	108.1(11)
P(1)-C(11)-C(12)	122.0(18)	P(2)-C(41)-C(42)	117.8(15)
P(1)-C(11)-C(16)	121.5(18)	P(2)-C(41)-C(46)	122.0(15)
C(16)-C(11)-C(12)	116.3(22)	C(46)-C(41)-C(42)	120.1(18)
C(11)-C(12)-C(13)	121.8(27)	C(41)-C(42)-C(43)	117.4(21)
C(12)-C(13)-C(14)	118.5(32)	C(42)-C(43)-C(44)	120.6(25)
C(13)-C(14)-C(15)	122.4(31)	C(43)-C(44)-C(45)	121.4(26)
C(14)-C(15)-C(16)	115.7(27)	C(44)-C(45)-C(46)	119.9(24)
C(15)-C(16)-C(11)	125.3(24)	C(45)-C(46)-C(41)	120.7(21)
P(1)-C(21)-C(22)	122.1(17)	P(2)-C(51)-C(52)	122.7(18)
P(1)-C(21)-C(26)	114.8(17)	P(2)-C(51)-C(56)	117.5(18)
C(26)-C(21)-C(22)	122.5(21)	C(56)-C(51)-C(52)	119.7(22)
C(21)-C(22)-C(23)	118.2(24)	C(51)-C(52)-C(53)	120.1(21)
C(22)-C(23)-C(24)	121.4(30)	C(52)-C(53)-C(54)	120.2(22)
C(23)-C(24)-C(25)	122.0(32)	C(53)-C(54)-C(55)	120.6(24)
C(24)-C(25)-C(26)	117.0(27)	C(54)-C(55)-C(56)	120.1(23)
C(25)-C(26)-C(21)	117.8(24)	C(55)-C(56)-C(51)	119.3(22)
P(1)-C(31)-C(32)	122.3(19)	P(2)-C(61)-C(62)	125.7(18)
P(1)-C(31)-C(36)	121.7(20)	P(2)-C(61)-C(66)	114.2(18)
C(36)-C(31)-C(32)	116.0(23)	C(66)-C(61)-C(62)	119.9(22)
C(31)-C(32)-C(33)	119.5(25)	C(61)-C(62)-C(63)	121.7(23)
C(32)-C(33)-C(34)	120.1(28)	C(62)-C(63)-C(64)	120.2(22)

Table 1-19. (continued)

Angle(°)		Angle(°)	
C(33)-C(34)-C(35)	120.3(28)	C(63)-C(64)-C(65)	115.7(22)
C(34)-C(35)-C(36)	117.0(30)	C(64)-C(65)-C(66)	121.9(24)
C(35)-C(36)-C(31)	126.9(28)	C(65)-C(66)-C(61)	120.0(25)
F(1)-P(3)-F(3)	179.3(14)	F(2)-P(3)-F(4)	171.3(21)
F(5)-P(3)-F(6)	178.0(21)		
F(1)-P(3)-F(2)	87.0(16)	F(1)-P(3)-F(4)	87.7(17)
F(1)-P(3)-F(5)	87.2(17)	F(1)-P(3)-F(6)	90.8(16)
F(2)-P(3)-F(3)	92.7(17)	F(2)-P(3)-F(5)	93.2(20)
F(2)-P(3)-F(6)	87.0(20)	F(3)-P(3)-F(4)	92.5(18)
F(3)-P(3)-F(5)	93.4(18)	F(3)-P(3)-F(6)	88.6(17)
F(4)-P(3)-F(5)	93.4(21)	F(4)-P(3)-F(6)	86.3(20)

Table 1-20. Least-squares planes in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (IIIa).

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 $Z = cz\sin\beta$.

(a) Plane defined by Pd, P(1) and P(2)

$-0.091X - 0.994Y + 0.059Z + 0.861 = 0.0$

(b) Coordination plane of Pd through Pd, P(1), P(2), S and C(1)

$-0.119X - 0.993Y + 0.005Z + 1.278 = 0.0$

Deviations of atoms from the plane(Å)

	Plane a	Plane b
Pd	0.0	+0.014
P(1)	0.0	+0.042
P(2)	0.0	-0.124
C(1)	+0.133*	+0.171
S	-0.200*	-0.066
C(2)	+1.413*	+1.590*

* Not included in the calculation of the plane.

Table 1-21. Dihedral angles between planes concerning the coordination geometry in $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(IIIa).

Plane	Atoms
(I)	Pd, P(1) and P(2)
(II)	Pd, S and C(1)
(III)	C(1), S and C(2)

Dihedral angle(°)

Plane	(II)	(III)
(I)	10.9	100.0
(II)		101.3

$[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$(IIIb)

Figure 1-16 shows an *ORTEP* drawing(Johnson, 1976) of the $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation. Atoms are represented by the thermal ellipsoids enclosing 30% probability levels. Bond lengths and bond angles are listed in Tables 1-22 ans 1-23.

Also in this complex, the perchlorate anion was so highly disordered that locations of three oxygen atoms of the ClO_4 anion could not be determined.

Figure 1-17 presents the coordination geometry around the palladium atom along with selected bond lengths and bond angles, which is vertially considered to be a planar coordination. The equations of the least-squares planes are shown in Table 1-24. The planarity of the coordination plane(the plane(b)) is not so good, the maximum deviation of atoms from the plane being 0.10 Å.

In the CH_2SCH_3 group, it is noteworthy that the S-C(1) bond length of 1.678(14) Å is relatively close to that of S=C double bond[1.61 Å] rather than the S-C single bond[1.82 Å] (Abrahams, 1956). This S-C(1) bond is also significantly shorter than those found in II and IIIa[1.756(6) and 1.77(4) Å]. On the other hand, the S-C(2) bond length of 1.86(4) Å is considered as that of the S-C single bond. In addition, it is remarkable that the Pd-C(1) bond length[2.208(13) Å], which is similar to the Pd-C length[2.18 Å] found in a palladium-styrene bond of $[Pd(\eta^5-C_5H_5)(PEt_3)(styrene)]BF_4$(Miki, Yama, Tanaka & Kasai, unpublished), is obviously longer than those found in II and IIIa[2.042(6) and 2.06(4) Å]. The Pd-S bond length of 2.303(6) Å, which is somewhat shorter than those observed in II

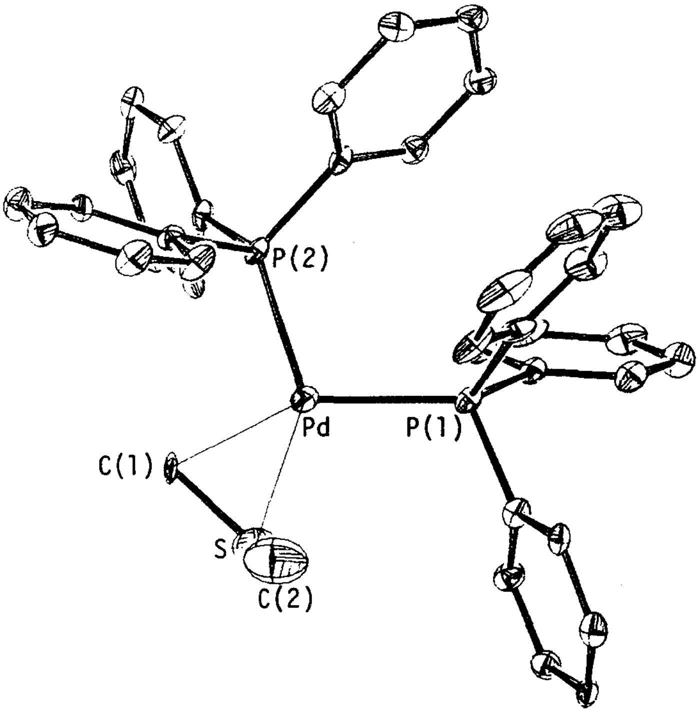


Fig. 1-16. An *ORTEP* drawing of [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$] cation in [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$]ClO$_4$·0.25CH$_2$Cl$_2$(IIIb). Atoms are represented by thermal ellipsoids enclosing 30% probability levels. The atomic numberings for the phenyl groups are omitted.

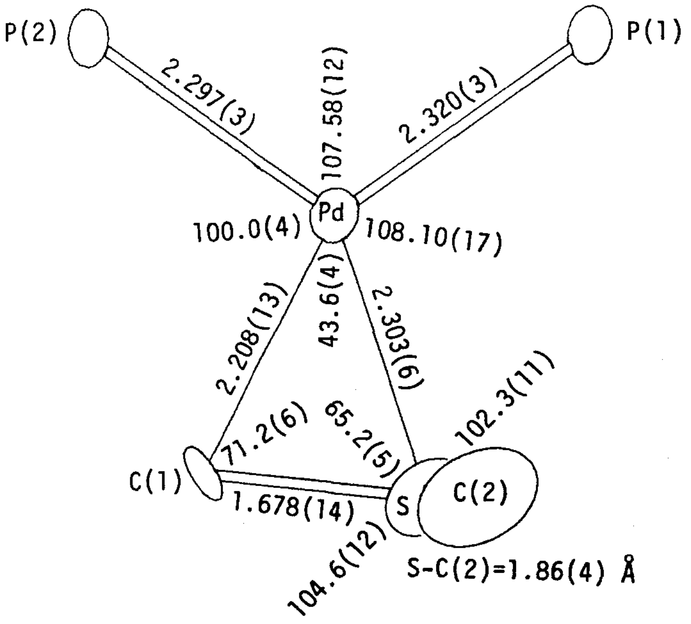


Fig. 1-17. The coordination geometry around the palladium atom in [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$]ClO$_4$·0.25CH$_2$Cl$_2$(IIIb).

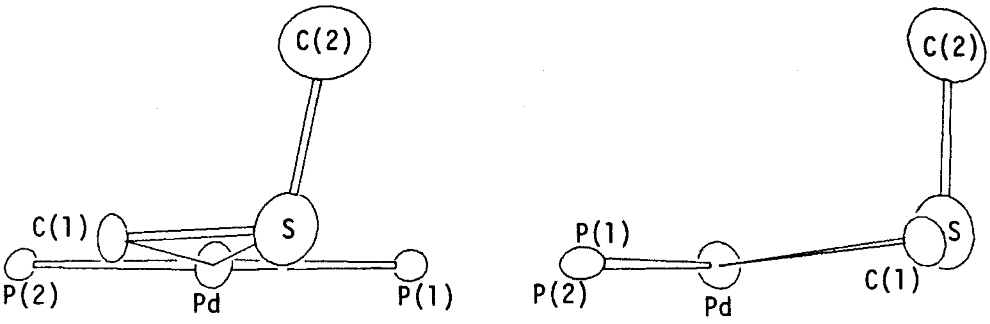


Fig. 1-18. Perspective views of the coordination plane in $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$(IIIb).

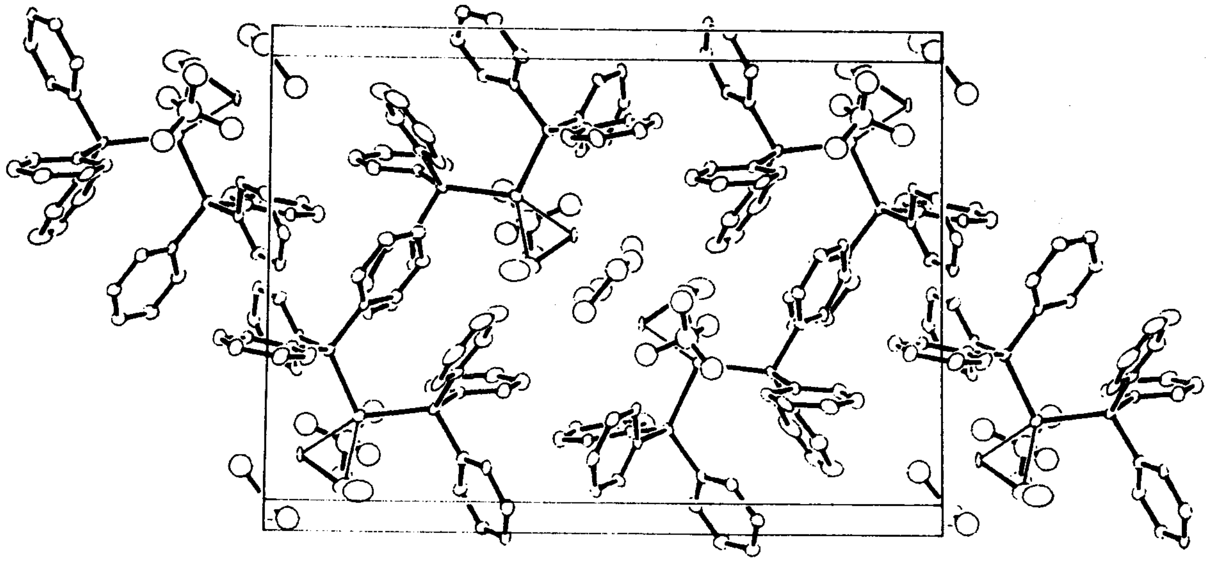


Fig. 1-19. The crystal structure of $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$(IIIb) projected along the a* axis. Atoms of $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation are represented by thermal ellipsoids at 30% probability levels while those of the ClO_4 anion and the solvated CH_2Cl_2 molecule are drawn by circles with B=7.0 Å^2. The locations of three oxygen atoms in the ClO_4 anion are estimated from stereochemical consideration.

Table 1-22. Bond lengths in $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$(IIIb). Estimated standard deviations in parentheses.

Length(Å)		Length(Å)	
Pd-P(1)	2.320(3)	Pd-P(2)	2.297(3)
Pd-S	2.303(6)	Pd-C(1)	2.208(13)
S-C(1)	1.678(14)	S-C(2)	1.86(4)
P(1)-C(11)	1.818(14)	P(2)-C(41)	1.814(13)
P(1)-C(21)	1.819(12)	P(2)-C(51)	1.822(13)
P(1)-C(31)	1.834(13)	P(2)-C(61)	1.826(13)
C(11)-C(12)	1.44(3)	C(41)-C(42)	1.43(2)
C(12)-C(13)	1.41(3)	C(42)-C(43)	1.42(2)
C(13)-C(14)	1.37(3)	C(43)-C(44)	1.38(2)
C(14)-C(15)	1.40(3)	C(44)-C(45)	1.40(2)
C(15)-C(16)	1.41(3)	C(45)-C(46)	1.40(2)
C(16)-C(11)	1.39(3)	C(46)-C(41)	1.38(2)
C(21)-C(22)	1.39(2)	C(51)-C(52)	1.38(2)
C(22)-C(23)	1.39(2)	C(52)-C(53)	1.39(2)
C(23)-C(24)	1.39(3)	C(53)-C(54)	1.42(3)
C(24)-C(25)	1.38(3)	C(54)-C(55)	1.39(3)
C(25)-C(26)	1.41(2)	C(55)-C(56)	1.43(2)
C(26)-C(21)	1.39(2)	C(56)-C(51)	1.43(2)
C(31)-C(32)	1.42(2)	C(61)-C(62)	1.41(2)
C(32)-C(33)	1.41(2)	C(62)-C(63)	1.40(3)
C(33)-C(34)	1.39(2)	C(63)-C(64)	1.42(3)
C(34)-C(35)	1.39(2)	C(64)-C(65)	1.40(2)
C(35)-C(36)	1.41(2)	C(65)-C(66)	1.39(2)
C(36)-C(31)	1.41(2)	C(66)-C(61)	1.40(2)
Cl(1)-O(1)	1.42(4)		
Cl(1S)-C(S)	1.69	Cl(2S)-C(S)	1.68

Table 1-23. Bond angles in $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4\cdot 0.25CH_2Cl_2$(IIIb). Estimated standard deviations in parentheses.

Angle(°)		Angle(°)	
P(1)-Pd-P(2)	107.58(12)	P(2)-Pd-C(1)	100.0(4)
P(1)-Pd-S	108.10(17)	C(1)-Pd-S	43.6(4)
Pd-S-C(1)	65.2(5)	Pd-S-C(2)	102.3(11)
C(1)-S-C(2)	104.6(12)	Pd-C(1)-S	71.2(6)
Pd-P(1)-C(11)	111.6(5)	Pd-P(2)-C(41)	113.8(5)
Pd-P(1)-C(21)	119.5(4)	Pd-P(2)-C(51)	120.2(5)
Pd-P(1)-C(31)	111.6(5)	Pd-P(2)-C(61)	108.2(5)
C(11)-P(1)-C(21)	108.2(6)	C(41)-P(2)-C(51)	101.2(6)
C(11)-P(1)-C(31)	104.0(7)	C(41)-P(2)-C(61)	107.2(6)
C(21)-P(1)-C(31)	100.5(6)	C(51)-P(2)-C(61)	105.3(6)
P(1)-C(11)-C(12)	115.1(11)	P(2)-C(41)-C(42)	117.8(10)
P(1)-C(11)-C(16)	123.5(12)	P(2)-C(41)-C(46)	122.9(10)
C(16)-C(11)-C(12)	121.3(14)	C(46)-C(41)-C(42)	119.3(12)
C(11)-C(12)-C(13)	118.2(15)	C(41)-C(42)-C(43)	118.0(12)
C(12)-C(13)-C(14)	119.8(18)	C(42)-C(43)-C(44)	121.0(13)
C(13)-C(14)-C(15)	122.0(20)	C(43)-C(44)-C(45)	120.8(13)
C(14)-C(15)-C(16)	119.9(19)	C(44)-C(45)-C(46)	118.5(13)
C(15)-C(16)-C(11)	118.6(16)	C(45)-C(46)-C(41)	122.5(12)
P(1)-C(21)-C(22)	119.2(10)	P(2)-C(51)-C(52)	118.4(10)
P(1)-C(21)-C(26)	120.2(10)	P(2)-C(51)-C(56)	120.2(10)
C(26)-C(21)-C(22)	120.5(12)	C(56)-C(51)-C(52)	121.3(12)
C(21)-C(22)-C(23)	120.3(13)	C(51)-C(52)-C(53)	120.8(13)
C(22)-C(23)-C(24)	119.5(14)	C(52)-C(53)-C(54)	119.4(14)
C(23)-C(24)-C(25)	120.9(15)	C(53)-C(54)-C(55)	120.3(14)
C(24)-C(25)-C(26)	120.0(14)	C(54)-C(55)-C(56)	120.7(14)
C(25)-C(26)-C(21)	118.9(13)	C(55)-C(56)-C(51)	117.5(13)
P(1)-C(31)-C(32)	115.9(10)	P(2)-C(61)-C(62)	117.0(10)
P(1)-C(31)-C(36)	124.1(10)	P(2)-C(61)-C(66)	122.4(10)
C(36)-C(31)-C(32)	120.0(12)	C(66)-C(61)-C(62)	120.5(12)
C(31)-C(32)-C(33)	119.6(12)	C(61)-C(62)-C(63)	120.1(14)
C(32)-C(33)-C(34)	120.5(13)	C(62)-C(63)-C(64)	119.3(14)

Table 1-23. (continued)

Angle(°)		Angle(°)	
C(33)-C(34)-C(35)	119.7(12)	C(63)-C(64)-C(65)	119.7(14)
C(34)-C(35)-C(36)	121.7(13)	C(64)-C(65)-C(66)	121.2(13)
C(35)-C(36)-C(31)	118.5(12)	C(65)-C(66)-C(61)	119.3(12)
Cl(1S)-C(S)-Cl(2S)	106.6		

Table 1-24. Least-squares planes in $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4\cdot 0.25CH_2Cl_2$(IIIb).

The equations 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 $Z = cz\sin\beta$.

(a) Plane defined by Pd, P(1) and P(2)

$-0.996X + 0.069Y - 0.063Z + 0.312 = 0.0$

(b) Coordination plane of Pd through Pd, P(1), P(2), S and C(1)

$0.993X - 0.117Y - 0.029Z + 0.174 = 0.0$

Deviations of atoms from the plane(Å)

	Plane a	Plane b
Pd	0.0	-0.101
P(1)	0.0	+0.036
P(2)	0.0	+0.045
C(1)	+0.263*	-0.042
S	+0.356*	+0.026
C(2)	+2.176*	+1.836*

* Not included in the calculation of the plane.

Table 1-25. Dihedral angles between planes concerning the coordination geometry in $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (IIIb).

Plane	Atoms
(a)	Pd, P(1) and P(2)
(b)	Pd, S and C(1)
(c)	C(1), S and C(2)

Dihedral angles(°)

Plane	(b)	(c)
(a)	8.9	91.3
(b)		97.0

$[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ *(IV)*

An *ORTEP* plot(Johnson, 1976) of the tetramer and solvent molecules viewed along the normal to the plane defined by Pd(1), Pd(2) and Pd(3) is given in Fig. 1-20, together with the atomic numbering scheme. Atoms are represented by thermal ellipsoids enclosing 50% probability levels. Tables 1-26 and 1-27 show bond lengths and bond angles along with their estimated standard deviations. Although the molecular structures of some cyclic complexes containing more than three palladium atoms have been determined by X-ray analysis, this compound is the first one which contains four palladium atoms in a molecule. The chemical stability of the complex may be due to the cyclic structure consisting of palladium atoms bridged by $CH_2SC_6H_5$ groups.

The skeletal part of the molecule projected on the least-squares plane of four palladium atoms is presented in Fig. 1-21. The molecule has approximate 222 symmetry. Four palladium atoms are located at the corners of a distorted rectangle. Two averaged Pd···Pd distances are 4.051 and 3.304 Å, respectively. Nonbonded Pd···Pd distances in some complexes containing more than three palladium atoms are listed in Table 1-28. Four coordination planes of palladium atoms are coupled in a cyclic manner. The coordination geometry around each palladium atom is essentially square-planar, which is shown in Fig. 1-22 viewed along the normal to the plane of palladium and two sulphur atoms. Selected bond lengths and bond angles are given in the figure. The equations of four coordination planes and some atomic deviations from these planes are shown in Table 1-29. As shown in Fig. 1-22, these four monomeric units are virtually equivalent.

However, the conformations of the phenyl groups are slightly different from each other. The dihedral angles between the phenyl planes and the coordination planes are listed in Table 1-30. The conformation of phenyl(2B) is obviously different from those of the others. The $CH_2SC_6H_5$ groups take *cis*-coordination.

In the $CH_2SC_6H_5$ groups the mean bond lengths of S-C(methylene) and S-C(phenyl) are 1.82 and 1.80 Å, respectively, which correspond to the expected values of the S-C(sp^3) and S-C(sp^2) single bonds, respectively. The S-C(methylene) bond lengths in this complex are compared with those found in I and II[1.796 and 1.756 Å, respectively.

The mean Pd-C bond length[2.05 Å] has a value expected for a Pd(II)-C(sp^3) σ-bond. The mean Pd-S bond length[2.400 Å] is relatively long compared with in which more than two palladium atoms are bridged by sulphur-containing ligands, as shown in Table 1-31. This may be partly due to the *trans*-influence of the carbon atom in the $CH_2SC_6H_5$ group.

With regard to sulphur atoms, there are two kinds of configurations. Although the crystal belongs to a centrosymmetric space group and absolute configuration does not exist, sulphur atoms numbered as S(nA) take *R*-configuration and the others (S(nB)) *S*-configuration in the enantiomer in Fig. 1-20 where $n = 1 \sim 4$. In this connexion, the conformation about the Pd-S(nA) bond is distinctly different from that of Pd-S(nB) as shown in Fig. 1-22. Mean bond angles around two types of sulphur atoms differ slightly; *e.g.* Pd-S(nA)-CH_2=111.1, Pd-S(nB)-CH_2=105.8, Pd-S(nA)-C(Ph)=111.7 and Pd-S(nB)-C(Ph)=108.3°.

The packing of molecules in a unit cell projected along the a* axis is given in Fig. 1-23. All intermolecular atomic contacts are considered to be the normal van der Waals distances, the shortest contact being 3.30(5) Å[C(4A4)(x,y,z)···C(4A4)(1-x, 1-y,$\bar{z}$)).

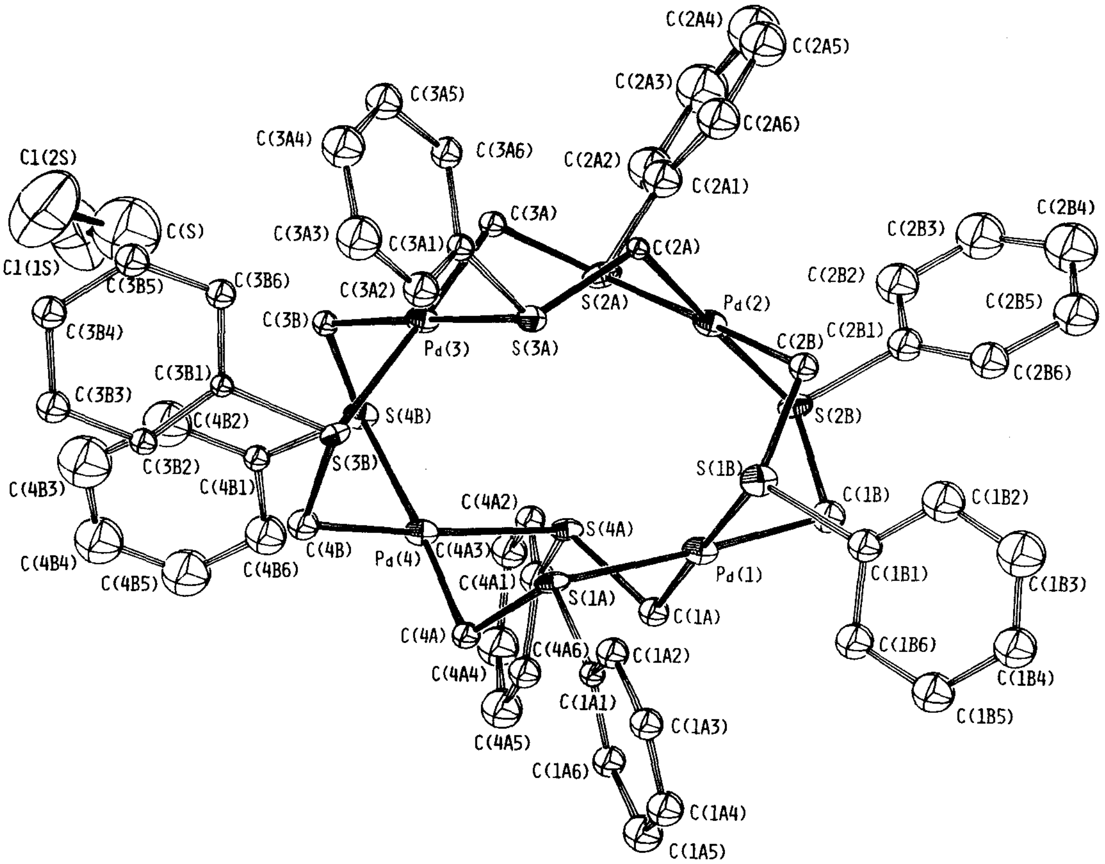
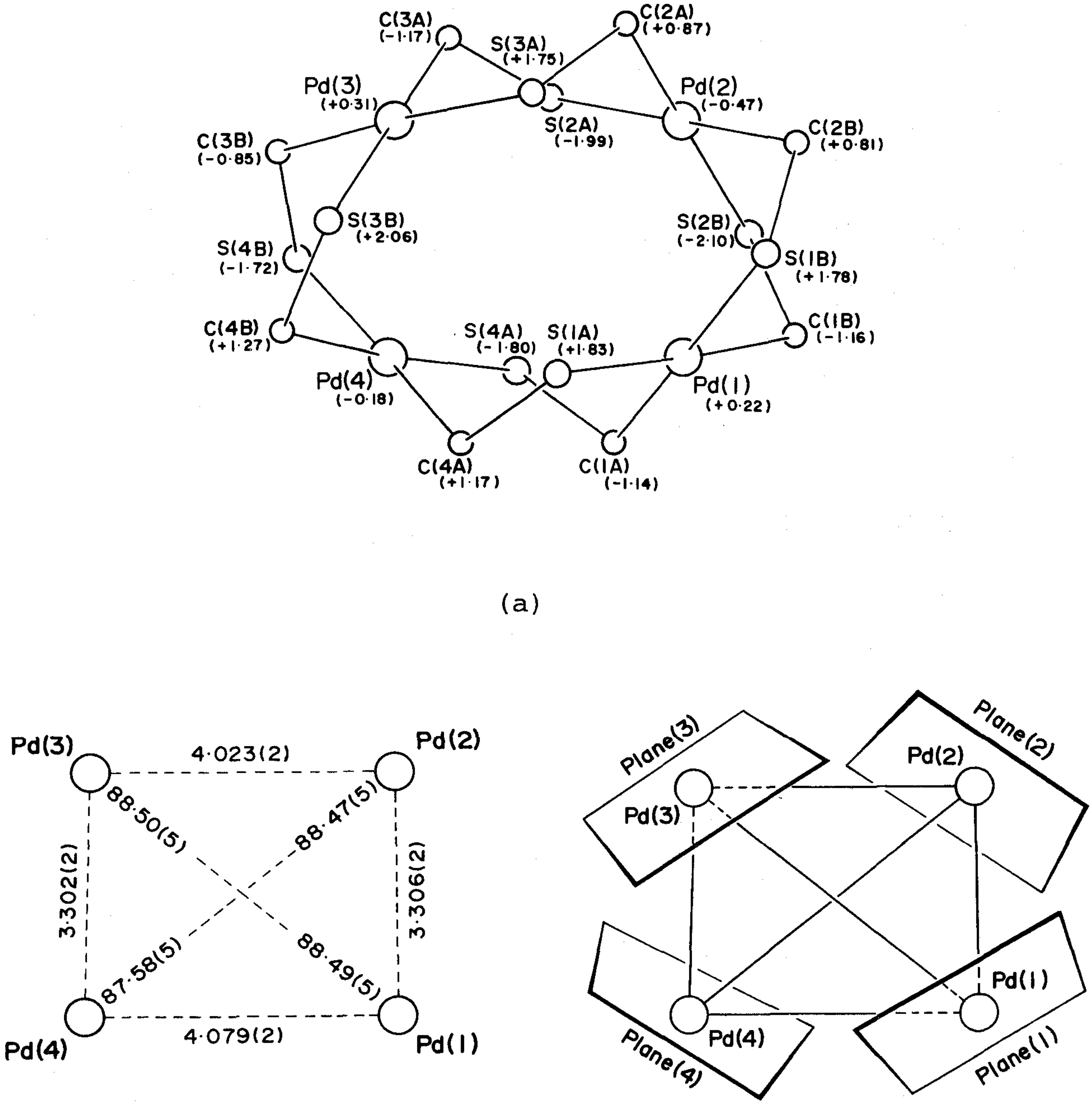


Fig. 1-20. An *ORTEP* plot of the tetramer and solvent molecules of $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$(IV). The thermal ellipsoids correspond to 50% probability level.



(a)

(b)

(c)

Fig. 1-21. The skeletal part of the complex projected onto the least-squares plane of four palladium atoms in $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$(IV).

(a) Deviations of atoms from the least-squares plane in parentheses.

(b) Inter-palladium distances and angles.

(c) Correlation of four coordination planes.

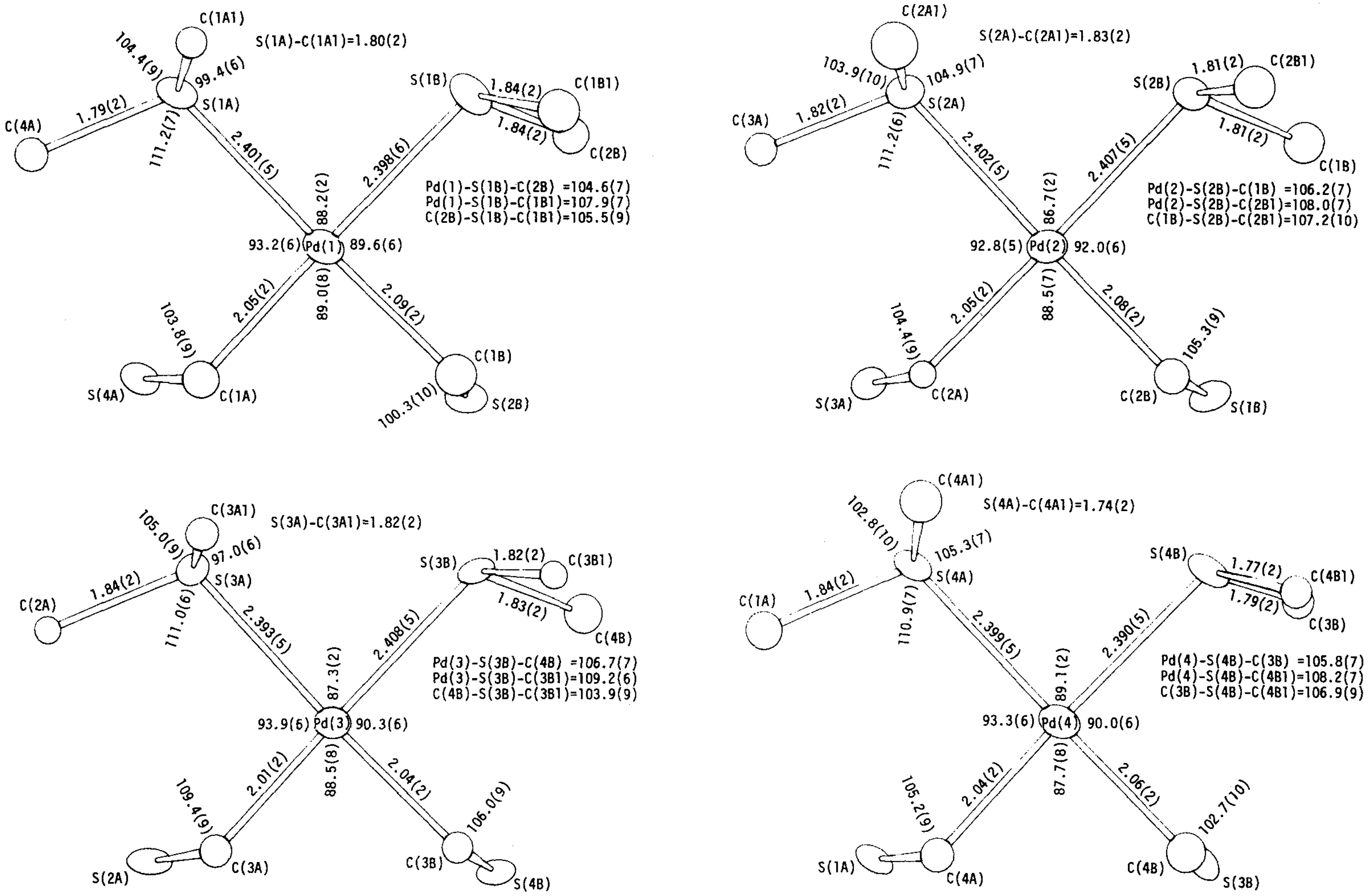


Fig. 1-22. The coordination geometry around each palladium atom in $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ (IV).

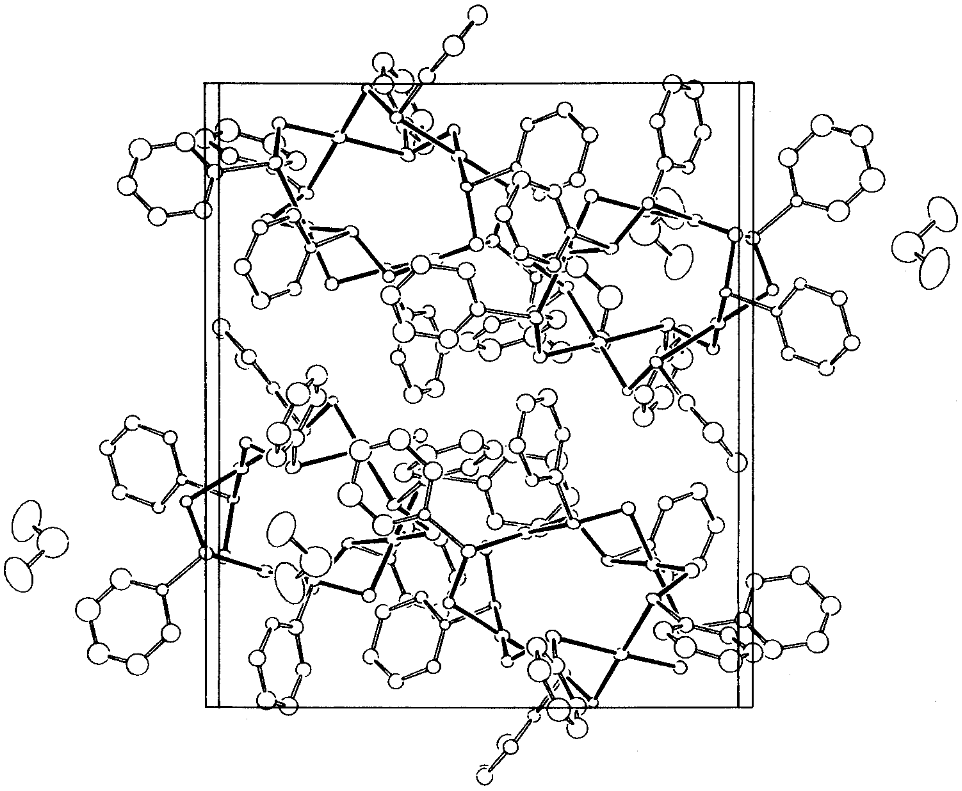


Fig. 1-23. The packing of the molecules of $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$(IV) projected along the a* axis. Atoms are represented by thermal ellipsoids at 50% probability levels.

Table 1-26. Bond lengths in $[\mathrm{Pd(CH_2SC_6H_5)_2]_4\cdot CH_2Cl_2}$ (IV). Estimated standard deviations in parentheses.

Length(Å)	n = 1	n = 2	n = 3	n = 4
Pd(n)-S(nA)	2.401(5)	2.402(5)	2.393(5)	2.399(5)
Pd(n)-S(nB)	2.398(6)	2.407(5)	2.408(5)	2.390(5)
Pd(n)-C(nA)	2.05(2)	2.05(2)	2.01(2)	2.04(2)
Pd(n)-C(nB)	2.09(2)	2.08(2)	2.04(2)	2.06(2)
	(m = 4)	(m = 3)	(m = 2)	(m = 1)
S(nA)-C(mA)	1.79(2)	1.82(2)	1.84(2)	1.84(2)
	(m = 2)	(m = 1)	(m = 4)	(m = 3)
S(nB)-C(mB)	1.84(2)	1.81(2)	1.83(2)	1.79(2)
S(nA)-C(nA1)	1.80(2)	1.83(2)	1.82(2)	1.74(2)
S(nB)-C(nB1)	1.84(2)	1.81(2)	1.82(2)	1.77(2)
C(nA1)-C(nA2)	1.39(3)	1.35(3)	1.40(3)	1.45(3)
C(nA2)-C(nA3)	1.41(3)	1.51(4)	1.43(3)	1.36(3)
C(nA3)-C(nA4)	1.33(3)	1.36(4)	1.38(4)	1.42(3)
C(nA4)-C(nA5)	1.46(3)	1.41(4)	1.42(3)	1.44(3)
C(nA5)-C(nA6)	1.42(3)	1.40(4)	1.45(3)	1.40(3)
C(nA6)-C(nA1)	1.39(3)	1.43(3)	1.42(3)	1.42(3)
C(nB1)-C(nB2)	1.33(3)	1.38(3)	1.37(3)	1.37(3)
C(nB2)-C(nB3)	1.40(4)	1.40(4)	1.42(3)	1.41(4)
C(nB3)-C(nB4)	1.37(4)	1.46(4)	1.45(3)	1.43(4)
C(nB4)-C(nB5)	1.38(3)	1.43(4)	1.38(3)	1.32(4)
C(nB5)-C(nB6)	1.42(3)	1.42(3)	1.41(3)	1.42(4)
C(nB6)-C(nB1)	1.41(3)	1.37(3)	1.38(3)	1.40(3)
Cl(1S)-C(S)	1.78(4)			
Cl(2S)-C(S)	1.65(4)			

Table 1-27. Bond angles in $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$(IV). Estimated standard deviations in parentheses.

Angle(°)	$n = 1$	$n = 2$	$n = 3$	$n = 4$
S(nA)-Pd(n)-S(nB)	88.2(2)	86.7(2)	87.3(2)	89.1(2)
S(nA)-Pd(n)-C(nA)	93.2(6)	92.8(5)	93.9(6)	93.3(6)
S(nB)-Pd(n)-C(nB)	89.6(6)	92.0(6)	90.3(6)	90.0(6)
C(nA)-Pd(n)-C(nB)	89.0(8)	88.5(7)	88.5(8)	87.7(8)
	($m = 4$)	($m = 3$)	($m = 2$)	($m = 1$)
Pd(n)-S(nA)-C(mA)	111.2(7)	111.2(6)	111.0(6)	110.9(7)
	($m = 2$)	($m = 1$)	($m = 4$)	($m = 3$)
Pd(n)-S(nB)-C(mB)	104.6(7)	106.2(7)	106.7(7)	105.8(7)
Pd(n)-S(nA)-C(nA1)	99.4(6)	104.6(7)	97.0(6)	105.3(7)
Pd(n)-S(nB)-C(nB1)	107.9(7)	108.0(7)	109.2(6)	108.2(7)
	($m = 4$)	($m = 3$)	($m = 2$)	($m = 1$)
C(mA)-S(nA)-C(nA1)	104.4(9)	103.9(10)	105.0(9)	102.8(10)
	($m = 2$)	($m = 1$)	($m = 4$)	($m = 3$)
C(mB)-S(nB)-C(nB1)	105.5(9)	107.2(10)	103.9(10)	106.9(9)
	($m = 4$)	($m = 3$)	($m = 2$)	($m = 1$)
Pd(n)-C(nA)-S(mA)	103.8(9)	104.4(9)	109.4(9)	105.2(9)
	($m = 2$)	($m = 1$)	($m = 4$)	($m = 3$)
Pd(n)-C(nB)-S(mB)	100.3(10)	105.3(9)	106.0(9)	102.7(10)

Table 1-27. (continued)

Angle(°)	*n* = 1	*n* = 2	*n* = 3	*n* = 4
S(*n*A)-C(*n*A1)-C(*n*A2)	117.9(15)	117.9(18)	117.6(15)	119.5(15)
S(*n*A)-C(*n*A1)-C(*n*A6)	121.8(15)	117.3(17)	119.9(15)	125.1(16)
C(*n*A6)-C(*n*A1)-C(*n*A2)	120.2(18)	124.8(21)	122.4(18)	115.4(18)
C(*n*A1)-C(*n*A2)-C(*n*A3)	118.5(18)	117.6(22)	119.7(20)	123.6(19)
C(*n*A2)-C(*n*A3)-C(*n*A4)	123.0(20)	117.3(24)	118.7(22)	119.4(20)
C(*n*A3)-C(*n*A4)-C(*n*A5)	119.7(20)	122.9(26)	122.6(22)	120.0(20)
C(*n*A4)-C(*n*A5)-C(*n*A6)	116.8(19)	120.9(23)	119.2(20)	117.8(20)
C(*n*A5)-C(*n*A6)-C(*n*A1)	121.6(19)	116.4(21)	117.3(18)	123.6(19)
S(*n*B)-C(*n*B1)-C(*n*B2)	120.6(17)	113.6(16)	118.5(14)	125.3(17)
S(*n*B)-C(*n*B1)-C(*n*B6)	115.5(16)	122.4(17)	117.1(14)	117.6(15)
C(*n*B6)-C(*n*B1)-C(*n*B2)	123.6(21)	123.9(20)	124.8(18)	117.1(20)
C(*n*B1)-C(*n*B2)-C(*n*B3)	118.5(22)	119.2(22)	119.8(18)	123.1(24)
C(*n*B2)-C(*n*B3)-C(*n*B4)	120.7(23)	118.8(23)	118.0(18)	117.3(25)
C(*n*B3)-C(*n*B4)-C(*n*B5)	120.7(23)	119.6(24)	117.9(19)	121.0(25)
C(*n*B4)-C(*n*B5)-C(*n*B6)	119.5(21)	118.6(22)	124.5(19)	120.2(24)
C(*n*B5)-C(*n*B6)-C(*n*B1)	116.8(20)	119.6(20)	115.3(18)	121.2(21)
Cl(1S)-C(S)-Cl(2S)	113.3(22)			

Table 1-28. Non-bonded Pd...Pd distances in some complexes containing three or more palladium atoms.

Pd complex	Pd...Pd distance(Å)	Mean value(Å)	Reference
$[Pd(CH_3COO)(ONC(CH_3)_2)]_3$	2.998(4) 3.009(5) 3.019(4)	3.009	Mawby & Prigle(1971)
$[Pd(SC_3H_7)_2]_6$	3.014(2) 3.157(2) 3.235(2)	3.135	Kunchur(1968)
$[Pd(CH_3COO)_2]_3$	3.105(1) 3.203(1)	3.15	Skapski & Smart(1970)
$[Pd(SC_2H_5)(S_2CSC_2H_5)]_3$	3.303(2) 3.307(2) 3.365(2)	3.422	Fackler Jr. & Zegarski(1973)
$[Pd(S_3C_4H_8)]_3$	3.407(12) 3.486(12) 3.662(12)	3.518	McPartlin & Stephenson(1969)
$[Pd(CH_2SC_6H_5)_2]_4$	3.302(2) 3.306(2)	3.304	this work(complex IV)
	4.023(2) 4.079(2)	4.051	

Table 1-29. Least-squares planes in $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$ (IV). 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 $Z = cz\sin\beta$.

Coordination plane of Pd.

Plane(*n*) indicates the coordination plane around the Pd(*n*) atom.

	Plane(1)	Plane(2)	Plane(3)	Plane(4)
A	0.720	-0.205	-0.592	-0.299
B	-0.525	-0.668	0.759	-0.954
C	-0.453	-0.715	-0.272	0.028
D	2.189	3.598	3.738	6.996

Deviations of atoms from the plane(Å)

	n = 1	*n* = 2	*n* = 3	*n* = 4
Pd(*n*)	-0.009	0.009	0.010	-0.028
S(*n*A)	0.027	0.016	-0.007	0.075
S(*n*B)	-0.023	-0.021	0.003	-0.059
C(*n*A)	-0.028	-0.024	0.003	-0.067
C(*n*B)	0.035	0.018	-0.009	0.082
C(*n*A1)*	-1.671	-1.733	-1.778	-1.496
C(*n*B1)*	-1.575	-1.686	-1.568	-1.541
	m = 4	*m* = 3	*m* = 2	*m* = 1
S(*m*A)*	1.688	1.715	1.647	1.604
C(*m*A)*	0.134	0.424	0.215	0.152
	m = 2	*m* = 1	*m* = 4	*m* = 3
S(*m*B)*	1.822	1.788	1.704	1.887
C(*m*B)	1.336	1.102	1.256	1.313

* Not included in the least-squares calculation.

Table 1-30. Dihedral angles between phenyl plane and coordination plane in $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$(IV).

Coordination plane	Phenyl plane*	Dihedral angle(°)
Plane(1)	Phenyl(1A)	86.2
	Phenyl(1B)	85.8
Plane(2)	Phenyl(2A)	87.7
	Phenyl(2B)	69.9
Plane(3)	Phenyl(3A)	88.2
	Phenyl(3B)	85.1
Plane(4)	Phenyl(4A)	77.4
	Phenyl(4B)	89.2

* Phenyl(nX) indicates the phenyl group which is attached to S(nX), where n = 1 ∿ 4 and X = A or B.

Table 1-31. Pd-S bond lengths of some complexes with more than two palladium atoms bridged by sulphur-containing ligands.

Pd complex	Bridging ligand	N[a]	Mean value (Å)	Range[b]	Esd[c]	Reference
$[Pd_3(SO_2)_2(Me_3CNC)_5]$	SO_2	4	2.261	13	8∿9	(a)
$[Pd(SCMe_3)(S_2CSCMe_3)]_2$	$SC(CH_3)_3$	2	2.320	10	3	(b)
$[Pd(SEt)(S_2CSEt)]_3$	SCH_2CH_3	6	2.324	12	4∿6	(b)
$[Pd(S_3C_4H_8)]_3$	$SCH_2CH_2SCH_2CH_2S$	6	2.331	124	30∿32	(c)
$[Pd(S(n\text{-}Pr))_2]_6$	$SCH_2CH_2CH_3$	12	2.350	172	4∿5	(d)
$[Pd(PPh_3)(SC_6F_5)_2]_2$(Form I)	SC_6F_5	4	2.371	21	11∿13	(e)
$[Pd(SCNMe_2)((MeO)_3P)Cl]_2$	$SCN(CH_3)_2$	1	2.382	—	2	(f)
$[Pd(PPh_3)(SC_6F_5)_2]_2$(Form II)	SC_6F_5	2	2.395	74	7	(g)
$[Pd(CH_2SC_6H_5)_2]_4$	$CH_2SC_6H_5$	8	2.400	18	5∿6	this work
$[Pd(SCN)(Ph_2PO)_2H]_2$	SCN	1	2.435	—	2	(h)

[a] The number of independent Pd-S bonds in a complex. [b] The range of bond lengths ($\times 10^{-3}$ Å).
[c] Esd of individual bond length ($\times 10^{-3}$ Å)

(a) Otsuka, Tatsuno, Miki, Aoki, Matsumoto, Yoshioka & Nakatsu (1973). (b) Fackler Jr. & Zegarski (1973). (c) McPartlin & Stephenson (1969). (d) Kunchur (1968). (e) Fenn & Segrott (1970). (f) Porter, White, Green, Angelici & Clardy (1973). (g) Fenn & Segrott (1972). (h) Naik, Palenik, Jacobson & Carty (1974).

1-5 Conclusion

The coordination behaviour of the $CH_2SR(R=CH_3, C_6H_5)$ groups to the palladium atom has been elucidated by the present structure determination of five palladium complexes containing these groups. In the complex I, the CH_2SCH_3 group is bonded to the palladium atom only through the Pd-C σ-bond and no donation of the sulphur to the metal atom is observed in this group. In the complex II, the CH_2SCH_3 group is bound to the palladium atom through both the Pd-C σ-bond and the Pd-S coordination bond, a metal-carbon-sulphur three-membered ring being formed. This group functions as a bidentate ligand. The coordination modes of the CH_2SCH_3 group in the cationic complexes IIIa and IIIb may be different from each other. In the complex IIIa, the coordination mode of the CH_2SCH_3 group is considered to be similar to that found in the complex II, while the form of the positively charged methylenemethylsulphonium ion plays a great contribution to the coordination of this group in IIIb. The CH_2SCH_3 group may function as a two-electron ligand in IIIb. On the other hand, the $CH_2SC_6H_5$ groups in the complex IV bridge four palladium atoms to form a stable tetrameric molecule. This group functions as a bridging ligand, which has been observed in the platinum complexes containing the CH_2SCH_3 group(Yoshida, Kurosawa & Okawara, 1977). Structures of five palladium complexes determined in this study are summarized schematically in Fig. 1-24.

It is surprising that the complex II was obtained from the repeated recrystallization of the complex I. The nucleophilicity of the sulphur to the matal atom is observed in the crystal

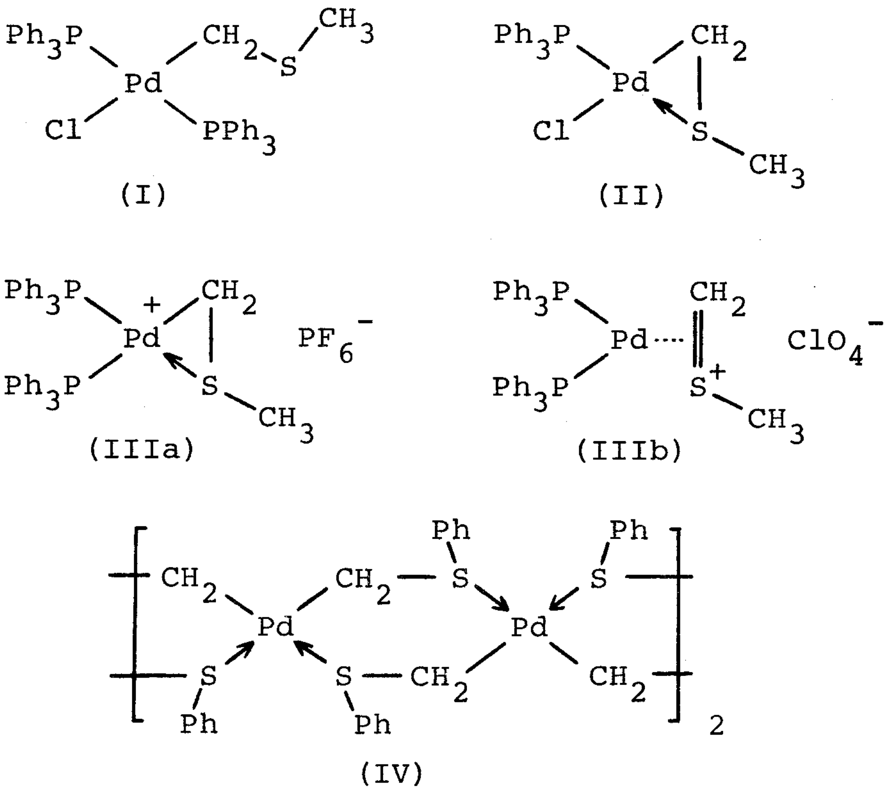
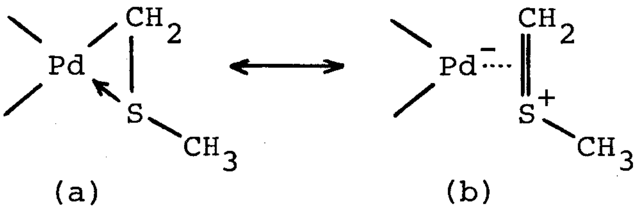


Fig. 1-24. Structures of five palladium complexes containing the CH_2SR(R=CH_3, C_6H_5) groups determined in this study.

structure of the complex I, which may be a driving force for the formation of the complex II. The cationic complexes IIIa and IIIb were obtained by the treatment of the complex I with NH_4PF_6 and $AgClO_4$, respectively. The resonance equilibrium between structures a and b presented below is suggested for the bonding of the CH_2SCH_3 group in the complexes II and III, which stabilizes these complexes. It is reasonable that the CH_2SCH_3 group is bonded to the palladium atom in the form of the methylenemethylsulphonium ion as observed in the complex IIIb, because



the resonance structure b is stabilized in the cationic complexes III. However, it is incomprehensible that the complex IIIa may have little contribution from the resonance structure b in the bonding of the CH_2SCH_3 group. This difference in the coordination modes between IIIa and IIIb may be partly caused by the strength of the negative charge in the PF_6 and ClO_4 anions. Table 1-32 presents distances between the $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation and the anion(PF_6 or ClO_4) in IIIa and IIIb. As both anions are considered to have the spherical symmetry, the distances between the palladium atom and the central atom of anions (the phosphorus and chlorine atoms for the PF_6 and ClO_4 anions, respectively) are compared with each other. The radius of the PF_6 anion(P-F = 1.54 Å) is larger than that of the ClO_4 anion (Cl-O = 1.42 Å). Nevertheless, the Pd...P(3) distances in IIIa are significantly shorter than those of the Pd···Cl(1) in IIIb, which suggests that the complex IIIa behaves as a stronger ion pair than the complex IIIb. This fact is probably one of the reasons why the coordination behaviour of the complexes IIIa

Table 1-32. Contacts between the $[Pd(CH_2SCH_3)(PPh_3)_2]$ cation and the anion (PF_6 or ClO_4) in the complexes IIIa and IIIb. The distances between the palladium atom(centre of the cation) and the phosphorus atom(for PF_6 in IIIa) or the chlorine atom (for ClO_4 in IIIb)(centre of the anion) are shown.

Distance(Å)	IIIa	IIIb
	Pd(x,y,z)···P(3)	Pd(x,y,z)···Cl(1)
Nearest	4.759(8)(x,y,z)	5.317(17)(x,y,z)
Second	5.252(8)(1-x,-1/2+y,1/2-z)	6.288(17)(-1+x,y,z)

and IIIb is somewhat different from each other.

Bond lengths and bond angles concerning the coordination around the palladium atom and the bonding of the CH_2SCH_3 and $CH_2SC_6H_5$ groups in the complexes I, II, IIIa, IIIb and IV are summarized in Table 1-33.

Table 1-33. Bond lengths and bond angles concerning the coordination of the palladium atom and the bonding of the CH_2SCH_3 and $CH_2SC_6H_5$ groups in the complexes I, II, IIIa, IIIb and IV.

Complex	(I)	(II)	(IIIa)	(IIIb)	(IV)*
Coordination of Pd					
Pd-Cl	2.408(1) Å	2.402(1) Å	---	---	---
Pd-P	2.346(1) 2.337(1)	2.267(1)	2.350(5) Å 2.271(6)	2.320(3) Å 2.297(3)	---
Pd-C	2.061(3)	2.042(6)	2.06(4)	2.208(13)	2.05(2) Å
Pd-S	---	2.371(1)	2.367(8)	2.303(6)	2.400(5)
Bonding of the CH_2SR groups					
R	CH_3	CH_3	CH_3	CH_3	C_6H_5
CH_2-S	1.796(3)	1.756(6)	1.77(4)	1.678(14)	1.82(2)
S-CH_3(C_6H_5)	1.817(5)	1.807(7)	1.78(4)	1.86(4)	1.80(2)
Pd-CH_2-S	100.64(14)°	76.9(2)°	75.8(13)°	71.2(6)°	105.7(9)° 103.6(10)
Pd-S-CH_2	---	56.98(19)	57.7(11)	65.2(5)	105.8(7) 111.1(7)
Pd-S-CH_3(C_6H_5)	---	106.7(2)	105.7(11)	102.3(11)	101.7(7) 108.3(7)
CH_2-S-CH_3(C_6H_5)	101.28(18)	103.8(3)	101.7(15)	104.6(12)	104.0(10) 105.9(9)

* mean values of four or eight equivalent bond lengths and bond angles.

CHAPTER 2

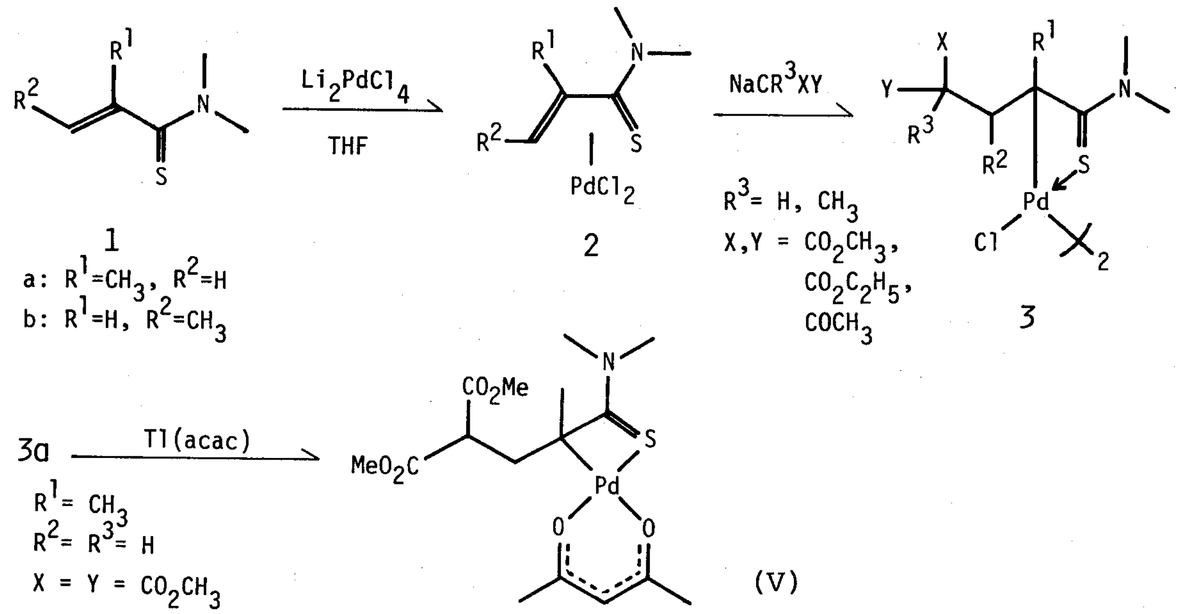
Molecular Structures of Palladium Complexes Containing Thia-allyl or Thioamidomethyl group

2.1 Introduction

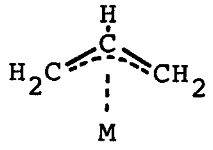
In this chapter, molecular structures of palladium complexes containing two kinds of sulphur-containing ligands, thia-allyl and thioamidomethyl groups, are described, and the coordination behaviour of these groups to the metal atom is discussed. A series of palladium-catalyzed reactions of thioamides have been studied by Yoshida and his co-workers(Tamaru, Kagotani & Yoshida, 1979a; 1979b). Those are summarized in Schemes 2-1 and 2-2.

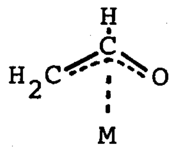
A thia-allyl palladium complex (V), which is the first "possible" thia-π-allyl complex, has been prepared by the palladium-assisted Michael addition of sodium dimethylmalonate to *N*,*N*-dimethylthiomethacrylamide as shown in Scheme 2-1(Tamaru, Kagotani & Yoshida, 1979a). Palladium complexes containing the π-allyl group have been widely studied from both viewpoints of synthetic and structural chemistry(Hartley, 1973a). The molecular structures of many π-allyl palladium complexes have been determined by means of X-ray diffraction. In addition, metal complexes containing the oxa-π-allyl or thia-π-allyl group, in which one of the terminal methylene group of the allyl group is replaced by a hetero atom such as oxygen or sulphur, have also been investigated although there are not so many reports of such complexes. Some of oxa-π-allyl

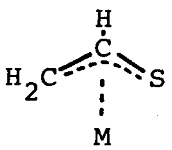
Scheme 2-1.



palladium complexes have been isolated(Yoshimura, Murahashi & Moritani, 1973) and have been suggested as reaction intermediates(Bierling, Kirshke, Oberender & Schulz, 1972; Wolff & Agosta, 1976; Ito, Hirao & Saegusa, 1978; Ito, Aoyama, Hirao, Mochizuki & Saegusa, 1979), however, none of their three-dimensional structures has been determined and the stereochemistry of the oxa-π-allyl metal complexes have not been established yet. On the other hand, no thia-π-allyl metal complex has been reported. It is therefore full of interest if the coordination mode of the oxa-π-allyl or thia-π-allyl group to the metal atom is elucidated from the three-dimensional structure.


π-allyl

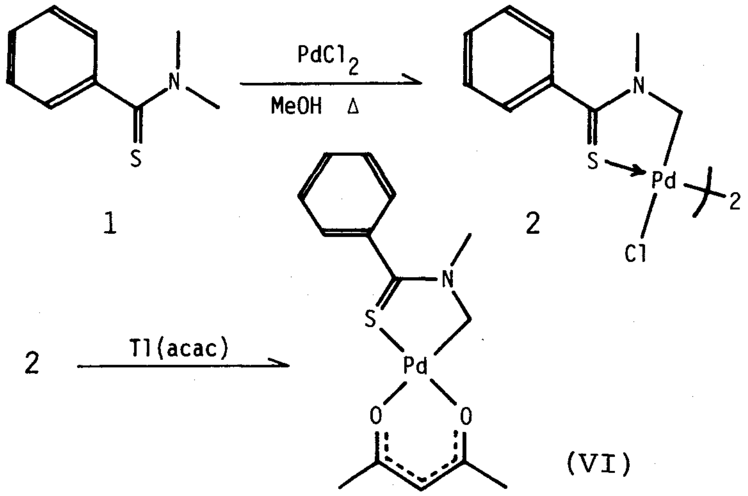

oxa-π-allyl


thia-π-allyl

A thioamidomethyl palladium complex (VI) has been afforded by the reaction between palladium chloride and *N*,*N*-dimethylthiobenzamide as shown in Scheme 2-2 (Tamaru, Kagotani & Yoshida, 1979b). The complex VI contains an *N*-methylthiobenzamidomethyl group which is expected to form a five-membered ring with the palladium atom.

The molecular structures of the complexes V and VI have been determined by means of X-ray diffraction to clarify the coordination behaviour of these sulphur-containing ligands to the metal atom. In order to obtain precise molecular structures, diffraction data collected at liquid nitrogen temperature and two or more symmetry-equivalent reflexion data were employed in the structure analyses for V and VI, respectively.

Scheme 2-2.



2.2 Experimental

Crystals used in this study were kindly supplied by Prof. Z. Yoshida and his co-workers. Crystals of thia-allyl palladium complex(V) are yellow plates, while those of thioamidomethyl palladium complex(VI) are yellow prisms. Well-shaped crystals with approximate dimensions 0.4×0.3×0.15 mm for V and 0.15×0.25×0.4 mm for VI were mounted on a Rigaku automated, four-circle, single-crystal diffractometer. The crystal setting was established with the aid of the Rigaku soft-ware system for the computer-controlled diffractometer. The crystal system was determined as monoclinic for V and as orthorhombic for VI, respectively. The each space group was uniquely determined as $P2_1/n$ for V and $P2_12_12_1$ for VI by the systematic absences of reflexions. Accurate cell dimensions were determined by a least-squares fit of 2θ values of 25 strong reflexions. Crystal data are shown in Table 2-1.

The data collection was carried out at both -160 and 20°C for V and only at 20°C for VI, respectively. The required low temperature was attained by the gas flow method using liquid nitrogen. Intensity data were collected on a Rigaku diffractometer by the θ-2θ scan technique with graphite-monochromatized Mo-$K\alpha$ radiation(λ=0.71069 Å, 40KV, 30mA). The scan speed was $4°\text{min}^{-1}$ and the scan width was $\Delta\theta=(1.0+0.35\tan\theta)°$. The background intensity was measured for 7.5 sec at each end of a scan. For the complex V, totals of 4186(at -160°C) and 4325(at 20°C) reflexions with 2θ less than 54° were collected and 318(at -160°C) and 643(at 20°C) reflexions were considered as unobserved. For the complex VI, two sets of Bijvoet pair

$|F(hkl)|$ and $|F(\overline{h}\overline{k}\overline{l})|$ reflexions, a total of 3720 reflexions was collected up to $2\theta=54°$ at 20°C and 198 reflexions were considered as unobserved. Four standard reflexions (0,0,10, 060, 501 and 444 for V and 600, 040, 0,0,10, and 224 for VI) were measured at regular intervals to monitor the stability and orientation of the crystal, and the intensity of these reflexions remained constant throughout each data collection. Lorentz and polarization corrections were carried out in the usual manner. No corrections for absorption and extinction effects were applied.

Table 2-1. Crystal data

	Complex V		Complex VI
Formula	$C_{16}H_{25}NO_6PdS$		$C_{14}H_{17}NO_2PdS$
Formula weight	465.8		369.8
$F(000)$	952		744
Crystal system	monoclinic		orthorhombic
Space group	$P2_1/n$		$P2_12_12_1$
	[-160°C]	[20°C]	[20°C]
a (Å)	8.752(3)	8.801(1)	11.200(2)
b (Å)	11.444(4)	11.562(2)	6.972(1)
c (Å)	19.095(5)	19.390(2)	19.034(3)
β (°)	92.06(3)	91.53(1)	
U (Å^3)	1911.3(9)	1972.3(4)	1486.4(4)
Z	4	4	4
Dc (g cm^{-3})	1.619	1.568	1.652
μ(Mo-$K\alpha$) (cm^{-1})	10.9	10.6	13.6

2.3 Structure Solution and Refinement

The both structures were solved by the conventional heavy atom method. The refinement of structures was carried out by the block-diagonal least-squares procedure using the *HBLS-V* programme(Ashida, 1979), the function minimized being $\sum w(|Fo|-|Fc|)^2$. The weighting scheme used was $w=(\sigma_{cs}{}^2+a|Fo|+b|Fo|^2)^{-1}$ for $|Fo|>0$, and $w=c$ for $|Fo|=0$, where σ_{cs} is the standard deviation obtained from the counting statistics and the values of a, b and c are the constants adjusted in the least-aquares refinement, although the unit weights were employed at the early stages of the refinement. The R and R_w (weighted R) values are defined by $R=\sum||Fo|-|Fc||/\sum|Fo|$ and $R_w=\{\sum w(|Fo|-|Fc|)^2/\sum w|Fo|^2\}^{1/2}$, respectively. The atomic scattering factors were taken from *International Tables for X-ray Crystallography*(1974) for non-hydrogen atoms and those of Stewart, Davidson & Simpson(1965) for hydrogen atoms.

All computations were carried out on an ACOS 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka university.

Thia-allyl Palladium Complex (V)

For the structure solution, intensity data obtained at 20°C were used. A three-dimensional Patterson map readily determined the location of the palladium atom. The subsequent Fourier map based on this atomic position revealed all locations of the remaining non-hydrogen atoms.

The structures at low and room temperatures were refined in parallel with each other. Several cycles of isotropic refinement converged the R values to 0.059(at -160°C) and 0.078 (at 20°C) for non-zero reflexions. A few more cycles of anisotropic refinement reduced the R indices to 0.044 and 0.049, respectively. At this stage, difference Fourier maps were calculated by the data at both temperatures, which reasonably found all the hydrogen atoms. The parameters of the hydrogen atoms were also refined isotropically in the further refinement. The final R indices are 0.033 and 0.039 for non-zero(0.039 and 0.056 for all) reflexions at -160 and 20°C, respectively. The final weighted R values(R_w) are 0.044(at -160°C) and 0.049(at 20°C) for all reflexions and the weighting parameters, a, b and c used at the final refinement are 0.0505, 0.0001 and 0.0923(at -160°C) and 0.0252, 0.0002 and 0.0864(at 20°C), respectively. The final atomic positional and thermal parameters at -160 and 20°C are listed in Tables 2-2 and 2-3.

Thioamidomethyl Palladium Complex (VI)

The coordinates of the palladium atom were easily determined from a Patterson synthesis. The remaining all the non-hydrogen atoms were located by the subsequent Fourier map.

The refinements were carried out without consideration of anomalous dispersion effect using 1886(1837 non-zero) reflexions which were obtained by averaging $|F(hkl)|$ and $|F(\overline{hkl})|$ reflexions. The agreement factor of equivalent reflexions defined by $R_{ref.}=\sum||F|-<|F|>|/\sum|F|$ is 0.014 for 3720 total reflexions, where $<|F|>$ is the averaged value of two or more equivalent reflexions. Several cycles of isotropic refinement of non-hydrogen atoms reduced the R value to 0.072 for non-zero reflexions. The further cycles of anisotropic refinement converged with R=0.040 for observed reflexions. All the hydrogen atoms were reasonably found in difference Fourier maps. After several more cycles of refinement were carried out anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms, five strong reflexions(200, 201, 002, 012 and 013) which showed large discrepancy between $|Fo|$ and $|Fc|$ ($|Fo|<|Fc|$) were omitted because they may be considered to be affected with extinction effects. The final R indices are 0.024 and 0.027 for non-zero and all reflexions, respectively. The final weighted R value(R_w) is 0.031 for all reflexions, and the weighting parameters used at the final stage of refinement are 0.0012, 0.0004 and 0.1450, respectively.

After all the refinements completed, the absolute configuration of the molecule was confirmed by the refinement of both models(x,y,z and $x,y,\bar{z}$), including hydrogen atom contributions, to convergence, although the present molecule contains no asymmetric atoms. For this refinement, $|F(hkl)|$ and $|F(\overline{hkl})|$ reflexions were treated as independent data(a total of 3252 reflexions) and anomalous dispersion effects were included, $\Delta f'$ and $\Delta f''$ components of which were taken from those of *International Tables for X-ray Crystallography*(1974). The chosen model had the R value of 0.0260 while the enantiomeric structure gave the R index of 0.0295. The R factor ratio test (Hamilton, 1965) applied to these R values obtained showed that alternate model($x,y,\bar{z}$) may be rejected at less than the 0.005 significant level. The final atomic parameters for the correct model are listed in Tables 2-4 and 2-5.

Table 2-2. Final atomic parameters for non-hydrogen atoms of Thia-allyl palladium complex (V)

Positional parameters in fraction of cell edges and 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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.04988(3)	0.112818(19)	0.185320(11)	0.00492(3)	0.002444(16)	0.000748(5)	-0.00030(4)	0.000458(19)	-0.000109(14)
S	-0.19051(9)	0.10591(8)	0.22491(5)	0.00429(9)	0.00407(7)	0.00117(2)	-0.00091(12)	0.00036(7)	-0.00147(6)
O(1)	0.2708(3)	0.15398(19)	0.16146(11)	0.0052(3)	0.00274(16)	0.00100(6)	-0.0006(4)	0.00119(19)	-0.00029(16)
O(2)	0.0413(3)	-0.01916(19)	0.10724(11)	0.0057(3)	0.00296(16)	0.00085(6)	-0.0015(4)	0.00049(19)	-0.00024(15)
O(3)	0.2338(3)	-0.08892(19)	0.42163(12)	0.0047(3)	0.00307(16)	0.00112(6)	0.0007(4)	-0.0007(2)	0.00096(16)
O(4)	0.3862(3)	0.0638(3)	0.40027(13)	0.0055(3)	0.00362(18)	0.00205(8)	-0.0010(4)	-0.0019(3)	0.00073(19)
O(5)	-0.0897(3)	-0.05703(19)	0.37068(12)	0.0045(3)	0.00275(16)	0.00144(6)	-0.0004(4)	0.0008(2)	0.00044(16)
O(6)	-0.0596(3)	0.10775(19)	0.43430(13)	0.0072(4)	0.00296(17)	0.00141(7)	0.0011(4)	0.0027(3)	0.00029(16)
N	-0.2142(3)	0.2774(3)	0.31906(14)	0.0052(4)	0.00275(19)	0.00110(7)	0.0020(4)	0.0008(3)	-0.00000(18)
C(1)	0.3397(4)	0.1108(3)	0.10992(16)	0.0050(4)	0.0023(3)	0.00096(8)	0.0011(5)	0.0006(3)	0.0006(2)
C(2)	0.1527(4)	-0.0425(3)	0.06856(15)	0.0063(4)	0.0023(3)	0.00076(7)	0.0002(5)	-0.0000(3)	0.0003(2)
C(3)	0.2906(4)	0.0183(3)	0.06662(16)	0.0063(4)	0.0030(3)	0.00087(8)	0.0004(5)	0.0018(3)	-0.0006(3)
C(4)	0.4897(4)	0.1685(3)	0.09441(18)	0.0051(4)	0.0035(3)	0.00156(9)	-0.0004(5)	0.0014(3)	-0.0004(3)
C(5)	0.1277(4)	-0.1468(3)	0.01998(17)	0.0082(5)	0.0035(3)	0.00110(8)	-0.0010(6)	0.0009(3)	-0.0010(3)
C(6)	-0.1258(4)	0.2162(3)	0.27859(15)	0.0048(4)	0.0023(3)	0.00076(7)	0.0007(5)	0.0001(3)	0.00048(19)
C(7)	0.0428(4)	0.2294(3)	0.26718(15)	0.0043(4)	0.0022(2)	0.00081(7)	-0.0004(5)	0.0007(3)	0.00013(19)
C(8)	0.1504(4)	0.1855(3)	0.32676(15)	0.0044(4)	0.0026(3)	0.00079(7)	-0.0008(5)	0.0004(3)	0.0001(2)
C(9)	0.1282(4)	0.0585(3)	0.34943(14)	0.0038(4)	0.00204(19)	0.00065(7)	0.0002(5)	-0.0000(3)	-0.00041(19)
C(10)	0.2654(4)	0.0141(3)	0.39367(15)	0.0043(4)	0.0025(3)	0.00074(7)	0.0007(5)	0.0005(3)	-0.00053(19)
C(11)	-0.0167(4)	0.0414(3)	0.39015(15)	0.0048(4)	0.0020(2)	0.00095(8)	0.0010(5)	0.0001(3)	0.0009(2)
C(12)	0.3573(4)	-0.1467(3)	0.46046(17)	0.0055(4)	0.0039(3)	0.00125(9)	0.0009(5)	-0.0007(3)	0.0004(3)
C(13)	-0.2286(4)	-0.0818(4)	0.4071(3)	0.0045(4)	0.0042(3)	0.00238(12)	0.0002(6)	0.0016(4)	0.0014(3)
C(14)	0.0893(4)	0.3517(3)	0.24285(16)	0.0080(5)	0.0023(3)	0.00103(8)	-0.0007(5)	0.0015(3)	0.0001(3)
C(15)	-0.3790(4)	0.2540(4)	0.3184(2)	0.0059(5)	0.0049(3)	0.00206(11)	0.0027(6)	0.0019(4)	-0.0015(3)
C(16)	-0.1556(4)	0.3595(3)	0.37202(17)	0.0079(5)	0.0025(3)	0.00128(9)	0.0018(5)	0.0013(4)	-0.0009(3)

Table 2-2. (continued)

(b) 20°C

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.05266(4)	0.10738(3)	0.187732(13)	0.01077(4)	0.00604(2)	0.001893(7)	-0.00122(5)	0.00074(3)	-0.00024(3)
S	-0.18638(12)	0.10132(11)	0.22695(6)	0.01007(13)	0.00982(11)	0.00299(4)	-0.00247(19)	0.00072(10)	-0.00342(10)
O(1)	0.2734(3)	0.1463(3)	0.16386(14)	0.0115(4)	0.0071(3)	0.00257(8)	-0.0026(5)	0.0022(3)	-0.0013(3)
O(2)	0.0445(3)	-0.0218(3)	0.10990(13)	0.0122(4)	0.0073(3)	0.00229(8)	-0.0048(5)	0.0014(3)	-0.0018(3)
O(3)	0.2375(3)	-0.0912(3)	0.41922(15)	0.0096(4)	0.0070(3)	0.00292(9)	0.0006(5)	-0.0017(3)	0.0015(3)
O(4)	0.3827(4)	0.0628(3)	0.4023(2)	0.0119(5)	0.0096(3)	0.00581(15)	-0.0052(6)	-0.0072(4)	0.0040(4)
O(5)	-0.0877(3)	-0.0588(3)	0.37174(16)	0.0097(4)	0.0069(3)	0.00382(10)	-0.0015(5)	0.0013(3)	0.0009(3)
O(6)	-0.0569(4)	0.1043(3)	0.43297(16)	0.0170(5)	0.0080(3)	0.00323(10)	0.0036(6)	0.0062(4)	0.0001(3)
N	-0.2113(4)	0.2713(3)	0.31873(17)	0.0122(5)	0.0067(3)	0.00279(11)	0.0041(6)	0.0015(4)	-0.0002(3)
C(1)	0.3402(5)	0.1064(4)	0.1120(2)	0.0102(5)	0.0056(3)	0.00253(11)	0.0004(7)	0.0011(4)	0.0005(3)
C(2)	0.1513(5)	-0.0426(4)	0.07016(19)	0.0134(6)	0.0063(3)	0.00187(10)	-0.0003(7)	-0.0005(4)	-0.0002(3)
C(3)	0.2891(5)	0.0181(4)	0.0686(3)	0.0120(6)	0.0063(4)	0.00256(12)	0.0006(7)	0.0024(4)	-0.0011(3)
C(4)	0.4887(5)	0.1636(5)	0.0971(3)	0.0114(6)	0.0086(4)	0.00400(16)	-0.0024(8)	0.0028(5)	-0.0019(5)
C(5)	0.1272(6)	-0.1418(4)	0.0206(3)	0.0180(8)	0.0081(4)	0.00267(13)	-0.0036(9)	0.0002(5)	-0.0029(4)
C(6)	-0.1225(5)	0.2101(4)	0.27931(19)	0.0110(5)	0.0060(3)	0.00210(10)	0.0020(6)	0.0005(4)	0.0010(3)
C(7)	0.0451(4)	0.2218(3)	0.26838(18)	0.0111(5)	0.0050(3)	0.00183(10)	-0.0005(6)	0.0014(4)	0.0001(3)
C(8)	0.1517(4)	0.1789(4)	0.32658(18)	0.0087(5)	0.0060(3)	0.00207(10)	-0.0021(6)	-0.0003(4)	0.0001(3)
C(9)	0.1298(4)	0.0542(4)	0.35023(17)	0.0086(5)	0.0056(3)	0.00182(9)	-0.0006(6)	0.0007(4)	-0.0008(3)
C(10)	0.2652(4)	0.0120(4)	0.39358(19)	0.0099(5)	0.0063(3)	0.00222(11)	0.0020(7)	0.0003(4)	-0.0006(3)
C(11)	-0.0148(4)	0.0380(4)	0.39011(19)	0.0101(5)	0.0053(3)	0.00224(10)	0.0029(6)	0.0001(4)	0.0018(3)
C(12)	0.3574(5)	-0.1487(4)	0.4581(3)	0.0129(7)	0.0090(4)	0.00317(14)	0.0047(8)	-0.0033(5)	0.0014(4)
C(13)	-0.2254(6)	-0.0817(5)	0.4074(4)	0.0106(7)	0.0095(5)	0.0064(3)	-0.0018(9)	0.0054(7)	0.0035(6)
C(14)	0.0928(5)	0.3431(4)	0.2444(3)	0.0174(7)	0.0051(3)	0.00277(13)	-0.0019(8)	0.0023(5)	0.0009(4)
C(15)	-0.3757(6)	0.2509(5)	0.3175(3)	0.0129(7)	0.0115(6)	0.0052(3)	0.0055(10)	0.0037(6)	-0.0035(6)
C(16)	-0.1541(6)	0.3543(4)	0.3698(3)	0.0180(8)	0.0072(4)	0.00366(16)	0.0051(9)	0.0003(6)	-0.0022(4)

Table 2-3. Final atomic parameters for hydrogen atoms of Thia-allyl palladium complex (V)

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

(a) -160°C

Atom	x	y	z	B
H(3)	0.360(4)	-0.003(3)	0.0366(17)	1.3(7)
H(4A)	0.549(7)	0.117(5)	0.077(3)	5.4(14)
H(4B)	0.536(7)	0.192(6)	0.138(3)	6.0(14)
H(4C)	0.471(7)	0.229(5)	0.068(3)	6.3(14)
H(5A)	0.107(5)	-0.212(4)	0.050(3)	3.0(9)
H(5B)	0.215(6)	-0.171(5)	0.002(3)	5.5(13)
H(5C)	0.050(6)	-0.130(5)	-0.001(3)	4.6(12)
H(8A)	0.246(4)	0.192(3)	0.3092(16)	0.8(6)
H(8B)	0.146(4)	0.236(3)	0.3669(17)	1.1(7)
H(9)	0.129(4)	0.016(3)	0.3139(16)	0.8(6)
H(12A)	0.307(5)	-0.210(4)	0.484(2)	2.4(8)
H(12B)	0.428(4)	-0.171(4)	0.4289(18)	1.4(7)
H(12C)	0.404(5)	-0.093(4)	0.492(3)	2.8(9)
H(13A)	-0.266(5)	-0.153(4)	0.388(3)	2.8(9)
H(13B)	-0.206(5)	-0.091(4)	0.453(3)	3.2(10)
H(13C)	-0.292(4)	-0.031(3)	0.3976(17)	1.1(7)
H(14A)	0.181(4)	0.347(3)	0.2206(17)	0.9(6)
H(14B)	0.010(5)	0.390(4)	0.217(3)	2.2(9)
H(14C)	0.108(5)	0.400(3)	0.2787(19)	1.6(8)
H(15A)	-0.427(5)	0.311(4)	0.336(3)	3.3(10)
H(15B)	-0.408(5)	0.252(4)	0.276(3)	2.7(9)
H(15C)	-0.394(6)	0.190(5)	0.345(3)	5.9(14)
H(16A)	-0.154(6)	0.326(5)	0.420(3)	4.5(12)
H(16B)	-0.063(6)	0.383(4)	0.366(3)	3.3(10)
H(16C)	-0.219(5)	0.418(4)	0.375(2)	2.3(8)

(b) 20°C

Atom	x	y	z	B
H(3)	0.359(5)	-0.002(4)	0.037(3)	5.4(11)
H(4A)	0.553(7)	0.106(5)	0.082(4)	9.6(18)
H(4B)	0.529(6)	0.180(5)	0.130(3)	8.2(15)
H(4C)	0.486(6)	0.212(5)	0.069(3)	8.4(15)
H(5A)	0.063(7)	-0.185(6)	0.037(3)	9.4(16)
H(5B)	0.217(7)	-0.176(6)	0.010(3)	9.7(17)
H(5C)	0.093(7)	-0.120(6)	-0.015(4)	10.1(19)
H(8A)	0.241(4)	0.182(3)	0.3099(17)	3.0(8)
H(8B)	0.145(5)	0.230(4)	0.368(3)	4.7(10)
H(9)	0.131(4)	0.018(4)	0.3142(18)	3.2(8)
H(12A)	0.322(7)	-0.195(6)	0.479(4)	11.7(20)
H(12B)	0.423(6)	-0.175(5)	0.427(3)	6.6(12)
H(12C)	0.401(6)	-0.100(4)	0.480(3)	6.1(12)
H(13A)	-0.248(6)	-0.156(5)	0.392(3)	6.3(12)
H(13B)	-0.202(7)	-0.102(5)	0.452(3)	8.5(16)
H(13C)	-0.291(6)	-0.030(5)	0.402(3)	7.0(13)
H(14A)	0.188(5)	0.332(4)	0.222(2)	4.3(9)
H(14B)	0.017(6)	0.371(5)	0.215(3)	6.5(13)
H(14C)	0.101(5)	0.394(4)	0.281(3)	4.8(10)
H(15A)	-0.425(6)	0.308(5)	0.336(3)	7.8(14)
H(15B)	-0.406(6)	0.239(5)	0.274(3)	8.2(15)
H(15C)	-0.399(6)	0.188(5)	0.332(3)	8.7(15)
H(16A)	-0.129(7)	0.319(6)	0.413(4)	10.4(18)
H(16B)	-0.067(6)	0.380(5)	0.363(3)	7.3(14)
H(16C)	-0.211(6)	0.416(5)	0.372(3)	7.5(14)

Table 2-4. Final atomic parameters for non-hydrogen atoms of Thioamidomethyl palladium complex (VI)

Positional parameters in fraction of cell edges and 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.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	0.17529(3)	0.03667(5)	0.064725(14)	0.006508(19)	0.01400(5)	0.002264(6)	0.00062(7)	0.00106(3)	0.00206(4)
S	0.21986(10)	0.15287(15)	-0.04213(6)	0.00814(9)	0.01480(19)	0.00229(3)	0.0057(3)	0.00233(8)	0.00203(12)
O(1)	0.1217(3)	-0.0374(5)	0.16431(14)	0.0096(3)	0.0186(7)	0.00251(8)	0.0052(9)	0.0027(3)	0.0029(5)
O(2)	0.2825(3)	-0.2109(4)	0.05793(14)	0.0075(3)	0.0161(6)	0.00254(8)	0.0013(7)	0.0014(3)	0.0029(4)
N	0.0829(3)	0.4083(5)	0.01720(16)	0.0055(3)	0.0137(7)	0.00227(9)	0.0010(7)	0.0004(3)	0.0009(4)
C(1)	0.1576(4)	-0.1828(6)	0.19727(19)	0.0080(4)	0.0167(9)	0.00201(10)	-0.0051(10)	-0.0002(4)	0.0019(5)
C(2)	0.2963(4)	-0.3277(7)	0.1084(3)	0.0061(4)	0.0150(8)	0.00281(12)	-0.0007(9)	-0.0008(4)	0.0010(6)
C(3)	0.2402(4)	-0.3189(7)	0.1736(3)	0.0077(4)	0.0185(9)	0.00246(12)	0.0022(10)	-0.0008(4)	0.0037(6)
C(4)	0.1063(6)	-0.2071(8)	0.2703(3)	0.0135(6)	0.0237(12)	0.00227(12)	-0.0010(15)	0.0018(5)	0.0034(7)
C(5)	0.3822(5)	-0.4907(7)	0.0950(3)	0.0086(4)	0.0173(11)	0.00389(15)	0.0039(11)	0.0005(5)	0.0016(7)
C(6)	0.1453(4)	0.3649(6)	-0.0388(2)	0.0061(3)	0.0138(8)	0.00217(10)	-0.0004(8)	0.0002(3)	0.0012(5)
C(7)	0.0748(4)	0.2702(6)	0.0749(3)	0.0066(4)	0.0157(8)	0.00242(12)	0.0010(9)	0.0017(4)	0.0013(6)
C(8)	0.0188(4)	0.5892(6)	0.0273(3)	0.0072(4)	0.0144(8)	0.00262(12)	0.0043(9)	-0.0002(4)	0.0002(5)
C(9)	0.1537(4)	0.4986(6)	-0.09978(19)	0.0082(4)	0.0133(9)	0.00207(10)	0.0028(9)	0.0013(3)	0.0010(5)
C(10)	0.2613(5)	0.5881(7)	-0.1155(3)	0.0089(4)	0.0203(11)	0.00289(13)	-0.0027(12)	-0.0001(4)	0.0027(6)
C(11)	0.2681(6)	0.7119(8)	-0.1714(3)	0.0124(5)	0.0208(11)	0.00368(16)	-0.0077(14)	0.0022(6)	0.0028(8)
C(12)	0.1705(6)	0.7451(7)	-0.2138(3)	0.0169(7)	0.0172(10)	0.00227(12)	0.0047(16)	0.0019(5)	0.0024(6)
C(13)	0.0659(5)	0.6572(9)	-0.1993(3)	0.0128(6)	0.0273(13)	0.00231(12)	0.0128(15)	-0.0007(5)	0.0032(7)
C(14)	0.0537(5)	0.5293(8)	-0.1426(3)	0.0090(4)	0.0257(11)	0.00242(11)	0.0049(13)	0.0001(4)	0.0020(7)

Table 2-5. Final atomic parameters for hydrogen atoms of Thioamidomethyl palladium complex (VI)

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$. Estimated standard deviations in parentheses.

Atom	x	y	z	B
H(3)	0.254(4)	-0.405(7)	0.206(3)	1.9(10)
H(4A)	0.074(6)	-0.339(13)	0.279(4)	8.(3)
H(4B)	0.164(6)	-0.187(13)	0.304(4)	8.(3)
H(4C)	0.070(6)	-0.103(13)	0.274(4)	9.(3)
H(5A)	0.453(7)	-0.457(12)	0.080(4)	9.(3)
H(5B)	0.375(7)	-0.573(13)	0.123(4)	8.(3)
H(5C)	0.369(7)	-0.550(11)	0.063(3)	7.(3)
H(7A)	0.107(5)	0.345(8)	0.118(3)	2.0(10)
H(7B)	-0.006(5)	0.224(9)	0.071(3)	4.3(14)
H(8A)	-0.039(5)	0.589(9)	0.007(3)	3.7(13)
H(8B)	0.028(5)	0.637(9)	0.074(3)	4.2(14)
H(8C)	0.052(4)	0.697(8)	0.002(3)	3.1(13)
H(10)	0.331(4)	0.562(7)	-0.092(3)	2.3(10)
H(11)	0.340(4)	0.759(8)	-0.181(3)	2.6(11)
H(12)	0.185(5)	0.824(8)	-0.260(3)	3.4(12)
H(13)	0.004(6)	0.667(9)	-0.228(3)	4.0(14)
H(14)	-0.027(5)	0.487(8)	-0.134(3)	2.6(11)

2.4 Results and Discussion

Thia-allyl Palladium Complex (V)

Figure 2-1 represents *ORTEP* drawings(Johnson, 1976) of the molecule at -160 and 20°C along with the numbering system of the atoms. The thermal ellipsoids correspond to 30% probability level. Bond lengths and bond angles along with their estimated standard deviations are listed in Tables 2-6 and 2-7.

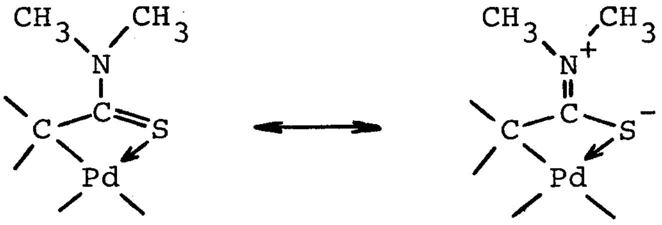
No essential difference is observed in the molecular structures at -160 and 20°C. However, the thermal ellipsoids of atoms at -160°C are much smaller than those at 20°C as shown in Fig. 2-1. Moreover, as shown in Table 2-6(a), most of bond lengths at 20°C are shorter than those at -160°C, which is considered mainly due to the larger thermal vibration of the molecule at 20°C. At -160°C, estimated standard deviations of bond lengths and bond angles are quite small, e.s.d.'s of C-C bond lengths in the acetylacetonato ligand being 0.005 Å. Hereafter, the description of the structure and the discussion will be mainly made on the low temperature structure.

The most remarkable feature of the molecular structure in this complex is that the thia-allyl group does not behave as a thia-π-allyl type but a thia-σ-allyl fashion. Palladium complexes containing π-allyl groups have been widely studied by means of X-ray diffraction(Hartley, 1973a). In π-allyl palladium complexes, the allyl(C_3H_5) plane inclines at 95 ∿ 125° to the coordination plane of the palladium(Hartley, 1973a) in order that the π-electron orbitals of the allyl group overlap with the orbitals of the metal atom. In a typical example of π-allyl palladium complex, $[(\pi\text{-}C_3H_5)PdCl]_2$(Rowe, 1962; Levdik

& Porai-Koshits, 1962; Oberhansli & Dahl, 1965; Smith 1965), the C_3H_5 plane inclines at 111.5° to the $(PdCl)_2$ plane(Smith, 1965). The Pd-C distances are all equal[2.11 and 2.12 Å] and two C-C bond lengths are equal to each other[1.38 Å](Smith, 1965). In the present complex, it is expected that the thia-allyl group takes similar coordination geometry to the π-allyl palladium complex, if this group is bound to the palladium by a π-type coordination. Figure 2-3 depicts the coordination behaviour of the thia-allyl group to the palladium atom. The plane defined by the S, C(6) and C(7) atoms is almost coplanar with the O(1)-Pd-O(2) plane, the dihedral angle between these two planes being 8.8°.

Figure 2-4 shows the coordination geometry around the palladium atom projected onto the coordination plane along with selected bond lengths and bond angles. The geometry around the palladium atom is essentially square-planar. The equation of the least-squares plane is given in Table 2-8. The Pd-C(7) bond length of 2.058(3) Å is a normal value for the Pd(II)-C(sp^3) σ-bond, whereas the Pd-C(6) distance is 2.670(3) Å. The Pd-S bond length[2.262(1) Å] is one of the shortest Pd-S bond lengths among palladium complexes containing the Pd-S bonds whose structures have been determined by the diffraction method[2.24 ∿ 2.47 Å], which may be partly due to the weak *trans*-influence of the oxygen atom in the acetylacetonato ligand.

In the thia-allyl group, the C(6)-C(7) bond length of 1.506(4) Å is an expected value for the C(sp^2)-C(sp^3) single bond, while the S-C(6) bond length[1.709(3) Å] falls between those of the S-C double and single bonds[1.61 and 1.82 Å, respectively] (Abrahams, 1956). However, the N-C(6) bond length of 1.315(4) Å is obviously shorter than those of the N-C(15) and N-C(16) bonds, which suggests the conjugation through the S-C(6) and N-C(6) bonds. Both resonance structures presented below play significant contributions in the present complex. The N, C(15) and C(16) atoms in the dimethylamino group are coplanar with the S, C(6) and C(7) plane in the thia-allyl group.



These facts imply that the coordination mode of the thia-allyl group is not a π-type but a σ-one. The thia-allyl group is bound to the palladium atom through the Pd-C σ-bond and the donation of the sulphur to the metal atom. The short Pd-S bond length in this complex shows the strong donation of the sulphur to the metal atom, which may be connected with the stability of the present complex as pointed out by Tamaru, Kagotani & Yoshida (1979a).

The geometry of two methoxy carbonyl groups is similar to those found in methyl ester of carboxylic acid derivatives such as dimethyl ester of *meso*-tartaric acid (Kroon & Kanters, 1973).

The crystal structure projected along the a* axis is shown in Fig. 2-5. No abnormally short intermolecular atomic contacts are observed, the shortest contact between non-hydrogen atoms being 3.305(5) Å[O(2)(x,y,z)···C(15)(-1/2-x,-1/2+y,1/2-z)].

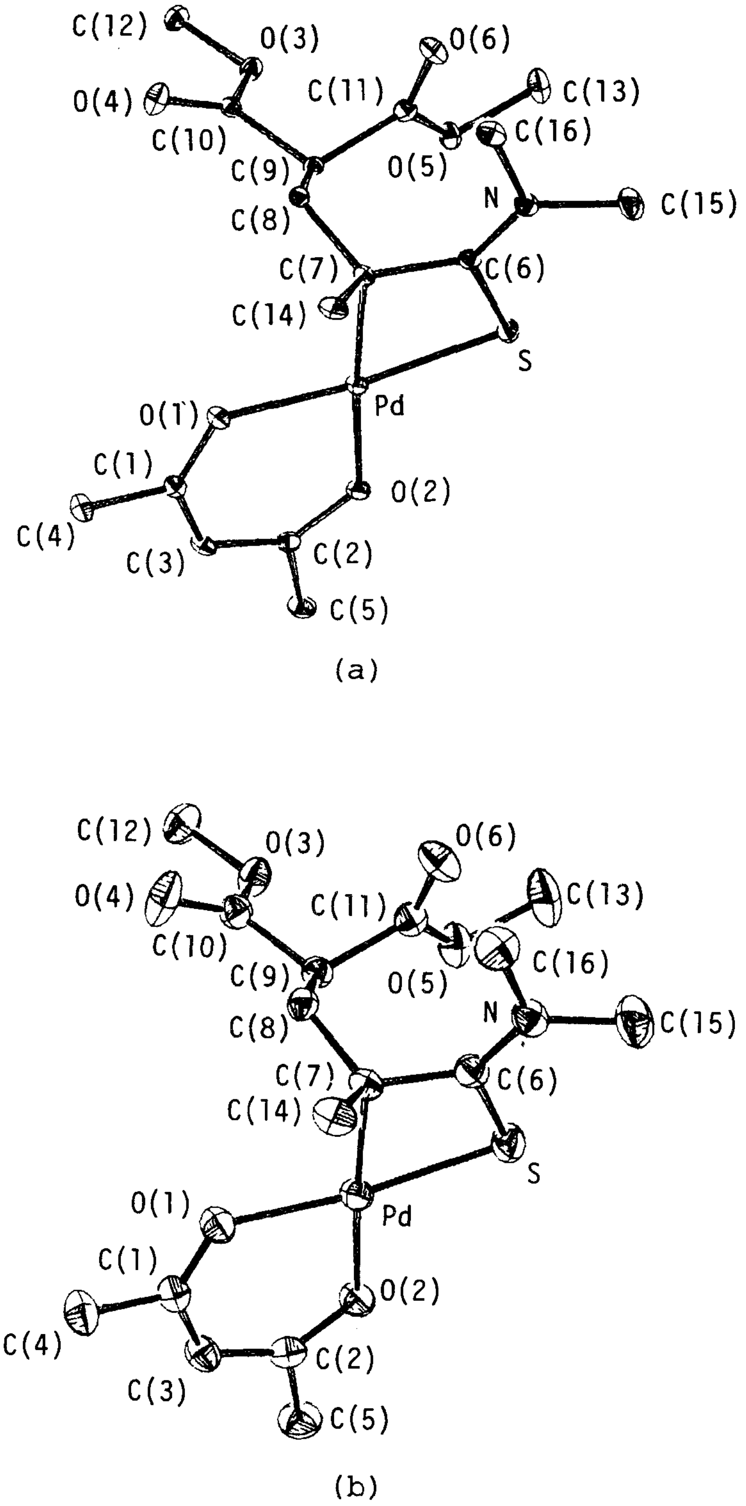


Fig. 2-1. *ORTEP* drawings of the molecule of Thia-allyl palladium complex (V) along with the numbering system of the atoms. The thermal ellipsoids correspond to 30% probability level. Hydrogen atoms are omitted for clarity. (a) -160°C, (b) 20°C.

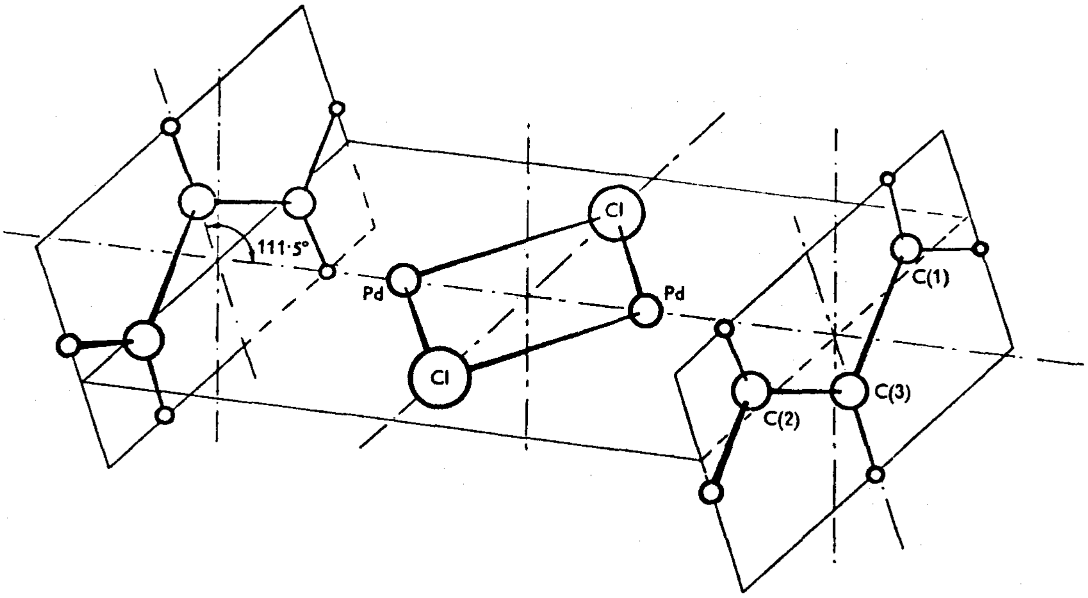


Fig. 2-2. The structure and the coordination behaviour in the π-allyl palladium chloride complex, $[(\pi\text{-}C_3H_5)PdCl]_2$ (Smith, 1965).

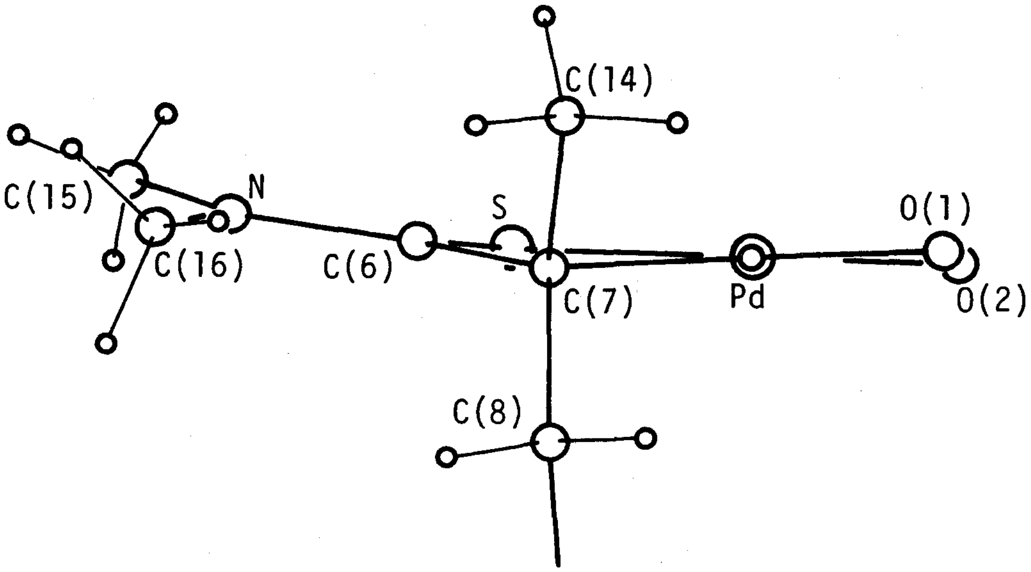


Fig. 2-3. A perspective view of the coordination behaviour of the thia-allyl group to the palladium atom in Thia-allyl palladium complex (V).

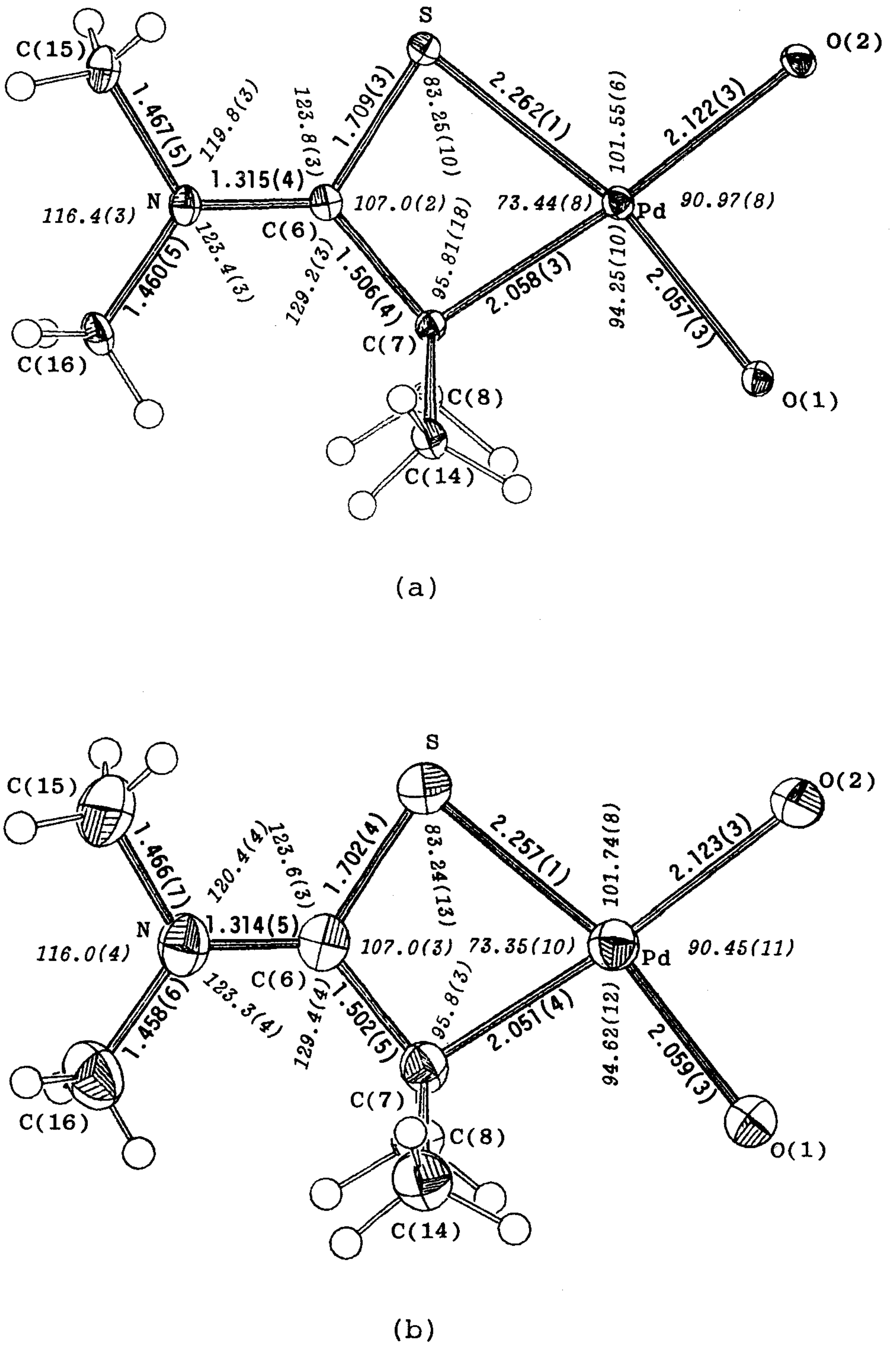
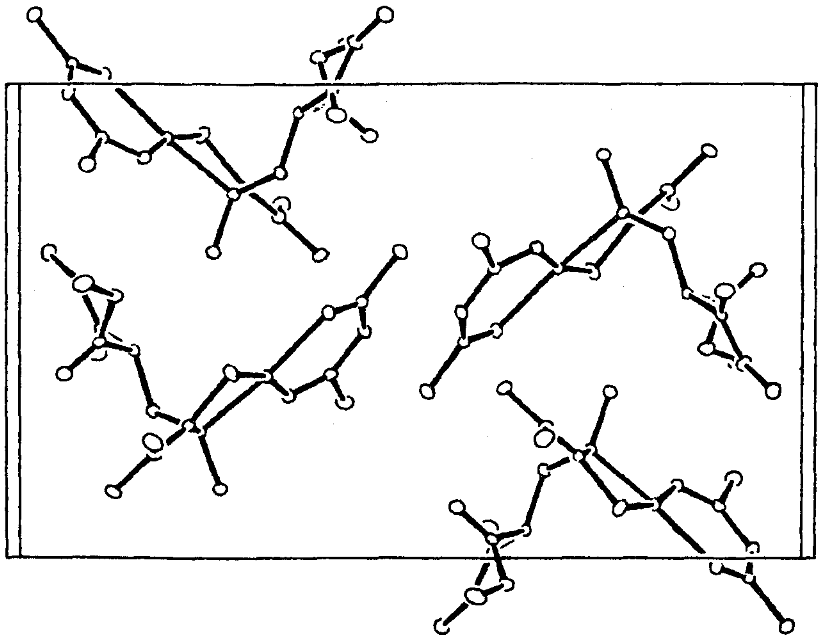
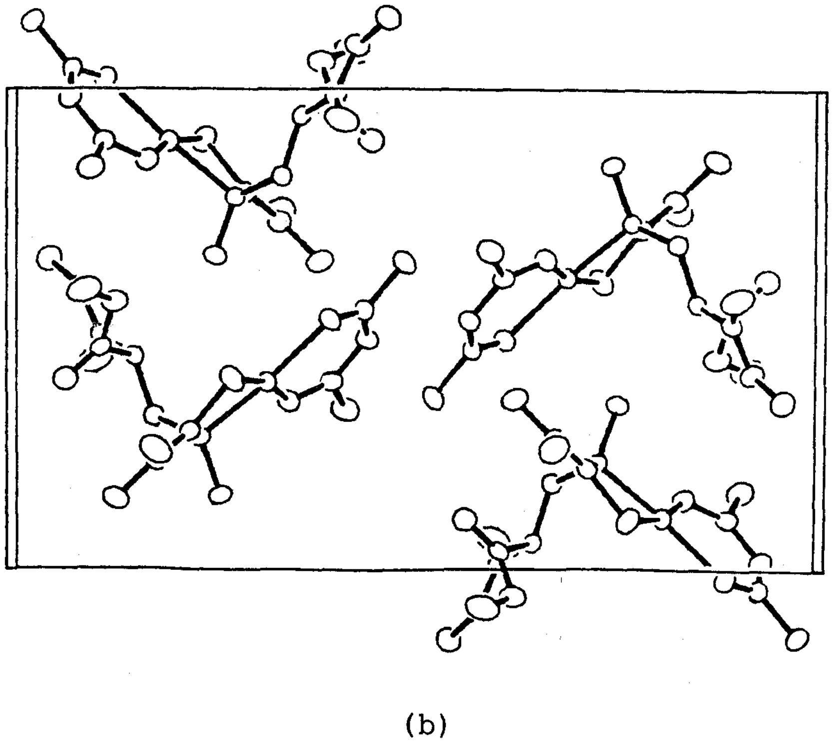


Fig. 2-4. The coordination geometry around the palladium atom and the coordination behaviour of the thia-allyl group in Thia-allyl palladium complex (V). (a) -160°C, (b) 20°C.



(a)



(b)

Fig. 2-5. The crystal structure of Thia-allyl Palladium Complex (V) projected along the a* axis. Atoms are represented by thermal ellipsoids at 30% probability levels. Hydrogen atoms are omitted for clarity. (a) -160°C, (b) 20°C.

Table 2-6. Bond lengths in Thia-allyl palladium complex (V). Estimated standard deviations in parentheses.

(a) Bonds involving non-hydrogen atoms

Length(Å)	[-160°C]	[20°C]
Pd-O(1)	2.057(3)	2.059(3)
Pd-O(2)	2.122(3)	2.123(3)
Pd-S	2.262(1)	2.257(1)
Pd-C(7)	2.058(3)	2.051(4)
O(1)-C(1)	1.272(4)	1.264(5)
O(2)-C(2)	1.272(4)	1.254(5)
C(1)-C(3)	1.401(5)	1.390(6)
C(1)-C(4)	1.509(5)	1.500(7)
C(2)-C(3)	1.395(5)	1.403(6)
C(2)-C(5)	1.523(5)	1.507(7)
S-C(6)	1.709(3)	1.702(4)
N-C(6)	1.315(4)	1.314(5)
N-C(15)	1.467(5)	1.466(7)
N-C(16)	1.460(5)	1.458(6)
C(6)-C(7)	1.506(4)	1.502(6)
C(7)-C(8)	1.535(5)	1.531(5)
C(7)-C(14)	1.534(5)	1.540(6)
C(8)-C(9)	1.532(5)	1.527(5)
C(9)-C(10)	1.530(5)	1.520(6)
C(9)-C(11)	1.523(5)	1.518(5)
O(3)-C(10)	1.327(4)	1.318(5)
O(3)-C(12)	1.448(5)	1.442(6)
O(4)-C(10)	1.203(4)	1.198(6)
O(5)-C(11)	1.341(4)	1.333(5)
O(5)-C(13)	1.449(5)	1.436(7)
O(6)-C(11)	1.205(4)	1.196(5)

Table 2-6. (continued)

(b) Bonds involving hydrogen atoms

Length(Å)	[-160°C]	[20°C]
C(3)-H(3)	0.88(4)	0.92(5)
C(4)-H(4A)	0.86(6)	0.92(7)
C(4)-H(4B)	0.95(6)	0.75(6)
C(4)-H(4C)	0.86(6)	0.78(6)
C(5)-H(5A)	0.96(5)	0.82(6)
C(5)-H(5B)	0.89(6)	0.91(7)
C(5)-H(5C)	0.80(6)	0.78(7)
C(8)-H(8A)	0.92(4)	0.86(4)
C(8)-H(8B)	0.96(4)	1.00(5)
C(9)-H(9)	0.84(4)	0.82(4)
C(12)-H(12A)	0.96(4)	0.75(7)
C(12)-H(12B)	0.92(4)	0.89(5)
C(12)-H(12C)	0.95(5)	0.80(5)
C(13)-H(13A)	0.95(5)	0.93(5)
C(13)-H(13B)	0.90(5)	0.92(6)
C(13)-H(13C)	0.82(4)	0.83(6)
C(14)-H(14A)	0.93(4)	0.97(4)
C(14)-H(14B)	0.94(4)	0.92(5)
C(14)-C(14C)	0.89(4)	0.92(5)
C(15)-H(15A)	0.85(5)	0.87(6)
C(15)-H(15B)	0.84(5)	0.88(6)
C(15)-H(15C)	0.91(6)	0.81(6)
C(16)-H(16A)	1.00(6)	0.95(7)
C(16)-H(16B)	0.87(5)	0.84(6)
C(16)-H(16C)	0.87(4)	0.87(6)

Table 2-7. Bond angles involving non-hydrogen atoms in Thia-allyl palladium complex (V). Estimated standard deviations in parentheses.

Angle(°)	[-160°C]	[20°C]
O(1)-Pd-O(2)	90.97(8)	90.45(11)
S-Pd-O(2)	101.55(6)	101.74(8)
S-Pd-C(7)	73.44(8)	73.35(10)
O(1)-Pd-C(7)	94.25(10)	94.62(12)
Pd-O(1)-C(1)	123.9(2)	124.1(3)
Pd-O(2)-C(2)	123.3(2)	124.1(3)
O(1)-C(1)-C(3)	127.3(3)	126.8(4)
O(1)-C(1)-C(4)	115.0(3)	114.8(4)
C(3)-C(1)-C(4)	117.7(3)	118.4(4)
O(2)-C(2)-C(3)	126.4(3)	125.4(4)
O(2)-C(2)-C(5)	114.9(3)	116.3(4)
C(3)-C(2)-C(5)	118.7(3)	118.3(4)
C(1)-C(3)-C(2)	127.5(3)	128.4(4)
Pd-S-C(6)	83.25(10)	83.24(13)
S-C(6)-C(7)	107.0(2)	107.0(3)
S-C(6)-N	123.8(3)	123.6(3)
N-C(6)-C(7)	129.2(3)	129.4(4)
Pd-C(7)-C(6)	95.81(18)	95.8(3)
Pd-C(7)-C(8)	108.44(18)	108.7(3)
Pd-C(7)-C(14)	110.22(19)	110.0(3)
C(6)-C(7)-C(8)	116.0(3)	116.9(3)
C(6)-C(7)-C(14)	114.1(3)	113.7(4)
C(8)-C(7)-C(14)	111.1(3)	110.5(3)
C(6)-N-C(15)	119.8(3)	120.4(4)
C(6)-N-C(16)	123.4(3)	123.3(4)
C(15)-N-C(16)	116.4(3)	116.0(4)
C(7)-C(8)-C(9)	116.1(3)	116.6(3)
C(8)-C(9)-C(10)	111.5(3)	111.5(3)
C(8)-C(9)-C(11)	112.5(3)	112.6(3)
C(10)-C(9)-C(11)	109.1(3)	109.5(3)

Table 2-7. (continued)

Angle(°)	[-160°C]	[20°C]
C(9)-C(10)-O(3)	110.2(3)	110.5(3)
C(9)-C(10)-O(4)	124.7(3)	125.6(4)
O(3)-C(10)-O(4)	125.0(3)	123.9(4)
C(9)-C(11)-O(5)	111.3(3)	111.8(3)
C(9)-C(11)-O(6)	124.2(3)	123.6(4)
O(5)-C(11)-O(6)	124.5(3)	124.6(4)
C(10)-O(3)-C(12)	116.6(3)	118.3(4)
C(11)-O(5)-C(13)	115.5(3)	115.6(4)

Table 2-8. Least-squares planes in Thia-allyl palladium complex(V)

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 $Z = cz\sin\beta$.

Coordination plane of Pd through Pd, O(1), O(2), C(7) and S

(a) -160°C

$-0.2900X + 0.6900Y - 0.6632Z + 1.5471 = 0.0$

(b) 20°C

$-0.2860X + 0.6980Y - 0.6565Z + 1.6281 = 0.0$

Acetylacetonato plane through O(1), O(2), C(1), C(2), C(3), C(4) and C(5)

(a) -160°C

$-0.3996X + 0.6392Y - 0.6571Z + 1.7043 = 0.0$

(b) 20°C

$-0.4109X + 0.6626Y - 0.6263Z + 1.7322 = 0.0$

Deviations of atoms from the plane(Å)

	Coordination plane of Pd		Acetylacetonato plane	
	[-160°C]	[20°C]	[-160°C]	[20°C]
Pd	0.003	0.001	0.082*	0.125*
O(1)	0.064	0.059	-0.097	-0.090
O(2)	-0.045	-0.042	0.104	0.094
C(1)	0.190*	0.221*	-0.022	-0.019
C(2)	-0.030*	0.021*	0.019	0.022
C(3)	0.124*	0.183*	0.005	0.007
C(4)	0.459*	0.497*	0.067	0.060
C(5)	-0.185*	-0.095*	-0.061	-0.060
S	0.065	0.060	0.387*	0.476*
C(6)	0.103*	0.120*	0.309*	0.454*
C(7)	-0.078	-0.071	-0.044*	0.068*

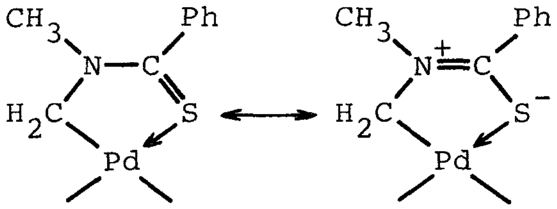
* Not included in the least-squares calculation.

Thioamidomethyl Palladium Complex (VI)

Figure 2-6 shows an *ORTEP* drawing of the molecule(Johnson, 1976) together with the atomic numbering scheme. The thermal ellipsoids correspond to 30% probability level. Bond lengths and bond angles are listed in Tables 2-9 and 2-10.

The geometry around the palladium atom is essentially square-planar. The palladium atom is surrounded by two oxygen atoms of the acetylacetonato ligand and the carbon and sulphur atoms of the thioamidomethyl group. This coordination geometry along with selected bond lengths and bond angles is shown in Fig. 2-7. The equation of the least-squares plane and atomic deviations from the plane are presented in Table 2-11.

The thioamidomethyl group, bound to the palladium atom through the Pd-C σ-bond and the donation of the sulphur to the metal atom, functions as a bidentate ligand forming a Pd-C-N-C-S five-membered ring. The Pd-C(7) bond length of 1.988(4) Å is somewhat short but fall into the range 1.97 ∿ 2.19 Å of the Pd(II)-C(sp^3) bond lengths reported hitherto. The Pd-S bond length[2.245(1) Å] in this complex is also one of the shortest Pd(II)-S bonds among palladium complexes whose structures have been determined by the diffraction method[2.24 ∿ 2.47 Å]. The S, N, C(6), C(7), C(8) and C(9) atoms in the thioamidomethyl group are coplanar with each other. The dihedral angle between this plane and the coordination plane of the palladium atom is 5.3°. Among three N-C bonds, the N-C(7) and N-C(8) bond lengths[both 1.463(5) Å] are considered to be normal values for the N-C(sp^3) single bond. On the other hand, the N-C(6) bond length[1.309(5) Å] is obviously shorter than those of the other two N-C bonds and may have partial double bond character. In this connexion, the S-C(6) bond[1.699(4) Å] is apparently lengthened over the S=C double bond[1.61 Å](Abrahams, 1956). These facts show the conjugation through the S-C(6) and N-C(6) bonds. Both resonance structures presented below contribute significantly to the bonding of the thioamidomethyl group in this complex, which is probably connected with the relatively short Pd-S bond.



The crystal structure as viewed down the b axis is presented in Fig. 2-8. All intermolecular distances are considered to be normal van der Waals contacts, the shortest contact of non-hydrogen atoms being 3.218(5) Å[C(8)(x,y,z)···O(2)(-1/2+x,1/2-y,-z)].

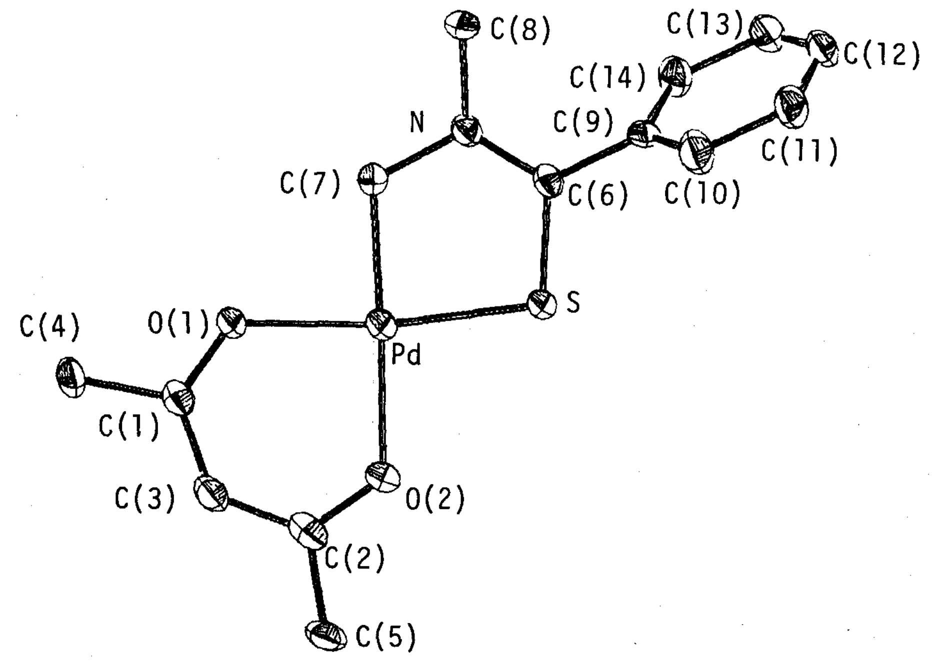


Fig. 2-6. An *ORTEP* drawing of the molecule of Thioamidomethyl palladium complex (VI) along with the numbering system of the atoms. The thermal ellipsoids correspond to 30% probability level. Hydrogen atoms are omitted for clarity.

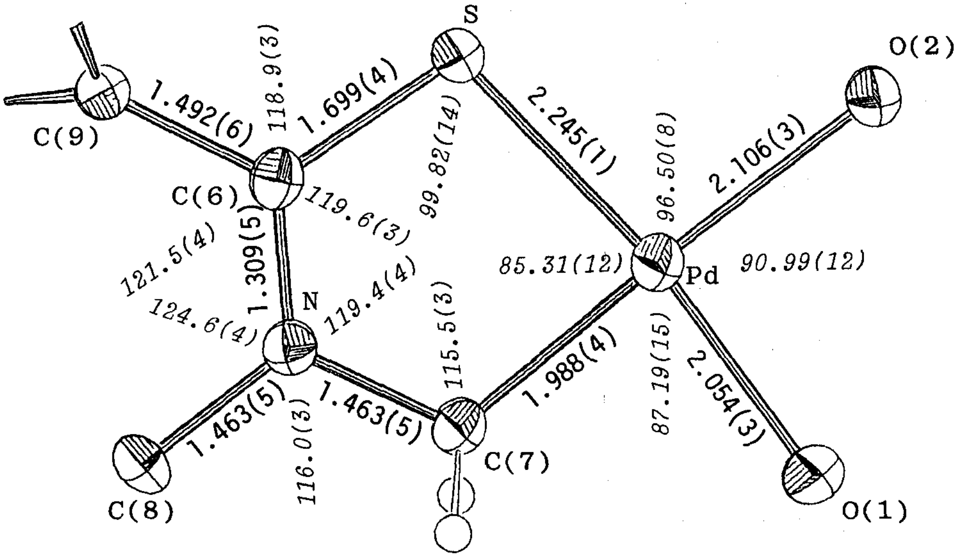


Fig. 2-7. The coordination geometry around the palladium atom and the coordination behaviour of the thioamidomethyl group in Thioamidomethyl palladium complex (VI).

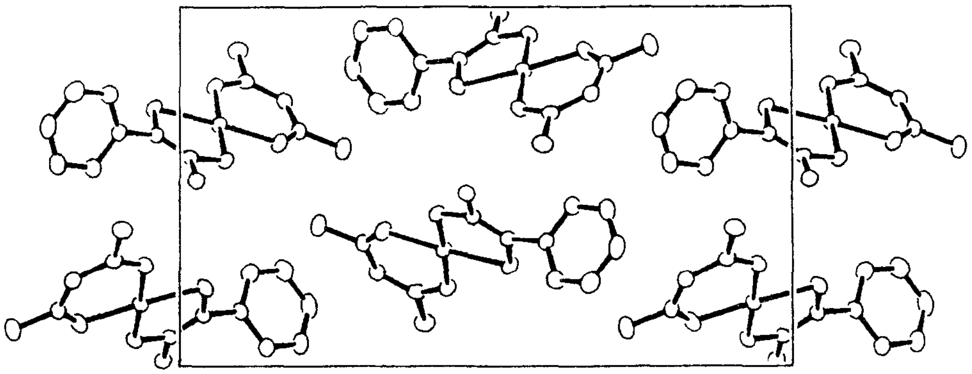


Fig. 2-8. The crystal structure of Thioamidomethyl palladium complex (VI) as viewed down the b axis. Atoms are represented by thermal ellipsoids at 30% probability levels. Hydrogen atoms are omitted for clarity.

Table 2-9. Bond lengths in Thioamidomethyl palladium complex (VI). Estimated standard deviations in parentheses.

(a) Bonds involving non-hydrogen atoms

Length(Å)		Length(Å)	
Pd-O(1)	2.054(3)	Pd-O(2)	2.106(3)
Pd-S	2.245(1)	Pd-C(7)	1.988(4)
O(1)-C(1)	1.258(5)	O(2)-C(2)	1.268(5)
C(1)-C(3)	1.400(6)	C(2)-C(3)	1.394(6)
C(1)-C(4)	1.514(7)	C(2)-C(5)	1.510(7)
S-C(6)	1.699(4)	N-C(6)	1.309(5)
N-C(7)	1.463(5)	N-C(8)	1.463(5)
C(6)-C(9)	1.492(6)		
C(9)-C(10)	1.389(6)	C(10)-C(11)	1.373(7)
C(11)-C(12)	1.379(8)	C(12)-C(13)	1.351(8)
C(13)-C(14)	1.406(8)	C(14)-C(9)	1.402(7)

(b) Bonds involving hydrogen atoms

Length(Å)		Length(Å)	
C(3)-H(3)	0.87(5)		
C(4)-H(4A)	1.00(9)	C(5)-H(5A)	0.88(9)
C(4)-H(4B)	0.92(9)	C(5)-H(5B)	0.79(9)
C(4)-H(4C)	0.83(9)	C(5)-H(5C)	0.75(8)
C(7)-H(7A)	1.03(6)	C(10)-H(10)	0.92(5)
C(7)-H(7B)	0.97(6)	C(11)-H(11)	0.89(5)
C(8)-H(8A)	0.76(6)	C(12)-H(12)	1.05(6)
C(8)-H(8B)	0.96(7)	C(13)-H(13)	0.89(6)
C(8)-H(8C)	0.97(6)	C(14)-H(14)	0.96(6)

Table 2-10. Bond angles involving non-hydrogen atoms in Thioamidomethyl palladium complex (VI). Estimated standard deviations in parentheses.

Angle(°)		Angle(°)	
O(1)-Pd-O(2)	90.99(12)	O(1)-Pd-C(7)	87.19(15)
S-Pd-C(7)	85.31(12)	S-Pd-O(2)	96.50(8)
Pd-O(1)-C(1)	124.7(3)	Pd-O(2)-C(2)	123.3(3)
O(1)-C(1)-C(3)	126.7(4)	O(2)-C(2)-C(3)	126.3(4)
O(1)-C(1)-C(4)	115.3(4)	O(2)-C(2)-C(5)	115.7(4)
C(3)-C(1)-C(4)	118.0(4)	C(3)-C(2)-C(5)	118.1(4)
C(1)-C(3)-C(2)	127.9(5)		
Pd-S-C(6)	99.82(14)	Pd-C(7)-N	115.5(3)
S-C(6)-N	119.6(3)	C(6)-N-C(7)	119.4(4)
S-C(6)-C(9)	118.9(3)	C(6)-N-C(8)	124.6(4)
N-C(6)-C(9)	121.5(4)	C(7)-N-C(8)	116.0(3)
C(6)-C(9)-C(10)	120.2(4)	C(6)-C(9)-C(14)	119.8(4)
C(10)-C(9)-C(14)	120.0(5)	C(9)-C(10)-C(11)	119.8(5)
C(10)-C(11)-C(12)	121.0(6)	C(11)-C(12)-C(13)	119.5(6)
C(12)-C(13)-C(14)	121.9(6)	C(13)-C(14)-C(9)	117.7(5)

Table 2-11. Least-squares planes in Thioamidomethyl palladium complex (VI).

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; $X = ax$, $Y = by$ and $Z = cz$.

(a) Coordination plane of Pd through Pd, O(1), O(2), C(7) and S

$$-0.7750X - 0.5006Y - 0.3858Z + 2.1346 = 0.0$$

(b) Plane of the thioamidomethyl group through S, N, C(6), C(7), C(8) and C(9)

$$-0.8081X - 0.4189Y - 0.4141Z + 2.0804 = 0.0$$

(c) Plane of the acetylacetonato ligand through O(1), O(2), C(1), C(2), C(3), C(4) and C(5)

$$-0.7533X - 0.5469Y - 0.3654Z + 2.0054 = 0.0$$

Deviations of atoms from the plane(Å)

	Plane a	Plane b	Plane c
Pd	0.010	-0.123*	-0.063*
S	0.002	-0.024	
N	-0.137*	0.002	
C(6)	-0.115*	0.005	
C(7)	-0.007	0.024	
C(8)	-0.285*	-0.026	
C(9)	-0.207*	0.019	
O(1)	0.002		-0.021
O(2)	-0.007		0.024
C(1)	-0.044*		0.001
C(2)	-0.090*		0.001
C(3)	-0.113*		-0.013
C(4)	-0.050*		0.018
C(5)	-0.168*		-0.009

* Not included in the least-squares calculation.

Acetylacetonato Ligand

In both complexes V and VI, each structure of the acetylacetonato ligand is similar to each other, which is compared with that found in [Pd(acac)$_2$] (Knyazeva, Shugam & Shkol'nikova, 1970; Sato, Miki, Kai, Yasuoka & Kasai, 1978). This ligand in each complex has high planarity and is coplanar with the palladium atom. The equations of the least-squares planes of this ligand in both complexes are presented in Tables 2-8 and 2-11. The deviations of the palladium atom from the acac plane are 0.082 and 0.063 Å for V and VI, respectively. Table 2-12 gives the comparison of bond lengths and bond angles concerning the acetylacetonato ligand among the complexes V, VI and [Pd(acac)$_2$]. In both V and VI, the Pd-O bond lengths are longer than those found in [Pd(acac)$_2$], which may be due to stronger *trans*-influence of the carbon and sulphur atoms in V and VI than that of the oxygen atoms in [Pd(acac)$_2$]. The Pd-O(1) bond lengths [2.057(3) and 2.054(3) Å] are obviously shorter than those of the Pd-O(2) bonds [2.122(3) and 2.106(3) Å] in the complexes V and VI. This fact is also probably caused by the difference of the *trans*-influence of the atoms attached to the *trans*-positions of two Pd-O bonds (C and S). The *trans*-influence of the alkyl carbon atom is significantly stronger than that of the sulphur atom. The O(1)-Pd-O(2) bond angles in V and VI [90.97(8) and 90.99(12)°] are relatively smaller than the corresponding angle found in [Pd(acac)$_2$] [95.21°]. It may be partly owing to the relatively narrower angles of S-Pd-C(7) [73.44(8)° for V and 85.31(12)° for VI] than 90° which is due to the formation of four- and five-membered rings in V and VI, respectively.

The other bond lengths and bond angles among three complexes presented in Table 2-12 are good agreement with each other, which are considered as standard values for an acetylacetonato ligand.

Table 2-12. Comparison of bond lengths and bond angles in the acetylacetonato ligand among the complexes V, VI and [Pd(acac)$_2$].

	Complex V	Complex VI	[Pd(acac)$_2$][a]
	(at -160°C)	(at 20°C)	(at -170°C)
Pd-O(1)(*trans* to S)	2.057 Å	2.054 Å	1.989 Å*
Pd-O(2)(*trans* to C)	2.122	2.106	
O(1)-C(1) O(2)-C(2)	1.273*	1.263*	1.275*
C(1)-C(3) C(2)-C(3)	1.398*	1.397*	1.402*
C(1)-C(4) C(2)-C(5)	1.516*	1.512*	1.506*
O(1)-Pd-O(2)	90.97°	90.99°	95.21°
Pd-O(1)-C(1) Pd-O(2)-C(2)	123.6*	124.0*	122.6*
O(1)-C(1)-C(3) O(2)-C(2)-C(3)	126.9*	126.5*	126.4*
O(1)-C(1)-C(4) O(2)-C(2)-C(5)	115.0*	115.5*	115.3*
C(3)-C(1)-C(4) C(3)-C(3)-C(5)	118.2*	118.1*	118.3*
C(1)-C(3)-C(2)	127.5	127.9	126.6

* Averaged value of two chemically equivalent bond lengths and bond angles

[a] Sato, Miki, Kai, Yasuoka & Kasai(1978).

CONCLUSION

The purpose of this study is that the molecular structures of the organopalladium complexes which have the sulphur-containing ligands(groups) are determined with high precision in order to elucidate the exact coordination behaviour of these ligands (groups) to the palladium atom.

In Chapter 1, the molecular structures of five palladium complexes containing the methylthiomethyl or phenylthiomethyl group(I, II, IIIa, IIIb and IV) have been determined at liquid nitrogen temperature and the coordination behaviour of these groups to the metal atom has been discussed.

In Chapter 2, the molecular structures of two palladium complexes containing the thia-allyl or thioamidomethyl group (V and VI) have been determined and the bonding modes of these groups to the metal atom have been elucidated.

Precision of the Structure Determination

In order to carry out the structure determination with high precision, the X-ray analyses for the complexes I ∿ V have been made at liquid nitrogen temperature(-160°C), while two or more independent sets of the equivalent reflexion data have been collected at room temperature for the complex VI. The data concerning the precision of the present structure determination are summarized in Table C-1. The structure analyses of the complexes I, II, V and VI have enough precision to make detailed discussions, in which the exact locations of hydrogen atoms are also determined. However, in the complexes IIIa and IIIb, the poor quality of the crystals, which is possibly connected with the disordered structures of the anions, reduced the precision of the structure determination. The complex IV are unstable at room temperature and its crystals are very thin, to which the relatively low precision of this structure analysis may be due. It has been established by the present structure analyses that the X-ray diffraction work at low temperature is a very effective method to obtain the precise molecular structure also in case of the organometallic compounds. However, the quality of crystals, of course, has an important influence upon the precision which is demonstrated in case of the complexes IIIa, IIIb and IV.

Table C-1. The precision of the present structure determination

Complex	I	II		IIIa	IIIb
Temperature (°C)	-160	-160	20	-160	-160
Final R value	0.035	0.049	0.068	0.141	0.102
E.s.d.'s of C-C bonds* (Å)	0.004 ∿0.006	0.007 ∿0.009	0.011 ∿0.015	0.03 ∿0.05	0.02 ∿0.03
H atoms	Yes	Yes	Yes	No	No

Complex	IV	V		VI
Temperature (°C)	-160	-160	20	20
Final R value	0.089	0.033	0.039	0.024
E.s.d.'s of C-C bonds* (Å)	0.03 ∿0.04	0.005	0.006 ∿0.007	0.006 ∿0.007
H atoms	No	Yes	Yes	Yes

* e.s.d.'s of C-C bond lengths in the phenyl groups for I, II, IIIa, IIIb and IV and in the acetylacetonato ligand for V and VI.

The Pd-S bond lengths

All the palladium complexes except for the complex I, whose structures have been confirmed in this study, contain palladium-sulphur bonds.

All the palladium complexes containing Pd-S bonds whose structures have already been determined by the diffraction method are listed up in Fig. C-1 with the aid of the XDC data base of the TOOL-IR system at the Computer Centre, the University of Tokyo(Yamamoto, Negishi, Ushimaru, Tozawa, Okabe & Fujiwara, 1975; Shimanouchi & Yamamoto, 1976), which is transcribed from the data base at Cambridge Crystallographic Data Centre(Kennard, Watson & Town, 1972; Allen, Kennard, Motherwell, Town & Watson, 1973; Allen, Isaacs, Kennard, Motherwell, Pettersen, Town & Watson, 1973; Allen, Kennard, Motherwell, Town, Watson, Scott & Larson, 1974; Kennard, Watson, Allen, Motherwell, Town & Rodger, 1975). All the Pd-S bond lengths fall in the range between 2.24 and 2.47 Å, as shown in Fig. C-1.

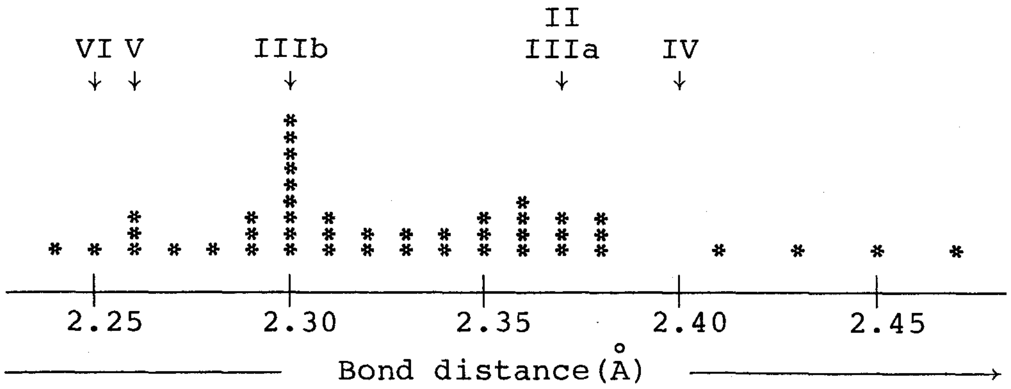


Fig. C-1. Pd-S bond lengths found in all the palladium complexes containing Pd-S bonds whose structures have been determined by the diffraction method.

Figure C-2 represents the Pd-S bond lengths classified by the coordination number and type of the sulphur atom. In Fig. C-2, the *n* appeared in parentheses of S(*n*) indicates the coordination number of the sulphur atom, where *n*= 2, 3 or 4. The prime(') and double-prime(") in S(*n*)' and S(*n*)" show the bond types as follows. The symbol S(2)(without prime) shows that the coordination number of the sulphur is 2 and that the Pd-S bond is formally considered as a σ-bond. The prime in S(2)' and S(3)' indicates the Pd-S coordination bond(the donation of the S to Pd atom). The double-prime in S(2)" and S(3)" shows that the Pd-S bond has both characters of the σ- and coordination bonds or that it is difficult to distinglish between these two. The symbol S(4) means only the coordination number of 4. The examples of the palladium complexes classified by these symbols are also shown in Fig. C-2.

Figure C-3 shows the relation between the Pd-S bond lengths and the atoms *trans* to the Pd-S bonds in the square-planar palladium(II) complexes. As pointed out by Hartley(1973b), the Pd-S bond lengths correlate signficantly with the electronegativity(Pauling, 1960) of the *trans*-atoms in Fig. C-3. The Pd-S bond length seems to be obviously affected with the *trans*-influence.

In the present complexes(II, IIIa, IIIb, IV, V and VI), the Pd-S bond lengths of II, IIIa and IV are relatively longer than the others classified in the same type in Fig. C-2, which may be partly due to the strain caused by the formation of the three-membered ring for II and IIIa and the bridging the palladium atoms for IV, respectively. On the other hand, the Pd-S

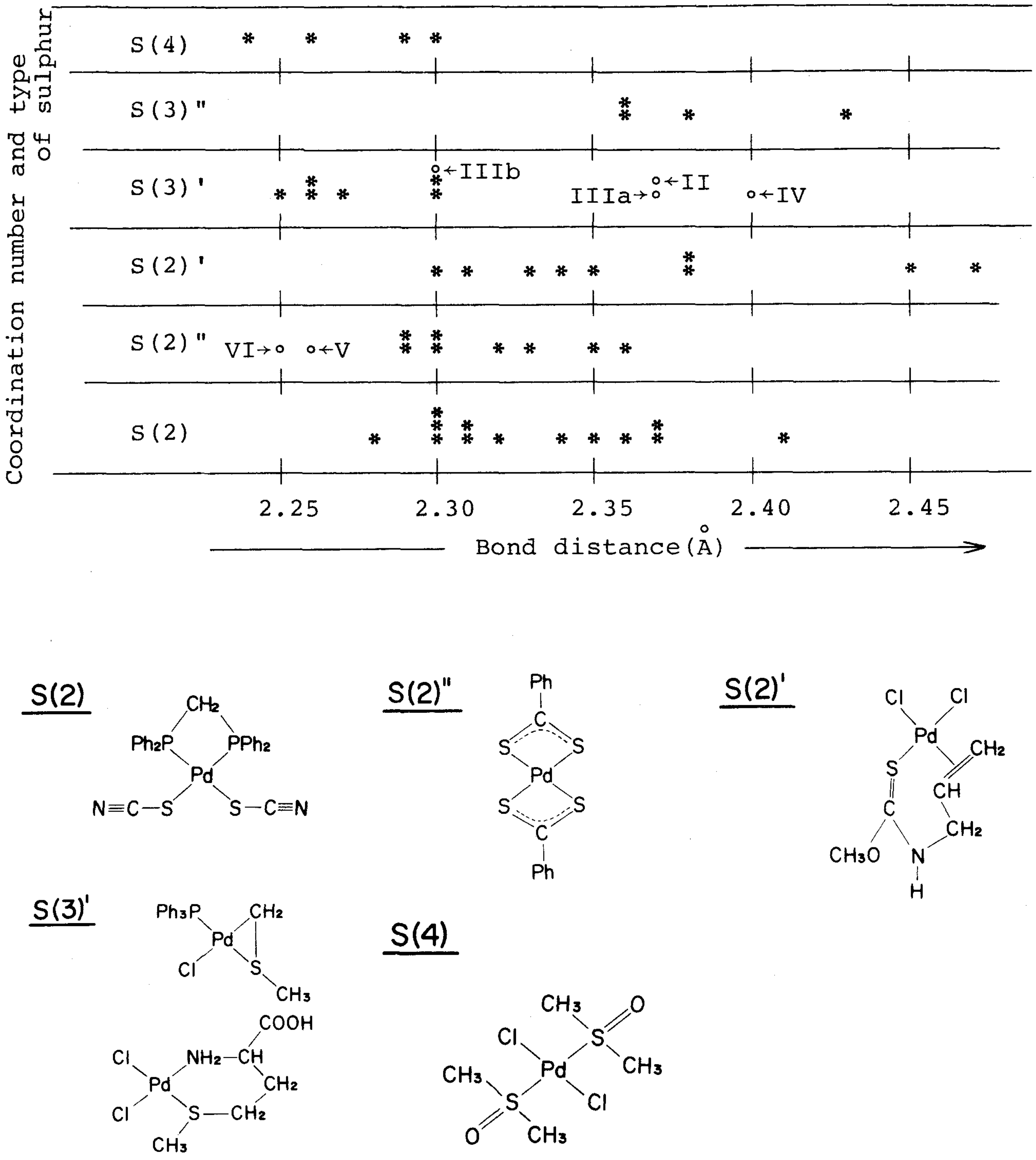


Fig. C-2. Relation between the bond length and the coordination number and type of the sulphur atom in Pd-S bonds. Notation of the symbols(*e.g.* S(2)) is shown in the text.

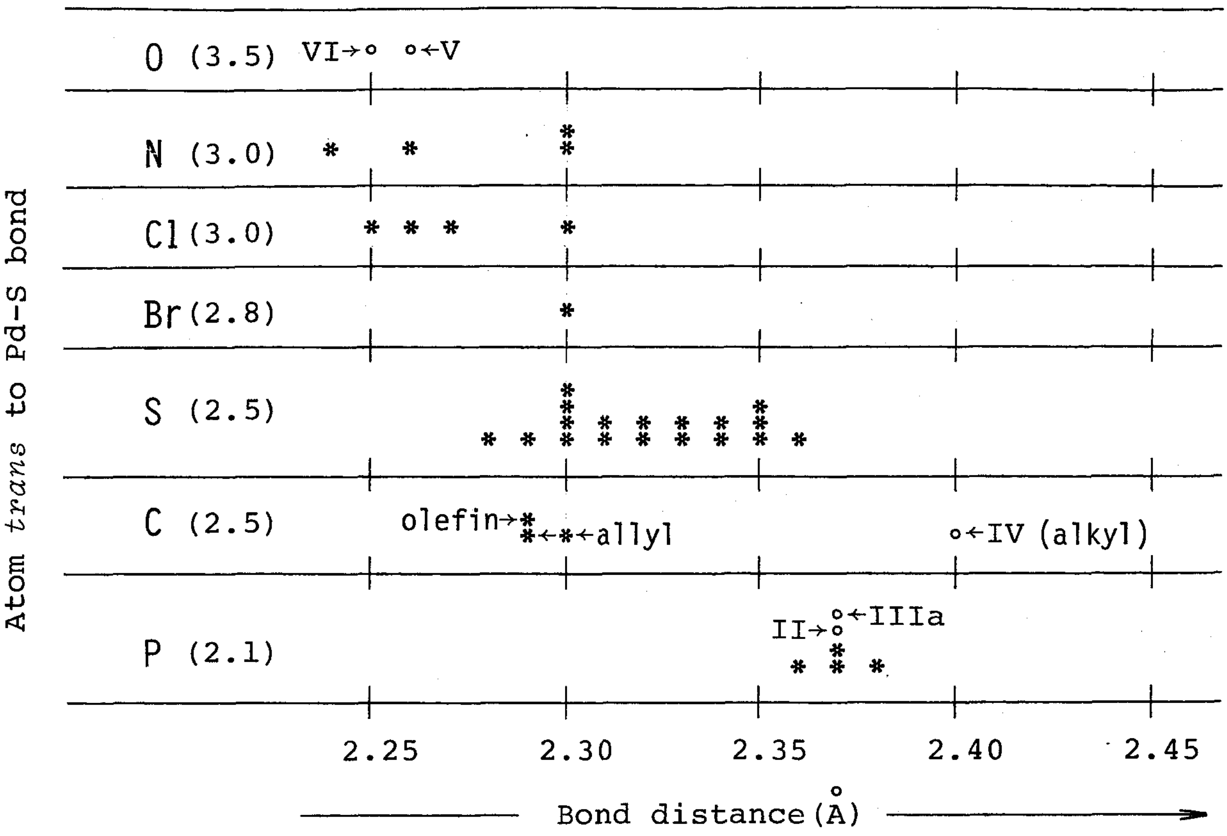


Fig. C-3. Relation between the Pd-S bond lengths and the *trans*-atoms of the sulphur atom. Pauling's electronegativity of the *trans*-atom is presented in parentheses.

bond lengths in V and VI are shorter than those found in most of palladium complexes listed in Fig. C-1. These short Pd-S bond lengths are probably due to the weak *trans*-influence of the oxygen atoms in the acetylacetonato ligand. The relatively long Pd-S bond lengths in IV may be understood also considering the strong *trans*-influence of the alkyl carbon atoms *trans* to the Pd-S bonds.

In the present study, the coordination modes of several sulphur-containing ligands to the palladium atom in seven organopalladium complexes have been elucidated from their three-dimensional structures. The sulphur-containing ligands take a variety of coordination modes to the metal atom, which is possibly due to the characteristics of the sulphur atom. It is very interesting that the structure and bonding of such organometallic compounds as those in the present study have been investigated from many different viewpoints of chemistry.

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LIST OF PUBLICATIONS

The content of this thesis is composed of the following papers;

1. The Molecular Structure of Chlorothiomethoxymethylbis(triphenylphosphine)palladium(II) Methylenechloride Solvate at -160°C

   K. Miki, Y. Kai, N. Yasuoka and N. Kasai
   J. Organomet. Chem., 165, 79(1979).

2. The Molecular Structure of Chlorothiomethoxymethyltriphenylphosphinepalladium(II) at -160 and 20°C.

   K. Miki, Y. Kai, N. Yasuoka and N. Kasai
   J. Organomet. Chem., 135, 53(1977).

3. The Molecular Structures of Thiomethoxymethylbis(triphenylphosphine)palladium Hexafluorophosphate and Perchlorate at -160°C

   K. Miki, Y. Kai, N. Yasuoka and N. Kasai
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4. The Preparation and X-ray Molecular Structure of A Novel Dialkyl Palladium(II) Compound Containing Bridged Thiophenoxymethyl Groups

   K. Miki, G. Yoshida, Y. Kai, N. Yasuoka and N. Kasai
   J. Organomet. Chem., 149, 195(1978).

5. The Molecular Structure of A Thia-allyl Palladium Complex at -160 and 20°C

   K. Miki, N. Tanaka and N. Kasai
   J. Organomet. Chem., in press.

6. Structure of Acetylacetonato[*N*-(methyl)thiobenzamidomethyl]-palladium(II)

   K. Miki, N. Tanaka and N. Kasai
   Acta Cryst., in press.

The other supplementary papers:

1. The Crystal and Molecular Structures of *trans*-Dichloro-bis(dimethylneomenthylphosphine)palladium(II) and *trans*-Dichloro(dimethylmenthylphosphine)palladium(II), Asymmetric Hydrosilylation Catalysts of Olefin

   K. Kan, K. Miki, Y. Kai, N. Yasuoka and N. Kasai
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2. Synthesis and Structure of α-Diazomethyl Palladium σ-Complexes; X-ray Crystal Structure of Chloro[diazo(ethoxy-carbonyl)methyl]bistriphenylphosphinepalladium

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3. The Crystal Structure of (Acetylacetonato)bis(dimethyl-amine)palladium(II) Acetylacetonate at -170°C

   S. Kotake, T. Sei, K. Miki, Y. Kai, N. Yasuoka and N. Kasai
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