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THE MOLECULAR STRUCTURE OF CHLOROTHIOMETHOXYMETHYLBIS(TRIPHENYLPHOSPHINE)PALLADIUM(II) METHYLENECHLORIDE SOLVATE AT —160°C

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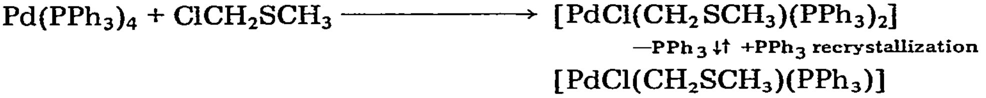
Summary

The precise molecular structure of [PdCl(CH_2SCH_3)(PPh_3)$_2$] has been determined from three-dimensional X-ray diffraction data collected at —160°C. The CH_2Cl_2 solvated crystal ([PdCl(CH_2SCH_3)(PPh_3)$_2$ · CH_2Cl_2]) belongs to the monoclinic system, space group $P2_1/n$, with four formula units in a cell of dimensions: a 14.973(3), b 15.333(3), c 17.377(3) Å and β 115.77(1)° at —160°C. The structure was solved by the conventional heavy atom method and refined by the least-sqaures procedure to R = 0.035 for observed reflections. The geometry around the palladium atom is square-planar. The phosphorus atoms of the two triphenylphosphine ligands are mutually *trans*. The CH_2SCH_3 group is bonded to the palladium atom only through the Pd—C σ-bond and the sulfur atom is not bonded to the metal atom (Pd—C(1) 2.061(3), S—C(1) 1.796(3), S—C(2) 1.817(5), Pd···S 2.973(1) Å, Pd—C(1)—S 100.64(14)° and C(1)—S—C(2) 101.28(18)°). The structure is in contrast to that of [PdCl(CH_2SCH_3)(PPh_3)], in which both the carbon and sulfur atoms of the CH_2SCH_3 group are bonded to the palladium atom.

Introduction

We have studied the coordination behavior of the CH_2SR (R = CH_3, C_6H_5) group in a series of palladium complexes, in particular, of the sulfur atom to the metal atom. We have already reported the molecular structures of [PdCl(CH_2SCH_3)(PPh_3)] [1] and [Pd($CH_2SC_6H_5$)$_2$]$_4$ [2] at liquid nitrogen temperature. In the former complex, the CH_2SCH_3 group is bonded to the metal atom through Pd—C and Pd—S bonds, forming a Pd, C, S three-membered ring which includes an intramolecular donation of the sulfur atom to the metal atom. On the other hand, in the latter complex, the $CH_2SC_6H_5$ groups bridge four palladium atoms, forming a cyclic crown-type tetramer which includes an internuclear coordination of the sulfur atom.

In this paper, we deal with the molecular structure of chlorothiomethoxymethylbis(triphenylphosphine)palladium(II), $[PdCl(CH_2SCH_3)(PPh_3)_2]$ and compare it with that of $[PdCl(CH_2SCH_3)(PPh_3)]$. The series of palladium complexes used in our study was prepared by Okawara and his coworkers of Osaka University according to the reaction scheme presented below [3]. It is very interesting



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

that the transformation between the above two complexes, addition and elimination of one of the triphenylphosphine groups, proceeds easily and reversibly only by several steps of recrystallization. The determination of the structures of the above complexes is indispensable in elucidating the correlation between these two complexes from the viewpoint of the coordination behavior of the CH_2SCH_3 group. The molecular structure of the present complex also has been determined at liquid nitrogen temperature (—160° C) in order to obtain the structure with greater precision.

We also have attempted the structure determination of $[PtCl(CH_2SCH_3)(PPh_3)_2]$ [4] in which the platinum atom takes the place of the palladium atom in $[PdCl(CH_2SCH_3)(PPh_3)_2]$ in order to compare the difference between two structures due to the difference in the metal atom. The structure of the platinum complex should have been determined at low temperature with the precision as high as that of the palladium complex so as to allow detailed discussion. However, the abnormal behavior of the crystal at low temperature prevented us from collecting intensity data (see Experimental). Therefore, the structure determination of the platinum complex has not been carried out.

Experimental

Slightly yellow, prismatic, methylene chloride solvated, crystals of $[PdCl(CH_2SCH_3)(PPh_3)_2]$ were kindly supplied by Professor R. Okawara and his coworkers. Preliminary oscillation and Weissenberg photographs taken at room temperature with Cu-K_α radiation showed the crystal to be monoclinic, and the systematic absences of reflections, $0k0$ with k odd and $h0l$ with $h + l$ odd, determined the space group as $P2_1/n$. Accurate cell dimensions at both —160 and 20° C were determined by a least-squares fit of 2θ values of 25 strong reflections measured on a Rigaku automated, four-cricle, single-crystal diffractometer. Crystal data are shown in Table 1.

Intensity data were collected at —160° C on a Rigaku diffractometer using graphite monochromatized Mo-K_α radiation (λ 0.71069 Å). The required low temperature was attained by the gas flow method using liquid nitrogen. The setting angles of each reflection were computed by the Busing—Levy method [5] on a FACOM U-200 computer attached to the diffractometer. A well-shaped crystal with approximate dimensions 0.3 × 0.3 × 0.35 mm was used for the intensity data measurement. The $\theta - 2\theta$ scan procedure with the width of $\Delta\theta = (1.0 + 0.35 \tan\theta)°$ was employed for the data collection. The integrated inten-

TABLE 1

CRYSTAL DATA

$C_{38}H_{35}ClP_2PdS \cdot CH_2Cl_2$, mol. wt. 812.5, $F(000) = 1656$
Monoclinic, Space group $P2_1/n$

	−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_α) (cm^{-1})	9.02	8.67
D_c (g cm^{-3})	1.503	1.444
D_m (g cm^{-3})		1.44
Z	4	4

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

sity was determined by scanning the peak at the rate of 4° min^{-1}, and subtracting the background measured for 5 s at both ends of a scan. A total of 7832 unique reflections was collected up to a 2θ value of 54°, and of these 700 reflections were recorded as zero. Four standard reflections (800, 80$\bar{4}$, 612 and 742) were measured at regular intervals and the intensities of these reflections remained constant throughout the data collection. Lorentz and polarization corrections were carried out in the usual manner. No extinction correction was applied. An absorption correction (linear absorption coefficient 9.02 cm^{-1}) was ignored due to the uniform shape of crystal [$0.14 < \mu R < 0.25$], which might limit the accuracy of the present structure determination.

Crystals of [$PtCl(CH_2SCH_3)(PPh_3)_2$] also supplied by Professor R. Okawara and his coworkers were colorless thick plates. The crystal setting was established with the aid of the Rigaku soft-ware system for computer-controlled diffractometers. The crystal system was determined as triclinic. Accurate cell dimensions were determined at 20°C in the same manner as for the palladium complex: a 12.326(6), b 14.515(7), c 11.123(5) Å, α 100.70(6), β 92.97(5), γ 79.56(7)° and U 1922.7(16) Å^3. The crystal of the platinum complex is not iso-structural with that of the palladium complex. The calculated density for $Z = 2$ and the formula, $C_{38}H_{35}ClP_2PtS$ (mol. wt. 816.3) is 1.41 g cm^{-3}. Although the crystal was cooled step by step to liquid nitrogen temperature slowly and carefully, abnormal reflections were observed below ca. −70°C. This phenomenon may be understood, provided that the phase transition occurs at lower temperatures. However, the transformation between high and low temperature phases was irreversible, and the crystals decomposed after a few cycles of temperature change. Therefore, the intensity measurement at low temperature was impossible and further investigation of the platinum complex was abandoned.

Structure solution and refinement

For the structure solution and through early stages of the refinement, a limited data set (3878 reflections $2\theta \leqslant 42°$) was used in order to save computer time. The structure was solved by the conventional heavy atom method. A three-

(continued on p. 84)

TABLE 2

FINAL ATOMIC PARAMETERS ON NON-HYDROGEN ATOMS (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	0.47809(2)	0.40375(2)	0.71944(2)	0.00167(1)	0.00113(1)	0.00126(1)	−0.00025(2)	0.00130(2)	−0.00019(2)
Cl(1)	0.52674(5)	0.53789(4)	0.79909(4)	0.00255(4)	0.00113(2)	0.00147(2)	−0.00041(5)	0.00118(5)	−0.00059(4)
S	0.49846(6)	0.21688(5)	0.76990(5)	0.00334(4)	0.00132(3)	0.00151(3)	−0.00041(5)	0.00169(6)	0.00019(4)
P(1)	0.31757(5)	0.41103(4)	0.71095(4)	0.00157(3)	0.00114(3)	0.00111(2)	−0.00015(4)	0.00132(5)	−0.00001(4)
P(2)	0.63063(5)	0.39872(4)	0.71292(4)	0.00142(3)	0.00106(3)	0.00105(2)	−0.00003(4)	0.00101(5)	0.00017(4)
C(1)	0.45010(20)	0.27834(17)	0.67222(17)	0.00193(14)	0.00113(10)	0.00156(10)	−0.00049(19)	0.0015(2)	−0.00039(17)
C(2)	0.4813(3)	0.1058(2)	0.7295(2)	0.0064(3)	0.00126(13)	0.00313(16)	−0.0002(3)	0.0034(3)	0.0004(2)
C(11)	0.2469(2)	0.50624(19)	0.65186(18)	0.00277(16)	0.00152(11)	0.00134(10)	0.0006(2)	0.0019(2)	−0.00002(17)
C(12)	0.1440(3)	0.5122(2)	0.6244(2)	0.00329(18)	0.00275(15)	0.00372(16)	0.0015(3)	0.0044(3)	0.0020(3)
C(13)	0.0918(3)	0.5864(2)	0.5831(3)	0.0037(2)	0.00309(16)	0.00372(17)	0.0031(3)	0.0040(3)	0.0025(3)
C(14)	0.1414(3)	0.6557(2)	0.5669(2)	0.0050(2)	0.00227(14)	0.00216(13)	0.0027(3)	0.0023(3)	0.0010(2)
C(15)	0.2416(3)	0.6496(2)	0.5911(2)	0.0045(2)	0.00228(14)	0.00284(15)	−0.0004(3)	0.0015(3)	0.0020(2)
C(16)	0.2949(2)	0.5755(2)	0.6328(2)	0.00309(17)	0.00241(13)	0.00198(12)	0.0000(2)	0.0012(2)	0.0012(2)
C(21)	0.3130(2)	0.41575(17)	0.81440(17)	0.00196(14)	0.00126(10)	0.00135(10)	−0.00035(19)	0.0019(2)	−0.00025(16)
C(22)	0.4004(2)	0.4171(2)	0.88901(20)	0.00183(15)	0.00312(14)	0.00179(12)	0.0004(2)	0.0018(2)	0.0008(2)
C(23)	0.3966(2)	0.4215(2)	0.96850(19)	0.00232(16)	0.00368(16)	0.00128(11)	0.0001(3)	0.0012(2)	0.0000(2)
C(24)	0.3074(2)	0.4255(2)	0.97322(19)	0.00307(17)	0.00238(13)	0.00176(12)	0.0000(2)	0.0028(2)	−0.0005(2)
C(25)	0.2197(2)	0.4237(3)	0.8982(2)	0.00249(17)	0.00492(19)	0.00210(13)	−0.0004(3)	0.0027(3)	−0.0005(3)
C(26)	0.2231(2)	0.4183(3)	0.8194(2)	0.00195(16)	0.00483(19)	0.00169(12)	−0.0005(3)	0.0015(2)	−0.0006(2)
C(31)	0.23611(20)	0.31987(18)	0.65772(17)	0.00160(13)	0.00149(11)	0.00157(10)	−0.00006(19)	0.00150(20)	−0.00011(17)

C(32)	0.2405(2)	0.2434(2)	0.70344(20)	0.00271(16)	0.00186(12)	0.00206(12)	−0.0006(2)	0.0017(2)	0.00058(20)
C(33)	0.1920(3)	0.1683(2)	0.6611(2)	0.00331(18)	0.00161(12)	0.00368(16)	−0.0010(2)	0.0031(3)	0.0004(2)
C(34)	0.1387(2)	0.1683(2)	0.5724(2)	0.00290(17)	0.00224(14)	0.00340(15)	−0.0021(2)	0.0025(3)	−0.0022(2)
C(35)	0.1315(2)	0.2440(2)	0.5270(2)	0.00245(16)	0.00320(15)	0.00199(12)	−0.0011(3)	0.0017(2)	−0.0017(2)
C(36)	0.1802(2)	0.3194(2)	0.56900(18)	0.00203(14)	0.00227(13)	0.00152(11)	−0.0005(2)	0.0013(2)	−0.00020(19)
C(41)	0.6483(2)	0.48472(18)	0.64788(17)	0.00233(14)	0.00159(11)	0.00123(10)	−0.0005(2)	0.0015(2)	0.00027(17)
C(42)	0.7208(2)	0.4770(2)	0.61784(20)	0.00291(16)	0.00190(12)	0.00224(12)	0.0000(2)	0.0029(2)	0.00075(20)
C(43)	0.7369(3)	0.5437(2)	0.5716(2)	0.00385(19)	0.00276(15)	0.00287(14)	−0.0002(3)	0.0044(3)	0.0010(2)
C(44)	0.6807(3)	0.6198(2)	0.5542(2)	0.00388(20)	0.00256(14)	0.00264(14)	−0.0002(3)	0.0030(3)	0.0021(2)
C(45)	0.6093(2)	0.6279(2)	0.5840(2)	0.00323(18)	0.00201(13)	0.00255(13)	0.0009(2)	0.0020(3)	0.0017(2)
C(46)	0.5916(2)	0.56100(20)	0.63017(19)	0.00209(15)	0.00178(12)	0.00216(12)	0.0007(2)	0.0016(2)	0.00132(19)
C(51)	0.7370(2)	0.40504(17)	0.81775(18)	0.00171(13)	0.00113(10)	0.00141(10)	0.00034(18)	0.00068(20)	−0.00007(16)
C(52)	0.7232(2)	0.3869(2)	0.89072(19)	0.00233(15)	0.00224(12)	0.00166(11)	−0.0002(2)	0.0019(2)	0.00061(19)
C(53)	0.8038(2)	0.3833(2)	0.97084(19)	0.00266(16)	0.00241(13)	0.00144(11)	0.0003(2)	0.0012(2)	0.00028(20)
C(54)	0.8988(2)	0.3986(2)	0.97913(20)	0.00229(16)	0.00216(13)	0.00172(12)	0.0011(2)	0.0001(2)	−0.00008(19)
C(55)	0.9131(2)	0.4175(2)	0.9073(2)	0.00182(15)	0.00233(13)	0.00256(13)	0.0002(2)	0.0013(2)	−0.0004(2)
C(56)	0.8330(2)	0.4205(2)	0.82681(20)	0.00211(15)	0.00198(12)	0.00208(12)	0.0004(2)	0.0017(2)	0.00056(20)
C(61)	0.65873(20)	0.29995(18)	0.66887(18)	0.00180(13)	0.00154(11)	0.00165(10)	−0.00011(19)	0.0021(2)	−0.00033(17)
C(62)	0.7028(2)	0.2293(2)	0.72178(19)	0.00334(17)	0.00184(12)	0.00165(11)	0.0009(2)	0.0016(2)	−0.00003(19)
C(63)	0.7136(3)	0.1499(2)	0.6875(2)	0.00370(19)	0.00197(13)	0.00273(14)	0.0011(3)	0.0016(3)	−0.0005(2)
C(64)	0.6806(2)	0.1411(2)	0.6002(2)	0.00312(17)	0.00202(13)	0.00312(14)	−0.0009(2)	0.0040(3)	−0.0017(2)
C(65)	0.6370(3)	0.2115(2)	0.5470(2)	0.00398(19)	0.00249(14)	0.00193(12)	−0.0017(3)	0.0032(3)	−0.0014(2)
C(66)	0.6254(2)	0.2904(2)	0.58083(19)	0.00295(16)	0.00200(12)	0.00175(11)	−0.0005(2)	0.0018(2)	−0.00031(19)
Cl(1S)	0.01002(10)	0.25798(7)	0.80760(7)	0.00945(9)	0.00268(4)	0.00261(4)	−0.00058(10)	0.00290(10)	−0.00024(6)
Cl(2S)	−0.04724(7)	0.35913(7)	0.65288(7)	0.00397(5)	0.00344(4)	0.00388(4)	0.00016(7)	0.00258(8)	0.00239(7)
C(S)	−0.0362(4)	0.2542(3)	0.6977(3)	0.0099(4)	0.00205(16)	0.00316(17)	−0.0007(4)	0.0047(4)	−0.0005(3)

dimensional Patterson map easily gave the approximate coordinates of the palladium atom. The remianing non-hydrogen atoms were located from successive Fourier maps based on this atomic position.

Structure refinement was carried out by the block-diagonal least-squares method using the HBLS-V program [6], the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. A few cycles of isotropic refinement converged with $R = 0.077$ for non-zero reflections, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Several subsequent cycles of anisotropic refinement reduced the R index to 0.052 for observed reflections. At this stage, a difference Fourier map was calculated, from which all the hydrogen atoms were reasonably located. Several more cycles of refinement

TABLE 3

FINAL ATOMIC PARAMETERS OF HYDROGEN ATOMS (Positional parameters in fraction of cell edges and thermal parameters in the form of exp $\{-B(\sin\theta/\lambda)^2\}$. Estimated standard deviations in parentheses).

Atom	*x*	*y*	*z*	*B*
H(12)	0.108(3)	0.460(3)	0.634(3)	3.8(10)
H(13)	0.016(3)	0.586(3)	0.564(3)	4.2(11)
H(14)	0.105(3)	0.709(3)	0.541(3)	4.0(10)
H(15)	0.279(3)	0.695(3)	0.580(3)	3.2(9)
H(16)	0.362(3)	0.568(3)	0.647(3)	4.3(11)
H(22)	0.471(3)	0.416(2)	0.889(2)	2.0(7)
H(23)	0.459(4)	0.425(3)	1.023(3)	5.0(12)
H(24)	0.306(3)	0.430(2)	1.029(2)	2.2(7)
H(25)	0.152(3)	0.422(3)	0.899(3)	3.6(10)
H(26)	0.156(3)	0.415(3)	0.767(3)	4.2(11)
H(32)	0.280(3)	0.244(3)	0.768(3)	3.2(9)
H(33)	0.195(3)	0.113(3)	0.692(3)	3.5(9)
H(34)	0.104(3)	0.112(3)	0.544(3)	3.2(9)
H(35)	0.094(3)	0.247(3)	0.463(3)	4.4(11)
H(36)	0.178(3)	0.377(3)	0.536(2)	2.4(8)
H(42)	0.763(3)	0.423(2)	0.629(2)	2.3(8)
H(43)	0.791(3)	0.539(3)	0.551(2)	2.9(8)
H(44)	0.691(3)	0.666(3)	0.518(3)	4.4(11)
H(45)	0.568(3)	0.680(3)	0.570(3)	3.2(9)
H(46)	0.541(3)	0.570(2)	0.648(2)	2.3(8)
H(52)	0.656(3)	0.373(3)	0.885(3)	3.2(9)
H(53)	0.790(3)	0.371(3)	1.022(2)	2.8(8)
H(54)	0.962(3)	0.395(2)	1.037(2)	2.5(8)
H(55)	0.980(3)	0.427(3)	0.910(3)	4.1(10)
H(56)	0.848(3)	0.434(3)	0.776(3)	3.8(10)
H(62)	0.732(3)	0.235(3)	0.789(3)	3.4(9)
H(63)	0.748(4)	0.097(3)	0.725(3)	4.2(11)
H(64)	0.692(3)	0.085(2)	0.576(3)	2.5(8)
H(65)	0.612(3)	0.203(3)	0.485(3)	3.5(9)
H(66)	0.588(3)	0.345(3)	0.537(3)	3.0(8)
H(1A)	0.380(2)	0.270(2)	0.642(2)	1.6(7)
H(1B)	0.487(3)	0.263(2)	0.639(2)	2.4(8)
H(2A)	0.401(3)	0.102(3)	0.695(3)	4.2(11)
H(2B)	0.528(4)	0.098(3)	0.697(3)	5.2(13)
H(2C)	0.503(3)	0.071(3)	0.780(3)	4.3(11)
H(1S)	−0.097(5)	0.221(4)	0.666(4)	8.9(18)
H(2S)	0.008(6)	0.223(6)	0.652(5)	12.4(25)

were carried out anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. The R index converged to 0.031 for non-zero reflections of the limited data set. Subsequently the remaining 3956 reflections were added, and further refinement was carried out for the total of 7832 reflections. The final R indices are 0.035 and 0.043 for 7132 non-zero and for all 7832 reflections respectively. The weighting scheme used was $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$ for $|F_o| > 0$, and $w = c$ for $|F_o| = 0$, where σ_{cs} is the 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 ($R_w = \Sigma\{w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$) is 0.054 for all reflections. The atomic scattering factors used were taken from ref. 7 for hydrogen atoms and from ref. 8 for non-hydrogen atoms.

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

Results and discussion

Figure 1 shows a perspective view of the molecule with atomic numbering. An ORTEP plot of the complex and solvent molecules with thermal ellipsoids at 50% probability levels is presented in Fig. 2. Bond lengths and bond angles along with their estimated standard deviations are given in Tables 4 and 5.

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 3 shows the coordination geometry around the palladium atom with selected bond lengths and bond angles. The remarkable feature of the molecular structure is that no donation of the sulfur 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. 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-sqaures planes including the palladium atom and atomic deviations from the planes are given in Table 6. 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 sulfur and metal atoms mentioned below. The molecule has an approximate mirror symmetry. 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°.

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* The table of structure factors has been deposited as NAPS Document No. 03354/40 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $10.00 for photocopies or $3.00 for microfiche. Advanced payment is required. Make checks payable to Microfiche Publications.

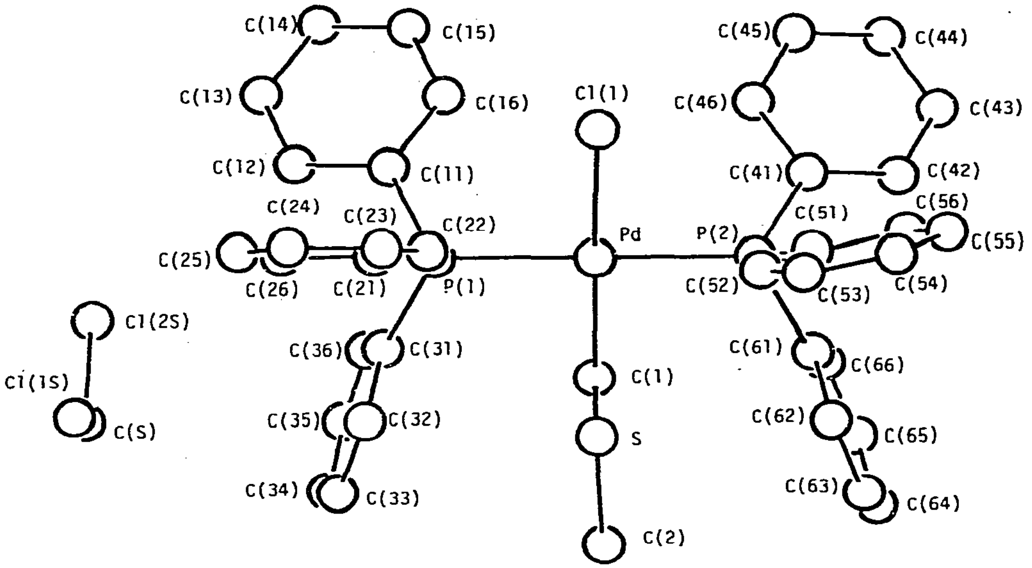

Fig. 1. A perspective view of the molecule and the numbering system of the atoms. Hydrogen atoms are omitted for clarity.

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) [9] 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 sulfur 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 [10]. Among the palladium complexes whose molecular structures have been determined by the X-ray diffraction method, the Pd—Cl distances in which

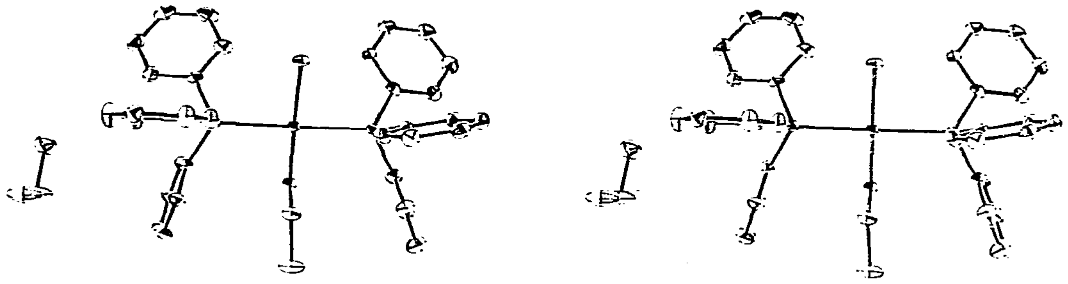

Fig. 2. ORTEP drawings of the molecule. The thermal ellipsoids correspond to 50% probability level. Hydrogen atoms are omitted for clarity.

TABLE 4

BOND LENGTHS ALONG WITH THEIR 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) [a]
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)

(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(2S)	1.32(9)

[a] Non-bonded distance.

TABLE 5

BOND ANGLES INVOLVING NON-HYDROGEN ATOMS ALONG WITH THEIR 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)
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)		

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 (2.408(1) Å) is normal. Table 7 * presents Pd—P bond lengths in all complexes hitherto reported in which the phosphorus atoms of two trialkylphosphine ligands are mutually *trans*. The Pd—P bond lengths in the present complex (2.346(1) and 2.337(1) Å) are fairly similar and are relatively long among those in Table 7.

It is of interest to compare the molecular structure of the present complex

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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 Center [11].

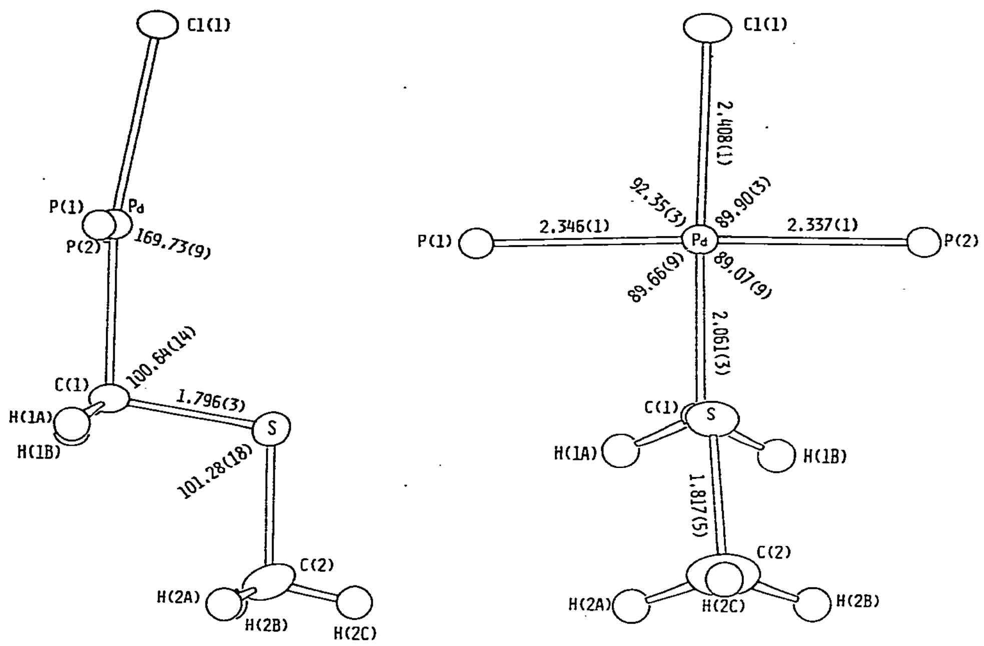

Fig. 3. The coordination geometry around the palladium atom.

with that of [PdCl(CH_2SCH_3)(PPh_3)] [1] in which the CH_2SCH_3 group behaves as a three-electron, bidentate ligand, forming a metallocyclic three-membered ring (see below). The Pd—C and Pd—Cl bond lenghts in complex I are in good agreement with those of complex II (Pd—C 2.042(6) and Pd—Cl 2.402(1) Å).

TABLE 6

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

(*a*) Coordination plane of Pd

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

(*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 [a]
P(2)	+0.148	—2.313 [a]
C(1)	—0.148	+0.031
S	—1.935 [a]	+0.043
C(2)	—2.116 [a]	—0.052

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

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[a] Not included in the least-aquares calculation.

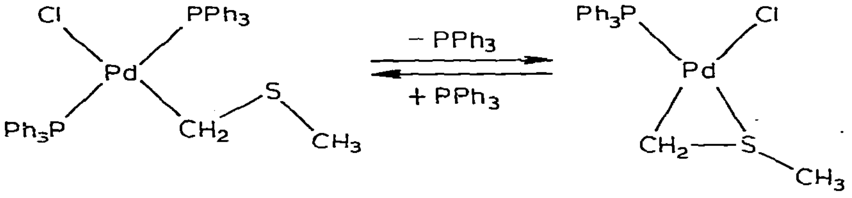
TABLE 7

Pd—P BOND LENGTHS OF PALLADIUM COMPLEXES IN WHICH THE PHOSPHORUS ATOMS OF TWO TRIALKYLPHOSPHINE GROUPS ARE MUTUALLY *trans*

Pd Complex	Length (Å)	Reference
$PdHCl(PEt_3)_2$	2.308(4) [a]	12
$PdCl(Azb)(PEt_3)_2$ [c]	2.309(9) [b]	13
$PdCl_2(PMe_2Men)_2$ [d]	2.310(5)	14
$Pd(SCN)_2\{P(OPh)_3\}_2$	2.312(1)	15
$PdCl(Dtt)(PPh_3)_2$ [e]	2.325(3) [a]	16
$PdCl(COCOOMe)(PPh_3)_2$	2.325(7) [a]	17
$Pd(SCN)_2\{PPh_2(C{=}CBu\text{-}t)\}_2$	2.326(3)	18
$PdI_2(PMe_2Ph)_2$ (orthorhombic form)	2.330(8) [a]	19
$PdI_2(PPh_3)_2$	2.331(2)	20
$PdI_2(PMe_2Ph)_2$ (monoclinic form)	2.333(7)	19
$PdCl(CH_2SCH_3)(PPh_3)_2$	2.342(1) [a]	this work
$PdBr\{C_4(COOMe)_4H\}(PPh_3)_2$	2.35 [a]	21
$PdCl_2(PMe_2neoMen)_2$ [d]	2.353(5) [a]	14

[a] Average value of two Pd—P bonds. [b] Average 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.

The averaged Pd—P bond length of 2.343(1) Å in complex I is longer than that of complex II (2.267(1) Å), which is mainly due to the difference of the *trans*-influence between phosphorus and sulfur atoms. In the previous paper [1], we concluded that both CH_2—S and S—CH_3 bonds in complex II are single bonds but that the former may have partial double bond character (CH_2—S 1.756(6) and S—CH_3 1.807(7) Å). The two sulfur—carbon bonds in complex I are also single bonds. However, the CH_2—S bond is 0.02 Å shorter than the S—CH_3 bond, which exhibits the same tendency as found in complex II. Although there is no double bond character in the CH_2—S bond of complex I, this slight shortening of the CH_2—S bond may be associated with an interaction between sulfur and palladium atoms.



Complex I(present work)

Complex II [1]

The crystal structure viewed along the *b* axis is given in Fig. 4. 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)($\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$)).

All computations were carried out on a NEAC 2200—700 computer at Osaka University and on a FACOM 230—60 computer at Kyoto University. Figures 2, 3 and 4 were drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP-II [22].

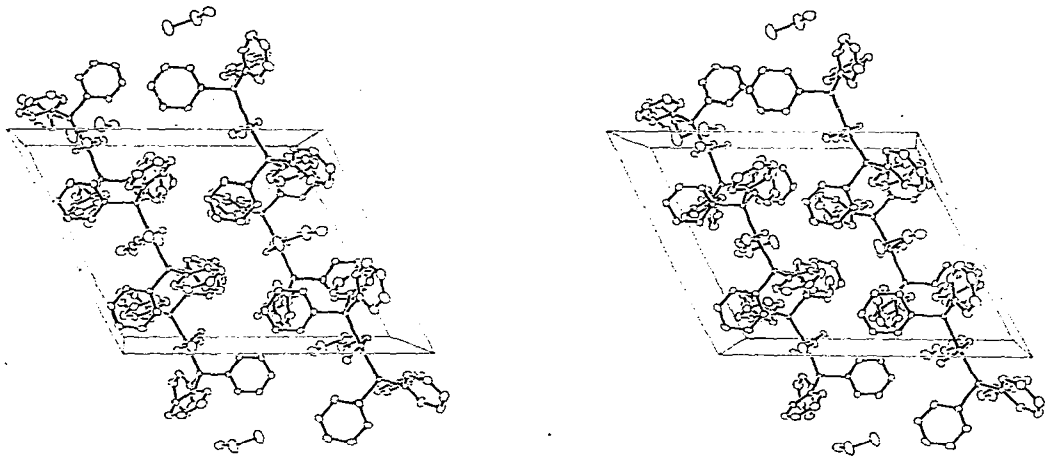


Fig. 4. The crystal structure as viewed down the *b* axis. Atoms are represented by thermal ellipsoids at 50% probability levels. Hydrogen atoms are omitted for clarity.

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