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The Molecular Structures of Thiomethoxymethylbis(triphenylphosphine)palladium Hexafluorophosphate and Perchlorate at $-160\,^\circ$C

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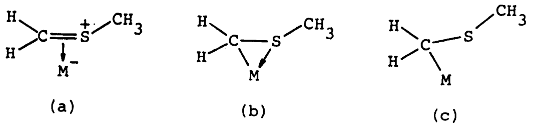
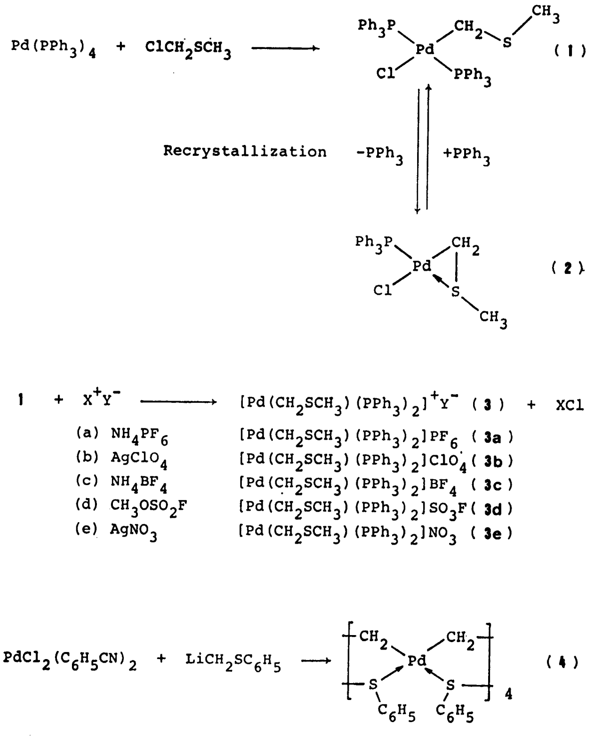
The molecular structures of $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$(**3a**) and $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4$(**3b**) at -160°C were determined by means of X-ray diffraction. Crystals of both complexes belong to the monoclinic system: **3a**, $a=11.535(2)$, $b=17.990(4)$, $c=17.754(2)$ Å and $\beta=101.07(1)$°, space group $P2_1/c$ with $Z=4$; **3b**·CH_2Cl_2 solvate, $a=11.496(5)$, $b=20.872(9)$, $c=15.056(6)$ Å and $\beta=94.77(4)$°, space group $P2_1/n$ with $Z=4$. Both structures were solved by the heavy atom method and refined by the least-squares procedure to $R=0.141$ for 3906 reflections and $R=0.102$ for 4595 reflections for **3a** and **3b** respectively. The geometry around the Pd atom in each complex is essentially planar. However, the coordination behavior of the CH_2SCH_3 group in **3a** and in **3b** seems to be different. In **3a**, the CH_2SCH_3 group is bonded to the Pd atom through the Pd–C σ-bond and the donation of the sulfur to the metal atom, forming a Pd–C–S three-membered ring [Pd–CH_2=2.06(4), Pd–S=2.367(8), CH_2–S=1.77(4) and S–CH_3=1.78(4) Å]. On the other hand, the CH_2SCH_3 group in **3b** is coordinated to the metal atom as a methylenemethylsulfonium ion, containing a C=S double bond[Pd–CH_2=2.208(13), Pd–S=2.303(6), CH_2–S=1.678(14) and S–CH_3=1.86(4) Å].

We have hitherto studied the structural chemistry of a series of palladium complexes containing the CH_2SR($R=CH_3$, C_6H_5) groups in order to elucidate their coordination behavior, especially that of the sulfur to the metal atom.[1–3] It is interesting that the CH_2SR group is coordinated to the transition metal not only as a monodentate ligand but also as a bidentate one.[4,5] Three types of coordination modes are possible for the thiomethoxymethyl(CH_2SCH_3) group, as shown below:



The CH_2SCH_3 group behaves as a π-bonded two-electron ligand in (a), as a bidentate ligand in (b), or as a σ-bonded monodentate ligand in (c).



Scheme 1.

Recently, a series of novel palladium complexes containing these CH_2SR groups have been prepared by Okawara, Yoshida, and their co-workers.[3,6–8] The outline of the reactions is summarized in Scheme 1.

We have previously carried out structure analyses of Complexes **1**,[1] **2**,[2] and **4**.[3] In Complex **1**,[1] the CH_2SCH_3 group is bound to the Pd atom through the Pd–C σ-bond (type c). On the other hand, in Complex **2**,[2] the CH_2SCH_3 group is coordinated with the type b mode to form a Pd–C–S three-membered ring. The thiophenoxymethyl ($CH_2SC_6H_5$) groups bridge four Pd atoms in Complex **4**,[3] which can be considered as an internuclear modification of type b. These differences in bonding modes may be due to the slight difference of the nucleophilicity of S atom in these complexes.

As a part of this study, we will report here the molecular structures of Complexes **3a** and **3b**, determined by means of X-ray diffraction at -160 °C, in order to reveal the coordination of the CH_2SCH_3 group in these cationic complexes.

Experimental

Several efforts were made for five kinds of complexes, **3a**—**e**, to obtain good single crystals from CH_2Cl_2 solutions. Crystals of $[Pd(CH_2SCH_3)(PPh_3)_2]SO_3F$(**3d**)[7] were too small to use for intensity data collection, and Complex **3e**, $[Pd(CH_2SCH_3)(PPh_3)_2]NO_3$, did not crystallize.[7] Crystals of $[Pd(CH_2SCH_3)(PPh_3)_2]BF_4$(**3c**)[7] were comparatively large, large enough to collect intensities. However, preliminary oscillation and Weissenberg photographs showed many diffuse spots near the normal Bragg reflections, suggesting a disordered structure. If all these diffuse spots can be disregarded, the **3c** crystals can be said to have a *C*-centered monoclinic unit cell with dimensions of $a=18.0$, $b=18.4$, $c=12.3$ Å, and $\beta=107$°.

The crystals of **3a** and **3b** are colorless needles and plates

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Table 1. Crystal data

	$[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (**3a**)		$[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (**3b**)	
Formula	$C_{38}H_{35}P_2PdS \cdot PF_6$		$C_{38}H_{35}P_2PdS \cdot ClO_4 \cdot 0.25CH_2Cl_2$	
Formula weight	837.1		812.8	
$F(000)$	1696		1658	
Crystal system	Monoclinic		Monoclinic	
Space group	$P2_1/c$		$P2_1/n$	
Z	4		4	
	[−160 °C]	[20 °C]	[−160 °C]	[20 °C]
a/Å	11.535(2)	11.650(2)	11.496(5)	11.526(4)
b/Å	17.990(4)	18.198(5)	20.872(9)	21.110(8)
c/Å	17.754(2)	17.956(3)	15.056(6)	15.328(5)
β/°	101.07(1)	101.24(2)	94.77(4)	94.42(4)
U/Å^3	3615.5(11)	3733.7(15)	3600(3)	3718(3)
D_c/g cm^{-3}	1.538	1.489	1.499	1.452
D_m/g cm^{-3} [a)]		1.49		1.44
μ (Mo $K\alpha$)/cm^{-1}	7.55	7.31	8.03	7.78

a) By flotation in carbon tetrachloride/hexane at 25 °C.

respectively. X-Ray structure analyses of these crystals have been performed, although they seemed not too suitable for X-ray diffraction study judging from their size, shape, and/or habits. Preliminary oscillation and Weissenberg photographs taken at room temperature with Cu $K\alpha$ raditaion determined their crystal system and space group. Accurate unit-cell dimensions at −160 and 20 °C were determined by a least-squares fit of the 2θ value of 25 strong reflections measured on a Rigaku diffractometer. The crystal data are summarized in Table 1.

Measurements of the integrated intensities were made at −160 °C on the Rigaku automated, four-circle, single-crystal diffractometer. The crystals used had approximate dimensions of 0.1 mm × 0.1 mm × 0.25 mm and 0.25 mm × 0.3 mm × 0.35 mm for **3a** and **3b** respectively. The low temperature was attained by the gas flow method using liquid nitrogen. The intensity data were collected by the θ-2θ scan technique, using graphite-monochromatized (for **3a**) and Zr-filtered (for **3b**) Mo $K\alpha$ radiation (λ=0.71069 Å). The scan speed was 4° min^{-1}, and the scan width was $\Delta 2\theta = (2.5+0.7 \tan\theta)^\circ$. The background intensities were measured for 5 s at both ends of a scan. Totals of 7899 and 7907 reflections with 2θ less than 54° were collected for **3a** and **3b** respectively, 3906 and 4595 reflections of which were considered as observed ($|F_o| > 3\sigma(|F_o|)$). The standard reflections (600, 019, and 219 for **3a** and 800, 555, 008 and 0, 10, 0 for **3b**) monitored at regular intervals were constant throughout the data collection. Corrections for Lorentz and polarization factors were carried out in the usual manner, while neither absorption nor extinction correction was made.

Structure Solution and Refinement

Both structures were solved by the heavy atom method. The structures were refined by the block-diagonal least-squares procedure (*HBLS*-V[9]), the function minimized being $\sum w(|F_o|-|F_c|)^2$. The unit weights were employed throughout the refinement. The atomic scattering factors were taken from International Tables for X-Ray Crystallography[10] for non-hydrogen atoms and from those of Stewart *et al.*[11] for hydrogen atoms. The final atomic positional parameters are presented in Table 2.†

*$[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (**3a**).* All the non-hydrogen atoms were reasonably located by the Patterson and Fourier syntheses. Several cycles of isotropic refinement reduced the R value ($R = \sum||F_o|-|F_c||/\sum|F_o|$) to 0.17. The temperature factors of the F atoms in the PF_6 anion showed relatively large values (maximum B=11.2 Å^2). Further anisotropic refinement in the usual manner did not go on straightforwardly, some abnormal temperature factors being observed. Therefore, the subsequent refinement was carried out step-by-step using small damping factors for the shifts of the parameters. On a Fourier map, a relatively high peaks, the peak height of which was about 80% of that of the C(1) atom, appeared 1.12 and 2.37 Å distant from the S and Pd atoms respectively. If this peak is identified as a disordered fragment of the S atom, the geometry around the Pd atom is far from the square-planar coordination. Therefore, this peak was ignored and not included in the subsequent refinement. The final R value is 0.141 for 3906 reflections.

*$[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (**3b**).* The Fourier synthesis based on the coordinates of the Pd atom, determined from a three-dimensional Patterson map, revealed the locations of all the non-hydrogen atoms in the cation. A few cycles of isotropic refinement reduced the R value to 0.14. A difference Fourier map revealed the location of only the Cl atom of the ClO_4 anion, and its electron density was relatively low and very broad. Subsequent difference Fourier maps could locate only one of the four O atoms in the ClO_4 anion. These Cl and O atoms indicated abnormally large temperature factors in the further refinement. In addition, three other peaks were found on a Fourier map. They were interpreted as those of the solvent CH_2Cl_2 molecule. The calculated density for the formula weight, assuming that one molecule of CH_2Cl_2 is included in an asymmetric unit [1.566 g cm^{-3}], is

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† Tables of the complete F_o—F_c data and of the final anisotropic temperature factors are deposited at the Chemical Society of Japan as Document No. 8150.

Table 2. Final atomic parameters

Estimated standard deviations are given in parentheses. B_{eq} values are equivalent isotropic temperature factors calculated from anisotropic thermal parameters.[12)]

(a) [Pd(CH_2SCH_3)(PPh_3)$_2$]PF_6 (**3a**)

Atom	x	y	z	$B_{eq}/Å^2$
Pd	0.67007(14)	0.02532(11)	0.22058(9)	2.0
S	0.4737(6)	0.0431(5)	0.1540(4)	3.5
P(1)	0.8027(5)	0.0113(3)	0.1363(3)	1.4
P(2)	0.7904(5)	0.0270(4)	0.3379(3)	1.6
C(1)	0.509(3)	0.0299(19)	0.2547(16)	4.0
C(2)	0.422(3)	−0.0465(16)	0.1216(17)	4.0
C(11)	0.9603(18)	0.0021(13)	0.1724(12)	2.0
C(12)	1.034(3)	0.0647(15)	0.1936(15)	3.1
C(13)	1.153(3)	0.057(3)	0.2267(16)	5.1
C(14)	1.201(2)	−0.0149(18)	0.2377(14)	3.5
C(15)	1.133(3)	−0.0780(18)	0.2190(14)	3.5
C(16)	1.0122(17)	−0.0656(14)	0.1866(11)	2.0
C(21)	0.7993(17)	0.0861(11)	0.0662(10)	1.2
C(22)	0.890(3)	0.0965(14)	0.0257(14)	2.7
C(23)	0.880(3)	0.1543(16)	−0.0267(14)	3.8
C(24)	0.782(4)	0.203(3)	−0.038(2)	5.6
C(25)	0.698(3)	0.2005(15)	0.0086(16)	3.2
C(26)	0.707(2)	0.1384(16)	0.0649(17)	3.6
C(31)	0.762(2)	−0.0702(14)	0.0806(13)	2.3
C(32)	0.791(3)	−0.0808(16)	0.0060(14)	3.2
C(33)	0.753(3)	−0.1461(16)	−0.0366(15)	4.1
C(34)	0.690(3)	−0.2019(14)	−0.0044(15)	3.3
C(35)	0.659(3)	−0.1909(18)	0.067(2)	4.9
C(36)	0.698(3)	−0.1252(16)	0.1053(16)	3.5
C(41)	0.7210(15)	0.0348(10)	0.4227(10)	1.1
C(42)	0.6496(19)	0.0966(12)	0.4276(12)	2.0
C(43)	0.599(3)	0.1029(15)	0.4932(16)	3.5
C(44)	0.621(3)	0.0489(16)	0.5508(13)	3.2
C(45)	0.687(2)	−0.0107(14)	0.5444(13)	2.7
C(46)	0.7395(19)	−0.0183(13)	0.4816(12)	2.1
C(51)	0.889(3)	0.1070(12)	0.3525(13)	2.2
C(52)	0.9790(19)	0.1157(13)	0.4191(13)	2.2
C(53)	1.055(2)	0.1755(13)	0.4251(13)	2.2
C(54)	1.042(3)	0.2272(13)	0.3686(15)	3.0
C(55)	0.954(3)	0.2195(13)	0.3025(12)	2.4
C(56)	0.877(3)	0.1587(14)	0.2950(12)	2.4
C(61)	0.8805(19)	−0.0566(12)	0.3545(11)	1.7
C(62)	1.000(3)	−0.0585(12)	0.3761(12)	2.3
C(63)	1.063(3)	−0.1269(14)	0.3881(12)	2.4
C(64)	0.999(3)	−0.1986(13)	0.3739(12)	2.1
C(65)	0.877(3)	−0.1935(14)	0.3518(13)	2.8
C(66)	0.817(3)	−0.1225(17)	0.3369(14)	3.3
P(3)	0.5228(7)	0.2723(4)	0.2220(4)	3.2
F(1)	0.4013(16)	0.2265(11)	0.2079(12)	5.8
F(2)	0.454(3)	0.336(2)	0.246(2)	15.2
F(3)	0.639(2)	0.3163(13)	0.2365(15)	8.1
F(4)	0.583(3)	0.2017(15)	0.207(3)	12.6
F(5)	0.493(3)	0.293(3)	0.1375(13)	13.0
F(6)	0.549(3)	0.249(3)	0.3079(13)	11.5

much larger than the observed value of 1.44 g cm^{-3}. These facts suggest a low occupancy of CH_2Cl_2. The occupancy factor for CH_2Cl_2 was then estimated as 0.25, which gives the calculated density of 1.452 g cm^{-3}. The coordinates of the C atom of CH_2Cl_2 were fixed in the further refinement. Several more cycles of refinement were carried out anisotropically for the Pd, S, P, and C atoms in the cation and isotropically for Cl, O, and C in the ClO_4 anion and the CH_2Cl_2 molecule. The final R factor is 0.102 for 4595 reflections.

(b) $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4 \cdot 0.25CH_2Cl_2$ (**3b**)

Atom	x	y	z	B_{eq} or B^*/Å^2
Pd	0.04915(9)	0.13720(5)	0.17868(7)	2.4
S	0.0116(6)	0.1166(3)	0.0287(4)	5.7
P(1)	0.0635(3)	0.24730(16)	0.1976(3)	1.9
P(2)	0.0470(3)	0.09187(15)	0.3175(3)	1.8
C(1)	0.0133(12)	0.0517(6)	0.0945(9)	2.3
C(2)	−0.145(3)	0.1380(16)	0.0090(16)	8.6
C(11)	−0.0487(11)	0.2778(7)	0.2647(9)	2.6
C(12)	−0.1645(12)	0.2541(8)	0.2405(11)	3.4
C(13)	−0.2558(13)	0.2746(10)	0.2911(13)	5.2
C(14)	−0.2320(15)	0.3146(11)	0.3623(12)	5.3
C(15)	−0.1190(16)	0.3373(10)	0.3864(12)	5.1
C(16)	−0.0253(14)	0.3176(9)	0.3382(11)	4.0
C(21)	0.2024(10)	0.2823(6)	0.2391(8)	1.9
C(22)	0.2981(11)	0.2424(7)	0.2590(9)	2.3
C(23)	0.4068(12)	0.2683(8)	0.2850(10)	2.9
C(24)	0.4196(13)	0.3344(8)	0.2908(10)	3.5
C(25)	0.3255(12)	0.3745(7)	0.2717(10)	3.0
C(26)	0.2145(12)	0.3485(7)	0.2455(9)	2.7
C(31)	0.0371(10)	0.2898(6)	0.0913(9)	2.1
C(32)	0.1283(12)	0.2868(7)	0.0336(9)	2.6
C(33)	0.1167(12)	0.3197(7)	−0.0484(9)	2.5
C(34)	0.0152(12)	0.3532(6)	−0.0742(9)	2.3
C(35)	−0.0743(11)	0.3556(7)	−0.0179(9)	2.6
C(36)	−0.0650(11)	0.3247(6)	0.0660(9)	2.1
C(41)	0.1782(10)	0.0470(6)	0.3522(9)	1.9
C(42)	0.2668(11)	0.0424(6)	0.2909(9)	2.1
C(43)	0.3702(11)	0.0079(7)	0.3183(9)	2.5
C(44)	0.3847(12)	−0.0205(7)	0.4013(10)	2.7
C(45)	0.2974(11)	−0.0162(6)	0.4608(9)	2.3
C(46)	0.1956(11)	0.0176(7)	0.4342(9)	2.3
C(51)	0.0327(11)	0.1422(6)	0.4149(9)	2.2
C(52)	0.1176(11)	0.1876(7)	0.4365(9)	2.4
C(53)	0.1115(14)	0.2267(7)	0.5105(9)	3.1
C(54)	0.0178(13)	0.2190(7)	0.5655(9)	3.0
C(55)	−0.0669(12)	0.1728(7)	0.5452(9)	2.8
C(56)	−0.0621(11)	0.1329(7)	0.4688(9)	2.5
C(61)	−0.0753(11)	0.0359(6)	0.3152(8)	2.1
C(62)	−0.1868(12)	0.0603(8)	0.2881(11)	3.2
C(63)	−0.2836(12)	0.0197(8)	0.2816(11)	3.4
C(64)	−0.2677(12)	−0.0464(7)	0.2998(10)	2.9
C(65)	−0.1563(12)	−0.0696(7)	0.3275(10)	2.9
C(66)	−0.0603(12)	−0.0293(6)	0.3350(9)	2.2
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	0.003	8.9(28)*

Results and Discussion

Bond lengths and bond angles in the two complexes are listed in Tables 3 and 4 respectively.

In spite of the low temperature measurements, the precision of neither structure is high enough to make a detailed discussion. This is considered mainly due to the poor quality of the **3a** and **3b** crystals. In both **3a** and **3b** crystals, the PF_6 and ClO_4 anions have rather disordered structures, which may also be connected with the precision of the present structures.

Structures of PF_6 and ClO_4 Anions. In **3a**, six F atoms of the PF_6 anion, especially four out of those, show abnormally low peak heights and a broadening in the electron density distribution. As an example, an electron density map on the plane formed by the P and four F atoms is given in Fig. 1. The ^{19}F NMR studies of **3a** suggested that the PF_6 anions are rapidly reorienting about the octahedral axes$^{13)}$ at random, or nearly so, even at liquid nitrogen temperature.$^{14)}$

The locations of three oxygen atoms in the ClO_4 anion

Table 3. Bond lengths, with their estimated standard deviations in parentheses

Length (l/Å)	**3a**	**3b**	Length (l/Å)	**3a**	**3b**
[Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$] cation					
Pd–P(1)	2.350(5)	2.320(3)	Pd–P(2)	2.271(6)	2.297(3)
Pd–S	2.367(8)	2.303(6)	Pd–C(1)	2.06(4)	2.208(13)
S–C(1)	1.77(4)	1.678(14)	S–C(2)	1.78(4)	1.86(4)
P(1)–C(11)	1.82(3)	1.818(14)	P(2)–C(41)	1.84(2)	1.814(13)
P(1)–C(21)	1.83(2)	1.819(12)	P(2)–C(51)	1.82(3)	1.822(13)
P(1)–C(31)	1.78(3)	1.834(13)	P(2)–C(61)	1.82(3)	1.826(13)
C(11)–C(12)	1.42(4)	1.44(3)	C(41)–C(42)	1.40(3)	1.43(2)
C(12)–C(13)	1.39(5)	1.41(3)	C(42)–C(43)	1.40(4)	1.42(2)
C(13)–C(14)	1.41(5)	1.37(3)	C(43)–C(44)	1.40(4)	1.38(2)
C(14)–C(15)	1.38(5)	1.40(3)	C(44)–C(45)	1.33(4)	1.40(2)
C(15)–C(16)	1.42(4)	1.41(3)	C(45)–C(46)	1.37(4)	1.40(2)
C(16)–C(11)	1.36(4)	1.39(3)	C(46)–C(41)	1.40(3)	1.38(2)
C(21)–C(22)	1.39(4)	1.39(2)	C(51)–C(52)	1.43(4)	1.38(2)
C(22)–C(23)	1.39(4)	1.39(2)	C(52)–C(53)	1.38(4)	1.39(2)
C(23)–C(24)	1.41(5)	1.39(3)	C(53)–C(54)	1.36(4)	1.42(3)
C(24)–C(25)	1.39(5)	1.38(3)	C(54)–C(55)	1.40(4)	1.39(3)
C(25)–C(26)	1.49(4)	1.41(2)	C(55)–C(56)	1.40(4)	1.43(2)
C(26)–C(21)	1.42(4)	1.39(2)	C(56)–C(51)	1.37(4)	1.43(2)
C(31)–C(32)	1.44(4)	1.42(2)	C(61)–C(62)	1.36(4)	1.41(2)
C(32)–C(33)	1.42(5)	1.41(2)	C(62)–C(63)	1.43(4)	1.40(3)
C(33)–C(34)	1.42(5)	1.39(2)	C(63)–C(64)	1.48(4)	1.42(3)
C(34)–C(35)	1.39(5)	1.39(2)	C(64)–C(65)	1.39(4)	1.40(2)
C(35)–C(36)	1.40(5)	1.41(2)	C(65)–C(66)	1.45(4)	1.39(2)
C(36)–C(31)	1.36(4)	1.41(2)	C(66)–C(61)	1.40(4)	1.40(2)
PF$_6$ and ClO$_4$ anions					
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)	
Cl(1)–O(1)a)		1.42(4)			
CH$_2$Cl$_2$, crystalline solvent					
Cl(1S)–C(S)		1.69b)	Cl(2S)–C(S)		1.68b)

a) The other O atoms in the ClO$_4$ anion could not be located. b) The coordinates of the C(S) atom were not refined.

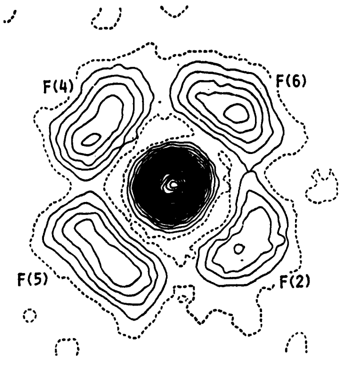


Fig. 1. Electron density distribution on the plane formed by the P(3), F(2), F(4), F(5), and F(6) atoms of the PF$_6$ anion in [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$]PF$_6$ (**3a**). The contours are drawn at the interval of 1.0 e/Å^3. Zero contours are shown as broken lines while negative contours are omitted.

could not be determined in **3b**, because the electron densities around the central Cl atom are very broad and relatively low except for the O(1) atom. Disordered structures and large thermal motions of the ClO$_4$ anion have been reported in some complexes.15)

Structures of [Pd(CH$_2$SCH$_3$)(PPh$_3$)$_2$] Cations. Figure 2 shows *ORTEP* drawings16) of the cations in these complexes. In Fig. 3, the coordination geometries around the Pd atom in **3a** and **3b** are compared with that of **2**.2) The geometry around the Pd atom in each complex is essentially square-planar. The equations of the least-squares planes and the deviation of atoms from the planes are presented in Table 5. The planarity of the coordination plane in each complex is not so high, the maximum deviations from the plane being 0.17 and 0.10 Å for **3a** and **3b** respectively, while that in **2** is only 0.04 Å.2)

Two PPh$_3$ groups are bonded to the Pd atom in *cis*-coordination. In both complexes, the Pd–P(1) bond lengths are slightly longer than those of the Pd–P(2). This is partly due to the difference in the *trans*-influences of the C and S atoms in the CH$_2$SCH$_3$ groups.

In the CH$_2$SCH$_3$ group in **3a**, the S–C(1) and S–C(2) bond lengths are close to the S–C single bond length [1.82 Å].17) The Pd–C(1) bond length is considered to be a normal value for the Pd(II)–C(sp^3) σ-bond. Since these bond lengths, as well as the Pd–S, are comparable to the corresponding ones in **2**,2) the coordination mode

TABLE 4. BOND ANGLES, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Angle (ϕ/°)	**3a**	**3b**
[$Pd(CH_2SCH_3)(PPh_3)_2$] cation		
P(1)–Pd–P(2)	103.2(3)	107.58(12)
P(1)–Pd–S	112.0(3)	108.10(17)
P(2)–Pd–C(1)	99.0(10)	100.0(4)
C(1)–Pd–S	46.5(10)	43.6(4)
Pd–S–C(1)	57.7(11)	65.2(5)
Pd–S–C(2)	105.7(11)	102.3(11)
C(1)–S–C(2)	101.7(15)	104.6(12)
Pd–C(1)–S	75.8(13)	71.2(6)
Pd–P(1)–C(11)	121.0(8)	111.6(5)
Pd–P(1)–C(21)	115.0(7)	119.5(4)
Pd–P(1)–C(31)	107.7(8)	111.6(5)
C(11)–P(1)–C(21)	101.3(10)	108.2(6)
C(11)–P(1)–C(31)	105.3(11)	104.0(7)
C(21)–P(1)–C(31)	105.1(10)	100.5(6)
Pd–P(2)–P(41)	117.7(7)	113.8(5)
Pd–P(2)–P(51)	113.3(8)	120.2(5)
Pd–P(2)–P(61)	111.5(8)	108.2(5)
C(41)–P(2)–C(51)	100.4(10)	101.2(6)
C(41)–P(2)–C(61)	104.8(10)	107.2(6)
C(51)–P(2)–C(61)	108.1(11)	105.3(6)
P(1)–C(11)–C(12)	122.0(18)	115.1(11)
P(1)–C(11)–C(16)	121.5(18)	123.5(12)
C(16)–C(11)–C(12)	116.3(22)	121.3(14)
C(11)–C(12)–C(13)	121.8(27)	118.2(15)
C(12)–C(13)–C(14)	118.5(32)	119.8(18)
C(13)–C(14)–C(15)	122.4(31)	122.0(20)
C(14)–C(15)–C(16)	115.7(27)	119.9(19)
C(15)–C(16)–C(11)	125.3(24)	118.6(16)
P(1)–C(21)–C(22)	122.1(17)	119.2(10)
P(1)–C(21)–C(26)	114.8(17)	120.2(10)
C(26)–C(21)–C(22)	122.5(21)	120.5(12)
C(21)–C(22)–C(23)	118.2(24)	120.3(13)
C(22)–C(23)–C(24)	121.4(30)	119.5(14)
C(23)–C(24)–C(25)	122.0(32)	120.9(15)
C(24)–C(25)–C(26)	117.0(27)	120.0(14)
C(25)–C(26)–C(21)	117.8(24)	118.9(13)
P(1)–C(31)–C(32)	122.3(19)	115.9(10)
P(1)–C(31)–C(36)	121.7(20)	124.1(10)
C(36)–C(31)–C(32)	116.0(23)	120.0(12)
C(31)–C(32)–C(33)	119.5(25)	119.6(12)
C(32)–C(33)–C(34)	120.1(28)	120.5(13)
C(33)–C(34)–C(35)	120.3(28)	119.7(12)
C(34)–C(35)–C(36)	117.0(30)	121.7(13)
C(35)–C(36)–C(31)	126.9(28)	118.5(12)
P(2)–C(41)–C(42)	117.8(15)	117.8(10)
P(2)–C(41)–C(46)	122.0(15)	122.9(10)
C(46)–C(41)–C(42)	120.1(18)	119.3(12)
C(41)–C(42)–C(43)	117.4(21)	118.0(12)
C(42)–C(43)–C(44)	120.6(25)	121.0(13)
C(43)–C(44)–C(45)	121.4(26)	120.8(13)
C(44)–C(45)–C(46)	119.9(24)	118.5(13)
C(45)–C(46)–C(41)	120.7(21)	122.5(12)
P(2)–C(51)–C(52)	122.7(18)	118.4(10)
P(2)–C(51)–C(56)	117.5(18)	120.2(10)
C(56)–C(51)–C(52)	119.7(22)	121.3(12)
C(51)–C(52)–C(53)	120.1(21)	120.8(13)
C(52)–C(53)–C(54)	120.2(22)	119.4(14)
C(53)–C(54)–C(55)	120.6(24)	120.3(14)
C(54)–C(55)–C(56)	120.1(23)	120.7(14)
C(55)–C(56)–C(51)	119.3(22)	117.5(13)
P(2)–C(61)–C(62)	125.7(18)	117.0(10)
P(2)–C(61)–C(66)	114.2(18)	122.4(10)
C(66)–C(61)–C(62)	119.9(22)	120.5(12)
C(61)–C(62)–C(63)	121.7(23)	120.1(14)
C(62)–C(63)–C(64)	120.2(22)	119.3(14)
C(63)–C(64)–C(65)	115.7(22)	119.7(14)
C(64)–C(65)–C(66)	121.9(24)	121.2(13)
C(65)–C(66)–C(61)	120.0(25)	119.3(12)
PF_6 anion		
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)	
CH_2Cl_2, crystalline solvent		
Cl(1S)–C(S)–Cl(2S)		106.6[a]

a) The coordinates of the C(S) atom were not refined.

of the CH_2SCH_3 group to the Pd atom in **3a** is considered to be virtually the same as in **2**. The CH_2SCH_3 group is bonded to the Pd atom by the Pd–C σ-bond, and also by the donation from the S to the Pd atom (the b-type mentioned above).

On the other hand, the coordination mode of the CH_2SCH_3 group to the Pd atom in **3b** is different from those in **2** and **3a**. In **3b**, the S–C(1) bond length is significantly shorter than those in **2** and **3a**, and it is close to the S=C double bond length [1.61 Å][17] rather than the S–C single bond length [1.82 Å].[17] The S–C(2) bond length is considered to be equal to the S–C single bond length. The Pd–C(1) distance is obviously longer than those in **2** and **3a**, and rather near to the Pd–C(olefin) lengths [2.174 and 2.233 Å] in [$Pd(\eta^5$-$C_5H_5)(PEt_3)$(styrene)]BF_4.[18] The Pd–S distance, somewhat shorter than those found in **2** and **3a**, is in good agreement with that in [$Pd(CS)_2(PPh_3)_2$][2.31 Å].[19] These facts imply that the a-type coordination mode, where the CH_2SCH_3 group functions as a methylene-methylsulfonium ion, makes a great contribution to the bonding of the CH_2SCH_3 group.

Perspective views of the coordination mode are shown in Fig. 4. The C(1)–S–C(2) plane is almost perpendicular to the P(1)–Pd–P(2) plane in **3b**. The dihedral angles between these planes are 91.3° in **3b**, whereas

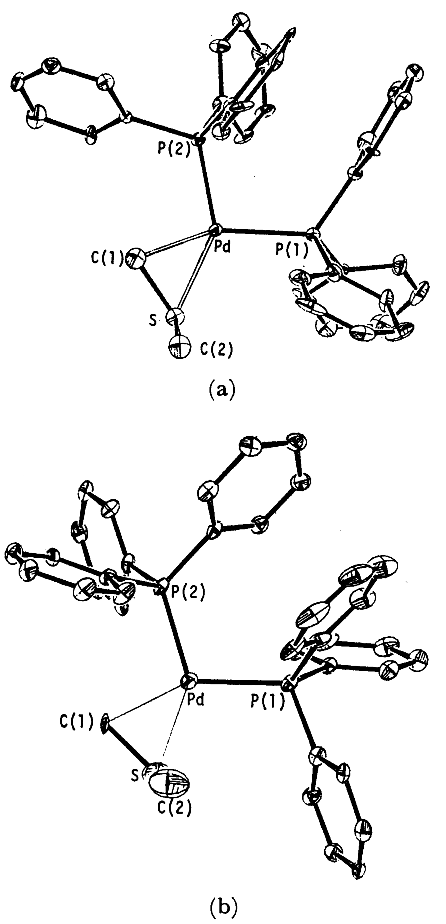


Fig. 2. An *ORTEP* drawing[16)] of the [Pd(CH_2SCH_3)(PPh_3)$_2$] cation. The thermal ellipsoids correspond to 30% probability levels. The atomic numberings for the phenyl groups of the triphenylphosphine groups are omitted. Six carbon atoms of the phenyl group are numbered as C(*n*1)—C(*n*6), where *n*=1—6. The C(11), C(21), and C(31) atoms are attached to the P(1) atom while C(41), C(51) and C(61) to P(2).
(a): [Pd(CH_2SCH_3)(PPh_3)$_2$]PF_6(**3a**), (b): [Pd(CH_2SCH_3)(PPh_3)$_2$]ClO_4(**3b**).

they are 100.0° in **3a** and 100.9° in **2**. As presented in Table 5, the C(1) and S atoms in **3a** are located on the opposite sides of the P(1)–Pd–P(2) plane, 0.13 and

Table 5. Least-squares planes and atomic deviations from the planes

The equation of the plane is of the form: $AX+BY+CZ+D=0$, 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, P(1), P(2), C(1), and S

(**3a**) $-0.119X-0.993Y+0.005Z+1.278=0$

(**3b**) $0.993X-0.117Y-0.029Z+0.174=0$

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

(**3a**) $-0.091X-0.994Y+0.059Z+0.861=0$

(**3b**) $-0.996X+0.069Y-0.063Z+0.312=0$

Deviations of atoms from the plane (l/Å)

	Plane (a)		Plane (b)	
	(**3a**)	(**3b**)	(**3a**)	(**3b**)
Pd	+0.014	−0.101	0	0
P(1)	+0.042	+0.036	0	0
P(2)	−0.124	+0.045	0	0
C(1)	+0.171	−0.042	+0.133[a)]	+0.263[a)]
S	−0.066	+0.026	−0.200[a)]	+0.356[a)]
C(2)	+1.590[a)]	+1.836[a)]	+1.413[a)]	+2.176[a)]

a) Not included in the calculation of the plane.

−0.20 Å away from it respectively, while in **3b** these two atoms deviate by 0.26 and 0.36 Å on the same side of the P(1)–Pd–P(2) plane.

The resonance structures (d) and (e) presented below are suggested for the bonding of the CH_2SCH_3 group to the Pd atom,[8)] which is connected with the stabilization of these complexes, although the main representation of the structure is probably (e). The contribution from (d) in the cationic complexes **3** may play a greater part than in a neutral complex such as **2**. However, the contributions from (d) in **3a** and **3b** seem to differ from each other, which may be due to the counter anions.

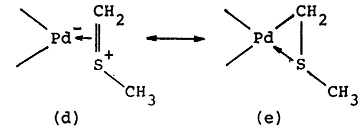


Table 6 shows the contacts between the [Pd(CH_2SCH_3)(PPh_3)$_2$] cation and the PF_6 or ClO_4 anion in **3a** and **3b**. Both anions are considered to have the

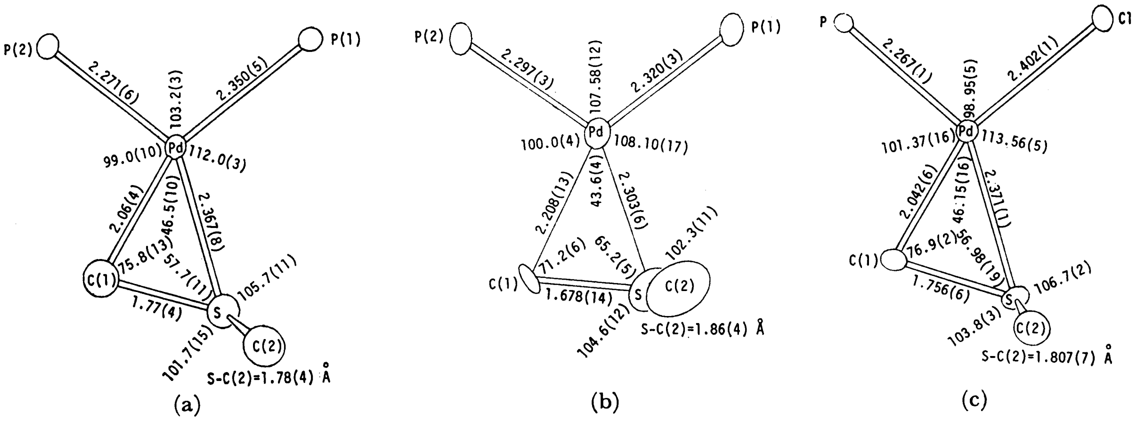


Fig. 3. The coordination geometry around the Pd atom along with selected bond lengths and bond angles.
(a): **3a**, (b): **3b**, (c): **2**.[2)]

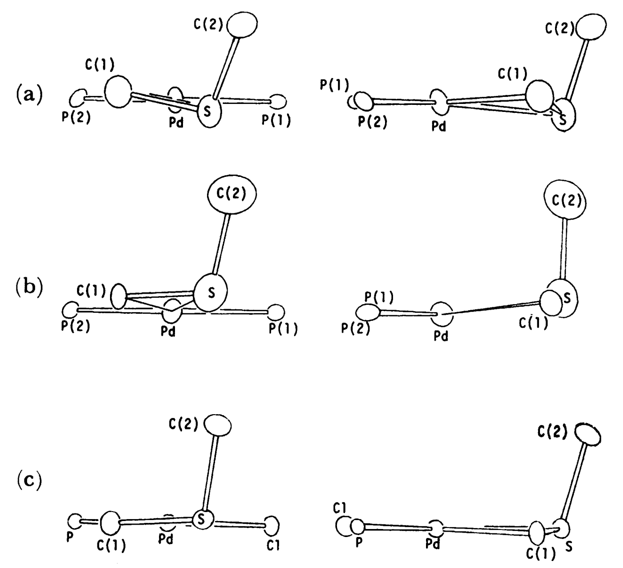


Fig. 4. Perspective views of the coordination geometry of the CH_2SCH_3 group to the Pd atom.
(a): **3a**, (b): **3b**, (c): **2**.[2)]

TABLE 6. CONTACTS BETWEEN THE $[Pd(CH_2SCH_3)(PPh_3)_2]$ CATION AND THE PF_6 OR ClO_4 ANION

Distances between the Pd atom (the center of the cation) and the P (for PF_6 in **3a**) or Cl (for ClO_4 in **3b**) atom (the center of the anion) are shown.

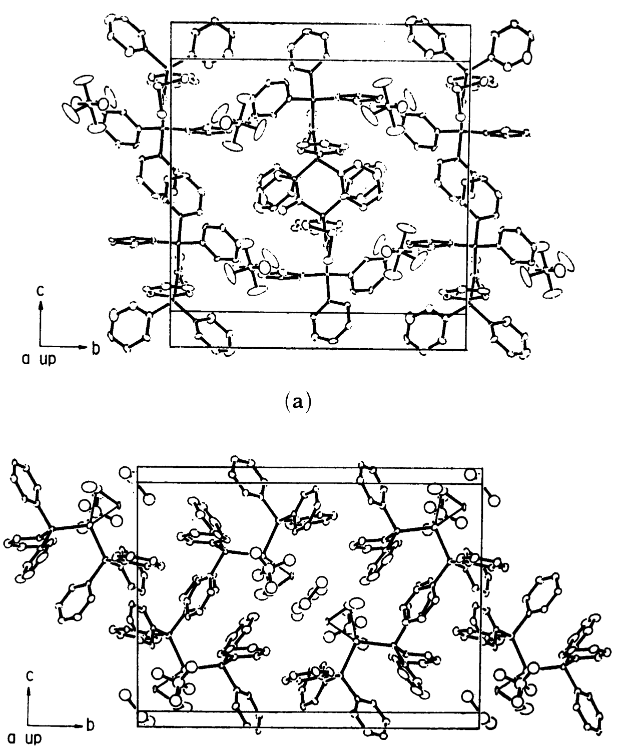
Distance (l/Å)	(**3a**)	(**3b**)
	Pd(x,y,z)···P(3)	Pd(x,y,z)···Cl(1)
Nearest	4.759(8)(x,y,z)	5.317(17)(x,y,z)
Second	5.252(8)(1−x, −1/2+y,1/2−z)	6.288(17) (−1+x,y,z)

As shown in Fig. 5, only the above two contacts may exemplify significant interaction between the cation and the anion.

spherical symmetry. The distances between the Pd atom and the central atom of the anions (the P and Cl atoms) are compared with each other in Table 6. 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 **3a** are sigificantly shorter than those of the Pd–Cl(1) in **3b**. These facts imply that **3a** may behave as a stronger ion-pair than **3b**, which is probably connected with the difference in the coordination modes between **3a** and **3b**.

Crystal Structure. The crystal structures of **3a** and **3b**, both projected along the a* axis, are given in Fig. 5. All the intermolecular atomic contacts in **3a** are considered as usual van der Waals distances, the shortest atomic contact being 3.22(4) Å [C(15)(x,y,z)···F(3)(2−x,−1/2+y,1/2−z)]. In **3b**, an abnormal short contact [2.82 Å] can be calculated for C(S)(x,y,z)···C(S)(1−x,−y,−z) distance. However, we can not discuss it further because of the low occupancy (0.25) of the CH_2Cl_2 molecule.

All the computations were carried out on NEAC 2200-700 and ACOS 800 computers at Computation Center, Osaka University, and on an ACOS 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University.



(a)

(b)

Fig. 5. The crystal structure projected along the a* axis.
(a) $[Pd(CH_2SCH_3)(PPh_3)_2]PF_6$ (**3a**).
Atoms are represented by thermal ellipsoids at 30% probability levels.
(b) $[Pd(CH_2SCH_3)(PPh_3)_2]ClO_4\cdot0.25CH_2Cl_2$ (**3b**).
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.

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