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THE MOLECULAR STRUCTURE OF A THIA-ALLYL PALLADIUM COMPLEX AT −160°C AND 20°C

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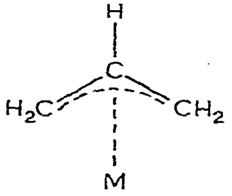
Summary

The molecular structure of a novel palladium complex containing a thia-allyl group has been determined from three-dimensional X-ray diffraction data collected at both −160°C and 20°C. The crystal belongs to the monoclinic system, space group $P2_1/n$, with four formula units in a cell of dimensions: a 8.752(3), b 11.444(4), c 19.095(5) Å and β 92.06(3)° at −160°C; a 8.801(1), b 11.562(2), c 19.390(2) Å and β 91.53(1)° at 20°C. The structure was solved by the heavy atom method, and refined by the least-squares procedure to R = 0.033 (−160°C) and 0.039 (20°C) for non-zero reflections. No essential difference is observed between molecular structures at −160 and 20°C. The coordination mode of the thia-allyl group ($(MeOCO)_2CHCH_2(Me)C(Me_2N)C{=}S$), which is bound to the palladium atom through the Pd—C σ-bond and the donation of the sulfur atom to the metal atom, is not a π-type but a σ-type [Pd—C(7) 2.058(3), Pd—S 2.262(1), C(6)—C(7) 1.506(4) and C(6)—S 1.709(3) Å at −160°C]. The relatively short Pd—S bond may show strong donation of the sulfur to the metal atom. The geometry around the palladium atom is essentially square-planar. The C(6), C(7) and S atoms in the thia-allyl group are almost coplanar with the palladium atom.

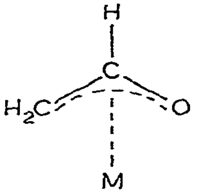
Introduction

Palladium complexes containing the π-allyl group have been widely studied from both viewpoints of synthetic and structural chemistry [1]. 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 groups of the allyl group is replaced by a hetero atom such as oxygen or sulfur, also have been investigated, although there are not so many reports of such complexes.

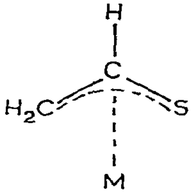
Some of oxa-π-allyl palladium complexes have been isolated [2] and have been



π—allyl



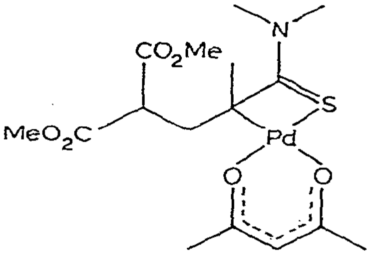
oxa—π—allyl



thia—π—allyl

suggested as reaction intermediates [3—5]. However, none of their three-dimensional structures has been determined and the stereochemistry of the oxa-π-allyl metal complexes has not been established yet. On the other hand, no thia-π-allyl metal complex has been reported. It was, therefore, of interest to elucidate the coordination mode of the oxa-π-allyl or thia-π-allyl group to the metal atom in the three-dimensional structure.

Very recently, a series of palladium-catalyzed reactions of thioamides have been studied by Tamaru, Kagotani and Yoshida [6]. The first "possible" thia-π-allyl palladium complex has been prepared by the palladium-assisted Michael addition of sodium dimethylmalonate to *N*,*N*-dimethylthiomethacrylamide [6].



In order to clarify the coordination of the thia-allyl group to the palladium atom (thia-π-allyl type or thia-σ-allyl mode) and as part of a series of structural studies on palladium complexes which have sulfur-containing ligands, the molecular structure of the present thia-allyl palladium complex has been determined precisely using X-ray diffraction data collected at liquid nitrogen temperature (—160° C). The molecular structure at room temperature (20° C) also has been determined and is compared with the low temperature structure.

Experimental

Crystals of the thia-allyl palladium complex supplied by Prof. Z. Yoshida and his coworkers are yellow plates. A well-shaped crystal with approximate dimensions 0.4 × 0.3 × 0.15 mm was 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 FACOM U-200-controlled diffractometer. The crystal system was determined as monoclinic. The space group was uniquely determined as $P2_1/n$ (No. 14) by the systematic absences of reflections. Accurate unit-cell dimensions were determined by a least-squares fit of

TABLE 1

CRYSTAL DATA

$C_{16}H_{25}NO_6PdS$, mol. wt. 465.8, $F(000) = 952$
Monoclinic, space group $P2_1/n$

	−160°C	20°C
a (Å)	8.752(3)	8.801(1)
b (Å)	11.444(4)	11.562(2)
c (Å)	19.095(5)	19.390(2)
β (°)	92.06(3)	91.53(1)
U (Å^3)	1911.3(9)	1972.3(4)
Z	4	4
D_c (g cm^{-3})	1.619	1.568
μ(Mo-K_α) (cm^{-1})	10.9	10.6

2θ values of 25 strong reflections. Crystal data are shown in Table 1.

The intensity data collection was carried out at both −160 and 20°C on the diffractometer by the θ—2θ scan technique with 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 scan speed was 4° min^{-1} and the scan width was $\Delta 2\theta = (2.0 + 0.7 \tan \theta)°$. The background intensity was measured for 7.5 s at both ends of a scan. Totals of 4186 (at −160°C) and 4325 (at 20°C) reflections with 2θ less than 54° were collected, and 318 (at −160°C) and 643 (at 20°C) reflections were considered as unobserved. Four standard reflections (0, 0, 10, 060, 501 and 444) were measured at regular intervals to monitor the stability and orientation of the crystal, and the intensity of these reflections remained constant throughout the data collection. Lorentz and polarization corrections were carried out in the usual manner. No corrections for absorption and extinction effects were applied [$(\mu R)_{max}$ = 0.3].

Structure solution and refinement

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 the locations of remaining non-hydrogen atoms.

The structures at low and room temperatures were refined in parallel with each other by the block-diagonal least-squares procedure using the HBLS-V program [7], the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Several cycles of isotropic refinement converged the R values to 0.059 (at −160°C) and 0.078 (at 20°C) for non-zero reflections, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. 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 located all the hydrogen atoms. The parameters of the hydrogen atoms were also refined isotropically in the further refinement. A final difference Fourier map at −160°C showed no peaks higher than 0.7 e/Å^3. The final R indices are 0.033 and 0.039 for non-zero (0.039 and 0.056 for all) reflections at −160 and 20°C, respectively. The

TABLE 2

FINAL ATOMIC PARAMETERS FOR NON-HYDROGEN ATOMS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(a) −160°C									
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)	0.0061(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(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)
(b) 20°C									
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)

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[a] Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE 3

FINAL ATOMIC PARAMETERS FOR HYDROGEN ATOMS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [a]

Atom	x	y	z	B
(a) —160°C				
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				
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)

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

final weighted R values ($R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$) are 0.044 (at —160° C) and 0.049 (at 20° C) for all reflections. The weighting schemes used were $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$ 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 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, although the unit weights were employed at the early stages of the refinement. The atomic scattering factors were taken from International Tables for X-ray Crystallography [8] for non-hydrogen atoms and those of Stewart et al. [9] for hydrogen atoms.

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

Results and discussion

Figure 1 represents ORTEP drawings of the molecule at —160 and 20° C with the numbering system of atoms. The thermal ellipsoids correspond to 30% probability level. Bond lengths and bond angles along with their estimated standard deviations are listed in Tables 4 and 5.

No essential difference is observed between 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. 1. Moreover, as shown in Table 4(a), most of the bond lengths at 20° C are shorter than those at —160° C, which is considered mainly due to the larger thermal motion of the molecule at 20° C. At —160° C, estimated standard deviations of bond lengths and bond angles are quite small, those of C—C bond lengths in the acetylacetonate ligand being 0.005 Å. The description of the structure and the discussion will be made on the low temperature structure, otherwise stated, hereafter.

The most remarkable feature of the molecular structure is that the thia-allyl group does not behave as a thia-π-allyl type but a thia-σ-allyl fashion. In π-allyl palladium complexes, the allyl (C_3H_5) plane inclines at 95—125° to the coordination plane of the palladium [1] in order that the π-electron orbitals of the allyl group overlap with the orbitals of the metal atom. In a typical example of the π-allyl palladium complex, $[(\pi\text{-}C_3H_5)PdCl]_2$ [10—13], the C_3H_5 plane inclines at 111.5° to the $(PdCl)_2$ plane [13]. 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] [13]. 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 bonded to the palladium by a π-type coordination. Figure 2 depicts the coordination 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°.

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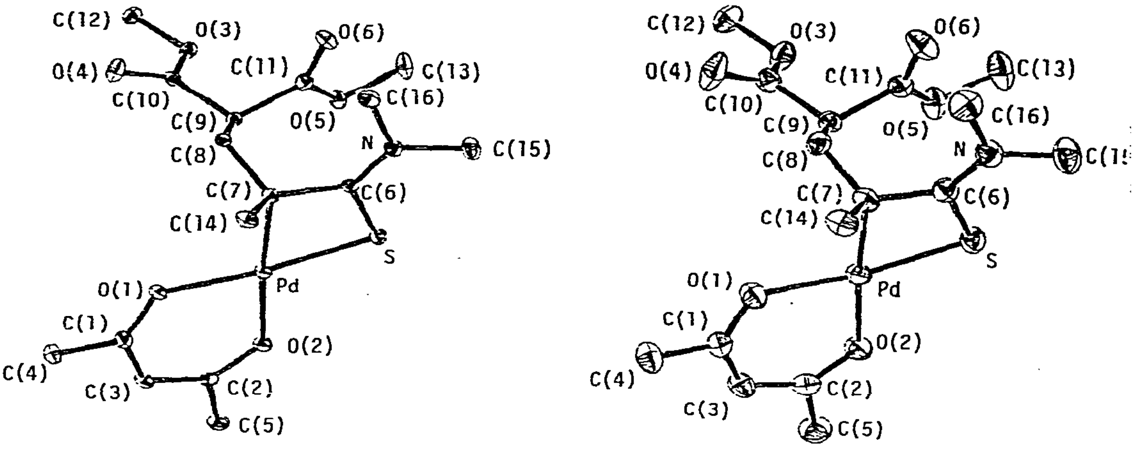


(a) (b)

Fig. 1. ORTEP drawings of the molecule 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.

TABLE 4

BOND LENGTHS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Length (Å)	—160°C	20°C	Length (Å)	—160°C	20°C
(a) Bonds involving non-hydrogen atoms			*(b) Bonds involving hydrogen atoms*		
Pd—O(1)	2.057(3)	2.059(3)	C(3)—H(3)	0.88(4)	0.92(5)
Pd—O(2)	2.122(3)	2.123(3)	C(4)—H(4A)	0.86(6)	0.92(7)
Pd—S	2.262(1)	2.257(1)	C(4)—H(4B)	0.95(6)	0.75(6)
Pd—C(7)	2.058(3)	2.051(4)	C(4)—H(4C)	0.86(6)	0.78(6)
O(1)—C(1)	1.272(4)	1.264(5)	C(5)—H(5A)	0.96(5)	0.82(6)
O(2)—C(2)	1.272(4)	1.254(5)	C(5)—H(5B)	0.89(6)	0.91(7)
C(1)—C(3)	1.401(5)	1.390(6)	C(5)—H(5C)	0.80(6)	0.78(7)
C(1)—C(4)	1.509(5)	1.500(7)	C(8)—H(8A)	0.92(4)	0.86(4)
C(2)—C(3)	1.395(5)	1.403(6)	C(8)—H(8B)	0.96(4)	1.00(5)
C(2)—C(5)	1.523(5)	1.507(7)	C(9)—H(9)	0.84(4)	0.82(4)
S—C(6)	1.709(3)	1.702(4)	C(12)—H(12A)	0.96(4)	0.75(7)
N—C(6)	1.315(4)	1.314(5)	C(12)—H(12B)	0.92(4)	0.89(5)
N—C(15)	1.467(5)	1.466(7)	C(12)—H(12C)	0.95(5)	0.80(5)
N—C(16)	1.460(5)	1.458(6)	C(13)—H(13A)	0.95(5)	0.93(5)
C(6)—C(7)	1.506(4)	1.502(6)	C(13)—H(13B)	0.90(5)	0.92(6)
C(7)—C(8)	1.535(5)	1.531(5)	C(13)—H(13C)	0.82(4)	0.83(6)
C(7)—C(14)	1.534(5)	1.540(6)	C(14)—H(14A)	0.93(4)	0.97(4)
C(8)—C(9)	1.532(5)	1.527(5)	C(14)—H(14B)	0.94(4)	0.92(5)
C(9)—C(10)	1.530(5)	1.520(6)	C(14)—H(14C)	0.89(4)	0.92(5)
C(9)—C(11)	1.523(5)	1.518(5)	C(15)—H(15A)	0.85(5)	0.87(6)
O(3)—C(10)	1.327(4)	1.318(5)	C(15)—H(15B)	0.84(5)	0.88(6)
O(3)—C(12)	1.448(5)	1.442(6)	C(15)—H(15C)	0.91(6)	0.81(6)
O(4)—C(10)	1.203(4)	1.198(6)	C(16)—H(16A)	1.00(6)	0.95(7)
O(5)—C(11)	1.341(4)	1.333(5)	C(16)—H(16B)	0.87(5)	0.84(6)
O(5)—C(13)	1.449(5)	1.436(7)	C(16)—H(16C)	0.87(4)	0.87(6)
O(6)—C(11)	1.205(4)	1.196(5)			

TABLE 5

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

Figure 3 shows the coordination geometry around the palladium atom projected onto the coordination plane. Selected bond lengths and bond angles also are given. The geometry around the palladium atom is essentially square-planar. The equation of the least-squares plane is given in Table 6. 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 Pd—S bonds whose structures have been determined by the diffraction method [2.24—2.45 Å].

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

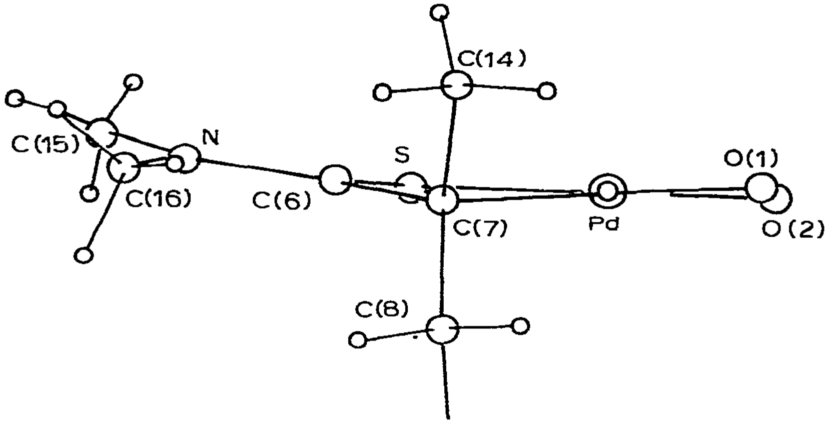


Fig. 2. A perspective view of the coordination behavior of the thia-allyl group to the palladium atom.

[1.61 and 1.82 Å, respectively] [14]. 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 conjugation through the S—C(6) and N—C(6) bonds. Both resonance structures presented below contribute significantly to the description of 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 sulfur to the metal atom.

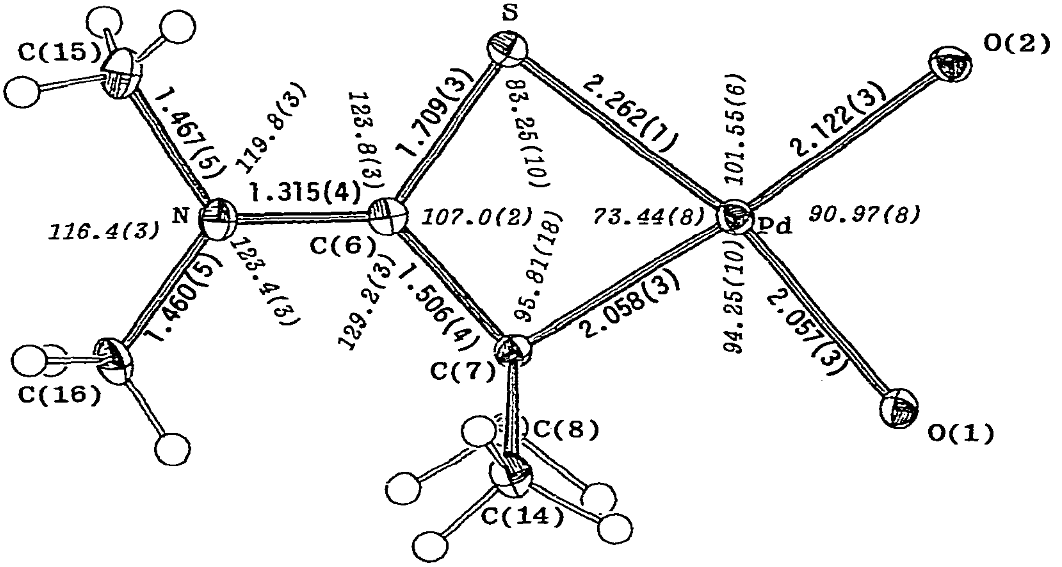


Fig. 3. The coordination geometry around the palladium atom and the coordination behavior of the thia-allyl group (at —160° C).

TABLE 6

LEAST-SQUARES PLANES (AT —160°C) [a]

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

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

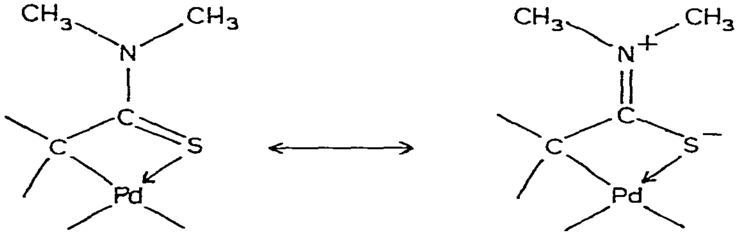
(b) Acetylacetonato plane through O(1), O(2), C(1), C(2), C(3), C(4) and C(5)

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

Deviations of atoms from the plane (Å) with e.s.d.'s in parentheses

	Plane (a)	Plane (b)
Pd	0.003(1)	0.082(3) [b]
O(1)	0.064(3)	—0.097(3)
O(2)	—0.045(3)	0.104(3)
C(1)	0.190(4) [b]	—0.022(4)
C(2)	—0.030(4) [b]	0.019(4)
C(3)	0.124(4) [b]	0.005(4)
C(4)	0.459(5) [b]	0.067(5)
C(5)	—0.185(5) [b]	—0.061(5)
S	0.065(2)	0.387(6) [b]
C(6)	0.103(4) [b]	0.309(7) [b]
C(7)	—0.078(4)	—0.044(6) [b]

[a] 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 $Z = cz \sin\beta$. [b] Not included in the least-squares calculation.



The short Pd—S bond length in this complex shows the strong donation of the sulfur to the metal atom, which may be connected with the stability of the present complex as pointed out by Tamaru et al. [6].

The geometry of the two methoxy carbonyl groups is similar to those found in methyl esters of carboxylic acid derivatives such as dimethyl ester of meso-tartaric acid [15].

The structure of the acetylacetonato ligand is comparable with that found in [Pd(acac)$_2$] [16,17]. This ligand has high planarity and is coplanar with the palladium atom. The equation of the least-squares plane of this ligand is also listed in Table 6. The deviation of the palladium atom from the plane is 0.063 Å. The Pd—O(1) bond length [2.057(3) Å] is significantly shorter than the Pd—O(2) bond length [2,122(3) Å], which may be caused by weak *trans*-influence of the electronegative sulfur atom located at the *trans*-position of the Pd—O(1) bond. The O(1)—Pd—O(2) angle of 90.97(8)° in this complex is smaller than that found in [Pd(acac)$_2$] (95.21°) [17], which may be partly owing to the relatively narrow angle of S—Pd—C(7) due to the formation of the Pd—C(6)—C(7)—S four-membered ring.

The crystal structure projected along the a^* axis is shown in Fig. 4. No

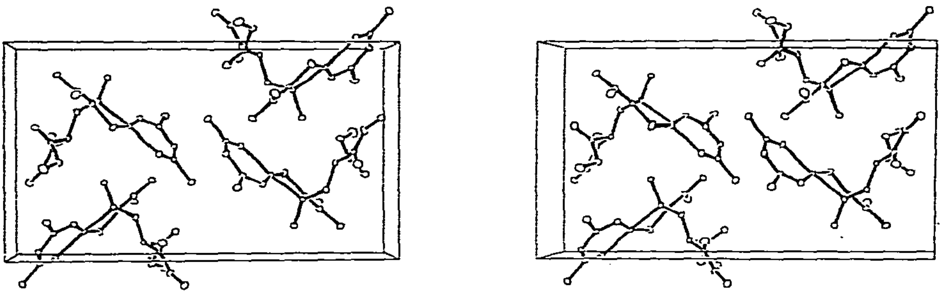


Fig. 4. A stereoscopic drawing of the crystal structure projected along the a^* axis (at −160°C). Atoms are represented by thermal allipsoids at 30% probability levels. Hydrogen atoms are omitted for clarity.

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) $(-1/2-x, -1/2+y, 1/2-z)$].

All computations were performed on an ACOS Series 77 NEAC System 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University. Figures 1, 3 and 4 were drawn by the ORTEP-II program [18].

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