Journal of Organometallic Chemistry, 149 (1978) 195—208

THE PREPARATION AND X-RAY MOLECULAR STRUCTURE OF A NOVEL DIALKYLPALLADIUM(II) COMPOUND CONTAINING BRIDGED THIOPHENOXYMETHYL GROUPS

KUNIO MIKI, GOHEI YOSHIDA, YASUSHI KAI, NORITAKE YASUOKA and NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)

(Received August 12th, 1977)

Summary

A stable homoleptic palladium compound, $[Pd(CH_2SC_6H_5)_2]_4$ was isolated by treatment of $(C_6H_5CN)_2PdCl_2$ with $LiCH_2SC_6H_5$, and its molecular structure has been determined by means of three-dimensional X-ray diffraction data at —160°C. The CH_2Cl_2 solvate ($[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$) forms orange-yellow, monoclinic crystals; a 16.302(3), b 19.394(4), c 18.552(3) Å and β 91.28(2)° at —160°C, space group $P2_1/n$ with $Z = 4$. The structure was solved by the conventional heavy atom method, and refined by the least-squares procedure to $R = 0.089$ for 4363 independent non-zero reflections. The fairly rigid cyclic tetramer is formed, which has approximate 222 symmetry. Four palladium atoms occupy the corners of a distorted rectangle and two averaged Pd···Pd distances are 4.051 and 3.304 Å, respectively. Four coordination planes around the palladium atom, the geometries of which are essentially square-planar, are equivalent with each other. The $CH_2SC_6H_5$ groups bridge four palladium atoms (mean S—C(methylene) 1.82, S—C(phenyl) 1.80 Å).

Introduction

In a series of studies on thioalkoxymethylmetal complexes [1], the coordination behavior of the CH_2SR ($R = CH_3$, C_6H_5) group, especially that of the sulfur atom, is of particular interest. The X-ray molecular structure of $[PdCl(CH_2SCH_3)(PPh_3)]$ has already been reported [2]. Recently, a novel dialkylpalladium(II) compound containing bridged thiophenoxymethyl groups has been prepared, which is of good thermal and hydrolytic stability for a homoleptic alkylpalladium(II) compound. In this paper, the preparation and structure of this crown-type palladium complex, bis(thiophenoxymethyl)palladium(II) tetramer, $[Pd(CH_2SC_6H_5)_2]_4$ are described. The molecular structure was determined at —160°C because of the instability of the crystals at room temperature. This is the first example of an X-ray molecular structure determination of a dialkylpalladium complex without a "stabilizing ligand" such as trialkylphosphine.

Experimental

Preparation of bis(thiophenoxymethyl)palladium(II) tetramer

To a dry benzene solution (20 ml) of $(C_6H_5CN)_2PdCl_2$ (3.94 mmol) cooled to 0°C, $LiCH_2SC_6H_5$ [3] (15.74 mmol in 15 ml of dry THF) was added dropwise. After it had been stirred for 4 h at 0°C, the mixture was hydrolysed with a saturated aqueous solution of ammonium chloride. The organic layer was dried over $MgSO_4$ at low temperature. Then the solvent was removed under reduced pressure to leave a yellow oily liquid, which was dissolved in a minimum volume of CH_2Cl_2, and n-hexane was added to give a yellow solid. Recrystallization from CH_2Cl_2/Et_2O gave orange-yellow plates (1.27 g, 74%); m.p. 164°C (decomp.). (Found: C, 47.90; H, 4.08; mol. wt. 1436 and 1446, osmometrically in 2.50 and 3.55 wt.% chloroform solutions at 25°C. $C_{14}H_{14}PdS_2$ calcd.: C, 47.66; H, 4.00%; mol. wt. 1412 as tetramer.)

X-ray structure determination

Crystals of $[Pd(CH_2SC_6H_5)_2]_4$ are unstable at room temperature and decompose after ca. 12 h at 25°C. Therefore, all the X-ray measurements mentioned below were carried out at low temperature (—160°C), which was attained by the gas flow method using liquid nitrogen.

A crystal with approximate dimensions 0.25 × 0.30 × 0.05 mm was mounted on a Rigaku automated, four-circle, single-crystal diffractometer. The crystal setting was established by the Rigaku soft-ware system for a FACOM U-200-controlled diffractometer based on the Busing—Levy method [4]. The crystal system was found to be monoclinic and the space group was uniquely determined as $P2_1/n$ by the systematic absence of reflections ($h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$).

Intensity data were collected by the $\theta - 2\theta$ scan technique with graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å). The scan width and the scan speed were $\Delta\theta = (1.0 + 0.35 \tan\theta)^\circ$ and 4° min^{-1}, respectively. The background was measured for 5 s at both ends of a scan. Totals of 5516 reflections with 2θ less than 40° were collected, of which 1153 were considered as unobserved. Relatively few intensities above background were observed in the range with 2θ larger than 40°. Four standard reflections (060, 305, $61\bar{3}$ and $90\bar{7}$) were measured at regular intervals to monitor the stability and orientation of the crystal. No intensity decrease was observed throughout the experiment. The data were corrected for Lorentz and polarization effects but not for absorption $[(\mu R)_{max} = 0.3]$ * and extinction.

The unit-cell parameters at —160°C were determined by a least-squares fit

---

* Although an absorption correction should not be ignored in such a thin plate as the present crystal, the instability of the crystal prevented us from carrying out any measurements necessary for an absorption correction. This might limit the accuracy of the present structure determination.

TABLE 1

CRYSTAL DATA OF $[Pd(CH_2SC_6H_5)_2]_4 \cdot CH_2Cl_2$

$C_{56}H_{56}Pd_4S_8 \cdot CH_2Cl_2$, mol. wt. 1496.1, $F(000)$ 2984
Monoclinic, Space group $P2_1/n$

	[−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(3)
μ(Mo-K_α) (cm^{-1})	15.82	15.33
D_c (g cm^{-3})	1.69	1.64
Z	4	4

using 2θ values of 25 strong reflections. The determination of the cell parameters at 18°C was also made quickly in the same way as at −160°C before the crystal collapsed. Crystal data are summarized in Table 1.

Structure solution and refinement

The structure was solved by the conventional heavy atom method. 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 sulfur 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.

Structure refinement was carried out by the block-diagonal least-squares procedure using the HBLS-V program [5], the function minimized being $\Sigma w(|F_0| - |F_c|)^2$. Through the early stage of the refinement 4175 reflections ($2\theta \leqslant 36.4°$) 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 reflections, where $R = \Sigma||F_0| - |F_c||\,|F_0|$. 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: $w = (\sigma_{cs}^2 + a|F_0| + b|F_0|^2)^{-1}$ for $|F_0| > 0$, and $w = c$ for $|F_0| = 0$, 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) reflections and 0.115 for all reflections, respectively, where $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$. 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 reflections 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) reflections. The final weighted R index (R_w) is 0.120 for all reflections and the weighting parameters, a, b and c used in the final refinement are 0.1120, 0.0018 and 0.0446, respectively. Atomic scattering factors are taken from ref. 6.

(continued on p. 200)

TABLE 2

FINAL ATOMIC PARAMETERS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Positional parameters of heavy atoms in fractions of cell edges and anisotropic thermal parameters in the form: exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd(1)	0.16800(9)	0.22963(8)	0.21040(8)	0.00175(7)	0.00094(5)	0.00086(5)	−0.00004(9)	0.00085(9)	0.00010(8)
Pd(2)	0.22687(9)	0.08501(8)	0.13267(8)	0.00174(7)	0.00082(5)	0.00093(5)	−0.00016(9)	0.00053(9)	−0.00006(8)
Pd(3)	0.45218(9)	0.11498(8)	0.21092(8)	0.00168(7)	0.00083(5)	0.00089(5)	−0.00007(9)	0.00058(9)	−0.00007(8)
Pd(4)	0.40930(9)	0.28021(8)	0.23964(8)	0.00174(7)	0.00081(5)	0.00089(5)	0.00004(9)	0.00072(9)	0.00009(8)
S(1A)	0.2547(3)	0.2355(3)	0.3166(3)	0.0015(2)	0.00068(15)	0.00071(16)	0.0004(3)	0.0010(3)	0.0001(3)
S(1B)	0.1110(3)	0.1253(3)	0.2573(3)	0.0017(2)	0.00100(17)	0.00141(18)	−0.0004(3)	0.0013(3)	0.0008(3)
S(2A)	0.3523(3)	0.1131(3)	0.0739(3)	0.0018(2)	0.00105(16)	0.00085(17)	0.0006(3)	0.0012(3)	0.0001(3)
S(2B)	0.1634(3)	0.1735(3)	0.0595(3)	0.0016(2)	0.00082(16)	0.00081(16)	0.0006(3)	0.0005(3)	0.0001(3)
S(3A)	0.3372(3)	0.0532(3)	0.2654(3)	0.0012(2)	0.00076(16)	0.00102(17)	−0.0002(3)	0.0005(3)	−0.0000(3)
S(3B)	0.4692(3)	0.1644(2)	0.3384(3)	0.0011(2)	0.00053(15)	0.00088(16)	0.0002(3)	0.0009(3)	0.0005(3)
S(4A)	0.3166(3)	0.2956(3)	0.1387(3)	0.0015(2)	0.00066(15)	0.00077(16)	0.0003(3)	0.0008(3)	−0.0000(3)
S(4B)	0.5161(3)	0.2511(3)	0.1579(3)	0.0016(2)	0.00098(16)	0.00092(17)	−0.0002(3)	0.0013(3)	−0.0000(3)
Cl(1S)	0.8602(6)	0.2868(6)	−0.0086(5)	0.0059(5)	0.0067(4)	0.0038(3)	−0.0040(7)	0.0006(6)	−0.0012(6)
Cl(2S)	0.8480(6)	0.2004(7)	0.1160(5)	0.0062(5)	0.0094(6)	0.0047(4)	0.0052(9)	0.0006(7)	0.0005(8)

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

ATOM	x	y	z	B		x	y	z	B
C(S)	0.797(2)	0.2350(20)	0.047(2)	7.6(9)	C(2B3)	0.0996(16)	0.0955(13)	−0.1337(14)	3.8(6)
C(1A)	0.2136(12)	0.3196(10)	0.1688(10)	1.5(4)	C(2B4)	0.0149(17)	0.0735(14)	−0.1253(14)	4.3(6)

C(1B)	0,0937(12)	0,2189(11)	0,1176(11)	1,8(4)
C(2A)	0,2813(11)	0,0078(9)	0,1923(9)	0,8(4)
C(2B)	0,1174(12)	0,0630(10)	0,1827(10)	1,4(4)
C(3A)	0.4405(11)	0,0744(10)	0,1205(10)	1,2(4)
C(3B)	0,5522(11)	0,1682(10)	0,1868(10)	1.1(4)
C(4A)	0,3236(11)	0,3075(10)	0,3128(10)	1.2(4)
C(4B)	0.4868(12)	0,2569(11)	0,3257(11)	1,7(4)
C(1A1)	0.1799(11)	0,2607(10)	0,3812(10)	1.1(4)
C(1A2)	0.1492(12)	0,2100(10)	0,4263(11)	1.6(4)
C(1A3)	0,0889(12)	0,2288(11)	0,4763(11)	1.7(4)
C(1A4)	0,0570(13)	0,2919(11)	0,4795(11)	2,1(4)
C(1A5)	0,0887(13)	0,3464(11)	0,4336(12)	2,4(4)
C(1A6)	0,1491(12)	0,3272(10)	0,3836(11)	1.7(4)
C(1B1)	0,0007(13)	0,1396(11)	0,2701(11)	1,9(4)
C(1B2)	—0,0537(14)	0,0918(12)	0,2511(12)	2,9(5)
C(1B3)	—0,1366(16)	0,1032(14)	0,2661(14)	3,8(6)
C(1B4)	—0,1604(14)	0,1616(12)	0,3010(12)	2,9(5)
C(1B5)	—0,1036(14)	0,2108(12)	0,3220(12)	2,8(5)
C(1B6)	—0,0196(13)	0,2008(11)	0,3065(11)	2,3(4)
C(2A1)	0,3463(13)	0,0671(11)	—0,0122(12)	2.4(4)
C(2A2)	0,3800(15)	0,0973(12)	—0,0699(13)	3.1(5)
C(2A3)	0,3738(17)	0,0596(14)	—0,1410(14)	4,2(6)
C(2A4)	0,3374(16)	—0,0037(14)	—0,1412(14)	4,3(6)
C(2A5)	0,3041(15)	—0,0336(13)	—0,0790(13)	3,4(5)
C(2A6)	0,3069(14)	0,0013(12)	—0,0129(12)	2,9(5)
C(2B1)	0,1017(13)	0,1317(11)	—0,0102(11)	1.9(4)
C(2B2)	0,1423(14)	0,1225(12)	—0,0741(12)	2,9(5)
C(2B5)	—0,0252(14)	0,0866(12)	—0,0591(13)	3,1(5)
C(2B6)	0,0214(13)	0,1146(11)	—0,0007(12)	2,3(4)
C(3A1)	0,3955(11)	—0,0135(10)	0,3125(10)	1,3(4)
C(3A2)	0,3971(13)	—0.0120(11)	0,3881(1)	2,1(4)
C(3A3)	0,4479(15)	—0,0597(13)	0,4274(13)	3,4(5)
C(3A4)	0,4917(15)	—0,1082(12)	0,3896(13)	3,0(5)
C(3A5)	0,4900(13)	—0,1113(11)	0,3130(11)	2,3(4)
C(3A6)	0,4385(12)	—0,0636(11)	0,2728(11)	1.7(4)
C(3B1)	0,5648(11)	0.1335(9)	0,3791(10)	0,9(4)
C(3B2)	0,6096(11)	0,1776(10)	0,4220(10)	1.2(4)
C(3B3)	0,6821(12)	0,1540(11)	0,4574(11)	1,8(4)
C(3B4)	0,7051(13)	0,0825(11)	0,4481(11)	1,9(4)
C(3B5)	0,6572(12)	0,0426(11)	0,4025(11)	1.9(4)
C(3B6)	0,5862(12)	0,0660(10)	0,3657(10)	1.5(4)
C(4A1)	0,3496(13)	0,3703(11)	0,0958(11)	1.9(4)
C(4A2)	0,3907(12)	0,3649(10)	0,0278(10)	1.4(4)
C(4A3)	0,4180(13)	0,4203(11)	—0,0098(11)	2,1(4)
C(4A4)	0,4019(14)	0,4878(12)	0,0159(12)	2,7(5)
C(4A5)	0,3628(14)	0,4971(12)	0,0843(12)	2.7(5)
C(4A6)	0,3358(12)	0,4383(10)	0.1203(11)	1.7(4)
C(4B1)	0,5970(11)	0.3101(10)	0,1712(10)	1.1(4)
C(4B2)	0,6741(15)	0.2934(13)	0,1960(14)	3.7(5)
C(4B3)	0,7365(17)	0,3426(15)	0,2072(15)	4.7(6)
C(4B4)	0,7169(16)	0.4130(13)	0,1914(14)	3.8(6)
C(4B5)	0,6438(16)	0,4304(14)	0,1652(14)	3.8(6)
C(4B6)	0,5813(14)	0.3798(12)	0,1568(12)	2,8(5)

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

Results and discussion

In the ^{1}H NMR spectra of the complex $[Pd(CH_2SC_6H_5)_2]_4$ in $CDCl_3$ at −60 to 23°C, the methylene proton signals appeared as a single AB pattern ($\delta(H_A)$ 2.89 and $\delta(H_B)$ 2.55 ppm, J_{AB} 6 Hz), suggesting that the sulfur atom in the thiophenoxymethyl group is asymmetric due to coordination to a palladium atom and each thiophenoxymethyl group in the tetrameric molecule is in a similar magnetic environment. This is the first example of a homoleptic alkylpalladium(II) complex without a "stabilizing ligand" such as trialkylphosphine.

An ORTEP plot 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, to-

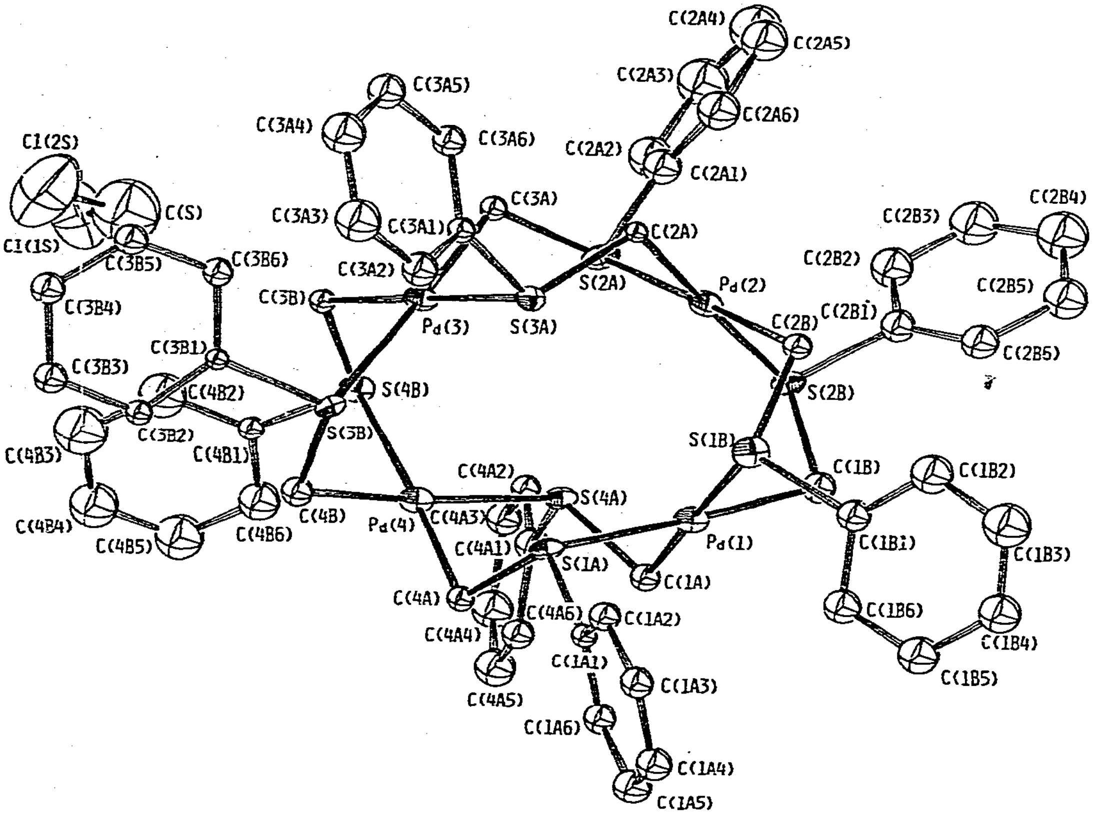


Fig. 1. An ORTEP plot of the tetramer and solvent molecules. The thermal ellipsoids correspond to 50% probability level.

---

* The table of structure factors has been deposited as NAPS Document No. 03201 (14 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 $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States and Canada, postage is $ 3.00 for a photocopy or $ 1.00 for a fiche.

TABLE 3

BOND LENGTHS ALONG WITH THEIR 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)
	$n = 1, m = 4$	$n = 2, m = 3$	$n = 3, m = 2$	$n = 4, m = 1$
S(nA)—C(mA)	1.79(2)	1.82(2)	1.84(2)	1.84(2)
	$n = 1, m = 2$	$n = 2, m = 1$	$n = 3, m = 4$	$n = 4, m = 3$
S(nB)—C(mB)	1.84(2)	1.81(2)	1.83(2)	1.79(2)
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
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)			

gether with the atomic numbering scheme. Tables 3 and 4 show bond lengths and bond angles along with their estimated standard deviations. Although the molecular structures of some cyclic complexes contianing more than three palladium atoms have been determined by X-ray analysis [7—12], 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. 2. 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 5. 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. 3 viewed along the normal to the plane of palladium and two sulfur 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 6. As

TABLE 4

BOND ANGLES ALONG WITH THEIR 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)
	n = 1, m = 4	m = 2, m = 3	n = 3, m = 2	n = 4, m = 1
Pd(n)—S(nA)—C(mA)	111.2(7)	111.2(6)	111.0(6)	110.9(7)
	n = 1, m = 2	n = 2, m = 1	n = 3, m = 4	n = 4, m = 3
Pd(n)—S(nB)—C(mB)	104.6(7)	106.2(7)	106.7(7)	105.8(7)
	n = 1	n = 2	n = 3	n = 4
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)
	n = 1, m = 4	n = 2, m = 3	n = 3, m = 2	n = 4, m = 1
C(mA)—S(nA)—C(nA1)	104.4(9)	103.9(10)	105.0(9)	102.8(10)
	n = 1, m = 2	n = 2, m = 1	n = 3, m = 4	n = 4, m = 3
C(mB)—S(nB)—C(nB1)	105.5(9)	107.2(10)	103.9(9)	106.9(9)
	n = 1, m = 4	n = 2, m = 3	n = 3, m = 2	n = 4, m = 1
Pd(n)—C(nA)—S(mA)	103.8(9)	104.4(9)	109.4(9)	105.2(9)
	n = 1, m = 2	n = 2, m = 1	n = 3, m = 4	n = 4, m = 3
Pd(n)—C(nB)—S(mB)	100.3(10)	105.3(9)	106.0(9)	102.7(10)
	n = 1	n = 2	n = 3	n = 4
S(nA)—C(nA1)—C(nA2)	117.9(15)	117.9(18)	117.6(15)	119.5(15)
S(nA)—C(nA1)—C(nA6)	121.8(15)	117.3(17)	119.9(15)	125.1(16)
C(nA6)—C(nA1)—C(nA2)	120.2(18)	124.8(21)	122.4(18)	115.4(18)
C(nA1)—C(nA2)—C(nA3)	118.5(18)	117.6(22)	119.7(20)	123.6(19)
C(nA2)—C(nA3)—C(nA4)	123.0(20)	117.3(24)	118.7(22)	119.4(20)
C(nA3)—C(nA4)—C(nA5)	119.7(20)	122.9(26)	122.6(22)	120.0(20)
C(nA4)—C(nA5)—C(nA6)	116.8(19)	120.9(23)	119.2(20)	117.8(20)
C(nA5)—C(nA6)—C(nA1)	121.6(19)	116.4(21)	117.3(18)	123.6(19)
S(nB)—C(nB1)—C(nB2)	120.6(17)	113.6(16)	118.5(14)	125.3(17)
S(nB)—C(nB1)—C(nB6)	115.5(16)	122.4(17)	117.1(14)	117.6(15)
C(nB6)—C(nB1)—C(nB2)	123.6(21)	123.9(20)	124.4(18)	117.1(20)
C(nB1)—C(nB2)—C(nB3)	118.5(22)	119.2(22)	119.8(18)	123.1(24)
C(nB2)—C(nB3)—C(nB4)	120.7(23)	118.8(23)	118.0(18)	117.3(25)
C(nB3)—C(nB4)—C(nB5)	120.7(23)	119.6(24)	117.9(19)	121.0(25)
C(nB4)—C(nB5)—C(nB6)	119.5(21)	118.6(22)	124.5(19)	120.2(24)
C(nB5)—C(nB6)—C(nB1)	116.8(20)	119.6(20)	115.3(18)	121.2(21)
Cl(1S)—C(S)—Cl(2S)	113.3(22)			

(continued on p. 206)

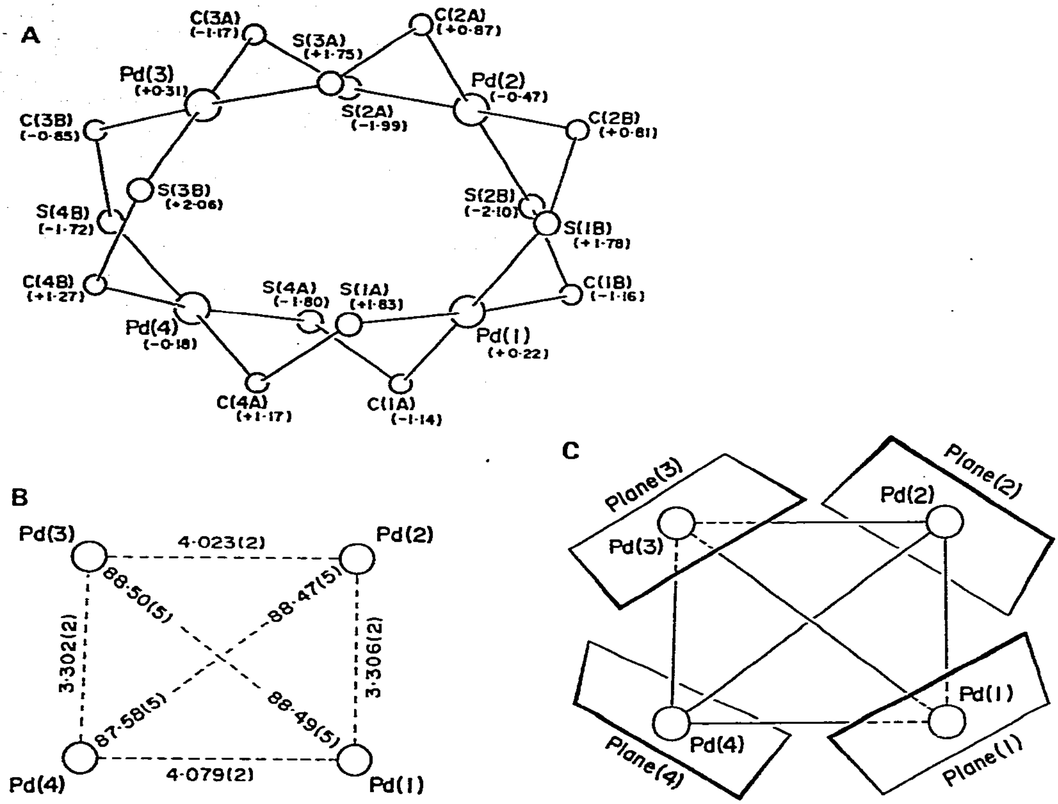
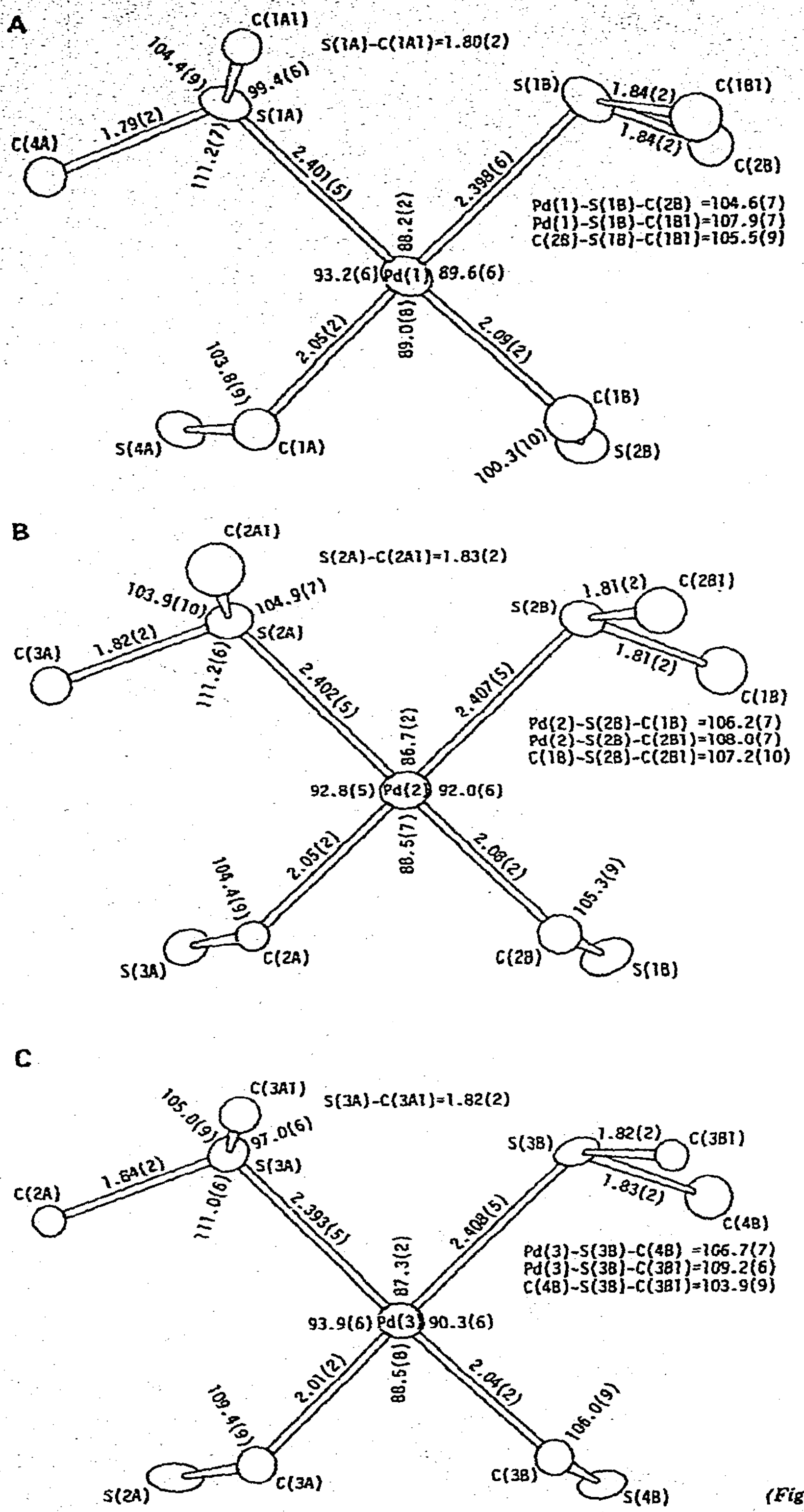


Fig. 2. The skeletal part of the complex projected onto the least-squares plane of four palladium atoms. (a) Deviations of atoms from the least-squares plane in parentheses. (b) Inter-palladium distances and angles. (c) Correlation of four coordination planes.

TABLE 5

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) 3.019(4) 3.009(5)	3.009	7
$[Pd(SC_3H_7)_2]_6$	3.014(2) 3.157(2) 3.235(2)	3.135	8
$[Pd(CH_3COO)_2]_3$	3.105(1) ~3.203(1)	3.15	9
$[Pd(SC_2H_5)(S_2CSC_2H_5)]_3$	3.303(2) 3.307(2) 3.655(2)	3.422	10
$[Pd(S_3C_4H_8)]_3$	3.407(12) 3.486(12) 3.662(12)	3.518	11
$[Pd(CH_2SC_5H_5)_2]_4$	3.302(2) 3.306(2)	3.304	this work
	4.023(2) 4.079(2)	4.051	



(Figure continued on next page)

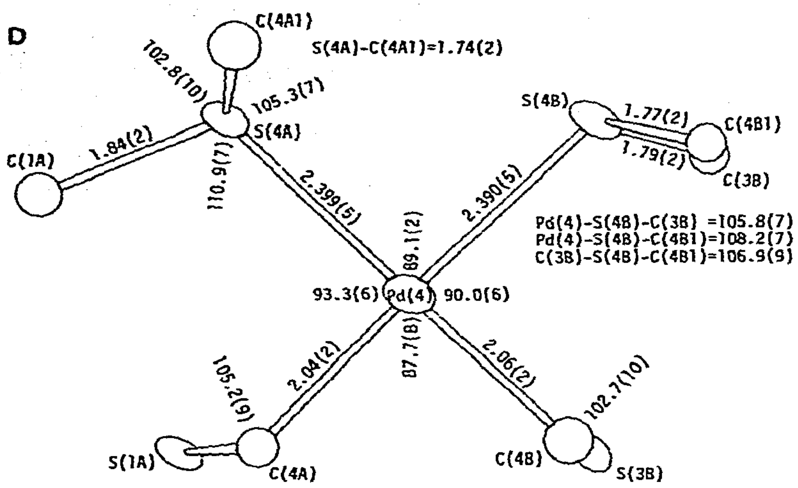


Fig. 3. The coordination geometry around each palladium atom.

shown in Fig. 3, 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

TABLE 6

LEAST-SQUARES PLANES AND DEVIATIONS OF ATOMS FROM THE PLANES

Equations of the planes are of the form: $AX + BY + CZ + D = 0.0$, where X, Y and Z are the orthogonal axes in Å units

	Plane (1)	Plane (2)	Plane (3)	Plane (4)
Square-planar planes of Pd				
Plane (n) indicates the coordination plane around the Pd(n) atom.				
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(nA)	0.027	0.016	−0.007	0.075
S(nB)	−0.023	−0.021	0.003	−0.059
C(nA)	−0.028	−0.024	0.003	−0.067
C(nB)	0.035	0.018	−0.009	0.082
C(nA1)[a]	−1.671	−1.733	−1.778	−1.496
C(nB1)[a]	−1.575	−1.686	−1.568	−1.541
	$m = 4$	$m = 3$	$m = 2$	$m = 1$
S(mA)[a]	1.688	1.715	1.647	1.604
C(mA)[a]	0.134	0.424	0.215	0.152
	$m = 2$	$m = 1$	$m = 4$	$m = 3$
S(mB)[a]	1.822	1.788	1.704	1.887
C(mB)[a]	1.336	1.102	1.256	1.313

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

TABLE 7

DIHEDRAL ANGLES BETWEEN PHENYL PLANE AND COORDINATION PLANE

Coordination plane	Phenyl plane[a]	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

[a] Phenyl (nX) indicates the phenyl group which is attached to S(nX), where $n = 1 \sim 4$ and X = A or B.

listed in Table 7. 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 (meth-

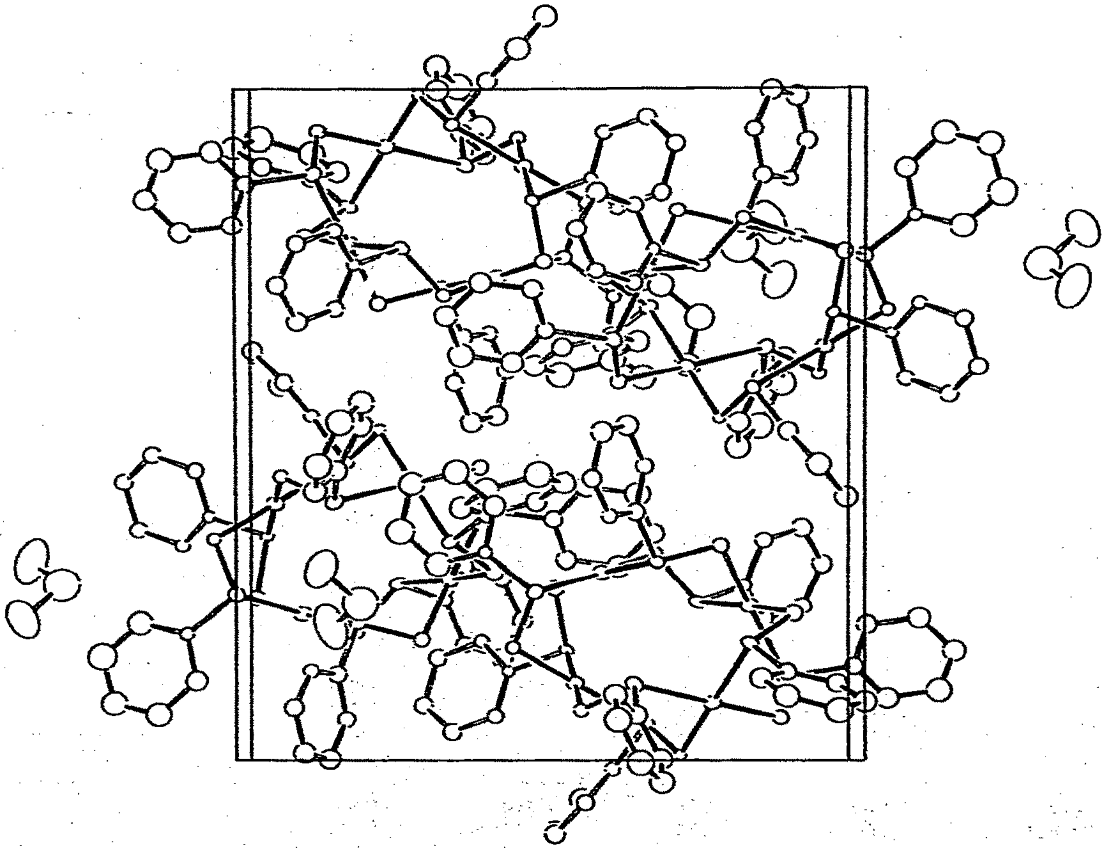


Fig. 4. The packing of the molecules in a unit cell projected along the a^* axis. Atoms are represented by thermal ellipsoids at 50% probability levels.

TABLE 8

Pd—S BOND LENGTHS OF SOME COMPLEXES WITH MORE THAN TWO PALLADIUM ATOMS BRIDGED BY SULFUR-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	12
$[Pd(SCMe_3)(S_2CSCMe_3)]_2$	$SC(CH_3)_3$	2	2.320	10	3	10
$[Pd(SEt)(S_2CSEt)]_3$	SCH_2CH_3	6	2.324	12	4~6	10
$[Pd(S_3C_4H_8)]_3$	$SCH_2CH_2SCH_2CH_2S$	6	2.331	124	30~32	11
$[Pd(S(n\text{-}Pr))_2]_6$	$SCH_2CH_2CH_3$	12	2.350	172	4~5	8
$[Pd(PPh_3)(SC_6F_5)_2]_2$ (Form I)	SC_6F_5	4	2.371	21	11~13	14
$[Pd(SCNMe_2)((MeO)_3P)Cl]_2$	$SCN(CH_3)_2$	1	2.382	—	2	15
$[Pd(PPh_3)(SC_6F_5)_2]_2$ (Form II)	SC_6F_5	2	2.395	74	7	16
$[Pd(CH_2SPh)_2]_4$	$CH_2SC_6H_5$	8	2.400	18	5~6	this work
$[Pd(SCN)(Ph_2PO)_2H]_2$	SCN	1	2.453	—	2	17

[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)

ylene) bond length in this complex is compared with that of 1.756 Å in [PdCl(CH_2SCH_3)(PPh_3)] [2], in which the CH_2SCH_3 group forms a metal—carbon—sulfur three-membered ring.

The mean Pd—C bond length (2.05 Å) has a value expected for a Pd^{II}—C(sp^3) σ-bond [13]. The mean Pd—S bond length (2.400 Å) is relatively long compared with complexes in which more than two palladium atoms are bridged by sulfur-containing ligands, as shown in Table 8. This may be partly due to the *trans*-influence of the carbon atom in the CH_2SCH_3 group.

With regard to sulfur atoms, there are two kinds of configurations. Although the crystal belongs to a centrosymmetric space group and absolute configuration does not exist, sulfur atoms numbered as S(nA) take *R*-configuration and the others[S(nB)] *S*-configuration in the enantiomer in Fig. 1, where $n = 1\sim4$. In this connection, the conformation about the Pd—S(nA) bond is distinctly different from that of Pd—S(nB) as shown in Fig. 3. Mean bond angles around two types of sulfur 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. 4. 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)($1-x$, $1-y$, $\bar{z}$)).

All computation were carried out on a NEAC 2200-700 computer at Osaka University. Figures 1, 3 and 4 were drawn on a NUMERICON 7000 system at Osaka University with the local version of ORTEP-II [18].

Acknowledgements

The authors express their deep thanks to Professor Rokuro Okawara of Osaka University for his continuous encouragement and helpful discussions, and to Dr. Donald J. Mullen who read the manuscript and improved its English.

References

1 (a) G. Yoshida, Y. Matsumura and R. Okawara, J. Organometal. Chem., 92 (1975) C53; (b) G. Yoshida, H. Kurosawa and R. Okawara, ibid., 113 (1976) 85.
2 (a) K. Miki, Y. Kai, N. Yasuoka and N. Kasal, Acta Cryst. A, 31 (1975) S138; (b) K. Miki, Y. Kai, N. Yasuoka and N. Kasai, J. Organometal. Chem., 135 (1977) 53.
3 E.J. Corey and D. Seebach, J. Org. Chem., 31 (1966) 4097.
4 W.R. Busing and H.A. Levy, Acta Cryst., 22 (1967) 457.
5 T. Ashida, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1973, p. 55.
6 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974, p. 71
7 A. Mawby and G.E. Pringle, J. Inorg. Nucl. Chem., 33 (1971) 1989.
8 N.R. Kunchur, Acta Cryst. B, 24 (1968) 1623.
9 A.C. Skapski and M.L. Smart, Chem. Commun., (1970) 658.
10 J.P. Fackler Jr. and W.J. Zegarski, J. Amer. Chem. Soc., 95 (1973) 8566.
11 E.M. McPartlin and N.C. Stephenson, Acta Cryst. B, 25 (1969) 1659.
12 S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumoto, H. Yoshioka and K. Nakatsu, J. Chem. Soc. Chem. Commun., (1973) 445.
13 M. Horike, Y. Kai, N. Yasuoka, N. Kasai, J. Organometal. Chem., 86 (1975) 269.
14 R.H. Fenn and G.R. Segrott, J. Chem. Soc. A, (1970) 3197.
15 S.K. Porter, H. White, C.R. Green, R.J. Angelici and J. Clardy, J. Chem. Soc. Chem. Commun., (1973) 493.
16 R.H. Fenn and G.R. Segrott, J. Chem. Soc. Dalton, (1972) 330.
17 D.V. Naik, G.J. Palenik, S. Jacobson and A.J. Carty, J. Amer. Chem. Soc., 96 (1974) 2286.
18 C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.