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

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The molecular structures of [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] and [PdCl$_2${(Me$_2$Men)P}$_2$], asymmetric hydrosilylation catalysts of olefin, were determined by means of X-ray diffraction. Both complexes form yellow prismatic crystals. The former belongs to the monoclinic system: $a=13.512(5)$, $b=13.082(1)$, $c=8.472(1)$ Å, and $\beta=97.00(2)°$, space group P2$_1$ with $Z=2$; the latter belongs to the tetragonal system: $a=9.662(1)$ and $c=32.459(2)$ Å, space group P4$_3$2$_1$2 with $Z=4$. Both structures were determined by the heavy atom method and have been refined anisotropically by a least-squares procedure ($R=0.0697$ for 2606 non-zero reflections for the former and $R=0.0713$ for 1388 non-zero reflections for the latter). The former molecules is not iso-structural with its nickel analog. The central palladium atom has *trans*-square planar geometry [Pd–Cl 2.304(5) and 2.297(5), Pd–P 2.344(4) and 2.361(5) Å]. The molecule has an approximate two-fold symmetry around the normal to the co-ordination plane. The neomenthyl groups are on the same side of the co-ordination plane. The latter molecule has exact C$_2$ symmetry: the two-fold axis passes through the Cl(1), Pd, and Cl(2) atoms which lie on the co-ordination plane. The geometry around the palladium slightly deviates from the *trans*-square planar [Pd–Cl 2.296(9) and 2.267(9) Å and Pd–P 2.310(6) Å]. The menthyl groups are located on either side of the co-ordination plane.

In a series of structural studies of catalytically active organometallic complexes, the molecular structures of some organoaluminium complexes have been determined;[1–4] their roles in the stereospecific polymerization of acetaldehyde have also been discussed.[4,5] The X-ray molecular structure of [Zn(OMe)$_2$(EtZnOMe)$_6$],*** which is considered as the key substance for the polymerization of methyloxirane, has recently been reported.[6]

A variety of dihalophosphine-transition metal(II) complexes have been found to be effective catalysts for the hydrosilylation of olefins and acetylenes by M. Kumada and co-workers.[7–9] *trans*-Dichlorobis(dimethylneomenthylphosphine)nickel(II) [NiCl$_2${(Me$_2$*neo*Men)P}$_2$]† and -palladium(II) [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] and *trans*-dichlorobis(dimethylmenthylphosphine)palladium(II) [PdCl$_2${(Me$_2$Men)P}$_2$]† are complexes in which each phosphine has a chiral substituent; they are catalysts for the asymmetric hydrosilylation of olefin.[10]

The X-ray molecular structure of the nickel complex [NiCl$_2${(Me$_2$*neo*Men)P}$_2$] has been reported very recently.[11] In this paper the molecular structures of the palladium analogs [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] and [PdCl$_2${(Me$_2$Men)P}$_2$] are described.

Experimental

Crystals of [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] and [PdCl$_2${(Me$_2$Men)P}$_2$] were provided by Professor M. Kumada and co-workers of Kyoto University. They are both yellow and prismatic. Preliminary photographic data showed that crystals of [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] and [PdCl$_2${(Me$_2$Men)P}$_2$] belong to monoclinic and tetragonal system, respectively. Since these complexes are both optically active, the corresponding space groups should be non-centrosymmetric. The systematic absence of reflections of the former ($0k0$, $k=2n+1$) indicated that its space group was P2$_1$; in the latter the absences ($h00$, $h=2n+1$ and $00l$, $l=2n+1$) suggested the space group P4$_1$2$_1$2 or P4$_3$2$_1$2.

The unit-cell dimensions of the two crystals were determined by the least-squares fit from 2θ values of 16 and 11 high-angle reflections measured on a G.E. single crystal orienter mounted on a Rigaku SG-2 goniometer. The crystal densities were measured by flotation in aqueous solutions of potassium tartarate. Crystal data of the two complexes are given in Table 1.

A crystal of [PdCl$_2${(Me$_2$*neo*Men)P}$_2$] with dimensions of 0.23×0.20×0.18 mm was chosen for the intensity measurement. A Rigaku automated four-circle diffractometer was used, with Zr-filtered Mo $K\alpha$ radiation. The θ-2θ scan technique was employed. The integrated intensities of each reflection were determined by scanning over a peak at a rate of 4 °min^{-1}, and subtracting the background obtained by averaging the two values measured for 5 s at both ends of a scan. The 2θ scan width was from $-1.0°$ for the $K\alpha_1$ peak to 1.0° for the $K\alpha_2$ peak. For the intensity data collection of [PdCl$_2${(Me$_2$Men)P}$_2$] the crystal used had dimensions of

TABLE 1. CRYSTAL DATA

	[PdCl$_2${(Me$_2$*neo*Men)P}$_2$] C$_{24}$H$_{50}$Cl$_2$P$_2$Pd	[PdCl$_2${(Me$_2$Men)P}$_2$] C$_{24}$H$_{50}$Cl$_2$P$_2$Pd
F. W.	577.9	577.9
Crystal system	Monoclinic	Tetragonal
Space group	P2$_1$	P4$_3$2$_1$2
a [Å]	13.512(5)	9.662(1)
b [Å]	13.082(1)	
c [Å]	8.472(1)	32.459(2)
β [°]	97.00(2)	
U [Å^3]	1486.4(6)	3030.2(4)
Z	2	4
D_m [g cm^{-3}]	1.29	1.27
D_c [g cm^{-3}]	1.29	1.27
μ [cm^{-1}]	9.1 (for Mo $K\alpha$)	77.6 (for Cu $K\alpha$)

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*** Me: methyl group, Et: ethyl group.

† *neo*Men: neomenthyl group, Men: menthyl group.

$0.20\times0.17\times0.15$ mm. This crystal was rather small to give sufficient intensity using Mo $K\alpha$ radiation, but no other good, larger crystal could be selected. It was therefore necessary to use Cu $K\alpha$ radiation in order to obtain strong reflection intensities. Intensity measurements were carried out in a way similar to those for $[\mathrm{PdCl_2\{(Me_2}neo\mathrm{Men)P\}_2}]$. Totals of 2814 independent reflections for $[\mathrm{PdCl_2\{(Me_2}neo\mathrm{Men)P\}_2}]$ and 1440 for $[\mathrm{PdCl_2\{(Me_2Men)P\}_2}]$ were collected at room temperature. In each case three standard reflections were measured after every 50 reflections. The intensities were corrected for the usual Lorentz and polarization effects. The absorption correction was ignored. This might limit the accuracy of the structures obtained, especially that of $[\mathrm{PdCl_2\{(Me_2Men)P\}_2}]$ ($\mu(\mathrm{Cu}\ K\alpha)=77.6\ \mathrm{cm^{-1}}$).

TABLE 2. POSITIONAL AND THERMAL PARAMETERS OF ATOMS FOR $[\mathrm{PdCl_2\{(Me_2}neo\mathrm{Men)P\}_2}]$ (e.s.d.'s in parentheses)

(a) Fractional co-ordinates ($\times10^4$).

Atom	x	y	z	Atom	x	y	z
Pd	−2711.6(6)	−2500	−191.5(10)	C(19)	758(18)	−2754(14)	3098(22)
Cl(1)	−1556(3)	−3779(3)	−355(5)	C(20)	1363(12)	−1741(16)	849(28)
Cl(2)	−3884(3)	−1229(3)	−184(6)	C(3)	−5145(11)	−3382(16)	−741(20)
P(1)	−1563(3)	−1300(3)	−926(4)	C(4)	−3723(12)	−4921(12)	−862(21)
P(2)	−3934(3)	−3727(3)	230(5)	C(31)	−2398(13)	−4688(18)	3331(20)
C(1)	−740(12)	−1835(13)	−2294(17)	C(32)	−3425(16)	−5039(15)	2868(22)
C(2)	−2210(14)	−321(13)	−2177(18)	C(33)	−4186(11)	−4161(13)	2219(19)
C(11)	−1907(11)	3085(15)	2205(18)	C(34)	−4194(13)	−3361(15)	3543(21)
C(12)	−1129(10)	4529(12)	1032(16)	C(35)	−3116(14)	−2975(15)	4041(19)
C(13)	−698(9)	−540(10)	504(14)	C(36)	−2432(16)	−3828(20)	4577(22)
C(14)	−195(10)	−1153(12)	1983(17)	C(37)	−1783(21)	−5577(25)	4018(30)
C(15)	−985(13)	−1368(15)	3085(18)	C(38)	−4943(14)	−2538(25)	3187(20)
C(16)	−1451(12)	−389(19)	3582(19)	C(39)	−4819(25)	−1661(23)	4458(29)
C(17)	−2278(16)	1350(19)	2752(26)	C(40)	−6026(16)	−2899(32)	3040(33)
C(18)	464(13)	−2073(11)	1613(19)				

(b) Anisotropic temperature factors ($\times10^4$) expressed 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	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	63.1(5)	60.2(5)	165.0(12)	−13.0(14)	13.0(11)	1.5(20)
Cl(1)	80.1(25)	65.4(25)	344.0(89)	4.9(40)	62.4(75)	−2.8(77)
Cl(2)	73.5(25)	82.5(29)	384.5(99)	20.8(44)	45.7(78)	13.0(91)
P(1)	81.0(24)	66.4(23)	145.4(47)	−12.5(39)	29.4(52)	5.2(57)
P(2)	75.0(24)	75.5(28)	232.8(68)	−29.6(43)	22.7(65)	−4.8(73)
C(1)	125(13)	113(14)	175(23)	−28(22)	134(29)	−55(30)
C(2)	158(16)	87(12)	174(24)	−18(23)	−44(31)	106(29)
C(11)	87(11)	139(17)	231(28)	−13(23)	17(28)	−118(37)
C(12)	80(9)	79(10)	213(24)	−8(16)	28(24)	−57(26)
C(13)	65(8)	66(9)	176(21)	−20(14)	55(20)	−37(22)
C(14)	80(10)	98(12)	219(25)	−49(18)	−16(24)	61(29)
C(15)	139(15)	122(16)	202(26)	−94(27)	−70(32)	31(35)
C(16)	99(13)	204(24)	195(27)	2(30)	22(30)	−49(43)
C(17)	146(19)	165(23)	429(51)	41(33)	60(50)	−314(60)
C(18)	137(14)	62(9)	302(33)	22(19)	−140(35)	−56(29)
C(19)	233(24)	89(18)	317(38)	66(31)	−179(49)	−9(37)
C(20)	79(12)	110(16)	607(62)	−61(23)	130(43)	−97(53)
C(3)	63(9)	160(18)	300(34)	−68(22)	−92(28)	70(42)
C(4)	96(12)	72(11)	354(37)	−66(19)	77(33)	−99(33)
C(31)	111(14)	181(23)	236(31)	−1(30)	−29(33)	89(45)
C(32)	180(20)	104(15)	288(36)	34(29)	116(44)	122(39)
C(33)	90(11)	91(12)	287(32)	−56(19)	116(30)	−0(32)
C(34)	114(14)	110(15)	297(34)	7(24)	126(36)	−8(37)
C(35)	137(15)	147(19)	216(28)	−76(27)	50(34)	−34(36)
C(36)	138(17)	213(28)	259(35)	−30(36)	7(39)	163(54)
C(37)	245(30)	264(37)	424(60)	331(58)	107(69)	237(79)
C(38)	163(16)	138(17)	333(35)	80(50)	169(39)	22(68)
C(39)	346(41)	188(29)	394(59)	218(60)	223(79)	−124(68)
C(40)	115(17)	408(73)	656(77)	154(57)	304(60)	281(119)

Table 2. (Continued)

(c) Calculated co-ordinates ($\times 10^3$) and assigned isotropic temperature factors for hydrogen atoms (except methyl hydrogen atoms).

Atom	*x*	*y*	*z*	*B*	Atom	*z*	*y*	*z*	*B*
H(11)	−256	−13	166	5.0	H(31)	−211	−434	230	5.0
H(12A)	−149	85	−1	5.0	H(32A)	−343	−563	193	5.0
H(12B)	−53	93	159	5.0	H(32B)	−371	−541	387	5.0
H(13)	−101	−36	−21	5.0	H(33)	−496	−441	196	5.0
H(14)	38	−68	262	5.0	H(34)	−439	−376	460	5.0
H(15A)	−158	−185	248	5.0	H(35A)	−284	−256	307	5.0
H(15B)	−66	−178	414	5.0	H(35B)	−312	−243	504	5.0
H(16A)	−88	3	433	5.0	H(36A)	−264	−419	563	5.0
H(16B)	−203	−59	434	5.0	H(36B)	−166	−356	484	5.0
H(18)	−5	−255	76	5.0	H(38)	−482	−236	194	5.0

Table 3. Positional and thermal parameters of atoms for $[PdCl_2\{(Me_2Men)P\}_2]$ (e.s.d.'s in parentheses)

(a) Fractional co-ordinates ($\times 10^4$).

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	−1962.3 (22)	−1962.3 (22)	0	C(13)	955 (14)	−3176 (15)	−529 (4)
Cl(1)	−282 (9)	−282 (9)	0	C(14)	1241 (15)	−4623 (16)	−356 (4)
Cl(2)	−3621 (9)	−3621 (9)	0	C(15)	2831 (19)	−4799 (21)	−311 (5)
P	−937 (4)	−2855 (5)	−585 (1)	C(16)	3563 (16)	−4660 (18)	−731 (5)
C(1)	−1676 (19)	−4435 (20)	−812 (5)	C(17)	3979 (20)	−3052 (27)	−1333 (6)
C(2)	−1171 (19)	−1594 (21)	−1006 (5)	C(18)	488 (18)	−4829 (19)	82 (6)
C(11)	3258 (17)	−3259 (20)	−912 (5)	C(19)	1103 (24)	−3989 (26)	436 (5)
C(12)	1667 (16)	−3026 (20)	−963 (5)	C(20)	557 (28)	−6399 (26)	209 (8)

(b) Anisotropic temperature factors ($\times 10^4$) expressed 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	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	99.6 (18)	99.6 (18)	11.3 (1)	15.1 (30)	−2.4 (13)	2.4 (13)
Cl(1)	151.4 (108)	151.4 (108)	34.8 (13)	−66.6 (139)	48.8 (97)	−48.8 (97)
Cl(2)	190.4 (122)	190.4 (122)	21.9 (9)	−142.6 (153)	24.1 (88)	−24.1 (88)
P	112.6 (47)	152.3 (58)	11.4 (4)	53.2 (89)	−3.6 (24)	5.6 (28)
C(1)	174 (28)	250 (33)	15 (2)	−44 (47)	−5 (13)	−66 (14)
C(2)	200 (28)	253 (34)	14 (2)	205 (51)	9 (12)	55 (13)
C(11)	103 (21)	201 (29)	23 (2)	52 (37)	21 (13)	10 (15)
C(12)	139 (22)	209 (27)	16 (2)	94 (45)	34 (11)	34 (14)
C(13)	104 (17)	118 (19)	14 (2)	68 (31)	−6 (9)	17 (10)
C(14)	129 (21)	162 (23)	11 (1)	77 (35)	13 (9)	7 (10)
C(15)	166 (27)	269 (35)	15 (2)	192 (51)	8 (13)	31 (15)
C(16)	115 (20)	180 (26)	17 (2)	70 (37)	−2 (11)	−4 (13)
C(17)	189 (30)	344 (45)	27 (3)	150 (69)	87 (17)	75 (22)
C(18)	208 (30)	186 (27)	20 (3)	159 (46)	33 (15)	58 (14)
C(19)	288 (41)	383 (50)	12 (2)	110 (77)	−14 (15)	−33 (17)
C(20)	349 (52)	272 (45)	37 (4)	118 (76)	52 (26)	118 (24)

(c) Calculated co-ordinates ($\times 10^3$) and assigned isotropic temperature factors for hydrogen atoms (except methyl hydrogen atoms).

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
H(11)	366	−251	−70	5.0	H(15A)	305	−581	−18	5.0
H(12A)	125	−379	−117	5.0	H(15B)	322	−402	−10	5.0
H(12B)	148	−200	−109	5.0	H(16A)	467	−478	−69	5.0
H(13)	137	−243	−32	5.0	H(16B)	320	−546	−94	5.0
H(14)	83	−540	−56	5.0	H(18)	−56	−446	4	5.0

Solution and Refinement of the Structure

Both structures were solved by the heavy-atom method, and refined anisotropically by the block-diagonal least-squares procedure using the HBLS V program.[12] The function minimized was $\Sigma(|F_o|-k\cdot|F_c|)^2$, where k is a scale factor. The atomic scattering factors used were those of Hanson, Herman, Lea, and Skillman.[13]

[$PdCl_2${(Me_2neoMen)P}$_2$]. From a three-dimensional Patterson function, the approximate co-ordinates of the palladium, two chlorine, and two phosphorus atoms were easily determined. All the non-hydrogen atoms were located in the subsequent Fourier synthesis. In the least-squares refinement, the y parameter of the palladium atom was fixed at 0.25 in order to define the origin of the unit-cell. When the R value fell down to 0.075, a difference synthesis revealed some but not all positions of the hydrogen atoms. All the hydrogen atoms except methyl hydrogen were then located assuming the C–H bond length of 1.08 Å and a tetrahedral angle for each carbon atom. In the subsequent refinement their contributions were included in the structure factor calculations, under the condition of fixed parameters. The effect of anomalous dispersion[14] for palladium, chlorine, and phosphorus atoms was then corrected for. The final R values for the structure obtained and its enantiomorph were 0.0702 (R_w=0.067) and 0.0697 (R_w=0.066) for 2606 non-zero reflections. The final positional and thermal parameters of the latter, which confirmed the absolute configuration of the neomenthyl group, are given in Table 2.[††]

[$PdCl_2${(Me_2Men)P}$_2$]. Since four molecules are contained in a unit-cell with the space group $P4_12_12$ or $P4_32_12$, the molecules must have special positions. The following two cases can satisfy the requirements: (1) only the palladium atom lies on the two-fold axis normal to the co-ordination plane, or (2) the palladium and the two chlorine atoms lie on the two-fold axis on the co-ordination plane.
A three-dimensional Patterson function could be interpreted for the latter case for the space group of either $P4_12_12$ or its enantiomorph $P4_32_12$; after assuming the $P4_32_12$ group, the subsequent Fourier synthesis revealed all the non-hydrogen atoms. At the final stage of the refinement, the effect of the anomalous dispersion for heavy atoms[14] was considered, and the contributions of all the hydrogen atoms except the methyl hydrogens were included in the structure factor calculations in the same manner as in [$PdCl_2${(Me_2*neo*Men)P}$_2$]. The final R value for the structure obtained and its enantiomorph was 0.0713 (R_w=0.0778) and 0.0803 (R_w=0.0899) for 1388 non-zero reflections. The former structure confirmed the absolute configuration of the menthyl group and determined the space group to be $P4_32_12$. The positional and thermal parameters are also given in Table 3.[†††]

Results and Discussion

The molecular structures of [$PdCl_2${(Me_2*neo*Men)P}$_2$] and [$PdCl_2${(Me_2Men)P}$_2$] are shown in Figs. 1 and 2 respectively, along with the numbering scheme of the atoms. The stereoscopic drawings of the molecules are given in Figs. 3 and 4. Bond lengths and bond angles are listed in Tables 4 and 5.

[$PdCl_2${(Me_2neoMen)P}$_2$]. The molecule has an approximate two-fold symmetry around the normal to the co-ordination plane, which passes through the palladium atom. The present complex is not iso-struc-

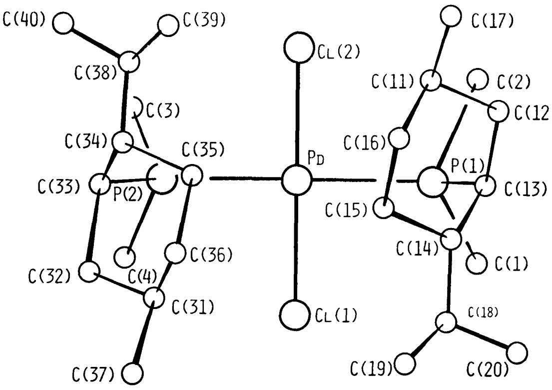

Fig. 1. Molecular structure of [$PdCl_2${(Me_2*neo*Men)P}$_2$] with the numbering scheme of atoms.

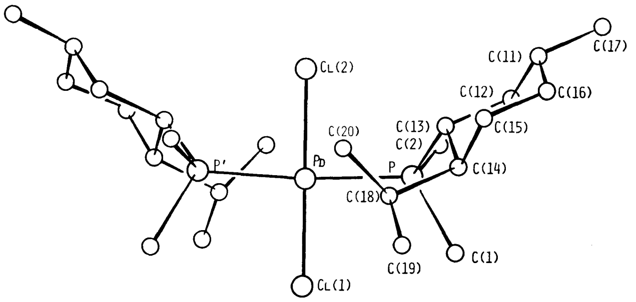

Fig. 2. Molecular structure of [$PdCl_2${(Me_2Men)P}$_2$] with the numbering scheme of atoms.

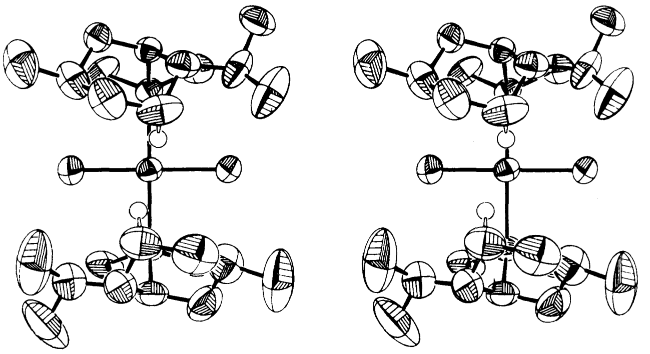

Fig. 3. A stereoscopic drawing of the [$PdCl_2${Me_2*neo*-Men)P}$_2$] molecule. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability levels.

[††] This table of observed and calculated structure factors is kept as Document No. 7806a at the Chemical Society of Japan.

[†††] This table of observed and calculated structure factors is kept as Document No. 7806b at the Chemical Society of Japan.

Table 4. Bond lengths and bond angles in $[\mathrm{PdCl_2\{(Me_2}\textit{neo}\mathrm{Men)P\}_2}]$ (e.s.d.'s in parentheses)

Bond lengths [l/Å]			
Pd-Cl (1)	2.304 (5)	Pd-Cl (2)	2.297 (5)
Pd-P(1)	2.344 (4)	Pd-P (2)	2.361 (5)
P (1) -C (1)	1.839 (18)	P (1) -C (2)	1.817 (19)
P (1) -C (13)	1.865 (14)	P (2) -C (3)	1.796 (21)
P (2) -C (4)	1.856 (18)	P (2) -C (33)	1.849 (17)
C (11) -C (12)	1.544 (25)	C (11) -C (16)	1.548 (31)
C (11) -C (17)	1.542 (31)	C (12) -C (13)	1.513 (20)
C (13) -C (14)	1.570 (21)	C (14) -C (15)	1.527 (25)
C (14) -C (18)	1.551 (24)	C (15) -C (16)	1.509 (31)
C (18) -C (19)	1.553 (30)	C (18) -C (20)	1.508 (29)
C (31) -C (32)	1.468 (32)	C (31) -C (36)	1.548 (36)
C (31) -C (37)	1.504 (41)	C (32) -C (33)	1.594 (27)
C (33) -C (34)	1.535 (25)	C (34) -C (35)	1.551 (28)
C (34) -C (38)	1.483 (38)	C (35) -C (36)	1.485 (33)
C (38) -C (39)	1.569 (47)	C (38) -C (40)	1.529 (53)
Bond angles [ϕ/°]			
C (1) -Pd-Cl (2)	176.7 (2)	Cl (1) -Pd-P (1)	89.7 (2)
Cl (1) -Pd-P (2)	90.4 (2)	Cl (2) -Pd-P (1)	89.7 (2)
Cl (2) -Pd-P (2)	89.8 (2)	P (1) -Pd-P (2)	173.3 (2)
Pd-P (1) -C (1)	112.5 (6)	Pd-P (1) -C (2)	109.8 (6)
Pd-P (1) -C (13)	124.6 (5)	Pd-P (2) -C (3)	112.0 (7)
Pd-P (2) -C (4)	110.1 (6)	Pd-P (2) -C (33)	123.8 (6)
C (13) -P (1) -C (1)	103.5 (7)	C (13) -P (1) -C (2)	102.8 (7)
C (1) -P (1) -C (2)	100.7 (8)	C (3) -P (2) -C (4)	99.8 (9)
C (33) -P (2) -C (3)	103.7 (9)	C (33) -P (2) -C (4)	104.6 (8)
C (12) -C (11) -C (16)	108.5 (16)	C (12) -C (11) -C (17)	110.9 (16)
C (16) -C (11) -C (17)	114.1 (18)	C (11) -C (12) -C (13)	113.7 (13)
C (12) -C (13) -P (1)	114.6 (10)	C (12) -C (13) -C (14)	110.3 (12)
C (14) -C (13) -P (1)	115.0 (10)	C (13) -C (14) -C (15)	108.4 (13)
C (13) -C (14) -C (18)	116.0 (13)	C (15) -C (14) -C (18)	116.2 (14)
C (14) -C (15) -C (16)	111.1 (16)	C (15) -C (16) -C (11)	115.5 (19)
C (14) -C (13) -C (19)	112.2 (15)	C (14) -C (16) -C (20)	112.1 (15)
C (19) -C (18) -C (20)	111.9 (17)	C (32) -C (31) -C (36)	107.7 (20)
C (32) -C (31) -C (37)	108.8 (21)	C (36) -C (31) -C (37)	111.0 (22)
C (31) -C (32) -C (33)	114.6 (18)	C (32) -C (33) -P (2)	110.7 (12)
C (32) -C (33) -C (14)	107.5 (14)	C (34) -C (33) -P (2)	118.4 (12)
C (33) -C (34) -C (35)	109.3 (15)	C (33) -C (34) -C (38)	114.3 (19)
C (35) -C (34) -C (38)	114.4 (19)	C (34) -C (35) -C (36)	111.6 (18)
C (35) -C (36) -C (31)	114.0 (20)	C (34) -C (38) -C (39)	112.2 (25)
C (34) -C (38) -C (40)	114.5 (27)	C (39) -C (38) -C (40)	107.6 (28)
Short atomic contact [l/Å] and angles [ϕ/°]			
Pd···H (15A)	2.71	P (1) ···Pd···H (15A)	71.8
H (15A) ···H (35A)	2.06	P (2) ···Pd···H (35A)	72.6

tural with its Ni-analog, $[\mathrm{NiCl_2\{Me_2neoMen)P\}_2}]$. A remarkable difference between these two complexes is the arrangement of the two neomenthyl groups about the co-ordination plane. The neomenthyl groups are located on the same side of the co-ordination plane in the present complex, whereas they are on opposite sides of the plane in the Ni-analog. This structural difference may affect the different catalytic activities of these two complexes in the hydrosilylation of olefins.

The co-ordination around the palladium atom is rather square-pyramidal, and deviates from the *trans*-square planar geometry; the deviations of the Pd, Cl(1), Cl(2), P(1), and P(2) atoms from the co-ordination plane are relatively large: 0.08, 0.02, 0.02, −0.04, and −0.06 Å, respectively. The Pd–Cl bond lengths are nearly equal, 2.304(5) and 2.297(5) Å (av 2.301 Å); these are the ordinary values found in *trans* Pd–Cl bonds.[15–20] The Cl(1)–Pd–Cl(2) is not linear, [176.7(2)°]. The Pd–P bond lengths are unequal, 2.344(4) and 2.361(5) Å (av 2.353 Å). These are the longest values so far reported for complexes which have the *trans* Pd–P bonds.[22–28] The P(1)–Pd–P(2) angle of 173.3(2)° significantly deviates from 180° (Fig. 5), in

TABLE 5. BOND LENGTHS AND BOND ANGLES IN $[\mathrm{PdCl_2\{Me_2Men)P\}_2}]$ (e.s.d.'s in parentheses)

Bond lengths [l/Å]			
Pd-Cl(1)	2.296(9)	Pd-Cl(2)	2.267(9)
Pd-P	2.310(5)	P-C(1)	1.839(20)
P-C(2)	1.843(20)	P-C(13)	1.863(16)
C(11)-C(12)	1.563(27)	C(12)-C(13)	1.575(24)
C(13)-C(14)	1.532(22)	C(14)-C(15)	1.552(26)
C(15)-C(16)	1.541(27)	C(16)-C(11)	1.504(26)
C(11)-C(17)	1.548(33)	C(14)-C(18)	1.610(25)
C(18)-C(19)	1.525(32)	C(18)-C(20)	1.573(33)
Bond angles [ϕ/°]			
Cl(1)-Pd-Cl(2)	180	P-Pd-P′	175.5(5)
Cl(1)-Pd-P	87.8(3)	Cl(2)-Pd-P	92.3(3)
Pd-P-C(1)	118.2(7)	Pd-P-C(2)	108.0(7)
Pd-P-C(13)	113.7(5)	C(1)-P-C(2)	101.8(9)
C(1)-P-C(13)	106.4(8)	C(2)-P-C(13)	107.6(8)
C(12)-C(11)-C(16)	111.3(15)	C(12)-C(11)-C(17)	109.2(17)
C(16)-C(11)-C(17)	111.9(17)	C(11)-C(12)-C(13)	108.7(15)
C(12)-C(13)-C(14)	109.5(13)	C(12)-C(13)-P	109.0(11)
C(14)-C(13)-P	111.4(10)	C(13)-C(14)-C(15)	108.2(14)
C(13)-C(14)-C(18)	110.9(13)	C(15)-C(14)-C(18)	110.6(14)
C(14)-C(15)-C(16)	111.2(16)	C(15)-C(16)-C(11)	109.5(15)
C(14)-C(18)-C(19)	115.0(16)	C(14)-C(18)-C(20)	109.3(16)
C(19)-C(18)-C(20)	107.5(18)		
Short atomic contact [l/Å]			
Pd···H(18)	2.78		

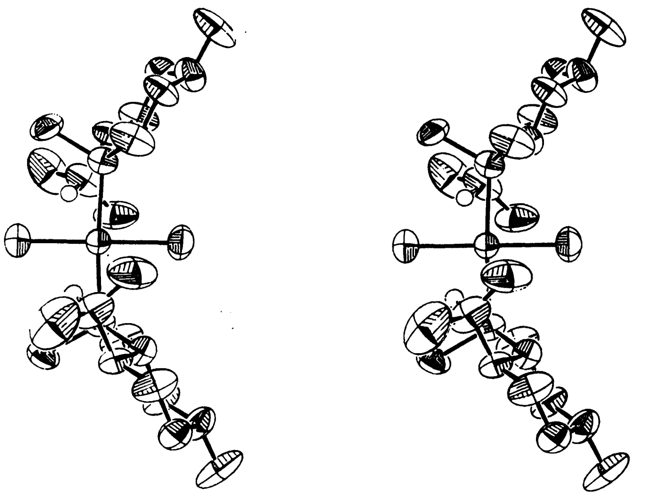

Fig. 4. A stereoscopic drawing of the $[\mathrm{PdCl_2\{(Me_2Men)P\}_2}]$ molecule.

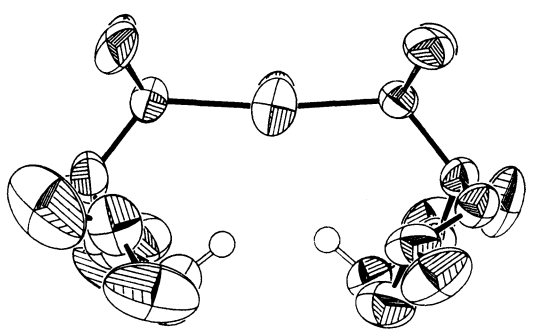

Fig. 5. $[\mathrm{PdCl_2\{(Me_2}$*neo*$\mathrm{Men)P\}_2}]$ molecule projected along the Cl(1)-Pd bond.

order to decrease the steric repulsion between two neomenthyl groups in the molecule.

The conformation about the P(1)–Pd–P(2) is approximately eclipsed (Fig. 6) in a way different from the Nickel analog. The P(1) and P(2) atoms deviates slightly away from the approximate co-ordination plane. There is no significant difference between the conformations about the P(1)–C(13) (Fig. 7) and P(2)–C(33) bonds, which are intermediates between the staggered and eclipsed conformations.

The P–C bond lengths, ranging from 1.796(21) to 1.865(14) Å, are equal within the limits of error. However, the geometries around the phosphorus atoms show distortions. The Pd–P(1)–C(13) and Pd–P(2)–C(33) angles, 124.6(5) and 123.8(6)°, deviate greatly from the tetrahedral angle, whereas the C–P–C angles are rather small [99.8(9)—104.6(8)°]. The large Pd–P(1)–C(13) and Pd–P(2)–C(33) angles are also due to the steric repulsion between the neomenthyl groups in the molecule.

The P(1)–C(13)–C(12), P(1)–C(13)–C(14), and P(2)–C(33)–C(34) angles 114.6(10), 115.0(10), and 118.4(12)°, are larger than the normal value of 109.5°. Similar distortions of the P–C–C angles, which are considered to be due to the steric hindrance between the neomenthyl and methyl groups, were observed in the Ni-analog.[11)]

$[\mathrm{PdCl_2\{(Me_2Men)P\}_2}]$. The molecule has C_2 symmetry; the two fold axis passes through the Cl(1),

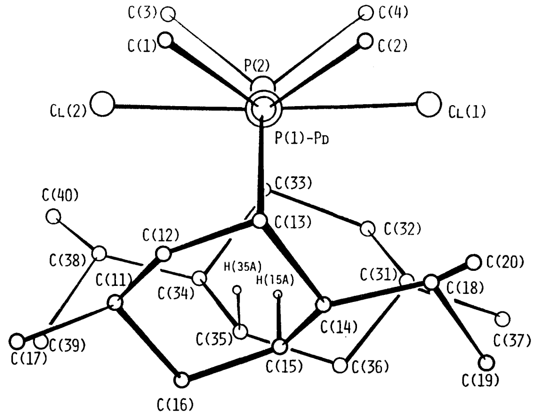

Fig. 6. The conformation about the P(1)-Pd bond in [PdCl$_2${(Me$_2$*neo*Men)P}$_2$].

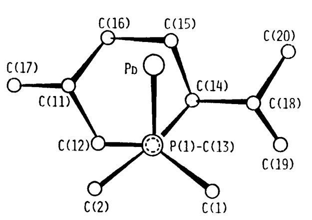

Fig. 7. The conformation about the P(1)-C(13) bond in [PdCl$_2${(Me$_2$*neo*Men)P}$_2$]. The conformation about the P(2)-C(33) bond is similar to this.

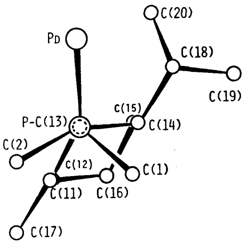

Fig. 8. The conformation about the P-C(13) bond in [PdCl$_2${(Me$_2$Men)P}$_2$].

Pd, and Cl(2) atoms which are on the co-ordination plane (Figs. 2 and 4). The geometry around the palladium atom is *trans*-square planar. The two menthyl groups are located on either side of the co-ordination plane.

The Pd–Cl bond lengths 2.296(9) and 2.267(9) Å (av 2.282 Å) are equal to those in [PdCl$_2${(Me$_2$*neo*-Men)P}$_2$]. The Pd–P bond length 2.310(5) Å is significantly shorter than those in [PdCl$_2${(Me$_2$*neo*Men)-P}$_2$]. The longer Pd–P lenghts in the latter are considered to result from the steric hindrance between the two neomenthyl groups. The P–Pd–P′ angle (175.5(5)°) is not linear.

The conformation about the P–C(13) bond (Fig. 8) is an intermediate between the staggered and eclipsed conformations, which is rather similar to the one in [NiCl$_2${Me$_2$*neo*Men)P}$_2$].

The conformation about the C(14)–C(18) bond of the menthyl group is different from those of the neomenthyl groups in [NiCl$_2${(Me$_2$*neo*Men)P}$_2$] and [PdCl$_2$-{(Me$_2$*neo*Men)P}$_2$], since the isopropyl group is rotated about 120° around the C(14)–C(18) bond. This is due to the steric interaction between the palladium atom and the isopropyl group of the menthyl group. Two hydrogen atoms, H(18) and H(18′), of the menthyl group occupy the vacant sites of the octahedron centered by the palladium and make short contacts (2.78 Å) with the palladium atom.

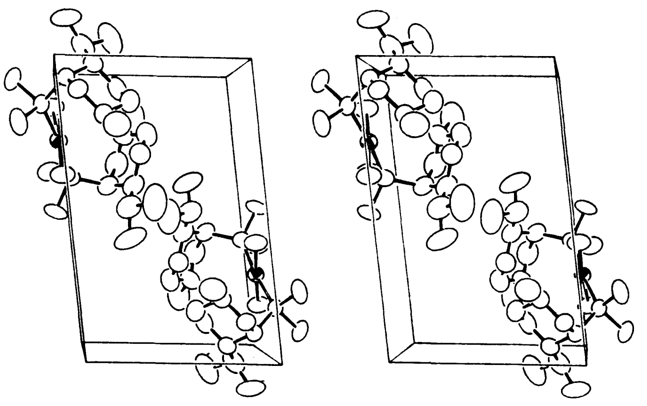

Fig. 9. A stereoscopic view of the crystal structure, [PdCl$_2${(Me$_2$*neo*Men)P}$_2$].

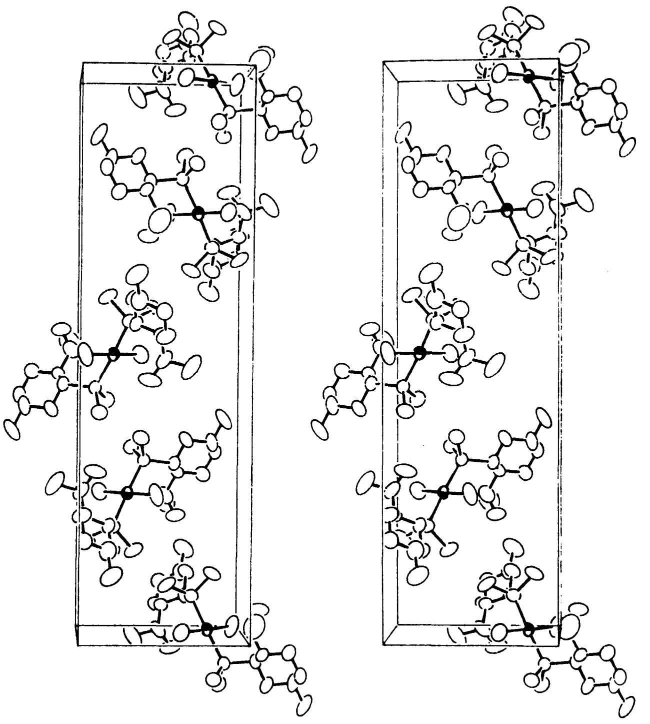

Fig. 10. A stereoscopic view of the crystal structure, [PdCl$_2${(Me$_2$Men)P}$_2$].

Crystal Structure. The Crystal structure of [PdCl$_2$-{(Me$_2$*neo*Men)P}$_2$] is given in Fig. 9. The packing of [PdCl$_2${(Me$_2$Men)P}$_2$] molecules in a unit-cell is shown in Fig. 10. There is no short intermolecular atomic contact less than 3.8 Å between non-hydrogen atoms in either crystal.

The calculations were carried out on the NEAC 2200-700 computer at Osaka University and the FACOM 230-60 at Kyoto University. Figures 3, 4, 5, 9, and 10 were drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP.[28)]

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