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The Crystal and Molecular Structure of Dichloro [*N*, *N*-dimethyl-*α*-methyl-*o*-(butylphenylphosphino)benzylamine] palladium(II)

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The crystal structure of dichloro[*N*,*N*-dimethyl-α-methyl-*o*-(butylphenylphosphino)benzylamine]palladium(II) has been determined from Mo*K*α diffraction data. The space group is $P2_1$ with $Z=2$, $a=9.255(2)$, $b=14.372(3)$, $c=8.584(1)$ Å, and $\beta=105.99(1)$°. The final *R* became 0.034 by least-squares refinement. The Pd atom has a square planar coordination of N, P, and two Cl atoms, which is considerably distorted by the intramolecular atomic repulsions. The Pd–N distance, 2.134(4) Å, which is longer than those found so far, is accompanied by a short distance 2.285(1) Å of trans Pd–Cl. A plot of Pd–Cl distance *versus* trans Pd–N distance in several Pd complexes, in which the nitrogen atom is not π-acceptor, shows a linear relationship with the correlation factor of −0.28(4).

N,*N*-Dimethyl-α-methyl-*o*-(butylphenylphosphino)-benzylamine, $(C_6H_5)P(C_4H_9)C_6H_4CH(CH_3)N(CH_3)_2$, prepared from (*S*)-α-methylbenzylamine, is a diastereomeric bidentate ligand. The rhodium complexes with the optically resolved ligand catalyze hydrogenation of certain olefins; the preferred configuration of the products depends primarily upon the chirality of the ligand.[1)] To determine the absolute configuration of the ligand, the title Pd complex was synthesized and its crystal structure was analyzed by the X-ray diffraction method.

Experimental

$Pd(C_6H_5CN)_2Cl_2$ (156 mg, 0.4 mmol) and $C_6H_5P(C_4H_9)C_6H_4CH(CH_3)N(CH_3)_2$ (124 mg, 0.4 mmol), a pure epimer, were dissolved in 15 ml of dry benzene. After 2 h stirring in N_2 atmosphere, deep yellow precipitates, 150 mg, were collected by filtration and recrystallized from a hexane–CH_2Cl_2 (1:2) solution. Calcd for $C_{20}H_{28}Cl_2NPPd$: C, 48.95; H, 5.75; N, 2.85%. Found: C, 48.41; H, 5.86; N, 2.84%; mp 196—197 °C (dec); $[\alpha]_D^{20}$ −202° (in CH_2Cl_2).

TABLE 1. CRYSTAL DATA

$Pd[C_6H_5P(C_4H_9)C_6H_4CH(CH_3)N(CH_3)_2]Cl_2$	
F.W. 490.7	
Monoclinic, $P2_1$ (systematic absence 0*k*0 $k=2n+1$)	
$a=9.255(2)$ Å	$Z=2$
$b=14.372(3)$	$D_m=1.48$ g cm^{-3} (by flotation)
$c=8.584(1)$	$D_x=1.485$ g cm^{-3}
$\beta=105.99(1)$°	μ (Mo*K*α) = 12.4 cm^{-1}

A crystal, 0.15×0.3×0.5 mm in size, was used for data collection on a Rigaku computer-controlled four-circle diffractometer, using graphite-monochromated Mo*K*α radiation ($\lambda=0.71069$ Å). The cell parameters were obtained by least-squares calculation with 22 high-angle reflexions. The crystal data are summarized in Table 1. Intensities were measured in ω-2θ scan mode with scan width of 1.5° (in 2θ) plus α_1-α_2 divergence at scan speed 4° (in 2θ) min^{-1}, using a large receiving slit 5.5×5.5 mm. By this scan technique, intensity profile of each reflexion showed a single peak, although the specimen gave twinned spots on Weissenberg photographs owing to a crack within it. Five reference reflexions, monitored after every 50 reflexions, indicated no significant intensity variations throughout the experiment. Out of 2616 independent reflexions in the range $2\leq 2\theta\leq 55$°, 88 weak reflexions which gave the counts under background were considered as zero-reflexions. The data were corrected for Lorentz and polarization factors but not for absorption effects. Bijvoet pairs of reflexions were collected on Weissenberg photographs using Cu*K*α radiation.

Structure Determination

The structure was solved by the heavy-atom method and its atomic parameters were refined by block-diagonal least-squares technique. All the hydrogen atoms, found on a difference map, were included. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, with $w=1/(\sigma_p^2+qF_o^2)$, where σ_p is due to counting statistics and q is 1.02×10^{-5} derived from the variation of the monitored reflexions.[2)] The zero-reflexions were included in least-squares calculation by assuming $F_o=F_{\rm lim}$ and $w=w(F_{\rm lim})$, where $F_{\rm lim}$ is 3.198, an observational threshold value, but those for which $|F_c|<F_{\rm lim}$ were omitted. The final *R* value was 0.034; the maximum shift of coordinates in the last cycle was 0.10σ for Pd, Cl, and P, 0.15σ for N, 0.44σ for C, and 1σ for H atoms. The absolute configuration was determined from a comparison of intensities of 22 Bijvoet pairs. Atomic parameters are listed in Table 2.[3)] A stereoscopic view of the molecule is shown in Fig. 1, and bond distances and angles in Fig. 2. Atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[4)]

Results and Discussion

As shown in Fig. 1, the Pd atom has a considerably distorted square planar coordination of the N, P, and two Cl atoms. The chlorine atoms are cis as required by the geometry of the bidentate chelating ligand. The absolute configuration of C(7) is sinister (*S*) and that of P is rectus (*R*). The methyl group C(9) and the butyl group are located above the coordination plane, while the methyl group C(8) lies below it. If the rhodium complexes[1)] take the same structure, such an arrangement might furnish the structural basis for the mechanism of the asymmetric hydrogenation. When the prochiral substrate approaches Rh above or below the coordination plane to form a π-complex, the steric constraint could determine the preferable enantiotropic face of the substrate.

The two Pd–Cl bond distances differ significantly to

TABLE 2. FRACTIONAL COORDINATES ($\times 10^5$ except for H and $\times 10^4$ for H) AND THERMAL PARAMETERS ($\times 10^5$ except for H)

The anisotropic temperature factor has the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Standard deviations are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	99449(4)	25000(5)	16950(3)	801(3)	520(2)	702(3)	112(8)	231(5)	−192(8)
Cl(1)	124579(13)	30288(12)	20426(15)	759(16)	861(11)	1260(20)	−139(22)	303(29)	−149(25)
Cl(2)	102713(14)	27693(10)	43939(12)	1181(17)	849(14)	593(14)	−87(22)	141(25)	−449(21)
P	75005(12)	23074(10)	15126(12)	758(14)	356(9)	598(13)	29(18)	185(22)	−87(18)
N	96901(39)	21581(29)	−7859(41)	871(52)	625(34)	984(57)	−13(62)	744(90)	−385(65)
C(1)	69109(49)	19602(35)	−18214(49)	973(67)	437(30)	747(65)	−135(75)	81(107)	−295(74)
C(2)	63386(44)	23003(35)	−5771(44)	866(55)	401(37)	685(54)	−157(73)	52(89)	72(72)
C(3)	48952(48)	26622(39)	−9506(50)	908(59)	447(41)	1105(64)	−60(79)	251(100)	222(86)
C(4)	39903(51)	27006(37)	−25415(58)	908(64)	470(44)	1547(79)	−248(77)	−622(113)	442(90)
C(5)	45535(53)	23563(50)	−37679(51)	1610(77)	508(40)	940(63)	−631(107)	−677(109)	148(98)
C(6)	59599(57)	20084(39)	−34239(52)	1477(84)	546(34)	754(68)	−321(88)	−107(122)	−304(81)
C(7)	84047(57)	15235(40)	−15367(52)	1429(84)	666(40)	694(69)	48(94)	544(123)	−639(86)
C(8)	85044(67)	5845(44)	−7573(69)	1935(109)	585(41)	1740(107)	353(112)	379(170)	−688(110)
C(9)	95094(67)	30608(49)	−16651(55)	2104(107)	973(49)	843(76)	−1146(120)	1254(150)	−109(104)
C(10)	110990(63)	16860(56)	−9063(69)	1338(94)	1304(64)	1673(105)	416(127)	1056(165)	−1365(139)
C(11)	69819(53)	12867(34)	24871(51)	1234(75)	319(28)	834(68)	−79(75)	470(116)	−271(72)
C(12)	80743(65)	7578(39)	35680(63)	1808(98)	408(34)	1450(94)	311(94)	645(154)	251(92)
C(13)	76495(76)	222(44)	43787(70)	2944(142)	458(38)	1866(114)	513(122)	1915(208)	347(113)
C(14)	61718(86)	−1653(44)	41526(75)	3944(179)	420(37)	1848(117)	−518(133)	2902(245)	−82(108)
C(15)	50856(70)	3288(47)	30864(68)	2515(128)	634(41)	1855(111)	−1180(130)	1847(196)	−377(118)
C(16)	54883(62)	10662(41)	22585(62)	1532(90)	541(38)	1293(88)	−241(95)	596(142)	172(94)
C(17)	67935(49)	32689(35)	24650(50)	881(65)	412(30)	882(67)	−16(73)	547(108)	−159(75)
C(18)	69954(60)	42268(37)	17770(63)	1440(85)	386(32)	1522(92)	−42(85)	1228(146)	−100(90)
C(19)	65642(64)	50198(41)	27250(74)	1753(104)	413(35)	2520(128)	302(100)	1529(187)	−120(117)
C(20)	76730(83)	51316(53)	43495(82)	3116(163)	804(56)	2594(148)	247(154)	1096(249)	−1619(158)

/Å²	x	y	z	B/Å²		x	y	z	B/Å²
H(3)	4470(44)	2924(29)	−122(49)	1.4(1.0)	H(19B)	5454(48)	4946(34)	2691(53)	1.9(1.1)
H(4)	3051(45)	2971(30)	−2747(47)	1.1(1.0)	H(7)	8519(56)	1423(40)	−2382(64)	4.0(1.4)
H(5)	4012(44)	2368(42)	−4809(48)	3.1(1.2)	H(20A)	7444(52)	4644(36)	5131(58)	3.1(1.3)
H(6)	6417(46)	1795(33)	−4171(51)	1.6(1.1)	H(20B)	7541(53)	5628(39)	4653(59)	3.9(1.4)
H(12)	9085(43)	905(29)	3766(48)	0.8(1.0)	H(20C)	8672(61)	5015(42)	4346(66)	5.1(1.6)
H(13)	8448(55)	−297(36)	5155(60)	3.2(1.3)	H(8A)	9372(56)	264(41)	−762(61)	4.7(1.5)
H(14)	5900(56)	−583(41)	4608(62)	4.3(1.5)	H(8B)	7798(48)	232(34)	−1099(52)	2.4(1.2)
H(15)	3988(54)	296(41)	2902(58)	3.8(1.4)	H(8C)	8415(48)	659(33)	199(51)	1.9(1.1)
H(16)	4818(44)	1459(31)	1632(47)	1.1(1.0)	H(9A)	10421(67)	3474(50)	−1050(75)	6.6(1.8)
H(17A)	5665(44)	3145(31)	2379(46)	0.7(0.9)	H(9B)	8396(52)	3537(36)	−1768(55)	2.7(1.2)
H(17B)	7219(41)	3240(30)	3372(44)	0.4(0.9)	H(9C)	9362(52)	2903(33)	−2883(54)	2.6(1.2)
H(18A)	8002(41)	4238(28)	1895(45)	0.0(0.8)	H(10A)	11934(48)	2094(33)	−454(53)	2.6(1.2)
H(18B)	6372(44)	4271(31)	615(49)	1.0(1.0)	H(10B)	11058(63)	1636(44)	−2028(67)	5.2(1.6)
H(19A)	6489(52)	5548(38)	2144(57)	3.3(1.3)	H(10C)	11276(55)	1140(37)	−191(60)	3.7(1.4)

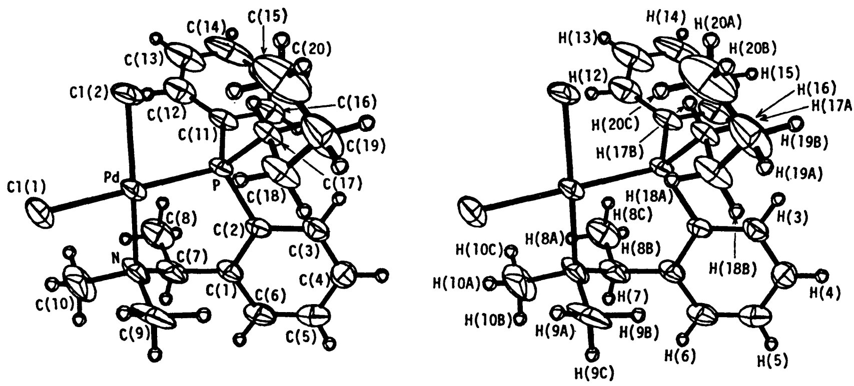

Fig. 1. Stereoscopic drawing of the molecule of dichloro[*N*,*N*-dimethyl-α-methyl-*o*-(butylphenylphosphino)benzylamine]palladium(II). The non-hydrogen atoms are represented by their thermal ellipsoids with 50% probability, while the hydrogen atoms are represented by arbitrary spheres.

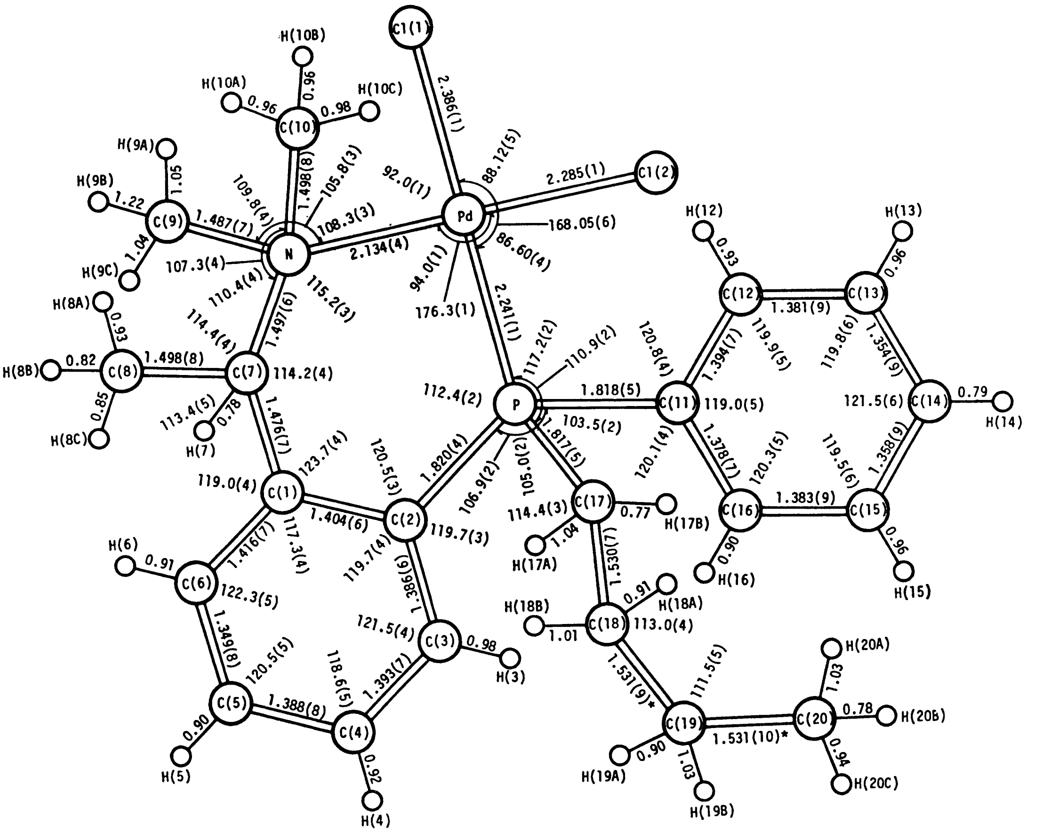

Fig. 2. Bond distances (l/Å) and bond angles (ϕ/°), with their e.s.d.'s in parentheses. Starred values are corrected for riding motion. Standard deviations of C–H bonds are 0.06 Å, and bond angles involving hydrogen atom are nearly tetrahedral or trigonal angle.

each other. The greater length of Pd–Cl(1) (trans to Pd–P) than Pd–Cl(2) (trans to Pd–N) is consistent with the observation that the Pd–Cl bond length decreases as the electronegativity of the trans atom increases.[5] The Pd–Cl(1) distance, 2.386(1) Å, is in the range expected for a Pd–Cl bond trans to Pd–P. On the other hand, the Pd–Cl(2) distance, 2.285(1) Å, is shorter and the Pd–N distance, 2.134(4) Å, is longer than those found so far in Cl–Pd–N systems. Figure 3 shows a plot of Pd–Cl distance *versus* trans Pd–N distance for several Pd complexes, in which the nitrogen atom is not a π-acceptor. Except for $Pd(NH_2CH_2CH_2NH_2)Cl_2$, a linear relationship is observed, the correlation factor is −0.28(4). This observation could be explained in terms of electrostatic interaction, as proposed for Cl–Pt–C system by Manojlovič-Muir and Muir.[11] The present Pd–N bond is lengthened by the geometrical constraints mentioned later. The "bend" deformation of the metal d_π orbital by electrostatic repulsion from the σ orbital of Pd–N bond would be small, so that the trans Cl(2) could approach the metal. The value of the correlation factor may be reasonable, since the repulsions from the deformed d_π is mitigated at a long distance of Pd–Cl(2).

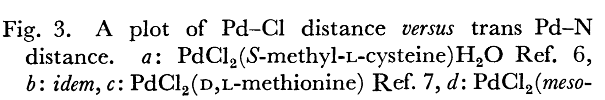

Fig. 3. A plot of Pd–Cl distance *versus* trans Pd–N distance. *a*: $PdCl_2(S\text{-methyl-L-cysteine})H_2O$ Ref. 6, *b*: *idem*, *c*: $PdCl_2(\text{D,L-methionine})$ Ref. 7, *d*: $PdCl_2(\textit{meso}\text{-}2,3\text{-diaminobutane})$ Ref. 8, *e*: *idem*, *f*: $PdCl_2(\text{ethylenediamine})$ Ref. 9, *g*: $PdCl_2(\text{tetrahydrogen-ethylenediaminetetraacetate})5H_2O$ Ref. 10, *h*: present work.

The geometrical constaint is indicated by the deviations of atoms from the mean plane through the four coordinating atoms, Pd −0.172, P 0.044, Cl(1) 0.056, Cl(2) −0.050, and N −0.423 Å. The deviation of P is due to repulsions from C(7) and C(8), and that of Cl(1) is caused by C(10); the close contacts are given in Fig. 4. At the same time these repulsions make the N–Pd–Cl(1) and N–Pd–P angles expand, so that P–Pd–Cl(1) deviates from a line. In addition the bond angles involving C(8), C(8)–C(7)–N and C(8)–C(7)–C(1), expand owing to the close contact between P and C(8). The 6-membered chelate ring is also constrained to enlarge the angles, P–Pd–N, Pd–N–C(7), N–C(7)–C(1), C(7)–C(1)–C(2), and Pd–P–C(2), from their normal values. The torsion angles about the C(17)–C(18) and C(18)–C(19) bonds are 186.8(4) and 70.8(6)°, respectively. The three P–C bond distances are 1.817—1.820 Å. The C–N bond distance is 1.494 Å in average. The bond lengths are apparently shortened

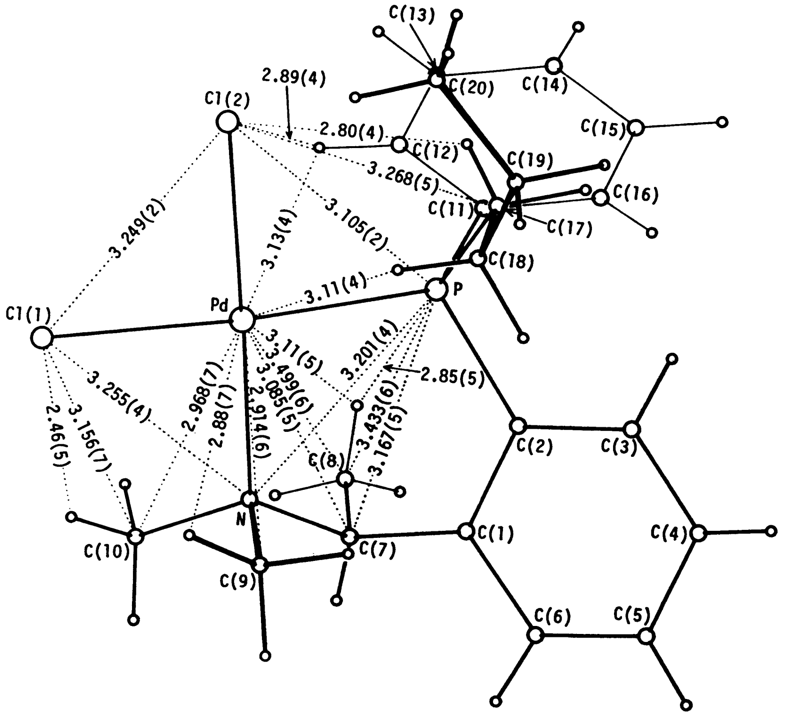

Fig. 4. Close contacts (in Å) around the palladium atom.

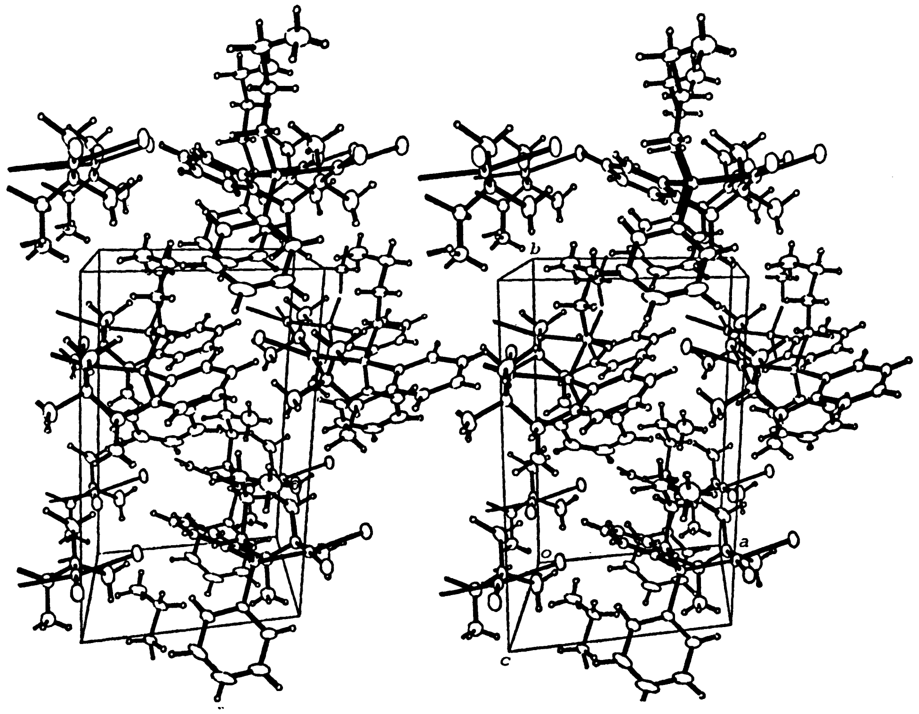

Fig. 5. Stereoscopic diagram showing the molecular packing.

at the periphery of the molecule by the large thermal motions.

As shown in Fig. 5, the complex molecules are packed by van der Waals interactions. A survey of the intermolecular distances indicates no abnormal contacts.

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