105. Crystal Structures of the (–)-DIOP Complexes of Nickel, Palladium and Platinum Dichloride

by **Volker Gramlich** and **Giambattista Consiglio**

Swiss Federal Institute of Technology, Department of Industrial and Engineering Chemistry, Universitätsstrasse 6, 8092 Zürich, Switzerland

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Summary

The crystal structures of $PdCl_2$[(–)-DIOP], $PtCl_2$[(–)-DIOP] and of $NiCl_2$-[(–)-DIOP] have been determined by X-ray analysis and refined by least-squares methods [(–)-DIOP = (–)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane]. The coordination around the nickel atom is tetrahedral, the coordination around palladium and platinum is square planar. The unit cell of the palladium complex contains two non-equivalent molecules with different conformations of the seven-membered chelate ring involving the metal and the two phosphorus atoms. $PtCl_2$[(–)-DIOP] is isostructural with the corresponding palladium complex.

Since its first preparation by *Dang & Kagan* [1] (–)-DIOP [(–)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane] has been extensively [2] used as a chiral ligand in transition metal catalyzed asymmetric reactions.

Thus, rhodium complexes have been used for asymmetric hydrogenation [3], hydroformylation [4] and hydrosilylation [5]; ruthenium complexes for asymmetric hydrogenation [6] [7]; platinum complexes for asymmetric hydroformylation [8]; palladium complexes for asymmetric cross-coupling reactions [9] and hydrocarboxylation [10]; nickel complexes for asymmetric cross-coupling reaction [11]. The efficiency of DIOP as asymmetric ligand of different metal atoms in various catalytic reactions has been ascribed to the property that the two phosphorus atoms become asymmetric centres on coordination to the metal atoms [12] and to the capacity of chelation of the diphosphine [3]: investigations of the conformation of this ligand in metal complexes in solution [13] [14] and in the solid state [15] [16] are therefore significant.

We report in this paper the crystal structures of some catalyst precursors, namely of $PdCl_2$[(–)-DIOP], $PtCl_2$[(–)-DIOP] as well as a refinement of the previously [15] reported structure of $NiCl_2$[(–)-DIOP].

Experimental Part

$PdCl_2$[(–)-DIOP] was prepared by stirring equimolar amounts of (–)-DIOP and $PdCl_2(PhCN)_2$ in ether for 24 h. After filtration, the crude product was dissolved in methylene chloride and reprecipitated by slow addition of heptane. Methylene chloride was then added to obtain a clear

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solution, which was allowed to evaporate in air. The crystalline pale yellow material was filtered off, washed with pentane and dried under vacuum; m.p. 278-79° (dec.).

$C_{31}H_{32}P_2O_2 \cdot PdCl_2$ (676.14) Calc. C 55.09 H 4.77 Cl 10.49% Found C 54.71 H 4.82 Cl 10.02%

A crystal with approximate dimensions $0.15 \times 0.20 \times 0.35$ mm^3 was selected for X-ray analysis. The unit cell is triclinic, space group $P1$, $a = 10.345$ Å, $b = 11.144$ Å, $c = 14.654$ Å (all ± circa 0.005 Å), $\alpha = 98.03°$, $\beta = 85.43°$, $\gamma = 118.18°$, and contains two molecules. Intensity measurements were made with a Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator) for 5177 reflections, of which 4556 were counted as significant observations ($I > 3\sigma(I)$). No absorption correction was applied.

The position of the Pd-atoms and subsequently of the ligand atoms could easily be read from *Patterson* and *Fourier* maps. *Stewart*'s X-ray system [17] was used for all calculations.

The Pt-complex was prepared and recrystallized following the same method as for the Pd-complex; m.p. 283° (dec.).

$C_{31}H_{32}P_2O_2 \cdot PtCl_2$	Calc. C 48.69	H 4.22	Cl 9.27	P 8.10%
(764.67)	Found „ 48.40	„ 4.01	„ 9.54	„ 8.01%

Space group $P1$, $a = 10.381$ Å, $b = 11.127$ Å, $c = 14.643$ Å (all ± circa 0.008 Å) $\alpha = 98.20°$, $\beta = 85.32°$, $\gamma = 118.30°$. 5177 reflections were measured, 4502 observed. $PtCl_2$[(−)-DIOP] and $PdCl_2$[(−)-DIOP] are isomorphous.

Ni-complex. The experimental conditions and the structure determination of this complex have been reported in a preliminary communication [15] (space group $P2_12_12_1$, $a = 10.785$ Å, $b = 14.441$ Å, $c = 19.396$ Å, 4 molecules per unit cell).

Structure Refinement. Group refinement for the phenyl rings was chosen in order to avoid excessive computer time. The idealized geometry of the phenyl rings with C−C bond lengths of 1.395 Å and angles of 120° was generated with the distance least-squares method [18] starting from the coordinates obtained after five cycles of isotropic block diagonal least squares refinement. The atoms of the phenyl groups were subsequently refined in the isotropic temperature factor mode, the remaining atoms were refined anisotropically. Calculated H-atoms with an assumed C−H bond length of 1.1 Å were introduced in the final cycles but not refined. Weights $w = \sigma^{-2}(F_0)$ from counting statistics were used for these final cycles. Scattering factors were taken from the analytical interpolation functions given by *Cromer & Mann* [19]. Anomalous dispersion corrections [20] were applied for Pt, Pd, Ni, P and Cl. The final conventional R-values for the Pd-, Pt- and Ni-complex were 4.5%, 6.7% and 7.5% respectively.

Results and Discussion. - Atomic coordinates with estimated standard deviations in units of the last digit are given in *Tables 1-3*. Bond lengths and angles are shown in the schematic drawings of *Figures 1-3*, additional bond angles are listed in *Table 4*. The orientation of the phenyl groups is specified by the dihedral angle between their planes and the planes containing metal, P and C *(Table 5)*. *Tolman* has reported in a review article [21] that graphitelike interactions (~ 3.4 Å spacings) tend to occur between phenyl groups in phenyl phosphines. *Table 5* shows that the planes of the two phenyl groups at each P-atom are roughly perpendicular, but that pairs of phenyl groups belonging to different P-atoms are roughly parallel. The shortest contacts between C-atoms of the nearly parallel phenyl groups are 3.3 Å and 3.7 Å for the Ni-complex. For these graphite-like interactions to occur, the ligands must distort severely from their highest possible symmetry (C_2) which is never observed *(cf. Fig. 4* and *5)*.

No unusual thermal parameters or bond distances have been observed. Nevertheless, the values obtained for the P-phenyl distances might be systematically influenced by the group refinement of the phenyl groups [27]. The Cl-Ni-Cl bond angle deviates largely from the ideal tetrahedral value. *Garton et al.* [22] observed a

Table 1. *Fractional coordinates of* $PdCl_2$*[(−)-DIOP]*, (a) *molecule I*, (b) *molecule II*. Standard deviations (in brackets) are given in units of the last digit.

Table 1a

	x	y	z
Pd	0.0	0.0	0.0
Cl(1)	0.9701(3)	0.1738(3)	0.0933(2)
Cl(2)	−0.2569(3)	−0.1321(3)	−0.0050(2)
P(1)	0.2478(3)	0.1309(3)	0.0102(2)
P(2)	0.0023(3)	0.8142(3)	0.9162(2)
O(1)	0.2871(8)	0.9048(7)	0.7173(5)
O(2)	0.4326(8)	0.1357(7)	0.7514(5)
C(1)	0.373(2)	0.076(1)	0.835(1)
C(2)	0.349(2)	0.184(1)	0.901(1)
C(3)	0.182(1)	0.838(1)	0.870(1)
C(4)	0.234(1)	0.948(1)	0.803(1)
C(5)	0.387(2)	0.027(1)	0.675(1)
C(6)	0.306(2)	0.056(2)	0.606(1)
C(7)	0.521(2)	0.013(2)	0.637(1)
C(1)-Ø(11)	0.310(3)	0.300(3)	0.081(2)
C(2)-Ø(11)	0.328(3)	0.414(3)	0.041(2)
C(3)-Ø(11)	0.379(3)	0.542(3)	0.094(2)
C(4)-Ø(11)	0.425(3)	0.558(3)	0.184(2)
C(5)-Ø(11)	0.416(3)	0.446(3)	0.222(2)
C(6)-Ø(11)	0.348(3)	0.315(3)	0.173(2)
C(1)-Ø(12)	0.337(3)	1.051(3)	0.064(2)
C(2)-Ø(12)	0.487(3)	1.094(3)	0.054(2)
C(3)-Ø(12)	0.552(3)	1.035(3)	0.100(2)
C(4)-Ø(12)	0.463(3)	0.924(3)	0.149(2)
C(5)-Ø(12)	0.314(3)	0.885(3)	0.162(2)
C(6)-Ø(12)	0.250(3)	0.944(3)	0.116(2)
C(1)-Ø(21)	0.943(3)	0.667(3)	−0.020(2)
C(2)-Ø(21)	1.043(3)	0.633(3)	0.013(2)
C(3)-Ø(21)	0.992(3)	0.516(3)	0.058(2)
C(4)-Ø(21)	0.842(3)	0.438(3)	0.075(2)
C(5)-Ø(21)	0.743(3)	0.478(3)	0.048(2)
C(6)-Ø(21)	0.793(3)	0.590(3)	−0.003(2)
C(1)-Ø(22)	0.899(3)	0.756(3)	0.809(2)
C(2)-Ø(22)	0.873(3)	0.628(3)	0.764(2)
C(3)-Ø(22)	0.813(3)	0.586(3)	0.676(2)
C(4)-Ø(22)	0.772(3)	0.668(3)	0.636(2)
C(5)-Ø(22)	0.788(3)	0.792(3)	0.684(2)
C(6)-Ø(22)	0.857(3)	0.838(3)	0.769(2)

Table 1b

	x	y	z
Pd	0.2608(1)	0.2791(1)	0.4537(1)
Cl(1)	0.5155(3)	0.4083(3)	0.4686(2)
Cl(2)	0.2941(3)	0.1041(3)	0.3674(2)
P(1)	0.2424(3)	0.4608(3)	0.5408(2)
P(2)	0.0169(3)	0.1419(3)	0.4415(2)
O(1)	0.9167(9)	0.1542(7)	0.7179(5)
O(2)	−0.0212(9)	0.3812(7)	0.7301(5)
C(1)	0.962(2)	0.328(1)	0.636(1)
C(2)	1.062(2)	0.445(1)	0.582(1)
C(3)	0.931(2)	0.094(1)	0.556(1)
C(4)	0.992(2)	0.208(1)	0.634(1)
C(5)	0.938(2)	0.268(2)	0.785(1)
C(6)	1.060(2)	0.302(2)	0.847(1)
C(7)	0.794(2)	0.242(2)	0.833(1)
C(1)-Ø(11)	0.346(3)	0.519(3)	0.647(2)
C(2)-Ø(11)	0.363(3)	0.639(3)	0.701(2)
C(3)-Ø(11)	0.431(3)	0.677(3)	0.786(2)
C(4)-Ø(11)	0.486(3)	0.598(3)	0.816(2)
C(5)-Ø(11)	0.463(3)	0.474(3)	0.765(2)
C(6)-Ø(11)	0.398(3)	0.438(3)	0.679(2)
C(1)-Ø(12)	0.322(3)	0.616(3)	0.479(2)
C(2)-Ø(12)	0.232(3)	0.668(3)	0.455(2)
C(3)-Ø(12)	0.290(3)	0.782(3)	0.407(2)
C(4)-Ø(12)	0.439(3)	0.844(3)	0.383(2)
C(5)-Ø(12)	0.530(3)	0.796(3)	0.410(2)
C(6)-Ø(12)	0.470(3)	0.678(3)	0.454(2)
C(1)-Ø(21)	0.924(3)	0.220(3)	0.393(2)
C(2)-Ø(21)	0.774(3)	0.173(3)	0.410(2)
C(3)-Ø(21)	0.702(3)	0.235(3)	0.375(2)
C(4)-Ø(21)	0.776(3)	0.336(3)	0.316(2)
C(5)-Ø(21)	0.927(3)	0.384(3)	0.300(2)
C(6)-Ø(21)	0.999(3)	0.322(3)	0.335(2)
C(1)-Ø(22)	0.940(3)	0.976(3)	0.375(2)
C(2)-Ø(22)	0.912(3)	0.961(3)	0.282(2)
C(3)-Ø(22)	0.866(3)	0.843(3)	0.229(2)
C(4)-Ø(22)	0.834(3)	0.719(3)	0.272(2)
C(5)-Ø(22)	0.866(3)	0.734(3)	0.365(2)
C(6)-Ø(22)	0.927(3)	0.864(3)	0.415(2)

similar effect in the $NiCl_2(Ph_3P)_2$ molecule where the Cl-Ni-Cl angle is 123° and the Ni-Cl distance is 2.27 Å. *Jarvis et al.* [23] explained the large Br-Ni-Br angle of 126° in the corresponding bromine complex as a consequence of steric repulsion. Similar arguments would be unsatisfactory for the Cl-containing complex where the Cl-Cl distance is 3.99 Å for both $NiCl_2$[(−)-DIOP] and $NiCl_2(Ph_3P)_2$, nearly 0.4 Å larger than the *van der Waals* diameter of Cl. The P-Ni-P angle of 103° is

Table 2. *Fractional coordinates of* $PtCl_2$*[(−)-DIOP]*, (a) *molecule I*, (b) *molecule II*. Standard deviations (in brackets) are given in units of the last digit.

Table 2a

	x	y	z
Pt	0.0	0.0	0.0
Cl(1)	0.9687(5)	0.1720(5)	0.0929(4)
Cl(2)	−0.2557(5)	−0.1294(5)	−0.0023(4)
P(1)	0.2469(5)	0.1292(4)	0.0114(3)
P(2)	0.0001(5)	0.8148(5)	0.9162(3)
O(1)	0.289(2)	0.906(2)	0.722(1)
O(2)	0.427(2)	0.134(2)	0.752(1)
C(1)	0.370(2)	0.079(2)	0.837(1)
C(2)	0.352(2)	0.185(2)	0.904(1)
C(3)	0.182(2)	0.839(2)	0.872(1)
C(4)	0.232(2)	0.947(2)	0.801(1)
C(5)	0.388(2)	0.024(2)	0.677(2)
C(6)	0.313(4)	0.061(4)	0.604(2)
C(7)	0.521(4)	0.013(4)	0.641(2)
C(1)-Ø(11)	0.310(5)	0.299(5)	0.084(3)
C(2)-Ø(11)	0.333(5)	0.413(5)	0.042(3)
C(3)-Ø(11)	0.386(5)	0.542(5)	0.094(3)
C(4)-Ø(11)	0.428(5)	0.559(5)	0.185(3)
C(5)-Ø(11)	0.414(5)	0.447(5)	0.225(3)
C(6)-Ø(11)	0.344(5)	0.315(5)	0.177(3)
C(1)-Ø(12)	0.334(5)	1.057(5)	0.070(3)
C(2)-Ø(12)	0.484(5)	1.100(5)	0.058(3)
C(3)-Ø(12)	0.548(5)	1.039(5)	0.102(3)
C(4)-Ø(12)	0.461(5)	0.926(5)	0.149(3)
C(5)-Ø(12)	0.312(5)	0.887(5)	0.164(3)
C(6)-Ø(12)	0.247(5)	0.948(5)	0.120(3)
C(1)-Ø(21)	0.937(5)	0.666(5)	−0.021(3)
C(2)-Ø(21)	1.038(5)	0.638(5)	0.018(3)
C(3)-Ø(21)	0.988(5)	0.521(5)	0.063(3)
C(4)-Ø(21)	0.838(5)	0.438(5)	0.075(3)
C(5)-Ø(21)	0.738(5)	0.472(5)	0.043(3)
C(6)-Ø(21)	0.787(5)	0.583(5)	−0.008(3)
C(1)-Ø(22)	0.896(5)	0.755(5)	0.813(3)
C(2)-Ø(22)	0.873(5)	0.630(5)	0.765(3)
C(3)-Ø(22)	0.812(5)	0.590(5)	0.677(3)
C(4)-Ø(22)	0.766(5)	0.673(5)	0.640(3)
C(5)-Ø(22)	0.780(5)	0.793(5)	0.691(3)
C(6)-Ø(22)	0.850(5)	0.838(5)	0.776(3)

Table 2b

	x	y	z
Pt	0.2557(1)	0.2790(1)	0.4554(1)
Cl(1)	0.5122(5)	0.4041(5)	0.4687(4)
Cl(2)	0.2928(5)	0.1049(5)	0.3673(4)
P(1)	0.2415(5)	0.4596(5)	0.5419(3)
P(2)	0.0158(5)	0.1423(5)	0.4443(3)
O(1)	0.913(2)	0.154(2)	0.717(1)
O(2)	−0.024(2)	0.384(2)	0.735(2)
C(1)	0.963(2)	0.329(2)	0.637(1)
C(2)	1.060(2)	0.446(2)	0.581(2)
C(3)	0.932(2)	0.095(2)	0.559(1)
C(4)	0.988(2)	0.209(2)	0.637(1)
C(5)	0.935(2)	0.270(2)	0.785(2)
C(6)	1.065(3)	0.307(3)	0.846(2)
C(7)	0.797(3)	0.244(3)	0.836(2)
C(1)-Ø(11)	0.342(5)	0.519(5)	0.651(3)
C(2)-Ø(11)	0.361(5)	0.642(5)	0.701(3)
C(3)-Ø(11)	0.428(5)	0.684(5)	0.786(3)
C(4)-Ø(11)	0.481(5)	0.605(5)	0.821(3)
C(5)-Ø(11)	0.456(5)	0.479(5)	0.773(3)
C(6)-Ø(11)	0.392(5)	0.438(5)	0.686(3)
C(1)-Ø(12)	0.322(5)	0.618(5)	0.482(3)
C(2)-Ø(12)	0.233(5)	0.671(5)	0.460(3)
C(3)-Ø(12)	0.290(5)	0.782(5)	0.408(3)
C(4)-Ø(12)	0.437(5)	0.840(5)	0.379(3)
C(5)-Ø(12)	0.528(5)	0.790(5)	0.405(3)
C(6)-Ø(12)	0.469(5)	0.674(5)	0.453(3)
C(1)-Ø(21)	0.922(5)	0.227(5)	0.401(3)
C(2)-Ø(21)	0.772(5)	0.176(5)	0.417(3)
C(3)-Ø(21)	0.696(5)	0.232(5)	0.379(3)
C(4)-Ø(21)	0.768(5)	0.330(5)	0.318(3)
C(5)-Ø(21)	0.919(5)	0.382(5)	0.303(3)
C(6)-Ø(21)	0.994(5)	0.327(5)	0.341(3)
C(1)-Ø(22)	0.955(5)	0.977(5)	0.380(3)
C(2)-Ø(22)	0.922(5)	0.964(5)	0.287(3)
C(3)-Ø(22)	0.871(5)	0.837(5)	0.234(3)
C(4)-Ø(22)	0.842(5)	0.721(5)	0.275(3)
C(5)-Ø(22)	0.880(5)	0.735(5)	0.366(3)
C(6)-Ø(22)	0.945(5)	0.864(5)	0.417(3)

significantly smaller than the tetrahedral angle. A discussion of the distortion of Ni(II) tetrahedra in terms of ligand field theory has been given by *Venanzi* [24].

The packing diagrams of the Pt-complex *(Fig. 6)* and of the Pd-complex reveal that the two molecules I and II are roughly related by a center of symmetry. The steric arrangements of the atoms around the metal appear mirror related if the two molecules are rotated to show the five-membered rings in parallel orientation. This

Table 3. *Fractional coordinates of NiCl$_2$[(−)-DIOP].* Standard deviations (in brackets) are given in units of the last digit.

	x	y	z		x	y	z
Ni	0.7030(2)	−0.0017(2)	−0.1710(1)	C(1)-Ø(12)	0.630(3)	0.225(3)	−0.124(2)
Cl(1)	0.8784(3)	−0.0058(3)	−0.1128(2)	C(2)-Ø(12)	0.712(3)	0.211(3)	−0.069(2)
Cl(2)	0.6513(4)	−0.0732(3)	−0.2672(2)	C(3)-Ø(12)	0.706(3)	0.267(3)	−0.011(2)
P(1)	0.6420(3)	0.1472(2)	−0.1970(2)	C(4)-Ø(12)	0.616(3)	0.337(3)	−0.006(2)
P(2)	0.5460(3)	−0.0530(2)	−0.1017(2)	C(5)-Ø(12)	0.531(3)	0.348(3)	−0.060(2)
O(1)	0.2279(7)	0.0632(6)	−0.1626(4)	C(6)-Ø(12)	0.539(3)	0.293(3)	−0.119(2)
O(2)	0.2874(8)	0.1201(8)	−0.2624(5)				
C(1)	0.396(1)	0.086(1)	−0.2352(6)	C(1)-Ø(21)	0.533(3)	−0.001(3)	−0.017(2)
C(2)	0.499(1)	0.157(1)	−0.2462(7)	C(2)-Ø(21)	0.644(3)	0.014(3)	0.019(2)
C(3)	0.394(1)	−0.042(1)	−0.1406(6)	C(3)-Ø(21)	0.641(3)	0.054(3)	0.084(2)
C(4)	0.360(1)	0.059(1)	−0.1614(6)	C(4)-Ø(21)	0.528(3)	0.077(3)	0.114(2)
C(5)	0.191(1)	0.122(1)	−0.2164(6)	C(5)-Ø(21)	0.418(3)	0.062(3)	0.078(2)
C(6)	0.084(2)	0.082(1)	−0.254(1)	C(6)-Ø(21)	0.421(3)	0.024(3)	0.012(2)
C(7)	0.166(2)	0.215(1)	−0.191(1)				
C(1)-Ø(11)	0.763(3)	0.203(3)	−0.251(2)	C(1)-Ø(22)	0.558(3)	−0.176(3)	−0.082(2)
C(2)-Ø(11)	0.825(3)	0.286(3)	−0.242(2)	C(2)-Ø(22)	0.666(3)	−0.224(3)	−0.098(2)
C(3)-Ø(11)	0.891(3)	0.326(3)	−0.296(2)	C(3)-Ø(22)	0.679(3)	−0.317(3)	−0.079(2)
C(4)-Ø(11)	0.892(3)	0.284(3)	−0.361(2)	C(4)-Ø(22)	0.579(3)	−0.364(3)	−0.050(2)
C(5)-Ø(11)	0.832(3)	0.199(3)	−0.370(2)	C(5)-Ø(22)	0.470(3)	−0.316(3)	−0.035(2)
C(6)-Ø(11)	0.769(3)	0.158(3)	−0.315(2)	C(6)-Ø(22)	0.460(3)	−0.222(3)	−0.050(2)

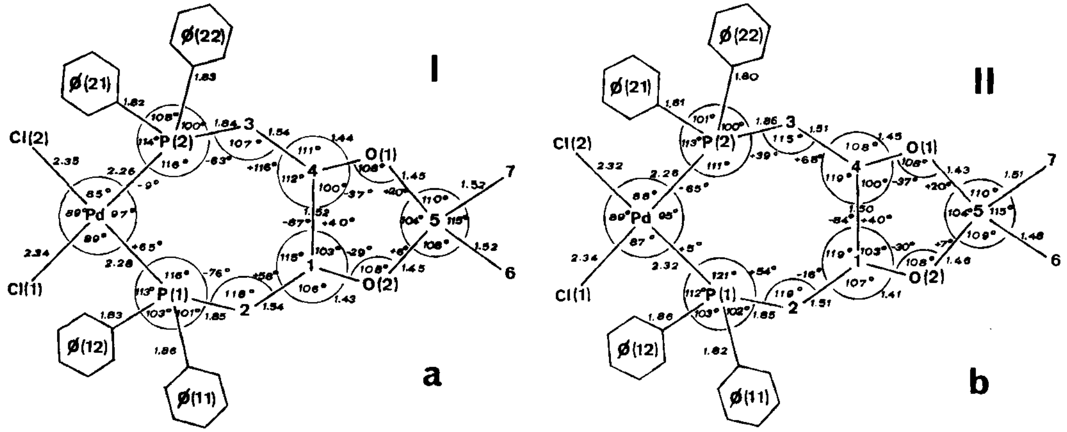

Fig. 1. *Bond lengths, bond angles and torsion angles of PdCl$_2$[(−)-DIOP],* (a) *molecule I,* (b) *molecule II.* Estimated standard deviations 0.01-0.02 Å for bond lengths, 1-2° for bond angles, 2-3° for torsion angles

is evident from *Figure 5* and can be verified by inspection of *Figures 1* and *2*, *Tables 4* and *5*.

The reported results do not provide an explanation for the high efficiency of the chiral ligand DIOP in asymmetric reactions. On the basis of the X-ray analysis of Ir(COD)((+)-DIOP)Cl the conformation of the seven membered ring [16] and the

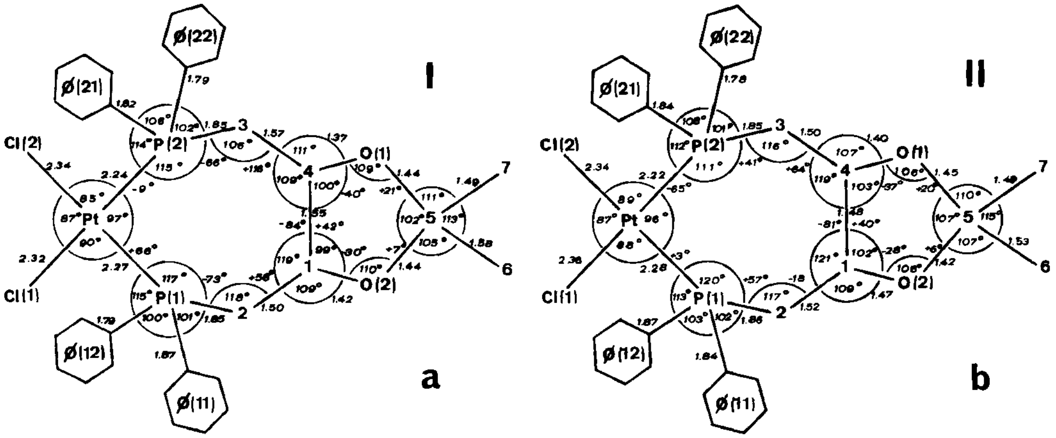

Fig. 2. *Geometry of $PtCl_2$[(−)-DIOP],* (a) *molecule I,* (b) *molecule II:* Standard deviations 0.02-0.05 Å (bonds), 2-5° (angles), 4-7° (torsions)

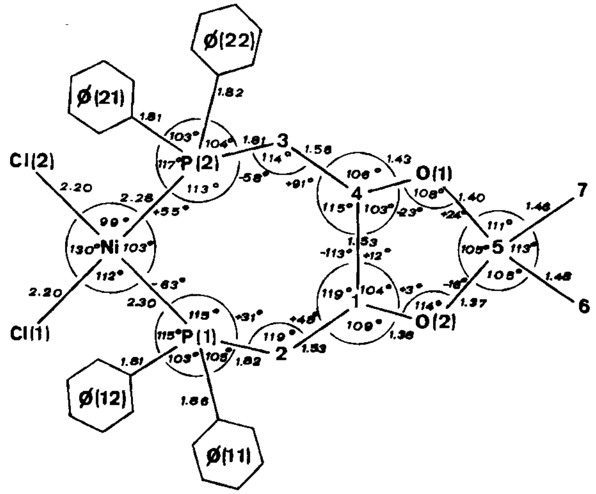

Fig. 3. *Geometry of $NiCl_2$[(−)-DIOP].* Standard deviations 0.02-0.03 Å (bonds), 2-3° (angles), 3-5° (torsions)

Table 4. *Bond angles* (to complete *Fig. 1-3*)

	Pd-complex		Pt-complex		Ni-complex
	molecule I	molecule II	molecule I	molecule II	
Bond angles					
Cl(1)-Metal-P(2)	173°	176°	172°	174°	109°
Cl(2)-Metal-P(1)	178°	177°	177°	175°	100°
Metal-P(1)-Ø(11)	115°	113°	115°	115°	109°
C(2)-P(1)-Ø(12)	106°	103°	107°	102°	107°
Metal-P(2)-Ø(22)	115°	123°	115°	118°	113°
C(3)-P(2)-Ø(21)	102°	107°	102°	106°	106°
O(1)-C(5)-C(6)	110°	111°	114°	110°	110°
O(2)-C(5)-C(7)	109°	107°	110°	108°	113°

Table 5. *Dihedral angles of the phenyl groups*

Angles between the planes of adjacent phenyl rings	Pd-complex		Pt-complex		Ni-complex
	molecule I	molecule II	molecule I	molecule II	
Ø(11)-Ø(12)	76°	82°	77°	85°	85°
Ø(12)-Ø(21)	7°	6°	8°	8°	36°
Ø(21)-Ø(22)	76°	83°	74°	80°	83°
Torsion angles					
Metal-P(1)-Ø(11)	−87°	−14°	−89°	−14°	66°
Metal-P(1)-Ø(12)	−18°	−62°	−14°	−58°	32°
Metal-P(2)-Ø(21)	76°	26°	80°	30°	−42°
Metal-P(2)-Ø(22)	17°	83°	16°	83°	12°

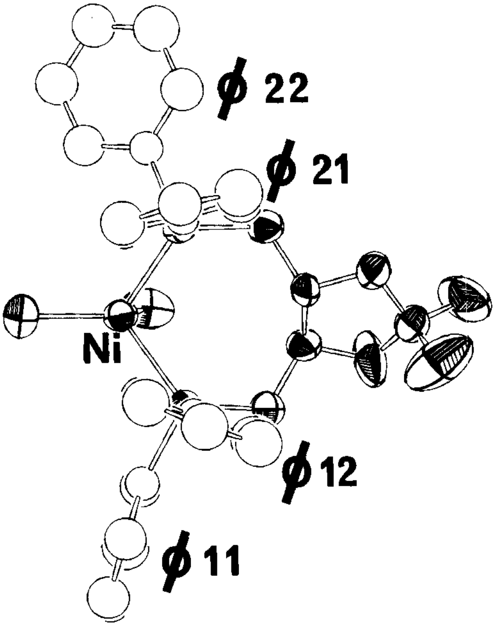

Fig. 4. *ORTEP-drawing [26] of the* $NiCl_2[(-)\text{-}DIOP]$ *molecule.* The 50% probability representations is chosen for the thermal ellipsoids

conformation of 'edge-face' phenyl rings on each P-atom [25] have been invoked to explain specificity in asymmetric catalysis by DIOP-complexes. The present investigation shows that for Pd- and Pt-complexes in the solid state, there are different conformations of the seven membered rings.

Different conformations of $Pt(DIOP)_2$ are known to occur in solution, the energy barrier of the interconversion being rather low $\Delta G^{\ddagger}_{250} \simeq 11.5$ Kcal mol^{-1} [14].

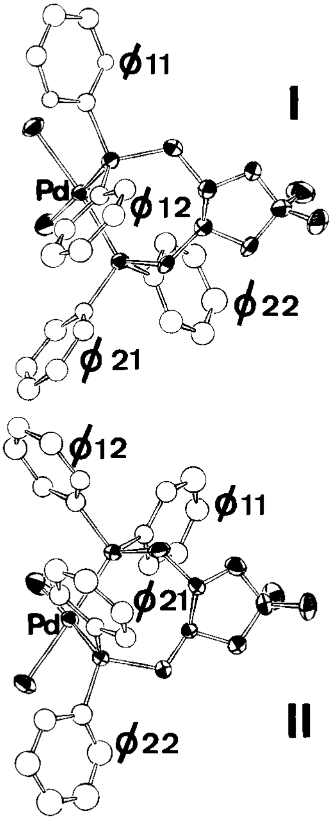

Fig. 5. *ORTEP-drawing of Pd* Cl_2*[(−)-DIOP], molecules I and II*

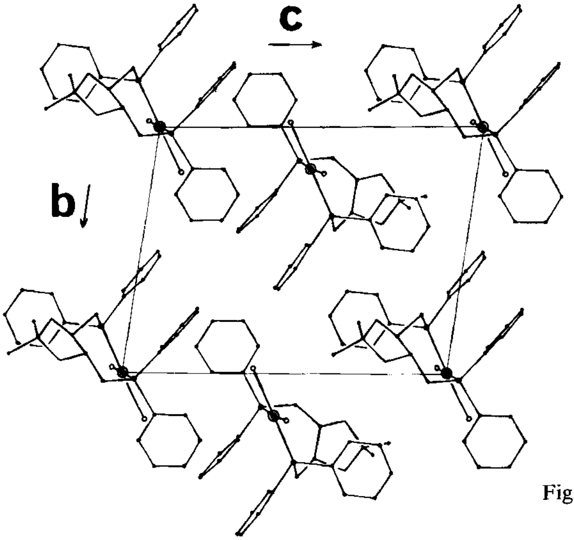

Fig. 6. *Packing diagram of Pt* Cl_2*[(−)-DIOP]*

A conformational adaptability of the ligand with respect to the substrate [13] in the catalyst-substrate-complex could well be an important factor in determining asymmetric induction by the above ligand.

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