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The Crystal and Molecular Structure of [*trans*-1,2-Bis(diphenylphosphinamino)cyclohexane](1,5-cyclooctadiene)rhodium(I) Perchlorate Dichloromethane Solvate

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The molecular structure of the title compound has been determined from three-dimensional X-ray diffraction data. The crystal belongs to the triclinic system: $P\bar{1}$, $a=11.488(2)$, $b=18.163(2)$, $c=10.998(2)$Å, $\alpha=101.70(2)$, $\beta=118.29(1)$, $\gamma=85.32(3)°$, $Z=2$. The structure has been refined by block-diagonal least-squares techniques using 3749 non-zero reflections to the final R value of 0.067. The rhodium atom is coordinated in a slightly distorted square-planar geometry by the bisphosphine and the diene ligand, with average Rh–P and Rh–C distances of 2.301(2) and 2.26(1)Å, respectively. The seven-membered chelate ring takes a distorted boat conformation, and the two phenyl groups of diphenylphosphine are arranged in a face-edge manner and those of the other diphenylphosphine are in a helical arrangement like a propeller, viewed from cyclooctadiene.

The stereoselectivity in the asymmetric hydrogenation of α-acylaminocinnamic acid by the rhodium complex with (1*R*,2*R*)-1,2-bis(diphenylphosphinamino)-cyclohexane has been reported to be inverted by *N*-methylation of the ligand.[1] We have been interested in such a chiral inversion of the stereoselectivity. In order to elucidate the stereochemistry of those complexes, the crystal structure of the title compound has been determined.

Experimental and Structure Determination

Preliminary Weissenberg photographs showed that crystals of [(1*S*,2*S*)-1,2-bis(diphenylphosphinamino)cyclohexane](1,5-cyclooctadiene)rhodium(I) perchlorate were unsuitable for X-ray analysis. Therefore, we determined the crystal structure of the racemic complex of [*trans*-1,2-bis(diphenylphosphinamino)cyclohexane](1,5-cyclooctadiene)rhodium(I) perchlorate.

Crystal and Intensity Data. Wine-red rhombohedral crystals were obtained from dichloromethane solution. Preliminary Weissenberg photographs suggested that the crystals were triclinic, and the space group was confirmed to be $P\bar{1}$ by the following structure analysis. The crystal chosen for data collection had approximate dimensions of $0.1\times 0.3\times 0.3$ mm. Accurate unit-cell parameters were obtained by least-squares refinement of 18 high angle reflections. The crystal data are summarized in Table 1. Intensity data were collected on a Phillips PW-1100 computer-controlled diffractometer using a θ-2θ scan technique with monochromated Cu $K\alpha$ radiation in the range of $2\theta\leqq 100°$. A total of 3749 non-zero independent reflections was collected at room temperature. Standard reflections monitored during the course of data collection showed that no significant decomposition and no mispositioning had occurred. No absorption correction was applied.

Structure Solution and Refinement. The positional parameters of the Rh atom were determined from a three-dimensional Patterson synthesis. All the non-hydrogen atoms were found from subsequent Fourier and difference electron density maps. The electron densities of all the oxygen atoms were broad, and particularly the O(1) atom showed only a half of the densities of the other oxygen atoms. The positional and thermal parameters were refined by block-diagonal least-squares techniques; seven cycles for isotropic and four cycles for anisotropic parameters of non-hydrogen atoms. Three types of weight factors were assigned, depending on the value of F_o: $w=0.5$ ($F_o\leqq 5.0$), $w=1$ ($5.0<F_o\leqq 20.0$), $w=20.0/F_o$ ($20.0<F_o$). The electron density map at this stage showed that the perchlorate anion was disordered, so that another oxygen atom O(1)′ occupied the opposite position across the Cl atom from O(1). The perchlorate anion was further refined by assuming a half occupancy for O(1) and O(1)′ atoms. The final R value was 0.067 for non-zero reflections. The positional and thermal parameters are given in Tables 2 and 3,[2] respectively. The observed and calculated structure factors are listed in Table 4.[2] Atomic scattering factors of the rhodium cation and the other neutral atoms were taken from International Tables for X-Ray Crystallography.[3]

Results and Discussion

A perspective view of the molecule is given in Fig. 1, together with the numbering system of the atoms. A stereographic drawing of the molecule is shown in Fig. 2. A stereographic drawing of the packing of the molecules in a unit cell is shown in Fig. 3, excluding the O(1)′ atom.

Bond distances and bond angles are listed in Table 5. The bond distances show that C(51)–C(58) and C(54)–C(55) are the double bonds in cyclooctadiene. The rhodium atom is coordinated in a slightly distorted square-planar geometry to the bisphosphine and the two double bonds in the diene ligand. The dihedral angle between the plane defined by P(1)–Rh–P(2) and the plane containing Rh and mid-points of the two double bonds is 20.0°. Bond distances of Rh–P(1) and Rh–P(2) are 2.286(2) and 2.315(2)

Table 1. Crystal data

$C_{39}H_{46}N_2O_4Cl_3P_2Rh$	$F.W.=878.01$
Triclinic	Space group $P\bar{1}$
$a=11.488(2)$ Å	$\alpha=101.70(2)°$
$b=18.163(2)$ Å	$\beta=118.29(1)°$
$c=10.998(2)$ Å	$\gamma=85.32(3)°$
$U=1978.5(4)$ Å^3	$F(000)=452$
$D_m=1.47$ g cm^{-3} (by flotation)	
$D_c=1.474$ g cm^{-3}	$Z=2$
μ(Cu $K\alpha$) $=47.9$ cm^{-1}	

TABLE 2. THE ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS
* Perchlorate ** Dichloromethane

Atom	x	y	z	Atom	x	y	z
Rh	0.09201(5)	0.21625(3)	0.43523(6)	C(24)	0.3242(10)	0.4516 (6)	0.9105(10)
P(1)	0.0651 (2)	0.3432 (1)	0.4475 (2)	C(25)	0.1934(10)	0.4732 (5)	0.8421(10)
P(2)	0.9723 (2)	0.2162 (1)	0.5554 (2)	C(26)	0.1141 (8)	0.4412 (5)	0.7012 (9)
*Cl	0.7225 (3)	0.3170 (2)	0.8379 (3)	C(31)	0.8469 (8)	0.1407 (5)	0.4788 (9)
*O(1)′	0.6566(49)	0.3859(19)	0.7967(63)	C(32)	0.7947 (9)	0.1073 (5)	0.3364(10)
*O(1)	0.8306(24)	0.2601(14)	0.8511(36)	C(33)	0.6841(10)	0.0601 (6)	0.2690(11)
*O(2)	0.6212(13)	0.2684 (7)	0.7378(10)	C(34)	0.6263(10)	0.0444 (6)	0.3477(14)
*O(3)	0.8123(16)	0.3394 (9)	0.8172(14)	C(35)	0.6780(10)	0.0774 (5)	0.4933(12)
*O(4)	0.7295(13)	0.3304(11)	0.9642(12)	C(36)	0.7889 (9)	0.1262 (5)	0.5583(11)
N(1)	0.9126 (6)	0.3763 (4)	0.3910 (7)	C(41)	0.0771 (8)	0.2002 (5)	0.7345 (9)
N(2)	0.8950 (6)	0.2946 (3)	0.5869 (7)	C(42)	0.1036 (9)	0.1265 (5)	0.7584(10)
C(1)	0.7943 (8)	0.3342 (5)	0.3541 (9)	C(43)	0.1908(11)	0.1156 (6)	0.8966(11)
C(2)	0.7777 (8)	0.3277 (5)	0.4804 (8)	C(44)	0.2481(10)	0.1780 (6)	0.0073(10)
C(3)	0.6492 (8)	0.2894 (6)	0.4351(10)	C(45)	0.2173 (9)	0.2485 (6)	−0.0207(10)
C(4)	0.5313 (9)	0.3304 (6)	0.3411(11)	C(46)	0.1341 (8)	0.2617 (5)	0.8443 (9)
C(5)	0.5443(10)	0.3371 (7)	0.2092(11)	C(51)	0.2295 (9)	0.1252 (5)	0.5273(11)
C(6)	0.6747 (8)	0.3727 (5)	0.2526 (9)	C(52)	0.3614(11)	0.1396 (7)	0.5355(14)
C(11)	0.1231 (8)	0.3903 (4)	0.3551 (9)	C(53)	0.3508(10)	0.1675 (6)	0.4095(13)
C(12)	0.2427 (9)	0.4358 (5)	0.4246(11)	C(54)	0.2344(10)	0.2188 (5)	0.3464(11)
C(13)	0.2781(11)	0.4699 (5)	0.3470(12)	C(55)	0.1076 (9)	0.1914 (5)	0.2381 (9)
C(14)	0.2036(13)	0.4612 (6)	0.2020(13)	C(56)	0.0695(13)	0.1114 (6)	0.1735(12)
C(15)	0.0864(12)	0.4171 (6)	0.1315(12)	C(57)	0.1051(13)	0.0558 (6)	0.2698(12)
C(16)	0.0490 (9)	0.3830 (5)	0.2110(11)	C(58)	0.1192(11)	0.0882 (5)	0.4161(11)
C(21)	0.1658 (8)	0.3856 (4)	0.6316 (8)	**Cl(1)	0.7068 (4)	0.0572 (3)	0.9014 (5)
C(22)	0.2926 (9)	0.3623 (5)	0.7011(10)	**Cl(2)	0.4982 (5)	0.1442 (5)	0.9261 (5)
C(23)	0.3763(10)	0.3965 (6)	0.8454(10)	**C(0)	0.6492(14)	0.1455 (8)	0.9328(18)

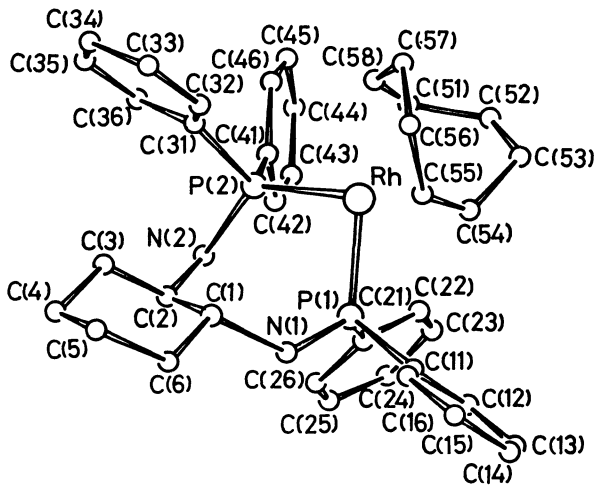

Fig. 1. Perspective view of the molecule with the numbering system of atoms.

Å, respectively, and the bond angle of P(1)–Rh–P(2) is 89.91(8)°.

A seven-membered chelate ring can take three types of conformations, boat, chair, and twist-chair forms, in which four atoms lie on a plane.[4] In the present complex, the seven-membered chelate ring consists of Rh, P(1), P(2), N(1), N(2), C(1), and C(2) atoms, and its conformation is a boat form, in which the nitrogen atom N(2) lies nearly on the plane of P(1)–Rh–P(2); the deviation of the N(2) atom from the plane is 0.21 Å. This conformation is, however, a little distorted and has no mirror symmetry, because the bond distance of N(2)–P(2) is not equal to that of Rh–P(1).

The chair conformation of seven-membered chelate ring has been observed in several complexes: *e.g.* in (1,5-cyclooctadiene)[(2*S*,4*S*)-*N*-pivaloyl-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine]-rhodium(I),[5] (1,5-cyclooctadiene)[(2*S*,4*S*)-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine]-rhodium(I),[6] chloro(1,5-cyclooctadiene)[(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]iridium(I),[7] and dichloro[(−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]nickel(II).[8] Thus the boat conformation of the present complex seems to be unusual. The intramolecular distance of Rh–C(1) is found to be 3.71(1) Å. Although the distance is not so short to make a bond,[9] it might be close enough to have some interaction.[10] The coordinates of the hydrogen atom bonded to C(1) are estimated to be (−0.1967, 0.2774, 0.3062) by assuming that the C(1) is sp^3 and that the C–H distance is 1.08 Å. A projection of this hydrogen atom on the P(1)–Rh–P(2) plane is shown in Fig. 4. As seen in this figure, the hydrogen projects toward the rhodium atom. The Rh–H distance thus calculated is 3.13 Å. Therefore, the boat conformation may be caused by the intramolecular interaction between rhodium and hydrogen.

The configuration of a product in the asymmetric

TABLE 5. BOND DISTANCES AND BOND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATION IN PARENTHESES

Bond distances [l/Å]

Rh-P(1)	2.286 (2)	C(11)-C(12)	1.445(15)	C(43)-C(44)	1.415(17)
Rh-P(2)	2.315 (2)	C(12)-C(13)	1.364(18)	C(44)-C(45)	1.358(16)
Rh-C(51)	2.235(12)	C(13)-C(14)	1.388(20)	C(45)-C(46)	1.392(15)
Rh-C(54)	2.275(12)	C(14)-C(15)	1.411(20)	C(46)-C(41)	1.399(14)
Rh-C(55)	2.212(11)	C(15)-C(16)	1.397(18)	C(51)-C(52)	1.516(19)
Rh-C(58)	2.301(13)	C(16)-C(11)	1.382(15)	C(52)-C(53)	1.517(20)
P(1)-N(1)	1.663 (8)	C(21)-C(22)	1.364(14)	C(53)-C(54)	1.522(18)
P(1)-C(11)	1.816(10)	C(22)-C(23)	1.442(16)	C(54)-C(55)	1.422(16)
P(1)-C(21)	1.823 (9)	C(23)-C(24)	1.375(16)	C(55)-C(56)	1.483(18)
P(2)-N(2)	1.679 (8)	C(24)-C(25)	1.389(16)	C(56)-C(57)	1.504(21)
P(2)-C(31)	1.835(10)	C(25)-C(26)	1.397(15)	C(57)-C(58)	1.532(20)
P(2)-C(41)	1.829(10)	C(26)-C(21)	1.407(13)	C(58)-C(51)	1.374(17)
N(1)-C(1)	1.456(13)	C(31)-C(32)	1.402(15)	Cl-O(1)	1.52 (4)
N(2)-C(2)	1.486(12)	C(32)-C(33)	1.388(17)	Cl-O(1)′	1.45 (7)
C(1)-C(2)	1.516(14)	C(33)-C(34)	1.394(20)	Cl-O(2)	1.38 (2)
C(2)-C(3)	1.398(14)	C(34)-C(35)	1.430(20)	Cl-O(3)	1.27 (2)
C(3)-C(4)	1.574(16)	C(35)-C(36)	1.407(18)	Cl-O(4)	1.33 (2)
C(4)-C(5)	1.556(17)	C(36)-C(31)	1.398(15)	Cl(1)-C(0)	1.72 (2)
C(5)-C(6)	1.498(16)	C(41)-C(42)	1.397(15)	Cl(2)-C(0)	1.70 (2)
C(6)-C(1)	1.526(14)	C(42)-C(43)	1.415(17)		

Bond angles [ϕ/°]

P(1)-Rh-P(2)	89.91(8)	C(23)-C(24)-C(25)	121.7(11)
Rh-P(1)-N(1)	118.2 (3)	C(24)-C(25)-C(26)	119.5(10)
Rh-P(1)-C(11)	118.7 (3)	C(25)-C(26)-C(21)	119.8 (9)
Rh-P(1)-C(21)	106.0 (3)	P(2)-C(31)-C(32)	120.5 (8)
N(1)-P(1)-C(11)	100.0 (4)	P(2)-C(31)-C(36)	118.4 (8)
N(1)-P(1)-C(21)	109.3 (4)	C(36)-C(31)-C(32)	120.0(10)
C(11)-P(1)-C(21)	103.6 (4)	C(31)-C(32)-C(33)	122.0(11)
Rh-P(2)-N(2)	119.6 (3)	C(32)-C(33)-C(34)	118.4(12)
Rh-P(2)-C(31)	114.2 (3)	C(33)-C(34)-C(35)	120.8(13)
Rh-P(2)-C(41)	112.1 (3)	C(34)-C(35)-C(36)	119.7(12)
N(2)-P(2)-C(31)	105.3 (4)	C(35)-C(36)-C(31)	119.0(11)
N(2)-P(2)-C(41)	100.4 (4)	P(2)-C(41)-C(42)	119.3 (8)
C(31)-P(2)-C(41)	103.3 (4)	P(2)-C(41)-C(46)	119.5 (7)
P(1)-N(1)-C(1)	126.3 (7)	C(46)-C(41)-C(42)	121.1 (9)
P(2)-N(2)-C(2)	126.1 (6)	C(41)-C(42)-C(43)	118.2(10)
N(1)-C(1)-C(2)	113.3 (8)	C(42)-C(43)-C(44)	120.4(11)
N(1)-C(1)-C(6)	108.2 (8)	C(43)-C(44)-C(45)	119.1(11)
C(2)-C(1)-C(6)	110.0 (8)	C(44)-C(45)-C(46)	122.2(10)
N(2)-C(2)-C(1)	112.3 (8)	C(45)-C(46)-C(41)	118.9 (9)
N(2)-C(2)-C(3)	113.6 (8)	C(58)-C(51)-C(52)	128.9(11)
C(1)-C(2)-C(3)	109.5 (8)	C(51)-C(52)-C(53)	114.3(12)
C(2)-C(3)-C(4)	114.5 (9)	C(52)-C(53)-C(54)	114.2(11)
C(3)-C(4)-C(5)	105.9 (9)	C(53)-C(54)-C(55)	122.9(11)
C(4)-C(5)-C(6)	110.3(10)	C(54)-C(55)-C(56)	125.9(11)
C(5)-C(6)-C(1)	114.4 (9)	C(55)-C(56)-C(57)	118.0(12)
P(1)-C(11)-C(12)	123.4 (8)	C(56)-C(57)-C(58)	115.5(12)
P(1)-C(11)-C(16)	118.6 (8)	C(57)-C(58)-C(51)	125.2(12)
C(16)-C(11)-C(12)	118.0(10)	O(1)-Cl-O(2)	94.4(16)
C(11)-C(12)-C(13)	119.5(11)	O(1)-Cl-O(3)	66.0(17)
C(12)-C(13)-C(14)	121.9(13)	O(1)-Cl-O(4)	103.5(17)
C(13)-C(14)-C(15)	119.8(13)	O(2)-Cl-O(3)	123.2(11)
C(14)-C(15)-C(16)	118.4(12)	O(2)-Cl-O(4)	114.4(11)
C(15)-C(16)-C(11)	122.5(11)	O(3)-Cl-O(4)	121.8(12)
P(1)-C(21)-C(22)	118.8 (8)	O(1)-Cl-O(1)′	150.8(31)
P(1)-C(21)-C(26)	120.8 (7)	O(2)-Cl-O(1)′	96.8(28)
C(26)-C(21)-C(22)	120.4 (9)	O(3)-Cl-O(1)′	85.4(29)
C(21)-C(22)-C(23)	120.2(10)	O(4)-Cl-O(1)′	96.2(29)
C(22)-C(23)-C(24)	118.4(10)	Cl(1)-C(0)-Cl(2)	113.0(12)

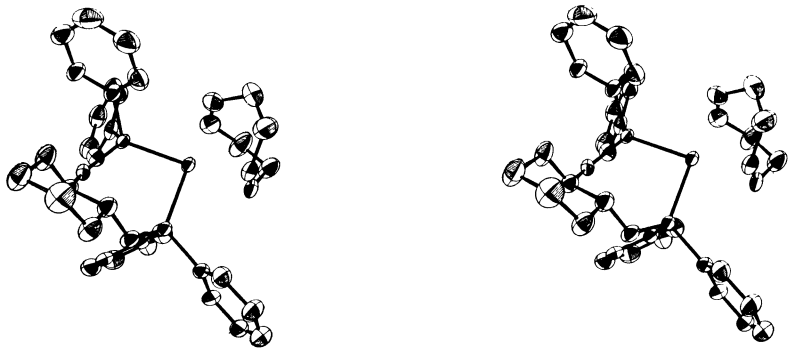

Fig. 2. Stereographic drawing of the molecule. Non-hydrogen atoms are represented by thermal ellipsoids of 50% probability.

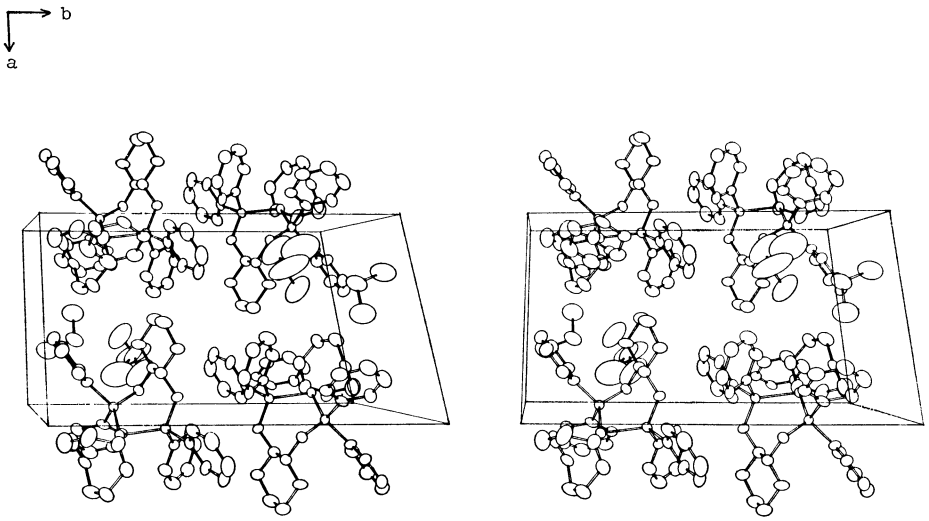

Fig. 3. Stereographic drawing of the packing of the molecules along the c axis.

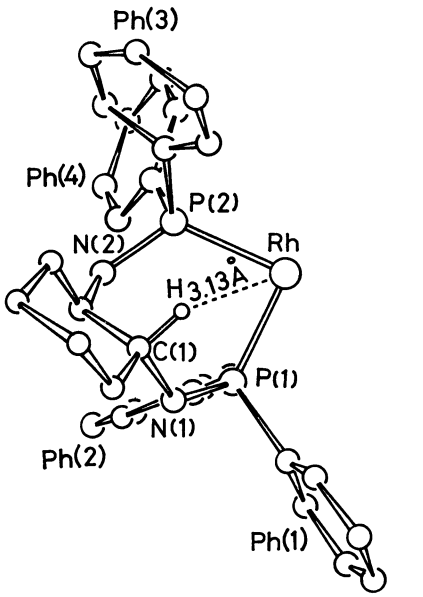

Fig. 4. Projection of the selected atoms on the P(1)–Rh–P(2) plane. Ph(1) is composed of C(11)–C(16), Ph(2) is composed of C(21)–C(26), Ph(3) is composed of C(31)–C(36), and Ph(4) is composed of C(41)–C(46).

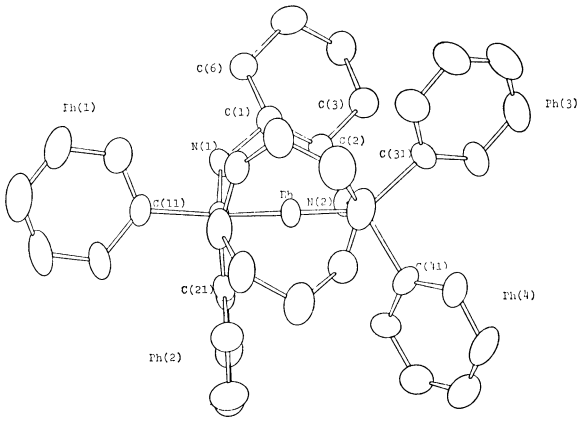

Fig. 5. The arrangement of the four phenyl groups.

hydrogenation may be derived from a chiral arrangement of the four phenyl groups which differentiate an enantiomeric face of a substrate. The arrangement of the phenyl groups, looked at from the side of cyclooctadiene, is shown in Fig. 5. As can be seen there, Ph(1) and Ph(2) are arrayed in a face-edge manner and, Ph(3) and Ph(4) are twisted like a propeller. Ph(2) and Ph(4) stretch out below the coordination lane so that there is a vacancy between Ph(1) and

Ph(3). If this structure is maintained in solution, the substrate may approach from the space between Ph(1) and Ph(3).

The positions of hydrogen atoms on N(1) and N(2) are estimated by assuming that the nitrogen atoms are sp^3 and that the N–H distance is 1.03 Å. The coordinates for N(1) are (H-1: −0.1073, 0.3964, 0.3021) or (H-2: −0.0814, 0.4209, 0.4684), and those for N(2) are (H-3: −0.0334, 0.3364, 0.6349) or (H-4: −0.1331, 0.2849, 0.6585). The shortest distances between each of the hydrogen atoms and their adjacent atoms are 2.4 Å for H-1···C(6), H-1···C(11), and H-1···C(16); 2.5 Å for H-2···C(2) and H-2···C(26); 2.4 Å for H-3···C(26); 2.5 Å for H-4···C(3). These distances are almost the same. Therefore, the hydrogen atoms on the nitrogens may actually occupy either of the two positions.

To examine the *N*-methylation effect, a hypothetical structure was given for the *N,N'*-dimethyl derivative on the basis of the present structure, and by assuming the N–C distance to be 1.45 Å. The coordinates of the methyl carbon on N(1) are (CH_3-1: −0.1154, 0.4045, 0.2658) or (CH_3-2: −0.0789, 0.4391, 0.5000), and those on N(2) are (CH_3-3: −0.0041, 0.3535, 0.6544) or (CH_3-4: −0.1446, 0.2810, 0.6877). The shortest distances between the methyl carbons and their adjacent atoms are 2.2 Å for CH_3-1···C(16); 2.3 Å for CH_3-2···C(26); 2.0 Å for CH_3-3···C(26); 2.7 Å for CH_3-4···C(3) and CH_3-4···C(41). Considering that the sum of the van der Waals radii of the methyl group and the carbon atom is 3.7 Å, there are no sufficient space for the methyl groups in the present structure. The complex with the *N,N'*-dimethylated ligand, therefore, seems to take another conformation.

References

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