

Structure and Absolute Configuration of [(+)₅₈₉-(R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl](8,9,10-trinorborna-2,5-diene)rhodium(I) Perchlorate, the Precursor of a Catalyst for Highly Enantioselective Hydrogenations

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Abstract

The molecular structure and absolute configuration of the title compound, [Rh(trinorbornadiene) {(+)-binap}](ClO₄), have been determined by the single-crystal X-ray diffraction method. The crystal data are: [Rh(C₇H₈)(C₄₄H₃₂P₂)]ClO₄, orthorhombic, *P*2₁2₁2₁, *Z* = 4, *a* = 11.104 (1), *b* = 35.238 (2), *c* = 10.892 (1) Å, *U* = 4261.6 (3) Å³, *D*_x = 1.430 Mg m⁻³, *μ*(Cu *Kα*) = 4.98 mm⁻¹. The structure has been refined, using 3249 independent reflections, to give an *R* value of 0.032. The Rh^I has square-planar coordination geometry involving two P atoms and the two C=C bonds of norbornadiene. The seven-membered chelate ring is fixed in a *λ* skew(*v*) conformation and this dissymmetry determines the orientation of the four phenyl rings on the P atoms. A chiral environment at the site of the olefin coordination is provided by the dispositions of the four phenyl rings in an alternating edge-face manner. The absolute configuration of the dextrorotatory diphosphine ligand has been assigned by the Bijvoet method as *R*.

Introduction

In recent years, chiral diphosphines have attracted much attention as ligands of transition-metal catalysts for a variety of asymmetric transformations (Knowles, Sabacky & Vineyard, 1974; Morrison, Masler & Hathaway, 1976; Kagan & Fiaud, 1978; Pino & Consiglio, 1979). 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl [(1), hereafter abbreviated to binap] (Miyashita, Yasuda, Takaya, Toriumi, Ito, Souchi & Noyori, 1980) has several interesting characteristics in this respect. It is a new type of bis(triaryl)phosphine having only an axial element of chirality, and will

coordinate to a wide variety of transition metals and metal ions through a change of the twist angle between the two naphthyl rings. In addition, the presence of a *C*₂ axis in the binaphthyl moiety can minimize the number of possible diastereomeric intermediates in the catalytic processes. We demonstrated the high effectiveness of (1) as a ligand for the Rh^I-catalyzed asymmetric hydrogenation of *α*-(acylamino)acrylic acids and esters (Miyashita, Yasuda, Takaya, Toriumi, Ito, Souchi & Noyori, 1980). The present paper describes the crystal structure of the title compound, [Rh(trinorbornadiene) {(+)-binap}](ClO₄), the precursor of the catalyst used in the asymmetric hydrogenation, which has been studied in order to determine the absolute configuration of the (+)-binap ligand and to investigate the chiral environment at the site of the olefin coordination provided by the coordinated (+)-binap.

Experimental

Dark-red mica-like crystals of [Rh(trinorbornadiene) {(+)-binap}](ClO₄) were obtained by recrystallization from methanol. Weissenberg photographs showed the crystals to be orthorhombic with space group *P*2₁2₁2₁. The cell dimensions (see *Abstract*) were determined by a least-squares calculation based on 19 *2θ* values in the range 20° < 2*θ*_{Cu *Kα*} < 31° measured on a Rigaku four-circle diffractometer. The calculated density of 1.430 Mg m⁻³ (*Z* = 4) is in the range expected for such compounds.

A crystal of dimensions 0.34 × 0.32 × 0.32 mm was glued to the interior of a thin-walled glass capillary which was sealed as a precaution against moisture sensitivity. The intensities were collected up to 2*θ* = 120° with graphite-monochromated Cu *Kα* radiation. The *θ*-2*θ* scan technique was employed, the scan range being (1.1 + 0.3 tan *θ*)°. A total of 3503 *hkl* reflexions were measured within the range 2° < 2*θ* < 120°, of

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Table 1. *Positional parameters* ($\times 10^5$) and *equivalent isotropic temperature factors for the non-hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} * (Å ²)
Cl	40962 (15)	12332 (5)	8578 (15)	5.06 (4)
O(1)	52525 (50)	10724 (16)	6209 (59)	7.90 (19)
O(2)	42960 (60)	16152 (15)	12586 (62)	8.50 (20)
O(3)	34672 (55)	10337 (17)	17906 (62)	9.25 (22)
O(4)	34053 (59)	12340 (24)	-2378 (55)	10.06 (24)
Rh	93161 (4)	10727 (1)	16026 (4)	2.94 (1)
P(1)	88551 (11)	16646 (3)	23720 (12)	2.41 (3)
P(2)	92917 (13)	8058 (3)	35505 (13)	3.15 (3)
C(1)	77256 (39)	16550 (13)	36022 (46)	2.57 (11)
C(2)	65375 (43)	17589 (16)	32867 (52)	3.48 (13)
C(3)	56180 (48)	17171 (19)	40847 (55)	4.46 (16)
C(4)	58115 (47)	15663 (17)	52695 (53)	3.84 (14)
C(5)	48417 (52)	15218 (21)	60937 (64)	5.24 (19)
C(6)	50262 (55)	13812 (23)	72433 (66)	5.80 (22)
C(7)	61867 (55)	12828 (21)	75929 (59)	4.91 (17)
C(8)	71400 (47)	13297 (16)	68230 (51)	3.77 (15)
C(9)	69832 (46)	14682 (15)	56260 (49)	3.16 (13)
C(10)	79609 (43)	15140 (13)	47620 (48)	2.72 (12)
C(11)	92065 (44)	14173 (13)	52175 (43)	2.58 (11)
C(12)	97411 (43)	16650 (14)	61184 (47)	2.84 (12)
C(13)	91976 (45)	20078 (15)	64869 (49)	3.36 (12)
C(14)	97447 (55)	22500 (17)	72937 (59)	4.36 (16)
C(15)	108852 (55)	21637 (19)	77782 (59)	4.68 (17)
C(16)	114395 (48)	18310 (18)	74528 (60)	4.37 (16)
C(17)	109085 (42)	15775 (15)	66068 (51)	3.33 (13)
C(18)	114590 (46)	12412 (17)	62414 (55)	3.75 (14)
C(19)	109593 (46)	10097 (15)	53913 (53)	3.50 (14)
C(20)	98356 (43)	10976 (13)	48423 (45)	2.78 (11)
C(21)	101830 (43)	18867 (13)	30244 (47)	2.80 (12)
C(22)	101362 (56)	22199 (15)	37236 (56)	4.00 (15)
C(23)	111940 (71)	23566 (18)	42597 (62)	5.24 (19)
C(24)	122528 (59)	21650 (19)	41065 (67)	5.16 (19)
C(25)	123094 (48)	18406 (17)	34244 (68)	4.69 (17)
C(26)	112714 (48)	17061 (15)	28756 (55)	3.57 (14)
C(27)	83002 (44)	20007 (14)	12255 (49)	2.95 (12)
C(28)	88523 (54)	23484 (15)	10149 (58)	3.92 (15)
C(29)	84024 (64)	25911 (17)	1094 (75)	5.43 (20)
C(30)	74447 (66)	24944 (19)	-5827 (59)	5.22 (18)
C(31)	68850 (60)	21493 (19)	-4008 (57)	4.97 (19)
C(32)	73048 (54)	19023 (15)	4966 (53)	3.78 (15)
C(33)	102211 (62)	3769 (15)	36101 (58)	4.49 (16)
C(34)	97646 (75)	212 (17)	38766 (78)	6.23 (22)
C(35)	104791 (87)	-2978 (20)	38370 (120)	9.59 (37)
C(36)	116145 (90)	-2695 (21)	35131 (116)	9.79 (38)
C(37)	121584 (74)	830 (24)	31966 (102)	8.28 (30)
C(38)	114267 (61)	4067 (19)	32183 (70)	5.46 (20)
C(39)	77936 (53)	6584 (15)	40004 (60)	3.99 (15)
C(40)	68494 (59)	6859 (17)	31893 (74)	5.29 (19)
C(41)	56892 (67)	5904 (21)	35485 (88)	7.16 (25)
C(42)	54611 (71)	4755 (23)	47265 (103)	8.06 (31)
C(43)	64001 (79)	4428 (20)	55429 (83)	6.78 (25)
C(44)	75535 (64)	5399 (17)	51950 (61)	4.93 (18)
C(45)	85775 (66)	10936 (20)	-2584 (58)	5.39 (19)
C(46)	96838 (72)	12450 (18)	-3150 (57)	5.25 (19)
C(47)	105318 (63)	9185 (22)	-6249 (65)	5.68 (20)
C(48)	97416 (68)	6765 (19)	-14519 (63)	5.57 (20)
C(49)	86915 (67)	6680 (20)	-5181 (73)	5.94 (21)
C(50)	94313 (95)	5294 (16)	6117 (61)	6.71 (26)
C(51)	105095 (71)	6860 (19)	5381 (67)	5.98 (21)

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j a_i a_j \beta_{ij}$$

which 3249 with $|F_o| > 0$ were used for the structure determination. To determine the absolute configuration of the structure, 725 hkl reflections ($2^\circ < 2\theta < 70^\circ$) were also measured. Lorentz-polarization and absorption ($\mu_{CuK\alpha} = 4.98 \text{ mm}^{-1}$) corrections were applied. A decrease in the intensities of 6%, which was detected in the intensities of three standard reflections monitored every 50 reflections, was also corrected.

The solution of the structure and the determination of the absolute configuration

The structure was solved by the heavy-atom method. Block-diagonal least-squares refinement with anisotropic thermal parameters gave R and R_w values of 0.053 and 0.073, respectively. The weighting scheme $w = [\sigma_c^2 + (0.015 |F_o|)^2]^{-1}$ was employed.

Least-squares calculation including the anomalous-scattering corrections for non-hydrogen atoms gave R and R_w values of 0.045 and 0.061, respectively. At this point the enantiomeric structure was refined under identical conditions to give R and R_w values of 0.067 and 0.091, respectively. Accordingly, the first model was used in subsequent calculations.

All the H atoms were located from the successive difference Fourier syntheses. The final block-diagonal least-squares refinement including the H atoms as isotropic contributions converged at residuals of $R = 0.032$ and $R_w = 0.041$ for all the 3249 structure amplitudes. The final positional parameters are listed in Table 1.* The atomic scattering factors and the

* Lists of positional and thermal parameters for H atoms, anisotropic thermal parameters for non-hydrogen atoms, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36451 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Observed and calculated structure factor relations between some hkl and hkl reflexions*

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o(hkl) $ [$ F_c(hkl) $]	$ F_o(h\bar{k}l) $ [$ F_c(h\bar{k}l) $]	$\frac{ F_o(h\bar{k}l) }{ F_o(hkl) }$ $\frac{ F_c(h\bar{k}l) }{ F_c(hkl) }$
1	4	1	67.0 [74.3]	87.4 [89.4]	1.30 [1.20]
1	6	1	53.1 [52.8]	44.1 [40.5]	0.83 [0.77]
5	2	1	26.8 [24.6]	34.8 [33.0]	1.30 [1.34]
1	1	2	55.1 [54.2]	42.9 [42.5]	0.78 [0.78]
1	3	2	37.7 [36.8]	25.8 [24.1]	0.68 [0.65]
2	1	2	55.2 [57.2]	64.4 [66.8]	1.17 [1.17]
2	6	2	50.4 [53.2]	38.8 [41.6]	0.77 [0.78]
3	4	2	75.0 [75.0]	59.6 [59.8]	0.79 [0.80]
4	8	2	41.8 [40.4]	57.3 [54.9]	1.37 [1.36]
1	1	3	59.3 [57.6]	42.5 [42.4]	0.72 [0.74]
2	10	3	90.4 [91.2]	83.2 [80.5]	0.92 [0.88]
2	7	4	53.9 [54.3]	63.8 [63.1]	1.18 [1.16]

anomalous-scattering corrections were taken from *International Tables for X-ray Crystallography* (1974). For H, the values given by Stewart, Davidson & Simpson (1965) were used.

The absolute configuration of the Rh complex was determined by the anomalous-scattering technique. The observed and calculated structure factors for some Bijvoet pairs are listed in Table 2 along with their relative intensity ratios. The results in Table 2 indicate that the absolute configuration of the dextrorotatory diphosphine ligand is *R*. As a confirmation the enantiomeric structure was also refined under identical conditions; this gave *R* and *R_w* values of 0.045 and 0.067, respectively. When the *R*-factor-ratio test is applied to *R_w* values, the alternative model can be rejected at the less than 0.005 significance level, assuming no systematic errors in the data.

Description of the structure

Fig. 1 shows a perspective view of the complex cation with the atom-numbering scheme. Bond lengths and angles are listed in Table 3.

The Rh has square-planar coordination geometry involving two P atoms and the two C=C bonds of trinorbornadiene. The complex has an approximate twofold axis passing through the Rh and bisecting the P(1)–Rh–P(2) angle. A stereoscopic view of the

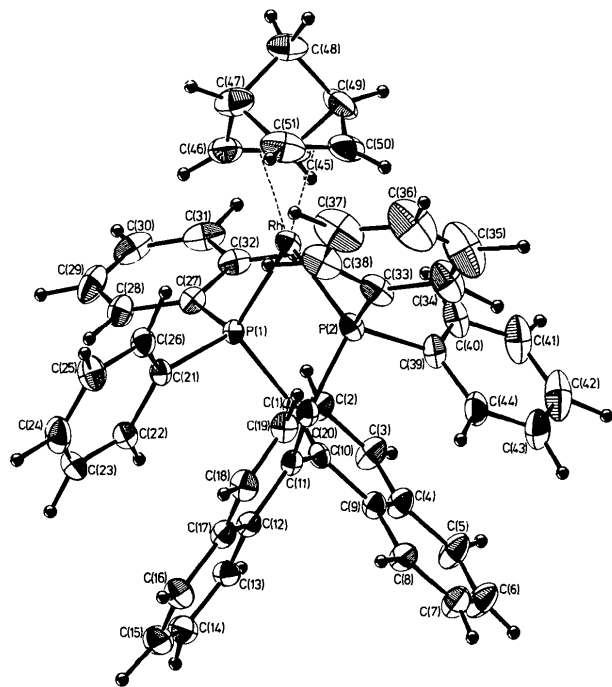


Fig. 1. A perspective drawing of $[\text{Rh}(\text{trinorbornadiene})(+)\text{-binap}]^+$, showing the atom-numbering scheme.

Table 3. Bond distances (Å) and angles (°) with their *e.s.d.*'s

Rh–P(1)	2.305 (1)	C(27)–C(28)	1.389 (7)
Rh–P(2)	2.321 (1)	C(28)–C(29)	1.398 (9)
P(1)–C(1)	1.836 (5)	C(29)–C(30)	1.347 (10)
P(1)–C(21)	1.814 (5)	C(30)–C(31)	1.380 (10)
P(1)–C(27)	1.828 (5)	C(31)–C(32)	1.389 (9)
P(2)–C(20)	1.844 (5)	C(27)–C(32)	1.404 (8)
P(2)–C(33)	1.831 (6)	C(33)–C(34)	1.383 (9)
P(2)–C(39)	1.810 (6)	C(34)–C(35)	1.377 (11)
C(10)–C(11)	1.508 (7)	C(35)–C(36)	1.313 (14)
C(1)–C(2)	1.412 (7)	C(36)–C(37)	1.424 (12)
C(2)–C(3)	1.349 (8)	C(37)–C(38)	1.401 (11)
C(3)–C(4)	1.412 (8)	C(33)–C(38)	1.409 (10)
C(4)–C(5)	1.411 (8)	C(39)–C(40)	1.374 (10)
C(4)–C(9)	1.401 (7)	C(40)–C(41)	1.388 (10)
C(5)–C(6)	1.362 (10)	C(41)–C(42)	1.369 (14)
C(6)–C(7)	1.388 (9)	C(42)–C(43)	1.375 (13)
C(7)–C(8)	1.361 (8)	C(43)–C(44)	1.379 (11)
C(8)–C(9)	1.403 (8)	C(39)–C(44)	1.392 (9)
C(9)–C(10)	1.446 (7)	Rh–C(45)	2.188 (7)
C(1)–C(10)	1.382 (7)	Rh–C(46)	2.213 (6)
C(11)–C(20)	1.387 (7)	Rh–C(50)	2.202 (6)
C(11)–C(12)	1.441 (7)	Rh–C(51)	2.227 (7)
C(12)–C(13)	1.409 (7)	C(45)–C(46)	1.341 (11)
C(12)–C(17)	1.435 (7)	C(50)–C(51)	1.321 (13)
C(13)–C(14)	1.367 (8)	C(45)–C(49)	1.531 (10)
C(14)–C(15)	1.405 (9)	C(46)–C(47)	1.525 (10)
C(15)–C(16)	1.371 (9)	C(50)–C(49)	1.558 (11)
C(16)–C(17)	1.412 (8)	C(51)–C(47)	1.509 (10)
C(17)–C(18)	1.392 (8)	C(47)–C(48)	1.519 (10)
C(18)–C(19)	1.353 (8)	C(48)–C(49)	1.548 (11)
C(19)–C(20)	1.418 (7)	Cl–O(1)	1.427 (6)
C(21)–C(22)	1.401 (7)	Cl–O(2)	1.432 (6)
C(22)–C(23)	1.397 (10)	Cl–O(3)	1.419 (7)
C(23)–C(24)	1.366 (10)	Cl–O(4)	1.419 (6)
C(24)–C(25)	1.365 (9)		
C(25)–C(26)	1.382 (8)		
C(21)–C(26)	1.376 (7)		
P(1)–Rh–P(2)	91.82 (5)	P(1)–C(21)–C(22)	123.0 (4)
Rh–P(1)–C(1)	113.60 (16)	P(1)–C(21)–C(26)	117.9 (4)
Rh–P(1)–C(21)	110.62 (16)	C(22)–C(21)–C(26)	119.0 (5)
Rh–P(1)–C(27)	114.37 (17)	C(21)–C(22)–C(23)	119.0 (5)
Rh–P(2)–C(20)	117.88 (16)	C(22)–C(23)–C(24)	120.1 (6)
Rh–P(2)–C(33)	111.12 (21)	C(23)–C(24)–C(25)	121.3 (6)
Rh–P(2)–C(39)	111.99 (21)	C(24)–C(25)–C(26)	119.0 (5)
C(1)–P(1)–C(21)	106.1 (2)	C(25)–C(26)–C(21)	121.5 (5)
C(1)–P(1)–C(27)	106.3 (2)	P(1)–C(27)–C(28)	122.4 (4)
C(21)–P(1)–C(27)	105.2 (2)	P(1)–C(27)–C(32)	119.4 (4)
C(20)–P(2)–C(33)	104.4 (3)	C(28)–C(27)–C(32)	118.2 (5)
C(20)–P(2)–C(39)	104.7 (3)	C(27)–C(28)–C(29)	119.9 (6)
C(33)–P(2)–C(39)	105.8 (3)	C(28)–C(29)–C(30)	121.5 (6)
P(1)–C(1)–C(10)	123.0 (4)	C(29)–C(30)–C(31)	119.9 (6)
P(1)–C(1)–C(2)	117.1 (4)	C(30)–C(31)–C(32)	120.1 (6)
P(2)–C(20)–C(11)	120.8 (4)	C(31)–C(32)–C(27)	120.5 (5)
P(2)–C(20)–C(19)	119.2 (4)	P(2)–C(33)–C(34)	123.3 (5)
C(1)–C(10)–C(11)	123.7 (4)	P(2)–C(33)–C(38)	117.6 (4)
C(9)–C(10)–C(11)	116.7 (4)	C(34)–C(33)–C(38)	118.7 (6)
C(10)–C(11)–C(20)	123.3 (4)	C(33)–C(34)–C(35)	121.5 (8)
C(10)–C(11)–C(12)	117.7 (4)	C(34)–C(35)–C(36)	120.0 (7)
C(2)–C(1)–C(10)	119.5 (4)	C(35)–C(36)–C(37)	122.6 (8)
C(1)–C(2)–C(3)	121.5 (5)	C(36)–C(37)–C(38)	117.4 (7)
C(2)–C(3)–C(4)	121.0 (5)	C(37)–C(38)–C(33)	119.7 (6)
C(3)–C(4)–C(5)	120.5 (5)	P(2)–C(39)–C(40)	120.5 (5)
C(3)–C(4)–C(9)	119.2 (5)	P(2)–C(39)–C(44)	121.0 (5)
C(5)–C(4)–C(9)	120.3 (5)	C(40)–C(39)–C(44)	118.4 (6)
C(4)–C(5)–C(6)	120.7 (6)	C(39)–C(40)–C(41)	120.7 (7)
C(5)–C(6)–C(7)	118.9 (6)	C(40)–C(41)–C(42)	120.5 (8)
C(6)–C(7)–C(8)	121.5 (6)	C(41)–C(42)–C(43)	119.4 (8)
C(7)–C(8)–C(9)	121.2 (5)	C(42)–C(43)–C(44)	120.4 (8)
C(8)–C(9)–C(10)	123.4 (5)	C(43)–C(44)–C(39)	120.6 (7)
C(4)–C(9)–C(8)	117.3 (5)	C(46)–C(45)–C(49)	107.8 (6)
C(4)–C(9)–C(10)	119.3 (5)	C(45)–C(46)–C(47)	106.0 (6)
C(9)–C(10)–C(11)	119.5 (4)	C(46)–C(47)–C(48)	101.4 (6)
C(12)–C(11)–C(20)	119.0 (4)	C(46)–C(47)–C(51)	102.3 (6)
C(11)–C(12)–C(13)	122.5 (4)	C(48)–C(47)–C(51)	100.6 (6)

Table 3 (cont.)

C(11)–C(12)–C(17)	119.6 (4)	C(47)–C(48)–C(49)	93.2 (5)
C(13)–C(12)–C(17)	117.8 (5)	C(45)–C(49)–C(48)	99.5 (6)
C(12)–C(13)–C(14)	121.9 (5)	C(45)–C(49)–C(50)	101.8 (6)
C(13)–C(14)–C(15)	120.4 (6)	C(48)–C(49)–C(50)	97.4 (6)
C(14)–C(15)–C(16)	119.5 (6)	C(49)–C(50)–C(51)	107.4 (6)
C(15)–C(16)–C(17)	121.5 (5)	C(47)–C(51)–C(50)	107.0 (6)
C(16)–C(17)–C(18)	122.8 (5)	O(1)–Cl–O(2)	106.8 (4)
C(12)–C(17)–C(16)	118.9 (5)	O(1)–Cl–O(3)	112.1 (4)
C(12)–C(17)–C(18)	118.3 (5)	O(1)–Cl–O(4)	109.6 (4)
C(17)–C(18)–C(19)	121.9 (5)	O(2)–Cl–O(3)	108.9 (4)
C(18)–C(19)–C(20)	121.2 (5)	O(2)–Cl–O(4)	109.8 (4)
C(19)–C(20)–C(11)	119.8 (4)	O(3)–Cl–O(4)	109.7 (4)

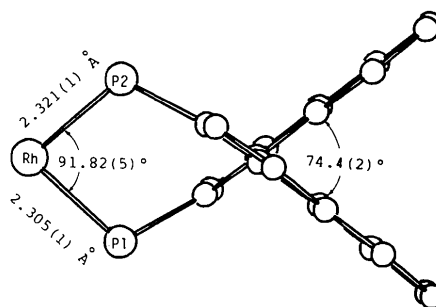


Fig. 4. The structure of the binaphthyl moiety.

structure along this axis is shown in Fig. 2, in which the binaphthyl moiety, for simplicity, is not depicted.

The Rh–P(1) and Rh–P(2) distances [2.305 (1) and 2.321 (1) Å, respectively] are comparable to the range of distances reported for other Rh–phosphine complexes (Nappier, Meek, Kirchner & Ibers, 1973; Ball & Payne, 1977; Chan, Pluth & Halpern, 1979; Ohga, Iitaka, Kogure & Ojima, 1978).

The (+)-binap ligand coordinates to the Rh to form a seven-membered chelate ring (Fig. 3) which is a typical skew(*v*) type (Kashiwabara, Hanaki & Fujita, 1980) and is very similar to one of the chelate rings in *trans*-[CoCl₂(1,4-butanediamine)₂]²⁺ (Nakayama, Ooi & Kuroya, 1974). The absolute configuration of the seven-membered skew(*v*) ring is designated as λ . Deviations of atoms from the P(1)–Rh–P(2) plane are: C(1) –1.095 (5), C(10) –0.812 (5), C(11) 0.519 (5), C(20) 0.935 (5) Å.

Non-hydrogen atoms of each naphthyl group are coplanar within 0.054 (5) Å. The angle between the least-squares planes through the two naphthyl rings is 74.4 (2)° (Fig. 4), in contrast to those found for free binaphthyl or its derivative bearing bulky substituents

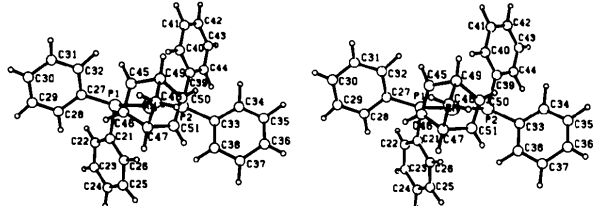


Fig. 2. A stereoscopic view of the structure along the pseudo twofold axis bisecting the P(1)–Rh–P(2) angle. The binaphthyl group is not depicted.

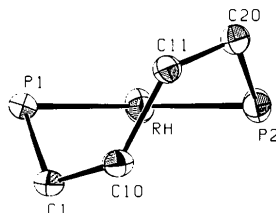


Fig. 3. The structure of the seven-membered chelate ring.

at the 2 and 2' positions [68° for 1,1'-binaphthyl (Kerr & Robertson, 1969) and 91.6° for 2,2'-bis(bromomethyl)-1,1'-binaphthyl (Harata & Tanaka, 1973)]. In view of the presence of two bulky diphenylphosphino groups, this angle in free binap can be considered to be much larger than the observed dihedral angle of 74.4 (2)° for the binap coordinated to Rh^I. This can be ascribed primarily as being the result of an induced-fit complexation with the Rh. The absolute configuration of (+)-binap that arises from this dissymmetry is designated as *R*.

The four phenyl rings on the P atoms are arranged in an alternating edge–face manner (Fig. 2), as was observed for the Rh^I complex of 1,2-bis(*o*-methoxyphenyl)phenylphosphinoethane (Knowles, Vineyard, Sabacky & Stults, 1979; Vineyard, Knowles, Sabacky, Bachman & Weinkauff, 1977). Two of the four phenyl rings orient approximately parallel to the naphthyl rings. The angle between the least-squares planes of phenyl ring (I) [C(21)–C(26)] and naphthyl ring (II) [C(11)–C(20)] is 15.6 (3)°, while that between phenyl ring (IV) [C(39)–C(44)] and naphthyl ring (I) [C(1)–C(10)] is 18.0 (3)°. Short intramolecular contacts within the complex cation are listed in Table 4, which shows that close contacts among the naphthyl and phenyl groups are uniformly distributed throughout the molecule. This results in the alternating edge–face disposition of the phenyl rings on the P atoms.

Kashiwabara, Hanaki & Fujita (1980) have shown that four phenyl rings on P atoms of a chiral diphosphine or aminophosphine coordinated to Rh^I have helical structures and the stereochemical arrangement of phenyl rings can be designated as *P* or *M* according to the Cahn, Ingold & Prelog (1966) notation. According to this, chiralities of both P(1) and P(2) in this compound are assigned as *P*.

The C(45)–C(46) and C(50)–C(51) double bonds are not coordinated perpendicularly to the P(1)–Rh–P(2) plane but are tilted, in the same direction, by 14.6 (4) and 16.1 (5)°, respectively. C(45) and C(46) lie 0.989 (7) Å above and 0.309 (7) Å below the plane and C(50) and C(51) 0.364 (8) Å above and 0.904 (7) Å below the plane, respectively. Close contacts between the double bonds

and the phenyl rings are noted: C(45)···C(32) 3.285 (9), C(51)···C(38) 3.245 (10) Å. These are responsible for the unsymmetrical coordination of the double bonds. Similar unsymmetrical coordination of double bonds has often been observed for other olefin-Rh complexes [for example, Ball & Payne (1977); Ohga, Iitaka, Achiwa, Kogure & Ojima (1978)]. The average Rh-C distance for the coordinated double bonds is 2.208 (16) Å and the two coordinated C=C bond lengths are 1.341 (11) [C(45)-C(46)] and 1.321 (13) Å [C(50)-C(51)]. These values are comparable to the range of distances observed for other similar structures [for example, Ball & Payne (1977); Ohga, Iitaka, Achiwa, Kogure & Ojima (1978); Churchill & Bezman (1972)].

Table 4. *Short intramolecular distances (Å) with their e.s.d.'s*

Naphthyl ring (I): C(1)-C(10)			
Naphthyl ring (II): C(11)-C(20)			
Phenyl ring (I): C(21)-C(26)			
Phenyl ring (II): C(27)-C(32)			
Phenyl ring (III): C(33)-C(38)			
Phenyl ring (IV): C(39)-C(44)			
(a) Phenyl ring (I) to naphthyl ring (II)			
C(21)···C(11)	3.101 (7)	C(22)···C(13)	3.272 (8)
C(22)···C(12)	3.289 (8)		
(b) Phenyl ring (I) to naphthyl ring (I)			
C(22)···C(1)	3.338 (7)		
(c) Phenyl ring (IV) to naphthyl ring (I)			
C(39)···C(10)	3.133 (7)	C(44)···C(9)	3.365 (8)
C(44)···C(8)	3.332 (8)		
(d) Phenyl ring (IV) to naphthyl ring (II)			
C(44)···C(20)	3.230 (8)		
(e) Phenyl ring (II) to naphthyl ring (I)			
C(27)···C(1)	2.931 (7)		
C(27)···C(2)	3.098 (7)	C(27)···H[C(2)]	2.66 (5)
C(32)···C(2)	3.196 (8)	C(32)···H[C(2)]	2.44 (5)
(f) Phenyl ring (II) to phenyl ring (I)			
C(28)···C(21)	3.102 (8)	H[C(28)]···C(21)	2.58 (5)
C(28)···C(22)	3.308 (9)	H[C(28)]···C(22)	2.56 (5)
(g) Phenyl ring (III) to naphthyl ring (II)			
C(33)···C(20)	2.094 (7)		
C(33)···C(19)	3.067 (8)	C(33)···H[C(19)]	2.57 (7)
C(38)···C(19)	3.223 (9)	C(38)···H[C(19)]	2.60 (6)
(h) Phenyl ring (III) to phenyl ring (IV)			
C(34)···C(39)	3.138 (9)	H[C(34)]···C(39)	2.63 (7)
C(34)···C(44)	3.381 (10)	H[C(34)]···C(44)	2.59 (7)
(i) Trinorbornadiene to phenyl rings (II) and (III)			
C(45)···C(32)	3.285 (9)	H[C(45)]···C(32)	2.55 (6)
C(51)···C(38)	3.245 (10)	H[C(51)]···C(38)	2.60 (6)
(j) Naphthyl ring (I) to naphthyl ring (II)			
C(8)···C(12)	3.214 (7)	C(9)···C(12)	3.185 (7)
C(8)···C(13)	3.326 (8)	C(9)···C(13)	3.247 (7)

The crystal consists of discrete Rh^I complex cations and perchlorate anions. The average Cl-O bond length is 1.424 (6) Å. Intermolecular contacts appear to be normal.

Discussion

The present compound is useful for obtaining products of high enantiomeric purity in the hydrogenation of α -acylaminoacrylic acids (Miyashita, Yasuda, Takaya, Toriumi, Ito, Souchi & Noyori, 1980). A ³¹P NMR study indicated that the binap-coordinated Rh^I complex has a very high enantioface-differentiation ability, though this might not necessarily follow the high efficiency of the asymmetric reactions (Chan, Pluth & Halpern, 1980). The chirality of the catalyst, which is originally provided by the molecular dissymmetry of the binaphthyl group, is transmitted to the sites of olefin coordination through the central Rh atom. One of the most important requirements for being an effective catalyst in asymmetric hydrogenation is rigidity of the chiral structure at the site of olefin coordination. The binap fulfills this requirement almost perfectly. The induced-fit coordination of (*R*)-binap to the Rh causes the dihedral angle of the two naphthyl planes to be fixed. The resulting seven-membered chelate ring adopts the chiral λ skew(*v*) conformation. For ordinary seven-membered chelate rings, various types of conformations are possible in the solid state: chair (Brunie, Mazan, Langlois & Kagan, 1976); skew(*v*) (Kashiwabara, Hanaki & Fujita, 1980; Nakayama, Ooi & Kuroya, 1974); skew(*h*) (Kashiwabara, Hanaki & Fujita, 1980; Nakayama, Ooi & Kuroya, 1974; Sato & Saito, 1975); twist-chair (Nakayama, Matsumoto, Ooi & Kuroya, 1973); and boat (Onuma & Nakamura, 1981). Usually, a seven-membered ring is more flexible than a five- or six-membered chelate ring, especially in solution states. But this is not the case in this complex. All the four C atoms incorporated into the chelate ring skeleton are of *sp*² hybridization type and are the constituent atoms of the naphthyl groups and, as a result, form a very rigid λ skew(*v*) ring. The rigidity would be maintained even in solution. The chiral, rigid seven-membered structure in turn determines the dispositions of the four phenyl rings on the P atoms. The rigid orientations of the phenyl groups are also effected by the steric interactions among the phenyl and naphthyl groups in close proximity. Consequently, the four phenyl rings are arranged in such a way as to exert steric influence against incoming prochiral olefins. The interactions between the phenyl rings and an incoming substrate are undoubtedly responsible for the preferred coordination of one enantioface of the prochiral olefinic ligand over the other. The important roles played by the phenyl rings have also been discussed for other systems (Knowles, Vineyard, Sabacky & Stults, 1979).

The calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS III* (Sakurai & Kobayashi, 1979).

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Structure of Disodium Guanosine 5'-Phosphate Heptahydrate

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Abstract

$\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_8\text{P}^{2-} \cdot 2\text{Na}^+ \cdot 7\text{H}_2\text{O}$ is orthorhombic, $P2_12_12_1$, with $a = 22.267(2)$, $b = 21.360(2)$, $c = 9.035(1)$ Å, $Z = 8$, $V = 4297(2)$ Å³, $M_r = 533.3$, $D_c = 1.65$, $D_o = 1.63$ Mg m⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $T = 299(\pm 1)$ K, $F(000) = 2224$. The intensity data were collected on an automated diffractometer, and the structure was solved by direct methods. Block-diagonal

least-squares refinement of the non-hydrogen atoms and placement of the H atoms from difference Fourier maps or at calculated positions resulted in an R of 0.056 for 3927 reflections. The two independent GMP molecules, fourteen water molecules and four Na⁺ ions in the asymmetric unit form an intricate network of hydrogen and coordination bonds, but the packing scheme does not include base–base hydrogen bonds or the base stacking often observed in crystal structures of guanine compounds. The sodium coordination shells, which can be described as distorted octahedra, involve no direct interactions with the ionized phosphate groups.

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