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Chiral Phosphine Ligands in Asymmetric Synthesis. Molecular Structure and Absolute Configuration of (1,5-Cyclooctadiene)-(2*S*,3*S*)-2,3-bis(diphenylphosphino)butanerhodium(I) Perchlorate Tetrahydrofuran Solvate

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Received October 23, 1976

AIC60770T

The molecular structure and absolute configuration of (1,5-cyclooctadiene)-(2*S*,3*S*)-2,3-bis(diphenylphosphino)butanerhodium(I) perchlorate·THF, [$Rh(\pi-C_8H_{12})(PPh_2CHCH_3CHCH_3PPh_2)]ClO_4 \cdot C_4H_8O$, have been determined from three-dimensional x-ray data collected by counter methods. The complex crystallizes in the monoclinic space group $P2_1$ with two formula units per unit cell. The unit cell dimensions are $a = 11.423$ (2) Å, $b = 18.555$ (3) Å, $c = 9.950$ (2) Å, and $\beta = 113.53$ (1)°. The structure has been refined by full-matrix least-squares techniques on F, using 6691 unique reflections for which $F^2 > 0$, to a final agreement factor of 0.0403. The cation is in a square-planar configuration (if the diene is viewed as a bidendate chelating ligand) with average Rh–P and Rh–C distances of 2.271 (4) and 2.24 (1) Å, respectively. The absolute configurations of the asymmetric carbon atoms of the phosphine ligand were determined by the Bijvoet method to be *S*,*S*.

Introduction

There is growing interest in the use of asymmetric catalyst systems for preparing optically active compounds. In particular the homogeneous catalysts based on rhodium complexes of chiral phosphines have been extensively investigated in regard to their ability to asymmetrically hydrogenate selected olefins.[1-3] The mechanism of the catalytic process involving these complexes has been investigated by Wilkinson and others,[4] who postulated the existence of an intermediate species in which the olefin is coordinated to the rhodium–phosphine complex. For an optically active alkane to be produced, the hydrogenation mechanism must give stereospecific cis addition, and the olefin used must necessarily be prochiral. The presence of an asymmetric site in the rhodium complex may influence the coordination of this prochiral olefin in such a way that a diastereomeric excess of one form of the rhodium–olefin complex results. Since the hydrogenation mechanism is stereospecific, the end result will be an enantiomeric excess of one hand of the resultant alkane.

Introducing this asymmetric site either on the phosphorus atom bound to the metal atom or as a side chain on the phosphorus atom are two methods which have met with some success.[2,5] However, the best results seem to be realized when a chelating diphosphine is used. In this case excellent optical yields can be achieved with the asymmetric site either at the phosphorus atom or on a side chain remote from the phosphorus.[3,5] This improvement in stereoselectivity can be attributed to the presence of a rigid ligand environment firmly bonded to the metal atom, which prevents any marked change in the asymmetric environment during the coordination and hydrogenation of the olefin.

As the stereochemistry of the phosphine ligand plays a major role in determining the optical stereospecificity as well as the efficiency of the catalytic action, we decided to examine the solid-state structures of these complexes to determine both the absolute configurations at the asymmetric sites in the phosphine ligand and the relationship between the environment provided by the phosphine ligand and the asymmetric catalytic ability of the complex. In the present case high optical yields for the hydrogenation of acrylic acid derivatives can be obtained using the norbornadiene complex as the catalyst precursor.[6] However crystals suitable for x-ray analysis could not be obtained, so the 1,5-cyclooctadiene (COD) complex was examined instead.

Experimental Section

Table I. Crystal Data

$C_{40}H_{48}ClO_5P_2Rh$	Fw 809.131
$a = 11.423$ (2) Å	Space group $P2_1$
$b = 18.555$ (3) Å	$Z = 2$
$c = 9.950$ (2) Å	Cell vol = 1933.5 Å^3
$\beta = 113.53$ (1)°	Density (obsd)^a = 1.397 (1) g cm^{-3}
μ(Cu K$\bar{\alpha}$) = 51.15 cm^{-1}	Density (calcd) = 1.390 g cm^{-3}

^{a} By neutral buoyancy in CCl_4 and *n*-pentane.

Table II. Experimental Conditions for Data Collection

Radiation: Cu Kα, Ni-foil prefilter (0.018 mm)
Takeoff angle: 1.4° (for 80% of maximum Bragg intensity)
Aperture: 5 × 5 mm, 31 cm from crystal
Data collected: $\pm h, \pm k, +l$, for $0 < 2\theta < 125°$; $\pm h, +k, +l$, for $125 < 2\theta < 130°$
Scan: θ–2θ corrected for dispersion, range 1.2° (symmetric) for $0 < 2\theta < 110°$; for $110° < 2\theta$ range of Kα_1 − 0.7° to Kα_2 + 0.6°
Scan speed: 2° min^{-1}
Background: 20-s stationary crystal, stationary counter at scan limits
Standards: Five recorded every 200 observations, 200, 002, 020, 011, $\bar{2}00$

Light-orange crystals of (1,5-cyclooctadiene)-2,3-bis(diphenylphosphino)butanerhodium(I) perchlorate–tetrahydrofuran, [$Rh(\pi-C_8H_{12})(PPh_2CHCH_3CHCH_3PPh_2)]ClO_4 \cdot C_4H_8O$, were supplied by Bosnich and Fryzuk. Preliminary Weissenberg and precession photography showed the crystals to be monoclinic with Laué symmetry $2/m$. The systematic absences observed, $0k0$ for k odd, and the requirement that an optically active species crystallize in an acentric space group determine the space group to be $P2_1$-C_2^2, No. 4.[7]

The crystal chosen for data collection was of approximate dimensions 0.38 × 0.22 × 0.12 mm. It was carefully measured on a microscope fitted with a filar eyepiece. An optical goniometry study revealed nine crystal faces, (110), ($\bar{1}$10), (011), (01$\bar{1}$), (010), {100}, and {001}. Two broken faces were best approximated as (2$\bar{3}$1) and (0$\bar{6}$1). The crystal was mounted on a Picker FACS-1 computer-controlled diffractometer with the long dimension of the crystal, [010], approximately 10° from coincidence with the spindle axis. Cell constants and an orientation matrix were obtained from a least-squares refinement of 26 intense, carefully centered reflections with $24 < 2\theta < 57°$. Prefiltered Cu Kα_1 radiation (λ 1.540 56 Å) was used at an ambient temperature of 20 °C. Crystal data are given in Table I.

The conditions used for data collection are summarized in Table II. Several ω scans of intense, low-angle reflections were recorded as a check on crystal mosaicity. The average width at half-height was 0.08°. Measurement of standard reflections over the course of data collection and an examination of crystal mosaicity at the end showed no significant decomposition had occurred.

The intensity data were processed[8] and the value for p, the "ignorance" factor, was chosen to be 0.02. An absorption correction[9] was applied to the 6697 data for which $F^2 > 0$. The maximum and

Table III. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	1866.3 (3)	3000	−124.6 (3)	379 (2)	385 (2)	347 (2)	27 (2)	150 (1)	−2 (2)
P(1)	1528.0 (13)	4196.5 (7)	−629 (2)	357 (6)	394 (7)	477 (8)	28 (5)	169 (6)	1 (7)
P(2)	1209.4 (10)	2894.0 (9)	−2586.5 (12)	387 (5)	456 (9)	372 (5)	4 (6)	173 (4)	−5 (6)
Cl	−2721 (2)	2792.3 (8)	669 (2)	790 (10)	625 (11)	786 (11)	−89 (7)	314 (9)	−27 (7)
O(1)	−2910 (8)	3194 (4)	−627 (7)	2155 (68)	1217 (65)	773 (36)	−265 (50)	586 (43)	38 (37)
O(2)	−3911 (6)	2657 (3)	733 (9)	1098 (46)	1306 (54)	1899 (74)	119 (38)	885 (51)	215 (48)
O(3)	−2193 (7)	2126 (4)	662 (12)	1238 (53)	771 (42)	3780 (134)	190 (39)	1262 (73)	39 (60)
O(4)	−1983 (8)	3213 (4)	1854 (7)	2345 (76)	1138 (60)	847 (39)	−588 (52)	−235 (47)	−15 (36)
C(1)	580 (5)	4322 (3)	−2603 (6)	475 (28)	525 (32)	530 (31)	50 (24)	177 (25)	62 (25)
C(2)	1154 (5)	3785 (3)	−3414 (6)	599 (33)	544 (33)	465 (31)	−50 (26)	241 (27)	30 (25)
C(3)	455 (7)	5095 (4)	−3159 (8)	940 (50)	707 (43)	698 (44)	209 (38)	209 (39)	205 (36)
C(4)	508 (8)	3810 (4)	−5085 (7)	1264 (63)	757 (45)	535 (40)	−21 (42)	412 (43)	97 (33)
C(5)	1672 (5)	2980 (5)	2030 (5)	772 (32)	689 (33)	385 (23)	87 (48)	290 (23)	−45 (39)
C(6)	1304 (7)	2225 (4)	2298 (8)	929 (49)	939 (52)	687 (43)	41 (41)	497 (40)	254 (39)
C(7)	1079 (7)	1680 (4)	1136 (8)	854 (46)	785 (47)	819 (49)	−92 (38)	452 (41)	158 (39)
C(8)	1762 (6)	1808 (3)	146 (7)	675 (39)	484 (35)	547 (37)	−8 (28)	193 (33)	41 (30)
C(9)	3013 (5)	1980 (3)	567 (7)	554 (31)	467 (31)	614 (35)	141 (25)	236 (28)	58 (26)
C(10)	3955 (6)	2040 (4)	2165 (8)	611 (36)	685 (42)	695 (42)	184 (31)	147 (33)	73 (34)
C(11)	4072 (6)	2752 (4)	2819 (7)	656 (38)	990 (58)	578 (37)	47 (34)	40 (31)	−43 (33)
C(12)	2877 (6)	3208 (3)	2292 (6)	708 (35)	653 (44)	376 (27)	68 (28)	139 (26)	−50 (24)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional and thermal parameters have been multiplied by 10^4. [b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

minimum transmission coefficients were 0.657 and 0.393, respectively, a variation of 67.2%.

To give a check on the quality of the data the 12 pairs of reflections collected which are equivalent by symmetry ($h00$ and $\bar{h}00$) were compared. The R factor for averaging for these data was 0.010 and these reflections were left as independent reflections during the refinement.

Structure Solution and Refinement

For the solution and preliminary refinement only those data with $2\theta \leq 90°$ and $F^2 > 3\sigma(F^2)$ were used. The positional parameters for the Rh atom were determined from a three-dimensional Patterson synthesis. A series of least-squares refinements and difference Fourier synthesis calculations located the remaining 43 non-hydrogen atoms of the anion and cation. Refinement of atomic parameters was carried out by full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes, respectively. The weighting factor w is given by $w = 4F_o^2/\sigma^2(F_o^2)$.

The neutral-atom scattering factors for the nonhydrogen atoms were those of Cromer and Waber[10] while those for the H atom were taken from Stewart, Davidson, and Simpson.[11] The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were those of Cromer and Liberman[12] and were included in the calculations for the Rh, P, and Cl atoms. Further refinement employed 6465 observations for which $F^2 > 3\sigma(F^2)$. One cycle of full-matrix least-squares refinement varying the positional and thermal parameters for the ion pair (omitting the THF of solvation) with the four phenyl rings constrained as rigid groups (D_{6h} symmetry, C–C = 1.392 Å) and employing anisotropic temperature factors for the Rh, P, and Cl atoms gave values of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.0846$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2} = 0.1223$. At this point the enantiomeric structure was refined under identical conditions to R_1 and R_2 values of 0.0684 and 0.1024, respectively. Accordingly, this second model was used in the subsequent calculations.

In order to locate the solvent molecule, a series of difference Fourier syntheses was computed, but these revealed only a torus of electron density containing no peaks higher than 1.4 e Å^{-3}. Since the presence of a solvent molecule had been confirmed by elemental analysis, the density determination, and ^{1}H NMR results, a disordered tetrahydrofuran molecule was postulated. After several trials a suitable model was achieved, employing a molecule of C_2 symmetry[13] exhibiting twofold disorder. The second molecule, superimposed upon the first, was rotated by approximately 180° about an axis perpendicular to the mean molecular plane. Optimal positional and thermal parameters for these atoms were obtained by including the two molecules as rigid groups, each of multiplicity 0.5, and by refining the group origin and individual isotropic thermal parameters. The parameters so obtained were not varied subsequently. One cycle of least-squares refinement on this model varying the positional and thermal parameters for all the atoms of the cation and anion, using the 3454 data not containing the Bijvoet pairs, resulted in R_1 and R_2 values of 0.0485 and 0.0644, respectively.

All 40 H atoms present in the cation were located in a difference Fourier synthesis and these positions compared favorably to idealized positional coordinates calculated assuming sp^2 and sp^3 coordination geometries about the C atoms and an H–C bond distance of 0.95 Å. The H atoms were assigned isotropic thermal parameters 1.0 Å^2 greater than those of the atom to which they are bonded. The contributions from the H atoms, in their calculated positions (excluding those of the tetrahydrofuran), were included in subsequent refinement cycles but no attempt was made to refine their parameters.

One cycle of full-matrix least-squares refinement using all of the data with $F^2 > 3\sigma(F^2)$ followed by recalculation of the H atom positions preceded the convergence of the model. In the final two cycles of refinement all 6697 data for which $F^2 > 0$ were used to refine 276 variables. This model converged at residuals of $R_1 = 0.0403$ and $R_2 = 0.0505$. In the final cycle the largest parameter shift was 0.98 of its estimated standard deviation and was associated with the z coordinate of O(3) of the perchlorate anion. The error in an observation of unit weight was 2.68 electrons. A statistical analysis of R_2 in terms of $|F_o|$, diffractometer setting angles χ and ϕ, and $\lambda^{-1}\sin\theta$ showed no unusual trends. A difference Fourier synthesis calculated from the final structure factors contained no features of chemical significance. The highest peak, with fractional coordinates −0.439, 0.415, −0.394, located near the disordered solvent molecule, had an electron density of 0.93 (12) e Å^{-3}. An examination of F_o and F_c showed no evidence for secondary extinction.

Final positional and thermal parameters for the nonhydrogen atoms are given in Tables III and IV; those for the H atoms are in Table V and the group parameters are given in Table VI. The structure factor amplitudes are presented in Table VII.[14]

Determination of Absolute Configuration

The absolute configuration of the cation, determined by the Bijvoet absorption edge technique, was confirmed by refinement of both models, including recalculated H atom contributions, to convergence. The chosen model had residuals of $R_1 = 0.0403$ and $R_2 = 0.0505$ while the enantiomeric structure gave R_1 and R_2 values of 0.0726 and 0.1021, respectively. When the R factor ratio test[15] is applied to R_2, the alternate model can be rejected at less than the 0.005 significance level assuming no systematic errors in the data. Table VIII lists a selection of structure amplitudes for the chosen model for which $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ differ by more than 25%, based on the final positional parameters. The observed F_o relationships for the same reflections confirm the choice of enantiomer.

Structure Description

A perspective drawing of the cation with the atom-numbering scheme is presented in Figure 1 and a stereoview of the

Table IV. Final Atomic Positional[a] and Thermal Parameters for the Phenyl Ring Atoms

Atom	*x*	*y*	*z*	*B*, Å^2
C(21)	682 (5)	4663 (3)	297 (6)	3.58 (9)
C(22)	−581 (6)	4479 (3)	−57 (7)	4.90 (12)
C(23)	−1216 (7)	4749 (4)	742 (8)	5.66 (14)
C(24)	−622 (6)	5191 (4)	1900 (7)	5.35 (13)
C(25)	606 (6)	5383 (4)	2280 (7)	5.56 (13)
C(26)	1274 (5)	5122 (3)	1482 (6)	4.53 (11)
C(31)	3013 (5)	4678 (3)	−206 (6)	3.87 (10)
C(32)	3100 (6)	5418 (3)	−266 (7)	4.87 (12)
C(33)	4292 (7)	5760 (4)	74 (8)	5.91 (15)
C(34)	5371 (7)	5344 (4)	437 (8)	6.0 (2)
C(35)	5291 (7)	4597 (4)	507 (8)	5.78 (14)
C(36)	4116 (5)	4265 (3)	147 (6)	4.41 (11)
C(41)	−400 (5)	2524 (3)	−3438 (6)	3.59 (9)
C(42)	−969 (6)	2305 (3)	−4893 (6)	4.55 (11)
C(43)	−2206 (6)	2008 (4)	−5457 (8)	5.67 (14)
C(44)	−2841 (7)	1934 (4)	−4569 (8)	6.06 (15)
C(45)	−2292 (6)	2165 (4)	−3131 (7)	5.38 (13)
C(46)	−1102 (5)	2465 (3)	−2580 (6)	4.33 (10)
C(51)	2215 (5)	2345 (3)	−3195 (5)	3.60 (9)
C(52)	3460 (6)	2611 (3)	−2881 (7)	4.39 (11)
C(53)	4330 (7)	2180 (4)	−3179 (8)	5.68 (14)
C(54)	4002 (7)	1510 (4)	−3771 (8)	5.98 (14)
C(55)	2780 (6)	1235 (4)	−4066 (8)	5.85 (14)
C(56)	1907 (5)	1661 (3)	−3754 (6)	5.31 (13)

[a] The positional parameters have been multiplied by 10^4.

Table V. Derived Hydrogen Atom Positional ($\times 10^4$) and Isotropic Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2
H1C(1)	−261	4164	−2787	5.15
H1C(2)	2020	3923	−3162	5.05
H1C(3)	1276	5295	−2874	7.46
H2C(3)	34	5084	−4201	7.46
H3C(3)	−38	5361	−2763	7.46
H1C(4)	578	4292	−5389	7.68
H2C(4)	921	3489	−5483	7.68
H3C(4)	−361	3689	−5379	7.68
H1C(5)	992	3338	1638	5.79
H1C(6)	1972	2044	3145	7.34
H2C(6)	539	2251	2457	7.34
H1C(7)	1345	1220	1592	6.80
H2C(7)	180	1657	549	6.80
H1C(8)	1244	1760	−887	5.58
H1C(9)	3343	2084	−170	5.22
H1C(10)	3664	1714	2713	6.55
H2C(10)	4771	1893	2242	6.55
H1C(11)	4333	2699	3856	7.20
H2C(11)	4707	3015	2640	7.20
H1C(12)	2991	3711	2124	5.48
H1C(22)	−1017	4179	−871	5.95
H1C(23)	−2077	4630	481	6.80
H1C(24)	−1068	5355	2438	6.24
H1C(25)	1025	5699	3067	6.48
H1C(26)	2142	5244	1753	5.43
H1C(32)	2344	5699	−524	5.79
H1C(33)	4327	6275	93	7.09
H1C(34)	6171	5570	588	7.10
H1C(35)	6041	4312	804	6.65
H1C(36)	4048	3752	151	5.47
H1C(42)	−508	2346	−5500	5.58
H1C(43)	−2608	1855	−6443	6.69
H1C(44)	−3666	1718	−4905	6.97
H1C(45)	−2755	2123	−2516	6.12
H1C(46)	−746	2620	−1585	5.25
H1C(56)	1083	1479	−3937	5.40
H1C(55)	2553	772	−4501	6.91
H1C(54)	4587	1225	−4015	7.19
H1C(53)	5159	2363	−2978	6.80
H1C(52)	3698	3067	−2476	6.41

overall geometry of the cation is shown in Figure 2. Selected bond distances and angles are listed in Table IX.

The Rh atom is coordinated in a square-planar geometry to the diphosphine and the diene ligands. The internal geometry of the diene is quite normal with average C(sp^3)–C(sp^3) and C(sp^2)–C(sp^3) distances of 1.47 (2) and 1.51 (1) Å, respectively, and an average internal angle at the sp^3 carbons

Table VI. Final Group Positional and Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2
		THF(1)		
O(6)[a]	0.6142	0.5108	0.6826	21.9519
C(61)	0.6853	0.4706	0.6180	18.5111
C(62)	0.5837	0.4234	0.4855	30.3335
C(63)	0.4675	0.4742	0.4346	26.4661
C(64)	0.4809	0.5074	0.5910	26.7729
		THF(2)		
O(7)	0.5457	0.4713	0.4846	29.0580
C(71)	0.4248	0.4642	0.4946	20.6063
C(72)	0.4528	0.4464	0.6644	27.4673
C(73)	0.5776	0.4032	0.7087	34.0254
C(74)	0.6452	0.4458	0.6164	26.8770

[a] The atoms are numbered sequentially around the ring starting at the O atom in each case.

Table VIII. Determination of Absolute Configuration

hkl	$F_c(hkl)$	Obsd F_o relationship	$F_c(h\bar{k}l)$
$\bar{6},\bar{14},3$	6.87	<	10.25
941	5.96	<	8.59
$\bar{11},\bar{11},2$	3.44	<	4.76
$6\bar{5}4$	7.38	<	10.20
$0\bar{8}6$	11.01	<	15.17
$\bar{11},4,5$	9.03	>	5.66
$\bar{7},\bar{15},7$	6.05	<	8.29
$\bar{3},\bar{16},7$	6.63	<	8.98
$\bar{3},12,2$	19.58	>	12.89
$0\bar{6}6$	16.88	<	22.24
$\bar{2},9,10$	2.68	>	1.84
$\bar{4}57$	16.49	<	21.40
$\bar{9}35$	17.69	>	12.70
$\bar{1}51$	40.03	>	29.21

Table IX. Selected Bond Distances (Å) and Angles (deg)

Rh–P(1)	2.275 (1)
Rh–P(2)	2.266 (1)
Rh–C(5)	2.241 (4)
Rh–C(8)	2.238 (6)
Rh–C(9)	2.247 (5)
Rh–C(12)	2.247 (5)
C(5)–C(12)	1.362 (8)
C(8)–C(9)	1.357 (8)
P(1)–C(1)	1.840 (6)
P(1)–C(21)	1.801 (5)
P(1)–C(31)	1.812 (5)
P(2)–C(2)	1.837 (6)
P(2)–C(41)	1.824 (5)
P(2)–C(51)	1.811 (5)
C(1)–C(3)	1.524 (8)
C(2)–C(4)	1.527 (8)
C(1)–C(2)	1.580 (8)
C(5)–C(6)	1.517 (11)
C(6)–C(7)	1.480 (10)
C(7)–C(8)	1.500 (9)
C(9)–C(10)	1.526 (9)
C(10)–C(11)	1.456 (9)
C(11)–C(12)	1.510 (8)
Cl–O(1)	1.429 (6)
Cl–O(2)	1.408 (6)
Cl–O(3)	1.378 (6)
Cl–O(4)	1.385 (6)

P(1)–Rh–P(2)	83.82 (6)
C(5)–Rh–C(8)	80.7 (3)
C(9)–Rh–C(12)	80.2 (2)
Rh–P(1)–C(1)	109.5 (2)
Rh–P(1)–C(31)	111.7 (2)
C(1)–P(1)–C(21)	106.2 (2)
C(21)–P(1)–C(31)	106.7 (2)
Rh–P(2)–C(2)	110.1 (2)
Rh–P(2)–C(51)	115.5 (2)
C(2)–P(2)–C(41)	106.4 (2)
C(41)–P(2)–C(51)	106.8 (2)
P(1)–C(1)–C(2)	106.2 (3)
P(1)–C(1)–C(3)	115.8 (4)
P(2)–C(2)–C(1)	106.6 (4)
P(2)–C(2)–C(4)	115.5 (4)
C(6)–C(5)–C(12)	125.7 (6)
C(5)–C(6)–C(7)	117.9 (5)
C(6)–C(7)–C(8)	115.5 (6)
C(7)–C(8)–C(9)	126.5 (6)
C(8)–C(9)–C(10)	123.8 (6)
C(10)–C(11)–C(12)	116.4 (5)
C(9)–C(10)–C(11)	115.6 (5)
C(5)–C(12)–C(11)	126.6 (6)
C(3)–C(1)–C(2)–C(4)	−50.5 (7)[a]
O(1)–Cl–O(2)	109.5 (5)
O(2)–Cl–O(3)	105.8 (4)
O(2)–Cl–O(4)	109.4 (5)
O(3)–Cl–O(4)	113.1 (6)

[a] When looking from C(1) to C(2) rotating C(3) about the C(1)–C(2) axis will superimpose its image upon C(4).

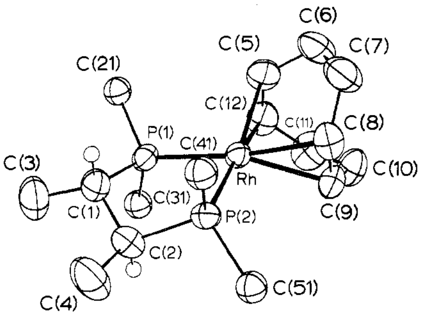

Figure 1. View of the cation, including selected H atoms, depicting the atom-numbering scheme. Only the α carbon atom of each phenyl ring is shown. Atoms other than H are represented by 50% probability thermal ellipsoids.

Table X

Selected Weighted Least-Squares Planes[a]

Plane 1: $A = 0.624, B = -14.7, C = 5.35, D = -6.64$[b]

C(21)	0.000 (5)	C(24)	0.003 (6)	P(1)	0.242
C(22)	0.003 (6)	C(25)	0.001 (7)		
C(23)	−0.005 (7)	C(26)	−0.002 (6)		

Plane 2: $A = -3.01, B = 0.951, C = 9.84, D = -0.674$

C(31)	0.009 (5)	C(34)	−0.006 (8)	P(1)	−0.006
C(32)	−0.005 (6)	C(35)	0.016 (7)		
C(33)	0.002 (7)	C(36)	−0.015 (6)		

Plane 3: $A = 3.47, B = -16.9, C = 1.33, D = -4.88$

C(41)	0.014 (5)	C(44)	0.014 (7)	P(2)	0.060
C(42)	−0.007 (6)	C(45)	0.004 (7)		
C(43)	−0.010 (7)	C(46)	−0.016 (6)		

Plane 4: $A = -0.544, B = -7.09, C = 8.61, D = -4.52$

C(51)	−0.009 (5)	C(54)	−0.010 (7)	P(2)	0.181
C(52)	0.011 (6)	C(55)	0.007 (7)		
C(53)	−0.003 (7)	C(56)	0.005 (7)		

Dihedral Angles between Planes

Plane	Plane	Angle, deg	Plane	Plane	Angle, deg
1	2	57.80	2	3	81.90
1	3	24.98	2	4	28.12
1	4	30.40	3	4	53.83

Displacements from the Rh-P(1)-P(2) Plane, Å

C(1)	0.437 (5)	C(21)	1.155 (5)
C(2)	−0.363 (6)	C(31)	−1.640 (5)
C(5)	0.891 (6)	C(41)	1.628 (5)
C(12)	−0.434 (6)	C(51)	−1.222 (5)
C(8)	0.427 (6)		
C(9)	−0.890 (6)		

[a] Distances given are displacements from the plane in Å with those without esd's related to atoms not included in the calculation of the plane. [b] The form of the plane equation is $Ax + By + Cz - D = 0$.

of 116 (1)°. The two coordinated C–C double-bond lengths are 1.362 (8) and 1.357 (8) Å. These values determined in this structure are comparable to the range of distances and angles observed for this ligand in other structures.[16,17] The average Rh–C distance for the coordinated double bonds is 2.24 (1) Å. The C(5)–C(12) and C(8)–C(9) double bonds are not coordinated perpendicular to the Rh–P(1)–P(2) plane but are tilted, in the same direction, by 13.3 and 13.9°, respectively, as often observed for coordinated double bonds. Also the C atoms of these two double bonds are not symmetrically disposed above and below the Rh–P(1)–P(2) plane, but rather the diene is coordinated with C(5) and C(9) approximately twice as far out of the plane as C(12) and C(8). A selection of least-squares planes and distances from the coordination plane is given in Table X.

The overall conformation of the five-membered chelating phosphine ring is δ with the absolute configuration of the two asymmetric carbon atoms designated *S,S* which places the two methyl groups, C(3) and C(4), in the expected equatorial dispositions.

The Rh–P(1) and Rh–P(2) distances are 2.275 (1) and 2.266 (1) Å, respectively. These are somewhat shorter than might be expected from other rhodium–phosphine structures,[18-20] but we are unable to comment on the significance, if any, of this observation. The P(1)–Rh–P(2) angle of 83.82 (6)° is comparable to values observed in other structures with five-membered chelating phosphine ligands.[19,20] The average P–C(alkyl) and P–C(aryl) distances of 1.838 (2) and 1.812 (5) Å are normal, as is the average C–C distance of 1.54 (2) Å. The four phenyl rings have the following average bond lengths and angles: R1 (C(21)–C(26)), 1.373 (8) Å, 120.0 (4)°; R2 (C(31)–C(36)), 1.391 (6) Å, 120.0 (3)°; R3 (C(41)–C(46)), 1.382 (7) Å, 120.0 (4)°; R4 (C(51)–C(56)), 1.392 (8) Å, 120.0 (4)°.

Alternatively, the ring geometries may be examined to see if there are significant deviations from the D_{6h} symmetry often imposed in group refinements. The C–C distances show no systematic deviations from the mean values with the largest difference being 2.5σ. The angles at the α carbon atoms and the ortho, meta, and para atoms have means of 118.5 (2), 120.5 (2), 120.1 (3), and 120.3 (1)°, respectively. These values indicate a significant (4.8σ) decrease of the internal angle at the α carbon atom of a phenyl ring from the expected angle of 120° for a group of D_{6h} symmetry.

The diphosphine ligand maintains an approximate C_2 symmetry after coordination as indicated by the disposition of the phenyl rings about the Rh–P(1)–P(2) plane. Thus the related α carbon atoms, C(21) and C(51), are approximately equidistant from the plane (Table X) as is the pair C(31) and C(41). It should also be noted that phenyl rings R1 and R4 are bent toward the COD ligand with P(1)–C(21)–C(24) and P(2)–C(51)–C(54) angles of 171.8 (3) and 172.7 (3)°, re-

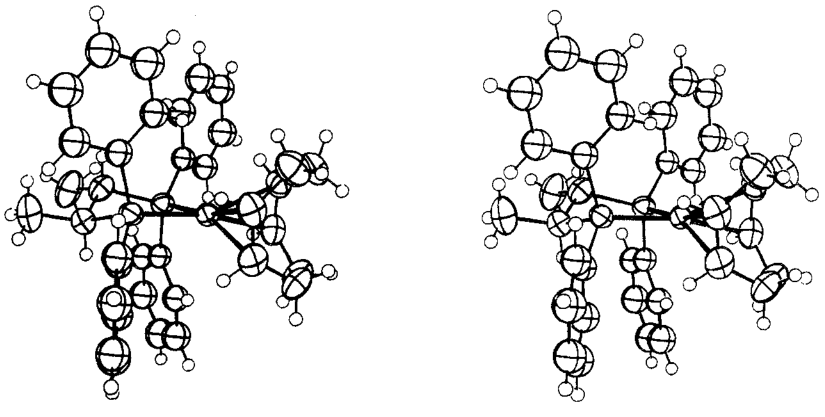

Figure 2. Stereoview of the cation showing the stereochemical arrangement of the phenyl rings.

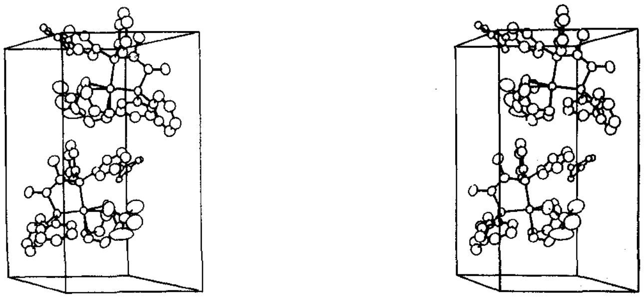

Figure 3. Stereoview of the unit cell content. For clarity only one molecule is shown at each tetrahydrofuran site, with reduced thermal parameters. The *c* axis runs from left to right, with the *b* axis vertical.

spectively. The corresponding angles for the other two rings are 176.6 (3) and 176.5 (3)°.

The geometry of the perchlorate anion is unexceptional, with an average Cl–O bond length of 1.40 (1) Å. There are no close contacts to the cation which might indicate a hydrogen-bonding network, for the distance of closest approach is 2.65 Å between O(3) and HC(32) on one phenyl ring. The shortest Rh–Cl and Rh–Rh distances are 5.616 (2) and 9.950 (2) Å, respectively. Thus the crystals are built up from discrete cations and anions, as is shown in the stereoview of the unit cell contents presented in Figure 3.

Discussion

A catalyst for asymmetric synthesis must show not only good catalytic activity but also high coordination stereospecificity in order to give a product of high enantiomeric purity. The catalyst systems which have been most successful in this latter respect contain a rigid ligand environment firmly bonded to the metal atom to provide the necessary asymmetry in the catalyst.

It has been found that a chelating diphosphine provides just such an environment and, in addition, permits the introduction of asymmetric sites at varying distances from the metal atom, either directly on the phosphorus atoms or on side chains in the chelate ring. If this latter method is used, it has the further advantage that the substituents cause the chelate ring to have a preferred conformation resulting in an enhancement of the rigidity of the ligand. However, the asymmetric sites are consequently more distant from the metal atom and the asymmetric environment must presumably be transmitted to the site of olefin coordination by the substituents on the phosphorus atoms.

The importance of the role played by the phenyl rings on a phosphine ligand was demonstrated nicely by Kagan.[21] In that instance a seven-membered chelating diphosphine was used to provide the asymmetric sites and excellent results were observed in the catalysis as long as the two phenyl rings on each of the phosphorus atoms were free to adopt their preferred configurations. In the case of the present diphosphine ligand, the chelate ring adopts the conformation in which the methyl substituents occupy equatorial positions, and the phenyl rings are arranged in positions where they present short-range interactions to incoming ligands. These interactions will result in either an attractive or a repulsive force between the phenyl rings and the incoming ligand. We are presently studying a system in which just such an interaction between a phenyl ring on a coordinated asymmetric sulfoxide ligand and the substituent upon the incoming prochiral olefin is responsible for the preferential coordination of one face of the olefin ligand.[22]

The choice of the cyclooctadiene derivative for this study was dictated by the need for crystals of a quality suitable for diffraction studies. Although the observed stereochemistry of the phosphine ligand must represent a preferred configuration, it is difficult to interpret stereospecific hydrogenation in terms of the disposition of the phenyl rings in this complex. Conclusions along these lines must await the analysis of a complex containing a prochiral olefin.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work.

Registry No. $[Rh(\pi\text{-}C_8H_{12})(PPh_2CHCH_3CHCH_3PPh_2)]ClO_4\cdot C_4H_8O$, 61886-03-1.

Supplementary Material Available: Table VII listing structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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