

Structure of (Bicyclo[2.2.1]hepta-2,5-diene)[(-)-(R,R)-2-exo,3-endo-bis(diphenylphosphino)bicyclo[2.2.1]heptane]rhodium(I) Perchlorate Tetrahydrofuran Solvate, $C_{38}H_{38}P_2Rh^+ \cdot ClO_4^- \cdot C_4H_8O$, the Penultimate Catalyst Precursor in Asymmetric Reductions using the Norphos Ligand

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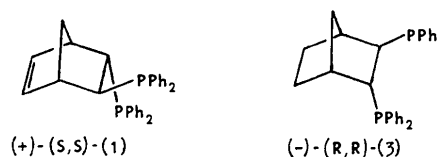
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(Received 26 January 1983; accepted 14 July 1983)

Abstract. $M_r = 831.08$, orthorhombic, $P2_12_12_1$, $a = 15.794$ (3), $b = 20.541$ (3), $c = 11.399$ (1) Å, $V = 3698.2$ Å³, $Z = 4$, $D_x = 1.492$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 6.57$ cm⁻¹, $F(000) = 1720$, $T = 238$ K. $R = 0.044$ for 4372 observed reflections. This structure is essentially isomorphous with that previously reported for the related unsaturated species. The most pronounced effect of the clockwise torque imposed on the rigid hydrocarbon framework upon chelation of the Rh^I species by the diphosphine ligand is the distortion of the PCCP dihedral angle from an ideal value of 120 to 64°. Other dihedral and bonding angles are also affected.

Introduction. The design, synthesis, and study of chiral auxiliaries for transition-metal-catalyzed asymmetric reactions continues to generate considerable interest (Merrill, 1981; Valentine & Scott, 1978; Glaser, Geresh & Twaik, 1980; Caplar, Comisso & Šunjić, 1981; Chan, Pluth & Halpern, 1980). An important class of such chiral modifiers is that of the chelating diphosphines, and many such systems have been described (Kagan & Dang, 1972; Vineyard, Knowles, Sabacky, Bachman & Weinkauff, 1977; Fryzuk & Bosnich, 1977, 1978; Achiwa, 1976; Lauer, Samuel & Kagan, 1979; Miyashita, Yasuda, Takaya, Toriumi, Ito, Souchi & Noyori, 1980; Toriumi, Ito, Takaya, Souchi & Noyori, 1982). One such system, (+)- and (-)-norphos {5,6-bis(diphenylphosphino)bicyclo[2.2.1]hept-2-ene}, (1), is characterized by its relative synthetic accessibility and its ability to induce high enantiomeric excesses when used as a ligand for Rh^I in the catalytic hydrogenation of prochiral enamides (Brunner & Pieronczyk, 1979; Brunner, Pieronczyk, Schönhammer, Streng, Bernal & Korp, 1981). We recently described the structure of [(+)-(S,S)-norphos]-Rh(bicyclo[2.2.1]hepta-2,5-diene)ClO₄, (2), and also presented evidence that the ligand in the operating catalyst is, in fact, renorphos {2,3-bis(diphenylphosphino)bicyclo[2.2.1]heptane}, (3), (Kyba, Davis, Juri & Shirley, 1981). That is, catalyst activation with

dihydrogen rapidly reduces the double bond in the coordinated norphos to give coordinated renorphos. One of our interests was to determine the way in which the 'rigid' bicyclo[2.2.1]hept-2-en-5,6-diyl system (1) adjusted to the torsional stress imposed upon it when chelation by the *exo*-5-*endo*-6-diphosphino moieties to Rh occurred. Study of Dreiding models indicated that severe distortions might be expected. Indeed this was observed in the structure of (2). THF (THF = tetrahydrofuran), the most notable deformation being in the dihedral angle, PCCP, from an ideal angle of 120 to 64°. Unfortunately, due to the steric similarity of the bridging methylene and ethylidene moieties in norphos, the structure of (2) was disordered with 1:1 interchange of these CH₂ and CHCH units. Thus a careful analysis of the effect of torsional stress on the [2.2.1] system was impossible. We now report the structure of the penultimate precursor to the actual chiral hydrogenation catalyst, [(-)-(R,R)-renorphos]Rh(bicyclo[2.2.1]hepta-2,5-diene)ClO₄, (4), in which the disorder difficulty encountered with (2) is not as significant.



Experimental. Ligand (3) and cationic complex (4) synthesized as described previously (Kyba *et al.*, 1981). X-ray-quality crystals of (4).THF grown from a THF solution at room temperature. Crystal vol. 0.0387 mm³, ten crystal faces. Syntex P2₁ autodiffractometer, graphite monochromator, Syntex LT-1 inert-gas (N₂) low-temperature delivery system. Unit-cell parameters obtained by least-squares refinement against observed setting angles of 30 locally intense reflections with 25.1 < 2θ < 26.5°. Data reduction carried out as described in Riley & Davis (1976). ω-scan mode, scan range symmetrically over 1.0° about Kα_{1,2} max., background offset 1.0 and -1.0° in ω from Kα_{1,2} max., scan rate 3.5° min⁻¹, exposure time 57.6 h.

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Crystal and instrument stability [computed $s = 0.00016$ (5), $t = -0.000002$ (1)] monitored by remeasurement of four check reflections after every 96 reflections, max. correction on $I = -0.3I$ [these data analyzed as detailed in Henslee & Davis (1975)]. Absorption correction, transmission factors 0.842–0.884. 2θ range 4.0–55°. 4745 total reflections (h 0–20, k 0–26, l 0–14), 4372 observed [$F > 4(\sigma_F)$]. Comparison of space group and unit-cell parameters for (4).THF and (2).THF (Kyba *et al.*, 1981) suggested that the two crystals were isostructural. [Recalculation of the X-ray density for (2).THF gives a corrected value, $D_x = 1.507$ g cm $^{-3}$.] Initial structure for (4).THF was therefore obtained directly from non-H atomic coordinates found for compound (2).THF. Since the (–)-enantiomer of (4) was used in this study, its

Table 1. Fractional coordinates (for Rh and P $\times 10^5$, for C $\times 10^4$) and U_{eq} (for Rh and P $\times 10^4$, for C $\times 10^3$) for non-rigid-group non-H atoms in (4).THF

	x	y	z	$U_{eq}*(\text{\AA}^2)$
Rh	16020 (3)	14381 (2)	17406 (4)	172 (1)
P(1)	11223 (8)	25080 (6)	17197 (14)	159 (3)
P(2)	7306 (9)	12743 (6)	1257 (12)	156 (4)
C(1)	–620 (4)	2214 (3)	–794 (5)	21 (2)
C(2)	–1261 (5)	2620 (4)	–155 (7)	49 (3)
C(3)	–787 (4)	3185 (4)	234 (7)	45 (3)
C(4)	74 (4)	3139 (3)	–267 (7)	30 (2)
C(5)	613 (4)	2591 (3)	289 (5)	16 (1)
C(6)	25 (3)	1989 (3)	138 (5)	15 (1)
C(7)	–141 (4)	2736 (4)	–1498 (6)	42 (2)
C(11)	3123 (4)	850 (3)	2446 (6)	29 (2)
C(12)	2745 (4)	1516 (3)	2817 (5)	23 (2)
C(13)	2074 (3)	1394 (3)	3556 (4)	21 (2)
C(14)	2013 (4)	631 (3)	3662 (5)	25 (2)
C(15)	1746 (4)	435 (3)	2399 (5)	27 (2)
C(16)	2420 (4)	561 (3)	1670 (6)	30 (2)
C(17)	2978 (4)	467 (3)	3598 (6)	29 (2)

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

coordinates were obtained by inverting those available for (+)-(2). THF. The four phenyl rings (including H atoms) were refined as rigid groups. The three disordered atoms C(2), C(3) and C(7) (see Fig. 1) were omitted from the first four cycles of full-matrix least-squares refinement. During these cycles, R decreased from 0.200 to 0.158. At this point, a difference density map revealed positions of the remaining bridging C atoms, and these were included in the next few cycles of refinement. One phenyl ring (Ph3) had exceptionally large changes in position during these cycles, accompanied by abnormally high thermal parameters. Three cycles of anisotropic refinement, including improved coordinates for phenyl rings Ph3 and Ph4 obtained from a difference density map, reduced R from 0.109 to 0.047. At this point, H atoms were located in a difference density map. With all atoms anisotropic except for rigid groups and THF, H atoms were added in ideal positions for five more cycles of least-squares refinement. The THF molecule and C(2),

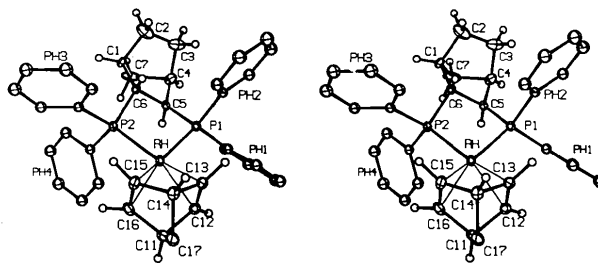


Fig. 1. Stereoscopic view of (4). Equiprobability ellipsoids of 30% probability are shown for non-H atoms; H atoms are represented as 0.25 Å spheres. The C(17) and phenyl ring H atoms have been omitted for clarity; the parentheses in atom labels have also been omitted.

Table 2. Selected bond lengths (Å) and angles (°) in (4).THF

1	2	3	1–2	1–2–3	1	2	3	1–2	1–2–3	1	2	3	1–2	1–2–3
P(1)	Rh	P(2)	2.325 (1)	86.3 (<1)	C(301)	P(2)	C(6)	1.820 (3)	106.7 (2)	P(1)	C(5)	C(4)	1.827 (6)	132.5 (4)
12,13*	Rh	P(1)	2.084 (8)	101.1 (2)	C(401)	P(2)	C(6)	1.820 (3)	107.1 (2)	C(6)	C(5)	P(1)	1.556 (8)	106.7 (4)
15,16*	Rh	P(1)	2.102 (8)	171.1 (3)	P(1)	C(101)	C(102)	1.831 (3)	117.6 (3)	C(4)	C(5)	C(6)		101.8 (4)
12,13	Rh	P(2)	2.084 (8)	172.5 (2)	P(1)	C(101)	C(106)		122.4 (3)	P(2)	C(6)	C(1)	1.843 (5)	129.3 (4)
15,16	Rh	P(2)		102.0 (3)	P(1)	C(201)	C(202)		120.2 (3)	P(2)	C(6)	C(5)		105.8 (4)
C(12)	Rh	C(13)	2.189 (6)	36.6 (2)	P(1)	C(201)	C(206)		119.7 (3)	C(1)	C(6)	C(5)		103.4 (4)
C(13)	Rh		2.201 (5)		P(2)	C(301)	C(302)		124.1 (3)	C(1)	C(7)	C(4)	1.538 (9)	90.4 (5)
C(15)	Rh	C(16)	2.205 (6)	36.3 (2)	P(2)	C(301)	C(306)		115.8 (3)	C(12)	C(11)	C(16)	1.550 (9)	102.7 (5)
C(16)	Rh		2.219 (6)		P(2)	C(401)	C(402)		122.4 (3)	C(12)	C(11)	C(17)		99.2 (5)
Rh	P(1)	C(101)		119.0 (1)	P(2)	C(401)	C(406)		117.6 (2)	C(16)	C(11)	C(17)	1.539 (9)	100.6 (5)
Rh	P(1)	C(202)		137.5 (1)	C(2)	C(1)	C(6)	1.501 (10)	106.1 (5)	C(11)	C(12)	C(13)		107.6 (5)
Rh	P(1)	C(5)		103.9 (2)	C(2)	C(1)	C(7)		101.4 (5)	C(12)	C(13)	C(14)	1.377 (8)	106.0 (5)
C(101)†	P(1)	C(201)	1.831 (3)	103.2 (2)	C(6)	C(1)	C(7)	1.542 (8)	104.1 (5)	C(13)	C(14)	C(15)	1.574 (8)	101.7 (4)
C(101)	P(1)	C(5)		107.9 (2)	C(1)	C(2)	C(3)		104.2 (6)	C(15)	C(14)	C(17)	1.553 (9)	99.6 (5)
C(201)	P(1)	C(5)	1.832 (4)	110.0 (2)	C(2)	C(3)	C(4)	1.450 (11)	107.8 (6)	C(17)	C(14)	C(13)	1.562 (9)	98.7 (5)
Rh	P(2)	C(301)	2.323 (1)	117.0 (1)	C(3)	C(4)	C(5)	1.477 (10)	113.2 (6)	C(14)	C(15)	C(16)		107.5 (5)
Rh	P(2)	C(401)		113.6 (1)	C(5)	C(4)	C(7)	1.547 (8)	95.4 (5)	C(15)	C(16)	C(17)	1.377 (9)	73.3 (4)
Rh	P(2)	C(6)		103.7 (2)	C(7)	C(4)	C(3)	1.664 (10)	99.8 (5)	C(11)	C(17)	C(14)	1.549 (9)	94.3 (5)
C(301)	P(2)	C(401)	1.832 (3)	108.0 (2)										

* 12,13 and 15,16 represent the midpoints of the C(12)=C(13) and C(15)=C(16) bonds respectively. The fractional coordinates of 12,13 are 0.24095, 0.14545, 0.31866 and those of 15,16 are 0.20831, 0.04979, 0.20344.

† An atom designated by C(*i*/*j*) is C atom *i* in phenyl ring *j*.

C(3) and C(7) were slightly disordered in this structure as evidenced by elevated thermal parameters, and an attempt to resolve this 10–15% disorder was unsuccessful. H atoms on C(2), C(3) and C(7) were fixed in ideal positions as were those on phenyl rings and THF. Refinement with coordinates describing (*S,S*) structure resulted in higher *R* and *wR* values (0.047 and 0.052 respectively), confirming assignment of current enantiomer as (–)-(*R,R*). In the final refinement (303 variables) *R* = 0.0439, *wR* = 0.0489 (*R* for all data = 0.0496), *S* = 2.58; function minimized $\sum w(F_o - F_c)^2$ where $w = (\sigma_F)^{-2}$, ignorance factor *p* = 0.02. $(\Delta/\sigma)_{\max}$ (non-H) = 0.452, $(\Delta/\sigma)_{\max}$ (H) = 0.733. Final $\Delta\rho$ peaks –0.70 to 1.16 e Å⁻³. No correction for secondary extinction. Neutral-atom scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computer programs used in data reduction and in structure refinement and analysis are as previously detailed (Gadol & Davis, 1982).

Discussion. Table 1 contains fractional coordinates and equivalent isotropic *U* values for (4).THF.* Bond distances (also somewhat distorted around the disordered atoms) and angles are given in Table 2. Fig. 1 shows a stereoview of (4).

The chelation of the Rh^I species by (–)-(*R,R*)-(3) puts a clockwise torque on the rigid hydrocarbon framework, as viewed from the perspective in front of the metal center towards the ligand. The most pronounced effect is that the PCCP dihedral angle is distorted from an ideal value of 120 to 64°, essentially the same as in complex (2), but about 12° more than when the organic ‘scaffolding’ is not constrained by a rigid ring, as in (5) (Cod = 1,5-cyclooctadiene) (Ball & Payne, 1977). Table 3 compares selected torsional angles in (4) with those in [2.2.1] systems, (6), which do not have the ‘chelation torque’ present (Fratini, Britts & Karle, 1967; Newton, Pantaleo, Kirbawy & Allinger, 1978). Another measure of the distortion caused by chelation is the dihedral angle *X*–C(5)–C(6)–C(1) (158°) as well as *Y*–C(6)–C(5)–C(4) (155°), compared with angles in the vicinity of 125° in unconstrained systems (Table 3, columns 4–6). The clockwise torque manifests itself not only in the dihedral angles but also in bonding angles. Thus angles C(1)–C(6)–P(2) (129°) and C(4)–C(5)–P(1) (133°) have opened considerably from the tetrahedral angle. The five-membered ring attached to the chelate ring is distorted, as evidenced by

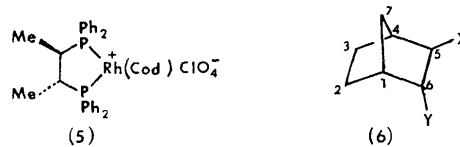
* Lists of structure factors, anisotropic thermal parameters of non-rigid-group non-H atoms, and the coordinates and isotropic thermal parameters for non-rigid-group H atoms and all atoms of the rigid groups, the perchlorate anion and the THF molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38820 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected dihedral angles (°) for the C atoms in [2.2.1] systems with the general structure and numbering shown in (6)

	(4) ^a	(2) ^b	(6a) ^c	(6b) ^d	(6c) ^e
(I) <i>X</i> –C(5)–C(6)– <i>Y</i>	–63	–64	–112	–110	
(II) <i>X</i> –C(5)–C(6)–C(1)	158	156	122	130	
(III) <i>Y</i> –C(6)–C(5)–C(4)	155	155	126	129	122
(IV) C(4)–C(5)–C(6)–C(1)	17	15	1	9	1
(V) C(4)–C(3)–C(2)–C(1)	6	3	–4	5	–3
(VI) C(3)–C(4)–C(5)–C(6)	53	50	62	64	70
(VII) C(2)–C(1)–C(6)–C(5)	–80	–73	–69	–78	–72
(VIII) C(5)–C(4)–C(3)–C(2)	–70	–64	–60	–74	–69
(IX) C(6)–C(1)–C(2)–C(3)	66	66	77	68	73
(X) <i>X</i> –C(5)–C(4)–C(3)	–72	–76	–64	–54	
(XI) <i>Y</i> –C(6)–C(1)–C(2)	156	161	166	160	167

Notes: (a) This work [(4).THF] is described in the text. The standard deviations for these torsion angles [and those for (2).THF] are all less than 1°. The numbering system for the other compounds has been changed to correspond with this system, with *X*, *Y* = P(Ph)₂–Rh⁺(bicyclo[2.2.1]hepta-2,5-diene)–P(Ph)₂. (b) The numbering system in (2).THF is as for (4).THF. The C(2)–C(3) bond is unsaturated. Since the structure determined (Kyba *et al.*, 1981) was of the (*S,S*) species, all dihedral angles have been multiplied by minus one. (c) *X* = *Y* = P(O)Ph₂. The C(2)–C(3) bond is unsaturated (Brunner *et al.*, 1981). (d) *X* = OH, *Y* = CH₂N(Me)CH₂Ph (Fratini *et al.*, 1967). (e) *X* = NHCOPh, *Y* = H (Newton *et al.*, 1978).

the dihedral angle C(4)–C(5)–C(6)–C(1), which is 17° for the renorphos complex and 15° for the norphos complex. Interestingly, unconstrained systems with 2-*exo*,3-*endo* substituents, (6a,b), also exhibit reasonable distortions in the same direction. Entries (VI) and (VII) in Table 3 show the distortion caused by chelation in the five-membered ring fused to the chelate. On the other hand, entries (V), (VIII) and (IX) reveal virtually no effect in the five-membered ring containing the C(2)–C(3) bridge, (2,4). It is apparent that the strain imposed on the organic scaffolding upon chelation is dissipated almost completely in the proximate ring of the [2.2.1] system. The presence of the double bond in the norphos system contributes little to making it more rigid.



Finally, we call attention to the fact that the bicyclo[2.2.1]hepta-2,5-diene ligand is bonded to the Rh center such that the double bonds are not perpendicular to the plane defined by PRhP. There are now four such cases, to our knowledge, involving norphos (Kyba *et al.*, 1981), chiraphos [2,3-bis(diphenylphosphino)butane] (Ball & Payne, 1977), binap [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] (Miyashita *et al.*, 1980; Toriumi *et al.*, 1982), and renorphos as the chiral ligands. In each case the diene ligand is twisted in the same sense relative to the chirality at the phosphines

imposed by the chiral organic framework. It is not clear from examination of interatomic distances in these complexes what causes the distorted olefin bonding to the Rh center. It is possible that there is an orbital bias caused by the chiral binding of the diphosphine which leads to the diolefin bonding in the twisted form observed in order to maximize orbital overlap. Whatever the cause of the skewed bonding of the diolefin, presumably it would be an important factor in asymmetric induction in hydrogenations of prochiral olefins using such Rh complexes as catalyst precursors.

This work was supported by the National Science Foundation (EPK, Grant No. 8113090) and The Robert A. Welch Foundation (RED, Grant No. F-233; EPK, Grant No. F-573). We are also indebted to the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer (Grant No. GP-37028).

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Acta Cryst. (1984). **C40**, 24–28

Structure de l'Aqua(aza-4 azonia-1 bicyclo[2.2.2]octane)trinitratocadmium(II), $Cd(C_6H_{13}N_2)(H_2O)(NO_3)_3$

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(Reçu le 9 mai 1983, accepté le 1 août 1983)

Abstract. $M = 429.6$, monoclinic, $P2_1$, $a = 7.032$ (3), $b = 7.068$ (7), $c = 13.791$ (5) Å, $\gamma = 94.01$ (5)°, $V = 684$ (1) Å³, $Z = 2$, $D_m = 2.02$ (3), $D_x = 2.09$ Mg m⁻³, $Mo K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.65$ mm⁻¹, $F(000) = 428$ e, $T = 294 \pm 1$ K, $R = 0.025$ for 1905 independent reflections. The structure consists of molecules linked together by hydrogen bonds and van der Waals

interactions. The coordination polyhedron of the Cd atom is a bipyramid with a hexagonal base made up of six O atoms which belong to three unsymmetrically bidentate nitrate groups. Both apical positions are occupied by the O atom of a water molecule and by one N atom of 4-aza-1-azoniabicyclo[2.2.2]octane. The molecule has approximately C_3 symmetry.

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