will be described in forthcoming reports.[23]

Registry No. $Cs_4[Rh_{14}(CO)_{25}]$, 75558-11-1; $[(C_2H_5)_4N]_4[Rh_{14}(CO)_{25}]$, 68714-70-5; $[PhCH_2N(C_2H_5)_3]_4[Rh_{14}(CO)_{25}]$, 75558-89-3; $[(CH_3)_4N]_4[Rh_{14}(CO)_{25}]$, 75548-81-1; $Rh(CO)_2acac$, 14874-82-9.

Supplementary Material Available: Complete tables of structural factors, atomic distances and angles, and positional and thermal parameters (14 pages). Ordering information is given on any current masthead page.

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(23) The wide use of the method may be hindered by the requirements for high-pressure equipment, although pressure bombs with a safety limit of ca. 1000 psi are often found in most laboratories. The time requred is less than ca. 2 days.

(24) The compositions of the $[Cs(CH_3OCH_2CH_2)_4OCH_3)_2]^+$ and $[Cs(C_{12}H_{22}O_6)_{1.9}]^+$ salts are proposed on the bases of their elemental analyses and ^1H NMR studies. It is proposed on the same bases that the side product soluble only in dimethyl sulfoxide could be the corresponding salt of $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ ($x = 0, 1$), a cluster previously observed by Chini et al. The glyme and 18-crown-6 solvates are obtained by conducting the synthesis of $[Rh_{14}(CO)_{25}]^{4-}$ described here in these solvents.

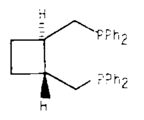
Contribution from the Chemical Research Department,
Hoffmann-La Roche Inc., Nutley, New Jersey 07110

Crystal Structure of (η^6-Hexadeuteriobenzene)[(1*R*,2*R*)-*trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane]rhodium(I) Perchlorate: A Model for the Resting State of an Asymmetric Hydrogenation Catalyst

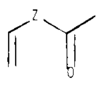
John M. Townsend* and John F. Blount

Received May 12, 1980

Catalytic asymmetric hydrogenation has become a practical synthetic method to prepare enantiomers of many organic substances.[1] Hydrogenations which proceed with the highest enantioselectivities at the fastest rates typically involve rhodium complexes of chiral chelating bis(phosphines) such as **1**.[2]



1



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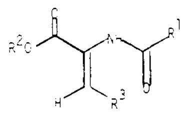
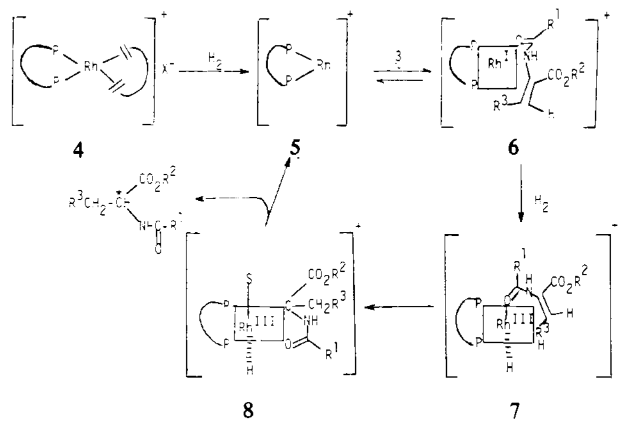
Z = NH, CH$_2$, O



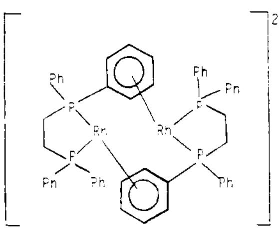
3

Substrates of general structure **2** which can also coordinate as bidentate ligands also give particularly good results. For the important case of hydrogenation of prochiral α-acylaminoacrylic acid derivatives such as **3** catalyzed by cationic rhodium(I) complexes of chelating bis(phosphines), reaction Scheme I is supported by considerable experimental evidence.[3-12]

Scheme I



Several crystal structures of cationic diolefin catalyst precursors **4** have been reported.[13-16] Under hydrogenation conditions, the diene is removed as saturated hydrocarbon to generate the highly coordinatively unsaturated "resting" state of the catalyst **5**. *In methanol or acetone*, these species have been characterized by ^{31}P NMR and other spectroscopic methods and appear to exist as methanol (or acetone) solvated monomers, or dimers held together by solvent bridges.[4-6,17-20] Another possibility is that of a dimer held together by π-arene bridges involving phenyl moieties of the phosphine. There is as yet no unambiguous evidence for this type of structure in solution, but it has been observed in the solid state for analogue **9**,[4] where 1,2-bis(diphenylphosphino)ethane serves as a close model for chiral bis(phosphines) of the dipamp[9] and chiraphos[21] type.



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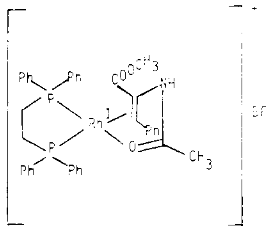

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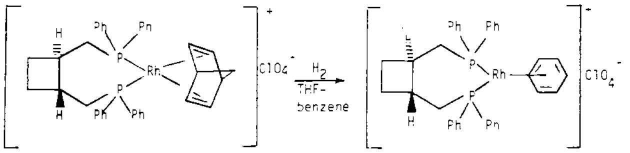
Table I. Crystal Data

formula	$C_{36}H_{30}D_6ClO_4P_2Rh$
fw	739.02
space group	$P2_1$
a	11.074 (1) Å
b	14.400 (1) Å
c	10.525 (1) Å
β	98.81 (1)°
Z	2
d_{calcd}	1.480 g cm^{-3}
μ(Cu Kα)	62.2 cm^{-1}

Species **5** do not add hydrogen under normal conditions, at least with cis-chelating bis(phosphines).[4,7,17,22] They do, however, readily add unsaturated species such as arenes[4,5] and olefinic hydrogenation substrates such as **3**. The resulting complexes **6** have been characterized by spectral methods,[3-6,12,17,18,20] especially ^{31}P and ^{13}C NMR methods, and, in one case, by an X-ray crystal structure determination on **10**.[23] Addition of hydrogen to **6** gives the as yet uncharacterized dihydride **7**. Apparently stepwise transfer of hydride leads through **8** (detected spectroscopically at low temperature in two cases)[3,8] to product and regenerates **5**.

This paper describes an X-ray crystal structure investigation of a complex which models the resting form of the catalyst **5**. Hydrogenation of diene precursor **11** in tetrahydrofuran–benzene results in solutions which are catalytically active for hydrogenation and which precipitate **12** upon standing. Complex **12** is thus a structurally characterized example of the arene complexes of **5** previously characterized[4,5] spectroscopically in solution.



11 **12**

Experimental Section

(Bicyclo[2.2.1]heptadiene)[(1*R*,2*R*)-*trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane]rhodium(I) Perchlorate (11). Orange-yellow crystals of **11** were obtained from [RhCl(bicyclo[2.2.1]heptadiene)]$_2$,[24] the chiral phosphine **1**,[2] and NaClO$_4$ by "method 2" of Schrock and Osborn.[25]

Anal. Calcd for $C_{37}H_{38}ClO_4P_2Rh$: C, 59.49; H, 5.13; Cl, 4.75; P, 8.29. Found: C, 59.25; H, 5.30; Cl, 4.86; P, 8.40.

Complex 12. A solution–suspension of 200 mg of **11** in 2 mL of 7:3 (v/v) tetrahydrofuran–benzene was stirred under 45 psi of hydrogen for several minutes, resulting in a gradual color change from orange-yellow to red-brown. After standing overnight, the mixture was filtered to give 106 mg (54%) of **12** as a red-brown powder. ^{31}P NMR[26] (CD$_2$Cl$_2$): δ +31.4 (d, $J_{\text{P,Rh}}$ = 201.4 Hz).

Anal. Calcd for $C_{36}H_{36}ClO_4P_2Rh$: C, 58.99; H, 4.95; Cl, 4.84. Found: C, 58.99; H, 4.82; Cl, 4.59.

Complex 12-*d*$_6$. A similar preparation carried out in 7:3 (v/v) tetrahydrofuran-benzene-d_6 was intended to provide a solution for NMR study. However, when the solution–suspension was allowed to stand under hydrogen for several days before filtration, red-brown crystals of **12**-d_6 suitable for X-ray analysis were formed. ^{31}P NMR[26] (CD$_2$Cl$_2$): δ +31.3 (d, $J_{\text{P,Rh}}$ = 201.3 Hz).

Anal. Calcd for $C_{36}H_{30}D_6ClO_4P_2Ph$: C, 58.51; H + D, 5.73. Found: C, 57.96; H + D, 5.03.

Table II. Selected Bond Lengths (Å) in **12** with Standard Deviations in Parentheses

Rh-P(1)	2.237 (2)	P(2)-C(41)	1.823 (9)
Rh-P(2)	2.252 (2)	C(1)-C(2)	1.524 (12)
Rh-C(51)	2.300 (10)	C(2)-C(3)	1.526 (12)
Rh-C(52)	2.332 (11)	C(2)-C(5)	1.539 (12)
Rh-C(53)	2.317 (12)	C(3)-C(4)	1.516 (12)
Rh-C(54)	2.297 (11)	C(3)-C(6)	1.577 (10)
Rh-C(55)	2.357 (10)	C(5)-C(6)	1.533 (12)
Rh-C(56)	2.373 (10)	C(51)-C(52)	1.416 (18)
Rh-Midp[a]	1.876	C(51)-C(56)	1.396 (19)
P(1)-C(1)	1.836 (8)	C(52)-C(53)	1.396 (18)
P(1)-C(11)	1.839 (10)	C(53)-C(54)	1.321 (21)
P(1)-C(21)	1.837 (10)	C(54)-C(55)	1.386 (20)
P(2)-C(4)	1.854 (8)	C(55)-C(56)	1.373 (19)
P(2)-C(31)	1.811 (9)		

[a] Midp is the center of the benzene ring.

Table III. Selected Bond Angles (Deg) in **12** with Standard Deviations in Parentheses

P(1)-Rh-P(2)	96.2 (1)	C(4)-P(2)-C(41)	100.8 (4)
P(1)-Rh-Midp	132.5	C(31)-P(2)-C(41)	104.2 (4)
P(2)-Rh-Midp	131.2	P(1)-C(1)-C(2)	112.8 (6)
P(1)-Rh-C(51)	96.4 (2)	C(1)-C(2)-C(3)	119.2 (7)
P(1)-Rh-C(54)	166.2 (2)	C(1)-C(2)-C(5)	119.2 (8)
P(2)-Rh-C(51)	167.1 (2)	C(3)-C(2)-C(5)	89.4 (6)
P(2)-Rh-C(54)	95.7 (2)	C(2)-C(3)-C(4)	118.9 (9)
C(51)-Rh-C(54)	72.2 (3)	C(2)-C(3)-C(6)	86.6 (6)
Rh-P(1)-C(1)	119.0 (3)	C(4)-C(3)-C(6)	118.5 (7)
Rh-P(1)-C(11)	109.7 (3)	P(2)-C(4)-C(3)	114.1 (6)
Rh-P(1)-C(21)	119.3 (3)	C(2)-C(5)-C(6)	87.7 (7)
C(1)-P(1)-C(11)	100.9 (4)	C(3)-C(6)-C(5)	87.7 (6)
C(1)-P(1)-C(21)	102.2 (4)	C(52)-C(51)-C(56)	121.7 (11)
C(11)-P(1)-C(21)	103.3 (5)	C(51)-C(52)-C(53)	118.5 (12)
Rh-P(2)-C(4)	123.2 (3)	C(52)-C(53)-C(54)	118.6 (13)
Rh-P(2)-C(31)	109.1 (3)	C(53)-C(54)-C(55)	123.6 (14)
Rh-P(2)-C(41)	115.5 (3)	C(54)-C(55)-C(56)	120.6 (13)
C(4)-P(2)-C(31)	101.7 (4)	C(51)-C(56)-C(55)	116.8 (13)

Another experiment confirmed that solutions from which **12** crystallizes are catalytically active. Complex **12** (0.0022 g) was stirred under hydrogen in tetrahydrofuran–benzene (10 mL) for several minutes and then vented. (*Z*)-*N*-Acetylaminocinnamic acid (2.0 g) was added to the solution under an argon atmosphere. The mixture was placed under 45 psi of hydrogen and stirred at room temperature. Hydrogen uptake ceased after ca. 15 min. Solvent removal gave (*R*)-*N*-acetylphenylalanine having $[\alpha]^{25}{}_{\text{D}}$ −29.8° (*c* 1.0, EtOH), corresponding to an optical purity of 65%.[27]

Crystallographic Experimental Data. The crystal chosen for data collection was obtained from the preparation of **12**-d_6 described above. The crystal data are summarized in Table I. The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ-2θ scans, pulse height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.15 × 0.18 mm; the data were corrected for absorption. Of the 2346 independent reflections for $\theta < 57°$, 2227 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by the heavy-atom method. The final refinement was carried out by block-diagonal least-squares methods in which the matrix was partitioned into two blocks. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. All nonhydrogen atoms were refined as individual atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The rhodium and chlorine scattering curves were corrected for the real and imaginary components of the anomalous dispersion. The final discrepancy indices

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(26) Proton noise-decoupled ^{31}P NMR spectra were obtained at 40.5 MHz on a Varian XL-100 spectrometer operating in the Fourier transform mode. Chemical shifts are in ppm relative to external 85% H_3PO_4, with decreasing field in the positive direction.

(27) Higher optical purities (90% op) were obtained previously[2] with this phosphine–substrate combination, but under somewhat different hydrogenation conditions, viz., rhodium chloride catalyst precursor, ethanol–benzene (2:1) solvent, 1 atm hydrogen pressure, and added triethylamine.

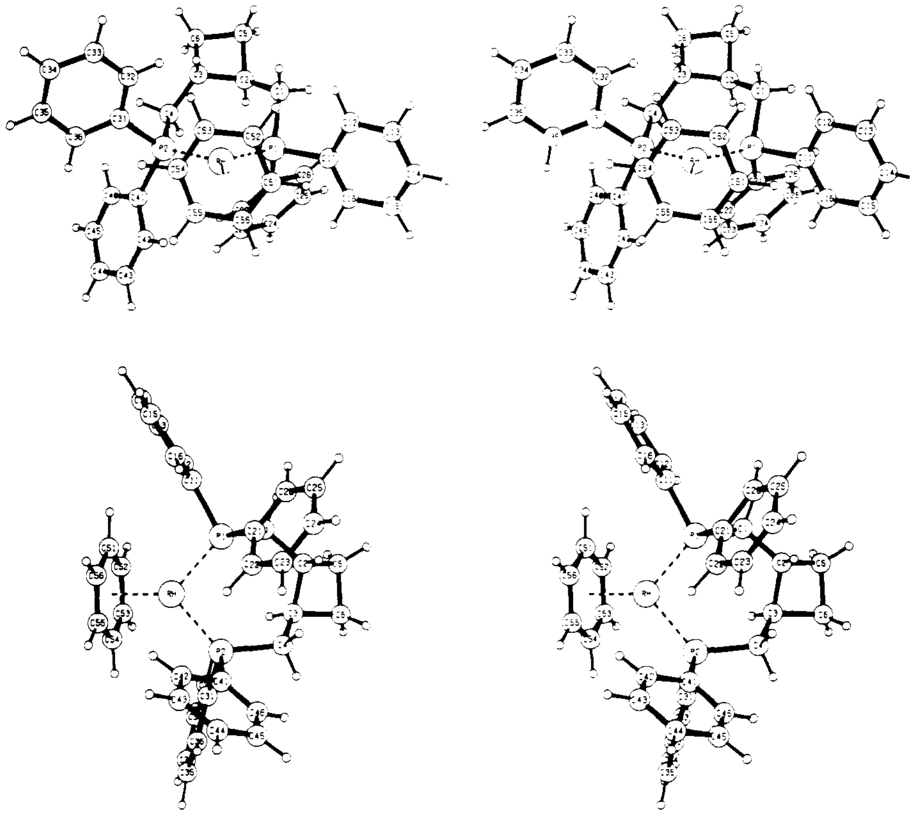

Figure 1. Stereoscopic drawings of the rhodium complex **12**. In the upper part, the view is approximately parallel to the P–Rh–P plane, and in the lower part, the view is approximately perpendicular to the P–Rh–P plane. It is especially apparent how far the cyclobutane ring is from the P–Rh–P plane. The environments about the two phosphorus atoms are not equivalent with respect to the P–Rh–P plane. About P(1), the P(1)–C(11) bond is in the plane with the P(1)–C(1) and P(1)–C(21) bonds out of the plane, whereas about P(2), the P(2)–C(4) bond is nearly in the plane and the two P-phenyl bonds, P(2)–C(31) and P(2)–C(41), are out of the plane.

are $R = 0.033$ and $R_w = 0.043$ for the 2227 observed reflections. The final difference map has no peaks greater than ± 0.7 e A^{-3}.[37]

Results and Discussion

Stereoscopic drawings of the cation of **12**-d_6 are shown in Figure 1. The structure consists of a coordinatively saturated mononuclear rhodium(I) ion (d^8) coordinated to two phosphorus atoms and to benzene in a symmetrical π-arene manner. The six benzene carbon atoms are almost equidistant from the rhodium atom. The benzene ring is oriented such that two of its carbon atoms lie approximately in the P–Rh–P plane [C(51) is 0.1 Å out of the plane and C(54) is 0.3 A out of the plane on the other side]. The four atoms P(1), P(2), C(51), and C(54) do not form a plane. They lie –0.10, 0.10, 0.12, and –0.12 Å, respectively, from their best plane. The rhodium atom is almost in this plane (0.04 A out) while the four atoms C(1), C(2), C(3), and C(4) are well out of the plane (–1.6, –1.7, –1.8, and –0.6 Å, respectively). The diherdral angle between this plane and the plane of the benzene ring is 88°. Selected interatomic distances and angles are given in Tables II and III.

π-Arene bonding in cationic rhodium complexes has been observed previously,[4,5,28-34] but **12** appears to be the first structurally characterized example involving a simple free arene. The observed structure illustrates one way in which the extreme ligand deficiency of species like **5** can be satisfied in the presence of an aromatic solvent. It is of interest that **5** apparently prefers coordination of benzene over solvation of tetrahydrofuran or, based on Halpern's results,[4,5] solvation by methanol.

The situation which prevails when the rhodium catalyst counterion is potentially coordinating halide rather than perchlorate or tetrafluoroborate is less clear,[17,35,36] despite the fact that use of a rhodium chloride catalyst precursor in an ethanol–benzene solvent system is very common for these reactions. Bis(phosphine), chloride, and η^6-benzene cannot all be accommodated by rhodium(I) without exceeding the 18-electron rule, so presumably in this case either chloride or one phosphorus ligand is displaced or benzene acts as a η^2 or η^4 ligand. These questions are presumably related to the significant differences obtained in catalytic asymmetric hydrogenations upon changing of the solvent, the rhodium counterion, or other variable (e.g., added triethylamine) and may be expected to be especially important with substrates that are less strongly coordinating than α-acylaminoacrylic acids. These factors await detailed elucidation.

Registry No. **11**, 74965-02-9; **12**, 74965-04-1; **12**-d_6, 74965-06-3; [RhCl(bicyclo[2.2.1]heptadiene)]$_2$, 12257-42-0; (*Z*)-*N*-acetylaminocinnamic acid, 55065-02-6; (*R*)-*N*-acetylphenylalanine, 10172-89-1.

Supplementary Material Available: Tables of final atomic parameters, final anisotropic thermal parameters, final F_o and F_c values, bond lengths, bond angles, and torsion angles (14 pages). Ordering information is given on any current masthead page.

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