

Chart I

	protonated amine	unreacted amine
	HIr(CO) ₄	O(CH ₂ CH ₂) ₂ N(CH ₃), PhN(CH ₃) ₂
↑ increase in acidity ↓	HCo(CO) ₄	O(CH ₂ CH ₂) ₂ N(CH ₃) PhN(CH ₃) ₂
	HRh(CO) ₄	O(CH ₂ CH ₂) ₂ N(CH ₃), PhN(CH ₃) ₂

HM(CO)₄ (M = Co, Rh, Ir) in this solvent, although in this respect the incomplete conversion of Rh₄(CO)₁₂ to Rh₂(CO)₈ (vide infra) was of concern and the insolubility of the ionic tetracarbonylmetalate salts was a limitation that only allows for the qualitative comparison of the respective ability of these hydrides to protonate amines.

Fourier subtraction techniques show that HIr(CO)₄ (1.5 mmol) does not react with *N*-methylmorpholine (10.0 mmol) while HCo(CO)₄ (2.4 mmol) reacts with this amine (1.0 mmol) (Figure 3) but it does not protonate the less basic *N,N*-dimethylaniline (1.0 mmol) in a detectable fashion at either 5 or 100 °C. Similar procedures were followed during the study of HRh(CO)₄, although the presence of Rh₄(CO)₁₂ and Rh₂(CO)₈ in this case resulted in a complex pattern already discussed. In any event, the decrease of the bands associated with HRh(CO)₄ is observed with *N,N*-dimethylaniline (1.0 mmol) (Figure 3). That this decrease does not correspond to a reaction of the hydride with Rh₄(CO)₁₂ or any cluster derived from it that could be formed by the presence of the amine is inferred from the constant absorbances for the infrared absorptions of this cluster and Rh₂(CO)₈.

With a quantitative evaluation of the relative acidity of HM(CO)₄ (M = Co, Rh, Ir) precluded, we turned to qualitative studies for the comparison of the acid-base properties

of the HM(CO)₄ species. A summary of these observations (Chart I) seems to indicate the larger acidity of HRh(CO)₄, although it should be kept in mind that such a conclusion may be affected by our considerations concerning Rh₄(CO)₁₂.

The position of HRh(CO)₄ is seen to be anomalous, and we do not have a readily available explanation for it. As we already mentioned, a somewhat related behavior has also been reported for the elements in the iron triads. For instance, [C₅H₅Fe(CO)₂]⁻ is a stronger nucleophile than its ruthenium analogue,³⁰ and the proton affinity of [(η-C₅H₅)₂Fe] is larger than that of [(η-C₅H₅)₂Ru].³¹ It appears, then, that a similar variation in the basicity of the metals, or, more specifically, of their complexes, could be present for both the iron and cobalt triads.

The characterization of HRh(CO)₄, a hitherto unobserved species, is also relevant in homogeneous catalysis by rhodium because this species has been proposed to be active in hydroformylation^{1-6,13} and in the hydrogenation of carbon monoxide to less oxidized species, e.g., methanol and ethylene glycol.¹¹

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Registry No. HCo(CO)₄, 16842-03-8; HRh(CO)₄, 75506-18-2; HIr(CO)₄, 25282-12-6; [PhCH₂PPh₃][Co(CO)₄], 42535-64-8; [PhCH₂PPh₃][Ir(CO)₄], 75556-03-5; [PhCH₂PPh₃][Rh(CO)₄], 75556-04-6; Co₂(CO)₈, 10210-68-1; Rh₄(CO)₁₂, 19584-30-6; Ir₄(CO)₁₂, 18827-81-1; Ir(CO)₂(acac), 14023-80-4; Rh(CO)₂(acac), 14874-82-9; Rh₂(CO)₈, 29658-60-4.

Supplementary Material Available: High-pressure infrared spectra of the fragmentation of Rh₄(CO)₁₂ solutions under CO and CO-H₂, IR spectra of the protonation of [M(CO)₄]⁻ with protonic acids under CO, and IR spectra of HM(CO)₄ (M = Co, Rh, Ir) (3 pages). Ordering information is given on any current masthead page.

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X-ray Structural Characterization and Catalytic Properties of Hydridobis[4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]rhodium(I)

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The compound HRh[(+)-diop]₂, (+)-diop = (4*S*,5*S*)-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with cell dimensions *a* = 17.253 (2) Å, *b* = 20.976 (2) Å, *c* = 16.336 (3) Å, and *Z* = 4. Of the 5726 reflections measured by counter methods (Mo Kα radiation), 3758 ≥ 3σ were used for the structure determination. Full-matrix least-squares refinement gave a conventional *R* value of 0.060. The rhodium(I) atom is coordinated to two chelating diop ligands, each with *S,S* chirality, and a hydride in a distorted trigonal bipyramid, the hydride (located in a difference Fourier, Rh-H = 1.6 Å) and a phosphorus being at the trans axial sites. The ³¹P and high-field ¹H NMR data reveal a fluxional structure at room temperature. Kinetic and spectroscopic studies on catalytic hydrogenation of styrene support earlier work on prochiral substrates and are consistent with an "unsaturate" mechanism via a HRh(diop)(diop*) species containing monodentate diop*. Optical induction at the substrate coordination stage is not readily attributed (by studying models) to interaction between the substrate and chiral ligand.

Introduction

Interest remains high in catalytic asymmetric synthesis using transition-metal complexes.¹ Asymmetric hydrogenation has

been the most widely studied reaction, using particularly rhodium catalysts containing chiral phosphine ligands, and attempts to explain the mechanism of optical induction have stemmed largely from investigations with these systems.²⁻⁴

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(2) B. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).

(3) D. A. Slack, I. Greveling, and M. C. Baird, *Inorg. Chem.*, **18**, 3125 (1979).

Table I

Crystal Data	
C ₆₂ H ₆₄ O ₄ P ₂ Rh	fw 1101.01
space group: P2 ₁ 2 ₁ 2 ₁	Z = 4
a = 17.253 (2) Å	D _{calcd} = 1.237 g cm ⁻³
b = 20.976 (2) Å	μ(Mo Kα) = 3.82 cm ⁻¹
c = 16.336 (3) Å	

Experimental Conditions for Data Collection

radiation: Mo Kα, graphite monochromator
 scan: ω-2θ, range of (0.50 + 0.35 tan θ)° in ω, extended 25% for backgrounds; speed from 1 to 10.1° min⁻¹ to give I/σ(I) ≥ 20
 aperture: (2.0 + 0.50 tan θ) × 4 mm; 173 mm from crystal
 stds: measd every hour of exposure time on (458), (458), (618), and (6,10,0)
 orientation: checked with 3 reflections after every 100; max deviation of any scattering vector 0.05°
 data collected: h, ±k, l for 2θ < 40°, hkl for 40 < 2θ < 50°
 σ(I): [Int + 4(BGR + BGL) + (0.03I)²]^{1/2}; Int is the integrated peak count, BGR and BGL are background counts, and I is the intensity

We reported recently⁵ the structure of *trans*-HRuCl(diop)₂, a hydrido-ruthenium(II) complex containing the well-known diop ligand,⁶ and this appears to be the first structural investigation of a transition-metal hydride with a ligand having a chiral center.⁷ The related rhodium complex HRh(diop)₂ was inadvertently synthesized in this laboratory while attempting to make a carbonyl-containing hydroformylation catalyst;⁸ the hydride was found to effect catalytic hydrogenation of olefinic substrates including prochiral ones under mild conditions (30 °C, 1 atm H₂),⁹ and this was initially surprising in view of earlier work^{10,11} reporting the relative inactivity of bis(diphos) analogues, diphos = 1,2-bis(diphenylphosphino)ethane. Other neutral and cationic rhodium(I)-bis(bis(tertiary phosphine)) chelate complexes have since been found active as hydrogenation catalysts.¹² A kinetic and mechanistic study⁹ on the asymmetric hydrogenation of methylenesuccinic acid catalyzed by HRh(diop)₂ was somewhat complicated by a slow decomposition of the rhodium hydride (by the protons of the substrate) to the cationic species Rh(diop)₂⁺.

This paper reports the X-ray investigation of HRh(diop)₂ (1) together with some spectroscopic data and a mechanistic study of the catalyzed hydrogenation of the nonacidic and nonprochiral substrate styrene.

Experimental Section

The HRh(+)-diop)₂ complex can be prepared according to literature procedures, either from RhCl₃·3H₂O (Johnson, Matthey, Ltd.)¹³ or from Rh[(+)-diop]₂Cl,¹² and recrystallization from benzene-ethanol solutions yielded crystals suitable for crystallographic analysis. (+)-diop, with S configuration at both chiral carbon centers, was obtained from Strem Chemicals. Experimental procedures, including kinetic measurements via gas-uptake measurements, have been described previously.⁹ The rhodium complex was added from a glass bucket held over the styrene solutions via the use of side arms in a reaction vessel containing a known pressure of hydrogen. Vigorous

shaking avoids diffusion control during the H₂ absorption which is measured at constant pressure. Styrene was passed through an alumina column and distilled under vacuum before use.

X-ray Intensity Data. A combination of photographic and diffractometric techniques showed the crystals to be orthorhombic with systematic absences, *h* odd for *h*00, *k* odd for 0*k*0, and *l* odd for 00*l*, unambiguously determining the space group to be P2₁2₁2₁, D₂²-No. 19.¹⁴

The crystal chosen for data collection had dimensions of approximately 0.22 × 0.25 × 0.31 mm and possessed 12 faces, {010}, {001}, and {111}; it was sealed in a Lindemann glass capillary and mounted in a nonspecific orientation on an Enraf-Nonius CAD-4 diffractometer. The cell constants and an orientation matrix were determined from a least-squares fit to 23 reflections having 33 < 2θ < 40°. The crystal data and experimental conditions for data collection are given in Table I. A total of 5726 unique reflections were measured and processed¹⁵ to give 3758 reflections with F² > 3σ(F²) which were used in the solution and refinement of the structure.

Structure Solution and Refinement

The positional parameters of the Rh atom were determined from a three-dimensional Patterson synthesis, and the remaining nonhydrogen atoms were found by use of three iterations of the usual combination of least-squares refinement and difference Fourier synthesis. In a difference synthesis, C atoms appeared with electron densities of approximately 3–5 e Å⁻³. The absolute configuration of the complex was chosen such that the diop ligands had the S,S configuration at the chiral carbons.⁷

Refinement of atomic parameters was carried out with use of full-matrix least-squares techniques on F, minimizing the function Σw(|F_o| - |F_c|)², where |F_o| and |F_c| are the observed and calculated structure factor amplitudes, respectively, and the weighting factor w is given by w = 4F_o²/σ²(F_o²). The neutral-atom scattering factors for all atoms were calculated from the analytical expression for the scattering factor curves.¹⁶ The f' and f'' components of anomalous dispersion were those of Cromer and Liberman¹⁷ and were included in the calculations for the Rh and P atoms.

Two cycles of least-squares refinement of the nonhydrogen atoms, in which all the atoms with the exception of the phenyl ring carbons were assigned anisotropic thermal parameters, resulted in values of R₁ = Σ(|F_o| - |F_c|)/ΣF_o = 0.068 and R₂ = (Σw(|F_o| - |F_c|)²/Σw(F_o²)^{1/2}) = 0.104.

Of the 64 H atoms in the molecule (not including the hydride), 52 (the nonmethyl hydrogens) were easily located in geometrically feasible positions by difference Fourier synthesis. Coordinates for the "ideal" positions for these H atoms were calculated, and, by use of a least-squares fit to the most reasonable electron density peaks near the methyl carbons, positions for the methyl H atoms were also calculated. The H atom positions were determined by using C-H = 0.95 Å and regular C_{sp²} and C_{sp³} geometries, and the hydrogen thermal parameters were assigned isotropic values 1.0 Å² greater than those of the C atoms to which they are bonded. The contributions from these hydrogens were calculated and included in a subsequent refinement cycle, giving residuals of R₁ = 0.064 and R₂ = 0.103.

At this point an examination of F_o and F_c showed evidence of extinction effects as well as the presence of some data with F_o ≫ F_c. Consequently, seven reflections which had the largest values for |F_o - F_c|/σ(F_o) were removed and an isotropic extinction parameter¹⁸ was introduced during subsequent refinement cycles. These changes resulted in an improvement of R₁ and R₂ to 0.060 and 0.084, respectively.

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 (15) The computer programs used in this analysis include locally written programs for data reduction and modifications of ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy for full-matrix least-squares refinement, FORDAP by A. Zalkin for Patterson and Fourier synthesis, ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy for distances and angles, and ORTEP by C. K. Johnson for crystal structure illustrations.
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Table II. Atomic Positional and Thermal Parameters^a

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Rh	31 (1)	4940.3 (4)	292 (1)	285 (5)	307 (5)	513 (6)	13 (6)	-42 (7)	-60 (6)
P(1)	578 (2)	5873 (2)	-244 (3)	354 (21)	323 (18)	375 (20)	13 (16)	15 (22)	-41 (19)
P(2)	1037 (2)	4231 (2)	197 (3)	316 (20)	295 (17)	415 (22)	13 (15)	3 (21)	42 (18)
P(3)	-1147 (2)	4788 (2)	-354 (3)	318 (21)	372 (18)	398 (21)	-35 (15)	-49 (20)	-3 (20)
P(4)	-254 (2)	5342 (2)	1577 (3)	314 (23)	494 (23)	438 (23)	25 (18)	3 (19)	52 (19)
C(1)	1509 (9)	6149 (7)	189 (10)	444 (92)	394 (75)	376 (90)	-57 (68)	-43 (84)	-61 (76)
C(2)	2218 (9)	5727 (8)	-21 (10)	265 (83)	549 (96)	463 (103)	-72 (74)	38 (75)	69 (75)
C(3)	2298 (9)	5117 (7)	448 (10)	282 (79)	439 (87)	560 (107)	-89 (68)	0 (73)	129 (85)
C(4)	2050 (9)	4501 (7)	20 (10)	321 (88)	415 (86)	522 (111)	-12 (69)	66 (79)	71 (73)
C(5)	3492 (11)	5631 (9)	325 (18)	347 (104)	604 (109)	1389 (207)	-88 (86)	-183 (147)	393 (154)
C(6)	3879 (17)	5495 (14)	-553 (26)	831 (209)	1221 (224)	2407 (409)	336 (176)	905 (259)	344 (253)
C(7)	4004 (17)	5860 (13)	978 (23)	916 (197)	1045 (207)	2322 (357)	-429 (169)	-1085 (238)	962 (235)
O(1)	2877 (6)	6082 (5)	194 (8)	339 (60)	490 (60)	787 (85)	-147 (51)	-127 (68)	222 (68)
O(2)	3117 (7)	5075 (6)	584 (8)	437 (69)	498 (67)	1116 (105)	-32 (60)	-252 (68)	314 (75)
C(8)	-1996 (8)	4981 (7)	292 (11)	353 (82)	463 (85)	559 (91)	-32 (77)	15 (85)	0 (107)
C(9)	-2027 (10)	5663 (9)	590 (11)	344 (97)	623 (109)	523 (107)	162 (84)	-121 (82)	-105 (86)
C(10)	-1830 (10)	5778 (8)	1492 (10)	430 (106)	624 (109)	409 (95)	151 (88)	75 (84)	38 (86)
C(11)	-1009 (9)	5967 (8)	1707 (10)	324 (90)	605 (101)	409 (90)	76 (83)	-9 (78)	-33 (82)
C(12)	-2946 (11)	6339 (9)	1164 (12)	407 (110)	657 (116)	628 (122)	157 (91)	56 (99)	-24 (100)
C(13)	-2966 (16)	7006 (11)	824 (15)	1133 (215)	723 (143)	807 (161)	88 (143)	-62 (160)	-37 (128)
C(14)	-3707 (13)	6200 (16)	1583 (17)	438 (143)	1940 (319)	1004 (189)	-60 (168)	118 (141)	131 (205)
O(3)	-2827 (7)	5865 (6)	551 (7)	560 (82)	808 (89)	609 (81)	357 (73)	-176 (66)	-222 (72)
O(4)	-2323 (8)	6306 (7)	1701 (8)	541 (87)	926 (101)	693 (88)	322 (76)	-160 (75)	-250 (77)

atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
1C1	-19 (9)	6600 (6)	-132 (8)	353 (30)	1C2	-675 (10)	6657 (7)	-607 (10)	447 (40)
1C3	-1164 (11)	7171 (9)	-520 (11)	578 (49)	1C4	-991 (12)	7619 (9)	80 (12)	615 (50)
1C5	-352 (11)	7596 (9)	544 (11)	591 (49)	1C6	158 (10)	7080 (7)	433 (10)	483 (40)
2C1	812 (10)	5949 (8)	-1353 (10)	420 (39)	2C2	799 (12)	6513 (9)	-1740 (12)	592 (50)
2C3	1004 (15)	6546 (11)	-2567 (14)	811 (65)	2C4	1239 (15)	5997 (12)	-2975 (15)	893 (73)
2C5	1272 (14)	5448 (10)	-2600 (14)	722 (60)	2C6	1068 (11)	5400 (8)	-1777 (11)	498 (46)
3C1	1024 (10)	3597 (7)	-596 (9)	414 (39)	3C2	1564 (12)	3125 (9)	-612 (12)	585 (49)
3C3	1537 (14)	2675 (10)	-1243 (14)	781 (65)	3C4	1012 (14)	2690 (11)	-1843 (14)	767 (61)
3C5	477 (15)	3180 (11)	-1896 (14)	836 (69)	3C6	500 (13)	3633 (9)	-1230 (12)	676 (55)
4C1	1190 (10)	3714 (7)	1092 (10)	413 (39)	4C2	1748 (12)	3811 (9)	1665 (12)	600 (50)
4C3	1809 (14)	3407 (10)	2380 (13)	734 (59)	4C4	1331 (14)	2920 (11)	2432 (14)	769 (63)
4C5	806 (15)	2804 (12)	1894 (15)	897 (71)	4C6	706 (12)	3181 (9)	1184 (11)	601 (51)
5C1	-1461 (9)	3958 (7)	-582 (9)	395 (38)	5C2	-1315 (13)	3499 (10)	-81 (13)	770 (62)
5C3	-1551 (16)	2868 (12)	-215 (18)	1002 (76)	5C4	-1976 (14)	2737 (11)	-889 (15)	808 (67)
5C5	-2169 (14)	3181 (11)	-1370 (15)	829 (68)	5C6	-1914 (14)	3818 (10)	-1251 (14)	744 (62)
6C1	-1366 (9)	5190 (7)	-1322 (9)	416 (38)	6C2	-2042 (13)	5561 (10)	-1451 (13)	651 (55)
6C3	-2133 (15)	5868 (11)	-2203 (14)	831 (67)	6C4	-1583 (15)	5830 (11)	-2797 (14)	813 (66)
6C5	-932 (14)	5463 (10)	-2663 (14)	753 (63)	6C6	-819 (10)	5149 (8)	-1933 (10)	526 (44)
7C1	543 (11)	5736 (8)	2133 (10)	506 (44)	7C2	588 (14)	6373 (10)	2281 (13)	740 (60)
7C3	1263 (17)	6636 (12)	2632 (16)	938 (78)	7C4	1863 (18)	6243 (13)	2839 (17)	1051 (87)
7C5	1809 (16)	5583 (12)	2760 (15)	925 (75)	7C6	1142 (14)	5316 (10)	2381 (13)	727 (62)
8C1	-544 (11)	4781 (8)	2420 (11)	555 (46)	8C2	-543 (14)	4184 (11)	2324 (13)	772 (63)
8C3	-745 (16)	3728 (12)	3005 (16)	932 (75)	8C4	-923 (16)	4002 (13)	3682 (17)	953 (77)
8C5	-921 (16)	4608 (12)	3845 (16)	933 (77)	8C6	-723 (12)	5022 (11)	3200 (13)	760 (58)

^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 10⁴. $U_{ij} = B_{ij}/(2\pi^2 a^* a^* \rho^* j) \text{ \AA}^2$. The thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

As these residuals were still somewhat higher than usually obtained by using modern diffractometer methods, we attempted to discover whether there were any systematic errors in the data or whether the structure had refined to a false minimum. Adjustments in the geometry of atoms C(6) and C(7) and phenyl rings 5 and 8 to give more acceptable values, as compared to those of the rest of the molecule, failed to make any improvement and these atoms refined back to their original positions. Likewise no systematic errors were found in an examination of the data, and accordingly the refinement was terminated after two further cycles upon convergence of the variable shifts to values of less than one standard deviation.

In the final cycle, with recalculated H atom contributions and all nonphenyl atoms with anisotropic thermal parameters, 401 variables were refined with the use of 3751 reflections having $F^2 > 3\sigma(F^2)$ to final agreement factors of $R_1 = 0.060$ and $R_2 = 0.083$. The largest variable shift was 0.97 times its esd, and the error in an observation of unit weight was 2.11 e.

The hydride was located in a difference Fourier map calculated over the region about the Rh atom. The largest peak, having an electron density of 0.3 e \AA^{-3} , was 1.6 \AA from the Rh atom with fractional coordinates $(-0.0387, 0.4350, 0.0745)$.

A difference Fourier map calculated from the final structure factors

contained no features of chemical interest, other than the hydride, with the largest peak located at $(0.507, 0.0, 0.027)$ with an electron density of 1.4 e \AA^{-3} . An examination of R_2 in terms of F_o , $\lambda^{-1}(\sin \theta)$, and combinations of Miller indices showed no significant trends.

A listing of the final structure factor amplitudes is available as supplementary material (see paragraph at the end of this paper), while the atomic and thermal motion parameters are given in Tables II and III.

Prior to the final refinement we ensured that the correct model had been chosen, in terms of absolute configuration, by refining the enantiomeric molecule under the same conditions as the original. This refinement resulted in an increase in R_2 from 0.090 to 0.109. Application of the R -factor ratio test¹⁹ indicates we may reject, at the 0.995 confidence level, the model in which the chiral carbons have the R,R absolute configuration.

Results and Discussion

Structural Data. The Rh atom is coordinated to two che-

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Table III. H Atom Positional and Isotropic Thermal Parameters ($\times 10^4$)

atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
H1C2	-790	6336	-1001	571	H1C3	-1610	7218	-858	709
H1C4	-1347	7961	167	747	H1C5	-245	7919	937	723
H1C6	624	7056	744	607	H2C2	650	6889	-1452	718
H2C3	986	6943	-2850	942	H2C4	1378	6020	-3549	1030
H2C5	1437	5078	-2886	842	H2C6	1102	5003	-1501	628
H3C2	1956	3102	-202	708	H3C3	1914	2334	-1245	928
H3C4	1005	2357	-2245	890	H3C5	120	3215	-2340	963
H3C5	135	3973	-1229	803	H4C2	2107	4149	1593	723
H4C3	2179	3494	2799	852	H4C4	1377	2640	2899	898
H4C5	464	2442	1986	1014	H4C6	325	3081	784	726
H5C2	-1028	3598	404	892	H5C3	-1420	2542	163	1126
H5C4	-2129	2303	-1004	951	H5C5	-2497	3082	-1829	963
H5C6	-2052	4145	-1629	878	H6C2	-2424	5599	-1035	774
H6C3	-2592	6108	-2306	951	H6C4	-1646	6054	-3302	940
H6C5	-550	5428	-3082	881	H6C6	-363	4902	-1852	648
H7C2	164	6643	2146	859	H7C3	1300	7083	2721	1070
H7C4	2331	6426	3055	1184	H7C5	2213	5314	2953	1044
H7C6	1106	4868	2297	845	H8C2	-411	4013	1804	913
H8C3	-739	3275	2944	1051	H8C4	-1080	3726	4120	1094
H8C5	-1051	4763	4379	1069	H8C6	-709	5469	3292	889
H1C(2)	2224	5641	-593	551	H1C(3)	2037	5153	958	561
H1C(9)	-1716	5928	251	618	H1C(10)	-1975	5415	1804	614
H1C(1)	1606	6568	-12	533	H2C(1)	1459	6165	768	533
H1C(4)	2387	4171	198	550	H2C(4)	2114	4562	-554	550
H1C(8)	-2452	4900	-19	584	H2C(8)	-1988	4708	756	584
H1C(11)	-1004	6097	2264	571	H2C(11)	-870	6319	1370	571
H1C(6)	4056	5066	-573	1622	H2C(6)	3504	5562	-972	1622
H3C(6)	4304	5776	-633	1622	H1C(7)	4402	5558	1076	1559
H2C(7)	4228	6257	821	1559	H3C(7)	3711	5921	1468	1559
H1C(13)	-2479	7100	578	1025	H2C(13)	-3364	7036	425	1025
H3C(13)	-3063	7298	1256	1025	H1C(14)	-3734	6433	2081	1249
H2C(14)	-4124	6322	1235	1249	H3C(14)	-3741	5756	1697	1249

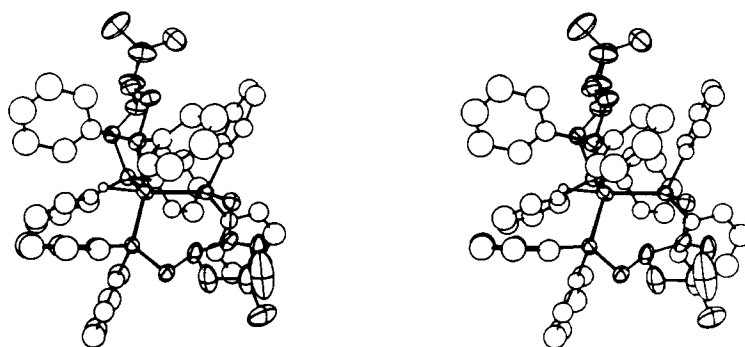


Figure 1. Stereoview of hydridobis[(+)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]rhodium(I). H atoms have been omitted except for the hydride which is drawn at an arbitrary size. The atoms are represented by 50% thermal ellipsoids.

lating diop ligands and a hydride in a distorted trigonal-bipyramidal arrangement. A stereoview of the molecule is shown in Figure 1, and the atom numbering scheme is illustrated in Figure 2. Selected bond distances and angles within the molecule are given in Table IV.

The P(2), P(3), and P(4) atoms that constitute the distorted trigonal environment around the Rh atom reveal a mean Rh-P bond length of 2.306 (12) Å. The axial P atom, P(1), is trans to the position chosen for the hydride; this Rh-P bond length, 2.342 (4) Å, is on the borderline (2.8σ) of being significantly longer than the mean of the other three, which would be consistent with the usual strong trans influence of the hydride ligand;^{7,20} however, in an ideal trigonal-bipyramidal structure, the axial bond should be longer anyway, and it is probably more realistic to consider the hydrogen as being trans to one phosphorus in a set of four that approximate to a tetrahedral

arrangement about the rhodium. Tertiary phosphine complexes of Rh(I) show Rh-P bond lengths ranging from 2.27 to 2.38 Å,²¹⁻²⁶ with those of chelating diphosphines tending to fall in the lower range. The values for complex 1 agree with this trend and in particular are close to those reported²² for the square-planar cationic complex $\text{Rh}(\text{diphos})_2^+\text{ClO}_4^-$.

Few crystallographic studies have appeared on complexes containing saturated seven-membered chelate rings. The archetypal seven-membered ring, cycloheptane, has been

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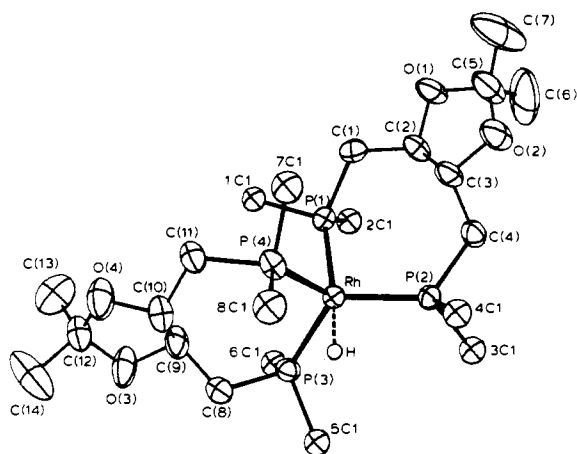


Figure 2. Perspective view of the molecule showing the atom numbering scheme. For clarity only the α -carbons of each phenyl ring are shown. The hydride is drawn at its inferred position with a dotted bond to the Rh atom.

Table IV. Selected Bond Distances (Å) and Angles (Deg)

Distances			
Rh-P(1)	2.342 (4)	C(2)-C(7)	1.50 (2)
Rh-P(2)	2.292 (4)	C(2)-O(1)	1.41 (2)
Rh-P(3)	2.311 (4)	C(3)-C(4)	1.53 (2)
Rh-P(4)	2.316 (5)	C(3)-O(2)	1.43 (2)
P(1)-C(1)	1.85 (2)	C(5)-O(1)	1.43 (2)
P(1)-1C1	1.85 (1)	C(5)-O(2)	1.40 (2)
P(1)-2C1	1.86 (2)	C(5)-C(6)	1.61 (4)
P(2)-C(4)	1.86 (2)	C(5)-C(7)	1.47 (3)
P(2)-3C1	1.86 (2)	C(8)-C(9)	1.51 (2)
P(2)-4C1	1.84 (2)	C(9)-C(10)	1.53 (2)
P(3)-C(8)	1.85 (2)	C(9)-O(3)	1.44 (2)
P(3)-5C1	1.86 (2)	C(10)-C(11)	1.51 (2)
P(3)-6C1	1.84 (2)	C(10)-O(4)	1.44 (2)
P(4)-C(11)	1.86 (2)	C(12)-O(3)	1.42 (2)
P(4)-7C1	1.84 (2)	C(12)-O(4)	1.39 (2)
P(4)-8C1	1.88 (2)	C(12)-C(13)	1.50 (3)
C(1)-C(2)	1.55 (2)	C(12)-C(14)	1.51 (3)
Angles			
P(1)-Rh-P(2)	102.2 (1)	C(3)-C(2)-O(1)	104 (1)
P(1)-Rh-P(3)	107.41 (1)	C(2)-C(3)-C(4)	117 (1)
P(1)-Rh-P(4)	96.9 (1)	C(2)-C(3)-O(2)	103 (1)
P(2)-Rh-P(3)	123.0 (1)	P(2)-C(4)-C(3)	117 (1)
P(2)-Rh-P(4)	117.3 (2)	C(2)-O(1)-C(5)	107 (1)
P(3)-Rh-P(4)	106.1 (2)	C(3)-O(2)-C(5)	111 (1)
Rh-P(1)-C(1)	118.0 (5)	O(1)-C(5)-O(2)	105 (1)
Rh-P(2)-C(4)	121.7 (5)	C(6)-C(5)-C(7)	117 (2)
Rh-P(3)-C(8)	114.0 (5)	P(3)-C(8)-C(9)	115 (1)
Rh-P(4)-C(11)	120.6 (5)	C(8)-C(9)-C(10)	117 (2)
1C1-P(1)-2C1	98.4 (7)	C(10)-C(9)-O(3)	102 (1)
3C1-P(2)-4C1	97.6 (6)	C(9)-C(10)-C(11)	118 (1)
5C1-P(3)-6C1	101.3 (7)	C(11)-C(10)-O(4)	107 (1)
7C1-P(4)-8C1	96.8 (8)	O(3)-C(12)-O(4)	107 (1)
P(1)-C(1)-C(2)	115 (1)	C(13)-C(12)-C(14)	109 (2)
C(1)-C(2)-C(3)	117 (1)		

subjected to conformational analysis,²⁷⁻²⁹ and the results suggest that the ring has four minimum-energy conformations, chair, twist-chair, twist-boat, and boat, with the first two being lowest in energy and hence preferred. Seven-membered rings in the 1,4-diaminobutane complexes of octahedral Co(III)³⁰ and square-planar Pt(II)³¹ and in a square-planar (L-ornithine-*N,N'*)palladium(II) complex³² show the chair or

twist-chair conformations with N-M-N angles of 86-90°. Only diop-ligated systems have been studied outside of the square and octahedral geometries.³³ The diop ligands in octahedral *trans*-HRuCl(diop)₂,⁷ and square-pyramidal IrCl(COD)(diop)³⁴ (COD = 1,5-cyclooctadiene), also adopt the twist-chair conformation and have P-M-P angles of 90.29 (6) and 92.4°, respectively. The ligands in the present distorted trigonal-bipyramidal structure again show the twist-chair conformation, the P-Rh-P chelate angles being 102.2 (1) and 106.1 (2)°. Crystal structures of the square-planar diene complexes [Rh(NBD)(diop)]⁺BPh₄⁻ and [Rh(COD)-(PPPM)]⁺ClO₄⁻ (NBD = norbornadiene, PPPM = (2*S*,4*S*)-*N*-pivaloyl-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine) have been carried out, but few details on the conformation of the seven-membered ring are available;⁴ a perspective view along the P-Rh-P plane (P-Rh-P = 98°) in the former complex is described as showing a "remarkably flat seven-membered ring", but it is probably not very different from those present in our complex 1.

Table V lists the torsion angles which define the conformation of the diop ligands in the three complexes for which these values have been reported. While the chelate ring is quite flexible, the conformations do not differ markedly between the complexes despite the differing coordination stereochemistries. As expected, the largest differences in the torsion angles are associated with those about the M-P bonds³⁵ and are concomitant with the changes in stereochemistry at the metal atom.

The diop ligands in 1 permit the approximately tetrahedral orientation of the P atoms which is presumably energetically more favorable than a square-pyramidal arrangement with an axial hydride. Since the cation [Rh(diphos)₂]⁺ is square planar, the difference must result from the bite angles available to five- and seven-membered rings. The more flexible seven-membered ring can give rise to a 90° bite angle (see above) or the larger tetrahedral one revealed here which reduces nonbonded repulsive interactions between ligands.

With the exception of C(6) and C(7), which show a lengthening and shortening, respectively, over the normal C-C bond length and larger than usual temperature factors, the geometry of the two diop ligands is normal. The average P-C(aryl) and P-C(alkyl) distances of 1.85 (2) and 1.848 (9) Å, respectively, are not significantly different from values observed in other structures of this and related ligands.^{7,21-24} The mean C-C and C-O bond lengths are 1.52 (4) and 1.42 (2) Å, respectively, and the internal angles in the diop ligand are unexceptional. The phenyl rings show no significant distortions from planarity with a mean C-C length of 1.38 (1) Å and a mean C-C-C angle of 119.98 (1)°.

The hydride, as located in a difference Fourier map, is 1.6 Å from the Rh atom, similar to other M-H distances,^{7,36} and is trans to P(1) with P(1)-Rh-H = 174.8°.

The molecules of a unit cell (Figure 3) display only the usual intermolecular distances in accord with normal van der Waals interactions.

Spectroscopic Data. The spectroscopic data for 1 have been reported previously.¹² The hydride is detected by IR, and the room-temperature solution high-field ¹H NMR (a doublet of quintets, *J*_{Rh-H} = 6 Hz, *J*_{P-H} = 17 Hz) and hydride-decoupled ³¹P NMR spectra (a sharp doublet, *J*_{Rh-P} = 146 Hz) reveal

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(35) The torsion angle, ω_1 , of the Ir complex is anomalously low considering the generally close agreement of the other angles.

(36) J. A. Ibers, *Adv. Chem. Ser.*, No. 167, 26 (1978).

Table V. Torsion Angles for Metal–diop Complexes

complex	ω_0^a	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ref
HRh(diop) ₂	101.1	-93.3	37.6	-15.4	-52.3	69.9	-76.9	this work
	95.0	-105.3	59.8	-2.2	-42.7	64.3	-69.2	
HRuCl(diop) ₂	88.7	-107.3	37.4	-30.9	-78.3	77.3	-55.7	7
IrCl(COD)(diop)	87	-77	38	-30	-72 ^b	74	-59	34

^a The torsion angles, ω_j , are defined as positive when a clockwise rotation is required to superimpose the projection of atom $j - 1$ on atom $j + 2$ when being viewed from atom j to $j + 1$. The numbering scheme is sequential about the ring with the metal atom as atom 4. ^b In the original paper this angle is given as positive which appears to be a misprint as all the other angles agree in sign.

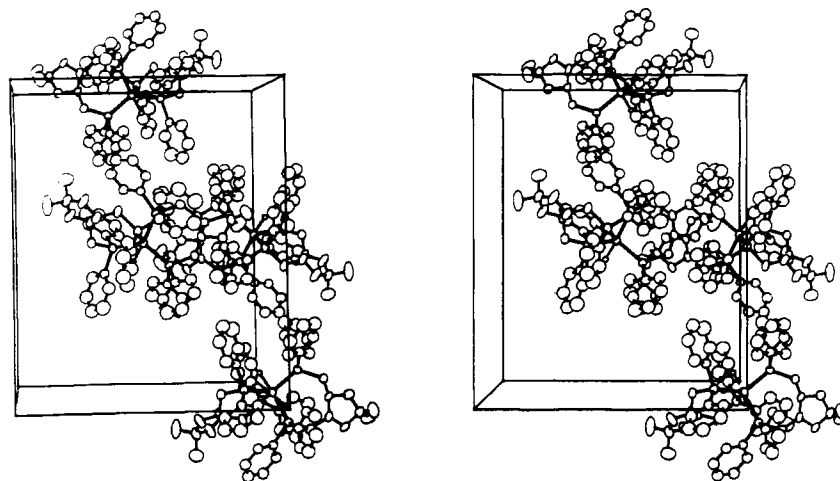


Figure 3. Stereoview of a unit cell. The cell axes are oriented with x horizontally to the right, y vertical, and z coming out of the page.

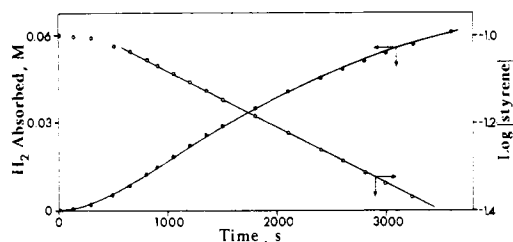
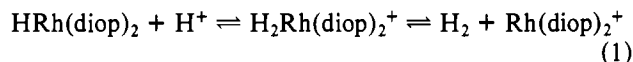


Figure 4. Hydrogen-uptake plot and corresponding log plot for the catalyzed hydrogenation of styrene: $[1] = 6 \times 10^{-3}$ M, $[\text{styrene}] = 0.1$ M, H_2 pressure 720 torr, 45°C .

equivalent phosphines at these conditions. Comparable NMR data for HRh(Ph₂PCH₃)₄ at -60°C had been attributed to a tetragonal-pyramid structure³⁷ although others have considered a fluxional C_{3v} structure more likely.³⁸ Our structure and a very similar one recently reported³⁹ for HIr(diphos)₂, which also shows equivalent phosphorus atoms in the room-temperature NMR, support the fluxionality concept. The structure of HRh(PPh₃)₄ with the hydrogen atom omitted is described as tetrahedral,⁴⁰ which is again analogous to that of the bis(diop) complex; the H atom in the triphenylphosphine complex almost certainly lies on a threefold axis of symmetry rather than be randomly disordered in the crystal.⁴¹ All of the above structures, and those of analogous HRh(P₂)₂ complexes, where P is a monodentate—or P₂ a bidentate—tertiary phosphine,¹² are thus considered likely to be approximately trigonal bipyramidal with the hydride at an axial site.

At lower temperatures the high-field ¹H NMR and ³¹P NMR resonances do start to broaden out. However, at -60°C the limiting spectrum had not been attained, but the complex spectrum must result from inequivalent phosphorus atoms. The four P atoms in the static structure are all inequivalent, and a complex limiting spectrum is predicted. The ¹H and ³¹P NMR spectra of HRh(diphos)₂ and HRh[PPh₂(CH₂)₃PPh₂]₂ at room temperature again show patterns due to four equivalent P atoms,¹² the spectra have now been found to be essentially unchanged at -60°C , and this is consistent with the usual behavior of increased fluxionality with decreasing chelate ring size.⁴²

Catalytic Hydrogenation. Complex 1 was found to catalyze the hydrogenation of terminal olefins under mild conditions. The hydrogenation of styrene to phenylethane proved convenient for kinetic purposes, and there was no complication due to reaction 1 that is evident when α,β -unsaturated carboxylic acid substrates⁹ are used.



A typical H₂-uptake plot in butanol–toluene (2:1) is shown in Figure 4. The curve initially shows autocatalytic behavior to approach a maximum rate which then falls in a manner that is strictly first order in styrene; the standard log plots (Figure 4) readily yield the pseudo-first-order rate constants (k_1) that obtain in the constant-pressure apparatus during any one experiment. The first-order dependence on styrene was demonstrated by using initial concentrations up to 0.25 M. k_1 was directly proportional to the Rh concentration ($1.0\text{--}6.0 \times 10^{-3}$ M and to a partial pressure of H₂ up to 720 mm (5.7×10^{-3} M atm⁻¹ at 45°C). The kinetic data were reproducible to within 5%, and the average overall third-order rate constant

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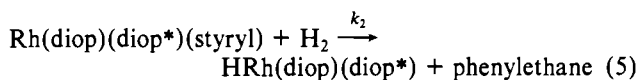
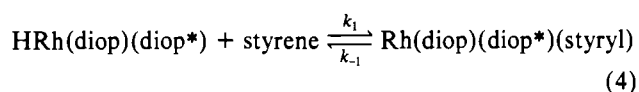
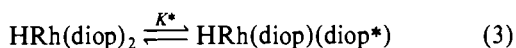
k for rate law 2 was $7.38 \text{ M}^{-2} \text{ s}^{-1}$ at 45°C .

$$-d[\text{H}_2]/dt = k[\text{Rh}][\text{styrene}][\text{H}_2] \quad (2)$$

Addition of even small amounts of diop had a remarkable inhibiting effect on the hydrogenation, and at an added diop:Rh ratio of 1:3 the rate is completely suppressed. It is of interest that addition of $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ had the same effect, while addition of PPh_3 or a nitrogen base (NEt_3) up to a 1:1 ratio had no effect on the hydrogenation rates.

The yellow solutions of **1** under argon ($\lambda_{\text{max}} 350 \text{ nm}$, $\epsilon 12300 \text{ M}^{-1} \text{ cm}^{-1}$) were unaffected on adding separately (i) 0.1 M styrene, (ii) 720 mm H_2 , or (iii) excess diop. When the solutions were sampled during catalytic hydrogenation, the visible and NMR spectra detected only $\text{HRh}(\text{diop})_2$.

Although an observed rate law of the type shown in eq 2 is particularly uninformative, taken together with the spectroscopic data, the very marked added diop inhibition, and the initial autocatalytic region, the data are consistent with the previously suggested "unsaturate" mechanism (i.e., binding of olefin prior to H_2 activation). This was based on more complex but informative kinetic dependences observed with olefinic acid substrates⁹ (eq 3–5, where diop* represents the monodentate, dangling diphosphine).



An alternative mechanism involving complete dissociation of a diop ligand is certainly not operable for the olefinic acid substrates (see ref 9) and in the present styrene system would lead to a dependence in Rh going from first to zero order with increasing catalyst concentration (reflected in an increasing denominator [diop] term in the rate law). However, in the closely related monodentate phosphine systems $\text{HRh}(\text{PPh}_3)_4$ ⁴³ and $\text{HRh}(\text{DBP})_4$ (DBP = 5-phenyl-5*H*-dibenzophosphole),⁴⁴ the most active catalysts are the bis(phosphine) species. The cationic $[\text{Rh}(\text{CO})_2(\text{diop})(\text{diop}^*)]^+\text{Cl}^-$ species has been isolated.⁴⁵

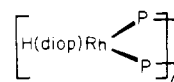
The mechanism of eq 3–5, with k_2 the rate-determining step (i.e., $k_2[\text{H}_2] \ll k_1$), gives the rate law $K^*K_1k_2[\text{Rh}][\text{styrene}][\text{H}_2]$, where all the detectable rhodium is present as $\text{HRh}(\text{diop})_2$ and $K_1 = k_1/k_{-1}$; the measured rate constant k is identified with $K^*K_1k_2$. Variation of k with temperature (7.38, 9.43, 12.66, and $14.04 \text{ M}^{-2} \text{ s}^{-1}$ at 45, 50, 55, and 60°C , respectively) yields a good Arrhenius plot and the activation parameters $\Delta H^\ddagger = 9.5 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -25 \pm 4 \text{ eu}$, which presumably refer to the composite constant $K^*K_1k_2$. If these activation parameters reflect mainly changes in the rate constant k_2 , they are reasonably consistent with oxidative addition of H_2 to a d^8 square-planar center (eq 5).⁴⁶

The autocatalytic region is attributed to a buildup of the steady-state concentration of the styryl complex that must result from a competition of the back-reaction of eq 3 with the forward reaction of eq 4.

The rates as determined by the mechanism of eq 3–5 should show no dependence on added diop, and yet there is a very marked inverse dependence (again, a "complete diop disso-

ciation mechanism" would lead, at a given Rh concentration, to a direct inverse dependence on added diop, contrary to the experimental findings).

We have suggested previously⁹ that added diop might result in the formation of catalytically inactive $\text{HRh}(\text{diop})(\text{diop}^*)_2$ species. However, in the styrene system, even if the maximum one-third of the rhodium were tied up in the experiments with added diop:Rh ratio of 1:3, the amount of kinetically available $\text{HRh}(\text{diop})(\text{diop}^*)$ catalyst would still be two-thirds that available in the system with no added diop, since the $\text{HRh}(\text{diop})(\text{diop}^*):\text{HRh}(\text{diop})_2$ ratio is fixed by the constant K^* ; the rate would be expected to decrease by one-third in contrast to the measured one of essentially zero. Addition of up to one PPh_3 or NEt_3 per Rh had no effect on the measured rates, which argues against any general-base-catalyzed reaction destroying the catalysis, and also tends to rule out formation of inactive species such as $\text{HRh}(\text{diop})(\text{diop}^*)(\text{PPh}_3)$. The inhibition by diop then remains unexplained; we tentatively suggest formation of polymeric species



containing bridging diop ligands. Complexes containing bridging diphosphines, including diop, are well documented,^{45,47–49} and polymerization via an initially formed $\text{HRh}(\text{diop})(\text{diop}^*)_2$ complex through a slight excess of diop ligand could explain the complete loss of activity at low diop:Rh ratios. Unfortunately we have been unable to obtain any evidence for such polymerization. Spectroscopically the polymer would likely be indistinguishable from complex **1**; cryoscopic data appear quite irreproducible, presumably as a result of the extreme oxygen sensitivity of the solutions. The inhibition by $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, a nonchiral analogue of diop, suggests that the dioxolane ring is not involved in the inhibition by added diop and is consistent with requirement of a potential bridging species for formation of a polymer.

It is of interest that $\text{HRh}[(+)\text{-diop}]_2$ -catalyzed asymmetric hydrogenation gives products of the same chirality as corresponding in situ 1:1 $\text{Rh}^1/(+)\text{-diop}$ catalysts, at least for the three substrates that we have studied, methylenesuccinic, α -phenylacrylic (atropic), and α -acetamidoacrylic acids (Table VI), although reaction rates are much slower with the bis-(diphosphine) system, $t_{1/2}$ being hours rather than minutes, under comparable conditions (20°C , 1 atm H_2 in butanol-toluene). Mono(diop) systems have also been known in certain cases to show dramatic solvent effects in terms of chirality of the product,⁵¹ which is consistent qualitatively with the presence of coordinated solvent in the catalytic species. The chirality induced in products by using **1** as a catalyst was invariant on use of butanol-toluene mixtures or *N,N*-dimethylacetamide; only one coordination site would be available (for the olefin) with a $\text{HRh}(\text{diop})(\text{diop}^*)$ intermediate, and solvent effects should be less marked.

In the mono(diop) and related mono(chelated-diphosphine) systems, the optical enrichment is thought to be induced during substrate coordination to, for example, a $\text{Rh}(\text{diop})(\text{solvated})^+$ species, one face of the olefin being preferentially coordinated due to a slightly more favored conformation of the rhodium-chelate ring in which the four phenyl groups approximate an

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Table VI. Catalyzed Hydrogenation of Prochiral Olefinic Substrates Using in Situ Solvated Rh[(+)-diop]Cl Species^a and HRh[(+)-diop]₂ (1)^b

olefinic acid	product % ee		
	in situ	1	ref
methylsuccinic	60 (R)	37 (R)	this work
α -acetamidoacrylic	73 (S)	56 (S)	6, 9
α -phenylacrylic	63 (R)	37 (R)	9, 50

^a From [Rh(C₈H₁₄)₂Cl]₂ or [Rh(COD)Cl]₂ + 2diop, at ~20 °C in 2:1 ethanol-benzene; [Rh] \approx 3 \times 10⁻³ M, [substrate] \approx 0.2 M, 760 torr; catalyst is likely to be cationic in this medium (see ref 2).

^b At ~20 °C in 2:1 butanol-toluene; [Rh] \approx 2 \times 10⁻³ M, [substrate] \approx 0.2 M, 760 torr.

edge-face arrangement;^{2,4} such reasoning depends very much on the substrate binding both via the olefinic link and at least one other functional group, commonly a carbonyl within an enamide substrate.^{4,52} The HRh(diop)(diop*) intermediate allows for coordination via the olefinic double bond only, and maximum hydrogenation rates measured for styrene (15 \times 10⁻⁶ M s⁻¹) and α -phenylacrylic acid (8 \times 10⁻⁶ M s⁻¹) under corresponding conditions ([substrate] = 0.1 M, [Rh] = 3 \times 10⁻³ M, in butanol-toluene at 50 °C and 1 atm pressure) indicate a lack of participation by the carboxylic group of the acid. The HRh(diop)₂ catalyst also shows a marked selectivity for hydrogenating substrates with terminal =CH₂ groups. Increasing substitution at the olefinic link decreases hydrogenation rates markedly;⁹ this is not apparent with mono(diop) catalysts which hydrogenate di- and trisubstituted olefins

equally readily.^{6,51,53-55} Such a difference again supports a more crowded rhodium center in the bis(diop) catalyst and thus favors the metal retaining both molecules of diop. The optical induction must result from a preferred binding of one of the faces of the olefin, but this is not obvious from the models after uncoordinating one of the phosphorus atoms. Asymmetric induction via interaction between the substrate and the chiral Rh atom in HRh(diop)(diop*), rather than interaction between substrate and ligand, cannot be ruled out,¹ and a kinetically preferred hydrogen transfer to one face of the olefin within two HRh(diop)(diop*)(olefin) diastereomers could also account for the induction.

Finally, the methylsuccinic acid hydrogenation catalyzed by HRh(diop)₂ is somewhat remarkable in that the optical purity of the methylsuccinic acid product *increases* to ~60% ee at temperatures of about 80 °C.⁵⁶ Such behavior is most unusual^{6,57,58} but could be rationalized in terms of some dissociation of a diop ligand at the higher temperatures to give a more effective mono(diop) catalyst.

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Supplementary Material Available: A listing of the structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of *trans*-Chlorohydridobis[(+)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]ruthenium(II) Toluene Solvate

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The molecular structure and absolute configuration of *trans*-chlorohydridobis[(+)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]ruthenium(II) has been determined by single-crystal X-ray diffractometry. The crystal is orthorhombic, of space group *P*2₁2₁2, with *a* = 20.506 (3) Å, *b* = 16.110 (2) Å, *c* = 11.085 (1) Å, and *Z* = 2. The structure has been refined by full-matrix least-squares techniques on *F*, using 4050 unique reflections for which *F*² > 3σ(*F*²), to a final agreement factor of 0.048. The molecules lie at special positions having twofold symmetry with the axis along the Ru-Cl bond. The absolute configuration at the asymmetric C atoms has been determined to be *S* by the Bijvoet absorption-edge technique.

Introduction

Rhodium and ruthenium complexes of optically active chelating diphosphines such as diop (4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane)¹ or other sim-

ilar diphosphines^{2,3} are capable of providing a strongly asym-

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