Inorg. Chem. **1981**, *20*, 261-265

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	product % ee 1	ref
methylenesuccinic	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(C_8H_{14})$_2$Cl]$_2$ or [Rh(COD)Cl]$_2$ + 2diop, at ~20 °C in 2:1 ethanol-benzene; [Rh] ≈ 3 × 10^{-3} M, [substrate] ≈ 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] ≈ 2 × 10^{-3} M, [substrate] ≈ 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 × 10^{-6} M s^{-1}) and α-phenylacrylic acid (8 × 10^{-6} M s^{-1}) under corresponding conditions ([substrate] = 0.1 M, [Rh] = 3 × 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 =CH_2 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 methylenesuccinic 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.

Acknowledgment. We thank the National Scientific and Engineering Research Council of Canada for financial support, the University of British Columbia Computing Centre for assistance, and Johnson, Matthey, Ltd., for loan of the rhodium.

Registry No. HRh[(+)-diop]$_2$, 65573-60-6.

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 $P2_12_12$, 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 $F^2 > 3\sigma(F^2)$, 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 similar diphosphines[2,3] are capable of providing a strongly asym-

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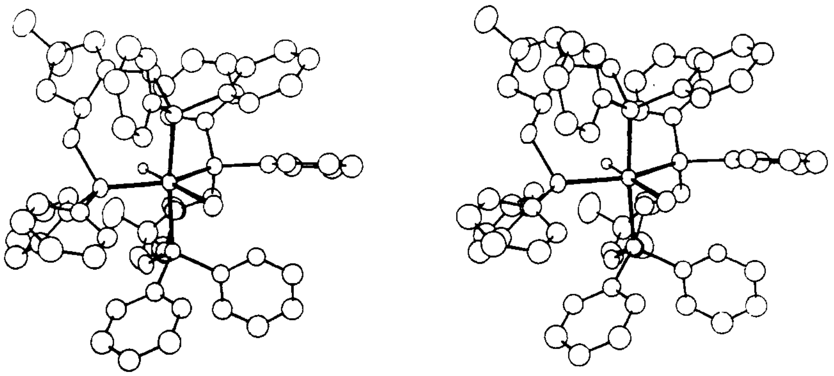


Figure 1. Stereoview of *trans*-chlorohydridobis[(+)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]ruthenium(II). The atoms, with the exception of the hydride which is arbitrarily small, are represented by 50% thermal ellipsoids.

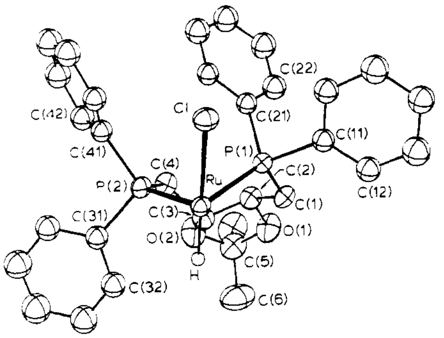


Figure 2. View of the unique portion of the molecule showing the atomic numbering scheme.

Table I. Crystal Data

$C_{76}H_{81}ClO_4P_4Ru$
space group: $P2_12_12$
$a = 20.506$ (3) Å
$b = 16.110$ (2) Å
$c = 11.085$ (1) Å

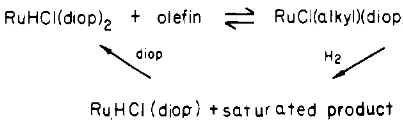
fw 1318.9
$Z = 2$
$D_{\text{calcd}} = 1.196$ g cm^{-3}
$D_{\text{obsd}} = 1.182$ (4) g cm^{-3} [a]
μ(Mo Kα) = 3.812 cm^{-1}

[a] By neutral bouyancy in benzene and dichloromethane.

Table II. Experimental Conditions for Data Collection

radiation: Mo Kα, graphite monochromator
scan: ω–2θ; range $(0.60 + 0.35 \tan\theta)^\circ$ in ω, extended 25% for backgrounds; speed from 1 to 10.1° min^{-1} to give $I/\sigma(I) \geqslant 20$
aperture: $(2.0 + 0.50 \tan\theta) \times 4$ mm; 173 mm from crystal
stds: reflections (20,0,0), $(\bar{2},14,0)$, (458), $(\bar{4}58)$; measured every hour of exposure time
orientation: checked with 3 reflections after every 100; 0.05° maximum deviation of any scattering vector
data collected: *hkl* to $2\theta < 40^\circ$; *hkl* and $\overline{hkl}$ for $40 \leqslant 2\theta < 60^\circ$
$\sigma(I)$: $[\text{Int} + 4(\text{BGR} + \text{BGL}) + (0.04I)^2]^{1/2}$; Int is integrated peak count, BGR and BGL are the background counts, and I is the intensity

metric environment about the metal atom. This environment permits discrimination with respect to the two enantiotopic faces of some prochiral olefins during the catalytic hydrogenation of these substrates.[1-4] Reports on the mechanism of homogeneous catalytic hydrogenation have generally concluded that a metal hydride species is an intermediate in the catalytic cycle. Indeed, for the Ru(II)–diop system it is proposed[4] that $RuHCl(diop)_2$ is involved in the catalytic cycle according to the mechanism (1).



(1)

The solid-state stereochemistries of some metal hydrides containing monodentate phosphines have been investigated[5-7] and usually found to be severely distorted from simple five- and six-coordinate geometries. However, to date, no structural investigations of metal hydrides with optically active chelating diphosphines have been reported. Consequently, we have undertaken the X-ray crystallographic examination of two such complexes, $RuHCl(diop)_2$[8] and $RhH(diop)_2$.[9] We report here the full structural details for the ruthenium complex.

Experimental Section

Light-orange crystals of $RuHCl(diop)_2 \cdot 2CH_3C_6H_5$ were kindly supplied by B. R. James and D. K. W. Wang. A preliminary photographic study showed the crystals to be orthorhombic and the systematic absences, *h* odd for *h*00 and *k* odd for 0*k*0, unambiguously determine the space group to be $P2_12_12$, D_2^3—No. 18.[10]

The crystal chosen for data collection was well formed with eight faces, {110} and {101}, and was of approximate dimensions 0.35 × 0.47 × 0.51 mm. The crystal was mounted on an Enraf-Nonius CAD-4 computer-controlled diffractometer in a nonspecific orientation. Cell constants were determined from a least-squares refinement of the setting angles of 21 reflections having $30 < 2\theta < 41^\circ$. The crystal data and the experimental conditions used during data collection are given in Tables I and II, respectively.

The 9784 reflections measured were processed[11] to give 6465 data for which $I > 3\sigma(I)$, including 2415 Bijvoet pairs measured for those data with $2\theta > 40^\circ$. The 4050 independent reflections were used for structure solution and preliminary refinement. No absorption correction was applied to the data.

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(10) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1962.

(11) A locally written program was used to apply corrections for background, Lorentz, and polarization effects to the intensity data. Other programs used in the analysis include 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, ORFE 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.

Table IV. Atomic Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0	5000	−2150.4 (3)	224 (1)	312 (2)	255 (2)	−4 (3)	0	0
P(1)	−3 (1)	6478 (1)	−2365 (1)	282 (3)	312 (4)	304 (4)	6 (7)	19 (9)	8 (3)
P(2)	1108.4 (4)	5034 (1)	−1591 (1)	254 (3)	373 (4)	316 (4)	−8 (6)	−22 (3)	6 (8)
Cl	0	5000	−4450 (1)	371 (5)	436 (6)	307 (5)	−25 (11)	0	0
C(1)	−53 (3)	7114 (3)	−983 (4)	334 (21)	405 (17)	353 (17)	24 (23)	53 (24)	−68 (14)
C(2)	580 (2)	7184 (3)	−281 (4)	410 (22)	448 (24)	368 (23)	−7 (19)	−21 (18)	−53 (20)
C(3)	905 (2)	6372 (3)	104 (4)	414 (22)	472 (24)	329 (22)	−8 (19)	−63 (18)	−21 (19)
C(4)	1376 (2)	5989 (3)	−780 (5)	317 (19)	388 (21)	415 (24)	−69 (16)	−55 (17)	−49 (20)
O(1)	446 (2)	7586 (3)	849 (4)	630 (22)	647 (24)	445 (21)	98 (19)	−64 (19)	−254 (19)
O(2)	1271 (2)	6642 (3)	1142 (4)	656 (24)	707 (26)	444 (22)	122 (21)	−203 (19)	−178 (20)
C(5)	904 (3)	7285 (4)	1720 (5)	550 (29)	674 (34)	398 (25)	−55 (25)	−79 (23)	−159 (27)
C(6)	518 (4)	6940 (7)	2787 (7)	810 (48)	1480 (85)	504 (37)	−133 (55)	39 (37)	114 (52)
C(7)	1380 (4)	7960 (5)	2092 (8)	704 (40)	849 (47)	834 (50)	−94 (37)	−128 (40)	−249 (45)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
C(11)	−663 (2)	6946 (3)	−3287 (5)	339 (12)	C(12)	−1217 (2)	7296 (3)	−2766 (5)	419 (9)
C(13)	−1700 (3)	7651 (4)	−3467 (5)	528 (12)	C(14)	−1621 (3)	7689 (3)	−4726 (5)	458 (11)
C(15)	−1067 (3)	7341 (3)	−5239 (5)	504 (12)	C(16)	−594 (2)	6974 (3)	−4525 (5)	392 (9)
C(21)	−677 (2)	3007 (3)	−3148 (5)	334 (12)	C(22)	−757 (2)	2149 (3)	−3070 (5)	457 (10)
C(23)	−1262 (3)	1755 (4)	−3687 (6)	541 (13)	C(24)	−1690 (3)	2209 (4)	−4355 (6)	523 (13)
C(25)	−1604 (2)	3061 (3)	−4490 (5)	467 (11)	C(26)	−1090 (2)	3460 (3)	−3896 (4)	352 (8)
C(31)	1357 (2)	4305 (3)	−382 (5)	391 (10)	C(32)	1022 (3)	4300 (3)	722 (5)	473 (11)
C(33)	1229 (3)	3830 (4)	1688 (7)	610 (14)	C(34)	1773 (4)	3313 (5)	1542 (7)	698 (17)
C(35)	2105 (3)	3287 (4)	473 (6)	610 (15)	C(36)	1907 (3)	3783 (3)	−490 (5)	473 (11)
C(41)	1801 (2)	4934 (3)	−2650 (3)	340 (7)	C(42)	2430 (3)	5196 (3)	−2345 (5)	475 (12)
C(43)	2926 (3)	5171 (3)	−3213 (5)	548 (13)	C(44)	2804 (3)	4871 (4)	−4366 (5)	551 (13)
C(45)	2174 (3)	4614 (4)	−4658 (5)	496 (11)	C(46)	1684 (2)	4652 (3)	−3802 (4)	380 (9)
C(51)	2632 (5)	5301 (6)	2043 (10)	1036 (29)	C(52)	3145 (4)	5376 (5)	1095 (8)	772 (20)
C(53)	3255 (4)	6132 (5)	537 (8)	781 (20)	C(54)	3730 (5)	6240 (6)	−281 (10)	997 (28)
C(55)	4129 (6)	5587 (8)	−670 (12)	1192 (37)	C(56)	4013 (5)	4814 (6)	−147 (10)	1048 (31)
C(57)	3527 (4)	4700 (5)	732 (9)	863 (23)	C(61)	5000	5000	−3552 (31)	2640 (145)
C(62)	5000	5000	−4944 (15)	1192 (43)	C(63)	5407 (5)	4499 (6)	−5617 (9)	956 (27)
C(64)	5399 (5)	4541 (7)	−6866 (10)	1061 (31)	C(65)	5000	5000	−7374 (16)	1312 (52)

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

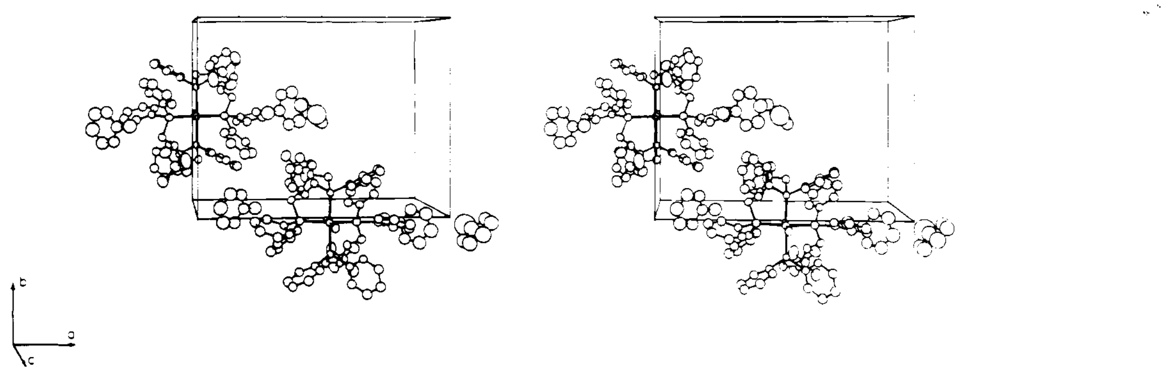

Figure 3. Stereoview of the contents of a unit cell.

Structure Solution and Refinement. The positional parameters for the Ru, Cl, and P atoms were determined from a three-dimensional Patterson synthesis. As there are only two molecules per unit cell, crystallographic twofold symmetry is imposed on the molecule with the Ru and Cl atoms lying on this axis at the special position $(0, {}^1/_2, z)$. The other nonhydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier syntheses.

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 the observed and calculated structure factor amplitudes, respectively, and the weighting factor w is given by $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral-atom scattering factors were calculated from the analytical expression for the scattering factor curves.[12] The f' and f'' components of anomalous dispersion were those of Cromer and Liberman[13] and were included in the calculations for the Ru, P, and Cl atoms.

One cycle of least-squares refinement in which all atoms, other than those of the phenyl rings or the toluene solvate molecules, were assigned anisotropic temperature factors gave values of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.068$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2} = 0.095$. At this point it appeared that the toluene molecule located at the special position $({}^1/_2, {}^1/_2, z)$ was disordered about the twofold axis. This disorder was not considered serious enough to justify refining a model to account for it; hence we have the higher than normal temperature factors and somewhat distorted geometry of this group.

Of the 46 independent H atoms in the molecule, not including the hydride ligand, only the six associated with the methyl groups of the two toluene molecules could not be located in feasible positions. Accordingly "ideal" positions were calculated for these 40 H atoms with the assumptions of C–H bond lengths of 0.95 Å, sp^3 or sp^2 geometries at the appropriate C atoms, and isotropic thermal parameters of 1.0 Å^2 greater than those of the atoms to which they are bonded. These parameters were not refined, but their contributions were included in subsequent calculations. The hydride was located in a difference Fourier synthesis at fractional coordinates (0.0, 0.5, −0.0638) by using those data with $\lambda^{-1}(\sin\theta) \leq 0.4$.

After recalculation of the H atom positions the refinement converged

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(12) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1972.

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

Table V. Hydrogen Atom Parameters ($\times 10^4$)

atom	x	y	z	U, Å^2
H	0	5000	−638	1013
H1C(12)	−1261	7293	−1913	556
H1C(13)	−2084	7866	−3099	654
H1C(14)	−1940	7950	−5215	580
H1C(15)	−1015	7351	−6091	637
H1C(16)	−220	6738	−4883	515
H1C(22)	−466	1832	−2586	581
H1C(23)	−1306	1167	−3641	665
H1C(24)	−2054	1943	−4716	648
H1C(25)	−1887	3368	−4994	593
H1C(26)	−1025	4040	−3996	470
H1C(32)	642	4632	804	595
H1C(33)	1012	3861	2442	736
H1C(34)	1920	2983	2193	841
H1C(35)	2465	2923	386	738
H1C(36)	2143	3768	−1227	612
H1C(42)	2522	5387	−1553	605
H1C(43)	3348	5373	−3023	686
H1C(44)	3145	4832	−4936	686
H1C(45)	2085	4415	−5444	626
H1C(46)	1255	4482	−4011	500
H1C(53)	2984	6591	747	899
H1C(54)	3791	6780	−614	1132
H1C(55)	4464	5678	−1253	1353
H1C(56)	4273	4362	−396	1201
H1C(57)	3459	4164	1071	989
H1C(63)	5692	4137	−5205	1089
H1C(64)	5698	4212	−7304	1196
H1C(65)	5057	5282	−8128	1393
H1C(2)	880	7504	−730	542
H1C(3)	587	5976	333	532
H1C(1)	−185	7658	−1205	496
H2C(1)	−373	6876	−469	496
H1C(4)	1762	5862	−353	504
H2C(4)	1468	6403	−1374	504
H1C(6)	682	7162	3517	1058
H2C(6)	69	7099	2701	1058
H3C(6)	547	6354	2794	1058
H1C(7)	1811	7786	1893	936
H2C(7)	1280	8454	1659	936
H3C(7)	1347	8056	2928	936

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

atoms	dist	atoms	angle
Ru-P(1)	2.393 (1)	P(1)-Ru-P(2)	90.29 (6)
Ru-P(2)	2.357 (1)	P(1)-Ru-P(1)′	168.60 (4)
Ru-H	1.65	P(2)-Ru-P(2)′	149.49 (5)
Ru-Cl	2.549 (1)	P(1)-Ru-Cl	84.30 (2)
P(1)-C(1)	1.845 (4)	P(2)-Ru-Cl	105.26 (2)
P(1)-C(11)	1.855 (5)	C(11)-P(1)-C(21)	96.3 (2)
P(1)-C(21)	1.839 (5)	Ru-P(1)-C(1)	118.0 (1)
P(2)-C(4)	1.864 (5)	C(1)-P(1)-C(11)	101.0 (2)
P(2)-C(31)	1.853 (5)	C(1)-P(1)-C(21)	100.6 (2)
P(2)-C(41)	1.850 (4)	C(4)-P(2)-Ru	115.5 (1)
C(1)-C(2)	1.518 (7)	C(4)-P(2)-C(31)	95.3 (3)
C(2)-C(3)	1.528 (7)	C(4)-P(2)-C(41)	98.7 (2)
C(2)-O(1)	1.437 (6)	C(31)-P(2)-C(41)	101.1 (2)
C(3)-O(2)	1.441 (6)	P(1)-C(1)-C(2)	114.7 (4)
C(3)-C(4)	1.509 (7)	C(1)-C(2)-C(3)	117.0 (4)
C(5)-O(1)	1.431 (7)	C(1)-C(2)-O(1)	108.5 (4)
C(5)-O(2)	1.432 (7)	C(2)-C(3)-C(4)	116.6 (4)
C(5)-C(6)	1.528 (10)	C(2)-C(3)-O(2)	101.1 (4)
C(5)-C(7)	1.519 (9)	C(3)-C(4)-P(2)	117.5 (3)
		O(1)-C(5)-O(2)	106.7 (4)
		C(6)-C(5)-C(7)	112.6 (6)

in two cycles of full-matrix least-squares refinement to final agreement factors of $R_1 = 0.048$ and $R_2 = 0.064$. In the final cycles 248 variables were refined by using 6465 data with $F^2 \geq 3\sigma(F^2)$. The largest parameter shift was 0.7 of its estimated standard deviation and was associated with the z coordinate of atom C(63) in the disordered solvate molecule. A statistical analysis of R_2 in terms of $|F_o|$, combinations of Miller indices, and $\lambda^{-1}(\sin\theta)$ showed no unusual trends. The highest peak on a difference Fourier synthesis, calculated from the final structure factors, has an electron density of 1.3 e Å^{-3} and fractional coordinates of (0.55, 0.44, −0.62), which are near those of the disordered toluene molecule.

Table VII. Selected Ruthenium-Phosphine Bond Lengths (Å) and Angles (Deg)

complex	Ru-P	P-Ru-P	ref
$Ru(pyS)_2(PPh_3)_2$ [a]	2.319 (2), 2.332 (2)	96.8 (1)	16
$RuCO(C_2S_2(CF_3)_2)(PPh_3)_2$ [b]	2.397 (2), 2.381 (2)	100.8 (1)	17
$Ru(S_2HC)_2(PPh_3)_2$ [b]	2.335 (3), 2.357 (2)	101.3	18
$Ru(NO)_2(PPh_3)_2$	2.337 (2), 2.353 (2)	103.85 (6)	19
$RuHNO(PPh_3)_3$	2.34 (1) av	115 (4)	7
$RuHCl(diop)_2$	2.357 (1)	149.49 (5)	this work
$RuHCl(PPh_3)_3$	2.361 (4), 2.329 (4)	153.1 (2)	5
$RuH(Oac)(PPh_3)_3$	2.363 (5), 2.351 (5)	154.9 (1)	6
$RuCl_2(PPh_3)_3$	2.374 (6), 2.412 (6)	156.4 (2)	20
$RuHCl(diop)_2$	2.393 (4)	168.60 (4)	this work
$RuCl_3NO(PPh_2Me)_2$	2.441 (2), 2.429 (2)	171.4 (6)	21
$[RuCl(CO)(HN_2Ph)(PPh_3)_2]^+$	2.439 (2), 2.415 (2)	176.83 (5)	22

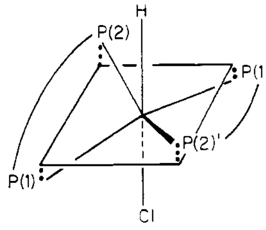
[a] Phosphines trans to N; pyS = pyridine-2-thiolato. [b] Phosphines trans to S.

That the correct absolute configuration has been chosen was determined by refinement of the centrosymmetrically related model. The weighted residual, R_2, for this refinement is 0.072 which, with use of Hamilton's significance test,[14] indicates this second model may be rejected with a confidence level greater than 0.995.

A listing of the final calculated and observed structure factors is given in Table III.[15] The final atomic parameters are given in Tables IV and V.

Discussion

A stereoview of the overall molecular geometry is presented in Figure 1, while the atom numbering scheme for the unique portion of the complex is shown in Figure 2. A listing of selected bond distances and angles is given in Table VI. The Ru atom is six-coordinate, in a distorted octahedral environment, with the hydride trans to Cl. The distortion from an ideal octahedral geometry is depicted in I in which the two phosphorus atoms P(1) and P(2) are displaced in opposing senses from the equatorial plane (the primed atoms are related to the unprimed by the twofold axis).



I

The Ru–P distances of 2.356 (1) and 2.393 (1) Å both fall within the wide range, 2.2–2.4 Å, of distances observed for ruthenium–phosphine complexes.[5–7,16–22] The difference be-

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tween the two bond lengths is 0.037 Å, which is crystallographically significant (>25σ), and may be ascribed to a stronger trans influence acting on the more nearly opposed atoms P(1) and P(1)'. By assigning the difference to trans influence, we imply that for a series of similar complexes we should expect to see a positive correlation between the Ru–P bond length and the P–Ru–P angle. Table VII lists a series of Ru complexes containing two or more tertiary P atoms bonded to the metal. While a variety of effects is presumed to be contributing to the observed Ru–P distances (coordination geometry, oxidation state, nature of the trans ligand, etc.), it is nonetheless interesting to note the trend of increasing Ru–P bond length with increasing P–Ru–P angle. Included in this table are the bond lengths for Ru–P(1) and Ru–P(2) which both fit into this series according to the appropriate P–Ru–P angle.

The Ru–Cl distance of 2.549 (1) Å is considerably longer than Ru–Cl bonds in which the chloro ligand is trans to Cl (2.398 (10) Å)[21] or P (2.421 (5) Å).[5] Although not many structures of hydride complexes are available for systematic comparison, it is usually felt that the hydride ligand does exert a strong trans influence. Thus this factor is used to explain the ca. 0.12 Å difference in Pt–Cl distances when the trans ligand is H as opposed to Cl.[23] However, it is of interest to note that the Rh–Cl distance in $RhHCl(SiCl_3)(PPh_3)_2$[24] is only slightly longer than that observed in $RhCl_3(PPhEt_2)_3$[25] (2.387 (4) and 2.362 (3) Å, respectively). Since there is no apparent structural element in the present complex which would prevent a shorter Ru–Cl bond, the closest nonbonded contact being 2.66 Å to HC(26), we conclude that the long Ru–Cl bond is the result of the trans influence of the hydride ligand. The implication of this long bond, that the Ru–Cl bond may be weaker than normal, derives support from the behavior of the complex as an electrolyte in nitromethane, which initially suggested the complex was five-coordinate with a chloride counterion.[4]

The Ru–H distance of 1.68 Å, as deduced from a difference Fourier synthesis, is in good agreement with the values of 1.68 Å in $RuH(acetate)(PPh_3)_3$,[6] 1.7 Å in $RuHCl(PPh_3)_3$,[5] and 1.67 Å in $RuH(naphthyl)(dmpe)_2$,[26] all located in a similar manner.

The internal geometry of the (+)-diop ligand is normal, with mean distances of 1.851 (9), 1.520 (7), and 1.475 (5) Å for the P–C, C–C, and C–O bonds, respectively. The geometry of the phenyl rings is as expected with mean C–C distances of 1.39 (1) Å and mean C–C–C angles of 120 (1)°. The absolute configuration at both C(2) and C(3) is *S*, which is consistent with a positive specific rotation for the ligand[27] and a crystal structure of an iridium complex containing (+)-diop.[28]

A stereoview of the unit cell packing is shown in Figure 3. There are no close intermolecular contacts, with the closest distance of approach being 2.19 Å between H1C(1) at (x, y, z) and H1C(22) at ($\bar{x}$, $1 - y$, z).

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Registry No. $RuHC(diop)_2 \cdot 2CH_3C_6H_5$, 75171-73-2.

Supplementary Material Available: Table III, a listing of structure factor amplitudes (85 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from Union Carbide Corporation,
South Charleston, West Virginia 25303

Rhodium Carbonyl Cluster Chemistry under High Pressure of Carbon Monoxide and Hydrogen. 2. Synthesis of $[Rh_{14}(CO)_{25}]^{4-}$

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The study of rhodium carbonyl clusters has been in process for some time in our laboratory.[2-4] As a result of that work, we have observed that high-yield, readily implemented synthetic procedures for rhodium carbonyl species could be developed by using high-pressure techniques as reported for $[Rh_{17}S_2(CO)_{32}]^{3-}$, $[Rh_9E(CO)_{21}]^{2-}$, $[Rh_{10}E(CO)_{22}]^{3-}$ (E = P, As), and an antimony-containing species under characterization.[5-10]

Transition-metal carbonyl clusters containing an unusually high number of rhodium atoms have been postulated as suitable models for the behavior of surfaces.[11] Specifically, the structural changes noted for $[Rh_{13}(CO)_{24}H_3]^{2-}$, $[Rh_{15}(CO)_{27}]^{3-}$, and $[Rh_{14}(CO_{25}]^{4-}$ have been correlated with those expected in the reconstruction of some surfaces.[12] The syn-

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