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Crystal and Molecular Structure and Solution Dynamics of Hydridotris(triphenylphosphine)rhodium(I)

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The structure of $RhH(PPh_3)_3{\cdot}HN(CH_3)_2{\cdot}THF$ has been determined by single-crystal X-ray methods. The dimethylamine and THF molecules are discrete solvates and are not coordinated to the rhodium atom. The coordination about the metal is nearly planar with the mutually trans phosphine ligands displaced toward the presumed position of the hydride ligand. There are no ortho hydrogen–rhodium distances shorter than 3.01 Å. Variable-temperature $^{31}P\{^1H\}$ NMR data in toluene-d_8 confirm a C_s or C_{2v} structure at −86 °C and demonstrate a rapid (230 s^{-1}) intramolecular rearrangement of the phosphine ligands at −13 °C. An upper limit of 0.4% is placed on the amount of $RhHP_2$ present in solution at 30 °C. The significance of these results with respect to the catalytic activity of $RhH(PPh_3)_3$ and $RhH(PPh_3)_4$ is discussed.

Introduction

Hydridotris(triphenylphosphine)rhodium(I), $RhHP_3$, has received some attention as an olefin isomerization catalyst,[2] in one case exhibiting the highest activity of a series of group 8 catalysts.[2b] It also is about 40 times more active than $RhClP_3$ as an ethylene hydrogenation catalyst.[3] In spite of these interesting catalytic properties only fragmentary and conflicting data have been reported about the structure and behavior of this hydride complex in solution.

Tetrahedral structures for both $RhHP_3$ and $Rh(CH_3)P_3$ were proposed based on ^1H NMR spectra,[4,5] but the more likely alternate explanation of rapidly rearranging square-planar structures was not considered. The extent of phosphine dissociation from $RhHP_3$ also is uncertain. Some data indicate that $RhHP_4$ loses two phosphine ligands in solution (reactions 1 and 2) to yield the bis(phosphine) complex $RhHP_2$,[6] while other data (using a phosphine other than triphenylphosphine) suggest that reaction 2 lies far to the left.[7]

$$RhHP_4 \rightleftharpoons RhHP_3 + P \quad (1)$$

$$RhHP_3 \rightleftharpoons RhHP_2 + P \quad (2)$$

In this work we report the solid-state and the solution structure of $RhHP_3$, as determined by X-ray diffraction methods and ^{31}P NMR spectroscopy, respectively. The NMR data also allow firm conclusions to be drawn about a room-temperature rearrangement of the phosphine ligands and about the extent of reaction 2.

Experimental Section

Standard vacuum line and inert atmosphere techniques[8] were employed since $RhHP_3$ is oxygen sensitive both in solution and in the solid state. Solvents were dried by distillation from lithium aluminum hydride or sodium borohydride. Chlorotris(triphenylphosphine)-rhodium(I) (Ventron Corp. or Strem Chemical Co.), lithium dimethylamide (Ventron Corp.), and toluene-d_8 (Wilmad Glass Co.) were used as received. Dimethylamine (Matheson Gas Products) was dried over lithium dimethylamide.

Hydridotris(triphenylphosphine)rhodium(I) was prepared by the reaction of $RhClP_3$ (1 mmol) and lithium dimethylamide (1 mmol) in THF (15 mL) containing an excess of dimethylamine (25 mmol).[9,10] Filtration of the resulting complex followed by recrystallization from THF/dimethylamine yielded yellow-orange crystals of $RhHP_3{\cdot}HN(CH_3)_2{\cdot}THF$.

The crystal structure determination was performed by Molecular Structure Corp., College Station, Texas. A crystal (0.2 mm × 0.2 mm × 0.35 mm) was mounted in a glass capillary in a nitrogen atmosphere. It was found to belong to the orthorhombic system and to display extinctions $h00$, $h \neq 2n$, $0k0$, $k \neq 2n$, and $00l$, $l \neq 2n$, which establish the space group $P2_12_12_1$. Unit cell dimensions, determined by a least-squares refinement of the angular positions of 25 computer-centered reflections, are as follows: a = 9.710 (4) Å, b = 21.230 (7) Å, c = 25.397 (4) Å, V = 5235 Å^3, density (calcd) = 1.29 g cm^{-3} for Z = 4 and formula weight = 1016.05 g mol^{-1}.

Data collection using Mo Kα radiation was carried out on an Enraf-Nonius CAD4 diffractometer. Of the 6748 reflections measured, 6640 are unique and of these 1701 have $F_o^2 > 3\sigma(F_o^2)$. The structure was solved by Patterson and difference Fourier syntheses. The rhodium atom and the three phosphorus atoms were refined anisotropically, and the remaining nonhydrogen atoms in the ligands and the THF molecule were refined isotropically. The dimethylamine was located in the final difference Fourier map. When the nitrogen and two carbon atoms of this molecule were included in the structure factor calculation R was reduced from 0.083 to 0.072 and R_w was reduced from 0.112 to 0.076. Although these three atoms could not be refined, it seems certain that dimethylamine is in the structure. This also was confirmed by elemental analytical data. The positions of the 18 ortho hydrogens were idealized using a C–H distance of 0.95 Å. Rhodium–ortho hydrogen interatomic distances were then calculated using standard crystallographic programs.

Listings of the observed and calculated structure amplitudes, bond distances, and bond angles are available as supplementary material. The final positional and thermal parameters appear in Table I. Selected bond distances and bond angles are given in Table II.

The purification of $RhClP_3$ and the preparation of $RhHP_3$ used for NMR spectroscopy have been described.[3] Solutions of the complexes (ca. 10 mM) in toluene-d_8 were prepared under nitrogen and were transferred to 8-mm NMR tubes via syringe. The tubes were then sealed under vacuum.

The proton-decoupled ^{31}P NMR spectra, abbreviated $^{31}P\{^1H\}$, were recorded on a Varian CFT-20 spectrometer operating at 32.199 MHz. The chemical shifts reported in this paper are with respect to external 85% H_3PO_4 at 30 °C. A negative sign indicates an upfield shift. The temperature at the sample was measured with a chromel–constantan thermocouple inserted coaxially into an 8-mm NMR tube containing acetone (below room temperature) or mineral oil (above room temperature) so that the thermocouple junction was positioned at the center of the transmitter coil.

Results and Discussion

Structure in the Solid State. Figure 1 shows the structure of the coordination sphere of the complex. Figure 2 is a view of the inner-coordination sphere. Selected bond distances and bond angles are given in Table II. The molecule is nearly planar with the rhodium atom displaced from the plane defined by the three phosphorus atoms by 0.164 Å.

Outside of the coordination sphere of the rhodium atom, a molecule of dimethylamine and a molecule of THF are present as solvates. These molecules are at least 3.5 Å from any other atom in the structure. Thus, the rhodium is strictly four-coordinate.

The hydride ligand was not located, but its position can be inferred from the large P_1–Rh–P_2 angle of 151.7 (2)°. Further evidence for the existence of the hydride ligand in this molecule is provided by spectroscopic measurements.[9,10] The Rh–P_3 bond distance is 0.048 (8) Å longer than the average of the Rh–P_1 and the Rh–P_2 bond distances, in harmony with the

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Rh	0.1082 (2)	−0.08723 (9)	0.19832 (7)	0.0085 (2)	0.00157 (3)	0.00092 (2)	−0.0004 (3)	−0.0005 (2)	−0.00007 (8)
P_1	−0.0221 (7)	−0.1062 (3)	0.1256 (2)	0.0068 (8)	0.0018 (2)	0.0013 (1)	0.0008 (7)	0.0002 (6)	−0.0004 (2)
P_2	0.1545 (6)	−0.0995 (3)	0.2850 (2)	0.0096 (10)	0.0017 (2)	0.0011 (1)	0.0003 (7)	−0.0005 (5)	−0.0001 (2)
P_3	0.2238 (7)	0.0052 (3)	0.1784 (2)	0.0094 (10)	0.0018 (2)	0.0012 (1)	−0.0009 (8)	0.0008 (6)	−0.0002 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O_{15}	0.722 (4)	0.144 (1)	0.369 (1)	19 (1)	C_{30}	0.245 (3)	−0.2007 (13)	0.3519 (10)	6.5 (8)
N_1	0.9256 (0)	0.2813 (0)	0.9766 (0)	25.0000 (0)	C_{31}	0.242 (3)	−0.0423 (10)	0.3255 (8)	3.2 (5)
C_1	−0.097 (3)	−0.0373 (9)	0.0948 (8)	3.5 (5)	C_{32}	0.185 (2)	0.0157 (10)	0.3342 (8)	3.5 (6)
C_2	−0.107 (3)	−0.0273 (10)	0.0410 (8)	4.0 (5)	C_{33}	0.254 (3)	0.0634 (11)	0.3676 (10)	5.7 (7)
C_3	−0.166 (3)	0.0278 (11)	0.0217 (9)	5.0 (7)	C_{34}	0.376 (3)	0.0502 (10)	0.3886 (8)	4.3 (6)
C_4	−0.227 (3)	0.0739 (12)	0.0561 (9)	5.8 (7)	C_{35}	0.447 (3)	−0.0089 (14)	0.3775 (11)	7.4 (9)
C_5	−0.232 (3)	0.0617 (12)	0.1086 (10)	6.0 (7)	C_{36}	0.380 (3)	−0.0545 (11)	0.3461 (8)	4.7 (6)
C_6	−0.160 (2)	0.0044 (11)	0.1298 (8)	3.8 (6)	C_{37}	0.282 (3)	0.0187 (10)	0.1096 (9)	3.9 (6)
C_7	−0.176 (3)	−0.1566 (11)	0.1360 (9)	4.0 (6)	C_{38}	0.176 (3)	0.0409 (12)	0.0743 (9)	5.0 (7)
C_8	−0.159 (3)	−0.2161 (11)	0.1658 (9)	4.5 (6)	C_{39}	0.223 (4)	0.0409 (13)	0.0195 (11)	7.5 (9)
C_9	−0.272 (3)	−0.2600 (12)	0.1696 (9)	5.6 (7)	C_{40}	0.346 (3)	0.0180 (12)	0.0020 (10)	6.3 (8)
C_{10}	−0.395 (4)	−0.2363 (12)	0.1519 (9)	6.1 (7)	C_{41}	0.439 (3)	−0.0024 (12)	0.0347 (9)	5.1 (7)
C_{11}	−0.416 (3)	−0.1811 (12)	0.1250 (10)	6.2 (7)	C_{42}	0.411 (3)	−0.0028 (11)	0.0933 (9)	5.1 (6)
C_{12}	−0.301 (3)	−0.1416 (11)	0.1140 (9)	4.5 (6)	C_{43}	0.384 (3)	0.0084 (9)	0.2128 (7)	2.8 (5)
C_{13}	0.058 (2)	−0.1439 (9)	0.0682 (7)	2.3 (5)	C_{44}	0.436 (2)	0.0645 (10)	0.2375 (9)	4.1 (6)
C_{14}	0.203 (3)	−0.1362 (11)	0.0639 (9)	4.5 (6)	C_{45}	0.575 (3)	0.0604 (11)	0.2612 (9)	4.9 (6)
C_{15}	0.264 (3)	−0.1610 (11)	0.0180 (9)	4.4 (6)	C_{46}	0.649 (3)	0.0052 (12)	0.2584 (12)	6.1 (7)
C_{16}	0.195 (3)	−0.1955 (11)	−0.0205 (8)	3.9 (6)	C_{47}	0.599 (3)	−0.0490 (10)	0.2341 (8)	4.1 (5)
C_{17}	0.056 (3)	−0.2040 (12)	−0.0149 (9)	5.0 (7)	C_{48}	0.469 (2)	−0.0470 (10)	0.2107 (9)	4.0 (6)
C_{18}	−0.016 (3)	−0.1780 (10)	0.0316 (9)	3.6 (6)	C_{49}	0.141 (2)	0.0818 (10)	0.1931 (8)	4.1 (5)
C_{19}	−0.009 (2)	−0.1094 (9)	0.3224 (7)	2.4 (5)	C_{50}	0.027 (2)	0.0802 (11)	0.2261 (8)	4.4 (6)
C_{20}	−0.001 (3)	−0.0981 (13)	0.3783 (9)	5.6 (7)	C_{51}	−0.045 (3)	0.1375 (13)	0.2371 (11)	7.5 (9)
C_{21}	−0.130 (3)	−0.1042 (13)	0.4084 (10)	7.5 (8)	C_{52}	0.005 (3)	0.1941 (12)	0.2163 (10)	6.1 (8)
C_{22}	−0.250 (3)	−0.1277 (13)	0.3832 (10)	7.0 (8)	C_{53}	0.123 (3)	0.1957 (11)	0.1856 (9)	6.3 (7)
C_{23}	−0.243 (3)	−0.1416 (11)	0.3293 (9)	5.2 (7)	C_{54}	0.199 (3)	0.1394 (12)	0.1715 (9)	5.4 (7)
C_{24}	−0.123 (3)	−0.1324 (9)	0.2999 (9)	4.3 (5)	C_{15}	0.804 (5)	0.1933 (20)	0.3798 (16)	15.0 (16)
C_{25}	0.249 (2)	−0.1733 (9)	0.3023 (9)	3.3 (5)	C_{25}	0.911 (6)	0.1700 (23)	0.4162 (20)	19.8 (19)
C_{26}	0.327 (3)	−0.1997 (11)	0.2614 (9)	4.6 (7)	C_{35}	0.865 (5)	0.1046 (20)	0.4310 (15)	15.1 (14)
C_{27}	0.412 (3)	−0.2551 (12)	0.2740 (10)	6.8 (8)	C_{45}	0.762 (6)	0.0951 (24)	0.3999 (18)	17.5 (17)
C_{28}	0.406 (3)	−0.2828 (11)	0.3230 (9)	5.6 (7)	C_{55}	1.140 (0)	0.2676 (0)	1.0009 (0)	25.0 (0)
C_{29}	0.328 (3)	−0.2561 (12)	0.3603 (10)	5.7 (7)	C_{65}	0.956 (0)	0.2231 (0)	1.0162 (0)	25.0 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{1,1}h^2 + B_{2,2}k^2 + B_{3,3}l^2 + B_{1,2}hk + B_{1,3}hl + B_{2,3}kl)]$.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in $RhHP_3{\cdot}HN(CH_3)_2{\cdot}THF$

Rh-P_1	2.274 (6)	P_2-C_{25}	1.87 (2)
Rh-P_2	2.262 (5)	P_2-C_{31}	1.80 (2)
Rh-P_3	2.316 (6)	P_3-C_{37}	1.86 (2)
P_1-C_1	1.81 (2)	P_3-C_{43}	1.79 (2)
P_1-C_7	1.85 (2)	P_3-C_{49}	1.85 (2)
P_1-C_{13}	1.84 (2)	P-C (av)	1.84
P_2-C_{19}	1.87 (2)		
P_1-Rh-P_2	151.7 (2)	Rh-P_2-C_{19}	109.8 (6)
P_1-Rh-P_3	104.0 (2)	Rh-P_2-C_{25}	115.0 (7)
P_2-Rh-P_3	102.4 (2)	Rh-P_2-C_{31}	124.8 (6)
Rh-P_1-C_1	115.6 (7)	Rh-P_3-C_{37}	119.0 (7)
Rh-P_1-C_7	115.7 (7)	Rh-P_3-C_{43}	110.3 (6)
Rh-P_1-C_{13}	119.0 (7)	Rh-P_3-C_{49}	119.4 (7)

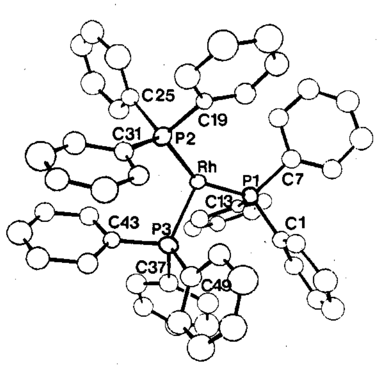


Figure 1. Structure of the $RhH(PPh_3)_3$ molecule.

observation that hydrides exert a slightly greater trans influence than phosphines.[11] The deviation of the P_1–Rh–P_2 angle from 180° demonstrates the reduced steric requirements of the hydride ligand. However, as has been noted for a large number of hydride complexes,[12] the stereochemical role of a hydride ligand is variable and depends on a subtle balance of steric and electronic effects.

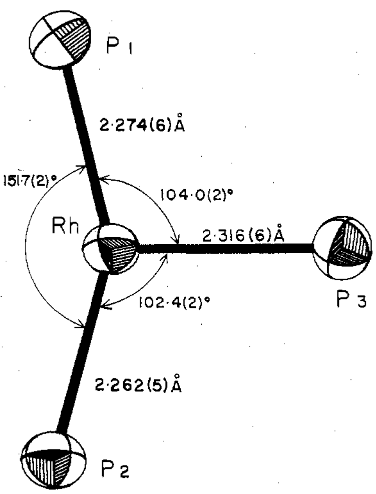


Figure 2. A view of the inner-coordination sphere of the $RhH(PPh_3)_3$ molecule.

A comparison of the structures of several rhodium hydride complexes allows this balance to be seen. In the solid-state structure of $RhHP_4$ the four triphenylphosphine ligands form, within experimental error, a regular tetrahedron around the rhodium atom.[13] The hydride ligand, which was not located, presumably sits on a tetrahedral face and thus is not ste-

Table III. A Comparison of Bond Distances (Å) and Bond Angles (deg) for Planar d^8 $MX(PPh_3)_3$ Complexes

complex	$M-P_1$[a]	$M-P_2$	$M-P_3$	P_1-M-P_2	P_1-M-P_3	P_2-M-P_3	ref
$RhH(PPh_3)_3$	2.274 (6)	2.262 (5)	2.316 (6)	151.7 (2)	104.0 (2)	102.4 (2)	*f*
$RhCl(PPh_3)_3$[b]	2.304 (4)	2.338 (4)	2.225 (4)	159.1 (2)	97.7 (1)	96.4 (2)	*g*
$RhCl(PPh_3)_3$[c]	2.334 (4)	2.322 (4)	2.214 (4)	152.8 (1)	97.9 (2)	100.4 (1)	*g*
$[Rh(PPh_3)_3]^+$	2.24[d]	—[e]	2.21[d]	159.3 (2)	102.4 (2)	97.7 (2)	*h*
$[PtH(PPh_3)_3]^+$	2.315 (6)	2.309 (6)	2.363 (6)	159.6 (2)	100.6 (2)	99.6 (2)	*i*

[a] P_1 and P_2 are mutually trans; P_3 is trans to the X ligand (H, Cl, or no ligand). [b] The orange allotrope. [c] The red allotrope. [d] Standard deviations were not reported. [e] This value was not reported. [f] This work. [g] Reference 15c. [h] Reference 16. [i] Reference 22.

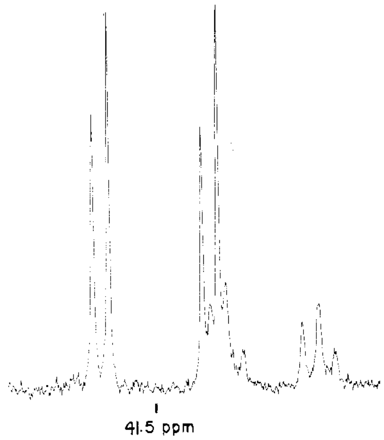


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $RhH(PPh_3)_3$ in toluene-d_8 at −86 °C. Chemical shifts are referenced to external 85% H_3PO_4 at 30 °C. H_0 increases to the right.

reochemically active. The interphosphine van der Waals repulsions are smaller for $RhHP_3$ then for $RhHP_4$, and the molecule is midway between a rigorous square-planar structure (P_1–Rh–P_2 = 180°) and a sterically ideal C_{3v} structure (P_1–Rh–P_2 ~ 120°). The interligand repulsions are smaller still in $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$ and in the solid state the P–Rh–P angle is 168.12 (3)°.[14]

Molecular structures have been determined crystallographically for several square-planar d^8 tris(triphenylphosphine) complexes. Bond distances and bond angles for these complexes are listed in Table III. Although the list includes complexes of two different metals, complexes having different ligands trans to P_3, and complexes having different charges (neutral and monopositive), the distances and angles are strikingly similar. A feature that apparently has a subtle influence on the geometry of these complexes is the interaction of an ortho hydrogen with the metal. The major difference between the two forms of $RhCl(PPh_3)_3$ is that in the orange allotrope there is an ortho hydrogen on P_3 that is 2.84 Å from the rhodium atom, while in the red allotrope it is an ortho hydrogen on P_2 that is close (2.77 Å) to the rhodium atom.[15] Despite the short (2.21 Å) Rh–P_3 distance and the absence of a ligand trans to P_3 in the $[Rh(PPh_3)_3]^+$ cation, the P_1–Rh–P_2 angle is rather large.[16] This is undoubtedly due to the close approach of a phenyl ring on P_1 to the rhodium atom, severely distorting the Rh–P_1–C angle to 75.6 (5)°. An ortho hydrogen on this phenyl ring is 2.56 Å from the rhodium atom (the ipso carbon on this phenyl ring is only 2.48 (2) Å from the metal center).[16] This ortho hydrogen–rhodium interaction is not observed for $RhH(PPh_3)_3$, however, since the closest ortho hydrogen–rhodium distance is 3.01 Å.

Structure and Dynamics in Solution. Figure 3 shows the $^{31}P\{^1H\}$ spectrum of $RhHP_3$ at −86 °C. The observed AB_2X pattern of a double doublet and a less intense double triplet is exactly that expected for a structure with C_s or C_{2v} symmetry, in full agreement with the virtually square-planar solid-state structure. The observed chemical shifts and coupling constants (tabulated in Table IV) can be compared to those for $RhClP_3$, $RhHP_4$, and RhH_2ClP_3 (the labeling of

Table IV. ^{31}P Chemical Shifts (ppm) and Coupling Constants (Hz)[a]

complex	$\delta(P_A)$	$\delta(P_B)$	J_{Rh-P_A}	J_{Rh-P_B}	$J_{P_A-P_B}$	ref
$RhH(PPh_3)_3$[b]	35.9	41.5	145	172	25	*f*
$RhH(PPh_3)_4$[c]	31.7	28.2	113	162	27	*g*
$RhCl(PPh_3)_3$[b]	45.3	28.8	192	145	38	*f*
$RhCl(PPh_3)_3$[d]	48.9	32.2	192	146	37.5	*h*
$RhH_2Cl(PPh_3)_3$[e]	20.7	40.3	90	114	17.5	*h*

[a] See 1, 2, and 3 for the labeling scheme used in this table. [b] In toluene-d_8 at −86 °C. [c] In toluene-d_8 at −78 °C. [d] In methylene chloride at 28 °C. [e] In methylene chloride at −25 °C. [f] This work. [g] Reference 3b. [h] Reference 20b.

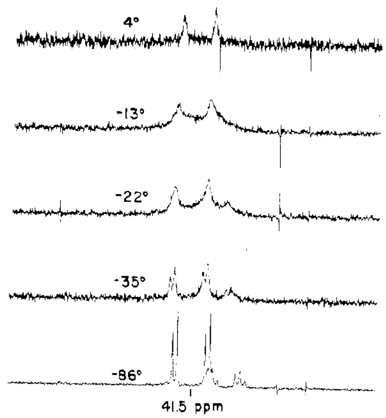
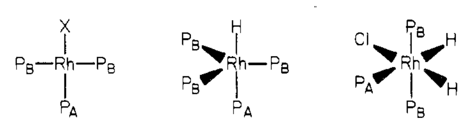


Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $RhH(PPh_3)_3$ in toluene-d_8. H_0 increases to the right.

the triphenylphosphine ligands is shown below for $RhXP_3$ (**1**; X = H, Cl), $RhHP_4$ (**2**), and RhH_2ClP_3 (**3**)). For the three



1, X = H, Cl **2** **3**

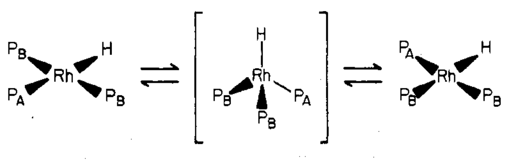
hydride complexes listed note that within each complex J_{Rh-P} is smaller for phosphorus trans to hydrogen than for phosphorus trans to phosphorus.

There is no change in the coupling constants or in the appearance of the spectrum of $RhHP_3$ as the temperature is raised from −86 to −43 °C. The chemiccal shifts, however, show linear temperature dependences over this range ($\Delta\delta(P_A)$ = 0.032 ppm deg^{-1}; $\Delta\delta(P_B)$ = 0.014 ppm deg^{-1}) which are similar in sign to but smaller in magnitude than those reported for other group 8 phosphine and phosphite complexes.[17] Extrapolations of these dependences were made into the temperature range where the chemical shifts could not be measured directly. Triphenylphosphine shows a similar linear dependence ($\Delta\delta_P$ = 0.023 ppm deg^{-1}; $\delta_P^{30 °C}$ = −5.9 ppm in toluene-d_8) over the temperature range −86 to +75 °C.

Above −43 °C there is a broadening of the spectrum with a concomitant loss of P–P coupling (Figure 4). At 4 °C the spectrum has sharpened up to a doublet: δ = 41.0, J_{Rh-P} =

164 Hz. The weighted average of the chemical shifts for P_A and P_B at 4 °C, taking into account their respective temperature dependences, is 41.5 ppm. The weighted average of J_{Rh-P_A} and J_{Rh-P_B} is 163 Hz. This is compelling evidence for a rapid intramolecular rearrangement of the three P ligands, unprecedented behavior for a four-coordinate $4d^8$ or $5d^8$ metal complex (except for one unrecognized example, see below). For example, both cis and trans forms of PtL_2X_2 complexes (L = trivalent phosphines, X = Cl, Br) can be isolated, since they do not interconvert at any measurable rate in solution.[18] While analogous palladium compounds are much more labile, affording isolation of only the equilibrium amounts of the cis and trans isomers,[19] the nature (inter- vs. intramolecular) and exact rate of any cis–trans isomerization have not been reported. NMR studies have shown that both $RhClP_3$[20] and $PtHP_3^+$[21] are structurally rigid in solution at room temperature (the latter complex is isoelectronic, isoleptic,[22] and isostructural[23] with $RhHP_3$). Moreover, *trans*-$PtH(PPH_3)(PEt_3)_2^+$ is stable in solution with respect to geometrical isomerization,[24] which places a lower limit on the rate of intramolecular (or intermolecular) isomerization of hours. To our knowledge there are no reports in which an intramolecular rearrangement for this type of complex is recognized. The one possible unrecognized case is $Rh(CH_3)P_3$, for which the ^1H NMR spectrum at 5 °C in benzene-d_6 shows the methyl protons coupled to three equivalent phosphines.[4] This was interpreted[4,5] as evidence supporting a tetrahedral structure, even though such a conformation is unknown for four-coordinate $4d^8$ or $5d^8$ complexes.[25] We suggest that a more reasonable explanation is that $Rh(CH_3)P_3$ is a square-planar complex that, like $RhHP_3$, is undergoing a rapid intramolecular rearrangement.

The simplest mechanism for the rearrangement is shown in reaction 3, in which the three phosphines are equivalent in

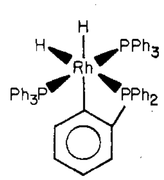


(3)

the tetrahedral intermediate. This mechanism has been adequately demonstrated for a large number of four-coordinate $3d^8$ complexes, which exist in solution at room temperature as an equilibrium mixture of tetrahedral and square-planar comformers yet are rapidly interconverting.[28] This is not a common feature for $4d^8$ or $5d^8$ complexes since the electronic energy difference between the square-planar and tetrahedral conformations increase $3d^8 < 4d^8 < 5d^8$[29] (cf. $RhClP_3$ and $CoClP_3$; the former is square planar[15] while the latter is believed to be tetrahedral based on magnetic measurements and electronic spectra[30]).

There is no compelling a priori argument that can explain why $\Delta G^‡$ for the rearrangement shown in reaction 3 is smaller for $RhHP_3$ and $Rh(CH_3)P_3$ than for $RhClP_3$. It seems likely, however, that the differences are based mainly on electronic factors since the van der Waals radii of covalently bonded chlorine and a methyl group are about the same.[31]

Alternate mechanisms involving an ortho-metalated intermediate, **4**, can be envisioned. Ortho metalation is now



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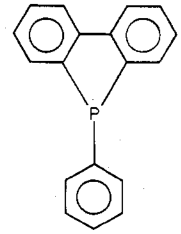
recognized to be a common reaction for triphenylphosphine complexes of Rh(I) and Ir(I).[3,32] However, any mechanism subsequent to ortho metalation that interchanges the phosphine ligands, such as a trigonal twist[33] or a tetrahedral jump,[34] would also interchange the hydride ligands. Thus, the hydride ligand in $RhHP_3$ would be exchanging with 18 ortho hydrogens on the phosphine phenyl rings. The observation of rhodium–hydrogen coupling in the ^1H NMR spectrum of $RhHP_3$ at 30 °C precludes these alternate mechanisms.[35]

Another possible rearrangement mechanism would involve the interaction of an ortho hydrogen on one of the phosphine phenyl groups with the rhodium atom, forming a pseudo-five-coordinate intermediate. In general, five-coordinate complexes undergo intramolecular rearrangements much more rapidly than four- or six-coordinate complexes.[34] However, the absence of a close ortho hydrogen–rhodium interaction for $RhHP_3$ in the solid state (see above) and the absence of a rapid intramolecular rearrangement for $RhClP_3$ (which does exhibit such an interaction in the solid state, see above) make this mechanism unlikely.

From 4 to 30 °C there is no change in J_{Rh-P} for the doublet or in the width of the peaks at half-height. The temperature dependence of the chemical shift of the doublet is smaller than the weighted average of the temperature dependences for P_A and P_B (see above). This cannot be due to exchange with dissociated phosphine since in that case Rh–P coupling would not be seen. This discrepancy can perhaps be attributed to a small error introduced by extrapolation of the temperature dependences measured in the −86 to −43 °C range. Since dissociated phosphine is not exchanging with the complex on the time scale of the experiment, one should observe a single sharp peak if any is present. The absence of a peak at −5.9 ppm in the 30 °C spectrum allows an upper limit of 0.4% to be placed on the amount of $RhHP_2$ present. This is in sharp contrast to the interpretation that reaction 2 lies far to the right, which was based on 1-hexene hydrogenation catalyzed by benzene solutions of $RhHP_4$.[6] Although the present findings demonstrate that reaction 2 lies far to the left, they do not preclude the possibility that a very small concentration of $RhHP_2$ is the major catalytic species for reactions catalyzed by $RhHP_4$[6] and $RhHP_3$,[2,3] as has been found for $RhClP_2$.[20b,39] However, the selectivity reported for catalysis by $RhHP_4$[6] (1-hexene was hydrogenated while 2-hexene was not) appears too high for a coordinatively unsaturated bis(phosphine) complex.[40] In a related system, a study of $RhHL_4$-catalyzed 1-hexene hydrogenation (L = 5-phenyl-5*H*-dibenzophosphole, **5**, a sterically more demanding ligand than triphenylphosphine)



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demonstrated that the tris(phosphine) complex $RhHL_3$ was the major rhodium-containing species in solution and that dissociation to the bis(phosphine) complex was finite but very small.[41]

Above 30 °C there is a gradual loss of Rh–P coupling accompanied by both a broadening of the doublet and an upfield shift (Figure 5). This is indicative of an intermolecular exchange with a gradual shift of reaction 2 to the right as the temperature is raised. The broad singlet is no sharper at 85 °C, the highest temperature used in this study. If the sample is cooled to −86 °C after several hours at 85 °C, no de-

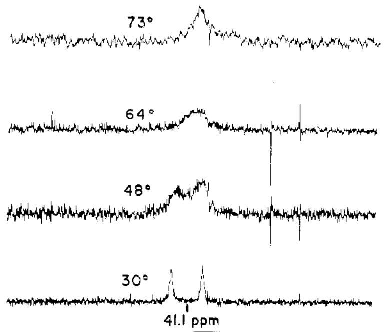

Figure 5. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $RhH(PPh_3)_3$ in toluene-d_8. H_0 increases to the right.

composition is evident.

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Registry No. $RhHP_3{\cdot}HN(CH_3)_2{\cdot}THF$, 67426-13-5; $RhClP_3$, 14694-95-2.

Supplementary Material Available: Structure of $RhH(PPh_3)_3$ and a listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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