was found in the reaction mixture, but it is quite possible that this was a result of the known tendency of hexafluorobut-2-yne to trimerize at elevated temperatures under autogenous pressure and not from the reaction of $RhCl(C_8F_{12})(Sb(C_6H_5)_3)_2$ with a third molecule of the acetylene.[15] The reaction involving $RhCl(As(C_6H_5)_3)_3$ represents an intermediate case in which the primary product, even at room temperature, is $RhCl(C_8F_{12})(As(C_6H_5)_3)_2$ with no complex corresponding to I being found. It thus appears that the tendency of $RhCl(As(C_6H_5)_3)_3$ and $RhCl(Sb(C_6H_5)_3)_3$ to form more stable derivatives than $RhCl(P(C_6H_5)_3)_3$[2] is once more illustrated with this isolation of a probable intermediate in the polymerization of hexafluorobut-2-yne by rhodium complexes.

Acknowledgments.—We are grateful to the National Institutes of Health for a postdoctoral fellowship to J. T. M., while at Imperial College, and to Johnson Matthey and Co. Ltd. for generous loans of rhodium trichloride. We also wish to thank Dr. Donald Moore of the U. S. Naval Ordnance Test Station, China Lake, Calif., for assistance in obtaining the nmr data.

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[15] J. F. Harris, R. J. Harder, and G. N. Sausen, *J. Org. Chem.*, **25**, 633 (1960).

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The Preparation and Nuclear Magnetic Resonance Spectra of Hydridophosphine Complexes of Ruthenium and Rhodium

BY K. C. DEWHIRST, W. KEIM,[1] AND C. A. REILLY

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The preparations of the complexes $H_2Ru((C_6H_5)_2PCH_3)_4$, $H_2Ru(CO)((C_6H_5)_2PCH_3)_3$, $HRh((C_6H_5)_3P)_4$, $HRh((C_6H_5)_3P)_3$, $HRh((C_6H_5)_2PCH_3)_4$, $((C_6H_5)_2PCH_3)_3RhCl$, and $((C_6H_5)_2PCH_3)_2(CO)RhCl$ are described. The nmr spectra of these complexes are discussed with regard to possible structures. The results confirm a rapid ligand exchange in these types of compounds.

Introduction

Hydrido complexes of the transition metals have been extensively investigated during the past decade.[2] Recently there has been considerable interest in the hydrido and chloro complexes of ruthenium and rhodium from the standpoint of their significance in homogeneous catalytic reactions.[3-5] It has been shown that compounds with a ruthenium or rhodium metal-to-hydrogen bond are the active intermediates in the homogeneous hydrogenation of olefins. There is relatively little information in the literature concerning low-valent ruthenium and rhodium hydrides, and still less is known about the stereochemistry of these types of complexes.

Molecular stereochemistries of transition metal hydrides have in many cases been deduced from nmr measurements.[6,7] From the P–H nuclear spin–spin coupling constants derived from the fine structure of the hydride resonance it is often possible to draw some firm conclusions about the geometrical arrangement of the phosphine ligands.

In the present paper we wish to report the synthesis and nmr studies of some novel hydrido and chloro complexes of ruthenium and rhodium, with special emphasis on structural elucidation.

Experimental Section

The nmr spectra were determined on a field-frequency stabilized Varian HR 100 using hexamethyldisiloxane as an internal reference (unless otherwise stated). The infrared spectra were determined *via* potassium bromide films. All preparations were carried out under an argon atmosphere.

Preparation of Compounds. ***cis*-Dihydridotetrakis(diphenylmethylphosphine)ruthenium(II).**—A mixture consisting of 2.5 g of $[((C_6H_5)_2PCH_3)_6Ru_2Cl_3]Cl$,[8] 2.5 ml of diphenylmethylphosphine, 25 ml of benzene, 25 ml of ethanol, and 10 ml of anhydrous hydrazine was pressured with 600 psig of hydrogen and warmed at 80° for 30 min. Upon cooling, the white separated solid was filtered and recrystallized from ethanol (2 g, 83% yield). *Anal.* Calcd for $((C_6H_5)_2PCH_3)_4RuH_2$: C, 69.1; H, 6.0; Ru, 11.2. Found: C, 68.8; H, 6.1; Ru, 11.0; mp 188–190°; γ(Ru–H) 1940, 1885 cm^{-1}.

***cis*-Dideuteriotetrakis(diphenylmethylphosphine)ruthenium(II).**—A benzene solution containing 1 g of $H_2Ru((C_6H_5)_2PCH_3)_4$ and a trace of hexene-1 was treated at 120° with 200 psig of deuterium for 3 hr. Upon cooling, a white solid separated which was subsequently filtered (0.6 g, 60% yield); γ(Ru–D) 1390, 1355 cm^{-1}.

***cis*-Dihydridocarbonyltris(diphenylmethylphosphine)ruthenium(II).**—A benzene solution containing 0.5 g of $H_2Ru((C_6H_5)_2P$-

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[1] To whom inquiries should be addressed.

[2] (a) A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, Marcel Dekker, Inc., New York, N. Y., 1965, p 111; (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965).

[3] J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Commun.*, 17 (1965).

[4] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

[5] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 305 (1967).

[6] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[8] J. Chatt and R. G. Hayter, *ibid.*, 896 (1961).

$CH_3)_4$ was treated with 200 psig of carbon monoxide at 90° for 1 hr. Upon cooling, the white precipitated complex was isolated by filtration (0.3 g, 74% yield). *Anal.* Calcd for $H_2Ru((C_6H_5)_2PCH_3)_3(CO)$: C, 65.7; H, 5.6; Ru, 13.8. Found: C, 65.6; H, 5.7; Ru, 14.1; mp 170–172°; γ(RuCO) 1920 cm^{-1}.

Hydridotris(triphenylphosphine)rhodium(I).—A suspension of 3 g of chlorotris(triphenylphosphine)rhodium(I) in 10 ml ether and 10 ml of *n*-hexane was treated with a solution of 0.7 g of aluminum triisopropyl at room temperature for 18 hr. The orange product was filtered and washed several times with hexane (1.74 g, 60% yield). *Anal.* Calcd for $HRh((C_6H_5)_3P)_3$: C, 72.8; H, 5.2; P, 10.4; Rh, 11.6. Found: C, 71.7; H, 5.1; P, 10.0; Rh, 11.1; γ(Rh–H) 2020 cm^{-1}.

Hydridotetrakis(triphenylphosphine)rhodium(I). (a) Preparation from Chlorotris(triphenylphosphine)rhodium(I).[9]—A mixture containing 1 g of chlorotris(triphenylphosphine)rhodium(I), 4.0 g of triphenylphosphine, 10 ml of benzene, 10 ml of ethanol, and 4.0 ml of anhydrous hydrazine was purged with hydrogen and heated at 80° for 30 min. The cooled reaction mixture was filtered to give a yellow product (1.1 g, 88% yield). *Anal.* Calcd for $HRh((C_6H_5)_3P)_4$: C, 75.0; H, 5.3; Rh, 8.9. Found: C, 74.5; H, 5.8; Rh, 9.3; mp 168° dec; γ(Rh–H) 2140 cm^{-1}.

(b) Preparation from Hydridotris(triphenylphosphine)rhodium(I).[9]—A suspension of 3 g of hydridotris(triphenylphosphine)rhodium(I), 9 g of triphenylphosphine, and 20 ml of toluene was heated at 80–90° for 1 hr. The complex went into solution and upon cooling a yellow compound precipitated (2.5 g, 64% yield). The ir and nmr spectra were identical with those of hydridotetrakis(triphenylphosphine)rhodium(I) prepared by method (a). *Anal.* Calcd for $HRh((C_6H_5)_3P)_4$: C, 75.0; H, 5.3; P, 10.8; Rh, 8.9. Found: C, 74.3; H, 5.5; P, 10.3; Rh, 9.1.

Hydridocarbonyltris(triphenylphosphine)rhodium(I).[10] **(a) Preparation from Hydridotetrakis(triphenylphosphine)rhodium(I).**—One gram of hydridotetrakis(triphenylphosphine)rhodium(I) was placed in a volumetric apparatus in benzene solution and 1.3 mole equiv of carbon monoxide was added within 5 min. The reaction mixture was diluted with ethanol and the precipitated complex filtered (0.4 g, 50% yield). The ir spectrum was identical with that of an authentic sample of $HRh(CO)((C_6H_5)_3P)_3$.

(b) Preparation from Hydridotris(triphenylphosphine)rhodium(I).—A suspension of 1 g of hydridotris(triphenylphosphine)rhodium(I) in 10 ml of ethanol was treated with carbon monoxide at room temperature and atmospheric pressure for 2 hr. The filtered complex (0.8 g, 81% yield) had identical ir and nmr spectra with those of an authentic sample of $HRh(CO)((C_6H_5)_3P)_3$.

Hydridotetrakis(diphenylmethylphosphine)rhodium(I).—A mixture of 3 g of chlorotris(diphenylmethylphosphine)rhodium(I), 6 g of diphenylmethylphosphine, 10 ml of benzene, 10 ml of ethanol, and 10 ml of anhydrous hydrazine was pressured with 450 psig of hydrogen and warmed at 80° for 1 hr. On cooling, a yellow complex precipitated, which was filtered and washed with ethanol and hexane (2.7 g, 73% yield). *Anal.* Calcd for $HRh((C_6H_5)_2PCH_3)_4$: C, 69.0; H, 5.9; Rh, 11.4; P, 13.7. Found: C, 68.3; H, 5.9; Rh, 10.9; P, 13.4; mp 174–178° dec; γ(Rh–H) 2005 cm^{-1}.

Chlorotris(diphenylmethylphosphine)rhodium(I).—A toluene solution of 0.5 g of μ-dichloro-tetraethylenedirhodium(I)[11] was treated with 3 g of diphenylmethylphosphine and warmed at 100° for 2 hr. On cooling, a yellow complex separated, which was filtered and washed with *n*-hexane (1.7 g, 90% yield). *Anal.* Calcd for $((C_6H_5)_2PCH_3)_3RhCl$: C, 63.5; H, 5.3; Rh, 14.0; P, 12.6; Cl, 4.8. Found: C, 63.0; H, 5.4; Rh, 13.5; P, 13.0; Cl, 5.0; mp 153° dec.

Chlorocarbonylbis(diphenylmethylphosphine)rhodium(I).—A toluene solution of 5.85 g of $[Rh(CO)_2Cl]_2$[12] was treated with 25 ml of $(C_6H_5)_2PCH_3$ and warmed at 60° for 30 min. Upon cooling and addition of *n*-hexane, a yellow complex precipitated which was filtered and washed with *n*-hexane (15.8 g, 71% yield). *Anal.* Calcd for $((C_6H_5)_2PCH_3)_2(CO)RhCl$: C, 57.2; H, 4.6; Rh, 18.2; P, 10.9; Cl, 6.2. Found: C, 57.8; H, 4.7; Rh, 17.6; P, 10.7; Cl, 6.1; mp 134–136°; γ(RhCO) 1980 cm^{-1}.

Results and Discussion

In order to stabilize the low-valent hydrido complexes of ruthenium and rhodium, we have prepared and studied complexes containing the ligands triphenylphosphine and diphenylmethylphosphine. Diphenylmethylphosphine has the advantage over triphenylphosphine in that complexes containing this ligand are in general readily soluble in aromatic solvents. In addition, the structure of these complexes can usually be readily ascertained from an analysis of the phosphine methyl group multiplets. The nmr data obtained for the compounds discussed in this paper are listed in Table I.

***cis*-Dihydridotetrakis(diphenylmethylphosphine)ruthenium(II).**—A method frequently used to prepare metal hydrides is to react a suitable complex with hydrazine. In this way $H_2Ru((C_6H_5)_2PCH_3)_4$ could be synthesized by treating $[Ru_2Cl_3((C_6H_5)_2PCH_3)_6]Cl$ with hydrazine and an excess of diphenylmethylphosphine under hydrogen pressure. The ir spectrum showed two bands of medium strength at 1940 and 1885 cm^{-1} for the Ru–H stretching frequencies. This is to be expected for *cis*-dihydro groups. The corresponding dideuterio complex showed two Ru–D stretching frequencies at 1390 and 1340 cm^{-1} (γ(Ru–H)/γ(Ru–D) = 1.4).

The nmr is consistent with an octahedral structure in which the hydrides occupy a *cis* position. The spectrum of the methyl groups consists of a triplet and a doublet with relative areas of 1:1 (see Figure 1). Upon irradiation of the P nuclei, each of these multiplets collapses to a singlet, the optimum decoupling frequency for the collapse of the doublet being 440 Hz (11 ppm) higher than that required for the collapse of the triplet. The spectrum observed for the hydride region is shown in Figure 2a. Upon irradiation of the P nuclei, this multiplet collapses to a doublet with weak, poorly resolved satellites when the frequency corresponds to that for optimum decoupling of the methyl triplet and to a clean triplet when the frequency corresponds to that for optimum decoupling of the methyl doublet.

The phosphorus and hydride spins in $H_2Ru((C_6H_5)_2PCH_3)_4$ form a system that can be best described as $AA'PP'X_2$, the coplanar H and P nuclei constituting the AA'PP' portion and the *trans*-P nuclei the X_2 portion. An analysis of the hydride resonance multiplet on this basis yields the calculated spectrum shown in Figure 2b in which all lines were calculated assuming each has a Lorentzian width of 5.0 Hz. It is evident that there is good agreement between the observed and calculated line positions. It is also evident that some of the lines in the observed spectrum are considerably broader than others and broader than the 5.0 Hz assumed for the spectral calculations. The reason for

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[9] W. Keim, *J. Organometal. Chem.* (Amsterdam), in press.

[10] S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).

[11] R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

[12] W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, **90**, 2425 (1957).

TABLE I

Nmr Parameters for Ruthenium Dihydrides[a]

Complex	∂CH₃, ppm downfield	∂P, ppm downfield	∂H, ppm upfield	J_{HRuH}, Hz	J_{PRuH}, Hz	J_{PCH_3}, Hz	J_{PRuP}, Hz
$(C_6H_5)_2PCH_3$	1.49	upfield 29	...	...	...	...	...
$H_2Ru((C_6H_5)_2PCH_3)_4$	L_3, L_4 = 1.39 L_5, L_6 = 1.29	L_3, L_4 = 21 L_5, L_6 = 32	H_1, H_2 = 9.54	−9.0	*cis*-L_4 = −25.0 L_5, L_6 = −29.0 *trans* = +74	$L_5 + L_6$ = 4.0 L_3, L_4 = 4.0	*trans* >> 0 *cis* ≈ 0
$H_2Ru(CO)((C_6H_5)_2PCH_3)_3$	L_4 = 1.42 L_5, L_6 = 1.82	L_4 = 25 L_5, L_6 = 37	H_1 = 8.02 H_2 = 6.80	−6.2	*cis*-L_4 = −19.5 L_5, L_6 = −27.1 *trans* = +75.4	$L_5 + L_6$ = 7.6 L_4 = 7.6	*trans* >> 0 *cis* ≈ 0

Nmr Parameters for Rhodium Hydrides and Chlorides[a]

Complex	∂CH₃, ppm downfield	∂P, ppm downfield	∂P, ppm upfield	J_{RhH}, Hz	J_{PH}, Hz	J_{PCH_3}, Hz
$HRh((C_6H_5)_2PCH_3)_4$	1.53	9	12.1	7.0	*cis* = 18.0	...
$ClRh((C_6H_5)_2PCH_3)_3$	2.06	*cis* = 14 *trans* = 34	...	...	...	3.0 (av)
$ClRh(CO)((C_6H_5)_2PCH_3)_2$	...	14	...	...	...	...
$HRh((C_6H_5)_3P)_4$	...	...	10.6	13.0	...	...
$HhR((C_6H_5)_3P)_3$	...	...	8.9	≈0	...	...
$CH_3Rh((C_6H_5)_3P)_3$	...	42	CH_3 = 0.35 (downfield)	J_{RhMe} = 3.6	J_{PCH_3} = 1.4	...

[a] Proton chemical shifts are referred to hexamethyldisiloxane as internal reference and phosphorus chemical shifts are referred to trimethyl phosphate as external reference. The *trans*-PRuH coupling constant is assumed positive; the signs of the remaining coupling constants in the ruthenium complexes are then most likely as indicated.

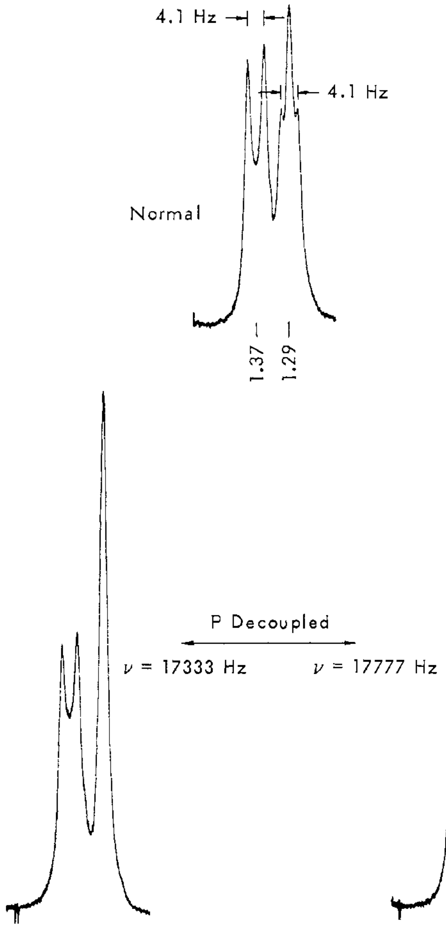

Figure 1.—Nmr spectrum of the methyl region of $((C_6H_5)_2PCH_3)_4$-RuH_2 in CH_2Cl_2 at 30°.

this is not certain but it may be a consequence of phosphine ligand exchange.

The assignment of P chemical shifts was made on the basis of an analysis of the methyl multiplets (Figure 1). The two pairs of phosphine ligands form an $A_3PP'A'_3$ spin system (A_3 = CH_3). It is known that P nuclei are strongly coupled when they are *trans* in complexes of this nature, but weakly coupled when they are *cis*.[7,13] If $J_{PP'} >> J_{PCH_3}$, then the spin states are mixed in such a way that the methyl resonance will be a triplet with a splitting given by the average of J_{PCH_3} and $J_{P'CH_3}$. On the other hand, if $J_{PP'} << J_{PCH_3}$, the methyl resonance will be a doublet with a splitting given by J_{PCH_3}. Both a doublet and a triplet are observed and the pairs of P nuclei can be identified accordingly.

The temperature dependence of the hydride multiplet is shown in Figure 3. The broadening of some of the lines with increasing temperature indicates the presence of a dynamic process—probably phosphine ligand exchange similar to that found in some triphenylphosphine–π-allylrhodium complexes.[14] If the hydride ligands were exchanging, it would be expected that all lines of the hydride multiplet, and not just some of them, would become broadened upon increasing the temperature. Independent evidence for phosphine ligand exchange is found in the observation that the methyl resonances are broadened with increasing temperature and merge at 80° showing that all methyl groups have become equivalent at this temperature.

***cis*-Dihydridocarbonyl(diphenylmethylphosphine)ruthenium(II).**—By treating $H_2Ru((C_6H_5)_2PCH_3)_4$ with CO at 80° the replacement of one diphenylmethylphosphine occurred and the white complex $H_2Ru((C_6H_5)_2P$-$CH_3)_3(CO)$ was formed. The ir spectrum showed only one strong band at 1920 cm^{-1} attributed to the Ru–CO stretching frequency. The Ru–H stretching frequencies were covered by the strong carbonyl band.

The nmr spectrum is consistent with an octahedral structure in which the carbonyl group occupies a position *trans* to one hydride group. In contrast to the complex $H_2Ru((C_6H_5)_2PCH_3)_4$, the normal spectrum of the methyl region shows a doublet and a triplet, but now the intensity of the triplet is twice that of the doublet, and the *trans*-phosphorus nuclei are less

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(13) J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. Ind.* (London), 859 (1958).

(14) C. A. Reilly and H. Thyret, *J. Am. Chem. Soc.*, in press.

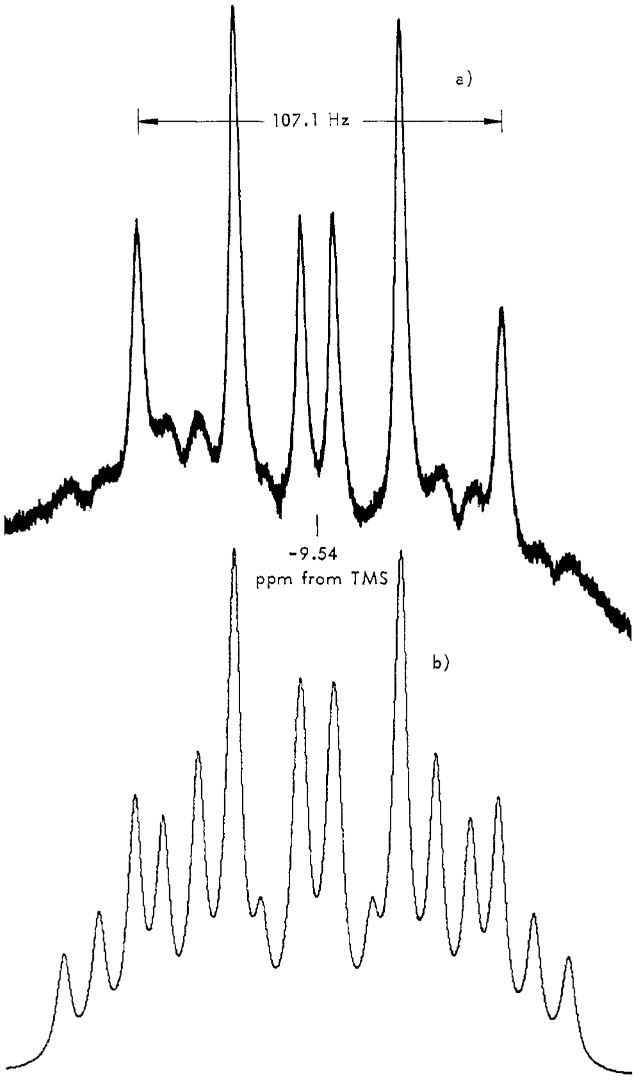

Figure 2.—Nmr spectrum of the hydride region of $((C_6H_5)_2PCH_3)_4RuH_2$: (a) observed in C_6H_5Cl at 50°; (b) calculated as a Gaussian distribution (width = 0.5 Hz) of Lorentzian lines (width = 5.0 Hz).

shielded than the *cis* one by about 500 Hz (12 ppm) (Figure 4). This conclusion is confirmed by a first-order analysis of the hydride resonance multiplet shown in Figure 5. The two protons are nonequivalent and are coupled together with $J = \pm 6.2$ Hz. When the *trans*-P nuclei are decoupled (ν 17,641 Hz), the spectrum from each proton consists of a doublet of doublets and when the *cis*-P nucleus is decoupled (ν 17,641 Hz), it consists of a triplet of doublets. The coupling constants given in Table I were obtained from the normal spectrum because the separations in the P decoupled spectra are too small owing to partial decoupling of one group of P nuclei when the other one is being irradiated.

Hydridotetrakis(triphenylphosphine)rhodium and Hydridotris(triphenylphosphine)rhodium.—The complex $HRh((C_6H_5)_3P)_4$ has been synthesized by treating $((C_6H_5)_3P)_3RhCl$[9] with hydrazine in an excess of $(C_6H_5)_3P$ under hydrogen pressure. The hydridotris(triphenylphosphine)rhodium[9] has been prepared by treating $((C_6H_5)_3P)_3RhCl$ with aluminum triisopropyl.

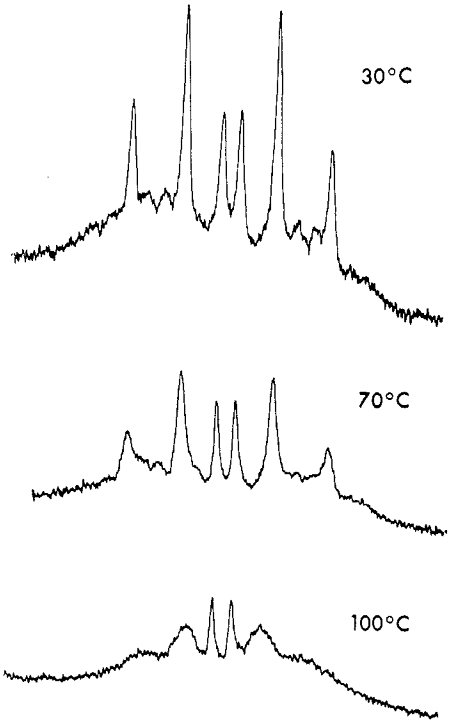

Figure 3.—Nmr spectrum of the hydride region of $((C_6H_5)_2PCH_3)_4RuH_2$ as a function of temperature in C_6H_5Cl.

Attempts were also made to establish the structures of these complexes by nmr analysis. At room temperature the hydride resonance of the compound $HRh((C_6H_5)_3P)_3$ is a broadened doublet, whereas the hydride resonance of $HRh((C_6H_5)_3P)_4$ gives only a broadened singlet. Figure 6 shows the observed spectra. There was no detectable change in the appearance of the lines on cooling to −60°. Apparently even at this low temperature the phosphine ligands are still exchanging rapidly enough to cause the line broadening. Further evidence for a rapid ligand exchange in these complexes has been obtained upon heating $HRh((C_6H_5)_3P)_4$ to 60–70°. The dissociation of $(C_6H_5)_3P$ takes place and the complex $HRh((C_6H_5)_3P)_3$ can be isolated. Conversely the addition of an excess of $(C_6H_5)_3P$ to a solution of $HRh((C_6H_5)_3P)_3$ gave the $HRh((C_6H_5)_3P)_4$ complex. These results can be explained by considering the equilibrium

$$HRh((C_6H_5)_3P)_4 \rightleftharpoons HRh((C_6H_5)_3P)_3 + (C_6H_5)_3P$$

The reaction of $HRh((C_6H_5)_3P)_3$ and $HRh((C_6H_5)_3P)_4$ with CO yielded Vaska's complex $HRh((C_6H_5)_3P)_3(CO)$[10] proving the composition of the above complexes.

Although there is no direct nmr evidence of the type given above for the ruthenium complexes to support particular structures for these complexes, the following indirect evidence may be cited.

The complex $HRh((C_6H_5)_3P)_3(CO)$ is known from X-ray studies to be a trigonal bipyramid.[15] We have determined its nmr spectrum and have confirmed the trigonal-bipyramidal structure in solution as well, although the solution must be cooled to about −30° to slow the exchange of the phosphine ligands. At −30°

(15) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

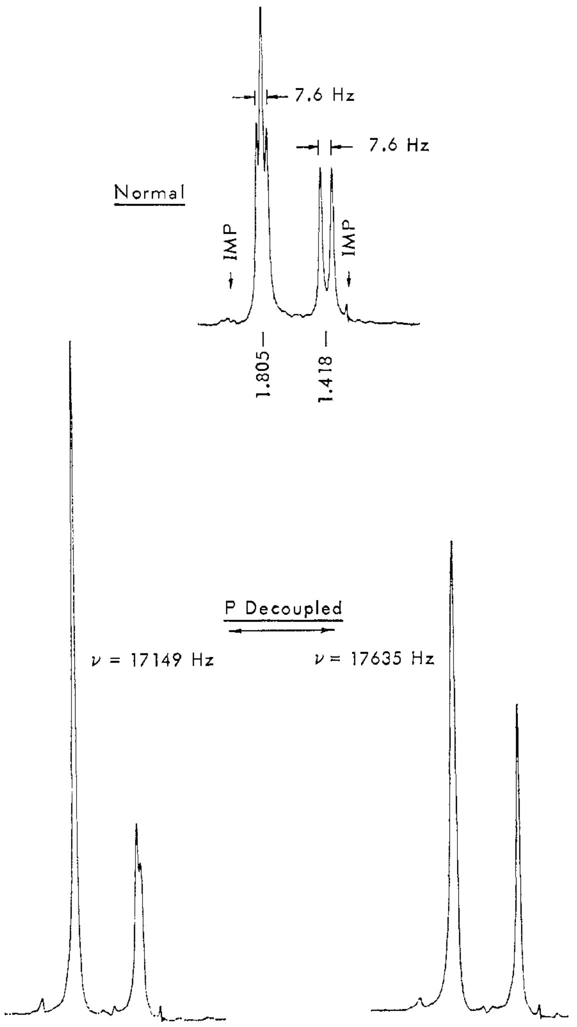

Figure 4.—Nmr spectrum of the methyl region of $((C_6H_5)_2PCH_3)_3(CO)RuH_2$ in C_6H_6 at 30°.

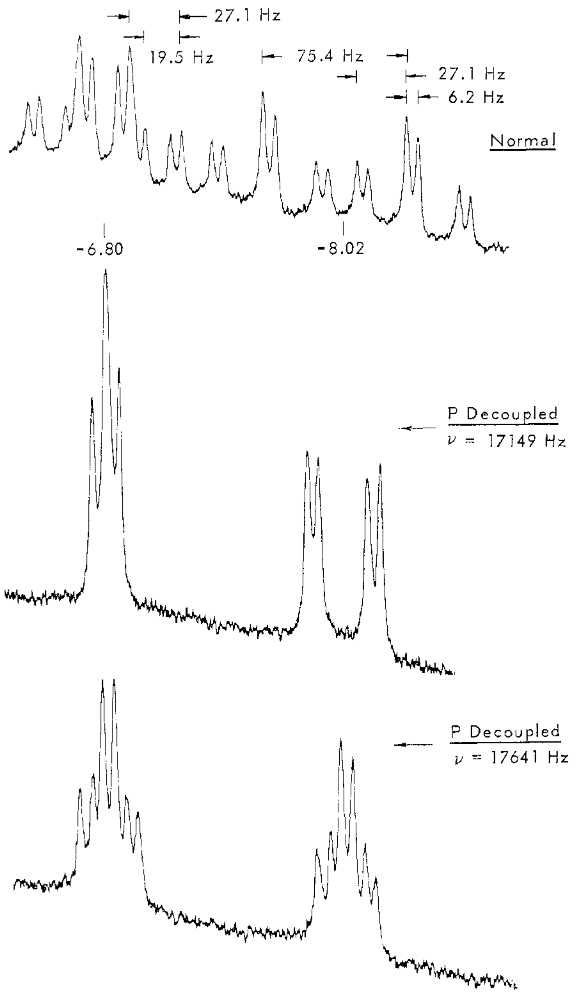

Figure 5.—Nmr spectrum of the hydride region of $((C_6H_5)_2PCH_3)_3(CO)RuH_2$ in C_6H_6 at 30°.

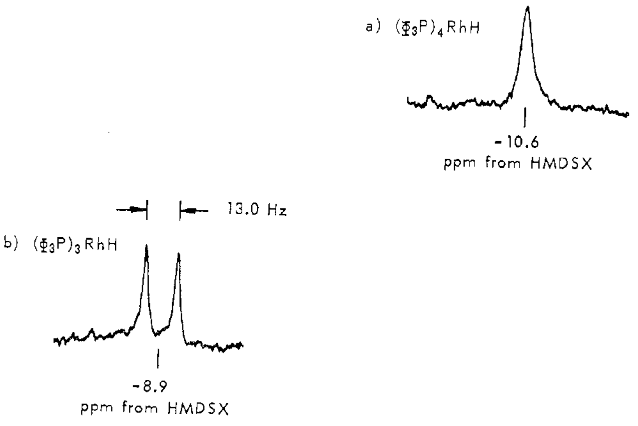

Figure 6.—Nmr spectrum of the hydride region in THF at 40°.

the hydride resonance is a 1:3:3:1 quartet arising from coupling of the hydride with three equivalent P nuclei. There is additional splitting of the quartet by Rh–H coupling ($J \sim 0.8$ Hz). The correspondingly small value (≤ 1 Hz) for J_{RhH} in $HRh((C_6H_5)_3P)_4$ suggests that it may also be a trigonal bipyramid.

Nmr evidence supporting a tetrahedral structure for $HRh((C_6H_5)_3P)_3$ can be derived by analogy with the known structure of $CH_3Rh((C_6H_5)_3P)_3$, in which the methyl resonance is split by interaction with the three equivalent P nuclei into a symmetrical quartet with relative intensities 1:3:3:1.[9] Each line is further split by rhodium into a doublet (see Figure 7). The nmr data are listed in Table I. These results strongly imply a tetrahedral (trigonal-pyramidal) structure for $CH_3Rh((C_6H_5)_3P)_3$. It is interesting to note that for most of the compounds possessing a terminal hydrogen bonded to a metal, there is an analogous alkyl compound with comparable physical properties. Apparently the metal–CH_3 bond is similar to the metal–H bond and a comparison of the structures of $CH_3Rh((C_6H_5)_3P)_3$ and $HRh((C_6H_5)_3P)_3$ can be made. Furthermore, on the basis of $J_{RhCH_3} = 1.4$ Hz in the methyl complex, one might expect J_{RhH} to be about 14 Hz in the corresponding hydride. The observed 13.0 Hz suggests a tetrahedral structure for $HRh((C_6H_5)_3P)_3$ also.

Hydridotetrakis(diphenylmethylphosphine)rhodium(I).—Since we have not been able to ascertain for certain the structures of the above rhodium hydrides by direct nmr evidence because of the rapid ligand exchange of $(C_6H_5)_3P$, it is reasonable to assume that a ligand having stronger π acidity might slow down the exchange. Therefore we prepared $HRh((C_6H_5)_2P$-

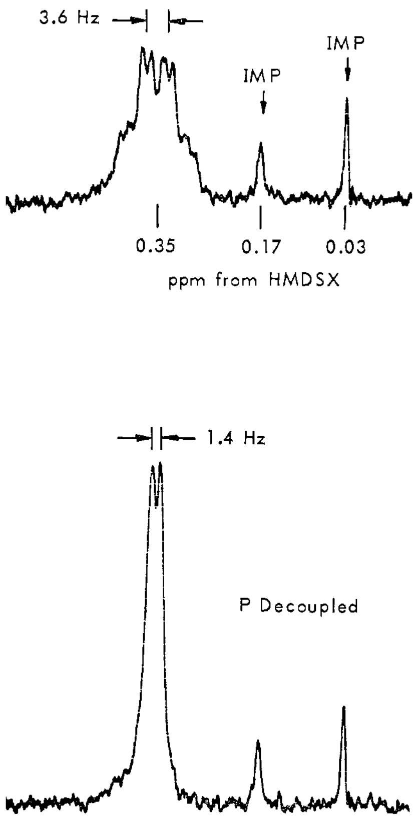

Figure 7.—Nmr spectrum of the methyl region of $((C_6H_5)_3P)_3Rh$-CH_3 in C_6D_6 at ~5°.

$CH_3)_4$ by treating $((C_6H_5)_2PCH_3)_3RhCl$ in an excess of $(C_6H_5)_2PCH_3$ with hydrazine. The nmr spectrum is consistent with a square-pyramidal structure evidenced as follows. The hydride region of the spectrum is shown in Figure 8 at 10 and −60°. At the latter temperature, exchange of the phosphine ligands is slowed sufficiently to show the coupling to the P nuclei. The normal spectrum clearly shows a typical *cis*-PH coupling of 18 Hz with no evidence for a much larger *trans*-PH coupling. The normal multiplet is evidently a quintet of doublets of which the center three are well resolved. The two outer components of the quintet show up only as shoulders, but there can be little doubt about their presence. Hence it is concluded that the structure must be square pyramidal with the four equivalent P nuclei forming the base and the hydride the apex. It will be noted that the Rh–H coupling constant for the square-pyramidal structure of $HRh((C_6H_5)_2PCH_3)_4$ is 7.0 Hz. This is just the average of those found for the $HRh((C_6H_5)_3P)_3$ and $HRh((C_6H_5)_3P)_4$ complexes (see Table II). These observations imply that the structures of the three complexes are not the same. If we assume the previous conclusions about the structures of $HRh((C_6H_5)_3P)_3$ and $HRh((C_6H_5)_3P)_4$ to be correct, we have the interesting results of Table II. All our attempts to synthesize the complex $HRh((C_6H_5)_2PCH_3)_3$ to complete the series have failed.

Chlorotris(diphenylmethylphosphine)rhodium(I) and Chlorocarbonylbis(diphenylmethylphosphine)rhodium(I).—Four-coordinated rhodium(I) complexes whose ligands consist of trivalent organophosphorus compounds are well known and can readily be obtained by the reaction of $[(C_2H_4)_2RhCl]_2$ with the phosphorus ligand. Little is known of the structures of these complexes. We prepared $((C_6H_5)_2PCH_3)_3RhCl$ by using $(C_6H_5)_2PCH_3$ as the phosphorus ligand.

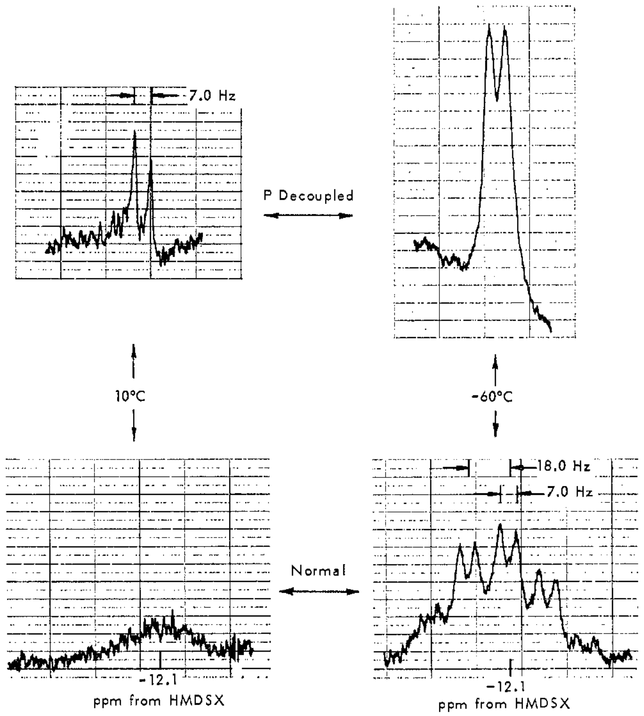

Figure 8.—Nmr spectrum of the hydride region of $((C_6H_5)_2$-$PCH_3)_4RhH$ in THF at 10 and −60°.

TABLE II

Complex	Structure	J_{RhH}, Hz
$HRh((C_6H_5)_3P)_3$	Tetrahedral (trigonal pyramidal)	13.7
$HRh((C_6H_5)_2PCH_3)_4$	Square pyramidal	7.0
$HRh((C_6H_5)_3P)_4$	Trigonal bipyramidal	0.0

The nmr spectrum is consistent with the square-planar configuration in that the methyl resonance is split into a doublet and a triplet very similar to those found for $H_2Ru((C_6H_5)_2PCH_3)_4$. The structure cannot be tetrahedral because this would require all P nuclei to be equivalent and *cis* to one another, giving rise to only a doublet in the methyl region.

The reaction of $[(CO)_2RhCl]_2$ with $(C_6H_5)_2PCH_3$ yielded $((C_6H_5)_2PCH_3)_2(CO)RhCl$ where the γ(RhCO) band is found at 1980 cm^{-1}. The nmr spectrum confirms the square-planar structure with the P nuclei at the ends of a diagonal. The methyl region consists of a triplet only and shows that the two P nuclei must be *trans* to one another.

Only a few experiments have been carried out to support the chemical composition of the hydrides described. The reaction of $H_2Ru((C_6H_5)_2PCH_3)_4$ with HCl gave the starting chloride and hydrogen. The formation of nearly quantitative amounts of hydrogen has also been observed by treating $HRh((C_6H_5)_3P)_3$ and $HRh((C_6H_5)_3P)_4$ with phenol thus forming the complexes $((C_6H_5)_3P)_nRhOC_6H_5$ ($n = 2$ or 3).[9]