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Activation of Ortho Carbon–Hydrogen Bonds in Triphenyl Phosphite Complexes

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Interactions between the central rhodium and ligand C–H bonds leading to exchange of hydrogen for deuterium have been observed in $[(C_6H_5O)_3P]_3RhCl$ and $[(C_6H_5O)_3P]_4Rh^+$. In $[(C_6H_5O)_3P]_4Rh^+$ this exchange is preceded by oxidative addition of hydrogen and an equilibrium loss of a proton. Reaction of $[(C_6H_5O)_3P]_3RhCl$ with phenylmagnesium chloride produces an air-sensitive ortho-bonded complex $[(C_6H_5O)_3P]_2(C_6H_5O)_2\overline{POC_6H_4Rh}$. Reactions of this complex with H_2, DCl, CO, and excess $(C_6H_5O)_3P$ are reported.

Introduction

Interactions between metal ions and carbon–hydrogen bonds of coordinated ligands are well-established phenomena, especially in complexes containing ligands such as arylphosphines and aryl phosphites.[1] Many of these interactions have been established by an exchange of deuterium for ligand protons which apparently occurs by sequential oxidative addition and reductive elimination reactions. Recently the exchange has been conclusively shown to occur in the ortho positions of the aryl groups attached to the phosphorus donor.[2] Although metal–(C–H bond) interactions occur in a variety of metal complexes, all the deuterium-exchange processes have been observed in complexes containing a hydride ligand or a metal–carbon bond which can cleave to form a metal hydride.

We now report the exchange of deuterium for ligand protons in $[(C_6H_5O)_3P]_3RhCl$, a complex which contains only phosphorus and halogeno ligands. An ortho-bonded species postulated as an intermediate in the exchange process has been synthesized by a novel route and its reactions with hydrogen and hydrogen chloride have been studied. In addition both oxidative addition of molecular hydrogen and exchange of ligand hydrogen have been observed in $[(C_6H_5O)_3P]_4Rh^+$ which is derived from $[(C_6H_5O)_3P]_3RhCl$ by metathesis.

Experimental Section

Tris(triphenyl phosphite)rhodium(I) Chloride.—This complex was prepared by the method described by Haines.[3]

Elimination of Triphenyl Phosphite from Tris(triphenyl phosphite)rhodium(I) Chloride.—When a small amount of tris(triphenyl phosphite)rhodium(I) chloride was heated in a sublimation apparatus, melting occurred at *ca.* 115°. At *ca.* 120–130° a colorless condensate formed on the cold finger and the yellow solid changed to orange. The infrared spectrum of the liquid from the cold finger was identical with that of authentic triphenyl phosphite. The orange residue was recrystallized from chloroform by addition of ethanol to give orange needles of di-μ-chloro-tetrakis(triphenyl phosphite)dirhodium(I), mp 161–164°. *Anal.* Calcd for $Rh_2C_{72}H_{60}O_{12}P_4Cl_2$: C, 56.97; H, 3.98; P, 8.16. Found: C, 56.33, 56.18; H, 3.81, 4.13; P, 8.12. This dimeric complex may also be prepared from 1,5-cyclooctadienerhodium(I) chloride dimer as described by Haines.[3]

Deuterium Exchange in Tris(triphenyl phosphite)rhodium(I) Chloride.—A solution of 0.5 g of tris(triphenyl phosphite)rhodium(I) chloride in 35 ml of methylene chloride was cooled to −78° in a pressure bottle with a stirring bar, evacuated, and then pressurized to 40 psig with deuterium gas. The solution was allowed to warm to room temperature and was stirred for 4 days. After this time the pressure was released; the solution was filtered and evaporated to *ca.* 10 ml. Petroleum ether (bp 30–60°) was added to crystallize the product. The infrared spectrum of this product contained new bands at 1480, 1110, 1070, 840, and 820 cm^{-1} which are not present in the starting material. The aromatic absorptions in the region 700–800 cm^{-1} are also changed.

In another run 2 g of complex in 25 ml of methylene chloride was stirred for 11 days under 60 psig deuterium pressure. The solution was filtered and evaporated to dryness. The oil which resulted was recrystallized from chloroform by addition of ethanol. The crystals of recovered $[(C_6H_5O)_3P]_3RhCl$ were dried at 0.1 mm and 78° for 16 hr. *Anal.* Calcd for $RhC_{54}H_{45}O_9P_3Cl$: C, 60.64; H, 4.21; P, 8.62; Cl, 3.31. Found: C, 60.68; H, 4.34; P, 8.53; Cl, 3.75.

In a third run 2 g of complex in 25 ml of methylene chloride was stirred under 40 psig D_2 pressure for 4 days. A small amount of the complex isolated as above was placed in a molecular still and evacuated on the vacuum line. The still was heated to 130–140° for 2–3 hr until 2 drops of condensate collected in the receiver flask. Mass spectral analysis showed triphenyl phosphite with the following composition, in mole per cent of deuterium: d_0, 4; d_1, 6.5; d_2, 11; d_3, 17; d_4, 22; d_5, 23; d_6, 17. The infrared spectrum of the free, partially deuterated phosphite contains absorptions at 1430, 1290, 1265, 1110, 1040, and 975 cm^{-1} which are not present in an undeuterated sample.

As a control experiment, a solution of 4 ml of triphenyl phosphite in 45 ml of methylene chloride was cooled, evacuated, and pressurized with 40 psig deuterium gas. The solution was stirred for 6 days; the pressure was then released and the methylene chloride was removed by evacuating the bottle through a trap. The infrared and mass spectra of the triphenyl phosphite recovered by molecular distillation were identical with those of undeuterated triphenyl phosphite.

Deuterium Exchange in Di-μ-chloro-tetrakis(triphenyl phosphite)dirhodium(I).—A solution of 50 mg (0.033 mmol) of $\{[(C_6H_5O)_3P]_2RhCl\}_2$ in 2 ml of methylene chloride was degassed and sealed in a 15-ml bulb with 0.236 mmol of D_2. After stirring for 3 days the gas phase was analyzed by mass spectroscopy. *Anal.* Calcd for 0.792 mmol of exchangeable hydrogen (mole per cent): H_2, 39.3; HD, 46.8; D_2, 13.9. Found: H_2, 25.2; HD, 46.6; D_2, 28.2.

Inhibition of Deuterium Exchange in Tris(triphenyl phosphite)rhodium(I) Chloride by Triphenyl Phosphite.—A solution of 4 ml (15 mmol) of triphenyl phosphite and 2 g (1.9 mmol) of tris(triphenyl phosphite)rhodium(I) chloride in 45 ml of methylene chloride was cooled, evacuated, and pressurized to 40 psig with D_2. The solution was stirred for 6 days at room temperature. It was evaporated to *ca.* half-volume and petroleum ether (bp 30–60°) was added to precipitate the complex. The filtrate was evaporated to an oil and distilled to give clear triphenyl phosphite for mass spectral analysis. Found (mole per cent): d_0, 92.5; d_1, 7; d_2, 0.5.

The precipitated solid was washed with petroleum ether and dried. A sample was heated in a molecular still and a sample of triphenyl phosphite was collected for mass spectral analysis. Found (mole per cent): d_0, 93; d_1, 6.5; d_2, 0.5.

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[1] G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

[2] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

[3] L. M. Haines, *Inorg. Nucl. Chem. Lett.*, **5**, 399 (1969); *Inorg. Chem.*, **9**, 1517 (1970).

Tetrakis(triphenyl phosphite)rhodium(I) Perchlorate.—To a solution of 2.13 g (2 mmol) of tris(triphenyl phosphite)rhodium(I) chloride and 0.8 g (2.5 mmol) of triphenyl phosphite in 25 ml of acetone was added 0.5 g (2.3 mmol) of silver perchlorate. The mixture was stirred for *ca.* 15 min and filtered. Evaporative cooling of the filtrate gave fine yellow needles of $[(C_6H_5O)_3P]_4RhClO_4$. These were collected, washed quickly with cool acetone and then ether, and were dried at 0.1 μ overnight; yield 1.5 g. (All operations were performed under nitrogen.) *Anal.* Calcd for $RhC_{72}H_{60}O_{16}P_4Cl$: C, 59.97; H, 4.19; P, 8.59; Cl, 2.45. Found: C, 60.24; H, 4.42; P, 8.50; Cl, 2.83.

The tetrafluoroborate salt was prepared similarly. The perchlorate salt can also be prepared by the reaction of 1,5-cyclooctadienerhodium(I) chloride dimer with a methanol solution of triphenyl phosphite followed by addition of sodium perchlorate.[3]

Reaction of Tetrakis(triphenyl phosphite)rhodium(I) Perchlorate with Hydrogen.—As reported by Haines[4] for the tetraphenylborate salt, tetrakis(triphenyl phosphite)rhodium(I) perchlorate dissolved in methylene chloride to give yellow solutions which decolorized rapidly on exposure to hydrogen or deuterium (40 psig). When pressure was released, the solutions again became yellow.

The Raman spectrum of the colorless product was obtained as follows. A slurry of tetrakis(triphenyl phosphite)rhodium(I) perchlorate in acetone was prepared so that all the solid dissolved when hydrogen was passed through the solution. Partial decoloration occurred in the process. A capillary for the Raman measurement was quickly filled with a syringe and the capillary was pressurized behind a shield to 30 psig. The spectrum of a fresh solution showed bands at 2000 and 735 cm^{-1} which are not present in solutions of $[(C_6H_5O)_3P]_4RhClO_4$. All other absorptions matched almost exactly. The absorption at 2000 cm^{-1} is assigned to the Rh–H stretching vibration. The band width is fairly large but resolution into two bands is not obvious. According to Adams[5] cis dihydrides in which both hydrides are opposite identical donors exhibit only one M–H stretch which may be broad.

The dihydride complex was isolated by vigorously bubbling H_2 though a suspension of the perchlorate salt in 15 ml of tetrahydrofuran. The yellow solid slowly dissolved and after a short time a white solid, presumably $\{[(C_6H_5O)_3P]_4RhH_2\}ClO_4$, formed. The white crystals were collected quickly. The infrared spectrum was almost identical with that of the parent compound except for a sharp band at 1995 cm^{-1}. After standing in air for *ca.* 30 min the white solid slowly turned yellow.

Reaction of Tetrakis(triphenyl phosphite)rhodium(I) Perchlorate with Hydrogen in the Presence of Triethylamine.—A suspension of 0.3 g of the perchlorate salt in 15 ml of THF was treated with hydrogen until white crystals of the dihydride began to appear. At this point *ca.* 0.5 ml of triethylamine was added and hydrogen was passed through the solution for 20–25 min, during which time all the solid dissolved to form a dark yellow solution. The volatile components were evaporated and benzene, 0.8 ml, was distilled onto the residual oil, presumably $[(C_6H_5O)_3P]_4RhH$. The yellow solution which formed was transferred to an nmr tube under nitrogen, and the spectrum was obtained at 220 MHz. The high-field region contained a doublet of quintets at τ 17.3 ($J_{PH} = 44$, $J_{RhH} = 6$), as reported for the neutral monohydride.[6]

Deuterium Exchange in Tetrakis(triphenyl phosphite)rhodium(I) Salts.—A solution of 50 mg (0.035 mmol) of tetrakis(triphenyl phosphite)rhodium(I) perchlorate in 2 ml of methylene chloride in a 15-ml bulb was degassed twice and pressurized at 0° to 620 mm deuterium pressure. The tube was sealed and rotated at room temperature for 12 days. The gas phase was subjected to mass spectral analysis. *Anal.* Calcd for 24 protons and 0.358 mmol of deuterium: H_2, 29.1; HD, 49.7; D_2, 21.2. Found: H_2, 38.8; HD, 44.9; D_2, 16.3.

A solution of tetrafluoroborate salt was treated with D_2 under the same conditions for 8 days. Evaporation gave a yellow crystalline solid with an ^1H nmr spectrum (220 MHz, CD_2Cl_2 solution) very similar to that of the original $[(C_6H_5O)_3P]_4RhBF_4$. However, some fine structure was lost from the τ 2.89 signal assignable to the meta and para protons. The signal at τ 3.16 assignable to ortho protons diminished in intensity corresponding to 11% replacement of H by D. Pyrolysis of the recovered complex at 180° under vacuum gave triphenyl phosphite which, by mass spectral analysis, contained 5–10% of the monodeuterated species.

Reaction of Tris(triphenyl phosphite)rhodium(I) Chloride with Phenylmagnesium Chloride.—Under nitrogen, 8.4 g (8 mmol) of tris(triphenyl phosphite)rhodium(I) chloride was dissolved in 150 ml of benzene which had been dried over 4A Molecular Sieves. This yellow solution was treated at room temperature with 4 ml of a 3 *M* solution of phenylmagnesium chloride in ether. After about 5 min the solution slowly changed to a darker yellow and a white solid precipitated. After being stirred for 3.5 hr, the mixture was filtered and the filtrate was evaporated under reduced pressure to leave an orange oil. This oil was dissolved in a minimum amount of warm 1:1 hexane–benzene. After filtration, the solution was allowed to stand at room temperature for several hours during which time yellow-orange crystals formed. These were recrystallized from warm benzene–hexane to give, after 3 days, large rhombic crystals. These were collected, washed with petroleum ether, and dried at 10^{-6} mm. *Anal.* Calcd for $RhC_{54}H_{44}O_9P_3 \cdot 0.5C_6H_6$: C, 63.87; Cl, 0.0; H, 4.42; P, 8.67. Found: C, 63.40, 63.57; Cl, 0.0; H, 4.55, 4.36; P, 8.84.

The infrared spectrum of this material is identical with that for tris(triphenyl phosphite)rhodium(I) chloride except for two additional bands at 1105 and 795 cm^{-1}. There are minor differences in the region 750–780 cm^{-1}. These two bands near 1100 and 800 cm^{-1} have previously been identified with ortho-bonded triphenyl phosphite.[2]

Reaction of $[(C_6H_5O)_3P]_2(C_6H_5O)_2\overline{POC_6H_4Rh}$ with Deuterium Chloride.—Under nitrogen, 1 g (1 mmol) of $[(C_6H_5O)_3P]_2(C_6H_5O)_2POC_6H_4Rh \cdot 0.5C_6H_6$ was dissolved in 25 ml of benzene which had been dried over 4A Molecular Sieves. Deuterium chloride, prepared by dropping 2 ml of a 38% deuterium chloride in deuterium oxide onto phosphorus pentoxide, was passed through a Dry Ice trap into the benzene solution. An immediate lightening in color was observed. After gas ceased to flow from the generator, the solution was evaporated overnight under a nitrogen stream to leave a semisolid. This material was dissolved in a minimum amount of chloroform and crystallized by addition of ethanol. The solid was dried *in vacuo* to give 0.75 g of yellow crystals.

A small amount of this yellow material (0.3 g) was heated under vacuum in a molecular still at 120–140° to liberate free phosphite. A sample of this material was submitted for mass spectral analysis. *Anal.* Found: d_0, 76; d_1, 22; d_2, 2. The estimated precision is ±2% for these values. Assuming a completely random removal of phosphite from tris(triphenyl phosphite)rhodium(I) chloride 33% of the recovered phosphite should be monodeuterated.

Reaction of $[(C_6H_5O)_3P]_2(C_6H_5O)_2\overline{POC_6H_4Rh}$ with Hydrogen and Deuterium.—Under nitrogen a pressure bottle was charged with 1 g of complex and 10 ml of benzene. After cooling and evacuating, the bottle was pressurized with 45 psig hydrogen and the solution was stirred for 3 days. After this time the solvent was evaporated to leave an oil. The bottle was opened under N_2 and the infrared spectrum of the oil was obtained. Changes in the infrared spectrum from that of the starting material were minor except for a band at 1940 cm^{-1}, assigned to Rh–H stretching vibration. All attempts to prepare crystalline material failed. The presence of 1100- and 800-cm^{-1} bands indicated carbon–metal bond cleavage was not complete.

A solution of 50 mg (0.047 mmol) of complex in 1 ml of benzene was degassed and sealed in a 15-ml bulb with 0.46 mmol of deuterium. After the bulb was agitated for 12 days, the gas phase was analyzed. *Anal.* Calcd for exchange of 17 protons: H_2, 21.6; HD, 49.75; D_2, 28.7. Found: H_2, 13.7; HD, 44.6; D_2, 41.7. A deuteriobenzene solution of the ortho-bonded complex (80 mg in 1.5–2 ml) was heated at 50° under an atmosphere of hydrogen for 2.5 hr. The darkened solution was transferred under nitrogen to an nmr tube. The proton spectrum showed broad signals in the hydride region.

Reaction of $[(C_6H_5O)_3P]_2(C_6H_5O)_2\overline{POC_6H_4Rh}$ with Carbon Monoxide.—A yellow benzene solution of $[(C_6H_5O)_3P]_2(C_6H_5O)_2\overline{POC_6H_4Rh}$ became colorless when exposed to carbon monoxide at 1 atm. The process was reversed by passing nitrogen through ths solution. The infrared spectrum of the colorless solution contained a sharp band at 2000 cm^{-1} with a shoulder on the low-

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[4] L. M. Haines, *Inorg. Chem.*, **10**, 1693 (1971).

[5] D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold Publishers, London, 1967.

[6] J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1405 (1968).

energy side. No absorption was observed in the region 1500–1700 cm^{-1} for an acyl C=O.

Preparation of Pentafluorophenyltris(triphenyl phosphite)rhodium(I).—This preparation was carried out similarly to the synthesis of the phenyl analog using 2.1 g (2 mmol) of tris(triphenyl phosphite)rhodium(I) chloride in 50 ml of benzene and 4 ml of a 1 *M* solution of pentafluorophenylmagnesium bromide in ether. The initial product was a benzene solvate. *Anal.* Calcd for $RhC_{66}H_{51}F_5O_9P_3$: C, 61.98; H, 4.01; P, 7.26. Found: C, 61.24; H, 4.20; P, 7.50.

Heating this compound *in vacuo* at 78° for 16 hr gave opaque yellow crystals with loss of benzene. *Anal.* Calcd for $RhC_{60}H_{45}F_5O_9P_3$: C, 60.01; H, 3.77. Found: C, 60.35, 60.40; H, 4.10, 3.83.

The infrared spectrum (Nujol) of this compound was similar to that of tris(triphenyl phosphite)rhodium(I) chloride with two additional bands at 1045 and 1055 cm^{-1} assigned to the pentafluorophenyl group. Other absorptions characteristic of this group were obscured. The ^{19}F nmr spectrum in toluene *vs.* trichlorofluoromethane as standard consisted of three resonances at +108.3, +162.6 (triplet, $J = 21$), and +165.4 ppm, assigned to the ortho, para, and meta fluorines, respectively.

Results and Discussion

Chemistry of $[(C_6H_5O)_3P]_4Rh^+$.—Tetrakis(triphenyl phosphite)rhodium(I) cation (**1**) is easily prepared by metathesis of $[(C_6H_5O)_3P]_3RhCl$ with silver perchlorate or tetrafluoroborate in acetone containing excess triphenyl phosphite. It readily undergoes oxidative-addition reactions as reported by Haines.[4] For example, solutions of **1** rapidly but reversibly react with hydrogen to give $\{H_2Rh[P(OC_6H_5)_3]_4\}^+$. We were able to isolate this complex as a white, metastable perchlorate salt by passing H_2 vigorously through a tetrahydrofuran solution of **1**. The metal–hydrogen stretching frequencies (2000 cm^{-1} Raman, 1995 cm^{-1} infrared) are consistent with cis stereochemistry.[4,5] The lability of this dihydride is in contrast to the apparent stability of the cationic dihydrides containing more basic phosphorus ligands such as $P(CH_3)_2C_6H_5$ and $P(CH_3)_3$.[7]

Ortho Hydrogen Exchange.—Reaction of deuterium with **1** proceeds similarly to the hydrogen reaction but is accompanied by H–D exchange. Analysis of the residual gas from such a reaction shows statistical introduction of H into the gas phase. The ^1H nmr spectrum of the recovered $\{[(C_6H_5O)_3P]_4Rh\}BF_4$ after dissociation of D_2 shows partial substitution of D for H in the ortho positions of the phenoxy groups.

The exchange between D_2 and the ortho hydrogens of **1** can be rationalized by a modification of the mechanism previously proposed[2] to account for exchange in hydrido complexes. In the H_2 or D_2 adduct of **1** the rhodium is formally trivalent and, hence, unlikely to undergo further oxidative addition of an ortho C–H bond. However, preequilibrium loss of a proton (eq 1) could give hydridotetrakis(triphenyl phosphite)rhodium (**3**) which has already been shown to undergo ortho hydrogen exchange.[2] Similar acid–base equilibria are

$$\underset{\mathbf{2}}{[(C_6H_5O)_3P]_4RhH_2^+} \rightleftharpoons \underset{\mathbf{3}}{[(C_6H_5O)_3P]_4RhH} + H^+ \qquad (1)$$

known for a number of metal hydrides.[8] Evidence for the acidity of one of the hydrogens and support for this mechanism were obtained by reaction of the dihydride with triethylamine. The product had a high-field ^1H nmr spectrum consisting of a quintet of doublet at τ 17.3 ($J_{PH} = 44$, $J_{RhH} = 6$) as reported[6] for **3**.

When tris(triphenyl phosphite)rhodium(I) chloride (**4**) in methylene chloride is reisolated after exposure to deuterium for a few days, the infrared spectrum contains new bands at 1480, 1110, 1070, 840, and 820 cm^{-1}. Recovery of analytically pure **4** from such experiments is typically 70–85%. On heating **4**, triphenyl phosphite is liberated with formation of the chloride-bridged dimer **5**

$$\underset{\mathbf{4}}{2[(C_6H_5O)_3P]_3RhCl} \xrightarrow{\Delta} 2(C_6H_5O)_3P + \underset{\mathbf{5}}{\{[(C_6H_5O)_3P]_2RhCl\}_2} \qquad (2)$$

Free phosphite from a typical run with deuterium was so isolated and analyzed by mass spectroscopy. The results indicated a substantial incorporation of deuterium; triphenyl-d_6 phosphite was the most heavily deuterated species observed. Deuterium incorporation is assumed to be in the ortho position as in previous work.[2] This exchange is substantially inhibited by the presence of excess phosphite.

The ortho hydrogen exchange observed with **4**, like that of **1**, can be readily explained if either a hydrido complex or an ortho-bonded compound of rhodium(I) can be generated in the system. As shown in Figure 1, the essential sequence for exchange between H_2 (or D_2) and ortho hydrogen is **6** $\rightleftharpoons$ **7** $\rightleftharpoons$ **8**, whether one starts with **1**, **4**, or the previously described $[(C_6H_5O)_3P]_4RhH$. From **4**, two intermediates in this sequence are accessible by dehydrochlorination of rhodium(III) species. The paths from **4** to **6** and from **4** to **8** superficially appear to be equally favorable and both reactions may occur simultaneously in solution. The two paths parallel chemistry known for the $[(C_6H_5)_3P]_3IrCl$[9] and $[(C_6H_5)_3P]_2(CO)IrCl$[10] systems. Ortho bonding similar to that proposed in **6** and **7** has been demonstrated crystallographically[11] for a triphenyl phosphite com-

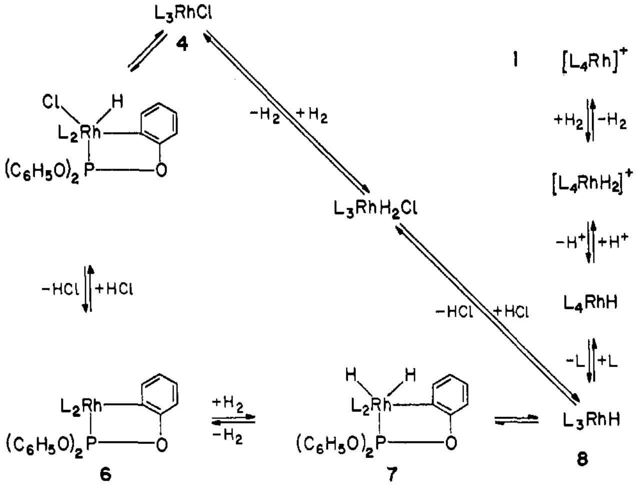

Figure 1.—Mechanism of ortho hydrogen exchange in triphenyl phosphite complexes of rhodium; L = $(C_6H_5O)_3P$.

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[7] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 2397 (1971).

[8] D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

[9] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

[10] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, **47**, 1431 (1969).

[11] J. M. Guss and R. Mason, *J. Chem. Soc. D*, 58 (1971).

plex of iridium.[12] Indeed, attempts to prepare the iridium analog of **4** lead directly to an ortho-bonded species.[13]

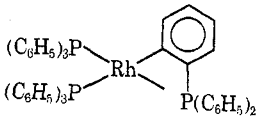
The dehydrochlorination reactions are reversible as shown by recovery of **4** from the exchange reaction. Thus, the base that effects removal of HCl must be quite mild, either triphenyl phosphite or **1** itself. A slow, apparently irreversible, abstraction of HCl from **4** was observed when the complex was treated with triethylamine in benzene. Use of a stronger base, a Grignard reagent, gave an isolable ortho-bonded complex as described below.

Isolation of the Ortho-Bonded Complex 6.—Several attempts to prepare phenyltris(triphenyl phosphite)-rhodium(I) by the reaction of **4** with phenylmagnesium chloride yielded a yellow solid whose analytical data were consistent only with the formulation $[(PhO_3)P]_3Rh \cdot 0.5C_6H_5$. The infrared spectrum of this compound contained bands at *ca.* 1100 and 800 cm^{-1} which have previously been attributed to ortho-bonded triphenyl phosphite.[2] The same compound was obtained using a *p*-tolyl Grignard reagent. Reaction of this compound with DCl gave **4** whose infrared spectrum did not contain the 1100- and 800-cm^{-1} bands. Analysis of triphenyl phosphite recovered by heating this sample of **4** *in vacuo* indicated the incorporation of approximately one deuterium per complex molecule in agreement with the formulation of this compound as **6**. Thus it appears that the initial reaction with the Grignard reagent must give first the aryl complex which subsequently eliminates benzene at room temperature to form the ortho-bonded complex. An authentic arylrhodium compound was obtained by reaction of **1** with pentafluorophenylmagnesium bromide. No loss of pentafluorobenzene was observed under ordinary conditions in the absence of hydrogen.

Reaction of **6** with hydrogen in benzene yielded, after evaporation of the solvent, an orange oil. The infrared spectrum of this oil contained an absorption at 1940 cm^{-1} which is assigned to a Rh–H stretch. No crystalline material could be obtained, and the hydride, presumably **7**, was not long-lived because of loss of hydrogen with reversion to **6**. Ortho hydrogen exchange with deuterium was observed at 1 atm as expected for such a labile system.

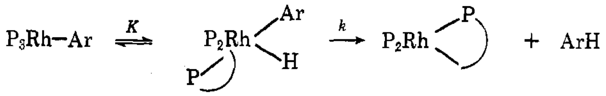
Yellow benzene solutions of **6** became colorless under a carbon monoxide atmosphere. Infrared spectra of these solutions contained a band at 2000 cm^{-1}. This band disappeared and the yellow color returned when nitrogen was passed through the solution. No absorptions in the region 1500–1700 cm^{-1} were observed; hence, no insertion product was formed under these conditions. No reaction was observed in liquid SO_2 at 25°.

Both the phenyl and methyl derivatives have been prepared from tris(triphenylphosphine)rhodium(I) chloride.[14] In contrast to the phosphite complexes these complexes are thermally quite stable and methane is lost only upon heating the methyl derivative to 80° in toluene with formation of the ortho-bonded compound



9

Insertion of carbon monoxide into the Rh–C bond of **9** has been observed.[15] Neglecting a large electronic difference between phosphine and phosphite donors, the absence of insertion in the present case may be attributed to the small energy change involved in going from a five- to six-membered ring. In the case of **9**, ring expansion by insertion of carbon monoxide relieves the strain associated with the four-membered ring. Similar arguments may be used to explain the large difference in thermal stability of the aryl and alkyl complexes mentioned previously. In the case of the phosphite complex oxidative addition of an ortho carbon–hydrogen bond to the central rhodium gives a five-membered chelate whereas in the case of the phosphine only a four-membered ring is formed. In the schematic representation shown below the rate constant *k* should be nearly the same for both complexes and the stability of the complexes is governed by the difference in *K* for the oxidative addition.



Addition of excess triphenyl phosphite to benzene solutions of **6** immediately lightens the yellow color. Evaporation produces colorless crystals. No analytical results have been obtained but it seems likely that this complex should be formulated as $[(C_6H_5O)_3P]_3$-$(C_6H_5O)_2\overline{POC_6H_4Rh}$. An authentic sample of this complex[12] prepared from hydridotetrakis(triphenyl phosphite)rhodium(I) produces pale yellow solutions in benzene, probably by dissociation into complex **6** and $(C_6H_5O)_3P$.

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[12] E. W. Ainscough and S. D. Robinson, *J. Chem. Soc. D*, 863 (1970).

[13] M. A. Bennett and R. Charles, *Aust. J. Chem.*, **24**, 427 (1971).

[14] W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

[15] W. Keim, *ibid.*, **19**, 161 (1969).