Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NEW σ-BONDED RHODIUM(I) COMPLEXES CONTAINING A METAL–CARBON BOND. I

W. KEIM
Shell Development Company, Emeryville, California 94608 (U.S.A.)

(Received April 12th, 1968)

SUMMARY

The synthesis of the new rhodium(I) complexes $(Ph_3P)_3RhR$ (R = Me, Ph) is reported. The compounds react with phenol giving the new phenoxy derivatives $(Ph_3P)_nRhOPh$ ($n = 2, 3$). Based on NMR evidence, a tetrahedral or trigonal pyramidal structure is proposed for $(Ph_3P)_3RhMe$. Upon heating, the latter one loses methane and it could be shown that the abstracted hydrogen comes from an *ortho*-position of one phenyl ring of the ligand Ph_3P, thus forming complex $(Ph_3P)_2(Ph_2PC_6H_4)Rh$, which is characterized by chemical and physical means.

INTRODUCTION

There has been considerable interest in recent years in the properties of low-valent σ-bonded complexes of transition metals because of their significance in oligomerization reactions of olefins. Complexes containing a metal–carbon bond have been described in scattered publications over the past decade. To our knowledge no organometallic rhodium(I) compounds possessing a rhodium–carbon bond have been reported in the literature.

In a preliminary note[1] the σ-bonded rhodium(I) complexes of the general formula $(Ph_3P)_3RhR$ (R = Me, Ph) were described. Subsequently a more detailed study of the properties and behavior of these complexes was made, and this paper gives a full account of the preparation and characterization of these compounds.

RESULTS AND DISCUSSION

The compounds $(Ph_3P)_3RhR$ (R = Me, Ph) were synthesized in high yields by reacting $(Ph_3P)_3RhCl$* with methyl- and phenylmagnesium bromide, respectively. Great difficulties were experienced in obtaining good elemental analyses of these complexes. They are very air and moisture sensitive, and they tend to include solvent molecules upon crystallization.

The IR spectra of $(Ph_3P)_3RhMe$ and $(Ph_3P)_3RhPh$ show mainly bands due to the ligand Ph_3P. The NMR spectrum of the phenyl complex is characterized by overlapping signals from the aromatic protons. The NMR spectrum of $(Ph_3P)_3RhMe$ is in agreement with the proposed structure in which the methyl group is bound

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* This compound has been obtained independently by several workers[2].

directly to the rhodium. The methyl resonance centered at $\delta(CH_3)=0.35$ (hexamethyldisiloxane as internal reference) [$\delta(P) = -41$] is split by interaction with the three equivalent ^{31}P nuclei into a symmetrical quarted with relative intensities 1/3/3/1 [$J(P-H)=3.6$ Hz]. Each line is further split by ^{103}Rh into a doublet [J-(Rh–H) = 1.4 Hz]. These results imply a tetrahedral or trigonal pyramidal structure for $(Ph_3P)_3RhMe$.

In order to ascertain the composition of $(Ph_3P)_3RhR$ (R = Me, Ph) by chemical means, the following reactions were carried out. The treatment of $(Ph_3P)_3RhR$ (R = Me, Ph) with hydrogen yielded in 54% yield (calculated for $(Ph_3P)_3RhMe$) methane and 93% benzene (calculated for $(Ph_3P)_3RhPh$) with isolation of the known hydrido complex $(Ph_3P)_3RhH$[3]:

$$(Ph_3P)_3RhR + H_2 \rightarrow (Ph_3P)_3RhH + RH \quad (R = Me, Ph)$$

The complexes $(Ph_3P)_3RhR$ (R = Me, Ph) readily undergo reaction with phenol to give the new compound $(Ph_3P)_3RhOPh$ and the corresponding hydrocarbons methane and benzene in 65% and 95% yield, respectively [based on the complexes $(Ph_3P)_3RhMe$ and $(Ph_3P)_3RhPh$]

$$(Ph_3P)_3RhR + PhOH \rightarrow (Ph_3P)_3RhOPh + RH \quad (R = Me, Ph)$$

Phenoxytris(triphenylphosphine)rhodium is a reddish-brown compound which easily loses one Ph_3P. The diphosphine complex which is isolated is presumably dimer and analogous to $Rh_2(CO)_4Cl_4$[4].

During our attempts to recrystallize the complex $(PH_3P)_3RhMe$ from aromatic solvents, a gas was evolved, the mass spectral analysis of which proved the formation of methane. Upon cooling, an orange-yellow complex (**1**) with the analytical composition $Rh/Ph_3P = 1/3$ crystallized. The question arises whether the methane is formed while the methyl group abstracts a hydrogen from the solvents or whether the hydrogen abstraction occurs from the ligand Ph_3P. In order to substantiate the origin of the hydrogen atom the following experiments were carried out. The complex $(Ph_3P)_3RhMe$ was heated in molten Ph_3P and the evolved gas consisted of only methane, which was formed in 98% yield referred to the calculated amount of $(Ph_3P)_3RhMe$. This experiment confirms that the abstracted hydrogen atom comes from Ph_3P, but it does not distinguish whether the hydrogen originates from the Ph_3P bonded as ligand or from the added Ph_3P. Therefore an additional experiment in which the neat complex $(Ph_3P)_3RhMe$ was thermally decomposed was carried out. The evolved gas showed only the presence of methane which was formed in 42% calculated for $(Ph_3P)_3RhMe$. The most conclusive result has been obtained upon heating of the deuterated $[(C_6D_5)_3P]_3RhMe$ in toluene. The resulting gas, which was formed in 68% yield based on the starting complex, contained only methane and monodeuterated methane in the ratio $CH_4/CH_3D = 10/90$, proven by mass spectral analysis. The latter finding strongly implies that the abstracted hydrogen comes from the ligand Ph_3P.

The loss of hydrogen from an aromatic ring of a ligand with the concomitant formation of a metal–carbon bond has been observed previously. In the examples described by Chatt and Davidson[5], Bennet and Milner[6], and Hata and Miyake[7], the hydrogen migrates to the metal forming a hydrido complex. In analogy we suggest the mechanism for the formation of **1**, as shown in Fig. 1.

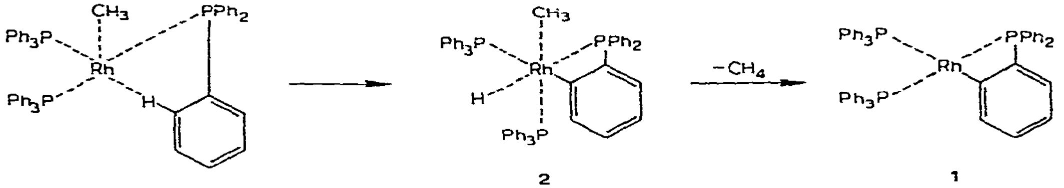

Fig. 1.

Based on NMR evidence we proposed a tetrahedral or trigonal pyramidal structure for $(Ph_3P)_3RhMe$. This configuration does not exlude that an α-hydrogen atom of one phenyl group occupies a coordination side (Fig. 1) similar to that found in the crystalline triphenylphosphine complexes of ruthenium(II) and palladium(II)[8]. The insertion of rhodium into the hydrogen–carbon bond occurs at the *ortho*-position, converting the d^8 complex $(Ph_3P)_3RhMe$ into a d^6 complex **2** (Fig. 1). The oxidative addition of an X–Y type molecule to a d^8 complex whereby a d^6 configuration results is a well-studied reaction[9]. The liberation of methane yields complex **1** for which the structure drawn in Fig. 1 is suggested.

Magnetic susceptibility measurements on compound **1** indicate diamagnetism, which is expected for a d^8 complex of square planar structure.

The cryoscopic determination of the molecular weight in benzene gave values much lower than the expected ones, which suggests that the complex dissociates in solution. A similar phenomenon has recently been reported for $(Ph_3P)_3RhCl$[10].

The NMR spectrum of compound **1** shows only absorption bands due to phenyl protons, and their splitting pattern does not allow to draw firm conclusions about the geometrical arrangement of the ligands.

IR investigations confirm structure **1** in which one hydrogen in *ortho*-position is abstracted. The intense shoulder at 746 cm^{-1} is assigned to the C–H out-of-plane deformation mode of an *ortho*-disubstituted benzene. The rhodium–carbon band is attributed to the absorption at 327 cm^{-1}.

The UV spectrum shown in Fig. 2 is also in agreement with the proposed

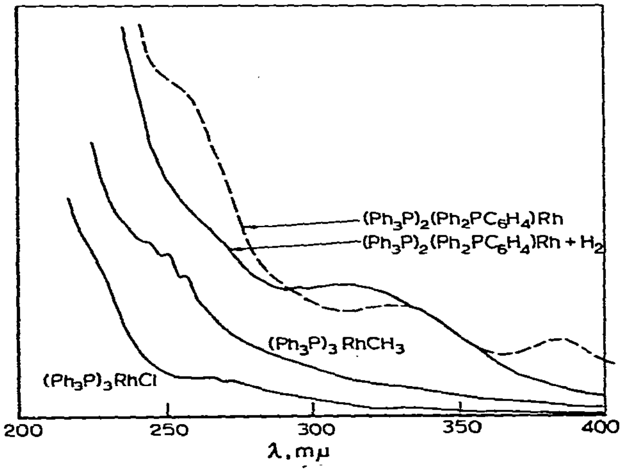

Fig. 2. UV spectrum of $(Ph_3P)_3RhR$ (R=Cl, CH_3) [solvent THF, conc. ~1 mg/ml, at 0.05 cm].

structure 1. The absorption at 384 mμ is assigned to the structure where the phenyl ring is σ-bonded to rhodium and phosphorus. Charge transfer with the aryl system directly bonded to the rhodium should show a bathochromic shift. The band at 384 mμ is not present in the complexes $(Ph_3P)_3RhCl$ and $(Ph_3P)_3RhMe$ (Fig. 2). However, upon warming of the tetrahydrofuran solution of $(Ph_3P)_3$ RhMe to 50° the band appears. Contrarily, upon bubbling of hydrogen through the solution of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$, the band at 384 mμ disappears (Fig. 2). We demonstrated that the addition of hydrogen to the complex $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ cleaves the carbon–rhodium bond and takes the following path:

$$(Ph_3P)_2(Ph_2PC_6H_4)Rh + H_2 \xrightarrow{Ph_3P} (Ph_3P)_4RhH$$

The complex $(Ph_3P)_4RhH$ was isolated and characterized by IR analysis. The spectrum was identical with that of an authentic sample of $(Ph_3P)_4RhH$[3].

EXPERIMENTAL

All reactions have been carried out under the exclusion of air and moisture, and argon was used as inert gas.

Methyltris(triphenylphosphine)rhodium

Chlorotris(triphenylphosphine)rhodium (4.1 g, 4.5 mmole) was suspended in absolute ether (100 ml) and excess methylmagnesium bromide (20 ml, 1.9 *M*) added. The mixture was stirred for 24 h at 0–10° and the orange-yellow precipitate separated by filtration, washed three times with ether, followed by washing with n-hexane. Upon drying in high vacuum an almost quantitative yield of $(Ph_3P)_3RhMe$ (3.9 g, 97%) was obtained; m.p. 120–140° (dec.). (Found: C, 72.8; H, 5.3; P, 10.3; Rh, 11.1. $C_{55}H_{48}P_3Rh$ calcd.: C, 73.0; H, 5.4; P, 10.3; Rh, 11.4%.)

Phenyltris(triphenylphosphine)rhodium

Chlorotris(triphenylphosphine)rhodium (6.5 g, 7.05 mmole), phenylmagnesium bromide (15 ml of a 2 *M* solution) and 100 ml of dry ether were stirred for 24 h at room temperature to give a yellowish precipitate which was filtered, washed a few times with dry ether and hexane, and dried at 10^{-4} mm Hg pressure (7.5 g, 90%); m.p. 160–170° (dec.). (Found: C, 74.1; H, 5.1; P, 9.8; Rh, 11.1. $C_{60}H_{50}P_3Rh$ calcd.: C, 74.5; H, 5.2; P, 9.6; Rh, 10.6%.)

Reaction of phenyltris(triphenylphosphine)rhodium with hydrogen

Phenyltris(triphenylphosphine)rhodium (1.9 g, 2 mmole) and 10 ml toluene were filled at 0° into a small autoclave and pressured with 650 psig hydrogen. After 20 h reaction time the formed benzene was distilled together with the toluene and analyzed by GLC analysis. The benzene amounted to 93%. The residue obtained after the distillation was recrystallized from toluene and the IR and NMR spectra were identical with those of $(Ph_3P)_3RhH$[3].

Reaction of methyltris(triphenylphosphine)rhodium with hydrogen

Methyltris(triphenylphosphine)rhodium (3.1 g, 3.4 mmole) was suspended in

5 ml toluene at 0°, filled into an autoclave and pressured with 650 psig hydrogen. The gas was analyzed by mass spectral analysis and 54% for the calculated amount of methane was found. The formed solid was identified by IR analysis to be $(Ph_3P)_3RhH$[3].

Reaction of methyltris(triphenylphosphine)rhodium with phenol

Methyltris(triphenylphosphine)rhodium (3.1 g, 3.4 mmole) was treated with 6 ml phenol. The resulting gas contained 65% of the calculated amount for methane. The red residue was washed with n-hexane, removing the excess of phenol, and recrystallized from toluene to yield 2.6 g (77%) $(Ph_3P)_3RhOPh$. (Found: C, 73.0; H, 4.9; P, 8.8; Rh, 9.5. $C_{60}H_{50}OP_3Rh$ calcd.: C, 73.3; H, 5.1; P, 9.5; Rh, 10.5%.)

Upon stirring of $(Ph_3P)_3RhOPh$ for 24 h in n-hexane and recrystallization from toluene, the complex $(Ph_3P)_2RhOPh$ was isolated. (Found: C, 69.4; H, 4.9; P, 8.7; Rh, 13.7. $C_{42}H_{35}OP_2Rh$ calcd.: C, 70.0; H, 4.8; P, 8.6; Rh, 14.3%.)

Reaction of phenyltris(triphenylphosphine)rhodium with phenol

Phenyltris(triphenylphosphine)rhodium (3.75 g, 4 mmole) was treated with 4 g phenol in 10 ml toluene. On heating to 100° a dark-red solution was obtained. The benzene formed and a part of the toluene was distilled and analyzed by GLC analysis. The benzene yielded 95% of the theory.

Recrystallization of methyltris(triphenylphosphine)rhodium in toluene

Upon heating of $(Ph_3P)_3RhMe$ (8 g, 8.9 mmole) in 200 ml toluene for 30 min at 100°, 85% for the calculated amount of methane evolved. The hot solution was filtered, and on cooling an orange-yellow complex $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ crystallized which was filtered and washed with n-hexane and dried at 10^{-4} mm Hg (5.1 g, 65%); m.p. 110–130° (dec.). (Found: C, 73.4; H, 5.3; P, 9.2; Rh, 10.8. $C_{54}H_{44}P_3Rh$ calcd.: C, 72.9; H, 5.1; P, 10.4; Rh, 11.6%.)

Thermal decomposition of methyltris(triphenylphosphine)rhodium

a. Decomposition in molten Ph_3P. Methyltris(triphenylphosphine)rhodium (2.3 g, 2.5 mmole) was heated in 8 g Ph_3P for 1 h at 90°. The methane formed amounted to 98% of the calculated amount for $(Ph_3P)_3RhMe$.

b. Decomposition of neat $(Ph_3P)_3RhMe$. Methyltris(triphenylphosphine)-rhodium (3.1 g, 3.4 mmole) was heated for 8 h at 110°. The gas evolved contained only methane which was formed in a yield of 42% calculated for $(Ph_3P)_3RhMe$.

Synthesis of deuterated methyltris(triphenylphosphine) rhodium

The fully deuterated $(C_6D_5)_3P$ was prepared according to standard organic methods starting from deuterobenzene which was converted to bromobenzene. The bromobenzene was transformed into the corresponding Grignard compound which gave with PCl_3 the fully deuterated $(C_6D_5)_3P$. In analogy, as described above, the deuterated $[(C_6D_5)_3P]_3RhMe$ was synthesized.

Reaction of the deuterated methyltris(triphenylphosphine)rhodium in toluene

The deuterated $[(C_6D_5)_3P]_3RhMe$ (0.8 g, 0.9 mmole) was heated in 15 ml toluene for 30 min at 100°. The evolved gas was analyzed by mass spectral analysis and exhibited the presence of only CH_3D and CH_4 in the ratio $CH_3D/CH_4 = 90/10$. The gas formed amounted to 68% of the calculated amount for $[(C_6D_5)_3P]_3RhMe$.

Reaction of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ *with hydrogen*

The complex $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (3 g, 3 mmole) was dissolved in 20 ml toluene and 2 g Ph_3P were added. This solution was pressured with 500 psig hydrogen and stirred for 1 h. Upon addition of 60 ml n-hexane a yellow complex precipitated (2.15 g, 72%), the IR spectrum of which was identical with that of $(Ph_3P)_4RhH$[3].

ACKNOWLEDGEMENTS

The assistance of Dr. C. A. REILLY, Dr. K. LOOS, and Dr. J. W. FORBES in the measurement and interpretation of the NMR, IR, and UV spectra is gratefully acknowledged.

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