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REACTIONS OF RHODIUM(I) COMPLEXES CONTAINING A METAL–CARBON BOND WITH CARBON MONOXIDE. III

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SUMMARY

The reaction of $(Ph_3P)_3Rh\text{–}R$ ($R = CH_3$, Ph) with carbon monoxide is described. In the case of $(Ph_3P)_3Rh\text{–}Ph$, the complex $(Ph_3P)_2(CO)RhPh$ could be isolated. Special attention was paid to study the carbon monoxide insertion into the rhodium–carbon bond via IR spectroscopy. Treatment of $(Ph_3P)_2RhC_6H_4PPh_2$ with carbon monoxide yielded the complex $(Ph_3P)_2(CO)Rh(CO)C_6H_4PPh_2$. The complex $(Ph_3P)_2RhC_6H_4PPh_2$ undergoes readily an oxidative reaction with benzoyl chloride and oxalyl chloride.

INTRODUCTION

Many papers have been published in recent years concerning the insertion of carbon monoxide into a carbon–metal bond[1,2]. Because of the potential practical application of the carbonylation exemplified by the hydroformylation process, this subject also attracted a great deal of industrial interest. During our investigations on rhodium(I) complexes containing a rhodium–carbon bond[3–5], we became interested in studying their reactions with carbon monoxide. The results obtained will be discussed in this paper.

RESULTS AND DISCUSSION

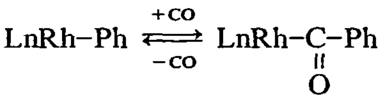
Reaction of phenyltris(triphenylphosphine)rhodium with carbon monoxide

When a toluene or tetrahydrofuran suspension of $(Ph_3P)_3RhPh$ is exposed to carbon monoxide at −40° at 1 atm and then slowly warmed to room temperature, a reddish-yellow solution is obtained. Upon addition of hexane, a yellow compound precipitates the analysis of which is in agreement with the empirical formula $(Ph_3P)_2$-$(CO)RhPh$ (I). The IR spectrum (Nujol mull) shows a sharp, strong band at 1960 cm^{-1}. This frequency is in the region of a terminal carbon monoxide group attached to rhodium(I). It may be noted that there is no evidence in the IR spectrum for a benzoyl group which would arise from carbon monoxide insertion into the rhodium–phenyl bond. Based on elemental analysis and IR studies, a square planar structure is proposed for (I). The cleavage of the rhodium–phenyl bond by treatment with phenol yielded 63% benzene. Thermal decomposition of (I) gave benzene, biphenyl, benzophenone and traces of benzil. All these products can be explained by considering the formation of phenyl radicals and their reaction with carbon monoxide.

The reaction of $(Ph_3P)_3RhPh$ with carbon monoxide was followed by IR spectroscopy. At the same time, the uptake of CO was measured volumetrically. It is worth mentioning that in organic solvents extensive dissociation of triphenylphosphine–rhodium complexes occurs and that this dissociation is concentration dependent[6–8]. Accordingly, the equilibrium (1) can be discussed.

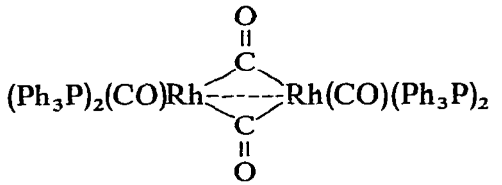
$$(Ph_3P)_3RhPh \underset{+Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} (Ph_3P)_2RhPh \tag{1}$$

At −20°, a tetrahydrofuran solution of $(Ph_3P)_3RhPh$ reacts with *ca* 2 moles CO [based on the dissociated species $(Ph_3P)_2RhPh$]. The IR spectrum at −20° shows two strong bands at 1930 cm^{-1} and 1970 cm^{-1} appropriate for terminal carbonyl stretching frequencies attached to rhodium(I). Both the presence of two IR absorptions and their intensity ratio are in agreement with a pentacoordinated species $(Ph_3P)_2(CO)_2RhPh$. This composition explains also the uptake of two moles of CO. On warming to 0°, no noticeable change in the IR spectrum could be observed. All attempts, however, to isolate $(Ph_3P)_2(CO)_2RhPh$ have failed, and it is very likely that this complex exists only in solution and uncer CO atmosphere. At room temperature and at prolonged reaction time, (60 min) the IR spectrum exhibits an additional band in the keto region at 1625 cm^{-1} indicating that insertion of CO into the rhodium–phenyl bond has occurred, thus forming a benzoyl complex (eqn. 2).



$$LnRh{-}Ph \underset{-CO}{\overset{+CO}{\rightleftharpoons}} LnRh{-}\underset{\underset{O}{\|}}{C}{-}Ph \tag{2}$$

These observations are in agreement with kinetic studies on carbonylation reactions demonstrating that the insertion is the slower step compared to CO coordination and that the CO coordination occurs readily at temperatures at which the insertion reaction does not take place at a measurable rate[9–11]. We have not been able to isolate a benzoyl complex; all our efforts led to the isolation of $(Ph_3P)_2(CO)RhPh$ only. It is known from the literature that the CO insertion reaction is frequently reversible, but sometimes only the reverse reaction, CO elimination is known[12,13]. Aryl compounds appear to undergo decarbonylation reactions more readily than alkyl compounds[14] and the decarbonylation of benzoyl complexes is even utilized in synthesizing phenyl complexes which are difficult or impossible to synthesize by other methods[15,16]. Therefore, it might be concluded that the benzoyl complex is very unstable and isomerizes easily to the phenyl complex as indicated in eqn. (2). Indeed, upon warming of the $(Ph_3P)_3RhPh/CO$ solution to 80°, the band at 1625 cm^{-1} disappears and a yellow complex precipitates, the analysis of which is in agreement with the composition $(Ph_3P)_2Rh(CO)_2$. The IR spectrum (Nujol mull) shows two terminal carbonyl groups at 2010 (medium) and 1980 cm^{-1} (strong). In addition, there are a strong band at 1770 cm^{-1} and a medium one at 1800 cm^{-1}, which both are appropriate for a $Rh^I{-}CO{-}Rh^I$ group. The structure of this compound is uncertain, but a complex of the analogous composition and a similar IR pattern has been recently described[17] and the structure (II) was assigned.



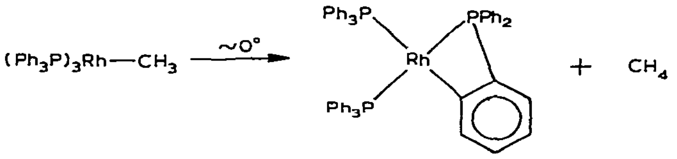
(II)

This structure does not explain the IR pattern found unless the presence of different isomers are considered.

The work up of the mother solution obtained after filtration of complex (II) revealed the expected products such as benzene 68%, biphenyl 21%, benzophenone 10%, and benzil (traces). These compounds can be explained as resulting from phenyl radicals which are formed from a homolytic fission of the phenyl–rhodium σ-bond.

Reaction of methyltris(triphenylphosphine)rhodium with carbon monoxide

It is known that metal–methyl and metal–phenyl bonds show a different behavior toward carbonylation[18]. Therefore, it appeared of interest to investigate also the reaction of $(Ph_3P)_3RhCH_3$ with carbon monoxide. It can be anticipated that this carbonylation reaction is complicated by reaction (3).



(3)

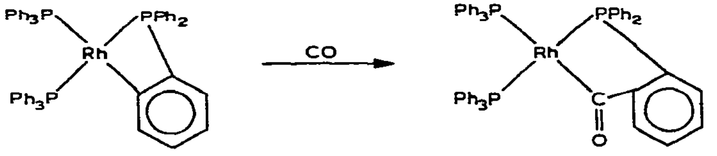
(III)

A full account of this reaction has been given in our previous paper[4]. Indeed, we have been unsuccessful in isolating an analytically pure complex on carbonylating $(Ph_3P)_3RhCH_3$ and therefore, our efforts were mainly directed toward studying the reaction path via IR spectroscopy.

When a toluene or tetrahydrofuran suspension of $(Ph_3P)_3RhCH_3$ is treated at −40° with carbon monoxide and warmed to −20°, one mole of complex reacts with *ca.* two moles of CO [based on $(Ph_2P)_2RhCH_3$], forming an orange-yellow solution. The IR spectrum of this solution exhibits two strong bands at 1980 and 1940 cm^{-1} attributable to the terminal stretching frequency of Rh^ICO. There is no evidence at this temperature of an CO insertion into the rhodium–methyl bond with formation of an acetyl complex. However, at 10° a new band at 1645 cm^{-1} appears which can be assigned to an acetyl group. Quenching of a part of this orange solution with hexane gives a pale yellow complex which still retains the keto stretch at 1640 cm^{-1}. Elemental analysis of this complex indicated inhomogenity and further purification could not be accomplished.

Upon warming of the remaining part of the orange solution to 60°, a gas evolves accompanied by the disappearance of the acetyl band. The mass spectral analysis of the gas revealed the presence of CO and methane [48% calculated for $(Ph_3P)_3RhCH_3$]. The solution contained acetone (28% for the calculated amount) and biacetyl (11% for the calculated amount). Upon heating, there was no color change, the solution stayed orange-yellow.

The addition of n-hexane to this orange-yellow solution gave a yellow precipitate which could not be characterized by elemental analysis and consists presumably of mixture of complexes. The mixed carbonyl product contains both terminal and acyl carbonyl groups, as shown by strong bands in the IR spectrum at 1950 and 1620 cm^{-1}. The band at 1620 cm^{-1} can be explained in the fashion depicted in eqn. (4). A carbon monoxide insertion into the rhodium–phenyl bond of (III) yields a complex of the type (IV).



(III) (IV) (4)

To substantiate the possibility of this type of CO insertion, a tetrahydrofuran solution of (III) was reacted with CO at 200 psi and 60°. The addition of n-hexane to the yellow solution produced a yellow precipitate. The IR spectrum (Nujol mull) shows a terminal carbonyl group [ν(CO) 1965 cm^{-1}] and a band at 1620 cm^{-1} appropriate for a carbonyl stretching vibration of a benzoyl derivative (Fig. 1). An intense shoulder at 746 cm^{-1} can be assigned to the CH out-of-plane deformation mode of an *ortho*-disubstituted benzene. Based on the IR data and on the elemental analysis, the structure (V) is proposed.

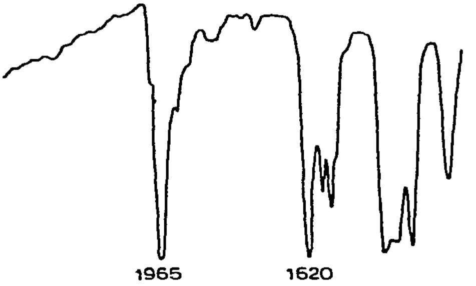
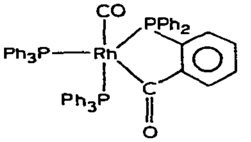


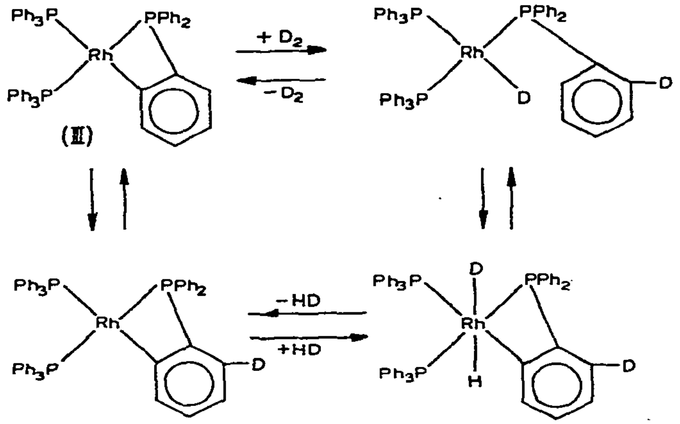
Fig. 1. Complex 5 in nujol mull.



(V)

It can be anticipated that the reaction of (V) with hydrogen would lead to a phosphorus compound containing the inserted CO. The treatment with hydrogen followed by decomposition of the complexes formed with H_2O_2 yielded only triphenylphosphine oxide. Apparently a decarbonylation took place. It is well known that various rhodium complexes decarbonylate aldehydes[19,20], alcohols[21,22], etc. A final determination of the structure must be done by X-ray analysis.

Stimulated by recent, elegant work in the literature[23], the complex (III) was treated with deuterium (50 psi) at 60°. Upon addition of H_2O_2, triphenylphosphine oxide was isolated and the NMR spectrum recorded in C_6D_6 on a Varian A 60 spectrometer. In C_6D_6, the *ortho*-proton signal of Ph_3PO is well separated from those of *meta*- and *para*-protons. The spectrum observed showed almost a complete absence of the *ortho*-signal, implying that the majority of the *ortho*-positions are occupied by deuterium. A possible explanation is that a rapid equilibrium occurs as outlined in the following scheme starting from (III).

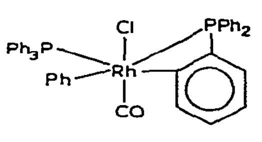


We could demonstrate that the complex (III) smoothly reacts with hydrogen yielding $(Ph_3P)_3RhH$[4]. A rapid equilibrium of the type $d^8 \rightleftarrows d^6$ in which the rhodium inserts by oxidative addition into the *ortho*-C–H bond can explain the labelling of *ortho*-positions only.

Decarbonylation of benzoyl and oxalyl chloride

As mentioned above, many rhodium complexes function as decarbonylation agents. The following part of this paper describes our decarbonylation studies using complex (III). Only two examples, benzoyl chloride and oxalyl chloride have been studied.

A toluene solution of (III) and benzoyl chloride were heated to 90°. A pale yellow, stable complex precipitated which analyzed correctly for $(Ph_3P)(CO)Cl\text{-}PhRhC_6H_4PPh_2$. The IR spectrum (KBr film) exhibits a strong terminal bond in the region for rhodium(III) carbonyls at 2050 cm^{-1}. There is no evidence for a ketonic acyl group. The reaction with phenol yielded benzene in 68% yield. Based on these results, the structure (VI) is proposed for this complex. The formation of (VI) is a

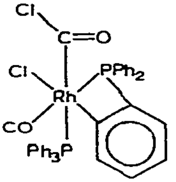


(VI)

further example where a coordinatively unsaturated d^8 complex is converted into an octahedral d^6 complex by the addition of a covalent molecule to the coordinate sphere. A plausible reaction path can be visualized by assuming a coordination of benzoyl chloride with concomitant cleavage of the carbon–halogen bond, thus forming a benzoyl complex which rearranges to (VI). A similar reaction scheme for the decarbonylation of benzoyl chloride using $(Ph_3P)_3RhCl$ has been described[19].

When catalytic amounts of (III) were heated with benzoyl chloride at 200°, chlorobenzene distilled off with the evolution of carbon monoxide.

Upon stirring a toluene solution of (III) at room temperature with oxalyl chloride, a pale yellow complex precipitated, the IR spectrum of which is in agreement with structure (VII).



(VII)

The terminal carbonyl vibration of Rh^{III}–CO is found at 2060 cm^{-1} and a very strong bond at 1680 cm^{-1} is assigned, to a Rh–CO–Cl group.

EXPERIMENTAL

All operations were conducted under argon. IR spectra of solids were obtained on nujol mulls or KBr film. Solution spectra were measured in 0.5 or 1 mm liquid cells and in a low temperature apparatus designed in our laboratories. A Beckman IR-5 spectrophotometer was used.

Reaction of $(Ph_3P)_3RhPh$ with CO

A tetrahydrofuran (30 ml) suspension of $(Ph_3P)_3RhPh$ (7.6 g, 79 mmols) was treated at −40° and 1 atm with CO. Upon warming to −20°, the CO uptake amounted to 2.1 moles CO per mole of $(Ph_3P)_2RhPh$. A clear reddish-yellow solution was obtained, which was stirred for 1 h at room temperature. This solution was divided in two equal parts and worked up as follows: The first part was quenched with n-hexane (50 ml) at 0° and a yellow complex precipitated, which was filtered and washed with n-hexane followed by drying in high vacuum (yield 1.1 g, 42%), m.p. 170–180° (dec.). (Found: C, 70.0; H, 4.8; P, 8.2; Rh, 13.9. $C_{43}H_{35}OP_2Rh$ calcd.: C, 70.5; H, 4.8; P, 8.5; Rh, 14.1%.)

The second part was heated for 30 min at 70–80° under CO atmosphere. A yellow complex precipitated, which was washed with a mixture of THF/hexane and dried at high vacuum (yield 1.05 g, 39%). (Found, C, 65.9; H, 4.4; P, 8.8; Rh, 15.5; $C_{38}H_{30}O_2P_2Rh$ calcd.: C, 66.8; H, 4.4; P, 9.1; Rh, 15.0%.) The mother solution was analyzed by GLC and benzene (68%), biphenyl (21%), benzophenone (10%) and benzil (< 1%) were found [% based on $(Ph_3P)_3RhPh$]. Mass spectral and IR analyses confirmed the presence of biphenyl and benzophenone.

The complex $(Ph_3P)_2(CO)RhPh$ (0.5 g) was heated in toluene with 2 g phenol to 140°. The toluene was distilled off and analyzed by GLC. Benzene (63%) was found [calculated for $(Ph_3P)_2(CO)RhPh$].

Reaction of $(Ph_3P)_3RhCH_3$ with CO

A tetrahydrofuran (50 ml) suspension of $(Ph_3P)_3RhCH_3$ (8.6 g, 92 mmol) was treated with CO at −40° and 1 atm. The suspension was warmed to −20° until an orange-yellow solution was obtained. The uptake of CO amounted to 2.05 mols per mol $(Ph_3P)_2RhCH_3$. After warming to 10° the solution was split into two equal parts.

The first part was quenched with 50 ml n-hexane and the yellow precipitate (2.1 g) washed and dried at the high vacuum. Elemental analysis showed inhomogenity of this precipitate. Repeated recrystallization gave no pure compound.

The second part was warmed to 60° and the gas collected. Mass spectral analysis of the gas gave methane [48% calculated for $(Ph_3P)_3RhCH_3$] and CO. GLC analysis of the solution gave acetone [28% calculated for $(Ph_3P)_3RhCH_3$] and biacetyl [11% calculated for $(Ph_3P)_3RhCH_3$]. IR analysis confirmed the presence of acetone and biacetyl. The addition of n-hexane to this solution gave a yellow precipitate, the analysis of which gave variable results.

Reaction of $(Ph_3P)_2RhC_6H_4PPh_2$ *with CO*

The complex $(Ph_3P)_2RhC_6H_4PPh_2$ (8.1 g, 91 mmols) and Ph_3P (2 g) were dissolved in benzene (60 ml) and pressured up with 200 psi CO and stirred for 2 h at 60°. Hexane (80 ml) was added to the orange-yellow solution and the precipitated yellow complex (4.2 g, 42% yield) was washed several times with n-hexane and dried at the high vacuum. A recrystallized (benzene) sample was analyzed, m.p. 180–200° (dec.). (Found: C, 71.3; H, 4.8; O, 3.5; P, 10.2; Rh, 10.9; $C_{56}H_{44}O_2P_3Rh$ calcd.: C, 71.2; H, 4.7; O, 3.4; P, 9.8; Rh, 10.3%.)

Reaction of $(Ph_3P)_2(CO)RhC_6H_4COPPh_2$ *with hydrogen*

A benzene solution of the complex (2.1 g) was pressured up with 200 psi hydrogen and warmed to 60° for 5 h. The yellow-orange solution was stirred with 30% H_2O_2 for 2 h and the phosphorus compounds isolated by chromatography on Al_2O_3. Only Ph_3PO could be isolated (0.9 g, 48% yield).

Reaction of $(Ph_3P)_2RhC_6H_4PPh_2$ *with deuterium*

A benzene solution of $(Ph_3P)_2RhC_6H_4PPh_2$ (5.1 g) was pressured up with 50 psi deuterium and stirred for 24 h at 60°. The gas, analyzed by mass spectrometry, contained H_2, HD and D_2. The extent of hydrogen exchange corresponds to 16.8 hydrogens per mol of rhodium complex. The reddish-yellow solution was stirred for 2 h with 30% H_2O_2 and the organic phase analyzed by chromatography on Al_2O_3. Triphenylphosphine oxide could be isolated in 38% yield.

Reaction of $(Ph_3P)_2RhC_6H_4PPh_2$ *with benzoyl chloride*

A mixture of 20 ml toluene and 10 ml benzoyl chloride was heated together with $(Ph_3P)_2RhC_6H_4PPh_2$ (3.8 g, 4.3 mmol) for 2 h at 90°. Upon cooling, the pale yellow precipitate (3.2 g, 73% yield) was filtered, washed with hexane and dried at the high vacuum. (Found: C, 66.8; H, 4.5; Cl, 4.3; O, 2.2; P, 8.1; Rh, 13.1; $C_{43}H_{34}ClOP_2Rh$ calcd.: C, 67.4; H, 4.5; Cl, 4.6; O, 2.1; P, 8.1; Rh, 13.5%.)

Reaction of $(Ph_3P)_2RhC_6H_4PPh_2$ *with oxalyl chloride*

When a toluene (25 ml) solution of $(Ph_3P)_2RhC_6H_4PPh_2$ (2.6 g, 2.9 mmols) was stirred at room temperature for 5 h with oxalyl chloride (1.5 ml) a pale yellow complex precipitated (1.3 g). The filtered and washed (n-hexane) complex was air stable. (Found; C, 60.5; H, 4.0; Cl, 9.4; O, 4.2; P, 8.3; Rh, 13.6; $C_{38}H_{29}Cl_2O_2P_2Rh$ calcd.: C, 61.0; H, 4.1; Cl, 9.4; O, 4.2; P, 8.8; Rh, 13.3%.)

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