REACTIONS OF $Rh(acac)[P(OPh)_3]_2$ WITH H_2, CO AND OLEFINS

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Summary

The reactions of $Rh(acac)[P(OPh)_3]_2$ with H_2, CO and olefins have been investigated using UV–VIS, IR, ^1H and ^{31}P NMR techniques. In the presence of H_2 and free phosphite, $Rh(acac)P_2$ produces $HRhP_4$, which was shown to catalyse isomerization reactions of olefins. Addition of CO to $HRhP_4$ produces $HRh(CO)P_3$, which is a good hydroformylation catalyst. The latter hydride can also be obtained directly from the starting complex in the presence of H_2, CO and free phosphite. No evidence for the formation of any hydride complexes could be found in the absence of free phosphite. The results are discussed with reference to earlier studies performed on these systems.

Introduction

The 16-electron, square planar $Rh(acac)[P(OPh)_3]_2$ (acac = acetylacetone) complex is a Rh(I) species suitable for use as a model homogeneous catalyst for the activation of diatomic molecules such as H_2 and CO, as well as olefins and aromatic hydrocarbons [1, 2]. This compound, produced in the substitution reaction [3]:

$$(acac)Rh(CO)_2 + 2P(OPh)_3 \longrightarrow (acac)Rh[P(OPh)_3]_2 + 2CO$$

is stable enough to be regarded as the precursor of catalytically active forms in hydrogenation (of olefins and aromatics), isomerization (of olefins) and, most important, hydroformylation reactions [2].

Quite recently [4] we have proposed the structure of complexes formed in this reaction system on the basis of our spectroscopic results.

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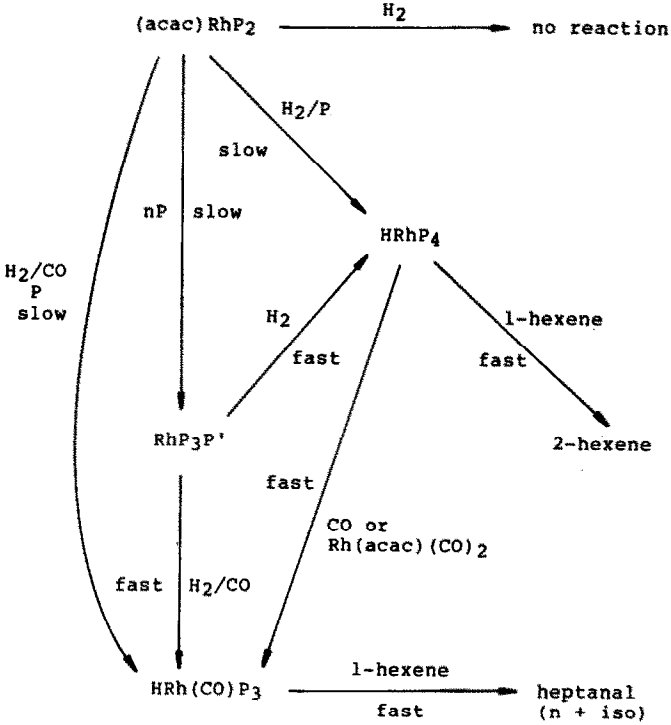
These results have indicated that the $Rh(acac)[P(OPh)_3]_2$ complex, in the presence of $P(OPh)_3$, may produce the active catalytic system for olefin hydroformylation, even under mild conditions. Our present investigations have allowed us to elucidate the structure of complexes formed in the reaction of $Rh(acac)[P(OPh)_3]_2$ with H_2 and CO in the presence of free $P(OPh)_3$.

Results and discussion

The $Rh(acac)[P(OPh)_3]_2$ complex does not undergo any structural changes under mild conditions in the presence of H_2, as evidenced by the lack of changes in the UV–VIS, IR, ^{31}P and ^1H NMR spectra. If, however, free $P(OPh)_3$ is present in solution, $Rh(acac)[P(OPh)_3]_2$ reacts with H_2 to produce the hydride complex (Scheme 1). The ^{31}P NMR spectrum exhibits two doublets (δ = 129.7 ppm, J(Rh—P) = 232.8 Hz, J(P—H) = 44 Hz), and in the hydride range of the ^1H NMR spectra a quintet of doublets appears (δ = −10.59 ppm, J(Rh—H) = 7 Hz, J(P—H) = 44 Hz) (Fig. 1a). Moreover, a shift of the CH_3 acetylacetone line from δ = 1.44 to 1.57 ppm (free acac position) is observed. The reaction with H_2 is relatively slow: within several minutes after introduction of H_2, the spectra show the corresponding changes, but more pronounced effects are observed after 24 h. The hydride



Scheme 1.

compound is stable in solution, and does not suffer decomposition in a hydrogen atmosphere even after 8 days.

On the basis of $^{31}P[^{1}H]$ NMR data, some of the authors of the present paper previously suggested the hydride complex to be $H_2Rh(acac)[P(OPh)_3]_2$ [4]. Our present ^{1}H NMR measurements, however, showed that the hydride complex produced in the reaction of $Rh(acac)[P(OPh)_3]_2$ with H_2 in the presence of $P(OPh)_3$ has the formula $HRh[P(OPh)_3]_4$. A sample of $HRh[P(OPh)_3]_4$, independently synthesized according to the method described in [5], exhibited identical ^{1}H and ^{31}P NMR characteristics [6].

The results of a detailed study of the ^{1}H and ^{31}P NMR spectra of the $Rh(acac)P_2 + nP$ system forced us to revise our earlier conclusions concerning the structure of the product formed in this reaction [7]. It appeared that the presence of an excess of free $P(OPh)_3$ caused the stepwise substitution of the acetylacetonate ligand and the formation of the five-coordinate orthometallated $Rh[P(OPh)_3]_3[P(OPh)_2(OC_6H_4)]$ complex via the reaction:

$$Rh(acac)P_2 + P \longrightarrow [Rh(acac)P_3)]^{\#}$$

$$\Big\downarrow P$$

$$RhP_3P' + Hacac \longleftarrow [RhP_4(acac)]^{\#}$$

where $P = P(OPh)_3$ and $P' = P(OPh)_2(OC_6H_4)$. The final product reacts more readily with H_2 than does the $Rh(acac)P_2 + P$ system. ^{31}P and ^{1}H NMR spectra indicate that RhP_3P' undergoes rapid oxidative addition by H_2 to produce a six-coordinate Rh(III) species [8], which is followed by a slightly slower reaction to produce $HRhP_4$ [7]. This process understandably depends on the reaction temperature, hydrogen concentration and the presence of free $P(OPh)_3$. It was observed that when RhP_3P' is contaminated with small traces of free $P(OPh)_3$, the reaction with H_2 to produce $HRhP_4$ is significantly faster. However, in the absence of free $P(OPh)_3$ we observed the formation of an intermediate species, which is presumably Rh(III) produced via an oxidative addition reaction [10]. This species was found to be stable over several days and only partially converts to $HRhP_4$. It is now understandable why the reaction of H_2 with the $Rh(acac)P_2 + P$ system is so slow, since the formation of RhP_3P' is rate-determining [9]. In the absence of free P, the $Rh(acac)P_2$ complex is stable and does not react with H_2.

$HRh[P(OPh)_3]_4$ formed in the above system reacts with olefins as proved for 1-hexene. We have studied the reaction $Rh(acac)[P(OPh)_3]_2$ + 1-hexene ([Rh]:[P]:[1-hexene] = 1:3:40) using ^{1}H and ^{31}P NMR. The ^{31}P NMR spectrum of a solution after saturation with hydrogen, shows the formation of $HRh[P(OPh)_3]_4$. The spectrum did not change in two days, and there are two doublets (identical to those shown in Fig. 1a), originating from the hydride complex and presumably unreacted $Rh(acac)[P(OPh)_3]_2$, respectively. Simultaneously, the isomerization of 1-hexene to 2-hexene also occurs. This reaction was examined by ^{1}H NMR in the proton range of the olefin carbons. After 2 days at room temperature, *ca.* 80% 1-hexene had

reacted to 2-hexene. This experiment led us to believe that $HRh[P(OPh)_3]_4$ is the active form of a catalyst for olefin isomerization.

In our previous studies [4] we found that the complex containing H^- and CO could be formed in reactions between CO and the above-described hydride complex, and also in the reaction of the $H_2 + CO$ mixture with a solution of $Rh(acac)[P(OPh)_3]_2 + P(OPh)_3$. In our present studies of the reactions with CO, we have used pure CO and $Rh(acac)(CO)_2$ as the CO donors. The latter complex is known to detach CO very readily in the presence of phosphite. Introduction of CO (or of $Rh(acac)(CO)_2$) to the system containing $HRh[P(OPh)_3]_4$ (produced from $Rh(acac)[P(OPh)_3]_2 + P(OPh)_3 + H_2$) results in instantaneous changes in the ^{31}P and ^1H NMR spectra. The intensity of lines in the ^{31}P NMR spectrum, characteristic for $HRh[P(OPh)_3]_4$ at $\delta = 129.7$ ppm (J(Rh—P) = 232.8 Hz), decreases and is replaced by a new doublet at $\delta = 140.5$ ppm (J(Rh—P) = 240 Hz) (Fig. 1b). In the ^1H NMR hydride range, the quintet at $\delta = -10.59$ ppm disappears and a doublet at $\delta = -10.2$ ppm appears (Fig. 1c). It follows from the observed splitting that J(Rh—H) = 3 Hz and that no P—H couplings are observed. The absence of any P—H couplings is not unusual since such *cis* couplings are usually very small compared to *trans* P—H couplings. We also observed no *cis* P—H couplings for the $H_2RhP_4^+$ species [10].

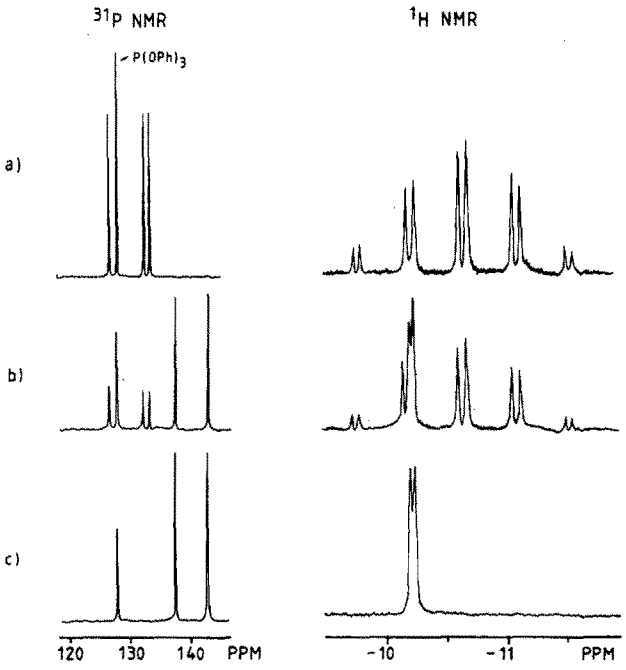


Fig. 1. ^1H and ^{31}P NMR spectra at 100 MHz and 40.5 MHz, respectively: (a) $HRh[P(OPh)_3]_4$ obtained in the reaction $Rh(acac)[P(OPh)_3]_2 + P(OPh)_3 + H_2$; (b) $HRh[P(OPh)_3]_4 + HRh(CO)[P(OPh)_3]_3$ obtained in the reaction $Rh(acac)[P(OPh)_3]_2 + P(OPh)_3 + H_2 + CO$; (c) $HRh(CO)[P(OPh)_3]_3$ obtained by saturation of solution (b) with CO.

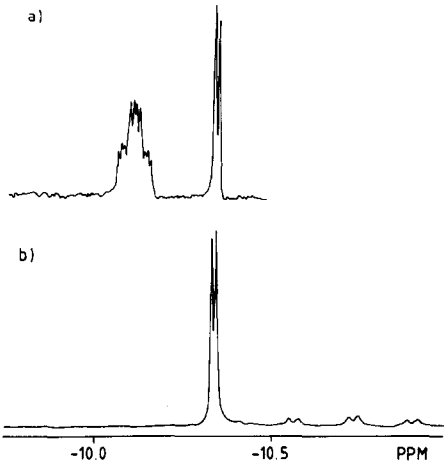


Fig. 2. ^1H NMR spectra at 100 MHz for the reaction $HRh(CO)(PPh_3)_3 + 3P(OPh)_3 \rightarrow HRh(CO)[P(OPh)_3]_3 + 3PPh_3$: (a) immediately after mixing; (b) after 18 h.

The complex produced in the reaction $RhP_3P' + H_2 + CO$ or $HRhP_4 + CO$ is the 18-electron five-coordinate species $HRh(CO)P_3$. The release of P can be clearly observed when such reactions are performed under argon atmosphere. Further evidence in favour of the $HRh(CO)P_3$ species was obtained from the reaction of $HRh(CO)(PPh_3)_3$ (prepared as in [11]) with $P(OPh)_3$ (ratio 1:3). The ^1H NMR spectrum recorded immediately after mixing (Fig. 2a) is in agreement with that for $HRh(CO)(PPh_3)[P(OPh)_3]_2$ and $HRh(CO)[P(OPh)_3]_3$. After 18 h (Fig. 2b), $HRh(CO)P_3$ is the main product, with some $HRhP_4$ formed. Similarly, the reaction of $HRh(CO)(PPh_3)_3$ with $P(OC_2H_5)_3$ (ratio 1:3) results in the formation of mainly $HRh(CO)[P(OC_2H_5)_3]_3$ and traces of $HRh[P(OC_2H_5)_3]_4$. In this case, the $HRh(CO)P_3$ species exhibits a quartet of doublets in the ^1H NMR spectrum, with $J(Rh—H) = 8$ Hz and $J(P—H) = 16$ Hz. We assume that the $P(OC_2H_5)_3$ ligands are slightly out of the trigonal plane, enabling P—H coupling to occur, in contrast to the $P(OPh)_3$ case where such coupling is absent. It follows that all the available evidence is in favour of the 18-electron $HRh(CO)P_3$ species with the phosphite ligands in the trigonal planar positions and the Rh—H bond perpendicular to this plane.

It should be noted that the rates of formation of $HRhP_4$ and $HRh(CO)P_3$ are different; the first is rather slow, while the reaction of the hydride complex with CO proceeds almost instantaneously. The difference in the rate of these reactions could be easily seen from the ^1H NMR spectra in the hydride range. A quintet of doublets (at $\delta = -10.59$ ppm) observed in the spectrum of the hydride complex solution ($HRhP_4$) disappeared immediately after introduction of $Rh(acac)(CO)_2$ or CO, and was replaced by the doublet at $\delta = -10.2$ ppm (assigned to $HRh(CO)P_3$). The same product is obtained in the reaction of $HRhP_4$ (prepared according to [5]) with CO. At insufficient concentrations of CO, the reaction was not com-

plete and the recorded spectra were those of mixtures of the complexes $HRhP_4$ and $HRh(CO)P_3$ (Fig. 1b). After introduction of more CO, only $HRh(CO)[P(OPh)_3]_3$ was present in solution (Fig. 1c). We examined these reactions under various conditions, *i.e.* by varying the sequence of the introduction of CO and H_2, and allowing different saturation conditions. In all cases, the NMR spectra indicated that, in the presence of H_2 and CO, the hydride complexes $HRhP_4$ and $HRh(CO)P_3$ exist in equilibrium, and their concentrations depend on the selected conditions.

The catalytic activity of $HRh(CO)P_3$ in hydroformylation reactions of 1-hexene was also studied by ^1H and ^{31}P NMR. The reaction was studied in a NMR tube with $Rh(acac)P_2$ + P + 1-hexene ([Rh]:[P]:[1-hexene] = 1:3:40). First the olefin-free solution was saturated with a H_2/CO mixture, which produced $HRh(CO)P_3$ in solution. 1-Hexene was then added, and after 24 h the two lines in the ^{31}P NMR spectrum characteristic of $HRh(CO)P_3$ had disappeared and were replaced by two doublets characteristic of $HRhP_4$. Addition of CO to the reaction mixture led to the formation of $HRh(CO)P_3$. The organic products were identified by ^1H NMR as aldehyde and 2-hexene. It follows that in the described system $HRh(CO)P_3$ and $HRhP_4$ are present; the former catalyses the hydroformylation and the latter the isomerization reaction.

The main goal of our studies on the interaction of Rh(I) complexes with olefins was the identification of the active forms of the complexes. Our present work enables us to estimate how well our system simulates a real catalytic system. We have discovered that an active catalyst for hydroformylation, *viz.* $HRh(CO)P_3$, can easily be obtained from the known compound $HRhP_4$. Its application as a catalyst, however, seems to be less convenient than the use of $Rh(acac)P_2$. First of all, the stability of these compounds is completely different: $HRhP_4$ is very unstable as a solid and cannot be stored; in contrast, $Rh(acac)P_2$ is stable for weeks. Furthermore, $Rh(acac)P_2$ can be synthesized with a much higher yield than can $HRhP_4$.

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