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Reactions of alkenes and alkynes with formaldehyde catalyzed by rhodium systems containing phosphine ligands

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Abstract. The reaction of alkenes (allyl alcohol, styrene and C₆ alkenes) with formaldehyde was efficiently performed by using Rh precatalysts formed *in situ* by the addition of triphenylphosphine (PPh₃), 1,2-bis(diphenylphosphino)ethane (dppe) or 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) to the complex Rh(acac)(CO)₂ at 130°C in 1,4-dioxane, yielding their corresponding aldehydes; the best catalytic system was Rh(acac)(CO)₂/2dppe, which generates the cationic complex [Rh(κ²-P,P-dppe)₂]⁺. However, the reaction of phenylacetylene with formaldehyde under the same reaction conditions generated styrene, which was found to be the product of transfer hydrogenation from formaldehyde.

Keywords: hydroformylation; formaldehyde; alkenes; alkynes; rhodium; phosphine.

Resumen. La reacción de alquenos (alcohol alílico, estireno y alquenos C₆) con formaldehído se realizó eficientemente usando precatalizadores de Rh formados *in situ* por adición de trifenilfosfina (PPh₃), 1,2-bis(difenilfosfino)etano (dppe) o 1,1,1-tris(difenilfosfinometil) etano (trifos) al complejo Rh(acac)(CO)₂ a 130°C en 1,4-dioxano, produciendo los correspondientes aldehídos. El mejor sistema catalítico fue Rh(acac)(CO)₂/2dppe, el cual genera el complejo catiónico [Rh(κ²-P,P-dppe)₂]⁺. Sin embargo, la reacción de fenilacetileno con formaldehído bajo las mismas condiciones de reacción generó estireno, el cual es el producto de la transferencia de hidrógeno del formaldehído.

Palabras clave: hidroformilación; formaldehído; alquenos; alquinos; rodio; fosfina.

Introduction

The hydroformylation of unsaturated substrates (alkenes, dienes and alkynes) is a well known synthetic tool for the synthesis of a wide range of organic molecules of high commercial value and it is also one of the largest industrial scale applications of organometallic catalysis for the manufacture of aldehydes and/or alcohols [1-4]. All industrial hydroformylation processes make use of highly toxic and flammable syn-gas (CO and H₂ mixture), which has restricted somehow the widely use of hydroformylation in industry and academia. Hence, performing hydroformylation without the use of syn-gas is highly desired and will contribute to the further advancement of sustainable chemistry. Formaldehyde, either in solution (formalin) or as solid (paraformaldehyde), is one of the surrogates for syn-gas in hydroformylation reactions [5].

However, the version of hydroformylation of alkenes with formaldehyde has received very little attention since the first report of Okano et al. [6] in 1982. In the following three decades, the hydroformylation of unsaturated substrates with formaldehyde has been reported intermittently [7-11] and only recently this area has attracted significant interest, as emphasized by Franke et al. [12] in a review on the hydroformylation

reaction and its applications. In fact, some of us reported the potential of rhodium catalysts containing triphenylphosphine (PPh₃), diphosphines [Ph₂P(CH₂)_nPPh₂; n = 2, 3 and 4] and 1,1,1-tris(diphenylphosphino)ethane (triphos) in the hydroformylation with formaldehyde of 1-hexene (Eq. 1) and other C₆ alkenes; the system Rh(acac)(CO)₂/2dppe [dppe: 1,2-bis(diphenylphosphino)ethane] was the most active precatalyst [13,14]. Morimoto et al. [15] reported the highly linear regioselective hydroformylation of 1-alkenes using formaldehyde to give aldehydes by using two rhodium catalysts: Rh₂Cl₂(binap)₂ [binap: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] and Rh-H(CO)₂(xantphos) [xantphos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene]. Taddei et al. [16] showed that this reaction may be accelerated under microwave dielectric heating. Other recent works on the reaction of alkenes, dienes and alkynes with formaldehyde have been also reported [17-23].

There are two possible pathways for the metal-catalyzed hydroformylation of alkenes with formaldehyde (Fig. 1), which proceed through the formation of a hydride-formyl complex, M(H)(CHO): i) the classical hydroformylation mechanism (path A), which consists in the decarbonylation of the hydride-formyl intermediate to give either a dihydride-carbonyl intermediate or syn-gas, with the subsequent traditional alkene

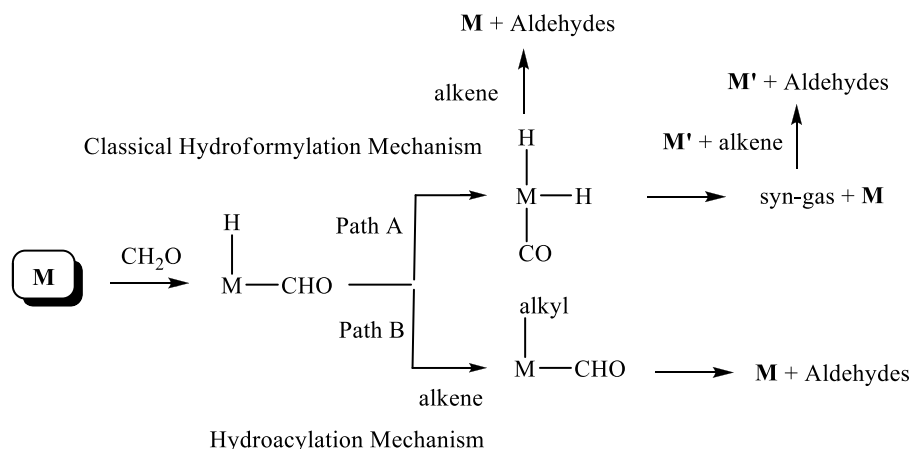
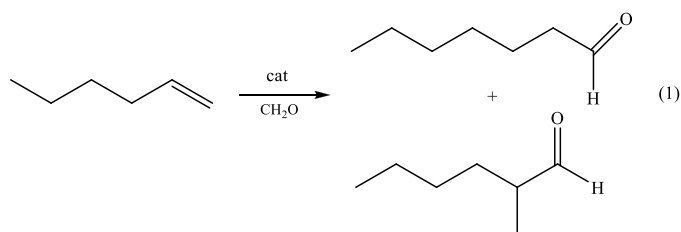


Fig. 1. Possible pathways for the catalytic hydroformylation of alkenes with formaldehyde.

hydroformylation catalyzed by either the same or other precatalyst, and ii) the hydroacylation mechanism (path B), which occurs by alkene insertion into the M-H bond and the reductive elimination of alkyl and formyl ligands.

Morimoto et al. [15] demonstrated that the hydroformylation of 1-alkenes proceeds through the formaldehyde decomposition to give syn-gas catalyzed by a rhodium-binap complex and the posterior classical alkene hydroformylation catalyzed by Rh-xantphos one. More recently, some of us reported a detailed kinetic and mechanistic study of the hydroformylation of 1-hexene with formaldehyde (Eq. 1) catalyzed by $[\text{Rh}(\kappa^2\text{-P,P-dppe})_2]\text{acac}$; experimental results and theoretical DFT calculations proportioned evidences on favor of a hydroacylation mechanism [24].



In the present work, we disclose the use of rhodium precatalysts containing PPh_3 , dppe and triphos for the reaction of other unsaturated substrates (allyl alcohol, styrene and phenylacetylene) with formaldehyde, including some coordination chemistry studies; the initial rates of these reactions were also compared with the hydroformylation of C_6 alkenes with formaldehyde.

Results and discussion

Catalytic reactions of unsaturated substrates with formaldehyde

The reaction of allyl alcohol, styrene and phenylacetylene with formaldehyde in 1,4-dioxane solution was studied using several

rhodium systems, which were formed *in situ* by the reaction of the complex $\text{Rh}(\text{acac})(\text{CO})_2$ with the corresponding equivalents of triphenylphosphine (PPh_3), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) at 130 °C.

In Table 1 are summarized the results of the hydroformylation of allyl alcohol (2-propen-1-ol) to produce 4-hydroxybutanal and 2-methyl-3-hydroxypropanal, products that were identified for the molecular ion peaks at M^+ 88, besides higher intensity peaks (base peaks) at m/z 42 and 57 u.m.a corresponding to the loss of 46 units (ethanol) and 31 units (methanol), respectively; propanal was also obtained (17-53% in 4 h), by isomerization of this substrate and subsequent tautomerization, as may be observed in Fig. 2.

Although the unmodified complex $\text{Rh}(\text{acac})(\text{CO})_2$ was catalytically inactive for the hydroformylation of allyl alcohol with formaldehyde, the addition of PPh_3 , dppe and triphos to this complex did induce the formation of the corresponding aldehydes (TON varying from 24 to 195) at 130°C. The highest activity (with the lowest percentage of isomerization-tautomerization to propanal) was obtained when two equivalents of dppe were added to $\text{Rh}(\text{acac})(\text{CO})_2$, which generates the cationic

Table 1. Hydroformylation of allyl alcohol with formaldehyde catalyzed by rhodium-phosphine systems

Precatalyst	% propanal	% hydroformylation	TON	l/b
$\text{Rh}(\text{acac})(\text{CO})_2/2 \text{ PPh}_3$	46	26	78	6
$\text{Rh}(\text{acac})(\text{CO})_2/3 \text{ PPh}_3$	48	25	75	7
$\text{Rh}(\text{acac})(\text{CO})_2/\text{dppe}$	53	14	42	23
$\text{Rh}(\text{acac})(\text{CO})_2/2 \text{ dppe}$	17	65	195	30
$\text{Rh}(\text{acac})(\text{CO})_2/\text{triphos}$	40	8	24	8

Conditions: $[\text{Rh}] = 3.3 \times 10^{-3} \text{ M}$, $[\text{allyl alcohol}] = 1.0 \text{ M}$, $[\text{CH}_2\text{O}] = 2.5 \text{ M}$, $T = 130^\circ\text{C}$, solvent = 1,4-dioxane, $t = 4 \text{ h}$, TON = mole of product per mole of catalyst; *l/b* = linear to branched ratio.

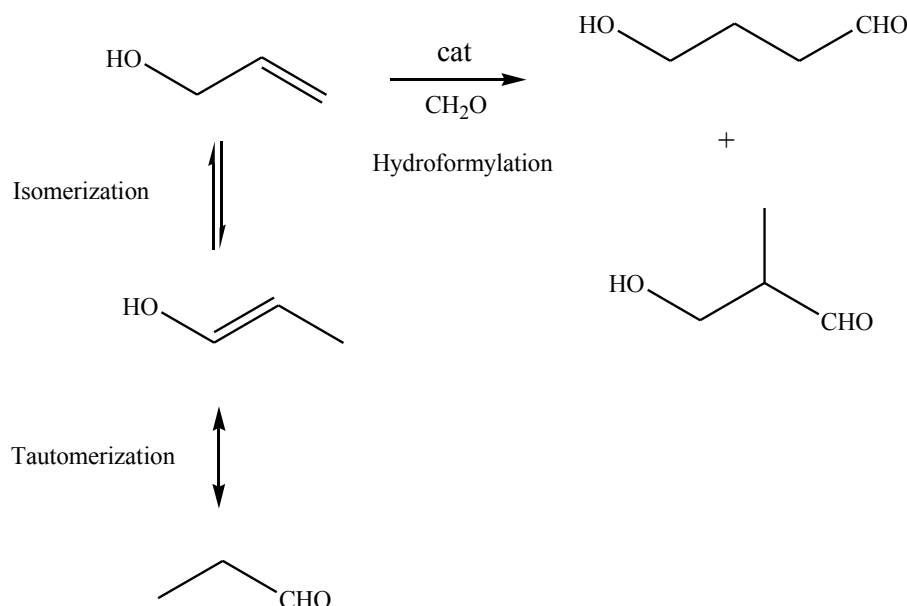
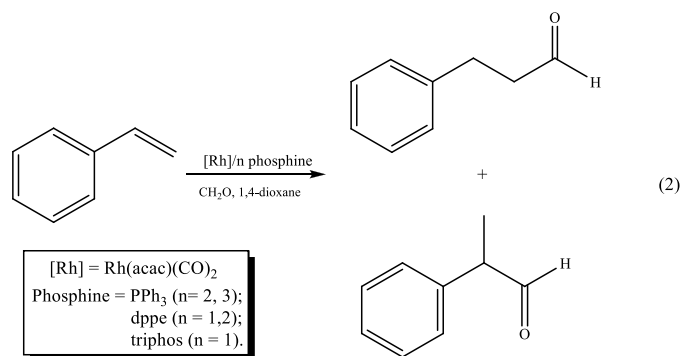


Fig. 2. Products of the catalytic reaction of allyl alcohol with formaldehyde.

complex $[\text{Rh}(\kappa^2\text{-P,P-dppe})_2]^+$, as reported by Rosales *et al.* [13,14,24]. The catalytic activity of this system was four times higher than the activity generated by addition of 1 eq dppe, twice higher than those generated by addition of 2 or 3 eq. of PPh_3 and eight times higher than that of the Rh/triphos system. Regioselectivities towards the corresponding linear aldehyde were from moderate to high, being the most selective system Rh/2 dppe ($I/b = 30$). For comparison, under the same reaction conditions, the complex $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ displayed a good activity (36 TON in 4h) with high regioselectivity toward the linear aldehyde ($I/b = 21$), results which are concordant with those reported by Seok *et al.* [11].

On the other hand, these systems were also active for the hydroformylation of styrene with formaldehyde (Eq. 2), under the same reaction conditions (see Table 2), obtaining the corresponding linear and branched aldehydes (3-phenyl- and 2-phenyl-propanal), which were identified by mass spectra (molecular ion peak M^+ at m/z 134); small amounts of the hydrogenation product (ethylbenzene) were found (< 2%). The systems Rh/ $n\text{PPh}_3$ showed low activities (conversions lower than 10%, TON in the range between 15 and 21, in 4 h), and also low regioselectivities toward the linear aldehyde ($I/b = 1.6\text{--}2.5$). The system Rh/2dppe also showed the highest activity (TON = 144), although the regioselectivity was moderate ($I/b = 2.0$). The production of appreciable amounts of the branched aldehyde (ca. 33%) in the reaction catalyzed by Rh/2dppe is of special interest for application to the highly enantioselective and regioselective asymmetric hydroformylation of vinylarenes (styrenes and naphthylethylenes) with formaldehyde, which could provide high added-value products such as non-steroidal anti-inflammatory drug intermediates [25].



The results obtained for the hydroformylation of allyl alcohol with formaldehyde catalyzed by rhodium systems containing phosphine ligands differ somewhat to those obtained for the reaction of 1-hexene [13, 14] and styrene with formaldehyde by using the same catalytic systems. In fact, for the hydroformylation of simple alkenes (1-hexene and styrene), the order of catalytic activity is Rh/2dppe > Rh/dppe > Rh/triphos > Rh/ $n\text{PPh}_3$, whereas for the hydroformylation of allyl alcohol (an alkene with oxygen atom in β position), the order is Rh/2dppe > Rh/ $n\text{PPh}_3$ > Rh/dppe > Rh/triphos. The higher activity of the Rh/ $n\text{PPh}_3$ systems for the hydroformylation of allyl alcohol compared with simple alkenes may be explained by the coordination of the OH group of the substrate to the metal center, which should hinder the decarbonylation of the formyl group; the coordination of OH group of the substrate to the metal center has been reported by Seok *et al* [11] for the hydroformylation of allyl alcohol and acrolein catalyzed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. Although the hydroformylation of alkenes with formaldehyde

Table 2. Hydroformylation of styrene with formaldehyde catalyzed by rhodium-phosphine systems.

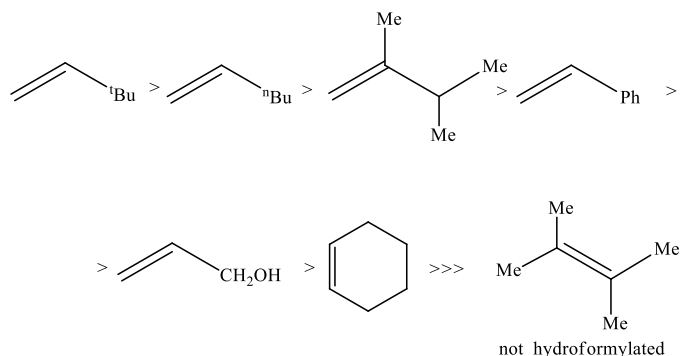
Catalytic System	% conversion	TON	<i>l/b</i>
Rh(acac)(CO) ₂ /2 PPh ₃	7	21	1.6
Rh(acac)(CO) ₂ /3 PPh ₃	5	15	2.5
Rh(acac)(CO) ₂ /dppe	35	105	1.4
Rh(acac)(CO) ₂ /2dppe	48	144	2.0
Rh(acac)(CO) ₂ /triphos	21	63	1.9

Conditions: [Rh] = 3.3×10^{-3} M, [styrene] = 1.0 M, [CH₂O] = 2.5 M, T = 130°C, solvent = 1,4-dioxane, t = 4 h, TON = mole of product per mole of catalyst; *l/b* = linear to branched ratio.

catalyzed by Rh/2dppe proceeds via hydroacylation mechanism [24], the reaction catalyzed by Rh/nPPh₃ and Rh/1dppe systems probably proceeds through a classic mechanisms in view of experimental evidences obtained in the coordination chemistry reported in the present work (*vide infra*). In fact, the Rh/3PPh₃ system is a more active precatalyst than Rh/dppe one for the alkene hydroformylation under syngas conditions.

For comparative effects, Table 3 shows the measured reaction rates for the hydroformylation with formaldehyde of some olefins catalyzed by [Rh(dppe)₂]acac, the most active precatalyst. 3,3-Dimethylbut-1-ene and 2,3-dimethylbut-1-ene were hydroformylated exclusively to their corresponding linear products (4,4- and 3,4-dimethylpentanal, respectively), presumably due to steric impediments for the formation of the branched alkyl intermediates. As may be observed, the simple alkenes without steric effect (3,3-dimethyl-1-butene and 1-hexene) were hydroformylated faster than 2,3-dimethyl-1-butene at 100°C, whereas styrene (vinyl arene), allyl alcohol (alkene with an oxygen in β position) and cyclohexene (cyclic alkene) require a higher temperature (130°C). Finally, the internal alkene, 2,3-dimethyl-2-butene, was not hydroformylated under these

reaction conditions due to steric hindrance. The order of reactivity of these alkenes is:



On the other hand, the *l/b* ratio was moderate for 1-hexene and styrene (*l/b* = 1.7 and 2.0, respectively) whereas a highly linear regioselective hydroformylation was observed for allyl alcohol substrate (*l/b* = 30). These results are interesting because the system Rh/2dppe catalyzes the hydroformylation with formaldehyde of either simple alkenes (aliphatic and cyclic alkenes and vinylarenes) or alkenes containing oxygen at the β position to the carbon-carbon double bond, contrary to the results obtained by Seok *et al.* [11], who found that the complex RhH(CO)(PPh₃)₃ was more active for the hydroformylation with formaldehyde of alkenes containing oxygen at the β position to the carbon-carbon double bond than for simple alkenes, for which lower activities were found.

Finally, the reaction of phenylacetylene with formaldehyde catalyzed by Rh/phosphine systems, under the same reaction conditions (130 °C, 4h), did not generate the corresponding unsaturated aldehydes (3-phenyl- and 2-phenyl-propenal). Instead, styrene was almost quantitatively obtained in these reactions in 4 h, which may be the product of hydrogen transfer product of the formaldehyde or from the 1,4-dioxane solvent [26]. To demonstrate this, the same reactions were carried out in absence of formaldehyde; under these conditions phenylacetylene

Table 3. Comparison of reaction rates for the olefin hydroformylation with formaldehyde catalyzed by [Rh(dppe)₂]acac.

Olefin	Hydroformylation Products	$10^5 r_i$ (Ms ⁻¹)	% Conversion (5 h)	<i>l/b</i>
1-hexene ^a	Heptanal 2-methylhexanal	8.09 ± 0.11	41	1.7
3,3-dimethyl-1-butene ^a	4,4-dimethylpentanal	14.8 ± 0.21	48	-
2,3-dimethyl-1-butene ^a	3,4-dimethylpentanal	0.18 ± 0.02	4	-
Styrene ^b	3-phenylpropanal 2-phenylpropanal	3.31 ± 0.05	23	2.0
Allyl alcohol ^b	4-hydroxybutanal 3-hydroxypropanal	1.66 ± 0.03	13	30.1
Cyclohexene ^b	Cyclohexylcarboxaldehyde	0.15 ± 0.03	5	-
2,3-dimethyl-2-butene ^b	-	-	0	-

Conditions: [Rh] = 1.7×10^{-3} M, [olefin] = 0.13 M, [CH₂O] = 0.5 M, T = 100°C^a, 130°C^b; *l/b* = linear to branched ratio.

was not hydrogenated, which indicates that the hydrogenation of this substrate proceeds through decomposition of formaldehyde [27] and hydrogen transfer toward the metal center yielding rhodium-dihydride species and subsequently from rhodium to phenylacetylene.

Reactions of the Rh/dppe systems with formaldehyde

In order to gain further understanding on the mechanism of hydroformylation of unsaturated substrates with formaldehyde, the interaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with dppe and formaldehyde was studied; the results are shown in Fig. 3. In previous works, we have reported that reaction of the dicarbonylrhodium complex with 2 equivalents of dppe in 1,4-dioxane solution under reflux produces the cationic complex $[\text{Rh}(\kappa^2\text{-P,P-dppe})_2]^+$ (**1**), as its acetylacetonate (acac) salt [13, 14]; coordination chemistry and theoretical DFT studies followed us to propose that complex **1** is the active catalytic species. When the reaction of

this complex with an excess of formaldehyde ($[\text{CH}_2\text{O}]/[\text{Rh}] = 10$) was carried out, it was impossible to detect any other species different than the cationic bis(dppe)rhodium complex [24]. We considered that the cationic bis(dppe)rhodium complex reacted reversibly with formaldehyde to produce $[\text{RhH}(\text{CHO})(\kappa^2\text{-P,P-dppe})_2]^+$ (**2**), which in absence of an unsaturated substrate (alkene or alkyne) come back to **1**. Now, we performed these reactions by using only one equivalent of dppe. When the reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with 1 equivalent of dppe was carried out, the presence of complex $[\text{Rh}(\kappa^2\text{-P,P-dppe})_2]^+$ (approximately 50 %) was observed as the only phosphorous complex; in some reactions, a small amount of a carbonyl complex was detected by IR (ν_{CO} in 1960 cm^{-1}), which is probably $\text{Rh}(\text{acac})(\text{CO})(\kappa^1\text{-P-dppe})$ (**3**) by comparison with the triphenylphosphine analogue complex, namely $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ [28]. The same reaction in the presence of an excess of formaldehyde mainly produces a mixture of two carbonyl complexes, as detected by IR ($\nu_{\text{CO}} = 2100, 2055$ and 2010 cm^{-1}) and $^{31}\text{P}\{^1\text{H}\}$

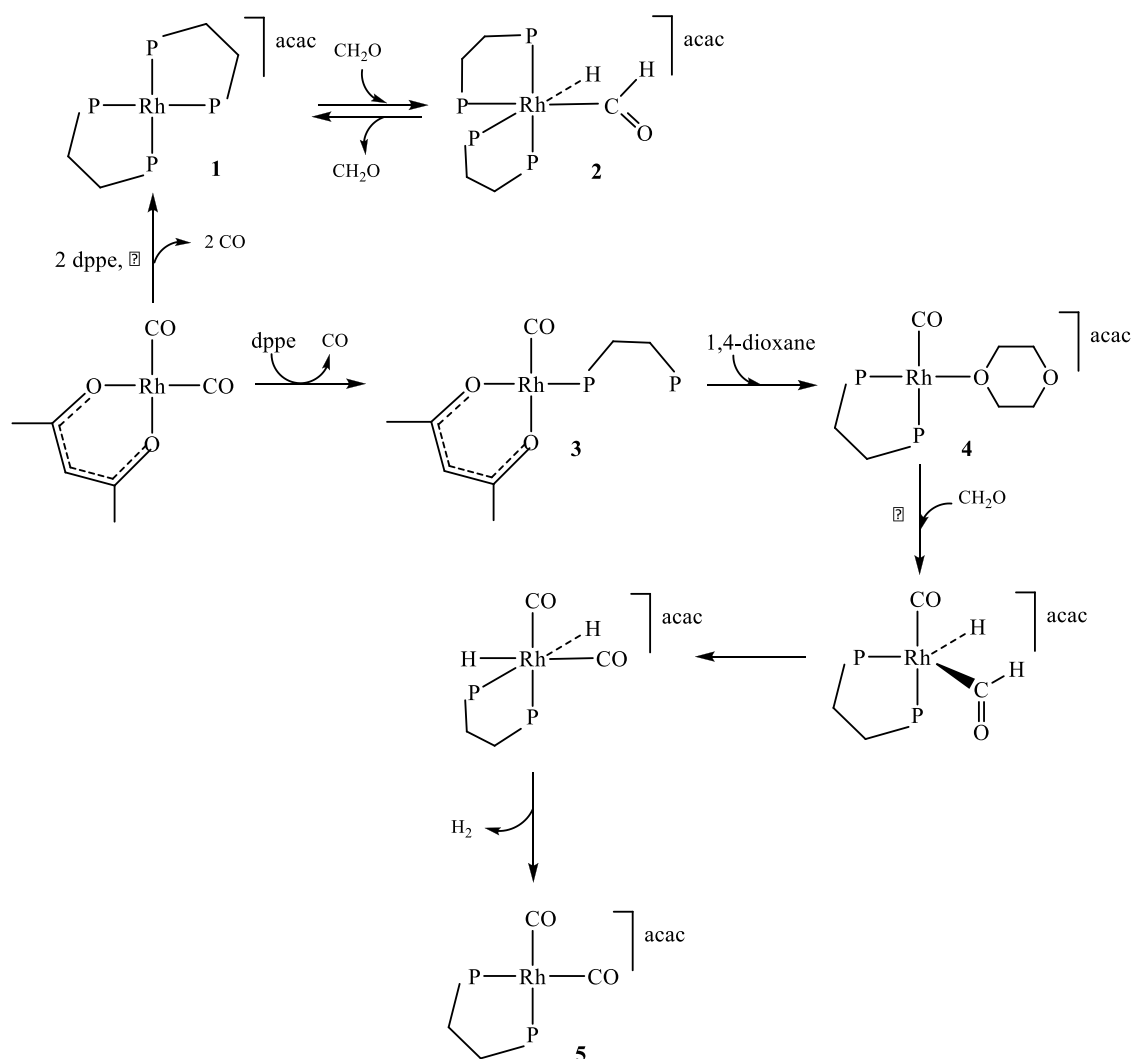


Fig. 3. Reactions of $\text{Rh}(\text{acac})(\text{CO})_2$ with dppe and formaldehyde.

NMR, a monocarbonyl complex, possibly $[\text{Rh}(\text{CO})(1,4\text{-dioxane})(\kappa^2\text{-P,P-dppe})]^+$ (**4**), and small amounts of the dicarbonyl one, namely $[\text{Rh}(\text{CO})_2(\kappa^2\text{-P,P-dppe})]^+$ (**5**). The monocarbonyl complex ($\nu_{\text{CO}} = 2010 \text{ cm}^{-1}$) showed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum two doublets of doublets (dd) centered at 67.0 and 66.9 ppm with coupling constants $^1J_{\text{Rh-P}} = 131 \text{ Hz}$ and $^2J_{\text{P-P}} = 12 \text{ Hz}$, whereas the dicarbonyl complex ($\nu_{\text{CO}} = 2100$ and 2055 cm^{-1}) showed a doublet at 67.0 ppm [$^1J_{\text{Rh-P}} = 155 \text{ Hz}$]. Complex **4** may be formed from **3** by dissociation of an acac ligand and the subsequent coordination of both the other arm of dppe ligand as well as of a molecule of 1,4-dioxane, whereas complex **5** may be obtained by the reaction of **4** with formaldehyde to produce initially a hydride-formyl intermediate, $[\text{RhH}(\text{CHO})(\text{CO})(\kappa^2\text{-P,P-dppe})]^+$, which suffers decarbonylation to generate a dihydride-dicarbonyl complex and finally the reductive elimination of dihydrogen. Fairlie and Bosnich [29] reported the synthesis of the ClO_4 salt of complex **5**, as well as similar

complexes related to **4**, namely $[\text{Rh}(\text{CO})(\text{ketone})(\kappa^2\text{-P,P-dppe})]\text{ClO}_4$ (ketone: acetone and cyclopentanone).

These results indicate that in presence of one equivalent of dppe, the rhodium-catalyzed hydroformylation with formaldehyde probably proceed through a classical mechanism via formaldehyde decomposition. Perhaps, the hydroformylation of alkenes with formaldehyde employing the Rh/nPPH_3 catalytic systems occurs through of a similar route than the Rh/dppe -catalyzed reaction.

Mechanistic proposal for the reactions of unsaturated substrates with formaldehyde

On the basis of experimental findings and the present knowledge of these reactions [15,24], we propose a plausible general mechanism for the reaction of the different substrates (alkenes and alkynes) with formaldehyde catalyzed by rhodium-phosphine systems, which is shown in Fig. 4. The catalytic cycle

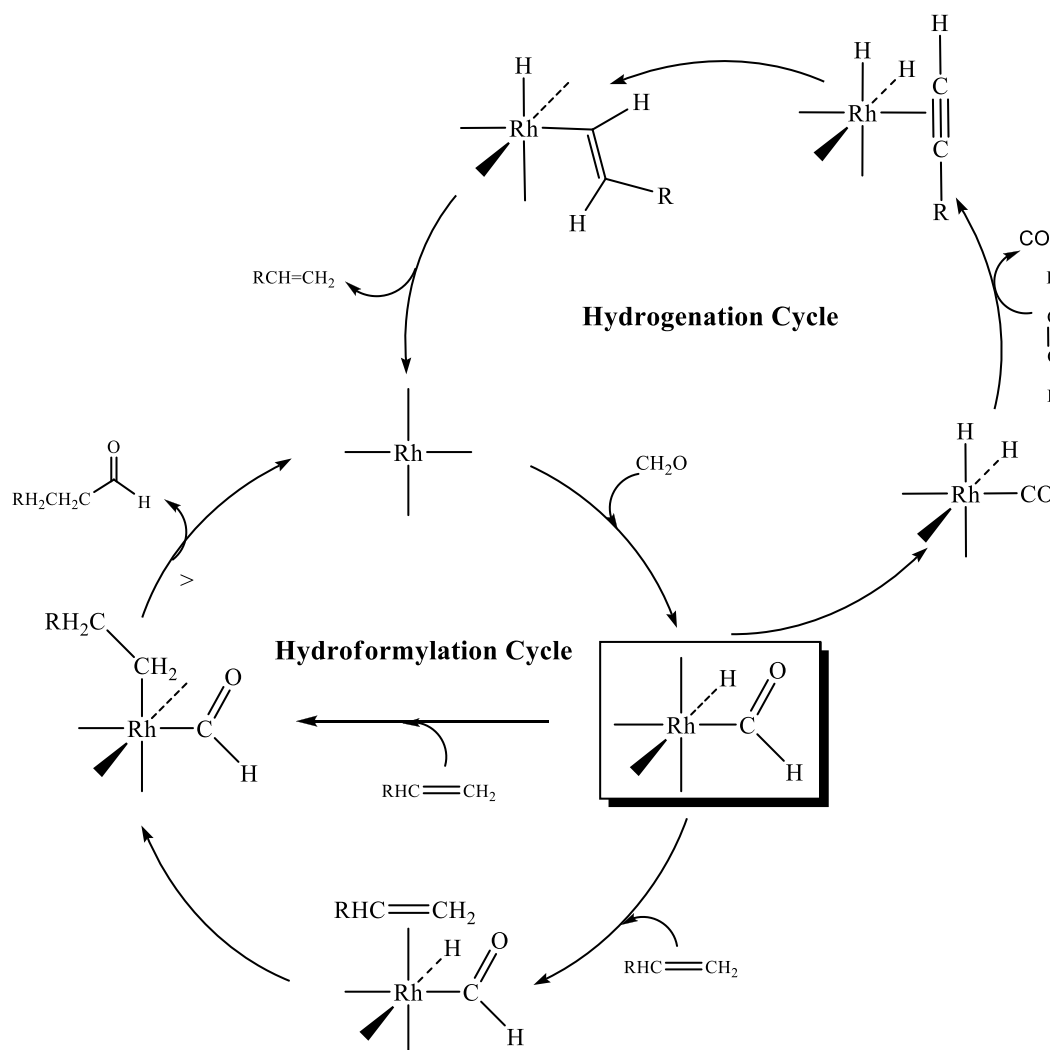


Fig. 4. Proposed catalytic cycle for the reaction of alkenes and alkynes with formaldehyde catalyzed by rhodium-phosphine systems.

is initiated with the oxidative addition of formaldehyde C-H bond to generate a hydride-formyl rhodium species, which we suppose is the key intermediate of both cycles. For hydroformylation of alkenes with Rh/2dppe system, the following steps are the insertion of olefin into the Rh-H bond to generate an alkyl-formyl species and, finally, the reductive elimination of the corresponding aldehydes to regenerate the active species and restart the cycle; when Rh/dppe or Rh/nPPh₃ systems are used as precatalysts, the reaction occurs probably through a classical hydroformylation mechanism (see Fig. 1). On the other hand, if the substrate is phenylacetylene, the hydride-formyl species suffers the decarbonylation of the formyl group to yield a dihydro-carbonyl species; substitution of CO ligand by phenylacetylene followed by the subsequent hydride transfer toward one of the carbon atom containing the triple bond and the reductive elimination of styrene completes the catalytic hydrogenation cycle.

Conclusions

The hydroformylation of the carbon-carbon double bond of allyl alcohol and styrene was performed with formaldehyde by using rhodium-phosphine precatalysts in dioxane at 130 °C. The best system was that formed *in situ* by addition of 2 eq of dppe to the complex Rh(acac)(CO)₂, yielding the cationic species [Rh(κ²-P,P-dppe)₂]⁺, which displayed the highest activity. However, the reaction of phenylacetylene with formaldehyde under the same reaction conditions did generate styrene, which is the product of hydrogen transfer from the formaldehyde.

Experimental Section

Chemicals

Substrates (1-hexene, allyl alcohol, styrene, 3,3-dimethyl-1-butene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and phenylacetylene) and the catalytic reaction solvent [1,4-dioxane (Riedel de Haens)] were purified by known procedures and distilled at reduced pressure before using [30]. CDCl₃ (Aldrich) was dried using activated molecular sieves. Other chemicals [RhCl₃·xH₂O, PPh₃, dppe and triphos (Stream Chemicals) and paraformaldehyde (Aldrich)] and solvents [toluene (Riedel de Haens), cycloheptane, ethylacetate and n-pentane (Merck)] were used as received.

General procedure

All manipulations were conducted with the rigorous exclusion of air using a vacuum line, an argon-filled Schlenk line and/or an argon-filled glovebox. Complex Rh(acac)(CO)₂ was prepared from RhCl₃·xH₂O by a published procedure [28] whereas formaldehyde was generated *in situ* in the reaction medium dissolving paraformaldehyde in 1,4-dioxane.

Physical measurements

The products of the catalytic reactions were analyzed by GC using a 3300 Series VARIAN instrument fitted with a flame ionization detector (FID) and a 2 m 20 % SP-2100 on a 0.1 % carbowax 100/120 Supelcoport column, using N₂ as carrier gas; the results were quantified with a VARIAN 4400 microcomputer. The products were additionally analyzed by a GC/MS HP 5890/5971 coupled system using a Quadrex PONA 5% phenyl methyl silicone, 25m, 320 μm column. Cycloheptane, ethyl acetate and toluene were used as internal standards for the reactions of C₆ alkenes, allyl alcohol and styrene and phenylacetylene, respectively. The IR spectra (in KBr disk) were recorded on a Shimadzu 8300 FT-IR instrument. ³¹P{¹H}-NMR spectra were recorded on a Bruker AM-300 spectrometer; chemical shift are expressed in p.p.m. upfield from H₃PO₄.

Catalytic reactions

The catalytic reactions were performed in a Fischer Porter reactor, in which a solution of Rh(acac)(CO)₂ (0.05 mmol), the required amount of the corresponding phosphine, the substrate (15 mmol), formaldehyde (1.125 g, 40 mmol), the corresponding internal standard (8.3 mmol) and 1,4-dioxane (total volume 15 mL) were placed in the reactor. The system was flushed three times with argon and then heated to the desired reaction temperature; after 4 h with constant stirring, the system was cooled in ice. At the end of the catalytic reactions, the products were analyzed by GC.

Measurements of the initial rate of reactions

In order to measure the initial rate of the hydroformylation of olefins with formaldehyde, all the runs were performed at low conversions [31], by using a Parr Instrument high-pressure reactor. This reactor was provided with an arrangement for sampling of liquid contents, besides of automatic temperature, pressure and variable stirrer speed controls. In a typical experiment, a solution of the catalytic system, the corresponding substrate, formaldehyde, the internal standard (8.3 mmol) and 1,4-dioxane (total volume 30 mL) was placed in the reactor. The solution was deoxygenated and charged with argon at atmospheric pressure and the reactor was heated to the desired temperature. Aliquots of the reaction mixture were taken at regular intervals of time, which were monitored by using GC.

The data of the reactions were plotted as molar concentration of the products *versus* time in seconds yielding straight lines, which were fitted by conventional linear regression programs ($r^2 > 0.95$); initial rates of the reaction (r_i) were obtained from the corresponding slopes.

Reactions of Rh(acac)(CO)₂ with dppe and formaldehyde

These reactions were performed by the interaction of Rh(acac)(CO)₂ (103 mg, 0.4 mmol) with one (160 mg, 0.4 mmol) or two equivalents (320 mg, 0.8 mmol) of dppe in the presence or

absence of a ten-fold excess of formaldehyde (120 mg, 4 mmol) in 1,4-dioxane (10 mL) under reflux for 2 h. The corresponding solution was evaporated until dryness and the solid was washed with n-pentane.

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