

Note

Hydroformylation of alkenes with paraformaldehyde catalyzed by rhodium–phosphine complexes

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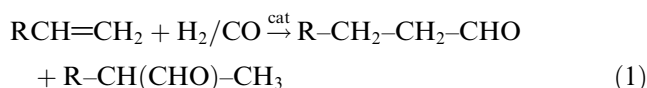
Abstract

The hydroformylation of medium-chain C₆ olefins and of allyl alcohol was achieved with paraformaldehyde in dioxane solution using rhodium catalysts with mono-, bi-, and tri-dentate phosphine ligands. The highest activities with *n/i* ratios around 2, were obtained for a system derived from [Rh(dppe)₂]⁺, prepared in situ by reaction of Rh(acac)(CO)₂ with 2 eq of dppe.
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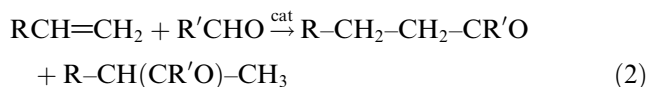
Keywords: Hydroformylation; Paraformaldehyde; Olefins; Rhodium; Phosphine

1. Introduction

The hydroformylation of alkenes (Eq. (1)) is a well-known synthetic tool for a wide range of organic molecules of commercial value and it is also one of the largest scale applications of homogeneous catalysis in industry, the manufacture of aldehydes and alcohols. The major capacity is based on the low pressure oxo process (LPO) using phosphine-modified rhodium carbonyl complexes [1] but in recent years, new applications for high added-value intermediates for the production of fine chemicals and pharmaceuticals and novel highly active and/or selective catalysts have emerged in the literature [2,3].



The related alkene hydroacylation reaction (Eq. (2)) has been employed in the synthesis of a variety of ketones by addition of an aldehyde to the C=C bond, including cyclic ketones by intramolecular hydroacylation [4].



This reaction represents a possible alternative to olefin hydroformylation, which avoids the use of high-pressure equipment and of highly toxic and explosive syngas mixtures, through its substitution by inexpensive formaldehyde (Eq. (2), R' = H). This version of olefin hydroformylation has received little attention [5–10]. Ahn et al. [10] reported the use of RhH(CO)(PPh₃)₃ for the hydroformylation of a number of alkenes with paraformaldehyde; the reaction was most adapted to olefins

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containing oxygen at the β position to the carbon–carbon double bond (allyl alcohol, acrolein and methylacrylate) but activities were rather low (<25% conversion in 7 h) although with excellent selectivity for linear aldehydes (*n/i* 20); less attractive results were obtained for simple olefins such as propylene, hex-1-ene and styrene. In this note, we disclose the potential of rhodium catalysts containing mono-, bi- and tri-dentate phosphines in the reaction of C₆ olefins with paraformaldehyde; as well as some preliminary studies on the possible active species involved in the catalytic cycle. The hydroformylation of medium-length C₅–C₈ alkenes is of interest in connection with naphtha upgrading [11,12].

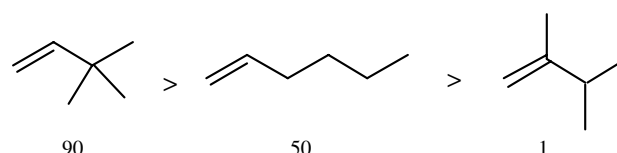
2. Results and discussion

The hydroformylation of hex-1-ene with paraformaldehyde in dioxane solution was studied using RhH(CO)(PPh₃)₃ (**1**), Rh(acac)(CO)₂ (**2**), and several systems formed in situ by the interaction of **2** with PPh₃, 1,2-bis(diphenylphosphino)ethane, dppe and 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, as summarized in Table 1.

At 100 °C, **1** displayed a rather low activity (ca. 14 TN in 4 h) with *n/i* = 1.4. Addition of up to 5 eq of PPh₃ did not produce substantial changes in the activity or the selectivity of the catalyst; these results are consistent with those obtained by Ahn et al. [10]. Under the same conditions, complex **2** (unmodified with phosphines) was catalytically inactive for the hydroformylation of hex-1-ene with paraformaldehyde; however, the addition of PPh₃, dppe and triphos to the system did induce the formation of the corresponding aldehydes. The highest activity was obtained when two equivalents of dppe were added to **2**, about six times higher than the catalyst generated by addition of 1 eq dppe, and four times higher than the one generated by addition of 1 eq triphos. Isomerization to hex-2-enes amounts to about 15% of the products. Selectivities for the linear aldehyde were moderate, the most selective systems being **2**/dppe and **2**/triphos (*n/i* ca. 2). When the temper-

ature was increased to 130 °C faster reaction rates were obtained for the in situ prepared catalysts; the activity of the **2**/2dppe system was four and six times higher than those of **2**/dppe and **2**/triphos, respectively, and close to 20 times more active than the other systems; raising the temperature did not produce any major effect on selectivity. At 150 °C, the catalytic activities obtained were lower than those accomplished at 130 °C and rather similar to those found at 100 °C; some catalyst decomposition may be occurring in that case.

The Rh(acac)(CO)₂/2dppe system was also an active precatalyst for the hydroformylation with paraformaldehyde of other C₆ olefins at 130 °C, the relative order of individual rates being: 3,3-dimethylbut-1-ene > 1-hexene > 2,3-dimethylbut-1-ene in an approximate ratio 90:50:1.



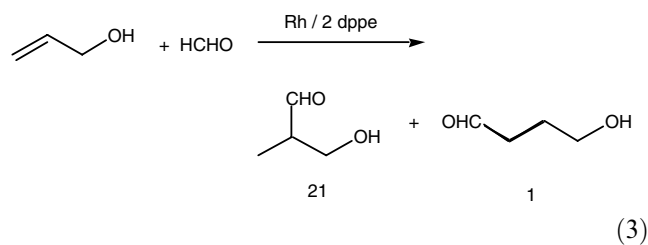
3,3-Dimethylbut-1-ene and 2,3-dimethylbut-1-ene were hydroformylated exclusively to their corresponding linear products (4,4- and 3,4-dimethylpentanal, respectively), presumably due to steric impediments for the formation of the branched alkyl or acyl intermediates. Cyclohexene was only slowly hydroformylated into cyclohexylcarboxaldehyde at 150 °C while the tetra-substituted 2,3-dimethylbut-2-ene could not be hydroformylated under these reaction conditions.

Also, the Rh(acac)(CO)₂/2dppe system is useful for the hydroformylation of allyl alcohol with paraformaldehyde with very high selectivity for the branched product under the same reaction conditions. A turnover number of 129 was achieved in 4 h, producing 2-methyl-3-hydroxypropanal and 4-hydroxybutanal in a 21:1 ratio (Eq. (3)); propanal was also obtained (up to 30% in 4 h), by isomerization of allyl alcohol and subsequent tautomerization.

Table 1
Hydroformylation of 1-hexene with paraformaldehyde catalyzed by rhodium systems

Catalyst	100 °C		130 °C		150 °C	
	TN	<i>n/i</i>	TN	<i>n/i</i>	TN	<i>n/i</i>
RhH(CO)(PPh ₃) ₃	14 ± 3	1.4 ± 0.2	9 ± 2	1.5 ± 0.2	8 ± 2	2.1 ± 0.3
Rh(acac)(CO) ₂	0	0	12 ± 3	2.8 ± 0.3	12 ± 5	2.7 ± 0.2
Rh(acac)(CO) ₂ /3PPh ₃	6 ± 1	1.3 ± 0.2	10 ± 2	3.0 ± 0.3	9 ± 1	2.1 ± 0.3
Rh(acac)(CO) ₂ /dppe	19 ± 3	1.9 ± 0.4	49 ± 8	1.8 ± 0.2	32 ± 10	1.8 ± 0.3
Rh(acac)(CO) ₂ /2dppe	123 ± 7	1.7 ± 0.2	201 ± 9	1.7 ± 0.2	97 ± 13	1.8 ± 0.1
Rh(acac)(CO) ₂ /triphos	56 ± 5	2.2 ± 0.2	32 ± 4	2.5 ± 0.3	21 ± 5	1.9 ± 0.2

Conditions: [Rh] = 3.3 × 10⁻³ M, [1-hexene] = 1 M, solvent = dioxane, *t* = 4 h, TN = mole of product per mole of catalyst *n/i* = linear to iso aldehyde ratio. TN and *n/i* are expressed in means ± s.e.m.; *P* = 0.05.



We found that under our reaction conditions the complex $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ reported by Ahn et al. [10], displayed a lower catalytic activity for the hydroformylation of allyl alcohol (24 TN in 4 h) than our system $\text{Rh}(\text{acac})(\text{CO})_2/2\text{dppe}$, and about 50% of the products was propanal. Interestingly, the regioselectivity in this case is toward the linear aldehyde ($n/i > 20$).

In order to gain some knowledge on the active species involved in olefin hydroformylation with paraformaldehyde catalyzed by $2/2\text{dppe}$, $\text{Rh}(\text{acac})(\text{CO})_2$ was allowed to react with 2 eq dppe in dioxane in the presence and in the absence of an excess of paraformaldehyde. In both cases, the cationic complex $[\text{Rh}(\text{dppe})_2]^+$ was generated (as the acac salt) as characterized by NMR spectroscopy; in the ^1H spectrum the phenyl protons appear as a complex multiplet at 7.7–7.2 ppm, the CH_2 signals of dppe are observed as a multiplet at 2.2 ppm and a singlet at 2.5 is assigned to the acac⁻ counter-anion. The $^{31}\text{P}\{^1\text{H}\}$ spectrum consists of only a doublet at 58.8 ppm, with $J(\text{Rh}-\text{P}) = 133$ Hz. James and Mahajan [13] have previously reported this complex as the BF_4 salt. We thus believe that this cationic bis(phosphine) species is the precursor entering the catalytic cycle.

In conclusion, olefin hydroformylation was achieved with paraformaldehyde by use of rhodium–phosphine catalysts in dioxane under moderate reaction conditions. The system formed by addition of 2 eq of dppe to $\text{Rh}(\text{acac})(\text{CO})_2$ displayed the highest activity at 130 °C. Although the n/i ratios obtained are modest, this catalyst could be of use in applications that do not require a high regioselectivity, such as naphtha upgrading [11,12]. Hydroformylation with paraformaldehyde offers several advantages over the conventional process with syn-gas: it enables the reaction to be performed under atmospheric pressure of an inert gas in conventional glassware, not requiring high-pressure equipment and avoiding the use of lethal carbon monoxide. A kinetic analysis of this reaction, as well as further coordination chemistry studies and calculations are in progress, aimed at better understanding this system and at improving the selectivity properties.

3. Experimental section

3.1. General procedure

Manipulations were performed under N_2 using standard Schlenk techniques. Solvents and olefins were dis-

tilled over appropriate standard agents under N_2 prior to use. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was obtained from Pressure Chemicals and alkenes from Aldrich. IR spectra were recorded in a Nicolet Magna 560 spectrophotometer and NMR spectra were obtained in a Bruker Avance (300 MHz for ^1H) instrument at room temperature in CDCl_3 . GC analyses were performed in a 610 Series UNICAM instrument fitted with a thermal conductivity detector, a 3m 10% SE-30 on Supelcoport glass column and a UNICAM 4815 data system using helium as the carrier gas.

3.2. Catalytic runs

In a typical experiment, a solution of the precatalyst (0.05 mmol), the required amount of the corresponding phosphine, hex-1-ene (1.9 mL, 15 mmol), paraformaldehyde (1.125 g, 40 mmol), cycloheptane as internal standard (1.0 mL, 8.3 mmol) and dioxane (total vol 15 mL) were placed in a glass ampoule; the system was flushed three times with argon and then closed and heated to the desired reaction temperature. After 4 h with constant stirring, the ampoule was cooled in ice and the products were analyzed by GC. Each reaction was repeated at least twice in order to ensure reproducibility of the results.

3.3. Stoichiometric reactions

Complex **2** (103 mg, 0.4 mmol) and dppe (320 mg, 0.8 mmol) in dioxane (10 mL) were stirred vigorously under reflux for 2 h; the solution was evaporated under vacuum to about 1/3 of its initial volume and the product was precipitated by addition of *n*-pentane, filtered and dried in vacuo. Yield 80%. The same complex was obtained when this reaction was carried out in the presence of an excess of paraformaldehyde (120 mg, 4 mmol). ^1H RMN (CDCl_3 , 25 °C): 7.7–7.2 (series of m, 40H, PPh_2), 2.5 (s, 6H acac) and 2.2 ppm (m, 8H, CH_2-P); $^{31}\text{P}\{^1\text{H}\}$ RMN (CDCl_3 , 25 °C): 58.8 ppm (d, $^2J_{\text{P}-\text{Rh}} = 133$ Hz).

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