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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.

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].

$$\begin{aligned}\mathrm{RCH{=}CH_2} + \mathrm{H_2/CO} &\overset{\mathrm{cat}}{\rightarrow} \mathrm{R{-}CH_2{-}CH_2{-}CHO}\\ &+ \mathrm{R{-}CH(CHO){-}CH_3} \qquad (1)\end{aligned}$$

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].

$$\begin{aligned}\mathrm{RCH{=}CH_2} + \mathrm{R'CHO} &\overset{\mathrm{cat}}{\rightarrow} \mathrm{R{-}CH_2{-}CH_2{-}CR'O}\\ &+ \mathrm{R{-}CH(CR'O){-}CH_3} \qquad (2)\end{aligned}$$

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 $RhH(CO)(PPh_3)_3$ for the hydroformylation of a number of alkenes with paraformaldehyde; the reaction was most adapted to olefins

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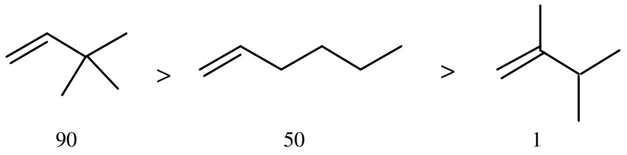
containing oxygen at the β position to the carbon–carbon double bond (allyl alcohol, acrolein and methylacrylate) but activities were rather low (<25% conversion in 7 h) although with excellent selectivity for linear aldehydes (*n*/*i* 20); less attractive results were obtained for simple olefins such 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 $RhH(CO)(PPh_3)_3$ (**1**), $Rh(acac)(CO)_2$ (**2**), and several systems formed in situ by the interaction of **2** with PPh_3, 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 PPh_3 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 PPh_3, 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 temperature 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 C_6 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 tetrasubstituted 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

Temperature	100 °C		130 °C		150 °C	
Catalyst	TN	*n*/*i*	TN	*n*/*i*	TN	*n*/*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: $[Rh] = 3.3 \times 10^{-3}$ 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.; $P = 0.05$.