Modified precursor systems for the hydroformylation of olefines

Carmen Claver*, Aurora Ruiz, Anna Maria Masdeu and **Nuria Ruiz**
Departament de Quimica, Facultat de Quimica, Pl. Imperial Tarraco 1, 43005 Tarragona (Spain)

Received March 6, 1990)

Abstract

Dichloroethane solutions of $[Rh(diolefin)(PR_3)_2]ClO_4$, diolefin = 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) and $[Rh(\mu\text{-}L)(COD)]_2$, L = OAc, OMe, complexes in the presence of different excesses of PR_3, R = Ph, OPh, OMe, have been used as catalysts precursor systems for the hydroformylation of 1-hexene at 5 bar and 80 °C. The influence of the nature of the PR_3 ligands and the effect of the different P/Rh ratios in the activity and selectivity of the hydroformylation reaction have been studied. Cyclohexene is also hydroformylated using $[Rh(\mu\text{-}L)(COD)]_2/P(OPh)_3$ as catalyst precursor.

Introduction

Much effort has been devoted to obtaining new rhodium complexes to be used as catalyst precursors in hydroformylation reactions. Of interest are the new dinuclear thiolate bridging ligand rhodium(I) complexes [1] and the related pyrazolate [2] and aminothiolate bridging ligands [3] which at low pressure behave as active and selective catalyst precursors in olefin hydroformylation.

Rhodium(I) mononuclear complexes containing a single β-diketonate ligand of the type $[Rh(acac)(PR_3)_2]$ have been recognized as catalyst precursors in hydroformylation of olefins and their catalytic activity has been recently studied in different hydroformylation conditions [4]. Many studies have been reported using the Wilkinson catalyst $[RhH(CO)(PPh_3)_3]$ in the presence of different phosphorous ligands [5–9].

However, in many cases the catalyst precursors are prepared *in situ* from solutions of the rhodium complexes in hydroformylation conditions and the presence of different phosphorous ligands [8–14]. Very often the rhodium complexes precursors are neutral, $[RhCl(CO)(PPh_3)_2]$ [7–9], $[Rh(\mu\text{-}Cl)(COD)]_2$ [9], $[Rh(\mu\text{-}Cl)(NBD)]_2$ [10, 12], $[Rh(\mu\text{-}Cl)(CO)_2]_2$ [8, 9, 13], $[Rh(\mu\text{-}OAc)(COD)]_2$ [11], $Rh_4(CO)_{12}$ [7–9], although the cationic complexes $[Rh(COD)(PR_3)_2]ClO_4$ [15] and [Rh(COD)(phenanthroline)]ClO_4 [16] have also been used.

Although it is known that in most cases the active species are probably the same as when using the Wilkinson catalyst, $[RhH(CO)(PPh_3)_3]$, the nature of the initial rhodium complex modifies the catalytic reaction. For instance in rhodium complexes containing chloride ligands, NEt_3 should be added to improve the hydroformylation activity [7, 8, 13].

On the other hand, the influence of the different phosphorous ligands on the activity and selectivity of the hydroformylation reaction has been observed: bulky phosphite ligands seem particularly suitable to hydroformylate hindered and cyclic olefins [11]. The effect of excess of the phosphorous ligand has been studied in catalyst precursors related to the Wilkinson catalyst [7, 8]. It has been shown that an excess of phosphorous ligand increases the selectivity, probably due to the steric hindrance produced by the formation of species with more phosphorous ligands bonded to the metal center and decreases the activity because of the stabilization of the species which must dissociate the phosphorous ligands during the catalytic cycle [7, 8]. However, the effect of the excesses strongly depends on the phosphorous ligand used. Recently, it has been reported that the activity and regioselectivity of rhodium hydroformylation catalysts containing 1,2,5-triphenylphosphole as ligand are independent of the excess in the catalytic hydroformylation of alkenes [13].

We report here the hydroformylation of 1-hexene and cyclohexene at low pressure ($P = 5$ bar, $T = 80$ °C) using catalyst precursors generated *in situ* from cationic and neutral rhodium complexes, modified by different PR_3 ligands.

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

The influence of the nature of the phosphorous ligand and the effect of the PR_3/Rh ratio on the catalytic activity and selectivity are discussed.

Experimental

All solvents were distilled and stored under nitrogen atmosphere. All preparations were carried out under nitrogen by Schlenk techniques. The complexes $[Rh(COD)(PPh_3)_2]ClO_4$ [17], $[Rh(\mu\text{-}OAc)(COD)]_2$ [18] and $[Rh(\mu\text{-}OMe)(COD)]_2$ [19] were prepared according to literature methods. The elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded on a Nicolet 5ZDX-FT instrument using KBr pellets or solutions.

Hydroformylation experiments were carried out in a 150 ml stainless steel magnetically stirred autoclave equipped with a glass inlet. The temperature was kept constant at 80 °C by circulating water through a double jacket. The mixture of syn gas ($H_2/CO = 1$) was introduced at a constant pressure of 5 bar from a gas tank. The drop of pressure in the tank was followed with a pressure transducer connected to an electronic unit of measurement and printing. A 1,2-dichloroethane solution of the rhodium complexes containing the amount of required phosphine or phosphite and the olefin were introduced into the evacuated autoclave. This was heated at 80 °C, and when the system had reached thermal equilibrium the syn gas was introduced at 5 bar and the stirring connected. After each run the solution was transferred from the autoclave into a Schlenk tube, and analyzed by IR spectroscopy and GLC on a Hewlett-Packard 5840A chromatograph equipped with an OV-17 on chromosorb W.H.P. 6 m × 1/8" column.

Results and discussion

$[Rh(diolefin)L_2]ClO_4$ precursors, diolefin = COD, NBD; L = PPh_3, $P(OPh)_3$, $P(OMe)_3$

$[Rh(COD)(APh_3)_2]ClO_4$ complexes, A = N, P, As, Sb, Bi, have been previously used as hydroformylation precursors in different conditions (15–150 bar, 25–100 °C) [14].

In this work, the systems $[Rh(diolefin)(PR_3)_2]ClO_4$/$PR_3$, diolefin = COD, NBD; R = Ph, OPh, OMe, are used as catalyst precursors for the hydroformylation of 1-hexene. We have focused on the influence of the different ligands and the effect of PR_3 in excess (P/Rh molar ratio = 5, 10) on the catalytic activity and selectivity. The results obtained with the different system precursors are shown in Table 1. Catalytic hydroformylation was achieved in all experiments and only branched and linear aldehydes were obtained. No hydrogenation or isomerization was observed.

In the case of L = PPh_3 with P/Rh = 10, a 93% conversion is obtained with a selectivity of 80% of the linear aldehyde. However when the molar ratio was reduced, P/Rh = 5, lower conversions were observed.

It is noteworthy that the cyclooctadiene systems $[Rh(COD)(PR_3)_2]ClO_4$/10 PR_3 are more active than the corresponding norbornadiene systems $[Rh(NBD)(PPh_3)_2]ClO_4$/10 PR_3. This effect has also been observed in olefin hydrogenation using $[Rh(COD)(SPPh_3)_2]ClO_4$ and $[Rh(NBD)(SPPh_3)_2]ClO_4$; it could be attributed to the higher π-acceptor capacity of the 2,5-norbornadiene which makes the oxidative addition of hydrogen to the rhodium(I) center difficult [20].

Concerning the nature of the PR_3 ligands, the experiments using a P/Rh molar ratio of 5/1 (Table 1) show decreasing activity in the order $P(OPh)_3 > PPh_3 > P(OMe)_3$; the selectivity in linear aldehyde is similar for PPh_3 and $P(OPh_3)$. Very low conversion is obtained in the case of $P(OMe)_3$.

According to the Tolman's cone angle data [21], the steric effect lies in the order $PPh_3 > P(OPh)_3 > P(OMe)_3$, and the basicities of the ligands, which describe electronic effects, decrease in the order $PPh_3 > P(OMe)_3 > P(OPh)_3$. No dependence on the steric or electronic effect can be observed, probably due to the combination of both effects and their different influence on the steps in the catalytic cycle.

$[Rh(\mu\text{-}L)(COD)]_2/PR_3$ systems L = OAc, OMe; R = Ph, OPh, OMe

As an alternative to the known $[Rh(\mu\text{-}Cl)(diolefin)]_2$/phosphorous ligand systems [7–9] we have studied the catalytic olefin hydroformylation activity of two related systems $[Rh(\mu\text{-}L)(COD)]_2$/$PR_3$, L = OAc, OMe. These two systems do not introduce chloride which is known to reduce the catalytic hydroformylation [7].

The data collected in Table 2 show the results of the hydroformylation of 1-hexene, with these precursor systems at 5 bar and 80 °C, using different P/[complex] molar ratio: 5, 10, 20 (P/Rh = 2.5, 5, 10). Higher conversions than in the case of the above reported cationic complexes were obtained, only linear and branched aldehydes were formed, no isomerization or hydrogenation were observed.

The effect of the excess of PR_3 is shown in Table 2. The same general trend has been observed for the complex precursors $[Rh(\mu\text{-}OAc)(COD)]_2$ and $[Rh(\mu\text{-}OMe)(COD)]_2$. When PR_3 is triphenylphos-

TABLE 1. Hydroformylation reactions with cationic rhodium complexes as catalyst precursors

Catalyst precursor	P/Rh	Reaction time(h)	Conversion (%)	n/iso
$[Rh(COD)(PPh_3)_2]ClO_4/PPh_3$[a]	5	5	3	3.4
$[Rh(COD)(PPh_3)_2]ClO_4/PPh_3$[b]	10	5	93	3.7
$[Rh(COD)(P(OPh)_3)_2]ClO_4/P(OPh)_3$[a]	5	19	76	3.6
$[Rh(COD)(P(OPh)_3)_2]ClO_4/P(OPh)_3$[a]	10	19	22	4.8
$[Rh(NBD)(PPh_3)_2]ClO_4/PPh_3$[a]	10	5	20	3.8
$[Rh(COD)(P(OMe)_3)_2]ClO_4/P(OMe)_3$[b]	5	5	15	

[a]Substrate = 1-hexene. [b]Substrate = 1-heptene. Reaction conditions: 0.1 mmol of complex, $CO/H_2 = 1/1$, [substrate]/[precursor] = 400/1, total pressure = 5 atm., temperature = 80 °C, solvent = 15 ml 1,2-dichlorethane.

TABLE 2. Hydroformylation of 1-hexene with $[Rh(\mu\text{-L})(COD)]_2/PR_3$ as catalyst precursors

Catalyst precursor	P/Rh	Reaction time (h)	Conversion (%)	n/iso
$[Rh(\mu\text{-OMe})(COD)]_2/PPh_3$	2.5	3	87	1.6
	5	3	86	2.4
	10	3	63	3.6
$[Rh(\mu\text{-OMe})(COD)]_2/P(OPh)_3$	2.5	5	83	0.6
	5	5	51	2.3
$[Rh(\mu\text{-OMe})(COD)]_2/P(OMe)_3$	2.5	3	93	3.4
	5	3	36	5.3
$[Rh(\mu\text{-OAc})(COD)]_2/PPh_3$	2.5	3	75	0.9
	5	3	82	2.8
	10	3	78	5.3
$[Rh(\mu\text{-OAc})(COD)]_2/P(OPh)_3$	2.5	3	96	0.5
	5	3	53	1.5
$[Rh(\mu\text{-OAc})(COD)]_2/P(OMe)_3$	2.5	3	88	1.8
	5	3	18	4.6

Substrate = 1-hexene. Reaction conditions: 0.1 mmol of complex, $CO/H_2 = 1/1$, [substrate]/[precursor] = 400/1, total pressure = 5 atm., temperature = 80 °C, solvent = 15 ml 1,2-dichlorethane.

phine the behaviour is different than in the case of phosphite ligands: an excess of PPh_3 increases the selectivity without decreasing the activity, except in the case of $[Rh(\mu\text{-OMe})(COD)]_2$ where a decrease in the conversion is observed when $PPh_3/Rh = 10$ (68%). The selectivity in n-heptanal achieves 78%, L = OMe, and 84%, L = OAc. Different results are observed when PR_3 is $P(OPh)_3$ or $P(OMe)_3$. The excess of phosphite ligands increases the selectivity but at the expense of decreasing the activity (80–50% 1-hexene conversion in aldehydes).

The different behaviour shown by triphenylphosphine and the phosphite ligands could be related to the formation of different species, when an excess of ligand is present in solution, depending on the nature of the ligand.

The smaller cone angle (PPh_3 $\theta = 145°$, $P(OPh)_3$ $\theta = 128°$, $P(OMe)_3$ $\theta = 107°$) [21] and the more π-acceptor capacities of the phosphite ligands, could allow the formation of rhodium species with more phosphorous ligands bonded to the metal center which produces a decrease in the activity.

The conversions of 1-hexene along the hydroformylation reaction catalyzed by $[Rh(\mu\text{-OAc})(COD)]_2/PR_3$, R = Ph, OPh, OMe, precursor systems when P/Rh = 2.5 are illustrated in Fig. 1.

As a control experiment the catalytic reaction was carried out with $[RhH(CO)(PPh_3)_3]$, under the same conditions. A conversion of 66% was achieved with a selectivity of 64% in linear aldehyde. When an excess of PPh_3 was used ($PPh_3/Rh = 20$) the conversion significantly decreased to 43% while the selectivity increased to 80%. As shown in Fig. 1, higher conversions are achieved with $[Rh(\mu\text{-OAc})(COD)]_2/PR_3$, in particular when PR_3 is a phosphite ligand.

The selectivities decrease in the order $P(OMe)_3 > PPh_3 > P(OPh)_3$ (Table 2).

Cyclohexene hydroformylation

Cyclic and internal olefins are much less reactive than terminal olefins in the rhodium catalyzed hy-

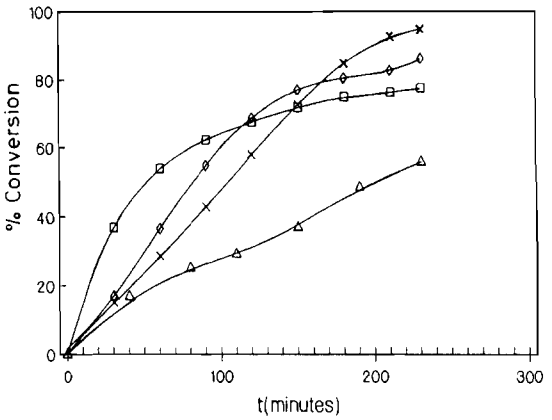


Fig. 1. Catalytic hydroformylation of 1-hexene using as catalyst precursors (–△–) $[RhH(CO)(PPh_3)_3]$ and $[Rh(\mu\text{-}OAc)(COD)]_2/PR_3$, excess P/Rh = 2.5, where PR_3 is: (–□–) PPh_3, (–×–) $P(OPh)_3$ and (–◇–) $P(OMe)_3$.

droformylation reaction [22] although the rate differences depend on the conditions and on the ligand modification of the catalyst. In general, the hydroformylation of the less reactive olefins is carried out at higher temperatures [23].

However, the study of precursor systems which are effective catalysts for hydroformylation of unreactive olefins in mild conditions is now of great interest due to their possible application in the syntheses of intermediates through hydroformylation reactions which could provide high regio and stereoselectivity.

The $[Rh(\mu\text{-}OAc)(COD)]_2/PR_3$ precursor systems have been previously used in hydroformylation of unreactive olefins at 14–20 bar and 70–90 °C and it has been shown that cyclohexene can be efficiently hydroformylated with a rhodium catalyst carrying bulky phosphite ligands [11].

In the present work we report the activity of the $[Rh(\mu\text{-}OAc)(COD)]_2/PR_3$ precursor system in the cyclohexene hydroformylation at 5 bar and 80 °C.

Almost total conversion (98%) in cyclohexanal is obtained when $P(OPh)_3$ is used in the ratio P/Rh = 2.5, although rates are lower than in the case of terminal olefins.

Lower conversions in cyclohexanal are obtained, 63%, when the $[Rh(\mu\text{-}OMe)(COD)]_2/P(OPh)_3$, P/Rh = 2.5 system is used as precursor.

IR study of rhodium species at the end of the hydroformylation reaction

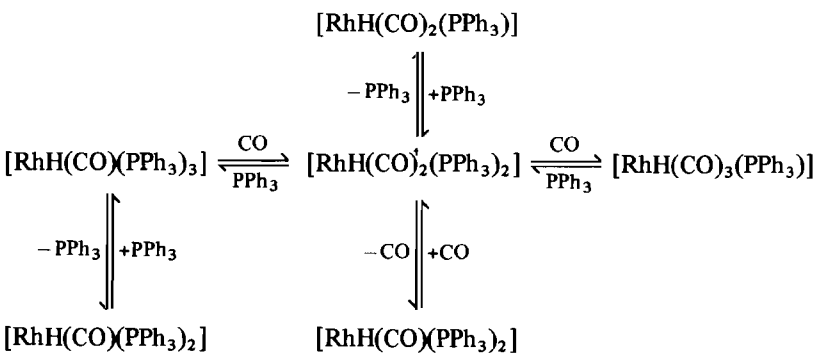
It is known that rhodium precursors related with the Wilkinson catalyst $[RhH(CO)(PPh_3)_3]$, in hydroformylation conditions, afford hydrido carbonyl rhodium species [24, 25]. Different rhodium species are in equilibrium in solution [7] (Scheme 1).

When triphenylphosphine is used the infrared spectra recorded at the end of the catalytic reaction for both systems $[Rh(\mu\text{-}OAc)(COD)]_2/PPh_3$ and $[Rh(\mu\text{-}OMe)(COD)]_2/PPh_3$ show a single strong carbonyl stretching absorption at 1979 cm^{-1} together with a weak band in the 2010–2030 cm^{-1} region corresponding to Rh–H absorption. The same frequencies are present when different P/Rh excess are used. Stable yellow solids can be isolated at the end of the reactions and their IR spectra recorded in KBr or in $CHCl_3$ solution show a single ν(CO) absorption.

Hydroformylation experiments with the Wilkinson catalyst $[RhH(CO)(PPh_3)_3]$, excess P/Rh ratio = 0.5, were carried out in the same conditions for comparative purpose and the IR spectra recorded at the end of the reaction also showed a single strong ν(CO) absorption at 1976 cm^{-1}.

When the precursor systems are $[Rh(\mu\text{-}L)(COD)]_2/PPh_3$, L = OAc, OMe, the elemental analyses of the yellow solids isolated (C ≈ 57%, H ≈ 4.5%) suggest that the *trans*-$[RhH(CO)_2(PPh_3)]$ or $[RhH(CO)_3(PPh_3)]$ species must be present at the end of the hydroformylation reaction.

It is known that both species show a single ν(CO) absorption [26] according to the IR spectrum observed in the solution obtained at the end of the reaction.



Scheme 1.

$[RhH(CO)_2(PPh_3)_2]$ which presents two bands in the $\nu(CO)$ region [25] has been described as unstable and difficult to isolate [24, 27].

When $PR_3 = P(OPh)_3$ or $P(OMe)_3$ and $P/Rh = 2.5$ only a $\nu(CO)$ absorption is observed whatever the precursor system is. These absorptions could be attributed to the same species as in the case of PPh_3 ($P/Rh = 2.5$). The variation of these frequencies, $\nu(CO)_{PPh_3} = 1978\ cm^{-1}$, $\nu(CO)_{P(OMe)_3} = 2004\ cm^{-1}$ and $\nu(CO)_{P(OPh)_3} = 2014\ cm^{-1}$, can be related with the electronic parameter τ [21] which indicates the donor ability of these ligands $PPh_3 > P(OMe)_3 > P(OPh)_3$, as suggested by the evidence given above.

Acknowledgements

We thank CICYT (project n. PB 85-0008-CO2-01) for financial support and Drs J. C. Bayón and J. Real for many helpful discussions.

References

1 (a) Ph. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern and A. Thorez, *J. Chem. Soc., Chem. Commun.*, (1983) 510. (b) Ph. Kalck, in A. de Meijere and H. tom Dieck (eds.), *Organometallics in Organic Synthesis*, Springer, Berlin, 1987, pp. 297–320.

2 (a) Ph. Kalck, A. Thorez, M. T. Pinillos and L. A. Oro, *J. Mol. Catal., 31* (1985) 311; (b) C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano and C. Foces-Foces, *J. Chem. Soc., Dalton Trans.*, (1988) 1523; (c) C. Claver, Ph. Kalck, L. A. Oro, M. T. Pinillos and C. Tejel, *J. Mol. Catal., 43* (1988) 1.

3 (a) J. C. Bayón, P. Esteban, J. Real, C. Claver and A. Ruiz, *J. Chem. Soc., Dalton Trans.*, (1989) 1579; (b) J. C. Bayón, J. Real, C. Claver, A. Polo and A. Ruiz, *J. Chem. Soc., Chem. Commun.*, (1989) 1056.

4 (a) H. Janecko, A. M. Trzeciak and J. J. Ziolkowski, *J. Mol. Catal., 26* (1984) 355; (b) A. M. Treziak and J. J. Ziolkowski, *J. Mol. Catal., 34* (1986) 213; *43* (1988) 335 and refs. therein.

5 (a) O. R. Hughues and J. D. Unruh, *J. Mol. Catal., 12* (1981) 71; (b) J. D. Unruh and J. R. Christeton, *J. Mol. Catal., 19* (1982) 19.

6 M. Matsumoto and M. Tamura, *J. Mol. Catal., 16* (1982) 209.

7 R. Pruett, in F. G. A. Stone and R. West (eds.), *Advances in Organometallic Chemistry*, Vol. 17, *Catalysis and Organic Syntheses*, Academic Press, New York, 1979, pp. 1–57.

8 J. Falbe (ed.), *New Synthesis with Carbon Monoxide*, Spring, Berlin, 1980.

9 (a) C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli and A. Gamba, *La Chimica e l'Industria, 62* (1980) 604; (b) C. Botteghi, R. Ganzerla, M. Lenarda and G. Moretti, *J. Mol. Catal., 40* (1987) 129.

10 (a) L. A. Oro, A. Manrique and M. Royo, *Transition Met. Chem., 3* (1978) 383; (b) M. Royo, F. Melo, A. Manrique and L. Oro, *Transition Met. Chem., 7* (1982) 44.

11 P. W. N. M. Van Leeuwen and C. F. Roobbek, *J. Organomet. Chem., 258* (1983) 343.

12 J. M. Brown and S. J. Cook, *Tetrahedron, 42* (1986) 5109.

13 C. Bergounhou, D. Neibecker and R. Réau, *J. Chem. Soc., Chem. Commun.*, (1988) 1370.

14 K. Prokai-Tátrai, S. Törös and B. Heil, *J. Organomet. Chem.*, 315 (1986) 231.

15 R. Usón, L. A. Oro, C. Claver, M. A. Garralda, J. M. Moretó, *J. Mol. Catal., 4* (1978) 231.

16 C. Claver, E. Marco, L. A. Oro, M. Royo and E. Pastor, *Transition Met. Chem., 7* (1982) 246.

17 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc., 93* (1971) 2397.

18 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1975) 4735.

19 R. Usón, L. A. Oro and J. M. Cabeza, *Inorg. Synth., 23* (1985) 126.

20 C. Claver, F. Gili, J. M. Viñas and A. Ruiz, *Polyhedron, 6* (1987) 1329.

21 Ch. A. Tolman, *Chem. Rev., 77* (1977) 313.

22 C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 2753.

23 H. Siegel and W. Himmele, *Angew. Chem., 92* (1980) 182.

24 D. Evans, G. Yagupski and G. Wilkinson, *J. Chem. Soc. A*, (1968) 220.

25 W. R. Moser, C. J. Papite, D. A. Brannon, R. A. Duwell and S. S. Weininger, *J. Mol. Catal., 41* (1987) 271.

26 R. L. Pruett and J. A. Smith, *J. Org. Chem., 34* (1969) 327.

27 A. F. Borowski, D. J. Cole-Hamilton and G. Wilkinson, *Nouv. J. Chim., 2* (1978) 137.