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Journal of Molecular Catalysis A: Chemical 208 (2004) 97–101
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Hydroformylation of 1-octene with rhodium catalysts in fluorous systems

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Received 25 February 2003; received in revised form 9 July 2003; accepted 9 July 2003

Abstract

Rhodium complexes associated with the fluorous phosphine $P(C_6H_4\text{-}4\text{-}OCH_2C_7F_{15})_3$ (**1**) are active catalysts in the hydroformylation of 1-octene in biphasic fluorous systems (TOF 380 h^{-1}). Selectivity in aldehydes was as much as 99% and regioselectivity in the linear aldehyde up to a *n*/*iso* ratio of 2.8. The system was efficiently recycled for two consecutive runs without decreasing conversion or selectivity. The loss of Rh in the organic layer after the first run was 0.78%. The activity increased using perfluoromethylcyclohexane as a sole solvent (TOF 1040 h^{-1}). Under pressure of CO/H_2 (40 bar) the hydrido species $[RhH(CO)(\mathbf{1})_3]$ and $[RhH(CO)_2(\mathbf{1})_2]$ were detected by high pressure NMR spectroscopy.

Keywords: Rhodium; Hydroformylation; Fluorous; NMR spectroscopy

1. Introduction

The hydroformylation of alkenes to obtain aldehydes using carbon monoxide and hydrogen is an important homogeneous catalysed industrial process [1,2]. It is successfully used to hydroformylate low alkenes ($<C_4$) because the products can be separated by simple distillation. For higher alkenes, the distillation requires higher temperatures, so the catalyst often decomposes. We can solve this problem by using biphasic systems in which the catalyst and the products dissolve in two different phases and can been easily separated.

Ruhrchemie/Rhône-Poulenc have applied a biphasic water/organic solvent system since 1984 for the industrial hydroformylation of propene [3–5] using the water soluble Rh-TPPTS (TPPTS = $P(C_6H_4\text{-}2\text{-}SO_3Na)_3$) catalyst [6]. However, this process is limited to short-chain alkenes (propene and 1-butene) because it requires a certain solubility of the alkene in water [7].

In 1994, the concept of the fluorous biphase system (FBS) was introduced by Horváth and Rábai and applied to the hydroformylation of 1-decene [8,9]. The FBS is based on the properties of perfluorinated solvents, which have a low affinity for non-fluorinated compounds. The catalyst, which contains ligands with fluorous chains, is therefore dissolved in the fluorous phase and the products can be separated by decantation. The ligands used were fluorous trialkyl phosphines $P[(CH_2)_2(CF_2)_5CF_3]_3$, in which the methylenic units were essential for insulating the strong electron-withdrawing groups from the phosphorus atom. Kinetic studies on the Rh-hydroformylation of 1-decene using this fluorous trioctylphosphines have been carried out [10]. The catalyst system was separated and recycled up to nine times, which proved the efficiency of the fluorous concept. High pressure NMR (HPNMR) experiments lead to the characterisation of $[RhH(CO)\{P((CH_2)_2(CF_2)_5CF_3)_3\}_3]$, which is in equilibrium under CO pressure with $[RhH(CO)_2\{P((CH_2)_2(CF_2)_5CF_3)_3\}_2]$.

Fluorous trialkylphosphines are efficient ligands for the Rh-hydroformylation but the activities are lower than when Rh/PPh_3 is used as the catalytic system. The activities and linear selectivity obtained with triaryl phosphines $P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$ and triaryl phosphites such as $P(OC_6H_4\text{-}4\text{-}C_6F_{13})_3$ were actually higher at lower ligand loadings than with

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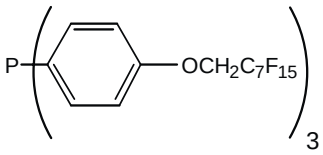
doi:10.1016/S1381-1169(03)00509-0



(1)

Fig. 1. Ligand **1**.

trialkyl phosphines [11–16]. These systems were even more efficient in the absence of organic solvent.

Mortreux and co-workers prepared triarylphosphites with two fluorous chains in the *ortho*- and *para*-positions [17]. In the hydroformylation of 1-decene, with the rhodium catalyst with substituents in the *ortho*-position, activity was very high (TOF > 10,000).

Diphenylphosphino moieties have also been used in fluorous soluble polymers. Selectivities in linear aldehydes obtained with rhodium systems with these polymers were high (*n*/*iso* up to 5.9 for the hydroformylation of 1-decene) but activities were relatively low (TOF of 136 mol h^{-1} for 1-decene) [18].

Some of us recently reported a suitable method for synthesising phosphines in which the fluorous substituent was introduced through an ether function [19,20]. The *ortho*-, *meta*- and *para*-phosphines, $P(C_6H_4\text{-}O(X)R_F)_3$ ($X = CH_2$, $(CH_2)_3$,$CH_2O(CH_2)_2$; $R_F = C_7F_{15}$, C_8F_{17}) as well as fluorous phosphines with a binaphthyl core were successfully used in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate [21], the Heck coupling reaction [22] and the hydrogenation of alkenes [23].

In this paper, we use the fluorous monophosphine, $P(C_6H_4\text{-}4\text{-}OCH_2C_7F_{15})_3$ (**1**) (Fig. 1) in the rhodium hydroformylation of 1-octene in the biphasic fluorous solvent/organic solvent system. We also use HPNMR methods to identify the species formed under pressure conditions.

2. Experimental

2.1. General methods

Solvents (toluene, perfluoromethylcyclohexane and perfluorooctane) were deoxygenated before use. All other reagents were used as supplied. The ligand **1** was prepared as previously described [19]. Gas chromatography (GC) analyses were performed using a Hewlett-Packard 5890A chromatograph in an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm Ø) to separate the products. The ^1H and ^{31}P NMR spectra were registered on a Varian 300 MHz instrument and the chemical shifts were quoted in ppm downfield from internal $SiMe_4$ (^1H) or external 85% H_3PO_4 (^{31}P). HPNMR experiments were carried out in a 10 mm diameter sapphire tube, with a titanium cap [24].

2.2. Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was kept in a Teflon vessel. The inside of the cap of the autoclave was also Teflon-covered to prevent the solution from coming into direct contact with the stainless steel. An electric heating mantle kept the temperature constant.

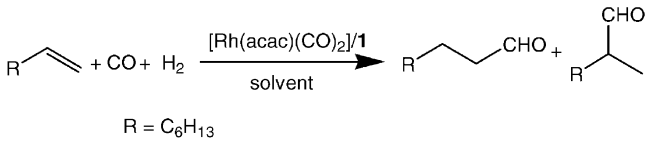
2.3. Standard hydroformylation experiment

The complex $[Rh(acac)(CO)_2]$ (5 mg, 0.019 mmol) and the ligand **1** (138 mg, 0.095 m mol) in the fluorous solvent (12 ml) were stirred for 1 h at 50 °C until complete dissolution. The substrate (alkene/Rh ratio 500 or 2000) and toluene (7.5 ml) were added. The resulting two-phase system was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure was attained. After the reaction time, the autoclave was cooled to room temperature and depressurised. The reaction mixture was separated under nitrogen atmosphere and the fluorous solvent was recycled. The toluene phase was analysed by GC. The Rh and P content in the toluene layer of experiment 5 were analysed by ICP–MS.

3. Results and discussion

3.1. Hydroformylation of 1-octene

We studied the hydroformylation of 1-octene (Eq. (1)) using $[Rh(acac)(CO)_2]$ with ligand **1** (P/Rh = 5) at 80 °C and 40 atm. Table 1 shows the results we obtained. The catalyst precursor was prepared in situ by adding **1** to a suspension of $[Rh(acac)(CO)_2]$ in the fluorous solvent and heating it up to 50 °C until dissolution.



(1)

Using the biphasic perfluoromethylcyclohexane/toluene system (60/40, v/v), the total conversion and selectivity in aldehydes were very high (>95%) after 1 h reaction (Table 1, entry 1). The TOF calculated was 380 h^{-1} (19% conversion). The regioselectivity in *n*-aldehyde was 72%. These results are similar to those obtained when PPh_3 was used as the ligand under similar conditions (Table 1, entry 2). This indicates that the fluorous chain is well insulated by the $–OCH_2$-spacer and does not, as reported previously, modify the electronic properties of the ligand [23]. Results were

Table 1
Hydroformylation of 1-octene using [Rh(acac)(CO)$_2$]/**1** as the catalyst precursor[a]

Entry	L	Run	Solvent	C_T (%)	S_{ald} (%)	*n/iso* (%)	S_{iso} (%)
1	**1**	1[b]	C_7F_{14}/toluene	98	97	72/28	3
		2[b]		98	77	63/37	23
2	PPh_3	1	Toluene	97	98	73/27	2
3	**1**	1[b]	C_8F_{18}/toluene	96	98	73/27	2
4	–	1	Toluene	98	68	58/42	32
5	**1**	1	C_7F_{14}/toluene	97	99	73/27	1
		2		96	97	73/27	3
		3[b]		94	91	71/29	9
		4[b]		97	75	65/35	25
6[c]	**1**	1[b]	C_7F_{14}/toluene	20	94	73/27	6
7[c]	**1**	1[b]	C_7F_{14}	68	96	74/26	4

[a] Reaction conditions: $P = 40$ bar (CO/H_2 = 1/1), $T = 80\,^{\circ}C$, $t = 1$ h, [Rh(acac)(CO)$_2$] 1.6×10^{-3} M, P/Rh = 5, substrate/catalyst = 500/1, fluorous solvent (12 ml)/toluene (7.5 ml). S_{ald} = selectivity in aldehydes, S_{iso} = selectivity in isomerisation products (2- and 3-octene).
[b] The toluene phase was coloured.
[c] Substrate/catalyst = 2000/1.

similar when perfluorooctane was used as the fluorous solvent (Table 1, entry 3).

The separation of the two phases by cooling the final solution in experiment 1–10 °C was good, but the ligand precipitated partially in the fluorous phase. Also, the toluene phase was coloured, which indicates that there was some leaching of the complex. The fluorous phase was recycled, but if the conversion in the second run was high, the decrease in selectivity in aldehydes and in regioselectivity in 1-nonanal indicated a partial loss of ligand **1**. To confirm this, we performed a reference experiment using [Rh(acac)(CO)$_2$] as the catalyst precursor without added ligand under the same conditions and effectively observed a low selectivity in aldehydes and regioselectivity in *n*-nonanal (68 and 58%, respectively) (Table 1, entry 4). This lower selectivity in aldehydes and regioselectivity in the linear isomer as the P/Rh ratio decreases in Rh/PPh_3 systems is well documented [25].

To prevent the ligand from precipitating, in experiment 5 (Table 1) the phases were separated after reaction at 50 °C. It has been reported that 2:2:1 mixtures of toluene:perfluoromethylcyclohexane:1-octene form two phases below 60 °C. The nonanals separated better at higher temperature and 2:2:1 mixtures of toluene:perfluoromethylcyclohexane:1-nonanal showed no apparent mixing up to 80 °C [12]. Under these conditions, the conversion and selectivity of the catalyst was the same for three consecutive runs and only started to drop only on the fourth run. Nevertheless, small amounts of aldehydes were detected by GC in the fluorous phase. The leaching of Rh and P in the toluene phase after the first run in experiment 5 (Table 1) was 0.78 and 15% of the total recovered.

At a higher substrate/Rh ratio (2000), the conversion after 1 h was still good (entry 6, Table 1) when the perfluoromethylcyclohexane/toluene system was used. The activity increased when perfluoromethylcyclohexane was used as the sole solvent. At a substrate/Rh ratio of 2000, the calculated TOF was 1040 h^{-1} (13% conversion) (Table 1, entry 7) and the regioselectivity in the linear aldehyde was maintained. A similar increase in activity has been reported with Rh-phosphite systems [11,17].

3.2. High pressure experiments

High pressure NMR $^{31}P\{^1H\}$ and ^1H NMR experiments under hydroformylation conditions were performed on the complex [Rh(acac)(CO)$_2$] associated with 5 eq. of ligand **1** under 40 bar of CO/H_2 (1/1). After shaking the system for 12 h at 50 °C, the solution turned yellow. The $^{31}P\{^1H\}$ NMR spectra at room temperature showed six signals (Fig. 2) at δ (ppm): 37.1 (d, $^1J_{P-Rh}$ = 154.4 Hz), 32.1 (d, $^1J_{P-Rh}$ = 136.4 Hz), 24.9 (s, oxide of **1**), 19.9 (broad d, $^1J_{P-Rh}$ = 159.0 Hz), 17.0 (broad d, $^1J_{P-Rh}$ = 152.7 Hz) and at 10.1 (singlet, free ligand). The ^1H NMR in the hydride region showed two broad signals at δ −9.1 and −9.3 ppm. By comparison with published data on triphenylphosphine complexes, the major signal at δ 37.1 ppm together with the hydride signal at δ −9.3 ppm were attributed to the triphosphine hydrido species [RhH(CO)(**1**)$_3$] (**2**). Reported data on the corresponding complex [RhH(CO)(PPh_3)$_3$] were a broad hydride signal at δ −9.9 ppm [26,27] (resolved at −35 °C in a quadruplet [26]) and a doublet in the ^{31}P NMR at δ 41.3 ($^1J_{P-Rh}$ = 153.9 Hz) [28]. The minor signals at δ 32.1 ppm (^{31}P) with the hydride signal at δ −9.1 ppm were attributed to the bis phosphino complex [[RhH(CO)$_2$(**1**)$_2$] (**3**) by comparing them with the data for [RhH(CO)$_2$(PPh_3)$_2$], which showed a broad doublet in dichloromethane at δ −9.6 ppm for the hydride signal [26] and a doublet at δ 32.1 ppm ($^1J_{P-Rh}$ = 138.7 Hz) for the phosphorous signal [28]. The small broad signals at δ 19.9 and 17.0 ppm were attributed to the binuclear rhodium species [(**1**)(CO)$_2$Rh(μ-CO)$_2$Rh(CO)$_2$(**1**)] (**4**) and [(**1**)$_2$(CO)Rh(μ-CO)$_2$Rh(CO)$_2$(**1**)] (**5**), which were

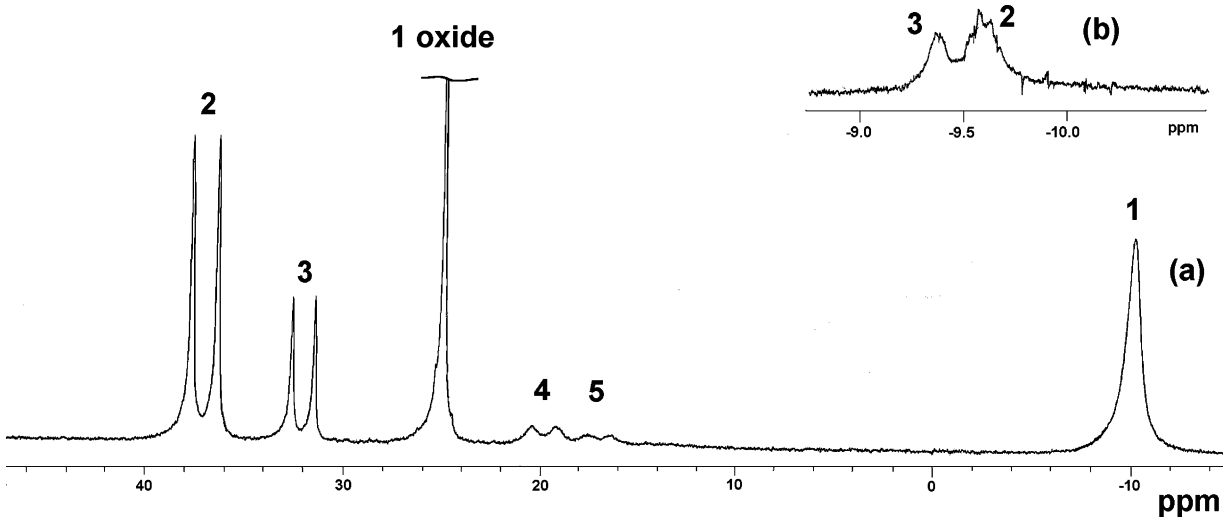


Fig. 2. (a) $^{31}P\{^{1}H\}$ NMR spectrum at 20 °C of [Rh(acac)(CO)$_2$]/**1** (P/Rh = 5) in $CF_3C_6H_{11}$ under 40 bar of CO/H_2 (1:1). (b) Hydride region of the ^{1}H NMR.

$$[RhH(CO)(\mathbf{1})_3] \underset{}{\overset{-\mathbf{1}\ /\ +CO}{\rightleftharpoons}} [RhH(CO)_2(\mathbf{1})_2] \underset{-\ \mathbf{1}}{\overset{+CO/\ -H_2}{\rightleftharpoons}} [Rh(CO)_2(\mathbf{1})]_2 \overset{+\mathbf{1}\ /\ -CO}{\rightleftharpoons} [Rh_2(CO)_5(\mathbf{1})_3]$$
2 **3** **4** **5**

Scheme 1.

reported to form at a high concentration of rhodium triphenylphosphine complex and a low pressure of hydrogen [26,28]. The analogous species of **5** with PPh_3 [$(PPh_3)_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)_2(PPh_3)$] also showed a broad doublet at −20 °C [28]. The spectra remained similar in the 0–60 °C temperature range.

When the NMR tube was depressurised, the signals corresponding to the species **3**–**5** in the ^{31}PP–$Rh\{^{1}H\}$ NMR spectra disappeared and only the signal corresponding to the triphosphine species **2** remained. When pressure of syn gas was again added to the tube, the signals corresponding to complexes **3**–**5** were recovered in the spectrum. This behaviour is consistent with an equilibrium between the species [RhH(CO)(**1**)$_3$] and [RhH(CO)$_2$(**2**)$_2$] by CO-**1** exchange, as is reported for triphenylphosphine complexes [27] (Scheme 1).

Finally, the tube was depressurised, 1-octene (1-octene/Rh ratio 5/1) was added, the tube was charged with 40 bar CO/H_2 (1/1), and the solution was shaken for 1 h at 50 °C. The spectra (^{31}P and ^{1}H) of the resulting solution (Fig. 3) showed the signals corresponding to species **2** and **3** in a ca. 40/60 ratio, and very small signals corresponding to the binuclear species **4** and **5**. Signals corresponding to the aldehydes were observed in the 9.5 ppm region in the ^{1}H NMR

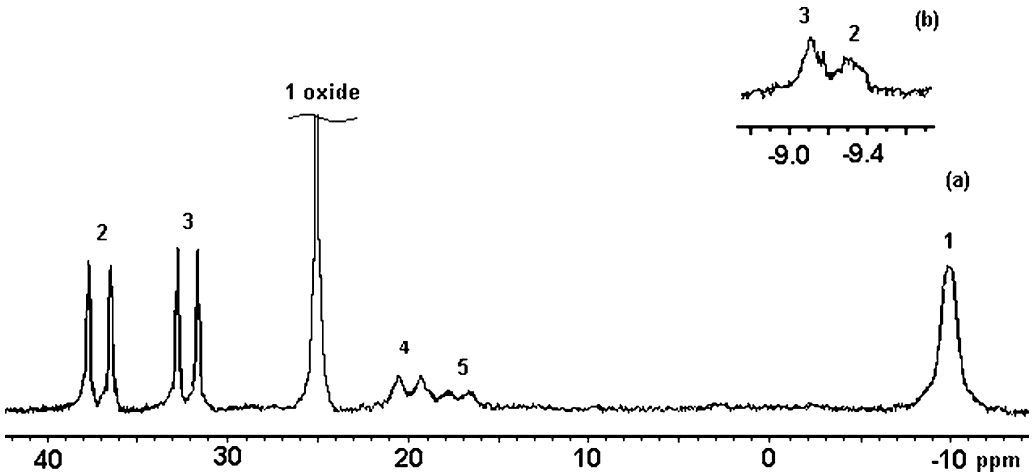


Fig. 3. (a) $^{31}P\{^{1}H\}$ NMR spectrum at room temperature of [Rh(acac)(CO)$_2$]/**1** (P/Rh = 5) in $CF_3C_6H_{11}$ with 1-octene (1-octene/Rh = 5) under 40 bar of CO/H_2 (1:1). (b) Hydride region of the ^{1}H NMR.

spectra, which indicated that hydroformylation took place. The lower relative concentration of species **2** may be due to a displacement of the equilibrium caused by the reaction of species **3** with the alkene. In the related Rh/PPh_3 system, it has been suggested that a CO molecule dissociates from the complex $[RhH(CO)_2(PPh_3)_2]$ to form the intermediate that reacts with the substrate [29,30].

In summary, the HPNMR experiments showed that, under CO/H_2 pressure conditions, the rhodium systems with fluorous ligand **1** behaved in a similar way to the Rh/triphenylphoshine system and the electronic effects of the fluorous chains did not essentially modify the nature of the species formed.

4. Conclusion

In conclusion, active catalyst in the hydroformylation of 1-octene in biphasic fluorous systems is obtained when $[Rh(acac)(CO)_2]/P(C_6H_4\text{-}4\text{-}OCH_2C_7F_{15})_3$ is used as the precursor. The selectivity in aldehydes was as much as 99% and the regioselectivity in the linear aldehyde was up to $n/iso = 2.8$. The system was efficiently recycled for two consecutive runs without decreasing conversion and selectivity. Under hydroformylation conditions, hydrido species $[RhH(CO)(\mathbf{1})_3]$ and $[RhH(CO)_2(\mathbf{1})_2]$ and rhodium dimers were detected by high pressure NMR spectroscopy.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología (PPQ2001-0452) and the Generalitat de Catalunya (Departament d'Universitats, Recerca i Societat de la Informació, Acció Integrada ACI2000-1) for financial support.

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