Journal of Organometallic Chemistry, 420 (1991) 353–358
Elsevier Sequoia S.A., Lausanne
JOM 22140

Influence of the modification of the ligands on hex-1-ene hydroformylation catalyzed by $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$. Catalytic activity of the system $[HRh\{P(OPh)_3\}_4] + Cp_2Zr(CH_2PPh_2)_2$

Anna M. Trzeciak, Józef J. Ziółkowski
Institute of Chemistry, University of Wrocław, 50-383 Wrocław (Poland)

and Robert Choukroun
Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex (France)

(Received February 7th, 1991)

Abstract

A study has been carried out of the catalytic activity of the systems formed by $[HRh\{P(OPh)_3\}_4]$ or $[HRh(CO)\text{-}\{P(OPh)_3\}_3]$ with the modifying ligands $P(OPh)_3$, PPh_3, diphos and $Cp_2Zr(CH_2PPh_2)_2$ in hydroformylation of hex-1-ene (at $p = 5$ bar). The best results were obtained with the system $[HRh\{P(OPh)_3\}_4] + Cp_2Zr(CH_2PPh_2)_2$ (75–85% yield of aldehydes).

Introduction

There has been increasing interest recently in applications of bimetallic catalytic systems [1–7]. Especially promising appear to be the catalysts containing two metal centers, one with low and the other with high electron density, within one molecule (e.g. d^0–d^8 Zr^{IV}–Rh^I). In such a system there could be simultaneous activation of carbon monoxide by both metallic centers, the d^0 metal interacting with the oxygen atom of the carbon monoxide molecule bonded to the d^8 metal [1]. The presence of the Zr–Rh bond also makes possible the migration of the hydrogen atom bonded to rhodium over to the zirconium ion. Such a possibility was supported by an X-ray structural determination of $[Cp_2Zr(CH_2PPh_2)_2Rh(H)(PPh_3)]$, which indicated the presence of an agostic interaction between the zirconium atom and the Rh–H bond [2].

Studies of hydroformylation reactions in systems containing various rhodium complexes along with the bisphosphine $Cp_2Zr(CH_2PPh_2)_2$ have revealed the promising catalytic properties of these systems [3–4]. With both $[HRh(PPh_3)_4]$ [3] and $[HRh(CO)(PPh_3)_3]$ [4] the rate of hydroformylation and the yield of aldehydes were raised by addition of $Cp_2Zr(CH_2PPh_2)_2$. The bimetallic complexes

Table 1

Product distribution in the hydroformylation of hex-1-ene [a] in the presence of $[HRh\{P(OPh)_3\}_4]$ [b] and a phosphorus ligand L [c]

[L]/[Rh]	$P(OPh)_3$		PPh_3		diphos		$Cp_2Zr(CH_2PPh_2)_2$	
	ald. [d] (%)	n/i	ald. (%)	n/i	ald. (%)	n/i	ald. (%)	n/i
1.1	55	2.3	60	2.6				
1.4					79	3.1	68	6.3
2.0	61	3.2	84	3.3			76	5.3
2.6					87	2.9	85	5.5
3.6					83	3.8	76	5.9
4.0	67	4.3	74	5.1			84	5.2

[a] In addition to the products shown, the mixture at the end of the reaction contained hex-2-ene. [b] $[Rh] = 1.25 \times 10^{-2}$ mmol. [c] L = $P(OPh)_3$, PPh_3, diphos(dppe), $Cp_2Zr(CH_2PPh_2)_2$. [d] Aldehyde.

$[Cp_2Zr(CH_2PPh_2)_2Rh(H)\text{-}(PPh_3)]$ [2,3], $[Cp_2Zr(CH_2PPh_2)_2Rh(H)(CO)(PPh_3)]$ [4] and $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2\text{-}Cp_2Zr(CH_2PPh_2)_2]$ [5,6] are also highly active.

We present below the results of study of hydroformylation of hex-1-ene catalyzed by $[HRh\{P(OPh)_3\}_4]$ or $[HRh(CO)\{P(OPh)_3\}_3]$ in the presence of various phosphorus ligands, viz. $P(OPh)_3$, PPh_3, diphos (dppe: 1,2-bis(diphenylphosphino) ethane) and $Cp_2Zr(CH_2PPh_2)_2$.

Results and discussion

Under hydroformylation conditions (5 bar CO/H_2 (1/1), 353 K), with a 400-fold ratio of hex-1-ene to rhodium in the absence of free phosphorus ligands, both $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$ are catalytically active, and bring about complete conversion of hex-1-ene in 70 min. However, the main reaction products are not aldehydes (44% and 32% yield for $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$, respectively), but hex-2-ene (56% and 68%), with a very low n/i ratio (2.4 and 1.3, respectively). The aldehyde yield and selectivity are markedly higher when modifying ligands such as $P(OPh)_3$, PPh_3, diphos and $Cp_2Zr(CH_2PPh_2)_2$ are present (Tables 1 and 2).

The results obtained with the $[HRh\{P(OPh)_3\}_4]$ catalyst and various modifying ligands are summarized in Table 1. The data reveal the specificity of some of the systems investigated. Thus, use of higher concentrations of PPh_3 and $P(OPh)_3$, i.e. $[L]:[Rh] > 2$, leads to higher yields of and selectivities towards the aldehydes. Less obvious is the concentration dependence for the bidentate modifying ligands, diphos (dppe: 1,2-bis(diphenylphosphino)ethane) and $Cp_2Zr(CH_2PPh_2)_2$, for which only 1.5-fold excess of a ligand suffices to give the maximum yield. Of the four systems studied, the highest n/i selectivity (5–6) is obtained with $Cp_2Zr(CH_2PPh_2)_2$. Since the yield of aldehydes in the latter system is 75–85%, modification of $[HRh\{P(OPh)_3\}_4]$ by $Cp_2Zr(CH_2PPh_2)_2$ must be regarded as the most favorable in terms of yield and selectivity. Compared with the system previously studied, i.e. the phosphine complex $[HRh\{P(Ph)_3\}_4]$ with $Cp_2Zr(CH_2PPh_2)_2$ (where $n/i = 2.76$) [3] the best result in respect of n/i values is obtained with the phosphite analog, $[HRh\{P(OPh)_3\}_4]$, which gives n/i values twice as large.

In the presence of $[HRh\{P(OPh)_3\}_4]$ and $Cp_2Zr(CH_2PPh_2)_2$ the yield of aldehy-

Table 2

Product distribution in the hydroformylation of hex-1-ene [a] in the presence of $[HRh(CO)\{P(OPh)_3\}_3]$ [b] and phosphorus ligands, L [c]

[L]/[Rh]	$P(OPh)_3$		PPh_3		diphos		$Cp_2Zr(CH_2PPh_2)_2$	
	ald. [d] (%)	n/i	ald. (%)	n/i	ald. (%)	n/i	ald. (%)	n/i
1.0	54	2.4	61	3.4			54	2.9
1.3					86	2.7		
1.7							83	3.0
2.0	77	5.0	87	2.8				
2.4					73	2.3		
2.9	73	5.2					74	3.5
4.0			87	7.0	90	2.4	73	3.6

[a,b,c,d] See Table 1.

des was increased to 98% under 10 bar pressure, but n/i fell to 3.4.

The results shown in Table 2 reveal the catalytic activity of the $[HRh(CO)\{P(OPh_3\}_3]$ systems in the presence of various modifying ligands. As in the case of $[HRh\{P(OPh)_3\}_4]$, the best results were obtained with an excess of the free ligand ([L] : [Rh] > 1.5). The highest aldehyde yield (> 80%) was obtained with diphos and PPh_3 while the systems containing $P(OPh)_3$ and $Cp_2Zr(CH_2PPh_2)_2$ gave slightly lower yields of aldehydes, viz. 75%. The previously studied system containing the phosphine complex $[HRh(CO)\{(PPh)_3\}_3]$ and $Cp_2Zr(CH_2PPh_2)_2$ gave a value of n/i of 2.6, whereas with the present system the n/i ratio is 3.4.

The best catalytic system $[HRh\{P(OPh)_3\}_4]$ and $Cp_2Zr(CH_2PPh_2)_2$ was examined for stability in two experiments. In the first experiment, after one hydroformylation reaction cycle was complete a further quantity of hex-1-ene was added to the reaction mixture and the autoclave was again filled with CO/H_2. After completion of the reaction a third quantity of hex-1-ene was introduced. The stabilities of all four examined systems (see Table 1) proved to be similar, i.e. the decrease of the initial pressure was already smaller in the third cycle, and in the post-reaction mixture unreacted hex-1-ene was detected. The highest aldehyde yield (58%) was achieved in the presence of $Cp_2Zr(CH_2PPh_2)_2$, but the yield upon addition of PPh_3 (54%) was not much lower (Table 3).

Table 3

Composition of the hex-1-ene hydroformylation products [a] for catalysis by $[HRh\{P(OPh)_3\}_4]$ in the presence of ligand L ($[Rh] = 1.25 \times 10^{-2}$ mmol; [L]/[Rh] = 4)

L	[hex-1-ene] = 3×5.2 mmol $p = 5$ bar			[hex-1-ene] = 12.1 mmol $p = 10$ bar	
	ald. (%)	hex-1 (%)	n/i	ald. (%)	n/i
$P(OPh)_3$	44	12	4.7	71	5.0
PPh_3	54	8	5.3	74	4.8
diphos	51	18	2.4	75	4.4
$Cp_2Zr(CH_2PPh_2)_2$	58	9	3.9	64	4.4

[a] See Table 1.

The second experiment was carried out at higher hex-1-ene concentration ([hex-1-ene]:[Rh] = 970) and under 10 bar pressure. The system $[HRh\{P(OPh)_3\}_4]$ $+ Cp_2Zr(CH_2PPh_2)_2$ gave only a 64% yield of aldehydes, whereas in the other three systems the aldehyde yield was 71–77% (Table 3).

Thus, addition of the diphosphine $Cp_2Zr(CH_2PPh_2)_2$ results in an increase in both the yield and selectivity of the hydroformylation reaction catalyzed by $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$. Particularly good results (80% aldehydes, $n/i = 5.7$) are achieved with the system based on $[HRh\{P(OPh)_3\}_4]$. After 800 cycles, however, the system loses its activity and its stability is thus comparable to that of systems containing $[HRh\{P(OPh)_3\}_4]$ and the other phosphorus ligands.

^1H and ^{31}P NMR monitoring allowed identification of the complexes formed in the initial stage of the reaction. Depending on the native properties of the ligand (L), substitution of one or two $P(OPh)_3$ ligands in the complex was observed.

The following reaction pattern can be proposed:

$$HRh\{P(OPh)_3\}_4 + L \rightarrow \underset{(1)}{HRh\{P(OPh)_3\}_3L}$$

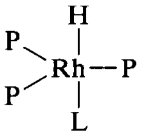
$L = PPh_3$, $Cp_2Zr(CH_2PPh_2)_2$

$$HRh\{P(OPh)_3\}_4 + \text{diphos} \rightarrow \underset{(2)}{HRh\{P(OPh)_3\}_2(\text{diphos})}$$

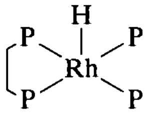
$$HRh(CO)\{P(OPh)_3\}_3 + L \rightarrow \underset{(3)}{HRh(CO)\{P(OPh)_3\}_2L}$$

$L = PPh_3$, $Cp_2Zr(CH_2PPh_2)_2$

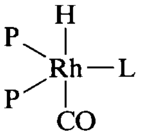
$$HRh(CO)\{P(OPh)_3\}_3 + \text{diphos} \rightarrow \underset{(4)}{HRh(CO)\{P(OPh)_3\}(\text{diphos})}$$



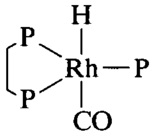
(1)



(2)



(3)



(4)

According to the ^1H and ^{31}P NMR spectra, one complex, $[HRh\{P(OPh)_3\}_2(\text{diphos})]$, has a square-pyramidal structure whereas the others show a trigonal bipyramid symmetry. The diphosphine $Cp_2Zr(CH_2PPh_2)_2$ reacts with $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$ complexes in monodentate fashion and the products, ($[HRh\{P(OPh)_3\}_3\text{-}\{Cp_2Zr(CH_2PPh_2)_2]$ and $[HRh(CO)$ $\{P(OPh)_3\}_2\{Cp_2Zr(CH_2PPh_2)_2\}]$), have geometries close to those of species obtained with PPh_3 under similar conditions. A complementary peak, located at δ -3.1 ppm, close to the signal for free $Cp_2Zr(CH_2PPh_2)_2$ [11], is attributed to the uncoordinated $ZrCH_2PPh_2$ moiety in the bimetallic complex.

Substitution of $P(OPh)_3$ by $Cp_2Zr(CH_2PPh_2)_2$ in $[HRh\{P(OPh)_3\}_4]$ and ($[HRh(CO)\{P(OPh)_3\}_3]$ produces products different from those obtained by substitution of PPh_3 in the corresponding $[HRh(PPh_3)_4]$ and $[HRh(CO)\{PPh_3\}_3]$ complexes, where $Cp_2Zr(CH_2PPh_2)_2$ coordinates as chelating ligand [4]. In $[HRh(CO)\{(PPh)_3\}\{Cp_2Zr(PPh_2)_2\}]$, the diphosphine $Cp_2Zr(PPh_2)_2$ is coordinated as a bidentate ligand [1].

Bridging coordination of $Cp_2Zr(CH_2PPh_2)_2$ between two rhodium centres was also considered. If such coordination took place, formation of $[HRh\{P(OPh)_3\}_3]_2[\mu\text{-}Cp_2Zr(CH_2PPh_2)_2]$ would be expected. However, ^{31}P NMR studies of the mixture containing $[Cp_2Zr(CH_2PPh_2)_2]:[Rh] = 0.43$ showed complete coordination of $Cp_2Zr(CH_2PPh_2)_2$ and the presence of about 50% of unchanged $[HRh\{P(OPh)_3\}_4]$. Complete conversion of $[HRh\{P(OPh)_3\}_4]$ was observed when the $[Cp_2Zr(CH_2PPh_2)_2]:[Rh]$ ratio was about 1.2. This provides confirmation of the structure of the rhodium complex proposed earlier, with the diphosphine coordinated via one phosphorus atom rather than as a bridging ligand.

As all previous reports [2–6] have shown that the bis(diphenylphosphinomethyl) complex $Cp_2Zr(CH_2PPh_2)_2$ reacts with rhodium phosphine complexes resulting in formation of derivatives of the type $\{[Rh][(\mu\text{-}PPh_2CH_2)_2ZrCp_2]\}$, in which there is a *trans* chelation of the phosphorus, it is surprising that in the case of the triphenylphosphite rhodium analogs, under identical conditions, only one phosphite site is replaced by the zirconium diphosphine. This difference in behavior can be attributed to the softer character of triphenyl phosphite, the most obvious variable with which increasing observed selectivity might be associated.

The reaction of $[HRh(CO)\{P(OPh)_3\}_3]$ with $Cp_2Zr(CH_2PPh_2)_2$ gave a mixture of $[HRh(CO)\{P(OPh)_3\}_2\{Cp_2Zr(CH_2PPh_2)_2\}]$ and $[HRh\{P(OPh)_3\}_3\}\{Cp_2Zr(CH_2PPh_2)_2\}]$, indicating that the CO/diphosphine substitution is possible. The same reaction conducted under a CO atmosphere gave a single product, $[HRh(CO)\{P(OPh)_3\}_3\{Cp_2Zr(CH_2PPh_2)_2\}]$. The same complex was obtained from the reaction of $[HRh\{P(OPh)_3\}_4]$ with $Cp_2Zr(CH_2PPh_2)_2$ and CO.

The results described above show that CO/diphosphine substitution in the system $[HRh(CO)\{P(OPh)_3\}_3] + Cp_2Zr(CH_2PPh_2)_2$ is rather slow. Along with the above reaction, replacement of CO by $P(OPh)_3$ in $[HRh(CO)\{P(OPh)_3\}_3]$ takes place, to give some $[HRh\{P(OPh)_3\}_4]$, which then reacts with $Cp_2Zr(CH_2PPh_2)_2$.

The complexes for which NMR spectroscopic data are presented in Table 4 are the final reaction products; increase in the [L]:[Rh] ratio ($L = PPh_3$, $Cp_2Zr(CH_2PPh_2)_2$) within the range 1–2 has no effect on the reaction products. For L = diphos even at a [L]:[Rh] ratio of 1.2 formation of $[HRh(diphos)_2]$ is observed ($\delta = 142.6$ ppm, $J(Rh\text{–}P) = 84.6$ Hz). With both $[HRh\{P(OPh)_3\}_4]$ and $[HRh(CO)\{P(OPh)_3\}_3]$, an increase in the diphos concentration results in an increase in the $[HRh(diphos)_2]$ concentration.

Experimental

The rhodium complexes were made by previously described methods: $[HRh\{P(OPh)_3\}_4]$ [8], $[HRh(CO)\{P(OPh)_3\}_3]$ [9], $[Rh(acac)(CO)_2]$ [10]. $Cp_2Zr(CH_2PPh_2)_2$ was obtained as described in ref. 11.

The ^{31}P and ^{1}H NMR spectra of complexes formed in reactions $[HRh\{P(OPh)_3\}_4] + L$ and $[HRh(CO)\{P(OPh)_3\}_3] + L$ were interpreted with the help of computer simulation by the LAOCN3 program.

Hydroformylation reaction procedure

1.25×10^{-2} mmol of a catalyst and appropriate amount of phosphine were weighed out into Teflon vessels and placed in a steel autoclave (40 cm^3) under N_2 and 0.65 or 1.5 cm^3 of hex-1-ene and 1.5 cm^3 of benzene were introduced. The

Table 4

^{1}H and ^{31}P NMR [a] data for products of the reaction of [HRh{P(OPh)$_3$}$_4$] and L and of [HRh(CO)-{P(OPh)$_3$}$_3$] and L (L = PPh$_3$, Cp$_2$Zr(CH$_2$PPh$_2$)$_2$, diphos)

	^{31}P NMR (δ (ppm), J(A–B) (Hz))	^{1}H NMR (δ (ppm), J(A–B) (Hz))
HRh{P(OPh)$_3$}$_4$ +		
PPh$_3$	δ 129.8 (d of d, J(Rh–P) 238.3) δ 34.5 (d of q, J(Rh–P) 131.3) J(P–P) 63.5	δ −10.8 (q of d of d) J(P–H) 55, J(P–H) 8, J(Rh–H) 4
Cp$_2$Zr(CH$_2$PPh$_2$)$_2$ [b]	δ 129.3 (d of d, J(Rh–P) 248.5) δ 15.5 (d of q, J(Rh–P) 112.8) J(P–P) 16.6	δ −11.2 (d of d of q) J(P–H) 72, J(P–H) 7, J(Rh–H) 2
diphos	δ 133.8 (d of t, J(Rh–P) 260.7) δ 68.0 (d of t, J(Rh–P) 125.0) J(P–P) 68.4	δ −9.7 (t of d of t) J(P–H) 56, J(P–H) 14, J(Rh–H) 8
HRh(CO){P(OPh)$_3$}$_3$ +		
PPh$_3$	δ 143.7 (d of d, J(Rh–P) 250.0) δ 35.8 (d of t, J(Rh–P) 150.4) J(P–P) 141.6	δ −10.0 (t of d of d) J(P–H) 10, J(P–H), J(Rh–H) 3
Cp$_2$Zr(CH$_2$PPh$_2$)$_2$ [b]	δ 144.2 (d of d, J(Rh–P) 249.0) δ 12.0 (d of t, J(Rh–P) 132.3) J(P–P) 129.9	δ −10.2 (d of d of t) J(P–H) 7, J(P–H) 9, J(Rh–H) 4
diphos	δ 144.5 (d of t, J(Rh–P) 252.9) δ 61.1 (d of d, J(Rh–P) 121.1) J(P–P) 66.4	δ −9.3 (t of d of d) J(P–H) 55, J(P–H) 14, J(Rh–H) 10

[a] d—doublet, t—triplet, q—quartet. [b] ^{31}P NMR of uncoordinated ZrCH$_2$PPh$_2$ is observed at −3.1 ppm.

autoclave was closed, flushed with hydrogen, then filled with a 1/1 CO/H$_2$ mixture to 5 or 10 bar. Reactions were carried out at 353 K for 70 min with magnetic stirring and the autoclave was then cooled to room temperature and opened. The products were analyzed by ^{1}H NMR (Tesla 567 BS 100 MHz spectrometer) and IR (Specord M-80) spectroscopy. ^{31}P NMR spectra were recorded on a Tesla BS 587 A spectrometer (at 32.35 MHz) with 85% H$_3$PO$_4$ as external standard.

References

1 L. Gelmini and D.W. Stephan, Organometallics, 7 (1988) 849.
2 R. Choukroun, A. Iraqi, D. Gervais, J.-C. Daran and Y. Jeannin, Organometallics, 6 (1987) 1197.
3 R. Choukroun, A. Iraqi and D. Gervais, J. Organomet. Chem., 311 (1986) C60.
4 R. Choukroun, D. Gervais, P. Kalck and F. Senocq, J. Organomet. Chem., 335 (1987) C9.
5 R. Choukroun, D. Gervais, J. Jaud, P. Kalck and F. Senocq, Organometallics, 5 (1986) 67.
6 F. Senocq, C. Randrianalimanana, A. Thorez, P. Kalck, R. Choukroun and D. Gervais, J. Mol. Cat., 35 (1986) 213.
7 G.S. Ferguson, P.T. Wolczanski, L. Parkanyi and M.C. Zonnevylle, Organometallics, 7 (1988) 1967.
8 A.M. Trzeciak and J.J. Ziolkowski, Transition Met. Chem., 12 (1987) 408.
9 A.M. Trzeciak, J. Organomet. Chem., 390 (1990) 105.
10 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.
11 N.E. Shore, S.J. Young and M. Olmstead, Organometallics, 2 (1983) 1769.