Journal of Organometallic Chemistry, 397 (1990) 119–125
Elsevier Sequoia S.A., Lausanne

JOM 21022

A new platinum-based catalyst system for olefin asymmetric homogeneous hydroformylation

S. Paganelli, U. Matteoli and A. Scrivanti *

Dipartimento di Chimica, Universitá di Venezia, Calle Larga S. Marta 2137, I-30123 Venice (Italy)

(Received April 9th, 1990)

Abstract

The complex [Pt(C_2H_4)((+)-DIOP)] interacts with [PtCl_2((+)-DIOP)] to give catalysts active in hydroformylation of styrene and 1-hexene. The activities of these systems depend upon the molar ratio of the two platinum complexes and the nature of the substrate. The systems display good chemioselectivity and induce asymmetry in the branched aldehydes formed. 2-Phenylpropanal can be isolated in ~27% optical purity from hydroformylation of styrene.

Introduction

A variety of Pt(II) diphosphino complexes in combination with $SnCl_2$ are active catalysts in olefin hydroformylation [1]. Great current interest in this subject stems from the remarkable results obtained with Pt(II) complexes of the type [PtCl_2(chiral chelating diphosphine)] in asymmetric catalytic hydroformylations [2–5]. For instance, Stille successfully used platinum-catalyzed asymmetric hydroformylation as a key step in a direct route to valuable biologically active products [6,7]. In continuation of our interest in these matters [8,9] we are searching for more active and selective catalytic systems and we recently reported that Pt(0) complexes of the type [Pt(ethylene)(chelating diphosphine)] become active catalysts for styrene hydroformylation when promoted by CH_3SO_3H [10]. We wish to report here that Pt(II) complexes can also activate Pt(0) complexes for the catalytic hydroformylation of alkenes.

Results

The new catalytic systems were prepared by mixing various amounts of complexes [Pt(C_2H_4)((+)-DIOP)] (**A**) and [PtCl_2((+)-DIOP)] (**B**) [DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] keeping the total platinum content constant.

0022-328X/90/$03.50

Table 1

Homogeneous hydroformylation of styrene catalyzed by Pt complexes

Run	Catalyst precursor	Conv. (%)	Ethylbenzene yield (%)	Aldehydes yield (%)	Selectivity to 3-phenyl-propanal (%)	o.p. (%) [a,b]	config [a,b]
1	**A**	11.6	1.2	10.4	38.4	n.d.	–
2	**A**/**B** (7/3)	50.6	1.7	48.9	32.5	27.9	(−)-*R*
3	**A**/**B** (1/1)	63.9	1.5	62.4	35.8	27.6	(−)-*R*
4	**A**/**B** (3/7)	59.6	1.9	57.7	41.7	27.7	(−)-*R*
5	**B**	49.0	2.1	46.9	55.7	24.2	(−)-*R*
6	**A**/**C** (3/7)	57.8	2.0	55.8	42.5	7.4	(−)-*R*

Styrene, 16 mmol; styrene/Pt(molar ratio), 230; toluene, 20 ml; $P(CO) = P(H_2)$, 50 atm; temperature, 100 °C; time, 72 h. Cat.: **A** = $[Pt(C_2H_4)((+)\text{-DIOP})]$; **B** = $[PtCl_2((+)\text{-DIOP})]$; **C** = $[PtCl_2((\pm)\text{-DIOP})]$.
[a] Determined with 2-phenylpropanal. [b] Calculated using a value of $[\alpha]^{21}_{D}$ max of 315.8 [2] (*c* 1.5, benzene) for the optically pure (+)-(*S*)-2-phenylpropanal.

Data for styrene hydroformylation are given in Table 1. Complex **A** is a poor catalyst, but complex **B** shows a much higher activity (runs 1 and 5). When we carried out the styrene hydroformylation in the presence of mixtures of complexes **A** and **B** we observed a catalytic activity that did not correspond to the sum of the activities of the complexes calculated by taking account of the stoichiometry of the mixture (runs 2–4) [11 *]. For instance, the catalytic system prepared by mixing complexes **A** and **B** in a 7/3 molar ratio yielded 48.9% aldehydes (run 2), a yield close to that obtained in the presence of pure complex **B**. The most active system was obtained by mixing complexes **A** and **B** in a 1/1 molar ratio (yield of aldehydes 62.4%, run 3). When the complex **A**/complex **B** molar ratio was reduced to 3/7 the yield of aldehydes fell to 57.7% (run 4). The chemioselectivity of these systems is very good (~ 98%), and the only side reaction observed is hydrogenation of the substrate to ethylbenzene. The regioselectivity towards the linear aldehyde depends on catalyst composition, ranging from 32.5 to 55.7%. The asymmetric inductions obtained with the mixed systems fall in a narrow range (27–28%, runs 2–4), and are a little higher than that provided by complex **B** (run 5). It is noteworthy that under the same conditions the widely-used system complex **B**/$SnCl_2$ gave 2-phenylpropanal with only 3.7% o.p. (see experimental section).

A catalytic reaction (not reported in Table 1) carried out at higher hydrogen pressure ($P(H_2) = 100$ atm, $P(CO) = 50$ atm) in the presence of complex **A**/complex **B** mixture (molar ratio 3/7) gave a higher yield of aldehydes (71.5%), the corresponding alcohols (12.5%), and small amounts of ethylbenzene (~ 9%). The branched aldehyde was obtained with the same regioselectivity, optical purity, and configuration as in the reaction at a lower hydrogen partial pressure. Run 6 involved an experiment carried out under the same conditions as run 4, but with racemic DIOP in the Pt(II) complex. The conversion, chemioselectivity and regioselectivity are almost identical in the two experiments; the optical purity of the branched aldehyde falls from 27.7 to 7.4% when the achiral complex is used.

In Table 2 are shown the results of the catalytic hydroformylation of 1-hexene. In all the experiments the only aldehydes formed were 1-heptanal and 2-methyl-

---

* Reference number with asterisk indicates a note in the list of references.

Table 2

Homogeneous hydroformylation of 1-hexene catalyzed by Pt complexes

Run	Catalyst precursor	Conv. (%)	n-Hexane yield (%)	Hexenes yield (%)	Aldehydes yield (%)	Selectivity to 1-heptanal (%)	o.p. (%) [a,b]	Config. [a,b]
1	**A**	6.2	0.9	0.8	4.5	81.7	n.d.	–
2	**A**/**B** (7/3)	68.0	1.3	2.5	64.2	86.8	10.9	(–)-*R*
3	**A**/**B** (1/1)	75.5	1.6	2.9	71.0	86.5	10.2	(–)-*R*
4	**A**/**B** (3/7)	89.7	1.7	2.8	85.2	86.3	10.4	(–)-*R*
5	**B**	71.5	1.9	3.0	66.6	82.9	6.2	(–)-*R*

1-Hexene, 16 mmol; 1-hexene/Pt(molar ratio), 230; toluene, 20 ml; $P(CO) = P(H_2)$, 50 atm; temperature, 100 °C; time, 72 h. Cat.: **A** = [Pt(C_2H_4)((+)-DIOP)]; **B** = [$PtCl_2$((+)-DIOP)].

[a] Determined with 2-methylhexanoic acid [15]. [b] Calculated using a value of $[\alpha]_D^{25}$ max of 22.105 [16] (neat) for the optically pure (+)-(*S*)-2-methylhexanoic acid.

hexanal. The overall behaviour resembles that observed in styrene hydroformylation. In this case the mixed systems were again more active than complex **A** or complex **B**. The highest activity was displayed by the catalytic system obtained by mixing complex **A** and complex **B** in 3/7 molar ratio (run 4). The side hydrogenation and isomerization reactions occurred to only a small extent, and the chemioselectivity was always > 95%. Complex **A** and **B** gave the same regioselectivity towards linear aldehyde (~ 82%), whereas the mixed catalysts gave a higher normal to branched aldehyde ratio (~ 86%). In the next to the last column of Table 2 are listed the optical purities of 2-methylhexanal. The mixed catalytic systems give moderate asymmetric inductions (o.p. ~ 10%) which are significantly higher than those obtained under the same conditions with complex **B** (o.p. 6.2%) or with the widely-used complex **B**/$SnCl_2$ system (o.p. 1.2%) (see experimental section).

Discussion

The data in Tables 1 and 2 show that complex [$PtCl_2$((+)DIOP)] (**B**) interacts with complex [$Pt(C_2H_4)$((+)DIOP)] (**A**) to produce a catalytically active system. The results suggest that the nature of the substrate plays a key role in this interaction, since the most active system for styrene hydroformylation is prepared by mixing complexes **A** and **B** in the molar ratio 1/1, whereas the best activity for 1-hexene hydroformylation is obtained in the presence of a mixture of complexes **A** and **B** in 3/7 molar ratio. In our opinion this means that the interaction does not produce a well-defined mono- or poly-nuclear platinum species. Some insights into this interaction were obtained by comparing the ^{31}P-NMR spectra recorded at the beginning and at the end of a styrene hydroformylation experiment (catalyst precursor: complexes **A** and **B** in 1/1 molar ratio) (see experimental section). The ^{31}P-NMR spectrum of the initial mixture shows a singlet (flanked by Pt-satellites) due to complex **B** and the pattern attributable to complex [Pt(styrene)((+)-DIOP)] (**D**), which is formed from complex **A** via ethylene displacement [12,13] (see experimental section). In the ^{31}P-NMR spectrum recorded at the end of the reaction the pattern due to complex **B** was unchanged, whereas the signals of complex **D** were replaced by a very intricate pattern indicating the presence of several species. In our opinion these findings suggest that the activation involves some major rearrangements of the starting platinum(0) derivative, and that the complex [$PtCl_2$((+)DIOP)] takes part reversibly in the catalysis.

It is of interest that in the 1-hexene hydroformylation the regioselectivity towards linear aldehyde and the asymmetric induction of the mixed systems are higher than those obtained with the pure complexes **A** or **B**. This feature is not surprising at high complex **A**/complex **B** molar ratios. Under these conditions only the free complex **A** and the activated species should be present in the system, but the contribution of the free complex **A** to the overall catalysis should be negligible owing to its low catalytic activity. Therefore, the regioselectivity and asymmetric induction are expected to be determined by the activated species. On the other hand, at low complex **A**/complex **B** molar ratios the presence of free complex **B** could exert a strong influence, lowering the regioselectivity and the asymmetric induction. Since this does not occur we believe that no free complex **B** is involved in 1-hexene hydroformylation under the conditions used.

The regio- and stereo-selectivity data for the styrene hydroformylation reveal a more complex behaviour. When the complex **A**/complex **B** molar ratio is lowered there is a roughly linear increase in the regioselectivity towards the linear aldehyde, whereas the asymmetric induction remains constant. In this case the most active system is formed by mixing complexes **A** and **B** in 1/1 molar ratio. At complex **A**/complex **B** molar ratios of ≥ 1 the catalysis must be due to free complex **A** and to the activated species. Under these conditions, as in the case of the 1-hexene hydroformylation, the regio- and stereo-selectivities are determined by the activated species. The higher regioselectivity obtained at complex **A**/complex **B** molar ratios of < 1 may be rationalized by assuming the presence of the free dichloro complex **B** which is active in catalysis. The data in run 4 of Table 1 thus represent the outcome of a balance between the specific activity of complex **B**, tending to produce much linear aldehyde, and that of the activated species, which produces much branched aldehyde. The steady values of the stereoselectivity probably represent a compromise between the two stereoselectivities, which are already very close.

Run 6 of Table 1 reveals very interesting results. When the styrene hydroformylation was carried out in the presence of a mixture of optically active complex **A** and racemic complex **B** 2-phenylpropanal was obtained in 7.4% o.p. It thus seems that the asymmetric induction is not derived from either complex **A** or complex **B**, but from the synergic interaction of the two species.

Conclusions

We suggest that the Pt(0)/Pt(II) system examined is of interest for several reasons, in particular:

(i) Pt(0) activation by a Pt(II) complex is unprecedented in both platinum chemistry and hydroformylation.
(ii) The catalytic system can be optimized, as suggested by the experiment carried out at $P(H_2)$ 100 atm, in which there was a higher reaction rate without loss of asymmetric induction in the branched aldehyde.
(iii) Even if the system is not optimized, asymmetric inductions are much higher than those provided by the widely used $[PtCl_2((+)\text{-DIOP})]/SnCl_2$ system under the same conditions.
(iv) An appropriate choice of the promotor Pt(II) complex could lead to generation of more active and/or more selective catalytic systems.

Experimental

GLC analyses were carried out on a C. Erba HRGC 5300 or on a Hewlett Packard HP 5890 gas chromatograph. Optical rotations were measured with a Perkin Elmer 241 polarimeter using a 1 dm tube. ^1H and ^{31}P NMR spectra were recorded on a Varian FT-80 A spectrometer operating at 79.542 and 32.203 MHz, respectively. IR spectra were recorded on a Biorad FTS-40 interferometer.

Styrene (C. Erba Analyticals) and 1-hexene (Janssen Chimica) were distilled before use. [(+)-DIOP] and [(−)-DIOP] were used as received from Strem Chemicals. Solvents were purified by standard procedures [14]. $[Pt(C_2H_4)((+)\text{-DIOP})]$, $[PtCl_2((+)\text{-DIOP})]$ and $[PtCl_2(\pm)\text{-DIOP}]$ were made as described previously [12].

Reaction products were identified by comparing their GLC retention times, NMR and IR spectra with those of authentic samples.

Hydroformylation reaction procedure

The freshly distilled substrate (16 mmol) was placed in a 150 ml stainless steel autoclave together with 20 ml of toluene and 0.069 mmol of the Pt catalyst. The reactor was pressurized to 100 atm with synthesis gas ($CO/H_2 = 1/1$) and heated to 100 °C (±0.1 °C). After 72 h the reactor was cooled to room temperature, the residual gases were removed, and the reaction mixture was analysed by GLC to determine the conversion, chemioselectivity and regioselectivity of the reaction.

In the case of hydroformylation of 1-hexene the aldehydes obtained were oxidized to the corresponding carboxylic acids by a standard procedure [15] for determination of the optical purities.

Hydroformylation in the presence of [PtCl$_2$((+)-DIOP)]

The freshly distilled substrate (16 mmol) was placed in the autoclave together with 20 ml of toluene, 0.069 mmol of [$PtCl_2$((+)-DIOP)] and 0.345 mmol of $SnCl_2$ (Pt/Sn = 1/5). The reactor was pressurized to 100 atm with synthesis gas ($CO/H_2 = 1/1$) and heated to 100 °C (±0.1 °C). After 4 h the reactor was cooled to room temperature, the gas vented off, and the mixture analyzed by GLC.

In styrene hydroformylation the yield of aldehydes was 76.8%, the regioselectivity towards the linear aldehyde 50.2%, the optical purity 3.7%, and the configuration (−)-*R*.

In 1-hexene hydroformylation the yield of aldehydes was 68.1%, the regioselectivity towards the linear aldehyde 86.3%, the optical purity 1.2%, and the configuration (−)-*R*.

NMR investigations

Freshly distilled styrene (32 mmol) was placed in a Schlenk flask together with 10 ml of toluene and 0.138 mmol of catalyst precursor (complex **A**/complex **B** in 1/1 molar ratio). The white suspension was stirred under nitrogen for 1 h and a 2 ml sample of the suspension was then withdrawn and evaporated under reduced pressure, and the residue dissolved in CD_2Cl_2 for NMR study. The ^{31}P NMR spectrum of the solution shows the presence of a singlet at −1.1 ppm flanked by Pt satellites ($^1J(Pt{-}P) = 3518$ Hz), due to complex **B**, and two AB quartets (with associated Pt satellites) had replaced the signals from complex **A**. This observation is consistent with a rapid ethylene displacement by styrene [13] to give the complex [Pt(styrene)((+)-DIOP)]. This latter exists as two diastereoisomeric forms, formed by binding of the *Si* and of the *Re* face of styrene to the [Pt((+)-DIOP)] moiety. Isomer I: $\delta(P_a) = 11.7$ ppm, $\delta(P_b) = 8.2$ ppm, $J(P{-}P) = 71$ Hz, $J(Pt{-}P_a) = 3634$ Hz, $J(Pt{-}P_b) = 3530$ Hz; isomer II: $\delta(P_a) = 10.2$ ppm, $\delta(P_b) = 9.4$ ppm, $J(P{-}P) = 75$ Hz, $J(Pt{-}P_a) = 3606$ Hz, $J(Pt{-}P_b) = 3615$ Hz.

The remaining suspension was transferred into a 150 ml stainless steel autoclave. The reactor was pressurized to 100 atm with synthesis gas ($CO/H_2 = 1/1$) and heated to 100 °C. After 10 h the reactor was cooled to room temperature and the gas vented off. The resulting clear solution was concentrated under reduced pressure and the red oily residue dissolved in CD_2Cl_2 and the solution transferred to an NMR tube.

References and notes

1 T. Hayashi, Y. Kawabata, T. Isoyama and I. Ogata, Bull. Chem. Soc. Jpn., 54 (1981) 3438.
2 G. Consiglio, P. Pino, L.I. Flowers and C.U. Pittman, Jr., J. Chem. Soc., Chem. Commun., (1983) 612.

3 L. Kollar, G. Consiglio and P. Pino, J. Organomet. Chem., 330 (1987) 305.
4 L. Kollar, J. Bakos, I. Toth and B. Heil, J. Organomet. Chem., 350 (1988) 277.
5 L. Kollar, J. Bakos, I. Toth and B. Heil, J. Organomet. Chem., 370 (1989) 257.
6 G. Parrinello, R. Deschenaux and J.K. Stille, J. Org. Chem., 51 (1986) 4189.
7 G. Parrinello and J.K. Stille, J. Am. Chem. Soc., 109 (1987) 7122.
8 A. Scrivanti, C. Botteghi, L. Toniolo and A. Berton, J. Organomet. Chem., 344 (1989) 261.
9 A. Scrivanti, S. Paganelli, U. Matteoli and C. Botteghi, J. Organomet. Chem., 385 (1990) 439.
10 C. Botteghi, S. Paganelli, U. Matteoli, A. Scrivanti, R. Ciorciaro and L.M. Venanzi, Helv. Chim. Acta, 73 (1990) 284.
11 In order to check the dependence of the catalytic activity upon concentration of complex **B**, we carried out some styrene hydroformylations at variable catalyst concentration. These experiments showed that the yield of aldehydes is roughly proportional to the concentration of complex **B**.
12 J.M. Brown, S.J. Cook and S.J. Kimber, J. Organomet. Chem., 269 (1984) C58.
13 D. Parker and R.J. Taylor, J. Chem. Soc., Chem. Commun., (1987) 1781.
14 D.D. Perrin and W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd edn., Pergamon Press, Oxford, 1988.
15 P. Pino, S. Pucci, F. Piacenti and G. Dell'Amico, J. Chem. Soc. C, (1971) 1640.
16 G. Consiglio, C. Botteghi, C. Salomon and P. Pino, Angew. Chemie, Int. Ed. Engl., 12 (1973) 669, and references therein.