*Journal of Organometallic Chemistry*, 417 (1991) C41–C45
Elsevier Sequoia S.A., Lausanne
JOM 21871PC

Preliminary communication

# Hydroformylation of olefins catalyzed by alkene complexes of platinum(0) *

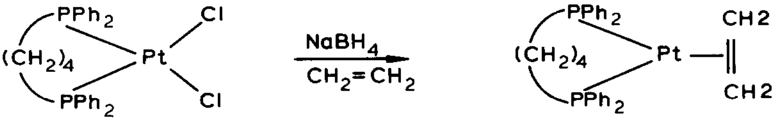
Carlo Botteghi * and Stefano Paganelli
*Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, I-30123 Venice (Italy)*

(Received February 25th, 1991)

## Abstract

In the presence of methanesulfonic acid the platinum(0) complex [Pt($C_2H_4$)(DPPB)] catalyses the hydroformylation of various olefins. In some cases there is quite good chemoselectivity and high regioselectivity towards n-aldehyde.

The well known and readily accessible platinum complexes of the type [Pt(alkene)(PP)] (PP = chelating ditertiary phosphine) are inactive in the hydroformylation of olefins [1], but are active in the presence of a strong organic acid with poor coordinating ability, such as methanesulfonic acid (MSA) [1]. Thus, the complex [Pt($C_2H_4$)(DPPB)], [DPPB = 1,4-bis(diphenylphosphino)butane] was prepared by a known procedure (see eq. 1) [2]:



and used in the presence of an equimolecular amount of MSA in the hydroformylation reaction of various olefinic substrates. The results are summarized in Table 1.

Under standard conditions (100 °C and 100 atm of an equimolecular mixture of CO and $H_2$ in toluene) and with a substrate-to-catalyst molar ratio of ca. 320, 1-alkenes are converted into the expected oxo-aldehydes with acceptable rates and with fair to good yields (see Table 1). The catalytic system is rather sensitive towards steric hindrance at the double bond; thus terminal alkenes bearing substituents in the 2- or 3-position, exemplified by α-methylstyrene and 3,3-dimethyl-1-butene respectively, react sluggishly with CO–$H_2$ under the conditions used (see Exp. 5 and 12). Furthermore, internal double bonds are rather unreactive, as shown by the hydroformylation of cyclohexene (see Exp. 6), but this can be exploited for

---

* Dedicated to the memory of Professor Piero Pino.

Table 1

Hydroformylation of various olefins catalyzed by [Pt($C_2H_4$)(DPPB)]/$CH_3SO_3H$

| Exp. | Substrate | *t* (h) | Substrate conversion (%) | Hydrogenated product yield (%) | Isomerized product yield (%) | Total aldehyde yield (%) | Selectivity towards n-aldehyde (%) | Total alcohol yield (%) | High boiling by-products yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Styrene | 22 | 94.2 | 2.6 | – | 78.9 | 89.2 | 6.0 | 6.7 |
| 2[a] | Styrene | 22 | 44.3 | 1.2 | – | 37.1 | 30.4 | 3.0 | 3.1 |
| 3[b] | Styrene | 22 | 91.3 | 2.0 | – | 80.4 | 89.5 | 3.9 | 5.0 |
| 4 | 1-Hexene | 24 | 95.9 | 1.9 | 25.7 | 58.0 | 94.9 | 4.7 | 5.6 |
| 5 | 3,3-Dimethylbutene | 45 | 38.4 | 0.3 | – | 31.8 | 99.1 | 5.3 | 1.0 |
| 6 | Cyclohexene | 68 | 22.3 | 0.4 | – | 18.3[h] | – | 3.1 | 0.5 |
| 7[c] | Cyclohexene | 48 | 27.7 | 1.0 | – | 23.7[h] | – | 2.2 | 0.8 |
| 8[d] | Cyclohexene | 48 | 52.3 | 0.8 | – | 17.9[h] | – | 23.8 | 9.8 |
| 9 | Ethyl-3-butenoate | 22 | 93.6 | 1.5 | 6.5 | 81.8[e] | 82.8 | – | 3.8 |
| 10 | 3-Vinylcyclohexene | 22 | 82.8 | 0.8 | – | 78.9[f] | 96.5 | – | 3.1 |
| 11 | Allylcyanide | 22 | 79.5 | 4.9 | 3.3 | 69.4 | 83.0 | – | 1.9 |
| 12 | α-Methylstyrene | 165 | 47.6 | 3.1 | – | 22.6[i] | – | 4.5 | 17.4 |
| 13 | *R*-(+)-Limonene | 43 | 14.3 | – | – | 13.9 | 78.2[g] | 0.4 | – |

Substrate: 16 mmol; catalyst: [Pt($C_2H_4$)(DPPB)]/$CH_3SO_3H$(1/1); substrate/catalyst = 320/1; toluene: 20 ml; $P(CO) = P(H_2) = 50$ atm; $T = 100$ °C.

[a] In the presence of [Pt($C_2H_4$)($PPh_3$)$_2$]/$CH_3SO_3H$ (1/1 molar ratio). [b] $P$(CO) to $P(H_2)$ ratio = 2/1 (total pressure 100 atm). [c] In the presence of [Pt($C_2H_4$)(DPPB)]/$CF_3SO_3H$ (1/1 molar ratio). [d] In the presence of [Pt($C_2H_4$)(DPPB)]/$CH_3SO_3H$ (1/3 molar ratio). [e] 8.8% yield of methyl-3-formylbutanoate and 5.3% yield of methyl-2-formylbutanoate. [f] 1.4% yield of 2-(3-cyclohexenyl)propanal and 1.4% yield of dialdehydes. [g] Diastereoisomeric ratio: 60.5/39.5 for 3-(4-methylcyclohex-3-enyl)butanal, determined by GLC (the absolute configurations of the diastereomers were not determined). [h] Only cyclohexane carboxaldehyde was formed. [i] Only 3-phenylbutanal was formed.

Table 2

Hydroformylation of 3,3-dimethylbutene catalyzed by [Pt($C_2H_4$)(DPPB)]/$CH_3SO_3H$ in various solvents

| Exp. | Solvent | $t$ (h) | Substrate conversion (%) | Hydro-genated product yield (%) | Total aldehyde yield (%) | Selectivity towards n-aldehyde (%) | Total alcohol yield (%) | High boiling by-products yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | Toluene | 45 | 38.4 | 0.3 | 31.8 | 99.1 | 5.3 | 1.0 |
| 2 | Methylene chloride | 19 | 84.7 | – | 65.5 | 97.6 | 17.0 | 2.2 |
| 3 | Ethanol | 22 | 82.5 [a] | 4.8 | 8.7 | 32.2 | 0.2 | 0.7 |
| 4 | Butan-2-one | 22 | 34.7 | 0.6 | 31.2 | 92.8 | 1.0 | 1.9 |
| 5 | Diethyl ether | 89 | 18.2 | 0.3 | 16.8 | 81.0 | 0.6 | 0.5 |
| 6 | Tetrahydrofuran | 72 | 11.7 | 0.3 | 11.0 | 98.8 | 0.3 | 0.1 |

Substrate: 16 mmol; catalyst: [Pt($C_2H_4$)(DPPB)]/$CH_3SO_3H$ (1/1); substrate/catalyst = 320/1; solvent: 20 ml; $P(CO) = P(H_2) = 50$ atm; $T = 100$ °C.

[a] 68.1% yield of 2-ethoxy-3,3-dimethylbutane was found.

selective hydroformylation reactions. For example, 3-vinylcyclohexene is more than 92% hydroformylated at the vinylic double bond (see Exp. 10).

The chemoselectivity of the reaction is generally good, however, although there is little hydrogenation of the substrate in most cases, migration of the double bond in the case of linear 1-alkenes constitutes a serious disadvantage. In the case of 1-hexene, for example, up to 25.7% of isomeric hexenes are formed (see Exp. 4). Surprisingly, such isomerization is much less important during hydroformylation of linear olefins containing functional groups, such as ethyl 3-butenoate and allyl cyanide (see Exp. 9 and 11).

Hydrogenation of the oxo-aldehydes to give the corresponding alcohols under the conditions used is generally more pronounced than the reduction of the substrate, but it can be controlled by stopping reaction at a low substrate conversion. The strong acid present can promote various other undesired processes, such as aldehyde condensation and substrate polymerization (particularly when the substrate is styrene or $\alpha$-methylstyrene).

The regioselectivity towards the formation of linear aldehydes is very good and comparable with that obtained with the most commonly used catalyst $[PtCl_2(PP)]/SnCl_2$ (PP = chelating diphosphine) [3]: the yield of linear aldehyde exceedes 96% in the case of 1-alkenes bearing substituents in 2- or 3-positions (see Exp. 5, 10 and 12).

The complex $[Pt(C_2H_4)(PPh_3)_2]$ [4] shows a lower catalytic activity than $[Pt(C_2H_4)(DPPB)]$ in the hydroformylation of styrene; interestingly, in this case the regioselectivity towards formation of the branched aldehyde is markedly higher (see Exp. 2).

The use of trifluoromethanesulfonic acid (TFMSA) results in a marked increase in both the conversion and yield of aldehyde (see Exp. 7); however, in the case of reactive olefins such as styrene and $\alpha$-methylstyrene, the predominant reaction is substrate polymerization. In contrast, the presence of an excess of MSA increases the reaction rate, but lowers the chemoselectivity (see Exp. 8).

The nature of the solvent exerts a marked influence on the rate and on the chemioselectivity (see Table 2). For example, the hydroformylation of 3,3-dimethyl-1-butene is much faster in methylene chloride (about 85% conversion after 19 h) than in toluene (about 38% conversion after 45 h). In the former solvent there is also a substantial amount of hydrogenation of the oxo-aldehydes to alcohols, whereas when ethanol is used as the solvent the yield of aldehydes was only 8.7%. Ethereal solvents reduce the catalytic activity: thus, use of diethyl ether or tetrahydrofuran leads to considerable reduction in the reaction rate, and when triethylorthoformate was used as the solvent or cosolvent [5] in the hydroformylation of styrene, the catalysis was completely inhibited.

A study of the influence of other reaction parameters is in progress with the aim of elucidating the reaction mechanism.

**Acknowledgement.** We thank Alvise Perosa for experimental assistance.

## References

1 C. Botteghi, S. Paganelli, U. Matteoli, A. Scrivanti, R. Ciorciaro and L.M. Venanzi, Helv. Chim. Acta, 73 (1990) 284.

2 A. Scrivanti, R. Campostrini and G. Carturan, Inorg. Chim. Acta, 142 (1988) 187.
3 Y. Kawabata, T. Hayashi and I. Ogata, J. Chem. Soc., Chem. Commun., (1979) 462.
4 U. Nagel, Chem. Ber., 115 (1982) 1998.
5 G. Parrinello and J.K. Stille, J. Am. Chem. Soc., 109 (1987) 7122.