31. A New Catalytic System for the Hydroformylation of Styrene Using Alkene Complexes of Platinum(0)

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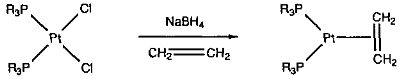
The platinum(0) complexes [Pt(C_2H_4)(PP)] (PP = 1,2-bis[(diphenylphosphino)methyl]benzene (**2**) and (+)-DIOP = (+)-1,4-bis(diphenylphosphino)-1,4-dideoxy-2,3-*O*-isopropyliden-D-threitol), when promoted by CH_3SO_3H, become active catalysts for styrene hydroformylation with total yields of aldehydes ranging from 44 to 67 % und selectivities towards 3-phenylpropanal ranging from 80 to 88 %. Smaller amounts of the corresponding alcohols (3–18 %) are also obtained with a selectivity towards 3-phenylpropanol of 94–96 %. When DIOP complexes were used, no stereoselectivity for asymmetric hydroformylation was observed.

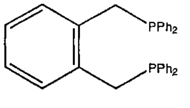
Introduction. – It is well-known that complexes of the type *cis*-[$PtCl_2$(PP)] (PP = chelating ditertiary phosphine), in the presence of $SnCl_2$, are efficient catalysts for the hydroformylation of 1-alkenes to linear aldehydes [1]. During a study of new and more efficient catalytic systems based on platinum we have investigated the activation of Pt(0) complexes for the catalytic hydroformylation of alkenes.

The synthesis of several alkene complexes of Pt(0) of the type [Pt(alkene)(PP)] (PP = chelating diphosphine), **I**, has been recently described [2–4]. These compounds can conveniently be obtained by the route developed for compounds *cis*-[$PtCl_2(PR_3)_2$] (*Scheme 1*) [5].

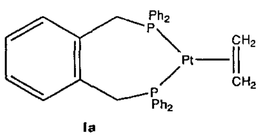
Scheme 1



Recent studies on the coordination properties of ligand **1** led to the isolation of [Pt(C_2H_4)**1**] (**Ia**) by the method described above starting from [$PtCl_2$(**1**)] [3]. This prompted the study of the reactivity of complex **Ia** and related compounds towards



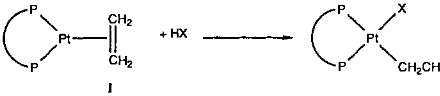
1



Ia

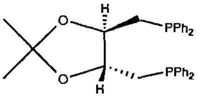
electrophylic reagents of the type HX (X = Cl, CH_3SO_3, CF_3CO_2, *etc.*). These have shown that, at least in the case of complex **Ia**, the π–σ transformation shown in *Scheme 2* proceeds satisfactorily, when HX was a strong acid with a counter-ion having moderate-to-

Scheme 2



good coordinating ability [6]. When complexes of type **I** are used, this reaction shows a marked regioselectivity, depending both on the phosphine ligand and on the anion X [7].

The formation of σ-alkyl complexes is one of the fundamental steps postulated in the catalytic cycle leading to the formation of aldehydes [8]. Furthermore, recent studies have shown that acidic species are involved in the hydroformylation catalytic cycle of linear α-alkenes promoted by the system *cis*-$[PtCl_2(PPh_3)_2]/SnCl_2$ [9]. Based on the above considerations, it appeared interesting to study the catalytic behaviour of alkene complexes of the type $[Pt(C_2H_4)(PP)]$, **I**, (PP = **1** or (+)-DIOP) in reactions of alkene hydroformylation using CH_3SO_3H, as promotor. As substrate, styrene was used as a model for vinyl-aromatic compounds which, recently, have been successfully employed as precursors for *valuable* biologically-active products [10].



(+)-DIOP

The *Table* summarizes the results of some hydroformylation experiments carried out under the conditions described in *Experimental*, using $[Pt(C_2H_4)(\mathbf{1})]$ (**Ia**) and $[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]$ (**Ib**). The data allow the following conclusions:

1) The complexes **Ia** and **Ib**, without CH_3SO_3H, do not show catalytic activity (*Exper. 1* and *2*).

2) Complexes **I**, in the presence of CH_3SO_3H as promotor, show a high degree of catalytic activity (*Exper. 3–6*), comparable to that of the system *cis*-$[PtCl_2\{(+)\text{-}(DIOP)\}]/SnCl_2$ (*cf. Exper. 5* and *10*).

3) The chemoselectivity of the reaction, particularly for high conversions, is lower than that given by the system Pt(II)/Sn(II). This is due to successive reactions such as the hydrogenation of aldehydes to alcohols, and aldehyde condensation, probably promoted by CH_3SO_3H.

4) The presence of an excess of CH_3SO_3H accelerates the reaction, but it is detrimental for the chemoselectivity *(Exper. 7)*.

5) The regioselectivity towards the formation of the linear isomer remains relatively high (the ratio linear/branched aldehyde $> 8:1$).

6) The stereoselectivity observed for the asymmetric hydroformylation (*Exper. 3, 5,* and *7*), carried out using complex **Ib**, is always zero probably because of the racemization of 2-phenylpropanal by CH_3SO_3H.

In view of the results obtained in the presence of CH_3SO_3H, we have also tested the effect of *Lewis* acids on the catalytic activity of complexes **Ia** and **Ib**. Thus, hydroformylation reactions were carried out in the presence of a stoichiometric amount of $SnCl_2$. As can be seen from the results of *Exper. 8* and *9*, the presence of $SnCl_2$ leads to a higher catalytic activity and a better chemoselectivity, although the reactions are accompanied by extensive decomposition of the catalytic system.

Table. *Styrene Hydroformylation Catalyzed by Pt(0) Complexes*[a])

Exper.	Catalytic precursors	t [h]	Alkene conversion [%]	Ethyl benzene yield [%]	Total aldehyde yield [%]	Selectivity towards 3-phenylpropanal [%]	Total alcohol yield [%]	Selectivity towards 3-phenylpropanol [%]	High boiling by-products yield [%]
1	$[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]$	24	0.75	–	0.75	93.3	–	–	–
2	$[Pt(C_2H_4)(\mathbf{1})]$	24	–	–	–	–	–	–	–
3	$[Pt(C_2H_4)[\{(+)\text{-}(DIOP)\}]/CH_3SO_3H$	4	80.0	2.9	67.3	88.3	2.9	96.5	6.9
4	$[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]/CH_3SO_3H$	24	91.4	3.7	52.7	85.0	11.6	94.8	23.4
5	$[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]/CH_3SO_3H$	72	97.5	4.5	44.3	83.3	18.3	94.5	30.4
6	$[Pt(C_2H_4)(\mathbf{1})]/CH_3SO_3H$	24	99.8	4.4	64.0	79.7	12.0	94.2	19.4
7	$[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]/CH_3SO_3H$	4	92.0	5.0	58.2	84.4	6.9	95.6	21.9
8	$[Pt(C_2H_4)\{(+)\text{-}(DIOP)\}]/SnCl_2$	4	100	12.0	84.8	58.7	2.8	67.8	traces
9	$[Pt(C_2H_4)(\mathbf{1})]/SnCl_2$	4	100	15.0	84.3	55.2	traces	–	traces
10	$[PtCl_2\{(+)\text{-}(DIOP)\}]/SnCl_2$	4	100	14.4	76.8	50.2	–	–	8.8

[a]) **1** = 1,2-Bis[(diphenylphosphino)methyl]benzene. Styrene = 16 mmol; styrene/Pt = 320; Pt/CH_3SO_3H = 1.1; Pt/Sn = 1, P(CO) = P(H_2) = 50 atm; temp. = 100°; solvent: toluene, 20 ml; for *Exper. 7*, Pt/CH_3SO_3H = 1/3; for *Exper. 10*, Pt/Sn = 1/3.

Catalytic systems for alkene hydroformylation based on Pt complexes which do not require the presence of $SnCl_2$ as co-catalyst have been reported in the literature [11–15] but do not appear to have been developed.

The catalytic system described here appears to be promising and experiments are in progress with the particular aim of obtaining a better control of chemo- and stereoselectivity.

Experimental Part

{1,2-Bis[(diphenylphosphino)methyl]benzene}(ethylene)platinum(0) (**Ia**) [3] and *((+)-DIOP)(ethylene)-platinum(0)* (**Ib**) [2b] were prepared according to literature methods. The results given in the *Table* were obtained as follows: 16 mmol of freshly distilled styrene were placed in a steel autoclave together with 20 ml toluene, 0.05 mmol of the complex (**Ia** or **Ib**) and an equivalent amount of CH_3SO_3H. The reactor was pressurized to 100 atm with synthesis gas (CO/H_2 1:1) and heated to 100° (±0.1°). After the desired reaction time, the reactor was cooled to r.t., the residual gases removed and the reaction mixture analysed for conversion, chemo-, regio-, and stereoselectivity of the catalytic process by GLC.

REFERENCES

[1] T. Hayashi, Y. Kawabata, T. Isoyama, I. Ogata, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3438.

[2] a) R.A. Head, *J. Chem. Soc., Dalton Trans.* **1982**, 1637; b) J.M. Brown, S.J. Cook, S.J. Kimber, *J. Organomet. Chem.* **1984**, *269*, C58.

[3] a) H. Rimml, Dissertation Nr. 7562, ETH Zürich, 1984, p. 113; b) M. Camalli, F. Caruso, S. Chaloupka, E.M. Leber, H. Rimml, L.M. Venanzi, in preparation.

[4] J.A. Ibers, S. Otsuka, T.H. Tulip, T. Yamagata, T. Yoshida, *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[5] U. Nagel, *Chem. Ber.* **1982**, *115*, 1998.

[6] R. Ciorciaro, unpublished observations and ref. [3a] p. 117.

[7] L.M. Venanzi, *Coord. Chem.* **1981**, *21*, 151, and ref. cit. therein.

[8] C. Masters, 'Homogeneous Transition-Metal Catalysis, a Gentle Art', Chapman and Hall, London, 1981, Chapt. 2.4.

[9] A. Scrivanti, S. Paganelli, U. Matteoli, C. Botteghi, to be published.

[10] G. Parrinello, J.K. Stille, *J. Am. Chem. Soc.* **1987**, *109*, 1987.

[11] P.W.N.M. van Leeuwen, C.F. Roobeck, R.L. Wife, J.H.G. Frijns, *Chem. Commun.* **1986**, 31.

[12] L. Slaugh, R.D. Mullineaux, U.S. Patent, 3239571, 1966 (*CA* : **1966**, *65*, 618).

[13] G.A. Rowe, G.B. Patent, 136834, 1974 (*CA* : **1975**, *83*, 142590).

[14] J.J. Mrowca, U.S. Patent, 3876672, 1975 (*CA* : **1976**, *84*, 30432).

[15] G. Longoni, P. Chini, *J. Am. Chem. Soc.* **1976**, *98*, 7225.