

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

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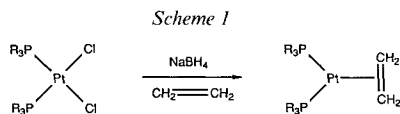
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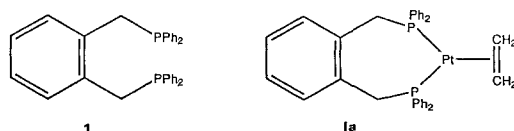
The platinum(0) complexes $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PP})]$ ($\text{PP} = 1,2\text{-bis}[(\text{diphenylphosphino})\text{methyl}]\text{benzene}$ (**2**) and (+)-DIOP = (+)-1,4-bis(diphenylphosphino)-1,4-dideoxy-2,3-*O*-isopropyliden-D-threitol), when promoted by $\text{CH}_3\text{SO}_3\text{H}$, become active catalysts for styrene hydroformylation with total yields of aldehydes ranging from 44 to 67% and 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 $\text{cis-}[\text{PtCl}_2(\text{PP})]$ ($\text{PP} = \text{chelating ditertiary phosphine}$), 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 $\text{Pt}(0)$ complexes for the catalytic hydroformylation of alkenes.

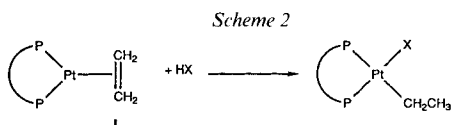
The synthesis of several alkene complexes of $\text{Pt}(0)$ of the type $[\text{Pt}(\text{alkene})(\text{PP})]$ ($\text{PP} = \text{chelating diphosphine}$), **1**, has been recently described [2–4]. These compounds can conveniently be obtained by the route developed for compounds $\text{cis-}[\text{PtCl}_2(\text{PR}_3)_2]$ (*Scheme 1*) [5].



Recent studies on the coordination properties of ligand **1** led to the isolation of $[\text{Pt}(\text{C}_2\text{H}_4)(\textbf{1})]$ (**1a**) by the method described above starting from $[\text{PtCl}_2(\textbf{1})]$ [3]. This prompted the study of the reactivity of complex **1a** and related compounds towards

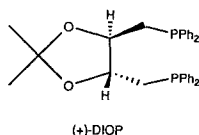


electrophilic reagents of the type HX ($\text{X} = \text{Cl}, \text{CH}_3\text{SO}_3, \text{CF}_3\text{CO}_2, \text{etc.}$). These have shown that, at least in the case of complex **1a**, the $\pi\text{-}\sigma$ transformation shown in *Scheme 2* proceeds satisfactorily, when HX was a strong acid with a counter-ion having moderate-to-



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*-[PtCl₂(PPh₃)₂]/SnCl₂ [9]. Based on the above



considerations, it appeared interesting to study the catalytic behaviour of alkene complexes of the type [Pt(C₂H₄)(PP)], **I**, (PP = **1** or (+)-DIOP) in reactions of alkene hydroformylation using CH₃SO₃H, 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].

The *Table* summarizes the results of some hydroformylation experiments carried out under the conditions described in *Experimental*, using [Pt(C₂H₄)(**1**)] (**Ia**) and [Pt(C₂H₄){(+)-DIOP}] (**Ib**). The data allow the following conclusions:

- 1) The complexes **Ia** and **Ib**, without CH₃SO₃H, do not show catalytic activity (*Exper. 1* and *2*).
- 2) Complexes **I**, in the presence of CH₃SO₃H as promotor, show a high degree of catalytic activity (*Exper. 3–6*), comparable to that of the system *cis*-[PtCl₂{(+)-DIOP}]/SnCl₂ (*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 CH₃SO₃H.
- 4) The presence of an excess of CH₃SO₃H 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 CH₃SO₃H.

In view of the results obtained in the presence of CH₃SO₃H, 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 SnCl₂. As can be seen from the results of *Exper. 8* and *9*, the presence of SnCl₂ 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)}

<i>Ex- per.</i>	Catalytic precursors	<i>t</i> [h]	Alkene conver- sion [%]	Ethyl benzene yield [%]	Total aldehyde yield [%]	Selec- tivity to- wards 3-phenyl- propanal [%]	Total alcohol yield [%]	Selec- tivity to- wards 3-phenyl- propanol [%]	High boiling by- products yield [%]
1	[Pt(C ₂ H ₄){(+)-(DIOP)}]	24	0.75	–	0.75	93.3	–	–	–
2	[Pt(C ₂ H ₄)(1)]	24	–	–	–	–	–	–	–
3	[Pt(C ₂ H ₄){(+)-(DIOP)}]/ CH ₃ SO ₃ H	4	80.0	2.9	67.3	88.3	2.9	96.5	6.9
4	[Pt(C ₂ H ₄){(+)-(DIOP)}]/ CH ₃ SO ₃ H	24	91.4	3.7	52.7	85.0	11.6	94.8	23.4
5	[Pt(C ₂ H ₄){(+)-(DIOP)}]/ CH ₃ SO ₃ H	72	97.5	4.5	44.3	83.3	18.3	94.5	30.4
6	[Pt(C ₂ H ₄)(1)]/CH ₃ SO ₃ H	24	99.8	4.4	64.0	79.7	12.0	94.2	19.4
7	[Pt(C ₂ H ₄){(+)-(DIOP)}]/ CH ₃ SO ₃ H	4	92.0	5.0	58.2	84.4	6.9	95.6	21.9
8	[Pt(C ₂ H ₄){(+)-(DIOP)}]/SnCl ₂	4	100	12.0	84.8	58.7	2.8	67.8	traces
9	[Pt(C ₂ H ₄)(1)]/SnCl ₂	4	100	15.0	84.3	55.2	traces	–	traces
10	[PtCl ₂ {(+)-(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/CH₃SO₃H = 1.1; Pt/Sn = 1, P(CO) = P(H₂) = 50 atm; temp. = 100°; solvent: toluene, 20 ml; for *Exper.* 7, Pt/CH₃SO₃H = 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 SnCl₂ 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) (**1a**) [3] and (+)-(DIOP)(ethylene)platinum(0) (**1b**) [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 (**1a** or **1b**) and an equivalent amount of CH₃SO₃H. The reactor was pressurized to 100 atm with synthesis gas (CO/H₂ 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.

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