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The role of additives in platinum-catalyzed hydroformylation

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Abstract

A study has been made of hydroformylation of styrene derivatives catalysed by several Pt–bisphosphine systems modified with various additives. The chain length of the chelating phosphines and the quality of the Lewis-acid type additives strongly influences the activity and the chemo- and regio-selectivity of the catalysts. The most active $PtCl_2$(bisphosphine) + $SnCl_2$ system was modified with amines of different basicities, and it was found that a strong base such as Et_3N stops the catalytic reaction by abstracting $HSnCl_3$ from the active platinum species. This reaction was monitored by NMR spectroscopy. Complexation of the chiral aminophosphine ((*S*)-(−)-*N*,*N*-dimethyl-1(2′-diphenylphosphinophenyl)-ethylamine, (*S*)-(−)-AMPHOS) with platinum has also been studied, and a chemical shift anisotropy relaxation mechanism observed.

Introduction

Asymmetric hydroformylation enables the synthesis of a wide variety of chiral compounds [1]. Although $PtCl_2(\widehat{P\ P}) + SnCl_2$ systems have already been used successfully in the hydrocarbonylation of several simple [2–4] and functionalized olefins [5,6], there has been little work on the role of various additives, especially amines, in these catalytic systems. Other group IVb metal halides have been used [8] instead of $SnCl_2$ ligand in association with $PtCl_2P_2$ complexes [7] but the catalysts so formed were at least an order of magnitude less active.

Strong dependence of the catalytic activity on the methylene chain length of the bisphosphine ligand was observed by Ogata and his coworkers [9]. In the hydroformylation of 1-pentene with $PtCl_2(Ph_2P(CH_2)_nPPh_2) + SnCl_2$ catalysts 1,4-bis(diphenylphosphino)butane ($n = 4$) proved to be the most suitable chelating phosphine.

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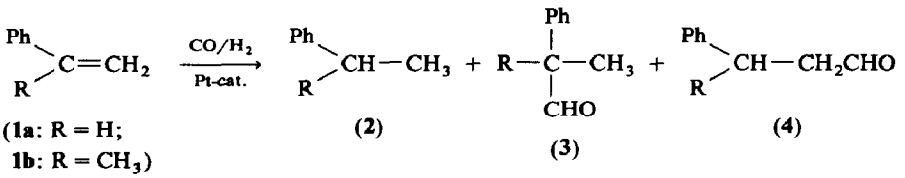
Although a number of *N*-containing compounds (amides, imides, lactams) were successfully used in the synthesis of various chiral building blocks [5,10–14], surprisingly no amino derivatives were hydroformylated in the platinum-catalyzed reaction.

We present here the results of a study of homogeneous hydroformylation of styrene-derivatives with platinum-bisphosphine complexes, involving examination of the influence of the chain length of the ligands as well as the effects of various additives, especially those of some amines of different basicities, on the catalytic reaction. The effects of amines and the complexation of the P–N-chelating ligand AMPHOS have also been studied by NMR spectroscopy.

Results and discussion

In our investigation styrene (**1a**) and 2-phenylpropene (**1b**) were chosen as substrates (Scheme 1). In addition to hydroformylation, hydrogenation of the olefins also takes place, to give ethylbenzene (**2a**) and isopropylbenzene (**2b**), respectively. From the hydroformylation of **1a** both regioisomers (**3a**,**4a**) were isolated, but the vinylidene-type olefin (**1b**) gave the linear aldehyde exclusively, as described previously [3,15].

The catalytic activity and regioselectivity of the hydroformylation (Table 1) were significantly influenced by the chain-length of the bisphosphine ligand. A reasonable extent of conversion was detected only for bisphosphines able to form six- or seven-membered chelate rings. Bis(diphenylphosphino)methane (dppm) (run 1) probably forms a dinuclear complex active under reductive conditions, as proposed previously [16,17]. Increase in the chelate ring of the catalysts has no marked change



Scheme 1

Table 1

Hydroformylation of **1a** and **1b** with $Pt/Ph_2P(CH_2)_nPPh_2/SnCl_2$ catalysts [a]

Run	Substrate	Bisphosphine (n)	Conversion [b] (%)	R_c [c] (%)	R_{RL} [d] (%)
1	**1a**	1	2 (4)	80 (85)	45 (44)
2	**1a**	2	9 (36)	72 (72)	28 (28)
3	**1a**	3	76	86	73
4	**1a**	4	71	80	57
5	**1b**	2	1 (3)	34 (38)	100 (100)
6	**1b**	3	64	80	100
7	**1b**	4	13 (36)	74 (80)	100 (100)

[a] Reaction conditions: 35 ml toluene; 0.1 mol substrate; Pt/substrate = 12000; $p(CO) = p(H_2) = 40$ bar; reaction temperature = 100 °C; reaction time 4 h (the results obtained in 12 h are in parenthesis). [b] (mol reacted substrate/mol initial substrate) × 100. [c] (mol aldehyde/mol reacted substrate) × 100. [d] (mol linear aldehyde/mol aldehyde) × 100.

Table 2

The effect of amine additives in the hydroformylation of **1a** with $Pt/dppb/SnCl_2$ catalysts [a]

Run	Amine	Conversion [b] (%)	R_c [c] (%)	R_{RL} [d] (%)	pK_a [e]
1	– [f]	71	80	57	
2	Et_3N [g]	0(1)	–	–	10.65
3	$PhEt_2N$	6(32)	83(84)	55(56)	6.56
4	Py	13(43)	85(86)	55(55)	5.2
5	Bz_3N	29(72)	85(85)	54(55)	5.6
6	Ph_2NH	31(80)	84(84)	55(56)	0.79
7	Ph_3N	73	83	56	~0
8	Et_2NCH_2PS [h]	(68)	(85)	(56)	
9	Et_3N [i]	50(76)	84(83)	55(55)	10.65

[a] Reaction conditions (unless otherwise stated): 35 ml toluene; 0.1 mol **1a**; Pt/**1a** = 1/2000; $p(CO) = p(H_2) = 40$ bar; $Pt/SnCl_2$/amine = 1/2/5; reaction temp. = 100 °C; reaction time = 4 h (the results obtained in 10 h are in parenthesis). [b,c,d]: See Table 1. [e] See Lit. 20. [f] The conversion was 3–5% (in 15 h) when $ZnCl_2$, $AlCl_3$ were used as cocatalyst. [g] The same effect was observed when Et_2NCH_2PS was used instead of Et_3N; Et_2NCH_2PS = diethylaminomethylpolystyrene ($Pt/SnCl_2/N = 1/2/5$). [h] After filtration of the polimer 2 equiv. $SnCl_2$ was added. [i] $Pt/SnCl_2/Et_3N = 2/2/1$.

in chemo-(R_c) and regioselectivity (R_{RL}) of the reaction, but, surprisingly, when dppe was used, formation of the branched aldehyde (**3a**) was favoured (run 2). In the hydroformylation of both styrene derivatives dppp proved to be the best ligand (run 6). Use of phosphines that form more flexible chelate rings ($n = 3,4$) results in a marked decrease in the extent of the hydrogenation reaction.

Other IVb group halides and Lewis-acid type additives ($ZnCl_2$, $AlCl_3$) were used instead of $SnCl_2$ as cocatalysts in the platinum-dppb catalyzed styrene hydroformylation, but the activities of the systems were rather low. However, an interesting effect noted previously for the $PtCl(SnCl_3)$(BDPP) catalyzed reaction [18] was again observed and shown to be independent of the cocatalyst used. This effect is that at lower temperatures the formation of the (*S*)-enantiomer predominates, but at higher temperature (125 °C) the *R*-enantiomer of **3a** predominates. The results can be accounted for in terms of the change in the conformation of the chelate ring, and consequently in terms of the stability of the catalytic intermediates and kinetic factors [19].

To the best of our knowledge the effects of amines on platinum-catalyzed hydroformylation have not previously been studied in detail. In our experiments, with catalysts prepared in situ from $Pt/dppb/SnCl_2$ (run 1) and several amines of different basicities [20] large changes in activity were observed (Table 2). Whereas the most basic amine (Et_3N) practically stopped the reaction, no poisoning effect of the less basic Ph_3N was observed (run 2–7). We found that Et_3N inhibits the catalysis at a $Pt : SnCl_2 : Et_3N$ ratio of 1 : 1 : 1, but further addition of $SnCl_2$ regenerates the activity (run 9). In the presence of a polymer containing the Et_2NCH_2 moiety, no catalytic activity was detected (run 2) but after removal of the polymer by filtration and addition of two equiv. of $SnCl_2$ the reaction started again (run 8).

For all the amines used, the regio- and chemoselectivity of the hydroformylation remained practically unchanged. This feature is consistent with the presence of the same active species at different concentrations, and can be attributed to partial (or

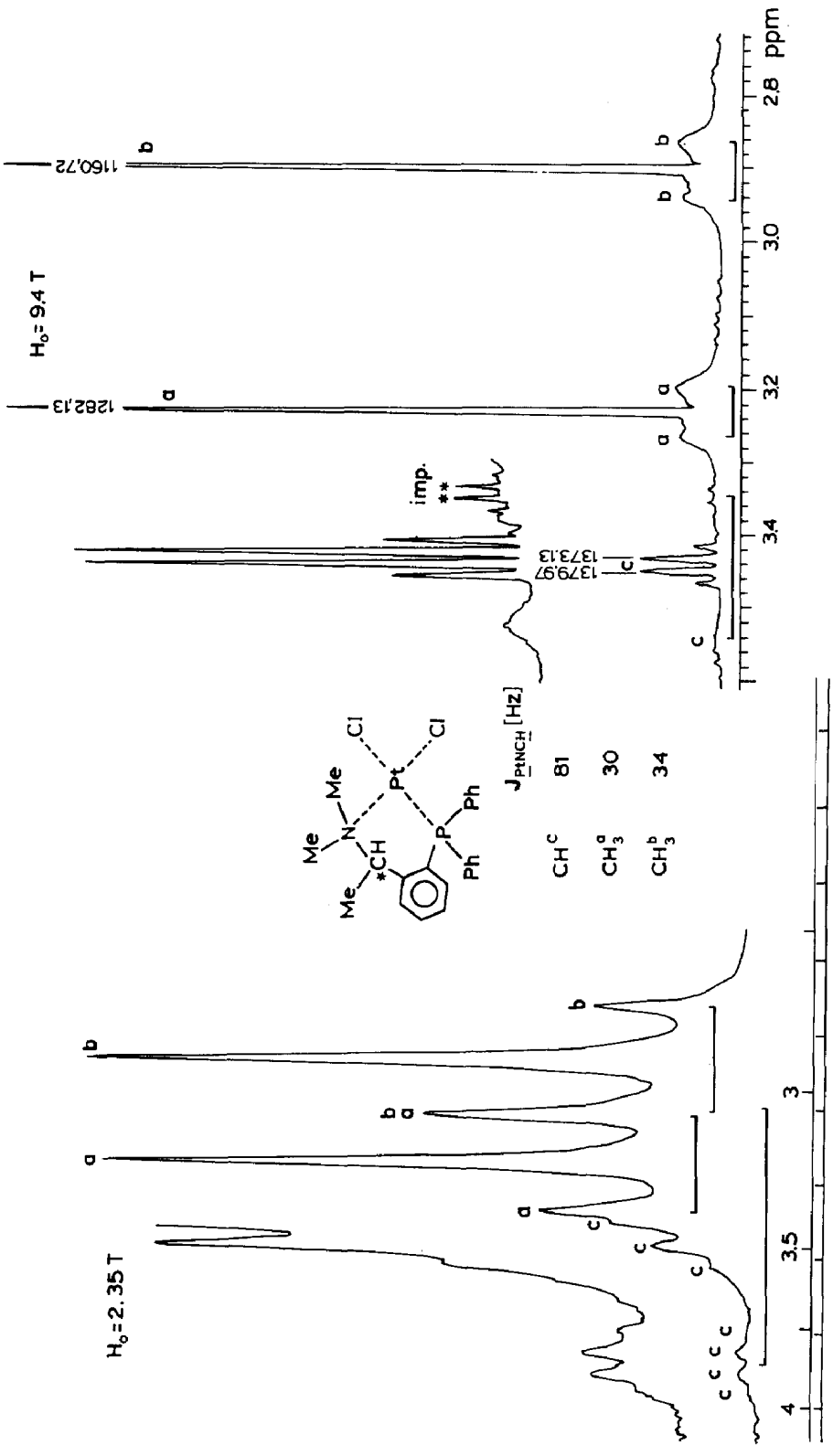


Fig. 1. The ^{1}H-NMR spectra of the $PtCl_2$(AMPHOS) complex (CH_3, CH region) at 80 and 400 MHz.

complete) $HSnCl_3$ abstraction by the amines from the $PtH(SnCl_3)$(bisphosphine) complexes formed under hydroformylation conditions. As a consequence of the elimination of $HSnCl_3$, the platinum complexes lose their catalytic activity [21].

The ^{31}P-NMR spectra of the catalytic precursors, $PtCl(SnCl_3)$(bisphosphine) showed no changes after addition of amines at room temperature under normal pressure, and so coordination of amines under these conditions can be ruled out.

The role of the amine function is quite different in the case of the chelating aminophosphine (AMPHOS). Direct coordination of the dimethylamino-group of AMPHOS was revealed by ^{1}H-NMR spectroscopy (Fig. 1). Both the methyl-groups and the methin-proton gave characteristic 1 : 4 : 1 patterns due to the coupling to the central platinum (natural abundance of spin-1/2 ^{195}Pt isotope is 33.88%). Although the signals in the 80 and 100 MHz spectra are sharp, at 400 MHz the central sharp singlet is symmetrically flanked by broad ^{195}Pt satellites, indicating a very significant chemical shift anisotropy (CSA) relaxation mechanism [22,23]. Owing to the chelation effect, AMPHOS coordinates to the central platinum as a $\widehat{P\,N}$ chelating ligand even when present in excess (Pt/AMPHOS = 1/2); coordination of the NMe_2 group results in a complex without any catalytic activity.

Experimental

Reagents

The $PtCl_2P_2$-type catalyst precursors and the $PtCl_2$(AMPHOS) complex were prepared from $PtCl_2(PhCN)_2$ by a standard method [18]. The anhydrous $SnCl_2$ used for the preparation of the in situ catalysts was made by dehydrating $SnCl_2 \cdot 2H_2O$ with a stoichiometric amount of acetic anhydride and washing it with ether. Toluene was distilled under argon from sodium in the presence of benzophenone. Styrene, 2-phenylpropene, and the liquid amines were freshly distilled before use.

The ^{1}H-NMR spectra were recorded for $CDCl_3$ solutions containing TMS as internal standard on a Varian XL-400 and Varian XL-100 spectrometers. The ^{31}P-NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 32.1 MHz. The optical rotations of the products were measured for the neat liquids isolated from the reaction mixture, on a Schmidt–Haensch LM visual polarimeter.

Hydroformylation experiment

In a typical experiment a suspension of 0.05 mmol of $PtCl_2$(bisphosphine) and 0.05 mmol (9.5 mg) $SnCl_2$ in 35 ml of toluene containing 0.1 mol of substrate was placed under argon in a 150 ml stainless steel autoclave. (When an amine additive was also used, it was dissolved in the catalyst.) The autoclave was pressurized to 80 bar total pressure ($CO/H_2 = 1/1$), placed in a thermostated electric oven, and agitated with an arm shaker. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was analyzed by GC and fractionally distilled for further characterisation of the products.

Characterization of the $PtCl_2$ (AMPHOS) complex

^{1}H-NMR (100 MHz, $CDCl_3$): δ 1.26 (d, J 6.8 Hz, 3H, CH_3CH); 2.90 (1 : 4 : 1 pattern, J(*Pt*NC*H*) 34 Hz; 3H, NCH_3^b); 3.21 (1 : 4 : 1 pattern, J(*Pt*NC*H*) 30 Hz, 3H, NCH_3^a); 3.44 (1 : 4 : 1 pattern of quartets, J 6.8 Hz, J (*Pt*NC*H*) 81 Hz, 1H, CH_3CH^c); 6.9–7.9 (m, 14H, aromatic protons) (See also Fig. 1).

^{31}P-NMR (32.1 MHz, CD_2Cl_2): $\delta = -6.8$ ppm; J(Pt–P) 3917 Hz.

Analysis. Found: C, 44.22; H, 4.10; N, 2.42. $C_{22}H_{24}NCl_2PPt$ calcd.: C, 44.09; H, 4.04; N, 2.34%.

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