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METALS IN ORGANIC SYNTHESES

X *. OLEFIN HYDROFORMYLATION AND HYDROCARBOALKOXYLATION COMPETITIVELY CATALYZED BY A $[PtCl_2(PPh_3)_2]/SnCl_2$ SYSTEM

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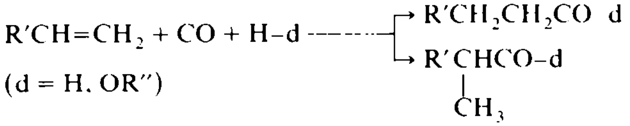
Summary

The system $[PtCl_2(PPh_3)_2]/SnCl_2$ significantly catalyzes only the hydroformylation of α-olefins at 100°C in EtOH, at $P(CO) = P(H_2) = 65$ atm; hydrocarboalkoxylation does not occur to an apreciable extent, even in the presence of potential activating agents (HCl, LiCl). The catalyst precursor has been recovered from the reaction medium, as the cationic complex $[PtH(CO)(PPh_3)_2](SnCl_3)$, having the $SnCl_3$ anion non-directly bound to the platinum atom, and as *trans*-$[PtCl(COR)(PPh_3)_2]$. The latter complex is a (precursor) intermediate leading to an active catalytic species possessing at least one Pt–Sn bond which plays a key role in the catalysis.

Introduction

The activity of the highly regioselective catalyst system $[PtCl_2(LPh_3)_2]/SnCl_2$, in hydroformylation (L = P) or hydrocarboalkoxylation (L = As) reactions, here depicted for reactions of an α-olefin, has been found to be greatly dependent on the nature of the solvent [2,3] (eq. 1).



$$R'CH{=}CH_2 + CO + H{-}d \longrightarrow \begin{cases} R'CH_2CH_2CO\ d \\ R'\underset{\substack{|\\CH_3}}{CH}CO{-}d \end{cases} \qquad (d = H, OR'') \tag{1}$$

The preferred solvents appear to be those of intermediate polarity and coordinating ability such as ketones; in highly polar or coordinating solvents, like *N,N'*-DMF, THF, or CH_3CN, the catalysis is inhibited [2,3].

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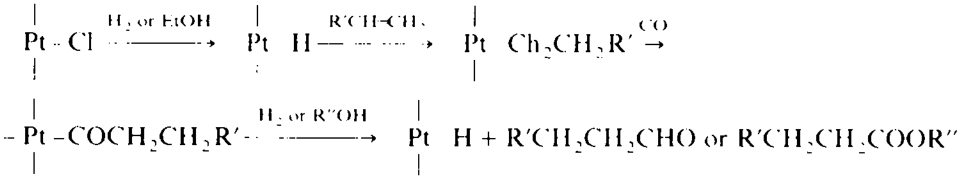
* Part IX: see ref. 1.

Very recently, *trans*-[$PtCl(COR)(PPh_3)_2$] (R = n-Pr and n-Hex) has been isolated in good yield in the course of olefin hydroformylation or hydrocarboalkoxylation employing the system *cis*-[$PtCl_2(PPh_3)_2$]/$SnCl_2$ in an alkanol, where no significant catalytic activity has been observed [1,4] *; with methyl isobutyl ketone as solvent, the catalytic system is very active in the hydroformylation only: under these conditions *trans*-[$Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2$] has been isolated [4]. It is believed that a complex of this type, having at least one Pt Sn bond, is the active (precursor) intermediate [4].

Since in an alkanol the catalytic system is recovered as *trans*-[$PtCl(COR)(PPh_3)_2$], and since the proposed reactions pathways can be represented as in eq. 2 it appears that the two reactions have much in common.



$$\mathrm{Pt{-}Cl} \xrightarrow{H_2\text{ or EtOH}} \mathrm{Pt{-}H} \xrightarrow{R'CH{=}CH_2} \mathrm{Pt{-}Ch_2CH_2R'} \xrightarrow{CO}$$
$$\mathrm{{-}Pt{-}COCH_2CH_2R'} \xrightarrow{H_2\text{ or }R''OH} \mathrm{Pt{-}H} + \mathrm{R'CH_2CH_2CHO} \text{ or } \mathrm{R'CH_2CH_2COOR''}$$

(2)

We report below the most relevant results on the olefin carbonylation carried out in the presence of molecular hydrogen with an alkanol as solvent in order to ascertain whether catalysis occurs at higher temperature and to find out which reaction is the most favored under competitive hydroformylation and hydrocarboxylation conditions.

Results and discussion

Most of the experiments were carried out in ethanol, at 100°C, at $P(CO) = P(H_2) = 65$ atm, using *cis*-[$PtCl_2(PPh_3)_2$]/$SnCl_2$ as catalyst precursor, with Pt/Sn/olefin ratios 1.5/5/100.

In every case only aldehydes, together with the corresponding acetals, are formed, in good yield **. With 1-hexene the observed regioselectivity (94%) is slightly higher than that achievable with propene (90%); analogous results are obtained when a ketone is used as solvent (93 and 83%, respectively).

The catalyst is recovered as *trans*-[$PtCl(COR)(PPh_3)_2$] from the reaction medium. When using this complex, in the hydroformylation of 1-hexene the regioselectivity is practically the same (95%) as that observed employing the precursor *cis*-[$PtCl_2(PPh_3)_2$], with either ethanol or a ketone as solvent. It is noteworthy that when propene is hydroformylated in a ketone as solvent a significantly higher selectivity is observed if *trans*-[$PtCl(COPr\text{-}n)(PPh_3)_2$] (93%; linear/branched isomer ratio 13) is used in place of the precursor (83%; linear/branched 4.9) [4].

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* Experiments were carried out under 100 120 atm, at 70°C under hydroformylation conditions, or at 70-100°C under hydrocarboalkoxylation conditions.

** It is of interest that with a $PdCl_2(PPh_3)_2$ catalytic system, which also yields an analogous (precursor) intermediate *trans*-$PdCl(COPr\text{-}n)(PPh_3)_2$, only hydrocarboalkoxylation occurs even in the absence of $SnCl_2$, and that in such a case the presence of molecular hydrogen increases the rate of ester formation without producing any aldehyde [5,6].

A possible rationalization for the different regioselectivity observed when propene is hydroformylated in a ketone has already been given; it involves the assumption that HCl intervenes in the regioselective steps of the catalysis ($[PtCl_2(PPh_3)_2]$ and $[PtCl(COPr\text{-}n)(PPh_3)_2]$ are equivalent during the catalysis except that they differ by a molecule of HCl [4]).

However, since in ethanol the observed regioselectivity is the same, when either the precursor or $[PtCl(COR)(PPh_3)_2]$ is used, it is reasonable to suppose that HCl does not modify the equilibria involved in the regioselective steps and/or that the solvent reduces any possible effect of HCl.

The facts that (i) no significant amount of aldehyde is detectable in the absence of $SnCl_2$ and (ii) the catalytic system is more active when a ketone is used as solvent *, from which medium it is recovered as *trans*-$[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$, and (iii) the catalyst system is recovered as *trans*-$[PtCl(COR)(PPh_3)_2]$ from an alkanol, give further support to the hypothesis that the active intermediate involves at least one Pt–Sn bond, and suggests that this species is present in a higher concentration in the ketone and/or that the slow catalytic step has a higher activation energy in EtOH.

In some experiments involving hydroformylation of 1-hexene in ethanol at 100°C, the catalyst was recovered as a mixture of *trans*-$[PtCl(COHex\text{-}n)(PPh_3)_2]$ and a hydrido carbonyl having a composition corresponding to $PtH(CO)(PPh_3)_2(SnCl_3)$. This complex is probably a four-coordinate ionic salt (Λ_m in nitromethane solution is 37 ohm^{-1} cm^2 mol^{-1}, slowly decreasing with time indicating some decomposition) with the $SnCl_3^-$ anion not directly bound to the platinum atom since IR bands attributable to ν(Sn–Cl) appear at 304vs, 290s, 280(sh) cm^{-1}, while for a metal $SnCl_3$ bond the ν(Sn–Cl) bands are expected to be at higher values [7]; in the Pt–H and C≡O region there are two bands at 2164 and 2050 cm^{-1}. An analogous complex, similarly formulated, was also isolated in the course of 1-pentene hydroformylation using benzene as solvent; this shows the same bands in the 2000 cm^{-1} region and bands attributable to ν(Sn–Cl) at 335, 314, and 292 cm^{-1}; no conductivity data were reported [8]. It seems unlikely that a complex of this type, with the $SnCl_3^-$ group not coordinated to the platinum atom, could be the active intermediate in this catalysis, implying that the role of $SnCl_2$ is to assist separation of the Cl^- ion, since under the reaction conditions, even in the absence of $SnCl_2$, equilibria of the type $[PtCl_2(PPh_3)_2] + CO \rightleftarrows [PtCl(CO)(PPh_3)_2]^+ Cl^-$ can be readily established. For example, it has been shown that this cationic complex can be prepared by bubbling CO into an acetone solution of $[PtCl_2(PPh_3)_2]$ under ambient conditions [9]; moreover, it was recently reported that the cationic complex $[PtCl(CO)(PPh_3)_2]^+(ClO_4)^-$ shows no significant catalytic activity in the hydroformylation of internal olefins unless $SnCl_2$ is added [10].

It has been reported that the closely related catalytic system $[PtCl_2(AsPh_3)_2]/SnCl_2$ is highly active in the hydrocarboalkoxylation of α-olefins, in a ketone as solvent, at 80°C and 240 atm of CO; under similar conditions the P analogue also shows catalytic activity, though to a lesser extent [3]. Rather surprisingly, the catalytic systems here described show no significant activity in ethanol at 100°C, P(CO) 100–130 atm. Moreover, it has been found that the system $[PtCl_2(LR_3)_2]/SnCl_2$ catalyzes the formation of acyl chlorides from olefins, carbon monoxide and hydrochloric acid in a suitable solvent [11]. In order to promote the

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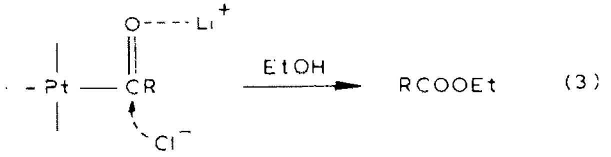
* In this solvent the catalyst is highly active even at 70°C [2].

formation of the ester, some reactions were carried out in the presence of an excess of HCl in EtOH as solvent, but without success: the precursor was recovered as *trans*-[$PtCl(COR)(PPh_3)_2$]. In addition, it has also been reported that a H_2PtCl_6/$SnCl_2$ system catalyzes the hydrocarboalkoxylation of α-olefins [12]. We examined the reaction in the presence of LiCl which would probably promote the formation of the ester by partially replacement of PPh_3 by Cl^- [1] and/or by yielding the acyl chloride; in addition Li^+ could interact with the oxygen atom of the acyl intermediate, thus favoring the attack of Cl^- (eq. 3). However, the formation of the ester


(3)

was not promoted even in the presence of relatively large amounts of LiCl; the catalyst was recovered as [$PtCl(COR)(PPh_3)_2$].

For the hydrocarboalkoxylation reaction a different reaction pathway has also been suggested. This begins with olefin insertion into a M–COOR bond [13] (eq. 4).

$$M{-}COOR \xrightarrow{C=C} M{-}C{-}C{-}COOR \xrightarrow{CO,\ ROH} M{-}COOR + H{-}C{-}C{-}COOR \qquad (4)$$

Experiments carried out employing [$PtCl(COOEt)(PPh_3)_2$] in place of [$PtCl_2(PPh_3)_2$] or [$PtCl(COR)(PPh_3)_2$] in EtOH, at 100°C, ended with unsignificant formation of ester and recovery of the catalyst as the last complex. These experiments prove that the Pt–C bond in $PtCl(COR)(PPh_3)_2$ is rather unreactive and does not undergo any cleavage under the action of agents such as HCl, Cl^- or the alcohol even in the presence of $SnCl_2$.

Experimental

Materials

Carbon monoxide and hydrogen were purchased from the S.I.O. Company. Propene was kindly supplied by the Montedison SpA.; it contained about 5% propane, traces of propyne and allene, but no C_4 or higher hydrocarbons. Alcohols and $SnCl_2 \cdot 2H_2O$ were commercial grade. 1-Hexene was passed through a column of neutral Al_2O_3 and distilled before use. The catalyst precursor *cis*-[$PtCl_2(PPh_3)_2$] was prepared from $H_2PtCl_6 \cdot 6H_2O$ and PPh_3 [14]. [$PtCl(COOEt)(PPh_3)_2$] was prepared by treating *cis*-[$PtCl_2(PPh_3)_2$] with carbon monoxide in EtOH in the presence of NEt_3 [15].

Hydroformylation and hydrocarboalkoxylation reactions

The previously described general procedure was used [1,4]. In a typical experiment 120 mg of *cis*-[$PtCl_2(PPh_3)_2$] and 113 mg of $SnCl_2 \cdot 2H_2O$ were added to 9 ml of EtOH and 10 mmol of 1-hexene in a bottle placed in an autoclave, which was purged with CO and charged with H_2 and CO (50/50 atm at room temperature). The mixture was allowed to react for 6 h at 100°C. After cooling, the recovered catalyst was identified by elemental analysis and IR spectroscopy (Perkin Elmer spectrophotometer Mod. 683 using CsI windows). The analysis of carbonylation products was carried out with a Hewlett–Packard gas chromatograph Model 5830 A equipped with a Hewlett–Packard GC terminal Model 18850, using a 6 ft long column 10 Pr. UCCW 982 on Chrom. AW-DMCS 80–100 mesh (1-hexene) or a 6 ft long column of SE 30 25% on Chrom. P followed by a 6 ft column of Porapak N.

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