METALS IN ORGANIC SYNTHESES

XI [*]. ^{31}P NMR AND REACTIVITY STUDIES ON THE SYSTEM *trans*-[PtCl(CO-n-hexyl)(PPh₃)₂]/SnCl₂, AN ACTIVE INTERMEDIATE IN THE CATALYTIC HYDROFORMYLATION OF 1-HEXENE

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Summary

The system *trans*-[PtCl(CO-n-hexyl)(PPh₃)₂]/SnCl₂ has been investigated by ^{31}P NMR spectroscopy. In CD₂Cl₂ or acetone-d_6 solutions two species (in equilibrium with the starting Pt complex) are observed at low temperature: one set of signals is attributed to the complex *trans*-[Pt(SnCl₃)(CO-n-hexyl)(PPh₃)₂]; the other set does not show Sn–P coupling and it is tentatively attributed to a complex having chloride bridging the Pt and Sn metal centers. Formation of the complex *trans*-[Pt(SnCl₃)(CO-n-hexyl)(PPh₃)₂] is prevented when ethanol is added to the CD₂Cl₂ or acetone-d_6 solutions. Treatment of the CD₂Cl₂ or acetone-d_6 solutions with molecular hydrogen gives n-heptanal and hydridoplatinum species; this reaction does not occur in the presence of ethanol, where only a complex having chloride bridging the Pt and Sn metal centers seems to be present.

These results are discussed in connection with the catalytic cycle of olefin hydroformylation promoted by the [PtCl₂(PPh₃)₂]/SnCl₂ system.

Introduction

The ligand-stabilized platinum(II) Group IVA metal halides system displays a high catalytic activity and selectivity in olefin hydroformylation comparable with

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[*] For Part X see ref. 7.

that of the well-known rhodium complexes [1–4]. The details of the reaction mechanism with these platinum(II) catalytic precursors are not yet well understood, especially as far as the role of $SnCl_2$ in the catalytic cycle is concerned. It has been found that olefin hydroformylation catalyzed by the platinum(II)-phosphine ligand/$SnCl_2$ system is strongly solvent dependent [1–7]. For instance, in methyl ethyl ketone the hydroformylation of propene proceeds smoothly at 70°C and P 100 atm $(CO/H_2 = 1/1)$ giving high yields of n-butanal; under these conditions *trans*-[Pt($SnCl_3$)(CO-n-propyl)(PPh$_3$)$_2$], which contains a Pt–Sn bond, has been isolated [5]. In ethanol solutions, under the same conditions, no catalysis was observed; and *trans*-[PtCl(CO-n-propyl)(PPh$_3$)$_2$] and *trans*-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] were isolated during hydroformylation of propene or 1-hexene [5–7]. These complexes can be obtained even in the absence of $SnCl_2$ [5–7].

These results prove that the presence of $SnCl_2$ is not necessary for formation of the σ-acyl-platinum(II) complexes. However, these complexes display high catalytic activity only in the presence of $SnCl_2$, in solvents of moderate or low polarity such as ketones or benzene [5–7].

In the present paper we report the results of ^{31}P NMR investigations of (i) the interaction of *trans*-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] with $SnCl_2$ in acetone-d_6, CD_2Cl_2 and ethanol; and, (ii) the reactions of the above systems with molecular hydrogen. The aim of the study was to ascertain the role played by $SnCl_2$ in the step involving hydrogenolysis of the σ-acyl-platinum(II) complex to give the final aldehyde.

Results and discussion

^{31}P NMR of trans-[PtCl(CO-n-hexyl)(PPh₃)₂] (1)

First, we studied the behaviour of the complex *trans*-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] (1) in both acetone and dichloromethane solutions, in which the hydroformylation of 1-hexene can be successfully carried out. In CD_2Cl_2, at 303 K, the ^{31}P {^{1}H} NMR spectrum of 1 displays a single resonance at 21.0 ppm flanked by [195]Pt satellites (^1J(Pt–P) 3537 Hz); this signal is moderately affected by temperature: at 203 K it is observed at 21.4 ppm (^1J(Pt–P) 3467 Hz). In acetone-d_6, at 303 K, the signal appears at 20.0 ppm (^1J(Pt–P) 3571 Hz); the poor solubility of complex 1 in acetone prevented recording of the spectrum at lower temperature.

These results indicate that the *trans*-phosphine configuration of complex 1 present in the solid state [6] is retained in solution; spectral changes are probably due to solvent and/or temperature effects.

^{31}P NMR spectra of the system 1 / SnCl₂ in CD₂Cl₂

Addition of an equivalent amount of $SnCl_2$ to 1, in CD_2Cl_2 gives an orange solution which shows a featureless ^{31}P NMR spectrum at 303 K. Upon cooling to 203 K the spectrum resolves into two distinct and equivalent signals at 17.6 ppm (^1J(Pt–P) 2940 Hz) and 15.7 ppm (^1J(Pt–P) 3220, ^2J(P–Sn) 283,295 Hz) indicated as A and B, respectively, in Fig. 1.

Signal B can be assigned to the complex *trans*-[Pt($SnCl_3$)(CO-n-hexyl)(PPh$_3$)$_2$] (2): the values of the P–Sn couplings prove the presence of a Pt–$SnCl_3$ bond in a *cis* position relative to two equivalent PPh$_3$ ligands mutually in a *trans* disposition in the coordination plane [8–10]. The breadth of signal A indicates that the relevant chemical species are involved in a relatively fast equilibrium.
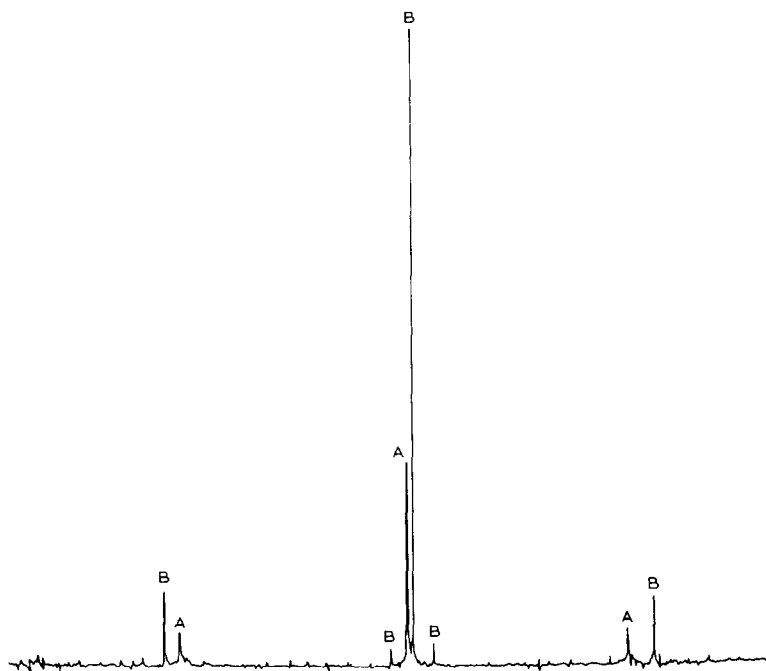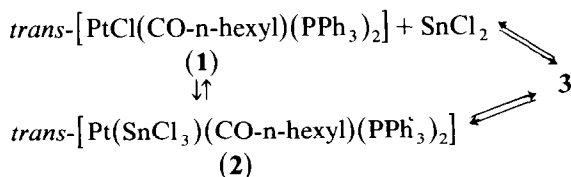
Fig. 1. ^{31}P NMR spectrum of *trans*-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$]/SnCl$_2$ (Sn/Pt = 1/1) in CD$_2$Cl$_2$ at 203 K.

The ^{31}P NMR spectra recorded in the presence of variable amounts of SnCl$_2$ (Sn/Pt ratios ranging from 0.3/1 to 1.2/1) show that peak *B* maintains its spectral features, whereas peak *A* moves from 21.1 ppm (^1J(Pt–P) 3465 Hz) at Sn/Pt ratio 0.3/1 to 17.0 ppm (^1J(Pt–P) 2935 Hz) at Sn/Pt ratio 1.2/1. The increase in the Sn/Pt ratio also results in a substantial enhancement of the intensity of signal *B* with respect to signal *A*. At the lowest Sn/Pt ratio peak *A* is close to the signal corresponding to the pure complex **1**. Thus signal *A* may be interpreted as the average resonance arising from a relatively fast equilibrium involving complex **1** and complex **3**, arising from the interaction of complex **1** with SnCl$_2$.

The observed ^{31}P NMR spectral behaviour can be interpreted in terms of the following scheme:

trans-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] + SnCl$_2$

(**1**)

$\downarrow\uparrow$

trans-[Pt(SnCl$_3$)(CO-n-hexyl)(PPh$_3$)$_2$]

(**2**)

3

Species **3** is in rapid equilibrium with complex **1**, whereas equilibria involving complex **2** are frozen out at 203 K. Complex **2** may be formed either via complex **3** or by direct attack of SnCl$_2$ on complex **1**. It is interesting to observe that the closely related complex *trans*-[Pt(SnCl$_3$)(CO-n-propyl)(PPh$_3$)$_2$] has been isolated during propene hydroformylation; in that case the presence of a Pt–SnCl$_3$ bond was suggested on the basis of IR data [5].

The following experimental observations affords other information on the nature of complex **3**: (i) the solutions containing **1** and $SnCl_2$ are non-conducting; (ii) the ^{31}P NMR spectrum of the cationic complex *trans*-[(solv)Pt(CO-n-hexyl)(PPh$_3$)$_2$]$^+$ (**4**) (solv = CD_2Cl_2), independently prepared, shows signals (see Table 1) different from those of **A** and **B**. It is thus reasonable to propose structures of types I or II for complex **3**.

(I)   (II)

Structures of types I and II have been found by X-ray diffraction of the complexes [Ag(SnCl$_3$)(PP)] (PP = 2,11-bis(diphenylphosphinomethyl)-benzo[c]-phenanthrene [11]) and [MoCl(SnCl$_2$CH$_3$)(2,2-bipyridyl)] [12]. Our results do not allow a definitive assignment for species **3**, since the equilibria cannot be frozen out even at 203 K.

It is noteworthy that in the case of the closely related complex *trans*-[Pt(SnCl$_3$)(CO-phenyl)(PPh$_3$)$_2$] in CDCl$_3$ solution a complex of type **2** has been observed, along with another species displaying no P–Sn couplings in the low temperature limiting spectrum; this latter species was tentatively formulated as an ion pair complex [13].

^{31}P NMR of the system $1/SnCl_2$ in acetone

The equilibria depicted in the scheme are strongly affected by the nature of the solvent. In acetone-d_6 at 203 K, the ^{31}P NMR of the system $1/SnCl_2$ (Pt/Sn = 1/1)

TABLE 1

^{31}P NMR DATA (chemical shifts are in ppm (positive values downfield referred to external 85% H$_3$PO$_4$ at room temperature). Coupling constants are in Hz (± 3))

	In CD$_2$Cl$_2$			In Acetone-d_6	
	δ(P)	^1J(Pt–P)	^2J(Sn–P)	δ(P)	J(Pt–P)
trans-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] ^{a} (**1**)	21.0	3537		20.0	3571
trans-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$] ^{b} (**1**)	21.4	3467			
trans-[Pt(SnCl$_3$)(CO-n-hexyl)(PPh$_3$)$_2$] ^{b} (**2**)	15.7^c	3220	283,295	15.1^c	3251
trans-[PtCl(CO-n-hexyl)(PPh$_3$)$_2$/SnCl$_2$] ^{b} (**3**)	17.6^c	2940		16.0^c	3103
trans-[(solv)Pt(CO-n-hexyl)(PPh$_3$)$_2$]$^+$ ^{a,d} (**4**)	23.1	3652			

^{a} Spectra measured at r.t. (303 K). ^{b} At 203 K. ^{c} Pt/Sn ratio 1/1. ^{d} Solv = CD_2Cl_2.

shows two signals, A' and B', having the following features: $A' =$ broad singlet (intensity 4) δ 16.0 ppm (^1J(Pt–P) 3103 Hz); $B' =$ singlet (intensity 1) δ 15.1 ppm (^1J(Pt–P) 3251 Hz); both signals show no phosphorus–tin couplings. The closeness of δ and J values of the B (Fig. 1) and B' signals suggests that signal B' may be attributed to complex 2, even though the P–Sn couplings can not be observed. The broad resonance A' is tentatively attributed to complex 3. The presence of an excess of $SnCl_2$ (Pt/Sn ratio up to 1/5) causes negligible changes in the spectrum.

The solvent effect on the relative amounts of complexes 2 and 3 in dichloromethane and acetone is noteworthy. A strong solvent effect has been observed also for the catalytic activity, which is high in a ketone and markedly depressed in an alkanol. This prompted us to study the effect of added ethanol on the spectral behaviour of the system $1/SnCl_2$ in acetone and dichloromethane solutions.

In acetone-d_6 at 203 K, at relatively low ethanol concentrations (Pt/EtOH molar ratio up to 1/50), δ and J values for resonance B' remain almost unchanged; for resonance A' the signals shift upfield and the ^1J(Pt–P) value increases; moreover the relative intensity of the signals A' and B' increases from 4/1 to 10/1. At higher EtOH concentrations (Pt/EtOH ~ 1/800, acetone/EtOH ~ 2/1) resonance B' is no longer observable, while resonance A' appears as a singlet at 16.7 ppm with ^1J(Pt–P) 3290 Hz. The same behaviour is observed in CD_2Cl_2 solutions. These results suggest that EtOH prevents the formation of the complex trans-$[Pt(SnCl_3)(CO$-n-hexyl)$(PPh_3)_2]$ and that only species 1 and 3, in equilibrium, are present in this solvent.

Reactions with hydrogen

In CD_2Cl_2 or acetone-d_6 solutions the system $1/SnCl_2$ reacts with molecular hydrogen under ambient conditions. In both solvents, n-heptanal is formed overnight in practically quantitative yield. The fate of complex 1, was investigated by ^1H and ^{31}P NMR. The spectra of the CD_2Cl_2 solution show that resonances A and B have disappeared and that the major species present is trans-$[PtH(SnCl_3)(PPh_3)_2]$ [14a]; a minor amount of other hydrido species can be recognized from a complex pattern of resonances in the ^{31}P and ^1H (hydride region) NMR spectra. In acetone only this complex pattern is recognizable: these signals are superimposable on those of the system trans-$[PtHCl(PPh_3)_2]/SnCl_2$ which was independently studied in acetone [14b].

It is noteworthy that the hydrogenolysis of the σ-acyl–Pt bond is quenched by ethanol. The ^{31}P NMR spectra of CD_2Cl_2/ethanol or acetone/ethanol solutions of system $1/SnCl_2$ show no variations after hydrogen treatment overnight.

Conclusions

The most remarkable result of our investigation is the detection of species 3 in equilibrium with complexes 1 and 2. The concentration of species 3 is comparable with that of 2 in CD_2Cl_2 and is higher in acetone; in acetone/ethanol species 3 is practically the only complex present.

In acetone/ethanol hydrogenolysis of the σ-acyl–Pt^{II} bond of species 3 does not occur under ambient conditions. In contrast, species 2, which contains a Pt–$SnCl_3$ bond, undergoes hydrogenolysis, even under such conditions to give the corresponding aldehyde.

Since ethanol inhibits the formation of complex 2 and the catalytic hydroformyla-

tion is strongly depressed in this alcohol [5–7] it seems reasonable to assume that only a species of type **2** is directly involved in the catalysis. In addition, since complex **1** can be synthesized from [PtCl$_2$(PPh$_3$)$_2$], 1-hexene, and hydrogen even in the absence of SnCl$_2$, and since SnCl$_2$ is necessary in order to observe catalysis, our data give further support to the suggestion that a Pt–SnCl$_3$ bond plays a key role in the last steps of the catalytic cycle [5–7].

More experimental work, more closely simulating "oxo" conditions, is needed to gain a deeper insight into the nature and activity of the Pt–Sn system.

Experimental

Complex **1** and *trans*-[PtHCl(PPh$_3$)$_2$] were prepared as described in the literature [6,15]. SnCl$_2 \cdot$ 2H$_2$O was dehydrated before use [16].

The ^{1}H and ^{31}P {^{1}H} NMR spectra were recorded on a Varian FT 80 A spectrometer at 79.542 and 32.203 MHz respectively. The solutions for the NMR experiments were prepared by stirring complex **1** with the appropriate amount of SnCl$_2$ under argon.

Complex **4** was prepared in situ by adding an equimolecular amount of AgBF$_4$ to complex **1** dissolved in CD$_2$Cl$_2$.

The reactions with hydrogen were performed by keeping the **1**/SnCl$_2$ solutions under this gas overnight.

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