

METALS IN ORGANIC SYNTHESSES

XI *. ^{31}P NMR AND REACTIVITY STUDIES ON THE SYSTEM *trans*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]/\text{SnCl}_2$, AN ACTIVE INTERMEDIATE IN THE CATALYTIC HYDROFORMYLATION OF 1-HEXENE

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Summary

The system *trans*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]/\text{SnCl}_2$ has been investigated by ^{31}P NMR spectroscopy. In CD_2Cl_2 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*- $[\text{Pt}(\text{SnCl}_3)(\text{CO-n-hexyl})(\text{PPh}_3)_2]$; 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*- $[\text{Pt}(\text{SnCl}_3)(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ is prevented when ethanol is added to the CD_2Cl_2 or acetone- d_6 solutions. Treatment of the CD_2Cl_2 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 $[\text{PtCl}_2(\text{PPh}_3)_2]/\text{SnCl}_2$ system.

Introduction

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

* 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 ($\text{CO}/\text{H}_2 = 1/1$) giving high yields of *n*-butanal; under these conditions *trans*- $[\text{Pt}(\text{SnCl}_3)(\text{CO-n-propyl})(\text{PPh}_3)_2]$, which contains a Pt–Sn bond, has been isolated [5]. In ethanol solutions, under the same conditions, no catalysis was observed; and *trans*- $[\text{PtCl}(\text{CO-n-propyl})(\text{PPh}_3)_2]$ and *trans*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ 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*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ 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*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ (**1**)

First, we studied the behaviour of the complex *trans*- $[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ (**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 $\{^1\text{H}\}$ NMR spectrum of **1** displays a single resonance at 21.0 ppm flanked by ^{195}Pt satellites ($^1J(\text{Pt}–\text{P})$ 3537 Hz); this signal is moderately affected by temperature: at 203 K it is observed at 21.4 ppm ($^1J(\text{Pt}–\text{P})$ 3467 Hz). In acetone- d_6 , at 303 K, the signal appears at 20.0 ppm ($^1J(\text{Pt}–\text{P})$ 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** / SnCl_2 in CD_2Cl_2

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 ($^1J(\text{Pt}–\text{P})$ 2940 Hz) and 15.7 ppm ($^1J(\text{Pt}–\text{P})$ 3220, $^2J(\text{P}–\text{Sn})$ 283,295 Hz) indicated as *A* and *B*, respectively, in Fig. 1.

Signal *B* can be assigned to the complex *trans*- $[\text{Pt}(\text{SnCl}_3)(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ (**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.

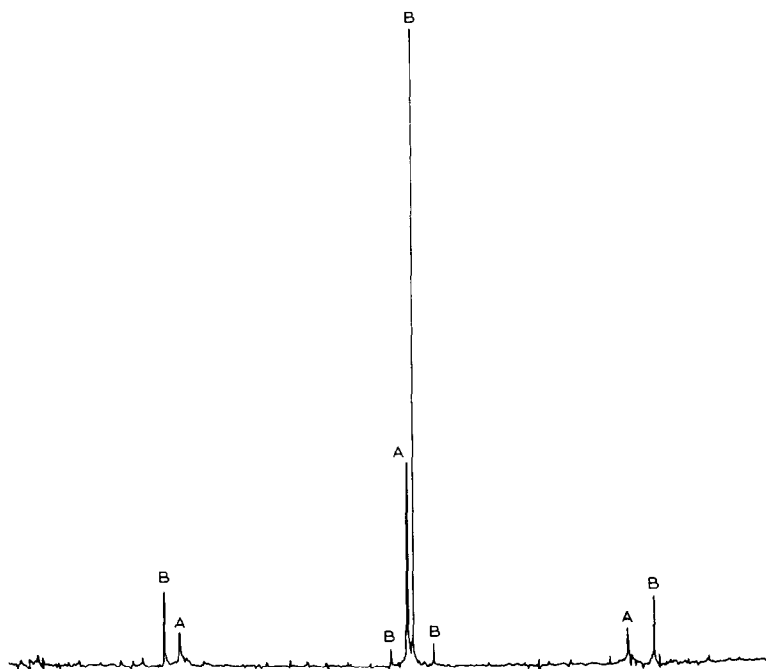
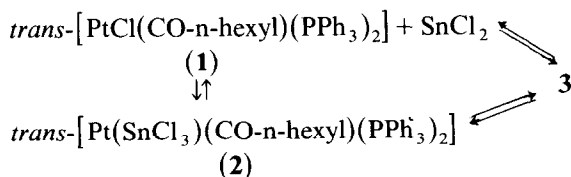


Fig. 1. ^{31}P NMR spectrum of $\text{trans}[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]/\text{SnCl}_2$ ($\text{Sn}/\text{Pt} = 1/1$) in CD_2Cl_2 at 203 K.

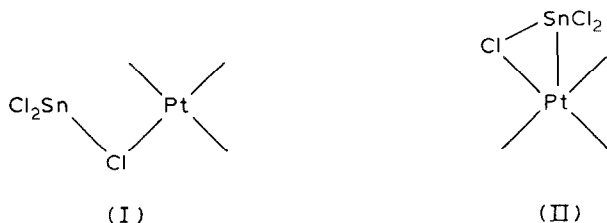
The ^{31}P NMR spectra recorded in the presence of variable amounts of SnCl_2 (Sn/Pt ratios ranging from 0.3/1 to 1.2/1) show that peak *B* maintains its spectral features, whereas peak *A* moves from 21.1 ppm ($^1J(\text{Pt-P})$ 3465 Hz) at Sn/Pt ratio 0.3/1 to 17.0 ppm ($^1J(\text{Pt-P})$ 2935 Hz) 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:



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 $\text{trans}[\text{Pt}(\text{SnCl}_3)(\text{CO-n-propyl})(\text{PPh}_3)_2]$ 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 $\text{trans}-[(\text{solv})\text{Pt}(\text{CO-n-hexyl})(\text{PPh}_3)_2]^+$ (**4**) ($\text{solv} = \text{CD}_2\text{Cl}_2$), 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**.



Structures of types I and II have been found by X-ray diffraction of the complexes $[\text{Ag}(\text{SnCl}_3)(\text{PP})]$ ($\text{PP} = 2,11\text{-bis}(\text{diphenylphosphinomethyl})\text{-benzo}[c]\text{-phenanthrene}$ [11]) and $[\text{MoCl}(\text{SnCl}_2\text{CH}_3)(2,2\text{-bipyridyl})]$ [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 $\text{trans}-[\text{Pt}(\text{SnCl}_3)(\text{CO-phenyl})(\text{PPh}_3)_2]$ 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 ($\text{Pt}/\text{Sn} = 1/1$)

TABLE 1

^{31}P NMR DATA (chemical shifts are in ppm (positive values downfield referred to external 85% H_3PO_4 at room temperature). Coupling constants are in Hz (± 3))

	In CD_2Cl_2			In Acetone- d_6	
	$\delta(\text{P})$	$^1J(\text{Pt-P})$	$^2J(\text{Sn-P})$	$\delta(\text{P})$	$J(\text{Pt-P})$
$\text{trans}-[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]^a$ (1)	21.0	3537		20.0	3571
$\text{trans}-[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]^b$ (1)	21.4	3467			
$\text{trans}-[\text{Pt}(\text{SnCl}_3)(\text{CO-n-hexyl})(\text{PPh}_3)_2]^b$ (2)	15.7 ^c	3220	283,295	15.1 ^c	3251
$\text{trans}-[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2/\text{SnCl}_2]^b$ (3)	17.6 ^c	2940		16.0 ^c	3103
$\text{trans}-[(\text{solv})\text{Pt}(\text{CO-n-hexyl})(\text{PPh}_3)_2]^+_{a,d}$ (4)	23.1	3652			

^a Spectra measured at r.t. (303 K). ^b At 203 K. ^c Pt/Sn ratio 1/1. ^d $\text{Solv} = \text{CD}_2\text{Cl}_2$.

shows two signals, A' and B' , having the following features: A' = broad singlet (intensity 4) δ 16.0 ppm ($^1J(\text{Pt-P})$ 3103 Hz); B' = singlet (intensity 1) δ 15.1 ppm ($^1J(\text{Pt-P})$ 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 $^1J(\text{Pt-P})$ 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 $\sim$ 1/800, acetone/EtOH $\sim$ 2/1) resonance B' is no longer observable, while resonance A' appears as a singlet at 16.7 ppm with $^1J(\text{Pt-P})$ 3290 Hz. The same behaviour is observed in CD_2Cl_2 solutions. These results suggest that EtOH prevents the formation of the complex *trans*- $[\text{Pt}(\text{SnCl}_3)(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ 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*- $[\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2]$ [**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*- $[\text{PtHCl}(\text{PPh}_3)_2]/\text{SnCl}_2$ 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-SnCl₃ 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 $[\text{PtCl}_2(\text{PPh}_3)_2]$, 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*- $[\text{PtHCl}(\text{PPh}_3)_2]$ were prepared as described in the literature [6,15]. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dehydrated before use [16].

The ^1H and ^{31}P (^1H) 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_2Cl_2 .

The reactions with hydrogen were performed by keeping the **1**/ SnCl_2 solutions under this gas overnight.

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