

Further studies of the $\text{Pt}^{\text{II}}/\text{SnCl}_2$ catalyzed hydroformylation

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Abstract

A convenient synthesis of the complexes *trans*- $[\text{PtCl}(\text{COEt})(\text{PMePh}_2)_2]$ and *trans*- $[\text{PtCl}(\text{COEt})(\text{PMe}_2\text{Ph})_2]$ is described, and their NMR spectra in the presence of SnCl_2 are discussed. These complexes have been examined as catalysts in 1-hexene hydroformylation in the presence of an excess of SnCl_2 . Their catalytic behaviour is compared with that of the systems based on complexes *trans*- $[\text{PtCl}(\text{COEt})(\text{PPh}_3)_2]$, *trans*- $[\text{PtHCl}(\text{PPh}_3)_2]$, *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$, and *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$.

Introduction

Olefin hydroformylation catalyzed by Pt^{II} complexes in the presence of Sn^{II} halides has been extensively studied because such systems allow formation of high yields of straight chain aldehydes from linear α -olefins [1] and give high stereoselectivities in asymmetric reactions [2–4]. Moreover, the stability of alkyl- and acyl-platinum(II) complexes has favoured extensive mechanistic investigations based on studies of the reactivity of model compounds. Recent studies [5–9] suggest that *trans*- $[\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2]$, *trans*- $[\text{PtR}(\text{SnCl}_3)(\text{PPh}_3)_2]$ and *trans*- $[\text{Pt}(\text{COR})(\text{SnCl}_3)(\text{PPh}_3)_2]$ (R = alkyl group) complexes are involved in the catalytic process promoted by the widely used Knifton system *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]/\text{SnCl}_2$. In particular, *trans*- $[\text{PtHCl}(\text{PPh}_3)_2]/\text{SnCl}_2$ [10] and *trans*- $[\text{PtCl}(\text{COR})(\text{PPh}_3)_2]/\text{SnCl}_2$ [11] have been successfully employed as catalytic precursors in hydroformylation. However, the relevant literature data are not comparable because the catalytic reactions were performed under different conditions, and so we decided to examine catalytic hydroformylations of 1-hexene in the presence of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]/\text{SnCl}_2$, *trans*- $[\text{PtHClL}_2]/\text{SnCl}_2$ (L = PPh_3 and PEt_3) and *trans*- $[\text{PtCl}(\text{COC}_2\text{H}_5)_2\text{L}_2]/\text{SnCl}_2$ (L = PPh_3 , PMePh_2 and PMe_2Ph) under the same conditions in order to compare the catalytic performances of these systems and to gain a deeper insight into: (a) the role played by hydride and acyl complexes in the catalytic cycle; (b) the effect of the phosphine basicity on the catalytic activity and (c) the role played by the phosphine basicity on the stability of trichlorostannate acyl complexes.

Complexes synthesis and NMR studies

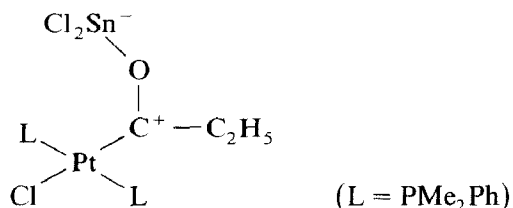
The acylplatinum(II) complexes *trans*-[PtCl(COC₂H₅)(PMePh₂)₂] (**2**) [12] and *trans*-[PtCl(COC₂H₅)(PMe₂Ph)₂] (**3**) [13] have been briefly described previously. We report here a one-pot synthesis of complexes **2** and **3** by a phosphine exchange method starting from the readily available complex *trans*-[PtCl(COC₂H₅)(PPh₃)₂] (**1**) [8]. The exchange is performed by suspending complex **1** in *n*-hexane and adding a stoichiometric amount of the appropriate ligand at room temperature under nitrogen. After 24 h analytically pure complex **2** or **3** can be filtered off.

The spectroscopic properties of complexes **2** and **3** are identical to those described in the literature [12,13]. Full characterization data are given in the Experimental section.

This synthetic method is convenient since it affords complexes **2** and **3** in high yield. It cannot, however, be used for the synthesis of acyl complexes bearing trialkylphosphines (e.g. triethylphosphine), since in this case the reaction product is soluble in *n*-hexane and its separation from triphenylphosphine difficult.

We have studied the solution behaviour of complexes **2** and **3** in the presence of an excess of SnCl₂ in order to ascertain the role played by the ligand basicity in stabilizing trichlorostannate acylplatinum(II) complexes. The reaction of complex **2** with SnCl₂ in CD₂Cl₂ afforded a yellow solution, which was studied by IR, ¹H and ³¹P NMR spectroscopy. The IR and ¹H NMR data confirmed the presence of the acyl moiety (see Experimental section). The CD₂Cl₂ low temperature (−70 °C) ³¹P NMR shows a singlet (δ 0.3 ppm) flanked by ¹⁹⁵Pt and ^{119,117}Sn satellites. The observed coupling constants (¹J(Pt–P) 3009 Hz and ²J(^{119,117}Sn–P) 288, 276 Hz) are in keeping with the formulation *trans*-[Pt(SnCl₃)(COC₂H₅)(PMePh₂)₂] [8,15]; no signals attributable to carbene species were detected. This result indicates that the PMePh₂ ligand stabilizes the trichlorostannate structure. The same effect was observed in the case of the related species *cis*-[Pt(SnCl₃)(COC₂H₅)(1,4-bis(diphenylphosphino)butane)] and *cis*-[Pt(SnCl₃)(COC₂H₅)(1,3-bis(diphenylphosphino)propane)] [16].

The reaction of complex **3** with SnCl₂ in CD₂Cl₂ afforded an orange solution containing acylplatinum species, as indicated by the IR and ¹H NMR data (see Experimental section). In this case, the low temperature ³¹P NMR spectrum showed two sets of signals of relative intensity ≈ 4/1. The spectral features of the more intense set (singlet at δ(P) −11.1 ppm, ¹J(Pt–P) 2871 Hz, ²J(^{119,117}Sn–P) 291, 280 Hz) are consistent with the structure *trans*-[Pt(SnCl₃)(COC₂H₅)(PMe₂Ph)₂], whereas the pattern for the minor species (broad singlet at δ(P) −7.29 ppm, ¹J(Pt–P) 2660 Hz, no Sn satellites) is attributable to a carbene-like structure in which the SnCl₂ acts as a Lewis acid towards the oxygen atom of the acyl ligand [8], as depicted below:



These results and those reported by others [8,14,16] (for instance, Pregosin observed no carbene-like structures in the case of the system *trans*-[PtCl(COPh)

($\text{PEt}_3)_2]/\text{SnCl}_2$) do not provide a basis for suggesting a relationship between the phosphine basicity and the stability of the trichlorostannate structures.

Catalytic hydroformylation

We carried out some hydroformylation experiments of 1-hexene using complexes **1–6** as the precatalysts in the presence of an excess of SnCl_2 . The aim of these experiments was to gain information about the influence of the phosphine basicity on the catalytic activity and the chemio- and regio-selectivity of the reaction. Therefore a fixed amount of the olefinic substrate was hydroformylated under standard conditions [1] (see Experimental section), and the chemical yield was determined after a fixed reaction time.

The hydroformylation results under several conditions are listed in Tables 1, 2 and 3. From the results of the catalytic runs in toluene (Table 1) it can be seen that the increase in the phosphine basicity in the σ -acyl complexes **1–3** leads to a substantial enhancement of the catalytic activity towards hydroformylation. Under the same conditions Knifton's system based on complex **4** gives the highest yield of

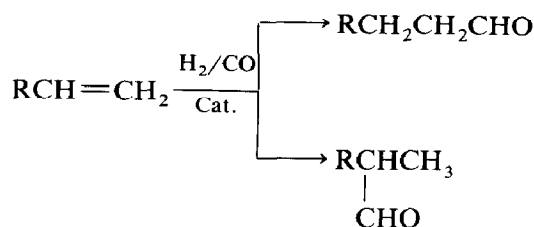


Fig. 1. Cat. = *trans*-[PtCl(COC₂H₅)(PPh₃)₂] (**1**); *trans*-PtCl(COC₂H₅)(PMePh₂)₂] (**2**); *trans*-[PtCl(COC₂H₅)(PMe₂Ph)₂] (**3**); *cis*-[PtCl₂(PPh₃)₂] (**4**); *trans*-[PtHCl(PPh₃)₂] (**5**); *trans*-[PtHCl(PEt₃)₂] (**6**).

Table 1

Results of hydroformylation in toluene (conditions: 1-hexene, 16 mmol; 1-hexene/Pt, 320; SnCl_2 /Pt, 5; $P(\text{CO})$, 50 atm; $P(\text{H}_2)$ 50 atm; reaction time, 3 h; temperature, 80 °C; solvent (toluene), 20 ml)

Catalyst precursor	Aldehydes (yield %)	Composition (%)		n-Hexane (yield %)	Hexenes (yield %)	Olefin conversion (%)
		Normal	Branched			
PtCl(COEt)(PPh ₃) ₂ (1)	33.7	94.2	5.8	2.6	2.4	38.7
PtCl(COEt)(PMePh ₂) ₂ (2)	49.2	94.1	5.9	7.9	6.9	64.0
PtCl(COEt)(PMe ₂ Ph) ₂ (3)	50.1	90.5	9.5	12.4	11.0	73.5
PtCl ₂ (PPh ₃) ₂ (4)	51.4	90.7	9.3	9.9	13.3	74.6
PtHCl(PPh ₃) ₂ (5)	33.9	93.8	6.2	2.7	2.4	39.0
PtHCl(PEt ₃) ₂ (6)	45.3	90.4	9.6	3.0	3.3	51.6

Table 2

Results of hydroformylation in dichloromethane (Conditions: 1-hexene, 16 mmol; 1-hexene/Pt, 320; SnCl_2/Pt , 5; $P(\text{CO})$, 50 atm; $P(\text{H}_2)$, 50 atm; reaction time, 3 h; temperature, 80 °C; solvent (CH_2Cl_2), 20 ml)

Catalyst Precursor	Aldehydes (yield %)	Composition (%)		n-Hexane (yield %)	Hexenes (yield %)	Olefin conversion (%)
		Normal	Branched			
$\text{PtClCOEt}(\text{PPh}_3)_2$ (1)	25.0	96.3	3.7	3.9	10.4	39.3
$\text{PtClCOEt}(\text{PMePh}_2)_2$ (2)	43.0	95.8	4.2	4.5	14.8	62.3
$\text{PtClCOEt}(\text{PMe}_2\text{Ph})_2$ (3)	62.0	95.5	4.5	6.3	22.9	91.2
$\text{PtCl}_2(\text{PPh}_3)_2$ (4)	63.4	93.0	7.0	5.0	27.8	96.2
$\text{PtHCl}(\text{PPh}_3)_2$ (5)	26.2	95.3	4.7	3.3	9.2	38.7
$\text{PtHCl}(\text{PEt}_3)_2$ (6)	55.4	94.5	5.5	3.0	8.1	66.5

aldehydes. The “oxo” activity of the hydrido complex **5** is much lower than that observed in the presence of complex **4**, and is very close to that of complex **1**. Comparison of the catalytic behaviour of the hydrido complexes **5** and **6** points to the influence of the phosphine basicity in promoting the aldehyde formation. The regio-selectivity of the “oxo” reaction is not significantly dependent on the nature of the procatalyst even if the decrease of the amount of linear aldehyde produced, observed on going from complex **1** to **3** and from **5** to **6**, is in keeping with the decreasing steric hindrance of the phosphine ligands. Furthermore the isomerization and hydrogenation side reactions of 1-hexene increase in both of the series **1–3** and **5–6**. This trend may be related to the increase in the phosphine basicity.

It is noteworthy that compared with the closely related complexes **1** and **5**, complex **4** gives a much higher olefin conversion but a lower chemoselectivity.

The hydroformylation data for the experiments performed in dichloromethane are shown in Table 2. In this solvent the overall behaviour is close to that observed in toluene. Comparison between the data in Tables 1 and 2 reveals that in dichloromethane the aldehyde yield is more affected by the phosphine basicity, the regio-selectivity towards linear aldehyde is higher, and the extent of 1-hexene isomerization is considerably enhanced, as reported by Knifton [1].

Discussion

The results obtained in the 1-hexene hydroformylation catalyzed by complexes **1–6** enable us to make some comments on the mechanism of the catalytic process.

The aldehyde formation from intermediate acylplatinum complexes has been suggested to be the rate-determining step of the catalytic cycle [1,17], and so the enhancement of activity observed with increasing phosphine basicity in both of the series **1–3** and **5–6** is in keeping with oxidative H_2 addition followed by reductive aldehyde elimination. It is well known that oxidative addition of H_2 is favoured by a higher electron density at the metal center [18,19].

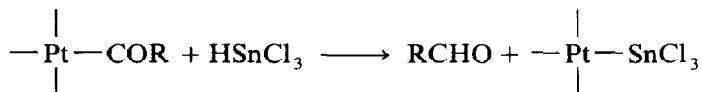
Table 3

Results of hydroformylation in toluene and in the presence of proton sponge (Conditions: 1-hexene, 16 mmol; 1-hexene/Pt, 320; SnCl_2/Pt , 5; $P(\text{CO})$, 50 atm, $P(\text{H}_2)$, 50 atm; reaction time, 3h; temperature, 80 °C; solvent (toluene), 20 ml; PS = proton sponge = 1,8-bis(dimethylamino)naphthalene)

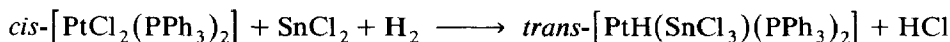
Catalyst Precursor	Aldehydes (yield %)	Composition (%)		n-Hexane (yield %)	Hexenes (yield %)	Olefin conversion (%)
		Normal	Branched			
$\text{PtCl}_2(\text{PPh}_3)_2$ (4)	51.4	90.7	9.3	9.9	13.3	74.6
$\text{PtCl}_2(\text{PPh}_3)_2$ + PS	31.9	86.7	13.3	1.9	2.9	36.7
$\text{PtHCl}(\text{PPh}_3)_2$ (5)	33.9	93.8	6.2	2.7	2.4	39.0

As far as the aldehyde yield is concerned, the most interesting speculations arise from the comparison of the catalytic behaviour of the complexes **1**, **4** and **5**. The results obtained with these complexes are somewhat surprising, since all these catalytic species are PPh_3 -based and are thought to belong to the same catalytic cycle. However, in both solvents (Tables 1 and 2) complex **4** shows a higher hydroformylating activity than complexes **1** and **5**, whose "oxo" activities are very similar.

To account for these features, it is reasonable to suggest that two separate mechanisms operate in the catalysis. Pino [20] previously suggested that the aldehyde-splitting can occur via interaction of HSnCl_3 with an acylplatinum complex:



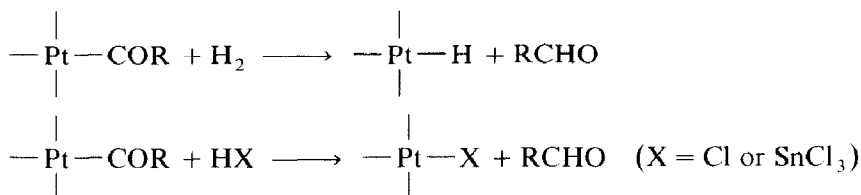
Furthermore, Pregosin [7] demonstrated that complex **4** promotes the heterolytic dissociation of hydrogen according to the following equation:



In Pregosin's experiments the presence of HCl was detected, but we cannot exclude the possibility that in the presence of SnCl_2 the species " HSnCl_3 " is formed [20]. In order to gain more information on the role played by acidic species in the catalytic cycle we carried out some hydroformylation experiments (Table 3) involving use of complex **4** in the presence of 1,8-bis(dimethylamino)naphthalene ("proton sponge", hereafter denoted by PS), which is said to be able to bind protons selectively while displaying negligible coordinating ability [21]. The aim of these experiments was to reduce strongly the contribution of acidic species to the catalysis without affecting the coordination sphere of the platinum. In the presence of one equivalent of PS (relative to Pt) the catalytic hydroformylating activity of complex **4** fell from 51.4 to 31.9%, and the overall catalytic behaviour became very close to that displayed by the hydrido complex **5**.

The importance of the role played by acidic species such as HCl in the catalytic cycle has also been pointed out by Marchionna [22], and is supported by the results of the reactivity experiments reported below. Thus upon treatment of the acyl complex $\text{trans-}[\text{PtCl}(\text{CO-n-hexyl})(\text{PPh}_3)_2]$ (**7**) with dry HCl in the presence of an

excess of SnCl_2 (see Experimental section) we observed the formation of a substantial amount of n-heptanal ($\sim 20\%$). We thus believe that for the aldehyde splitting both of the following pathways operate:



although further studies will be necessary to determine the relative contributions of these two routes. The presence of acidic species also accounts for the higher isomerization and hydrogenation activities displayed by complex **4** compared with the related complexes **1** and **5** (Tables 1 and 2). The chemio-selectivity obtained with complex **4** in the presence of PS came very close to that displayed by complex **5** (Table 3).

It is noteworthy that the very similar results obtained in catalysis with the acyl complex **1** and the hydrido complex **5** strongly support the hypothesis that these species belong to the same catalytic cycle.

Experimental

NMR spectra were recorded on a Varian FT 80 A spectrometer operating at 79.542 MHz for ^1H and 32.203 MHz for ^{31}P spectra. IR spectra were recorded on a Perkin Elmer 683 spectrophotometer. GLC analyses were carried out with a C. Erba HRGC 5300 gas chromatograph. GC-MS spectra were recorded with a 5970 Hewlett-Packard mass spectrometer linked to a HP 5890 gas chromatograph.

Solvents were purified by standard procedures [23]. Deuterated solvents were dried over molecular sieves. Anhydrous SnCl_2 was used as received from Fluka A.G.. The phosphine ligands were purchased from Strem Chemicals and used without further purification. "Proton sponge" [1,8-bis(dimethylamino)naphthalene] was purchased from Aldrich.

Complexes *trans*-[PtCl(COC₂H₅)(PPh₃)₂] (**1**) [8], *trans*-[PtHCl(PPh₃)₂] (**4**) [24], *cis*-[PtCl₂(PPh₃)₂] (**5**) [25], *trans*-[PtHCl(PEt₃)₂] (**6**) [24] and *trans*-[PtCl(CO-n-hexyl)(PPh₃)₂] (**7**) [8] were prepared by published procedures.

The catalytic hydroformylations were carried out in a 150 cm³ stainless steel autoclave. In a typical experiment, the autoclave was charged under a nitrogen purge with 0.05 mmol of the platinum catalyst, 0.25 mmol of anhydrous SnCl_2 , a solution of 16 mmol of 1-hexene in 20 ml of the solvent, and, if required, 0.05 mmol of "proton sponge". The autoclave was then sealed and pressurized to 100 atm (measured at room temperature) with synthesis gas (CO/H₂ 1/1). The reactor was heated with stirring at 80 °C ($\pm 0.5^\circ\text{C}$); after 3 h it was cooled and the gas vented off. The reaction mixture was analyzed by GLC to determine the degree of conversion and the product composition.

Synthesis of trans-[PtCl(COC₂H₅)(PMePh₂)₂] (**2**) and *trans*-[PtCl(COC₂H₅)(PMe₂Ph)₂] (**3**)

To a suspension of 1.22 g of *trans*-[PtCl(COC₂H₅)(PPh₃)₂] (**1**) (1.5 mmol) in

carefully degassed n-hexane (80 ml) was added 0.6 ml of PMePh_2 (3 mmol). The mixture was stirred overnight at room temperature, then the white suspension was filtered and the collected solid was washed with n-hexane to give complex **2** as a white powder (yield: 0.93 g, 90%). Analytical data: Found: C, 50.24; H, 4.50. $\text{PtC}_{29}\text{H}_{31}\text{ClOP}_2$ calcd.: C, 50.62; H, 4.54%. IR (Nujol mull): 1640 cm^{-1} ($\nu(\text{CO})$).

^1H NMR (CD_2Cl_2): -0.04 ppm, t, CH_3CH_2 (J 7.1 Hz); 1.60 ppm, q, CH_3CH_2 ; 2.15 ppm, tt, PCH_3 ($J(\text{P-H})$ 3.7 Hz, $J(\text{Pt-H})$ 36 Hz); 7.2 – 7.7 ppm phenyl protons.

^{31}P NMR (CD_2Cl_2): singlet at 6.4 ppm flanked by Pt satellites, $J(\text{Pt-P})$ 3351 Hz.

Complex **3** was obtained similarly in 60% yield. Analytical data: Found: C, 40.55; H, 4.87. $\text{PtC}_{19}\text{H}_{27}\text{ClOP}_2$ calcd.: C, 40.47; H, 4.83%. IR (Nujol mull): 1625 cm^{-1} ($\nu(\text{CO})$).

^1H NMR (CD_2Cl_2): 0.40 ppm, t, CH_3CH_2 (J 7.0 Hz); CH_3CH_2 masked by PCH_3 resonance; 1.77 ppm, tt, PCH_3 ($J(\text{P-H})$ 4.0 Hz, $J(\text{Pt-H})$ 37 Hz); 7.2 – 7.8 ppm phenyl protons.

^{31}P NMR (CD_2Cl_2): singlet at -6.1 ppm flanked by Pt satellites, $J(\text{Pt-P})$ 3175 Hz.

NMR studies: 30 mg of acyl complex **2** were added to a stirred suspension of SnCl_2 (100 mg) in CD_2Cl_2 (1 ml) under nitrogen. After 1 h the suspension was filtered and the clear yellow filtrate transferred to an NMR tube. ^1H NMR (CD_2Cl_2 , -25°C): -0.32 ppm, t, CH_3CH_2 (J 7.0 Hz); 1.54 ppm, q, CH_3CH_2 ; 2.52 ppm, tt, PCH_3 ($J(\text{P-H})$ 3.6 Hz, $J(\text{Pt-H})$ 37 Hz); 7.2 – 7.8 ppm phenyl protons; IR (CH_2Cl_2): 1635 cm^{-1} ($\nu(\text{CO})$).

The reaction of complex **3** with SnCl_2 is carried out similarly; ^1H NMR (CD_2Cl_2 , -25°C): 0.51 ppm, t, CH_3CH_2 (J 7.0 Hz); CH_3CH_2 masked by PCH_3 resonance; 1.94 ppm, tt, PCH_3 ($J(\text{P-H})$ 3.6 Hz, $J(\text{Pt-H})$ 37 Hz); 7.2 – 7.8 ppm phenyl protons; IR (CH_2Cl_2): 1622 cm^{-1} ($\nu(\text{CO})$).

Reaction of complex 7 with HCl: A solution of complex **7** (55 mg, 0.06 mmol) in 5 ml of CH_2Cl_2 , was treated with a five-fold excess of SnCl_2 under nitrogen. After 1 h a gentle stream of dry HCl was passed through the suspension and the mixture was left under an atmosphere of HCl for three days. GC-MS analysis indicated the presence of $\sim 24\%$ of n-heptanal, $\sim 50\%$ of condensation products, and $\sim 26\%$ of unidentified organic products.

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