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On the mechanism of platinum(II)/$SnCl_2$ catalyzed hydroformylation of olefins. Studies of the reactivity of alkyl complexes containing chelating diphosphines

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Abstract

The complexes *cis*-$PtCl(C_2H_5)$(diphosphine) (diphosphine = 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane) have been used as model compounds for the hydroformylation of olefin catalyzed by the system $PtCl_2$/diphosphine/$SnCl_2$. They react with $SnCl_2$ to yield the corresponding trichlorostannate complexes *cis*-$Pt(SnCl_3)(C_2H_5)$(diphosphine), which in the absence of free ethylene decompose to form the dichloro species *cis*-$PtCl_2$(diphosphine) via an unstable hydrido species. Both the chloro- and trichlorostannate-alkyl complexes react with CO to give the acyl species *cis*-$PtX(COC_2H_5)$(diphosphine) (X = Cl or $SnCl_3$). When the diphosphine is 1,4-bis(diphenylphosphino)butane, oligomeric acyl complexes of *trans* geometry are formed. Preliminary studies of the reactivity of the acyl complexes with molecular hydrogen show that only the complexes bearing the Pt–$SnCl_3$ moiety react at ambient conditions giving propanal as the only observed organic product.

Introduction

The system $PtCl_2$/chelating diphosphine/$SnCl_2$ efficiently catalyzes the hydroformylation of 1-alkenes when the diphosphine is able to give a seven-membered ring upon coordination of the Pt metal center [1]. Moreover, the highest optical yield in asymmetric hydroformylation has been obtained by using the $PtCl_2$/$SnCl_2$ catalytic system in the presence of (–)DIPHOL, which also gives a seven-membered ring upon coordination to platinum [2]. Although these observations have attracted much interest [3], the ability of a seven-membered ring to improve the catalytic performance of the Pt–Sn system has received only speculative consideration [1,4] and, to our knowledge, no detailed mechanistic studies have been reported.

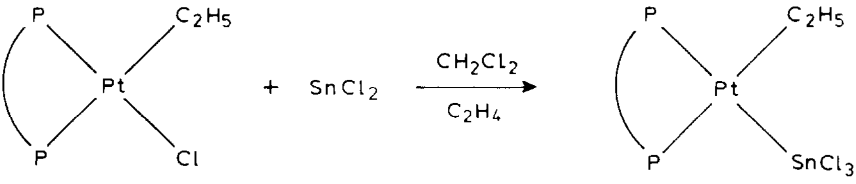
The catalytic system $PtCl_2(PPh_3)_2/SnCl_2$ has been considered in some detail [5–9]. We noted recently that complexes of the type *cis*-$Pt(SnCl_3)(C_2H_5)(PPh_3)_2$ are likely to be involved in the catalytic cycle of the hydroformylation of ethylene [9], and we thus thought it of interest to extend our investigation to the reactivity of the system *cis*-$PtCl(C_2H_5)$(diphosphine)/$SnCl_2$ towards CO and hydrogen. The aim of the present study is concerned with the role of the tin cocatalyst, and that of the diphosphine ligand.

The diphosphines chosen for the present study were 1,3-bis(diphenylphosphino)-propane (thereafter, DPPP) and 1,4-bis(diphenylphosphino)butane (thereafter DPPB). This latter (which forms seven-membered chelate rings) is the more interesting because the DPPB-based system shows a catalytic activity four times higher than that of the DPPP-based system. The DPPP catalyst shows a catalytic activity comparable with that of the system $PtCl_2(PPh_3)_2/SnCl_2$ [1].

Results and discussion

Reactivity of complexes cis-PtCl(C_2H_5)(PP) with $SnCl_2$

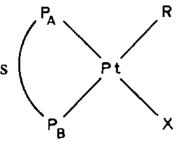
Complexes *cis*-$PtCl(C_2H_5)$(PP) (**1a**,**b**) (**a**: PP = DPPP; **b**: PP = DPPB) were prepared as described by published methods [10]. They were found to react with an equimolecular amount of $SnCl_2$ in dichloromethane under ethylene to give the corresponding trichlorostannate derivatives **2a** and **2b**:



(**1a**, **b**) (**2a**, **b**)

The formation of complexes **2a**,**b** in solution is confirmed by ^1H and ^{31}P NMR studies. At room temperature the ^{31}P NMR spectra of complexes **2a**,**b** consist of broad signals which sharpen on cooling, and at −80 °C they show an AB pattern flanked by ^{195}Pt and $^{117,119}Sn$ satellites. Such patterns arise from the non-equivalence of the P atoms of the diphosphine ligands. The resonance of the P atom *trans* to the ethyl group is easily recognized by its low ^1J(P–Pt) (ca. 1700 Hz) and ^2J(P–Sn) (ca. 250 Hz) coupling constants, while that of the P atom *trans* to the $SnCl_3$ group is characterized by much higher (^1J(P–Pt) (ca. 3800 Hz) and ^2J(P–Sn) (ca. 3500 Hz) values. The observed spectral parameters (see Table 1) agree well with the literature data for related systems [9], and in particular the values of the ^2J(P–Sn) are diagnostic for the presence of a $SnCl_3$ ligand bonded to the Pt metal center [11,12]. Since at −80 °C the ^1H NMR spectra of **2a**,**b** show broad resonances for the ethyl groups that are partially overlapped with the signals due to the methylene protons of the diphosphine ligand, their exact spectral assignments could not be made, but the integration ratios between aromatic and aliphatic protons are consistent with the proposed formulae.

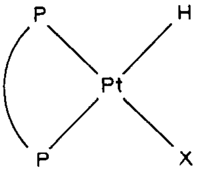
Table 1

^{31}P NMR data [a] for complexes  (X = Cl or SnCl$_3$)

Complex	$\delta(P_A)$ [b]	$\delta(P_B)$ [c]	$J(Pt-P_A)$	$J(Pt-P_B)$	$J(P_A-P_B)$	$J(P_A-Sn)$	$J(P_B-Sn)$
cis-Pt(SnCl$_3$)(Et)(DPPP) [d] (**2a**)	10.5	−4.2	3668	1634	28	3543,3389	262 [e]
cis-Pt(SnCl$_3$)(Et)(DPPB) [e] (**2b**)	30.6	8.4	3956	1772	19	3653,3493	236 [e]
cis-PtCl(COEt)(DPPP) (**6a**)	−4.2	−5.5	4448	1315	29		
cis-PtCl(COEt) (**6b**)	12.8	3.8	4706	1349	20		
trans-[PtCl(COEt)(DPPB)]$_3$ (**7**)	15.3		3381				
cis-Pt(SnCl$_3$)(COEt)(DPPP) [f] (**8a**)	−6.3	−13.8	3590	1540	35	2696 [e]	240 [e]
cis-Pt(SnCl$_3$)(COEt)(DPPB) [f] (**8b**)	23.8	−2.1	4014	1574	26	2896,2770	298 [e]
trans-Pt(SnCl$_3$)(COEt)(DPPB) [f] (**9**)	9.7		3090			271 [e]	

[a] Chemical shifts are in ppm (positive values downfield referred to 85% H_3PO_4 at room temperature); coupling constants are in Hz (±3); the spectra were recorded in CD_2Cl_2. [b] P_A is *trans* to R. [c] P_B is *trans* to X group. [d] Spectrum recorded at −80 °C. [e] Average coupling to ^{117}Sn and ^{119}Sn. [f] Spectrum recorded at −50 °C.

We were able to characterize complexes **2a** and **2b** spectroscopically only in solution, since they are stable only under an ethylene atmosphere. In the absence of an excess of olefin they decompose rapidly with loss of ethylene (as shown by GC-MS examination of the evolved gas). In the ^{1}H NMR spectrum there is a singlet at 5.43 ppm for the formed ethylene, and along with this there are two weak resonances in the hydrido region. These signals are quite broad indicating, that they arise from a dynamic species, and the spectra at −90 °C show a doublet of doublets. These patterns indicate the presence of Pt^{II}-hydride species of type **3**.



X = Cl or SnCl$_3$

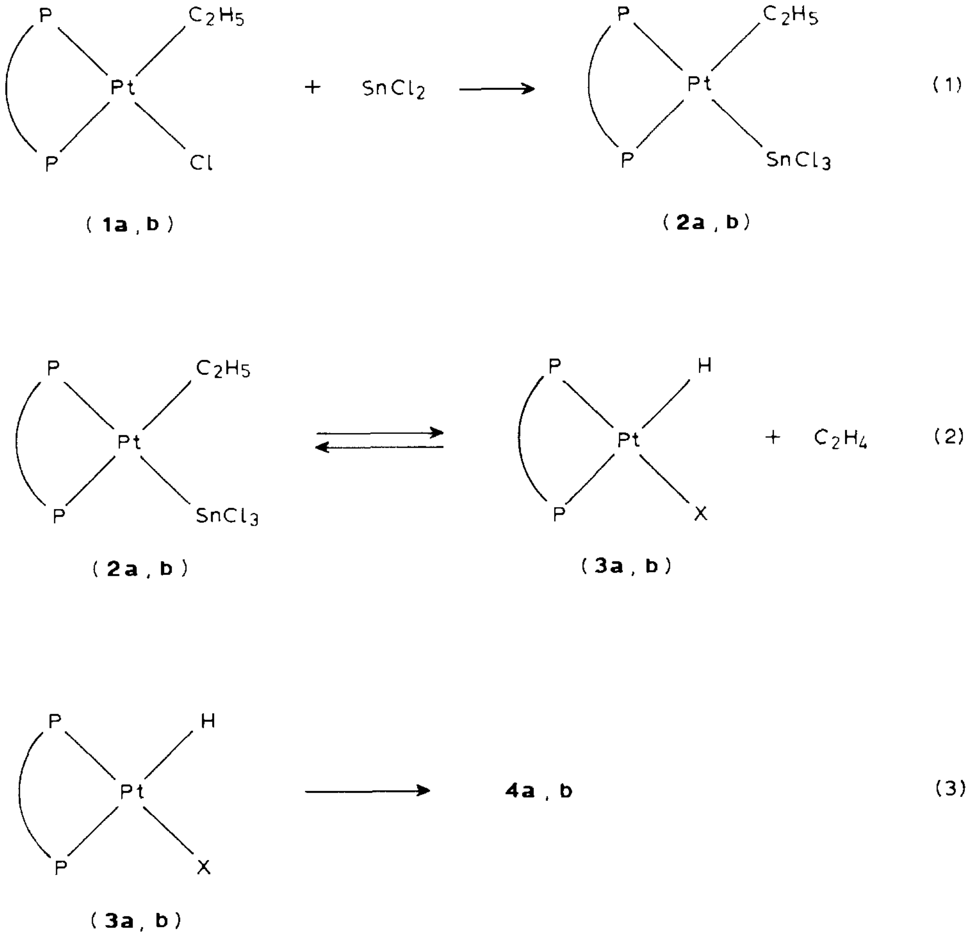
(**3a** , **b**)

Thus the observed spectral parameters (**3a**: δ(H) −11.35 ppm, $^2J(H-P_{trans})$ 146, $^2J(H-P_{cis})$ 11 Hz; **3b**: δ(H) −11.66 ppm, $^2J(H-P_{trans})$ 147, $^2J(H-P_{cis})$ 7 Hz) are similar to those reported by Shaw for the only *cis*-hydridochlorodiphosphine Pt^{II} complex for which relevant data are available, [13], and agree well with those for *cis*-PtH(SnCl$_3$)(PPh$_3$)$_2$ [14].

The lability of complexes **3a**,**b** prevented a full characterization. Moreover, the hydrido signals of these complexes disappear even when the solutions are kept at low temperature and yellow precipitates are formed. After recrystallization these precipitates were identified by IR spectroscopy and elemental analysis as the complexes $[PtCl_2(PP)]_n$ (**4a**,**b**) (**4a**: $n = 2$, **4b**: $n = 3$) [15], the yields of complexes **4a**,**b** account for ca. 70% of the starting complexes **2a**,**b**. Furthermore, after the precipitates are filtered off, the ^{31}P NMR spectra of the clear solutions show that complexes **4a**,**b** are practically the only species present. When complexes **1a** and **1b** are treated with half of the stoichiometric amount of $SnCl_2$, only ca. 50% of the complexes of type **1** is converted into the dichloro species **4**, the rest being unaffected. These experiments confirm that the chlorine atom required for the formation of complexes **4** is supplied by $SnCl_2$.

The overall transformations observed are summarized in Scheme 1.

The insertion of $SnCl_2$ into a Pt–Cl bond is a well known reaction [16]. Ethylene contributes to the stability of complexes **2** by driving equilibrium (2) to the left. The



Scheme 1

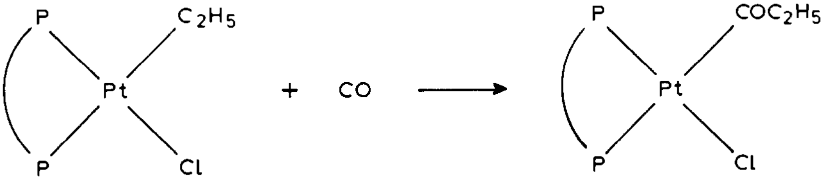
ethylene extrusion process probably occurs via a β-elimination reaction with the assistance of a readily available coordination site on the metal, either through an associative or an dissociative mechanism. In the latter case a vacant site would be provided through dissociation of $SnCl_3^-$, a process well known for Pt–$SnCl_3$ complexes [7,9]. In order to confirm this latter suggestion, we studied the behaviour of complexes **1a,b** in the presence of $AgBF_4$ in dichloromethane solutions. The immediate formation of AgCl was accompanied by gas evolution and the solutions turned red. GC-MS analysis showed the gas evolved is a mixture of ethylene and ethane. The results thus parallel those obtained by Baird, who observed ethane and ethylene evolution upon treatment of complexes **1a,b** with $Ph_3C^+BF_4^-$ [10]. Since in the decomposition shown in eq. 2 of Scheme 1 the formation of ethane is not observed, it appears that reaction (2) does not involve the formation of cationic intermediates via dissociation of the $SnCl_3^-$ ligand.

The instability of the hydrides of Pt^{II} having *cis* geometry is not surprising since very few complexes of this type are known [13,14,17]. While we have little experimental information to account for the formation of complexes **4**, we suggest that the reaction path could include as a first step the formation of a Pt^0 species via reductive elimination of HX, which would be favoured by the mutual *cis* position of the hydride and X ligand. This Pt^0 species might extract chlorine atoms from a Sn–Cl bond to yield the final dichloride **4**. The fate of the Sn-containing residue has not been investigated.

It is noteworthy that the ethylene deinsertion process shown in eq. 2 is slowed considerably in the presence of an excess of $SnCl_2$. As matter of fact, whereas olefin extrusion is complete in about 15 min at a Pt/Sn ratio 1/1, slurries obtained by stirring complexes **1a** or **1b** with a 3-fold the stoichiometric amount of $SnCl_2$ show only minor (< 10%) ethylene evolution after 1 h at room temperature. At a Pt/Sn ratio 1/3 the ethylene extrusion is complete in ca. 10 h, and the low temperature ^{31}P NMR spectra then show that the final products are the species $PtCl(SnCl_3)(PP)$ (**5a,b**) (see Experimental section). Probably $SnCl_2$ competes with the coordination site on the metal responsible for the β-elimination, as postulated for the insertion of $SnCl_2$ into a Pt–Cl bond [18].

Carbonylation reactions of complexes of type 1

Carbonylation of complex **1a**, at atmospheric pressure gives the acyl complex **6a** having *cis* geometry:



(4)

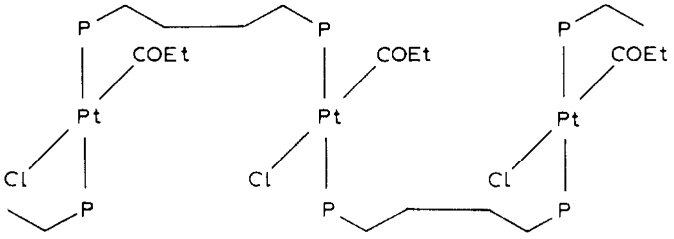
(**1a**) (**6a**)

P⌒P = DPPP

The IR spectrum of **6a** shows an intense CO stretching at 1640 cm^{-1} due to the acyl moiety [19,20] and a weak one at 295 cm^{-1} due to the Pt–Cl vibration [21]. The

^1H NMR spectrum shows the expected triplet and quartet of the ethyl group (CH_3 triplet at 0.40 ppm, J 7.0 Hz, CH_2: quartet at 2.09 ppm). The ^{31}P NMR spectrum confirms the *cis* geometry of complex **6a**, showing an AB pattern flanked by ^{195}Pt satellites; the spectral parameters are listed in Table 1 and are consistent with those reported for related systems [20].

In the case of complex **1b** the carbonylation proceeds in a different way. When a 5×10^{-2} M dichloromethane solution of complex **1b** is treated with CO at atmospheric pressure the formation of an acyl moiety is indicated by the presence of a strong absorption at 1638 cm^{-1}. The Pt–Cl stretching band is observed at 260 cm^{-1}, a rather low value for a Pt–Cl stretching *trans* to a P atom [21]. In the ^1H NMR spectrum only the resonance due to the CH_3 group is clearly recognized as a broad triplet centered at -0.01 ppm (J 7.2 Hz), and the CH_2 signals are not resolved from the broad signals from the aliphatic chain of the diphosphine ligand. The ^{31}P NMR spectrum shows a singlet at 15.2 ppm flanked by ^{195}Pt satellites (^1J(P–Pt) 3381 Hz), and does not change on lowering of the temperature to -70 ° C. The overall picture is consistent with the formation of an acyl-chloro complex having two P atoms in mutual *trans* disposition, indeed, the observed Pt–Cl stretching frequency is consistent with a Cl ligand *trans* to an acyl group [22], and the ^1J(Pt–P) value is in keeping with those of the related complexes *trans*-$PtCl(COR)(PPh_3)_2$ (R = aryl or alkyl) [23]. Elemental analysis is consistent with the formulation $PtCl(COC_2H_5)(DPPB)$. Molecular weight determinations give a mass of 1980, thus indicating an oligomeric species with the formula $[PtCl(COC_2H_5)(DPPB)]_3$. On the basis of these findings, we suggest for this species a network of Pt atoms bridged together by the diphosphine ligand:

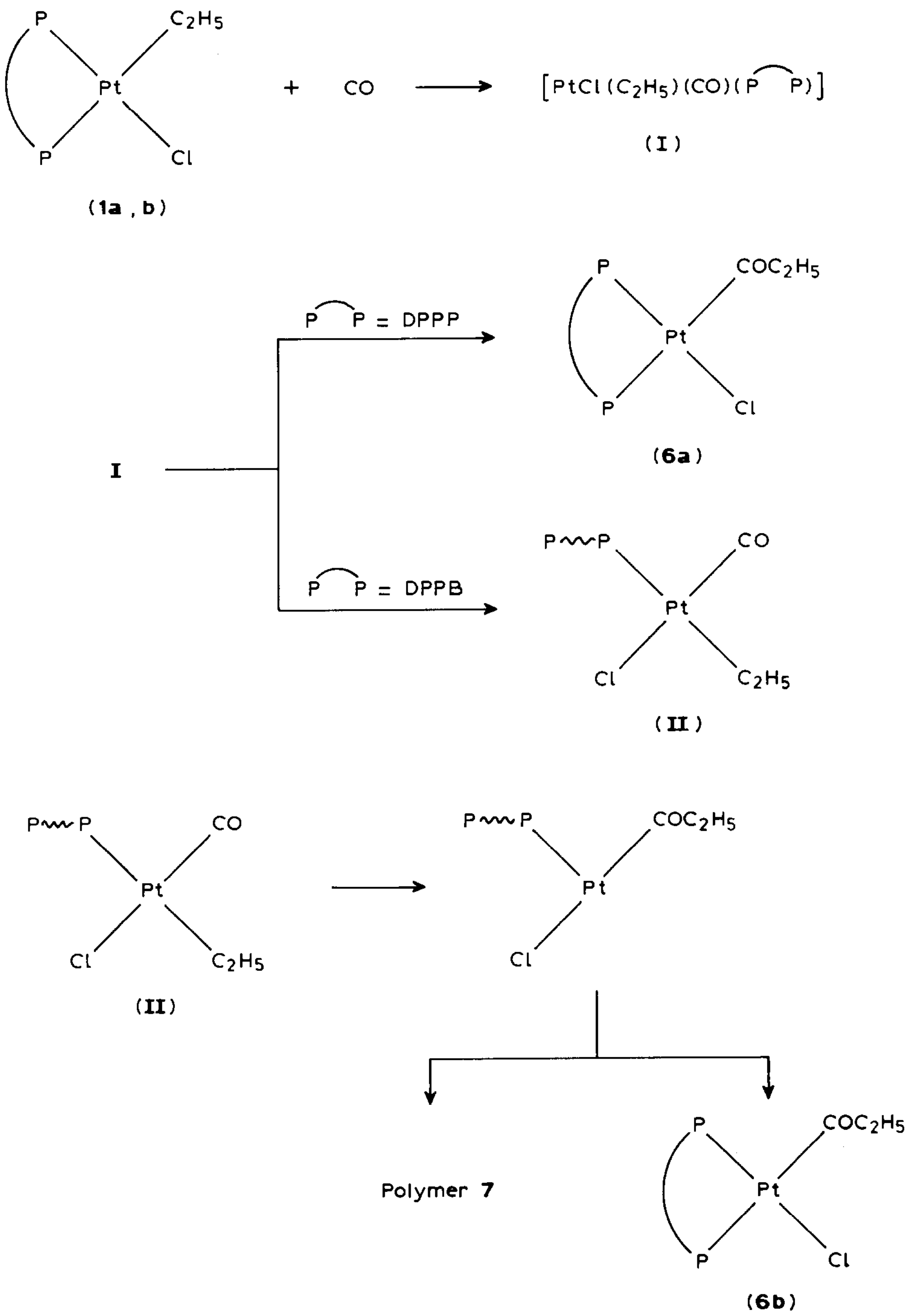


(**7**)

The formation of oligomeric complexes with DPPP and DPPB phosphine has been recognized previously in Pt^{II} chemistry [15].

The observed difference in the behaviour towards the CO insertion can be accounted for by the different chelating capabilities of the DPPP and DPPB ligands. A reasonable mechanism for the carbonylation of complexes **1a** and **1b** is outlined in Scheme 2.

The first step involves the interaction between the starting complexes **1a,b** and an incoming CO molecule to form the five-coordinate intermediate **I**. When PP = DPPP, intermediate **I** gives the monomeric acyl complex **6a** via an associative mechanism. This hypothesis is supported by the fact that when the carbonylation of complex **1a** was carried out in the presence of an excess of elemental sulphur and monitored by ^{31}P NMR spectroscopy, no signals attributable to CH_2–$PPh_2(S)$ moieties were


P
C2H5
Pt
P
Cl
(1a , b)
+
CO
[PtCl(C2H5)(CO)(P P)]
(I)
P P = DPPP
COC2H5
(6a)
I
P P = DPPB
P~P
CO
(II)
Polymer 7
(6b)

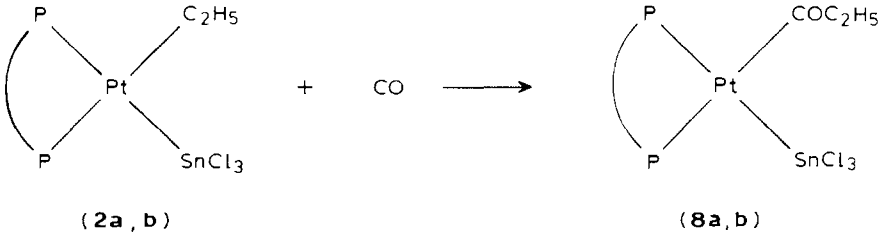
Scheme 2

detected, indicating no dissociation of either the DPPP ligand as a whole or one of its ends occurs during the process. An associative mechanism has been proposed by Anderson [20] for the carbonylation of the closely related complex *cis*-PtCl(Ph)(DPPP).

When PP = DPPB dissociation of one end of the diphosphine probably occurs, giving a four-coordinate intermediate such as **II**. Thus the different behaviour of complexes **1a** and **1b** can be related to the difference in the stabilities of the six- and seven-membered rings of the intermediates formed in the reaction with CO. The final steps of the carbonylation reaction lead to the acyl complex. This process might be assisted by the concomitant re-coordination of a diphenylphosphino group, otherwise these steps could imply some coordinatively unsaturated acyl species as outlined in Scheme 2. If the importance of the chelate effect is reduced, the incoming phosphino group can be provided from another platinum centre, giving rise to the oligomeric species **7**. If this is correct, there should be an increase in the amount of the monomeric *cis*-acyl complex **6b** when working with dilute solutions of complex **1b**, and this was shown to be the case by treating a 5×10^{-3} *M* dichloromethane solution of complex **1b** with CO. After concentration of the solution under reduced pressure, its ^{31}P NMR spectrum shows the presence, alongside the signals from the presumed trimeric species **7**, of an AB spin system (flanked by ^{195}Pt satellites), with spectral parameters identical to those of an authentic sample of *cis*-$PtCl(COC_2H_5)(DPPB)$ (**6b**) (see below). Examination of the integrated spectrum indicates that under these conditions complex **6b** is formed in ca. 30% yield.

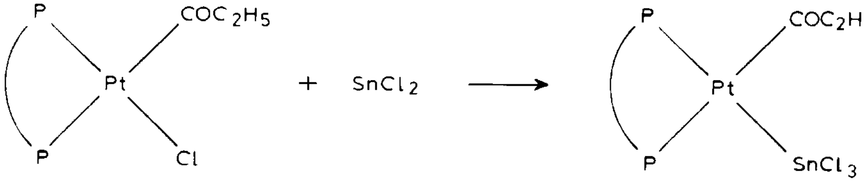
Carbonylation of complexes of type 2

Under a CO atmosphere, complexes **2a** and **2b** undergo a smooth insertion to yield the corresponding *cis*-acyl species:



(5)

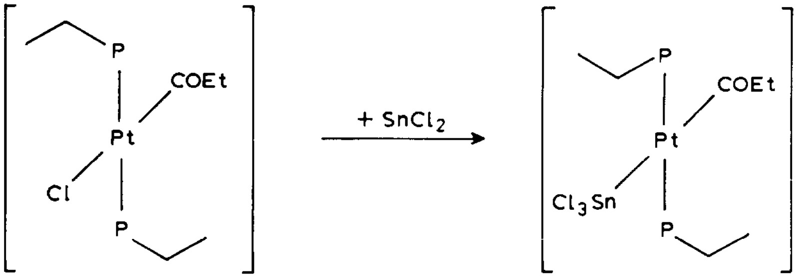
Reaction 5 is at least 10 times faster than the carbonylation of complexes **1a** and **1b**. The identities of complexes **8a** and **8b** were confirmed by IR and NMR spectroscopy. A strong absorption at 1640 cm^{-1} in the IR spectrum indicates the presence of an acyl moiety. The ^{1}H NMR spectra show the expected triplet and quartet patterns for the ethyl group (**8a**: CH_3: triplet at 0.35 ppm, *J* 7.1 Hz, CH_2: quartet at 2.14 ppm; **8b**: CH_3 at 0.34 ppm, *J* 7.0 Hz, CH_2 at 2.05 ppm). The *cis* geometry for these complexes is inferred from the ^{31}P NMR spectra recorded at $-50\,^{\circ}C$ (the r.t. spectra are dynamic), which show AB patterns flanked by Pt and Sn satellites. The relevant parameters are presented in Table 1, and fit well into the general trend observed for Pt-diphosphine complexes bearing a $SnCl_3$ ligand [11]. Further support for the proposed structure is given by the fact that complex **8a** can also be prepared by treating complex **6a** with an equimolecular amount of $SnCl_2$ in dichloromethane:



(**6a**) (**8a**)

(6)

The low temperature ^{31}P NMR spectrum of complex **8b** reveals the presence of a minor component (ca. 6% by integration), which gives rise to a singlet at 9.6 ppm. To identify this minor species we treated the trimeric acyl-chloro complex **7** with an equimolecular amount of $SnCl_2$, and obtained an orange product that contains the acyl ligand, as indicated by the presence of a CO stretch at 1660 cm^{-1}. The usual triplet and quartet patterns are present in the ^{1}H NMR spectrum: CH_3: triplet at -0.15 ppm, CH_2: quartet at 2.09 ppm, J(H,H) 7.1 Hz. The low temperature ^{31}P NMR spectrum of this species shows a singlet at 9.7 ppm flanked by Pt and Sn satellites. These features are consistent with the formation of a polymeric species derived from **7** by formal substitution of the Cl by the $SnCl_3$ ligand:



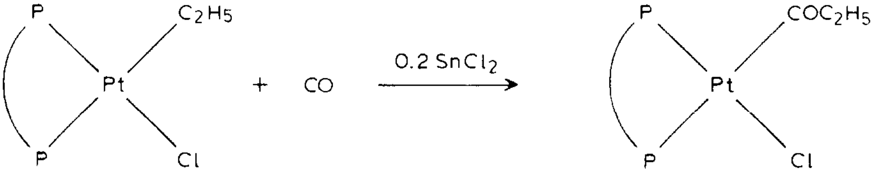
(**7**) (**9**)

(7)

On the basis of these data we assume that the low intensity signal at 9.6 ppm in the ^{31}P NMR spectrum of complex **8b** is attributable to the presence of a small amount of complex **9**.

Comparison of the results of the carbonylation reactions carried out on complexes **1b** and **2b** reveals that the presence of the $SnCl_3$ ligand induces operation of a mechanism different from that outlined in Scheme 2. Further studies of this feature are necessary but, it should be noted that an associative path was proposed by Clark [7] for the carbonylation of the closely related system *trans*-$Pt(SnCl_3)(Ph)(PPh_3)_2$.

Our findings prompted us to examine the carbonylation of complex **1b** in the presence of a catalytic amount of $SnCl_2$, which should favour the formation of the monomeric acyl complex **6b**. Reaction 8 was, indeed, found to proceed well, and recrystallization of the product gave complex **6b** in 60% yield:



(8)

(**1b**) (**6b**)

Characterization of complex **6b** was carried out by IR, ^1H and ^{31}P NMR spectroscopy. The IR spectrum shows an intense band at 1641 and a weaker one at 292 cm^{-1} attributable respectively to the CO and Pt–Cl stretching. The ^1H NMR spectrum shows a triplet at 0.37 ppm (J 7.2 Hz) and a quartet at 2.05 ppm due to the ethyl group. The *cis* geometry of complex **6b** gives rise to an AB ^{31}P spin system flanked by Pt satellites in the ^{31}P NMR spectrum; the relevant parameters are reported in Table 1, and are consistent with those of complex **6a**.

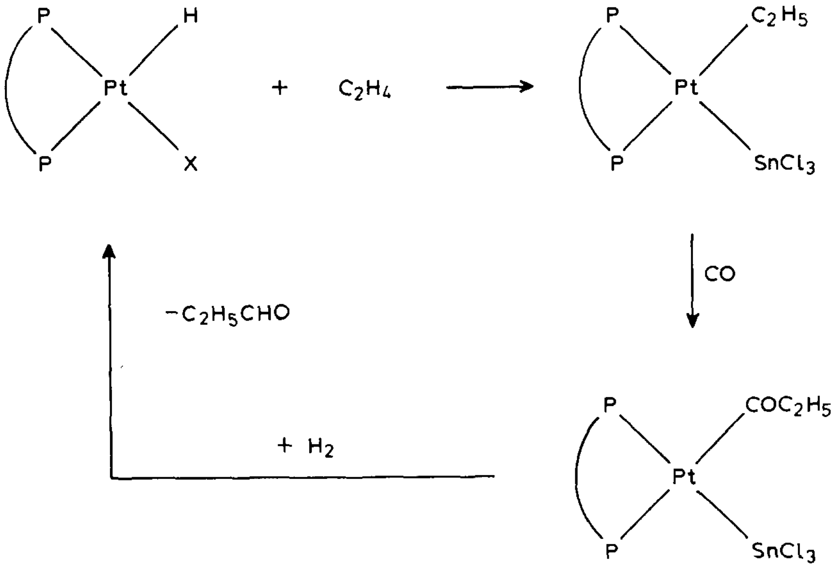
We should point out that when complex **1b** is treated with CO, under the same conditions but in the presence of a 3-fold excess of $SnCl_2$, practically no complex **8b** is formed: after a 2–4-min induction period, there is extensive precipitation of a yellow-orange material, the IR spectrum of which is superimposable upon that of authentic **5b**.

It is noteworthy that complexes **8a**, **8b**, **9** are the only species formed in these carbonylation reactions. It should also be recalled that carbonylation of the strictly related system $PtCl(R)(PPh_3)_2/SnCl_2$ (R = alkyl or aryl group) affords, along with $Pt(SnCl_3)(COR)(PPh_3)_2$ complexes, species in which the $SnCl_2$ acts as a Lewis acid and is involved in coordination with the oxygen atom of the acyl moiety [23]. (In some cases, depending on the nature of R, the proportion of such adducts may be as high as 70%). In contrast, in the present case we found no signals from such species in the solution, and conclude that the complexes containing the trichlorostannate ligand are much more stabile. Further studies are in progress to reveal the reasons for this enhanced stability.

Reactions with molecular hydrogen

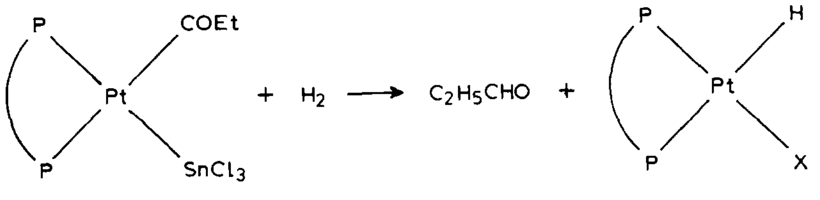
Hydrogenolysis of acyl complexes to yield the corresponding aldehyde and metal-hydrido complexes is thought to be the rate-determining step in the catalytic cycle of the hydroformylation reaction [1,8]. Thus we examined the reactions of complexes of type **6**, **7**, **8** and **9** with molecular hydrogen in order to obtain a better insight into the role played by the $SnCl_2$-cocatalyst and the influence of the structure of the diphosphine ligand. The reactions were carried out under ambient conditions and monitored by observing the decrease of the acyl carbonyl stretching in the IR spectra and by ^1H and ^{31}P NMR spectroscopy.

Only complexes of types **8** and **9**, which contain the trichlorostannate ligand, react with hydrogen, giving propanal as the only observed organic product. This supports our previous conclusions [9,23,24] on the need to form a Pt–$SnCl_3$ bond in order to have hydrogen activation. The reactivity order found (the time required for the complete reaction of 0.1 mmol of each species is shown in brackets) in **8b** (7 h) > **9** (12 h) $\gg$ **8a**. This order agrees well with that observed by Hayashi [1] in other catalytic reactions involving the same diphosphine ligands.

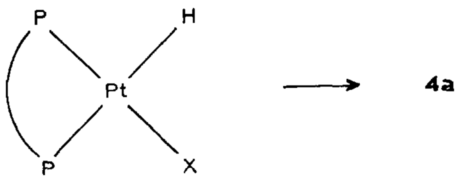


Scheme 3

The hydrogenolysis of complex **8a** affords a yellow solution that contains the dichloro complex **4a**, as the main component, and the low temperature ^1H NMR spectrum indicates that traces of the hydrido complex **3a** are also present. The reaction of complex **8a** with hydrogen can thus be formulated as:



(8a) **(3a)**



(3a)

The results suggest that the path depicted in Scheme 3 provides a reasonable model for the catalytic cycle when the ligand is DPPP.

The steps of Scheme 3 are closely related to those proposed for the catalytic hydroformylation carried out in the presence of the complex *trans*-$PtH(SnCl_3)(PPh_3)_2$ [9], the main differences arising from the poor stability of the *cis* hydrido species compared with that of the *trans* analogue, and the enhanced stability of the acyl-trichlorostannate complex **8a**.

For the diphosphine DPPB, when the monomeric acyl complex **8b** or its oligomeric counterpart **9** are treated with hydrogen, a deep red solution containing propanal is produced. The IR spectra of these solutions show a medium absorption at 2080 cm^{-1} that indicate the probable presence of Pt–H bonds. The relevant ^1H NMR spectra were recorded at $-80\,^\circ C$ but showed only weak and broad resonances in the hydrido region; and the ^{31}P NMR spectra were very complex, suggesting the presence of several species. It is relevant to note that the system *trans*-$PtHCl(PPh_3)_2/SnCl_2$ in acetone gives rise to at least six different hydrido species [14].

Concluding remarks

Although the conditions used of the present study are rather remote from the conditions normally used in the catalytic hydroformylation, the results provide useful information on the role played by $SnCl_2$ and on the influence of the nature of the diphosphine ligand.

Initially, $SnCl_2$ reacts with a Pt–Cl bond to give a Pt–$SnCl_3$ moiety. We have found that the presence of a trichlorostannate ligand directly bonded to platinum assists the CO insertion and confirmed that it is essential for hydrogen activation. In this connection the role of $SnCl_2$ seems not to be different from that observed for the corresponding PPh_3-based catalytic system. Furthermore, our results reveal the some previously unknown effects associated with the presence of an excess of $SnCl_2$, namely stabilization of the alkyl complexes of type **2** and inhibition of the carbonylation of complex **1b**. The observations could give a deeper insight into the still open question of the role played by an excess of $SnCl_2$ in the catalytic hydroformylation.

The most striking observations arising from the presence of the diphosphine ligands in the Pt complexes studied can be summarized as follows: (i) DPPB promotes the formation of oligomeric species; (ii) both DPPP and DPPB stabilize the trichlorostannate-acyl complexes of type **8** and **9**; and (iii), the acyl complex **8b** containing DPPB is more reactive towards H_2 than the corresponding DPPP complex **8a**.

In connection with point (i) it should be noted that its relevance to the catalysis is questionable, since the formation of the oligomeric acyl complexes is favoured in relatively concentrated solutions and in absence of $SnCl_2$. Our results indicate that for these species the preferred geometry is *trans*.

Points (ii) and (iii) may help to elucidate the role played by DPPB and related diphosphines in catalytic hydroformylation, in particular to enhancing the reaction rate relative to that for catalytic systems based on PPh_3 and other ligands with different frameworks. In connection with point (ii), we have previously shown that the reactivity towards H_2 of solutions containing acyl-trichlorostannate complexes is strongly dependent on the concentration of the species with Pt–$SnCl_3$ moiety like **8** and **9** [9,23]. As for point (iii), it is difficult to give a soundly-based explanation for the differing reactivities displayed by **8a** and **8b**. This feature represents, the most interesting outcome of the present work, and merits further investigation.

Experimental

NMR spectra were recorded with a Varian FT 80 A spectrometer, at 79.542 MHz for ^1H and 32.203 MHz for ^{31}P spectra. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer. GC-MS analyses were carried out on a Finnigan-MAT 700 ion trap detector mass spectrometer connected to a C. Erba Fractovap 4160 gas chromatograph. Molecular weight determinations, on dichloroethane solutions, were performed with a Knauer Vapor Pressure Osmometer.

Deuterated solvents were dried over molecular sieves. Anhydrous $SnCl_2$ was used as received from Fluka AG. The diphosphine ligands were purchased from Strem Chemicals and used without further purification.

Complexes *cis*-$PtCl(C_2H_5)$(DPPP) (**1a**) [10], *cis*-$PtCl(C_2H_5)$(DPPB) (**1b**) [10], *cis*-$[PtCl_2(DPPP)]_2$ (**4a**) [15] and *cis*-$[PtCl_2(DPPB)]_3$ (**4b**) [15] were prepared by published procedures.

Oxygen was excluded from all reactions by standard techniques.

cis-$Pt(SnCl_3)(C_2H_5)$(DPPP) (2a) and cis-$Pt(SnCl_3)(C_2H_5)$(DPPB) (2b)

A suspension of $SnCl_2$ (19 mg, 0.1 mmol) in CD_2Cl_2 (1 mmol) was cooled to −10 °C in a small Schlenk tube and saturated with ethylene. *Cis*-$PtCl(C_2H_5)$(DPPP) (**1a**) (67 mg, 0.1 mmol) was added under an ethylene atmosphere to this suspension, and the mixture was stirred until the $SnCl_2$ had completely dissolved. The clear pale yellow solution was quickly transferred to a NMR tube for the spectroscopic measurements.

A solution of *cis*-$PtCl(C_2H_5)$(DPPB) (**2b**) was prepared by a similar procedure.

cis-$[PtCl(SnCl_3)(DPPP)]$ (5a) and cis-$[PtCl(SnCl_3)(DPPB)]$ (5b)

To a suspension of *cis*-$[PtCl_2(DPPP)]_2$ (**4a**) (500 mg, 0.74 mmol) in CH_2Cl_2 (5 ml) was added anhydrous $SnCl_2$ (140 mg, 0.74 mmol). The mixture was stirred under nitrogen for 2 h at room temperature, and the pale yellow precipitate formed separated by filtration and dried in vacuo. Yield 560 mg, 87%. IR (Nujol mull): ν(Sn–Cl) at 322 and 297 cm^{-1}. ^{31}P NMR (CD_2Cl_2, −60 °C) δ(P) (*trans* to $SnCl_3$) 0.9 ppm, ^2J(P–P) 24, ^1J(P–Pt) 2804, ^2J(P–Sn) 3130 Hz (average value of ^2J(P–^{117}Sn) and ^2J(P–^{119}Sn); δ(P) (*trans* to Cl) −9.2 ppm, ^1J(P–Pt) 3248, ^2J(P–Sn) 226 Hz (average value of ^2J(P–^{117}Sn) and ^2J(P–^{119}Sn)). Anal. Found: C, 36.5; H, 3.0. $C_{27}H_{26}P_2Cl_4SnPt$ calc: C, 37.36; H, 3.02%.

Complex **5b** was prepared similarly. Yield 90%. IR (Nujol mull): ν(Sn–Cl) at 321 and 300 cm^{-1}. ^{31}P NMR (CD_2Cl_2, −60 °C) δ(P) (*trans* to $SnCl_3$) 20.0 ppm, ^2J(P–P) 19, ^1J(P–Pt) 2928, ^2J(P–Sn) 3119 Hz (average value of ^2J(P–^{117}Sn) and ^2J(P–^{119}Sn)); δ(P) (*trans* to Cl) 7.2 ppm, ^1J(P–Pt) 3372, ^2J(P–Sn) 212 Hz (average value of ^2J(P–^{117}Sn) and ^2J(P–^{119}Sn)). Anal. Found: C, 37.8; H, 3.1. $C_{28}H_{28}P_2Cl_4SnPt$ calc: C, 38.12; H, 3.20%.

Molecular weight determinations indicate that the parent complexes **4a** and **4b** are oligomeric species [15], the molecular weights of complexes **5a** and **5b** were not determined because in solutions of such complexes there are usually equilibria involving the Pt–$SnCl_3$ moiety [12].

*cis-PtCl(COC_2H_5)(DPPP) (**6a**) and trans-[PtCl(COC_2H_5)(DPPB)]$_3$ (**7**)*

A solution of complex **1a** (670 mg, 1 mmol) in CH_2Cl_2 (20 ml) was degassed under vacuum and saturated with CO. After 24 h the yellow solution obtained was diluted with diethyl ether (60 ml) under CO to give **6a** as white powder. This was filtered off, washed with n-hexane, and dried under vacuum. Yield: 520 mg, 74%. Molecular weight found 684, calc 700. Anal. Found: C, 51.6; H, 4.5. $C_{30}H_{31}OP_2ClPt$ calc: C, 51.47; H, 4.46%.

A similar procedure gave complex **7**. Yield 70%. Molecular weight: found 1980, calc for the monomeric species 714. Anal. Found: C, 52.0; H, 4.6. $C_{31}H_{33}OP_2ClPt$ calc: C, 52.14; H, 4.65%.

*cis-PtCl(COC_2H_5)(DPPB) (**6b**)*

A solution of complex **1b** (685 mg, 1 mmol) was degassed, saturated with ethylene and cooled to −10 °C. Anhydrous $SnCl_2$ (38 mg, 0.2 mmol) was added, and the suspension was stirred until the $SnCl_2$ had completely dissolved. This solution was stirred for 6 h under CO, then treated with a small amount of charcoal, filtered, and concentrated. Addition of CH_3OH precipitated an off-white compound, which was filtered off, washed with diethyl ether and n-hexane, and dried under vacuum. Yield 430 mg, 60%. Molecular weight: found 705, calc 714. Anal. Found: C, 51.9; H, 4.5. $C_{31}H_{33}OP_2ClPt$ calc: C, 52.14; H, 4.65%.

*trans-Pt($SnCl_3$)(COC_2H_5)(DPPB) (**9**)*

A solution of the oligomeric complex **7** (213 mg) in CH_2Cl_2 (15 ml) was degassed and kept under nitrogen. An excess of anhydrous $SnCl_2$ (100 mg) was added, and this mixture stirred for 2 h under nitrogen. The residual tin salt was filtered off, and the yellow-orange solution diluted with n-hexane to give an orange precipitate, which was filtered off and dried under vacuum. Yield 180 mg, 66%. IR (Nujol mull) ν(CO) at 1660 and ν(Sn–Cl) at 322 and 300 cm^{-1}. Anal: Found: C, 40.3, H, 3.6. $C_{31}H_{33}OP_2Cl_3SnPt$ calc: C, 40.97; H, 3.66%.

*cis-Pt($SnCl_3$)(COC_2H_5)(DPPP) (**8a**) and cis-Pt($SnCl_3$)(COC_2H_5)(DPPB) (**8b**)*

A suspension of anhydrous $SnCl_2$ (190 mg, 1 mmol) in 20 ml of CH_2Cl_2 was degassed, purged with ethylene, and cooled to −10 °C. Complex **1a** (685 mg, 1 mmol) was added and the mixture was stirred at −10 °C until the $SnCl_2$ had completely dissolved. The clear pale yellow solution was saturated with CO and the mixture allowed to warm to room temperature during 2 h. After the usual work up, complex **6a** was obtained: yield 700 mg, 80%. IR (Nujol mull) ν(CO) at 1640 and ν(Sn–Cl) at 339 and 319 cm^{-1}. Anal: Found: C, 39.8; H, 3.4. $C_{30}H_{31}OP_2Cl_3SnPt$ calc: C, 40.50; H, 3.51%.

A similar procedure gave complex **8b**: yield 75%. IR (Nujol mull) ν(CO) at 1642 and ν(Sn–Cl) at 337 and 315 cm^{-1}. Anal. Found: C, 39.9; H, 3.4. $C_{31}H_{33}OP_2Cl_3SnPt$ calc: C, 40.97; H, 3.66%.

*Reactions of complexes **6a**, **6b**, **7**, **8a**, **8b** and **9** with H_2*

A solution, thermostatically controlled at 25 °C, of the relevant complex (0.1 mmol) in 6 ml of dichloromethane was kept under hydrogen atmosphere. The progress of the reaction was monitored by examining the carbonyl absorption (2500–1500 cm^{-1}) in the IR spectrum of samples removed at intervals. When the reaction was complete, the solvent was evaporated off under reduced pressure and the residue dissolved in CD_2Cl_2 for ^1H and ^{31}P NMR examination.

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