METALS IN ORGANIC SYNTHESES

XIV *. NMR, IR, AND REACTIVITY STUDIES ON THE OLEFIN HYDROFORMYLATION CATALYZED BY Pt–Sn COMPLEXES

ALBERTO SCRIVANTI*, ADRIANO BERTON

Centro di Chimica Metallorganica del CNR, via Marzolo 9, Padova (Italy)

LUIGI TONIOLO,

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, University of Padova (Italy)

and CARLO BOTTEGHI

Dipartimento di Chimica, University of Venezia (Italy)

Summary

Among the several hydrides formed when *trans*-[PtHClL$_2$] (L = PPh$_3$) reacts with SnCl$_2$, only *trans*-[PtH(SnCl$_3$)L$_2$] rapidly inserts ethylene, at $-80°$C, to yield *cis*-[PtEt(SnCl$_3$)L$_2$]. At $-10°$C, *cis*-[PtEt(SnCl$_3$)L$_2$] irreversibly rearranges to the *trans*-isomer, thus indicating that the *cis*-isomer is the kinetically controlled species, and that the *trans*-isomer is thermodynamically more stable.

At $-50°$C, a mixture of *trans*-[PtHClL$_2$] and *trans*-[PtH(SnCl$_3$)L$_2$] reacts with ethylene to give *cis*-[PtEtClL$_2$] and *cis*-[PtEt(SnCl$_3$)L$_2$] and this has been attributed to the catalytic activity of SnCl$_2$ which dissociates from *cis*-[PtEt(SnCl$_3$)L$_2$] at this temperature.

Carbon monoxide promotes the *cis–trans* isomerization of *cis*-[PtEt(SnCl$_3$)L$_2$], which occurs rapidly even at $-80°$C. This rearrangement is followed by a slower reaction leading to the cationic complex *trans*-[PtEt(CO)L$_2$]$^+$ SnCl$_3^-$. At $-80°$C, this complex does not react further, but when it is kept at room temperature ethyl migration to coordinated carbon monoxide takes place, to give several Pt-acyl complexes, i.e. *trans*-[PtCl(COEt)L$_2$], *trans*-[Pt(SnCl$_3$)(COEt)L$_2$], *trans*-[PtCl-(COEt)L$_2$ · SnCl$_2$], and *trans*-[Pt(COEt)(CO)L$_2$]$^+$ SnCl$_3^-$. This mixture of Pt-acyl complexes reacts with molecular hydrogen to yield n-propanal and the same complex mixture of platinum hydrides as is obtained by treating *trans*-[PtHClL$_2$] with SnCl$_2$.

Trans-[PtH(SnCl$_3$)L$_2$] reacts with carbon monoxide to yield the five-coordinate complex [PtH(SnCl$_3$)(CO)$_2$L$_2$], which has been characterized by NMR and IR spectroscopy; ethylene does not insert into the Pt–H bond of this complex at low temperature. At room temperature, *trans*-[PtH(SnCl$_3$)L$_2$] reacts with a mixture of CO and ethylene to yield the same mixture of Pt-acyl species as is obtained when *trans*-[PtEt(SnCl$_3$)L$_2$] is allowed to react with CO.

The role of a Pt–Sn bond in these reactions is discussed in relation to the catalytic cycle for the hydroformylation of olefins.

Introduction

The hydroformylation of olefins catalyzed by platinum complexes in combination with Group IVA metal halides is of great current interest, for two main reasons, viz. (i) these systems are highly active and selective, their catalytic activity being comparable to that of the well-known rhodium systems which are industrially used [2–7]; and (ii) remarkable results have been achieved in asymmetric hydroformylation [8,9].

Typical catalyst precursors are: *trans*-[PtHCl(PR$_3$)$_2$] [2], *cis*-[PtCl$_2$(PR$_3$)$_2$] [4], *cis*-[PtCl$_2$(CO)(PR$_3$)] [6] (R = alkyl or aryl), [PtCl$_2$(P–P)] (P–P = diphosphine) [7] in combination with SnCl$_2$, usually in a Pt/Sn ratio between 1/1 and 1/10. The catalytic activity is strongly solvent dependent; for example the first two of the above-mentioned precursors are highly active in solvents of low or moderately low polarity, such as benzene or ketones, but much less active in coordinating solvents, such as acetonitrile, or in highly polar solvents, such as alkanols, [2–4].

From hydroformylations involving the catalyst precursor *cis*-[PtCl$_2$L$_2$]/SnCl$_2$ (L = PPh$_3$) and ethanol as solvent, acyl complexes of type *trans*-[PtCl(COR)L$_2$] (R = n-propyl, n-hexyl, 2-phenylethyl) have been isolated [10–13]. Furthermore, these acyl complexes show a higher catalytic activity in a ketone than in ethanol, and moreover the catalytic activity is observed only in the presence of SnCl$_2$ even though the acyl complexes are formed in the absence of SnCl$_2$. These facts suggest that a Pt–Sn bond plays a fundamental role in the last step of the catalytic cycle, i.e. the hydrogenolysis of the Pt-acyl intermediate [10–13].

A ^{31}P NMR study on the reaction of *trans*-[PtCl(CO-n-hexyl)L$_2$] with SnCl$_2$ has been described recently [14]. In acetone or dichloromethane, two species (in equilibrium with the starting platinum-acyl complex) are observed: one is *trans*-[Pt(SnCl$_3$)(CO-n-hexyl)L$_2$] and the other is a complex containing platinum and tin but not containing a Pt–Sn bond.

Under ambient conditions, upon treatment with molecular hydrogen, the above system yields n-heptanal and a complex mixture of platinum hydrides; when ethanol is added to the system, the formation of *trans*-[Pt(SnCl$_3$)(CO-n-hexyl)L$_2$] is prevented, and there is no reaction with hydrogen. These results give further support to the hypothesis that a Pt–Sn bond plays a key role in the last step of the catalysis [14].

Since the acyl complex is probably formed through insertion of the olefin into a Pt–H bond, followed by insertion of carbon monoxide into the resulting platinum-alkyl intermediate, we decided to undertake an NMR and IR study of the reaction of hydrido complexes with an olefin and with carbon monoxide. *Trans*-[PtHClL$_2$]

was chosen as starting hydride because upon reaction with $SnCl_2$ it gives the same complex mixture of hydrides as is formed when the system trans-[PtCl(CO-n-hexyl)L_2]/$SnCl_2$ reacts with molecular hydrogen [14]. Ethylene was used as the model olefin.

We report here the results of our studies on:

(i) the reaction of ethylene with the hydrides formed by treating trans-[PtHClL_2] with $SnCl_2$;

(ii) the reactions with CO of the σ-alkyl complexes cis- and trans-[PtEt($SnCl_3$)L_2], obtained in step (i);

(iii) the reactions of the resulting acyl complexes with molecular hydrogen;

(iv) the reaction of trans-[PtH($SnCl_3$)L_2] with carbon monoxide and with a mixture of carbon monoxide and ethylene.

The involvement of the above steps in the catalytic cycle of the hydroformylation of olefins, and the role of the co-catalyst $SnCl_2$ are also discussed.

Results and discussion

(a) Reaction of trans-[PtHClL]$_2$/$SnCl_2$ with ethylene in CD_2Cl_2

It is well known that in dichloromethane complex trans-[PtHClL_2] (1) (L = PPh_3) reacts with $SnCl_2$ to yield trans-[PtH($SnCl_3$)L_2] (2) or at room or at low temperature [17]:

$$1 + SnCl_2 \rightarrow 2 \tag{1}$$

Complex 2, prepared in CD_2Cl_2 by mixing complex 1 with $SnCl_2$ in the ratio 1/1, reacts with ethylene at $-80°C$, as shown in eq. 2, the reaction being complete within a few minutes at this temperature:

$$2 + C_2H_4 \xrightarrow{-80°C} cis\text{-}\left[PtEt(SnCl_3)L_2\right] \tag{2}$$
$$(3)$$
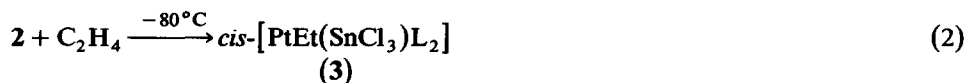
Reaction 2 has been briefly reported by other authors [16], but we have made more detailed studies. The progress of the reaction can be monitored by ^{31}P NMR spectroscopy (see Fig. 1).

Figure 1A shows the ^{31}P NMR spectrum of the starting complex 2 (the platinum satellites are omitted for clarity). Figure 1B shows the spectrum recorded ca. 50 s after the addition of ethylene. The chemical shift (δ 27.2 ppm) is significantly different from that of complex 2, and the signal is rather broad, but its ^1J(Pt–P) 2666 Hz is the same as that for complex 2; it can thus be concluded that the spectrum in Fig. 1B is due to a rapid equilibrium involving complex 2 and a five-coordinate species arising from the interaction of ethylene with the starting complex. The spectrum in Fig. 16 was recorded ca. 3 min after the addition of ethylene: together with the broad resonance of Fig. 1B there is a doublet of doublets, indicating that a platinum complex of cis geometry is forming. After ca. 10 min only the latter pattern is present (Fig. 1D), and no further change occurs when the solution is kept at this temperature. The spectral features closely match those of an authentic sample of cis-[PtEt($SnCl_3$)L_2] (see Experimental) confirming the assignment of the product as that shown in eq. 2.

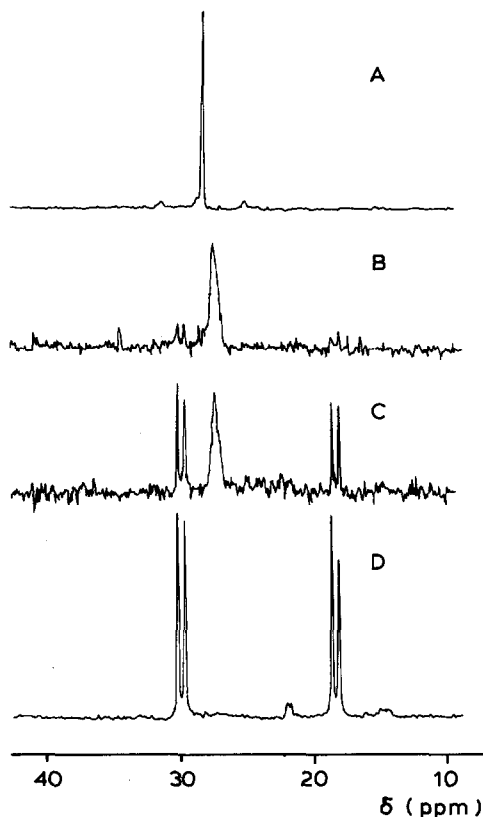When the temperature is increased, the spectrum of complex 3 slightly broadens

Fig. 1. ^{31}P NMR spectra during the reaction of complex 2 with ethylene: (A) ^{31}P NMR spectrum of complex 2 in CD_2Cl_2 at $-80\,^{\circ}C$ (^{195}Pt satellites omitted for clarity); (B) Spectrum recorded within 50 s after ethylene addition; (C) Spectrum recorded after 3 min; (D) Final spectrum of complex 3, the up-field resonance is due to the phosphorus atom *trans* to the ethyl group.

without changing substantially up to ca. $-20\,^{\circ}C$. At $-10\,^{\circ}C$ complete *cis* to *trans* isomerization takes place to give *trans*-$[PtEt(SnCl_3)L_2]$ (4) (eq. 3).

$$3 \xrightarrow{\;-10\,^{\circ}C\;} trans\text{-}\left[PtEt(SnCl_3)L_2\right] \tag{3}$$
$$\textbf{(4)}$$

This isomerization is not reversible, indicating that complex 3 is the kinetically controlled product of reaction 2 and that complex 4 is the thermodynamically stable species.

In the absence of $SnCl_2$ complex 1 does not yield the insertion reaction even at room conditions [18]. Thus when ethylene is added at $-80\,^{\circ}C$ to a mixture of complexes 1 and 2 (prepared by mixing complex 1 with a deficiency of $SnCl_2$ (for example with a Pt/Sn ratio of 3/1)) only complex 2 undergoes insertion of the olefin to yield complex 3. When the same experiment is carried out at $-50\,^{\circ}C$, complex 1 also reacts to give *cis*-$[PtEtClL_2]$ (5) (eq. 4):

$$1 + 2 \xrightarrow[\;C_2H_4\;]{\;-50\,^{\circ}C\;} 3 + 5 \tag{4}$$

Moreover, at $-50\,°C$ the $^2J(P-Sn)$ couplings are no longer observable for complex **3**, indicating that the equilibrium shown in eq. 5, exists; it must however, lie far over to the left since the ^{31}P NMR spectrum is the same as that at $-80\,°C$ except for the disappearance of the P–Sn couplings.

$$3 \underset{}{\overset{-50\,°C}{\rightleftharpoons}} 5 + SnCl_2 \tag{5}$$

The formation of complex **5** can be rationalized by assuming that dissociated $SnCl_2$ reacts with complex **1** to yield complex **2**, which in turn reacts with ethylene to give complex **3** (reactions 1 and 2):

$$SnCl_2 + 1 \rightarrow 2 \tag{1}$$

$$2 + C_2H_4 \rightarrow 3 \tag{2}$$

Thus free $SnCl_2$ acts as a catalyst for the insertion of ethylene into complex **1** even at this temperature ($-50\,°C$).

Since reactions 1 and 2 are rapid and quantitative even at $-80\,°C$, the results suggest that at this temperature ethylene insertion into complex **2** does not involve appreciable concomitant dissociation of $SnCl_2$.

In Scheme 1 are presented two possible pathways for the insertion reaction.

The first step involves coordination of the olefin to form a five-coordinate intermediate, as suggested by the spectral change observed upon addition of ethylene to the starting complex **2**. The ability of the $SnCl_3^-$ ligand to stabilize five-coordinate platinum(II) complexes is well-known [19]; moreover olefin adducts of this type have been characterized, although not with ethylene [20]. This step is common to both reaction pathways. Pathway (A), which was also postulated by Bogdashkina et al. [16], involves insertion of ethylene into the Pt–H bond of a five-coordinate intermediate, without dissociation of any ligands. Indeed, dissociation of a ligand (PPh_3 and $SnCl_3^-$) seems to be unlikely for the following reasons: (i) the broad resonance of Fig. 1B and 1C shows that the Pt–P coupling is retained; (ii) dissociation of $SnCl_3^-$ also seems unlikely since in the case of the insertion of ethylene into the closely related system $trans$-$[PtHCl(PEt_3)_2]/SnCl_2$ kinetic evidence had ruled out this possibility [21].

Pathway (B) involves a dissociative mechanism similar to that suggested by Ros et al. for the insertion of an olefin into the Pt–H bond of hydridocyanoalkyl complexes of platinum(II) [22]. At present we lack the kinetic information necessary for deeper insight into the mechanism of reaction 2, and so the participation of a spectroscopically non-detectable (but kinetically significant) four-coordinate species cannot be ruled out.

(b) Reaction of trans-[PtHClL$_2$] / SnCl$_2$ with ethylene in acetone

In acetone complex **1** reacts with $SnCl_2$ to give a mixture of several hydrides, as indicated by the appearance of a complex pattern in the low temperature ^1H and ^{31}P NMR spectra. Bogdashkina and co-workers have observed the presence of complex **1**, the cationic complex $trans$-$[PtHL_3]^+$ (**6**) and the complex cis-$[PtH(SnCl_3)L_2]$ (**7**); the presence of the anionic $trans$-$[PtH(SnCl_3)_2L]^-$ (**8**) and of another hydride which does not contain phosphine ligands was also tentatively proposed; the possibility of the presence of the hydrido complex **2** has not previously been mentioned [16].

374
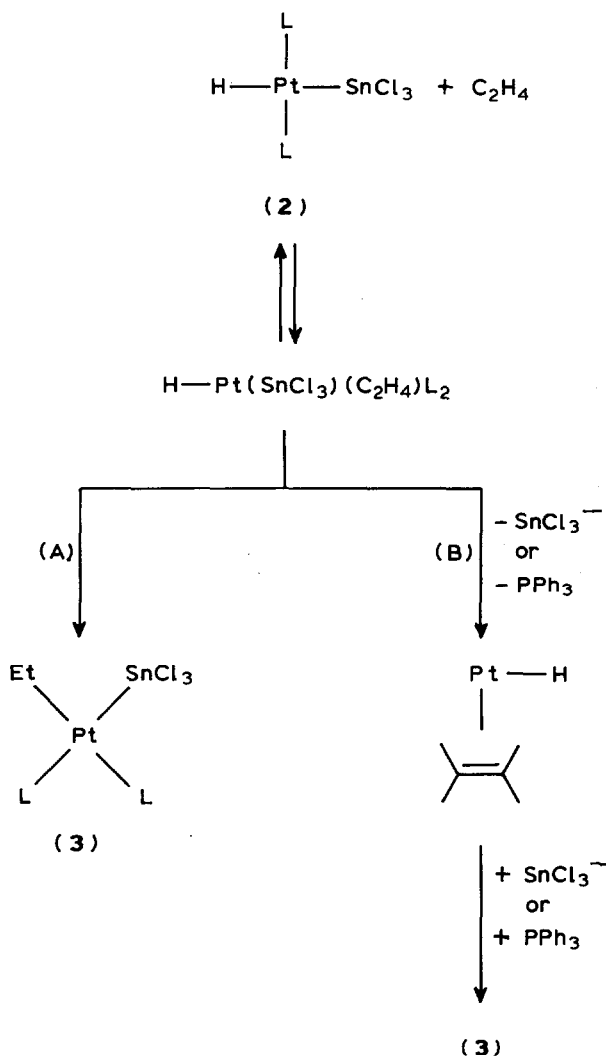
SCHEME 1

We have found, however, that when a stoichiometric amount of $SnCl_2$ is used, the ^1H and ^{31}P NMR spectra also show the presence of the resonance characteristic of complex **2**, whereas, when an excess of $SnCl_2$ is used (Pt/Sn = 1/3) a unique broad resonance centered at δ 27.5 ppm for ^{31}P is observed instead of the resonances due to complexes **1** (δ 27.2 ppm) and **2** (δ 28.2 ppm) even at $-90°C$. This indicates that the two species are involved in a fast exchange (the resonances due to the other hydrides remaining unchanged).

When the system complex $1/SnCl_2$ (Pt/Sn = 1/1) is treated with ethylene at $-80°C$, complex **2** reacts rapidly to yield complex **3**, while complex **7** reacts much more slowly, to yield the same product; the other hydrides do not react at all under these conditions. These results confirm the findings of Bogdashkina et al. [16], who studied the reaction of ethylene with complex **2** and complex **7**, separately.

When $SnCl_2$ is present in excess, the broad resonance arising from the fast equilibrium between complex **1** and complex **2** disappears upon ethylene addition, giving way to the AB spin system coming from complex **3**. Thus, under such conditions complex **1** also apparently reacts, probably as a result of its re-equilibration with complex **2**.

At room temperature all the complexes present in solution are in rapid equilibrium, and upon ethylene addition the *trans* complex **4** is formed quantitatively.

*(c) Reaction of cis-[PtEt(SnCl₃)L₂] with carbon monoxide*

When complex **3** is treated with carbon monoxide at atmospheric pressure in CD_2Cl_2 at $-80°C$, *cis-trans* isomerization takes place within a few seconds:

$$3 \xrightarrow[-80°C, \text{ fast}]{CO} 4 \qquad (6)$$

Thus carbon monoxide catalyzes this rearrangement, which probably occurs via an associative-dissociative mechanism through a five-coordinate carbonyl intermediate.

It is worth noting that under these conditions ethylene does not promote the same isomerization (compare with reactions 2 and 3).

Reaction 6 is followed by a slower one that leads to a cationic carbonyl ethyl complex and takes a few minutes:

$$4 \xrightarrow[-80°C]{CO} trans\text{-}[PtEt(CO)L_2]^+ SnCl_3^- \qquad (7)$$
$$(9)$$
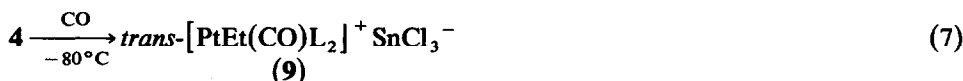
The formation of complex **9** has been confirmed by comparing its NMR spectral features with those of an authentic sample of *trans*-[PtEt(CO)L₂]⁺ BF₄⁻ (see Table 1 and Experimental).

At low temperature this complex does not react further; when the solution of reaction 7 is allowed to warm to room temperature, ethyl migration to coordinated carbon monoxide takes place, as indicated by the growth of a strong absorption at 1665 cm⁻¹ in the IR spectrum:

$$9 \xrightarrow{\text{r.t.}} \text{Pt-acyl complexes} \qquad (8)$$

TABLE 1

³¹P NMR DATA [a]

	δ(P)	¹J(Pt–P)	²J(P–¹¹⁹Sn,P–¹¹⁷Sn)	²J(P–P)
cis-[PtEt(SnCl₃)L₂] (3)	{ 29.8 P *trans* to Sn	3990	3784, 3616	17
	{ 17.8 P *trans* to Et	1855	256, 244	
trans-[PtEt(SnCl₃)L₂] (4)	25.7	3014	247, 236	
trans-[PtEt(CO)L₂]⁺ BF₄⁻ (9)	20.0	2817		
trans-[PtCl(COEt)L₂] (10)	20.7	3407		
trans-[Pt(SnCl₃)(COEt)L₂] (11)	15.7	3186	286, 273	
trans-[PtCl(COEt·SnCl₂)L₂] (12)	17.1	2925		
trans-[Pt(COEt)(CO)L₂]⁺ BF₄⁻ (13)	13.2	3070		
trans-[PtH(CO)L₂]⁺ BF₄⁻	23.5	2550		
[PtH(SnCl₃)(CO)L₂] [b] (15)	13.5	2865		

[a] Chemical shifts are in ppm (positive values downfield referred to 85% H_3PO_4 at room temperature). Coupling constants are in Hz (± 3). Spectra registered at 193 K in CD_2Cl_2. [b] Spectrum registered at 193 K.

The NMR spectra of this solution are dynamic at room temperature, indicating that there are some equilibria present. However the ^{31}P NMR spectrum of this solution at $-80°C$ is superimposable on that of a solution prepared by treating an authentic sample of trans-[PtCl(COEt)L$_2$] (10) (see Experimental) with an equivalent amount of SnCl$_2$. This confirms that formal CO insertion into the Pt–C σ-bond has occurred.

At $-80°C$ the ^{31}P NMR spectrum shows two independent patterns (A and B) of relative intensity 1/1. Pattern A consists of a sharp singlet centered at 15.7 ppm and flanked by ^{195}Pt and ^{119,117}Sn satellites. The values of these couplings (^1J(Pt–P) 3186, ^2J(P–^{119,117}Sn) 286, 273 Hz) unambiguously indicate the presence of a trichlorostannate ligand bonded to platinum in cis positions relative to two equivalent and mutually trans triphenylphosphine ligands [23,24]; thus this pattern is attributed to the complex trans-[Pt(SnCl$_3$)(COEt)L$_2$] (11). Pattern B consists of a relatively broad singlet ($\nu_{1/2}$ 14 Hz) at 17.1 ppm flanked by ^{195}Pt satellites (^1J(Pt–P) 2925 Hz); no P–Sn couplings are detectable.

The overall picture closely reproduces that observed for the strictly analogous system trans-[PtCl(CO-n-hexyl)L$_2$]/SnCl$_2$ [14]. In that case a pattern of type B is assumed to arise from a labile adduct, involving some interaction between the starting acyl complex and SnCl$_2$, which does not contain the trichlorostannate moiety. Most recent work in our laboratory in cooperation with Prof. Pregosin has shown that the behaviour described can be observed for many systems of the type trans-[PtCl(COR)L$_2$]/SnCl$_2$ (L = PPh$_3$, R = alkyl, aryl). Extensive multinuclear NMR studies suggest that in the labile adduct the SnCl$_2$ behaves as a Lewis acid towards the oxygen atom of the acyl moiety to form species 12:
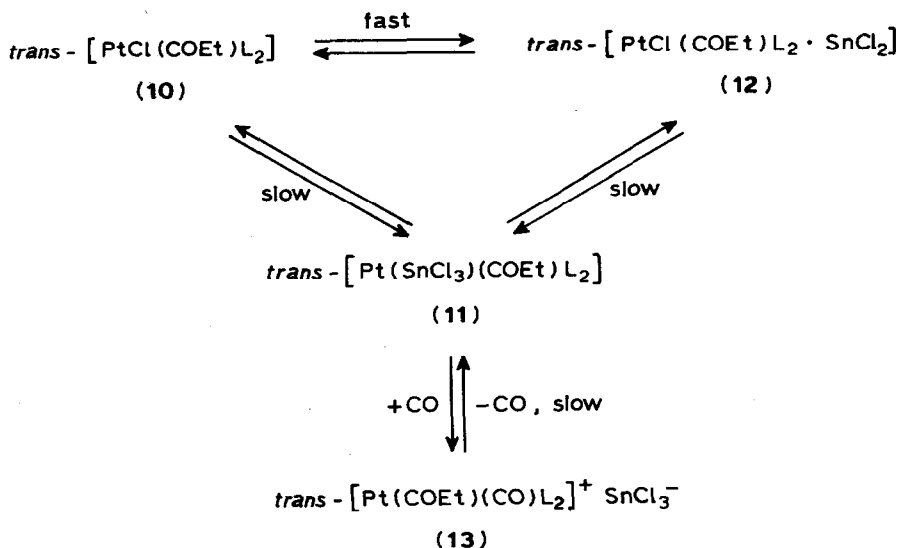

(12)
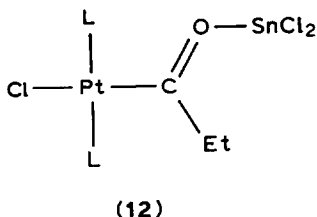
Details will be presented in a forthcoming publication [25].

In the presence of a large excess of CO an additional species is formed as indicated by the presence of a new band in the IR spectrum at 2109 cm^{-1}. This signal, and the corresponding one in the low temperature ^{31}P NMR spectrum, arise from the cationic complex trans-[Pt(COEt)(CO)L$_2$]$^+$ SnCl$_3$$^-$ (13) as its NMR and IR spectral features are identical to those of trans-[Pt(COEt)(CO)L$_2$]$^+$BF$_4$$^-$ (see Experimental). The formation of complex 13 is reversible since this complex disappears, to give complexes 10–12, when a nitrogen stream is passed through the solution, and it reappears when carbon monoxide is readmitted.

Scheme 2 summarizes the equilibria present in solution.

Reactions 7 and 8 also occur in acetone, the main difference being that in this solvent carbon monoxide insertion is faster.

The results here presented closely parallel those obtained by Clark for carbon monoxide insertion into the Pt–C σ-bond of trans-[PtClPhL$_2$] in the presence of SnCl$_2$ [26].

trans - $[PtCl(COEt)L_2]$ $\underset{\longleftarrow}{\overset{fast}{\longrightarrow}}$ trans - $[PtCl(COEt)L_2 \cdot SnCl_2]$

(10)   (12)

slow   slow

trans - $[Pt(SnCl_3)(COEt)L_2]$

(11)

$+CO$ $\updownarrow$ $-CO$, slow

trans - $[Pt(COEt)(CO)L_2]^+ SnCl_3^-$

(13)

SCHEME 2

(d) Reaction of trans-[PtCl(COEt)L$_2$] / SnCl$_2$ with molecular hydrogen

In CD_2Cl_2 or acetone-d_6 the above system reacts with molecular hydrogen to give propanal and the same mixture of hydrides as is produced when complex **1** is treated with $SnCl_2$. This hydrogenolysis does not occur in the presence of ethanol, and that the formation of complex **11** is prevented.

These results closely parallel those obtained with the system *trans*-[PtCl(CO-n-hexyl)L$_2$]/SnCl$_2$, and are in line with the suggestion that a Pt–Sn bond plays a key role in the last step of the catalysis [14].

(e) Reaction of trans-[PtHClL$_2$] / SnCl$_2$ with carbon monoxide

Hsu and Orchin have reported that treatment of complex **2** with carbon monoxide (100 atm) and molecular hydrogen (100 atm) in benzene at 100°C affords a greenish yellow complex whose elemental analysis is consistent with the formulation "PtH(SnCl$_3$)(CO)L$_2$" [2].

Under similar conditions, but employing the system *cis*-[PtCl$_2$L$_2$]/SnCl$_2$ as catalyst precursor in ethanol for 1-hexene hydroformylation, we have isolated an off-white complex having the same composition, but giving different ν(PtH), ν(CO) and ν(SnCl) bands in the IR spectrum [12]; on the basis of IR data only, it is not possible to decide unambiguously whether the complex is a five-coordinate species or the four-coordinate complex [PtH(CO)L$_2$]$^+$SnCl$_3^-$.

Thus we have examined the spectroscopic behaviour of complex **2** in the presence of carbon monoxide. At room temperature, the ^{31}P NMR spectrum of complex **2** in CD_2Cl_2 solution shows a broad resonance ($\nu_{1/2}$ 10 Hz) centered at 27.6 ppm with ^1J(Pt–P) 2688 Hz. Upon addition of a small excess of carbon monoxide, this resonance shifts upfield considerably (δ 15.5 ppm, ^1J(Pt–P) 2850 Hz, $\nu_{1/2}$ 40 Hz), indicating the formation of a new species, probably involved in some equilibrium. At -70°C, the resonance is sharper, and shifted to higher fields (δ(P) 13.5 ppm, ^1J(Pt–P) 2865 Hz), yet no P–Sn coupling is detectable. Further lowering of the

temperature causes only a broadening of the signals due to the precipitation of yellow-orange microcrystals.

In order to better understand the nature of the species formed we studied the ^{1}H NMR behaviour of this solution in the presence of ^{13}C-enriched carbon monoxide. At room temperature, the ^{1}H NMR spectrum shows a broad resonance at -9.58 ppm with ^1J(Pt–H) 715 Hz. When the temperature is lowered this resonance sharpens, and at $-70\,^{\circ}$C it shows the coupling between the hydride and the ^{13}C enriched carbon monoxide (δ(H) -9.80 ppm, ^1J(Pt–H) 627, ^2J(H–C) 59 Hz), thus indicating that at low temperature carbon monoxide is in the coordination sphere of platinum. However, this spectrum is quite unusual, since at low temperature the resonance observed shows no H–P coupling. Neither do the ^{31}P NMR spectra of this solution at low and room temperature, show either ^2J(P–C) or ^2J(R–Sn) couplings. (The low solubility of the species prevented us from recording ^{119}Sn NMR spectra.)

The IR spectrum of these solutions closely matches that observed by Orchin for the solid state, showing an intense absorption at 2176 cm^{-1} for ν(Pt–H) and another at 2060 for ν(CO); moreover, a low intensity band is present at 2082 cm^{-1}, and this corresponds exactly to the ν(CO) stretching absorption observed in the same solvent for the cationic complex *trans*-[PtH(CO)L$_2$]$^+$ BF$_4^-$ (**14**) [27].

Thus the IR data complete the information obtained by NMR spectroscopy, where no signals (δ(P) 23.5 ppm, ^1J(Pt–P) 2550 Hz) associated with the cationic complex **14** are observed, probably owing to its low concentration.

It is noteworthy that when a carbon monoxide stream is passed through an acetone solution of complex **1** and SnCl$_2$ (Pt/Sn = 1/1) yellow-orange micro-crystals immediately separate. The IR spectrum (Nujol mull) of the product shows ν(Pt–H) at 2177 cm^{-1} and ν(CO) at 2066 cm^{-1}; these values match the high intensity ones observed in solution; ν(Sn–Cl) appears at 311 and 303 cm^{-1}, indicating a SnCl$_3^-$ moiety bonded to platinum [28].

The results strongly suggest that the most abundant species present in solution is a five-coordinate complex (the tendency of the SnCl$_3^-$ ligand to stabilize five-coordination in platinum(II) complexes is well known [19]), and that this complex is involved in the equilibria shown in Scheme 3:

These equilibria largely favour the five-coordinate complex **15**, even at room temperature (the absence of the ^{1}H–^{13}C couplings in the ^{1}H NMR spectrum of complex **15** at this temperature indicates that fast CO exchange occurs in solution).
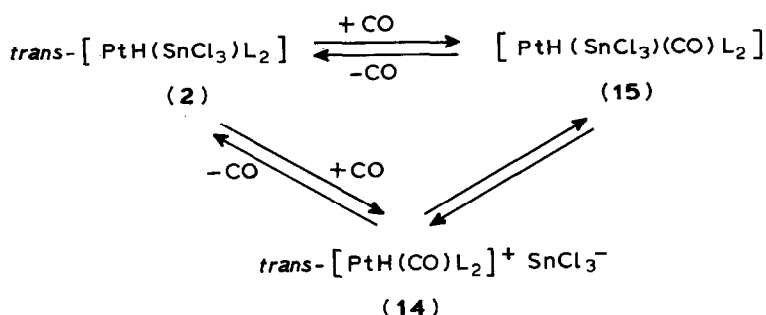
SCHEME 3

The absence of H–P, P–C and P–Sn couplings in the low temperature NMR spectra of the five-coordinate complex **15** is probably due to possible dynamic behaviour of this species, stereochemical non-rigidity being a common feature of five-coordinate structures. Usually the barriers to intramolecular rearrangements in such cases are low, and rigid structures are obtained only at very low temperatures [29], which we cannot reach owing to the low solubility of complex **15**.

It should be mentioned that the IR spectrum of a CH_2Cl_2 solution of the yellow-orange crystals isolated from acetone shows the presence of both complexes **14** and **15**. This indicates that in this solvent complex **15** re-equilibrates with complex **14**.

It is noteworthy that all the hydrides present in an acetone solution of complex **1** and $SnCl_2$ (see section (b)) react with carbon monoxide to yield the five-coordinate complex **15**.

(f) Reaction of trans-[PtHClL$_2$] / SnCl$_2$ with a gas mixture of carbon monoxide and ethylene

When ethylene is introduced into a CD_2Cl_2 solution containing complex **15** at −60°C, no reaction occurs. This is in line with a five-coordinate formulation of this complex. On the other hand, when a 1:1 mixture of carbon monoxide and ethylene is passed through a CD_2Cl_2 solution of complex **2**, at −60°C, the ^{31}P NMR spectrum recorded immediately after gas addition shows an intense and broad band centered at 14 ppm. The pattern associated with complex **3** is also present, but is of much lower intensity. After ca. 10 min only the resonances from the complexes **15** and **4** are present; later on formation of complex **9** is observed. Thus it appears that carbon monoxide competes with ethylene in coordinating to the metal center. This may possibly be related to the fact that the rate of hydroformylation catalyzed by the precursor *cis*-[PtCl$_2$L$_2$]/SnCl$_2$ is inversely proportional to $\sqrt{(P(CO))}$. (However, it should be noted that the composition of the species present in solution under forcing "oxo" conditions may be quite different from that under our conditions).

Since at room temperature complex **15** rapidly exchanges with carbon monoxide in solution, we have treated complex **2** with a 1:1 mixture of ethylene and carbon monoxide under ambient conditions and monitored the reaction by IR spectroscopy. A 5×10^{-2} M of complex **2** in CH_2Cl_2 was treated with the gas mixture, and after·5 min the absorptions due to the five-coordinate complex **15**, and the cationic complex **9** appeared. After 15 min, the cationic complex **9** is the most abundant species present in the solution, and some acyl complexes also appear. After 2 h, only a mixture of acyl complexes, which is the same as that obtained by treating complex **4** with carbon monoxide, is present. Thus it appears that under ambient conditions the equilibria shown in Scheme 3 provide a kinetically significant concentration of complex **2** which undergoes the ethylene insertion.

Conclusions

The reactions we have studied are closely related to the catalytic cycle of the hydroformylation of olefins. The results allow a better understanding of the role played by the tin co-catalyst.

Thus $SnCl_2$ can act in several ways:

(i) it may behave as a Lewis acid, as it does in the formation of complex **12**;

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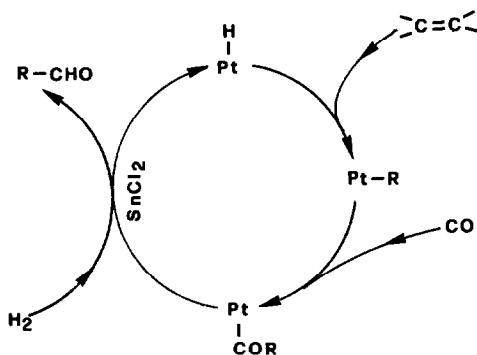
SCHEME 4

(ii) it may be the source of $SnCl_3^-$, which may act as a counter ion, as observed in the formation of the cationic complex **9** at low temperature;

(iii) it may act as a ligand directly bonded to platinum, a fact which is of crucial importance in the catalysis.

The well-known ability of the $SnCl_3^-$ ligand to promote the formation of five-coordinate species of platinum is an important factor; species containing the $Pt-SnCl_3$ moiety are found to be strongly involved in the catalytic cycle as intermediates, namely:

(i) in the insertion of the olefin into the Pt–H bond;

(ii) in the insertion of carbon monoxide into the Pt–C bond of the σ-alkyl intermediate formed;

(iii) in the hydrogenolysis of the resulting acyl intermediate, which leads to the formation of the final product, the aldehyde, and regeneration of the starting hydride.

Under "oxo" conditions the first two steps occur easily even without the tin co-catalyst, while the last step requires the formation of at least one Pt–Sn bond [10–14]. As in cobalt- or rhodium-catalyzed hydroformylation [30,31], the last step of the catalytic cycle probably involves oxidative addition of molecular hydrogen to the metal followed by reductive elimination of the aldehyde.

It is well known that the $SnCl_3^-$ ligand is a strong σ donor [28] as well as a strong π acceptor, as recently confirmed by extensive multinuclear NMR studies on Pt–Sn complexes [23]. This may account for the unique role played by $SnCl_3^-$ in activating molecular hydrogen. As a σ donor it may increase the electron density on the platinum metal, thus favouring the oxidative addition of hydrogen [32]. The π acceptor nature of $SnCl_3^-$ may also play an important role in favouring the oxidative addition of molecular hydrogen, as suggested by theoretical and experimental studies [33,34].

It is worth noting that other σ and π acceptor ligands may also be present in the coordination sphere of platinum; for example, carbon monoxide, especially under operative "oxo" conditions. Moreover, the acyl ligand itself, besides giving rise to a strong σ-bond, is also a π acceptor, as suggested by X-ray structure determinations [10–13]. However, our results reveal the unique role played by the $Pt-SnCl_3$ moiety in the last steps of the catalytic cycle.

Experimental

NMR spectra have been recorded with a Varian FT 80 A spectrometer operating at 79.542 MHz for ^{1}H and 32.203 MHz for ^{31}P in the FT mode. IR spectra were recorded with a Perkin–Elmer 983 spectrophotometer.

Deuterated solvents were dried by storage over molecular sieves. Analytical grade $SnCl_2 \cdot 2H_2O$ was dehydrated before use [35].

Complexes trans-[PtHClL$_2$] [15], cis-[PtEtClL$_2$] [36], trans-[PtEtClL$_2$] [36], and trans-[PtH(CO)L$_2$]$^+$ BF$_4^-$ [27] were prepared by published methods.

Complex trans-[PtH(SnGl$_3$)L$_2$] was prepared by stirring a 1/1 molar ratio of trans-[PtHClL$_2$] and anhydrous $SnCl_2$ in dichloromethane. The method described by Orchin [2] was also used.

Complex trans-[PtCl(COEt)L$_2$] was prepared as described for the n-hexyl analog [11]; IR (CH$_2$Cl$_2$ solution) ν(CO) 1642 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): CH$_3$: 0.15 ppm (triplet, J 7.0 Hz), CH$_2$: 1.55 ppm (quartet), phenyl protons: 7.2–8.1 ppm. Anal. Found: C, 57.8; H, 4.0. calcd.: C, 57.6; H, 4.3%.

Preparation of the solutions containing cis- or trans-[PtEt(SnCl$_3$)L$_2$]

To a cold ($-80°C$) CD$_2$Cl$_2$ solution of cis-[PtEtClL$_2$] (100 mg in 3 ml) was added a stoichiometric amount (24 mg) of SnCl$_2$. After 1 h stirring at low temperature, the yellow-orange solution was rapidly transferred to a 10 mm NMR tube for the spectroscopic investigations. ^{1}H NMR: two unresolved partially overlapping multiplets at 1.44 and 0.74 ppm for the aliphatic protons which integrate satisfactorily relative to the phenyl protons (7.2–8.1 ppm) (CD$_2$Cl$_2$ at $-80°C$).

The same procedure was used to prepare the solution of the *trans* isomer. ^{1}H NMR: CH$_3$: -0.06 ppm (triplet, J 7.0 Hz), CH$_2$: 1.00 ppm (unresolved multiplet), phenyl protons 7.2–8.1 ppm.

Attempts to obtain analytically pure materials from these solutions were unsuccessful, since eq. 2 represents an equilibrium which does not lie completely over to the right at room temperature.

Preparation of trans-[PtEt(CO)L$_2$]$^+$ BF$_4^-$

Complex trans-[PtEtClL$_2$] (300 mg) was dissolved in 10 ml of dichloromethane under a CO atmosphere at room temperature. Addition of AgBF$_4$ (74 mg) gave a precipitate of AgCl. Dilution of the filtered solution with diethyl ether yielded the product as white microcrystalline powder (yield 300 mg, 90%). IR (CH$_2$Cl$_2$ solution) ν(CO) at 2095 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): CH$_3$: -0.11 ppm (triplet, J 6.5 Hz); CH$_2$: 1.63 ppm (quartet flanked by platinum satellites: ^2J(Pt–H) 74 Hz); phenyl protons: 7.2–8.3 ppm. Anal. Found: C, 54.2; H, 4.1 calcd.: C, 54.1; H, 4.0%.

Preparation of trans-[Pt(COEt)(CO)L$_2$]$^+$ BF$_4^-$

Complex trans-[PtCl(COEt)L$_2$] (290 mg) was dissolved in 10 ml of dichloromethane at room temperature under a CO atmosphere. Addition of a stoichiometric amount (70 mg) of AgBF$_4$ gave a precipitate of AgCl. The solution was filtered then diluted with diethyl ether under CO atmosphere to give trans-[Pt(COEt)(CO)L$_2$]$^+$ BF$_4^-$ as white powder, which was filtered off and dried in a CO stream (yield 260 mg, 83%). IR (CH$_2$Cl$_2$ solution) ν(CO) at 2109 and 1665 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): CH$_3$: -0.18 ppm (triplet J 6.3 Hz); CH$_2$: 1.32 ppm (quartet); phenyl protons 7.3–8.3 ppm. Anal. Found: C, 53.6; H, 4.0. calcd.: C, 53.9; H, 3.9%.

Preparation of complex [PtH(SnCl₃)(CO)L₂]

To a CH_2Cl_2 solution of *trans*-[PtHClL₂] (250 mg in 15 ml) was added a stoichiometric amount (63 mg) of $SnCl_2$. The mixture was stirred until the tin salt completely dissolved, then the yellow-orange solution was evaporated in a slow CO stream. The orange product analyzed as [PtH(SnCl₃)(CO)L₂] (yield 230 mg, 88%). IR (Nujol mul) ν(Pt–H) at 2177, ν(CO) at 2066, ν(Sn–Cl) at 311 and 303 cm^{-1}. ¹H NMR (CD_2Cl_2): Hydride: -9.80 ppm (^1J(Pt–H) 627 Hz); phenyl protons 7.2–8.2 ppm. Anal. Found: C, 45.7; H, 3.2. calcd.: C, 45.6; H, 3.2%.

Preparation of the solutions containing complexes 11 and 12

Complexes **11** and **12** were observed only in solution. The solution was prepared by treating complex *trans*-[PtCl(COEt)L₂] with one equivalent of $SnCl_2$ in dichloromethane. Owing to the existence of the fast equilibria depicted in Scheme 2, addition of diethyl ether to these solutions causes separation of orange solids which do not give reproducible analytical data. On the other hand the starting compound is recovered from the solutions upon adding methanol and keeping the mixture in the refrigerator overnight.

Reactions with ethylene and carbon monoxide

The reactions with gases were performed in the NMR spectrometer. Typically, 3 ml of a CD_2Cl_2 solution (generally concentrations in the range 3–5×10^{-2} M have been used) of the substrate complex was placed in a 10 mm NMR tube. The tube was sealed with a rubber septum and allowed to reach the reaction temperature in the NMR probe. The reactions were carried out by injecting the stoichiometric amount of gas ($\sim$ 1 ml) through the septum into the solution.

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