Inorganica Chimica Acta, 77 (1983) L53–L55

Chemistry of Mixed Ligand Complexes of Platinum: a Study of the Carbon Monoxide Reaction with Trichlorostannyl–platinum(II) Complexes*

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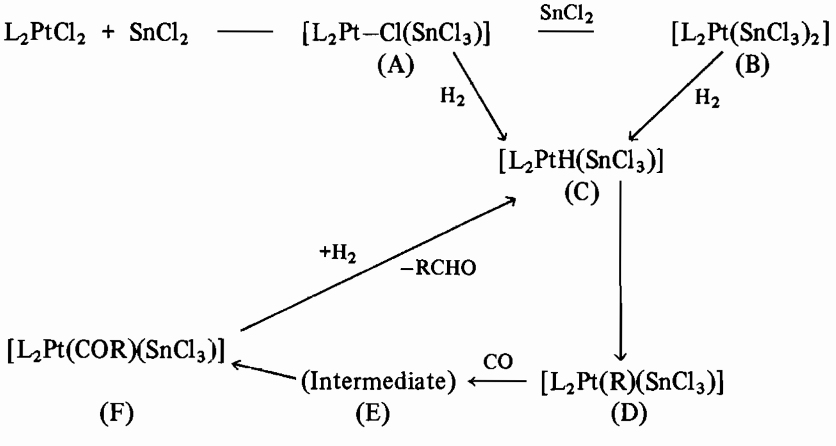
Received March 14, 1983

Metal complexes of low symmetry containing mixed ligands can be useful in studies such as (i) *trans*-effects of ligands having variable electronic and steric parameters [1–7], (ii) asymmetric synthesis catalyzed by metal complexes and (iii) homogeneous hydrogenation and hydroformylation catalysis [3, 4]. In particular, platinum–phosphine complexes in conjunction with tin(II) chloride have been used in homogeneously catalyzed hydrogenation and hydroformylation reactions [3, 4, 8–10].

The reaction sequence shown in Scheme 1 is considered to be the stoichiometric series that results in the hydroformylation catalysis of unsaturated hydrocarbons catalyzed by Platinum(II) chloride–Sn(II) chloride system. Existence of some of the intermediates proposed in Scheme 1 has been supported either by isolating them or by identifying them in solutions by spectroscopic means. For instance, platinum(II) chloride complexes are known to react with tin(II) chloride to yield trichlorostannyl–platinum(II) complexes (A or B) via migratory insertion reactions [4, 11]. Such trichlorostannyl–platinum complexes have been shown to react with H_2 to yield the corresponding hydrido–$PtSnCl_3$ complexes [12] (C). The hydrido-complex undergoes insertion reaction with unsaturated hydrocarbons (*e.g.* activated acetylene) [11] to yield the alkyl–platinum complex D. The intermediate D has been considered to react with CO resulting in the insertion product F via some intermediate (E) which upon subsequent reaction with H_2 produces the aldehyde product and the hydrido–platinum complex (C). Although as described above, various evidence in support of the existence of these intermediates (A–D) is available, little is known about the step involving the reaction of CO with trichlorostannyl–platinum(II) complex leading to the intermediate [13]. We wish to describe here our studies dealing with this particular step of the hydroformylation reaction.

In order to minimize complications such as isomerization, dissociation of alkyl group and possible rapid insertion of CO in the Pt–R bond, complexes of the type $[PtSnCl_3(P\text{-}C)L]$ (*1*) (where P-C) = $Bu^t_2PCMe_2CH_2$) have been selected as the model for intermediate D. These mixed ligand complexes (*1*) containing carbon–platinum and trichlorstannyl–platinum bonds have been obtained in high yield from the reaction of an excess (up to 5 fold) of $SnCl_2 \cdot H_2O$ with the corresponding chloro–platinum complexes *trans*-$[PtCl(P\text{-}C)L]$ [1, 5] (*2*) in solvents such as CH_2Cl_2 or benzene at room temperature (eqn. 1):



Scheme 1

$$\textit{trans}\text{-}[PtCl(P\text{-}C)L] + SnCl_2 \longrightarrow \textit{trans}\text{-}[Pt\text{–}SnCl_3(P\text{-}C)L] \qquad (1)$$

(*2*) (*1*)

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*Presented in part by A. B. Goel at the 3rd National Conference of Organometallics at Jaipur, Rajasthan (India) on February 22, 1982.

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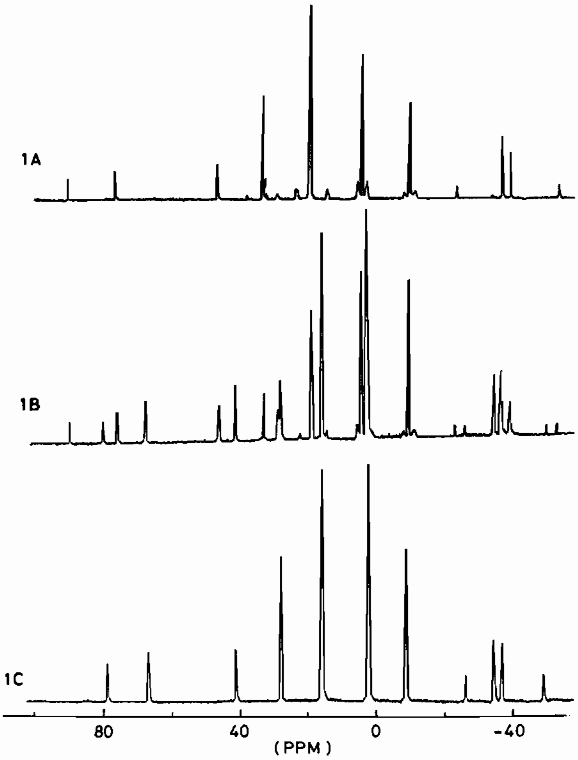


Fig. 1. ^{31}P NMR spectrum of the system (A) *trans*-[PtSnCl$_3$-(P-C)PPh$_3$] (*1*) (δP$_m$ = 2.41 ppm, JPtP$_m$ = 2026 Hz, JSnP$_m$ = 71 Hz; δP = 26.09 ppm, JPtP = 2746 Hz, JSnP = 205Hz, JP$_m$P = 336 Hz) (B) reaction of complex (*1*) with CO producing *trans*-[Pt(P-C)(PPh$_3$)CO]$^+$SnCl$_3^-$ (δP$_m$ = –3.27 ppm, JPtP$_m$ = 1851 Hz, JP$_m$P = 300 Hz, δP = 21.86 ppm, JPtP = 2500 Hz) and (C) *trans*-[Pt(P-C)(PPh$_3$)CO]$^+$PF$_6^-$ (δP$_m$ = –3.27 ppm, JPtP$_m$ = 1851 Hz, JP$_m$P = 300 Hz, δP = 21.89 ppm, JPtP = 2500 Hz and PF$_6$ as a set of seven signals centered at –144.69 (not shown in figure)) in CH$_2$Cl$_2$/C$_6$D$_6$ at room temperature. Scale ≈ 217.6 Hz/cm.

(where L = Ph$_3$As, CO, PCy$_3$, PBu$^t_2$R, PPh$_2$Me, P(C$_6$H$_4$Y)$_3$ (Y = Cl, F, H, CH$_3$, OCH$_3$)]

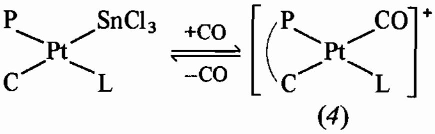
The *trans*-geometry for the complexes (*1*) (where L = PR$_3$) has been determined by the ^{31}P NMR spectral data which shows, in addition to the 12 lines pattern typical of mixed phosphines platinum(II) complexes of the type (*2*) containing non-equivalent phosphorus nuclei at mutually *trans*-position, lines due to tin–phosphorus couplings. A typical spectrum of the complex *1* (L = PPh$_3$) is shown in Fig. 1A. A CH$_2$Cl$_2$ solution of complex *1* reacts readily with CO under ambient conditions (room temperature and atmospheric pressure) yielding the CO containing platinum complex. Typically, when a slow stream of CO is bubbled through a solution of complex [PtSnCl$_3$(P-C)PPh$_3$] for 2–5 min the infrared spectrum of the solution shows a sharp band at 2085 cm^{-1} due to νCO. The ^{31}P NMR spectrum of this solution (10% C$_6$D$_6$ added) shows a complex pattern consisting of signals due to the starting complex *1* (L = PPh$_3$) and 12 additional lines (Fig. 1B) with no satellites due to tin–phosphorus couplings. Further reaction with Co at room temperature leads to complete conversion of starting complex *1* and the ^{31}P NMR spectrum shows only the later 12 lines pattern with no tin satellites. This indicates the dissociation of SnCl$_3^-$ from the platinum centre and suggests the formation of an ionic complex, [Pt(P-C)(PPh$_3$)(CO)]$^+$-SnCl$_3^-$ (*3*). In order to support this, a cationic platinum complex [Pt(P-C)(PPh$_3$)(CO)]$^+$PF$_6^-$ (*4*) with the same groups as in complex (*3*) has been prepared from the reaction of [PtCl(P-C)PPh$_3$] (*2*) with AgPF$_6$ followed by the treatment with CO (eqns. 3 and 4):

$$[\mathrm{PtCl(P\text{-}C)PPh_3}] + \mathrm{AgPF_6} \xrightarrow{-\mathrm{AgCl}} [\mathrm{Pt(P\text{-}C)PPh_3}]^+ + \mathrm{PF_6^-} \qquad (3)$$

$$[\mathrm{Pt(P\text{-}C)PPh_3}]^+\mathrm{PF_6^-} + \mathrm{CO} \longrightarrow [\mathrm{Pt(P\text{-}C)(PPh_3)CO}]^+\mathrm{PF_6^-} \qquad (4)$$

(*4*)

The ^{31}P NMR spectrum of complex (*4*) in CH$_2$Cl$_2$/C$_6$D$_6$ (Fig. 1C) shows an identical pattern to that observed in the reaction of CO with [PtSnCl$_3$(P-C)-PPh$_3$]. This 12 line pattern is consistent with the *trans*-orientation of the two non-equivalent phosphorus nuclei. Reactions of other complex *1* with CO also yield the corresponding cationic platinum complexes (*4*) (eqn. 5):



$$\mathrm{[PtSnCl_3(P\text{-}C)L]} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} [\mathrm{Pt(P\text{-}C)(CO)L}]^+ \; \mathrm{SnCl_3^-} \qquad (5)$$

(*4*)

It appears that the presence of a trichlorostannyl group on platinum not only aids in the formation of hydrido–platinum intermediates but also favours substitution by CO thus facilitating the CO insertion into Pt–R. However, such insertion of CO into Pt–C bonds of the above complex *4* did not take place probably due to (i) the chelating metalated phosphine and (ii) the steric effect of the ligands forcing the molecule to be in *trans*-position (insertion reactions have been considered to take place in molecules with *cis*-dispositions of alkyl or hydrogen and CO).

The intermediates and the steps proposed in Scheme 1 for the platinum(II) chloride, tin(II) chloride catalyzed hydroformylation reactions is undoubtedly an oversimplification of the overall process and is only intended to illustrate some of the most probable reaction pathways.

After the preparation of this manuscript, a series of papers by Clark and co-workers [14] dealing with the reactions of CO with trichlorostannyl–platinum(II) chloride complexes appeared [14]. These workers have reported an interesting solvent effect on the reaction pathway and showed the displacement of $SnCl_3^-$ by CO in solvents such as acetone or acetonitrile. However, no such ligand rearrangement has been reported to occur in chloroform. Contrary to this we have observed, as described above, the displacement of $SnCl_3^-$ by CO even in CH_2Cl_2 or CH_2Cl_2/C_6D_6 mixture. This difference in the reactivity may be due to the fact that the complexes we utilized in our studies were organoplatinum species containing platinum–carbon bonds whereas these workers used platinum–chloride complexes. It is known that the alkyl groups have a higher *trans*-effect than chloride groups, thus helping in the cleavage of $Pt-SnCl_3$ bonds.

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