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Synthesis and Characterization of Trichlorostannyl–Platinum(II) Complexes Containing a Platinum–Carbon Bond and Mixed Ligands

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Several trichlorostannyl-platinum(II) complexes containing platinum–carbon bond and mixed ligands, trans-*[$PtSnCl_3$(P–C)L] (1) [where (P–C) = $Bu_2{}^tPCMe_2CH_2$ and L = Ph_3As, Ph_3Sb, CO, PCy_3, $PBu_2{}^tR$, PPh_2Me, $P(C_6H_4Y)_3$ (Y = Cl, F, H, CH_3, OCH_3) have been prepared by the reaction of tin(II) chloride with the corresponding chloro–platinum(II) complexes,* trans-*[PtCl(P–C)L] (2). Complexes 1 have been characterized by their elemental analysis, ^1H and ^{31}P NMR spectral data. ^{31}P NMR spectra of these complexes show complex patterns with platinum–phosphorus and tin–phosphorus couplings. The* trans-*configuration has been assigned to these complexes containing mixed phosphine ligands on the basis of ^{31}P NMR spectra which show large phosphorus–phosphorus coupling constants ($^2J(PP') \sim 307–339$ Hz). The* trans-*effect of the* para-*substituted phosphines has been related to their electronic parameters by measuring the platinum–phosphorus coupling constants (J Pt–P) of the metalated phosphine present at the* trans *position which follows the trend Cl < F < H < CH_3 < CH_3O.*

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 to homogeneously catalyze both hydrogenation and hydroformylation reactions [3, 4, 8–11]. The actual catalysts in these systems have been considered to be trichlorostannyl–platinum(II) complexes formed by the reactions of platinum(II) chloride with tin(II) chloride [4, 12]. In the course of the reactions these trichloro-stannyl–platinum complexes react with H_2 to yield the corresponding hydrido–$PtSnCl_3$ complexes [13] which undergo insertion reactions with the unsaturated hydrocarbons (*e.g.*, activated acetylene) [12] to yield the alkyl–$PtSnCl_3$ complexes. In the hydroformylation catalysis these intermediate alkyl–$PtSnCl_3$ react with CO resulting in the insertion products which upon subsequent reaction with H_2 produce the aldehyde product. In the course of our studies on platinum catalyzed hydroformylation reactions, we isolated a series of trichlorostannyl–platinum(II) complexes containing a carbon-platinum bond and two non-equivalent phosphine ligands. We wish to describe here the preparation and the structural characterization of these complexes.

Results and Discussion

The trichlorostannyl–platinum(II) complexes containing a carbon–platinum bond and mixed ligands, [$PtSnCl_3$(P–C)L] (*1*) (P–C) = $Bu_2{}^tPCMe_2CH_2$ and L = Ph_3As, Ph_3Sb, CO, PCy_3, $PBu_2{}^tR$, PPh_2Me, $P(C_6H_4Y)_3$ (Y = Cl, F, H, CH_3, OCH_3) have been obtained in high yields 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–C)L] [2, 6] (*2*). The reaction of chloro–platinum(II) complexes, (*2*), with powdered $SnCl_2 \cdot H_2O$ in solvents such as CH_2Cl_2 or benzene proceeds rapidly at ambient temperatures. The reactions are usually complete within a few hours. The trichlorostannyl–platinum(II) complexes, (*1*) can be isolated by extracting the reaction mixture with CH_2Cl_2. Further re-crystallization in CH_2Cl_2/hexane (or benzene/hexane) gives white (or pale) crystalline products (Table I).

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TABLE I. Elemental Analysis of the Complex, *trans*-[$PtSnCl_3(P-C)L$].

S. No.	Complex $PtSnCl_3(P-C)L$	Yield (%)	Analysis (%) Found (calcd.)			
			C	H	Cl	P
	L =					
1	$P(C_6H_4Cl)_3$	89	36.6 (36.5)	3.92 (3.85)		6.51 (6.28)
2	$P(C_6H_4F)_3$	87	38.1 (38.4)	4.01 (4.05)		6.75 (6.62)
3	$P(C_6H_5)_3$	94	40.7 (40.8)	4.61 (4.64)	12.3 (12.1)	7.32 (7.02)
4	$P(C_6H_4Me)_3$	87	42.7 (42.8)	5.13 (5.08)	11.9 (11.5)	6.87 (6.70)
5	$P(C_6H_4OMe)_3$	85	40.3 (40.7)	4.80 (4.83)	11.2 (10.9)	6.59 (6.37)
6	PCy_3	88	40.3 (39.9)	6.70 (6.55)	11.6 (11.8)	6.81 (6.88)
7	$P(Bu_2{}^tMe)$	85	32.7 (32.3)	6.10 (6.02)	13.7 (13.6)	7.97 (7.94)
8	$P(Ph_2Me)$	79	36.3 (36.6)	4.72 (4.75)	13.7 (13.0)	7.83 (7.55)
9	$AsPh_3$	85	38.7 (38.8)	4.37 (4.42)	11.7 (11.5)	
10	$SbPh_3$	75	37.4 (37.0)	4.45 (4.21)	10.6 (10.9)	
11	CO	74	24.4 (24.0)	4.12 (4.00)	16.7 (16.4)	4.93 (4.78)

Complexes 1–6 and 10 were crystallized from CH_2Cl_2/hexane and complexes 7–9 and 11–12 were crystallized either from CH_2Cl_2/hexane or benzene/hexane.

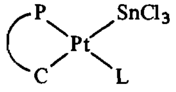
$$\underset{2}{trans\text{-}[PtCl(P-C)L]} + SnCl_2 \longrightarrow \underset{1}{trans\text{-}[Pt-SnCl_3(P-C)L]} \qquad (1)$$

The trichlorostannyl–platinum complexes (*1*) are air stable solids and are soluble in CH_2Cl_2 and benzene.

The *trans*-geometry for the complexes (*1*) has been determined by the ^{31}P NMR spectral data (Table II) which show large phosphorus–phosphorus coupling constants of the order of $^2J(PP') = 307–339$ Hz (due to magnetically non-equivalent phosphorus nuclei). With two such phosphorus nuclei, a twelve line spectrum is expected [2, 6] (each phosphorus giving a doublet with ^{195}Pt satellites). In addition to the 12 lines pattern typical of mixed phosphine platinum(II) complexes of the type (*2*) containing non-equivalent phosphorus nuclei at mutually *trans*-position, additional lines due to tin-phosphorus couplings are also expected. Indeed, complex ^{31}P NMR spectra consisting of large phosphorus–phosphorus couplings, platinum–phosphorus couplings of the order of JPtP = 1860–2773 Hz, and tin–phosphorus couplings, JSnP = 40–209 Hz (observed generally associated with the main large-signals) have been observed. A typical 12 lines spectrum (neglecting tin–satellites) is observed except in some cases (*e.g.*, L = Ph_2MeP) where instead of twelve lines, only ten lines are observed. In these spectra the two phosphine main signals appear as doublet sand the ^{195}Pt satellites down field from the main doublet signals appear as expected doublets; however, the upfield satellites are observed as singlets. It is interesting to note here that the sum of the [½J(PtP) + ½J(PtP')] (low field side) obtained by taking the mean values is observed to be equal to the sum of [½J(PtP) + ½J(PtP')] (high field side). Analysis of these spectra clearly indicates that the platinum satellite signals which appeared as two singlets are not a consequence of accidental overlap of the two doublets. Meek *et al.* [14] have recently observed a similar non-uniform spectra behavior in the case of $[Pt(tpp)X]^+$ complexes which has been explained on the basis of a second order approximation.

In these complexes (*1*), since metalated phosphine is a constant component for one 'side' of each molecule, the values for JPtP (metalated phosphine) may well then reflect just the effect of the phosphine or other ligand of the *trans*-position (*trans*-influence of the ligands [15]). Upon examination of these

TABLE II. ^{31}P NMR Spectral Data of *trans*-[$PtSnCl_3(P-C)L$] Complexes.

S. No.	Complex	Signals Due to Metalated Phosphine			Signals Due to Non-Metalated Phosphine			
	 L =	δ P_A (ppm)	$JPtP_A$ (Hz)	$JSnP_A$ (Hz)	δ P_B (ppm)	$JPtP_B$ (Hz)	$JSnP_B$ (Hz)	JP_AP_B (Hz)
1	$P(C_6H_4Cl)_3$	−3.67	2056	71	24.88	2754	200	337
2	$P(C_6H_4F)_3$	−3.57	2036	71	24.12	2764	195 204	337
3	$P(C_6H_5)_3$	−2.41	2026	71	26.09	2764	200 209	336
4	$P(C_6H_4Me)_3$	−2.76	2007	69	23.72	2769	198 208	336
5	$P(C_6H_4OMe)$	−2.77	1987	73	21.87	2773	193 203	339
6	PCy_3	−0.35	1860	90	28.25	2681	173	307
7	$P(Bu_2^tMe)$	−4.42	1909	95	24.74	2656	181	316
8	PPh_2Me	−4.17	2090	107	10.5	2588	156	336
9	$AsPh_3$	−2.31	2456	42				
10	$SbPh_3$	−4.62	2632	40				
11	CO	−6.94	2253					

Spectra were recorded at room temperature in solvents CH_2Cl_2/C_6D_6. Chemical Shift values are with respect to H_3PO_4 (external) standard. In some cases the signals due to tin–phosphorus [$J(^{117}SnP)$ and $J(^{119}SnP)$] coupling were not well resolved and the values are given as an average.

values (Table II), it is observed that in the series of Ph_3E (E = P, As, Sb), as the electronegativity of the element E decreases, the JPtP (metalated) value increases, suggesting a decreasing order of *trans*-influence (*i.e.*, when the basicity order is $Ph_3P > Ph_3As > Ph_3Sb$, then the *trans*-influence order is $Ph_3P > Ph_3As > Ph_3Sb$). For the aryl phosphine ligands the dominant factor for *trans*-influence should also be electronic rather than steric as no appreciable steric bulkiness is changed by changing the substituents at the *para*-position [1]. Upon examining the JPtP (metalated phosphine) values, it is observed that the value of JPtP decreases as the electron donating tendency of the *para*-substituent on phenylphosphines increases, suggesting an increasing order of *trans*- effect. In other words, when electronic parameters (ν cm^{-1}) [1] of the ligand (p-$YPh)_3P$ follow the order: Y = $CH_3O < CH_3 < H < F < Cl$, then the *trans*-effect follows the order: Y = $CH_3O > CH_3 > H > F > Cl$. It is further observed that the value of platinum–phosphine coupling constant (JPtP′) in the substituted triphenyl phosphine ligands increases systematically as the electron donating tendency of the *para* substituent increases. Another interesting observation has been made relating to the tin-phosphorus coupling constants. The values of the JSnP of the metalated phosphine have been observed to be smaller (~40–90 Hz) than that of the non-metalated phosphine (~200 Hz). It is well known that the *trans*- tin-phosphorus coupling constants are much larger than that of *cis*-tin-phosphorus. In the complex *1*, although both phosphorus nuclei are at *cis*-position to that of $SnCl_3$ group, the dissimilar values of JSnP (metalated) and JSnP′ (non-metalated) suggests a distortion in the molecule.

The ^1H NMR spectral parameters for complexes *trans*-[$PtSnCl_3(P-C)L$] (*1*) are given in Table III. Where L is other than a phosphine ligand, the metalated tri-t-butylphosphine shows signals due to tert-butyl (t-Bu_2P) and methyl (CMe_2) group protons as doublets in the ratio 3:1. The methylene protons are also observable as a doublet with ^{195}Pt satellites. For example, complex *1* (L = Ph_3Sb) shows doublets due to tert-butyl and methyl groups at δ1.56 [J(PH) = 14.3 Hz] and δ1.44 ppm [J(PH) = 14.6 Hz] respectively. The methylene proton signals are observed at δ1.26 ppm as doublet [J(PH) = 14 Hz] with platinum satellites [J(PtH) = 92 Hz]. Some of the spectra for complexes containing two magnetically non equivalent phosphines at positions *trans* with respect to each other, *e.g.*, *trans*-[$PtSnCl_3(P-C)(PR_3)$], show signals due to the tert-butyl groups

TABLE III. Proton NMR Spectral Data of *trans*-[Pt(SnCl$_3$(P–C)L] Complexes.

S. No.	Complex [PtSnCl$_3$(P–C)L] L =	Signals due to metalated phosphine					methylene (C–CH$_2$–Pt)			Signals due to monodentate ligand δ (ppm) + J(PH) (Hz)
		t-Butyl (P–Bu$_2^t$)			dimethyl (P–CMe$_2$)		δ (ppm)	J(PH) (Hz)	J(PtH) (Hz)	
		δ(ppm)	^{3}J(PH) (Hz)	^{5}J(PH) (Hz)	δ(ppm)	J(PH) (Hz)				
1	P(C$_6$H$_4$Cl)$_3$	1.53(dd)	13.5	1.2	1.38(d,br)	13.0	0.89(dd)	6.5	82	Ph = 7.71(d) JPH = 5.2
2	P(C$_6$H$_4$F)$_3$	1.56(dd)	13.5	1.0	1.41(d)	13.0	1.10(dd)	6.5	82	Ph = 7.5(m)
3	P(C$_6$H$_5$)$_3$	1.61(dd)	13.5	0.5	1.37(d)	12.5	1.08(dd)	7	84	Ph = 7.41(m)
4	P(C$_6$H$_4$Me)$_3$	1.56(dd)	13.5	1.1	1.40(d,br)	12.5	1.13(dd)	6.5	83	Me = 3.35(s) Ph = 7.44(t) 2,6 H JPH = 8.4; 7.23 (dd) 3,5H, JPH = 2, JHH = 7
5	P(C$_6$H$_4$OMe)$_3$	1.56(dd)	13.2	1.1	1.40(d)	13.0	1.16(dd)	6.5	83	OMe = 3.78(s) Ph = 7.48(t) – 2,6H JPH = 9 6.95 (dd) – 3,5H JPH = 1,6, JHH = 8
6	PCy$_3$	1.61(d)	12.9	–	1.42(d)	12.8	'a'	'a'	'a'	Cy = 1.0–3.0(br)
7	P(Bu$_2^t$Me)	1.59(dd)	12.9	2.3	1.52(d)	12.5	'a'	'a'	'a'	Bu^t = 1.36(dd) ^{3}JPH = 14.1; ^{5}JPH = 1.5 Me = 2.36(dd) ^{3}JPH = 6.2; ^{5}JPH = 2.3; JPtH = 32
8	P(Ph$_2$Me)	1.56(dd)	10	4.8	1.38(d)	9.4 4.4	1.05(dd)	7.9	80	Ph = 7.45(m); Me = 2.51 ^{3}JPH = 6.7; ^{5}JPH = 2.1; JPtH = 32
9	AsPh$_3$	1.74(d)	14.1	–	1.42(d)	14.0	1.26(d)	13.2	85	Ph = 7.48(s)
10	SbPh$_3$	1.56(d)	14.3	–	1.44(d)	14.6	1.26(d)	14	92	Ph = 7.4
11	CO	1.54(d)	14.7	–	1.57(d)	15.4	1.63(d)	13	'a'	–

Spectra were recorded in CDCl$_3$/CH$_2$Cl$_2$ (complexes 1–5) and in CDCl$_3$ (complexes 6–11) at room temperature and chemical shift values are with respect to TMS (as internal standard)

'a' values could not be determined due to overlapping with other signals.

protons as double doublets due to the splitting by both phosphorus nuclei. The methylene proton signals are observed as two sets of doublets. In particular, the spectrum of complex *1* [$PR_3 = P(C_6H_4Cl)_3$] shows a double doublet due to tert-butyl protons at δ 1.53 ppm [$^3J(PH)$ = 13.5 Hz and $^5J(PH)$ = 1.2 Hz] and a doublet with some broadening due to methyl protons at δ 1.38 ppm [$^3J(PH)$ = 13.0 Hz]. The methylene protons ($C-CH_2-Pt$) are observed as a double-doublet at δ 0.89 ppm [J(PH) = 6.5 Hz] with J(PtH) = 82 Hz.

Preliminary results on the reaction of carbonmonoxide with a solution of trichlorostannyl platinum complexes (*1*), indicate a rapid interaction of CO yielding ionic complexes of the type $[Pt(P-C)(CO)L]^+SnCl_3^-$. Details of these reactions will be reported later on.

Experimental

All the solvents used were of spectroanalyzed grade. Reactions and other manipulations such as purifications were carried out in air. The chloro-bridged dinuclear complex, $[Pt(\mu\text{-}Cl)(P-C)]_2$, (P–C) = $Bu_2{}^tPCMe_2CH_2$, was prepared as reported earlier from the reaction of $Bu_3{}^tP$ with $PtCl_2(NCPh)_2$. Mixed phosphine platinum(II) chloride complexes, *trans*-[PtCl(P–C)L] were obtained by the bridge splitting reaction [2, 6] and a general preparation is given below.

Elemental analyses were performed by M. H. W. Laboratories, Phoenix, Arizona and Atlantic Microlab, Atlanta. Proton and ^{31}P NMR spectra were recorded on a Brucker-60 Fourier transform spectrometer. TMS was used as an internal standard for ^1H NMR and phosphoric acid (85%) was used as external standard for ^{31}P NMR spectra. ^{31}P chemical shifts to high frequency (low field) are reported as positive. ^{31}P NMR spectra were recorded in a mixed CH_2Cl_2/C_6D_6 solvent.

Preparation of [PtCl(P–C)L] Complexes

Typically, ligands such as tertiary phosphine were added in 2:1 molar ratio a to the dimeric complex, $[PtCl(P-C)]_2$ in benzene solution, and the reaction mixture was allowed to react for 1–2 hours at temperatures of 40–50 °C. After concentrating the solution, crystals of the compound [PtCl(P–C)L] (*2*), were obtained in high yields by addition of hexane or ethanol.

Preparation of [PtSnCl$_3$(P–C)L] from the Reaction of [PtCl(P–C)L] with Excess SnCl$_2$·H$_2$O in CH$_2$Cl$_2$

Typically, to a solution of [PtCl(P–C)L] (1.0 mmol) in CH_2Cl_2 was added an excess of powdered $SnCl_2 \cdot H_2O$ (5.0 mmol) and the reaction was stirred at room temperature for 4 hr. The solution was filtered and concentrated to a small volume. Addition of hexane afforded white (or pale colored) crystals of trichlorostannyl–platinum complex, $[PtSnCl_3(P-C)L]$, in high yields (65–94%). Analytical and spectroscopic data for these complexes are given in Tables I–III.

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