Inorg. Chem. **1984**, *23*, 3223-3229

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Trichlorostannate Complexes of Platinum. Synthesis, Multinuclear NMR Spectroscopy, and X-ray Crystallography of *trans*-[$Pt(SnCl_3)_2(P(OPh)_3)_2$] and Related Complexes

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Received July 14, 1983

The preparation and ^{195}Pt, ^{119}Sn, and ^{31}P NMR spectroscopy of the complexes $PtCl_n(SnCl_3)_{2-n}(P(OR)_3)_2$ (n = 0, 1; R = Et, *i*-Pr, Ph), $[Pt(SnCl_3)_3(P(OR)_3)_2]^-$ (R = Me, Et, Ph), $[PtCl_2(SnCl_3)L]^-$ (L = PEt_3, $PTol_3$, $P(OEt)_3$, $P(OPh)_3$, $AsEt_3$, $AsPh_3$), $[PtCl(SnCl_3)_2L]^-$ (L = PEt_3, $PTol_3$, $AsEt_3$, $AsPh_3$), $[Pt(SnCl_3)_3(AsEt_3)]^-$, and $[Pt(SnCl_3)_4(PEt_3)]^{2-}$ are reported. These studies support the relative stability of poly(trichlorostannate) complexes of Pt(II). The structure of the complex $Pt(SnCl_3)_2(P(OPh)_3)_2$ has been determined by X-ray analysis and shown to have *trans*-$SnCl_3^-$ ligands and an overall square-planar arrangement. The possible involvement of poly(trichlorostannate) complexes in catalytic homogeneous hydrogenation is discussed. Crystal data: a = 11.177 (1), b = 13.181 (2), c = 14.489 (3) Å; β = 98.52 (1)°; V = 2111.0 Å^3; space group $P2_1/n$; Z = 2.

Introduction

The chemistry of the trichlorostannate ligand, $SnCl_3^-$, has received attention in various laboratories due to the capability of platinum(II)/tin(II) mixtures, usually as chloride salts, to homogeneously catalyze the hydroformylation,[1-3] carbonylation,[4-6] and hydrogenation[7-9] reactions. The catalysis functions best with group 5 ligands;[1,10] however, $K_2[PtCl_4]$ and excess $SnCl_2$ are sufficient.[1,11,12] Not surprisingly there have been a number of fundamental studies on "Pt–$SnCl_3$" complexes.[13-16]

For some time we have been involved in multinuclear NMR and preparative studies of (trichlorostannato)phosphine complexes of Pt(II),[17-24] Rh(I),[25,26] Ir(I),[26] and Ir(III).[27] Using excess tin(II) chloride, we have observed,[17] isolated,[17-21] and determined the structure[24] of platinum phosphine and arsine complexes that contain more than one coordinated $SnCl_3^-$ ligand. In particular we have found that the five-coordinate anionic complexes $[Pt(SnCl_3)_3L_2]^-$ (L = PR_3, AsR_3, diolefin) are quite stable[21] with small R groups such as Me, Et, and OEt. On the other hand, $Pt(SnCl_3)_2L_2$ complexes are more difficult to isolate. Given the implication that poly(trichlorostannate) complexes may be important in hydrogenation[8-16] and the reports by Clark and co-workers[28-31] on catalytic hydroformylation with $PtCl_2(CO)(ER_3)/SnCl_2$, which show best results with a Sn/Pt ratio ≥2, we have given further attention to complexes containing the "$Pt(SnCl_3)_2$" fragment. We report here multinuclear NMR spectroscopy of several new representatives of this class, as well as the solid-state structure for *trans*-[$Pt(SnCl_3)_2(P(OPh)_3)_2$].

Results

1. NMR Spectroscopy. The solution structures of all of our complexes were deduced from ^{31}P, ^{119}Sn, and ^{195}Pt NMR spectroscopic methods. Our efforts[17-27] and those of several other groups[32-39] have led to the following useful empiricisms: (a) $^1J(^{195}Pt,^{119}Sn)$ is of the order of kHz (sometimes >30 khz) and depends on the trans ligand[40] in a way reminiscent of $^1J(^{195}Pt,^{31}P)$[41] and $^1J(^{195}Pt,^{15}N)$.[42] (b) $^2J(^{119}Sn,^{117}Sn)$ is also of the order of kHz, with the trans geometry bringing values routinely in excess of 20 000 Hz,[21-24,33,34,36] whereas *cis*-$SnCl_3^-$ ligands afford far more "modest" values of <10 kHz. In five-coordinate $M(SnCl_3)_nL_{5-n}$ compounds, in which dynamic processes can average the various types of ^2J, this coupling constant can be as small as 619 Hz, as in (PPN)[$Pt(SnCl_3)_3(1,5\text{-COD})$],[23] or as large as the 20 990-Hz value found in $[Pd(SnCl_3)_3(PEt_3)_2]^-$.[21] (c) $^2J(^{119}Sn,^{31}P)_{cis}$ at 102-317 Hz[21-26] ≪ $^2J(^{119}Sn,^{31}P)_{trans}$ at 3044-4848 Hz.[17-21] (d) The ^{119}Sn chemical shift ranges over several hundred ppm with typical values between δ −39 and −387.[32-43] (e) $\delta(^{195}Pt)$ shifts

Scheme I

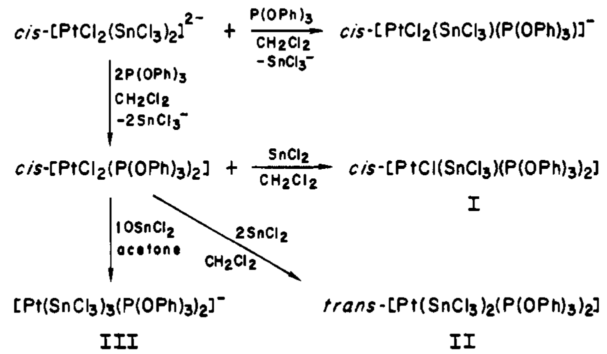

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Table I. NMR Data[a] for the Phosphite Complexes

compd	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$\delta(^{195}Pt)$	J(Pt,P)	J(Pt,Sn)	J(Sn,Sn)	J(Sn,P)
cis-$[PtCl_2(P(OMe)_3)_2]$	73.8			5705			
cis-$[PtCl_2(P(OEt)_3)_2]$	68.2		−4363	5657			
cis-$[PtCl_2(P(O\text{-}i\text{-}Pr)_3)_2]$	62.2		−4333	5815			
cis-$[PtCl_2(P(OPh)_3)_2]$	59.4		−4298	5800			
cis-$[PtCl(SnCl_3)(P(OEt)_3)_2]^b$	84.1/80.1	−1		4807/5430	16 068		6497/221
cis-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]^b$	77.4/76.5	−27	−4551	4899/5460	15 964		6550/218
cis-$[PtCl(SnCl_3)(P(OPh)_3)_2]^b$	74.8/73.5	−39		4695/5642	18 066		6750/195
trans-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]^b$	95.0	−267		3674			226
trans-$[Pt(SnCl_3)_2(P(OEt)_3)_2]^c$	104.4	−22	−5132	3610	20 741	32 556	268
trans-$[Pt(SnCl_3)_2(P(O\text{-}i\text{-}Pr)_3)_2]^c$	105.4	−27	−5136	3400	20 708	31 177	260
trans-$[Pt(SnCl_3)_2(P(OPh)_3)_2]^c$	97.0	−12		3930	19 043		256
$[Pt(SnCl_3)_3(P(OMe)_3)_2]^{-\,d}$	83.3	−121	−5390	2939	18 445	15 674	311
$[Pt(SnCl_3)_3(P(OEt)_3)_2]^{-\,e}$	77.0	−117	−5234	2883	19 049	16 504	317
$[Pt(SnCl_3)_3(P(OPh)_3)_2]^{-\,f}$	71.0	−184	−5629	4705	12 778	9 489	316

[a] Chemical shifts are in ppm; ±0.1 ppm for ^{31}P, ±0.2 ppm for ^{119}Sn and ^{195}Pt. Coupling constants are in Hz; ±1 for data from ^{31}P measurements, ±12 for data from ^{119}Sn and ^{195}Pt measurements. [b] $CH_2Cl_2/CDCl_3$, 1/1, −40 °C. [c] $CH_2Cl_2/CDCl_3$, 1/1, −50 °C. [d] Acetone-d_6, −90 °C. [e] Acetone-d_6, −40 °C. [f] Acetone-d_6, −50 °C.

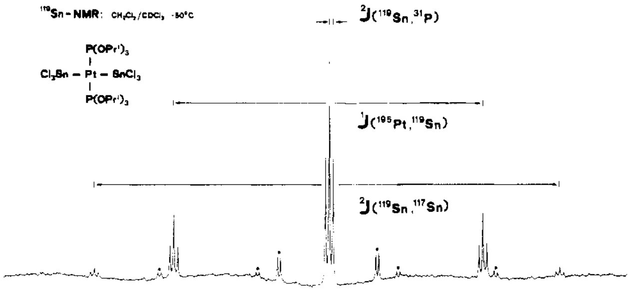

Figure 1. ^{119}Sn NMR spectrum of *trans*-$[Pt(SnCl_3)_2(P(O\text{-}i\text{-}Pr)_3)_2]$. The smaller signals marked with an asterisk stem from *cis*-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]$. The triplet multiplicity arises from the equivalent ^{31}P spins. Note that $^2J(^{119}Sn,^{117}Sn) \gg {}^1J(^{195}Pt,^{119}Sn)$; $\delta(^{119}Sn) = -27$.

to higher field by several hundred ppm when Cl^- is replaced by $SnCl_3^-$.[19,21,22,32]

Using these data we have identified a variety of mono-, bis-, and tris(trichlorostannate) complexes and begin our discussion with the chemistry of bis(phosphite) complexes.

Scheme II[a]

A.

$$[PtCl_3(PEt_3)]^- \xrightarrow{SnCl_2} cis\text{-}[PtCl_2(SnCl_3)(PEt_3)]^-\ (IV) \xrightarrow{SnCl_2}$$

$$trans\text{-}[PtCl(SnCl_3)_2(PEt_3)]^-\ (V) \xrightarrow{SnCl_2} Pt_2Cl_2(SnCl_3)_2(PEt_3)_2 +$$

$$[PtCl(SnCl_3)_2(PEt_3)]^- + [Pt(SnCl_3)_4(PEt_3)]^{2-} \xrightarrow{SnCl_3^-}$$

$$[Pt(SnCl_3)_4(PEt_3)]^-$$

B.

$$[PtCl_3(AsEt_3)]^- \xrightarrow{SnCl_2} cis\text{-}[PtCl_2(SnCl_3)(AsEt_3)]^-\ (VII) \xrightarrow{SnCl_2}$$

$$cis\text{-}[PtCl_2(SnCl_3)(AsEt_3)]^- + cis/trans\text{-}[PtCl(SnCl_3)(AsEt_3)_2]\ (VIII)^b +$$

$$[Pt(SnCl_3)_3(AsEt_3)]^- \xrightarrow{SnCl_2} [Pt(SnCl_3)_3(AsEt_3)]^-\ (IX)$$

[a] Solvent is CH_2Cl_2 in all cases. [b] Observed in solution.

a. Complexes Containing Two $P(OR)_3$ Ligands. Scheme I shows some typical reactions of $SnCl_2$ with *cis*-$[PtCl_2(P(OPh)_3)_2]$, from which *cis*-$[PtCl(SnCl_3)(P(OPh)_3)_2]$ (I), *trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$ (II), and the anion $[Pt(SnCl_3)_3(P(OPh)_3)_2]^-$ (III) can be prepared. Compounds related to III, e.g. with $P(OEt)_3$, can be precipitated by large cations, as described previously.[21] Our experience is that the five-coordinate complexes are frequently obtained in polar solvents such as methanol or acetone,[21] and specifically that *trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$ (II) is only obtainable in less polar solvents such as methylene chloride or chloroform.

Interestingly, reaction of the $[PtCl_2(SnCl_3)_2]^{2-}$ with *two* $P(OPh)_3$ ligands results in displacements of both $SnCl_3^-$ ligands (see Scheme I) whereas one phosphite ligand affords *cis*-$[PtCl_2(SnCl_3)(P(OPh)_3)]^-$. Best results for the poly(trichlorostannate) complexes were obtained starting from *cis*-$[PtCl_2(P(OPh)_3)_2]$.

Data for the analogous complexes with several $P(OR)_3$ ligands are shown in Table I, along with NMR results for the starting materials. Figure 1 shows a typical ^{119}Sn spectra. Note: (a) The multiplicity due to ^{31}P splitting defines the number of phoshorus ligands. This is important as many of these complexes are labile.[21] (b) The ^{195}Pt satellites are clearly observable, thereby assuring that we have coordinated $SnCl_3^-$. (c) The ^{117}Sn satellites are also visible, thus supporting the presence of more than one $SnCl_3^-$ ligand. The mono(trichlorostannate) complexes are mostly cis, with the exception of *trans*-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]$. The bis(trichlorostannate) derivatives all have the trans geometry, and the five-coordinate tris(trichlorostannate) compounds such as III are all sufficiently dynamic on the NMR time scale between −40 and −90 °C to prevent an assignment of their static structures. We note that $^2J(^{119}Sn,^{117}Sn)$ for the anion [Pt-

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(43) $\delta(^{119}Sn)$ for the $[PtCl_3(SnCl_3)]^{2-}$ dianion is at yet higher field, δ −596.

Table II. NMR Data[a] for the Monophosphine and -Arsine Complexes

L	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$\delta(^{195}Pt)$	$^1J(Pt,P)$	$^1J(Pt,Sn)$	$^2J(P,Sn)$
			cis-$[PtCl_2(SnCl_3)(L)]^-$			
PEt_3[b]	7.0	−340	−4359	3416	311 52	217
$PTol_3$[c]	8.6	−354	−4329	3734	304 44	197
$P(OEt)_3$[d]	70.7	−328	−4310	5577	314 00	149
$P(OPh)_3$[d]	63.6	−294	−4311	6077	295 85	130
$AsEt_3$[c]		−382	−4275		298 67	
$AsPh_3$[e]		−386	−4284		285 43	
			trans-$[PtCl(SnCl_3)_2(L)]^-$			
PEt_3[c,f]	9.0	−88	−4728	3235	240 85	196
$PTol_3$[g]	5.1	−114	−4617	3478	241 50	186
$AsEt_3$		−105	−4857		231 59	
$AsEt_3$[h]		−227	−4738		262 38	
		−38			164 64	
$AsPh_3$		−116			223 43	

complex	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$\delta(^{195}Pt)$	$^1J(Pt,P)$	$^1J(Pt,Sn)$	$^2J(P,Sn)$
$[Pt(SnCl_3)_3(AsEt_3)]^-$[i]		−25	−5510		208 12	
		−19			142 32	
$[Pt(SnCl_3)_4(PEt_3)]^{2-}$[j]	4.0	−83	−5633	2100	192 26	207
		−162			64 70	2405

[a] Chemical shifts and coupling constants are as in Table I. [b] Room temperature. [c] −20 °C. [d] 0 °C. [e] −40 °C. [f] $^2J(^{119}Sn,^{117}Sn)$ = 46 582 Hz. [g] −30 °C, $^2J(^{119}Sn,^{117}Sn)$ = 47 241 Hz. [h] Cis isomer. [i] $^2J(^{119}Sn,^{117}Sn)$ = 2100 Hz. [j] −90 °C, $^2J(^{119}Sn_{eq},^{117}Sn_{eq})$ = 159 55 Hz.

$(SnCl_3)_3(P(OPh)_3)_2]^-$ at 9480 Hz is considerably smaller than that found for $[Pt(SnCl_3)_3(P(OEt)_3)_2]^-$, 16 504 Hz, and suggest that the time-averaged structure for the former complex may differ from that containing the smaller phosphite ligands. This suggestion is also supported by the differences in $^1J(^{195}Pt,^{31}P)$, $^1J(^{195}Pt,^{119}Sn)$, and $\delta(^{119}Sn)$. The tris(trichlorostannate) complex with $P(OEt)_3$ has been isolated previously[21] as has the complex anion $[Pt(SnCl_3)_3(AsMe_3)_2]^-$ whose structure in the solid state is a trigonal bipyramid with axial arsine ligands.[24a]

Although there are large variations in the values $\delta(^{119}Sn)$, $\delta(^{195}Pt)$, $^1J(^{195}Pt,^{119}Sn)$, and $^2J(^{119}Sn,^{117}Sn)$ throughout the complexes I–III, the patterns follow those for the PEt_3 and $AsEt_3$ complexes described previously.[21] There is a minor point of interest concerning $^2J(^{119}Sn,^{31}P)_{trans}$. For the complexes *cis*-$[PtCl(SnCl_3)(P(OR)_3)_2]$ the observed values of 6497–6750 Hz are larger than those found in the tertiary phosphine analogoues, thereby making these the largest two-bond spin–spin coupling constants involving ^{31}P.

b. Complexes Containing One PR_3 or AsR_3 Ligand. Scheme II shows synthetic chemistry beginning from the trichloro anionic complexes $[PtCl_3L]^-$ (L = PEt_3, $AsEt_3$). The phosphine sequence involves the generation of the anions *cis*-$[PtCl_2(SnCl_3)(PEt_3)]^-$ (IV), *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ (V) (observed previously[29]), and the five-coordinate $[Pt(SnCl_3)_4(PEt_3)]^{2-}$ (VI). The complexes IV and VI have been isolated (see Experimental Section) and characterized as PPN^+ (and sometimes NEt_4^+) salts. Figure 2 shows the ^{119}Sn NMR spectrum of the $[PtCl(SnCl_3)_2(PTol_3)]^-$ anion. Once again the multiplicity data from $^2J(^{119}Sn,^{31}P)$, $^1J(^{195}Pt,^{119}Sn)$, and $^2J(^{119}Sn,^{117}Sn)$ are important for the proper characterization of this complex.

The relatively small value of $^2J(^{119}Sn,^{31}P)$, 186 Hz, and the very large $^2J(^{119}Sn,^{117}Sn)$, 47 241 Hz, place the Sn atoms in trans position to each other and cis to the phosphorus spin. $^1J(^{195}Pt,^{119}Sn)$ at 24 150 Hz is acceptable for $SnCl_3^-$ trans to $SnCl_3^-$. Interestingly, the tris(trichlorostannate) square-planar PEt_3 complex is not observed, perhaps due to the relative stability of the five-coordinate VI. However, for $AsEt_3$, the complex anion $[Pt(SnCl_3)_3(AsEt_3)]^-$ (IX) *is* formed, whereas we do not see the five-coordinate $[Pt(SnCl_3)_4(AsEt_3)]^{2-}$. Interestingly, there is a tendency to avoid PEt_3 trans to $SnCl_3^-$, but this is not so marked for $AsEt_3$. Note that addition of the third tin ligand gives a complicated equilibrium mixture that converts completely to the five-coordinate species when the fourth tin ligand is added.

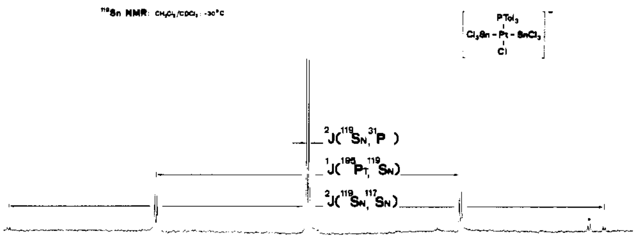
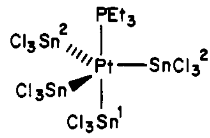


Figure 2. ^{119}Sn NMR spectrum of *trans*-$[PtCl(SnCl_3)_2(PTol_3)]^-$. The weak signals marked with an asterisk arise from *cis*-$[PtCl_2(SnCl_3)(PTol_3)]^-$; $\delta(^{119}Sn)$ = −114.

NMR data for these phosphine and arsine complexes are shown in Table II, and the ^{119}Sn NMR spectrum of VI, with



VI

the appropriate simulations, in Figure 3. This compound is noteworthy in that it represents one of the few cases for which we have obtained the limiting solution structure for a five-coordinate $SnCl_3^-$ complex. There are two types of ^{119}Sn in the ratio of 3 to 1: $\delta(Sn^1)$ −162, $^1J(^{195}Pt,^{119}Sn)$ = 6470 Hz, $^2J(^{119}Sn,^{31}P)$ = 2405 Hz; $\delta(Sn^2)$ −83, $^1J(^{195}Pt,^{119}Sn)$ = 19 226 Hz, $^2J(^{119}Sn,^{31}P)$ = 207 Hz. The axial ^{119}Sn resonance shows the large $^2J(^{119}Sn,^{31}P)$ value expected for a trans orientation of these spins (see above), and an analysis of the various remaining NMR parameters supports the assignment of a trigonal-bipyramidal structure to VI, with PEt_3 in an apical position (remember that there are *two* different $^2J(^{119}Sn,^{117}Sn)$ values for Sn^2_{cis} as well as a $^2J(^{119}Sn,^{119}Sn)$ coupling. Table II reveals a number of interesting features: (a) $^2J(^{119}Sn,^{117}Sn)$ values for the $[PtCl(SnCl_3)_2(PR_3)]^-$ anions (R = Et, Tol) at 46 582 and 47 241 Hz represent the largest known spin–spin coupling constants of any kind. (b) $^1J(^{195}Pt,^{119}Sn)$ varies ≃25 000 Hz from 6470 to 31 400 Hz. (c) The values $^1J(^{195}Pt,^{31}P)$ are normal (>3 khz) for P trans to Cl. (d) For the complexes *cis*-$[PtCl_2(SnCl_3)L]^-$ there is a cis effect on $\delta(^{119}Sn)$ amounting to 92 ppm. (e) $\delta(^{195}Pt)$ varies over 1358 ppm, with

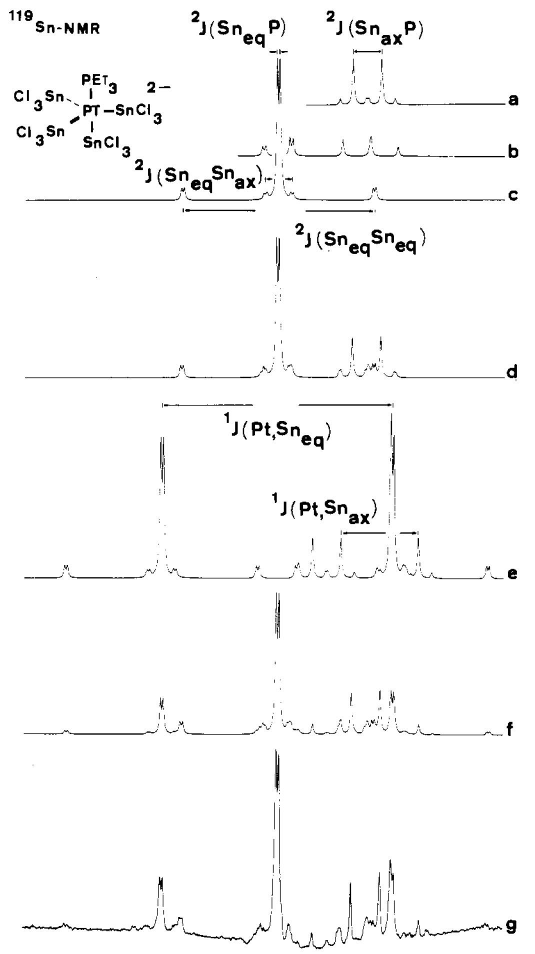


Figure 3. ^{119}Sn NMR spectrum of $(PPN)_2[Pt(SnCl_3)_4(PEt_3)]$ ($CDCl_3/CH_2Cl_2$, −90 °C). Spectrum g shows the experimental spectrum whereas simulations are shown in a–f: (a) ^{119}Sn axial, with one ^{117}Sn equatorial; (b) ^{119}Sn axial, with one ^{119}Sn equatorial; (c) ^{119}Sn equatorial with ^{117}Sn equatorial, plus ^{117}Sn axial; (d) sum of (a), (b), and (c) without ^{195}Pt; (e) calculation for 100% ^{195}Pt isotopomer; (f) complete simulation (33.7% ^{195}Pt).

resonances appearing at higher field than δ −5000.

Given point (a) we may now strengthen one NMR empiricism set out at the beginning. Specifically, $^2J(^{119}Sn,^{117}Sn)_{trans}$ will be routinely *very* large. This fact casts doubt on the recent assignment of a $^2J(^{119}Sn,^{117}Sn)$ value of ≃5800 Hz to the structure *trans*-$[PtCl(SnCl_3)_2(CO)]^-$.[29] Further, given (c), we question the decision[29] to assign the structure *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ to a compound having $^1J(^{195}Pt,^{31}P)$ = 2161 Hz (in acetone) in view of our value of 3235 Hz for the same complex ($CDCl_3/CH_2Cl_2$).

2. X-ray Structure of *trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$. A perspective view of the molecule is given in Figure 4, and a list of relevant interatomic distances can be found in Table III.

Due to the presence of a crystallographic inversion center, on which the Pt atom lies, only half of the molecule is crystallographically independent.

The complex has square-planar geometry, and the two $SnCl_3$ ligands are trans. There seem to be no pronounced distortions in the molecule, and the angles about platinum (P–Pt–Sn = 91.3 (1)°) are in the normal range for square-planar Pt(II) complexes. The $SnCl_3^-$ ligand shows Cl–Sn–Cl angles (average 99.5°) that are in agreement with those found in a number of transition-metal complexes.[37,40,44-54]

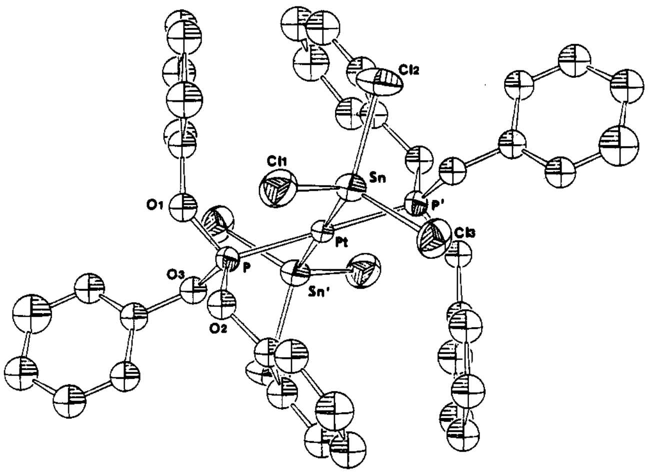


Figure 4. ORTEP view of the molecule *trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$ with numbering scheme.

Table III. Interatomic Distances (Å) and Bond Angles (deg) for $Pt(SnCl_3)_2(P(OPh)_3)_2$

	Distances		
Pt-Sn	2.599 (2)	P-O(2)	1.57 (1)
Pt-P	2.272 (3)	P-O(3)	1.64 (1)
Sn-Cl(1)	2.346 (6)	O(1)-C(13)	1.46 (1)
Sn-Cl(2)	2.332 (3)	O(2)-C(7)	1.43 (1)
Sn-Cl(3)	2.347 (4)	O(3)-C(1)	1.48 (1)
P-O(1)	1.60 (1)	⟨C-C⟩	1.40 (6)[a]
	Angles		
P-Pt-P	180.0	P-O(1)-C(1)	120.4 (8)
P-Pt-Sn	91.3 (1)	Cl(1)-Sn-Cl(2)	97.8 (2)
Pt-Sn-Cl(1)	121.5 (1)	Cl(1)-Sn-Cl(3)	98.2 (2)
Pt-Sn-Cl(2)	117.9 (2)	Cl(2)-Sn-Cl(3)	102.6 (2)
Pt-Sn-Cl(3)	115.1 (1)	O(1)-P-O(2)	108.4 (4)
Pt-P-O(1)	117.9 (2)	O(1)-P-O(3)	93.2 (6)
Pt-P-O(2)	109.5 (4)	O(2)-P-O(3)	108.0 (5)
Pt-P-O(3)	118.5 (2)	O(3)-C(13)-C(18)	108.0 (1.5)
P-O(3)-C(13)	120.8 (7)	O(2)-C(7)-C(8)	119.4 (9)
P-O(2)-C(7)	127.8 (7)	O(1)-C(1)-C(6)	116.6 (1.2)
	Internal Rotation Angles		
Pt-P-O(1)-C(1)	−39.0 (1.1)	P(1)-Pt-Sn-Cl(1)	1.5 (8)
Pt-P-O(2)-C(7)	−177.3 (1.0)	P(1)-Pt-Sn-Cl(2)	121.8 (9)
Pt-P-O(2)-C(13)	34.6 (1.0)	P(1)-Pt-Sn-Cl(3)	−116.7 (9)

[a] Average value (mean square deviation from the mean).

The platinum–tin separation of 2.599 (2) Å falls in the expected range although it lies at the high end of the reported M–Sn bond lengths in M–$SnCl_3$ complexes (2.35–2.64 Å). (Table IV shows a compilation of X-ray data for trichlorostannate complexes of group 8). For the square-planar complexes, the shortest Pt–Sn separations are associated with weaker ligands trans to $SnCl_3^-$, e.g., μ-Cl or Cl, whereas the longer distances are found for $SnCl_3^-$ trans to Pd (in $Pd_2Cl(SnCl_3)(Ph_2PCH_2PPh_2)_2$),[45] to the π-allyl carbon in $Pd(\eta^3\text{-}C_3H_5)(SnCl_3)(PPh_3)$,[46] or another $SnCl_3^-$. Many of the five-coordinate Ir(I) and Pt(II) compounds have relatively long M–Sn bonds.

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Table IV. Bond Separations (Å) in Some $SnCl_3^-$ Complexes[a]

no.	complex	⟨Mn–Sn⟩	⟨Sn–Cl⟩	ref
1	*cis*-$[PtCl_2(SnCl_3)_2]^{2-}$	2.355 (8)	2.352 (2), 2.787 (2)	37
2	$[PtCl(SnCl_3)(PEt_3)]_2$[c]	2.487 (3)	2.32 (2)	40
3	$PtCl(SnCl_3)(PhC(NH_2)=NOH)(PEt_3)$[b]	2.501 (1)	2.340 (3)	49
4	$[Pt(SnCl_3)_5]^{3-}$	2.553 (7)[g] 2.572 (10)[h]	2.347 (5) 2.372 (5)	38
5	*trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$	2.599 (2)	2.342 (4)	this work
6	$[Pt(SnCl_3)_3(AsMe_3)_2]^-$[d]	2.602 (2)	2.380 (7)	24
7	$Pd(SnCl_3)(\eta\text{-}C_3H_5)(PPh_3)_2$	2.56 (1)	2.38 (2)	46
8	$Pd_2Cl(SnCl_3)(Ph_2PCH_2PPh_2)$	2.585 (2)	2.394 (4)	45
9	$Ir(SnCl_3)(1,5\text{-}COD)_2$[e]	2.642 (2)	2.395 (10)	50
10	$Ir(SnCl_3)(NBD)(PMe_2Ph)_2$	2.587 (1)	2.406 (2)	51
11	$RuCH_3(SnCl_3)(\eta^6\text{-}C_6H_6)(Ph_2PNHCH(CH_3)Ph)$	2.543 (1)	2.372 (4)	53
12	$Ru_2Cl_3(SnCl_3)(CO)_5$	2.565 (4)	2.35 (1)	52
13	$RuCl(SnCl_3)(CO)(acetone)(PPh_3)_2$	2.594 (1)	2.374 (2)	54
14	$[RuCl(SnCl_3)_5]^{4-}$	2.553[f] (2) 2.579 (1)	2.367 (4) 2.393 (5)	36
15	$Au(SnCl_3)(PMe_2Ph)_2$	2.881 (1)	2.450	44

[a] Average values when there is more than one ⟨M–Sn⟩ and/or ⟨Sn–Cl⟩. [b] $SnCl_3$ trans to Cl. [c] Sym-trans. [d] Axial $AsMe_3$ ligands. [e] Pseudoequatorial $SnCl_3^-$. [f] Trans to Cl. [g] Axial. [h] Equatorial.

Interestingly, although the Pt–Sn bond length can vary by more than 0.1 Å, the corresponding Sn–Cl bond distances seem far less sensitive. Specifically, for *trans*-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$, $\langle Pt\text{–}Sn\rangle_{av} = 2.599$ (2) Å, with $\langle Sn\text{–}Cl\rangle_{av} = 2.342$ (4) Å, whereas for $[Pt(\mu\text{-}Cl)(SnCl_3)(PEt_3)]_2$, $\langle Pt\text{–}Sn\rangle_{av} = 2.482$ (3) Å and $\langle Sn\text{–}Cl\rangle_{av} = 2.32$ (2) Å. Nevertheless, these two bond separations do correlate roughly with one another to the extent that longer Pt–Sn distances (2.55–2.64 Å) are more often found together with longer Sn–Cl distances (see entries 1–4 vs. 5–14) in Table IV). This general trend is in keeping with the idea of incorporating more s character in the Sn–Cl bonds with increasing rehybridization at Sn, due to coordination. Note that the $SnCl_3^-$ anion in $Cs(SnCl_3)$[48] shows an average Sn–Cl bond of 2.52 Å, with the angle Cl–Sn–Cl = 89.8°, suggestive of extensive p character in these bonds. Rehybridization is expected to open the Cl–Sn–Cl angles while shortening the Sn–Cl bond lengths. In this context the structure of $Au(SnCl_3)(PMe_2Ph)_2$[44] is illustrative in that the very long Au–Sn interaction (2.881 (1) Å) is accompanied by a value of 2.450 (3) Å for $\langle Sn\text{–}Cl\rangle_{av}$.

The Pt–P distance at 2.272 (2) Å is long compared with the values of 2.182 (2) and 2.23 (3) Å found for *cis*-$[PtCl_2(P(OPh)_3)(PEt_3)]$[55] and $[Pt(SPEt_2)_2(P(OPh)_3]_2$.[56] The Pt(0) complexes $Pt(Sn(acac)_2)_2(P(OPh)_3)_2$[57] and $FePt_2(CO)_5(P(OPh)_3)_3$[58] have metal–phosphorus separations of 2.261 (4) and 2.223 (3) Å, respectively, although here $d\pi$–$d\pi$ back-bonding might contribute to shortening these values. Since there have been relatively few structures determined containing "$Pt(P(OPh)_3)$" units, it is difficult to comment further.

Both the two $SnCl_3^-$ and $P(OPh)_3$ groups are in a staggered configuration due to the centrosymmetry imposed on the molecule; their conformation with respect to the coordination plane is normal, as can be judged from the values of the relevant torsion angles reported in Table III. The packing in the cell is due to van der Waals interactions, and no short intermolecular contacts are present.

Discussion

The addition of the anions $[PtCl_2(SnCl_3)L]^-$, $[PtCl(SnCl_3)_2L]^-$, $[Pt(SnCl_3)_3(AsEt_3)]^-$, and $[Pt(SnCl_3)_4(PEt_3)]^{2-}$ to our list of stable compounds demonstrates that complexes with between one and five $SnCl_3^-$ ligands are all relatively stable. Moreover, it seems quite clear that the presence of $SnCl_3^-$ strongly promotes five-coordination in the chemistry of Pt(II). Although the overall chemistry is complicated by a number of equilibria, many of the species are readily identified.

Accepting the existence of these poly(trichlorostannate) complexes both in the solid state and in solution, we turn now to their possible relevance in homogeneously catalyzed reactions. The following facts require consideration:

1. For $PtCl_2P_2$ as cocatalyst, best results are obtained with a Sn/Pt ratio of 5 or more;[7] $PtCl_2P_2$ alone is not active.
2. For the hydroformylation with $PtCl_2(CO)(ER_3)$ as cocatalyst, a Sn/Pt ratio of ~2 is best.[28-31]
3. The $[Pt(SnCl_3)_5]^{3-}$ anion is an active hydrogenation catalyst as is $K_2[PtCl_4]$ and excess $SnCl_2$;[1] $K_2[PtCl_4]$ alone is not active.
4. The best yields of *trans*-$[PtH(SnCl_3)(P(p\text{-}XC_6H_4)_3)_2]$ (X = CH_3O, CH_3, H, F, Cl), a known catalyst, are obtained when $[PtCl_2(P(p\text{-}XC_6H_4)_3)_2]$ are treated with 2 equiv of $SnCl_2$ and molecular hydrogen.[20]
5. For the bis(triphenylphosphine)platinum(II) chloride system in nonpolar solvents (e.g., CH_2Cl_2, toluene), the hydroformylation catalyst is only moderately soluble and long induction periods are found,[1] but in highly polar solvents such as DMF, THF, and CH_3CN the catalysis is inhibited.
6. For the PPh_3 system of point 5, excess phosphine slows the reaction.[1]

We feel that all of these points are compatible with the presence of poly(trichlorostannate)—perhaps bis(trichlorostannate)—complexes during the *early* stages of the catalysis. The Pt–$SnCl_3$ complexes promote the activation of molecular hydrogen such that hydride complexes are formed. This does *not* mean that $SnCl_3^-$ must be involved in the rate-determining step in either the hydrogenation or hydroformylation reactions, although a ligand that readily stabilizes five-coordination and can also function as a good leaving group[28,31] might reduce the activation energies of certain subsequent steps.

The specific composition of the complex that activates the hydrogen, as well as the mechanism of the activation, remain unknown; however, it is tempting to think that a complex with a single phosphine such as $Pt(SnCl_3)_2(solvent)(PPh_3)$ might be involved. This *speculation* is supported by the following observations:

1. The complexes $PtCl(SnCl_3)(E(aryl)_3)_2$ are dynamic on the NMR time scale and in such a way as to involve exchange of $E(aryl)_3$. Specifically, a 1/1 mixture of $PtCl(SnCl_3)(PTol_3)_2$ and $PtCl(SnCl_3)(AsTol_3)_2$ affords the statistically expected

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amount of $PtCl(SnCl_3)(PTol_3)(AsTol_3)$;[21] therefore, loss of phosphine is possible.

2. In the presence of excess $SnCl_2$, we have observed tris(phosphine) complexes (eq 1 and 2). These are the readily

$$cis\text{-}[PtCl_2L^1{}_2] + 2SnCl_2 \xrightarrow[\text{reflux 1 h}]{CHCl_3} [PtClL^1{}_3]^+ + PtCl(SnCl_3)L^1{}_2 + ? \quad (1)$$

$$L^1 = P(p\text{-}ClC_6H_4)_3$$

$$cis\text{-}[PtCl_2L^2{}_2] + 10SnCl_2 \xrightarrow[\text{room temp}]{\text{acetone}} [PtClL^2{}_3]^+ + PtCl(SnCl_3)L^2{}_2 + [Pt(SnCl_3)_5]^{3-} \quad (2)$$

$$L^2 = P(p\text{-}CH_3OC_6H_4)_3$$

identified products, although NMR signals for additional complexes are observed. As in point 1 we take the presence of $[PtClL_3]^+$ to mean that phosphine dissociation takes place and that there are unobserved counterparts which are deficient in L.

3. We do not find the ligand exchange described in (1) and (2) for L = PEt_3 and $P(OR)_3$ and R = Et, *i*-Pr, Ph, and these Pt complexes are known to be poorer cocatalysts.

4. As mentioned above, excess phosphine slows the reaction. Indeed, $PtCl(SnCl_3)(P(p\text{-}CH_3OC_6H_4)_3)_2$ reacts with 1 equiv of $P(p\text{-}CH_3OC_6H_4)_3$ (eq 3) to give the tris(phosphine) cation.

$$cis/trans\text{-}[PtCl(SnCl_3)L^2{}_2] + L^2{}_2 \xrightarrow[CH_2Cl_2]{} [PtClL^2{}_3]^+ + SnCl_3^- \quad (3)$$

The implication of poly(trichlorostannate) complexes in homogeneous hydrogenation catalysts is not new.[8-16] Since the $[Pt(SnCl_3)_5]^{3-}$ anion is a catalyst, one or more of the $[PtCl_n(SnCl_3)_{5-n}]^{3-}$ anions can dissociate a ligand and the resulting coordinatively unsaturated complex activates H_2. We have recently characterized the 16-electron dianion $[Pt(SnCl_3)_4]^{2-}$ in solution, and a related hydride $[PtH(SnCl_3)_4]^{3-}$ is known.[13] Clearly, the substituion of phosphine or phosphite ligands for Cl is only a modification of the cocatalyst. Nevertheless, it might be useful to be able to specify which type of phosphine (phosphite) complex is most active, and further studies in this direction are in progress.

Experimental Section

NMR spectra were measured as $CDCl_3/CH_2Cl_2$ 1/2 solutions in 10-mm tubes using a Bruker WM-250 MHz spectrometer operating at 101.3, 93.3, and 53.8 MHz for ^{31}P, ^{119}Sn, and ^{195}Pt, respectively. See Tables I and II and ref 21 and 23 for further details. IR spectra were measured as KBr pellets using a Beckmann IR 4250 spectrometer.

Reagents. All the trichlorostannate complexes were prepared from the known $PtCl_2L_2$ and $[PtCl_3L]^-$ compounds. No precautions were taken with regard to the presence of either molecular oxygen or water. Both K_2PtCl_4 (Johnson-Matthey) and anhydrous $SnCl_2$ (Fluka AG, Buchs) were obtained commercially and used without further purification. PPN = bis(triphenylphosphine)nitrogen(1+) ion, $(PPh_3)_2N^+$. The following preparations are typical:

***cis*-{(PPN)[PtCl$_2$(SnCl$_3$)(PEt$_3$)]}. Method 1.** Solid tin(II) chloride (19 mg, 0.10 mmol) was added to a solution of $(PPN)[PtCl_3(PEt_3)]$ (96 mg, 0.10 mmol) in 3 mL of CH_2Cl_2. Stirring for 1 h was accompanied by a change in color such that the original yellow solution became orange and then a lighter yellow. Addition of 15 mL of ether precipitated the product, which was collected by filtration and further washed with ether; 106 mg (92%). Anal. Calcd for $C_{42}H_{45}Cl_5NP_3PtSn$: C, 43.95; H, 3.95; N, 1.22; Cl, 15.44. Found: C, 43.94; H, 3.96; N, 1.18; Cl, 15.45.

Method 2. Solid $(PPN)SnCl_3$ (77 mg, 0.10 mmol) was added to a solution of *sym-trans*-$[Pt_2Cl_4(PEt_3)_2]$ (39 mg, 0.050 mmol) in 5 mL of CH_2Cl_2. The orange solution became yellow, and after it was stirred for 0.5 h, the solution was filtered. The filtrate was covered with 15 mL of ether (such that the two layers do not mix) and the resultant mixture left to stand at −20 °C for 3 days. Decanting the filtrate followed by washing with ether affords the product as yellow crystals, 101 mg (88%).

The complexes $(Ph_4As)[PtCl_2(SnCl_3)(PTol_3)]$ and $(Ph_4P)[PtCl_2(SnCl_3)(AsEt_3)]$ were prepared in an identical fashion on a 0.1-mmol scale and gave 84% (99 mg) and 86% (85 mg) yields, respectively. Anal. Calcd for $C_{30}H_{35}AsCl_5PPtSn$: C, 36.30; H, 3.55; Cl, 17.86. Found: C, 35.56; H, 3.52; Cl, 17.71.

(Et$_4$N)$_2$[Pt(SnCl$_3$)$_4$(PEt$_3$)]. To a solution of *sym-trans*-$[Pt_2Cl_4(PEt_3)_2]$ (39 mg, 0.050 mmol) in 5 mL of CH_2Cl_2 was added first solid Et_4NCl (34 mg, 0.20 mmol) and then solid $SnCl_2$ (76 mg, 0.40 mmol). Stirring for 2 h was followed by filtration and careful treatment of the filtrate with 20 mL of ethylacetate such that the layers do not mix. Storing for 1 week at 0 °C is accompanied by the precipitation of orange needles. These were collected by filtration and washed with ether; 124 mg (84%). Anal. Calcd for $C_{22}H_{55}Cl_{12}N_2PPtSn_4$: C, 17.93; H, 3.76; N, 1.90. Found: C, 17.96; H, 3.67; N, 1.97.

The complex $(NEt_4)_2[Pt(SnCl_3)_4(PTol_3)]$ was prepared in a similar fashion on a 0.1-mmol scale; 87 mg (54%). Anal. Calcd for $C_{37}H_{61}Cl_{12}N_2PPtSn_4 \cdot 0.5CH_2Cl_2$: C, 26.45; H, 3.67; Cl, 27.07. Found: C, 26.51; H, 3.82; Cl, 27.38.

***trans*-[Pt(SnCl$_3$)$_2$(P(OPh)$_3$)$_2$].** A suspension of $PtCl_2(P(OPh)_3)_2$ (89 mg, 0.10 mmol) and $SnCl_2$ (38 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 was stirred for 2 h at room temperature, during which time the solids dissolved. Filtration was followed by covering with 10 mL of petroleum ether, 30–60 °C, and storing at −20 °C for 1 week. The crystalline product that precipitated became opaque when the solvent was removed. After drying under vacuum, 99 mg (78%) was obtained. Anal. Calcd for $C_{36}H_{30}Cl_6O_6P_2PtSn_2$: C, 34.16; H, 2.39; Cl, 16.81. Found: C, 34.05; H, 2.35; Cl, 16.89. The crystal used for the structure determination was kept in contact with solvent until shortly before data collection.

Solutions for NMR Spectroscopy. The solutions of the *trans*-$[PtCl(SnCl_3)_2L]^-$ and $[Pt(SnCl_3)_3L]^-$ anionic complexes were prepared by reaction of the correct number of equivalents of $SnCl_2$ with the appropriate chloroplatinum complex in 3 mL of $CDCl_3/CH_2Cl_2$. The mono(trichlorostannate) complexes PPN–*cis*-$[PtCl_2(SnCl_3)(P(OR)_3)]$ (R = Et, Ph) could be prepared by dropwise addition of 10 mL of 5×10^{-3} M ligand (CH_2Cl_2) to $(PPN)_2[PtCl_2(SnCl_3)_2]$ (90 mg, 0.050 mmol) in 20 mL of CH_2Cl_2 with vigorous stirring. Removal of the solvent in vacuo was followed by addition of 3 mL of $CDCl_3/CH_2Cl_2$ and immediate measurement. For R = Ph, the solution contains ≃80% *cis*-$[PtCl_2(SnCl_3(P(OPh)_3)]^-$, 10% $PtCl_2(P(OPh)_3)_2$, and 10% $[Pt(SnCl_3)_5]^{3-}$. For R = Et, the three components are found in the ratio 1/2/1 plus one part of unreacted *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ anion. Addition of a second eqivalent of $P(OR)_3$ leads to quantitative formation of *cis*-$[PtCl_2(P(OR)_3)_2]$.

Determination and Refinement of the Structure

Colorless crystals of $Pt(SnCl_3)_2(P(OPh)_3)_2$ were obtained by slow evaporation from a CH_2Cl_2/pentane solution and are air-stable.

A suitable crystal of prismatic habit was chosen for the data collection and mounted on a glass fiber at an arbitrary orientation. Crystal data are listed in Table V.

An Enraf-Nonius CAD4 computer-controlled diffractometer was used both for the determination of the lattice parameters and for the data collection (room temperature). From the systematic absences ($h00$, $h = 2n$; $k00$, $k = 2n$; $00l$, $l = 2n$; $h0l$, $h + l = 2n$) the space group was unambiguously determined as $P2_1/n$.

The cell parameters were obtained by a least-squares fit of the 2θ values of 25 higher order reflections ($20.0 \leq 2\theta \leq 30.0°$) by the centering routine installed on the CAD4/SDP system.[60] A group of three standard reflections (6,−1,−3; 2,−6,0; 4,6,−2) were measured every 2 h to check the stability of the experimental conditions and of the crystal. No significant variation was detected. An empirical absorption correction was applied by using azimuthal (Ψ) scans of two reflections at high-χ angle: 4,2,−1 and 8,4,−2. Transmission factors were in the range 0.74–0.98. The SDP system of programs[60] was used for both absorption correction and the data reduction.

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(60) "SDP Structure Determination Package—Users Manual"; Enraf-Nonius: Delft, Holland, 1975.

Table V. Crystal Data and Intensity Collection Parameters for $Pt[(SnCl_3)(PO_3C_{18}H_{15})]_2$

formula	$C_{36}H_{30}O_6P_2Cl_6PtSn_2$
fw	1265.77
cell parameters	
a	11.177 (1) Å
b	13.181 (2) Å
c	14.489 (3) Å
β	98.52 (1)°
V	2111.0 Å^3
Z	2
d_{calcd}	1.991 g cm^{-3}
space group	$P2_1/n$
cryst dimens	0.20 × 0.30 × 0.30 mm
radiation	Mo K$\bar{\alpha}$ (graphite monochromated; $\lambda = 0.71069$ Å)
abs coeff (μ)	50.19 cm^{-1}
θ range	$1.5 \leq \theta \leq 25.5°$
scan mode	$\omega/2\theta$
scan width	$(1.0 + 0.35 \tan \theta)°$
scan speed	4°/min
max scan time	30 s
total bkgd/scan time	0.5
receiving aperture (hor, mm)	2.0 tan θ
receiving aperture (vert, mm)	4.0
no. of data collcd	2192 ($\pm h, +k, +l$)
no. of obsd data ($I \geq 3\sigma(I)$)	1907
$R = \Sigma \lvert \Delta F \rvert / \Sigma \lvert F_o \rvert$	0.063 (0.069 with unobsd reflcns included)
$R_w = (\Sigma \lvert \Delta F \rvert / \Sigma w \lvert F_o \rvert^2)^{1/2}$	0.076

Table VI. Final Positional Parameters

atom	*x/a*	*y/b*	*z/c*
Pt	0.0	0.0	0.0
Sn	−0.07111 (7)	0.04651 (6)	0.15753 (11)
Cl(1)	−0.05886 (34)	−0.07024 (28)	0.28080 (50)
Cl(2)	−0.27265 (28)	0.09389 (34)	0.15473 (52)
Cl(3)	0.03408 (34)	0.18050 (26)	0.23987 (46)
P	0.05805 (23)	−0.15702 (18)	0.05373 (40)
O(1)	0.15276 (65)	−0.16491 (54)	0.15143 (92)
O(2)	0.11432 (61)	−0.21628 (51)	−0.02348 (88)
O(3)	−0.03995 (61)	−0.22840 (47)	0.09129 (90)
C(1)	0.2479 (9)	−0.0884 (7)	0.1746 (15)
C(2)	0.3241 (10)	−0.0664 (8)	0.1068 (16)
C(3)	0.4164 (15)	−0.0049 (9)	0.1366 (21)
C(4)	0.4374 (13)	0.0385 (11)	0.2285 (18)
C(5)	0.3654 (15)	0.0172 (12)	0.2856 (20)
C(6)	0.2597 (12)	−0.0503 (10)	0.2646 (17)
C(7)	0.1664 (9)	−0.3155 (8)	−0.0174 (14)
C(8)	0.2858 (10)	−0.3299 (8)	0.0308 (18)
C(9)	0.3343 (11)	−0.4219 (9)	0.0309 (16)
C(10)	0.2755 (13)	−0.5048 (9)	−0.0219 (18)
C(11)	0.1588 (17)	−0.4886 (12)	−0.0611 (20)
C(12)	0.1069 (11)	−0.3927 (8)	−0.0672 (15)
C(13)	−0.1666 (9)	−0.2306 (7)	0.0433 (14)
C(14)	−0.1921 (12)	−0.2368 (9)	−0.0436 (16)
C(15)	−0.3224 (12)	−0.2396 (9)	−0.0858 (16)
C(16)	−0.4051 (12)	−0.2328 (9)	−0.0216 (16)
C(17)	−0.3681 (12)	−0.2228 (9)	0.0740 (16)
C(18)	−0.2470 (13)	−0.2238 (10)	0.1060 (17)

Structure factors were calculated in the usual way (Lp corrections applied) on the assumption of ideally imperfect monochromatization. The standard deviations on the intensities were calculated in terms of statistics alone, considering as observed the reflections having $I_{net} \geq 3\sigma(I)$. There are two independent molecules in the unit cell ($Z = 2$), each molecule being on a crystallographic inversion center.

The structure was solved by standard Patterson and Fourièr methods and refined by block-diagonal least squares (the function minimized is $\sum w(|F_o| - (^1/_k)|F_c|)^2$ with w obtained from a Cruickshank[61] weighting scheme).

Anisotropic temperature factors were used for Pt, P, Cl, and Sn atoms and isotropic factors for the others. The hydrogen atoms were placed at their ideal calculated positions (C–H = 1.08 Å)[62] and assigned isotropic temperature factors $B = 5.5$ Å^2; during the final least-squares cycles their contribution was taken into account but not refined. No extinction correction was deemed necessary.

The scattering factors were taken from the literature,[63] and a correction for the real part of the anomalous scattering was taken into account for the Pt, Sn, and Cl atoms.

Upon convergence (no shifts greater than 0.5σ) the conventional agreement factor was 0.064 (cf. Table V); a final difference Fourier map showed no significant features.

All the calculations were performed on a UNIVAC 1100 using a local version of the structure factors, Fourier, least-squares, and bond angles calculations; the drawing was made by using the ORTEP program,[64] with thermal ellipsoids drawn at 50% probability.

Acknowledgment. H.R. thanks the ETH for support, and we thank the Johnson-Matthey Research Center for the loan of platinum metals.

Registry No. I, 67619-55-0; II, 67619-56-1; III, 91409-79-9; (PPN)(IV), 91409-81-3; V, 83719-71-5; $(NEt_4)_2$(VI), 91409-83-5; (Ph_4P)(VII), 91409-85-7; *trans*-VIII, 91423-95-9; *cis*-VIII, 91409-96-0; IX, 91409-86-8; *sym-trans*-$[Pt_2Cl_4(PEt_3)_2]$, 17522-94-0; *sym-trans*-$[Pt_2Cl_4(PTol_3)_2]$, 86322-36-3; *sym-trans*-$[Pt_2Cl_4(AsEt_3)_2]$, 17522-98-4; $(Ph_4As)[PtCl_2(SnCl_3)(PTol_3)_2]$, 91409-88-0; $(NEt_4)_2[Pt(SnCl_3)_4(PTol_3)]$, 91409-90-4; (PPN)-*cis*-$[PtCl_2(SnCl_3)(P(OEt)_3)]$, 91409-92-6; (PPN)-*cis*-$[PtCl_2(SnCl_3)(P(OPh)_3)]$, 91409-94-8; *cis*-$[PtCl_2(P(OMe)_3)_2]$, 28374-51-8; *cis*-$[PtCl_2(P(OEt)_3)_2]$, 15390-95-1; *cis*-$[PtCl_2(P(O\text{-}i\text{-}Pr)_3)_2]$, 70191-35-4; *cis*-$[PtCl(SnCl_3)(P(OEt)_3)_2]$, 91464-44-7; *cis*-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]$, 91464-45-8; *trans*-$[PtCl(SnCl_3)(P(O\text{-}i\text{-}Pr)_3)_2]$, 91464-46-9; *trans*-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$, 67619-54-9; *trans*-$[Pt(SnCl_3)_2(P(O\text{-}i\text{-}Pr)_3)_2]$, 74153-68-7; $[Pt(SnCl_3)_3(P(OMe)_3)_2]^-$, 91409-97-1; $[Pt(SnCl_3)_3(P(OEt)_3)_2]^-$, 83161-36-8; *cis*-$[PtCl_2(SnCl_3)(AsPh_3)]^-$, 91409-98-2; *trans*-$[PtCl(SnCl_3)_2(PTol_3)]^-$, 91423-96-0; *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$, 48055-16-9; *cis*-$[PtCl_2(P(OPh)_3)_2]$, 30053-58-8; $(PPN)[PtCl_3(PEt_3)]$, 91409-95-9; $Pt_2Cl_2(SnCl_3)_2(PEt_3)_2$, 83719-68-0; $[PtCl_3(AsEt_3)]^-$, 44968-34-5.

Supplementary Material Available: Listings of calculated and observed structure factors (Table S1) and positional and thermal parameters (Tables S2 and S3) (11 pages). Ordering information is given on any current masthead page.

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(61) Cruickshank, D. W. J. In "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970.

(62) A reviewer has suggested that a C–H value of 0.95 Å is preferable. Using this value we find no significant differences in the results.

(63) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(64) Johnson, C. K. "ORTEP, A Fortran Thermal Ellipsoid Program for Crystal Structure Illustrations", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.