1 (L = $P(OPh)_3$), 75030-86-3; **1** (L = $P(O\text{-}o\text{-}MeC_6H_4)_3$), 88229-58-7; **1** (L = $PPh_2(o\text{-}MeOC_6H_4)$), 88229-59-8; $P(OCH_2)_3CEt$, 824-11-3; $P(OEt)_3$, 122-52-1; $P(OMe)_2Ph$, 2946-61-4; PMe_2Ph, 672-66-2; $P(n\text{-}Bu)_3$, 998-40-3; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; CO, 630-08-0.

Supplementary Material Available: Measured rate constants for $Ru(CO)_3(L)(SiCl_3)_2$ compounds (Table SI) and infrared (Table SII) and analytical (Table SIII) data for new complexes of the type *mer*-$Ru(CO)_3(L)(SiCl_3)_2$ (9 pages). Ordering information is given on any current masthead page.

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A Multinuclear NMR Investigation of Stannous Chloride Promoted Ligand Exchange of Platinum Phosphole Complexes

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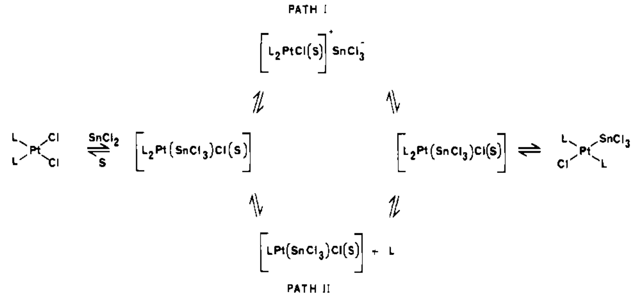
A thorough investigation by $^{31}P\{^1H\}$, ^{119}Sn, and $^{195}Pt\{^1H\}$ NMR spectroscopy of solutions containing dichlorobis(1-R-3,4-dimethylphosphole)platinum(II) (L_2PtCl_2) and $SnCl_2$ under a variety of conditions [various solvents, substituents (R = CH_3, $n\text{-}C_4H_9$, $t\text{-}C_4H_9$, C_6H_5, and $C_6H_5CH_2$), stoichiometries, times, and temperatures] demonstrated that the addition of solid anhydrous $SnCl_2$ to solutions of the phosphole complexes labilizes these phosphole complexes toward complete ligand exchange producing several species in solution. These include *cis*- and *trans*-$L_2Pt(SnCl_3)Cl$, *trans*-$L_2Pt(SnCl_3)_2$, *cis*-L_2PtCl_2, and, surprisingly, the pentacoordinate species L_3PtCl_2. The L_3PtCl_2 species are significant as their presence demonstrates that addition of a chloride acceptor ($SnCl_2$) to a solution of a noble-metal complex not only labilizes the metal–chloride bond as anticipated but also labilizes the other metal–ligand bonds as well.

Introduction

The interaction of platinum chlorides with stannous chloride has a long and interesting history.[2] As early as 1907, Wohler[3] noted the intense colors of these solutions and this later served as a basis for the analytical determination of platinum.[4] The exact nature of all the species responsible for the colors of these solutions remains in some doubt, but we have recently shown by ^{119}Sn and ^{195}Pt NMR spectroscopy and X-ray crystallography that one yellow species is[5,6] *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and a deep red species is[5,7] $[Pt(SnCl_3)_5]^{3-}$. Our efforts in this area were aided greatly by the seminal NMR investigations of Pidcock[8] and Pregosin.[9]

The original NMR investigations were prompted by several observations. Stannous chloride catalyzes the formation of analogues to Zeise's salt, $[PtCl_3(RCH{=}CH_2)]^-$, from $PtCl_4^{2-}$ and alkenes.[10,11] Stannous chloride combined with either $PtCl_6^{2-}$ or $(R_3P)_2PtCl_2$ becomes an efficient homogeneous catalyst for hydrogenation and isomerization of alkenes and alkynes,[12] including asymmetric hydrogenation.[13] These same mixtures have also been found to be good catalysts for hydroformylation,[14] carboalkoxylation,[15] and the water gas shift reaction.[16]

Scheme I



While the catalytic mechanisms are still being actively investigated,[17] the work to date clearly establishes that the in-

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Table I. ^{31}P, ^{119}Sn, and ^{195}Pt NMR Data for (1-R-3,4-dimethylphosphole)$_2$Pt(SnCl$_3$)$_n$Cl$_{2-n}$ Complexes in CH$_2$Cl$_2$ at 223 K

R	*n*	geometry	$^{31}P^a$	$^{119}Sn^a$	$^{195}Pt^a$	$^1J_{PtP}$	$^2J_{SnP}{}^b$	$^1J_{PtSn}$
CH_3	1	trans	−2.0	−357	−4940	1875	255	NO[c]
CH_3	2	trans	−20.1	−96	−5442	1481	286	20 312
n-C_4H_9	1	trans	−7.9	−357	NO	1492	291, 278	NO
n-C_4H_9	2	trans	−9.2	−96	−5463	1482	286, 273	NO
t-C_4H_9	1	trans	36.5	−484	−5006	2041	232, 222	28 259, 27 016
t-C_4H_9	1	cis[d]	39.2 (Cl)	−296	−4885	3252 (Cl)	250 (Cl)	
			31.8 (Sn)			2778 (Sn)	3875 (Sn)	25 714
t-C_4H_9	2	trans	28.3	−349	−5470	1912	244	22 778
C_6H_5	1	trans	8.5	−316	−4775	1927	246	24 488
C_6H_5	2	trans	−3.2	−134	−5436	1628	256	21 680, 20 727
$C_6H_5CH_2$	1	trans	−7.3	NA[e]	−5312	1858	256	NO
$C_6H_5CH_2$	2	trans	−11.2	−103	−5480	1494	281	NO

[a] ^{31}P, ^{119}Sn, and ^{119}Pt relative to external 85% H_3PO_4, Me_4Sn, and H_2PtCl_2, respectively, with downfield shifts positive in ppm and *J* values in Hz. [b] Where only one value is given, it is the average of $^2J_{^{117}SnP}$ and $^2J_{^{119}SnP}$, which were not resolved. [c] NO = not observed. [d] $^2J_{PP}$ = 15 Hz. [e] NA = not available.

teraction of the platinum–chloride bond with stannous chloride forms a Pt–SnCl$_3$ moiety containing a platinum–tin bond by a mechanism yet to be fully elucidated.[9] Since a vacant coordination site has been suggested by Collman as "the single most important property of a homogeneous catalyst",[18] it has been proposed that SnCl$_2$ promotes catalysis by platinum complexes by the sequence of reactions in (1)[17] (see also Scheme I, path I).[19]

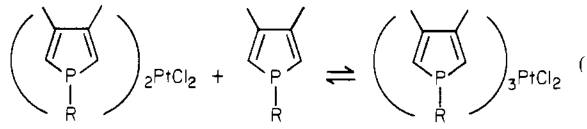
$$\text{Pt–Cl} + \text{SnCl}_2 \rightleftharpoons \text{Pt–SnCl}_3 \rightleftharpoons \text{Pt}^+ + \text{SnCl}_3^- \qquad (1)$$

(other supporting ligands omitted for clarity)

However, several studies have shown that the SnCl$_3^-$ ligand has both a high trans effect and a high trans influence by virtue of its weak σ-donor and high π-acceptor properties.[17] If this is the case, then coordinately unsaturated species could be formed by the equilibria[20] shown in Scheme I, path II, which has gained some experimental support.[21]

Further, we note that, in general, the reaction of *cis*-(R$_3$P)$_2$PtCl$_2$ with SnCl$_2$ immediately produces a mixture of *trans*-(R$_3$P)$_2$Pt(SnCl$_3$)Cl and *trans*-(R$_3$P)$_2$Pt(SnCl$_3$)$_2$ containing only minor amounts of *cis*-(R$_3$P)$_2$Pt(SnCl$_3$)Cl for most phosphines studied.[9,22] This requires a rapid geometrical isomerization at the platinum center that could proceed by either consecutive anionic or neutral ligand displacement mechanisms or both.[23] Unlike the (R$_3$P)$_2$PdCl$_2$ complexes, which spontaneously isomerize, isomerization of the more inert (R$_3$P)$_2$PtCl$_2$ requires either catalysis by excess phosphine or photolysis.[24]

If the equilibria illustrated in Scheme I, path II, occur, then phosphine, L, would be liberated. Our observation[24] that, in the dichlorobis(phosphole)platinum systems, pentacoordinate species of the formula L$_3$PtCl$_2$ were thermodynamically favored and rapidly formed (reaction 2) led us to investigate the



(2)

reaction of platinum phosphole complexes with SnCl$_2$. Reaction of SnCl$_2$ to form solvo species and consequently liberate free phosphole would then be expected to lead to the formation of stable pentacoordinate species observable by ^{31}P NMR spectroscopy.

Due to the marked dependence[12-17] of platinum–tin catalyst' efficiency and selectivity upon solvent, stoichiometry, and temperature, these variables were also studied.

Experimental Section

The dichlorobis(1-R-3,4-dimethylphosphole)platinum(II) complexes were prepared as previously reported.[24] To 10 mL of an approximately 0.1 M solution of the phosphole complex (~500 mg) was added a weighed quantity of commercial (Alpha) anhydrous SnCl$_2$ under nitrogen. The resultant heterogeneous mixture was stirred magnetically for 1 h. The volume was then reduced to approximately 5 mL with flowing nitrogen, and the resultant yellow, orange, or red solution was filtered under nitrogen directly into a 10-mm NMR tube. Generally less than 10 mg of insoluble material was removed by filtration. See Table II for further details. The tube was then sealed with Teflon tape to minimize exposure to atmospheric moisture. The $^{31}P\{^1H\}$, ^{119}Sn, and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 40.26, 37.10, and 21.28 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode with ^7Li external lock. The chemical shifts were measured relative to external 85% H$_3$PO$_4$, Me$_4$Sn, and H$_2$PtCl$_6$ with shifts to low field (high frequency) positive. The spectra were obtained with 50-kHz (^{119}Sn, ^{195}Pt) or 10-kHz (^{31}P) spectral widths by using 8K data points resulting in 1 ppm (^{119}Sn, ^{195}Pt) or 0.2 ppm (^{31}P) chemical shift accuracies. Coupling constants are belived accurate to 3 Hz (^{31}P spectra) or 12 Hz (^{119}Sn, ^{195}Pt spectra). The species present in these solutions were identified by comparison of the NMR parameters (Table I) to those of known compounds[8,9,24] and quantified (Table II) by integration of their ^{31}P resonances. The quantities are believed to be accurate to within 5%. Variable-temperature spectra were measured by using a commercially available temperature regulator (1 °C) and temperatures were monitored with both an alcohol thermometer and a thermocouple inserted directly into the probe.

Results and Discussion

When solid SnCl$_2$ is added to a very pale yellow solution of a dichlorobis(1-R-3,4-dimethylphosphole)platinum(II) complex, the SnCl$_2$ slowly dissolves to produce an orange (Sn/Pt = 1) or deep red (Sn/Pt = 2) solution. The $^{31}P\{^1H\}$ NMR spectra for these solutions at 300 K have very narrow

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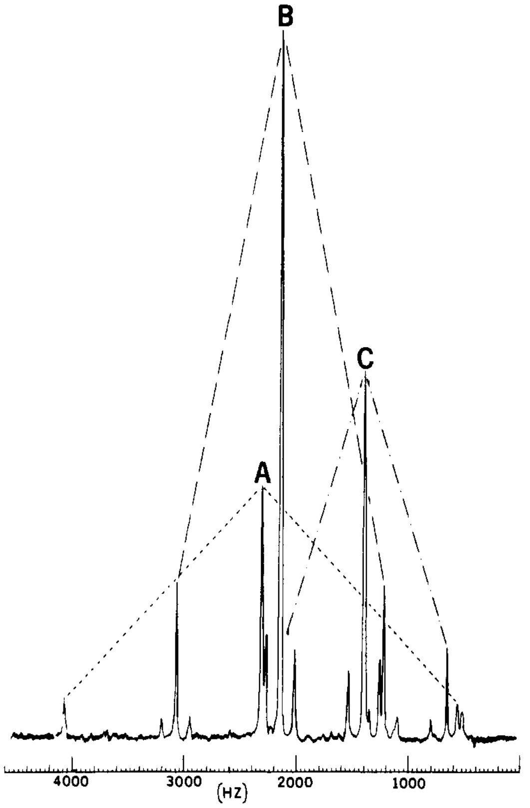

Figure 1. 40.26-MHz $^{31}P\{^1H\}$ NMR spectrum of (A) *cis*-L_2PtCl_2, (B) *trans*-$L_2Pt(SnCl_3)Cl$, and (C) *trans*-$L_2Pt(SnCl_3)_2$ in CH_2Cl_2 at 223 K. The solution was prepared by adding 2 equiv of anhydrous $SnCl_2$ to 1 equiv of *cis*-L_2PtCl_2. L = 1-benzyl-3,4-dimethylphosphole.

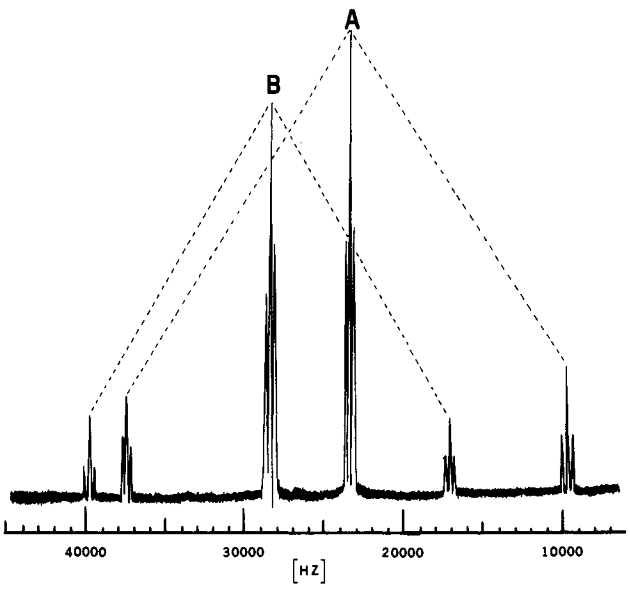

Figure 2. 37.10-MHz ^{119}Sn NMR spectrum of *cis*-L_2PtCl_2 plus $SnCl_2$ in CH_2Cl_2 at 223 K: (A) *trans*-$L_2Pt(SnCl_3)Cl$; (B) *trans*-$L_2Pt(SnCl_3)_2$. L = 1-*tert*-butyl-3,4-dimethylphosphole. By $^{31}P\{^1H\}$ NMR this solution contains 70% A and 30% B. The ^{195}Pt "satellites" are connected to their respective central resonances by dotted lines. The solution was prepared by adding 2 equiv of anhydrous $SnCl_2$ to 1 equiv of the platinum complex.

line widths and exhibit platinum–phosphorus coupling, but do not exhibit phosphorus–tin coupling. This suggests that tin exchange is occurring faster than the increase in magnitude of the phosphorus–tin coupling constant (214–286 Hz, Table I) at this temperature. Lowering the temperature of these solutions to 223 K deepens their color, and the $^{31}P\{^1H\}$ NMR spectra become well-resolved multiplets exhibiting phosphorus–tin coupling. Similar temperature dependence of phosphorus–tin coupling has previously been observed,[25] for both $(Et_3P)_2Pt(SnCl_3)Cl$ and $(Et_3P)_2Pt(SnCl_3)_2$ in acetone. It has also been noted that $[Pt(Ph_3P)_2(SnCl_3)Cl]$ rapidly decomposes into $(Ph_3P)_2PtCl_2$ in acetone.[26] These results all imply that equilibria 1 occur fast on the NMR time scale in these solutions at 300 K. The observation of platinum–phosphorus spin correlation throughout the entire temperature range (203–323 K) suggests that phosphorus exchange occurs more slowly than tin exchange. A typical $^{31}P\{^1H\}$ NMR spectrum at 223 K is illustrated in Figure 1. The nature of the species present in these solutions is readily discerned by multinuclear NMR spectroscopy. The nuclei of interest include[27] ^{31}P ($I = {}^1/_2$, 100% abundance), ^{119}Sn ($I = {}^1/_2$, 8.58% abundance), ^{117}Sn ($I = {}^1/_2$, 7.61% abundance), and ^{195}Pt ($I = {}^1/_2$, 33.8% abundance). The $^{31}P\{^1H\}$ NMR spectra of the starting L_2PtCl_2 complexes[24] display singlets due to 66.2% of the phosphorus nuclei coordinated to platinum nuclei other than ^{195}Pt, with a superimposed doublet from the remaining 33.8% of the phosphorus nuclei coupled to ^{195}Pt. The three lines labeled A in Figure 1 are exemplary of the 1:4:1 "pseudotriplets" typical of these species. The ^{195}Pt NMR spectra of L_2PtCl_2 show straightforward first-order 1:2:1 triplets (see A of Figure 4). From both the $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ $^1J_{PtP}$ can be obtained, and its value (~3300 Hz) indicates that these complexes have the cis geometry.[24] Aside from a temperature-dependent chemical shift change, the resonances associated with *cis*-L_2PtCl_2 are unaffected by the presence of $SnCl_2$. However, new resonances are observed in the $^{31}P\{^1H\}$, ^{119}Sn and $^{195}Pt\{^1H\}$ NMR of solutions containing cis-L_2PtCl_2 and $SnCl_2$. The species *trans*-$L_2Pt(SnCl_3)Cl$ (labeled B in Figure 1) are characterized by ^{31}P resonances that are generally found upfield of those for *cis*-L_2PtCl_2 (see Table I). These resonances are flanked by both ^{195}Pt and ^{119}Sn satellites whose intensities[28] should be respectively 25.5% and 4.7% of the central resonance. If, however, the ^{117}Sn satellites are not resolved from the ^{119}Sn satellites (as in Figure 1), then these combined (^{117}Sn + ^{119}Sn) satellite intensites will represent 10.3% of the central line.[29] The $L_2Pt(SnCl_3)Cl$ complexes are also characterized by the magnitudes of the respective coupling constants with typical values being $^1J_{PtP} \approx 1800$ Hz and $^2J_{SnP} \approx 250$ Hz. Likewise, the ^{195}Pt chemical shift of $L_2Pt(SnCl_3)Cl$ is 500–1100 ppm upfield of that of L_2PtCl_2. In both the ^{119}Sn (Figure 2) and ^{195}Pt NMR, $^1J_{PtSn}$, when observed, is found to exceed 20 kHz, which is typical of a Pt–Sn bond.[5-9] The NMR spectral parameters of the $L_2Pt(SnCl_3)_2$, complexes (Table I) are similar to those of $L_2Pt(SnCl_3)Cl$ complexes. Both ^{31}P and ^{195}Pt resonances for $L_2Pt(SnCl_3)_2$ appear upfield of the $L_2Pt(SnCl_3)Cl$ resonances, but the converse is true for ^{119}Sn NMR (see Figure 2). In general, $^1J_{PtP}$ is 300–500 Hz less for $L_2Pt(SnCl_3)_2$ than for $L_2Pt(SnCl_3)Cl$, suggesting that the platinum–phosphorus bond may weaken as additional platinum–tin bonds are formed.[8,30] The ^{119}Sn satellites in the ^{31}P

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Table II. Speciation of Reaction Mixtures of *cis*-(1-R-3,4-dimethylphosphole)$_2$PtCl$_2$ Complexes with SnCl$_2$

			product compn, %[a]				
R	Sn/Pt	solvent system	*cis*-L$_2$Pt-(SnCl$_3$)Cl	*trans*-L$_2$Pt-(SnCl$_3$)Cl	*trans*-L$_2$Pt-(SnCl$_3$)$_2$	L$_3$PtCl$_2$	*cis*-L$_2$PtCl$_2$
CH$_3$	1	CH$_2$Cl$_2$		22			78
CH$_3$	1	acetone		64			36
CH$_3$	1	heated in acetone		27		9[b]	58
CH$_3$	2	CH$_2$Cl$_2$		63	37		
CH$_3$	2	30% acetone/70% CH$_2$Cl$_2$		17	83		
CH$_3$	2	10% CH$_3$OH/90% CH$_2$Cl$_2$		2	98		
n-C$_4$H$_9$	1	CH$_2$Cl$_2$		27			73
n-C$_4$H$_9$	1	acetone		57			43
n-C$_4$H$_9$	2	CH$_2$Cl$_2$		46	54		
n-C$_4$H$_9$	2	30% acetone/70% CH$_2$Cl$_2$			98		2
t-C$_4$H$_9$	1	CH$_2$Cl$_2$		98			2
t-C$_4$H$_9$	1	CDCl$_3$		66			34
t-C$_4$H$_9$	2	CH$_2$Cl$_2$		70	30		
t-C$_4$H$_9$	2	acetone		9		60	
t-C$_4$H$_9$	2	heated in acetone		98			2
t-C$_4$H$_9$	2	30% acetone/70% CH$_2$Cl$_2$	27	48		9	12
t-C$_4$H$_9$	2	10% CH$_3$OH/90% CH$_2$Cl$_2$	16	28			56
C$_6$H$_5$	1	CH$_2$Cl$_2$		98		1	1
C$_6$H$_5$	1	heated in acetone		19		22	49
C$_6$H$_5$	2	CH$_2$Cl$_2$ fresh		87			13
		aged 1 day		36		31	18
		aged 2 days		36		31	18
		aged 1 week		47		35	
C$_6$H$_5$	2	30% acetone/70% CH$_2$Cl$_2$			14	57	
C$_6$H$_5$	2	heated in acetone			18	55	
C$_6$H$_5$CH$_2$	1	CH$_2$Cl$_2$		25	20		55
C$_6$H$_5$CH$_2$	1	aged 1 week in CH$_2$Cl$_2$		51	29		20
C$_6$H$_5$CH$_2$	1	heated in acetone		9	36	19	26
C$_6$H$_5$CH$_2$	1	30% CDCl$_3$/70% acetone			30		70
C$_6$H$_5$CH$_2$	2	aged 1 week in CH$_2$Cl$_2$			98		2
C$_6$H$_5$CH$_2$	2	30% acetone/70% CH$_2$Cl$_2$		86			14
C$_6$H$_5$CH$_2$	2	10% CH$_3$OH/90% CH$_2$Cl$_2$			98		2

[a] ±5% from integration of ^{31}P{^{1}H} spectra. [b] Percentage of unknown platinum-containing species assumed to be equal to half the percentage of L$_3$PtCl$_2$; see text for discussion.

NMR spectra of L$_2$Pt(SnCl$_3$)$_2$ complexes represent 9% (20% if ^{117}Sn and ^{119}Sn satellites overlap) of the central resonance (see Figure 1), and consequently, the satellite intensity gives a strong indication of the number of tin atoms bound to platinum.[9] For the *cis*-L$_2$Pt(SnCl$_3$)Cl complex, the ^{31}P NMR spectrum is an AX doublet of doublets (with associated satellites) having one ^{31}P chemical shift quite close to that of *cis*-L$_2$PtCl$_2$ and one considerably upfield. The small value of $^2J_{PP}$ = 15 Hz places[24] the two phospholes mutually cis. The chemical shifts may be assigned to the phosphole trans to tin ($\delta(^{31}P)$ = 31.8 ppm, $^2J_{SnP}$ = 3875 Hz) and trans to chloride ($\delta(^{31}P)$ = 39.2 ppm, $^2J_{SnP}$ = 250 Hz) on the basis of the magnitude of the Sn–P coupling constants. It is interesting to note[8] that $^1J_{PtP}$ is also a function of whether the phosphole is trans to tin ($^1J_{PtP}$ = 2778 Hz) or trans to chloride ($^1J_{PtP}$ = 3252 Hz). The latter value is only slightly smaller than $^1J_{PtP}$ observed for the analogous L$_2$PtCl$_2$ complex (3306 Hz). On the basis of both the ^{31}P chemical shifts and the Pt–P coupling constants, it appears that the Pt–P bond trans to tin is weaker than the Pt–P bond trans to chloride, in concert with SnCl$_3^-$ having a higher trans influence than chloride. Both the geometry and stoichiometry of the species present in these solutions are readily ascertained from the combined ^{31}P, ^{119}Sn, and ^{195}Pt NMR data. Pertinent NMR parameters are listed in Table I.

With this knowledge, it is possible to investigate the influence of time, solvent, stoichiometry, and temperature on the concentration of the various species in solution. The most obvious observation is that with these heterogeneous reactions (SnCl$_2$ is not very soluble in halocarbons) equilibrium is approached very slowly. With increasing time or with solvents that better dissolve SnCl$_2$ (methanol or acetone), the quantity of the SnCl$_3^-$ complexes increases (Table II). The quantity of the SnCl$_3^-$ complexes is not a simple function of either the basicity or steric bulk of the phosphole, but this may simply be a result of nonequilibrium measurements. The data do suggest that the Pt–SnCl$_3$ complexes are formed rather quickly when the SnCl$_2$ is in fact in solution and that they are thermodynamically more stable in solution than the chloride complexes from which they are formed. Attempts to grow crystals of the platinum–tin complexes by slow evaporation of solvent consistently resulted[31] in the isolation of the less soluble starting L$_2$PtCl$_2$ complexes.

When, however, an attempt was made to hasten the formation of the Pt–SnCl$_3$ complexes by either heating the solutions or using a solvent system that dissolved all the SnCl$_2$, a marked darkening of the solution to deep red, typical of L$_3$PtCl$_2$, occurred and the NMR spectra became broad and unresolved at 300 K. Cooling these solutions gave sharp, well-defined multiplets at 223 K, as illustrated in Figures 3 and 4. Thus, when more SnCl$_2$ is present in solution or the solutions are heated, a redistribution of the phosphole ligands occurs.

The NMR samples were prepared so as to contain 1:1 and 1:2 mole ratios of platinum to tin. However, before the spectra were recorded, the solutions were filtered to remove any insoluble materials (no platinum metal was found), whether undissolved SnCl$_2$ or reaction products. The presence of

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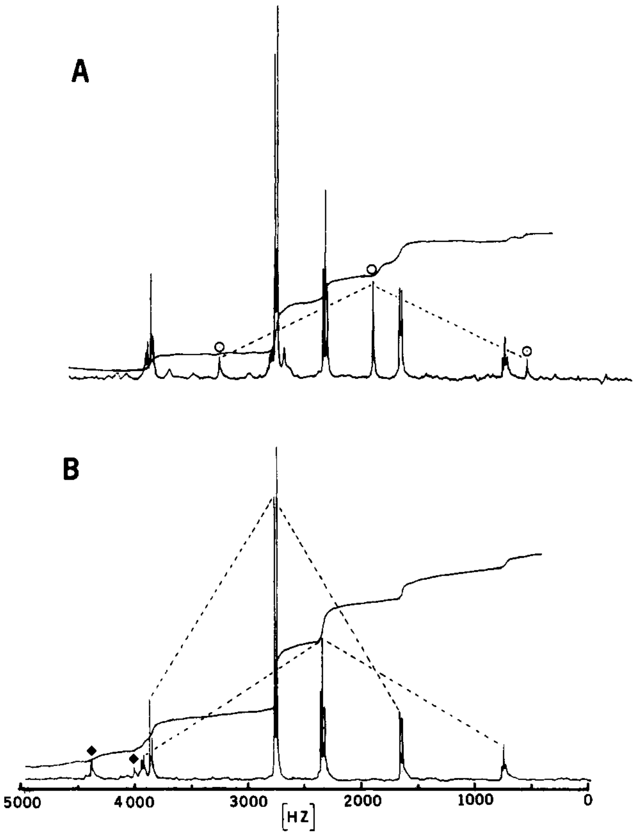

Figure 3. 40.26-MHz $^{31}P\{^1H\}$ NMR spectra of (A) a 1/2 mixture of *cis*-L_2PtCl_2 + $SnCl_2$ in acetone at 223 K, where open circles represent *trans*-$L_2Pt(SnCl_3)Cl$ and the other resonances L_3PtCl_2, and (B) L_3PtCl_2 in CH_2Cl_2 at 223 K, where solid diamonds represent $[L{=}O]_2$ and the other resonances the pentacoordinate species. The solution was prepared by adding 1 equiv of L to 1 equiv of *cis*-L_2PtCl_2 at 300 K. L = 1-*tert*-butyl-3,4-dimethylphosphole. (See ref 24 for further details on the discussion of this system.)

L_3PtCl_2 species in these solutions was established by examining the $^{31}P\{^1H\}$ and ^{195}Pt spectra. See ref 24 for a complete discussion of the assignments of these spectra. Representative spectra are shown in Figures 3 and 4, respectively. The spectra of a mixture of L_2PtCl_2 and $SnCl_2$ contain resonances due to *trans*-$L_2Pt(SnCl_3)Cl$ and/or *trans*-$L_2Pt(SnCl_3)_2$ in addition to resonances that are identical with those of independently prepared L_3PtCl_2 complexes.

The stoichiometry of the reaction requires the formation of some phosphole-deficient species. One plausible explanation would be the formation of chloro-bridged dimers $[LPtCl_2]_2$. This possibility is remote, however, as these dimers are typically very soluble in the solvents studied and would be expected[17,32] to show resonances in the ^{31}P chemical shift range observed. A more reasonable proposal is a species that contains no phosphorus such as $[PtCl_2(SnCl_3)_2]^{2-}$ or other platinum–tin clusters, which would have no ^{31}P resonance and which are typically poorly soluble.

In any event, it is the existence of the L_3PtCl_2 complexes that is most significant as their presence demonstrates that $SnCl_2$ labilizes the platinum–phosphole bond. The significance of this observation lies in its relevance to the catalytic mechanisms of the $(R_3P)_2PtCl_2/SnCl_2$ mixtures. For these systems, it has commonly been assumed that $SnCl_2$ renders the platinum complex both labile and coordinatively unsaturated by virtue of equilibrium 1. In support of this assumption, the starting L_2PtCl_2 complexes are wholly cis in solution but the resultant $L_2Pt(SnCl_3)Cl$ complexes are generally trans and the $L_2Pt(SnCl_3)_2$ complexes always trans. Thus, formation of the Pt–$SnCl_3$ species (by whatever mechanism) occurs concomitantly with geometrical isomerization at the platinum center. It is quite possible that equilibria such as those depicted in Scheme I are important under catalytic conditions (especially elevated temperatures), and further work is under way in our laboratories to clarify this point.

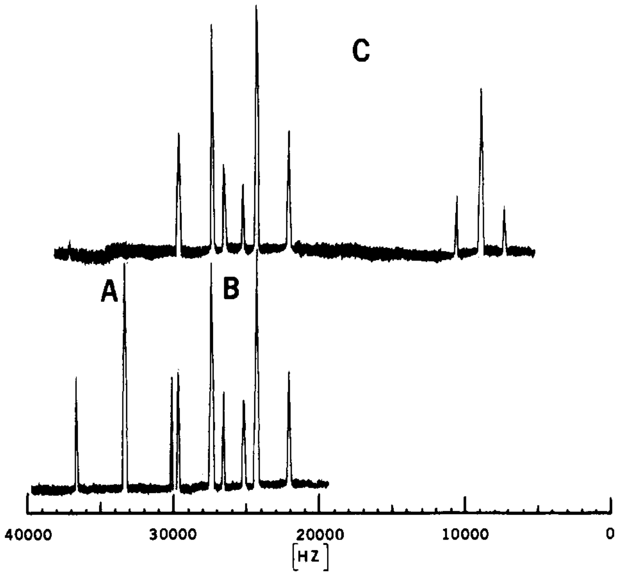

Figure 4. 21.88-MHz $^{195}Pt\{^1H\}$ NMR spectra of (A) L_2PtCl_2 in $CDCl_3$ at 300 K, (B) L_3PtCl_2 in CH_2Cl_2 at 203 K, and (C) a 1/2 mixture of L_2PtCl_2 + $SnCl_2$ in CH_2Cl_2 at 223 K. For (C) the solution was prepared by heating an acetone solution at 323 K for 1 h, evaporating to dryness under nitrogen, dissolving the residue in CH_2Cl_2, filtering into a 10-mm NMR tube, and cooling to 223 K. The high-field triplet represents *trans*-$L_2Pt(SnCl_3)_2$. L = 1-phenyl-3,4-dimethylphosphole.

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Registry No. *trans*-$L_2Pt(SnCl_3)Cl$ (R = CH_3), 88303-44-0; *trans*-$L_2Pt(SnCl_3)_2$ (R = CH_3), 88303-45-1; *trans*-$L_2Pt(SnCl_3)Cl$ (R = *n*-C_4H_9), 88303-46-2; *trans*-$L_2Pt(SnCl_3)_2$ (R = *n*-C_4H_9), 88303-47-3; *trans*-$L_2Pt(SnCl_3)Cl$ (R = *t*-C_4H_9), 88303-48-4; *cis*-$L_2Pt(SnCl_3)Cl$ (R = *t*-C_4H_9), 88335-38-0; *trans*-$L_2Pt(SnCl_3)_2$ (R = *t*-C_4H_9), 88303-49-5; *trans*-$L_2Pt(SnCl_3)Cl$ (R = C_6H_5), 88303-50-8; *trans*-$L_2Pt(SnCl_3)_2$ (R = C_6H_5), 88303-51-9; *trans*-$L_2Pt(SnCl_3)Cl$ (R = $C_6H_5CH_2$), 88303-52-0; *trans*-$L_2Pt(SnCl_3)_2$ (R = $C_6H_5CH_2$), 88303-53-1; L_3PtCl_2 (R = *t*-C_4H_9), 81011-74-7; L_3PtCl_2 (R = C_6H_5), 88303-54-2; L_3PtCl_2 (R = $C_6H_5CH_2$), 88303-55-3; *cis*-L_2PtCl_2 (R = CH_3), 81011-50-9; *cis*-L_2PtCl_2 (R = *n*-C_4H_9), 81011-51-0; *cis*-L_2PtCl_2 (R = *t*-C_4H_9), 81011-52-1; *cis*-L_2PtCl_2 (R = C_6H_5), 81011-54-3; *cis*-L_2PtCl_2 (R = $C_6H_5CH_2$), 81011-53-2; $SnCl_2$, 7772-99-8; ^{195}Pt, 14191-88-9; ^{119}Sn, 14314-35-3.

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