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## Role of the Trichlorostannyl Ligand in Homogeneous Catalysis. 4. Correlations of Solution Structure with Catalytic Activity in *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O and [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O (L = PR<sub>3</sub>, CO, Thioether, Amine; R = Aryl, Alkyl). Olefin Hydrogenation and Hydroformylation Systems<sup>1</sup>

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The catalytic activities of *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems in olefin hydrogenation (L = SR'<sub>2</sub>, *p*-XC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>; R = aryl) and olefin hydroformylation (L = CO, R = aryl, alkyl) are discussed. Comparison of *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)] with *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] and *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] shows that the first is the most effective catalyst precursor in the presence of tin(II) chloride. In the light of previous NMR studies on the reactions of these complexes with SnCl<sub>2</sub>·2H<sub>2</sub>O, the catalytic results are discussed and the roles of the PR<sub>3</sub> group, the ligand, L, the solvent, and SnCl<sub>2</sub>·2H<sub>2</sub>O are described. The catalytic activities of [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems are found to be very similar to those for mononuclear systems, particularly where the same catalyst precursor can be easily generated from the dinuclear species. Not surprisingly, the dinuclear systems show a greater solvent dependence arising from the ability of a given solvent to facilitate catalyst rearrangement processes.

### Introduction

Platinum(II) halo complexes, containing two different neutral ligands, have a particularly rich and interesting chemistry. Recently we have described synthetic procedures for the preparation of *trans*-[PtCl<sub>2</sub>(PR<sub>3</sub>)(PEt<sub>3</sub>)] (PR<sub>3</sub> = PPh<sub>3</sub>, PMePh<sub>2</sub>, P(*i*-Pr)<sub>3</sub>, P(*c*-Hx)<sub>3</sub>,<sup>2</sup> *trans*-[PtCl<sub>2</sub>(L)(P(*c*-Hx)<sub>3</sub>)] (L = PMePh<sub>2</sub>, P(*o*-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, CO, SMe<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N, AsPh<sub>3</sub>, *t*-BuNC)<sup>3</sup>, and *cis*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)] (PR<sub>3</sub> = PEt<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, PMePh<sub>2</sub>, PPh<sub>3</sub>, P(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, P(*c*-Hx)<sub>3</sub>)<sup>4</sup> and have described some stoichiometric<sup>2</sup> and catalytic<sup>5-7</sup> reactions of such complexes. One major area of interest is the application of these types of complexes to the systematic study of homogeneous catalytic reactions, where it is possible to vary just one ligand in a controlled fashion and hence, we believe, to gain some insight into the role of each neutral ligand in the catalytic process.

Initially, we described our preliminary results<sup>5,6</sup> on the ability of *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)] (L = thioether, amine; R = aryl) complexes to function as catalyst precursors, in the presence of SnCl<sub>2</sub>·2H<sub>2</sub>O, for olefin hydrogenation. These systems were found to be much more active than the corresponding *cis*-[PtCl<sub>2</sub>L<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O or *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O catalyst precursors. It was observed<sup>5</sup> that catalytic hydrogenation was retarded by addition of carbon monoxide to the system, an observation that led to the development<sup>7</sup> of a *cis*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O catalyst precursor that effected efficient olefin hydroformylation, with little competing olefin hydrogenation.

Dimeric complexes, of the type [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>], are of interest in this context as these are formally derived by the complete removal of the ligand, L, from the complexes [PtCl<sub>2</sub>(L)(PR<sub>3</sub>)] and are closely related in terms of reactivity. The preceding papers in this series<sup>1</sup> have described our spectroscopic studies of the precatalytic chemistry that occurs when *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)] and [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>Cl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (L = CO,

Table I. Effects of Variation in the PR<sub>3</sub> Ligand of *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PR<sub>3</sub>)] on the Catalytic Hydrogenation of Styrene<sup>a</sup>

PR <sub>3</sub>	turnover no. <sup>b</sup>	PR <sub>3</sub>	turnover no. <sup>b</sup>
P( <i>p</i> -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	2600	P( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	3700
PPh <sub>3</sub>	3400 <sup>c</sup>	P( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	4100

<sup>a</sup> Catalysis by *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PR<sub>3</sub>)] in acetone solution containing SnCl<sub>2</sub>·2H<sub>2</sub>O (Pt/Sn = 1/2) and styrene (Pt/olefin = 1/10 000) at 333 K under 600 psi of H<sub>2</sub> for 2 h. <sup>b</sup> Moles of styrene converted to ethylbenzene per mole of platinum per hour. <sup>c</sup> Typical value; five separate experiments gave values of 3085, 3200, 3420, 3430, and 3625 (mean of 3352). The spread of values obtained limits observations to gross trends in activity only.

Table II. Effects of Variation in the Ligand, L, of *cis*-[PtCl<sub>2</sub>(L)(PPh<sub>3</sub>)] on the Catalytic Hydrogenation of Styrene<sup>a</sup>

L	turnover no. <sup>b</sup>	L	turnover no. <sup>b</sup>
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3300	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	4000
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3500 <sup>c</sup>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	4400
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	3700		

<sup>a</sup> Catalysis by *cis*-[PtCl<sub>2</sub>(L)(PPh<sub>3</sub>)] in acetone solution containing SnCl<sub>2</sub>·2H<sub>2</sub>O (Pt/Sn = 1/2) and styrene (Pt/olefin = 1/10 000) at 333 K under 600 psi of H<sub>2</sub> for 2 h. <sup>b</sup> Moles of styrene converted to ethylbenzene per mole of platinum per hour. <sup>c</sup> Typical value; three separate experiments gave values of 3575, 3515, and 3500 (mean 3530).

Table III. Effects of the Pt(II)/Sn(II) Ratio on the Hydrogenation of Styrene by *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PPh<sub>3</sub>)]<sup>a</sup>

<i>n</i> SnCl <sub>2</sub> ·2H <sub>2</sub> O	turnover no. <sup>b</sup>	<i>n</i> SnCl <sub>2</sub> ·2H <sub>2</sub> O	turnover no. <sup>b</sup>
1	2000	3	2000
2	3400 <sup>c</sup>	5	1400

<sup>a</sup> Catalysis by *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PPh<sub>3</sub>)] in acetone solution containing *n* equiv of SnCl<sub>2</sub>·2H<sub>2</sub>O and styrene (Pt/olefin = 1/10 000) at 333 K under 600 psi of H<sub>2</sub> for 2 h. <sup>b</sup> Moles of styrene converted to ethylbenzene per mole of platinum per hour. <sup>c</sup> See footnote *c* in Table I.

SMe<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N, *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>; R = aryl, alkyl) complexes react with SnCl<sub>2</sub>·2H<sub>2</sub>O. It is important to note that such descriptions of precatalytic chemistry do not imply a knowledge of the actual catalytic processes that occur under operating conditions. To date, our attempts to study platinum(II)/tin(II) systems under operating conditions, by high-pressure infrared spectroscopy, have been largely uninformative because the

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**Table IV.** Catalytic Activity of *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] and *cis*-[PtCl<sub>2</sub>L<sub>2</sub>] Complexes in the Hydrogenation of Styrene<sup>a</sup>

PR <sub>3</sub> or L	<i>n</i> SnCl <sub>2</sub> ·2H <sub>2</sub> O <i>n</i>	turnover no. <sup>b</sup>
P( <i>p</i> -FC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	10.0	410
P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	10.0	430
PPh <sub>3</sub>	10.0	800
P( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	10.0	830
P( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	10.0	910
SMe <sub>2</sub>	2.0	190 <sup>c</sup>
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	2.0	340

<sup>a</sup> Catalysis by the named complex in acetone solution containing *n* equiv of SnCl<sub>2</sub>·2H<sub>2</sub>O and styrene (Pt/olefin = 1/10 000) at 333 K under 600 psi of H<sub>2</sub> for 2 h. <sup>b</sup> Moles of styrene converted to ethylbenzene per mole of platinum per hour. <sup>c</sup> Some polystyrene also formed; ca. 940 equiv of styrene polymerized over 2 h (estimated by weight).

major solvents of interest, acetone and acetonitrile, are far from ideal for the study of the metal hydride and carbonyl region of the infrared spectrum.

In this paper we describe the nature of the catalyst precursors generated in *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)] and [Pt<sub>2</sub>(μ-Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (L = PR<sub>3</sub>, CO, SMe<sub>2</sub>, amine; R = aryl, alkyl) systems in the presence of SnCl<sub>2</sub>·2H<sub>2</sub>O cocatalyst and comment on the roles of the neutral ligands, the solvent, and SnCl<sub>2</sub>·2H<sub>2</sub>O in relation to their effects on catalytic olefin hydrogenation and hydroformylation reactions.

## Results and Discussion

The results of our catalytic studies employing *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O precursors in the hydrogenation of styrene to ethylbenzene in acetone solution at 333 K under 600 psi H<sub>2</sub> pressure are presented in Tables I–III. Table I shows that variation in the electronic parameters<sup>8</sup> associated with triarylphosphines of the same steric bulk<sup>8</sup> affects the catalytic activity, with the presence of electron-donating para substituents causing enhancement. Conversely, Table II shows that the presence of electron-withdrawing para substituents on the arylamine ligand, L, also changes catalytic activity. It is tempting to rationalize these results by inferring that the ligand L will act as a leaving group during the catalytic reaction and that the more powerful triarylphosphine donor ligands will electronically stabilize any coordinatively unsaturated intermediates and, further, promote oxidative addition.<sup>9</sup> While there may be some element of truth in these statements, the situation will be shown to be more complex and understandable, in part, only through a knowledge of the precatalytic chemistry.

The dependence of catalytic activity on the platinum(II)/tin(II) ratio for the *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PPh<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O olefin hydrogenation system is shown in Table III. Clearly, catalytic activity reaches a maximum at a Pt(II)/Sn(II) ratio of 1/2, a situation entirely analogous to that observed for the *cis*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O olefin hydroformylation system<sup>10</sup> but different from that for the more common *cis*-

[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems, where maximum activity is observed<sup>11</sup> with Pt(III)/Sn(II) ratios of 1/10. Again, the simple rationale of these differences, in terms of the different equilibrium positions for the formation of trichlorostannyll complexes from the various precursors, represents a major oversimplification of the actual chemistry that occurs.

Data obtained for analogous olefin hydrogenation reactions utilizing *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O and *cis*-[PtCl<sub>2</sub>L<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems are presented in Table IV. In no case was activity obtained comparable to that of the *cis*-[PtCl<sub>2</sub>(L)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems. However, a consideration of the precatalytic chemistry that occurs in the simple *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O system demonstrates that even comparisons between analogous systems, where only a PR<sub>3</sub> ligand is changed, can be far from straightforward. For example, Pregosin and co-workers have shown<sup>12</sup> that a CH<sub>2</sub>Cl<sub>2</sub> solution of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] reacts with 5.0 equiv of SnCl<sub>2</sub>·2H<sub>2</sub>O in acetone to yield a precipitate, identified by its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in CH<sub>2</sub>Cl<sub>2</sub> as *cis*-[PtCl(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>]. In order to determine whether this result was applicable to the precatalytic chemistry occurring in the acetone solutions of 1/10 *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O that we had examined as catalysts, we performed similar experiments. It was found that the reaction of a suspension of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with either 1.0 or 10.0 equiv of SnCl<sub>2</sub>·2H<sub>2</sub>O in acetone caused an immediate color change to form a yellow solution but that a white precipitate formed rapidly. The yellow solution exhibited no <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, even at 213 K, indicating that little, if any, platinum phosphine complex remained in solution. Indeed, Wilkinson and co-workers observed some years ago<sup>13</sup> that [PtCl(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] reverts to SnCl<sub>2</sub> and the insoluble *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in acetone solution. The situation for the analogous PET<sub>3</sub> system is somewhat different, and its has been shown<sup>14</sup> that *cis*- or *trans*-[PtCl<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>] reacts with anhydrous SnCl<sub>2</sub> in acetone solution to produce equilibrium mixtures of [PtCl<sub>2-n</sub>(SnCl<sub>3</sub>)<sub>n</sub>(PET<sub>3</sub>)<sub>2</sub>] (*n* = 0–2) complexes. With Pt(II)/Sn(II) ratios of 1/5, the complex *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>] alone is identified<sup>14</sup> in solution at 200 K. We have confirmed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy that identical chemistry occurs when hydrated tin(II) chloride is employed (see Experimental Section for spectroscopic data) and similarly find that the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of *trans*-[PtCl(SnCl<sub>3</sub>)(PET<sub>3</sub>)<sub>2</sub>] and *trans*-[Pt(SnCl<sub>3</sub>)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>] show evidence of <sup>117,119</sup>Sn/<sup>31</sup>P coupling only at very low temperatures. Indeed, in acetone solution coupling is observed at 193 K but lost at 213 K. As <sup>195</sup>Pt/<sup>31</sup>P coupling is maintained at 213 K, a dissociative process involving loss of SnCl<sub>3</sub><sup>-</sup> is apparent, as previously proposed.<sup>14</sup>

Attempts to compare trends in catalytic rates for the [PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O systems (R = Ph, Et) in terms of the abilities of the different PR<sub>3</sub> ligands to promote substrate coordination, oxidative addition of H<sub>2</sub>, etc., would clearly be misleading. Any observable trends will not only reflect the abilities of the ligands to function effectively in these areas but will also be governed by the solubilities of the precursors in acetone and hence, indirectly, the positions of the equilibria between the chloro and trichlorostannyll complexes.

The problem encountered here, that of the extent to which precatalytic chemistry governs the nature of the species in solution at the start of a catalytic reaction, is met in both the *cis*-[PtCl<sub>2</sub>(SMe<sub>2</sub>)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O hydrogenation system and the *cis*-[PtCl<sub>2</sub>(CO)(PR<sub>3</sub>)]/SnCl<sub>2</sub>·2H<sub>2</sub>O hydroformylation

(8) The data of Tolman provide some relative comparisons of steric and electronic effects of PR<sub>3</sub> ligands. For the ligands employed here, the electronic parameters are as follows: P(*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, 2066.1; P(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, 2066.7; PPh<sub>3</sub>, 2068.9; P(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, 2071.3. The cone angles of all of these ligands are ca. 145°. See: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(9) That is if the electron count is increased at the metal center, the complex is expected to be more capable of maintaining a low coordination number and is more prone to oxidative addition.

(10) In the hydroformylation of hex-1-ene in acetonitrile solution at 353 K under 600 psi CO/H<sub>2</sub> (1/1) with a *cis*-[PtCl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub>]/SnCl<sub>2</sub>·2H<sub>2</sub>O precursor, turnover numbers varied with the Pt(II)/Sn(II) ratio as follows: TN = 0 (1/0), 14 (1/1), 139 (1/2), 150 (1/5), and 116 (1/10). In terms of experimental precision, the results for Pt(II)/Sn(II) ratios of 1/2 to 1/10 are considered to be approximately constant but are significantly higher than those for ratios of 1/0 and 1/1.

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**Table V.** Species Identified at Different Pt(II)/Sn(II) Ratios in Acetone Solutions of the  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  Olefin Hydroformylation Catalyst Precursor<sup>a</sup>

Pt(II)/ Sn(II)	<i>cis</i> - [PtCl <sub>2</sub> - (CO)(PPh <sub>3</sub> )]	<i>trans</i> - [PtCl- (CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	[Pt(SnCl <sub>3</sub> ) <sub>3</sub> ] <sup>3-</sup>	<i>trans</i> - [PtCl- (SnCl <sub>3</sub> ) <sub>2</sub> (CO)] <sup>-</sup>	<i>trans</i> - [PtCl- (SnCl <sub>3</sub> ) <sub>2</sub> (PPh <sub>3</sub> )] <sup>-</sup>
1/0	100				
1/1	35	32	26	6	
1/2 <sup>b</sup>		50	20	20	
1/5		48	50		2

<sup>a</sup> Additionally, indirect evidence suggests the presence of hydroxytin cations derived from  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , although these have not been observed spectroscopically. Figures refer to approximate percentages of platinum accounted for by each species, estimated from NMR data.

<sup>b</sup> At this ratio, a further unidentified platinum/tin complex, containing neither  $\text{PPh}_3$  nor CO ligands, was observed spectroscopically, accounting for ca. 10% of the total platinum-containing species.

system. In each of these cases, the precatalytic chemistry is extensive and highly complex, resulting in the formation of several species in solution.<sup>1</sup> Evidently, it is possible that only one of the species formed is necessary to establish the catalytic cycle under operating conditions. If this were to be the case, then the formation of other precatalytic species merely represents an undesirable, artificial lowering of the true catalyst precursor concentration. This problem is particularly difficult to resolve without ambiguity, but nonetheless, our studies<sup>1</sup> on the  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  system and, to a lesser extent, the thioether analogue do suggest that the multicomponent system is necessary to establish the catalytic cycle.

The effects of the Pt(II)/Sn(II) ratios on the activities of the two systems are indicative of this. For the carbonyl system,<sup>10</sup> the nature of the species present in solution at different Pt(II)/Sn(II) ratios<sup>1</sup> is indicated in Table V. Maximum catalytic activity is reached at a Pt(II)/Sn(II) ratio of 1/2 and remains approximately constant as the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  concentration is increased further. At such Pt(II)/Sn(II) ratios, the starting material,  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]$ , has been completely converted to the ionic complexes and, further, in the absence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , the parent complex exhibits no catalytic activity.<sup>10</sup> The cationic precursors,  $\text{trans-}[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+$ , accounts for ca. 50% of the total platinum, but extensive investigations<sup>15</sup> into the chemistry of  $\text{trans-}[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{X}]$  ( $\text{X} = \text{BF}_4, \text{ClO}_4$ , etc.) complexes have shown that these cations do not exhibit the catalytic activity for which their isoelectronic, neutral rhodium(II) and iridium(I) analogues are well-known. The  $[\text{Pt}(\text{SnCl}_3)_3]^{3-}$  anion is an effective catalyst precursor for hydrogenation of olefins,<sup>16</sup> and yet it does not appear that it is the presence of this complex alone that leads to access to the catalytic cycle and subsequent activity. If this were the case, the activity should increase as the amount of  $[\text{Pt}(\text{SnCl}_3)_3]^{3-}$  generated in the precatalytic reaction increases (i.e., as the Pt(II)/Sn(II) ratio is increased from 1/2 to 1/5). In fact, no significant increase in activity is observed and studies of stoichiometric reactions with  $\text{H}_2$  (vide infra) support the idea that the  $[\text{Pt}(\text{SnCl}_3)_3]^{3-}$  anion is not an isolated precursor<sup>17</sup> in this system. The  $\text{trans-}[\text{PtCl}(\text{SnCl}_3)_2(\text{CO})]^-$  anion<sup>18</sup> is produced during the precatalytic rearrangement reaction, but at high  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  concentra-

tions all CO is lost from the anionic products and this ion is no longer present. As the hydroformylation reaction is performed under high pressures of CO (300 psi, typically), it is not possible to eliminate this anion as an isolated precursor<sup>17</sup> as it may be regenerated under the reaction conditions.<sup>18</sup> The  $\text{trans-}[\text{PtCl}(\text{SnCl}_3)_2(\text{PPh}_3)]^-$  anion is only produced in trace amounts at high  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  concentrations, and hence there are insufficient data to comment on the possible role of this anion as an isolated catalyst precursor.<sup>17</sup>

A further piece of indirect evidence suggests that the entire multicomponent system is involved in the generation of the catalytic cycle. Acetone solutions of both the  $\text{cis-}[\text{PtCl}_2(\text{SMe}_2)(\text{PPh}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  system and the carbonyl analogue react with molecular hydrogen under ambient conditions. The thioether system yields  $[\text{PtH}(\text{SnCl}_3)(\text{SMe}_2)(\text{PPh}_3)]$  (isomer with H and  $\text{PPh}_3$  mutually trans),<sup>1</sup> and the carbonyl system yields an as yet unidentified platinum hydride, which contains  $\text{PPh}_3$  ligands. Undoubtedly, the very forcing conditions employed in catalytic syntheses may result in the formation of entirely different products, but nonetheless these reactions show that a multicomponent rearrangement is possible.<sup>19</sup>

Some other points of interest are also noteworthy in connection with the high catalytic activities of the  $\text{cis-}[\text{PtCl}_2(\text{L})(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems. The formation of  $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$  is evident in the precatalytic processes, this occurring rapidly where  $\text{L} = p\text{-MeC}_6\text{H}_4\text{NH}_2$  and very slowly where  $\text{L} = \text{CO}$ .<sup>1</sup> The catalytic activities of  $\text{cis-}[\text{PtCl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems in hydrogenation (Table IV) and hydroformylation suggest that the formation of this complex does not provide easy access to the catalytic cycles and is not responsible for the high activities of the amine or carbonyl systems. Additionally, it has long been known<sup>15</sup> that  $\text{trans-}[\text{PtCl}(\text{CO})(\text{PR}_3)_2][\text{X}]$  ( $\text{X} = \text{BF}_4, \text{ClO}_4$ , etc.) complexes react with water to yield the corresponding hydrides,  $\text{trans-}[\text{PtHCl}(\text{PR}_3)_2]$ . As the reaction of  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]$  with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in acetone solution yields  $\text{trans-}[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+$  as a major product (Table V), it seemed possible that the hydride may be generated by a subsequent reaction with water.<sup>20</sup> Accordingly,  $\text{trans-}[\text{PtHCl}(\text{PPh}_3)_2]$  was prepared independently and its activity as a catalyst examined, in the presence of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The results of these experiments (see Experimental Section), and further detailed studies on the catalytic activity of  $\text{trans-}[\text{PtHCl}(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems,<sup>21</sup> demonstrate that the  $\text{PPh}_3$  complex is an inefficient precursor and so the possibility of its formation in the  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  system is not likely

(15) Clark, H. C.; Dixon, K.; Jacobs, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 2259; **1969**, *91*, 1346.

(16) Cramer, R. D.; Jenner, E. L.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1691; **1965**, *87*, 658 and references therein.

(17) The term "isolation precursor" is used to represent a species capable of allowing facile entry into the catalytic cycle without interaction with the other platinum complexes in solution. That is, if such an isolated precursor was prepared independently, its catalytic activity would be the same as that of the multicomponent system.

(18) A synthetic procedure for  $[\text{PtCl}(\text{SnCl}_3)_2(\text{CO})]^-$  has been described (Kinston, J. V.; Scollary, G. R. *J. Chem. Soc. A* **1971**, 3765), but the geometry was assigned as *cis*. Spectroscopic data (ref 1) demonstrate conclusively that the complex formed in the present system is *trans*. Interestingly, this complex is reported to be involved in the Pt(II)/Sn(II)-catalyzed water gas shift reaction (Cheng, C. H.; Eisenberg, R. J. *Am. Chem. Soc.* **1978**, *100*, 5968).

(19) The  $[\text{Pt}(\text{SnCl}_3)_3]^{3-}$  anion alone reacts with  $\text{H}_2$  to yield  $[\text{PtH}(\text{SnCl}_3)_4]^{3-}$  (Cramer, R. D.; Lindsey, R. V.; Prewitt, C. T.; Stolberg, U. G. *J. Am. Chem. Soc.* **1965**, *87*, 658). Clearly, for the formation of the observed products, ligand migration reactions must occur during the reaction with  $\text{H}_2$ .

(20) <sup>1</sup>H NMR spectroscopy indicates that the acetone solvent contains substantial amounts of water and, additionally, hydrated tin(II) chloride is employed in the reaction.

(21) Billard, C.; Clark, H. C.; Wong, C. S., unpublished results.

to be an explanation for the high catalytic activity of the carbonyl precursor.

Hsu and Orchin isolated<sup>22</sup> an unstable complex of the form  $[\text{PtH}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2]$  from the reaction of *trans*- $[\text{PtHCl}(\text{PPh}_3)_2]$  with excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in benzene under high  $\text{H}_2/\text{CO}$  pressures. Hydroformylation of 1-pentene under these conditions (100 °C, 3000 psi) produced a high *n*/*iso* aldehyde ratio, but the activity was lower than for the *cis*- $[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  system, and much milder conditions were employed in the latter case. Thus the above complex cannot account for the activity observed for the *cis*- $[\text{PtCl}_2(\text{CO})(\text{PPh}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  system.

The catalytic activities of the *cis*- $[\text{PtCl}_2(\text{CO})(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and *cis*- $[\text{PtCl}_2(\text{SMe}_2)(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems differ in their dependence upon the nature of the  $\text{PR}_3$  ligand. In the carbonyl system, no predictable dependence upon either steric or electronic parameters was observed,<sup>7</sup> while the thioether analogue shows a strong dependence upon the electronic nature of  $\text{PR}_3$  (Table I). NMR studies<sup>1</sup> have shown that the precatalytic rearrangement reactions of *cis*- $[\text{PtCl}_2(\text{CO})(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems in acetone solution proceed at similar rates for  $\text{PR}_3 = \text{P}(p\text{-MeC}_6\text{H}_4)_3$ ,  $\text{PPh}_3$ , and  $\text{P}(p\text{-FC}_6\text{H}_4)_3$  but are very much slower for the  $\text{PEt}_3$  analogue. In subsequent olefin hydroformylation reactions,<sup>7</sup> the  $\text{PPh}_3$  and  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$  systems shows similar activity, but the  $\text{P}(p\text{-FC}_6\text{H}_4)_3$  analogue is much more active. In the case of the  $\text{PEt}_3$  complex, where the rearrangement reaction is very slow, activity is intermediate between those for the  $\text{P}(p\text{-FC}_6\text{H}_4)_3$  and  $\text{PPh}_3$  systems. Evidently, the effect of the  $\text{PR}_3$  ligands is not merely as a rate-controlling factor in the precatalytic reaction but genuinely has an effect upon the subsequent chemistry. For the three triarylphosphine systems, all the available  $\text{PR}_3$  ligands are accounted for in the formation of the unreactive<sup>15</sup> *trans*- $[\text{PtCl}(\text{CO})(\text{PR}_3)_2]^+$  cation during the rearrangement process. Accordingly, if the species were not involved in the catalysis, no  $\text{PR}_3$  effect would be observed. Similarly, if a rearrangement product such as  $[\text{Pt}(\text{SnCl}_3)_3]^{3-}$  or *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{CO})]^-$ , without  $\text{PR}_3$  ligands, was an isolated catalyst precursor,<sup>17</sup> then no  $\text{PR}_3$  effect would be expected. These observations thus provide further evidence that the multicomponent system is involved in the generation of the catalytic cycle.

The observed increase in catalytic activity with the electron-donating ability of  $\text{PR}_3$  and electron-withdrawing ability of L in the *cis*- $[\text{PtCl}_2(\text{L})(\text{PR}_3)]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (L = thioether, amine) systems, compared with the lack of correlation with the electronic nature of  $\text{PR}_3$  in the carbonyl analogues, may be related to the geometry of the rearrangement products. In both the thioether and carbonyl cases, tertiary phosphine displacement is involved in the formation of  $[\text{PtCl}(\text{L})(\text{PR}_3)_2]^+$  cations and *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PR}_3)]^-$  anions. In the carbonyl system, the cation is of *trans* geometry, an observation expected in terms of the possible arrangements of two strong  $\pi$ -acceptor ligands ( $\text{PR}_3$  and CO) about an electron-deficient metal center.<sup>23</sup> The corollary of this is that the carbonyl ligand is *trans* to  $\text{Cl}^-$ , a low-*trans*-influence group and that the molecule is static on the NMR time scale.<sup>1</sup> Accordingly, the *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PR}_3)]^-$  anion, which is believed to be related to the cation via an equilibrium (vide infra), is rarely observed and is only present in minor amounts.

In the thioether analogue, the cation is of *cis* geometry as the two strongest  $\pi$ -acceptor ligands (now both  $\text{PR}_3$  groups) are again reluctant to assume a *trans* geometry.<sup>23</sup> Accordingly, the thioether is *trans* to a  $\text{PR}_3$  ligand and as such is exceptionally labile, as demonstrated by variable-temperature NMR

Table VI. Catalytic Activity of Dimeric Complexes in the Hydrogenation of Styrene<sup>a</sup>

complex	$n\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$		turnover no. <sup>b</sup>
	<i>n</i>	solvent	
$[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]^c$	20	acetone	1300
$[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]^d$	20	$\text{CH}_2\text{Cl}_2$	350
$[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PEt}_3)_2]^e$	20	acetone	1400
$[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PEt}_3)_2]^d$	20	$\text{CH}_2\text{Cl}_2$	220
$[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PPh}_3)_2]^d$		$\text{CH}_2\text{Cl}_2$	370
$[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PEt}_3)_2]^d$		$\text{CH}_2\text{Cl}_2$	250

<sup>a</sup> Catalysis by the given complex in the appropriate solvent containing styrene at 333 K under 600 psi of  $\text{H}_2$ . <sup>b</sup> Moles of styrene converted to ethylbenzene per mole of platinum (i.e., half a dimeric unit) per hour. <sup>c</sup>  $\text{Pt}/\text{olefin} = 1/5000$ ; time 2 h. <sup>d</sup>  $\text{Pt}/\text{olefin} = 1/2000$ ; time 4 h. <sup>e</sup>  $\text{Pt}/\text{olefin} = 1/4000$ ; time 2 h.

experiments.<sup>1</sup> The lability of the  $\text{SMe}_2$  group leads to a facile exchange reaction, resulting in the interconversion of *cis*- $[\text{PtCl}(\text{SMe}_2)(\text{PR}_3)_2]^+$  and *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PR}_3)]^-$ . In general terms, the more powerful electron-donor  $\text{PR}_3$  groups and the less basic ancillary ligands, L, would be expected to facilitate this exchange process and thus be responsible for the generation of substitutionally labile species. This then appears to be reflected in subsequent reactions connected with the catalytic systems.

A final point to consider is the effect of the solvent on the catalytic behavior, a factor inherently expected to be related to the ability of a given solvent to facilitate rearrangement processes, via stabilization of ionic products. A relatively straightforward example concerns the solution chemistry of  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  systems. With use of the halocarbon solvents<sup>1</sup>  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ , the dimeric complexes  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$  (R = Ph, Et) react with excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  via a simple insertion of  $\text{SnCl}_2$  into the terminal Pt-Cl bonds to yield the corresponding  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PR}_3)_2]$  complexes.<sup>24</sup> In acetone solution,<sup>1</sup> however, a more complex reaction occurs to yield the *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PR}_3)]^-$  anion as the sole platinum-containing species. Indirect evidence suggests that hydroxytin cations are formed, via some hydrolytic process involving  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , to maintain electroneutrality.

The differences between the two classes of solvent are emphasized by the fact that no simple pathway exists for the formation of ionic products in halocarbon solution. Only by introduction of a powerful nucleophile such as  $\text{PPh}_3$  have we been able to observe rearrangement to yield ionic products in these solvents.<sup>1</sup> Accordingly, the two systems are expected to exhibit different catalytic behavior as, even if the same catalytic cycle is operative in both cases, the points of entry into (and hence the ease of entry into) such a cycle will be very different. Catalytic studies (Table VI) show that a  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$  precursor, in the presence of 20.0 equiv of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , exhibits a different catalytic activity in styrene hydrogenation with either dichloromethane or acetone as solvent. The ionic precursors (acetone systems) exhibit the higher activity, as we have generally observed. Additionally, as the reaction of  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$  with excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  solution yields only  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PR}_3)_2]$ , a complex that is stable in  $\text{CH}_2\text{Cl}_2$  solution in the absence of excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , the activities of the preformed precursor and the precursor generated *in situ* are expected to be the same, provided the excess  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  has no further role in the catalytic reaction. This was experi-

(22) Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

(23) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299.

(24) A novel reaction of  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PEt}_3)_2]$  with activated acetylenes is noteworthy in connection with this chemistry; in the reaction with activated acetylenes, insertion into the terminal Pt-Sn bond occurs, yielding the dimeric product with olefinic bridges between Pt and Sn, whose structure has been confirmed by X-ray crystallography: Clark, H. C.; Ferguson, G.; Goel, A. B.; Ruhl, B., manuscript in preparation.

mentally confirmed by comparison of  $[\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PR}_3)_2]$  and  $1/20 [\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]/\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  as precursors in styrene hydrogenation (Table VI).

One further example to confirm that the generation of in situ catalyst precursors and the use of preformed catalyst precursors can be employed interchangeably, provided the precatalytic chemistry is understood, comes from a comparison of the thioether and dimeric systems. Thus, reaction of  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]$  with excess  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in acetone solution generates the *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PPh}_3)]^-$  anion, which will react with  $\text{SMe}_2$  to yield an equilibrium mixture of *cis*- $[\text{PtCl}(\text{SMe}_2)(\text{PPh}_3)_2]^+$  and *trans*- $[\text{PtCl}(\text{SnCl}_3)_2(\text{PPh}_3)]^-$  as the only phosphine-containing products.<sup>1</sup> The same equilibrium mixture is obtained by the reaction of *cis*- $[\text{PtCl}_2(\text{SMe}_2)(\text{PPh}_3)]$  with  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in acetone solution. A comparison of the catalytic activity of such systems, performed with use of the  $\text{SPh}_2$  analogues, was made. A precursor generated by the reaction of  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]$  with 4.0 equiv of  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in acetone solution, followed by addition of 4.0 equiv of  $\text{SPh}_2$ , was compared with the standard  $1/2$  *cis*- $[\text{PtCl}_2(\text{SPh}_2)(\text{PPh}_3)]/\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  precursor in acetone solution. For the hydrogenation of styrene at 333 K under 600 psi of  $\text{H}_2$ , the former system gave a turnover number of 4400, while the latter gave 4300.

In conclusion, although we have been unable to study these catalytic systems under actual operating conditions, studies of the precatalytic chemistry have aided in the understanding of our catalytic results. Clearly, in systems of such complexity, attempts to rationalize catalytic results on the basis of ligand effects, solvent effects, etc., without an understanding of at least the precatalytic reactions, would be without any sound basis. Mechanistic discussion, based solely on catalytic data, should evidently be treated with extreme caution.

### Experimental Section.

The complexes  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$  ( $\text{R} = \text{Et}, \text{Ph}, p\text{-FC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4$ ) were prepared by the general method previously described.<sup>25</sup> The complexes *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$  ( $\text{R} = p\text{-FC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, \text{Ph}, p\text{-MeC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$ ) were prepared by the general literature method.<sup>26</sup> *cis*- $[\text{PtCl}_2(p\text{-XC}_6\text{H}_4\text{NH}_2)(\text{PPh}_3)]$  ( $x = \text{MeO}, \text{Me}, \text{H}, \text{Cl}, \text{O}_2\text{N}$ ) complexes were prepared by dissolving the dimer  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2]$  in  $\text{CH}_2\text{Cl}_2$  and adding a solution of  $p\text{-XC}_6\text{H}_4\text{NH}_2$  ( $\text{Pt}/\text{L} = 1/1.05$ ) in  $\text{CH}_2\text{Cl}_2$ . After 2 h of stirring, the solution was filtered and reduced to small volume in vacuo, and a solid was precipitated with hexane. The solid was isolated and recrystallized from  $\text{CH}_2\text{Cl}_2$  by dropwise addition of diethyl ether, and the crystalline product was dried in vacuo. *cis*- $[\text{PtCl}_2(\text{SMe}_2)(\text{PR}_3)]$  ( $\text{R} = p\text{-XC}_6\text{H}_4; \text{X} = \text{F}, \text{H}, \text{Me}, \text{MeO}$ ) were prepared from the appropriate dimers,  $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ , with use of a ca. 20-fold

excess of  $\text{SMe}_2$ , by the general method described above.

Phosphine ligands were obtained from Strem, and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  was purchased from Fisher (technical grade). Styrene (Aldrich 99%) was passed down columns of Florisil (Fisher, 100–200 mesh) and alumina (Fisher, basic Brockman activity 1, 80–200 mesh) and deoxygenated prior to use. Acetone (Fisher, spectroanalyzed) and dichloromethane (Fisher Certified) were deoxygenated prior to use in catalytic reactions.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained on a Bruker WP 60 spectrometer operating in the Fourier transform mode at 24.3 MHz. Chemical shifts are relative to external 85%  $\text{H}_3\text{PO}_4$ ; more positive shifts represent deshielding.

Reaction of *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$  with 1.0 equiv of  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in 90% acetone/10% acetone- $d_6$  solution was monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR. At 193 K, three species were identified: *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = 10.2, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 3477 \text{ Hz}$ ), *trans*- $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = 9.1, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 2080 \text{ Hz}, ^2J(^{117,119}\text{Sn}, ^{31}\text{P}) = 256 \text{ Hz (av)}$ ), and *trans*- $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = -11.2, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 1453 \text{ Hz}, ^2J(^{117,119}\text{Sn}, ^{31}\text{P}) = 266, 281 \text{ Hz}$ ). At 213 K, the spectrum showed the same three species but with no evidence of  $^{117,119}\text{Sn}, ^{31}\text{P}$  coupling: *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = 9.5, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 3479 \text{ Hz}$ ), *trans*- $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = 11.8 \text{ (br)}, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 2058 \text{ Hz}$ ), and *trans*- $[\text{Pt}(\text{SnCl}_3)_2(\text{PEt}_3)_2]$  ( $\delta(\text{P}) = -11.6, ^1J(^{195}\text{Pt}, ^{31}\text{P}) = 1455 \text{ Hz}$ ).

Catalytic reactions were typically performed at 333 K under 600 psi  $\text{H}_2$  pressure with use of a method analogous to that which we have previously described.<sup>7</sup> Gas chromatographic analyses were performed on an Aerograph Autoprep 700 chromatograph equipped with a 32 ft  $\times$  0.25 in. (o.d.) Carbowax 4000 (60–80 mesh) column by comparison with known standards.

The activity of  $[\text{PtHCl}(\text{PPh}_3)_2]$  as a catalyst precursor for styrene hydrogenation was examined. The following results were obtained: (1) solvent methanol,  $\text{Pt(II)}/\text{Sn(II)} = 1/1$ , temperature 333 K,  $\text{H}_2$  pressure 600 psi, turnover number 6; (2) solvent methanol,  $\text{Pt(II)}/\text{Sn(II)} = 1/5$ , temperature 333 K,  $\text{H}_2$  pressure 600 psi, turnover number 14; (3) solvent  $\text{CH}_2\text{Cl}_2$ ,  $\text{Pt(II)}/\text{Sn(II)} = 1/1$ , temperature 333 K,  $\text{H}_2$  pressure 600 psi, turnover number 38; (4) solvent  $\text{CH}_2\text{Cl}_2$ ,  $\text{Pt(II)}/\text{Sn(II)} = 1/5$ , temperature 333 K,  $\text{H}_2$  pressure 600 psi, turnover number 220.

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**Registry No.**  $\text{SnCl}_2$ , 7772-99-8; *cis*- $[\text{PtCl}_2(\text{SMe}_2)(p\text{-FC}_6\text{H}_4)_3]$ , 83915-76-8; *cis*- $[\text{PtCl}_2(\text{SMe}_2)(\text{PPh}_3)]$ , 52543-06-3; *cis*- $[\text{PtCl}_2(\text{SMe}_2)(p\text{-MeC}_6\text{H}_4)_3]$ , 83915-77-9; *cis*- $[\text{PtCl}_2(\text{SMe}_2)(p\text{-MeOC}_6\text{H}_4)_3]$ , 83915-78-0; *cis*- $[\text{PtCl}_2(p\text{-MeOC}_6\text{H}_4\text{NH}_2)(\text{PPh}_3)]$ , 83915-79-1; *cis*- $[\text{PtCl}_2(p\text{-MeC}_6\text{H}_4\text{NH}_2)(\text{PPh}_3)]$ , 40192-48-1; *cis*- $[\text{PtCl}_2(\text{C}_6\text{H}_5\text{NH}_2)(\text{PPh}_3)]$ , 839915-80-4; *cis*- $[\text{PtCl}_2(p\text{-ClC}_6\text{H}_4\text{NH}_2)(\text{PPh}_3)]$ , 83915-81-5; *cis*- $[\text{PtCl}_2(p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2)(\text{PPh}_3)]$ , 83915-82-6; *cis*- $[\text{PtCl}_2(p\text{-FC}_6\text{H}_4)_3]$ , 72124-15-3; *cis*- $[\text{PtCl}_2(p\text{-ClC}_6\text{H}_4)_3]$ , 67670-75-1; *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ , 15604-36-1; *cis*- $[\text{PtCl}_2(p\text{-MeC}_6\text{H}_4)_3]$ , 31173-67-8; *cis*- $[\text{PtCl}_2(p\text{-MeOC}_6\text{H}_4)_3]$ , 67773-08-4; *cis*- $[\text{PtCl}_2(\text{SMe}_2)_2]$ , 17836-09-8; *cis*- $[\text{PtCl}_2(p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2)_2]$ , 29857-46-3;  $\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPh}_3)_2$ , 15349-80-1;  $\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PEt}_3)_2$ , 15692-96-3;  $\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PPh}_3)_2$ , 83719-67-9;  $\text{Pt}_2(\mu\text{-Cl})_2(\text{SnCl}_3)_2(\text{PEt}_3)_2$ , 83719-68-0; *cis*- $\text{PtCl}_2(\text{PEt}_3)_2$ , 15692-07-6; *trans*- $\text{PtHCl}(\text{PPh}_3)_2$ , 16841-99-9; styrene, 100-42-5.

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