kinetics identical with that of the reaction of $[Fe(CO)_3NO]^-$ and MeI alone; i.e., the phosphine reacts with an intermediate in a step following the rate-determining reaction between the metalate and MeI. No reaction may be observed between the metalate and $Ph_3P$.[47] Using Occam's Razor, in conjunction with the very high yields of the phosphine product, we have assigned the intermediate the structure of the alkyliron complex. It is not surprising that we are unable to isolate or observe this species since it is electronically equivalent to the $[Co(CO)_4CH_3]$ complex, which decomposes at temperatures in excess of −30 °C.[48] We have made no attempts to discover the fate of the alkyl group in the reactions performed in the absence of phosphine ligand.

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**Registry No.** $[Fe(CO)_3(NO)]^-Na^+$, 25875-18-7; $[Fe(CO)_3(NO)]^-PPN^+$, 61003-17-6; $[Fe(CO)_3(NO)]^-K^+$, 25875-19-8; $PPh_3$, 603-35-0; 18-C-6, 17455-13-9; $(NH_2)_2DBC$, 60016-77-5; $Br_4DBC$, 62667-75-8; $(NO_2)_2DBC$, 29721-41-3; MeI, 74-88-4.

**Supplementary Material Available:** Comments relating to the treatment of the disorder problem and a listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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(47) This comment refers to thermal reactions. If the metalate is treated with triphenylphosphine and irradiation, we have observed facile CO displacement. We are examining the new metalate formed under these conditions.

(48) W. Beck and R. E. Nitzschmann, *Chem. Ber.*, **97**, 2098 (1964).

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# Role of the Trichlorostannyl Ligand in Homogeneous Catalysis. 2. Spectroscopic Studies of the Reaction of *cis*-$[PtCl_2(CO)(PR_3)]$ with $SnCl_2·2H_2O$: Ligand Rearrangement Reactions in the Formation of an Olefin Hydroformylation Catalyst Precursor[1]

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The complex *cis*-$[PtCl_2(CO)(PPh_3)]$ reacts with $SnCl_2·2H_2O$ in acetone to yield solutions that are active in the catalytic hydroformylation of olefins. Studies by $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{119}Sn\{^1H\}$, and $^{195}Pt$ NMR spectroscopy, including experiments utilizing $^{13}C$-labeled carbon monoxide, have shown that *cis*-$[PtCl_2(CO)(PPh_3)]$ reacts with $SnCl_2·2H_2O$ via a ligand rearrangement process. A cationic complex, *trans*-$[PtCl(CO)(PPh_3)_2]^+$, and four anionic complexes, three of which are identified as $[Pt(SnCl_3)_5]^{3-}$, *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, and *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$, are formed. One minor anionic product remains unidentified. Similar chemistry occurs with the analogous $P(p\text{-}MeC_6H_4)_3$ and $P(p\text{-}FC_6H_4)_3$ complexes, but the rearrangement reaction occurs much more slowly with the basic $PEt_3$ ligand. Some conclusions concerning the mechanism of the reaction are presented; $SnCl_2·2H_2O$ not only serves as a source of $SnCl_2$ moieties, which undergo insertion reactions, but also generates secondary cationic species, which maintain electroneutrality in the system. Attempted isolation of the ionic species leads to a further rearrangement reaction, ultimately yielding *cis*-$[PtCl_2(PPh_3)_2]$ as the only isolable product.

## Introduction

Platinum(II) halide complexes are known to react with tin(II) chloride[2a] to produce solutions, usually intensely colored, that are often catalytically active in the homogeneous hydrogenation[3,4] and hydroformylation[5,6] of olefins. It has been appreciated for some years[7] that $SnCl_2$ will react with certain transition-metal complexes containing a M–Cl bond to yield trichlorostannyl complexes, via migratory insertion reactions. Such complexes are believed to be key intermediates in the homogeneous catalytic activation of organic unsaturates. Support for these ideas has become available in recent years through the application of multinuclear magnetic resonance techniques,[8] which allow complex systems such as the $[PtCl_2(PR_3)_2]/SnCl_2·2H_2O$ catalyst precursor to be probed by $^1H$, $^{31}P$, $^{117,119}Sn$, and $^{195}Pt$ NMR methods and much structural information to be acquired concerning the species present in solution.

Extensive NMR studies by Pregosin and co-workers[9-11] have shown that halocarbon solutions of $[PtCl_2(PR_3)_2]$ complexes react with tin(II) chloride according to eq 1. The geometry of **1** may be either cis or trans, depending upon the nature of R, whereas **2** is always of trans geometry and reacts with $H_2$

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(1) Part 1: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.

(2) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Wiley: New York, 1973: (a) p 93; (b) p 96.

(3) Billard, C.; Clark, H. C.; Wong, C. S. IXth International Conference on Organometallic Chemistry, Dijon, France, 1979, Abstract No. C3; *J. Organomet. Chem.* **1980**, *190*, C3.

(4) See for examples: Cramer, R. D.; Jenner, E. L.; Lindsey, R. V.; Stolberg, U. G. *J. Am. Chem. Soc.* **1963**, *85*, 1691. Tayim, H. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 3420. Bailar, J. C., Jr.; Itatani, H.; Crespi, M. J.; Geldard, J. *Adv. Chem. Ser.* **1967**, *No. 62*, 103. Bailar, J. C., Jr. *Platinum Met. Rev.* **1971**, *15*, 2. Itatani, H.; Bailar, J. C., Jr. *Ind. Eng. Chem. Prod. Res. Dev.* **1972**, *11*, 146. James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.

(5) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503.

(6) Schwager, I.; Knifton, J. F., German Patent 2 322 751, 1973. Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553. Consiglio, G.; Pino, P. *Helv. Chim. Acta* **1976**, *59*, 642. Schwager, I.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256.

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(8) Davies, J. A. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, in press.

(9) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1979**, *61*, 1848.

(10) Ostaja-Starzewski, K. A.; Pregosin, P. S.; Ruegger, H. *Inorg. Chim. Acta* **1979**, *36*, L445.

(11) Pregosin, P. S. Biennial Inorganic Chemistry Symposium of the Chemical Institute of Canada and the American Chemical Society, Guelph, Canada, 1980.

0020-1669/83/1322-0427$01.50/0

$$[PtCl_2(PR_3)_2] \xrightarrow{SnCl_2} \underset{\mathbf{1}}{[PtCl(SnCl_3)(PR_3)_2]} \xrightarrow{SnCl_2} \underset{\mathbf{2}}{[Pt(SnCl_3)_2(PR_3)_2]} \quad (1)$$

to yield *trans*-$[PtH(SnCl_3)(PR_3)_2]$. The hydrido complex reacts with activated acetylenes to yield insertion products.[10] This reaction sequence is a stoichiometric series that reproduces the chemistry expected to occur in a catalytic cycle for the activation of unsaturated hydrocarbons. Studies of the $[PtCl_2(PEt_3)_2]/SnCl_2$ system by $^{31}P$ and $^{117}Sn$ NMR techniques have shown[12] that the use of acetone as a solvent causes the chemistry described by eq 1 to be complicated by equilibria, as exemplified by eq 2, involving the elimination of $SnCl_2$ from a M–$SnCl_3$ bond.

$$trans\text{-}[PtCl(SnCl_3)(PEt_3)_2] \rightleftharpoons cis\text{-}[PtCl_2(PEt_3)_2] + SnCl_2 \quad (2)$$

Nonetheless, the simple insertion of $SnCl_2$ into a M–Cl bond is often assumed to yield the primary intermediate in a catalytic cycle, although this is by no means proven under the conditions employed for actual catalytic syntheses. Such reactions are generally performed under elevated conditions of temperature and pressure,[3–6] and yet catalytic cycles derived from simple stoichiometric reaction series and equilibria, of the types shown in eq 1 and 2, are described in even the most modern critical texts on homogeneous catalysis.[13,14]

In a recent paper[5] we described the development of a new series of catalyst precursors for olefin hydroformylation. The precursors were formed by the reaction of *cis*-$[PtCl_2(CO)(PR_3)]$ (R = *p*-$FC_6H_4$, Ph, *p*-$MeC_6H_4$, Et, *n*-Bu, c-Hx)[15] with $SnCl_2{\cdot}2H_2O$. In addition to the expected variations in catalytic activity with $CO/H_2$ ratios, total pressures, and operating temperatures, marked dependences on the Pt(II)/Sn(II) ratio, the nature of the R group in the $PR_3$ ligand, and the nature of the solvent were observed. Catalytic activity was approximately constant[16] with Pt(II)/Sn(II) ratios of 1/2 to 1/10 but declined rapidly when ratios employing less $SnCl_2{\cdot}2H_2O$ were used. No correlation of activity with either steric or electronic parameters associated with the $PR_3$ ligands was observed, and efficient catalysis was obtained with use of only acetone or acetonitrile as solvent; use of both methanol and tetrahydrofuran resulted in a total loss of activity.[5] This behavior is so markedly different from that of the well-known $[PtCl_2(PR_3)_2]/SnCl_2$ catalyst system[6] that it seemed possible that chemistry of the type described by eq 1 and 2, although taken to be entirely general for such Pt(II)/Sn(II) reaction systems, may not be operative in the present case.

## Results and Discussion

For many of our catalytic studies[5] we employed the complex *cis*-$[PtCl_2(CO)(PPh_3)]$ as a model catalyst precursor and utilized acetone as the solvent; accordingly, it was this system that we first investigated by NMR spectroscopy.

The addition of $SnCl_2{\cdot}2H_2O$ to acetone suspensions of *cis*-$[PtCl_2(CO)(PPh_3)]$ generates an immediate bright red coloration, and the evolution of gas could be visually detected in clear solutions of the more concentrated samples. The $^{31}P\{^1H\}$ NMR spectra of such solutions were recorded at ambient temperature after the addition of 1.0, 2.0, 2.5, and 5.0 equiv of $SnCl_2{\cdot}2H_2O$. The disappearance of the starting material ($\delta(P) = 9.05$, $^1J(^{195}Pt,^{31}P) = 3057$ Hz)[17] was accompanied by the formation of a single observable new phosphorus-containing species ($\delta(P) = 18.50$, $^1J(^{195}Pt,^{31}P) = 2034$ Hz). After the addition of 2.0 equiv of $SnCl_2{\cdot}2H_2O$, the resonances associated with *cis*-$[PtCl_2(CO)(PPh_3)]$ were no longer present and no change in the spectrum was observed upon further additions. If chemistry analogous to eq 1 had occurred, the expected products would be $[PtCl(SnCl_3)(CO)(PPh_3)]$ and/or $[Pt(SnCl_3)_2(CO)(PPh_3)]$, and yet the $^{31}P\{^1H\}$ NMR spectra showed no evidence of coupling between $^{31}P$ and $^{117,119}Sn$, even when recorded at 213 K.[18]

It was found that samples prepared in the absence and in the presence of air had identical $^{31}P\{^1H\}$ NMR spectra and that sealed samples could be stored for several days without any deterioration being apparent. Purging solutions of *cis*-$[PtCl_2(CO)(PPh_3)]$ with molecular oxygen during the slow addition of $SnCl_2{\cdot}2H_2O$ considerably retarded the reaction, however,[19] and indeed, it has been shown[20] that $SnCl_2$ is oxidized by dioxygen in the presence of donor solvents according to eq 3 (where $x = 1, 2$). Under the conditions normally

$$2SnCl_2 + O_2 + 2x(\text{solvent}) \rightarrow 2SnOCl_2(\text{solvent})_x \rightarrow SnCl_4(\text{solvent})_2 + SnO_2 + 2(x-1)\text{solvent} \quad (3)$$

employed during this study (see Experimental Section), such oxidation of $SnCl_2{\cdot}2H_2O$ was not observed.

The $^{195}Pt$ NMR spectrum of an acetone solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ to which 2.0 equiv of $SnCl_2{\cdot}2H_2O$ had been added[21] was recorded at 213 K. The spectrum showed the presence of a single species in the range +2800 to −4400 ppm (relative to $K_2PtCl_4$(aq)) as a 1/2/1 triplet ($\delta(Pt) = -2822$, $^1J(^{195}Pt,^{31}P) = 2063$ Hz). No coupling to $^{117,119}Sn$ was observed. The $^{31}P\{^1H\}$ and $^{195}Pt$ NMR data indicate that a single observable platinum/phosphine complex is formed that contains *two* equivalent $PPh_3$ ligands per metal center. The magnitude of $^1J(^{195}Pt,^{31}P)$ indicates that the two equivalent $PPh_3$ ligands are trans to groups of relatively high trans influence,[22] which tends to rule against CO or $Cl^-$ as possible candidates. As the presence of the high-trans-influence $SnCl_3^-$ ligand is eliminated by the absence of coupling to $^{117,119}Sn$, the magnitude of $^1J(^{195}Pt,^{31}P)$ suggests that the two $PPh_3$ ligands are mutually trans.

In order to probe the nature of the rearrangement product further, we prepared a sample of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ by cleavage of the dimeric complex, $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$, with carbon-13 monoxide. The carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum of an acetone solution of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ showed the expected doublet,[23] exhibiting coupling to $^{195}Pt$ ($\delta(C) = 157.7$, $^1J(^{195}Pt,^{13}C) = 1766$ Hz, $^2J(^{31}P,^{13}C)$

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(12) Koch, B. R.; Fazakerley, G. V.; Dijkstra, E. *Inorg. Chim. Acta* **1980**, *45*, L51.

(13) Masters, C "Homogeneous Transition-Metal Catalysis—A Gentle Art"; Chapman and Hall: London, 1981; p 131 (paperback edition).

(14) Kahn, M. M. T.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. I, p 60.

(15) Abbreviations are as follows: Ph = $C_6H_5$, Me = $CH_3$, Et = $C_2H_5$, *n*-Bu = $CH_2(CH_2)_2CH_3$, c-Hx = cyclohexane.

(16) Catalytic activity was found to be constant within experimental error for Pt(II)/Sn(II) ratios of 1/2 and 1/5 with possibly a very slight decrease upon changing to a ratio of 1/10. See ref 5 for discussion.

(17) Data as previously reported: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 1636.

(18) Tin has three isotopes of $I = {}^1/_2$, $^{119}Sn$ (8.68%), $^{117}Sn$ (7.67%), and $^{115}Sn$ (0.35%). The low abundance of $^{115}Sn$ makes the observation of coupling to this isotope uncommon.

(19) Purging solutions with molecular oxygen was also found to inhibit the catalytic activity of such precursors during olefin hydroformylation. See ref 5 for discussion.

(20) Messin, G.; Janier-Dubry, J. L. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 409.

(21) The $^{195}Pt$ NMR spectrum of *cis*-$[PtCl_2(CO)(PPh_3)]$ itself consists of a doublet resonance ($\delta(Pt) = -3517$, $^1J(^{195}Pt,^{31}P) = 3112$ Hz for a $Me_2CO$ solution).

(22) The values of $^1J(^{195}Pt,^{31}P)$ in typical square-planar platinum(II) complexes vary with the nature of the trans ligand, L, according to the series L = P(III) ligand < sp C ligand < $Cl^-$. (a) For examples, see: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 944. (b) For a discussion of the NMR trans influence, see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 355.

(23) Data as previously reported: Anderson, G. K.; Cross, R. J.; Rycroft, D. S. *J. Chem. Res., Miniprint* **1979**, 1601.

**Table I.** $^{119}Sn\{^1H\}$ NMR Spectroscopic Data[a]

| obsd species | $\delta(^{119}Sn)$ | $^1J(^{195}Pt,^{119}Sn)$/Hz | $^2J(^{119}Sn,^{117}Sn)$/Hz | $\nu_{1/2}$/Hz |
|---|---|---|---|---|
| A | −120.9 | 15 875 | 6090 | 210 |
| B[b] | −141.6 | 14 960 | 5810 | <50 |
| C | −124.5 | ca. 15 850 | not obsd | ca. 350 |
| D[c] | −109.4 | ca. 18 600 | not obsd | *d* |

[a] Recorded in acetone solution at 213 K. [b] $^2J(^{119}Sn,^{13}C)$ = 195 Hz for the $^{13}CO$ analogue. [c] $^2J(^{119}Sn,^{31}P)$ = 266 Hz. [d] Resonance of insufficient intensity for $\nu_{1/2}$ to be measured.

= 6 Hz).[24] Addition of 2.0 equiv of $SnCl_2{\cdot}2H_2O$ to such a solution caused the original resonances to disappear and new signals, of reduced relative intensity, to appear as a 1/2/1 triplet, exhibiting coupling to $^{195}Pt$ ($\delta$(C) = 161.0, $^1J(^{195}Pt,^{13}C)$ = 1852 Hz, $^2J(^{31}P,^{13}C)$ = 10 Hz). The magnitude of $^2J(^{31}P,^{13}C)$[24] and the multiplicity of the resonance indicate that one or more carbonyl groups are bonded to platinum with two $PPh_3$ ligands, each in a cis geometry relative to the carbonyl group(s). The value of $\delta$(C) demonstrates that no bridging carbonyl groups are present.[25]

The $^{31}P\{^1H\}$ NMR spectrum of such a sample was recorded at 213 K. The resonance appeared as a doublet ($\delta$(P) = 17.2, $^1J(^{195}Pt,^{31}P)$ = 2073 Hz, $^2J(^{31}P,^{13}C)$ = 10 Hz), demonstrating that there is only one carbonyl group per molecule. The nature of the remaining ligand was still uncertain, but $Cl^-$ seemed a likely possibility as the magnitude of $^1J(^{195}Pt,^{13}C)$ was in accord with the known trans influence of the chloride ligand.[26]

Accordingly, the known complexes $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][X]_2$ (X = $ClO_4$, $SO_3CF_3$)[27] were cleaved with CO and $^{13}CO$ to yield *trans*-$[PtCl(CO)(PPh_3)_2][X]$[27] and its carbon-13 monoxide analogue. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of these complexes (see Experimental Section) were identical with those of the products of the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with 2 equiv of $SnCl_2{\cdot}2H_2O$ in acetone solution. These results thus conclusively identify the cationic part of the rearrangement product as the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ ion.

A consideration of the stoichiometry of the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with $SnCl_2{\cdot}2H_2O$ to yield the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation indicates the formal loss of a "$[PtCl_3(CO)]^-$" moiety from two molecules of *cis*-$[PtCl_2(CO)(PPh_3)]$. The evolution of gas during the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with $SnCl_2{\cdot}2H_2O$ and the reduced relative intensity of the resonances in the $^{13}C\{^1H\}$ NMR spectrum of the product (vide supra) indicate that some CO may be evolved during the rearrangement reaction. Accordingly, the anionic species, which must also be generated in this reaction, are a formal product of the reaction of "$[PtCl_3]^-$" and $SnCl_2{\cdot}2H_2O$, possibly containing some CO also, in a substoichiometric quantity.

The $^{195}Pt$ NMR spectrum at 213 K of the product of the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ and 2.0 equiv of $SnCl_2{\cdot}2H_2O$ in acetone solution showed only the resonances assigned to the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ ion, and no resonances attributable to any anionic species were observed within the range studied (+2800 to −4400 ppm).[28] Accordingly, $^{119}Sn\{^1H\}$ NMR spectroscopy was employed in order to gain structural information concerning the anionic products.[28] Initially,[5] $^{119}Sn\{^1H\}$ NMR spectra were measured at 93.07 MHz; the spectrum at 213 K of an acetone solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ to which 2.0 equiv of $SnCl_2{\cdot}2H_2O$ had been added showed a single resonance exhibiting coupling to $^{195}Pt$ ($\delta$(Sn) = −126.8, $^1J(^{195}Pt,^{119}Sn)$ = 15 968 Hz). Subsequently, it was found that spectra measured at 149.16 MHz allowed the observation of more than a single resonance for an identical sample and so all further measurements were made at the higher field.

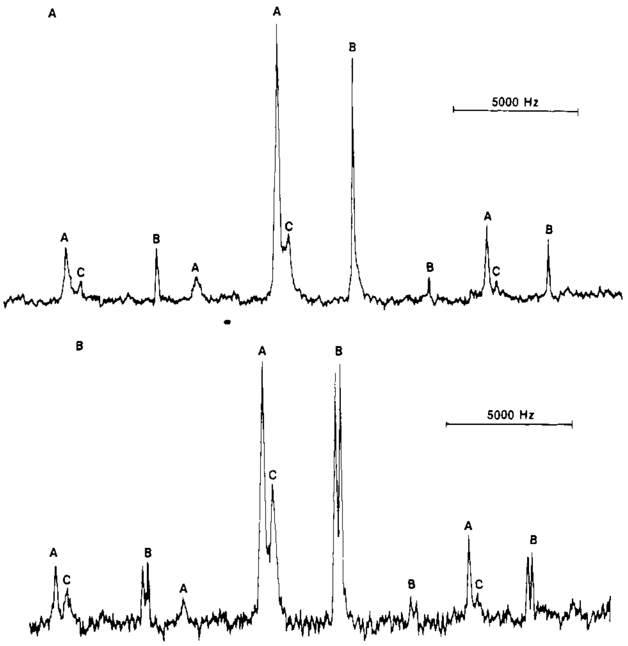

**Figure 1.** $^{119}Sn\{^1H\}$NMR spectra (acetone solution, 2.0 equiv of $SnCl_2{\cdot}2H_2O$ added): (A) *cis*-$[PtCl_2(CO)(PPh_3)]$; (B) *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$.

$^{119}Sn\{^1H\}$ NMR spectra were recorded at 213 K for acetone solutions of *cis*-$[PtCl_2(CO)(PPh_3)]$ to which 1.0, 2.0, and 5.0 equiv of $SnCl_2{\cdot}2H_2O$ had been added. The spectrum obtained with 1 equiv of $SnCl_2{\cdot}2H_2O$ exhibited two distinct resonances, A and B (Table I), in the ratio 4/1.

A spectrum obtained with 2.0 equiv of $SnCl_2{\cdot}2H_2O$ added allowed a more satisfactory S/N ratio to be obtained and showed the presence of both of the resonances previously observed (species A and B), and a third species, C (Table I), was observed as a very broad resonance exhibiting coupling to $^{195}Pt$. The ratio of the species present was A/B/C = 2/2/1, as estimated from integrated intensities.

Species A was the major one observed (>95%) when a $^{119}Sn\{^1H\}$ NMR spectrum was obtained for an acetone solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ to which 5.0 equiv of $SnCl_2{\cdot}2H_2O$ had been added. Resonances associated with species B and C were no longer observable. Additionally, a minor component, D (Table I), was observed. It is particularly noteworthy

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(24) The magnitude of $^2J(^{31}P,^{13}C)$ is an excellent probe of geometry in platinum(II) complexes containing tertiary phosphine and carbonyl ligands. For example, in the cis isomer of $[PtCl_2(^{13}CO)(PEt_3)]$, $^2J(^{31}P,^{13}C)$ = −6.7 Hz whereas in the trans isomer, $^2J(^{31}P,^{13}C)$ = +159.6 Hz. For further examples, see: Anderson, G. K.; Cross, R. J.; Rycroft, D. S. *J. Chem. Res., Synop.* **1980**, 240.

(25) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1975**, *20*, 299.

(26) Although comparative data are less common, the magntidue of $^1J(^{195}Pt,^{13}C)$ appears to follow the same trans influence series as $^1J(^{195}Pt,^{31}P)$, discussed in ref 22. For example, two of the isomers of $[PtClPh(CO)(PPh_2Me)]$ have values of $^1J(^{195}Pt,^{13}C)$ 1427 Hz (isomer with CO trans to P) and 1947 Hz (isomer with CO trans to $Cl^-$). No directly comparable value for CO trans to an sp C ligand is available. See ref 24 for further examples.

(27) Clark, H. C.; Dixon, K. R.; Jacobs, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 2259.

(28) The range of $^{195}Pt$ chemical shifts is very large, and resonances attributable to anionic platinum complexes encompass the entire known range, ca. 13 000 ppm (i.e., the $[PtF_6]^{2-}$ and $[PtI_6]^{2-}$ ions have resonances separated by 13 385 ppm). Accordingly, a diligent search for resonances attributable to anion rearrangement products was not considered profitable and $^{119}Sn\{^1H\}$ NMR spectroscopy was employed as an alternative. The known chemical shift range of $^{119}Sn$ is ca. 2500 ppm, and the presence of both $^{119}Sn$ and $^{117}Sn$ in a statistical percentage of molecules containing more than one tin nucleus, which leads to the generation of $^{119}Sn/^{117}Sn$ coupling, makes $^{119}Sn\{^1H\}$ NMR a most attractive technique. See ref 8 for discussion.

that on no occasion was a resonance observed for uncomplexed tin(II) chloride.[29]

Clearly, the $^{119}$Sn{$^1$H} NMR data are not straightforward, the relative proportions of species A–D being determined by the Pt(II)/Sn(II) ratio. As the three major species, A–C, were clearly observable for the case where the Pt(II)/Sn(II) ratio was 1/2, it was this system that we chose to study in greater depth. An acetone solution of *cis*-$[PtCl_2(CO)(PPh_3)]$, to which 2.0 equiv of $SnCl_2{\cdot}2H_2O$ had been added, was examined 30 min after the addition of the tin(II) chloride and again after 2.5 and 48 h of standing under a nitrogen atmosphere at room temperature. The final spectrum is shown in Figure 1A. The three species A–C are evident, with species C present in only a minor amount. The series of spectra indicated a relative increase in intensity of the resonance associated with species A, at the expense of B and C, over the first 2.5-h period, but then the relative intensities appear unchanged over the following 45.5 h. A similar series of experiments was performed with use of the carbon-13 monoxide complex, *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$. The final spectrum is shown in Figure 1B. This spectrum clearly shows that the central resonance of species B and the satellites resulting from coupling to $^{195}$Pt and $^{117}$Sn appear as well-defined doublets, due to coupling to $^{13}$C.

These data allow some questions concerning the nature of the anionic species to be answered. The experiments with the carbon-13 labeled carbonyl complex demonstrate that neither species A nor species C contains a carbonyl ligand. The $^{119}$Sn{$^1$H} NMR data of species A are very similar to those reported for the $[Pt(SnCl_3)_5]^{3-}$ anion. The data of Nelson et al.[30] for this anion include similar values of $^1J(^{195}Pt,^{119}Sn)$ and $^2J(^{119}Sn,^{117}Sn)$ (16024 and 6230 Hz, respectively) but differ with respect to the chemical shift (−142 ppm, erroneously reported as −387 ppm in the original paper).[30] Although tin chemical shifts cover a substantial range[28] and changes in temperature and solvent can appreciably affect the shift of many classes of tin compounds, the external standard used by ourselves (10% $Me_4Sn$ in $CDCl_3$ at ambient temperature) and Nelson et al. ($Me_4Sn$, presumably neat, temperature undefined) is known to display only a minor shift dependence on the nature of the solvent.[31] Accordingly, the anion, $[Pt(SnCl_3)_5]^{3-}$, was prepared independently by the reaction of $[K][PtCl_3(C_2H_4)]$ with $SnCl_2{\cdot}2H_2O$ in acetone solution, and the $^{119}$S{$^1$H} NMR spectrum was recorded at 213 K under our standard operating conditions (see Experimental Section). The spectrum obtained ($\delta(Sn) = -121.2$, $^1J(^{195}Pt,^{119}Sn) = 15995$ Hz, $^2J(^{119}Sn,^{117}Sn) = 6185$ Hz) confirmed that a complex identical with species A had been formed. Analysis of the satellite intensities[32] confirmed a Pt(II)/Sn(II) ratio of 1/5, defining the product conclusively as the $[Pt(SnCl_3)_5]^{3-}$ anion.

The data obtained for species B suggest a four-coordinate complex and allow a structure to be assigned. A single resonance is observed, demonstrating equivalence of all $^{119}$Sn nuclei in each molecule, and the magnitudes of $^1J(^{195}Pt,^{119}Sn)$ and $^2J(^{119}Sn,^{117}Sn)$ show that there are two tin nuclei in mutually trans positions.[33] The coupling to $^{13}$C is of the magnitude expected for a cis arrangement of CO and $SnCl_3^-$ ligands. The earlier $^{13}$C{$^1$H} NMR studies at 15.1 MHz of the reaction of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ with $SnCl_2{\cdot}2H_2O$ (vide supra) had allowed observation of the resonances associated with the *trans*-$[PtCl(^{13}CO)(PPh_3)_2]^+$ cation, but the anionic species B, known to contain a carbonyl ligand from the $^{119}$Sn{$^1$H} NMR data, was not observed. Accordingly, these studies were repeated, with the obtainment of $^{13}$C{$^1$H} NMR spectra at 100.1 MHz, and resonances attributable to species B were indeed observed ($\delta(C) = 152.5$, $^1J(^{195}Pt,^{13}C) = 1794$ Hz), although the minor nature of this species prevented observation of $^{119}$Sn/$^{13}$C coupling in the $^{13}$C{$^1$H} spectrum. The magnitude of $^1J(^{195}Pt,^{13}C)$ is indicative of a carbonyl group trans to a ligand of relatively low trans influence,[34] and accordingly, the fourth ligand is likely to be $Cl^-$. The species B is thus proposed to be the *trans*-$[PtCl(SnCl_3)_2(CO)]^-$ anion.[34]

The $^{119}$Sn{$^1$H} NMR data of species C do not allow a structure to be assigned for this complex. The minor nature of species C prevented observation of $^{119}$Sn/$^{117}$Sn coupling, should any be present, and accordingly the Pt(II)/Sn(II) ratio cannot be defined by analysis of satellite intensities. The very broad resonances associated with species C suggest that a polynuclear structure may be possible,[35] although, other than the conclusion that this minor species contains no CO or $PR_3$ ligands, further discussion would be speculative and unwarranted.

Addition of further $SnCl_2{\cdot}2H_2O$ to solutions containing *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, $[Pt(SnCl_3)_5]^{3-}$, and species C caused both *trans*-$[PtCl(SnCl_3)_2(CO)]^-$ and species C to be converted to the $[Pt(SnCl_3)_5]^{3-}$ anion, thus resulting in the total loss of CO from the anionic rearrangement products and generating a dominant anionic species.

The species D formed, in ca. 5% yield (by peak heights in the $^{119}$Sn{$^1$H} NMR spectrum), along with the dominant anion, $[Pt(SnCl_3)_5]^{3-}$, by the reaction of an acetone solution of *cis*-$[PtCl_2(CO)(PPh_3)]$ with 5.0 equiv of $SnCl_2{\cdot}2H_2O$ remained unidentified. The $^{119}$Sn{$^1$H} NMR data showed the presence of a doublet of separation 266 Hz, a value typical of $^2J(^{119}Sn,^{31}P)$ in platinum(II) complexes with cis $PR_3$ and $SnCl_3^-$ ligands.[9,12] The $^{31}$P{$^1$H} NMR spectra of such reaction mixtures showed only resonances attributable to the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation (vide supra) until a spectrum was obtained with a S/N ratio of ca. 300, which showed the presence of a second species, in <2% abundance,[36] as a resonance at 13.8 ppm. The very minor nature of this species precluded the observation of coupling to $^{117,119}$Sn and $^{195}$Pt.

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(29) The $^{119}$Sn{$^1$H} NMR spectrum of a saturated acetone solution of $SnCl_2{\cdot}2H_2O$ shows a single broad resonance ($\delta(Sn) = -218$, $\nu_{1/2}$ ca. 1200 Hz, measured at 213 K).

(30) Nelson, J. H.; Cooper, V.; Rudolph, R. W. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 263. For correct values of $\delta$(Sn), see: *Ibid.* **1980**, *16*, 587.

(31) Tupčiauskas, A. P.; Sergeyev, N. M.; Ustynyuk, Yu. A. *Liet. Fiz. Rinkinys* **1971**, *11*, 93. Smith, P. J.; Tupčiauskas, A. P. *Annu. Rep. NMR Spectrosc.* **1978**, *8*, 292.

(32) Rudolph, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4629.

(33) Values of $^1J(^{195}Pt,^{119}Sn)$ depend upon the nature of the trans ligand, much as expected. For example, in *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ and *trans*-$[PtCl(SnCl_3)(PEt_3)_2]$, both with $SnCl_3^-$ trans to $Cl^-$, $^1J(^{195}Pt,^{119}Sn)$ is ca. 28000 Hz[9,12] whereas in *trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$, with $SnCl_3^-$ ligands mutually trans, $^1J(^{195}Pt,^{119}Sn)$ is ca. 20000 Hz.[12] Data concerning $^2J(^{119}Sn,^{117}Sn)$ in platinum(II) complexes are scarce; the value for the mutually cis $SnCl_3^-$ ligands in *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$ is 2485 Hz. The much larger value of 5811 Hz obtained here demonstrates that the $SnCl_3^-$ ligands are trans.

(34) For example, $^1J(^{195}Pt,^{13}C) = 1757$ Hz in the directly comparable $[PtCl_3(CO)]^-$ ion. See ref 24 for discussion. The $[PtCl(SnCl_3)_2(CO)]^-$ anion is reported to be the product of the reaction of $[K]_2[PtCl_4]/SnCl_2$ with CO. The geometry was assigned as cis on the basis of IR data, which showed several unusual features (Kingston, J. V.; Scollary, G. R. *J. Chem. Soc. A* **1971**, 3765). In the present preparation, the geometry is undoubtedly trans. Interestingly, the $[PtCl(SnCl_3)_2(CO)]^-$ ion is reported to be involved in the catalysis of the water gas shift reaction (Cheng, C. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1978**, *100*, 5968).

(35) Polynuclear anions, derived from the reaction of $PtCl_2$, $SnCl_2$ and $Cl^-$, are known. See: Lindsey, R. V., Jr.; Parshall, G. W.; Stolberg, U. G. *Inorg. Chem.* **1966**, *5*, 109.

(36) Thus, species D represents <2% of the total $PR_3$-containing species but ca. 5% of the total $SnCl_3^-$-containing species; the intensity data from the $^{31}$P{$^1$H} and $^{119}$Sn{$^1$H} NMR spectra are therefore not incompatible, as they take no account of the fact that species D contains two $SnCl_3^-$ ligands but only one $PPh_3$ ligand.

The identity of the species D was not elucidated until our studies on the reactivity of dimeric platinum(II) halo complexes with tin(II) salts[37] showed that an acetone solution of $[\mathrm{Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2}]$ reacted with 4.0 equiv of $\mathrm{SnCl_2{\cdot}2H_2O}$ (i.e., Pt(II)/Sn(II) = 1/2) to yield the species D as the sole phosphorus-containing product. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum consisted of a single resonance exhibiting coupling to $^{195}$Pt and $^{117,119}$Sn ($\delta$(P) = 13.8, $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 2456 Hz, $^2J(^{117,119}\mathrm{Sn},^{31}\mathrm{P})$ = 246 Hz (av)). Analysis of the intensities of the satellites due to coupling to $^{117,119}$Sn and $^{195}$Pt indicates a Pt(II)/Sn(II) ratio of 1/2, and the magnitude of $^2J(^{117,119}\mathrm{Sn},^{31}\mathrm{P})$ demonstrates that the $\mathrm{PPh_3}$ and $\mathrm{SnCl_3^-}$ ligands are cis,[9] as postulated from the $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR data of species D (vide supra). The magnitude of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ is consistent[38] with coordination of a ligand of relatively low trans influence such as $\mathrm{Cl^-}$ trans to the $\mathrm{PPh_3}$ group. The ion may thus be assigned the structure *trans*-$[\mathrm{PtCl(SnCl_3)_2(PPh_3)}]^-$.

The data so far discussed have shown that the complex *cis*-$[\mathrm{PtCl_2(CO)(PPh_3)}]$ reacts with $\mathrm{SnCl_2{\cdot}2H_2O}$ in acetone solution to yield the cation *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}]^+$ and a number of anions, $[\mathrm{Pt(SnCl_3)_5}]^{3-}$, *trans*-$[\mathrm{PtCl(SnCl_3)_2(CO)}]^-$, *trans*-$[\mathrm{PtCl(SnCl_3)_2(PPh_3)}]^-$, and one minor unidentified species C, via a ligand rearrangement process. The relative abundances of the various anionic species are evidently determined by the Pt(II)/Sn(II) ratio, with the $[\mathrm{Pt(SnCl_3)_5}]^{3-}$ ion dominant at high tin(II) chloride concentrations.

At this stage, the stoichiometry of the reaction must be considered. The reaction of *cis*-$[\mathrm{PtCl_2(CO)(PPh_3)}]$ with 5.0 equiv of $\mathrm{SnCl_2{\cdot}2H_2O}$ has been shown to yield the cation, *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}]^+$, and two anions, $[\mathrm{Pt(SnCl_3)_5}]^{3-}$ (95%) and *trans*-$[\mathrm{PtCl(SnCl_3)_2(PPh_3)}]^-$ (5%), only. Evidently, these products account for only ca. 50% of the $\mathrm{SnCl_2{\cdot}2H_2O}$ added and yet no $^{119}$Sn NMR evidence for free $\mathrm{SnCl_2{\cdot}2H_2O}$ was observed (vide supra). Additionally, further work[37] has shown that in acetone solution the complex *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}][\mathrm{SO_3CF_3}]$ reacts with free $\mathrm{SnCl_2{\cdot}2H_2O}$. Accordingly, it seems evident that the additional $\mathrm{SnCl_2{\cdot}2H_2O}$ in the above reaction system, which does not affect the *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}]^+$ cation, has undergone some secondary reaction to yield a less reactive product. Indeed, the cation/anion ratio of the platinum-containing products shows that some secondary cationic species must be formed in order to preserve electroneutrality. Previously reported studies[39] of the $\mathrm{SnCl_2}$-catalyzed oxidation of benzene in aqueous acetone solution under ambient conditions have shown that a complex series of tin-containing cations is formed in this system. The nature and ratio of the various cations is dependent upon the amount of water present in the acetone solvent. As the amount of water increases, the concentration of $[\mathrm{Sn}]^{2+}$(aq) decreases while the concentration of the polynuclear cation $[\mathrm{Sn_3(OH)_4}]^{2+}$ increases. Less dominant cations, $[\mathrm{Sn_2(OH)_2}]^{2+}$ and $[\mathrm{Sn(OH)}]^+$, are also reported to be present.

In our system, the stoichiometry dictates that secondary cationic species are formed and the indirect evidence demonstrates that no free $\mathrm{SnCl_2{\cdot}2H_2O}$ is present in solution. Analysis of the 90% acetone/10% acetone-$d_6$ solvent employed for these studies by $^1$H NMR shows that substantial and variable amounts of water are present. Accordingly, it seems probable that electroneutrality is maintained in the system by the formation of complex hydroxytin cations. No $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR evidence for the formation of such species has been obtained, although the complexity of the solvent-dependent equilibria and polynuclear nature of the proposed cations may be an explanation for this.

The observed rearrangement reaction involves the transfer of a $\mathrm{PPh_3}$ ligand from on metal center to another. Accordingly, the nature of the $\mathrm{PR_3}$ ligand itself may be involved in determining the course of the reaction, and so analogous systems were investigated with use of complexes of para-substituted triarylphosphines, $\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$ and $\mathrm{P(\mathit{p}\text{-}FC_6H_4)_3}$, and a trialkylphosphine, $\mathrm{PEt_3}$, in order to determine the extent of electronic control exerted by these ligands.

The reactions of *cis*-$[\mathrm{PtCl_2(CO)(PR_3)}]$ (R = $\mathit{p}$-$\mathrm{MeC_6H_4}$, $\mathit{p}$-$\mathrm{FC_6H_4}$) with 2.0 equiv of $\mathrm{SnCl_2{\cdot}2H_2O}$ in acetone solutions were monitored by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. In both cases, quantitative formation of the appropriate *trans*-$[\mathrm{PtCl(CO)(PR_3)_2}]^+$ cation was observed, exactly as occurred with the $\mathrm{PPh_3}$ analogue. Indeed, use of a mixture of equimolar ratios of the precursors *cis*-$[\mathrm{PtCl_2(CO)(PPh_3)}]$ and *cis*-$[\mathrm{PtCl_2(CO)(PR_3)}]$ (R = $\mathit{p}$-$\mathrm{FC_6H_4}$, $\mathit{p}$-$\mathrm{MeC_6H_4}$) leads to formation of a statistical distribution of *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}]^+$, *trans*-$[\mathrm{PtCl(CO)(PR_3)_2}]^+$, and the mixed-phosphine complex *trans*-$[\mathrm{PtCl(CO)(PPh_3)(PR_3)}]^+$. The ligand-transfer process must thus occur at similar rates for $\mathrm{PPh_3}$, $\mathrm{P(\mathit{p}\text{-}MeC_6H_4)_3}$, and $\mathrm{P(\mathit{p}\text{-}FC_6H_4)_3}$. Only when the reaction of *cis*-$[\mathrm{PtCl_2(^{13}CO)(PEt_3)}]$ with 2.0 equiv of $\mathrm{SnCl_2{\cdot}2H_2O}$ in acetone solution was monitored by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy were substantial differences in behavior seen to occur.

In this case, the reaction was found to proceed very slowly and, even after a solution was heated at 323 K for 3 h, the major species in solution was unreacted *cis*-$[\mathrm{PtCl_2(^{13}CO)PEt_3}]$ (see Experimental Section). Two reaction products were also observed: the major product as a doublet resonance exhibiting coupling to $^{117,119}$Sn and $^{195}$Pt ($\delta$(P) = $-6.0$, $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 2012 Hz, $^2J(^{119,117}\mathrm{Sn},^{31}\mathrm{P})$ = 254 Hz (av), $^2J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 103 Hz) and the minor product as a singlet, exhibiting coupling to $^{195}$Pt only ($\delta$(P) = $-1.4$, $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 2207 Hz). The magnitudes of $^2J(^{119,117}\mathrm{Sn},^{31}\mathrm{P})$ and $^2J(^{31}\mathrm{P},^{13}\mathrm{C})$ in the spectrum of the major product indicate that the $\mathrm{PEt_3}$ ligand is cis to $\mathrm{SnCl_3^-}$[9] and trans to $^{13}$CO.[24] The ratios of the satellite intensities give a Pt(II)/Sn(II) ratio of 1/1, and the multiplicity of the resonance demonstrates the presence of a single carbonyl group. This product is accordingly assigned the formula $[\mathrm{PtCl(SnCl_3)(CO)(PEt_3)}]$ and is present as the isomer with $\mathrm{PEt_3}$ and CO ligands trans to each other. The identity of the minor product was not elucidated until later studies[37] on the reactivity of dimeric platinum(II) halo complexes with $\mathrm{SnCl_2{\cdot}2H_2O}$ showed that an acetone solution of $[\mathrm{Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2}]$ reacted with 4.0 equiv of $\mathrm{SnCl_2{\cdot}2H_2O}$ to yield exclusively an identical product. As in the case of the $\mathrm{PPh_3}$ complex (vide supra), this product was identified as the *trans*-$[\mathrm{PtCl(SnCl_3)_2(PEt_3)}]^-$ anion.[38] Although coupling to $^{195}$Pt is clearly evident in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of this anion at 213 K, coupling to $^{117,119}$Sn was only observed in cooling to 183 K ($\delta$(P) = $-2.4$, $J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 2161 Hz, $^2J(^{119,117}\mathrm{Sn},^{31}\mathrm{P})$ = ca. 215 Hz (av, br)), indicating that the anion is very labile, even at these low temperatures.

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(37) Anderson, G. K.; Clark, H. C.; Davies, J. A., following paper in this issue.

(38) This value of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ reflects not only the trans influence of the $\mathrm{Cl^-}$ ligand but also the cis influence of the $\mathrm{SnCl_3^-}$ groups. Thus, we have recorded the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of *trans*-$[\mathrm{PtCl_2(PEt_3)_2}]$, *trans*-$[\mathrm{PtCl(SnCl_3)(PEt_3)_2}]$, and *trans*-$[\mathrm{Pt(SnCl_3)_2(PEt_3)_2}]$ (see also ref 12) and obtained values of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ of 2415, 2058, and 1455 Hz, respectively (acetone solution, 213 K). Clearly, substitution of $\mathrm{Cl^-}$ by $\mathrm{SnCl_3^-}$ cis to $\mathrm{PEt_3}$ reduces the magnitude of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ by ca. 15% (monosubstitution) to 40% (disubstitution). For the $[\mathrm{PtCl_3(PEt_3)}]^-$ ion, $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 3704 Hz (see: Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095), and hence disubstitution to yield the *trans*-$[\mathrm{PtCl(SnCl_3)_2(PEt_3)}]^-$ ion is expected to give rise to a value of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ of ca. 2220 Hz. Synthesis of this ion (see text) and measurement of its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum yielded a value of 2207 Hz, as predicted. As couplings involving $\mathrm{PPh_3}$ are generally ca. 10% higher than those involving $\mathrm{PEt_3}$ (compare *trans*-$[\mathrm{PtCl_2(PR_3)_2}]$, where $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ = 2415 Hz for R = Et and 2637 Hz for R = Ph[22a]), the value of $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$ for the *trans*-$[\mathrm{PtCl(SnCl_3)_2(PPh_3)}]^-$ ion is predicted to be ca. 2430 Hz. The observed value is 2456 Hz, consistent with the proposed structure.

(39) Berentsveig, V. V.; Pleskach, N. I.; Rudenko, A. P. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1980**, *54*, 124.

The neutral product of this reaction, $[PtCl(SnCl_3)(CO)(PEt_3)]$, is the formal product of a simple insertion of $SnCl_2$ into one M–Cl bond of *cis*-$[PtCl_2(CO)(PEt_3)]$ followed by isomerization. Such a reaction is intuitively expected to be an initial step in the complex rearrangement process, which occurs much more slowly with the more basic $PEt_3$ ligand.[40] The presence of only one charged species, the *trans*-$[PtCl(SnCl_3)_2(PEt_3]^-$ anion, again suggests that secondary cationic species are formed.

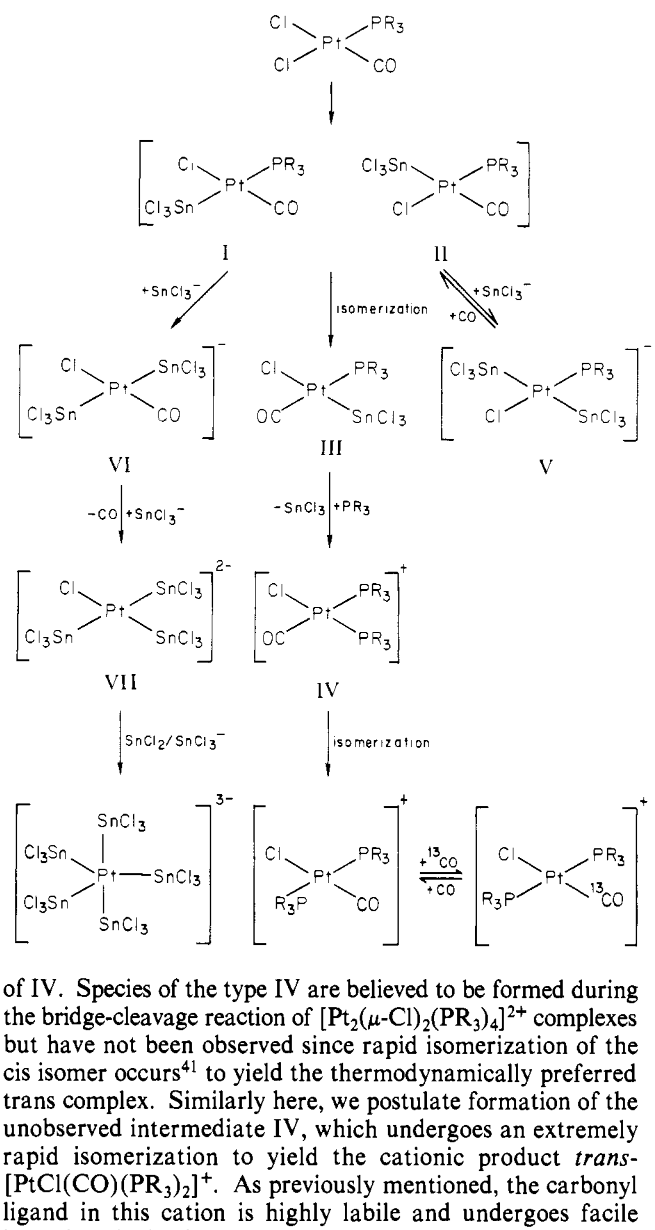
Only after the acetone solution of *cis*-$[PtCl_2(^{13}CO)(PEt_3)]\cdot 2.0SnCl_2 2H_2O$ was heated at 323 K for 96 h did the $^{31}P\{^1H\}$ NMR spectrum show that the *trans*-$[PtCl(^{13}CO)(PEt_3)_2]^+$ cation was the major phosphorus-containing species in solution (see Experimental Section). The nature of this species was confirmed by independent synthesis of the complex *trans*-$[PtCl(^{13}CO)(PEt_3)_2][SO_3CF_3]$ (see Experimental Section). Nonetheless, even after 96 h at 323 K, both unreacted *cis*-$[PtCl_2(^{13}CO)(PEt_3)]$ and *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ could still be identified in solution, indicating that the more basic tertiary phosphine retards the ligand rearrangement reaction quite dramatically.

The reaction of *cis*-$[PtCl_2(^{13}CO)(PEt_3]$ with 5.0 equiv of $SnCl_2\cdot 2H_2O$ in acetone solution proceeds to ca. 80% completion at room temperature. Monitoring the $^{31}P\{^1H\}$ NMR spectrum of such a reaction mixture at 213 K shows that the major phosphorus-containing species in solution is *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ although both the insertion/isomerization product, $[PtCl(SnCl_3)(^{13}CO)(PEt_3)]$, and the cationic rearrangement product, *trans*-$[PtCl(^{13}CO)(PEt_3)_2]^+$, could also be detected.

The importance of the anionic *trans*-$[PtCl(SnCl_3)_2(PR_3)]^-$ complexes as intermediates in these rearrangement reactions is emphasized by the reaction of the $PPh_3$ complex with carbon monoxide. An acetone solution of *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ was generated by the reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ with 4.0 equiv of $SnCl_2\cdot 2H_2O$ and allowed to react with $^{13}CO$ at 193 K. After 3 h, the $^{31}P\{^1H\}$ NMR spectrum of this solution at 213 K showed that considerable conversion to the cation, *trans*-$[PtCl(^{13}CO)(PPh_3)_2]^+$, had occurred. Only this cation and the anionic precursor were detected. Further reaction with CO at room temperature led to complete conversion to *trans*-$[PtCl(CO)(PPh_3)_2]^+$ in ca 5 min at atmospheric pressure. This result demonstrates an unusually facile anion/cation conversion and additionally shows that the carbonyl ligand in the cationic product is very labile, as isotopic exchange of $^{12}CO$ for $^{13}CO$ occurred rapidly.

The complexity of these rearrangement processes limits the number of deductions that can be made concerning the reaction mechanism. An approximate model, depicting the overall features of the reaction process, is shown in Scheme I. Clearly, the role of $SnCl_2\cdot 2H_2O$ is not merely to provide $SnCl_2$ units to undergo insertion processes with M–Cl-containing species but also to provide secondary sources of free $SnCl_3^-$ ions and hydroxytin cations, via some hydrolytic reaction, to maintain electroneutrality, and to provide the platinum(II) species with a means of generating the most stable possible products. Scheme I depicts the first stage of the reaction as the classical insertion of $SnCl_2$ into one Pt–Cl bond of the *cis*-$[PtCl_2(CO)(PR_3)]$ molecule to generate the complexes I and/or II. At no time have we obtained any spectroscopic evidence for the existence of these species, although, following the central reaction path, the isomerization product, III, was identified during the slower reaction of the $PEt_3$ complex. Reaction of III with $PR_3$, generated during a secondary reaction (vide infra), would result in displacement of the poorly nucleophilic $SnCl_3^-$ ion[1] and lead to formation of IV. Species of the type IV are believed to be formed during the bridge-cleavage reaction of $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4]^{2+}$ complexes but have not been observed since rapid isomerization of the cis isomer occurs[41] to yield the thermodynamically preferred trans complex. Similarly here, we postulate formation of the unobserved intermediate IV, which undergoes an extremely rapid isomerization to yield the cationic product *trans*-$[PtCl(CO)(PR_3)_2]^+$. As previously mentioned, the carbonyl ligand in this cation is highly labile and undergoes facile isotopic substitution.

Scheme I. Some Probable Pathways in the Reaction of *cis*-$[PtCl_2(CO)(PR_3)]$ with $SnCl_2\cdot 2H_2O$



It seems probable that the initial reaction of *cis*-$[PtCl_2(CO)(PR_3)]$ with $SnCl_2\cdot 2H_2O$ does yield both insertion products, I and II. Clearly, reaction of II with $SnCl_3^-$ (right-hand pathway) would generate the observed species V and the reverse reaction, forced to completion in the presence of excess CO, would lead to conversion of V to the final products via the alternative pathways. This process is entirely analogous to one that we have recently described in which displacement of $SnCl_3^-$ from *trans*-$[PtPh(SnCl_3)(PPh_3)_2]$ by CO occurs and the slow reattack of $SnCl_3^-$ to yield aroyl products, via carbonyl insertion, may be prevented entirely by utilizing an excess of CO, hence maintaining the equilibrium such that the carbonyl complex is favored. Alternatively, the intial insertion product I would react via displacement of $PR_3$ by $SnCl_3^-$ to yield the observed anion VI. Reaction of VI with additional $SnCl_3^-$ would result in loss of CO to form an unobserved intermediate of the type VII, which reacts further with $SnCl_2/SnCl_3^-$ to yield the stable five-coordinate anion $[Pt(SnCl_3)_5]^{3-}$.

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[40] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[41] Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299.

Undoubtedly, this scheme represents an oversimplification of the overall process and is only intended to illustrate some of the most probable reaction pathways. It is important to bear in mind the relationship of these reactions to the catalytic system previously described.[5] In the case of the $PPh_3$ complex, the rearrangement reaction is rapid and will have occurred prior to addition of olefin and pressurization with $H_2/CO$. The analogous reaction of the $PEt_3$ complex is very slow and accordingly will have proceeded to only a minor extent upon addition of olefin and pressurization. Here then, we have described the precatalytic chemistry, and as we have repeatedly emphasized,[5,8] extrapolation to actual catalytic reactions is unwarranted and has no sound basis.

Preliminary studies on the reactivity of the $PPh_3$ system with molecular hydrogen have been performed. It is well-known[4] that the $[Pt(SnCl_3)_5]^{3-}$ anion reacts with $H_2$ to yield the five-coordinate hydride $[PtH(SnCl_3)_4]^{3-}$, but in the present system, where *trans*-$[PtCl(CO)(PPh_3)_2]^+$ and $[Pt(SnCl_3)_5]^{3-}$ are both present in solution, a hydridic product is formed that contains $PPh_3$ ligands. As the cation *trans*-$[PtCl(CO)(PPh_3)_2]^+$ itself is reported[27] to be unreactive toward $H_2$, it seems likely that further rearrangement reactions occur.

A final observation, which demonstrates clearly the importance of studying reaction mechanism spectroscopically, relates to the attempted isolation of the rearrangement products of one of these reactions. The reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with 2.0 equiv of $SnCl_2{\cdot}2H_2O$ was performed in acetone solution, and via slow evaporation and cooling, a crystalline product was obtained in very low yield. The product was identified crystallographically as *cis*-$[PtCl_2(PPh_3)_2]$.[42] Undoubtedly, a second rearrangement process, which ultimately yields this highly insoluble complex, occurs over several days of standing in air. No ionic products could be isolated at all from the reaction system, although these clearly dominate the chemistry in solution. The following paper[37] in this series demonstrates the importance of solvent effects on this reaction system and shows that this type of chemistry is general for other related catalyst precursors.

## Experimental Section

The following complexes were prepared by reported methods: *cis*-$[PtCl_2(CO)(PR_3)]$ (R = Ph, *p*-$MeC_6H_4$, *p*-$FC_6H_4$, Et)[17] $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (R = Ph, Et),[43] and $[K][PtCl_3(C_2H_4)]$.[44] $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][X]_2$ complexes (R = Ph, X = $ClO_4$, $SO_3CF_3$; R = Et, X = $SO_3CF_3$) were prepared by the method reported for R = *n*-Bu, X = $ClO_4$.[41] *trans*-$[PtCl(CO)(PR_3)_2][X]$ (R = Ph, Et) complexes were prepared by cleavage of $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][X]_2$ with CO, as reported.[27] The labeled complexes *cis*-$[PtCl_2(^{13}CO)(PR_3)]$[23] and *trans*-$[PtCl(^{13}CO)(PR_3)_2][X]$ were prepared by stirring $CHCl_3$ suspensions of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ and $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][X]_2$, respectively, under an atmosphere of $^{13}CO$ for ca. 3 h, followed by standard isolation procedures.

Carbon-13 monoxide (90%) was purchased from Prochem, phosphine ligands were obtained from Strem Chemicals, and $SnCl_2{\cdot}2H_2O$ was purchased from Fisher (technical grade) and Aldrich ("Gold Label", 99.999%). The solvent mixture prepared for use in NMR experiments was a mixture of 90% acetone (Fisher, 99.5%) and 10% acetone-$d_6$ (Merck Sharp and Dohme, 99% deuterated).

NMR spectra were obtained as follows: $^1H$ (60.0 MHz), $^{13}C\{^1H\}$ (15.1 or 100.1 MHz), $^{31}P\{^1H\}$ (24.3 MHz), $^{119}Sn\{^1H\}$ (93.07 or 149.16 MHz), and $^{195}Pt$(53.75 MHz) NMR spectra were obtaind on Bruker WP60, W250, and W400 NMR spectrometers operating in the Fourier transform mode. Chemical shift standards were as follows: $^1H$ (internal $Me_4Si$), $^{13}C\{^1H\}$ (internal $Me_4Si$), $^{31}P\{^1H\}$ (external 85% $H_3PO_4$ at ambient temperature), $^{119}Sn\{^1H\}$ (external 10% $Me_4Sn$ in $CDCl_3$ solution at ambient temperature), $^{195}Pt$ (external saturated aqueous $K_2PtCl_4$ at ambient temperature). More positive shifts represent deshielding.

In a typical reaction of *cis*-$[PtCl_2(CO)(PR_3)]$ with $SnCl_2{\cdot}2H_2O$, the metal complex (30–40 mg) was weighed into a NMR tube (10-mm diameter) and solid $SnCl_2{\cdot}2H_2O$ (1.0, 2.0, 2.5, or 5.0 equiv) added. The solids were mixed by shaking, and the solvent (ca. 2 mL, 90% acetone/10% acetone-$d_6$) was added. Gentle shaking caused a clear red-orange solution to be formed, and gas evolution could be visually detected. After a period of ca. 15 min, the NMR spectrum was recorded, at the temperature cited in the text.

Use of either reagent grade or 99.999% $SnCl_2{\cdot}2H_2O$ did not alter the $^{31}P\{^1H\}$ NMR spectra of the samples. Certain samples were prepared by the above method and by anaerobic methods with use of solvent degassed by three freeze–pump–thaw cycles and NMR tubes sealed with serum caps. Both modes of preparation yielded solutions with identical $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra, although only sealed samples could be stored, because of solvent evaporation from capped samples.

The reaction of $[K][PtCl_3(C_2H_4)]$ with $SnCl_2{\cdot}2H_2O$ was performed by weighing the metal complex (45–55 mg) into a NMR tube (10-mm diameter) and adding solid $SnCl_2{\cdot}2H_2O$ (2.0 equiv). Addition of solvent (2 mL, 90% acetone/10% acetone-$d_6$) caused the formation of a clear red solution. The $^{119}Sn\{^1H\}$ NMR spectrum was obtained at 149.16 MHz and identified the sole tin-containing product as the $[Pt(SnCl_3)_5]^{3-}$ anion. The spectrum was recorded at 213 K.

NMR data not cited in the text are as follows: *trans*-$[PtCl(^{13}CO)(PPh_3)_2][SO_3CF_3]$, $\delta(P) = 17.1$, $^1J(^{195}Pt,^{31}P) = 2073$ Hz, $^2J(^{31}P,^{13}C) = 10$ Hz ($Me_2CO$, 213 K); *trans*-$[PtCl(^{13}CO)(PEt_3)_2][SO_3CF_3]$, $\delta(P) = 26.7$, $^1J(^{195}Pt,^{31}P) = 1816$ Hz, $^2J(^{31}P,^{13}C) = 8$ Hz ($Me_2CO$, 213 K); *trans*-$[PtCl(CO)(PPh_3)_2][ClO_4]$, $\delta(P) = 19.0$, $^1J(^{195}Pt,^{31}P) = 1999$ Hz ($Me_2CO$, ambient temperature); *cis*-$[PtCl_2(^{13}CO)(PEt_3)]$, $\delta(P) = 23.0$, $^1J(^{195}Pt,^{31}P) = 2756$ Hz, $^2J(^{31}P,^{13}C) = 7$ Hz ($Me_2CO$, ambient temperature); *trans*-$[PtCl(CO)(P(p\text{-}MeC_6H_4)_3)_2][X]$, $\delta(P) = 17.9$, $^1J(^{195}Pt,^{31}P) = 1958$ Hz ($Me_2CO$, ambient temperature); *trans*-$[PtCl(CO)(P(p\text{-}FC_6H_4)_3)_2][X]$, $\delta(P) = 14.9$, $^1J(^{195}Pt,^{31}P) = 2092$ Hz ($Me_2CO$, 213 K); *trans*-$[PtCl(CO)(PPh_3)(PR_3)][X]$, R = *p*-$MeC_6H_4$, central resonances coincident at $\delta = 17.5$, $^1J(^{195}Pt,^{31}P) =$ ca. 2062 Hz (av); *trans*-$[PtCl(CO)(PPh_3)(PR_3)][X]$, R = *p*-$FC_6H_4$, central resonances coincident at $\delta$ 16.3, $^1J(^{195}Pt,^{31}P) =$ ca. 2083 Hz (av) ($Me_2CO$, 213 K); *cis*-$[PtCl_2(PPh_3)_2]$, $\delta(P) = 15.5$, $^1J(^{195}Pt,^{31}P) = 3679$ Hz ($CDCl_3$, ambient temperature).

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