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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Guelph Campus, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Role of the Trichlorostannyl Ligand in Homogeneous Catalysis. 3. Solvent Effects on the Reactions of *cis*-$[PtCl_2(L)(PR_3)]$ and $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (L = CO, SMe_2; R = Ph, Et) with $SnCl_2 \cdot 2H_2O$[1]

GORDON K. ANDERSON, HOWARD C. CLARK,* and JULIAN A. DAVIES

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The reactivity of *cis*-$[PtCl_2(CO)(PPh_3)]$ toward $SnCl_2 \cdot 2H_2O$ has been studied with use of acetone, acetonitrile, and chloroform as solvents. In acetone and acetonitrile, ligand rearrangement reactions occur, but in chloroform only the simple insertion of $SnCl_2$ into one Pt–Cl bond is observed. Similar solvent effects are observed in the reactions of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ with $SnCl_2 \cdot 2H_2O$, which yield the *trans*-$[PtCl(SnCl_3)_2(PR_3)]^-$ anions in acetone solution but the simple insertion products, $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PR_3)_2]$, in chloroform solution. Reactions of the related complexes *cis*-$[PtCl_2(L)(PPh_3)]$ (L = SMe_2, C_5H_5N, *p*-$MeC_6H_4NH_2$) with $SnCl_2 \cdot 2H_2O$ in acetone solution also occur via ligand rearrangements. ^1H, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR methods, utilizing ^{13}C-labeled carbon monoxide as a probe of geometry, have been employed to assign solution structures and to monitor reaction pathways.

Introduction

In the preceding paper[1] we described the novel rearrangement that occurs when *cis*-$[PtCl_2(CO)(PR_3)]$ (R = Ph, Et) reacts with $SnCl_2 \cdot 2H_2O$ in acetone solution to produce ionic species that are catalyst precursors for olefin hydroformylation.[2] Here we describe the importance of solvent effects upon this reaction and demonstrate that the observed type of rearrangement is not an isolated case but is general for complexes of the type *cis*-$[PtCl_2(L)(PR_3)]$ (where L is a modest σ-donor ligand such as CO, thioethers, amines, etc.), including the previously reported[3] *cis*-$[PtCl_2(SMe_2)(PR_3)]/SnCl_2 \cdot 2H_2O$ olefin hydrogenation catalyst precursor. Some relevant reactions of the dimeric complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ with $SnCl_2 \cdot 2H_2O$ are also described. ^1H, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR methods have been employed to determine solution structures and to monitor reaction pathways.

The data presented in this paper demonstrate that three basic processes appear to be operative in the reactions of *cis*-$[PtCl_2(L)(PR_3)]$ complexes with $SnCl_2 \cdot 2H_2O$. The first process involves the simple insertion of $SnCl_2$ into one Pt–Cl bond of the parent complex, and this reaction can be observed in $CDCl_3$ solution. The nature of the PR_3 ligand appears to govern the equilibrium position for this process. The second reaction to occur is a ligand migration process to generate ionic species, and this reaction is only seen to occur readily in coordinating solvents capable of stabilizing the ionic products. The final process that we have observed involves a further rearrangement with displacement of the ligands, L, from the cationic complexes, $[PtCl(L)(PR_3)_2]^+$, to generate the neutral products, *cis*-$[PtCl_2(PR_3)_2]$. This process appears to be governed by the donor ability of the ligand L, being fast for L = *p*-$MeC_6H_4NH_2$ and slow for L = CO, while it has not been observed for L = SMe_2 and C_5H_5N.

Results and Discussion

cis-$[PtCl_2(CO)(PPh_3)]$ reacts with $SnCl_2 \cdot 2H_2O$ in acetone solution to produce the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation and a series of anions[4] of which $[Pt(SnCl_3)_5]^{3-}$ is the dominant species at high $SnCl_2 \cdot 2H_2O$ concentrations. The formation of hydroxytin cations is postulated to occur, thus generating a source of $SnCl_3^-$ ions and maintaining electroneutrality.[1] The *cis*-$[PtCl_2(CO)(PR_3)]/SnCl_2 \cdot 2H_2O$ olefin hydroformylation system was found[2] to be effective with use of both acetone and acetonitrile as solvents. Accordingly, the reactions of *cis*-$[PtCl_2(CO)(PR_3)]$ (R = Ph, *p*-MeC_6H_4) with 2.0 equiv of $SnCl_2 \cdot 2H_2O$ were performed in acetonitrile solution and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Spectra measured at ambient temperature (Table I) showed that quantitative conversion to the corresponding *trans*-$[PtCl(CO)(PR_3)_2]^+$ ions occurred.[5]

Consideration of the stoichiometry of the reactions demonstrates that $[Pt,Sn]^{n-}$ anions are again formed. Both acetone and acetonitrile are coordinating solvents[6] which promote ionization, and so it was of interest to utilize a halocarbon solvent, in which ionization is expected to be unfavorable and to investigate the solution chemistry of the *cis*-$[PtCl_2(CO)(PPh_3)]/SnCl_2 \cdot 2H_2O$ system. In order to be able to make sound structural assignments from NMR data, we synthesized the ^{13}C-labeled carbonyl complex *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ and monitored its reaction with excess $SnCl_2 \cdot 2H_2O$ in $CDCl_3$ solution at 213 K by $^{31}P\{^1H\}$ NMR spectroscopy. The resonances associated with *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ (Table I) were replaced by a resonance at 22.6 ppm, exhibiting coupling to ^{13}C, ^{117}Sn, ^{119}Sn, and ^{195}Pt ($\delta(P)$ = 22.6 (d), $^1J(^{195}Pt,^{31}P)$ = 2407 Hz, $^2J(^{31}P,^{13}C)$ = 7 Hz, $^2J(^{119}Sn,^{31}P)$ = 4028 Hz, $^2J(^{117}Sn,^{31}P)$ = 3853 Hz). The magnitude of $^2J(^{31}P,^{13}C)$[7] and multiplicity of the resonance show that the PPh_3 ligand is cis to a single carbonyl group, while the magnitudes of $^1J(^{195}Pt,^{31}P)$[8] and $^2J(^{117,119}Sn,^{31}P)$[9] demonstrate that the PPh_3 ligand is trans to the high-trans-influence $SnCl_3^-$ ligand. The ratios of the satellites due to coupling to ^{195}Pt and $^{117,119}Sn$ define the Pt(II)/Sn(II) ratio as 1/1. The complex is thus assigned the formula $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ and is present as the isomer with PPh_3 and $SnCl_3^-$ trans to each other. This product evidently results from the simple insertion of $SnCl_2$ into the Pt–Cl bond trans to the tertiary phosphine to yield the observed isomer. In the analogous reaction in acetone solution we have

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(1) Part 2: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.*, preceding paper in this issue.

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

(3) Clark, H. C.; Billard, C.; Wong, C. S. *J. Organomet. Chem.* **1980**, *190*, C105.

(4) Four anions were observed spectroscopically, and three were identified as $[Pt(SnCl_3)_5]^{3-}$, *trans*-$[PtCl(SnCl_3)_2(CO)]^-$, and *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$. The fourth minor anion was not identified. In referring to this general class of anions, where their precise nature is undetermined, the abbreviation $[Pt,Sn]^{n-}$ will be employed.

(5) For comparable $^{31}P\{^1H\}$ NMR data in Me_2CO solution see ref 1.

(6) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79.

(7) Anderson, G. K.; Cross, R. J.; Rycroft, D. S. *J. Chem. Res., Synop.* **1980**, 240.

(8) The $SnCl_3^-$ ligand exhibits a strong NMR trans influence, and hence the magnitude of $^1J(^{195}Pt,^{31}P)$ is expected to be low in a complex with trans PR_3 and $SnCl_3^-$ ligands; for examples, see: Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1979**, *61*, 1848.

(9) The ratio of $^2J(^{119}Sn,^{31}P)/^2J(^{117}Sn,^{31}P)$ = 1.045, close to the value of 1.046 for the ratios of the magnetogyric moments of $^{119}Sn/^{117}Sn$. Values of $^2J(^{117,119}Sn,^{31}P)$ are of the order of 200–300 Hz for cis $SnCl_3^-$ and PR_3 ligands but are generally ca. 4 kHz for trans complexes. See: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.

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Table I. $^{31}P\{^1H\}$ NMR Spectroscopic Data

obsd species	temp/K	solvent	$\delta(P)$	$^1J(^{195}Pt,^{31}P)$/Hz	$^2J(^{31}P,^{13}C)$/Hz	$^2J(^{117,119}Sn,^{81}P)$/Hz	$^2J(^{31}P,^{31}P)$/Hz
trans-$[PtCl(CO)(PPh_3)_2]^+$	ambient	CD_3CN	18.3	2062			
trans-$[PtCl(CO)(P(p\text{-}MeC_6H_4)_3)_2]^+$	ambient	CD_3CN	18.1	1948			
cis-$[PtCl_2(^{13}CO)(PPh_3)]$	213	$CDCl_3$	9.5 (d)	3062	5		
$[PtCl(SnCl_3)(PPh_3)(^{13}CO)]^a$	213	$CDCl_3$	22.6 (d)	2407	7	4028, 3863	
$[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2]^b$	213	$CDCl_3$	7.5	3721		210 (av)	
$[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PEt_3)_2]^c$	213	$CDCl_3$	12.5	3425		234, 244	
$[PtCl(SnCl_3)(PEt_3)(^{13}CO)]^a$	213	$CDCl_3$	33.9 (d)	2239	7	3516, 3679	
cis-$[PtCl_2(^{13}CO)(PEt_3)]$	213	$CDCl_3$	23.8 (d)	2783	7		
$[PtCl(PPh_3)_3]^+$	213	$CDCl_3$	23.5 (d)	2463			17
			11.9 (t)	3606			17
cis-$[PtCl(SnCl_3)(PPh_3)_2]^d$	213	$CDCl_3$	28.8 (d)	3066			12
			10.9 (d)	3626			12
cis-$[PtCl_2(PPh_3)_2]$	213	$CDCl_3$	14.3	3677			
trans-$[PtCl(SnCl_3)_2(PPh_3)]^-$	183	$(CD_3)_2CO$	14.1	2449		247 (av)	
trans-$[PtCl(SnCl_3)_2(PEt_3)]^-$	183	$(CD_3)_2CO$	2.4	2161		215 (av,br)	
cis-$[PtCl(SMe_1)(PPh_3)_2]^+$	213	$(CD_3)_2CO$	16.0 (d)	3179			18
			13.0 (d)	3577			18
cis-$[PtCl(C_5H_5N)(PPh_3)_2]^+$	213	$(CD_3)_2CO$	4.2 (d)	3179			18
			15.3 (d)	3686			18
cis-$[PtCl_2(C_5H_5N)(PPh_3)]$	213	$(CD_3)_2CO$	6.9	3896			
trans-$[PtCl_1(C_5H_5N)(PPh_3)]$	213	$(CD_3)_2CO$	2.3	3584			
cis-$[PtCl_2(p\text{-}MeC_6H_4NH_2)(PPh_3)]$	213	$(CD_3)_2CO$	3.3	3774			

[a] Isomer with $SnCl_3^-$ trans to PR_3. [b] $^2J(^{195}Pt,^{195}Pt) = 165$ Hz; $^4J(^{31}P,^{31}P) < 2.5$ Hz. [c] $^2J(^{195}Pt,^{195}Pt)$ not observed; $^4J(^{31}P,^{31}P) < 2.5$ Hz. [d] $^2J(^{117,119}Sn,^{31}P)$ not observed.

postulated[1] that this species is one product of the first step in the rearrangement reaction, although no spectroscopic evidence for its formation could be obtained. The reaction in $CDCl_3$ solution, which proceeds no further than simple insertion, suggests that this postulate is correct. Our suggested mechanism for the rearrangement reaction in acetone also involved the formation of the isomer of $[PtCl(SnCl_3)(CO)(PPh_3)]$ with CO and $SnCl_3^-$ ligands mutually trans as an unobserved intermediate in a closed secondary reaction pathway. In order to investigate the possible synthesis of this isomer, we prepared the dimeric complex $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2]$ by the reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ with excess $SnCl_2{\cdot}2H_2O$ in $CDCl_3$ solution and examined its cleavage by ^{13}CO. Bridge cleavage trans to PPh_3 would yield the isomer of $[PtCl(SnCl_3)(CO)(PPh_3)]$ previously obtained, while cleavage trans to $SnCl_3^-$ would yield the unobserved isomer. Cleavage by ^{13}CO at ambient temperature was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 213 K, which showed the disappearance of the resonances associated with $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2]$ (Table I) and the appearance of resonances due to the previously observed isomer of $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ and a minor amount of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$. No resonances attributable to the isomer of $[PtCl(SnCl_3)(CO)(PPh_3)]$ with $SnCl_3^-$ and CO ligands mutually trans were observed. When the cleavage reaction was performed at 213 K and the $^{31}P\{^1H\}$ NMR spectrum recorded at this temperature, the same spectroscopic data were obtained, except that the relative amount of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ had increased. Although the desired isomer of $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ was not observed during these reactions, the formation of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ indicates that some cleavage of the dimer trans to $SnCl_3^-$ does indeed occur. The observed isomer of $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ does not undergo extrusion of $SnCl_2$ from the Pt–$SnCl_3$ bond in $CDCl_3$ solution[10] and so cannot be a source of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$. More likely is extrusion of $SnCl_2$ from a M–$SnCl_3$ bond where $SnCl_3^-$ and CO are trans to each other. Two strong π acceptors in trans positions are likely to have a destabilizing effect upon the complex, and so reversion to the stable CO trans to Cl^- arrangement of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ seems likely. These results suggest that the postulated involvement of one, and possibly both, isomers of the simple insertion product in the first step of the reaction of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ with $SnCl_2{\cdot}2H_2O$ in acetone solution is not unreasonable.

Identical chemistry occurs with the analogous PEt_3 system; thus, $[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ reacts with excess $SnCl_2{\cdot}2H_2O$ in $CDCl_3$ solution to yield $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PEt_3)_2]$ (Table I), which is cleaved by ^{13}CO to produce $[PtCl(SnCl_3)(^{13}CO)(PEt_3)]$ (isomer with $SnCl_3^-$ trans to PEt_3, Table I) with a minor amount of *cis*-$[PtCl_2(^{13}CO)(PEt_3)]$ (Table I). Interestingly, the reaction of *cis*-$[PtCl_2(^{13}CO)(PEt_3)]$ with excess $SnCl_2{\cdot}2H_2O$ in $CDCl_3$ solution to yield $[PtCl(SnCl_3)(^{13}CO)(PEt_3)]$ does not proceed to completion over a 2-h time period. (The analogous reaction with the PPh_3 complex occurs in the time of mixing.) The rearrangement reaction of *cis*-$[PtCl_2(^{13}CO)(PEt_3)]$ in its reaction with $SnCl_2{\cdot}2H_2O$ in acetone solution is also very slow but is not directly comparable with the simple insertion, as the former process involves transfer of a PEt_3 ligand from one metal center to another. The differences observed between the PPh_3 and PEt_3 complexes in their simple insertion reactions probably reflect the equilibrium positions for the formation of the corresponding trichlorostannyl complexes.[11]

The complex $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ (PPh_3 trans to $SnCl_3^-$) did not undergo any further reaction with excess $SnCl_2{\cdot}2H_2O$ over a 24-h period in $CDCl_3$ solution. The addition of acetone to a $CDCl_3$ solution of $[PtCl(SnCl_3)(^{13}CO)(PPh_3)]$ also had no effect, but the addition of an acetone solution of $SnCl_2{\cdot}2H_2O$ caused a quantitative rearrangement to yield the *trans*-$[PtCl(^{13}CO)(PPh_3)_2]^+$ cation, identified by its $^{31}P\{^1H\}$ NMR spectrum. The stoichiometry again indicates formation of $[Pt,Sn]^{n-}$ anions. These data demonstrate that such rearrangement reactions do not occur in $CDCl_3$ solution, irrespective of the Pt(II)/Sn(II) ratio, and that acetone, or a similar solvent, is necessary to promote the reaction. However, the formation of ionic products in $CDCl_3$ solution can be promoted in a closely related system, by altering the Pt(II)/PPh_3 ratio. Thus, the reaction of a $CDCl_3$ solution of $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2]$ with 2.0 equiv of PPh_3

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(10) Such reactions are observed in related systems with use of ethanol as solvent; see: Kubota, M.; Phillips, D. A.; Jacobsen, J. E. *J. Coord. Chem.* **1980**, *10*, 125.

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

(i.e., 1.0 equiv of PPh_3 added per Pt) at 213 K yields three species that were observable in the ^{31}P{^{1}H} NMR spectrum at 213 K. The complexes $[PtCl(PPh_3)_3]^+$,[12] *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$,[13] and *cis*-$[PtCl_2(PPh_3)_2]$[14] (Table I) were observed in the approximate ratio of 4/2/1. Clearly, over half of the platinum/phosphine species produced have a Pt(II)/PPh_3 ratio of 1/3, although the overall stoichiometry dictate that a ratio of 1/2 must be maintained on average. The formation of anionic $[Pt,Sn]^-$ species, without phosphine ligands, seems likely in order to maintain both the stoichiometry and the electroneutrality.

The ability of the solvent to govern the course of a reaction is exemplified by the reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ with excess $SnCl_2\cdot 2H_2O$. In $CDCl_3$ solution, the dimeric complex reacts quantitatively to yield $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2]$, where insertion at the terminal M–Cl bonds has occurred (vide supra). In acetone solution, however, an ionic product is formed. Monitoring the reaction by ^{31}P{^{1}H} NMR spectroscopy at 183 K showed the formation of a single platinum/phosphine complex (δ(P) = 14.1, $^{1}J(^{195}Pt,^{31}P)$ = 2449 Hz, $^{2}J(^{117,119}Sn,^{31}P)$ = 247 Hz (av)). The magnitude of $^{2}J(^{117,119}Sn,^{31}P)$ demonstrates that the $SnCl_3^-$ and PPh_3 ligands are cis,[9] while analysis of the satellite intensities[15] resulting from coupling to ^{195}Pt and ^{117,119}Sn defines the Pt(II)/Sn(II) ratio as 1/2. The magnitude of $^{1}J(^{195}Pt,^{31}P)$ is as expected for coordination of PPh_3 trans to a low-trans-influence ligand such as Cl^-, when the expected cis influence of the $SnCl_3^-$ groups is considered.[1] Accordingly, the product of this reaction is assigned the structure *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ (Table I).

The generation of this anion as the sole phosphine-containing product from the reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ with excess $SnCl_2\cdot 2H_2O$ in acetone solution is further evidence that secondary cationic species such as hydroxytin complexes are also formed to maintain electroneutrality. The same solvent effect is observed with the reactions of the analogous PEt_3 complex, which yields $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PEt_3)_2]$ exclusively in $CDCl_3$ solution but the *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ anion (Table I) in acetone solution. Interestingly, the ^{31}P{^{1}H} NMR spectrum of *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$ showed a loss of coupling to ^{117,119}Sn on raising the temperature from 183 to 213 K, although this coupling was clearly observable for the PPh_3 analogue at 213 K. These data suggest that the PEt_3 complex may be more labile in solution and may undergo dissociative processes, possibly involving the reversible loss of $SnCl_3^-$, which are only inhibited at very low temperatures.

The postulate that the rearrangement reactions observed in acetone solution are accompanied by the formation of secondary cationic species, derived from $SnCl_2\cdot 2H_2O$,[16] remains unproven as these species have neither been observed spectroscopically nor been isolated. The considerable amount of indirect evidence for the existence of such species is further supported by observations relating to the reactivity of the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation. Thus, in the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with 5.0 equiv of $SnCl_2\cdot 2H_2O$, the products observed spectroscopically in acetone solution are the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation and the $[Pt(SnCl_3)_5]^{3-}$ anion, together with a minor amount of *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$.[1] The Pt(II)/Sn(II) ratio of the products thus accounts for ca. 50% of the added $SnCl_2\cdot 2H_2O$. Accordingly, it is necessary to determine whether the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation reacts with $SnCl_2\cdot 2H_2O$ in acetone solution. If this is indeed the case, then the remaining $SnCl_2\cdot 2H_2O$ in the above system has undoubtedly undergone a secondary reaction, which prevents attack on the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation. The reaction of *trans*-$[PtCl(^{13}CO)(PPh_3)_2]$ $[SO_3CF_3]$ with excess $SnCl_2\cdot 2H_2O$ in acetone solution was monitored by ^{31}P{^{1}H} NMR spectroscopy at 213 K. The spectroscopic data demonstrated that a reaction indeed occurred, yielding both $[PtCl(PPh_3)_3]^+$ and *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$, together with a small amount of triphenylphosphine oxide (δ(P) = 26.4).

The data so far discussed illustrate the basic differences between the $CDCl_3$ and acetone solvent systems. Reactions in $CDCl_3$ tend to proceed via simple insertion processes, and rearrangement reactions to yield ionic products are only observed upon addition of the powerful nucleophile PPh_3. In acetone solution, however, insertion processes are believed to be an initial step but are followed by rapid, highly complex ligand rearrangement reactions with quantitative formation of ionic species.

The system we have so far considered is rather unusual in that the carbonyl ligand may be lost from the reaction system as gaseous carbon monoxide during any labilization steps in the rearrangement reaction. Accordingly, we have examined some similar reactions of *cis*-$[PtCl_2(SMe_2)(PPh_3)]$, which is an effective catalyst precursor for olefin hydrogenation in the presence of $SnCl_2\cdot 2H_2O$ in acetone solution.[3]

The reaction of *cis*-$[PtCl_2(SMe_2)(PPh_3)]$ with 5.0 equiv of $SnCl_2\cdot 2H_2O$ in acetone solution was monitored by ^{31}P{^{1}H} and ^{119}Sn{^{1}H} NMR spectroscopies. Spectra were obtained sequentially at 213 K for the same solution. The ^{31}P{^{1}H} NMR spectrum consisted of a doublet of doublets exhibiting coupling to ^{195}Pt (δ(P) = 16.0, $^{1}J(^{195}Pt,^{31}P)$ = 3179 Hz; δ(P) = 13.0, $^{1}J(^{195}Pt,^{31}P)$ = 3577 Hz, $^{2}J(^{31}P,^{31}P)$ = 18 Hz), which was complicated by partial overlap with a singlet resonance, also exhibiting coupling to ^{195}Pt (δ(P) = 13.4, $^{1}J(^{195}Pt,^{31}P)$ = 2468 Hz). The singlet resonance also displayed closely spaced satellites due to coupling to ^{117,119}Sn, whose magnitude could not be reliably measured because of the overlapping resonance due to the former species. By analogy with the *cis*-$[PtCl_2(CO)(PPh_3)]/SnCl_2\cdot 2H_2O$ system, the products of this reaction, which are observable by ^{31}P{^{1}H} NMR spectroscopy, are expected to be the $[PtCl(SMe_2)(PPh_3)_2]^+$ cation and the *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ anion. The anionic species is clearly identified by the singlet resonance by comparison with the data previously obtained for this complex (Table I). For the $[PtCl(SMe_2)(PPh_3)_2]^+$ cation to be present, the two PPh_3 groups must be inequivalent and hence of cis geometry. For a confirmation of this, the reactions of $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][X]_2$ (X = ClO_4, SO_3CF_3) with excess SMe_2 in $CDCl_3$ solution were monitored by ^{31}P{^{1}H} NMR spectroscopy. The products were found to have spectra identical with that of the unknown component in the above reaction system, which is therefore assigned the structure *cis*-$[PtCl(SMe_2)(PPh_3)_2]^+$. The ^{119}Sn{^{1}H} NMR spectrum confirmed the presence of the *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ anion as a minor component (δ(Sn) = −109.8 (d), $^{2}J(^{119}Sn,^{31}P)$ = ca. 250 Hz, $^{1}J(^{195}Pt,^{119}Sn)$ and $^{2}J(^{119}Sn,^{117}Sn)$ not observed)[1] and identified the major tin-containing species as the $[Pt(SnCl_3)_5]^{3-}$ anion (δ(Sn) = −122.1, $^{1}J(^{195}Pt,^{119}Sn)$ = 16 110 Hz, $^{2}J(^{119}Sn,^{117}Sn)$ = 6330 Hz).[17]

Clearly, the thioether and carbonyl systems are very similar; both undergo ligand rearrangement reactions to yield the same anionic species, at this concentration of $SnCl_2\cdot 2H_2O$, and both yield the corresponding $[PtCl(L)(PPh_3)_2]^+$ cations. The cation

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(12) Data as previously reported: Wongnawa, S.; Schram, E. P. *Inorg. Chim. Acta* **1979**, *36*, 45.

(13) Data as previously reported; see ref 8.

(14) Data as previously reported; see ref 1.

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

(16) A 10^{-4} molar solution of $SnCl_2\cdot 2H_2O$ in acetonitrile, which also facilitates the ligand rearrangement reactions, has a molar conductivity, Λ_M, of 75.5 Ω^{-1} cm^2 mol^{-1}, indicating considerable formation of ionic species. See: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(17) Nelson, J. H.; Cooper, V.; Rudolph, R. W. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 263. See also errata (*Ibid.* **1980**, *16*, 587) for correct chemical shift of $[Pt(SnCl_3)_5]^{3-}$.

is of trans geometry for L = CO and of cis geometry for L = SMe_2. The major difference between the two systems is in the relationship between the $[PtCl(L)(PPh_3)_2]^+$ cation and the *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ anion. Thus, generation of *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ from the reaction of $[Pt_2(\mu-Cl)_2Cl_2(PPh_3)_2]$ and excess $SnCl_2 \cdot 2H_2O$ in acetone solution followed by reaction with CO at room temperature causes quantitative formation of the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation.[1] Reaction of *trans*-$PtCl(SnCl_3)_2(PPh_3)]^-$ with excess SMe_2 at room temperature in acetone solution causes only partial rearrangement however; both *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ and *cis*-$[PtCl(SMe_2)(PPh_3)_2]^+$ are identified in the $^{31}P\{^1H\}$ NMR spectrum, recorded at 213 K, with the ratios of the two species being approximately the same as that previously obtained in the reaction of *cis*-$[PtCl_2(SMe_2)(PPh_3)]$ with excess $SnCl_2 \cdot 2H_2O$ in acetone solution. The $^{31}P\{^1H\}$ NMR spectrum of this solution, when recorded at room temperature, shows no resonance due to the *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ anion, and the spectrum due to the *cis*-$[PtCl(SMe_2)(PPh_3)_2]^+$ cation appears considerably changed. Thus, the doublet at 13.0 ppm (PPh_3 trans to Cl^-) is sharp and well resolved whereas the resonance at 16.0 ppm (PPh_3 trans to SMe_2) is collapsed to a broad singlet. It seems evident therefore that the cation and anion are in equilibrium in the presence of free SMe_2 and that the cation is undergoing a dynamic process at room temperature, involving thioether dissociation, possibly promoted by the trans PPh_3 group. In the case of the carbonyl analogue, the carbonyl group is trans to Cl^- and as such is nonlabile.

A facile equilibrium between an anion and a cation may initially seem to be rather an unusual process but is believed to occur in the present system via the displacement of a formally negatively charged ligand, $SnCl_3^-$, by a neutral ligand, SMe_2, accompanied by a second such process involving replacement of $SnCl_3^-$ by PR_3. The replacement of the two negative ligands by two neutral ligands and vice versa results in the anion/cation interconversion. The carbonyl system is expected to be nonlabile as a result of the trans geometry of the $[PtCl(CO)(PR_3)_2]^+$ cation. The alternative cis geometry is expected to be exceedingly unstable, as a result of the presence of two strong π acceptors, CO and PR_3, in mutually trans positions. The low electron count on such a cation would not stabilize such a geometry,[18] and hence the expected trans arrangement is favored.

The close relationship between the carbonyl and thioether systems is demonstrated by the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with 2.0 equiv of $SnCl_2 \cdot 2H_2O$ in acetone solution, which generates the *trans*-$[PtCl(CO)(PPh_3)_2]^+$ cation and traces of the *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$ anion, followed by addition of excess SMe_2. The $^{31}P\{^1H\}$ NMR spectrum of such a reaction system at 213 K showed the presence of *cis*-$[PtCl(SMe_2)(PPh_3)_2]^+$, *trans*-$[PtCl(CO)(PPh_3)_2]^+$, and *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$, showing that the two cations may be readily interconverted.

Reactions of these ionic systems with molecular hydrogen have proved to be extremely complex. It is noteworthy that some years ago we showed[19] that complexes of the type *trans*-$[PtCl(CO)(PR_3)_2][X]$ (X = BF_4, ClO_4, etc.), although isoelectronic with Vaska's compound, do not react readily via the oxidative addition of small molecules. No reaction of molecular hydrogen was observed (for R = Et, X = BF_4) at 1 atm pressure at 298 K.[19] Similarly, we have now observed that the complex *cis*-$[PtCl(SMe_2)(PPh_3)_2][X]$ (X = ClO_4, SO_3CF_3) in acetone solution does not react with H_2 over a 30-min period at 1 atm and room temperature. Some reactions of the *cis*-$[PtCl_2(SMe_2)(PPh_3)]/SnCl_2 \cdot 2H_2O$ system with H_2 have been investigated by ^1H NMR spectroscopy, however, and show that hydridoplatinum species are formed under ambient conditions. The ^1H NMR spectrum of *cis*-$[PtCl_2(SMe_2)(PPh_3)]$ itself in $CDCl_3$ solution at 218 K shows a broad resonance due to the thioether protons ($\delta = 2.2$, $^3J(^{195}Pt,^1H) = 44.0$ Hz) and the expected multiplet for the phenyl protons of PPh_3. The reaction of *cis*-$[PtCl_2(SMe_2)(PPh_3)]$ with 4.0 equiv of $SnCl_2 \cdot 2H_2O$ in acetone produces a solution whose ^1H NMR spectrum shows only a broad resonance at 2.48 ppm for the SMe_2 protons, with no observable coupling, even at 193 K. Reaction with molecular hydrogen for 20 min produces a solution whose ^1H NMR spectrum shows a relatively sharp resonance for the SMe_2 protons ($\delta = 2.60$, $^3J(^{195}Pt,^1H) = 46.9$ Hz) and evidence for metal hydride formation by a complex multiplet centered at −13.14 ppm. The resonance appears as a doublet due to coupling to ^{31}P ($^2J(^{31}P,^1H) = 139.6$ Hz) and exhibits satellites due to coupling to ^{195}Pt ($^1J(^{195}Pt,^1H) = 390.6$ Hz) and $^{117,119}Sn$ ($^2J(^{117,119}Sn),^1H) = 43.9$ Hz (av)). These data suggest a possible structure for this product of the type $[PtH(SnCl_3)(PPh_3)(SMe_2)]$ (isomer with H and PPh_3 trans to each other). The importance of this result is that it clearly demonstrates that H_2 does not merely react with the $[Pt(SnCl_3)_5]^{3-}$ anion, a reaction known to yield $[PtH(SnCl_3)_4]^{3-}$, but rather initiates a further rearrangement process. Attempts to extrapolate such data to interpret actual catalytic reactions, performed under high pressures of H_2, in the presence of organic substrates, would obviously not be meaningful.

The rearrangement processes observed in the reactions of *cis*-$[PtCl_2(L)(PPh_3)]$ complexes (L = CO, SMe_2) with $SnCl_2 \cdot 2H_2O$ in acetone solution were found to be complicated by the formation of other products in the cases where the ligand, L, is a nitrogen donor. Reactions of $[PtCl_2(C_5H_5N)(PPh_3)]$, either as the trans isomer alone or as a 1/1 mixture of cis and trans isomers, with 2.0 equiv of $SnCl_2 \cdot 2H_2O$ in acetone yielded solutions with identical $^{31}P\{^1H\}$ NMR spectra. In both cases, the $^{31}P\{^1H\}$ NMR spectra at 213 K showed the complete disappearance of the starting materials (Table I) and the formation of a number of new products, including the *cis*-$[PtCl(C_5H_5N)(PPh_3)_2]^+$ cation as a major component. This complex was identified by comparison of its $^{31}P\{^1H\}$ NMR spectrum with that of an independently synthesized sample of *cis*-$[PtCl(C_5H_5N)(PPh_3)_2]^+$ (Table I) prepared via bridge cleavage of the dimeric complex $[Pt_2(\mu-Cl)_2(PPh_3)_4][ClO_4]_2$ with excess pyridine. Undoubtedly, a number of other unidentified products are also formed in the rearrangement reaction, but nonetheless, the formation of the $[PtCl(L)(PPh_3)_2]^+$ cation indicates that this reaction also belongs to the class under discussion. A somewhat different rearrangement process occurs in the reaction of *cis*-$[PtCl_2(p\text{-}MeC_6H_4NH_2)(PPh_3)]$ with 2.0 equiv of $SnCl_2 \cdot 2H_2O$ in acetone solution. The $^{31}P\{^1H\}$ NMR spectrum of such a solution at 213 K clearly shows the total disappearance of the starting material (Table I) and formation of a number of new products, including *cis*-$[PtCl_2(PPh_3)_2]$ as a major component. No formation of *cis*-$[PtCl(p\text{-}MeC_6H_4NH_2)(PPh_3)_2]^+$ was evident from the spectrum, and independent synthesis of this complex via bridge cleavage (vide supra) confirmed that this was not an observed product of the reaction. The formation of substantial amounts of *cis*-$[PtCl_2(PPh_3)_2]$ does indicate, however, that a process involving transfer of PPh_3 from one metal center to another indeed occurs. In the consideration of the formation of *cis*-$[PtCl_2(PPh_3)_2]$ in this reaction, it is particularly noteworthy that although the cationic complex *trans*-$[PtCl(CO)(PPh_3)_2]^+$ is formed in the reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with $SnCl_2 \cdot 2H_2O$ in acetone, it is the *cis*-$[PtCl_2(PPh_3)_2]$ complex alone that is isolable from the

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

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

carbonyl system.[1] It is thus possible that failure to observe the $[PtCl(p\text{-}MeC_6H_4NH_2)(PPh_3)_2]^+$ cation is merely a reflection of the rate of formation of *cis*-$[PtCl_2(PPh_3)_2]$ from the various $[PtCl(L)(PPh_3)_2]^+$ complexes. The fundamental observation in the reactions of the amine complex is that a ligand-transfer process occurs, even though no cationic complex was identified.

The following paper in this series[20] describes the use of some of these systems as precursors in the catalytic hydrogenation and hydroformylation of olefins and illustrates how a consideration of the precatalytic chemistry may be a useful tool in the understanding of new catalyst systems.

Experimental Section

The complexes *cis*-$[PtCl_2(CO)(PR_3)]$ (R = Et, Ph, p-MeC_6H_4),[21] *cis*-$[PtCl_2(^{13}CO)(PR_3)]$ (R = Et, Ph),[1] $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (R = Et, Ph),[22] and $[K][PtCl_3(C_2H_4)]$[23] were prepared by reported methods. $[Pt_2(\mu\text{-}Cl)_2(PR_3)_4][X]_2$ (R = Ph, Et; X = ClO_4, SO_3CF_3) complexes were prepared by the method reported for R = *n*-Bu, X = ClO_4.[18] The complexes *trans*-$[PtCl_2(C_5H_5N)(PPh_3)]$ (single isomer), *cis*- and *trans*-$[PtCl_2(C_5H_5N)(PPh_3)]$ (mixture of isomers), and *cis*-$[PtCl(C_5H_5N)(PPh_3)_2][ClO_4]$ were prepared as previously described.[24] The complexes *cis*-$[PtCl(L)_2(PPh_3)]$ and *cis*-$[PtCl(L)(PPh_3)_2][ClO_4]$ were prepared by the slow addition of a dilute solution of L (L = SMe_2, excess; L = p-$MeC_6H_4NH_2$, stoichiometric amount) to a solution of the complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ or $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][ClO_4]_2$ in CH_2Cl_2. Standard isolation procedures were employed.

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%). Solvents used for NMR experiments were $CDCl_3$ (Merck Sharp and Dohme, 99.8% deuterated), a mixture of 90% acetone (Fisher, 99.5%) and 10% acetone-d_6 (Merck Sharp and Dohme, 99% deuterated), or a mixture of 90% acetonitrile (MCB, Spectroquality) and 10% acetonitrile-d_3 (Merck Sharp and Dohme, 99% deuterated). ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker WP60 spectrometer operating in the Fourier transform mode at 60.0 and 24.3 MHz, respectively. $^{119}Sn\{^1H\}$ NMR spectra were obtained on a Bruker W400 spectrometer operating in the Fourier transform mode at 149.16 MHz. Chemical shift standards were Me_4Si (internal, ^1H), H_3PO_4 (external 85% at ambient temperature, ^{31}P), and Me_4Sn (external 10% solution in $CDCl_3$ at ambient temperature, ^{119}Sn). More positive shifts represent deshielding.

The following reactions were performed with use of the same general method: *cis*-$[PtCl_2(CO)(PR_3)]$ + 2.0 equiv of $SnCl_2{\cdot}2H_2O$ (MeCN); $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ + excess $SnCl_2{\cdot}2H_2O$ (ca. 20 equiv, Me_2CO); $[PtCl(CO)(PPh_3)_2][SO_3CF_3]$ + excess $SnCl_2{\cdot}2H_2O$ (ca. 20 equiv, Me_2CO); *cis*-$[PtCl_2(SMe_2)(PPh_3)]$ + 5.0 equiv of $SnCl_2{\cdot}2H_2O$ (Me_2CO); *cis*-$[PtCl_2(p\text{-}MeC_6H_4NH_2)(PPh_3)]$ + 2.0 equiv of $SnCl_2{\cdot}2H_2O$ (Me_2CO); *trans*-$[PtCl_2(C_5H_5N)(PPh_3)]$ + 2.0 equiv of $SnCl_2{\cdot}2H_2O$ (Me_2CO); *cis*- and *trans*-$[PtCl_2(C_5H_5N)(PPh_3)]$ + 2.0 equiv of $SnCl_2{\cdot}2H_2O$ (1/1 mixture of isomers, Me_2CO). In each case, the complex and $SnCl_2{\cdot}2H_2O$ were weighed directly into an NMR tube (10-mm diameter) and the solids mixed by shaking. The solvent (ca. 2 mL) was then added and the solution shaken gently until a homogeneous solution resulted.

The reaction of *cis*-$[PtCl_2(^{13}CO)(PPh_3)]$ with $SnCl_2{\cdot}2H_2O$ in $CDCl_3$ solution was performed by mixing the solid complex (ca. 30 mg) with excess $SnCl_2{\cdot}2H_2O$ (ca. 20-fold excess) in a 5-mL flask. Addition of $CDCl_3$ (ca. 2 mL) was followed by stirring for 30 min. The sample was then filtered into an NMR tube and examined spectroscopically. The reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ with excess $SnCl_2{\cdot}2H_2O$ in $CDCl_3$ solution was performed similarly.

Cleavage reactions of $[Pt_2Cl_2(SnCl_3)_2(PR_3)_2]$ with ^{13}CO (R = Et, Ph) or PPh_3 (R = Ph) were performed by cooling a $CDCl_3$ solution of the dimer (ca. 40 mg in 2 mL) to 213 K (chloroform/liquid nitrogen) and stirring under an atmosphere of ^{13}CO or adding a cooled solution of PPh_3 (2 equiv in 0.5 mL) dropwise with stirring. The solutions were then transferred to precooled NMR tubes and examined spectroscopically.

Reactions with H_2 were performed by purging solutions with the gas at ambient temperature for the appropriate length of time (see text) and maintaining constant volume by occasional addition of fresh solvent.

NMR data of model compounds not cited in Table I are as follows: *cis*-$[PtCl(SMe_2)(PPh_3)_2][SO_3CF_3]$, $\delta(P) = 12.5$ (d), $^1J(^{195}Pt,^{31}P) = 3552$ Hz, $\delta(P) = 16.0$ (d), $^1J(^{195}Pt,^{31}P) = 3186$ Hz, $^2J(^{31}P,^{31}P) = 19$ Hz (Me_2CO at 213 K); *cis*-$[PtCl(SMe_2)(PPh_3)_2][ClO_4]$, $\delta(P) = 13.8$ (d), $^1J(^{195}Pt,^{31}P) = 3557$ Hz, $\delta(P) = 16.4$ (d), $^1J(^{195}Pt,^{31}P) = 3203$ Hz, $^2J(^{31}P,^{31}P) = 18$ Hz ($CDCl_3$, ambient temperature); *cis*-$[PtCl(p\text{-}MeC_5H_4NH_2)(PPh_3)_2][ClO_4]$, $\delta(P) = 12.6$ (d), $^1J(^{195}Pt,^{31}P) = 3774$ Hz, $\delta(P) = 5.3$ (d), $^1J(^{195}Pt,^{31}P) = 3342$ Hz, $^2J(^{31}P,^{31}P) = 19$ Hz ($CDCl_3$, ambient temperature).

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Registry No. *trans*-$[PtCl(CO)(PPh_3)_2]^+$, 20683-70-9; *trans*-$[PtCl(CO)(P(p\text{-}MeC_6H_4)_3)_2]^+$, 83719-65-7; *cis*-$[PtCl_2(CO)(PPh_3)$, 19618-78-1; $PtCl(SnCl_3)(PPh_3)(CO)$, 83719-66-8; $Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PPh_3)_2$, 83719-67-9; $Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PEt_3)_2$, 83719-68-0; $PtCl(SnCl_3)(PEt_3)(CO)$, 83719-69-1; *cis*-$[PtCl_2(CO)(PEt_3)]$, 65466-58-2; $[PtCl(PPh_3)_3]^+$, 47899-38-7; *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$, 18583-20-5; *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; *trans*-$[PtCl(SnCl_3)_2(PPh_3)]^-$, 83719-70-4; *trans*-$[PtCl(SnCl_3)_2(PEt_3)]^-$, 83719-71-5; *cis*-$[PtCl(SMe_2)(PPh_3)_2]^+$, 83719-72-6; *cis*-$[PtCl(C_5H_5N)(PPh_3)_2]^+$, 83719-73-7; *cis*-$[PtCl_2(C_5H_5N)(PPh_3)]$, 60268-99-7; *trans*-$[PtCl_2(C_5H_5N)(PPh_3)]$, 60243-31-4; *cis*-$[PtCl_2(p\text{-}MeC_6H_4NH_2)(PPh_3)]$, 83719-74-8; $SnCl_2$, 7772-99-8; ^{119}Sn, 14314-35-3; $(CH_3)_2O$, 67-64-1; CH_3CN, 75-05-8; $CHCl_3$, 67-66-3.

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