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Preparation and Structural Characterization of Ionic Five-Coordinate Palladium(II) and Platinum(II) Complexes of the Ligand Tris[2-(diphenylphosphino)ethyl]phosphine. Insertion of $SnCl_2$ into M–Cl Bonds (M = Pd, Pt) and Hydroformylation Activity of the Pt–$SnCl_3$ Systems

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The five-coordinate palladium(II) and platinum(II) complexes [M(PP_3)Cl]Cl [M = Pd (**1**), Pt (**2**)] (PP_3 = tris[2-(diphenylphosphino)ethyl]phosphine) were prepared by interaction of aqueous solutions of MCl_4^{2-} salts with PP_3 in $CHCl_3$. Complexes **1** and **2** undergo facile chloro substitution reactions with KCN in 1:1 and 1:2 ratios to afford complexes [M(PP_3)(CN)]Cl [M = Pt (**3**)] and [M(PP_3)(CN)](CN) [M = Pd (**4**), Pt (**5**)] possessing M–C bonds, both in solution and in the solid state. The reaction of **1** and **2** with $SnCl_2$ in $CDCl_3$ occurs with insertion of $SnCl_2$ into M–Cl bonds leading to the formation of [M(PP_3)($SnCl_3$)]($SnCl_3$) [M = Pd (**6**), M = Pt (**7**)]. The isolation as solids of complexes **6** and **7** by addition of $SnCl_2$ to the precursors requires the presence of PPh_3 which activates the cleavage of M–Cl bonds, favors the $SnCl_2$ insertion, and does not coordinate to M in any observable extent. Solutions of **6** in $CDCl_3$ undergo tin dichloride elimination in higher proportion than solutions of **7**. The reaction of complexes **1** and **2** with $SnPh_2Cl_2$ leads to [M(PP_3)Cl]$_2$[$SnPh_2Cl_4$] [M = Pd (**8**)]. Complexes **2**, **5**, **7**, and **8** were shown by X-ray diffraction to contain distorted trigonal bipyramidal monocations [M(PP_3)X]$^+$ [M = Pt, X = Cl^- (**2**), X = CN^- (**5**), X = $SnCl_3^-$ (**7**); M = Pd, X = Cl^- (**8**)], the central P atom of PP_3 being trans to X in axial position and the terminal P donors in the equatorial plane of the bipyramids. The "preformed" catalyst **7** showed a relatively high aldehyde selectivity compared to most of the platinum catalysts.

1. Introduction

Tertiary phosphines are generally excellent ligating agents to d^8 metal ions and are very important constituents of compounds for catalysis.[1,2] Thus, platinum−chiral diphosphine complexes in the presence of tin(II) chloride and PtCl($SnCl_3$)(chiral diphosphines) "preformed" catalysts,[3–6] despite their low activities compared to the rhodium analogues,

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proved to be efficient in enantioselective hydroformylation. Especially, the hydroformylation of unsatured esters and vinyl aromatics resulted in chiral building blocks and compounds of pharmacological interest. The branched aldehydes obtained in hydroformylation of vinyl aromatics can be further oxidized to the corresponding acids which are used as effective nonsteroidal analgesics.[7,8] The insertion of $SnCl_2$ into the Pt−Cl bond of a $PtCl_2(P_2)$ precursor (P_2 = two monophosphines or chelating diphosphine) results in the formation of a trichlorostannato ligand affording complexes of the type $PtCl(SnCl_3)(P_2)$.[9] However, by addition of monophosphine, the cleavage of the Pt−Sn bond occurs with formation of ionic complexes containing $SnCl_3^-$ as counteranion, $[PtCl(P_3)](SnCl_3)$, $[PtCl(P)(P_2)](SnCl_3)$.[5] In consequence, when a catalytic system such as $PtCl_2(COD)/PPh_3/SnCl_2$ is used in hydroformylation, the Pt/PPh_3 ratio influences the products of reaction.[10] The addition of PPh_3 to square-planar compounds containing a tridentate triphosphine such as [M(triphos)Cl]Cl (M = Pd, Pt; triphos = bis[2-(diphenylphosphino)ethyl]phenylphosphine) in the presence of $SnCl_2$ leads to a chloro substitution reaction[11] with formation of the ionic complexes $[M(triphos)(PPh_3)](SnCl_3)_2$. Likewise, the σ-carbon donor ligand CN^- is able to displace the chloro ligand from the coordination sphere of M(II) affording new M−C bonds in $[M(triphos)(CN)]^+$ complexes which by addition of another equivalent of CN^- form neutral five-coordinate compounds of the type $[M(triphos)(CN)_2]$.[11]

The kinetics for ligand substitution reactions in square-planar palladium(II) and platinum(II) complexes have been well established, and an associative mechanism via a trigonal bipyramidal transition state has been generally proposed.[12] Five-coordinate hydride species containing the tripodal polyphosphine tris[2-(diphenylphosphino)ethyl]phosphine) (PP_3) and related ligands have been prepared with several low spin d^8 ions including Co(I), Ni(II), Pd(II), and Pt(II).[13−15] Likewise, S. Funahashi et al. have prepared relatively stable five-coordinate trigonal bipyramidal palladium(II) complexes by using the PP_3 ligand $[Pd(PP_3)X]^+$ ($X = Cl^-, Br^-, I^-$)[16] demonstrating that the order of stabilization of the axial halo ligand X is $I^- > Br^- > Cl^-$. In the presence of free trimethyl phosphite, the halo ligand substitution takes place with formation of $[Pd(PP_3)(P(OCH_3)_3)]^{2+}$.[17] These facts are consistent with expectations that reduction of the electronic repulsion is essential to give a higher coordination number than that usually observed, such as five-coordinate for palladium(II) complexes, and that only the donor orbitals on the relatively higher energy levels can form effective σ bonding in such complexes, compared with ordinary square-planar ones. The higher selectivity of the axial coordination site in $[Pd(PP_3)X]^+$ complexes for thiolate sulfur atoms compared with the corresponding square-planar $[Pd(P_3)X]^+$ compounds[18a] (P_3 = linear triphosphine) can be applied to separation of sulfur-containing amino acids from other amino acids and selective determination of the reduced form of glutathione, which is quite important in the biological redox and detoxification systems.[18b]

Following the investigations previously developed with square-planar complexes, the present work deals with the syntheses and characterization of trigonal bipyramidal compounds of the type $[M(PP_3)(CN)]^+$ and $[M(PP_3)(SnCl_3)]^+$ (M = Pd, Pt) and the potential role of the $Pt-SnCl_3$ systems in the hydroformylation of styrene. We report an unusual procedure for isolation of the solids $[M(PP_3)(SnCl_3)](SnCl_3)$ starting from $[M(PP_3)Cl]Cl$ and $SnCl_2$ in the presence of PPh_3. The behavior as a Lewis acid of $SnPh_2Cl_2$ versus $[M(PP_3Cl]Cl$ just binding Cl^- excludes the possibility of formation of M−Sn bonds but provides a way for obtaining well-ordered crystals containing trans $[SnPh_2Cl_4]^{2-}$ anions. The crystal structures for $[M(PP_3)X]X$ ($X = Cl^-, CN^-, SnCl_3^-$) and $[Pd(PP_3)Cl]_2[SnPh_2Cl_4]$ are reported, and the trans influence of the anionic ligands X is discussed.

2. Results and Discussion

2.1. Syntheses. Scheme 1 shows all complexes prepared with tris[2-(diphenylphosphino)ethyl]phosphine (PP_3). Complexes **1** ($[Pd(PP_3)Cl]Cl$) and **2** ($[Pt(PP_3)Cl]Cl$) were prepared as hydrates [(**1**)$\cdot 4H_2O$ and (**2**)$\cdot 2H_2O$] starting from aqueous solutions of MCl_4^{2-} salts and following a variation[19] of the method previously used by R. B. King et al.[20]

The reactions of **1** and **2** in $CHCl_3$ with KCN in CH_3OH led to the formation of $[Pt(PP_3)(CN)]Cl$ (**3**) and $[M(PP_3)(CN)](CN)$ [M = Pd (**4**), Pt (**5**)]. The solids of **4** and **5** were obtained as chloroform solvates [(**4**)$\cdot CHCl_3$ and (**5**)$\cdot CHCl_3$]. Solutions of **1** and **2** in chloroform react under stirring (ca. 12 h) with $SnCl_2$, added as a solid, to form complexes $[M(PP_3)(SnCl_3)](SnCl_3)$ [M = Pd (**6**), Pt(**7**)]. However, all attempts to prepare complexes **6** and **7** quantitatively as solids

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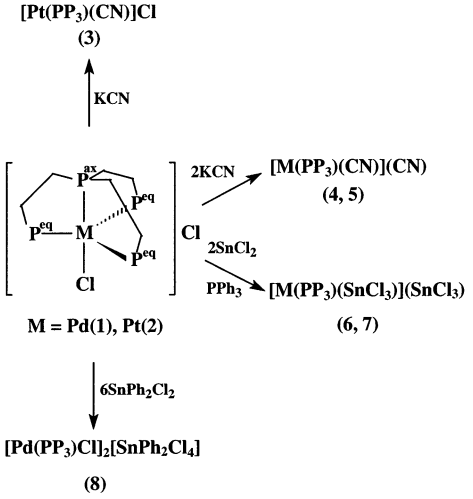
Scheme 1. Complexes Prepared with PP_3 Showing Labels for Donor Atoms



by reaction of the precursors **1** and **2** with $SnCl_2$ in excess were unsuccessful. The M−$SnCl_3$ complexes were achieved, as chloroform solvates [(**6**)·$CHCl_3$ and (**7**)·$CHCl_3$] using PPh_3 as additive ($M/PPh_3 = 1/1$). Crystals of complex **8** ([Pd(PP_3)Cl]$_2$[$SnPh_2Cl_4$]) were obtained as hydrates (**8**)·$4H_2O$ from the reaction {[Pd(PP_3)Cl]Cl (**1**) ($CDCl_3$) and 6 equiv of $SnPh_2Cl_2$ (CD_3OD)}.

Complexes **1**−**7** were prepared in excellent yields (81−92%), and the higher solubilities were found in coordinating solvents such as DMSO or DMF. However, the cyano complexes were not soluble in DMF.

2.2. Mass Spectometry and Infrared Spectroscopy. The FAB MS for complexes **1**, **2**, and **4**−**7** showed peaks assigned to M(PP_3)X fragments in all cases.

The far-infrared spectra (400−100 cm^{-1}) for complexes **1** and **2** show bands at 348 and 351 cm^{-1}, respectively, assigned to terminal M−Cl stretching vibrations. For complexes **6** and **7**, bands were detected at ~320 cm^{-1} assignable to Sn−Cl stretches of the $SnCl_3^-$ ligand. The near-infrared spectra (4000−500 cm^{-1}) for complexes **3** and **5** show bands around 2120 cm^{-1} characteristic of ν(CN) of the cyano ligand.[21,22] Likewise, the band at 2077 cm^{-1} observed for complex **3*** was assigned to $\nu(^{13}CN)$.

Table 1. $^{31}P\{^1H\}$ NMR Data (rt) in $CDCl_3$ for (**1**)·$4H_2O$, (**2**)·$2H_2O$, **3**, **3***, (**4**−**7**)·$CHCl_3$, and (**8**)·$4H_2O$ and Reactions of **1** and **2**

cmpd	$\delta P^{eq\ a}$	$^1J(^{195}Pt, ^{31}P^{eq})$	$\delta P^{ax\ a}$	$^1J(^{195}Pt, ^{31}P^{ax})$
(**1**)·$4H_2O$	29.5s		134.1s	
(**2**)·$2H_2O$	25.0s	2590	118.3s	2505
3^b	26.4d	2543	124.3q	1811
3*^{b,c}	26.4dd	2543	124.3dq	1811
(**4**)·$CHCl_3$	47.3s		154.3s	
(**5**)·$CHCl_3$	30.6s	2539	131.6s	1825
(**6**)·$CHCl_3$	44.6s^d		160.0s	
(**7**)·$CHCl_3$	28.4s^e	2450	137.8s^e	1695
(**7**)·$CHCl_3$^{f}	29.2s	2441	141.5s	2005
(**8**)·$4H_2O$^{g}	29.5s		133.0s	
(**2**)·$2H_2O$ + 6 equiv $SnPh_2Cl_2$^{g}	25.0s	2590	118.3s	2505
(**1**)·$4H_2O$ + 1 equiv PPh_3^{h}	29.5s		134.0s	
(**2**)·$2H_2O$ + 1 equiv PPh_3^{h}	25.0s	2590	118.3s	2505

^{a} See Scheme 1 for labeled atoms. ^{b} $^2J(^{31}P^{eq}, ^{31}P^{ax}) = 4.5$ Hz. ^{c} $^2J(^{31}P^{eq}, ^{13}C) = 15$ Hz, $^2J(^{31}P^{ax}, ^{13}C) = 102$ Hz. ^{d} $^2J(^{117/119}Sn, ^{31}P^{eq}) = 339$ Hz. ^{e} $^2J(^{117/119}Sn, ^{31}P^{eq}) = 298$ Hz, $^2J(^{117/119}Sn, ^{31}P^{ax}) = 2609/2729$ Hz. ^{f} Spectrum recorded in $CDCl_3$/DMF (1/1), $^2J(^{117/119}Sn, ^{31}P^{eq}) = 300$ Hz. ^{g} Spectrum recorded in $CDCl_3/CD_3OD$ (1/1). ^{h} $\delta P(PPh_3)$ −7.3.

2.3. NMR Spectra. 2.3.1. NMR Characterization of Complexes 1 and 2. The $^{31}P\{^1H\}$ NMR spectrum of complexes **1** and **2** ([M(PP_3)Cl]Cl) in $CDCl_3$ (Table 1) shows two signals with integration ratios 3:1 assignable to the equatorial and axial phosphorus (P^{eq}, P^{ax}) of the ligand, respectively, in a five-coordinate compound with a trigonal bipyramidal structure (Scheme 1).[16,18] The $^1J(^{195}Pt, ^{31}P)$ values of 2590 and 2505 Hz for **2** are in accordance with the terminal and central P of PP_3 occupying the equatorial and axial positions, respectively,[13,23] of the bipyramid. The $^1J(^{195}Pt, ^{31}P^{ax})$ value of 2505 Hz is lower than the coupling constants due to P trans to Cl in other homo- and heteronuclear phosphine complexes containing square-planar Pt(II) centers (3000−3600 Hz).[11,24−26] The proton decoupled ^{195}Pt spectrum of **2** (Figure 2a) in DMSO-d_6 consists of an overlapped doublet of (1:3:3:1) quartets centered at δ −4373. This resonance was strongly shifted toward a lower field compared with the corresponding value of the analogous hydrido complex $[Pt(PP_3)H]^+$ [13] ($\delta = -5474$) and also shifted lower field compared with the values ($\delta = -4858$ to −4592) for square-planar Pt(II) complexes.[24−26] The only coupling constant available from the multiplet is $^1J(^{195}Pt, ^{31}P^{eq}) = 2590$ Hz.

2.3.2. NMR Spectra for Complexes 3, 3*, and 4−8. The ^{31}P NMR spectra for solutions in $CDCl_3$ of [Pt(PP_3)(CN)]Cl (**3**) and [Pt(PP_3)(^{13}CN)]Cl (**3***) (prepared by interaction of **3** and 1 equiv of $K^{13}CN$) consist of two signals: a doublet (**3**), a doublet of doublets (**3***), at δ 26.4, and a quartet (**3**), a doublet of quartets (**3***), at δ 124.3. The signals were assigned to the P^{eq} and P^{ax} atoms, respectively, in a trigonal bipyramidal arrangement (Scheme 1). The couplings $^1J(^{195}Pt, ^{31}P^{eq}) = 2543$ Hz, $^1J(^{195}Pt, ^{31}P^{ax}) = 1811$ Hz, and $^2J(^{31}P^{eq}, ^{31}P^{ax}) = 4.5$ Hz are in accordance with this structure. The proton decoupled ^{13}C NMR spectrum of **3*** consists of a doublet of quartets at δ 105.5 (Figure 1b) from which the couplings $^1J(^{195}Pt, ^{13}C) = 911$ Hz, $^2J(^{31}P^{ax}, ^{13}C) = 102$ Hz, and $^2J(^{31}P^{eq}, ^{13}C) = 15$ Hz confirm again the trigonal bipyramidal structure. The same structure can be proposed on the basis of the $^{31}P\{^1H\}$ NMR data for solutions of [Pd(PP_3)(CN)](CN) (**4**) and [Pt(PP_3)(CN)](CN) (**5**) in $CDCl_3$.

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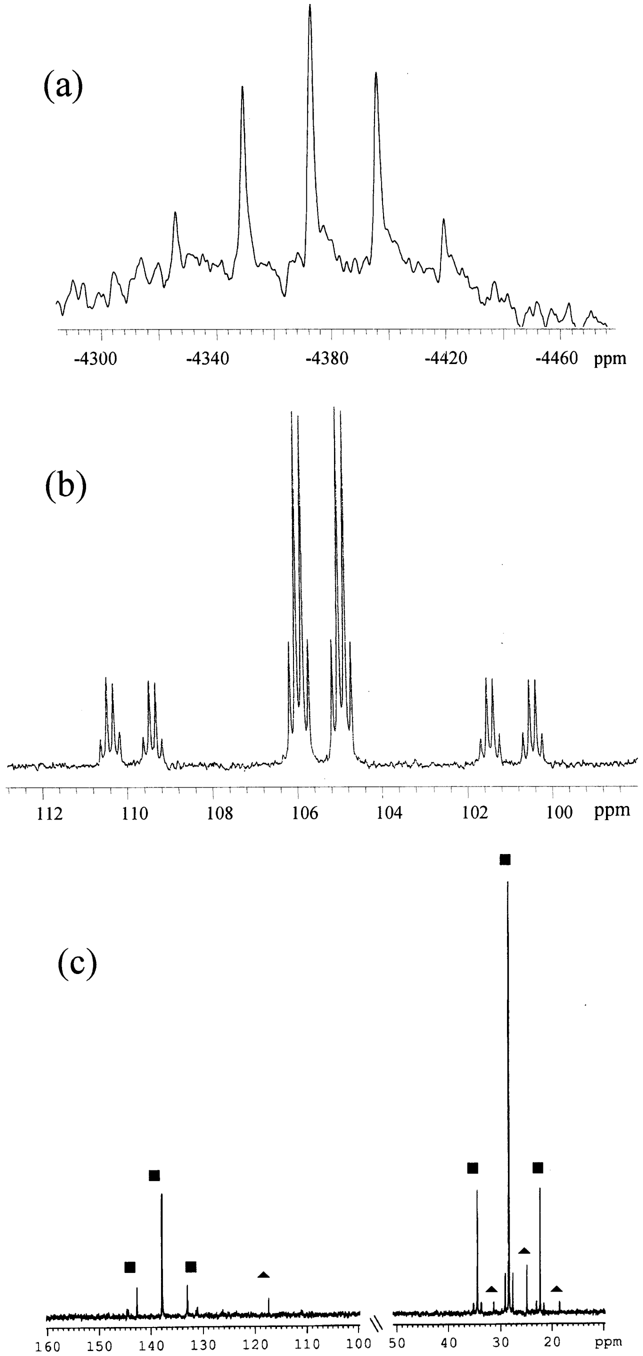

Figure 1. NMR spectra for solutions of (a) (**2**)·$2H_2O$ in DMSO-d_6, (b) **3*** in $CDCl_3$, and (c) (**7**)·$CHCl_3$ in $CDCl_3$ at rt: (a) ^{195}Pt, (b) ^{13}C, (c) $^{31}P\{^1H\}$ (peaks and satellites are labeled as ▲ for (**2**)·$2H_2O$ and ■ for (**7**)·$CHCl_3$).

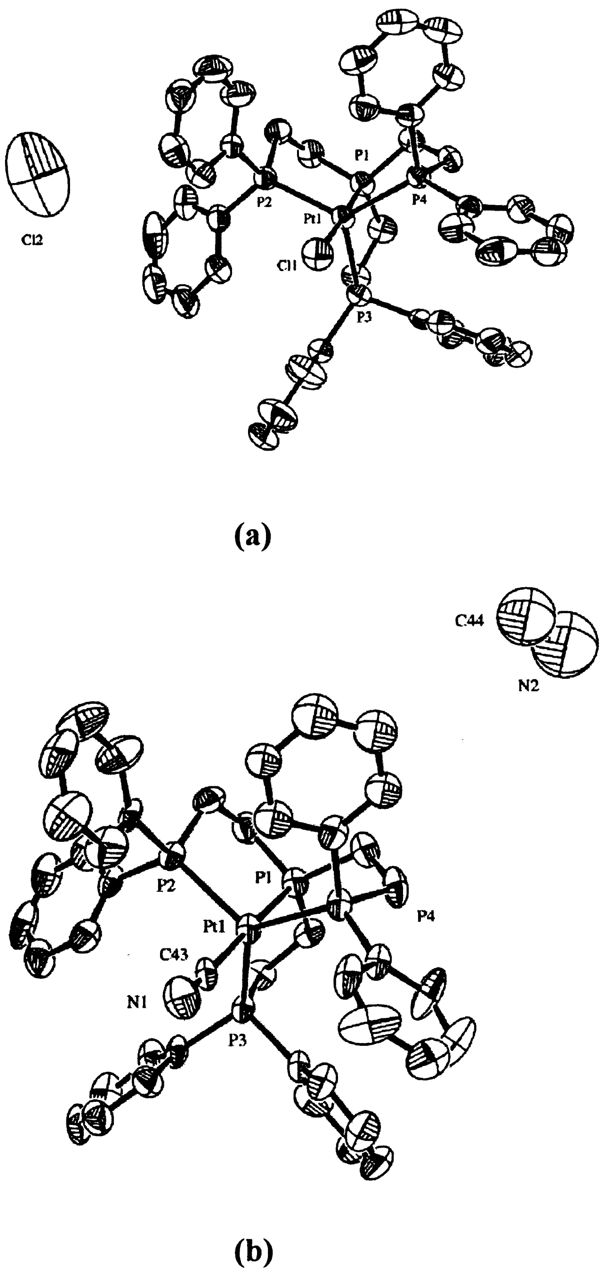

Figure 2. ORTEP diagram for **2** and **5**.

The insertion of $SnCl_2$ into M−Cl bonds was observed in solution by addition of $SnCl_2$, as a solid, to solutions of **1** and **2** in $CDCl_3$ under stirring.

Because the square-planar complexes [M(triphos)Cl]Cl react with PPh_3 in the presence of $SnCl_2$ to form [M(triphos)(PPh_3)]($SnCl_3$)$_2$ (prepared as solids),[11] the analogous reaction was carried out with [M(PP_3)Cl]Cl. It was surprisingly observed that when **1** and **2** (in $CHCl_3$) react with 2 equiv of $SnCl_2$ (in CH_3OH) in the presence of PPh_3 (M/PPh_3 = 1/1) the formation of complexes **6** and **7** occurs, respectively, with there being no reaction between [M(PP_3)Cl]$^+$ and PPh_3 (Table 1). The use of this procedure allowed the preparation of complexes **6** and **7** as solids.

The $^{31}P\{^1H\}$ NMR spectrum for **6** and **7** dissolved in $CDCl_3$ and the spectrum for **7** in $CDCl_3$/DMF (1/1) show two sets of two signals assignable to P^{ax} and P^{eq} in [M(PP_3)Cl]$^+$ and [M(PP_3)($SnCl_3$)]$^+$ complexes. This indicates that the trichlorostannato ligand undergoes tin dichloride elimination to some extent (Figure 1c). The presence of M−Sn bonds is evident from the couplings $^2J(^{117/119}Sn, ^{31}P^{eq}) = 339$ Hz (M = Pd) and 298 Hz (M = Pt) as well as $^2J(^{117/119}Sn, ^{31}P^{ax}) = 2609/2729$ Hz and $^1J(^{195}Pt, ^{31}P^{ax}) = 1695$ Hz (M = Pt). Despite the lower value of $^1J(^{195}Pt, P^{ax})$ in $CDCl_3$ for **7** (1695 Hz) compared to **5** (1825 Hz), the facile elimination of $SnCl_2$ from $SnCl_3^-$ ligand is indicative of weaker coordinating behavior for $SnCl_3^-$ versus CN^-, and the

Table 2. $SnCl_2$ Elimination for **6** and **7** and Insertion of $SnCl_2$ into M−Cl Bonds for **1** and **2** in $CDCl_3$

cmpd	$[M(PP_3)(SnCl_3)]^+$ (%)	$[M(PP_3)Cl]^+$ (%)
$[Pd(PP_3)(SnCl_3)](SnCl_3)$ (**6**)	75.4	24.6
$[Pt(PP_3)(SnCl_3)](SnCl_3)$ (**7**)	90.0	10.0
$[Pt(PP_3)(SnCl_3)](SnCl_3)$ (**7**)[a]	45.0	55.0
$[Pd(PP_3)Cl]Cl$ (**1**) + 1 equiv $SnCl_2$	100.0	0.0
$[Pt(PP_3)Cl]Cl$ (**2**) + 1 equiv $SnCl_2$	64.4	35.6
$[Pt(PP_3)Cl]Cl$ (**2**) + 2 equiv $SnCl_2$	100.0	0.0

[a] $CDCl_3$/DMF (1/1).

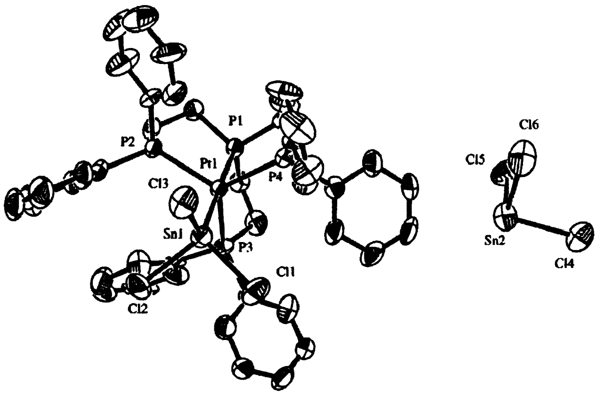

Figure 3. ORTEP diagram for **7**.

sequence proposed for the trans influence[27] in complexes **1**, **5**, **7**, and $[Pt(PP_3)H]^+$ ($^1J(^{195}Pt,^{31}P) = 1467$ Hz)[13a] is $H^- > CN^- > SnCl_3^- > Cl^-$.

The broad signals observed at δ −65.4 and −66.6 in the ^{119}Sn NMR spectra ($CDCl_3$) for **6** and **7**, respectively, did not allow us to distinguish between $SnCl_3^-$ ligand and counterion.[28]

The $^{31}P\{^1H\}$ NMR spectra for (**1** + 6 equiv $SnPh_2Cl_2$ = **8**) and (**2** + 6 equiv $SnPh_2Cl_2$) show signals (Table 1) in the same position as those for precursors **1** and **2**, respectively. $SnPh_2Cl_2$ reacts here as general-type Lewis acid, just binding Cl^-, and the different behavior compared to $SnCl_2$ (a specific complexing reagent for platinum group metals) is probably because of steric and electronic factors.

2.3.3. Elimination of $SnCl_2$ for Complexes 6 and 7 and Insertion of $SnCl_2$ into M−Cl Bonds for Complexes 1 and 2. Table 2 shows the percentages of $[M(PP_3)(SnCl_3)]^+$ versus $[M(PP_3)Cl]^+$ detected by $^{31}P\{^1H\}$ NMR for solutions of **6** and **7** ("preformed" systems) and titrations of **1** and **2** with $SnCl_2$ (in situ systems) in $CDCl_3$.

The tin dichloride elimination from **6** dissolved in $CDCl_3$ occurs in higher proportion (24.6%) than from **7** (10%). The use of the solvent mixture $CDCl_3$/DMF (1/1) for dissolving **7**, as expected, increases this elimination (55%).

The total insertion of $SnCl_2$ into the M−Cl bonds requires the addition of 1 and 2 equiv of $SnCl_2$ to solutions in $CDCl_3$ of **1** and **2**, respectively.

Thus, palladium(II) complexes **1** and **6** undergo more facile tin dichloride insertion and elimination reactions in $CDCl_3$ than platinum(II) compounds **2** and **7**, respectively, undergo.

2.4. Structural Characterization of 2, 5, 7, and 8 by X-ray Diffraction. Suitable crystals for X-ray diffraction studies of **2**, **5**, and **8** were obtained as hydrates (**2**)·H_2O, (**5**)·H_2O, and (**8**)·$4H_2O$. Crystals of **7** were obtained as the chloroform solvate (**7**)·$CHCl_3$. Crystal parameters, data collection, and refinement for all crystal structures are given in Table 3. The ORTEP diagrams with numbering schemes for complexes **2** and **5** are given in Figure 2, and for **7** and **8**, in Figures 3 and 4, respectively. Selected bond distances and angles for all crystals are listed in Table 4. While crystals of **2**, **5**, and **7** are made up of discrete units $[Pt(PP_3)X]X$ [X = Cl^- (**2**), CN^- (**5**), $SnCl_3^-$ (**7**)] containing one monocation and one monoanion, crystals of **8** consist of two monocations $[Pd(PP_3)Cl]^+$ symmetrically located in relation to one dianion $[SnPh_2Cl_4]^{2-}$, the tin atom being the center of symmetry. The cations $[M(PP_3)X]^+$ adopt, in all cases, a slightly distorted trigonal bipyramidal geometry where PP_3 acts as a tetradentate chelating ligand with the central phosphorus in axial position (P^{ax}) trans to the donor atom of the anionic ligand X and the terminal phosphorus in the equatorial plane (P^{eq}) of the bipyramid. All M−P^{eq} distances are longer than the M−P^{ax} for each complex. This can be attributed not only to the strong σ interaction of the axial bond in the trigonal bipyramidal geometry but also to the participation of the P^{ax} in three fused five-membered chelate rings to M. Similar trends with different axial and equatorial bond distances were observed in analogous d^8 metal complexes such as $[Co(PP_3)(P(OCH_3)_3)]^+$ [16] and $[Ni(PP_3)(P(OCH_3)_3)]^{2+}$,[14] and regardless of geometry, the shortest metal−phosphorus distances for other polyphosphine complexes ($[RuCl_2(tetraphos)]$,[29] [Ni(Te−Te)(triphos)],[30] [Pt(triphos)Cl]Cl[24]) also corresponded to the P donor atoms involved in more than one chelate ring to a metal center. For the present complexes, each M(II) in $[M(PP_3)X]^+$ [M = Pt (**2**, **5**, **7**), Pd (**8**)] is displaced by 0.161−0.197 Å from the equatorial plane defined by the three equatorial phosphorus atoms toward the X ligand, with the sequence of this displacement being **8** > **7** > **5** > **2**.

The Pt−P^{ax} bond distances for **2**, **5**, and **7** [2.2214(2), 2.259(5), and 2.294(3) Å, respectively] increase ca. 0.035 Å from **2** to **5** and from **5** to **7**. The unexpected increase for **7** compared to **5** (CN^- is stronger trans ligand)[27] can be attributed to a steric effect with the $SnCl_3^-$ coordinated complex, leading to more distortion of the tetrapod ligand chelate rings. Likewise, the lower trans effect of the axial ligand $SnCl_3^-$ compared with H^- results in a Pt−P^{ax} bond distance for **7** higher than the same distance for the hydrido complex $[Pt(PP_3)H](BPh_4)$ [2.266(1) Å][15], the general trend (on the basis of $^{31}P\{^1H\}$ NMR data) being in the opposite sense. The Pd−P^{ax} bond distance for complex **8**, 2.217(2) Å, is shorter than the same distance for complex **1** (2.237(3) Å).[16] The Pt−P^{eq} bond lengths are in the same range 2.340(1)−2.400(1) Å for all three complexes **2**, **5**, and **7** and

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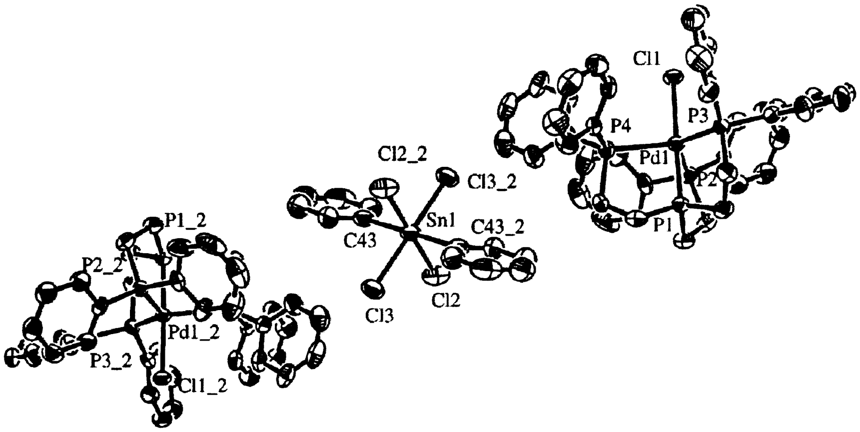

Figure 4. ORTEP diagram for **8**.

Table 3. Summary of Crystal Parameters, Data Collection, and Refinement for (**2**)·6H_2O, (**5**)·H_2O, (**7**)·$CHCl_3$, and (**8**)·4H_2O

	(**2**)·6H_2O	(**5**)·H_2O	(**7**)·$CHCl_3$	(**8**)·4H_2O
empirical formula	$C_{42}H_{42}P_4Cl_2O_{5.5}Pt$	$C_{44}H_{42}N_2OP_4Pt$	$C_{43}H_{42}Cl_9P_4PtSn_2$	$C_{48}H_{47}Cl_3P_4PdSn_{0.5}O_2$
fw	1024.63	933.77	1434.17	1051.83
temp (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst size (mm^3)	0.33 × 0.20 × 0.06	0.38 × 0.29 × 0.02	0.62 × 0.09 × 0.08	0.34 × 0.17 × 0.07
color/habit	orange/prisms	yellow/plates	yellow/needles	red/plates
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	10.275(2)	10.306(4)	12.514(3)	10.112(2)
b (Å)	10.630(2)	10.488(4)	42.380(11)	12.028(3)
c (Å)	20.770(4)	21.012(8)	10.552(3)	21.282(5)
α (deg)	80.244(4)	80.411(6)	90	92.903(4)
β (deg)	86.006(4)	86.458(6)	113.165(4)	101.721(4)
γ (deg)	75.924(4)	76.204(6)	90	111.854(4)
V (Å^3)	2167.7(8)	2174.2(15)	5145(2)	2329.4(9)
Z	2	2	4	2
calcd d (Mg/m^3)	1.570	1.426	1.851	1.500
abs coefft (mm^{-1})	3.551	3.408	4.298	1.008
F(000)	1020	932	2764	1066
θ range for data collection (deg)	1.00−26.44	0.98−26.44	0.96−26.41	0.99−26.42
index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$	$-15 \le h \le 15$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-12 \le k \le 13$	$-35 \le k \le 52$	$-15 \le k \le 15$
	$0 \le l \le 25$	$0 \le l \le 26$	$-13 \le l \le 11$	$0 \le l \le 26$
reflns collected	24811	24054	33126	17131
indep reflns	8840 [$R_{int} = 0.0363$]	8834 [$R_{int} = 0.0724$]	10514 [$R_{int} = 0.0767$]	9339 [$R_{int} = 0.0515$]
max and min transmission	0.8152 and 0.3870	0.9350 and 0.3575	0.7249 and 0.1758	0.9420 and 0.6488
data/restraints/params	8840/0/493	8834/0/421	10514/0/532	9339/0/519
GOF on F^2	0.980	1.251	0.992	0.958
final R indices	R1 = 0.0302	R1 = 0.1126	R1 = 0.0658	R1 = 0.0566
	wR2 = 0.0672	wR2 = 0.2920	wR2 = 0.1363	wR2 = 0.1384
largest diff. peak and hole (e·Å^{-3})	0.716 and −0.796	7.443 and −4.948	1.401 and −2.168	1.157 and −1.701

are slightly longer than the analogous distances for the hydrido complex [2.313(1)−2.343(1) Å]. Pd−P^{eq} bond distances for **8** are similar to those for complex **1**.[16] The Pt−Cl and Pd−Cl bond distances for **2** and **8**, respectively, are coincident and slightly longer than Pt−Cl (2.364(2) Å) and Pd−Cl (2.358(2) Å) distances in square-planar complexes of the type [M(triphos)Cl]$_2$[$SnPh_2Cl_4$] (M = Pd, Pt).[31] The Pt−C distance for **5** is in the same range of distances found for other heterobimetallic cyano complexes such as [PtRh(μ-dppm)$_2$(CNBu^t)$_2$(CN)$_2$](PF_6) and [AgPt(dppm)$_2$(CN)$_2$(CF_3SO_3)] [dppm = bis(diphenylphosphino)methane] [2.02(2)−2.035(2) and 2.00(2) Å].[22] The C−N distances in CN$^-$ ligand and counterion are 1.14(2) and 0.96(6) Å, respectively, revealing, as expected, a decrease in the CN bond order for CN$^-$ ligand compared with the counteranion. This is a consequence of the significant π-acceptor ability of the ligand.

The Pt−Sn bond length for **7** (2.5741(2) Å) is longer than the average axial Pt−Sn distances in [Pt($SnCl_3$)$_5$]$^{3-}$ (2.553 Å), almost coincident with the average equatorial Pt−Sn lengths (2.572 Å) in the same five-coordinate complex[32a] and slightly shorter than the Pt−Sn bonds in square-planar complexes such as *trans*-[PtH($SnCl_3$)(PPh_3)$_2$] (2.601(1) Å)[32b]

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Table 4. Selected Distances (Å) and Angles (deg) for Complexes (**2**)·$6H_2O$, (**5**)·H_2O, (**7**)·$CHCl_3$, and (**8**)·$4H_2O$

	(**2**)·$6H_2O$[a]	(**5**)·H_2O[a,b]	(**7**)·$CHCl_3$[a]	(**8**)·$4H_2O$[a]
M(1)−P(1)	2.2214(2)	2.259(5)	2.294(3)	2.217(2)
M(1)−P(2)	2.3404(2)	2.377(5)	2.382(3)	2.419(2)
M(1)−P(3)	2.4008(2)	2.359(4)	2.378(3)	2.400(2)
M(1)−P(4)	2.3672(2)	2.344(5)	2.362(3)	2.469(2)
M(1)−X[a]	2.4201(2)	2.029(2)	2.5741(2)	2.4202(2)
Sn(1/2)−Cl(1/4)			2.355(4)/2.494(4)	
Sn(1/2)−Cl(2/5)			2.370(4)/2.479(5)	2.608(3)
Sn(1/2)−Cl(3/6)			2.344(4)/2.506(5)	2.566(2)
Sn(1)−C(43)				2.145(9)
P(1)−M(1)−P(2)	84.40(4)	84.22(2)	84.34(2)	83.40(8)
P(1)−M(1)−P(3)	84.59(5)	84.96(17)	84.21(2)	84.29(8)
P(1)−M(1)−P(4)	85.40(4)	84.06(2)	83.75(2)	83.59(7)
P(2)−M(1)−P(3)	119.01(4)	119.51(2)	117.46(2)	129.67(8)
P(2)−M(1)−P(4)	124.80(4)	123.06(2)	120.13(2)	112.68(8)
P(3)−M(1)−P(4)	113.74(4)	114.60(2)	119.28(2)	114.09(8)
P(1)−M(1)−X[a]	177.30(5)	178.4(5)	178.44(8)	178.56(9)
P(2)−M(1)−X[a]	93.13(4)	97.2(5)	96.30(8)	96.87(7)
P(3)−M(1)−X[a]	97.57(5)	95.1(5)	96.74(9)	94.46(7)
P(4)−M(1)−X[a]	95.16(5)	94.6(5)	94.70(8)	83.59(7)
Pt(1)−Sn(1)−Cl(1)			119.09(2)	
Pt(1)−Sn(1)−Cl(2)			118.62(2)	
Pt(1)−Sn(1)−Cl(3)			120.53(1)	
Cl(1/4)−Sn(1/2)−Cl(2/5)			97.57(2)/92.15(2)	
Cl(1/4)−Sn(1/2)−Cl(3/6)			99.40(2)/93.48(2)	
Cl(2/5)−Sn(1/2)−Cl(3/6)			96.80(2)/94.41(2)	90.23(9)
Cl(2)−Sn(1)−Cl(2)#				180.00(2)
C(43)−Sn(1)−C(43)#				180.0(7)
C(43)−Sn(1)−Cl(2)				90.3(3)
C(43)−Sn(1)−Cl(3)				89.7(3)

[a] M = Pt (**2**, **5**, **7**), M = Pd (**8**); X = Cl(1) (**2**, **8**), X = C(43) (**5**), X = Sn (1) (**7**). [b] C(43)−N(1) = 1.14(2) Å, C(44)−N(2) = 0.96(6) Å.

and PtI($SnCl_3$)(bdpp) [bdpp = 2,4-bis(diphenylphosphino)pentane] (2.6113(2) Å).[5] This metal−tin bond is shorter than the sum of the appropriate atomic radii, in agreement with similar trends observed for other metal−$SnCl_3$ [metal = Ru(II), Ir(I), Pd(I)] complexes.[32a] All Sn−Cl distances in $SnCl_3^-$ ligand are shorter than those corresponding to $SnCl_3^-$ counteranion. Despite the high calculated density for **7** (1.851 Mg/m^3) compared to **2**, **5**, and **8** (1.570, 1.426, and 1.500 Mg/m^3, respectively), the crystal packing does not impose any unusual platinum−tin or tin−tin intermolecular contacts.

The Sn−Cl and Sn−C distances for $[SnPh_2Cl_4]^{2-}$ in **8** are in agreement with the values found in [Pd(triphos)Cl]$_2$[$SnPh_2Cl_4$].

The average value for P−M−P angles involving P^{ax} (84.30°) and P^{eq} (119.0°) reveals in all structures a light distortion from the trigonal bipyramidal geometry. The chelate bite angles P^{ax}−M−P^{eq} below 90° are presumably a consequence of the chelate strain of the five-membered P−C−C−P chelate rings formed. The angles P(1)−M(1)−P(3) (84.21(2)°) and P(1)−M(1)−P(4) (83.75(2)°) for **7** are smaller than the same angles for **5** (and **2**). This is in accordance with phosphorus donors P(3) and P(4) (and their phenyl rings) bent back more in the more sterically bulky $SnCl_3^-$ coordinated complex producing the unexpected increase in the Pt−P^{ax} distance. The averages for P−M−X angles (X = Cl, C, Sn) (178.20° and 94.62° for P^{ax}−M−X and P^{eq}−M−X, respectively) are also in accordance with a certain distortion. While the Pt−Sn−Cl angles for **7** are ca. 120°, the Cl−Sn−Cl angles for $SnCl_3^-$ ligand are above 95° showing a distortion for the $PtSnCl_3$ moiety from the tetrahedral geometry. The pyramidalization of $SnCl_3^-$ counteranion is evident from its Cl−Sn−Cl angles which are below 95°.

Table 5. Hydroformylation of Styrene with Pt Complexes Containing PP$_3$[a]

catalyst	R time (h)	conversion (%)	R_c (%)[b]	R_{br} (%)[c]
[Pt(PP$_3$)Cl]Cl + $SnCl_2$[d]	140	2	38	63
[Pt(PP$_3$)Cl]Cl + 5 $SnCl_2$[d]	110	11	42	62
[Pt(PP$_3$)($SnCl_3$)]($SnCl_3$)	50	12	99	75

[a] Reaction conditions: Pt/styrene = 1/4000; 100 °C; p(CO/H_2 = 1/1) = 100 bar; toluene solvent. [b] R_c = Chemoselectivity toward hydroformylation: (B + C)/(B + C + D) × 100. [c] R_{br} = regioselectivity toward branched aldehyde: B/(B + C) × 100. [d] ~30% of the substrate (styrene) polymerized.

The dianion $[SnPh_2Cl_4]^{2-}$ for **8** shows a *trans*-octahedral geometry with the phenyl rings in coplanarity. The angles trans C−Sn−C or Cl−Sn−Cl [180.00(11)°], and C−Sn−Cl [~90.0°], confirm this *trans*-octahedral arrangement.

2.5. Hydroformylation of Styrene with Pt Complexes Containing PP$_3$ as Catalysts. Styrene (**A**) as the model substrate was reacted either in the presence of the platinum precursor complex [Pt(PP$_3$)Cl]Cl (**2**) and anhydrous tin(II) chloride or in the presence of the "preformed" catalyst [Pt(PP$_3$)($SnCl_3$)]($SnCl_3$) (**7**) with CO/H_2 (1/1) at 100 °C and a pressure of 100 bar (Table 5).

$$\underset{\mathbf{A}}{PhCH{=}CH_2} \xrightarrow{CO/H_2} \underset{\mathbf{B}}{PhCH(CH_3)CHO} + \underset{\mathbf{C}}{PhCH_2CH_2CHO} + \underset{\mathbf{D}}{PhC_2H_5}$$

The highest activity among the systems was found for the "preformed" catalyst [Pt(PP$_3$)($SnCl_3$)]($SnCl_3$) (**7**) followed by the in situ prepared catalyst (**2** + 5 equiv of $SnCl_2$). (It has to be mentioned that the hydroformylation under harsh conditions and elevated reaction times is accompanied by polymerization of the substrate, as well as the dimerization of the aldehyde regioisomers **B** and **C** (in smaller extent) resulting in low reproducibility of the reaction.) The regio- and chemoslectivities were rather low when in situ systems were used. However, excellent aldehyde selectivity was obtained in the presence of the "preformed" catalyst **7**.

In general, Pt−PP$_3$ systems show very low catalytic activities compared to those of platinum−diphosphine tin(II) chloride systems[4,32] and especially to those of widely used rhodium-containing systems.[33] It is presumably due to the four phosphorus donor atoms of the ligand blocking the coordination sites. The absence of easily available vacant sites substantially hinders the facile activation of the reactants (carbon monoxide, olefin).

The hydrofomylation activity of the coordinatively saturated 18-electron complex, [Pt(PP$_3$)($SnCl_3$)]$^+$, can be explained by two reasons. (i) The complete dissociation[10b] of the trichlorostannate ligand provides a vacant coordination site. This fact is known from mechanistic studies carried out

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by high-pressure NMR.[34] The importance of the $SnCl_3^-$ acting as a counterion has been proved in elementary steps such as carbon monoxide activation, insertion to Pt−alkyl bond, and aldehyde forming step. (However, to the best of our knowledge, the role of $SnCl_2$ "cocatalyst" in olefin activation is still uncertain, and no mechanistic evidence has been reported.) (ii) The "arm off" dissociation of the PP_3 ligand leads to vacant coordination site(s), too. This effect has been observed in case of $HRh(CO[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ precursor under even less severe conditions (30 bar, room temperature).[35] The branched selectivities of 60−75% typical for various Pt−diphosphine systems, obtained also by the Pt−PP_3 systems, might be due to the dissociation of two phosphorus donors, that is, PP_3 acting as a bidentate ligand in square-planar catalytic intermediates.

In case of the in situ systems, the insertion of $SnCl_2$ into the Pt−Cl bond is not quantitative in noncoordinating toluene solvent; so, lower activity and different activation modes for the reactants could be expected. Although in DMF complete dissociation of $SnCl_3^-$ can be observed, much less active systems have been obtained because of solvent coordination.

3. Conclusions

The five-coordinate complexes $[M(PP_3)Cl]^+$ (M = Pd, Pt) exhibit a trigonal bipyramidal structure both in solution and solid state where PP_3 acts as tetradentate chelating ligand with the central phosphorus in axial position trans to Cl and the terminal ones in the equatorial plane of the bipyramid. The reactions of these chloro complexes with KCN or $SnCl_2$ maintain their geometries leading to the formation of new M−C or M−Sn bonds in the axial positions. However, the reactions of $[M(PP_3)Cl]Cl$ with $SnPh_2Cl_2$ occur with formation of $[SnPh_2Cl_4]^{2-}$ anions. The isolation of complexes $[M(PP_3)(SnCl_3)](SnCl_3)$ as solids by addition of $SnCl_2$ to the precursors requires the presence of PPh_3. The tin dichloride insertion and elimination in chloroform was more favored for Pd(II) than for Pt(II). Although the catalytic activity for solutions of the "preformed" complex $[Pt(PP_3)(SnCl_3)](SnCl_3)$ in the hydroformylation of styrene is very low, the potential formation of a vacant site by dissociation may be responsible for its excellent aldehyde selectivity.

4. Experimental Section

4.1. General Procedures. Dichloromethane was redistilled under nitrogen over $CaCl_2$. Potassium tetrachloroplatinate(II), palladium(II) chloride, and tin(II) chloride were purchased from Strem Chemicals, and tris[2-(diphenylphosphino)ethyl]phosphine and diphenyltin(IV) chloride, from Aldrich. Potassium cyanide was purchased from Panreac, and potassium cyanide-^{13}C, from Cambridge Isotope Laboratories. Microanalyses were performed on a Fisons Instrument EA 1108 CHNS-O. Fast atom bombardment (FAB) mass spectra were obtained in a Micromass Autospec spectrometer using 3-nitrobenzyl alcohol as the matrix. Infrared spectra were recorded at ambient temperature as KBr pellets (4000−500 or 4000−400 cm^{-1}) and Nujol mulls (500−100 cm^{-1}) on a Nicolet IMPACT 400 with a DTGS detector and a Mattson Cygnus 100 spectrophotometer. The bands are reported as s = strong, m = medium, b = broad. $^{31}P\{^1H\}$, ^{195}Pt, and ^{119}Sn NMR spectra were recorded on a Bruker AMX500 spectrometer at 202.46, 107.52, and 186.5 MHz, respectively. ^{13}C and some $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Inova 400 spectrometer at 100.6 and 161.9 MHz, respectively. Chemical shifts are reported relative to external standard $SiMe_4$ (^{13}C), 85% H_3PO_4 (^{31}P), 1 M Na_2PtCl_6 (^{195}Pt), and $SnMe_4$ (^{119}Sn); δ = chemical shift in ppm, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, q = quartet, dq = doublet of quartets, m = multiplet, bs = broad signal, J = coupling constant in hertz. Conductivities were measured at 25 °C using 10^{-3} M solutions in DMF on a WTW model LF-3 instrument.

4.2. Preparations and Titrations. Preparation of $[Pd(PP_3)Cl]Cl$ (1). Complex **1** was prepared as (**1**)$\cdot 4H_2O$. A suspension of $PdCl_2$ (0.0158 g, 0.2922 mmol) and NaCl (0.0342 g, 0.5844 mmol) in H_2O (14 mL) was heated on a water bath (80 °C) until a clear solution was obtained. This was allowed to cool to room temperature, and a solution of PP_3 (0.1959 g, 0.2922 mmol) in $CHCl_3$ (30 mL) was added dropwise. The mixture was stirred for 24 h at room temperature, and $CHCl_3$ was removed in vacuo to leave a red precipitate in the aqueous phase. It was filtered off, washed with H_2O and Et_2O, and dried in vacuo. Yield: 92%, mp 260 °C. Found: C, 55.0; H, 5.4. $C_{42}H_{50}P_4O_4PdCl_2$ requires: C, 55.6; H, 5.6%. IR ν_{max}/cm^{-1}: (Pd−Cl) 348m. MS (FAB): m/z 811 ($M^+ -$ Cl, 55.6%); 776 ($M^+ -$ 2Cl, 2.0%); 563 ($M^+ -$ 2Cl $-C_2H_4PPh_2$, 3.3%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): See Table 1. Λ(DMF) = 77.1 ohm^{-1} cm^2 mol^{-1}.

4.3. Preparation of $[Pt(PP_3)Cl]Cl$ (2). Complex **2** was obtained as (**2**)$\cdot 2H_2O$. To a solution of K_2PtCl_4 (0.1729 g, 0.4160 mmol) in H_2O (15 mL) was added dropwise a solution of PP_3 (0.2793 g, 0.4160 mmol) in $CHCl_3$ (30 mL), and the mixture was stirred for 12 h. $CHCl_3$ was removed in vacuo to leave a yellow precipitate in the aqueous phase which was filtered off, washed with H_2O and Et_2O, and dried in vacuo. Suitable crystals for X-ray diffraction were obtained from a solution of the complex in $CHCl_3$. Yield: 85%, mp 281 °C. Found: C, 51.4; H, 4.7. $C_{42}H_{46}P_4O_2PtCl_2$ requires: C, 51.8; H, 4.7%. IR ν_{max}/cm^{-1}: (Pt−Cl) 351m. MS (FAB): m/z 900 ($M^+ -$ Cl, 45.1%); 865 ($M^+ -$ 2Cl, 1.3%); 652 ($M^+ -$ 2Cl $-C_2H_4PPh_2$, 1.2%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): See Table 1. ^{195}Pt NMR (DMSO-d_6): δ −4373 (m) (overlapped dq). Λ(DMF) = 72.1 ohm^{-1} cm^2 mol^{-1}.

4.4. Titrations of (1)$\cdot 4H_2O$ and (2)$\cdot 2H_2O$ with KCN, $SnCl_2$, $SnPh_2Cl_2$, and PPh_3. To a solution of complexes (**1**)$\cdot 4H_2O$ and (**2**)$\cdot 2H_2O$ in $CDCl_3$ were added solutions of KCN and $SnPh_2Cl_2$ in CD_3OD or PPh_3 in $CDCl_3$ in different stoichiometric ratios. The $^{31}P\{^1H\}$ NMR spectra were recorded after each addition. Tin dichloride was added as a solid to 13 × 10^{-3} M solutions of (**1**)$\cdot 4H_2O$ and (**2**)$\cdot 2H_2O$ in $CDCl_3$, and the $^{31}P\{^1H\}$ NMR spectra were recorded after stirring for 12 h. The results for titrations with $SnPh_2Cl_2$ and PPh_3 are given in Table 1 and with $SnCl_2$ in Figures S1−S2 (Supporting Information).

4.5. Preparation of $[Pt(PP_3)(CN)]Cl$ [CN = ^{12}CN (3); ^{13}CN (3*)]. Complex $[Pt(PP_3)Cl]Cl\cdot 2H_2O$ (0.4683 g, 0.5 mmol) was added to a solution of KCN (**3**) or $K^{13}CN$ (**3***) (0.5 mmol) dissolved in CH_3OH (15 mL). The powder did not dissolve completely but was kept in suspension at 50 °C with constant stirring for 10 h. The white powderlike crystals were filtered, washed with water, methanol, and ether, and dried. The crystallization was carried out in a benzene/methanol mixture. Yield: 90%, mp 276 °C. Found: C, 56.0; H, 4.8; N, 1.6. $C_{43}H_{42}NP_4PtCl$ requires: C, 55.7; H, 4.6; N, 1.5%. IR ν_{max}/cm^{-1}: (^{12}CN) 2123m, (^{13}CN) 2077m. $^{31}P\{^1H\}$

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NMR ($CDCl_3$): See Table 1. ^{13}C NMR ($CDCl_3$) (**3***): δ 105.5 (dq), $^1J(^{195}Pt, ^{13}C) = 911$ Hz, $^2J(^{31}P^{ax}, ^{13}C) = 102$ Hz, $^2J(^{31}P^{eq}, ^{13}C) = 15$ Hz.

4.6. Preparation of $[Pd(PP_3)(CN)](CN)$ (4). This compound was prepared as (**4**)$\cdot CHCl_3$. To a solution of $[Pd(PP_3)Cl]Cl\cdot 4H_2O$ (0.1068 g, 0.1259 mmol) in $CHCl_3$ (25 mL) was added a solution of KCN (0.0164 g, 0.2519 mmol) in CH_3OH (16 mL), and immediately, the color of the solution changed from bright red to yellow. The mixture was stirred for 24 h at ambient temperature, and after that, Et_2O (80 mL) was added to precipitate a yellow solid, which was filtered off and dried in vacuo. Yield: 91%, mp 285 °C. Found: C, 57.5; H, 4.5; N, 3.1. $C_{45}H_{43}N_2P_4PdCl_3$ requires: C, 57.0; H, 4.6; N, 3.0%. IR ν_{max}/cm^{-1}: (CN) 2124m. MS (FAB): *m*/*z* 802 ($M^+ - CN$, 24.4%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): See Table 1.

4.7. Preparation of $[Pt(PP_3)(CN)](CN)$ (5). The complex was obtained as (**5**)$\cdot CHCl_3$. To a solution of $[Pt(PP_3)Cl]Cl\cdot 2H_2O$ (0.1095 g, 0.1169 mmol) in $CHCl_3$ (30 mL) was added a solution of KCN (0.0152 g, 0.2338 mmol) in CH_3OH (15 mL) dropwise, and immediately, the color of the solution turned from yellow to colorless. The mixture was stirred for 12 h, and after that, Et_2O was added to precipitate a white solid, which was filtered off and dried in vacuo. Suitable crystals for X-ray diffraction were obtained from a mixture of $[Pt(PP_3)Cl]Cl\cdot 2H_2O$ and KCN in $CDCl_3/CD_3OD$. Yield: 82%, mp > 300 °C. Found: C, 52.0; H, 4.0; N, 2.6. $C_{45}H_{43}N_2P_4PtCl_3$ requires: C, 52.1; H, 4.2; N, 2.7%. IR ν_{max}/cm^{-1}: (CN) 2122m. MS (FAB): *m*/*z* 891 ($M^+ - CN$, 47.5%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): See Table 1. ^{195}Pt NMR (DMSO-d_6): δ −4768 (brs).

4.8. Preparation of $[Pd(PP_3)(SnCl_3)](SnCl_3)$ (6). The compound was prepared as (**6**)$\cdot CHCl_3$. To a solution of $[Pd(PP_3)Cl]Cl\cdot 4H_2O$ (0.1080 g, 0.1274 mmol) in $CHCl_3$ (25 mL) was added a solution of PPh_3 (0.0241 g, 0.1274 mmol) in $CHCl_3$ (5 mL). After that, a solution of $SnCl_2$ (0.0668 g, 0.2548 mmol) in CH_3OH (15 mL) was added, and the mixture was stirred for 24 h during which an orange precipitate was formed. Et_2O (100 mL) was added to precipitate completely the solid that was filtered off and dried in vacuo. Yield: 81%, mp 212 °C. Found: C, 38.8; H, 3.4. $C_{43}H_{43}P_4Sn_2PdCl_9$ requires: C, 38.3; H, 3.2%. IR ν_{max}/cm^{-1}: $(Sn-Cl)_{as}$ 290m,br, 249m,br; $(Sn-Cl)_{coord}$ 322s. MS (FAB): *m*/*z* 1003 ($M^+ - SnCl_3$, 0.5%); 503 ($M^+ - 2SnCl_3 - C_2H_4PPh_2$, 1.6%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): See Table 1. ^{119}Sn NMR ($CDCl_3$): δ −65.4 (brs). Λ(DMF) = 77.0 ohm^{-1} cm^2 mol^{-1}.

4.9. Preparation of $[Pt(PP_3)(SnCl_3)](SnCl_3)$ (7). Complex **7** was isolated as (**7**)$\cdot CHCl_3$. To a solution of $[Pt(PP_3)Cl]Cl\cdot 2H_2O$ (0.1380 g, 0.1473 mmol) in $CHCl_3$ (35 mL) was added a solution of PPh_3 (0.0386 g, 0.1473 mmol) in $CHCl_3$ (6 mL). After that, a solution of $SnCl_2$ (0.0559 g, 0.2946 mmol) in CH_3OH (8 mL) was added, and the mixture was stirred for 24 h during which a yellow precipitate was formed. Et_2O (90 mL) was added to precipitate completely the solid that was filtered off and dried in vacuo. Suitable crystals for X-ray diffraction were obtained from a $CDCl_3$ solution. Yield: 90%, mp 250 °C. Found: C, 35.4; H, 3.2. $C_{43}H_{43}P_4Sn_2PtCl_9$ requires: C, 35.9; H, 3.0%. IR ν_{max}/cm^{-1}: $(Sn-Cl)_{as}$ 290m,b, 247m,b; $(Sn-Cl)_{coord}$ 323s,b. MS (FAB): *m*/*z* 563 ($M^+ - 2SnCl_3 - C_2H_4PPh_2$, 0.1%). $^{31}P\{^1H\}$ NMR ($CDCl_3$ or $CDCl_3$/DMF = 1/1): See Table 1. ^{119}Sn NMR ($CDCl_3$) = δ −66.6 (brs). Λ(DMF) = 75.0 ohm^{-1} cm^2 mol^{-1}.

4.10. Preparation of $[Pd(PP_3)Cl]_2[SnPh_2Cl_4]$ (8). To a solution of (**1**)$\cdot 4H_2O$ in $CDCl_3$ was added a solution of $SnPh_2Cl_2$ (6 mol equiv) in CD_3OD. Suitable crystals for X-ray diffraction of (**8**)$\cdot 4H_2O$ appeared in the mixture solution after some days. $^{31}P\{^1H\}$ NMR ($CDCl_3/CD_3OD$ = 1/1): See Table 1.

4.11. X-ray Crystallography. Orange prisms of (**2**)$\cdot 6H_2O$, yellow plates of (**5**)$\cdot H_2O$, yellow needles of (**7**)$\cdot CHCl_3$, and red plates of (**8**)$\cdot 4H_2O$ were mounted on glass fibers and used for data collection. Crystals data were collected at 293(2) K, using a Bruker SMART CCD 1000 diffractometer. Crystals of (**5**)$\cdot H_2O$ were of lower quality than those of (**2**)$\cdot 6H_2O$, (**7**)$\cdot CHCl_3$, and (**8**)$\cdot 4H_2O$; this lowered the precision of the crystal structure, which can be taken to establish chemical connectivity. Graphite monochromated Mo Kα radiation was used throughout. The data were processed with SAINT,[36] and empirical absorption correction was made using SADABS.[37] The structures were solved by direct methods using the program SIR92[38] and refined by full-matrix least-squares techniques aginst F^2 using SHELXL-97.[39] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically, and positional parameters were refined using a riding model. Atomic scattering factors were obtained with the use of International Tables for X-ray Crystallography.[40] Molecular graphics were obtained from ORTEP-3 for Windows.[41]

4.12. Hydroformylation Experiments. In a typical experiment, a solution of 0.025 mmol of $[Pt(PP_3)Cl]Cl$ and 0.125 mmol of $SnCl_2$ in 30 mL of toluene containing 0.1 mol of styrene was transferred under argon into a 150 mL stainless steel autoclave. The reaction vessel was pressurized to 100 bar total presure ($CO/H_2 = 1/1$) and placed in an oil bath kept at 100 °C, and the mixture was stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC. The same procedure was used for hydroformylation experiments with $[Pt(PP_3)Cl]Cl/SnCl_2$ in 1/1 ratio and with $[Pt(PP_3)(SnCl_3)](SnCl_3)$.

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Supporting Information Available: A crystallographic information file (CIF), containing structural data for **2**, **5**, **7**, and **8**. Figures S1 and S2 showing the titrations of complexes **1** and **2** with 1 and 2 equiv of $SnCl_2$. Figure S3 showing the $^{31}P\{^1H\}$ NMR spectrum for solutions in $CDCl_3$ + DMF of the solid obtained from the reaction (**2** + 4 equiv $SnCl_2$). This material is avaliable free of charge via the Internet at http://pubs.acs.org.

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