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Dehydrogenative stannane coupling by platinum complexes

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In honor of Professor Pierre Braunstein

Abstract

The complexes $Pt(acac)_2$, $(PhMe_2P)_2PtMe_2$, $(dppe)PtMe_2$ (dppe = bis(diphenylphosphino)ethane), and the $(P\cap N)PtMe_2$ complexes $[(\kappa^2\text{-P,N})\text{–}Ph_2PCH_2CH_2CH_2NMe_2]PtMe_2$ and $[(\kappa^2\text{-P,N})\text{–}Ph_2PCH_2CH_2NMe_2]PtMe_2$ catalyse the formation of distannanes by dehydrogenative coupling of triphenyltin hydride or tri-n-butyltin hydride. While $Pt(acac)_2$ appears to react by a radical mechanism, the bis(stannyl) complexes $(PhMe_2P)_2Pt(SnR_3)_2$ and $(dppe)Pt(SnR_3)_2$ were observed in the reaction of $(PhMe_2P)_2PtMe_2$ and $(dppe)PtMe_2$. At longer reaction periods the complexes $(PhMe_2P)_2Pt(H)SnBu_3$ and $(PhMe_2P)_2Pt(Ph)SnHPh_2$, respectively, were formed. There is evidence that the distannanes are formed by a similar mechanism when $(P\cap N)PtMe_2$ is employed as the catalyst instead of $(R_3P)_2PtMe_2$. However, the presence of the P,N-chelating ligand results in the stabilisation of the intermediate $(P\cap N)Pt(Me)SnR_3$ and in the formation of redistribution products.

Keywords: Platinum complexes; Stannyl complexes; Homogeneous catalysts; Hemilabile ligands

1. Introduction

The reactivity of platinum complexes towards silanes is greatly enhanced when hemilabile chelating P,N ligands are employed as opposed to the more common bis-phosphine complexes [1]. While an interesting variety of catalytic and stoichiometric reactions were found in which silicon–carbon or silicon–oxygen bonds were formed from hydrogenosilanes and chlorosilanes, dehydrogenative silane coupling was conspicuously absent. The formation of Si–Si bonds ($Ph_2Me_4Si_2$) was only observed when $[(\kappa^2\text{-P,N})\text{–}Ph_2PCH_2CH_2NMe_2]PtMe_2$ was reacted with $ClSiMe_2Ph$. The platinum complex acted as the chlorine scavenger in this stoichiometric reaction [2]. In extending our investigations to analogous reactions with organotin hydrides, we hoped to gain more insight into the electronic and energetic parameters that govern the outcome of a particular reaction when hemilabile ligands are used in reactions of Group IV compounds.

The formation of Sn–Sn bonds by dehydrogenative coupling is much more favourable than the formation of Si–Si bonds due to the weaker H–Sn bond (252 kJ mol^{-1}) compared with the H–Si bond (323 kJ mol^{-1}) [3]. Organotin hydrides $HSnR_3$ are known to undergo dehydrogenative dimerization with various types of catalyst, e.g. amines or transition metal catalysts such as $(Ph_3P)_2PdCl_2$ or $Pd(Ph_3P)_4$ [4]. Whether these reactions proceed or not depends strongly on the substituents at the tin atom. Dehydrogenative stannane dimerizations do not normally proceed at ambient temperatures or spontaneously. For example, using AIBN as a catalyst to form Sn_2Ph_6 from $HSnPh_3$ requires temperatures of over 100 °C [5].

It was hoped that a comparison of different platinum complex catalysts would allow some conclusions on how the ligands, especially hemilabile ligands, influence the outcome of the reaction. For this purpose, the reactions of the complexes $Pt(acac)_2$ (acac = acetylacetonate) (**1**), $(PhMe_2P)_2PtMe_2$ (**2**), $(dppe)PtMe_2$ (dppe = bis(diphenylphosphino)ethane) (**3**), and the $(P\cap N)PtMe_2$ complexes $[(\kappa^2\text{-P,N})\text{–}Ph_2PCH_2CH_2CH_2NMe_2]PtMe_2$

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(PC3NPtMe$_2$) (**4**) and [(κ^2-P,N)–Ph$_2$PCH$_2$CH$_2$NMe$_2$]-PtMe$_2$ (PC2NPtMe$_2$) (**5**), with triphenyltin hydride (HSnPh$_3$) and tri-n-butyltin hydride (HSn^{n}Bu$_3$) were investigated.

2. Results and discussion

When the stannanes were added to any of the three platinum complexes, strong gas evolution occurred in all cases, and the corresponding distannane, R$_3$Sn–SnR$_3$, was formed as the main product. The reactions were monitored by ^{1}H, ^{31}P{^{1}H} and ^{119}Sn NMR spectroscopy and distinct differences were observed.

2.1. Reaction with Pt(acac)$_2$ (*1*)

On addition of a stoichiometric amount, or a 20- or 100-fold excess of HSnPh$_3$ to a benzene solution of **1**, crystals of the distannane Ph$_3$Sn–SnPh$_3$ were formed within 5 min. When a ratio of 1:20 was employed, about 85% of the stannane was converted to distannane during this 5 min period (integration of ^{1}H NMR spectra). In the case of larger excesses, i.e. 1:100, the same products were identified, but only roughly 20% conversion to distannane was observed within 24 h at room temperature, determined from NMR spectra. Even after heating at 60 °C for 3 h conversion to distannane was only about 30%. The starting tin hydride and Sn$_2$Ph$_6$ were the only tin species identified throughout the course of the reaction by NMR spectroscopy. In addition, ^{195}Pt{^{1}H} NMR spectra only showed the presence of **1**, and there appeared to be no change of the acetylacetonate coordination since no spectroscopic indication of de-coordinated acetylacetone or η^1-coordinate acetylacetonate ligands was found. This indicates that the distannane is formed via a radical mechanism.

Analogous results were obtained when HSnBu$_3$ was used as the reagent stannane except for reaction being much faster. In the reaction of either stannane there was no evidence of elemental platinum.

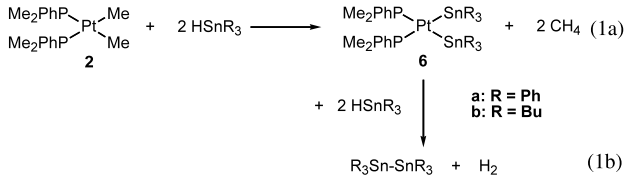
Experiments were also carried out in a similar manner to those described but the two different tin hydrides, HSnPh$_3$ and HSnBu$_3$, were added simultaneously in equal amounts to **1** in a benzene solution. The total platinum complex to tin hydride ratio was 1:40. The main product were the homogeneous distannanes, i.e. Sn$_2$Ph$_6$ and Sn$_2$Bu$_6$, although some asymmetric distannanes were observed in addition to the original tin hydrides. The preferred formation of the symmetrical distannanes may be due to the different reactivity of both stananes in radical reactions. No evidence was found to suggest some sort of equilibrium between asymmetrical distannanes and the, evidently favoured, symmetrical distannanes. Complete consumption of the reactant stannanes was not achieved after 3 days at room temperature.

2.2. Reaction with (PhMe$_2$P)$_2$PtMe$_2$ (*2*)

On reaction of **2** with HSnPh$_3$ or HSnBu$_3$ there was complete consumption of the reagent stannane within 24 h at **2**:HSnR$_3$ ratios of 1:1–1:5 and 1:20. Analogous complexes and tin species were observed with both tin hydrides used, though rates of conversion to distannane did alter.

^{31}P NMR spectra taken in the initial stages of the reactions with either stannane showed the immediate partial loss of the starting platinum complex and formation of a new platinum complex, with satellites from platinum and tin [6]. The phosphorus atoms of this platinum complex in addition to be equivalent, exhibit a typical *cis*-^1J(PPt) coupling of 2443 Hz [7]. Both also show *cis*- and a weak *trans*-PPtSn coupling, hence it must be the bis(stannyl) complex, *cis*-(PhMe$_2$P)$_2$Pt-(SnR$_3$)$_2$ (**6a**: R = Ph, **6b**: R = ^{n}Bu). In the case of HSnPh$_3$ when ratios of 1:2 or greater were used, the methyl/stannyl exchange at platinum occurs to an extent of approximately 90% at room temperature within 60 min. When HSnBu$_3$ was employed, **6b** was only identified in traces within this time period, the reasoning for this will be discussed later. The mono-substituted complex, (PhMe$_2$P)$_2$Pt(Me)SnR$_3$ was not observed in either case, it must therefore, be assumed that exchange of the second methyl group proceeds faster then that of the first.

At this point with HSnPh$_3$, i.e., the first 60 min of the reaction at room temperature, a maximum of three tin species were present (HSnR$_3$, Sn$_2$R$_6$ and **6a**). At 1:1 ratios only **6a** was observed, once the 1:2 ratio had been reached, distannane was also present. In the case of larger excesses, reactant stannane was still observed in the ^{119}Sn and ^{1}H NMR spectra. No evidence was found for the formation of MeSnPh$_3$, thus indicating that the methyl groups are eliminated as methane (see below).

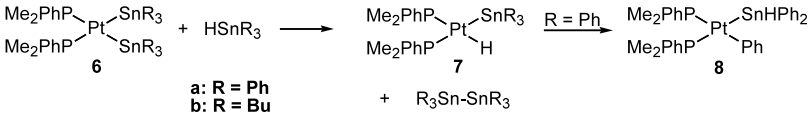


With HSnBu$_3$ at ratios of 1:1, Sn$_2$Bu$_6$ is the only tin species observed, while **2** is still present. At higher ratios complex **6b** was observed. With longer reaction times and ratios 1:2, traces of MeSnBu$_3$ were observed. This would imply that catalytic distannane formation must occur already at this ratio (1:1). This could be dependent on the stannane used HSnBu$_3$ which has a weaker H–Sn bond than HSnPh$_3$, and thus could facilitate the formation of the distannane.

The reaction of **2** with $HSnR_3$ obviously proceeds in two steps; the bis(stannyl) complexes **6** are formed first, which then produce Sn_2R_6 in a catalytic reaction. The difference in reactivity between $HSnPh_3$ and $HSnBu_3$ implies that for R = Bu the distannane formation is faster than the formation of **6**, for R = Ph the opposite is true.

At periods >90 min, complexes **6a** and **6b** in turn began to disappear, and a new complex **7b** was formed from **6b**, and a new complex **8** from **6a**. This can be followed well in ^{31}P NMR where the proportion of **6** decreases with formation of the new complexes **7b** or **8**. In the ^{119}Sn NMR spectrum a new peak can be assigned to the new complexes. A consumption of the complex **6** was observed with both stannanes and at all ratios, but to different extents. When an 1:20 ratio was employed, transformation of **6** to **7b** or **8** was complete after 24 h, this coincides with the disappearance of the first new platinum complex **6**. With a lower stoichiometric ratio, approximately 35% of **6** was consumed within 24 h.

One can imagine that complex **7** is formed through addition of a $HSnR_3$ group to complex **6**, and then loss of distannane, $R_3Sn–SnR_3$, occurs leaving **7**. In the case of $HSnBu_3$ this complex **7b** could be stable given work carried out on analogous silicon complexes [8]. It could be imagined that with aromatic substituents at tin (**7a**), a rearranged complex of structure **8** would be more stable due to the higher migration tendency of phenyl groups, and to the more stable *trans* influence achieved through the phenyl ligand compared with an alkyl group. Given that complex **8** is the more stable form for R = Ph and that rearrangement occurs quickly, this would explain the absence of spectroscopic evidence of **7a** in both ^{31}P NMR and ^{1}H NMR spectra.

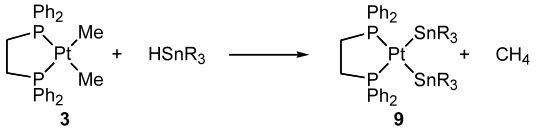


(2)

The formation of complex **7** has been explained by further addition of $HSnR_3$, however in the lower ratios NMR spectra imply the complete consumption of the reactant stannane which poses a problem for its formation. It could be that dissolved hydrogen is still present in solution but is not spectroscopically visible.

2.3. Reaction with (dppe)$PtMe_2$ (3)

If the reactions of **2** proceed via intermediates in which a phosphine ligands is de-coordinated, the presence of a chelate ligand would influence the outcome of the reaction. Therefore, the reactions of the bis-phosphine complex (dppe)$PtMe_2$ (**3**) was also tested. The reactivity of complex **3** may also serve as a reference for that of (P∩N)$PtMe_2$ complexes discussed below. Within the first 10 min of the reaction, the reactant platinum complex disappeared, and a new platinum complex was formed. In accordance with what was observed with **2**, the corresponding complexes **9** (**9a**: R = Ph, **9b**: R = ^{n}Bu) were formed.



(3)

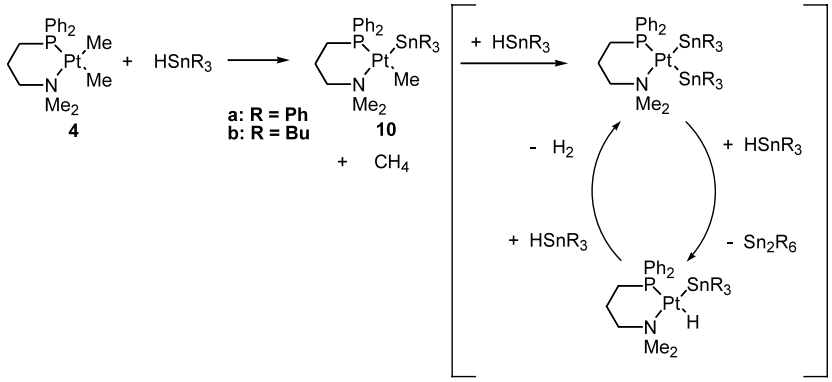
This complex is well supported with NMR data. In the ^{1}H NMR spectrum, the methyl groups are no longer present, for both $HSnBu_3$ and $HSnPh_3$ as reactant stannane. In the ^{31}P NMR spectrum, the characteristic coupling between the tin atom and phosphorus is seen, and this with tin atoms in both the *cis* and *trans* position to phosphorus [6].

Reaction of **3** with the stannanes is slower than for **2**. Conversion to the corresponding distannane with complex **3** in ratios of 1:20 after 3 h at room temperature was only about 7 and 15% for $HSnBu_3$ and $HSnPh_3$, respectively, compared with 90% for **2** with $HSnBu_3$ and at least 23% for $HSnPh_3$. Apart from this platinum complex no further ^{31}P NMR signals, and hence platinum complexes were identified. Reactions at different ratios or with either of the stannanes showed no great difference in reactivity, or further products formed.

2.4. Reaction with (P∩N)$PtMe_2$ (4)

In contrast to reactions of **2** with $HSnBu_3$ and $HSnPh_3$, where both stannanes resulted in analogous reactions and products, the outcome of the reaction of (PC3N)$PtMe_2$ (**4**) depended slightly on the kind of employed stannane.

When the reaction between **4** and $HSnBu_3$ was carried out in a stoichiometric ratio (1:1), the tin hydride had completely reacted within the first 5 min (as monitored by ^{1}H NMR spectroscopy). Gas evolution was observed



Scheme 1.

on addition of the stannane, which must be methane, considering the absence of other by-products. The only tin species identified by ^{119}Sn NMR spectroscopy were distannane, $MeBuSn_3$ and a platinum stannyl complex, **10b**.

As soon as an 1:1 ratio was exceeded, complex **10b** was the major platinum species present and could be identified immediately. This new platinum complex **10b**, and the reactant complex **4** were also identified by ^{195}Pt NMR spectroscopy which at this point (at 1:1 ratios, after 2 h) gave no suggestion of further platinum species.

Complex **10b** may be on the route to the formation of the distannane. From the reactions of **4** with $HSiR_3$ it is known that the second methyl ligand is exchanged much slower than the first [1], due to the different *trans* influence of the coordinated nitrogen and phosphorus atoms. It is reasonable to assume that the same is true for the Me/SnR_3 exchange. The fact that only **10b** and Sn_2R_6 are observed in the reaction mixture implies that the intermediate bis(stannyl) complex leads to fast formation of distannane. It is suggested that the reaction mechanism is along the lines of Scheme 1, where the first step is slow (initial addition of $HSnR_3$, and loss of CH_4), and the next step, and generation of Sn_2R_6 (further addition of $HSnR_3$ and loss of H_2 as shown in the brackets) is much faster. Given that the reaction is catalytic, the platinum complexes shown within the brackets would only be present in very small amounts for production of distannane, and given the timescale, not spectroscopically visible.

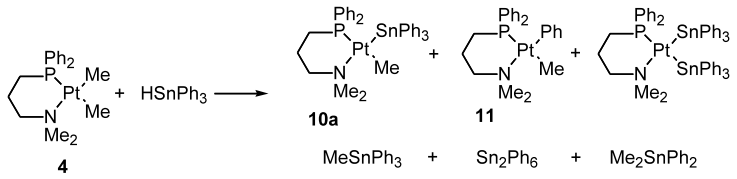
The remaining methyl group on platinum *trans* to phosphorus can be tentatively assigned in the ^{1}H NMR spectrum at stoichiometric ratios. In order confirm that, experiments were undertaken with CD_3 groups on the platinum complex instead of CH_3 groups. In this case the PC2N complex **5** instead of the PC3N complex **4** was used. Initial control experiments were carried out with the CH_3 platinum complex. The results were analogous to those found for complex **4**. The reactions of (PC2N)Pt$(CD_3)_2$ with $HSnBu_3$ and with $HSnPh_3$ were carried out at stoichiometric ratios and was monitored by ^{2}H NMR spectroscopy. Here the platinum bonded methyl groups of the reactant platinum complex were easily identified. During the course of the reaction a new CD_3 group was identified, this could be assigned to the remaining *trans*-methyl group at the platinum centre.

When the reaction between **4** and *HSnPh₃* was carried out in a stoichiometric ratio (1:1), the tin hydride also reacted completely within the first 5 min (as monitored by ^{1}H NMR spectroscopy), but in this case Sn_2Ph_6 and $MeSnPh_3$ were identified by ^{119}Sn NMR spectroscopy. The occurrence of $MeSnPh_3$ indicates a similar mechanism as in the reaction of (P∩N)$PtMe_2$ with H*Si*R_3 leading to mono- and bis-(silyl) complexes, (P∩N)Pt(SiR_3)Me and (P∩N)Pt$(SiR_3)_2$. In this reaction, one methyl ligand was eliminated as methane and the second as methylsilane [9]. At ratios from 1:1 to 1:4 no reactant stannane was observed after 5 min. At stoichiometric ratios with $HSnPh_3$, no new platinum complexes were initially identified. However, after a period of 2 h, a new platinum complex was observed, present in approximately the same ratio as the still present **4**. This new complex was also identified as the mono-substituted platinum complex **10a**.

When $HSnPh_3$ was reacted in larger than stoichiometric ratios, further tin and platinum species were observed. The main tin-containing product was still the expected distannane, however three new platinum complexes were observed by ^{31}P NMR spectroscopy. Among them is obviously **10a**. Another complex is almost certainly the phenyl substituted platinum complex **11**, and the final complex may be the bis(stannyl) complex.

In addition to these platinum complexes, several other tin compounds, such as $MeSnPh_3$, Me_2SnPh_2 and Me_3SnPh were observed with NMR spectroscopy.

This phenomena was tested in separate experiments, where **4** was reacted with $MeSnPh_3$ and $SnPh_4$ at room temperature and then at 60 °C. The same individual tetraalkylstannanes were observed as seen in the reaction of **4** with $HSnPh_3$. Here again complex **11** was also observed in the ^{31}P NMR spectrum, this was the same



(4)

platinum complex, which was seen in the reaction with $HSnPh_3$. No further platinum complexes were identified. When this same reaction was carried out with **1** or **2** no reaction was observed.

The reaction with the deuterated platinum complex **5** and $HSnPh_3$ further supports these findings. Here deuterated **10a** was seen, and further CD_3-substituted organotin species were identified.

The compounds Me_xSnPh_{4-x} are obviously formed by oxidative addition of Sn–Ph groups (Sn–Ph groups are easier added than Sn–Me groups [10]) followed by further redistribution reactions at the platinum centre.

2.5. Comparison of the platinum complexes

By examining the ^{31}P NMR spectra of the reaction mixtures with phosphorus-containing platinum complexes it is possible to compare qualitatively the relative reactivity of these complexes. The most obvious point is that on reaction with $HSnPh_3$ the $(P\cap N)PtMe_2$ complexes (**4** and **5**) immediately produce the corresponding distannane from ratios of 1:1, while in the reactions of the bis-phosphine complexes (**2** and **3**) the corresponding bis(stannyl) complexes (**6** and **9**) are first observed before distannane builds up. When comparing an 1:20 ratio 5 min into the reaction, in the case of **4** an approximately 50% conversion to distannane is observed compared only with 5% with **2**. These figures are only rough guides, especially in the case of Sn_2Ph_6, which is poorly soluble in benzene. However, the trend is clear that the $(P\cap N)PtMe_2$ complex **4** appears more effective at producing distannane. Complex **3** is even less efficient, where after 60 min at room temperature only 15% conversion has been observed. This would indicate, in comparison with **2**, that that some flexibility in the platinum complex could be necessary for the addition of the $HSnPh_3$/loss of Sn_2Ph_6.

It is also interesting to note that the complexes **2**–**5** do not react in the same manner as **1**. It still seems preferable for all Pt–Me complexes to react with the incoming $HSnR_3$ by oxidative addition rather than induce a radical type reaction.

The reaction with $HSnBu_3$ to form distannanes appears to be more favourable (probably due to reasons discussed previously), though in both cases a platinum–tin moiety is observed at some point during the reaction. Even with this stannane a slight improvement is seen with the $(P\cap N)PtMe_2$ complex. At a 1:20 ratio, after 60 min at room temperature, reaction of **4** results in approximately 97% of tin moieties as distannane (the rest being Pt–Sn) compared with 90% with complex **2**. Complex **3** produces exactly analogous results as with $HSnPh_3$, though conversion to distannane is lower, 3% at 60 min.

3. Conclusions

The first observation when looking at the different reactions is that $HSnBu_3$ has a higher affinity to form the distannane in the metal-catalysed reactions. This can be seen throughout the course of the reactions, even in the case of **1**, which is considered to react via a different reaction pathway.

Although the corresponding distannane is the main or only tin-containing product in each case the results indicate that the platinum complexes $Pt(acac)_2$, $(P\cap N)PtMe_2$ and $(R_3P)_2PtMe_2$ react by different reaction pathways with $HSnPh_3$ and $HSnBu_3$. $Pt(acac)_2$ clearly seems to react via a radical mechanism, which does not appear to be the case with the other platinum complexes. These obviously react by oxidative addition/reductive elimination mechanisms, that involves exchange of the methyl ligands for stannyl groups. There is strong evidence that bis(stannyl) complexes are involved in the formation of the distannanes.

The results also show again the differences between the bis-phosphine (**2** and **3**) and the P,N-chelated complexes (**4** and **5**). In the latter complexes, the differently activated methyl ligands result in different exchange rates. With the $(P\cap N)PtMe_2$ complexes, initially at least, only the methyl group *trans* to nitrogen is exchanged as a result of the weaker Pt–C bond *trans* to nitrogen. This is similar to the phenenoma seen with the reaction of $(P\cap N)PtMe_2$ complexes with the silicon analogues, where single substitution is always seen [1]. Furthermore, the effect of the hemilable chelating ligand leads to several by-products, which originate from the activation of Sn–C bonds, at least in the case of $HSnPh_3$. Such rearrangement reactions were not observed with the bis(phosphine) complexes **2** and **3**, or with **1**.

4. Experimental

All reactions were carried out using standard Schlenk techniques in an argon atmosphere. Argon was purified using Cu and molecular sieve (4 Å). All NMR measurements were carried out in deuterated benzene (C_6D_6), the samples were filled and sealed in an argon atmosphere. Benzene-d_6 was pre-dried using a molecular sieve (4 Å) and then made oxygen-free using the freeze–pump–thaw method.

The tin hydrides used were either purchased from Sigma Aldrich and in the case of $HSnPh_3$ also prepared from the corresponding chlorostannane using $LiAlH_4$. Purity was controlled using ^1H and ^{119}Sn NMR spectra. The platinum complexes were prepared as reported in the literature [11,9], the bis-phosphine complexes were prepared as stated the literature except the platinum reagent used was $nbdPtCl_2$ (prepared as in Ref. [12]). LiMe was used as methylating agent and diethyl-ether as the solvent. $Pt(acac)_2$ was purchased from Sigma Aldrich and then made oxygen-free.

NMR experiments were taken on Bruker Avance 300 and 250 MHz spectrometers at room temperature (r.t.), unless otherwise stated, using external standard (TMS, 85% H_3PO_4; Me_4Sn and $Na_2Pt(H_2O)_6$, respectively). All pulse programs used were obtained from the standard Bruker software library. Assignment of ^{119}Sn NMR signals was also based on HSn-HMQC experiments. ^{31}P, ^{195}Pt and ^{13}C NMR spectra were proton decoupled, 1D ^{119}Sn NMR spectra were obtained using the inversed gated technique. ^2H NMR experiments were carried out using a standard ZG30 PULSE program without lock.

4.1. General reaction procedure

The platinum complex was weighed into the NMR tube (Schlenk tube) under argon and then dissolved/suspended in C_6D_6. The stannane was then added at r.t., as quickly as possible via a syringe. At catalytic ratios, the pure, undiluted stannane was added to the platinum complex. At stoichiometric ratios, the stannane was diluted with C_6D_6 and then added to the platinum complex. The reaction was allowed to subside and then immediately NMR spectra were taken. The reaction was then followed by spectra taken at regular intervals.

All NMR signals seen throughout the course of the reaction are given here, including those which are only seen at certain ratios or specific reaction times, e.g. in some cases the reagent peaks are only seen in the stoichiometric reaction mixtures or at the beginning of a reaction. Further specific information is given in the main text. The majority of peaks are seen throughout the course of the reaction, and only the intensity of a few specific signals alter. For these reasons chemical shifts are given without integration as this varies throughout the course of the reaction—see text for noteworthy integration comparisons.

4.2. Reaction of $Pt(acac)_2$ (**1**) with $HSnPh_3$

A) $HSnPh_3$ (8.9 mg, 0.025 mmol) was added at r.t. to 10 mg (0.025 mmol) of **1** in 0.5 ml of C_6D_6. Light gas evolution was observed.

B) $HSnPh_3$ (178 mg, 0.51 mmol) was added at r.t. to 10 mg (0.025 mmol) of **1** in 0.5 ml of C_6D_6. Very strong gas evolution was observed, and a yellow solution was present. Distannane crystals began to form after 15 min. They were collected and dried. Their identity as $Ph_3SnSnPh_3$ was achieved through XRD power diffraction in comparison with an authentic sample. Crystal yield 149 mg (0.213 mmol, 84%).

C) $HSnPh_3$ (133 mg, 0.38 mmol) was added at r.t. to 1.5 mg (0.004 mmol) of **1** in 0.5 ml of C_6D_6. The sample turned yellow. Crystals of $Ph_3SnSnPh_3$ were formed from the reaction solution within 24 h. Crystal yield approximately 111 mg (0.088 mmol, 46%).

^1H NMR: δ (ppm) 1.59 (s, with satellites $^4J(PtOCCH) = 128$ Hz, $Pt(OCCH_3)$), 5.09 (s with satellites, $^4J(PtOCCH) = 159$ Hz, $Pt(OCCHCO)$), 7.01 (s with satellites, $^1J(^{117}SnH) = 1849$ Hz, $^1J(^{119}SnH) = 1934$ Hz, *H*Sn), 7.19–7.76 (m, *H*–PhSn); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −163.2 (s, $HSnPh_3$), −141.6 (s, $Ph_3SnSnPh_3$); $^{13}C\{^1H\}$ NMR: δ (ppm) 25.21 (s, $Pt(OCCH_3)$), 102.85 (s, $Pt(OCCHCO)$), 129.14 (s with satellites, unresolved, $C_{ar}SnH$), 129.33 (s with satellites, unresolved, $(C_{ar}Sn)_2$), 137.83 (s with sats), $^1J(CC) = 5$ Hz, $C_{ar}SnH$), 138.02 (t, $^1J(CC) = 4$ Hz, $(C_{ar}Sn)_2$), 185.47 (s, $Pt(OCCH_3)$); $^{195}Pt\{^1H\}$ NMR: δ (ppm) −400.3 (s, $Pt(acac)_2$).

4.3. Reaction of $Pt(acac)_2$ (**1**) with $HSnBu_3$

A) $HSnBu_3$ (5.9 mg, 0.020 mmol) was added at r.t. to 8 mg (0.020 mmol) of **1** in 0.5 ml of C_6D_6. After 90 min at r.t., in which time NMR spectra were taken in regular intervals, another equivalent of $HSnBu_3$ (5.9 mg, 0.020 mmol) and the process repeated (ca. 90min). A further equivalent was then added, and the process repeated again until a ratio of 1:5 was achieved.

B) $HSnBu_3$ (148 mg, 0.5 mmol) was added at r.t. to 10 mg (0.025 mmol) of **1** in 0.5 ml of C_6D_6. On addition of the stannane, hefty gas evolution was observed, and a colouring of the solution to yellow. After 75 min at r.t., another 20 equiv. of $HSnBu_3$ (148 mg, 0.5 mmol) was added, more gas evolution was observed and the spectrum remained unchanged except for the corresponding integrals in ^1H NMR.

^{1}H NMR: δ (ppm) 1.07 (t, ^3J(HCCH) = 7.3 Hz, *H*–Bu), 1.20–1.32 (t(1.23)+m, ^3J(HCCH) = 7.2 Hz, *H*–Bu), 1.51 (sxt, ^3J(HCCH) = 7.5 Hz, *H*–Bu), 1.58 (s, Pt(OCCH_3)), 1.75 (quin+m, ^3J(HCCH) = 8.1 Hz, *H*–Bu), 5.09 (s, Pt(OCC*H*CO)); ^{119}Sn{^{1}H} NMR: δ (ppm) −83.48 (s with satellites, ^1J(SnH) = 2492 Hz, Sn–Sn); ^{13}C{^{1}H} NMR: δ (ppm) 10.44 (s with satellites, ^1J(CC) = 40 Hz, ^1J(C^{117}Sn) = 230 Hz ^1J(C^{119}Sn) = 240 Hz, C_{Bu}–Sn), 13.70 (s with satellites, ^2J(CC$^{117/119}$Sn) = , C_{Bu}–Sn), 24.75 (s, Pt(OC*C*H$_3$)), 27.66 (s with satellites, ^1J(CC) = 54 Hz, C_{Bu}–Sn), 39.90 (t, ^1J(C$^{117/119}$Sn) = 8.2 Hz, C_{Bu}–Sn), 102.30 (s, Pt(OC*C*HCO)), 184.86 (s, Pt(O*C*CH$_3$)); ^{195}Pt{^{1}H} NMR: δ (ppm) −400.3 (s, Pt(acac)$_2$).

4.4. Reaction of Pt(acac)$_2$ (1) with HSnBu$_3$ and HSnPh$_3$

Seven hundred and thirty nine milligram (2.54 mmol) of HSnBu$_3$ and 892 mg (2.54 mmol) of HSnPh$_3$ were added at r.t. to 5 mg (0.013 mmol) of **1** in 0.5 ml of C_6D_6. On addition of the stannane a slight colouring of the solution to yellow was observed. NMR spectra were recorded.

After being left a RT for 5d crystals were formed, whose identity was confirmed to be Sn_2Ph_6 through a powder XRD analysis.

^{119}Sn{^{1}H} NMR: δ (ppm) −68.4 (s, *Sn*Bu/Ph) −84.5 (s, *Sn*–*Sn*, Sn_2Bu_6), −89.2(s, with satellites, *Sn*–H, HSnBu$_3$), −129.8 (s, *Sn*Bu/Ph), −148.3 (s, Ph$_3$*Sn*Sn-Ph$_3$), −163.0 (s, with satellites, *Sn*–H, HSnPh$_3$).

4.5. Reaction of (PhMe$_2$P)$_2$PtMe$_2$ (2) with HSnPh$_3$

A) Seven milligram (0.0199 mmol) of HSnPh$_3$ was added at r.t. to 10 mg (0.0199 mmol) of **2** in 0.5 ml of C_6D_6. After 90 min at r.t., in which time NMR spectra were taken, another equivalent of HSnBu$_3$ (7.0 mg, 0.0199 mmol) and the process repeated (ca. 90min). A further equivalent was then added, and the process repeated again until a ratio of 1:5 was achieved.

B) One hundred and forty milligram (0.4 mmol) of HSnPh$_3$ was added at r.t. to 10 mg (0.0199 mmol) of **2** in 0.5 ml of C_6D_6. After being left a RT for 7d crystals were formed, whose identity was confirmed to be Sn_2Ph_3 through a powder XRD analysis.

^{1}H NMR: δ (ppm) 0.9–1.0 (m, *H*–MePt), 1.68 (t with satellites, ^2J(HCP) = 2.84 Hz, ^3J(HCPPt) = 34 Hz, *H*–MeP), 7.01 (s with satellites, ^1J(^{117}SnH) = 1849 Hz, ^1J(^{119}SnH) = 1934 Hz, *H*Sn), 7.08–7.10 (m, *H*–PhP), 7.46–7.59 (m, *H*–PhP); ^{31}P{^{1}H} NMR: δ (ppm) −9.81(s, with satellites, ^1J(PtP) = 2660 Hz, (PhMe$_2$P)$_2$Pt(SnPh$_3$)$_2$ (**6a**), −10.03 (s, with satellites, ^1J(PtP) = 1821 Hz, (PhMe$_2$P)$_2$PtMe$_2$ (**2**), −12.89 (s with satellites, ^1J(PtP) = 2443 Hz, ^2J(SnPtP) = 184 Hz, (PhMe$_2$P)$_2$Pt(SnPh$_3$)$_2$ (**6a**), −55.66 (s with satellites, ^1J(PtP) = 1796 Hz, *cis*-P–PtSn, (**6a**), −56.71 (s with satellites, ^1J(PtP) = 1981 Hz, *tr*-P–PtSn, (**6a**); ^{119}Sn{^{1}H} NMR: δ (ppm) −9.46 (s, Pt–Sn, **6a**), −141.5 (s, Sn–Sn), −229.9 (s, HPh*Sn*–Pt, **8a**); ^{195}Pt{^{1}H} NMR: δ (ppm) −4586.4 (t, ^1J(PPt) = 1819 Hz, **2**), −4971.2 (t, ^1J(PPt) = 2662 Hz, *tr*-(PhMe$_2$P)$_2$-Pt(SnPh$_3$)$_2$), −5340.8 (t, ^1J(PPt) = 2442 Hz, **6a**)

4.6. Reaction of (PhMe$_2$P)$_2$PtMe$_2$ (2) with HSnBu$_3$

A) HSnBu$_3$ (5.8 mg, 0.0199 mmol) was added at r.t. to 10 mg (0.0199 mmol) of **2** in 0.5 ml of C_6D_6. After 90 min at r.t., in which time NMR spectra were taken, another equivalent of HSnBu$_3$ (5.8 mg, 0.0199 mmol) and the process repeated, (ca. 90 min). A further equivalent was then added, and the process repeated again until a ratio of 1:5 was achieved.

B) Fifty eight milligram (0.199 mmol) of HSnBu$_3$ was added at r.t. to 5 mg (0.0099 mmol) of **2** in 0.5 ml of C_6D_6.

^{1}H NMR: δ (ppm) 0.94–1.01 (m, *H*–Bu), 1.05–1.11 (m, *H*–Bu, *H*–MePt), 1.09 (t, ^3J(HCCH) = 7.3 Hz, *H*–Bu), 1.25–1.38 (m, *H*–Bu, *H*–MePt), 1.49–1.59 (m, *H*–Bu, *H*–MePt), 1.52 (sxt, ^3J(HCCH) = 7.7 Hz, *H*–Bu), 1.74–1.85 (m, *H*–Bu), 5.08 (quin with satellites, ^2J(HSnC) = 1.9 Hz, ^1J(H^{117}Sn) = 1517 Hz, ^1J(H^{119}Sn) = 1590 Hz, *H*–Sn), 7.08–7.10 (m, *H*–PhP), 7.46–7.59 (m, *H*–PhP); ^{31}P{^{1}H} NMR: δ (ppm) −10.03 (s, with satellites, ^1J(PtP) = 1821 Hz, **2**), −6.7 (s with satellites, ^1J(PtP) = 2816 Hz, **6b**), −44.04 (s, **7b**); ^{119}Sn{^{1}H} NMR: δ (ppm) −84.1 (s, Sn–Sn), −6.4 (s, MeSnBu$_3$), −12.3 (s, Pt–Sn).

4.7. Reaction of (dppe)PtMe$_2$ (3) with HSnPh$_3$

Fifty six milligram (0.16 mmol) of HSnPh$_3$ was added at r.t. to 5 mg (0.008 mmol) of **3** in 0.5 ml of C_6D_6.

^{1}H NMR: δ (ppm) 1.72–1.85 (m, ^3J(HCP) = 9.5 Hz, C_2H_4) 7.02 (s with satellites, ^1J(^{117}SnH) = 1849 Hz, ^1J(^{119}SnH) = 1934 Hz, *H*–Sn), 7.02–7.08 (m, *H*–PhP), 7.51–7.80 (m, *H*–PhP/*H*–PhSn); ^{31}P{^{1}H} NMR: δ (ppm) 58.63 (s, with satellites, ^1J(PtP) = 2263 Hz, ^2J(*tr*-^{117}SnPtP) = 1577 Hz, ^2J(*tr*-^{119}SnPtP) = 1598 Hz, ^2J(*cis*-^{117}SnPtP) = 119 Hz, ^2J(*cis*-^{119}SnPtP) = 144 Hz, **9a**); ^{119}Sn{^{1}H} NMR: δ (ppm) −46.1 (s, Sn–Pt, **9a**), −141.6 (s, Sn–Sn), −163.2(s, *Sn*–H, HSnPh$_3$).

4.8. Reaction of (dppe)PtMe$_2$ (3) with HSnBu$_3$

A) HSnBu$_3$ (4.7 mg, 0.016 mmol) was added at r.t. to 10 mg (0.016 mmol) of **3** in 0.5 ml of C_6D_6. After 90 min at r.t., in which time NMR spectra were taken,

another equivalent of $HSnBu_3$ (4.7 mg, 0.016 mmol) and the process repeated (ca. 90 min). A further equivalent was then added, and the process repeated again until a ratio of 1:4 was achieved.

B) $HSnBu_3$ (46.7 mg, 0.16 mmol) was added at r.t. to 5 mg (0.008 mmol) of **3** in 0.5 ml C_6D_6.

^1H NMR: δ (ppm) 0.9–1.6 (m, *H*–Bu, H–MePt), 1.40–1.55 (m, *H*–Bu), 1.61–1.76 (m, *H*–Bu/*H*–MePt), 1.91–2.02 (m, $^3J(HCCP) = 8.2$ Hz, C_2H_4), 5.18 (quin with satellites, $^2J(HSnC) = 1.9$ Hz, $^1J(H^{117}Sn) = 1517$ Hz, $^1J(H^{119}Sn) = 1590$ Hz, *H*–Sn), 7.13 (m, *H*–PhP), 7.77 (t, $^1J(HC) = 6.8$ Hz, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 48.11 (s, with satellites, $^1J(PtP) = 1778$ Hz, **3**), 56.62 (s, with satellites, $^1J(PtP) = 2124$ Hz, **9b**); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −14.5 (s, Sn–Pt, **9b**), −84.5 (s, Sn–Sn), −89.2(s, *Sn*–H, $HSnBu_3$).

4.9. Reaction of (PC3N)$PtMe_2$ (4) with $HSnBu_3$

A) $HSnBu_3$ (5.86 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **4** in 0.5 ml of C_6D_6. After 90 min at r.t., in which time NMR spectra were taken, another equivalent of $HSnBu_3$ (7.1 mg, 0.02 mmol) and the process repeated (ca. 90 min). A further equivalent was then added, and the process repeated again until a ratio of 1:5 was achieved.

B) Fifty eight-milligram (0.2 mmol) of $HSnBu_3$ was added at r.t. to 5 mg (0.01 mmol) of **4** in 0.5 ml of C_6D_6. On addition of the stannane, very strong gas evolution was observed.

^1H NMR: δ (ppm) 0.95–1.14 (m, *H*–Bu), 1.22–1.32 (m, *H*–Bu), 1.40–1.86 (m, *H*–Bu), 1.99–2.33(m, PC_3H_6N), 2.43 (s with satellites, $^3J(PtNCH) = 18$ Hz N–(CH_3)$_2$), 5.08 (quin with satellites, $^2J(HSnC) = 1.9$ Hz, $^1J(H^{117}Sn) = 1517$ Hz, $^1J(H^{119}Sn) = 1590$ Hz, *H*–Sn), 6.99–7.55 (m, *H*–PhP), 7.75–7.94 (tt, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 15.27 (s, with satellites, $^1J(PtP) = 2088$ Hz, **4**), 16.97 (s with satellites, $^1J(PtP) = 2158$ Hz, **10b**); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −84.04 (s, Sn–Sn), −6.57 (s, $MeSnBu_3$), −12.6 (s, Pt–Sn, **10b**); $^{13}C\{^1H\}$ NMR: δ (ppm) 9.25 (s, C_{Me}–Pt), 9.89 (s, C_{Me}–Pt), 10.61 (s, C_{Bu}–Sn), 14.12 (s, C_{Bu}–Sn), 25.32 (s, C_{Me}–Pt), 27.92 (d, $^1J(PC) = 13$ Hz, PC_3H_6N), 28.09 (s with satellites, $^1J(SnC) = 58$ Hz, C_{Bu}–Sn), 29.83 (d, $^1J(PC) = 12$ Hz, PC_3H_6N), 31.34 (s, C_{Bu}–Sn), 45.31 (s, NCH_3), 126.17 (s, C_{ar}–P), 131.33 (s, C_{ar}–P); $^{195}Pt\{^1H\}$ NMR: δ (ppm) −4051 (d, $^1J(PPt) = 1032$ Hz, **4**).

4.10. Reaction of (PC2N)$PtMe_2$ (5) with $HSnBu_3$

Eleven milligram (0.039 mmol) of $HSnBu_3$ was added at r.t. to 9.5 mg (0.020 mmol) of **5** in 0.5 ml of C_6D_6. Light gas evolution and a colour change to pink–brown was observed.

^1H NMR: δ (ppm) 1.09 (t, $^3J(HCCH) = 7.4$ Hz, *H*–Bu), 1.25–1.33 (m, *H*–MePt/*H*–BuSn), 1.54 (sxt, $^3J(HCCH) = 7.2$ Hz, *H*–Bu), 1.78 (sxt, $^3J(HCCH) = 7.5$ Hz, *H*–Bu), 1.8–2.2 (m, PC_2H_4N), 2.36 (s with satellites, $^3J(PtNCH) = 17.9$ Hz, N–(CH_3)$_2$), 7.09–7.21 (m, *H*–PhP), 7.80–7.85 (m, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 36.33 (s, with satellites, $^1J(PtP) = 2072$ Hz, *P*C2NPtMe$_2$ (**5**); ^{119}Sn NMR: δ (ppm) −84.04 (s, *Sn*–*Sn*), −6.9 (s, *Sn*–Pt); $^{195}Pt\{^1H\}$ NMR: δ (ppm) −4046 (d, $^1J(PPt) = 2095$ Hz, PC2N*Pt*Me$_2$ (**5**).

4.11. Reaction of (PC2N)$Pt(CD_3)_2$ (5) with $HSnBu_3$

Fifteen milligram (0.052 mmol) of $HSnBu_3$ was added at r.t. to 13 mg (0.027 mmol) of (PC2N)Pt(CD_3)$_2$ in 0.5 ml of C_6D_6. Light gas evolution and a colour change to pink–brown was observed.

^1H NMR: δ (ppm) 1.09 (t, $^3J(HCCH) = 7.3$ Hz, *H*–Bu), 1.25–1.33 (m, *H*–BuSn), 1.54 (sxt, $^3J(HCCH) = 7.4$ Hz, *H*–Bu), 1.72–1.83 (m, *H*–Bu), 1.91–2.07 (m, PC_2H_4N), 2.37 (s with satellites, $^3J(PtNCH) = 17.9$ Hz, N–(CH_3)$_2$), 7.15–7.17 (m, *H*–PhP), 7.79–7.85 (m, *H*–PhP) ^2H NMR: δ (ppm) 0.46 (s, with satellites, $^3J(PtCD) = 52.0$ Hz, *D*-MePt, (PC2NPt(CD_3)($SnBu_3$)), 1.52(d, with satellites, $^2J(HD) = 1.0$ Hz, $^2J(PtCD) = 9.6$ Hz, *D*-MePt, **5**′D), 1.79(d, with satellites, $^2J(HD) = 0.95$ Hz, $^2J(PtCD) = 12.2$ Hz, *D*-MePt, **5**′D); $^{31}P\{^1H\}$ NMR: δ (ppm) 36.33 (s, with satellites, $^1J(PtP) = 2072$ Hz, **5**′D); ^{119}Sn NMR: δ (ppm) −84.07 (s, *Sn*–*Sn*), −7.0 (s, *Sn*–Pt); $^{195}Pt\{^1H\}$ NMR: δ (ppm) −4046 (d, $^1J(PPt) = 2095$ Hz, PC2N*Pt*Me$_2$).

4.12. Reaction of (PC3N)$PtMe_2$ (4) with $HSnPh_3$

A) $HSnPh_3$ (274.8 mg, 7.8 mmol) was added at r.t. to 34 mg (7.8 mmol) of **4** in 5 ml of C_6D_6.

B) $HSnPh_3$ (7.1 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **4** in 0.5 ml of C_6D_6. After 75 min at r.t., in which time NMR spectra were taken, another equivalent of $HSnPh_3$ (7.1 mg, 0.02 mmol) and the process repeated (ca. 90 min). A further equivalent was then added, and the process repeated again until a ratio of 1:5 was achieved. After being left a RT for 3d crystals were formed, whose identity was confirmed to be Sn_2Ph_3 through a powder XRD analysis.

C) $HSnPh_3$ (42 mg, 0.12 mmol) was added at r.t. to 3 mg (0.006 mmol) of **4** in 0.5 ml of C_6D_6. After being left a RT for 3d crystals were formed, whose identity was confirmed to be Sn_2Ph_3 through a powder XRD analysis.

^1H NMR: δ (ppm) 1.05 (d, $^3J(PPtCH) = 7.5$ Hz, *tr*-Pt–CH_3, (**10a**), 1.12 (d, with satellites, $^3J(PPtCH) = 8.5$ Hz, $^2J(PtCH) = 88$ Hz, *tr*-Pt–CH_3 (**4**), 1.29 (d, with satellites, $^3J(PPtCH) = 7.6$ Hz, $^2J(PtCH) = 32$ Hz, *cis*-

Pt–CH_3, (**4**), 1.89–2.09 (m, $PC_2H_4CH_2N$), 2.25–2.28 (m, $PC_2H_4CH_2N$), 2.43 (s with satellites, ^3J(PtNCH) = 18 Hz, N–(CH_3)$_2$, (**4**), 2.71 (s with satellites, ^3J(PtNCH) = 12.6 Hz, N–(CH_3)$_2$, (**10a**), 6.86–6.99 (m, *H*–PhP), 7.04 (s with satellites, $^1J(H^{117}Sn) = 1849$ Hz $^1J(H^{119}Sn) = 1935$ Hz, *H*–Sn), 7.11–7.24 (m, *H*–PhP), 7.53–7.77 (m, *H*–PhSn), 7.80–7.86 (m, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 10.67 (s with satellites, ^1J(PtP) = 1901 Hz, **11**), 12.76 (s with satellites, ^1J(PtP) = 1978 Hz, **10a**), 13.69 (s with satellites, ^1J(PtP) = 1978 Hz, *P*C3NPt(SnPh$_3$)$_2$), 15.27 (s, with satellites, ^1J(PtP) = 2088 Hz, **4**); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −148.3 (s, Ph$_3$*Sn*Sn*Sn*Ph$_3$), −127.5 (s,) −91.6 (s, Me*Sn*Ph$_3$), −59.9 (s, Me$_2$*Sn*Ph$_2$), −30.8 (s, Me$_3$*Sn*Ph), −2.3 (s, *Sn*–Pt, **10a**); $^{195}Pt\{^1H\}$ NMR: δ (ppm) −4038 (d, ^1J(PPt) = 1043 Hz, **4**), −3844 (d, ^1J(PPt) = 1985 Hz, **10a**).

4.13. Reaction of (PC2N)PtMe$_2$ (5) with HSnPh$_3$

HSnPh$_3$ (7.28 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **5** in 0.5 ml of C_6D_6. Slight gas evolution was observed. After being left a RT for 7d crystals were formed, whose identity was confirmed to be Sn_2Ph_3 through a powder XRD analysis.

^{1}H NMR: δ (ppm) 1.33 (d, with satellites, ^3J(PPtCH) = 7.7 Hz, ^2J(PtCH) = 67 Hz, *tr*-Pt–CH_3 (**5**), 1.59 (d, with satellites, ^3J(PPtCH) = 7.3 Hz, ^2J(PtCH) = 91 Hz, *cis*-Pt–CH_3 (PC2NPtMe$_2$)), 1.71–1.75 (m, PCH_2CH$_2$N and satellites), 1.90–2.02 (m, PCH$_2$CH_2N), 2.36 (s with satellites, ^3J(PtNCH) = 17.6 Hz, N–(CH_3)$_2$ (**5**), 7.07–7.18 (m, H–PhP), 7.04 (s with satellites, $^1J(H^{117}Sn) = 1849$ Hz $^1J(H^{119}Sn) = 1935$ Hz, H–Sn), 7.51–7.87 (m, *H*–PhP/*H*–PhSn); $^{31}P\{^1H\}$ NMR: δ (ppm) 10.64 (s with satellites, ^1J(PtP) = 2659.5 Hz, PC2NPtMe(SnPh$_3$)), 36.33 (s, with satellites, ^1J(PtP) = 2072 Hz, **5**); ^{119}Sn NMR: δ (ppm) −141.6 (s, Ph$_3$*Sn*Sn*Sn*Ph$_3$), −91.05 (s, Me*Sn*Ph$_3$).

4.14. Reaction of (PC2N)Pt(CD$_3$)$_2$ (5) with HSnPh$_3$

HSnPh$_3$ (7.2 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **5** in 0.5 ml of C_6D_6.

^{1}H NMR: δ (ppm) 1.71–1.79, (m, PCH_2CH$_2$N), 1.91–2.04 (m, PCH$_2$CH_2N), 2.37 (s with satellites, ^3J(PtNCH) = 17.9 Hz, N–(CH_3)$_2$, **5**′D), 2.71 (s with satellites, ^3J(PtNCH) = 13.0 Hz, N–(CH_3)$_2$, PC2NPt(SnPh$_3$)Me), 6.91–7.23 (m, H–PhP), 7.04 (s with satellites, $^1J(H^{117}Sn) = 1849$ Hz $^1J(H^{119}Sn) = 1935$ Hz, H–Sn), 7.51–7.65 (m, *H*–PhP), 7.80–7.87 (m, *H*–PhSn); ^{2}H NMR: δ (ppm) 0.40 (d, ^2J(HD) = 1.9 Hz, *D*-MeSn), 0.79 (s, with satellites, ^3J(PtCD) = 7.8 Hz, *D*-MePt, PC2NPt(CD$_3$)(SnPh$_3$)), 1.43 (d, with satellites, ^2J(HD) = 1.0 Hz, ^2J(PtCD) = 9.4 Hz, *D*-MePt, **5**′D), 1.70 (d, with satellites, ^2J(HD) = 0.98 Hz, ^2J(PtCD) = 14.2 Hz, *D*-MePt, **5**′D); $^{31}P\{^1H\}$ NMR: δ (ppm) 10.69 (s with satellites, ^1J(PtP) = 2660 Hz, PC2NPt(CD$_3$)Ph), 16.50 (s, PC2NPt(CD$_3$)(SnPh$_3$)) 28.51 (s, with satellites, ^1J(PtP) = 4550 Hz, **5**′D); ^{119}Sn NMR: δ (ppm) −141.1 (s, Ph$_3$*Sn*Sn*Sn*Ph$_3$), −126.9 (s, *Sn*Ph$_4$), −90.5 (s, Me*Sn*Ph$_3$).

4.15. Reaction of (PC3N)PtMe$_2$ (4) with SnPh$_4$

SnPh$_4$ (8.6 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **4** in 0.5 ml of C_6D_6. After 5 h at r.t., the sample was heated over night at 60 °C which then resulted in a reaction.

^{1}H NMR: δ (ppm) 0 (d, ^3J(PPtCH) = 0 Hz, *tr*-Pt–CH_3 (**4**), 1.12 (d, with satellites, ^3J(PPtCH) = 8.5 Hz, ^2J(PtCH) = 88 Hz, *tr*-Pt–CH_3 (PC3NPtMe$_2$)), 1.29 (d, with satellites, ^3J(PPtCH) = 7.6 Hz, ^2J(PtCH) = 32 Hz, *cis*-Pt–CH_3 (PC3NPtMe$_2$)), 1.89–2.09 (m, $PC_2H_4CH_2N$), 2.25–2.28 (m, PC$_2$H$_4$CH_2N), 2.43 (s with satellites, ^3J(PtNCH) = 18 Hz, N–(CH_3)$_2$ (PC3NPtMe$_2$)), 6.86–6.99 (m, *H*–PhP), 7.11–7.24 (m, *H*–PhP), 7.53–7.77 (m, *H*–PhSn), 7.80–7.86 (m, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 10.67 (s with satellites, ^1J(PtP) = 1907 Hz, *P*C3NPtMePh); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −127.1 (s, SnPh$_4$), −91.2 (s, Me*Sn*Ph$_3$), −60.7 (s, Me$_2$*Sn*Ph$_2$), −30.5 (s, Me$_3$*Sn*Ph), −2.3 (s, *Sn*–Pt).

4.16. Reaction of (PC3N)PtMe$_2$ (4) with MeSnPh$_3$

MeSnPh$_3$ (7.4 mg, 0.02 mmol) was added at r.t. to 10 mg (0.02 mmol) of **4** in 0.5 ml of C_6D_6. After 5 h at r.t., the sample was heated over night at 60 °C which then resulted in a reaction.

^{1}H NMR: δ (ppm) 0.15 (s, with satellites, $^2J(HC^{117}Sn) = 52$ Hz, $^2J(HC^{119}Sn) = 65$ Hz, (*H*$_3$C)$_2$SnPh$_2$), 0.64 (s, with satellites, $^2J(HC^{117}Sn) = 64$ Hz, $^2J(HC^{119}Sn) = 67$ Hz, *H*$_3$CSnPh$_3$), 1.12 (d, with satellites, ^3J(PPtCH) = 8.5 Hz, ^2J(PtCH) = 88 Hz, *tr*-Pt–CH_3, (**4**), 1.29 (d, with satellites, ^3J(PPtCH) = 7.6 Hz, ^2J(PtCH) = 32 Hz, *cis*-Pt–CH_3, **4**), 1.89–2.09 (m, $PC_2H_4CH_2N$), 2.25–2.28 (m, PC$_2$H$_4$CH_2N), 2.43 (s with satellites, ^3J(PtNCH) = 18 Hz, N–(CH_3)$_2$, (**4**), 6.86–6.99 (m, *H*–PhP), 7.11–7.24 (m, *H*–PhP), 7.53–7.77 (m, *H*–PhSn), 7.80–7.86 (m, *H*–PhP); $^{31}P\{^1H\}$ NMR: δ (ppm) 10.67 (s with satellites, ^1J(PtP) = 1901 Hz, **11**); $^{119}Sn\{^1H\}$ NMR: δ (ppm) −90.1 (s, Me*Sn*Ph$_3$), −60.1 (s, Me$_2$*Sn*Ph$_2$), −30.5 (s, Me$_3$*Sn*Ph), −1.9 (s, *Sn*–Pt).

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