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CHEMISTRY OF PLATINUM HYDRIDES

XXV *. PREPARATION AND CHARACTERIZATION OF PLATINUM(II) HYDRIDOTIN COMPLEXES CONTAINING BULKY PHOSPHINES

H.C. CLARK*, A.B. GOEL and C. BILLARD

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Chemistry Department, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)

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Summary

Platinum(II) hydridotin complexes containing bulky phosphine ligands, *trans*-Pt(H)L_2(SnR_3) have been prepared from: (i) the equimolar reaction between corresponding platinum(II) dihydride complexes and $HSnR_3$ (Cy = cyclohexyl), P-i-Pr_3, P-t-BuPh_2, P-t-Bu_2Me; R = Ph), (ii) the oxidative addition of the corresponding zerovalent complexes, Pt^0L_2, with $HSnR_3$ (L = P-i-Pr_3, P-t-BuPh_2; R = Ph), (iii) the reaction of the corresponding platinum(II) dihydride complexes with $ClSnR_3$ in the presence of pyridine in benzene (L = P-i-Pr_3, P-t-BuPh_2; R = CH_3, n-Bu), (iv) the sodium borohydride reduction of the corresponding hydridochloride complexes Pt(H)Cl(PR_3)$_2$ with $ClSnR_3$ in THF (L = PCy_3; R = Ph), these compounds have been characterized by their elemental analysis, infrared, ^{1}H and ^{31}P NMR spectral data.

Introduction

Compounds containing transition metal—Group IVB metal bonds have been extensively investigated, in part because of their possible use as catalysts in homogeneous hydrogenation [1—13]. Thus, compounds containing covalent Pt—Si [13—16], Pt—Ge [14—16], Pt—Sn [14—18], Pt—Pb [14] bonds, among others, have been reported. They have been prepared mostly by the reactions of transition metal halides with derivatives of Group IVB elements of the type R_3MLi, or by the oxidative addition of triorganometal halides to zerovalent transition-metal complexes. In this last case, a recent study [17] has shown that organotin chlorides react with complexes of platinum(0) to give products of insertion into the Sn—C rather than the Sn—Cl bond as reported previously.

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* For part XXIV see ref.

Compounds containing a metal—metal as well as a metal—hydrogen bond have previously been prepared containing either small [14,15,19—22] or chelating [15] phosphine ligands coordinated to the transition metal. Such platinum(II) hydridotin complexes were obtained by the reaction of H_2 on platinum(II) ditin complexes [14] or by oxidative addition of $HSnR_3$ to platinum(0) complexes containing chelating phosphines [15]. We have now found that such compounds containing bulkier tertiary phosphines can be prepared more conveniently by the reaction of $HSnR_3$ with the corresponding dihydride complexes.

Results and discussion

The method [13] reported earlier for the preparation of platinum—metal bonded complexes involving the reaction of R_3MLi with the platinum halides has been used in an attempt to prepare hydridoplatinum—tin complexes containing two tertiary phosphine ligands. The reactions between R_3SnLi (R = Me, n-Pr) and $PtH(Cl)(L)_2$ (L = PEt_3, P-i-Pr_3, P-t-BuPh_2, PCy_3 (Cy = cyclohexyl) and PMe-t-Bu_2) take place extremely slowly, giving poor yields of the products, *trans*-$Pt(H)L_2(SnR_3)$ (I). Hence, this procedure was little used for the preparation of complexes I since (a) the reactivity of $PtH(Cl)L_2$ is dependent on the size of L and for L = PMe-t-Bu_2 or PCy_3, no product at all could be obtained even after prolonged reaction overnight; and (b) the air and moisture sensitivity which requires the use of inert atmosphere techniques makes the use of the R_3SnLi reagents inconvenient.

The oxidative addition of trialkyltin hydrides to zerovalent complexes of iridium [21—23] and platinum containing chelating phosphine ligands [25] has also been found useful for the preparation of hydridometal—tin complexes. In our study, we have found that triphenyltin hydride reacts smoothly with platinum(0) complexes, PtL_2 (L = P-i-Pr_3, PPh_2-t-Bu), under ambient conditions to give *trans*-$PtH(SnPh_3)L_2$. However, this reaction is also dependent on the size of the phosphine:

$$PtL_2 + HSnPh_3 \rightarrow trans\text{-}Pt(H)(SnPh_3)L_2 \qquad (1)$$

(L = P-i-Pr_3, PPh_2-t-Bu)

For bulkier phosphine complexes (i.e. L = PCy_3, P-n-Bu-t-Bu_2, or P-t-Bu_3), no product could be obtained and the starting $HSnPh_3$ was converted to hexaphenylditin, Ph_6Sn_2.

$$PtL_2 + HSnPh_3 \rightarrow PtL_2 + \tfrac{1}{2}Sn_2Ph_6 + \tfrac{1}{2}H_2 \qquad (2)$$

(L = PCy_3, P-t-Bu_3)

The synthetic method of reaction 1 has the further disadvantage that the starting zerovalent platinum complexes have a strong affinity towards oxygen, so that even traces of oxygen react immediately with PtL_2 in solution to give $Pt(O_2)L_2$ [32].

The reactions of triphenyltin hydride with platinum(II) dihydrides, $PtH_2(L)_2$, provide a more general and convenient route for the synthesis of platinum—tin complexes. Equimolar amounts of PtH_2L_2 (L = PPh_2-t-Bu, P-i-Pr_3, PCy_3 or PMe-t-Bu_2 and triphenyltin hydride react readily at room temperature with hydrogen gas evolution to give *trans*-$Pt(H)L_2(SnPh_3)$. While our work was in progress, a report appeared [33] describing a similar type of oxidative addition reaction of Me_3SnH with $(Ph_2PCH_2CH_2PPh_2)PtMe_2$ to give $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ with methane evolution, by reductive elimination, although the hydrido-platinum—tin complex was not isolated.

The nature of the products from the reactions of PtH_2L_2 with $HSnPh_3$ is found to be independent of the mode of addition of the reactants for L = $PMe\text{-}t\text{-}Bu_2$ or PCy_3. This was not the case, however, for L = $P\text{-}i\text{-}Pr_3$ or $PPh_2\text{-}t\text{-}Bu$. When a benzene solution of Ph_3SnH was added dropwise to a stirred solution of PtH_2L_2 (L = $PMe\text{-}t\text{-}Bu_2$, or PCy_3) in benzene, an immediate gas evolution took place, with the formation of the product $PtH(SnPh_3)L_2$ being complete in 15 min. The compound $Pt(SnPh_3)_2L_2$ is not formed even on the addition of an excess of Ph_3SnH. The slow addition of Ph_3SnH avoids any local excess and prevents the further reaction of Ph_3SnH with *trans*-$PtH(SnPh_3)L_2$ (L = $P\text{-}i\text{-}Pr_3$, $PPh_2\text{-}t\text{-}Bu$) to give $Pt(SnPh_3)_2L_2$.

$$PtH(SnPh_3)L_2 + Ph_3SnH \rightarrow Pt(SnPh_3)_2L_2 + H_2 \qquad (4)$$

Thus, when Ph_3SnH is added rapidly, a mixture of $PtH(SnPh_3)L_2$ and $Pt(SnPh_3)_2L_2$ along with unreacted PtH_2L_2 was obtained after 15 min. However, on allowing slow redistribution to occur between PtH_2L_2 and $Pt(SnPh_3)_2L_2$ over ~2—4 h, the desired product $PtH(SnPh_3)L_2$ was obtained.

$$PtH_2L_2 + Pt(SnPh_3)_2L_2 \rightarrow 2\ PtH(SnPh_3)L_2 \qquad (5)$$

When a benzene solution of PtH_2L_2 (L = $P\text{-}i\text{-}Pr_3$, $PPh_2\text{-}t\text{-}Bu$) was added slowly to a stirred solution of Ph_3SnH in benzene, a mixture of $PtH(SnPh_3)L_2$, $Pt(SnPh_3)_2L_2$ and PtH_2L_2 was first obtained after 15 min. which on further stirring (~4 h) gave only $PtH(SnPh_3)L_2$. The preparation of $PtH(SnPh_3)L_2$ with L = $P\text{-}n\text{-}Bu\text{-}t\text{-}Bu_2$ or $P\text{-}t\text{-}Bu_3$ could not be achieved by any of the above methods, and reaction with Ph_3SnH gave unreacted PtH_2L_2 and hexaphenylditin.

$$PtH_2L_2 + HSnPh_3 \rightarrow PtH_2L_2 + \tfrac{1}{2}Sn_2Ph_6 + \tfrac{1}{2}H_2 \qquad (6)$$

(L = $P\text{-}t\text{-}Bu_3$ and $P\text{-}t\text{-}Bu_2\text{-}n\text{-}Bu$)

In some cases, *trans*-$PtH(SnPh_3)L_2$ can be prepared by the reaction of PtH_2L_2 with Ph_3SnCl in the presence of pyridine, as exemplified in the reaction when L = $P\text{-}i\text{-}Pr_3$.

$$PtH_2(P\text{-}i\text{-}Pr_3)_2 + Ph_3SnCl \xrightarrow{py} PtH(SnPh_3)(P\text{-}i\text{-}Pr_3)_2 + PyHCl \qquad (7)$$

The complexes $PtH(SnPh_3)L_2$ can also be obtained in excellent yields when mixtures of $PtH(Cl)L_2$ and Ph_3SnCl are reduced by $NaBH_4$:

$$PtH(Cl)L_2 + Ph_3SnCl \xrightarrow{NaBH_4} PtH(SnPh_3)L_2 + 2\ NaCl \qquad (8)$$

Actually, in this reaction, sodium borohydride reacts with $PtH(Cl)L_2$ and Ph_3SnCl to produce PtH_2L_2 and Ph_3SnH in situ and these produce the desired

TABLE 1

IR, ^1H NMR AND ^{31}P NMR FOR PLATINUM(II) COMPLEXES[a]

IR (cm^{-1})				^1H NMR						^{31}P NMR		
Complexes	ν(Pt—H)	ρ(Sn—Ph)	ν(Pt—P)	τ(PR_3) (ppm)	τ(Sn—Ph) (ppm)	τ(Pt—H) (ppm)	J(P—H) (Hz)	J(Pt—H) (Hz)	J(Sn—H) (Hz)	δ(P) (ppm)	J(Pt—P) (Hz)	J(Sn—Pt—P) (Hz)
$HPt(PCy_3)_2$-($SnPh_3$)	2040 s	700 vs 725 vs	450 m	8.47	2.64 1.83	15.86	11.71	918	104	41.823	2624.5	144.0
$HPt(P\text{-}i\text{-}Pr_3)_2$-($SnPh_3$)	2035 s	680 vs 700 vs 730 vs	450 m	8.91	2.68 1.82	15.83	11.70	901	102	53.684	2629.4	148.9
$HPt(P\text{-}t\text{-}Bu_2Me)_2$-($SnPh_3$)	2038 s	700v s 730 vs	460 m	8.52	2.63 1.82	15.85		892		48.557	2634.3	146.5
$HPt(P\text{-}t\text{-}BuPh_2)_2$-($SnPh_3$)	2090 s	700 vs 730 vs	450 m	9.03	2.66 1.98	15.91	11.80	920		51.573	2636.0	
$Pt(P\text{-}i\text{-}Pr_3)_2$-$(SnPh_3)_2$[b]		700 vs 750 vs	450 m							53.483	2629.4	
$Pt(PBu\text{-}t\text{-}Ph_2)_2$-$(SnPh_3)_2$[b]		700 vs 730 vs	450 m							51.573	2635.0	

[a] ^1H NMR spectra were recorded in C_6D_6 with TMS as an external reference. ^{31}P NMR spectra in C_6D_6 with H_3PO_4 as an external reference. IR spectra were recorded as Nujol mulls. [b] ^1H NMR spectrum could not be resolved.

$PtH(SnPh_3)L_2$

$$PtH(Cl)L_2 \xrightarrow{NaBH_4} PtH_2L_2 + NaCl \qquad (9)$$

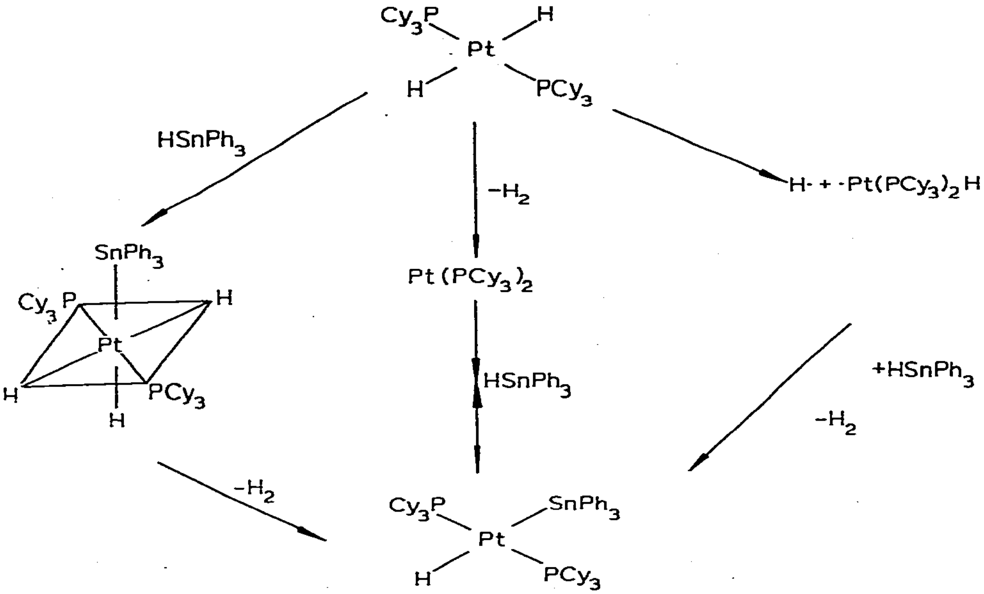
$$Ph_3SnCl \xrightarrow{NaBH_4} Ph_3SnH + NaCl \qquad (10)$$

$$PtH_2L_2 + HSnPh_3 \rightarrow HPt(L)_2(SnPh_3) \qquad (11)$$

The hydridoplatinum—tin complexes, $HPtL_2(SnPh_3)$ are off-white solids. The complexes with L = $P\text{-}i\text{-}Pr_3$ and PCy_3 are stable in the solid state for about one week in air, the ones with L = $P\text{-}t\text{-}Bu_2Me$ and $P\text{-}t\text{-}BuPh_2$ are stable for about one day in similar conditions. They can all be stored under nitrogen for much longer periods without signs of decomposition. In solution, they tend to decompose slowly when exposed to air, probably by reaction with oxygen. Their infrared spectra show strong bands in the region 2035—90 cm^{-1} due to ν(Pt—H). It has been suggested previously [24] that the *trans*-configuration can be assigned on the basis of an observed single infrared band in the region 420—400 cm^{-1} due to the Pt—P stretching vibration, while a *cis*-phosphine complex shows two bands at approximately 440 and 425 cm^{-1}. The use of these infrared spectral assignments, in predicting configuration, however, is not particularly reliable [27]. Thus, the above complexes show only a single infrared band at the somewhat higher frequency of ca. 450 cm^{-1}, but the *trans*-configuration can be assigned unambiguously on the basis of ^{31}P NMR spectral data which show a singlet with ^{195}Pt satellites (J(Pt—P) 2625—2636 Hz) characteristic of a *trans*-bis(phosphine) complex [25]. In addition to ^{195}Pt satellites, the signals also exhibit tin satellites due to phosphorus—tin coupling. However, instead of separate sets of satellites due to coupling to ^{117}Sn and ^{119}Sn, only one set is observed apparently due to very similar values of $J(^{117}Sn\text{—}P)$ and $J(^{119}Sn\text{—}P)$. Pidcock [17] has made similar observations for some *cis*-phosphineplatinum—tin complexes. The proton NMR spectra of these complexes, $HPtL_2(SnPh_3)$, show a triplet due to the hydridic proton at $\tau \sim 15.8\text{—}15.9$ with J(P—H) ~ 11.7, J(Sn—H) ~ 104, J(Pt—H) ~ 910 Hz, consistent with a *trans*-geometry of the phosphines. The complete spectroscopic data are given in Table 1.

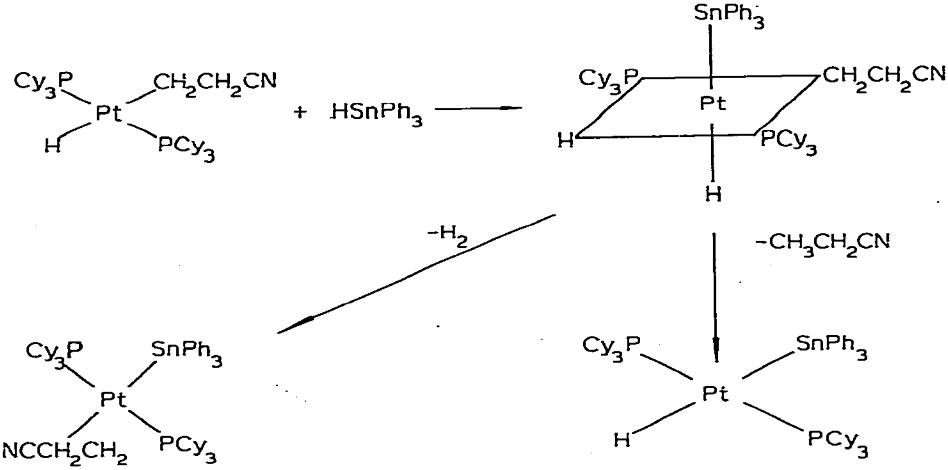
Several mechanistic possibilities can be suggested to describe the reaction of $H_2Pt(PR_3)_2$ with $HSnPh_3$. The first would involve the formation of a six-coordinate octahedral platinum(IV) species as intermediate, as suggested by Glockling [19,33], followed by reductive elimination of hydrogen. The second possibility would involve the formation of the zerovalent complex PtL_2, by reductive elimination of H_2, and this then oxidatively adds $HSnPh_3$ to give the product. This seems to be ruled out by our observation that $Pt(PCy_3)_2$ does not undergo oxidative addition with $HSnPh_3$. Thirdly, a free radical mechanism may be involved, since both $HSnPh_3$ and H_2PtL_2 [32] are known to participate in free radical processes (Scheme 1). To explore this possibility, ESR studies of these reactions are in progress and will be described later.

The likely importance of a possible oxidative addition process to give a platinum(IV) species is emphasized by the fact that, in the reaction of $HSnPh_3$ with $PtH(CH_2CH_2CN)(PCy_3)_2$, a mixture of $HPt(PCy_3)_2(SnPh_3)$ and $(CNCH_2CH_2)Pt(PCy_3)_2(SnPh_3)$ is obtained. This suggests that a six-coordinate intermediate, SCHEME 1



$H_2Pt(CH_2CH_2CN)(PCy_3)_2(SnPh_3)$, is formed, which by reductive elimination of either H_2 or CH_3CH_2CN gives the two products (Scheme 2).

SCHEME 2



The observed variations in the reactivity of PtL_2 and H_2PtL_2 towards $HSnPh_3$, and of $HPtClL_2$ with $LiSnR_3$ as L is varied, can probably be attributed to steric effects of the phosphine ligands. For phosphines such as $t\text{-}BuPh_2P$ and $i\text{-}Pt_3P$ which are relatively small [26—28], the reactions of $HSnPh_3$ with PtL_2 and H_2PtL_2 occur smoothly to give $HPtL_2(SnPh_3)$ and $PtL_2(SnPh_3)_2$, respectively. However, for the larger phosphines, no such reactions of $HSnPh_3$ with PtL_2 or H_2PtL_2 occur except for $H_2Pt(PCy_3)_2$ which with $HSnPh_3$ gives only $HPtL_2(SnPh_3)$. These steric effects of L are summarized in Table 2.

TABLE 2

STERIC EFFECTS OF THE PHOSPHINE LIGAND L ON THE REACTIONS: $H_2PtL_2 + HSnPh_3 \rightarrow H_{2-x}PtL_2(SnPh_3)_x$. $PtL_2 + HSnPh_3 \rightarrow H_nPtL_2(SnPh_3)_{2-n}$

L	θ^0 [a]	x	n
P-t-BuPh$_2$	107	1,2	1
P-i-Pr$_3$	109	1,2	1
PCy$_3$	113	1	0
P-t-Bu$_2$Me	116	1	0
P-t-Bu$_2$-n-Bu	121	0	0
P-t-Bu$_3$	130	0	0

[a] Minimum cone angle θ^0 as in ref. 26. θ^0 may also be regarded, as a first approximation, as equivalent to $2x_2\theta^0$ as in ref. 27.

Experimental

Reactions were carried out under a dry nitrogen atmosphere using Schlenk tube techniques. Infrared spectra were recorded with a Beckman IR 12 double beam spectrophotometer using KBr plates. Proton and ^{31}P NMR spectra were obtained with Varian A60 and Bruker 60 Fourier transform spectrometers. Analyses were obtained from M—H—W Laboratories, Phoenix, Arizona. As previous workers have found, carbon analyses tend to deviate substantially from theoretical values, apparently caused by the simultaneous presence of Pt, Sn and P in the compounds. The compounds $LiSnR_3$ were prepared by the procedure of Gilman and Rosenberg [29] from $SnCl_2$ and LiR in ether. The complexes $HPtL_2Cl$ were prepared by the procedure of Parshall [30], by reduction of PtL_2Cl_2 with hydrazine. The compounds PtL_2Cl_2 were obtained from K_2PtCl_4 and L [31]. In the case of the complex with tricyclohexylphosphine as ligand, $HPtL_2Cl$ was prepared by the displacement of PEt_3 from $HPt(PEt_3)_2Cl$. Zerovalent PtL_2 complexes were prepared by the reduction of the corresponding PtL_2Cl_2 compounds by sodium naphthalenide in THF under a nitrogen atmosphere followed by extraction with hexane. The hydrides H_2PtL_2 were prepared by reduction of the corresponding peroxycarbonato complexes by $NaBH_4$ in ethanol [32]. Triphenyltin hydride was used as received from Alfa Products.

1. *Reaction between $HPt(PEt_3)_2Cl$ and $LiSn(CH_3)_3$ in THF*

$HPt(PEt_3)_2Cl$ (468 mg; 1 mmol) was dissolved in dry THF (5 ml) and the solution of $LiSn(CH_3)_3$ (171 mg; 1 mmol) in dry THF (6 ml) was added dropwise under nitrogen at room temperature. The reaction mixture immediately turned brown and it was then refluxed for 4 h giving a black mixture. The solvent was removed under vacuum and the product extracted with benzene. The IR and ^1H NMR spectra identified the compound as the reactant $HPt(PEt_3)_2Cl$.

2. *Reaction between $HPt(PEt_3)_2Cl$ and $LiSn(C_4H_9)_3$ in THF*

$HPt(PEt_3)_2Cl$ (250 mg; 0.54 mmol) was dissolved in dry THF (5 ml) and a solution of $LiSn(C_4H_9)_3$ (0.54 mmol) in dry THF (5 ml) was added dropwise under nitrogen at 0°C. The reaction mixture was light tan; it was allowed to react at room temperature for 72 h. The colour changed slowly from tan, to black, to yellow. The solution was reduced in volume and hexane added to precipitate the product in cooling at 0°C. The pale yellow material was washed twice with hexane and dried under vacuum, which was identified as $HPt(PEt_3)_2Sn(C_4H_9)_3$. Yield ~15%. The compound decomposed at 140°C.

3. Reactions of triphenyltin hydride with platinum(0) complexes

(a) $Pt(P\text{-}t\text{-}Bu_3)_2$. A solution of $Pt(P\text{-}t\text{-}Bu_3)_2$ (75 mg; 0.125 mmol) was prepared in hexane (20 ml) and $HSnPh_3$ (44 mg; 0.125 mmol) was added dropwise under N_2. The solution turned light yellow with evolution of hydrogen. After one hour at room temperature, the solvent was removed under vacuum. The IR spectrum (Nujol) showed the absence of any band that could be assigned to ν(Pt—H) in the 1600—2400 cm^{-1} region. The residue was extracted with 15 ml of hexane and the extract was identified as $Pt(P\text{-}t\text{-}Bu_3)_2$ by its ^1H NMR spectrum. The insoluble residue was identified as Sn_2Ph_6 from its m.p. and IR spectrum.

(b) $Pt(PCy_3)_2$. To a hexane (20 ml) solution of $Pt(PCy_3)_2$ (83 mg, 0.1 mmol), $HSnPh_3$ (35 mg, 0.1 mmol) was added dropwise under nitrogen. The solution turned light yellow with evolution of hydrogen. After an hour at room temperature, a white solid precipitated out. This was filtered, washed three times with cold hexane and dried. It was identified spectroscopically as Sn_2Ph_6. The hexane-soluble part was found to be $Pt(PCy_3)_2$.

(c) Preparation of trans-$PtH(P\text{-}i\text{-}Pr_3)_2(SnPh_3)$ by reaction 3. $Pt(P\text{-}i\text{-}Pr_3)_2$ (65 mg, 0.125 mmol) in hexane solution (20 ml), and $HSnPh_3$ (44 mg, 0.125 mmol) was mixed under nitrogen. Evolution of hydrogen occurred. After 5 min at room temperature, the solvent was removed. The residue was treated with 3 X 5 ml of cold hexane under nitrogen; the white insoluble solid obtained was dried under vacuum. Yield: 100 mg (90%). This compound decomposed at 140—143°C and analyzed as $HPt(P\text{-}i\text{-}Pr_3)_2(SnPh_3)$ (Found: C, 49.65; H, 6.45. $C_{36}H_{58}P_2PtSn$ calcd. C, 49.88 H, 6.69%.) Spectroscopic data are given in Table 1.

(d) Preparation of trans-$PtH(P\text{-}t\text{-}BuPh_2)_2(SnPh_3)$ by reaction 3. Reaction between $Pt(P\text{-}t\text{-}BuPh_2)_2$ (85 mg; 0.125 mmol) and $HSnPh_3$ (44 mg, 0.125 mmol) in hexane was carried out as above to give a white product. Yield: 110 mg (85%). This compound decomposed at 135—139°C and gave analyses consistent with $PtH(P\text{-}t\text{-}BuPh_2)_2(SnPh_3)$. Found: C, 56.65 H, 5.12 $C_{50}H_{54}P_2PtSn$. calcd.: C, 58.25; H, 5.24%). Spectroscopic data are given in Table 1.

The above two compounds (c) and (d) are not very stable in benzene solution. (c) is stable for approximately one week and (d) for one day in contact with air in their solid state. They are better stored under nitrogen.

4. Reactions of triphenyltinhydride with H_2PtL_2

(a) $H_2Pt(P\text{-}t\text{-}Bu_3)_2$. $H_2Pt(P\text{-}t\text{-}Bu_3)_2$ (75 mg; 1.25 mmol) was dissolved in dry benzene (20 ml) and $HSnPh_3$ (44 mg; 0.125 mmol) in benzene (5 ml) was added dropwise under N_2. The solution turned light yellow with evolution of hydrogen gas. After 1 h at room temperature the solvent was removed under vacuum, and the residue was washed with hexane. The hexane insoluble solid was identified to be Sn_2Ph_6. The hexane soluble portion was evacuated to dryness and characterized as $Pt(P\text{-}t\text{-}Bu_3)_2$ by IR and ^1H NMR spectra.

(b) $H_2Pt(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Bu)_2$. $H_2Pt(P\text{-}t\text{-}Bu_2\text{-}n\text{-}Bu)_2$ was allowed to react in the same conditions and similar to the above reaction, Sn_2Ph_6 was formed. However, the

dihydridoplatinum complex was remained unchanged as observed by IR (ν(Pt—H) 1730 cm^{-1}) and ^1H NMR spectra.

(c) Preparation of trans-PtH(P-t-Bu$_2$Me)$_2$(SnPh$_3$) by reaction 4. To a stirred solution of $H_2Pt(P\text{-}t\text{-}Bu_2Me)_2$ (150 mg; 0.29 mmol) in dry benzene (20 ml), $HSnPh_3$ (102 mg; 0.29 mmol) was added dropwise under nitrogen resulting in an immediate evolution of hydrogen gas. After 15 min the solvent was removed under vacuum. The yellowish residue was treated with 3 × 5 ml of cold hexane. The resulting white compound was then dried under vacuum. Yield: 220 mg (85%). This compound decomposed at 110—114°C and analyzed as PtH(P-t-Bu$_2$Me)$_2$(SnPh$_3$). Found: C, 48.40, H, 6.99. $C_{36}H_{58}P_2PtSn$ calcd.: C, 49.88, H, 6.69%. Spectroscopic data are given in Table 1.

(d) Preparation of trans-PtH(PCy$_3$)$_2$(SnPh$_3$). $H_2Pt(PCy_3)_2$ (175 mg; 0.24 mmol) was dissolved in dry benzene (20 ml) and $HSnPh_3$ (84 mg; 0.24 mmol) was added dropwise under nitrogen. The same experimental manipulations as above gave a white compound. Yield: 220 mg (85%). This compound decomposed at 158—162°C and analyzed as PtH(PCy$_3$)$_2$(SnPh$_3$). Found: C, 58.87; H, 7.21. $C_{54}H_{82}P_2PtSn$ calcd.: C, 58.59; H, 7.41%.) Spectroscopic data are given in Table 1.

(e) Preparation of trans-PtH(P-i-Pr$_3$)$_2$(SnPh$_3$). $H_2Pt(P\text{-}i\text{-}Pr_3)_2$ (510 mg; 1.1 mmol) was dissolved in dry benzene (50 ml) and $HSnPh_3$ (386 mg; 1.1 mmol) was added dropwise under nitrogen. A white compound was obtained. Yield: 684 mg (80%). This compound decomposed at 175—180°C and analyses identified it as HPt(P-i-Pr$_3$)$_2$(SnPh$_3$). Found: C, 49.65; H, 6.45. $C_{36}H_{58}P_2PtSn$ calcd.: 49.88; H, 6.69%. Spectroscopic data are given in Table 1. A mixture of HPt(P-i-Pr$_3$)$_2$(SnPh$_3$) and Pt(P-i-Pr$_3$)$_2$(SnPh$_3$)$_2$ was obtained when $H_2Pt(P\text{-}i\text{-}Pr_3)_2$ was added to a benzene solution of $HSnPh_3$ and the reaction was carried out for ~15 min. However after 4 h, the only product obtained was HPt(P-i-Pr$_3$)$_2$(SnPh$_3$).

(f) Preparation of trans-Pt(P-i-Pr$_3$)$_2$(SnPh$_3$)$_2$. $H_2Pt(P\text{-}i\text{-}Pr_3)_2$ (350 mg; 0.68 mmol) was dissolved in dry benzene (20 ml) and $HSnPh_3$ (237 mg; 1.36 mmol) was added dropwise under nitrogen. A pale yellow compound was obtained. Yield: 440 mg (75%). This compound decomposed at 175—178°C and was identified by analyses as Pt(P-i-Pr$_3$)$_2$(SnPh$_3$)$_2$. Found: C, 53.73; H, 6.10. $C_{54}H_{72}P_2PtSn_2$ calcd. C, 53.33; H, 5.92%. Spectroscopic data are given in Table 1.

(g) Preparation of trans-PtH(P-t-BuPH$_2$)$_2$(SnPh$_3$). $HSnPh_3$ (51 mg; 0.146 mmol) was added dropwise under N_2 to a stirred solution of $H_2Pt(P\text{-}t\text{-}BuPh_2)_2$ (100 mg; 0.146 mmol) in benzene (20 ml). An off-white compound was obtained. Yield: 120 mg (80%). This compound decomposed at 135—139°C and was spectroscopically identical to that obtained in 3d.

(h) Preparation of trans-Pt(P-t-BuPh$_2$)$_2$(SnPh$_3$)$_2$. $H_2Pt(P\text{-}t\text{-}BuPh_3)_2$ (80 mg; 0.46 mmol) was dissolved in dry benzene (20 ml) and $HSnPh_3$ (82 mg; 0.232 mmol) was added dropwise under nitrogen. A pale yellow compound was obtained. Yield: 110 mg (75%). The compound decomposed at 110—115°C and analyzed as Pt(P-t-BuPh$_2$)$_2$(SnPh$_3$)$_2$. Found: C, 56.92, H, 5.04. $C_{68}H_{68}P_2PtSn_2$ calcd.: C, 59.17; H, 4.93%. Spectroscopic data are given in Table 1.

5. *Reaction of H_2PtL_2 with $ClSnPh_3$ in the presence of pyridine in benzene*

$H_2Pt(P\text{-}i\text{-}Pr_3)_2$ (100 mg; 0.193 mmol) was dissolved in dry benzene (20 ml). $ClSnPh_3$ (75 mg; 0.195 mmol) and pyridine (76 mg; 0.97 mmol) in dry benzene

(10 ml) was added dropwise at room temperature under nitrogen. The solution was allowed to react at 45°C for 1 h. The solution became yellow; the solvent was removed under vacuum, and the residue was washed with 3 × 5 ml cold hexane. The white compound obtained was spectroscopically identical to HPt-(P-Pr_3)$_2$($SnPh_3$) from 4e. Yield: 105 mg (60%).

6. *Reaction of HPt(PCy_3)$_2$Cl with Cl$SnPh_3$ in the presence of $NaBH_4$ in THF*

HPt(PCy_3)$_2$Cl (158 mg; 0.20 mmol) was dissolved in dry THF (20 ml). $NaBH_4$ (~10 fold excess) was added under nitrogen and the mixture was allowed to react at room temperature for 2 h, followed by the addition of Ph_3SnCl (92 mg; 0.20 mmol). The mixture turned yellow. After 15 min, the solvent was removed under vacuum. The product was extracted with benzene, the solvent removed compound obtained was similar to HPt(PCy_3)$_2$($SnPh_3$) from 4d. Yield: 215 mg (90%).

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