The Reaction between Carbonatobis(phosphine)platinum(II) Complexes and Triorganotin Hydrides. Formation of Sn–Pt^{IV} Bonds

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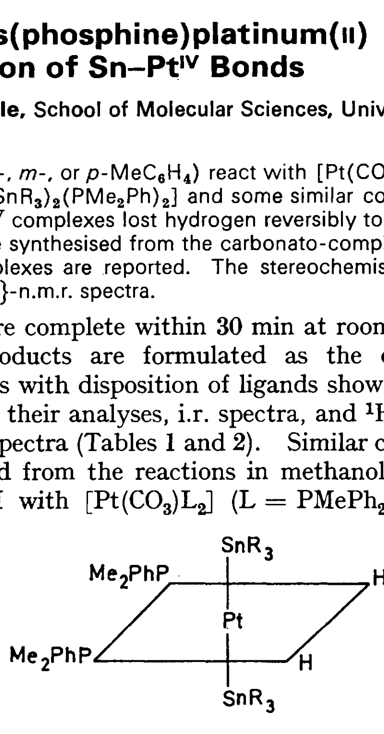
The triorganotin hydrides R_3SnH (R = Ph, $PhCH_2$, and *o*-, *m*-, or *p*-MeC_6H_4) react with $[Pt(CO_3)(PMe_2Ph)_2]$ in methanol to give the Pt^{IV} complexes *cis,trans,cis*-$[PtH_2(SnR_3)_2(PMe_2Ph)_2]$ and some similar complexes of PEt_3, $PMePh_2$, and diphos were obtained. In benzene the Pt^{IV} complexes lost hydrogen reversibly to form complexes such as *trans*-$[Pt(SnR_3)_2(PMe_2Ph)_2]$, which may also be synthesised from the carbonato-complexes in benzene. The factors favourable to the isolation of the Pt^{IV} complexes are reported. The stereochemistries of the Pt^{IV} and Pt^{II} complexes were determined from ^1H and $^{31}P\{^1H\}$-n.m.r. spectra.

OXIDATIVE-ADDITION of Group IV organometallic compounds, especially hydrides, to platinum(0) complexes $[PtL_n]$ (L = tertiary phosphine, $n = 3$ or 4) and $[Pt(C_2H_4)(PPh_3)_2]$ is a well-established method of forming compounds containing a Group IV metal bonded to platinum.[1-5] The carbonato-complexes $[Pt(CO_3)L_2]$ are reported to be reduced to Pt^0 complexes $[PtL_2]$ in alcohols,[6,7] and since they are more conveniently prepared than Pt^0 complexes and are probably obtainable with a wider range of ligands L, we have examined their reactions with triorganotin hydrides and some related compounds [Me_3SnBr, Et_3SnBr, Ph_3SnCl, (*p*-$MeC_6H_4)_3SnCl$, $MePh_2SiH$, and Ph_3GeH].

Solutions of the complex $[Pt(CO_3)(PMe_2Ph)_2]$ in methanol or ethanol were found to react rapidly with the hydrides R_3SnH (R = Ph, $PhCH_2$, and *o*-, *m*-, or *p*-$CH_3C_6H_4$) to give precipitates of the Pt^{IV} complexes $[PtH_2(SnR_3)_2(PMe_2Ph)_2]$. The reactions were accompanied by evolution of gas, presumably carbon dioxide,[6] and were complete within 30 min at room temperature. The products are formulated as the octahedral dihydrides with disposition of ligands shown in (I) on the basis of their analyses, i.r. spectra, and ^1H and $^{31}P\{^1H\}$-n.m.r. spectra (Tables 1 and 2). Similar complexes were obtained from the reactions in methanol or ethanol of Ph_3SnH with $[Pt(CO_3)L_2]$ (L = $PMePh_2$ or PEt_3) or $[Pt(CO_3)(diphos)]$ [diphos = 1,2-bis(diphenylphosphino)ethane], though the product from the latter complex was characterised only by i.r. spectra; its elemental analysis was somewhat unsatisfactory, and neither recrystallisation nor n.m.r. measurements were possible because upon dissolution in benzene it immediately



(I)

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[7] D. M. Blake and L. M. Leung, *Inorg. Chem.*, 1972, **11**, 2879.

evolved hydrogen with formation of $[Pt(SnPh_3)_2(diphos)]$. Reactions of $[Pt(CO_3)(PMe_2Ph)_2]$ with Et_3SnH or $Pr^i{}_3SnH$ gave only oils which smelled of phosphine.

Although Pt^{IV} compounds containing Sn–Pt bonds are undoubtedly formed in many oxidative-addition reactions of Pt complexes, they have been isolated only rarely because of their tendency in solution to undergo rapid reductive elimination of, for example, H_2, R_3SnH, or R_3SnCl, with formation of Pt^{II} complexes (which may or may not contain Sn–Pt bonds).[2,3] We have made a brief investigation of the factors favourable to the isolation of such Pt^{IV} compounds.

(i) The Pt^{IV} complexes $[PtH_2(SnPh_3)_2L_2]$ (L = PMe_2Ph or PEt_3) eliminate hydrogen when dissolved in benzene, and the Pt^{II} complexes *trans*-$[Pt(SnPh_3)_2L_2]$ are slowly deposited. The similar reaction of $[PtH_2(SnPh_3)_2(diphos)]$ has been mentioned previously. The complex *trans*-$[Pt(SnPh_3)_2(PMe_2Ph)_2]$ redissolves in benzene upon passage of hydrogen, and the Pt^{IV} complex can be isolated by addition of hexane. Thus, although the Pt^{IV} complexes are unstable in benzene with respect to elimination of hydrogen, the dissociation pressure is <1 atm for the dimethylphenylphosphine complexes.

TABLE 1

Data for the products $[PtH_2(SnR_2)_2L_2]$ obtained from reactions between R_3SnH and $[Pt(CO_3)L_2]$ in methanol

R	L	Yield (%)	M.p. (t/°C)	ν(Pt–H)(cm⁻¹)	Found (%)		Required (%)	
					C	H	C	H
Ph	PMe_2Ph	70	176—177	2085, 2110	53·4	4·7	53·2	4·6
o-MeC_6H_4	PMe_2Ph	70	140	2145	55·6	5·3	55·4	5·3
m-MeC_6H_4	PMe_2Ph	74	155	2095, 2120	55·8	5·4	55·4	5·3
p-MeC_6H_4	PMe_2Ph	79	204—208	2100	55·8	5·6	55·4	5·3
$PhCH_2$	PMe_2Ph	84	101—103	2080, 2095	55·4	5·4	55·4	5·3
Ph	$PMePh_2$	56	125	2125	57·4	4·6	57·4	4·5
Ph	PEt_3	85	174—176	2085, 2125	50·8	5·5	50·9	5·5
Ph	$\frac{1}{2}(Ph_2PCH_2CH_2PPh_2)$	65	210—215	2100, 2120, 2150	56·6	4·5	57·5	4·4
Ph	$AsEt_3$ [a]	61	120—122	2115, 2150	49·0	5·1	47·2	5·1

[a] Prepared from $[Pt(CO_3)(AsEt_3)_2]$ (ref. 9); sample contaminated with hexaphenyldistannoxane.

TABLE 2

^1H and ^{31}P N.m.r. parameters (τ, δ, J) * for the complexes $[PtH_2(SnR_3)_2L_2]$ [a]

L	R	τ(PtH) [b]	τ(PCH₃)	δ(P) [c]	^1J(Pt–H)	$^2J(PPtH)_{cis}$	$^2J(PPtH)_{trans}$	^1J(Pt–H)	^2J(PPtP)	^2J(PPtSn)	^2J(Sn-PtH)	^2J(PCH) [d]	^3J(PtPCH)	Other data
PMe_2Ph	Ph	20·70	8·6	+191·6	660	14	184	1731	12	95	18	9	20	7·6 τ($C_6H_4CH_3$)
PMe_2Ph	*o*-MeC_6H_4 [e]		8·6									8		
PMe_2Ph	*m*-MeC_6H_4	20·51	8·5	+191·6	666	14	184	1724	11	93	15	9	20	7·8 τ($C_6H_4CH_3$)
PMe_2Ph	*p*-MeC_6H_4	20·58	8·5	+191·3	666	14	185	1729	11	93	17	9	20	7·85 τ($C_6H_4CH_3$)
PMe_2Ph	$C_6H_5CH_2$	21·76	8·7	+199·7	685	14	187	1716	9	90	37	9	20	7·6 τ($C_6H_5CH_2$), ^2J(SnCH) 38 Hz
$PMePh_2$	Ph	20·05	8·2	+165·5	655		168 [f]	1826		88		4 [g]		
PEt_3	Ph	21·09		+164·2	625		161 [f]	1760		93				
$AsEt_3$	Ph	21·99			784						14			

* δ In p.p.m. and J in Hz. [a] All complexes show phenyl resonances between τ 2·0 and 3·2. Assignments of ^1H spectra of phosphine complexes assume the presence of coupling between hydride protons and Sn nuclei. Such Sn satellites are undoubtedly present in the spectrum of the arsine complex. [b] Relative to Me_4Si τ 10·00; recorded in C_6D_6. [c] Positive shifts are to high field of the external reference $(MeO)_3P$ in C_6D_6. [d] Doublet separation, strictly $|^2J(PCH) + {}^4J(PPtPCH)|$ (R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275). [e] Complex unstable. ^{31}P spectrum poorly resolved. Hydride resonances not observed. [f] Incomplete resolution prevented analysis; value given is $|^2J(PPtH)_{trans} + {}^2J(PPtH)_{cis}|$. [g] Broad doublet with obscured satellites.

(ii) Starting materials other than the carbonato-complexes may be used for the synthesis of Pt^{IV} compounds: $[Pt(PMe_2Ph)_4]$ reacts with Ph_3SnH in ethanol to give a precipitate of $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$, and the same complex is deposited when a *concentrated* solution of *trans*-$[PtHCl(PMe_2Ph)_2]$ in toluene is mixed at 0 °C with Ph_3SnH and set aside for a few hours. Furthermore, the i.r. spectra of the products indicate that *cis*-$[PtCl_2(PMe_2Ph)_2]$ is partially converted into the Pt^{IV} complex by Ph_3SnH in methanol.

(iii) The carbonato-complexes $[Pt(CO_3)L_2]$ (L = PMe_2Ph or PEt_3) dissolved in benzene containing Ph_3SnH and the solutions slowly deposited *trans*-$[Pt(SnPh_3)_2L_2]$. The complex $[Pt\{Sn(C_6H_4Me\text{-}p)_3\}_2(PMe_2Ph)_2]$ was obtained similarly. Treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with Ph_3SnH in ether or with Et_3SnH alone gave rather vigorous reactions from which only Pt^{II} complexes were isolated. However, addition of hexane during the reaction of $[Pt(CO_3)(PMe_2Ph)_2]$ with Ph_3SnH in benzene immediately after the carbonato-complex had completely dissolved (*ca.* 15 min) gave a precipitate of $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$.

These observations imply that the Pt^{IV} complexes in solution are unstable when set aside, but that they can be obtained from a variety of starting complexes and from benzene or toluene solutions provided that the procedures followed are favourable to the relatively rapid deposition of solid Pt^{IV} complexes. The synthesis from the carbonato-complexes in alcohols is especially suitable because of the adequate solubility of the starting materials and insolubility of the Pt^{IV} complexes in such solvents.

Insolubility of Pt^{IV} complexes in the reaction media also appears to be a feature of syntheses of other compounds containing Sn–Pt^{IV} bonds. Baird[8] found that $[PtCl_2(SnCl_3)_2(PPh_3)_2]$ precipitated rapidly from a solution of *trans*-$[PtHCl(PPh_3)_2]$ and $SnCl_4$ in warm benzene and that attempts to recrystallise the Pt^{IV} complex led to formation of $[PtCl(SnCl_3)(PPh_3)_2]$. Clemmitt and Glockling[2] obtained $[PtHCl(SnMe_3)_2(diphos)]$ as a brown

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[8] M. C. Baird, *J. Inorg. Nuclear Chem.*, 1967, **29**, 367.

deposit from a mixture of [$PtCl_2$(diphos)] and Me_3SnH, and found that [Pt(diphos)$_2$] was converted into [PtH($SnMe_3$)$_3$(diphos)] in contact with Me_3SnH. Both compounds lost Me_3SnH upon attempted recrystallisation from benzene.[2] A compound apparently analogous to one of the diphos complexes was obtained as a by-product from the reaction of [Pt(CO_3)(PMe_2Ph)$_2$] with Ph_3SnH in benzene. After removal of *trans*-[Pt($SnPh_3$)$_2$(PMe_2Ph)$_2$] by filtration, light petroleum (b.p. 40—60 °C) was added to the filtrate to precipitate a pale-brown solid which gave a correct analysis for [PtH($SnPh_3$)$_3$(PMe_2Ph)$_2$]. This is presumably formed by oxidative-addition of Ph_3SnH to the small amount of *trans*-[Pt($SnPh_3$)$_2$(PMe_2Ph)$_2$] remaining in solution.

The reactions of triorganotin halides R_3SnX with [Pt(CO_3)L_2] were briefly studied. As expected, no useful result could be obtained with methanol or ethanol solutions because of the solvolysis of the halides to generate HX; only the complexes *cis*-[PtX_2L_2] were isolated. From [Pt(CO_3)(PMe_2Ph)$_2$] with Ph_3SnCl or (*p*-MeC_6H_4)$_3$SnCl in refluxing benzene the complexes *trans*-[PtClR(PMe_2Ph)$_2$] (R = Ph or *p*-MeC_6H_4) were produced. Baird has reported that [PtCl($SnPh_3$)(PPh_3)$_2$] is converted into [PtClPh(PPh_3)$_2$] when heated under reflux in acetone,[8] but recent work in this laboratory [9] suggests that Baird's starting material may have been a mixture containing the phenyl complex, so as yet there is no reliable evidence that a tin-containing complex is an intermediate in the formation of the phenyl complex.

The reactions of a silicon hydride, Ph_2MeSiH, and a germanium hydride, Ph_3GeH, with [Pt(CO_3)(PPh_3)$_2$] in methanol were examined, but the products were the known Pt^{II} species [PtH($SiMePh_2$)(PPh_3)$_2$] [4] and [PtH($GePh_3$)(PPh_3)$_2$].[10]

Spectra and Stereochemistry.—Although the Pt^{IV} complexes eliminate hydrogen in benzene solution, it was possible to obtain satisfactory ^1H and $^{31}P\{^1H\}$-n.m.r. spectra for the complexes [PtH_2(SnR_3)$_2$(PMe_2Ph)$_2$] (R = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4, or $PhCH_2$) in deuteriobenzene by rapid acquisition of data with a Fourier transform instrument. The ^1H spectra of the hydride protons (A) are of $[AX]_2$ types due to coupling with ^{31}P (X), with additional coupling from ^{195}Pt. The form of the spectra eliminates structures involving *trans*-phosphines or *trans*-hydride ligands, and since the hydrides and phosphines must be chemically equivalent structure (I) is unequivocally established. The derivation of parameters from the spectra involves some ambiguity, because certain of the expected lines appear to overlap and satellite lines from coupling to Sn nuclei may also be present (Table 2). As expected from structure (I), the methyl groups of the phosphines give essentially doublet spectra with additional splitting by ^{195}Pt.

The $^{31}P\{^1H\}$ spectra imply a single phosphorus environment with coupling to ^{195}Pt. Additionally, each resonance is a *ca.* 1 : 5 : 1 triplet due to coupling with Sn nuclei of spin 1/2. The nuclei ^{117}Sn and ^{119}Sn have magnetogyric ratios which differ only by 5%, so the satellites from each nucleus are expected to overlap when the coupling constants are relatively small. Since the combined abundance of these isotopes is 16·3%, molecules containing two Sn nuclei of spin 1/2 have abundance of only 2·7% and need not be considered further. For configuration (I), molecules with one Sn nucleus of spin 1/2 (27·2% abundance) couple with both ^{31}P nuclei, to give a 1 : 1 doublet, so the ^{31}P resonances are calculated to appear as triplets of intensity ratios 1 : 5·1 : 1 in good agreement with observation. Full details of the n.m.r. parameters are given in Table 2. The spectra of the complexes [PtH_2($SnPh_3$)$_2$$L_2$] (L = $PMePh_2$ or PEt_3) are similar in form, but owing to instrumental difficulties arising from the low relative intensity of the hydride resonances the resolution of the ^1H spectra was inadequate for complete analysis. The spectra do, however, establish structure (I). The complexes [PtH_2\{Sn(C_6H_4Me-*o*)$_3$\}$_2$(PMe_2Ph)$_2$] and [PtH($SnPh_3$)$_3$(PMe_2Ph)$_2$] were insufficiently stable in solution for spectra to be obtained. It is unlikely that the stereochemistries of the Pt^{IV} complexes differ in solution and the solid state; for many of the complexes the presence of *cis*-hydrido-ligands in the solids can be inferred from the presence of two ν(Pt–H) bands in the i.r. spectra.

Spectra were also obtained for the Pt^{II} complexes (Table 3) except for [Pt\{Sn(C_6H_4Me-*p*)$_3$\}$_2$(PMe_2Ph)$_2$], which was too insoluble. The $^{31}P\{^1H\}$ spectrum of [Pt($SnPh_3$)$_2$(diphos)] is a simple 1 : 4 : 1 triplet with ^1J(Pt–P) 2290 Hz; there are some indications of Sn-satellite lines, but their intensities are less than 5% of those of the principal lines and they are obscured by noise. The absence of *P*PtSnC*H* coupling in [Pt($SnMe_3$)$_2$(diphos)] has been noted previously and tentatively attributed to averaging due to a rate process involving opening of the chelate ring.[2] This explanation appears to be rather improbable, and for our complex it is virtually eliminated by the presence of Pt–P coupling that is certainly not abnormally small. As noted previously, effects due to molecules containing two Sn nuclei of spin 1/2 may be neglected, so Sn satellites derive from molecules (27·2% abundance) that contain

TABLE 3

N.m.r. parameters for complexes [Pt($SnPh_3$)$_2$$L_2$]

Complex	δ(P)/ p.p.m.[a]	^1J(Pt–P)/ Hz	^2J(SnPtP)/ Hz
trans-[Pt($SnPh_3$)$_2$(PMe_2Ph)$_2$] [b]	+154·6	2437	190
trans-[Pt($SnPh_3$)$_2$(PEt_3)$_2$] [c]	+135·1	2349	171
[Pt($SnPh_3$)$_2$(diphos)]	+83·3	2290	*d*

[a] See footnote to Table 2. [b] *trans*-Stereochemistry established by ^1H spectrum of P–CH_3: τ 8·4 (t), ^2J(PCH) + ^4J(PPtPCH) 6 Hz, ^3J(PtPCH) 16 Hz. [c] *trans*-Stereochemistry established by ^1H spectrum of PCH_2CH_3: τ 9·3, 1 : 4 : 6 : 4 : 1 quintet (line separation 8 Hz). [d] Not observed, see text.

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[9] C. Eaborn, A. Pidcock, and B. R. Steele, unpublished observations.

[10] C. Eaborn, A. Pidcock, and F. Waugh, unpublished observations.

one such nucleus. By analogy with couplings ^2J(PPtP),[11] the coupling constants ^2J(SnPtP) to the phosphorus nuclei *cis* and *trans* to Sn are expected to differ by >1 kHz, so the Sn satellites are the AA′ part of an AA′X spectrum, with the couplings to the Sn nucleus leading to an effective chemical shift between the two phosphorus nuclei (A,A′).[12] This reduces the intensity of the Sn satellites quite markedly in comparison with the Pt^{IV} complexes considered earlier, since the lines from the A and A′ nuclei will not be superimposed and they will be split further by phosphorus–phosphorus coupling. The apparent intensity of the Sn satellites would also be reduced by non-coincidence of lines from the ^{117}Sn and ^{119}Sn nuclei.

If we make the reasonable assumption that the *trans*-Pt^{II} complexes (Table 3) are formed directly by (*cis*) elimination of H_2 from the Pt^{IV} compounds, then the $SnPh_3$ groups remain *trans* and the phosphines change from *cis* to *trans* for L = PMe_2Ph and PEt_3, whereas in the elimination from [$PtH_2(SnPh_3)_2$(diphos)], the $SnPh_3$ groups change from *trans* to *cis*.

EXPERIMENTAL

General.—All reactions were carried out under dry nitrogen. Solvents were dried and degassed before use.

Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 457 grating spectrometer. The n.m.r. spectra were recorded for hexadeuteriobenzene solutions (Pt^{IV} complexes) or dichlorodideuteriomethane solutions (Pt^{II} complexes) with tetramethylsilane as internal ^{1}H reference. The ^{1}H spectra of the Pt^{IV} compounds and ^{31}P{^{1}H} spectra were obtained with a JEOL PFT-100 Fourier transform spectrometer; trimethyl phosphite in hexadeuteriobenzene was the external ^{31}P reference.

Organotin Hydrides.—Triorganotin hydrides were prepared by treatment of the corresponding halides with lithium aluminium hydride in ether. Triphenyltin hydride was purified by vacuum distillation and *o*-tolyl, *p*-tolyl, and benzyl compounds by recrystallisation from methanol or aqueous methanol. The *m*-tolyl compound was obtained as an oil, and attempts to purify it by distillation led to decomposition, so the oil from the reduction was used directly.

Carbonatoplatinum Complexes.—The complexes [$Pt(CO_3)(PPh_3)_2$], [$Pt(CO_3)(PMePh_2)_2$], and [$Pt(CO_3)$(diphos)] were prepared as previously described.[7,13] The complexes [$Pt(CO_3)(PMe_2Ph)_2$] and [$Pt(CO_3)(PEt_3)_2$] were prepared analogously, as follows.

An excess of silver carbonate (15 g) (freshly prepared from silver nitrate and sodium carbonate in water, and dried after washing successively with water, ethanol, and acetone), was added to *cis*-[$PtCl_2(PMe_2Ph)_2$] (5·0 g) in dichloromethane (150 ml). The mixture was stirred with protection from light for 2 h and then filtered (Celite). The filtrate was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane–ether to give *carbonatobis(dimethylphenylphosphine)platinum*(II) (4·8 g, 90%) as colourless crystals, m.p. 160 °C; ν(C–O) 1615, 1635, and 1660 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): τ 2·5 (centre of phenyl resonance) and 7·26 [P–CH_3 group, ^2J(PCH) 11·6, ^3J(PtPCH) 17·3 Hz] (Found: C, 38·8; H, 4·3. $C_{17}H_{22}O_3P_2Pt$ requires C, 38·4; H, 4·0%).

Similarly prepared was *carbonatobis(triethylphosphine)platinum*(II) (55%), m.p. 160—170° (decomp.); ν(C–O) 1613, 1635, and 1660 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): complex multiplets centred at τ 8·1 and 8·9 (Found: C, 32·0; H, 6·4. $C_{13}H_{30}O_3P_2Pt$ requires C, 31·8; H, 6·15%).

Reactions between Carbonato-complexes and Triorganotin Hydrides.—(a) *In methanol.* In a typical reaction the tin hydride (4 molar proportions) was added to carbonato-complex (*ca.* 0·2 g) in methanol (5 ml) at room temperature. A gas was evolved and a solid separated which was filtered off after 30 min, washed with methanol and then several times with ether, and then dried under vacuum to give complexes [$PtH_2(SnR_3)_2L_2$]; yields, analytical data, and some physical parameters are given in Table 1. Ethanol was shown to be an equally satisfactory reaction medium.

From the reactions of Et_3SnH and Pr^i_3SnH with [$Pt(CO_3)(PMe_2Ph)_2$] only oils were obtained; these smelled of phosphine and exhibited ν(Pt–H) bands, but were not further characterised. The complex [$PtH_2(SnPh_3)_2$(diphos)] decomposed to [$Pt(SnPh_3)_2$(diphos)] (identical to an authentic sample, see below) upon attempted recrystallisation and its n.m.r. spectra could not be obtained. The crude material was characterised by i.r. spectroscopy and somewhat unsatisfactory analytical data (Table 1).

(b) *In benzene.* (i) These reactions provide convenient syntheses of the complexes [$Pt(SnR_3)_2L_2$]. A large excess of triphenyltin hydride was added to a stirred suspension of [$Pt(CO_3)$(diphos)] in benzene at room temperature. Addition of hexane to the homogeneous solution formed after 15 min gave 1,2-*bis(diphenylphosphino)ethanebis(triphenylstannyl)platinum*(II), m.p. 215 °C (Found: C, 56·9; H, 4·2. $C_{62}H_{54}P_2PtSn_2$ requires C, 57·6; H, 4·2%).

In the reaction of [$Pt(CO_3)(PMe_2Ph)_2$] with triphenyltin hydride the mixture was stirred overnight at room temperature. The solid formed was collected by filtration, washed with benzene and then ether, and dried under vacuum to give trans-*bis(dimethylphenylphosphine)bis(triphenylstannyl)platinum*(II), m.p. 175 °C (Found: C, 52·6; H, 4·6. $C_{52}H_{52}P_2PtSn_2$ requires C, 53·3; H, 4·5%). Similarly prepared were *bis(dimethylphenylphosphine)bis(tri-*p*-tolylstannyl)platinum*(II), m.p. 207—210 °C (decomp.) (Found: C, 55·6; H, 5·2. $C_{58}H_{64}P_2PtSn_2$ requires C, 55·1; H, 5·1%) and trans-*bis(triethylphosphine)bis(triphenylstannyl)platinum*(II), m.p. 175 °C (Found: C, 50·9; H, 5·5. $C_{48}H_{60}P_2PtSn_2$ requires C, 51·0; H, 5·4%).

The filtrate obtained during one preparation of *trans*-[$Pt(SnPh_3)_2(PMe_2Ph)_2$] was treated with light petroleum (b.p. 40—60 °C) and the solution was set aside for several days. The pale brown solid, m.p. 158—160 °C (yield 17%) was probably *bis(dimethylphenylphosphine)hydridotris(triphenylstannyl)platinum*(IV), ν(Pt–H) 2050 cm^{-1} (Found: C, 55·2; H, 4·4. $C_{70}H_{68}P_2PtSn_3$ requires C, 55·2; H, 4·5%).

(ii) When the reaction of triphenyltin hydride with [$Pt(CO_3)(PMe_2Ph)_2$] was interrupted by addition of hexane after the original suspension had given a clear yellow solution (*ca.* 15 min), a pale yellow solid separated. This was shown to be [$PtH_2(SnPh_3)_2(PMe_2Ph)_2$] by the identity of its i.r. spectrum with that of an authentic sample. A solution of the solid in the minimum amount of benzene

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[11] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

[12] A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 1958, 118.

[13] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.

was set aside overnight and the yellow precipitate which formed was filtered off and shown to be *trans*-$[Pt(SnPh_3)_2(PMe_2Ph)_2]$.

Miscellaneous Reactions forming $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$.—(*a*) Hydrogen was passed for 15 min through a suspension of *trans*-$[Pt(SnPh_3)_2(PMe_2Ph)_2]$ (0·05 g) in benzene. A small amount of residual solid was filtered off and the filtrate treated with hexane. The pale yellow precipitate formed (0·04 g) was collected and shown to be $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$ by the identity of its i.r. spectrum with that of an authentic sample.

(*b*) A concentrated solution of *trans*-$[PtHCl(PMe_2Ph)_2]$ in toluene was treated at 0 °C with triphenyltin hydride (4 molar proportions) and the solution was set aside at room temperature after gas evolution had subsided. Precipitation of a white solid, m.p. 175 °C, identified as $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$, was completed by addition of hexane.

(*c*) A suspension of *cis*-$[PtCl_2(PMe_2Ph)_2]$ in ethanol was treated with triphenyltin hydride (4 molar proportions). Following the evolution of gas, a pale yellow solid was filtered off and shown by i.r. spectroscopy to be a mixture of $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$ [ν(Pt–H) 2085 and 2110 cm^{-1}] and *cis*-$[PtCl_2(PMe_2Ph)_2]$ [ν(Pt–Cl) 288 and 307 cm^{-1} (authentic sample, 289 and 309 cm^{-1})].

(*d*) Triphenyltin hydride (0·8 g) was added to a stirred suspension of $[Pt(PMe_2Ph)_4]$ [5] (0·11 g) in ethanol (5 ml). Some evolution of gas occurred and after 3 h the mixture was filtered and the residue washed with ether to give a grey-yellow solid (0·15 g), m.p. 175 °C, shown to be mainly $[PtH_2(SnPh_3)_2(PMe_2Ph)_2]$ by i.r. spectroscopy [ν(Pt–H) 2085 and 2115 cm^{-1}].

Miscellaneous Reactions forming Pt^{II} *Complexes*.—(a) (i) Addition of triphenyltin hydride (0·047 g) to a mixture of $[Pt(C_2H_4)(PPh_3)_2]$ (0·1 g) and ether (5 ml) resulted in some gas evolution and the formation of a precipitate of cis-*hydridobis*(*triphenylphosphine*)(*triphenylstannyl*)-*platinum*(II) (0·07 g), m.p. 155—160 °C (decomp.), ν(Pt–H) 2055 cm^{-1} (Found: C, 59·05; H, 4·50. $C_{54}H_{46}PPtSn$ requires C, 60·56; H, 4·30%).

(ii) Triethyltin hydride (0·5 ml) was added dropwise to solid $[Pt(C_2H_4)(PPh_3)_2]$ (0·2 g). Following vigorous effervescence an orange-yellow paste remained. This was washed with hexane to give *bis*(*triethylstannyl*)*bis*(*triphenylphosphine*)*platinum*(II) as a pale yellow solid (0·1 g), m.p. 70—72 °C (Found: C, 51·1; H, 5·05. $C_{48}H_{60}P_2PtSn_2$ requires C, 50·96; H, 5·34%).

(b) *Reactions of triorganotin halides*. (i) Trimethyltin bromide (0·55 g) was added to $[Pt(CO_3)(PMe_2Ph)_2]$ (0·15 g) in ethanol (10 ml). The white precipitate was filtered off and dried and shown to be *cis*-$[PtBr_2(PMe_2Ph)_2]$, m.p. 200—203 °C (*lit.*,[14] 200—204 °C) (Found: C, 30·6; H, 3·9. Calc. for $C_{16}H_{22}Br_2P_2Pt$: C, 30·45; H, 3·5%). Its infrared spectrum was identical to that of an authentic sample. Triphenyltin chloride and triethyltin bromide reacted analogously with $[Pt(CO_3)(PPh_3)_2]$ and $[Pt(CO_3)(PMe_2Ph)_2]$ to give *cis*-dihalide complexes.

(ii) A mixture of triphenyltin chloride (0·145 g), $[Pt(CO_3)(PMe_2Ph)_2]$ (0·2 g), and benzene (15 ml) was refluxed for 5 h. A solid [possibly $(Ph_2SnO)_x$, ν(Sn–O) 575 and 552 cm^{-1} (lit.,[15] 571 and 553 cm^{-1})] was filtered off, and the filtrate evaporated. The residue was washed with hexane and dried, and identified as *trans*-$[PtClPh(PMe_2Ph)_2]$, m.p. 112—115 °C, ν(Pt–Cl) 275 cm^{-1}, ^{1}H n.m.r. (C_6D_6) τ 8·71 (t, PCH_3) [lit.,[16] m.p. 119—120 °C, ν(Pt–Cl) 274 cm^{-1}, ^{1}H n.m.r. ($CDCl_3$) τ 8·51 (t)] (Found: C, 45·5; H, 4·9. Calc. for $C_{22}H_{27}ClP_2Pt$: C, 45·25; H, 4·6%). Tri-*p*-tolyltin chloride similarly gave trans-*chlorobis*(*dimethylphenylphosphine*)(p-*tolyl*)*platinum*(II), m.p. 145—147 °C, ^{1}H n.m.r. τ 8·7 (t, PCH_3) (Found: C, 46·0; H, 4·9. $C_{23}H_{29}ClP_2Pt$ requires C, 46·2; H, 4·9%).

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