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Synthesis of 1,2-Bis(diphenylphosphino)ethane-bis-(trimethylstannyl)palladium(II) and Its Infrared Spectrum; the Infrared and Raman Spectra of 1,2-Bis(diphenylphosphino)ethane-bis-(trimethylstannyl)platinum(II)

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Abstract

The hitherto missing palladium complex $(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)_2$ has been successfully prepared by a simple method involving replacement of the chlorides in the complex $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ by Me_3Sn groups using neat trimethylstannane. The complex is more susceptible to decomposition in non-aqueous solution and less stable to thermolysis than its platinum analogue. The infrared spectra of the two complexes are compared. They show many similar features. The Raman spectrum and proton NMR spectra of the analogous platinum complex in deuterobenzene and in phosphorus tribromide are also reported. The spectra confirm the presence of platinum–tin bonds in the complex. In phosphorus tribromide the platinum complex decomposed giving trimethyltin(II)bromide and dimethyltin(II)dibromide. A possible reaction leading to the formation of dimethyltin(II)dibromide is proposed. Attempted synthesis of non-chelated palladium–tin complexes by oxidative addition of trimethylstannane to palladium(II) halides and palladium(0) complexes was unsuccessful.

Introduction

Although platinum is known to form several metal–metal bonded complexes with ligands of the type R_3M (R = alkyl or aryl; M = Si, Ge, Pb), similar complexes of palladium are relatively few and the best known are the germyl and plumbyl derivatives [1]. It has been a generally held view that palladium does not form complexes with organosilyl and organostannyl ligands as a result of the 'alternation effect' proposed by Phillips and Williams [2]. According to this hypothesis, palladium can form thermodynamically stable complexes only with carbon, germanium and lead. Although it is generally observed that complexes of palladium–group IVB elements are thermodynamically and kinetically less stable than the platinum analogues [1] there is insufficient convincing evidence to support the hypothesis. The more plausible explanation for the missing complexes in the palladium series, namely the silyl and stannyl complexes, is that there has not been enough effort made to prepare the missing members. Besides, complexes of palladium containing the $-Sn(OR)_3$ and $-Sn(OCPh_3)_3$ groups have been reported by Coulson and Sciwell [3], and those containing the $SnCl_3$ moiety are also known [4].

In this paper we report our attempts to prepare palladium(II)–organotin complexes containing chelating and non-chelating phosphine, arsine and thio ligands. We also report on the infrared spectrum of one of the palladium complexes we have successfully synthesised and compare it with that of its platinum analogue. We further report our attempts to obtain the Raman and ^1H NMR spectra of both complexes.

Experimental

Trimethyltin(II)hydride was prepared by established methods [5, 6]. The preparation of the 1,2-bis(diphenylphosphino)ethane-bis-(trimethylstannyl)-platinum(II) complex has been described [7, 8]. The preparation of the palladium–organotin complexes of the general formula $L_2Pd(SnR_3)$; ($L = Ph_3P$, Ph_3PCH_2-, Me_3As, and Et_2SCH_2-; R = Me, n-But) was attempted by two routes. One of the methods involved reacting palladium(II) halide directly with Me_3SnH. This method was attempted with the following halides which were available in analytically pure form. The other involved reacting the hydride with palladium(0) complexes.

(1) Reaction between $(EtSCH_2CH_2SEt)PdCl_2$ and Trimethylstannane (Me_3SnH)

Trimethylstannane (2.45 g, 14.8 mmol) was dissolved in pure dry and degassed benzene (5 cm^3) and the solution was condensed on to the palladium(II) halide (1.17 g, 3.7 mmol) at −196 °C in an evacuated break-seal tube. An excess of trimethylstannane was used in an attempt to drive the reaction to completion. When the reaction mixture was left to warm up to room temperature, a vigorous reaction ensued; a black mass and a mirror were immediately

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formed. The tube was opened to the vacuum line and the gaseous product (methane, 0.26 mmol) and other volatiles, which included $(Et_2SCH_2)_2$, unreacted Me_3SnH, benzene and tetramethylstannane were collected by trap to trap vacuum distillation. The black residue which was extracted several times with warm dry benzene, gave a dark red solution from which a sticky red polymeric material was isolated. Attempted recrystallisation from dichloroethane, dichloromethane, acetone (propanone), petroleum ether or absolute ethanol yielded no crystals from the red solid. The infrared spectrum of the red solid was recorded as a Nujol mull.

(2) Reaction between $(Ph_3P)_2PdCl_2$ and Me_3SnH

This reaction was attempted in the absence of a solvent. Neat trimethylstannane (0.93 g, 5.67 mmol) was condensed on the palladium complex (0.31 g, 0.442 mmol) in a break-seal tube as described in (1). No apparent change was immediately visible. The reaction mixture was kept at room temperature for one week. During this time a black solid was deposited. Opening the tube to the vacuum line gave hydrogen, methane and unreacted MeSnH as some of volatiles identified. The residue was extracted several times with dry benzene under an atmosphere of dry nitrogen. The extract gave a dark brown solution from which a brown powdery solid was recovered. The infrared spectrum of the powder showed bands which are characteristic of $\nu(CH_3)$ in the 3000–2800 cm^{-1} region and a band where the rock of the CH_3 of $Sn\text{-}CH_3$ occurs. Attempted recrystallisation from cyclohexane, acetone or ethanol resulted in further decomposition. Elemental analysis and mass spectrometry failed to establish conclusively the nature of the compound in the brown powder. Extracting the residue with THF and treating the extract with petroleum ether (40–60 °C) yielded the starting material $(Ph_3P)_2PdCl_2$.

(3) Reaction between $(Me_3As)_2PdBr_2$ and Me_3SnH

A solution of trimethylstannane (0.454 g, 2.77 mmol) was prepared in benzene (5 cm^3) and added to the palladium complex (0.31 g, 0.442 mmol) as described in (1). As the tube warmed to room temperature, some effervescence was observed which ceased after four days at room temperature. During this time a mirror was formed on the walls of the tube. On opening the tube to the vacuum line, Me_3As, Me_4Sn (GLC–mass spectrometric identification), hydrogen and trace CH_4 were collected. The residue was extracted as before and only Me_3SnBr was isolated.

(4) Reaction between $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ and Me_3SnH

A solution of trimethylstannane (0.5190 g, 3.15 mmol) in dry and degassed benzene (5 cm^3) was added to the palladium complex (0.0814 g, 0.141 mmol) as described in reaction (1). As the reaction mixture warmed up to room temperature, effervescence was observed and a light yellow solid was deposited after 4 days at room temperature. The tube was opened to the vacuum line fitted with a calibrated Töpler pump and hydrogen (4.48 cm^3) was collected.

The rest of the volatiles (unreacted trimethylstannane, benzene and Me_3SnCl) were isolated from the reaction mixture by trap to trap vacuum distillation. The light yellow solid was identified as $(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)_2$ (0.050 g). Melting point *c.* 130 °C (decomposed into a black powder). *Anal.* Found: C, 45.91; H, 4.94. Calc. for $(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)$: C, 46.16; H, 5.09%.

Attempted recrystallisation of the complex from solvents like THF, acetone, chloroform and dimethylformamide led to decomposition of the solid into a black mass.

(5) Reaction between $(Ph_3P)_4Pd$ and $n\text{-}But_6Sn_2$

Freshly prepared tetrakis(triphenylphosphino)palladium(0) [9] (0.629 g, 0.54 mmol) was added to $n\text{-}But_6Sn_2$ (0.31 g, 0.54 mmol) in benzene under dry and oxygen-free nitrogen. The mixture was stirred at room temperature for 30 min. At the end of this period no apparent change had occurred. The mixture was then refluxed for 2 h. The palladium complex dissolved and on cooling the solution to room temperature, a yellowish crystalline solid precipitated and was identified as unreacted starting material. Further work of the filtrate yielded only $n\text{-}But_6Sn_2$.

(6) Reaction between $(Ph_3P)_4Pd$ and Me_6Sn_2

Freshly prepared Me_6Sn_2 [5] was added to the palladium complex in the same ratios as in (5) and the same solvent. After refluxing for 2 h, only starting materials could be isolated from the reaction mixture.

(7) Reaction between $(Ph_3P)_4Pd$ and neat Me_3SnH

This experiment was attempted at three temperatures.

(a) At –78 °C

Trimethylstannane (0.7982 g) was condensed on the palladium complex (0.400 g) in a previously evacuated break-seal tube. The tube was transferred to a bath kept at –78 °C and left at this temperature for 2 days. At the end of this period no reaction had taken place.

(b) At 70 °C

The reaction was repeated and kept at this temperature for 2 days. A slow reaction was observed which lead to formation of a mirror on the walls of the break-seal tube. The tube was opened to the vacuum line and hydrogen (3.97 mmol) was collected via a

Tõpler pump system; the other volalite product was identified as tetramethylstannane (GLC and mass spectroscopy). Extraction of the black solid residue with hot benzene afforded a yellowish solid whose infrared and mass spectra indicated the presence of a Me_3Sn group but attempts to recrystallise the solid resulted in decomposition. No further analysis was carried out.

(c) At 120 °C

When the reaction was repeated at this temperature for the same duration as in (a) and (b) and for a shorter duration of 1 h, extensive decomposition occurred and some of the products isolated included H_2, CH_4, Me_4Sn, Ph_3P and palladium metal. No product containing Pd–Sn bonds was isolated.

Recording of the Spectra

The infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer as CsI, KBr discs or Nujol mulls. The Raman spectrum was recorded on a Cary 83 spectrophotometer with a Laxel Ion Laser, model 75. The ^1H NMR spectrum was recorded on a Brucker WH90 Fourier Transform spectrometer. The mass spectra were recorded with an AEIMS902 instrument.

Results and Discussion

As has been pointed out in 'Experimental', two routes to the palladium–stannyl complexes were attempted; interaction between trimethylstannane and palladium(II) halides and from zerovalent palladium complexes. The first method has been successfully used to prepare several monosilyl, monogermyl and monostannyl complexes of platinum(II) [1]. This route has also been successfully used to isolate optically active silyl complexes of platinum [10]. In both chelated and non-chelated platinum(II) chlorides it was observed that the reaction involves replacement of only one chloride by a group IVB moiety. The reaction is represented by the scheme below.

$$L_2PtCl_2 + R_3MH \longrightarrow L_2PtCl(MR_3) + HCl \qquad (1)$$

L = phosphine or arsine ligand; R = alkyl or aryl group; M = Si, Ge, Sn, Pb

However, reaction (1) has not been fully explored as a means of preparing the palladium analogues. We therefore decided to test a number of palladium(II) halides in an attempt to prepare complexes in which palladium is bonded to the trimethylstannyl group. Our investigations have shown that when palladium(II) chlorides or bromides, with non-chelating phosphine or arsine ligands, are treated with trimethylstannane in the presence or absence of a solvent, decomposition occurs even under very moderate temperatures. A number of unexpected products have been isolated from the decomposition reactions save the required complexes. We suspect that most of the observed decomposition products are formed by the catalytic action of the freshly deposited palladium metal.

When trimethylstannane was added to a suspension of the complex $(EtSCH_2CH_2SEt)PdCl_2$ in dry benzene in the absence of air, a rapid reaction took place in which the mixture turned from an orange suspension to a dark brown suspension and finally to a black mass with a palladium mirror. Work up of the reaction mixture yielded methane which is likely to come from the decomposition of trimethylstannane on the palladium mirror. This type of decomposition has been observed in a different kind of reaction [11]. The other compounds isolated included the free ligand $EtSCH_2CH_2SEt$ and a red sticky polymeric material which was shown by infrared spectroscopy to contain the Me_3Sn group. No definite palladium–stannyl complex was isolable. We suspect that the failure of this complex to give a definite palladium–tin bonded complex can be attributed to the inability of the sulphur atom to stabilise the palladium–tin bond by an inductive effect due to its low electronegativity which makes it less able to participitate in electron backdonation.

In a similar experiment, when trimethylstannane was reacted with $(Me_3As)_2PdBr_2$ in benzene decomposition again occurred rapidly with liberation of hydrogen, methane, Me_3As and other products which are not fully characterised. Again no product containing the palladium–tin bond could be isolated. On the other hand *trans*-$(Ph_3P)_2PdCl_2$ reacted slowly under similar conditions with the hydride, Me_3SnH, over a period of one week, to give methane in low quantity, hydrogen and a black mass. A dark brown solid was isolated from the black mass after extracting with benzene and although the infrared and the mass spectra indicated the presence of the trimethylstannyl group, attempts to purify it resulted in further decomposition. This reaction is in contrast with the behaviour of *trans*-$(Et_3P)_2PdCl_2$ towards trimethylgermane, Me_3GeH. From the latter reaction, *trans*-$(Et_2P)_2PdHCl$ was the main product isolated [12].

A stable *trans*-$(Ph_3P)_2PdCl(SnMe_3)$ or *trans*-$(Ph_3P)_2Pd(SnMe_3)_2$ was expected since such platinum complexes have been isolated and the triphenylphosphine is a strong π-acceptor ligand which helps to stabilise the metal–metal bond. This is another example of the low stability (kinetic or thermodynamic) of the palladium–group IVB complexes. We are of the view that palladium–stannyl complexes are much more difficult to isolate than the platinum analogues due to the stronger labilising effect of the Me_3Sn moiety which facilitates the decomposition reaction in the former.

When the reaction was repeated with the chelate complex, $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ at room temperature, no decomposition occurred which was rather surprising. Instead the reaction gave hydrogen and the complex $(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)_2$ which precipitated out of the reaction mixture as a pale yellow solid. As far as we know, this is the first palladium compound of this kind. The compound has been characterised in the same way as its platinum analogue whose spectroscopic properties are also reported here. The interesting feature of the reaction is the ease with which the two chlorides are displaced from the palladium atom by trimethylstannyl groups. We propose that the replacement of the two chlorides as opposed to one which is observed in the platinum complexes, is a reflection of the higher labile nature of the palladium complexes. The isolation of this complex also emphasises the significance of the 'chelate-effect'. The five-membered ring about the palladium atom is the least strained which enhances the overall stability of the complex in the thermodynamic sense. The absence of HCl in the volatile products and the isolation of hydrogen gas is probably due to the reaction between HCl and excess Me_3SnH which produces Me_3SnCl. The reaction which gives the complex can be represented by eqn. (2).

$$(Ph_2PCH_2CH_2PPh_2)PdCl_2 + (excess)Me_3SnH \longrightarrow \underset{\textbf{I}}{(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)} + H_2 + Me_3SnCl \qquad (2)$$

It is also interesting to note that complex I unlike its platinum analogue, does not form the six-coordinated palladium(IV) hydrido complex [7, 8]. This perhaps reflects the reluctance of palladium(II) to undergo oxidative addition to palladium(IV). Complex I was also found to be less stable to thermolysis than the platinum complex. Complex I decomposed at 130 °C whereas the platinum complex was found to be stable up to 200 °C for a period of three weeks [7].

The complex also showed a tendency to decompose in a number of solvents which made the recording of its ^{13}C and ^{1}H NMR spectra difficult. Like the platinum complex, it decolourised a solution of iodine in benzene but the reaction was accompanied by decomposition. However when reacted with a slight excess of hydrogen in benzene, it gave the dichloride $(Ph_2PCH_2CH_2PPh_2)PdCl_2$ which demonstrates that reaction (2) is reversible. A similar reaction is undergone by the platinum complex.

The infrared spectrum of complex I in CsI disc (Fig. 1) and of the platinum complex $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ in the same medium (Fig. 2) are identical save for the shift in the frequencies of the bands to the lower side in the spectrum of the palladium complex. It was not possible to obtain a Raman spectrum of complex I due to rapid decomposition in the laser beam even when the beam was defocused. However that of the platinum complex was recorded and is reproduced in Fig. 3. No meaningful polarisation studies were carried out as the complex has low solubility in most suitable

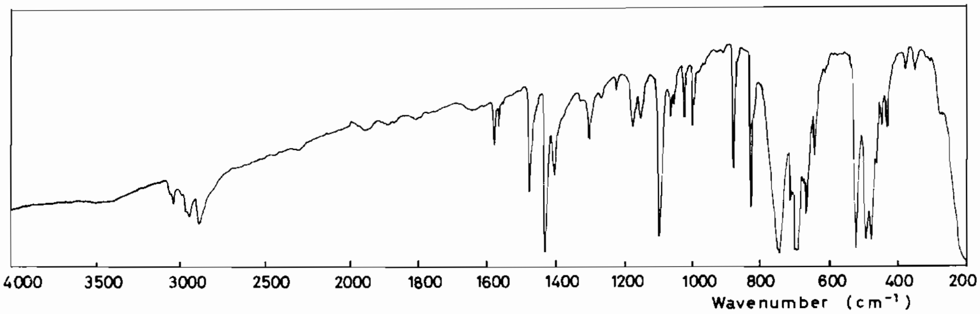

Fig. 1. The infrared spectrum of $(Ph_2PCH_2CH_2PPh_2)Pd(SnMe_3)_2$ in CsI disc.

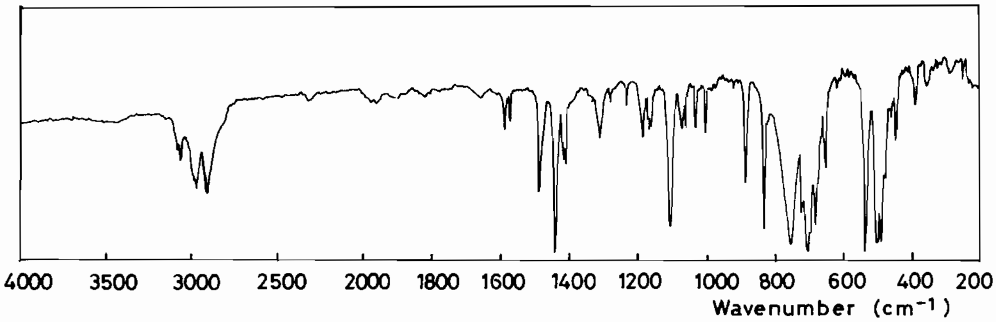

Fig. 2. The infrared spectrum of $(Ph_2CH_2CH_2PPh_2)Pt(SnMe_3)_2$ in CsI disc.

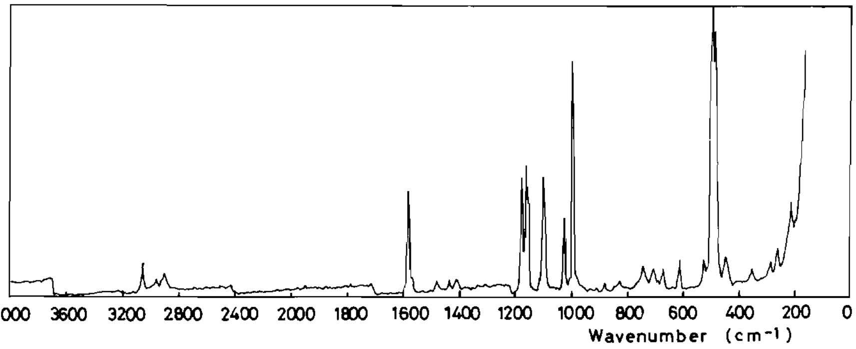

Fig. 3. The solid state Raman spectrum of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$.

solvents and in case of the chlorinated solvents the complex reacts, which makes the spectrum more complex.

The infrared spectra of the two complexes have several bands of varying intensities in the 1600–800 cm^{-1} region which are characteristic of the skeletal vibrations of the ligand $Ph_2PCH_2CH_2PPh_2$. Definite assignment in this region is difficult. In the Raman spectrum this region is less crowded and assignment is possible. It is observed that the strongest band in this region in the Raman spectrum is at 998 cm^{-1}. This band is characteristic of the phenyl ring vibrations. In the same spectrum a doublet (at 1179 cm^{-1} sharp, medium and 1160 cm^{-1}, medium) is assigned to $\rho(CH_3)$ of the $(CH_3)Sn$ group. This assignment is confirmed by the absence of the two bands in the Raman spectrum of $(Ph_2PCH_2CH_2PPh_2)PtCl_2$. The band at 758 cm^{-1} (broad, shoulder) in the infrared spectrum of the platinum complex and at 749 cm^{-1} in the spectrum of complex I is assigned to the CH_3 rock of the Sn–CH_3. This is considered to be one of the diagnostic bands for the $(CH_3)_3Sn$ group. In the Raman spectrum of the platinum complex it is at 742 cm^{-1}. The other important bands occur at 505 and 489 cm^{-1} in the infrared spectrum of the platinum complex and at 461 and 420 cm^{-1} in the spectrum of complex I. In the Raman spectrum the two bands are centred at 500 and 495 cm^{-1}, respectively and they are the strongest bands in the entire spectrum. The two bands are assigned to ν_a(Sn–C) and ν_s(Sn–C), respectively. By infrared spectroscopy alone unambiguous assignment is not possible due to the presence of other strong absorption bands in this region such as ν(Pt–P).

The presence of the Sn–C stretches in this region establishes fully the presence of Pt–Sn and Pd–Sn linkages. In tetramethylstannane, $SnMe_4$, which is assumed to have *Td* symmetry about the Sn atom, ν_a(Sn–C) occurs at 529 cm^{-1} in the infrared (liquid) and ν_s(Sn–C) is at 508 cm^{-1} [14]. If the difference between the absorption frequencies in the liquid and solid phases is assumed to be negligible, it can be inferred that the lowering of the two types of stretches when the $SnMe_3$ group is bonded to either palladium or platinum is due in part to a change in symmetry about the Sn atom from *Td* to C_{3v} and in part to the *trans* effect of palladium and platinum which reduces the force constant of the Sn–C bond. The other bands which are diagnostic of the $SnMe_3$ group are $\nu_a(CH_3)$ and $\nu_s(CH_3)$ which in the infrared spectra of the two complexes appear as two broad bands of weak to medium intensity at 3062 and 2970 cm^{-1}, respectively for the platinum complex and at 2970 and 2890 cm^{-1}, respectively for the palladium complex. They can be differentiated from the ν_a and ν_s of Pt–CH_3 and Pd–CH_3 by the band pattern [1]. In the Raman spectrum the two bands are of diminished intensity.

Difficulty was experienced in recording the ^{1}H NMR spectrum of complex I due to reasons already given. However the spectrum of the platinum complex [13] was re-examined using a spectrometer with higher resolution and at a frequency of 90 MHz with a view to establishing the presence or total absence of the long range coupling $^4J(^{31}P\text{–}H)$ which had not been observed by Clemit. The spectrum was recorded in deutero-benzene and was found to be similar to that recorded in the same solvent at 60 MHz. The CH_3 resonance appears as a triplet centred at 9.60 τ in the intensity ratio of 1:4:1. The triplets are flanked by the ^{117}Sn and ^{119}Sn satellites; $^2J(^{119}Sn\text{–}H)$, 39.2 Hz; $^2J(^{117}Sn\text{–}H)$, 30.0 Hz. The triplet arises from the coupling of Pt–H, $^3J(^{195}Pt\text{–}H)$, 8.54 Hz. It is still puzzling as to why this compound does not show the phosphorus–proton coupling when such coupling has been observed in the monostannyl complex, $(Ph_2PCH_2CH_2PPh_2)Pt(C{\equiv}CPh)(SnMe_3)$ and the spectra of the corresponding silyl complexes [7].

When the spectrum was recorded in anhydrous phosphorus tribromide the platinum-195 satellite disappeared which indicated cleavage of the platinum–tin bonds (Fig. 4). Precipitation occurred and after filtering the solution, two distinct signals flanked by tin-117 and tin-119 satellites appeared. The two signals (Fig. 4) are assigned to Me_3SnBr

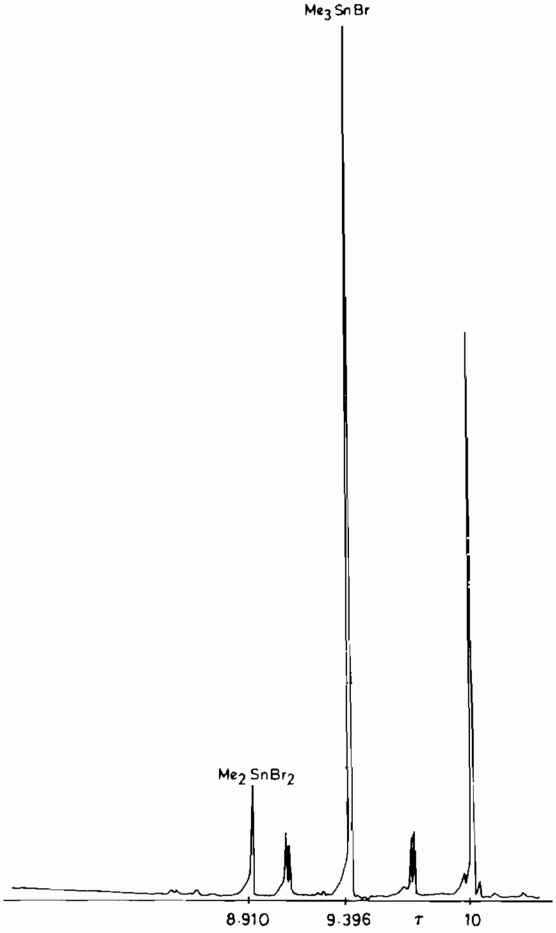

Fig. 4. ^{1}H NMR spectrum of $(Ph_2PCH_2CH_2PPh_2)Pt(SnMe_3)_2$ in phosphorus tribromide.

($\tau = 9.40$); $^2J(^{119}Sn–H)$, 56.6 Hz; $^2J(^{117}Sn–H)$, 54.4 Hz and tentatively to Me_2SnBr_2 ($\tau = 8.90$); $^2J(^{119}Sn–H)$, 66.4 Hz; $^2J(^{117}Sn–H)$, 61.04 Hz.

The signal due to Me_2SnBr_2 is weak which is indicative of its low concentration in the solution; however its formation is surprising and not fully understood. We suspect it is probably a bromide–methyl exchange of the type

$$PBr_3 + Me_3SnBr \longrightarrow MePBr_2 + Me_2SnBr_2 \qquad (3)$$

Further work is planned to study the origin of the second signal which we have tentatively assigned to Me_2SnBr_2 since the signal due to MePBr appears to be absent from the spectrum.

The second method we investigated as a possible means of preparing palladium–stannyl complexes was to start with palladium(0) complexes. As it turned out this route has not been as successful as was hoped. It is well known that platinum(0) complexes undergo dissociative-oxidative addition when reacted with R_3MH and R_6M_2 compounds under very mild conditions (R = alkyl or aryl group; M = group IVB element) giving $L_2Pt(MR_3)_2$ complexes [1]. By analogy palladium(0) was expected to behave the same way. It has turned out that with the palladium(0) complexes we have so far examined, the expected products are not isolated. The reactions attempted have shown that palladium(0) complexes containing non-chelating phosphine ligands are inert to R_6Sn_2 (R = n-But or Me) and are decomposed by Me_3SnH at slightly elevated temperatures. It was initially suspected that lack of reaction between n-But_6Sn_2 and tetrakis(triphenylphosphino)palladium(0) was due to steric hinderance arising from the bulkiness of the butyl group. However lack of reaction with Me_6Sn_2 which is much less bulky showed that if steric factors play any role in these reactions, it is only a minor one. The major decomposition products from the reaction between $(Ph_3P)_4$-Pd and Me_3SnH were hydrogen, methane and tetramethylstannane which are believed to be formed by the catalytic action of the freshly deposited palladium metal as has been observed elsewhere [11]. These investigations appear to strengthen the view that palladium–stannyl complexes are less easy to prepare than the corresponding platinum complexes. We attribute the difference in behaviour largely to the different sizes of the two elements.

Acknowledgements

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