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THE SYNTHESIS OF (TRIMETHYLSTANNYL)PHOSPHINE: THE OBSERVATION OF PHOSPHORUS–TIN NUCLEAR SPIN–SPIN COUPLING

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SUMMARY

(Trimethylstannyl)phosphine, $(CH_3)_3SnPH_2$, has been prepared in high yield by the reaction of $LiAl(PH_2)_4$ with $(CH_3)_3SnCl$. The product has been characterized by elemental analysis, ^1H and ^{31}P NMR, IR, and mass spectral data. Reactions between $(CH_3)_3SnPH_2$ and acidic reagents have been studied. The first measurement of $^1J(Sn{-}P)$ has been made.

INTRODUCTION

Compounds containing tin–phosphorus bonds have been reported previously; however, in every case the compounds have been substituted with organo-substituents on both the tin and phosphorus atoms[1-3]. During the course of our studies of the phosphination of Group IV halides[4,5], we have prepared the first example of a PH_2-substituted tin compound, $(CH_3)_3SnPH_2$. Besides being a compound with potentially interesting chemical properties, it appears to be the first example of a molecule in which nuclear spin–spin coupling between directly bonded tin and phosphorus has been observed. The preparation and properties of this new phosphino–tin compound and the measurement of $^1J(^{117}Sn{-}^{31}P)$ and $^1J(^{119}Sn{-}^{31}P)$ are the subject of this report.

RESULTS AND DISCUSSION

Synthesis and properties of (trimethylstannyl)phosphine

Trimethyltin chloride and $LiAl(PH_2)_4$ react at −30° in triglyme to form $(CH_3)_3SnPH_2$ in good yield according to eqn. (1). Trimethylstannane and PH_3 are

$$4(CH_3)_3SnCl + LiAl(PH_2)_4 \rightarrow LiCl + AlCl_3 + 4(CH_3)_3SnPH_2 \qquad (1)$$

also obtained from the reaction. The former apparently arises due to reduction of $(CH_3)_3SnCl$ by residual Al–H containing species in the $LiAl(PH_2)_4$ solutions. However, the reaction(s) by which PH_3 is formed has not been established at the present time.

The characterization of $(CH_3)_3SnPH_2$ is based on data obtained from elemental analysis, infrared, ^1H and ^{31}P NMR, and mass spectra. Since $(CH_3)_3SnPH_2$ is thermally unstable and air-sensitive, elemental analysis was accomplished by quantitative measurement in the vacuum system of the products of HCl-cleavage reactions. The mass spectrum of $(CH_3)_3SnPH_2$ exhibits the expected fragmentation pattern. The presence of a molecular ion at *m/e* 202 $[(CH_3)_3{}^{124}SnPH_2^+]$ provides confirmation of the molecular weight and compound stoichiometry.

The infrared spectrum shows several prominent absorptions which can be assigned. The absorptions at 2975 and 2910 cm^{-1} can be attributed to CH_3 group C–H stretching modes[6] and the strong absorptions at 2285 cm^{-1} are clearly characteristic of PH_2 group P–H stretching vibrations[6,7]. In addition, tentative assignments of the absorptions at 1058 and 772 cm^{-1} to PH_2 deformation and CH_3 rocking modes, respectively, appears reasonable.

TABLE 1

NUCLEAR MAGNETIC RESONANCE PARAMETERS FOR $(CH_3)_3SnPH_2$[a]

Measurement	Value	Measurement	Value
Coupling constant data (Hz)			
$^1J(^{117}$Sn–P)	443 ± 3^b	^1J(P–H)	169.5 ± 0.5
$^1J(^{119}$Sn–P)	463 ± 3^b	^3J(P–Sn–C–H)	1.60 ± 0.1
$^2J(^{117}$Sn–P–H)	60.0 ± 0.3	$^2J(^{117}$Sn–C–H)	53.6 ± 0.3
$^2J(^{119}$Sn–P–H)	62.5 ± 0.3	$^2J(^{119}$Sn–C–H)	55.7 ± 0.3
$^1J(^{13}$C–H)	130 ± 0.3		
Chemical shift data (ppm)			
$\delta(PH_2)$	-1.00 ± 0.02^c		
$\delta(CH_3)$	-4.22 ± 0.02^c		
$\delta(^{31}P)$	$+269 \pm 2^{b,d}$		

[a] Data from ^1H NMR spectrum unless noted otherwise. Recorded in tetramethylsilane (ca. 50% solution). [b] Obtained from ^{31}P spectrum of neat sample. [c] Chemical shifts relative to internal $(CH_3)_4Si$. [d] Chemical shift relative to external 85% H_3PO_4.

The ^1H and ^{31}P NMR spectral data provide final confirmation for the formulation of $(CH_3)_3SnPH_2$. Spectral parameters are given in Table 1. Doublets at δ −4.22 ppm and δ −1.00 ppm in the proton spectrum of relative area 9.00/2.04 are assigned readily to the CH_3 and PH_2 protons, respectively. The ^{31}P NMR spectrum (Fig. 1) exhibits the expected widely spaced 1/2/1 triplet [^1J(P–H)] in which each triplet member appears as ten lines in the binomial intensity distribution [^3J(P–Sn–C–H)].

In addition to the main triplet resonance shown in the ^{31}P NMR spectrum (relative intensity 83.9%), twelve symmetrically distributed satellite peaks, b and b′ (relative intensity 16.1%) are clearly evident. The main triplet observed in the spectrum corresponds to the PH_2 resonance of $(CH_3)_3SnPH_2$ molecules containing non-spin tin isotopes (83.65% natural abundance). The satellite peaks, which appear as two doublets of triplets, arise from molecules containing ^{117}Sn (7.67%) and ^{119}Sn (8.68%). From the satellite spectrum, absolute values of $^1J(^{117}Sn-^{31}P)$ and $^1J(^{119}Sn-^{31}P)$ of 443±2 Hz and 463±2 Hz, respectively, are obtained. The signs of the coupling constants were not determined in this study. The ratio of $^1J(^{119}$Sn–P$)/^1J(^{117}$Sn–P)

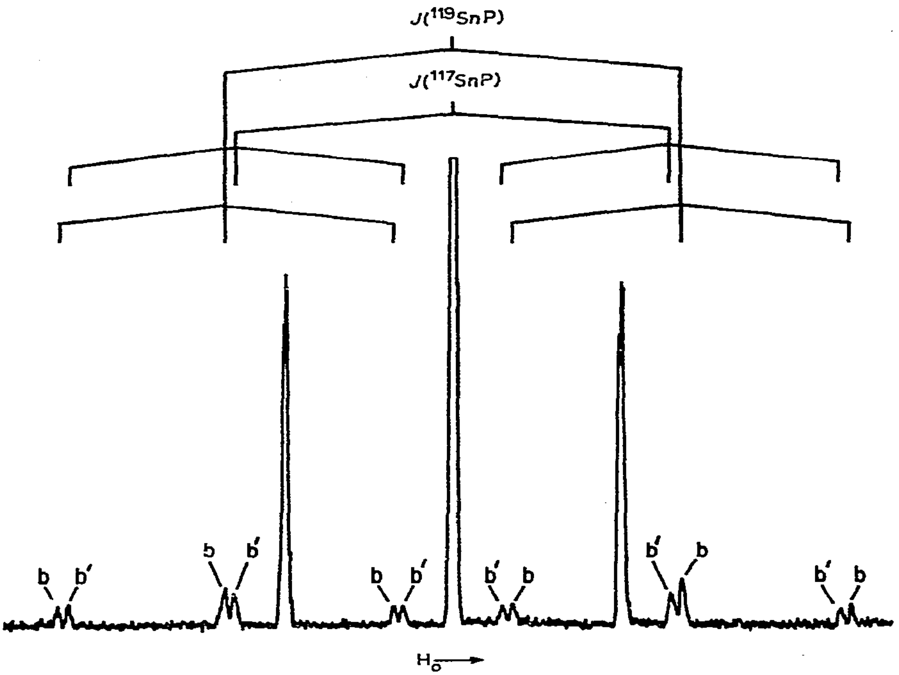

Fig. 1. The ^{31}P NMR spectrum of $(CH_3)_3SnPH_2$ showing the main triplet resonance and the ^{119}Sn (b) and ^{117}Sn (b′) satellite peaks.

measured here is found to be 1.045 in good agreement with the value of 1.046 expected from the ratio of gyromagnetic ratios. Although a variety of coupling constants between phosphorus and a variety of directly bonded nuclei have been reported[8], this appears to be the first system in which phosphorus–tin one-bond coupling has been observed.

(Trimethylstannyl)phosphine is a colorless, low-volatility liquid which reacts rapidly with air and water. The compound has a very strong odor and probably is extremely toxic. It decomposes slowly at room temperature, yielding PH_3 and very-low-volatility products. In view of the stoichiometry of the decomposition, the isolation of a small quantity of $[(CH_3)_3Sn]_2PH$, and analogy with previously studied silyl- and germyl-phosphine systems[1,2], it is proposed that the thermal decomposition is a disproportionation reaction as shown in eqn. (2). Formation of $[(CH_3)_3Sn]_3P$ undoubtedly involves intermediate formation of $[(CH_3)_3Sn]_2PH$.

$$3(CH_3)_3SnPH_2 \rightarrow [(CH_3)_3Sn]_3P+2\ PH_3 \qquad (2)$$

Acidic reagents react with $(CH_3)_3SnPH_2$ to effect cleavage of the tin–phosphorus bond. Reaction with HCl yields $(CH_3)_3SnCl$ and PH_3 quantitatively [eqn. (5)]. Reaction with BCl_3 below $-78°$ appears to yield an adduct $(CH_3)_3SnPH_2 \cdot BCl_3$ [eqn. (3)] which decomposes rapidly at higher temperatures forming $(CH_3)_3SnCl$ and an intractable polymer [eqn. (4)]. Analogous reactions for silyl- and germyl-phosphines are well known[1,2].

$$n(CH_3)_3SnPH_2+n\ BCl_3 \rightarrow [n(CH_3)_3SnPH_2\cdot BCl_3] \qquad (3)$$

$$[n(CH_3)_3SnPH_2 \cdot BCl_3] \rightarrow \frac{1}{n}(PH_2BCl_2)_n + n(CH_3)_3SnCl \qquad (4)$$

Further studies of the chemistry of $(CH_3)_3SnPH_2$ are in progress and will be reported later.

EXPERIMENTAL

Apparatus

All manipulations were performed using standard high-vacuum apparatus. Infrared spectra were obtained using a Perkin–Elmer Model 337 spectrophotometer. Mass spectra were measured with a Varian MAT CH-5 spectrometer. Proton nuclear magnetic resonance spectra were obtained on a Varian Associates A-60A spectrometer. Phosphorus-31 nuclear magnetic resonance data were obtained using a Varian HA-100 spectrometer equipped with standard 40.5 MHz probe and r.f. unit accessories. Spectra were obtained in the HR mode and were calibrated using the audio-frequency integrator side bands. This calibration was verified by comparing the value for $^1J(P\text{–}H)$ obtained from the ^{31}P spectrum with that obtained from the ^1H spectrum.

Materials

Trimethyltin chloride (Alfa Inorganics, Beverly, Massachusetts), BCl_3, HCl, and PH_3 (Matheson Company, East Rutherford, New Jersey) were purified by routine fractional condensation. Lithium tetrahydroaluminate ($LiAlH_4$) was recrystallized from diethyl ether and stored under dry nitrogen. Triglyme [1,2-bis(2-methoxyethoxy)ethane] was distilled at reduced pressure from $LiAlH_4$.

Preparation of lithium tetraphosphinoaluminate

The $LiAl(PH_2)_4$ solutions were prepared from the reaction of PH_3 with $LiAlH_4$ in triglyme during 96 h in a manner similar to that described previously[4,5,9]. Based on the quantity of PH_3 which was consumed in this reaction the percent conversion of $LiAlH_4$ to $LiAl(PH_2)_4$ was determined. In this study, solutions were used in which at least 92% conversion had been achieved.

(Trimethylstannyl)phosphine

In a typical reaction, $(CH_3)_3SnCl$ (10.1 mmoles) was condensed at −196° into a 1-liter bulb which contained 2.62 mmoles of $LiAl(PH_2)_4$ in 10 ml of triglyme. The reaction was allowed to proceed by slowly warming the reactants to −30° for 20 min and room temperature for 5 min. Upon completion of the reaction, volatile materials (excepting bulk triglyme) were pumped into the vacuum line and separated by repeated fractional condensation through a series of traps maintained at 0, −45°, −95° and −196°. The −160° trap contained PH_3 (0.87 mmoles), the −95° trap contained $(CH_3)_3SnH$ (0.66 mmoles; confirmed by IR spectrum), and the 0° trap condensed triglyme solvent. The −45° trap collected $(CH_3)_3SnPH_2$, (1.220 g, 6.21 mmoles, 62% yield). The 0° vapor tension of $(CH_3)_3SnPH_2$, is 1.0 ± 0.2 mm. Owing to the thermal instability of $(CH_3)_3SnPH_2$, vapor pressure *vs.* temperature data were not obtained.

Characterization of (trimethylstannyl)phosphine

Elemental analysis of $(CH_3)_3SnPH_2$ was accomplished by allowing a weighed sample (2.04 mmoles) to react with anhydrous HCl (3.52 mmoles). After 15 min at room temperature the reaction mixture was separated and found to consist of PH_3 (1.96 mmole; confirmed by IR and mass spectra), unreacted HCl (1.52 mmoles) and $(CH_3)_3SnCl$ (2.01 mmoles, confirmed by IR, ^1H NMR spectra). The ratio of $(CH_3)_3SnPH_2/HCl/(CH_3)_3SnCl/PH_3$ according to the reaction (5) is calcd., 1.00/1.00/1.00/1.00; found, 1.04/1.02/1.02/1.00.

$$(CH_3)_3SnPH_2 + HCl \rightarrow (CH_3)_3SnCl + PH_3 \tag{5}$$

The mass spectrum of (trimethylstannyl)phosphine exhibits peak envelopes which can be assigned to CH_x^+, PH_x^+, CH_xSn^+, $C_2H_xSn^+$, $C_3H_xSn^+$, and $C_3SnPH_x^+$ ion fragments. The highest-mass peak in the spectrum occurs at *m/e* 202 and can be assigned to the $(CH_3)_3{}^{124}SnPH_2^+$ molecular ion. The parent peak at *m/e* 202 is 1.1% as intense as the 100% peak at *m/e* 165, corresponding to $(CH_3)_3{}^{120}Sn^+$.

The infrared spectrum of $(CH_3)_3SnPH_2$ in the range 4000–400 cm^{-1} was obtained on a gaseous sample in a 10-cm cell equipped with KBr windows. The spectrum exhibits absorptions at 2975 (m), 2910 (m), 2285 (s), 1600 (w, br), 1315 (w, br), 1195 (m), 1135 (w), 1058 (w), 800 (m, sh), 772 (vs), 721 (w, sh), 591 (w) and 528 (vs) cm^{-1}.

Thermal decomposition of (trimethylstannyl)phosphine

A 1.53 mmole sample of $(CH_3)_3SnPH_2$ was allowed to stand at ambient temperature (24–27°) for 19 h. Slight effervesence from the liquid was evident during this time. Upon completion of the reaction the volatile materials were removed and separated. Phosphine (0.96 mmole; confirmed by IR spectrum), unreacted $(CH_3)_3SnPH_2$ (ca. 0.05 mmole) and a trace of a very low volatility liquid (I) was obtained. An involatile oil remained in the reaction vessel and it was not studied further. The mass spectrum of (I) showed it to be $[(CH_3)_3Sn]_2PH$, contaminated with a small amount of $(CH_3)_3SnPH_2$.

(Trimethylstannyl)phosphine/boron trichloride

(Trimethylstannyl)phosphine (1.61 mmoles) and BCl_3 (1.81 mmoles) were condensed at −196° into a reaction vessel and allowed to warm slowly to −78°. A white solid formed, which appeared to be decomposing slowly at −78°. The reactants were warmed to room temperature over 5 min. Upon completion of the reaction, volatile reaction materials were removed, separated and found to consist of $(CH_3)_3SnCl$ (1.40 mmoles; confirmed by mass spectrum) and BCl_3 (0.20 mmole; confirmed by IR spectrum). An intractable solid which remained in the reactor was not analyzed further.

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