*Inorganica Chimica Acta, 161* (1989) 105–111

# NMR Investigation of Diorganoyltin(IV)dihalide Complexes with Secondary Phosphines and Diorganoylphosphino-*N*-phenyl(thioformamido) Ligands

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(Received January 27, 1989)

## Abstract

Phosphorus-31 and tin-119 NMR spectroscopies have been used to study the formation of a series of organoyltin(IV)phosphine and phosphido complexes $R_2SnX_2(HPR'_2)$, $R_2SnX(PR'_2)$ and $R_2Sn(PR'_2)_2$ (where R = Ph, Me, Bu; R′ = c-$C_6H_{11}$, Ph; X = Cl, Br) in dichloromethane solution. Tin-119 chemical shifts indicate that $R_2Sn(PR'_2)_2$ are four coordinate whereas $R_2SnX_2(HPR'_2)$ and $R_2SnX(PR'_2)$ are five coordinated, the latter probably being dimeric via bridging halides. PhNCS inserts into the Sn–P bonds of $R_2SnX(PR'_2)$ and $R_2Sn(PR'_2)_2$ to give the new series of tin compounds $R_2SnX[R'_2PC(S)NPh]$ and $R_2Sn[R'_2PC(S)NPh]_2$ where ligand coordination is through the sulphur and nitrogen atoms resulting respectively, in five and six coordination about the tin atom. The series $R_2SnX[R'_2PC(S)NPh]$ and $R_2Sn[R'_2PC(S)NPh]_2$ may also be generated by reaction between diorganophosphino-*N*-phenyl(thioformamide) ligands, $R'_2PC(S)N(H)Ph$ and diorganoyltin(IV)dihalides; ligand deprotonation is spontaneous in one case (for $Ph_2SnX[(c\text{-}C_6H_{11})_2PC(S)NPh]$) whereas addition of base is necessary to generate the other members of the series.

## Introduction

The interactions between organoyltin(IV)halide compounds, $R_nSnX_{4-n}$ ($n$ = 1–3), with tertiary phosphines have been well documented and the general reaction is one of simple adduct formation leading to an increase of coordination number about the tin atom [1–4]. Fewer studies have appeared involving the use of secondary phosphines instead of tertiary phosphines. Reactions with secondary phosphines are interesting because of the further reactions, beyond simple adduct formation, that are possible. These reactions should also be dependent on the Lewis acidity of the initial organoyltin(IV)halide used. For example, $Ph_3SnCl$ does not form a simple adduct with $HPR'_2$ but does form phosphido compounds in the presence of a suitable Brönsted base [5]. Furthermore, the tin–phosphorus bonds in such compounds may undergo insertion reactions with 1,2-dipolar molecules such as $CS_2$ and PhNCS leading to formation of either a tin–sulphur or a tin–nitrogen bond [6]. Relevant to these complexes formed by insertion of a small molecule into an existing tin–ligand bond are diorganophosphino-*N*-phenyl(thioformamide) ligands, $R_2PC(S)N(H)Ph$, which usually coordinate through the phosphorus atom [7, 8] whereas deprotonated forms of the ligands are potentially mono- or bidentate or bridging ligands which may involve phosphorus, sulphur or nitrogen as donor atoms [9–11].

We have extended our studies of triorganoyltin(IV)halide with secondary phosphines and diorganophosphino-*N*-phenyl(thioformamide) ligands [12, 13] and now report the results of our studies of diorganoyltin(IV)dihalides with these ligands.

## Experimental

NMR spectra were generally recorded with broad band decoupling on a JEOL FX 100 spectrometer, phosphorus-31 at 40.26 MHz and tin-119 at 37.08 MHz using an external $^7Li$ lock. Phosphorus-31 spectra were referenced against external 85% $H_3PO_4$ and tin-119 against external $Me_4Sn$. Temperatures were maintained using a JEOL 5471 controller. Infrared spectra were recorded using a Perkin-Elmer 457 Grating Infrared Spectrometer. Elemental analyses were carried out by AMDEL, Port Melbourne, Australia.

Reactions were carried out under a dry argon atmosphere. Dicyclohexylphosphine, $HP(c\text{-}C_6H_{11})_2$, dbu (1,8-diazabicyclo(5.4.0)undec-7-ene), $Ph_4Sn$ and $Bu_2SnCl_2$ were purchased from commercial sources

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0020-1693/89/$3.50

and used without further purification. Diphenylphosphine, $HPPh_2$, was prepared from triphenylphosphine [14]. The compounds $Ph_2SnCl_2$ and $Ph_2SnBr_2$ were prepared from redistribution reactions between $Ph_4Sn$ and the appropriate tin(IV)tetrahalide [15]. The ligands dicyclohexylphosphino-*N*-phenyl(thioformamide) and diphenylphosphino-*N*-phenyl(thioformamide) were prepared by literature methods [16]. The adducts $R_2SnCl_2[HPPh_2]$ and $R_2SnX_2[HP(c\text{-}C_6H_{11})_2]$ were not isolated but were prepared *in situ* from the appropriate diorganoyltin(IV)dihalide and phosphine. The compounds $Ph_2SnX(PPh_2)$ (X = Cl, Br) $Me_2SnCl(PPh_2)$ and $R_2SnX[P(c\text{-}C_6H_{11})_2]$ (X = Cl, Br; R = Me, Bu) (excluding $Bu_2SnBr[P(c\text{-}C_6H_{11})_2]$) were made *in situ* by reacting equimolar quantities of diorganoyltin(IV)dihalide, phosphine and dbu. Compounds of the type $R_2Sn(PR'_2)_2$ (R' = Ph, c-$C_6H_{11}$) were prepared similarly but using two mole equivalents of base ($Et_3N$ or dbu). Alternatively, these compounds may be prepared by addition of phosphine and dbu to $R_2SnX(PR'_2)$. Isolation of the complexes $Ph_3Sn(PPh_2)$ and $Ph_2Sn(PPh_2)_2$ have been described previously [17].

## Results and Discussion

### *Reactions of $R_2SnX_2$ with $HP(c\text{-}C_6H_{11})_2$*

The room temperature $^{31}P$ spectrum of a dichloromethane solution containing equimolar proportions of $HP(c\text{-}C_6H_{11})_2$ and $Ph_2SnCl_2$ contains a single broad resonance near $-20$ ppm. At $-70$ °C the spectrum sharpens and a single resonance, with clearly resolved tin-119 and tin-117 satellites, is observed at 14.0 ppm. The proton-coupled $^{31}P$ spectrum comprises a doublet, $J$(P–H) 390 Hz. The $^{119}Sn$ spectrum consists of a doublet at $-296$ ppm [$J$(Sn–P) 710 Hz]. Addition of a further mole equivalent of $HP(c\text{-}C_6H_{11})_2$ causes the resonances to broaden. At $-95$ °C the $^{31}P$ spectrum again sharpens and comprises a resonance with broad tin satellites at $\delta(^{31}P)$ 13.5 ppm and a resonance at the position of uncoordinated phosphine. The $^{119}Sn$ spectrum at $-95$ °C shows only one, very broad, doublet resonance at $-297$ ppm [$J$(Sn–P) 700 Hz]. These NMR spectra are consistent with the formation of a 1:1 adduct, $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$. Addition of amounts of phosphine above that required for formation of the 1:1 adduct induce rapid intramolecular phosphine exchange but there is no evidence for formation of a 1:2 adduct. Diphenyltin(IV)dibromide reacts similarly with $HP(c\text{-}C_6H_{11})_2$, forming only the 1:1 adduct, $Ph_2SnBr_2[HP(c\text{-}C_6H_{11})_2]$.

The $^{31}P$ spectrum of a dichloromethane solution at $-70$ °C containing $Ph_2SnCl_2$, $Ph_2SnBr_2$ and $HP(c\text{-}C_6H_{11})_2$ in 1:1:2 molar proportions shows three resonances of approximate relative intensities 1:2:1 (each accompanied by tin satellites). The outermost resonances are identified by their chemical shift and coupling constant values as due to $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ and $Ph_2SnBr_2[HP(c\text{-}C_6H_{11})_2]$, whilst the central resonance is assigned to the mixed halide species $Ph_2SnClBr[HP(c\text{-}C_6H_{11})_2]$. The $^{119}Sn$ spectrum at this temperature consists of three doublets of relative intensities 1:2:1 and confirms the assignment made from the $^{31}P$ spectrum. These observations indicate not only that halide exchange can be slowed on the NMR time scale but also that these adducts must be considered as essentially five coordinate in solution at low temperature. The similarity of the NMR parameters for the chloro and bromo adducts is in accordance with the phosphine occupying an equatorial position of a trigonal bipyramid [1].

Dimethyltin(IV)dichloride, $Me_2SnBr_2$, and $Bu_2SnCl_2$ react similarly with $HP(c\text{-}C_6H_{11})_2$ to form 1:1 adducts in dichloromethane solution. In each case the spectra were recorded below $-70$ °C in order to slow intermolecular phosphine exchange. In each case the proton-coupled $^{31}P$ spectra show $J$(P–H) (Table 1). In contrast to the aryl analogues, halide exchange cannot be slowed sufficiently to allow observation of mixed-halide species for the alkyl derivatives. A dichloromethane solution containing an equimolar proportion of $Bu_2SnBr_2$ and $HP(c\text{-}C_6H_{11})_2$ has a single, very broad, $^{31}P$ resonance near $-40$ ppm. The corresponding $^{119}Sn$ spectrum contains a very broad singlet near $-204$ ppm (cf. 93 ppm for $Bu_2SnBr_2$). Although cooling to $-100$ °C does not slow intermolecular phosphine exchange sufficiently to permit observation of Sn–P coupling, the change in $^{119}Sn$ chemical shift neverless implies the formation of a 1:1 adduct, albeit a particularly labile one.

### *Reactions of $R_2SnX_2$ with $HP(c\text{-}C_6H_{11})_2$ and Base*

Dicyclohexylphosphine is itself not deprotonated by the base dbu. However $Ph_2SnCl_2$ and $Ph_2SnBr_2$ both react with dbu; the $^{119}Sn$ spectra of these solutions contain a variety of singlet resonances in the region $-200$ to $-500$ ppm, the intensities being dependent on the concentration of added dbu. The species in solution are probably partially hydrolysed species similar to 'ladder complexes' which have previously been described [18]. In the case of $Ph_2SnCl_2$ one of these products was isolated and characterised by its infrared spectrum and microanalyses as $[Ph_4Sn_2O(OH)_2]_2$ (Calc. C, 48.32; H, 3.99. Found C, 48.94; H, 4.08%).

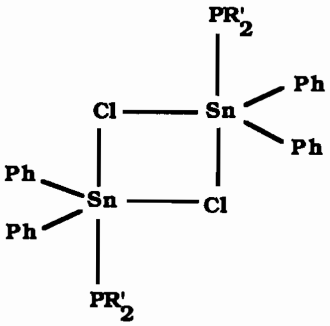
The $^{31}P$ spectrum of a dichloromethane solution at $-20$ °C containing equimolar quantities of $HP(c\text{-}C_6H_{11})_2$ and $Ph_2SnCl_2$ to which dbu had been added shows a resonance at 13.9 ppm with clearly defined tin-119 and tin-117 satellites and a resonance at the chemical shift position for uncoordinated $HP(c\text{-}C_6$-

TABLE 1. Phosphorus-31 and tin-119 NMR data for organoyltin(IV)phosphine and phosphido complexes in dichloromethane solution

| Species | $\delta(^{31}P)$ | $\delta(^{119}Sn)$ | $J(Sn-P)$ | $J(P-H)$ | Temperature (°C) |
|---|---|---|---|---|---|
| $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ | 14.3 | -296d | 710 | 390 | -90 |
| $Ph_2SnBr_2[HP(c\text{-}C_6H_{11})_2]$ | 18.8 | -303d | 595 | 400 | -90 |
| $Ph_2SnClBr[HP(c\text{-}C_6H_{11})_2]$ | 18.2 | -298d | 667 | 396 | -110 |
| $Me_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ | 6.6 | -176d | 341 | 392 | -90 |
| $Me_2SnBr_2[HP(c\text{-}C_6H_{11})_2]$ | 4.9 | -208d | 293 | 390 | -90 |
| $Bu_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ | 6.4 | -198d | 98 | 386 | -90 |
| $Ph_2SnCl[P(c\text{-}C_6H_{11})_2]$ | 13.9 | -221d | 945 | | -70 |
| $Ph_2Sn[P(c\text{-}C_6H_{11})_2]_2$ | -33.8 | -71t | 890 | | -90 |
| $Me_2SnCl[P(c\text{-}C_6H_{11})_2]$ | -6.5 | -79d | 879 | | -90 |
| $Me_2SnBr[P(c\text{-}C_6H_{11})_2]$ | -4.7 | -33d | 940 | | -90 |
| $Me_2Sn[P(c\text{-}C_6H_{11})_2]_2$ | -35.7 | -40t | 788 | | -90 |
| $Bu_2SnCl[P(c\text{-}C_6H_{11})_2]$ | -6.8 | -81d | 913 | | -90 |
| $Bu_2Sn[P(c\text{-}C_6H_{11})_2]_2$ | -32.3 | -46t | 830 | | -90 |
| $Ph_2SnCl_2[HPPh_2]$ | -11.0 | -291d | 570 | 300 | -100 |
| $Ph_2SnCl[PPh_2]$ | -7.4 | -291d | 730 | | -100 |
| $Ph_2SnBr[PPh_2]$ | -12.5 | -231d | 891 | | -115 |
| $Ph_2Sn[PPh_2]_2$ | -53.8 | -99t | 841 | | -115 |
| $Me_2SnCl[PPh_2]$ | -25.8 | -99d | 718 | | -90 |
| $Me_2Sn[PPh_2]_2$ | -53.5 | -2t | 768 | | -90 |
| $Bu_2Sn[PPh_2]_2$ | -53.5 | -13t | 810 | | -90 |
| $HP(c\text{-}C_6H_{11})_2$ | -28.9 | | | 200 | 25 |
| $HPPh_2$ | -40.0 | | | 219 | 25 |

d, doublet; t, triplet.

$H_{11})_2$. The resonance at 13.9 ppm shows no proton coupling in the $^{31}P$ proton-coupled spectrum. Although the $^{31}P$ spectrum shows clearly resolved tin-119 and tin-117 satellites at −20 °C, cooling to −70 °C is required before a $^{119}Sn$ spectrum could be observed. At this temperature the spectrum comprises a doublet [−221 ppm, $J(Sn-P)$ 945 Hz], consistent with formation of $Ph_2SnCl[P(c\text{-}C_6H_{11})_2]$. However the position of the tin-119 resonance implies that the tin atom is greater than four coordinated and is more consistent with five coordination [1]. Five coordination can be achieved by dimerisation through bridging chlorides (structure I). In such a dimer, it is likely that the bridging halides exchange rapidly at temperatures above −70 °C [19] which would explain the sharp $^{31}P$ spectrum (showing clear tin satellites) at −20 °C but the absence of a $^{119}Sn$ spectrum until −70 °C. Addition of a second mole equivalent of phosphine and additional dbu gives rise to a new $^{31}P$ resonance at −33.8 ppm with $J(Sn-P)$ 890 Hz and no $J(P-H)$ coupling in the proton-coupled $^{31}P$ spectrum. The $^{119}Sn$ spectrum comprises a triplet at −71 ppm, which is now in the range for four coordinated tin(IV) species, and these results are consistent with formation of a monomeric compound, $Ph_2Sn[P(c\text{-}C_6H_{11})_2]_2$.



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The $^{119}Sn$ spectrum at −90 °C of a dichloromethane solution of $Ph_2SnBr_2$ with $HP(c\text{-}C_6H_{11})_2$ (1:1) and dbu is complicated and there is no clear evidence to allow assignment of resonances due to $Ph_2SnBr[P(c\text{-}C_6H_{11})_2]$. However, the $^{119}Sn$ spectrum of a 1:2 solution of $Ph_2SnBr_2$ and $HP(c\text{-}C_6H_{11})_2$ plus added dbu consists of a triplet at −71 ppm, $J(Sn-P)$ 880 Hz, consistent with the formation of $Ph_2Sn[P(c\text{-}C_6H_{11})_2]_2$.

The NMR spectra at −90 °C of dichloromethane solutions of $Me_2SnCl_2$ with an equimolar quantity of $HP(c\text{-}C_6H_{11})_2$ in the presence of dbu are consistent with formation of a species $Me_2SnCl[P(c\text{-}C_6$-

$H_{11})_2]$. Reaction between two mole equivalents of $HP(c\text{-}C_6H_{11})_2$ with $Me_2SnCl_2$ in the presence of dbu gives rise to resonances due to $Me_2Sn[P(c\text{-}C_6H_{11})_2]_2$. Similarly, the NMR spectra of solutions of $Me_2SnBr_2$ or $Bu_2SnCl_2$ with $HP(c\text{-}C_6H_{11})_2$ indicate the formation of $Me_2SnBr[P(c\text{-}C_6H_{11})_2]$ and $Me_2Sn[P(c\text{-}C_6H_{11})_2]_2$, or $Bu_2SnCl[P(c\text{-}C_6H_{11})_2]$ and $Bu_2Sn[P(c\text{-}C_6H_{11})_2]_2$, respectively. NMR data are given in Table 1.

### *Reactions of $R_2SnX_2$ with $HPPh_2$*

The $^{31}P$ spectrum of a dichloromethane solution containing 1:1 proportions of $Ph_2SnCl_2$ and diphenylphosphine at room temperature comprises a broad resonance near the chemical shift position for uncoordinated $HPPh_2$. At $-110$ °C an additional $^{31}P$ resonance at $-11.0$ ppm with broad tin satellites is observed; the proton-coupled spectrum shows $J$(P–H) of 390 Hz. The $^{119}Sn$ spectrum comprises a somewhat broad doublet at $-291$ ppm, $J$(Sn–P) 570 Hz. These observations are consistent with the formation of a five coordinate adduct, $Ph_2SnCl_2[HPPh_2]$. Addition of a second mole equivalent of phosphine causes broadening of the resonances due to rapid intermolecular phosphine exchange. No evidence was found for formation of a 1:2 adduct. Results are presented in Table 1. NMR spectra, in the temperature range 30 to $-105$ °C, of a dichloromethane solution containing an equimolar ratio of $Ph_2SnBr_2$ and $HPPh_2$, show broad resonances near the chemical shift positions for the starting materials and provide no evidence for adduct formation.

The $^{119}Sn$ spectra of solutions of $HPPh_2$ with $Me_2SnCl_2$, $Me_2SnBr_2$ and $Bu_2SnCl_2$ each show only single broad resonances at substantially lower frequencies than those observed for the starting compounds. Formation of 1:1 adducts is postulated for these compounds although phosphine exchange is too rapid to enable observation of $J$(Sn–P) coupling. The different behaviour between $HP(c\text{-}C_6H_{11})_2$ and $HPPh_2$ presumably results from differences in basicities of the two phosphines, $HP(c\text{-}C_6H_{11})_2$ being the stronger base and the more reactive of the two.

### *Reactions of $R_2SnX_2$ with $HPPh_2$ and Base*

The $^{31}P$ spectrum at $-100$ °C of a dichloromethane solution containing equimolar quantities of $Ph_2SnCl_2$ and $HPPh_2$ to which dbu has been added consists of a resonance at $-19.3$ ppm (without tin satellites) and a resonance at the chemical shift position for uncoordinated phosphine. The $^{119}Sn$ spectrum contains a number of poorly defined resonances between $-210$ and $-297$ ppm. Although no clear assignment is possible, the range is that usually associated with five coordinate rather than four coordinate tin(IV) species and it is possible that associated species such as that depicted in structure I are also formed in the present circumstances. Addition of a second mole equivalent of $HPPh_2$ gives rise to an additional $^{31}P$ resonance at $-52.2$ ppm (with tin satellites) which shows no $J$(P–H) in the proton-coupled spectrum. The $^{119}Sn$ spectrum at $-70$ °C comprises a triplet at $-99$ ppm, $J$(Sn–P) 850 Hz, which is consistent with formation of a four coordinate species $Ph_2Sn[PPh_2]_2$. Solutions of $Ph_2SnBr_2$ and less than two molar equivalents of $HPPh_2$ and dbu have $^{31}P$ and $^{119}Sn$ spectra which remain unassigned at present, however when the ratio of $Ph_2SnBr_2$ to $HPPh_2$ is 1:2, the spectra again indicate formation of $Ph_2Sn[PPh_2]_2$.

The reaction of $Me_2SnCl_2$ with an equimolar equivalent of $HPPh_2$ in the presence of dbu at $-90$ °C displays two $^{31}P$ resonances accompanied by tin satellites. The $^{119}Sn$ spectrum consists of a doublet at $-99$ ppm, assigned to $Me_2SnCl[PPh_2]$ and a triplet at $-2$ ppm due to $Me_2Sn[PPh_2]_2$. A solution of $Me_2SnCl_2$ and $HPPh_2$ in 1:2 proportions in the presence of dbu has NMR spectra consistent with the presence of $Me_2Sn[PPh_2]_2$. Reaction of $Me_2SnBr_2$ with dbu and any proportion of $HPPh_2$ results only in the formation of $Me_2Sn[PPh_2]_2$. Similarly, mixtures of $HPPh_2$, dbu and $Bu_2SnCl_2$ or $Bu_2SnBr_2$ give NMR spectra consistent with formation of $Bu_2Sn[PPh_2]_2$. No evidence was observed for formation of $Bu_2SnX[PPh_2]$. NMR data for all the observed species are given in Table 1.

### *Reactions of $Ph_2SnX_2$ with $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$*

The $^{31}P$ spectrum of $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ in dichloromethane solution at room temperature consists of two sharp resonances of relative intensities 3:2 assigned to $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ [$\delta(^{31}P)$ 40.0 ppm] and $HP(c\text{-}C_6H_{11})_2$ [$\delta(^{31}P)$ $-28.9$ ppm, $J$(P–H) 200 Hz] respectively. Addition of excess PhNCS causes the $HP(c\text{-}C_6H_{11})_2$ resonance to disappear leaving only the $^{31}P$ resonance due to $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$. These observations are consistent with the equilibrium

$$(c\text{-}C_6H_{11})_2PC(S)N(H)Ph \longleftrightarrow (c\text{-}C_6H_{11})_2PH + PhNCS$$

The $^{31}P$ spectrum of a dichloromethane solution of $Ph_2SnCl_2$ with an equimolar proportion of $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ contains two resonances, each with tin satellites [$\delta(^{31}P)$ 14.3 ppm, $J$(Sn–P) 710 Hz, $J$(P–H) 390 Hz and $\delta(^{31}P)$ 3.2 ppm, $J$(Sn–P) 72 Hz], the former is attributed to the five coordinated tin adduct $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$. The latter resonance shows no $J$(P–H) whilst the magnitude of the coupling constant $J$(Sn–P) suggests that bonding is not directly through phosphorus but rather that the ligand is bonded through the sulphur and/or nitrogen atoms [13]. The $^{119}Sn$ spectrum at $-90$ °C consists of two doublets ($-211$, $-297$ ppm) of equal intensity with $J$(Sn–P) the same as observed in the corresponding $^{31}P$ spectra. The combination of a small coupling constant $J$(Sn–P) and the relative position of the $^{119}Sn$ resonance (at −211 ppm) implies that the second species may also be five coordinate and it is tentatively assigned to the deprotonated ligand species $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Five coordination could be achieved either by the ligand being bidentate through sulphur and nitrogen, or by a monodentate ligand accompanied by dimerisation as was proposed above for $Ph_2SnCl[P(c\text{-}C_6H_{11})_2]$. When a mole equivalent of PhNCS is added to the above solution, the $^{31}P$ and $^{119}Sn$ resonances attributed to $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ are diminished in intensity relative to those assigned to the deprotonated species, $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Addition of a further mole equivalent of PhNCS results in the observation of only the deprotonated species. This suggests that addition of PhNCS to a 1:1 solution of ligand and tin salt shifts the equilibrium towards exclusive formation of $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ and subsequently to the formation of $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Addition of PhNCS to a solution containing the 1:1 adduct $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ also gives rise to spectra consistent with the formation of $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Attempts at isolation of $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ were unsuccessful.

The $^{31}P$ and $^{119}Sn$ NMR spectra of a 1:2 mixture of $Ph_2SnCl_2$ and $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ in dichloromethane solution are identical to spectra of the 1:1 mixture, but contain additional $^{31}P$ resonances due to uncoordinated ligand and $HP(c\text{-}C_6H_{11})_2$. Addition of two mole equivalents of PhNCS causes the $^{31}P$ and $^{119}Sn$ resonances assigned to $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$ to diminish while the intensity of the $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ resonances increase. Addition of a further two mole equivalents of PhNCS does not alter the $^{31}P$ spectrum except for the disappearance of the resonance due to $Ph_2SnCl_2[HP(c\text{-}C_6H_{11})_2]$. The $^{119}Sn$ spectrum comprises a doublet due to $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$.

Addition of dbu to an equimolar solution of $Ph_2SnCl_2$ and $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ at room temperature results exclusively in formation of $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ and coupling $J(Sn\text{–}P)$ is seen at room temperature. The $\delta(^{31}P)$ resonance moves from 66.8 ppm at room temperature to 2.9 ppm at −90 °C. Addition of a second mole equivalent of $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ causes a change in the $^{31}P$ spectrum, which now shows a resonance near 3 ppm (with tin satellites) and resonances due to uncoordinated $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ and $HP(c\text{-}C_6H_{11})_2$. The $^{119}Sn$ spectrum at −90 °C consists of a triplet [$\delta(^{119}Sn)$ −293 ppm, $J(Sn\text{–}P)$ 55 Hz] assigned to $Ph_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$. The magnitude of the $^{119}Sn$ chemical shift is consistent with six coordinate tin and leads to the postulation of bidentate S, N coordination of the ligand to tin.

Diphenyltin(IV)dibromide is apparently unreactive towards $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ at room temperature. However at −100 °C the $^{31}P$ spectrum shows a very intense resonance due to free ligand and additional, very weak, resonances at 19.1, 10.4 and 3.3 ppm. The $^{119}Sn$ spectrum shows a broad resonance at −164 ppm and two doublets, one at −231 ppm, $J(Sn\text{–}P)$ 73 Hz, the other at −303 ppm, $J(Sn\text{–}P)$ 611 Hz. The latter is due to $Ph_2SnBr_2[HP(c\text{-}C_6H_{11})_2]$ whilst the former is, by analogy with $Ph_2SnCl_2$ reactions, assigned to a five coordinate species $Ph_2SnBr[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Addition of dbu results exclusively in formation of $Ph_2SnBr[(c\text{-}C_6H_{11})_2PC(S)NPh]$. Addition of further ligand leads to the exclusive formation of $Ph_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$.

No evidence is observed for reaction of $Me_2SnX_2$ (where X = Cl, Br) with $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ in dichloromethane solution over the temperature range 20 to −100 °C. However, addition of base does induce reaction and a dichloromethane solution containing equimolar quantities of $Me_2SnCl_2$, $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ and dbu has a $^{31}P$ spectrum containing a resonance at 5.1 ppm with $J(Sn\text{–}P)$ 73 Hz whilst the $^{119}Sn$ spectrum comprises a doublet at −70 ppm. These data are consistent with formation of the species $Me_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. The proximity of the $^{119}Sn$ chemical shift value to that observed for the four coordinate species $Me_2Sn[P(c\text{-}C_6H_{11})_2]_2$ implies that $Me_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ is also four coordinate in solution. The small $J(Sn\text{–}P)$ value is consistent with three-bond tin–phosphorus coupling and, together with the $^{119}Sn$ chemical shift value, implies that the ligand is coordinated in a monodentate fashion, either via sulphur or nitrogen, although NMR cannot distinguish between the two possibilities.

NMR spectra of solutions containing 1:1 molar proportions of $Me_2SnBr_2$ and $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ and base are consistent with formation of $Me_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$. The $^{119}Sn$ spectrum at −10 °C consists of a triplet at −166 ppm. The $^{31}P$ spectrum contains several resonances, one at 3.6 ppm with $J(Sn\text{–}P)$ 46 Hz equal to that derived from the $^{119}Sn$ spectrum. The small observed value of $J(Sn\text{–}P)$ is consistent with three- bond coupling and hence it is apparent that tin is not directly bonded to the phosphorus atom of the ligand. The $^{119}Sn$ shift is similar to values observed for five coordinate species $Me_2SnX_2HP(c\text{-}C_6H_{11})_2$ (Table 1) which implies that the tin atom in $Me_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$ is also effectively five coordinate. Rapid intramolecular monodentate–bidentate exchange of the sulphur and nitrogen atoms of the two ligands would have the effect of giving an effective coordination number greater than four but less than six, whilst still retaining the observed $^3J(Sn\text{–}P)$ coupling. The only other phosphorus resonance assigned is that of uncoordinated $HP(c\text{-}C_6H_{11})_2$. A 1:2 dichloromethane solution of $Me_2SnBr_2$, ligand and base contains the

TABLE 2. Phosphorus-31 and tin-119 NMR data for diorganoyltin(IV) complexes of $[R_2PC(S)NPh]^-$ in dichloromethane solution

| Species | $\delta(^{31}P)$ | $\delta(^{119}Sn)$ | $J(Sn-P)$ | Temperature (°C) |
|---|---|---|---|---|
| $Ph_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ | 3.2 | −211d | 72 | −100 |
| $Ph_2SnBr[(c\text{-}C_6H_{11})_2PC(S)NPh]$ | −0.9 | −238d | 52 | −20 |
| $Ph_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$ | 0.2 | −293t | 53 | −90 |
| $Me_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ | 5.1 | −70d | 73 | 25 |
| $Me_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$ | 3.6 | −166t | 46 | 0 |
| $Bu_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$ | 5.6 | −67d | 70 | 25 |
| $Bu_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$ | 3.5 | −142t | 46 | −10 |
| $Ph_2SnCl[Ph_2PC(S)NPh]$ | 0.4 | −217d | 52 | 30 |
| $Ph_2SnBr[Ph_2PC(S)NPh]$ | 0.1 | −238d | 59 | 0 |
| $Ph_2Sn[Ph_2PC(S)NPh]_2$ | −0.8 | −318t | 44 | −90 |
| $Me_2SnCl[Ph_2PC(S)NPh]$ | −0.6 | −80d | 56 | 25 |
| $Me_2SnBr[Ph_2PC(S)NPh]$ | −0.4 | −108d | 54 | 25 |
| $Me_2Sn[Ph_2PC(S)NPh]_2$ | 0.3 | −165t | 46 | 25 |
|  | −0.4 | −171t | 49 | 0 |
| $Bu_2SnCl[Ph_2PC(S)NPh]$ | 0.3 | −75d | 61 | 25 |
| $Bu_2Sn[Ph_2PC(S)NPh]_2$ | −1.1 | −151t | 45 | −10 |
| $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ | 44.3 |  |  | 25 |
| $Ph_2PC(S)N(H)Ph$ | 20.0 |  |  | 25 |

d, doublet; t, triplet.

same species, $Me_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$. NMR results are given in Table 2.

No reaction occurs between $Bu_2SnCl_2$ and $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$. However addition of dbu to an equimolar mixture of these compounds results in NMR spectra which are consistent with formation of $Bu_2SnCl[(c\text{-}C_6H_{11})_2PC(S)NPh]$. The $^{31}P$ spectrum at room temperature exhibits a single resonance at 5.6 ppm with tin satellites. The corresponding tin spectrum comprises a doublet at −67 ppm with $J(Sn-P)$ 70 Hz. Addition of further $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$ and dbu leads to the formation of $Bu_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$, which is probably six coordinate.

### *Reactions of Phosphine Adducts with PhNCS*

The $^{31}P$ spectrum of a dichloromethane solution containing equimolar amounts of $R_2SnX[P(c\text{-}C_6H_{11})_2]$ (X = Cl, Br) and phenylisothiocyanate, PhNCS, consists of a single resonance accompanied by tin satellites. The corresponding $^{119}Sn$ spectrum consists of a doublet. In each case the observed NMR data are consistent with formation of the species $R_2SnX[(c\text{-}C_6H_{11})_2PC(S)NPh]$ and confirm that insertion of PhNCS into the Sn–P bond of $R_2SNX[P(c\text{-}C_6H_{11})_2]$ has occurred. The $^{31}P$ spectrum of an equimolar solution of PhNCS and $R_2Sn[P(c\text{-}C_6H_{11})_2]_2$ consists of two resonances accompanied by tin satellites. The $^{119}Sn$ spectrum consists of two doublets of equal intensity and the data are in accord with the presence of $R_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$ and unreacted $R_2Sn[P(c\text{-}C_6H_{11})_2]_2$. No evidence was observed for the existence of the mixed-ligand species $R_2Sn[P(c\text{-}C_6H_{11})_2][(c\text{-}C_6H_{11})_2PC(S)NPh]$. NMR data for a 1:2 solution of $R_2Sn[P(c\text{-}C_6H_{11})_2]_2$ and PhNCS are consistent with formation of the insertion product $R_2Sn[(c\text{-}C_6H_{11})_2PC(S)NPh]_2$.

### *Reactions of $R_2SnX_2$ with $Ph_2PC(S)N(H)Ph$*

Unlike $(c\text{-}C_6H_{11})_2PC(S)N(H)Ph$, the ligand $Ph_2PC(S)N(H)Ph$ does not dissociate in dichloromethane solution. The $^{31}P$ and $^{119}Sn$ spectra of dichloromethane solutions of $Ph_2SnX_2$ (X = Cl, Br) and $Ph_2PC(S)N(H)Ph$ in various proportions, recorded between room temperature and −100 °C, show resonances due only to starting materials. However addition of base does induce reaction and the $^{31}P$ spectrum of an equimolar mixture of $Ph_2SnX_2$, $Ph_2PC(S)N(H)Ph$ and base (dbu or $Et_3N$) consists of a single resonance, accompanied by tin satellites. The $^{119}Sn$ spectrum in each case shows a doublet with the $J(Sn-P)$ coupling values consistent with three-bond coupling.

Addition of base to 1:2 proportions of $Ph_2SnCl_2$ and $Ph_2PC(S)N(H)Ph$ in dichloromethane at room temperature gives a $^{31}P$ spectrum consisting of a single broad resonance at about 0 ppm. Cooling to −60 °C sharpens the resonance and tin satellites become apparent. The $^{119}Sn$ spectrum at −60 °C is a triplet at −318 ppm. These spectra are consistent with the presence of a single species $Ph_2Sn[Ph_2PC(S)NPh]_2$ which has two equivalent phosphorus ligands coordinated to the tin atom. NMR spectra of solutions of 1:2 proportions of $Ph_2SnBr_2$ and $Ph_2PC(S)N(H)$-Ph and base also indicate formation of $Ph_2Sn[Ph_2$-$PC(S)NPh]_2$. The magnitude of the coupling constant, 44 Hz, implies that the ligand is coordinated not through phosphorus but rather through sulphur and nitrogen. NMR data are recorded in Table 2.

Neither $Me_2SnCl_2$ nor $Me_2SnBr_2$ apparently react with $Ph_2PC(S)N(H)Ph$ in the absence of base. However, the deprotonation reactions of mixtures of $Me_2$-$SnX_2$ and $Ph_2PC(S)N(H)Ph$ are facile. Equimolar quantities of $Me_2SnX_2$, $Ph_2PC(S)N(H)Ph$ and base have $^{31}P$ spectra each consisting of a single resonance with tin satellites and in each case the $^{119}Sn$ spectrum is a doublet, assigned to $Me_2SnX[Ph_2PC(S)NPh]$. The spectra are unaffected by changes in temperature. Reaction between $Me_2SnX_2$ and two molar equivalents of $Ph_2PC(S)N(H)Ph$ and base results in spectra consistent with exclusive formation of the six coordinate species, $Me_2Sn[Ph_2PC(S)NPh]_2$.

There is no reaction between $Bu_2SnCl_2$ and $Ph_2$-$PC(S)N(H)Ph$ (1:1) in the absence of base. Addition of base to the above solution leads to formation of $Bu_2SnCl[Ph_2PC(S)NPh]$. Addition of base to a 1:2 mixture of $Bu_2SnCl_2$ and $Ph_2PC(S)N(H)Ph$ gives spectra consistent with formation of $Bu_2Sn[Ph_2$-$PC(S)NPh]_2$. In the case of $Bu_2SnBr_2$, there is no evidence for formation of $Bu_2SnBr[Ph_2PC(S)NPh]$ and only $Bu_2Sn[Ph_2PC(S)NPh]_2$ was observed in both 1:1 and 1:2 solutions of $Bu_2SnBr_2$ and $Ph_2$-$PC(S)N(H)Ph$.

## Conclusions

PhNCS readily inserts into the Sn–P bonds of $R_2SnX(PR'_2)$ and $R_2Sn(PR'_2)_2$ to give the new series of tin compounds $R_2SnX[R'_2PC(S)NPh]$ and $R_2$-$Sn[R'_2PC(S)NPh]_2$. Although these new compounds have so far not been isolated, tin-119 spectroscopic data imply that ligand coordination is through the sulphur and nitrogen atoms resulting, respectively, in five and six coordination about the tin atom, in dichloromethane solution.

## Acknowledgement

We are grateful for a Commonwealth Postgraduate Research Award to C.L.R.

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