

Organotin(IV) triazadiphosphorines: Synthesis and characterization

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ABSTRACT: Organotin(IV) triazadiphosphorines, $[N(PPh_2NR')_2]_nSnR_2X_{2-n}]$ and $[N(PPh_2NR')_2SnR_3]$ (where $R' = -Ph$ or $-SiMe_3$, $R = -CH_3$, $-CH_2Ph$ or $-CH_2C_6H_4CH_3$, $n = 1$ or 2 and $X = Cl$) have been isolated by the reaction of acyclic bis-phenylated (**A**) and bis-silylated (**B**) phosphazene ligands, $[HN(PPh_2NR')_2]$, with Me_2SnCl_2 and R_3SnCl in refluxing methylene dichloride and toluene in different stoichiometric ratio. These pale yellow moisture sensitive derivatives have been characterized by elemental analyses (C, H, N, Cl and Sn), molecular weight determinations, mass, IR and NMR (1H , ^{13}C and ^{31}P) spectroscopy.

Key Words: Triazadiphosphorines, bis-phenylated and bis-silylated phosphazenes

Introduction

The six-membered cyclotriazaphosphazene (2,2,4,4,6,6-hexasubstituted-1,3,5,2λ⁵,4λ⁵,6 λ⁵-triazatriphosphorines) is by far the best investigated phosphorus-nitrogen compound,¹⁻³ particularly, in view to its metathesis reactions with a wide variety of nucleophiles.⁴⁻⁷ Initial report on metal-phosphorus-nitrogen compounds⁸ was appeared in 1962 while first synthesis of the metal-phosphorus and metal-nitrogen bonds become available in the late 1970's followed by isolation of heterometallacycloposphazenes⁹ in 1986. Afterward a large number of cyclometallaphosphazenes having transition metals as building blocks are discovered.¹⁰⁻¹⁶ Organotin compounds are used for molding rubbers, precursors for ceramics¹⁸ and are known to form polymers,¹⁷ which may possess average molecular weight up to 1×10^6 . Tin compounds are also known to possess potential biological activity, especially to those of triorganotin species. Literature survey revealed that little is known about the chemistry of cyclophosphazenes derivatives containing Sn-N bonds and till date no six-membered cyclophosphazene of tin(IV) is reported.¹⁹⁻²⁰ Keeping the view of our past efforts in synthesizing the new heterometallacycloposphazenes, we report herein on the syntheses of first organotin(IV) triazadiphosphorines (or heterotriazacycloposphazenes) with the assumption that they may find their utility as potential bioactive species or as precursor in the synthesis of the complex oxide materials of "high-tech" applications.

Experimental

In view of the sensitive nature of the ligands as well as complexes, utmost precautions were taken to exclude moisture to maintain anhydrous conditions. All experimental manipulations were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques and vacuum line. Solvents (toluene, methylene dichloride, diethyl ether) were freshly dried prior to use. The bis-phenylated (**A**) and bis-silylated (**B**) phosphazene ligands were synthesized by using literature methods.²¹⁻²² The Me_2SnCl_2 was procured commercially and tris-(benzyl)tin(IV) chloride and tris-(4-methylbenzyl)tin(IV) chloride was prepared in the laboratory by the reaction of tin metal and benzyl chloride and 4-methyl benzyl chloride.²³ respectively. Tin was estimated as SnO_2 and chloride was estimated using Volhard's method.²⁴

Molecular weights were determined in freezing benzene by cryoscopic method. Elemental analyses (C, H and N) were carried out in the microanalytical laboratory, Regional Research Laboratory, Jammu. IR spectra were recorded in KBr on Perkin Elemer-377 spectrophotometer in the range $4000-400\text{ cm}^{-1}$. 1H and ^{13}C NMR spectra were recorded on Jeol FX 90 Q MHz using TMS as external reference. ^{31}P NMR was done on Burkner DRX 300 (120 MHz) using 85% H_3PO_4 as external reference. The mass spectrometric analysis (EI) was carried out on ESQUIRE-3000 (BRUKER-DALTONICS).

Syntheses of the complexes

Reactions of Me_2SnCl_2 with $[HN(PPh_2NR')_2]$

To methylene dichloride solution (30 ml) of dimethyltin dichloride, Me_2SnCl_2 , was added dropwise methylene dichloride solution (30 ml) of phenylated phosphazene, $[HN(PPh_2NPh)_2]$, or bis-silylated phosphazene ligand, $[HN(PPh_2NSiMe_3)_2]$, alongwith triethylamine in 1:1 and 1:2 molar ratios with constant stirring at room temperature. The contents were then refluxed for ~5 hours. Now, excess of CH_2Cl_2 was removed under reduced pressure, which left a solid mass. This solid mass was dissolved in toluene to

separate triethylamine hydrochloride thus formed; which was removed by filtration using Schlenk funnel fitted with G-4 disc. Evaporation of excess of toluene under reduced pressure yielded pale yellow solid in 93-96% yield.

Reactions of $(C_6H_5CH_2)_3SnCl$ or $(CH_3C_6H_4CH_2)_3SnCl$ with $[HN(PPh_2NR')_2]$

To toluene suspension (~30 ml) of tris(benzyl)tinchloride, $(C_6H_5CH_2)_3SnCl$, or tris-(4-methylbenzyl)tinchloride, $(CH_3C_6H_4CH_2)_3SnCl$, was added dropwise to a toluene solution of bis-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, or bis-silylated phosphazene ligand, $[HN(PPh_2NSiMe_3)_2]$ alongwith triethylamine in 1:1 molar ratio. The reaction mixture was stirred at room temperature for 2 hours then refluxed for ~6 hours, the color of the content was changed from colorless to pale yellow. The precipitate of triethylamine hydrochloride was filtered off by Schlenk funnel fitted with G-4 disc and the excess of solvent was removed from the filtrate under reduced pressure, which resulted in the formation of a pale yellow solid in 93-95% yield.

The synthetic and analytical data of these complexes are summarized in the Table 1.

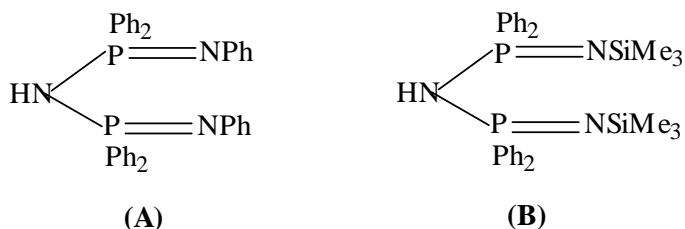
Table 1. Synthetic and analytical data of complexes of organotin(IV)triazadiphosphorines

S.No	Ligand $[HN(PPh_2NR')_2]$ g(mmol)	Metal g(mmol)	Molar ratio	Product (Physical state)	Yield(%) (m.p. °C)	Mol.Wt. Found (Calcd.)	Analyses (%) Found/Calcd.				
							Sn	C	H	N	Cl
1	1.41 (2.04)	Me_2SnCl_2 0.45(2.04)	1:1	$[N(PPh_2NSiMe_3)_2SnMe_2Cl]$ (yellow solid)	94 (61)	740 (742.1)	15.91 (15.99)	51.71 (51.73)	5.83 (5.92)	5.79 (5.67)	4.79 (4.78)
2	1.32 (2.36)	Me_2SnCl_2 0.26(1.18)	2:1	$[N(PPh_2NSiMe_3)_2]_2SnMe_2$ (yellow solid)	93 (67)	1260 (1264.6)	9.42 (9.38)	58.81 (58.82)	6.42 (6.48)	6.53 (6.64)	-
3	1.27 (2.27)	Me_2SnCl_2 0.41(2.27)	1:1	$[N(PPh_2NPh)_2]_2SnMe_2Cl$ (yellow solid)	95 (93)	745 (750.1)	15.77 (15.82)	63.74 (60.78)	6.47 (4.79)	6.15 (5.59)	5.92 (5.93)
4	2.00 (3.52)	Me_2SnCl_2 0.38(1.72)	2:1	$[N(PPh_2NPh)_2]_2SnMe_2$ (yellow solid)	96 (75)	1261 (1280.6)	9.23 (9.36)	67.50 (67.46)	5.92 (4.68)	5.50 (6.55)	-
5	1.17 (2.09)	R_3SnCl 0.89 (2.09)	1:1	$[N(PPh_2NSiMe_3)_2Sn(CH_2C_6H_5)_3]$ (yellow solid)	93 --	945 (949.6)	12.57 (12.49)	64.66 (64.44)	6.17 (6.21)	4.19 (4.42)	-
6	1.24 (2.21)	R_3SnCl 0.93(2.21)	1:1	$[N(PPh_2NPh)_2]_2Sn(CH_2C_6H_5)_3]$ 95 (yellow solid)	95 --	960 (957.6)	12.45 (12.39)	71.67 (71.42)	5.16 (5.32)	4.13 (4.38)	-
7	0.97 (1.73)	R_3SnCl 0.82(1.73)	1:1	$[N(PPh_2NSiMe_3)_2Sn(CH_2C_6H_4Me)_3]$ (yellow solid)	94 --	981 (991.6)	11.71 (11.96)	65.31 (65.34)	6.19 (6.55)	4.29 (4.23)	-
8	1.12 (2.00)	R_3SnCl 0.93(2.00)	1:1	$[N(PPh_2NPh)_2]_2Sn(CH_2C_6H_4Me)_3]$ (yellow solid)	95 --	969 (999.6)	11.83 (11.87)	72.00 (72.02)	5.17 (5.70)	4.31 (4.20)	-

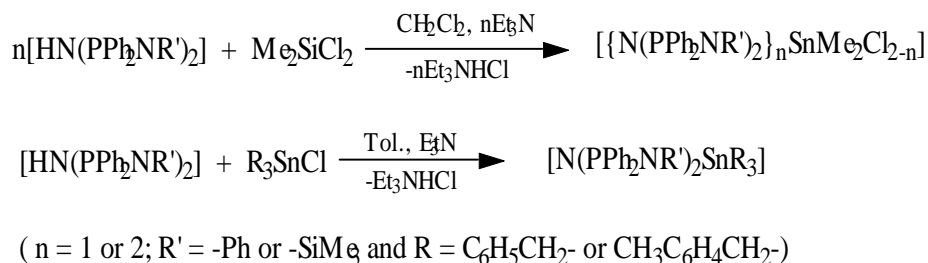
where $R' = -Ph$ or $-SiMe_3$ and $R = -CH_2C_6H_5$ or $-CH_2C_6H_4Me$

Results and discussion

The following two acyclic bis-phenylated (A) and bis-silylated phosphazene (B) ligands have been used which are known to form M-N bond with several transition as well as non-transition atoms.



The 1:1 and 1:2 molar reactions of these acyclic ligands, $[HN(PPh_2NR')_2]$ with dimethyltin dichloride, Me_2SnCl_2 , in presence of triethylamine, Et_3N , under refluxing condition in CH_2Cl_2 yielded pale yellow complexes corresponded to $[N(PPh_2NR'_2)]_nSnR_2X_{2-n}]$, ($n = 1$ or 2). The complexes were fairly soluble in common organic solvent except CCl_4 and obtained in quantitative yield. Similarly, these ligands on reactions with R_3SnCl (where $R = -CH_2Ph$ or $-CH_2C_6H_4CH_3$) in refluxing toluene yielded the complexes of the type $[N(PPh_2NR')_2SnR_3]$ (Scheme 1).



Scheme 1

These pale yellow solids are soluble in common organic solvents except in *n*-hexane and CCl_4 and appear to be highly moisture-sensitive, however, no ageing phenomenon was observed when kept under dried and inert atmosphere. The monomeric nature of the complexes has been confirmed by their molecular weight determination in freezing benzene. The elemental analyses (C, H, N, Cl and Sn) were found in accordance with the composition of the complexes. Mass spectrum of $[\{\text{N}(\text{PPh}_2\text{NPh})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3]$ have shown the molar ion (M^+) peak at m/z 956 (35%), beside the usual fragmentation pattern that occurs for phosphazene complexes. The base peak for the complex was found at 348 (100%) which correspond to $[(\text{Ph}_2\text{P})_2\text{NSn}]^+$ ion.

The symmetric nature of P-N-P ring system has been supported by the appearance of bands for $\nu\text{P-N}$ in the region $1260\text{-}1030\text{ cm}^{-1}$. Further, the appearance of new strong bands in the region $520\text{-}470\text{ cm}^{-1}$ and $460\text{-}430\text{ cm}^{-1}$ for $\nu\text{Sn-N}$ and $\nu\text{Sn-C}$, as well as disappearance of a strong band for νNH at 3345 cm^{-1} indicated the complexation. The bands of sharp to medium intensity in the region $1490\text{-}1260\text{ cm}^{-1}$ may be assign to $\nu\text{P=N}$ vibration. The bands of weak intensity in the region $370\text{-}367\text{ cm}^{-1}$ may be ascribed to $\nu\text{Sn-Cl}$. The relevant IR data are given in the Table 2.

Table 2. IR spectral data of Organotin(IV) triazadiphosphorines (in cm^{-1})

S. No.	Compounds	$\nu\text{P=N}$	$\nu\text{P-N-P}$	$\nu\text{Sn-N}$	$\nu\text{Sn-C}$	$\nu\text{Sn-Cl}$
1	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{SnMe}_2\text{Cl}]$	1482,vs	1261-1022	543,vs	510,vs	370,s
2	$[\{\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{SnMe}_2]$	1436,vs	1261-1025	550,vs	514,vs	367,s
3	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{SnMe}_2\text{Cl}]$	1481,vs	1260-1036	512,vs	442,vs	-
4	$[\{\text{N}(\text{PPh}_2\text{NPh})_2\}_2\text{SnMe}_2]$	1436,vs	1261-1026	547,vs	510,vs	-
5	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3]$	1457,vs	1260-1025	540,vs	500,vs	-
6	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3]$	1452,vs	1255-1029	530,vs	512,vs	-
7	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_3]$	1482,vs	1261-1039	550,vs	513,vs	-
8	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_3]$	1462,vs	1260-1023	545,vs	512,vs	-

where vs = very strong, s = strong, m = medium and w = weak.

^1H NMR spectra indicated de-protonation of ligand as no chemical shift was observed for the -NH proton (in the range 4.5-5.0 ppm). The phenyl protons for -PPh₂ and -NPh of ligand (**A**) were found as two multiplets in the region 6.20-8.20 ppm and phenyl protons for the complexes with ligand (**B**) were found as a multiplet in the region 6.0-8.40 ppm. Methyl protons of trimethylsilyl group did not show any appreciable change in their chemical shift value. A singlet was observed for methyl protons attached to Sn atom in the region 1.9-2.10 ppm. Methylene protons, -CH₂, of benzyl group gave the signal in the region 3.6-4.2 ppm while phenyl protons were observed in the region 6.0-8.2 ppm.

^{31}P NMR spectra of the complexes show only one singlet in each complex of either bis-phenylated (**A**) or bis-silylated (**B**) phosphazene ligand but with a downfield shift of 5-12 ppm compared to the parent ligand. The occurrence of the singlet in these complexes may, probably, be due to the equivalence of the phosphorus nuclei in the molecule as well as symmetric nature of the complexes.

The ^{13}C NMR spectra of the complexes do not show any appreciable change in their chemical shift compare to the parent moiety. The carbons of trimethylsilyl, methyl and the phenyl groups were observed

without any change except marginal shift in case of the methylene group. ^1H , ^{13}C and ^{31}P NMR spectral data of these complexes are summarized in Table 3.

Table 3. ^1H , ^{13}C and ^{31}P NMR data of organotin(IV)triazadiphosphorines in CDCl_3 (ppm)

S. No	Compounds	^1H NMR	^{31}P NMR	^{13}C NMR
1	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{SnMe}_2\text{Cl}]$	0.12, s, 18H (-SiMe ₃) 1.13, s, 6H (-CH ₃) 6.30 - 8.15, m, 20H (PPh ₂)	16.15, s	3.8, s (-SiMe ₃) 25.5, s (-Me ₂) 122-139, m (-Ph)
2	$[\{\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\}_2\text{SnMe}_2]$	0.12, s, 36H (-SiMe ₃) 1.10, s, 6H (-CH ₃) 6.45-8.20, m, 40H (-PPh ₂)	15.17, s	3.8, s (-SiMe ₃) 27.30, s (-Me ₂) 120-124, m (-Ph)
3	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{SnMe}_2\text{Cl}]$	1.15, s, 6H (-CH ₃) 6.40-7.20, m, 10H (-NPh) 7.45-8.10, m, 20H (-PPh ₂)	17.13, s	27.70, s (-Me ₂) 121-138, m (-Ph)
4	$[\{\text{N}(\text{PPh}_2\text{NPh})_2\}_2\text{SnMe}_2]$	1.20, s, 6H, (-CH ₃) 6.20-7.45, m, 10H (-NPh) 7.60 - 8.40, m, 40H (PPh ₂)	18.87, s	23.42, s (-Me ₂) 122-140, m (-Ph)
5	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3]$	0.12, s, 18H (-SiMe ₃) 2.7-3.2, s, 4H (-CH ₂) 6.45-7.20, m, 10H (-NPh) 7.60 - 8.15, m, 20H (PPh ₂)	24.10, s	3.9, s (-SiMe ₃) 41.90, s (-CH ₂) 119-140, m (-Ph)
6	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3]$	2.80, s, 6H (-CH ₂) 6.40-7.20, m, 10H (-NPh) 7.30-8.15, m, 20H (-PPh ₂)	19.13, s	42.30, s (-CH ₂) 120-138, m (-Ph)
7	$[\text{N}(\text{PPh}_2\text{NSiMe}_3)_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_3]$	0.12, s, 18H (-SiMe ₃) 1.25, s, 9H (-CH ₃) 2.90, s, 6H (-CH ₂) 6.40 - 8.15, m, 20H (-PPh ₂)	22.15, s	3.9, s (-SiMe ₃) 43.72, s (-CH ₂) 21.95, s (-Me ₂) 120-140, m (-Ph)
8	$[\text{N}(\text{PPh}_2\text{NPh})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_4\text{Me})_3]$	1.20, s, 9H (-CH ₃) 2.85, s, 6H (-CH ₂) 6.20-7.30, m, 10H (-NPh) 7.40-8.20, m, 20H (-PPh ₂)	18.12, s	41.5, s (-CH ₂) 22.25, s (-Me ₂) 120-140, m (-Ph)

Where s = singlet, d = doublet, m = multiplet

Structural features

Though, it would not be appropriate to predict precisely on the structure of these complexes since the efforts to obtain the suitable crystal for single crystal X-ray analysis were not successful. However, literature survey revealed that out of the various structural possibilities for these complexes, a square planar and regular octahedral geometries for 5- and 6-coordination, respectively, have been known.²⁵⁻²⁶ Since these ligands commonly depict the bidentate mode of bonding,¹²⁻¹⁶ therefore, in conjunction with the above studies, a square pyramidal geometry (I) for the complexes $[\{\text{N}(\text{PPh}_2\text{NR}')_2\}_2\text{SnR}_2\text{Cl}]$ having 5-coordinated tin atom and an octahedral geometry (II) for the complexes $[\{\text{N}(\text{PPh}_2\text{NR}')_2\}_2\text{SnR}_2]$ having 6-coordinated tin atom may plausibly be proposed (Figure 1).

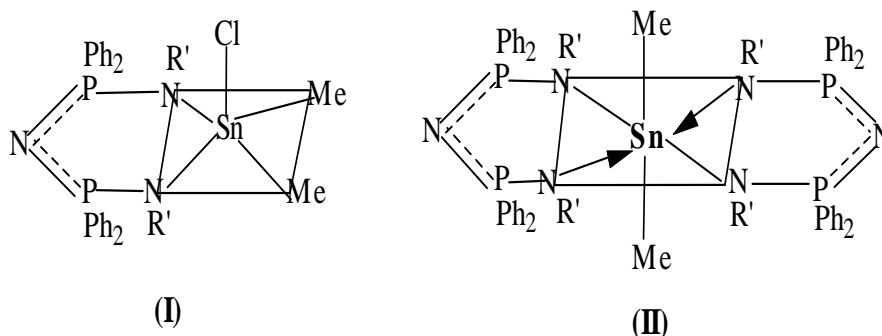


Figure 1. Proposed square pyramidal (I) and octahedral (II) geometries for the complexes $[\text{N}(\text{PPh}_2\text{NR}')_2\text{SnMe}_2\text{Cl}]$ and $[\{\text{N}(\text{PPh}_2\text{NR}')_2\}_2\text{SnMe}_2]$ (where $\text{R}' = -\text{Ph}$ or $-\text{SiMe}_3$)

Single crystal X-ray analysis of $\text{Ph}_3\text{Sn}[\text{S}_2\text{POCMe}_2\text{CMe}_2\text{O}]$ have shown that dithiophosphate ligand behaved in anisobidentate manner around the tin atom, which concludes an intermediate structure between

tetrahedral and trigonal bipyramidal geometry.²⁷ Considering monomeric nature of the complexes, appearance of vSn-N band and no shifting in the position of P=N in IR, disappearance of chemical shift for -NH in ¹H NMR and occurrence of a singlet with substantial downfield shift in ³¹P NMR, it is assumed that tris-benzyltin phosphazene complexes, [$\text{N}(\text{PPh}_2\text{NPH})_2\text{Sn}(\text{CH}_2\text{C}_6\text{H}_5)_3$], might possess an intermediate position between four coordinated tetrahedral (ligand behaved as monodentate) and five coordinated trigonal bipyramidal (ligand behaved as anisobidentate) geometry (Figure 2).

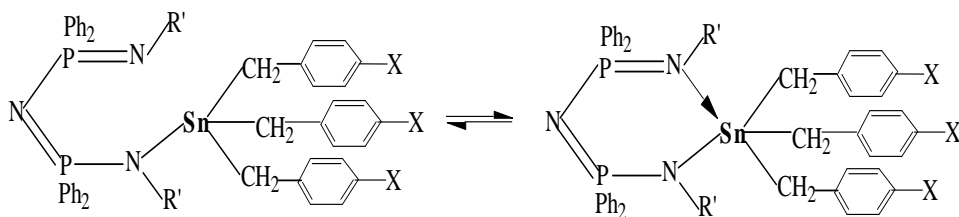


Figure 2. Proposed t_4 - tbp intermediate geometry for $[\text{N}(\text{PPh}_2\text{NR}')_2\text{SnR}_3]$ (where $\text{X} = \text{CH}_3$ or absent)

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