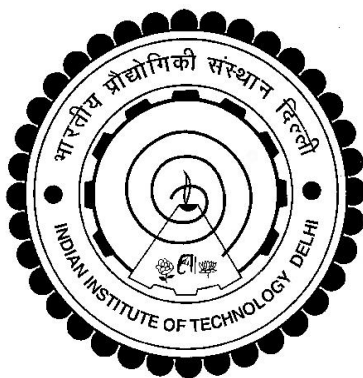


**SYNTHESIS AND CHARACTERIZATION OF
DIORGANOTIN(IV) COORDINATION POLYMERS
DERIVED FROM SILAALKYLPHOSPHONATE AND
SULFONATE BASED LIGANDS**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2016**

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by

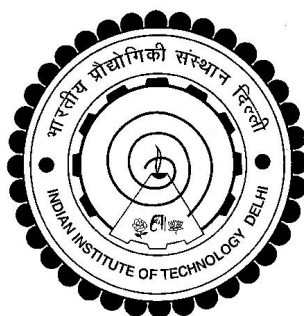
NISHA SINGLA

Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2016

Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled “*Synthesis and characterization of diorganotin(IV) coordination polymers derived from silaalkylphosphonate and sulfonate based ligands*” being submitted by **Ms. Nisha Singla** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Nisha Singla has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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CONTENTS

	Page No.
Abstract	i-ii
List of Figures	iii-v
List of Tables	vi-viii
Glossary of Symbols and Abbreviations	ix-x
CHAPTER I Introduction	1-21
Scope and aim	22
CHAPTER II Materials and methods	23-39
CHAPTER III Synthesis and characterization of mixed-ligand diorganotin(IV) coordination polymers bearing silaalkylphosphonate and methanesulfonate ligands	40-70
CHAPTER IV Synthesis and characterization of soluble diorganotin(IV) phosphonates and their miniaturization into colloidal domain	71-102
CHAPTER V Reactivity studies of diethyl trimethylsilylmethylphosphonate and its implication in organotin chemistry	103-126
REFERENCES	127-141
APPENDIX Figures and Tables	142-153

BIODATA OF THE AUTHOR

ABSTRACT

The work embodied in the thesis relates to the synthesis and structural studies of diorganotin(IV) based coordination assemblies derived from silaalkylphosphonic acids, $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OH})_2$, $\text{R}^1\text{R}^2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ ($\text{R}^1, \text{R}^2 = \text{Et}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$) and $\text{Me}_3\text{SiC}(\text{CH}_3)_2\text{P}(\text{O})(\text{OH})_2$. The choice of these ligands is driven by a desire to improve the solubility of the resulting coordination frameworks and take advantage of this property to transform the as-synthesized compounds into nano/colloidal domains using solution based approach. The thesis has been divided into five chapters.

Several diorganotin complexes of composition, $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_x\text{SiR}^1\text{R}^2\}(\text{OSO}_2\text{Me})$ (**4-12**) have been synthesized by following the synthetic protocol reported earlier from our group. The X-ray crystallographic studies of a few such compounds reveal the formation of one-dimensional/layered/lamellar structural motifs, depending upon the nature of organic substituents on tin and phosphonate groups. The results are included in chapter III.

The incorporation of the silaalkylphosphonate groups in diorganotin(IV) phosphonates, $\text{R}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ [$\text{R} = \text{Et}$ (**13**), $n\text{-Bu}$ (**14**)], $\text{R}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiR}^1\text{R}^2\}$ [$\text{R}^1, \text{R}^2 = \text{Et}$ (**15**, **16**); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (**17**, **18**)] and $\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_x\text{SiR}^1\text{R}^2\}_2$ [$x = 1$, $\text{R}^1, \text{R}^2 = \text{Me}$ (**19**); $x = 3$; $\text{R}^1, \text{R}^2 = \text{Et}$ (**20**), $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (**21**)] imparts ready solubility in common organic solvents including hydrocarbons and ethers. This property has been utilized to transform the as-synthesized compounds into nano/colloidal domains *via* ultrasonication of their solutions in ethanol-chloroform mixture. Depending upon the nature of the alkyl substituents on tin and phosphonate ligands, rod, disc or spherical morphologies are obtained. A preliminary screening of the complexes, **13-18** for their antibacterial activity against Gram-positive bacteria, *Bacillus subtilis* reveal that the colloidal particles show antibacterial activity while no inhibition zone was observed for their bulk counterparts.

The work embodied in this chapter also includes spectral studies of diorganotin bis(hydrogenphosphonate)s, $R_2Sn\{OP(O)(OH)CH_2SiMe_3\}_2$ [$R = Et$ (**22**), n -Bu (**23**)] and $R_2Sn\{OP(O)(OH)(CH_2)_3SiR^1R^2\}_2$ [$R^1, R^2 = Et$ (**24**, **25**); $R^1 = Ph, R^2 = Me$ (**26**, **27**)] in solution. Based on multinuclear NMR studies, it has been suggested that these compounds adopt a dimeric structure bearing bridging and terminal hydrogenphosphonate groups. The results emerging from these studies are included in chapter IV.

The content of chapter V provides an insight into the reactivity studies of diethyl trimethylsilylmethylphosphonate $Me_3SiCH_2P(O)(OEt)_2$ (**1a**) and its implications in organotin chemistry. The chemical transformation of **1a** into $Me_3SiC(CH_3)_2P(O)(OH)_2$ (**H₂L**) and the isolation of a few mixed-ligand diorganotin(IV) coordination polymers, $R_2Sn(HL)(OSO_2Me)$ [$R = Me$ (**29**), n -Bu (**31**)] and $(Et_2Sn)_6(L)_4(OSO_2Me)_4$ (**30**) are discussed in this section. These compounds have been characterized by IR, multinuclear NMR as well as X-ray crystal structure analysis (for **30**). The isolation of $MeP(O)(OEt)O^- Na^+$ (**32**) is achieved from the reaction of **1a** with ethanolic sodium hydroxide under optimized conditions. Using this ligand, a few diorganotin bis(*O*-ethylmethylphosphonate)s $R_2Sn\{OP(O)(OEt)Me\}_2$ [$R = Me$ (**33**), Et (**34**), n -Bu (**35**)] have been isolated and characterized by spectroscopic methods as well as X-ray crystal structure analysis of **35**. We also examined the reactivity of **1a** towards diorganotin oxides in the presence of triethylamine. This approach has been useful to synthesize α -functionally substituted tetraorganotin compounds, $R_2Sn\{CH_2P(O)(OEt)_2\}_2$ [$R = Me$ (**36**), Et (**37**), n -Bu (**38**)]. A putative mechanism for the formation of these compounds has been proposed by considering phosphonate-stabilized carbanion, $(EtO)_2P(O)CH_2^-$ as the intermediate.

LIST OF FIGURES

Figure No.	Description	Page No.
Chapter III		
3.1	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OEt})_2$ (1a).	45
3.2	(a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of $\text{PhMe}_2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OEt})_2$ (3a).	45
3.3	^1H NMR spectrum of $\text{Et}_3\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ (2).	49
3.4	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{PhMe}_2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ (3).	49
3.5	(a) Asymmetric unit of 1 . (b) 2D layered structure of 1 featuring O-H $\cdots$ O hydrogen bonding (view along <i>c</i> -axis).	51
3.6	(a) Asymmetric unit of 3 . (b) A perspective view of O-H $\cdots$ O hydrogen bonding interactions along <i>c</i> -axis. (c) 3D supramolecular assembly (view along <i>a</i> -axis).	53
3.7	(a) 1D structure of 5 viewed along <i>c</i> -axis. (b) 2D structure of 5 in <i>ab</i> -plane showing intermolecular hydrogen bonding interactions.	56
3.8	(a) Asymmetric unit of 9 . Layered structure of 9 in <i>ab</i> -plane.	58
3.9	(a) Asymmetric unit of 12 . (b) 2D structure of 12 (view along <i>a</i> -axis). (c) Lamellar structure of 12 (view along <i>b</i> -axis).	59
3.10	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}(\text{OSO}_2\text{Me})$ (5).	64
3.11	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiEt}_3\}(\text{OSO}_2\text{Me})$ (9).	64
3.12	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiPhMe}_2\}(\text{OSO}_2\text{Me})$ (12) in (a) solution and (b) in solid state.	65
Chapter IV		
4.1	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiPhMe}_2\}$ (17).	77
4.2	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}$ (16).	77
4.3	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}$ (15).	79
4.4	Solid state ^{119}Sn (CP-MAS) NMR spectrum of	

Figure No.	Description	Page No.
	$\text{Et}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}$ (15).	79
4.5	Rod-like morphologies of as synthesized (a) 13 and (b) 15 ; (c) flake-like particles of 14 (d) Rosette-like morphologies of 16 .	81
4.6	(a) SEM and (b) HR-TEM micrographs of nanorods of $\text{Et}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ (13) and $\text{Et}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}$ (15).	83
4.7	(a) SEM micrograph of nano particles of $n\text{-Bu}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ (14) and (b) HR-TEM image of disk shape particles of $n\text{-Bu}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}$ (16).	83
4.8	Inhibition zone for 13-16 against Gram-positive bacteria <i>B. subtilis</i> . (a) colloidal particles (b) bulk samples (S1) ethanol-chloroform (5:1) (S2) chloroform.	84
4.9	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}_2$ (20).	87
4.10	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiEt}_3\}_2$ (20) (a) in CDCl_3 (b) in solid state.	88
4.11	SEM images of (a) as synthesized and (b) spherical nano particles of 20 (Inset: HR-TEM image).	90
4.12	Thermogravimetric analysis of (A) $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}_2$ (22) (B) $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiEt}_3\}_2$ (24) and (C) $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiPhMe}_2\}_2$ (26).	93
4.13	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}_2$ (23) (a) in CDCl_3 and (b) in solid state.	98
4.14	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}_2$ (23) in CD_3OD .	99
4.15	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiEt}_3\}_2$ (25).	99

Chapter V

- 5.1 (a) ORTEP view of asymmetric unit of **28**. The thermal ellipsoids are set at 40% probability. (b) 1D ribbon-like structural motif of **28** (view along *b*-axis), showing O-H $\cdots$ O

Figure No.	Description	Page No.
	hydrogen bonding interactions.	106
5.2	(a) Asymmetric unit of 30 . (b) Extended 2D layered structure (view along <i>b</i> -axis).	108
5.3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{Et}_2\text{Sn})_6\{\text{O}_3\text{PC}(\text{CH}_3)_2\text{SiMe}_3\}_4(\text{OSO}_2\text{Me})_4$ (30).	111
5.4	(a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $(\text{Et}_2\text{Sn})_6\{\text{O}_3\text{PC}(\text{CH}_3)_2\text{SiMe}_3\}_4(\text{OSO}_2\text{Me})_4$ (30).	111
5.5	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (35).	116
5.6	(a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (34).	116
5.7	(a) Asymmetric unit of 35 . (b) One-dimensional structure viewed along <i>b</i> -axis.	117
5.8	ESI-MS (positive ion mode) spectrum of $n\text{-Bu}_2\text{Sn}\{\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2$ (38).	123
5.9	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Me}_2\text{Sn}\{\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2$ (36).	123
5.10	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $n\text{-Bu}_2\text{Sn}\{\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2$ (38).	124
5.11	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2$ (37).	124
Appendix		
A1	Powder X-ray diffraction pattern of $\text{Et}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ (13). (a) as synthesized sample and (b) after immersed in water.	147
A2	SEM micrographs of as synthesized (a) $\text{Et}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiPhMe}_2\}$ (17) and (b) $n\text{-Bu}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiPhMe}_2\}$ (18).	148
A3	SEM micrographs of as synthesized (a) $\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)_2$ (19) and (b) $\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiPhMe}_2\}_2$ (21).	148

LIST OF TABLES

Table No.	Description	Page No.
Chapter III		
3.1	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OEt})_2$ (1a) and $\text{R}^1\text{R}^2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OEt})_2$ [$\text{R}^1, \text{R}^2 = \text{Et}$ (2a); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (3a)]	44
3.2	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OH})_2$ (1) and $\text{R}^1\text{R}^2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ [$\text{R}^1, \text{R}^2 = \text{Et}$ (2); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (3)]	48
3.3	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}(\text{OSO}_2\text{Me})$ [$\text{R} = \text{Me}$ (4), Et (5), $n\text{-Bu}$ (6)]	61
3.4	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiEt}_3\}(\text{OSO}_2\text{Me})$ [$\text{R} = \text{Me}$ (7), Et (8), $n\text{-Bu}$ (9)]	62
3.5	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiPhMe}_2\}(\text{OSO}_2\text{Me})$ [$\text{R} = \text{Me}$ (10), Et (11), $n\text{-Bu}$ (12)]	66
Chapter IV		
4.1	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ [$\text{R} = \text{Et}$ (13), $n\text{-Bu}$ (14)] and $\text{R}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiR}^1\text{R}^2\}$ [$\text{R}^1, \text{R}^2 = \text{Et}$, $\text{R} = \text{Et}$ (15), $n\text{-Bu}$ (16); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R} = \text{Et}$ (17), $n\text{-Bu}$ (18)]	74
4.2	$^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}(\text{O}_3\text{PCH}_2\text{SiMe}_3)$ [$\text{R} = \text{Et}$ (13), $n\text{-Bu}$ (14)] and $\text{R}_2\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_3\text{SiR}^1\text{R}^2\}$ [$\text{R}^1, \text{R}^2 = \text{Et}$, $\text{R} = \text{Et}$ (15), $n\text{-Bu}$ (16); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R} = \text{Et}$ (17), $n\text{-Bu}$ (18)]	75
4.3	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Sn}\{\text{O}_3\text{P}(\text{CH}_2)_x\text{SiR}^1\text{R}^2\}_2$ [$x = 1$, $\text{R}^1, \text{R}^2 = \text{Me}$ (19); $x =$	

	3, $R^1, R^2 = \text{Et}$ (20); $R^1 = \text{Ph}, R^2 = \text{Me}$ (21)	86
4.4	^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}_2$ [$\text{R} = \text{Et}$ (22), $n\text{-Bu}$ (23)] and $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiR}^1\text{R}^2\}_2$ [$\text{R}^1, \text{R}^2 = \text{Et}, \text{R} = \text{Et}$ (24), $n\text{-Bu}$ (25); $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Me}, \text{R} = \text{Et}$ (26), $n\text{-Bu}$ (27)]	94
4.5	$^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}_2$ [$\text{R} = \text{Et}$ (22), $n\text{-Bu}$ (23)] and $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiR}^1\text{R}^2\}_2$ [$\text{R}^1, \text{R}^2 = \text{Et}, \text{R} = \text{Et}$ (24), $n\text{-Bu}$ (25); $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Me}, \text{R} = \text{Et}$ (26), $n\text{-Bu}$ (27)]	95
Chapter V		
5.1.	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Me}_3\text{SiC}(\text{CH}_3)_2\text{P}(\text{O})(\text{OH})_2$ (28), $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{C}(\text{CH}_3)_2\text{SiMe}_3\}(\text{OSO}_2\text{Me})$ [$\text{R} = \text{Me}$ (29), $n\text{-Bu}$ (31)] and $(\text{Et}_2\text{Sn})_6\{\text{O}_3\text{PC}(\text{CH}_3)_2\text{SiMe}_3\}_4(\text{OSO}_2\text{Me})_4$ (30)	110
5.2	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{MeP}(\text{O})(\text{OEt})\text{O}^-\text{Na}^+$ (32), and $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ [$\text{R} = \text{Me}$ (33), Et (34), $n\text{-Bu}$ (35)]	114
5.3	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{CH}_2\text{P}(\text{O})(\text{OEt})_2\}_2$ [$\text{R}^1 = \text{Me}$ (36), Et (37), $n\text{-Bu}$ (38)]	121
Appendix		
A1	Summary of the crystallographic data for $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OH})_2$ (1) and $\text{PhMe}_2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ (3)	142
A2	Selected Bond Lengths ($\text{\AA}$) and Angles (deg) for $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OH})_2$ (1)	143
A3	Selected Bond Lengths ($\text{\AA}$) and Angles (deg) for $\text{PhMe}_2\text{Si}(\text{CH}_2)_3\text{P}(\text{O})(\text{OH})_2$ (2)	143
A4	Summary of the crystallographic data for $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})\text{CH}_2\text{SiMe}_3\}(\text{OSO}_2\text{Me})$ (5), $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiEt}_3\}(\text{OSO}_2\text{Me})$ (9) and $n\text{-Bu}_2\text{Sn}\{\text{OP}(\text{O})(\text{OH})(\text{CH}_2)_3\text{SiPhMe}_2\}(\text{OSO}_2\text{Me})$ (12)	144

A5	Selected Bond Lengths (Å) and Angles (deg) for Et ₂ Sn{OP(O)(OH)CH ₂ SiMe ₃ }(OSO ₂ Me) (5)	145
A6	Selected Bond Lengths (Å) and Angles (deg) for <i>n</i> - Bu ₂ Sn{OP(O)(OH)(CH ₂) ₃ SiEt ₃ }(OSO ₂ Me) (9)	145
A7	Selected Bond Lengths (Å) and Angles (deg) for <i>n</i> - Bu ₂ Sn{OP(O)(OH)(CH ₂) ₃ SiPhMe ₂ }(OSO ₂ Me) (12)	146
A8	Summary of the crystallographic data for Me ₃ SiC(CH ₃) ₂ P(O)(OH) ₂ (28) and (Et ₂ Sn) ₆ {O ₃ PC(CH ₃) ₂ SiMe ₃ } ₄ (OSO ₂ Me) ₄ (30)	149
A9	Selected Bond Lengths (Å) and Angles (deg) for Me ₃ SiC(CH ₃) ₂ P(O)(OH) ₂ (28)	150
A10	Selected Bond Lengths (Å) and Angles (deg) for (Et ₂ Sn) ₆ {O ₃ PC(CH ₃) ₂ SiMe ₃ } ₄ (OSO ₂ Me) ₄ (30)	151
A11	Summary of the crystallographic data for <i>n</i> - Bu ₂ Sn{OP(O)(OEt)Me} ₂ (35)	152
A12	Selected Bond Lengths (Å) and Angles (deg) for <i>n</i> - Bu ₂ Sn{OP(O)(OEt)Me} ₂ (35)	153

Glossary of Symbols and Abbreviations

%	percent
°	degree
°C	degree centigrade
Å	Angstrom
AFM	atomic force microscopy
ATR	attenuated total reflectance
br	broad signal
b.p.	boiling point
d	Doublet
D	dimensional
ϵ	molar absorptivity
eq.	Equation
ESI	electrospray ionization
Et	ethyl
FT	fourier transform
g	gram
h	hour
HR-TEM	High resolution transmission electron microscopy
Hz	hertz
ICP	infinite coordination polymer
IR	infrared
J	coupling constant
λ	wavelength
μ	micro

m	multiplet
m.p.	melting point
Me	methyl
MHz	mega hertz
mL	milliliter
mmol	millimole
MOF	metal organic framework
<i>n</i> -Bu	<i>n</i> -butyl
nm	nanometer
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
q	quartet
rt	room temperature
SEM	scanning electron microscopy
t	triplet
<i>t</i> -Bu	<i>t</i> -butyl
TGA	thermogravimetric analysis
TMS	tetrametylsilane
δ	chemical shift
ν	frequency