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REDUCED MAIN GROUP COMPOUNDS:
STANNIDES AND PHOSPHIDES

Frédéric Guérin, B.Sc.

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ABSTRACT

The intermetallic phase, Na_4Sn, can be synthesised by a solid state reaction starting from stoichiometric quantities of the elements. It crystallizes in the orthorhombic space group P*nam* with 4 asymmetric units per unit cell (a=9.744(3)Å, b=22.751(10)Å, c=5,5390(15)Å). The reactivity of Na_4Sn with organic and inorganic halides, elements and organic cations was investigated.

The interconversion between P_{21}^{3-} and P_{16}^{2-} has been demonstrated. Coordinating solvents, such as THF and pyridine, stabilise the more reduced P_{21}^{3-} while the less reduced P_{16}^{2-} is favored when a non-coordinating solvent like EtOH is used. The reaction of P_{21}^{3-} with Bu_3SnCl yields the new polyphosphides P_{14}^{2-}. The structure of this new anion was deduced from ^{31}P studies.

ACKNOWLEDGEMENTS

I would like to thank Professor D. Richeson for his help during the last two years. Without him this work would not have been possible.

I would also like to thank Professor S. Gambarotta for his fruitful suggestions throughout this research.

Finally, I would like to thank my co-workers for their support.

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LIST OF ABBREVIATIONS

Bu	butyl
Bz	benzyl
Cp	cyclopentadienyl
DSC	differential scanning calorimetry
en	ethylenediamine
Et	ethyl
FTIR	Fourier transformed infra-red
Glyme (DME)	1,2-dimethoxyethane
HMPA	hexamethylphosphoric triamine
M.S.	mass spectrometry
Me	methyl
NMR	nuclear magnetic resonance
Ph	phenyl
PPNCl	bis(triphenylphosphine)ammonium chloride
RT	room temperature
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
XRD	X-ray diffraction
XRF	X-ray fluorescence

INTRODUCTION

The last few decades have seen a growing interest in the synthesis and characterization of the binary and ternary compounds formed between the electropositive alkali metals or alkaline earth metals and p-block elements such as Sn, Ge, P, or Te. These compounds are of general interest for several reasons: *(i)* their unusual structural features *(ii)* their potential use as starting material for the preparation of useful compounds and *(iii)* their physical properties related to their stoichiometry and structure.

The products obtained from these reactions can be classified into two major groups with the defining features being the interaction of the metal cation with the reduced p-block element. The first group, which will be referred to as binary or ternary *phases*, includes all the intermetallic compounds in which isolated molecular units are not found. Although varying degrees of interaction between the constituent atoms are discernable, their structures are infinite and uniform. As a general trend, these materials tend to have a high metal to p-block element ratio. In other words, the p-block element is, in a formal sense, highly reduced. One of the interesting features of these compounds is their covalent character. Recent literature examples include $Ca_{31}Sn_{20}$[1] and the related $Sr_{31}Pb_{20}$ as well as $LiSbTe_2$[2].

The second group can be classified as binary *anions* and is composed of all the molecular anionic species, both in the solid state or in solution. The ionic character of these compounds is greater than for their extended counter parts and may be sufficient to allow solvation of the cation with polar solvents.

Both classes of materials are known for the heavy elements of group 14, 15 and 16[3]. Particular emphasis has been directed toward Sn and Pb in group 14, P in group 15 and S, Se, and Te in group 16. One of the problems associated with structural characterisation of these species has been the difficulty in obtaining crystalline material and, for this reason, multinuclear NMR have been used extensively for their characterisation.

Surprisingly, there have been few studies concerning the reactivity of these species. Their potential use as precursors for the synthesis of semi-conductor materials has recently been demonstrated[4]. They may also provide an entry to new materials and molecules by functioning as ligands for organometallic complexes or as starting materials for the synthesis of inorganic polymers. Such polymers could have interesting electrical or magnetic properties based on the main group core. Ultimately, the polymerisation of these species would help to elucidate the transition between molecules and solid state compounds.

With these facts in mind, we have decided to focus our attention on the compounds containing phosphorus and/or tin as the main group elements. As starting materials for further exploration of the reactivity of these compounds they are among the most thoroughly characterised. In addition, the fact that they possess NMR active nuclei should allow the determination of the structural features of the products without relying on single crystal preparation. Table I shows useful data concerning these nuclei.

Table I Characteristics of ^{31}P, ^{117}Sn and ^{119}Sn

	^{31}P	^{117}Sn	^{119}Sn
Nuclear Spin	1/2	1/2	1/2
Natural abundance (%)	100	7.61	8.58
Receptivity (vs ^{13}C)	377	19.5	25.2
Chemical shift range *(a)* **(ppm)**	-500 to 300	*(b)*	-2000 to 500

(a) Reference to Me_4Sn for ^{119}Sn and to H_3PO_4 10% in water for ^{31}P

(b) Because of its higher relative abundance, ^{119}Sn is generally prefered

The high relative abundance of ^{31}P makes the homonuclear coupling easy to observe and structures of complex species can be proposed based solely on NMR data. In the case of tin, the presence of two nuclei often results in characteristic splitting pattern even in highly symmetrical species.

In the following sections, a brief overview of the related literature is presented. This is followed by a description of the results of our investigations of the binary and ternary phases and anions of tin and phosphorus.

CHAPTER 1: STANNIDES

BACKGROUND

The investigation of binary compounds of group 14 with the electropositive elements of groups 1 and 2 goes back to the beginning of the century. The first evidence of their existence was given by Johannis[5] who, while studying the addition of lead to ammonia solutions of sodium, noticed dramatic color changes. Intrigued by these observations, Smyth[6], Peck[7] and Kraus(8,9) began studies of this system but they were not able to explain these observations. Shortly thereafter Zintl[10] reported the first systematic investigation of these ammonia solutions. By employing potentiometric titration of $Na/NH_{3(l)}$ with PbI_2 he was able to identify the polyanions Pb_9^{4-} and Pb_7^{4-}. However, problems arose due to contamination of the solutions with alkali metal halides and the inability to observe the same effects with lighter elements, such as tin, forced him to search for new synthetic approaches to these compounds.

The first success was achieved by Zintl, Harder[11] and Dullenkopf[12] through the extraction of binary alloys, formed by fusion of the elements, with liquid ammonia. Starting from alloys of composition (Sn,Pb)/Na = 2.25 to 2.75, they were able to extract the homoatomic polyanions M_9^{4-} (M=Sn, Pb).

At this point, the investigation of these unusual alloys took two routes. The first approach was directed at obtaining crystalline binary phases directly via solid state synthesis. Recent examples include the high-pressure synthesis of LiSi[13], LiGe[14] and LiSn[15]. The second was to focus on the soluble products obtained from extraction of alloys of group 14 and electropositive group 1 elements with amine solvents such as ammonia or ethylenediamine.

Following the first approach, Zintl and Harder investigated the solid state alloys of the (Sn,Pb)/Na system and reported, based on X-ray diffraction, the crystal structures of two isostructural phases of composition $Na_{15}Pb_4$ and $Na_{15}Sn_4$[16]. These materials were reported to have a body-centered cubic structure with a_o=13.32Å and 76 (4*19) atoms per unit cell. This contrasted with a previous report[17] in which a phase of composition $Na_{31}Pb_8$ was reported to have a face centered cubic structure with a_o=13.30Å and 78 (2*39) atoms per unit cell. Moreover, earlier thermal analysis work by Mathewson[18], Boesch and Calingaert[19] indicated the existence of only one phase. In 1955, Shoemaker and co-workers reported the results of their analysis of the Na-Pb system[20]. Using different alloy preparation procedures which included annealing at 280°C for 60 hours followed by $N_{2(l)}$ quench or slow cooling, they were only able to reproduce Zintl's observation and found only the $Na_{15}Pb_4$ phase. The structure of the related "$Na_{15}Sn_4$" phase was not defined and the identity of the phase commonly referred to as Na_4Sn remained uncertain.

During the same period of time attempts to follow the second approach, the isolation of soluble polyanions, were unsuccessful. Simply evaporating the solvent only gave amorphous solids. This was believed to be a result of the instability of the solvent free cation which in order to achieve greater stability undergoes a back transfer of electrons from the polyanion to the cation with decomposition of the anion (equation 1a).

$$(Na(NH_3)_n^+)_4\, Pb_9^{4-} \rightarrow 4NaPb_{2.25} + 4nNH_3 \tag{1a}$$

The replacement of ammonia with ethylenediamine as the extraction solvent enabled Kummer and Diehl[21] to isolate, for the first time, a crystalline compound with the formula $[Na_4(en)_7]Sn_9$ (en=ethylenediamine). The crystal structure of this compound revealed the naked cluster anion Sn_9^{4-} and confirmed the earlier work of Zintl (Figure 1a).

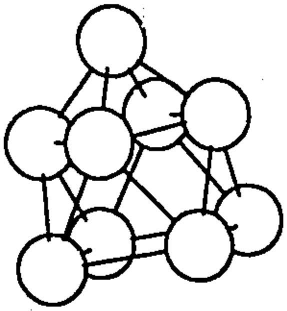

Figure 1a Crystal structure of the naked anion Sn_9^{4-}

Further attempts to crystallise other polyanions using ethylenediamine to both extract and stabilize the cation were unsuccessful and it rapidly became obvious that other methods to stabilize the cation had to be found.

In 1968, Corbett[22] showed that the cation complexing agent 2,2,2crypt[23] (Figure 1b) provided the needed stabilisation energy and allowed the crystallisation of a variety of anions. Table 1A lists some of the homopolyatomic anions that were crystallised with the use of crypt.

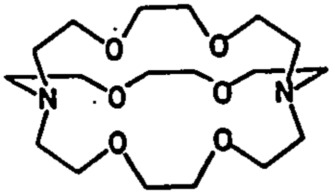

Figure 1b 2,2,2-Crypt

Table 1A Some group 14 homopolyatomic anions (crypt complexes)

Anion	**Symmetry**	**Characteristics**	p e$^-$	**ref**
Ge_9^{2-}	C_{2v}	Dark red rods	20	[24]
Ge_9^{4-}	C_{4v}	"	22	
Sn_9^{4-}	C_{4v}	"	22	[25]
Sn_9^{3-}	D_{3h}	Dark red plates	23*	[26]
Sn_5^{2-}	D_{3h}	Orange-brown plates	12	[27]
Pb_5^{2-}	D_{3h}	Ruby-red prisms	12	

* only known paramagnetic polyatomic anion

Following Corbett's work, Rudolph investigated the synthesis of heteroatomic polyanions with the general formula $(Sn_{9-x}M_x)^{4-}$ (x=0-

9) by extraction (M=Pb[28], Ge[29]) or electrolysis (M=Pb[30]) of ternary alloys. All of these investigations were based on multinuclear NMR studies and no crystal structures were reported.

The effectiveness of crypt at cation stabilization also enabled the isolation of mixed element clusters. This not only provided additional structural examples but also allowed the combination of electron poor (group 13) or electron rich (group 15 or 16) elements to form "doped" anions. Table 1B presents some of the known mixed polyanions.

Table 1B Some known "doped" polyanions

Anion	***p* e$^-$**	**ref**
$TlSn_8^{3-}$	20	31
$TlSn_9^{3-}$	22	"
$SnTe_4^{4-}$	22	32
$Sn_2Te_6^{4-}$	32	"
$Sn_2Bi_2^{2-}$	12	33
$SnAs_{14}^{4-}$	48	34

More recently[35], the use of other alkali metal cation coordinating agents such as HMPA (hexamethylphosphoric triamide) have been demonstrated to provide enough stabilisation to allow the crystallisation of some anions. The replacement of the alkali metal cation with tetraalkylammonium salts[35], such as Me_4N^+, has shown some limited success and allowed the isolation of the highly insoluble $(Me_4N)_4Sn_9$. However, the compounds obtained in these two cases are thermally unstable and decompose slowly at 25°C.

Finally, what is believed to be the "next frontier" in this area is the use of transition metal complexes to stabilise the cluster core. Only one example is known and was given by Huttner[36] in 1993. Starting from $SnCl_2$ and $K_4[Cr(CO)_5]$, he was able to synthesis the first octahedral main group polyanion $[Sn_6\{Cr(CO)_5\}_6]^{2-}$.

RESEARCH GOALS

1. Investigate the formation of sodium/tin binary alloys in order to provide a better understanding of the mechanisms involved in their formation. This could then allow a better control of their synthesis and ultimately lead to the formation of new species

2. Examine the reactivity of these alloys toward metathesis reactions with both organic and inorganic halides. Such reactions could provide alternative routes for the synthesis of useful compounds which are normally prepared via high temperatures solid state reactions.

3. Study the ability of these alloys to act as precursors for the synthesis of new mixed polyanions by introduction of a third component in the system. The resulting species could possess new and unusual structural features as well as interesting properties.

RESULTS AND DISCUSSION

Alloy preparation : synthesis of Na_4Sn

Several phases are present in the Na/Sn phase diagram (Figure 1c). Among these some controversy exists as to the structure and identity of the compound richest in Na, Na_4Sn. Our investigations of this system began with the preparation of binary alloys by heating, under dynamic $N_{2(g)}$ in a glass tube, the two elements to 300°C for 30 minutes. The reaction tubes were then cooled, the solid ground and extracted with ethylenediamine or liquid ammonia to remove any soluble species or unreacted metallic sodium. A summary of the reaction conditions used for the synthesis of these alloys is presented in Table 1C.

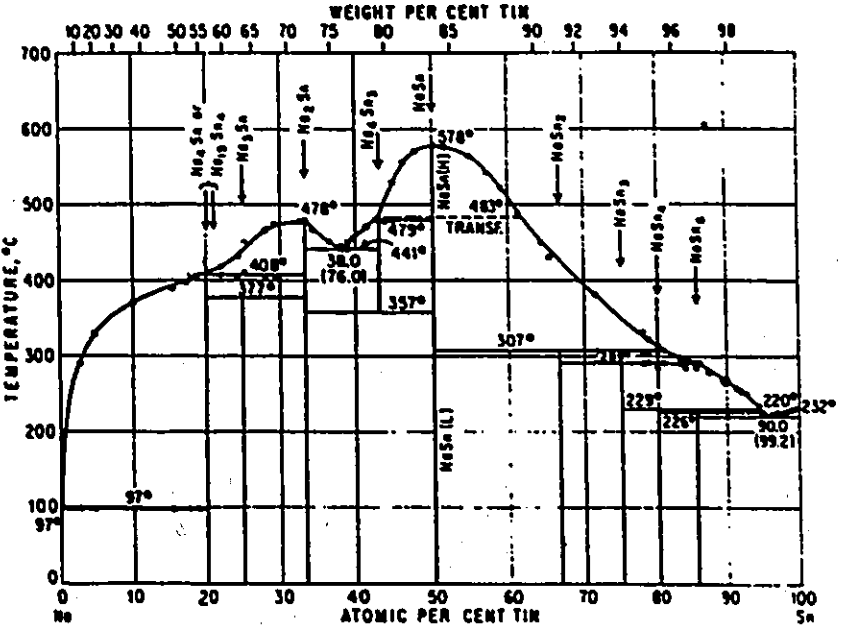

Figure 1c Na/Sn phase diagram (from: Constitution of binary alloys, second edition, Hansen, McGraw Hill book company, 1958, 1005)

Table 1C Synthesis of Na/Sn alloys : reaction conditions

Stoichiometry	**Products**	**Extraction products**
Na/Sn < 3.8/1	black alloys	ethylenediamine : Sn_9^{4-}
Na/Sn = (3.8-4.1)/1	metallic grey crystals	no soluble products were formed
Na/Sn > 4.1/1	crystals	$NH_{3(l)}$: Na

All the sodium-poor alloys, those with a Na/Sn ratio lower than 3.8, gave upon extraction with ethylenediamine or $NH_{3(l)}$, very dark red solutions for which the ^{119}Sn NMR showed a 0.060:0.311:1.000:0.309:0.030 pseudo quintet centered at 1230ppm upfield from the tetramethyltin signal (Figure 1d). The calculated relative intensities of the multiplet for a 9 atoms cluster are 0.044:0.311:1.000:0.311:0.044 based on abundances of 8.58% and 7.61% for ^{119}Sn and ^{117}Sn, respectively. This signal confirmed that the only soluble Sn compound was the nonastannide tetraanion (Sn_9^{4-})[28]. However, the best yield of Sn_9^{4-} were obtained with alloys of composition $NaSn_{2.25}$. As indicated by the phase diagram, pure, congruently melting Na_4Sn should be obtained for the alloys of composition Na/Sn = 4/1. Reaction with this stoichiometry yielded metallic grey crystalline material in quantitative yield. Similar results were obtained when a slight excess sodium was used. However, in these cases, the excess sodium remained unreacted and had to be removed by washing with $NH_{3(l)}$. DSC studies (Figure 1e) of the crystals showed, consistent with the phase diagram, a reversible endotherm at 407°C which corresponds to the melting of the compound.

It is important to notice that the melting point of the crystals is higher than the temperature at which they are formed (300°C). A likely explanation may be that the sodium (T_m=98°C) act as a flux, in the early stage of the reaction, there is enough $Na_{(l)}$ to dissolve the compound. As the reaction proceeds, the amount of sodium left unreacted is smaller and the solution become saturated and starts to crystallise. Finally, when all the sodium has reacted the compound precipitates. This hypothesis could also explain the higher crystallinity of the products obtained when a slight excess sodium is used.

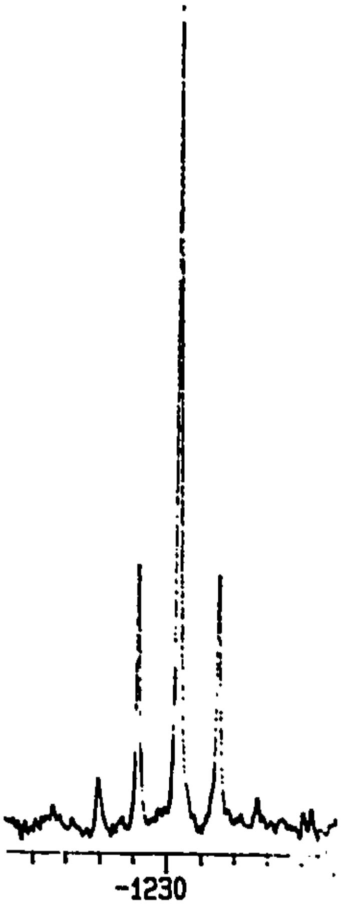

Figure 1d ^{119}Sn NMR of Sn_9^{4-} (in ethylenediamine)

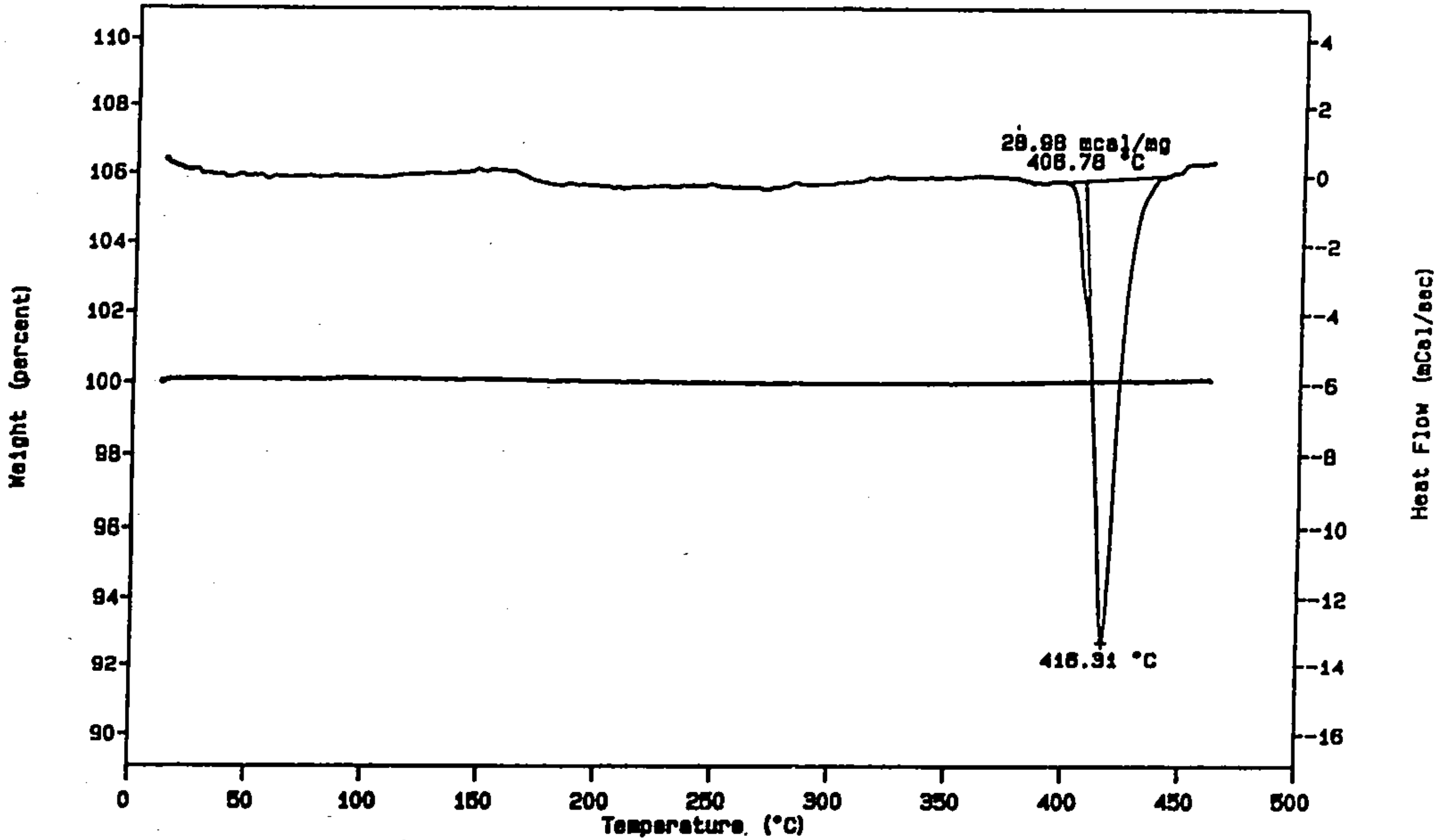

Figure 1e DSC of Na_4Sn

Crystal structure of Na_4Sn

Table 1D Crystal structure of Na_4Sn: Experimental details

Empirical formula	Na_4Sn
Formula weight	210.65
Crystal shape	cube
Crystal dimensions(mm)	0.4*0.3*0.3
Crystal system	orthorhombic
No. reflection used for unit cell dimension (2θ range)	25 (40°-50°)
Lattice parameters	a=9.744(3) b=22.751(10) c=5.5390(15)
Space group	Pnam
Z value	8
Dcalc (g/cm^3)	2.279
F(000)	746.14
μ (mm^{-1})	4.30
No of reflection measured	1202
No of reflection unique	1202
No of reflection observed	1052
No of atoms	10
No of variables	62
Rf (sign refl)	0.071
Rw (sign refl)	0.111
Rf (all refl)	0.097
Rw (all refl)	0.112
Goodness of fit	4.29
last difference Fourier map	
max peak	0.2550
min peak	-3.950

The Na_4Sn extended structure is based on the asymmetric unit shown in Figure 1f with the tin atoms emphasized to demonstrate the two different environments. The first tin atom (Sn1) lies on one corner of a tetragon completed with three sodium atoms (Na4, Na8 and Na1), it also forms a pseudo-octahedron with the other five sodium environments (Na6, Na5, Na3, Na2 and Na7). The other tin atom (Sn2) is sticking out of the asymmetric unit and is attached to Na1. A view of one unit cell of Na_4Sn along the a axis is given in Figure 1g. The unit cell is composed of four asymmetric units with alternating orientation. Expansion to two unit cell along the b axis (Figure 1h) shows the columnar character of the structure. The Sn2 atoms bridges between the Na1 atoms of adjacent asymmetric units forming columns. These columns are then oriented alternatively head-to-head and tail-to-tail to expand the structure in the c dimension. The position of the Sn2 atoms relative to the columns is better shown in Figure 1i. This figure also shows the interpenetration of the tetragonal planes of alternating columns.

A few features are striking in the structure: *(i)* it is not a closest packed structure like one might expect for a simple alloy *(ii)* there is no significant Sn-Sn interaction *(iii)* the presence of two different tin environments.

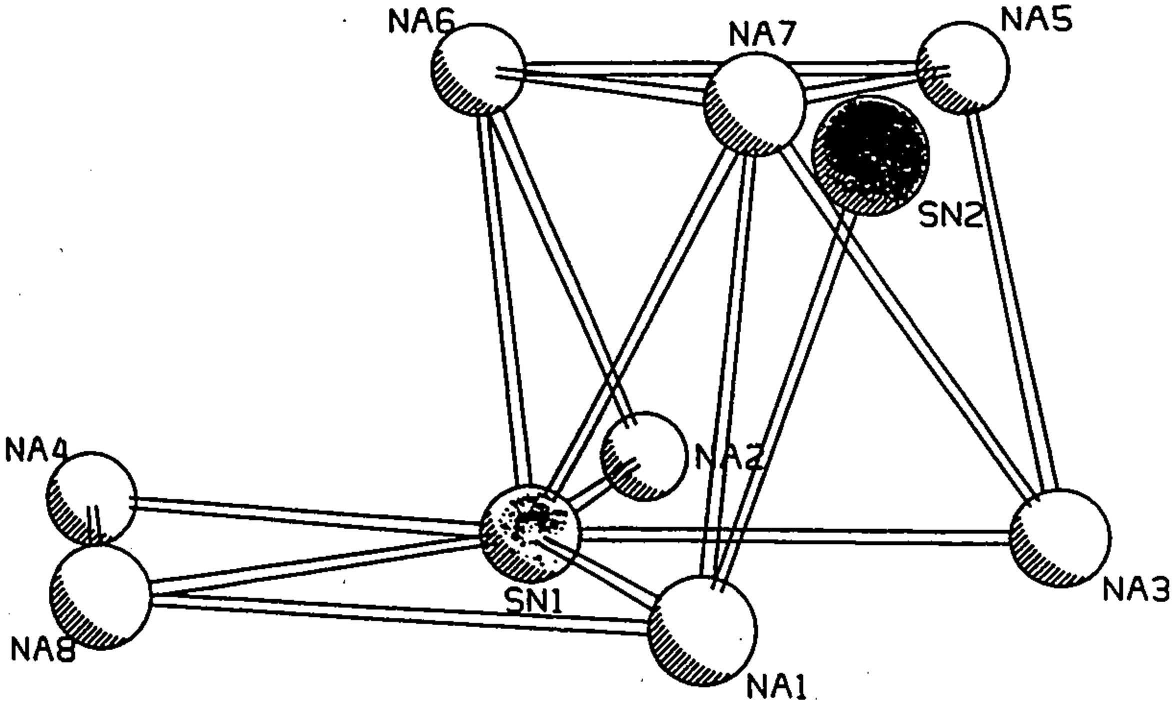

Figure 1f Na_8Sn_2 asymetric unit with the tin atoms emphasized. (Sn1 light, Sn2 dark)

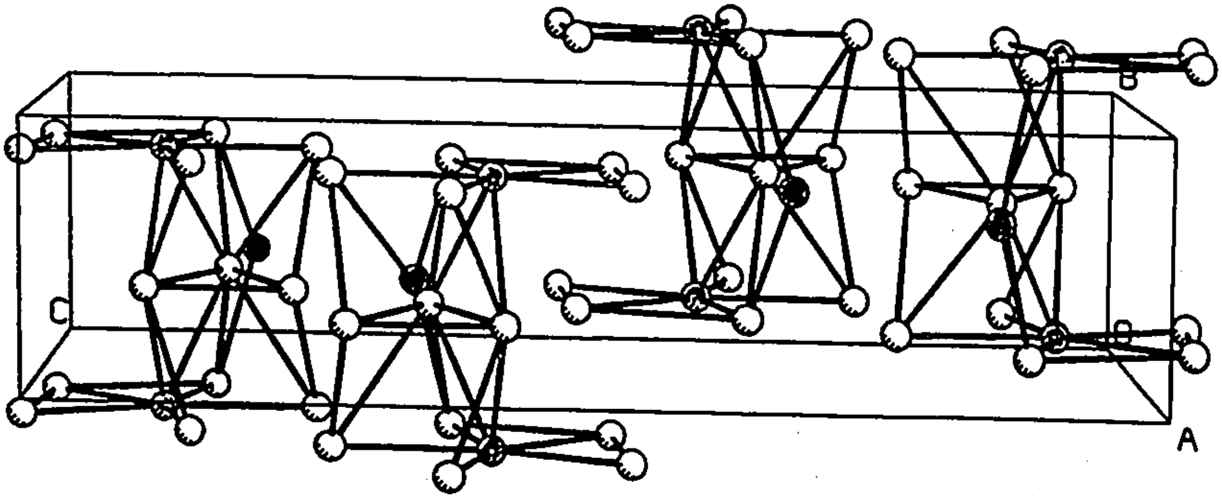

Figure 1g View along the a axis of one unit cell of Na_4Sn with the tin atoms emphasized

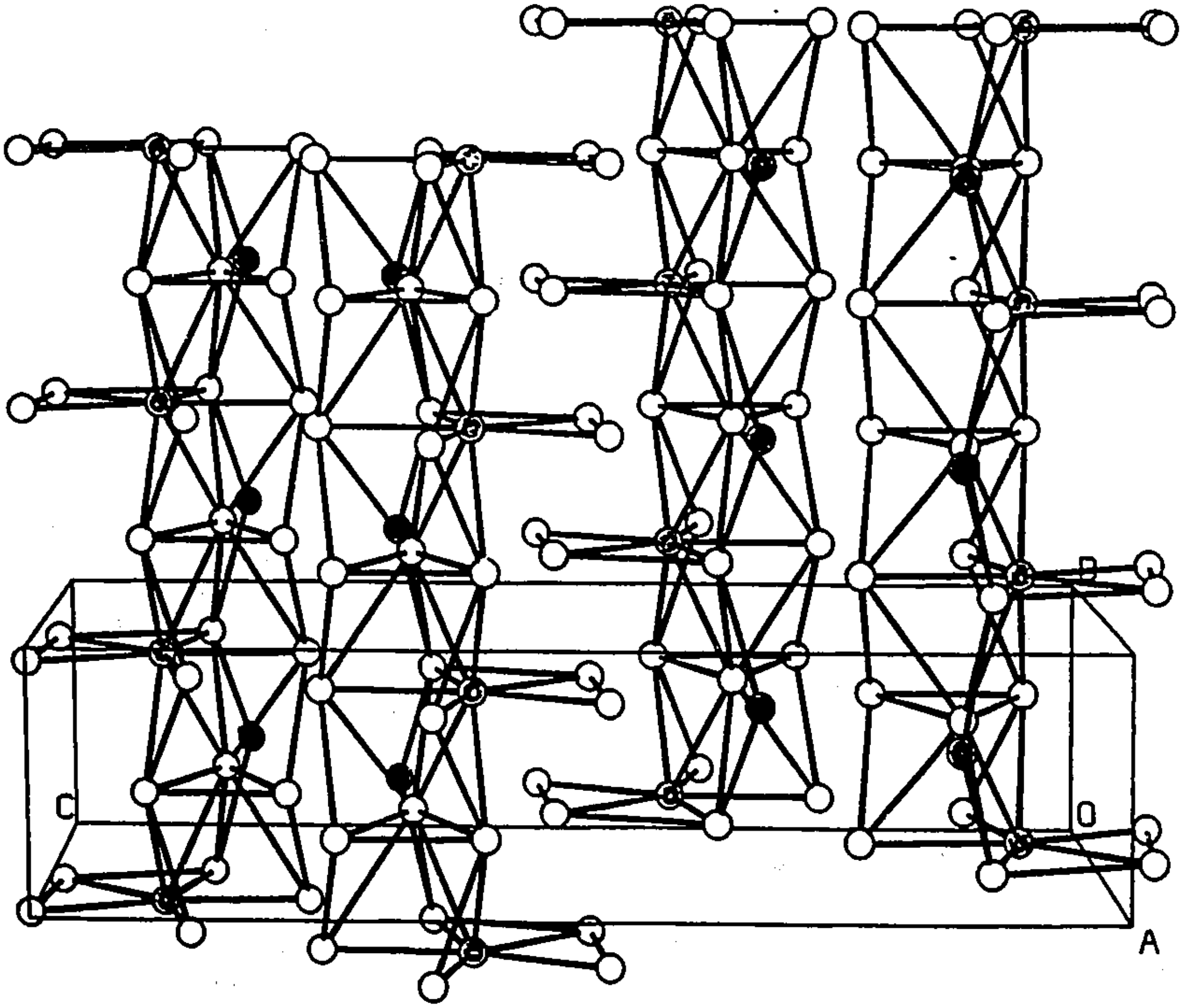

Figure 1h View along a of Na_4Sn, expanded by 2 unit cell along b

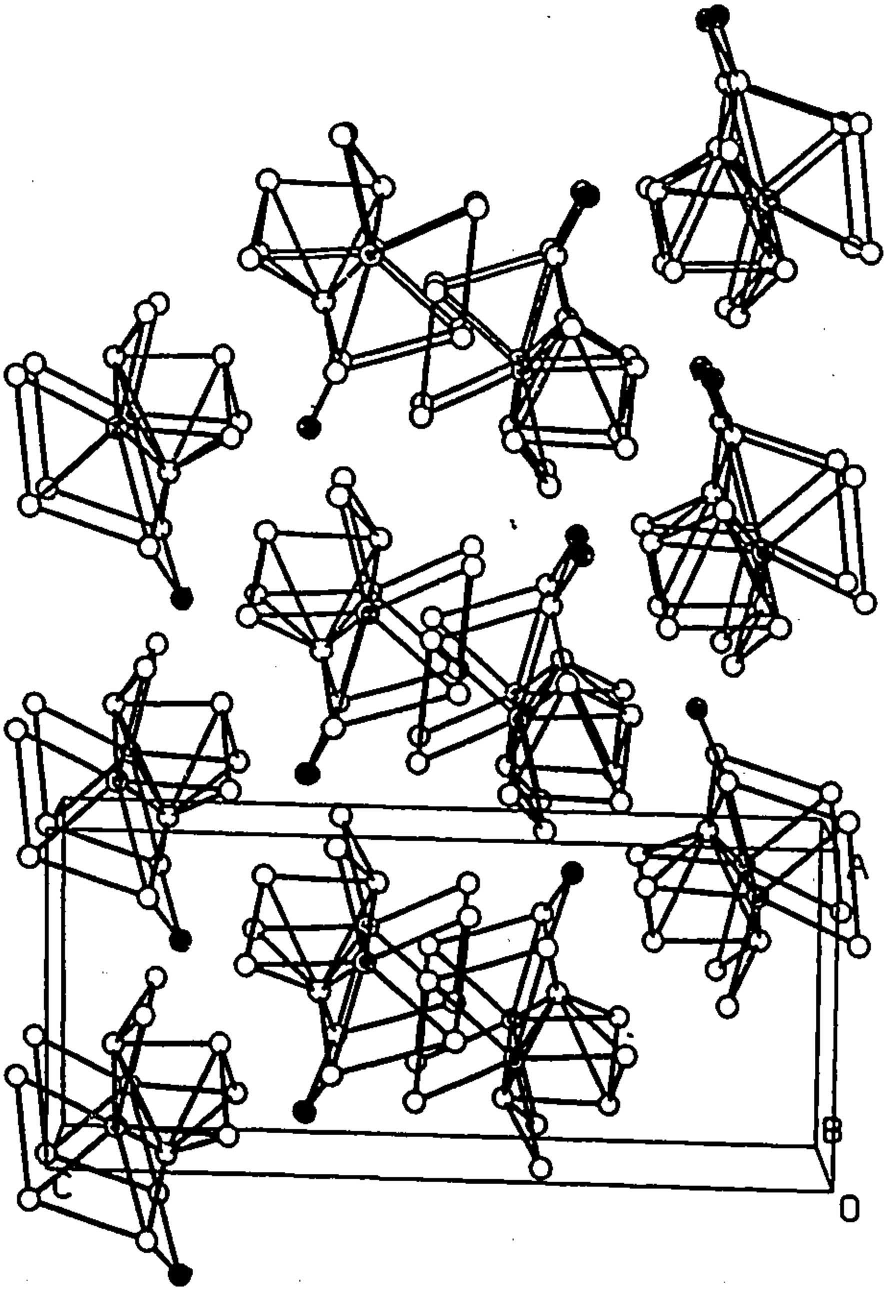

Figure 11 View along b of Na_4Sn, expanded by two unit cell in the a dimension

Comparison of the powder pattern calculated from the crystal structure (Table 1E) with the one obtained experimentally demonstrated the macroscopic homogeneity of the crystalline powder.

Table 1E Calculated and experimental powder patterns for Na_4Sn

Experimental		**Calculated**	
2	**int.(%)**	**2**	**int.(%)**
		14.8	12
15.6	31	15.6	29
16.5	11		
18.1	48	18.1	51
		18.6	43
18.8	40	18.8	54
		19.9	20
20.0	26	20.0	33
21.6	11	21.7	11
		21.9	21
31.9	51	31.9	38
		32.3	46
32.8	100	32.9	100
34.0	48	34.0	70
		37.2	16
37.4	24	37.5	13
38.2	27		

Reactivity of Na_4Sn

In order to define the reactivity of Na_4Sn four types of reactions were performed : reactions with elements, inorganic and organic halides and organic cations. The results of these reactions are discussed below.

Reactions of Na_4Sn with elements

The synthesis of mixed main group ternary phases or mixed element anions generally involves high temperature reactions of the elements in sealed tubes. This technique allows very little control of the reaction products and low yields are commonly obtained. The reaction of Na_4Sn with main group elements may provide a more controlled route for the synthesis of such compounds. Our first efforts were directed toward the investigation of the reaction of Na_4Sn with elemental phosphorus and sulfur. The reasons for this are two-fold. First, phosphorus and sulfur are known to make a wide variety of catenated phases and anions. Second, our experience with ^{31}P NMR spectroscopy[a] in the characterisation of polyphosphides could be of some importance.

Reactions of Na_4Sn with red phosphorus were performed by heating the two powders in a sealed tube at 150°C for 8 hours. For the reactions with white phosphorus, the Na_4Sn was refluxed in

---

[a] see chapter II, Polyphosphides

toluene solution of white phosphorus for 8 hours. Both procedures yielded black amorphous powders and no diffraction pattern was observed by powder XRD. Addition of ethylenediamine to these powders gave dark orange solutions as well as gas evolution. ^{119}Sn NMR of the orange solution showed the presence of Na_4Sn_9 (quintet at -1230ppm) while the ^{31}P NMR of that same solution showed only one signal at -273.1 ppm characteristic of $NaPH_2$[60]. The gas was characterised by mass spectrometry and ^1H NMR spectroscopy and identified as a mixture of $MeNH_2$ and $EtNH_2$[b].

These observations and the corresponding ones obtained from the reaction of Na_3P with ethylenediamine can be explained by proposing reaction 1b for the interaction of Na_4Sn and P^a.

$$Na_4Sn + x\,P \rightarrow x\,Na_3P + Na_{4-3x}Sn_{alloy} \tag{1b}$$

In this reaction the Na_4Sn acts as a reducing agent toward phosphorus to form Na_3P and an alloy containing the remaining sodium and tin. Extraction of this mixture with ethylenediamine results in a simple extraction of a tin-rich Na/Sn alloy to give Na_4Sn_9 while the Na_3P reacts with the ethylenediamine to form the $NaPH_2$, the $MeNH_2$ and the $EtNH_2$.

Unlike the reactions with elemental phosphorus, the reactions of Na_4Sn with elemental sulfur were extremely violent and self-

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[b] see discussion on the synthesis $NaPH_2$ for the identification of the products (page 48)

initiated when the two powders were put in contact. The products of these reactions were heterogeneous and amorphous rending their characterisation nearly impossible.

Reactions of Na_4Sn with inorganic halides

Reaction of inorganic halides and reduced main group element compounds may offer an alternative to the high temperature, direct reaction of element commonly employed in solid state synthesis. In these reactions, high $\Delta H_{reaction}$ supplies the energy for the propagation. Such solid state metathesis reactions have recently[4] been used in the synthesis of groups III-V semiconductors. Sodium and lithium pnictides, Na_3E and Li_3E (E=N,P,As,Sb) react with metal halides such as $GaCl_3$ or $TiCl_4$ to form GaE or TiE (equation 1c and 1d).

$$GaCl_3 + Na_3P \rightarrow GaP + 3\ NaCl \rightarrow GaP \qquad (1c)$$

$$3MCl_4 + 4Li_3N \rightarrow 12LiCl + 3MN + 0.5N_2 \qquad (1d)$$

where M = Ti, Zr, Hf or V[37]

Metathesis reactions starting from Na_4Sn and metal halides were explored in an effort to prepare new stannides and to offer alternative methods for the synthesis of known ones. The advantage of such reactions is that they could provide low temperature alternatives to the high temperature and pressure routes normally involved in the synthesis of these materials.

The phase diagrams for both Al/Sn and Ga/Sn systems are typical of a two component system which does not form any compounds. The reactions of Na_4Sn with $AlCl_3$ and $GaCl_3$ self-initiated within seconds when the two powders were simply placed in contact of one another. In order to prevent self initiation, the reactions were performed in a two zone tube, with one of the components in each zone. The tube was then sealed under vacuum and the metal halides slowly sublimed into the zone containing the Na_4Sn. Even in these conditions, the reactions were extremely violent and the products heterogenous. Grinding and annealing of the powders did not improve the homogeneity of the products. However, DSC studies allowed the identification of metallic tin as one of the products.

Three compounds are seen in the Nb/Sn phase diagram: Nb_3Sn, Nb_6Sn_5 and $NbSn_2$. Of these, Nb_3Sn is of particular interest due to the fact that it exhibits one of the highest superconducting transition temperatures (T_c = 18.05 K) for a simple binary alloy. The reactions between Na_4Sn and $NbCl_5$ self-initiated upon grinding with a mortar and pestle. In order to obtain homogeneous products, the separate components were placed in a teflon lined acid digestion bomb and the reaction was thermally initiated at 150°C. The temperature was then held constant for 12 hours after which a black powder was obtained. Removal of the NaCl from this black powder by successive washing with H_2O, EtOH and Et_2O yielded a black powder with a typical composition of Nb_3Sn. SEM and XRD of the black powder revealed its homogeneous and amorphous nature. Thermal studies showed that heating the sample in an inert atmosphere to 1200°C does not result in an increased crystallinity nor does it cause a decomposition. However decomposition was observed at 500°C when the powder was heated in air. Variable temperature conductivity measurements on the powder showed a temperature dependence of the conductivity (Figure 1j) which is typical of a semiconductor and no drop in resistance was noted near T_c of 18.05k.

Reactions of Na_4Sn with organic halides

Based on the high reactivity of Na_4Sn with inorganic halides, one might expect that when put in contact with organic halides, Na_4Sn would react to eliminate NaCl and form the metathesis SnR_4 products. Moreover, it has been demonstrated[38] that Na_3P reacts violently with trimethylsilyl chloride to form the phosphine with formation of NaCl. However, as presented in Table 1F, Na_4Sn did not react with any organic halides. Even under forcing conditions, neat reagent and reflux, the starting materials remained unchanged.

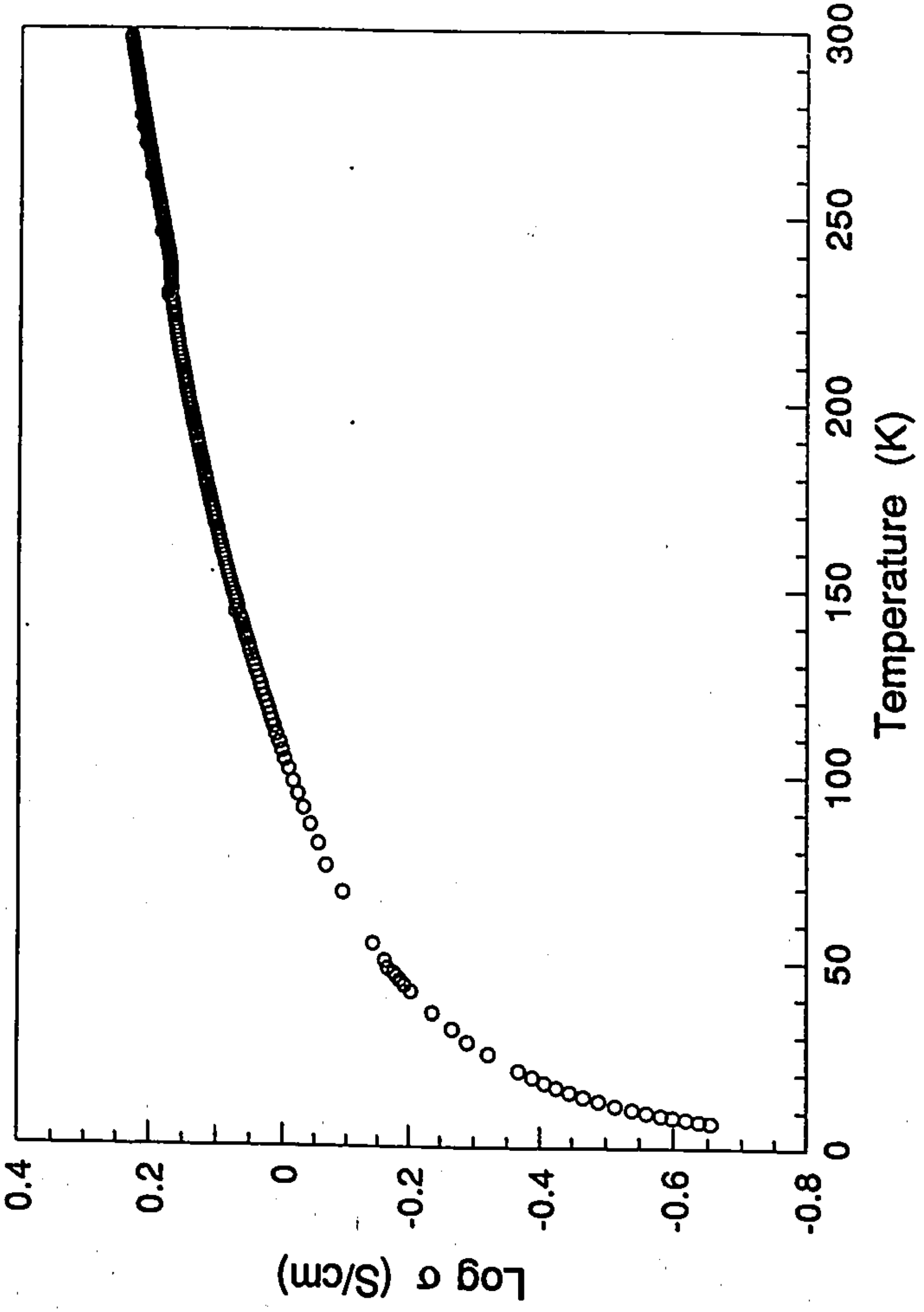

Figure 1j Nb$_3$Sn: conductivity vs temperature

Table 1F Summary of the reactions of Na_4Sn with organic halides

Halide	**Treatment**	**Stoichiometry/solvent**	**Result**
Ph_3SnCl	**A**	4 equivalents in THF	N.R.[a]
Me_3SiCl	**A**	4 equivalents in THF	[a]
Me_3SiCl	**A,B**	neat	[a]
CCl_4	**A,B**	neat	[a]
BzBr	**A**	4 equivalents in THF	[a]
PhCl	**A**	4 equivalents in THF	[a]

A : stirred at room temperature for 12 hours
B : refluxed under $N_{2(g)}$ for 12 hours
a : no reaction

Reactions of Na_4Sn with organic cations

It is well known that some Na/Sn alloys are precursors to soluble polystannide anions[39]. Based on the results of washing the solid with ethylenediamine it was clear that a simple extraction of Na_4Sn would not work and no soluble species would be formed. However, complete or partial replacement of the sodium cations with organic cations may increase the solubility which could then lead to the formation of new soluble species. The reactions of Na_4Sn with organic cations were performed by stirring, at room temperature, either THF or ether suspensions containing stoichiometric amounts of both starting materials. In the cases where no observable reactions were occurring, this was followed by 12 hours of reflux. Table 1G summarizes the results of these reactions with different organic cations.

Table 1G Reactions of Na_4Sn with organic cations

Cation	**Reaction conditions**	**Products**
R_4N^+ (R=Me,Bu)	Refluxing THF (12h)	no reaction
Me_3BzN^+	"	"
Et_3BzN^+	RT in THF (1h)	unidentified
Ph_4P^+	RT in Et_2O (12h)	PPh_3, PPh_5
$(Ph_3P)_2N^+$	RT in THF (30m)	PPh_3 + unidentified

As shown in Table 1G, the ammonium salts containing only alkyl substituents such as methyl or butyl did not react with Na_4Sn while the ones with only aryl substituents all reacted quite readily. In the intermediate cases where both alkyl and substituted alkyl substituents were present, a reaction was observed with Et_3BzN^+ but not with the methylated equivalent, Me_3BzN^+.

The first reaction to be studied was the reaction between Na_4Sn and the Ph_4P^+ cation. Stirring an ether suspension containing Na_4Sn and Ph_4PBr resulted in the formation of a dark orange solution within 12 hours at room temperature. The ^{31}P NMR of the crude reaction mixture showed two major signals at δ=-4.9 and -85.1ppm (Figure 1k) in a 1:1 ratio. These two resonances were attributed to PPh_3 and PPh_5 respectively based on values obtained by ^{31}P NMR of commercially available samples. The other signals detected in the ^{31}P NMR spectrum indicated the presence of impurities that might be responsible for the dark orange color of the solution. Recrystallisation from toluene allowed the isolation of PPh_5 which was further characterised by ^{1}H and ^{31}P NMR, IR and X-Ray crystallography (the preliminary crystal structure is presented in Figure 1l). No soluble Sn compounds were detected by ^{119}Sn NMR spectroscopy.

For the reaction of Na_4Sn with $[(Ph_3P)P]_2NCl$, a color change was observed within 30 minutes. However, unlike the case of Ph_4P^+, the reaction was not quantitative and unreacted starting material was still found after 12 hours of reflux. The ^{31}P NMR of the orange solution was quite complicated (Figure 1m) and only PPh_3 (δ=-4.9ppm) was identified as one of the products.

Based on these observations, a two step mechanism for the reaction of Na_4Sn with Ph_4P^+ salts can be proposed. The first step (equation 1e) involves an electron transfer from Na_4Sn to the organic salts. This generates two equivalents of NaX, tin metal, **PPh_3** and the active species (NaPh). The second step (equation 1f) is the reaction of this active species with unreacted organic salts to form the other two equivalents of NaX and **PPh_4**.

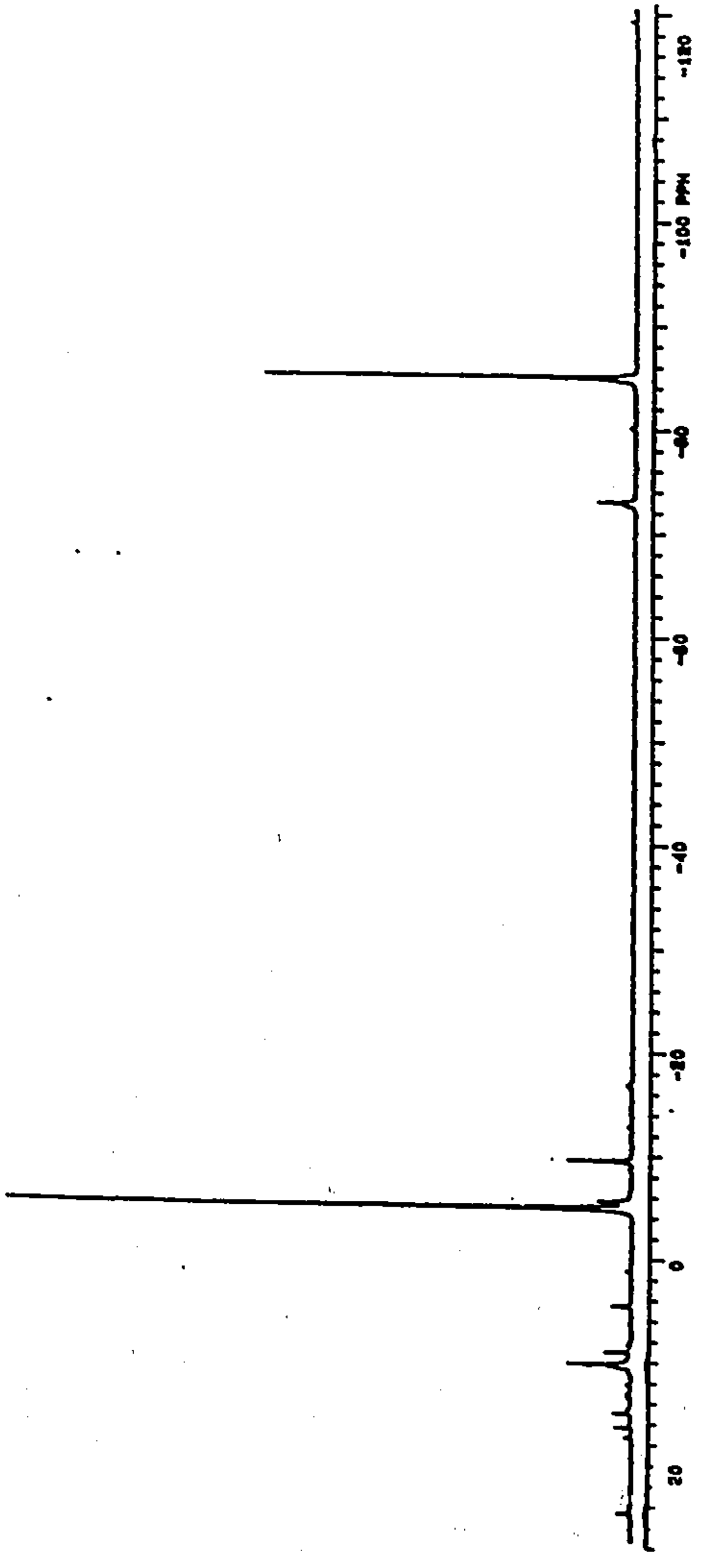

Figure 1k ^{31}P NMR of the crude solution from the reaction of Na_4Sn with Ph_4PBr

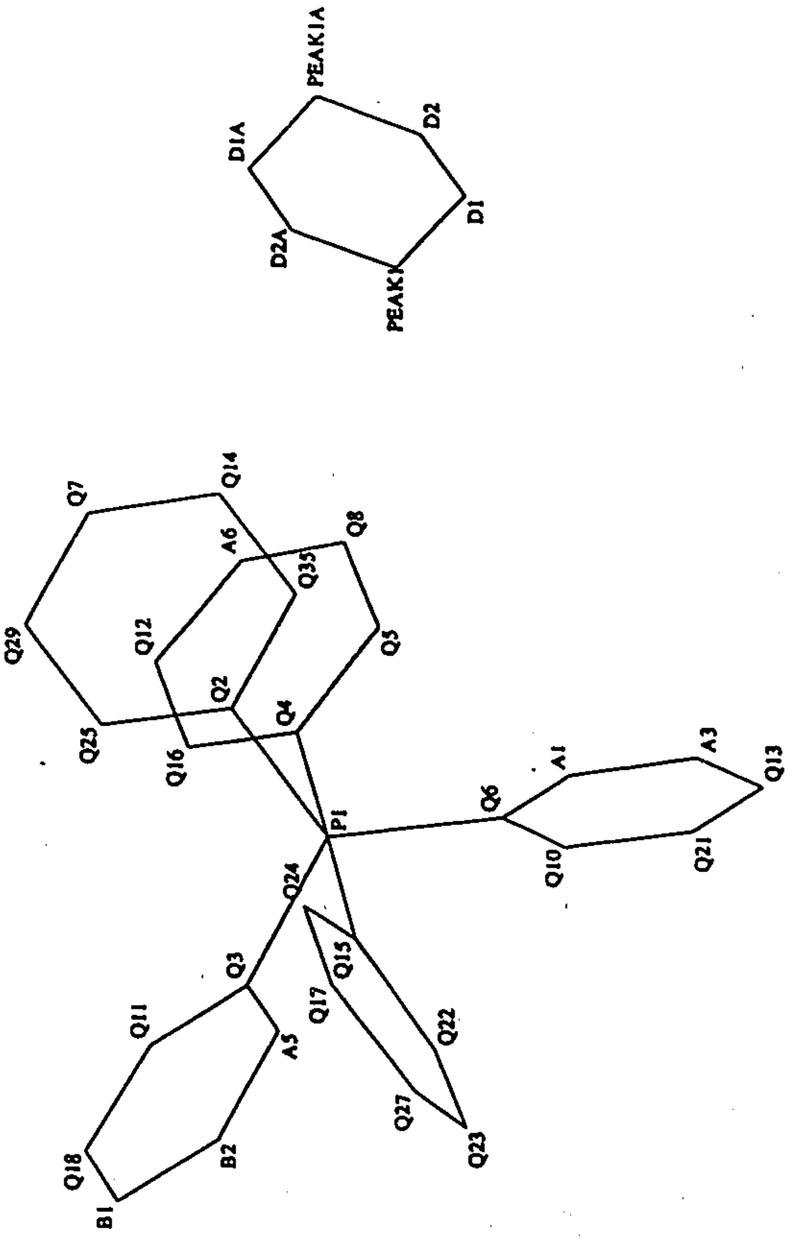

Figure 11 Preliminary crystal structure of PPh$_5$ • 0.5 toluene

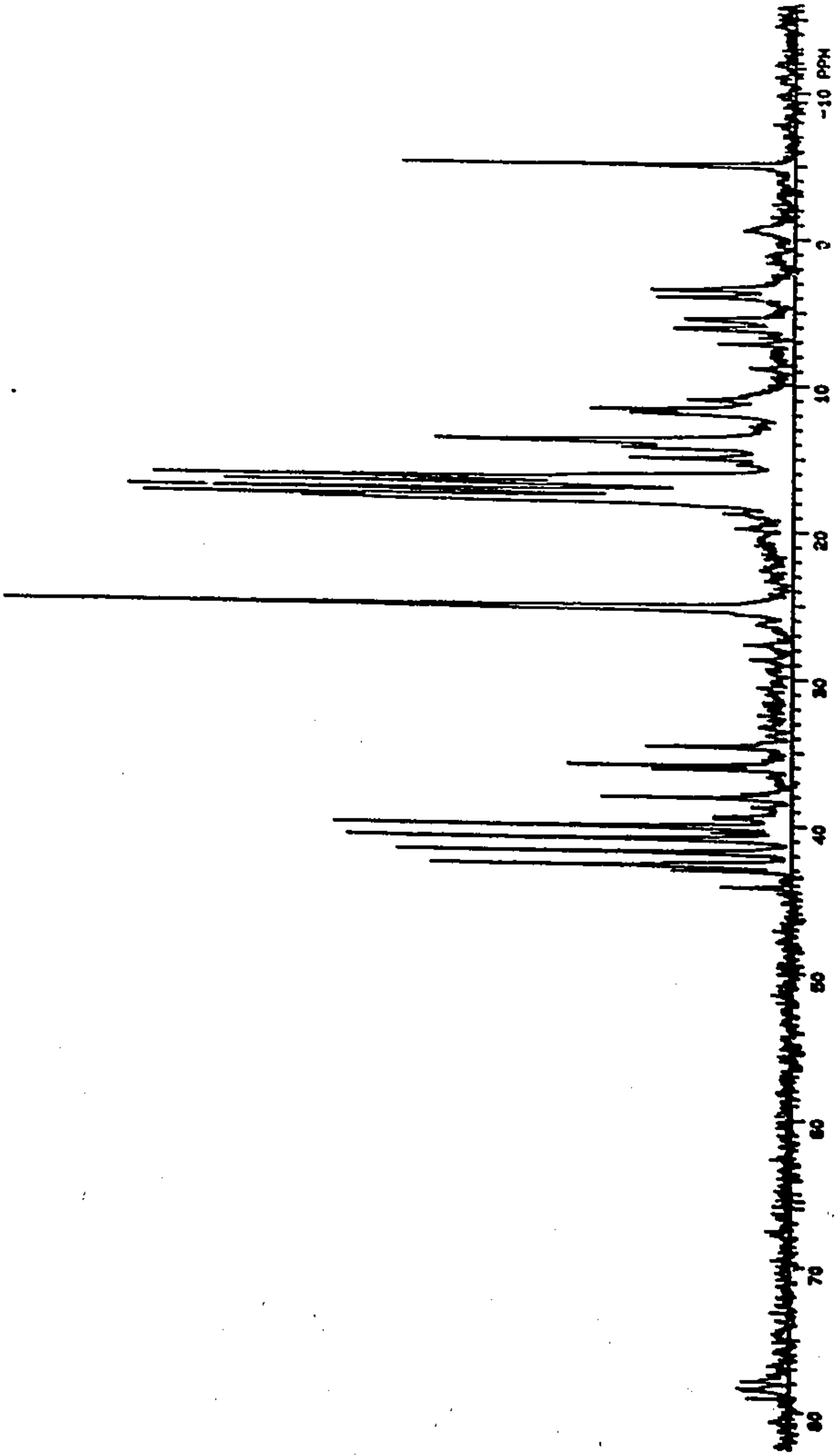

Figure 1a ^{31}P NMR of the crude solution obtained from the reaction of Na_4Sn with bis(triphenylphosphine)ammonium chloride

Step one: electron transfer

$$Na_4Sn + 2\ Ph_4PBr \rightarrow 2\ NaBr + Sn^{(0)} + 2\ PPh_3 + 2\ NaPh \qquad (1e)$$

Step two: reaction with NaPh

$$2\ NaPh + 2\ Ph_4PBr \rightarrow 2\ NaBr + 2\ PPh_5 \qquad (1f)$$

However, for $(Ph_3P)_2N^+$, the active species must involve less stable imido intermediates which can decompose to other amines or phosphines or react with left over starting material.

The reaction between the Et_3BzN^+ cation and Na_4Sn is completed in an hour at room temperature yielding a dark orange solution and a white solid which contained unreacted ammonium salts. Table 1H summarised the results of ^1H NMR studies of this reaction.

Table 1H ^1H NMR studies of the Et_3BzN^+ reaction

Treatments	**Aliphatic signals (ppm)**[a]		
	A	**B**	**C**
Crude reaction mixture	0.98(dt)	1.85(q)	2.15(dd)
Sublimed product	0.98(dt)	1.85(q)	---
reaction in C_6D_6	---	---	2.15(dd)

(a) aromatic signals omitted for clarity

dt : doublet of triplet

q : quartet

dd : doublet of doublet

The NMR of the crude reaction mixture consisted of what appeared to be a mixture of 2 species, **AB** and **C**. Sublimation of this mixture allowed the recovery of only one of the two compounds, **AB** (Figure 1n). Elemental analysis[c] of this oil gave a composition of C 88.89%, H 6.51% and N 5.02% which correspond to the reduced formula $C_{21}H_{19}N$ (C 88.38%, H 6.71% and N 4.91%).

If the reaction is performed in benzene instead of diethyl ether, the other product, **C**, is obtained (Figure 1o). Coupling between the signals **A** and **B** as well as between the signals **A** and **C** as shown in the ^1H 2D COSY NMR (figure 1p) is against the hypothesis of two compounds. Two protons on two different species should not be coupled together and no cross-peaks should be observed between **A** and **C** if there are in fact two species.

Attempts to do the reaction using simpler ammonium salts such as tetramethylammonium chloride and tetrabutylammonium bromide or trimethylbenzylammonium chloride were unsuccessful and no reactions were observed. Attempts to explain these results using the mechanism proposed for the reaction of Na_4Sn with PhP_4^+ were unsuccessful, the formation of a penta coordinated nitrogen being impossible. As of now, the mechanism and the products of these reactions are still unknown and further investigations will be needed.

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[c] Average of two separate analysis

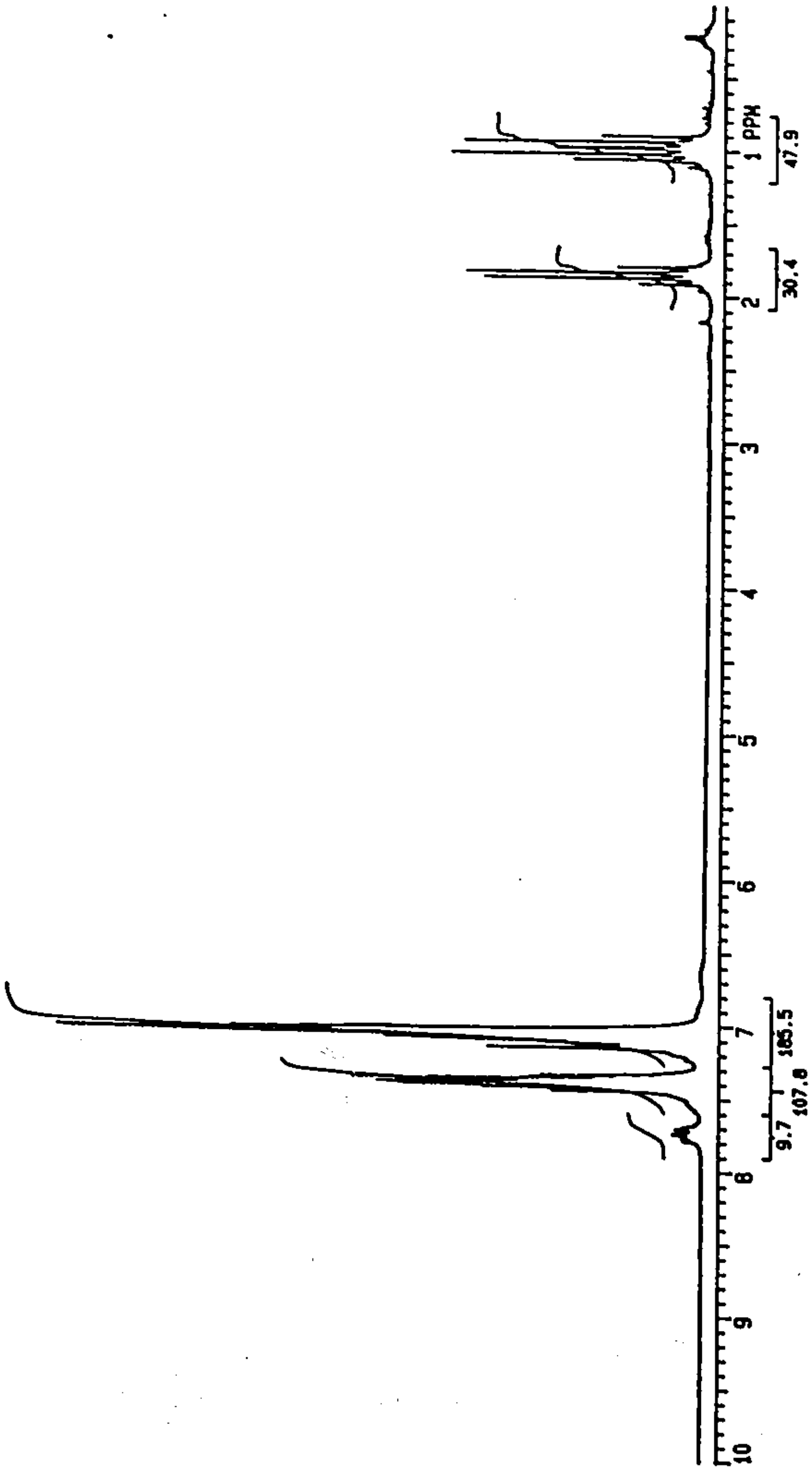


Figure 1n ^{1}H NMR spectra of the sublimed product from the reaction of Na_4Sn and $BzEt_3NCl$

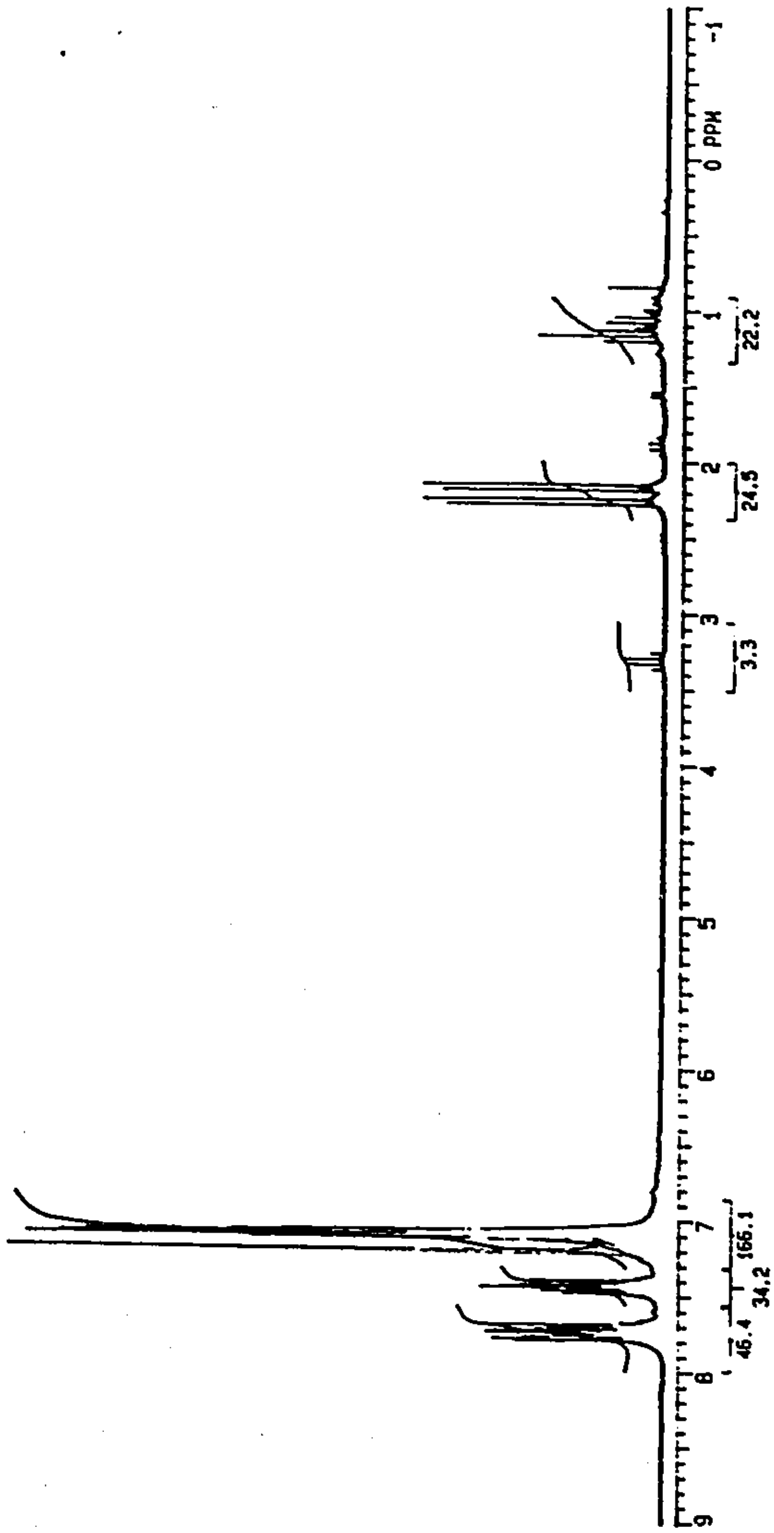


Figure 10 ^1H NMR of the product obtained from the reaction of Na_4Sn and $BzEt_3NCl$ done in benzene

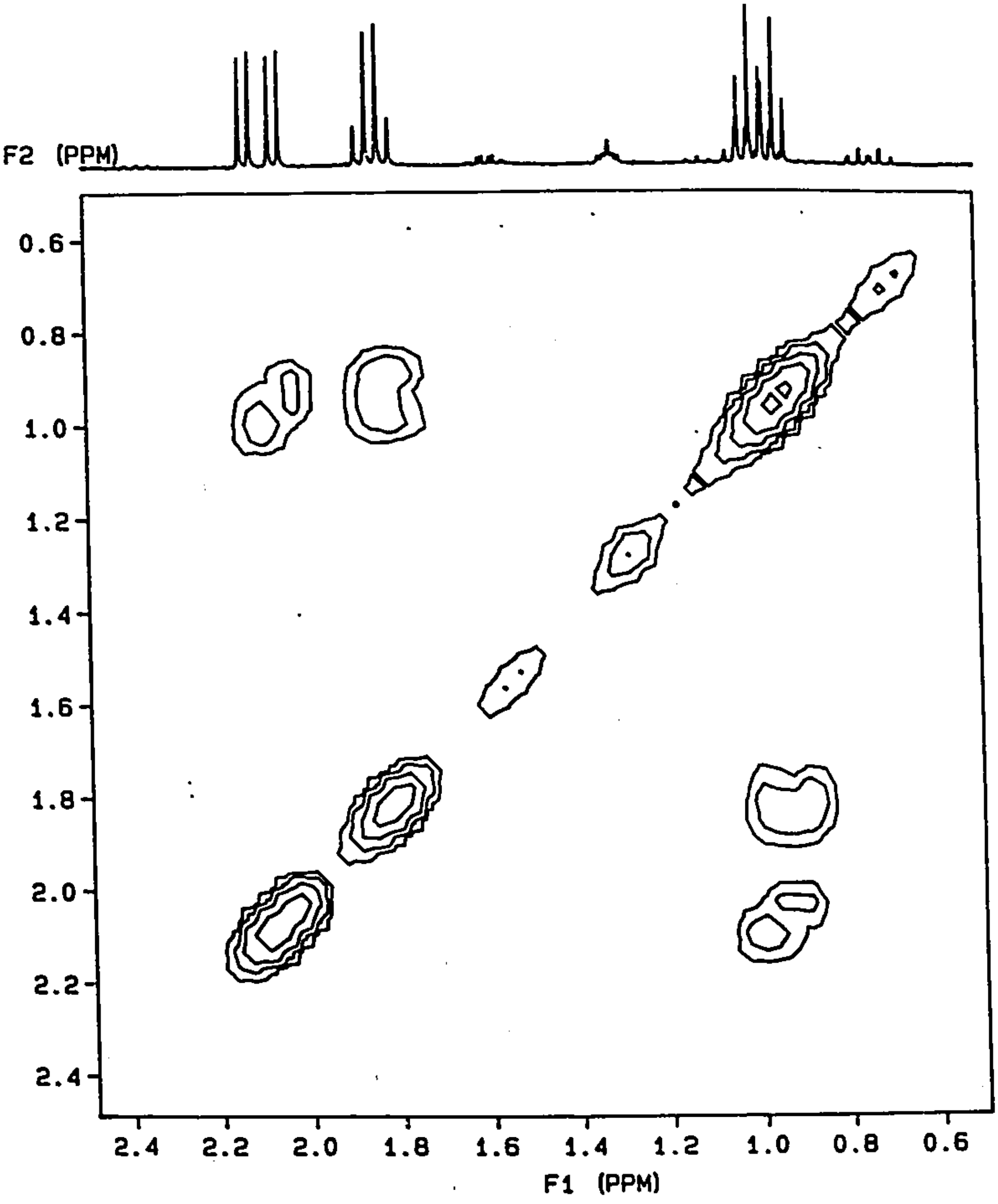


Figure 1p ^{1}H 2D COSY NMR of the crude mixture obtained from the reaction of Na_4Sn and Et_3BzNCl in THF.

CONCLUSIONS

Unlike what might be expected for a simple alloy, the structure of the new intermetallic phase, Na_4Sn, is not a closest packed structure and the two different tin environments is a particulary striking feature. Investigations of its reactivity, with inorganic and organic halides, elements, and organic cations show that it functions mainly as a reducing agent.

Further studies of its uses as a tin precursor in solid state metathesis reactions with other transition metal halides may help to develop alternative synthesis to the high temperature synthesis of transition metal-stannides.

CHAPTER 2: PHOSPHIDES

BACKGROUND

Since the isolation of the first binary phosphides, Li_3P and Na_3P, by Zintl[40] in 1937, there has been considerable investigation concerning the synthesis and characterisation of the binary species formed by the reaction of phosphorus with group 1 or 2 elements. Similar to the case of polystannides, the first synthetic routes to polyphosphides involved the preparation of alloys of phosphorus and the electropositive metal at high temperatures. Careful control of the conditions during the synthesis of these alloys has lead to the isolation of crystalline polyphosphides (Table 2A).

Table 2A Some solvent-free polyphosphides

Compound	Cluster	p e$^-$	ref
$Rb_3[P_{7-x}As_x]$	$P_{7-x}As_x^{3-}$	24	41
M_4P_6 (M=Rb,Cs)	P_6^{4-}	22	42
Sr_3P_{14}	$2*P_7^{3-}$	2*24	43
Li_3P_7	P_7^{3-}	24	44

The extraction of these alloys with liquid ammonia yielded mainly solvated phosphides. Destabilisation of the alkali cation upon solvent evaporation resulted in a back electron transfer from the anions to the alkali metal forming amorphous and highly reactive solids. The use of amine solvents, such as ethylenediamine and TMEDA (tetramethylethylediamine), or cation sequestering agents, such as 2,2,2-crypt has enabled the isolation of crystalline species including $Li_3(tmeda)_3P_7$[45] (Figure 2a) or $K_3(crypt)_3P_{11}$[46].

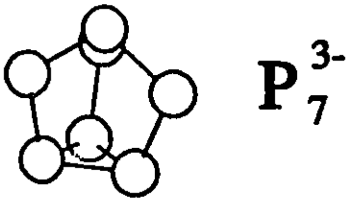


Figure 2a Structure of the P_7^{3-}anion

The limitations of these high temperature methods became rapidly obvious and include: *(i)* the inhomogeneous nature of the products which required several annealing/grinding steps and *(ii)* reactions between the reagents and the container at the temperatures for reaction.

An alternative to the direct reaction of the elements at high temperature was to perform the reactions at lower temperatures in refluxing solvents such as glyme or THF using stoichiometric amounts of soluble white phosphorus (P_4) with metallic sodium or potassium. Using this technique large polyphosphide species such as M_3P_7, M_2P_{16}, M_3P_{19}, M_3P_{21} (M=Na or K) and Na_4P_{26} were synthesised[47,48,49] and their solution structures (Figure 2b) deduced from ^{31}P NMR studies. These results also revealed the importance of the P_7 unit in the building of "higher polyphosphides".

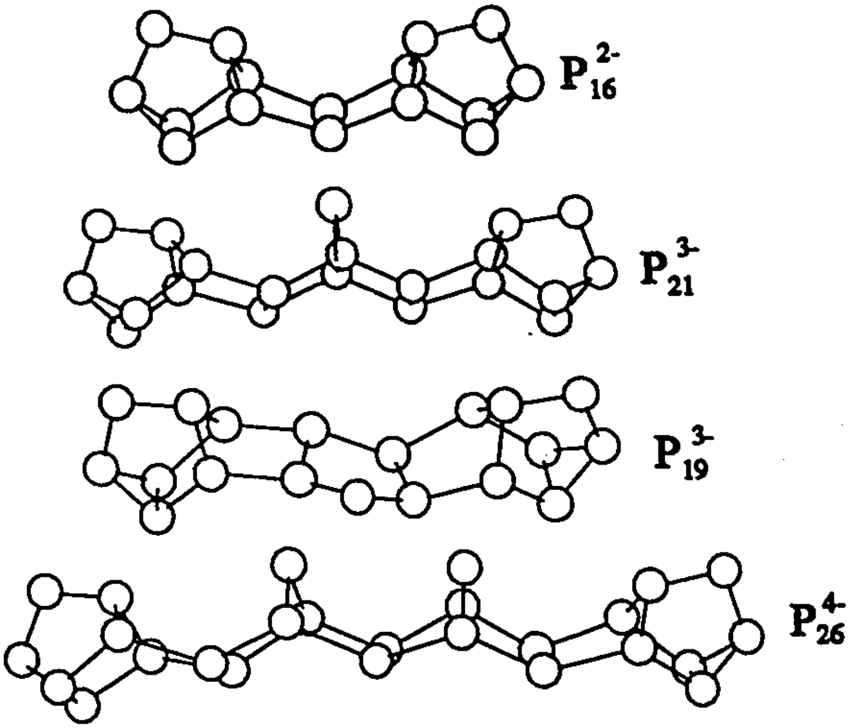


Figure 2b Structure of some polyphosphides deduced from NMR studies

One of the main problems associated with this synthetic methodology is the lack of selectivity. A mixture of clusters was almost always formed and low yields were common.

A more efficient route to the synthesis of a variety of polyphosphides[50] was offered by the nucleophilic cleavage of white phosphorus with lithium dihydrogenphosphide ($LiPH_2$) (equations 2a and 2b) or the disproportionation of Li_2HP_7[51] (equation 2c). However, the difficulties of handling highly reactive phosphine (PH_3) in the preparation of $LiPH_2$ together with a lack of selectivity have limited the use of this method.

$$3\ P_4 + 6\ LiPH_2 \rightarrow 2\ Li_3P_7{\bullet}3DME + 4\ PH_3 \tag{2a}$$

$$23\ P_4 + 12\ LiPH_2 \rightarrow 6\ Li_2P_{14}{\bullet}8THF + 8\ PH_3 \tag{2b}$$

$$3\ P_4 + 8\ Li_2HP_7 \rightarrow 4\ Li_4P_{16} + 2\ P_2H_4 \tag{2c}$$

To date, there is only one reported[52] crystal structure for these high polyphosphides. It was obtained by the oxidation of Na_3P_7 in THF solution in the presence of PPh_4Cl. The resulting compound had the formula $(PPh_4)_2P_{16}$ and its solid state structure was similar the one deduced from NMR studies.

Surprisingly, there have been very little investigation of the reactivity of these phosphides. The few reports involved alkylation, silylation or protonation of the heptaphosphide trianion. Table 2B summarizes the results of these reactions.

Table 2B Reactions with P_7^{3-}

Starting compound	Reagent	Product	ref
Li_3P_7	Me_3SiCl	$(Me_3Si)_3P_7$ and $(Me_3Si)_4P_{14}$	[53]
$(Me_3Si)_3P_7$	MeOH	H_3P_7	[54]
H_3P_7	$LiPH_2$	Li_3P_7	[*]
Li_3P_7	MeBr	Me_3P_7	[55]

RESEARCH GOALS

1. Investigate the solution synthesis of these polyphosphides starting from white phosphorus and potassium or sodium. This synthetic route may provide a more systematic and efficient approach for their synthesis thus expanding the accessibility of these species for further investigations of their reactivity. It may also allow the synthesis of new polyanions.

2. Explore the features that influence the interconversions between polyphosphides. Carry out "aimed isomerization" reactions.

3. Study the nucleophilic character of these clusters by using them as ligands for transition metal or main group element complexes. This may provide the stabilisation needed in order to prevent decomposition back to the alloy and allow the isolation of new species.

RESULTS AND DISCUSSION

Our investigation of the synthesis of sodium or potassium phosphides was divided into two approaches. The first approach was to study binary alloys of the alkali metal and phosphorus and their reactivity. The solution synthesis of polyphosphides from potassium and white phosphorus was also examined.

Na_3P: synthesis and extraction

The simplest binary alloy in the Na/P system, trisodium phosphide (Na_3P), was prepared by heating stoichiometric amounts of the elements to 500°C for 3 hours. Grinding the powder and annealing it at 500°C for another 12 hours was necessary in order to obtain homogeneous products. Addition of ethylenediamine to Na_3P resulted in gas evolution together with the formation of a dark orange solution. The gas was trapped using a Toepler pump system and analyzed by M.S. and ^1H NMR (Figure 2c) spectroscopy. From these data, the gas was identified as a mixture of $MeNH_2$ (major product) and $EtNH_2$. The IR spectrum of the yellow solid obtained by evaporation of the ethylenediamine from the orange solution showed a broad band at $3300cm^{-1}$ and a sharp peak at $2380cm^{-1}$ characteristic of P-H groups. The singlet at -273ppm in the $^{31}P\{^1H\}$ NMR spectra of the orange solution (Figure 2d*(a)*) can be attributed to $NaPH_2$[60]. The triplet obtained in the ^{31}P NMR (Figure 2d*(b)*) and the doublet ($^1J_{H-P}$=140Hz) at -1.5ppm in the ^1H NMR spectra of the same solution

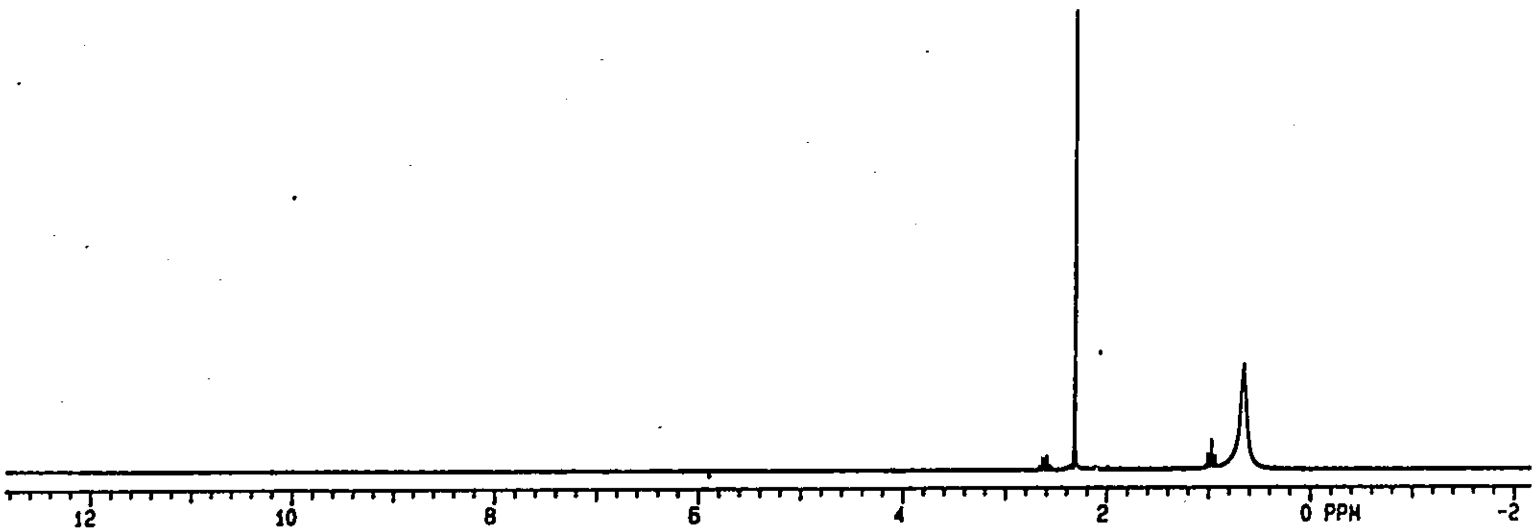


Figure 2c ^1H NMR of the gas evolved during the reaction of Na_3P with ethylenediamine, in benzene-d_6.

confirm this hypothesis. Similar results were obtained when ethylenediamine was allowed to react with K_3P and KPH_2 was formed.

This reaction provides an alternative to the use of highly reactive phosphine, PH_3, for the synthesis of alkali metal dihydrogenphosphides.

Figure 2d ^{31}P NMR spectra of $NaPH_2$, in ethylenediamine, *(a)* ^1H decoupled, *(b)* not ^1H decoupled

Reaction of Na_3P with $NbCl_5$

The importance of solid state metathesis reaction in the synthesis of group III-V semi conductors has recently been demonstrated[4]. A similar synthetic route has also been used for the synthesis of some transition metal nitrides[37]. With these facts in mind, we decided to study the reaction between Na_3P and $NbCl_5$. A mixture containing stoichiometric amounts of Na_3P and $NbCl_5$ was heated to 300°C for 12 hours, under vacuum. This procedure yielded a black powder which was then washed with H_2O, EtOH and Et_2O to remove the NaCl formed during the reaction and any unreacted starting material. The black powder obtained had a composition of

Nb_3P_5 based on XRF analysis and only broad features were observed by powder XRD. This material was thermally stable below 1000°C when heated under inert atmosphere but decomposed at 400°C when heated in air.

In an effort to increase the crystallinity of this material and aid in its identification, the powder was annealed at 600°C, under $N_{2(g)}$, for 12 hours in a quartz tube. During this procedure a small amount of red phosphorus sublimed out of the powder. The powder pattern of the resulting powder as well as the one of the original powder are shown in Figure 2e and compared with literature values for the NbP phase in Table 2C.

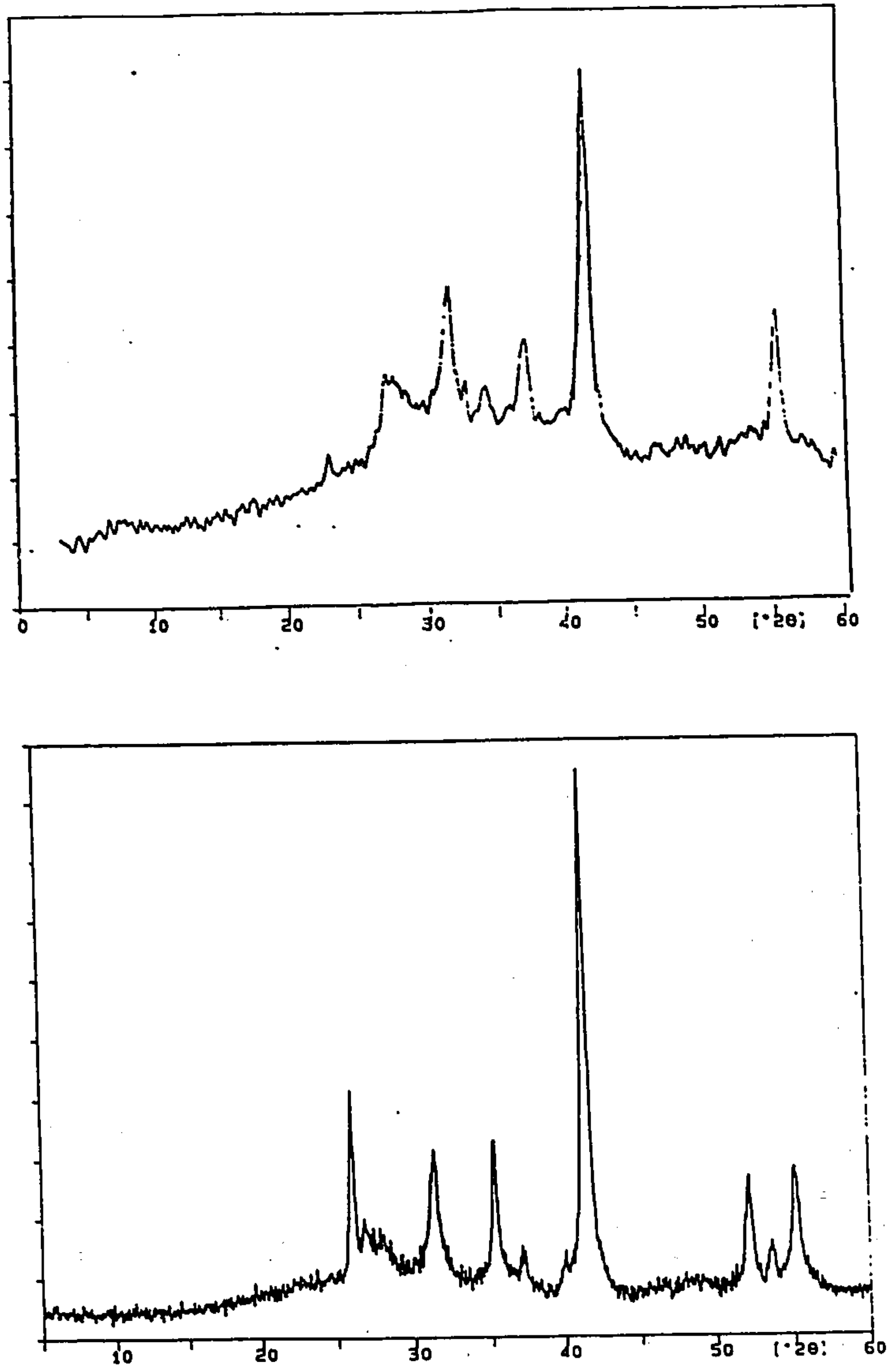


Figure 2e Powder pattern of NbP (top) original product (bottom) after annealing

Table 2C Powder XRD data for NbP (0°<2θ<60°)

literature[56]					experimental	
d (Å)	rel.int. [%]	h	k	l	d (Å)	rel.int. [%]
3.200	60	1	0	1	3.422	33
2.843	30	0	0	4	2.854	24
2.503	55	1	0	3	2.539	27
2.178	100	1	1	2	2.174	100
1.879	30	1	0	5	1.751	21
1.668	25	2	0	0	1.665	24

Na/2P alloy: synthesis of P_7^{3-}

An alloy of ratio Na/2P was prepared by heating, under $N_{2(g)}$, the elements in stoichiometric amounts to 300°C for 30 minutes. The powder was then ground with a mortar and pestle and extracted with ethylenediamine. The solution was then stirred at room temperature for 12 hours after which a light orange solution was obtained upon filtration. The ^{31}P NMR spectra (Figure 2f) of the orange solution showed a broad singlet at -122ppm, characteristic of P_7^{3-} [44].

Ternary alloys: P/Sn/M (M=Na,K)

In an effort to examine the possibility of introducing Sn into one of the phosphide anions, ternary phosphorus/tin/alkali metal alloys were prepared by heating to 300°C for 30 minutes stoichiometric amounts (1:1:1) of the elements. Unlike in the case of binary alloys, the ternary alloys did not look homogeneous and the presence of some metallic tin was observed. Nevertheless, the alloys were ground and extracted with ethylenediamine. Filtration of the resulting solution yielded a dark orange solution. The ^{31}P solution NMR showed the presence of P_7^{3-} and MPH_2 (M=Na,K) in a 20:3 ratio while no signal was observed between +500 and -1800 ppm in the ^{119}Sn NMR spectra.

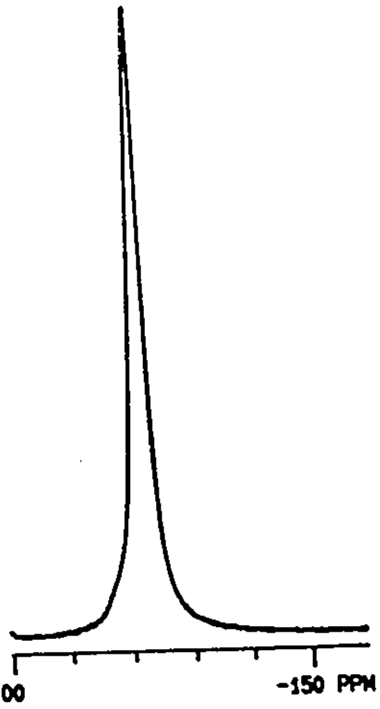


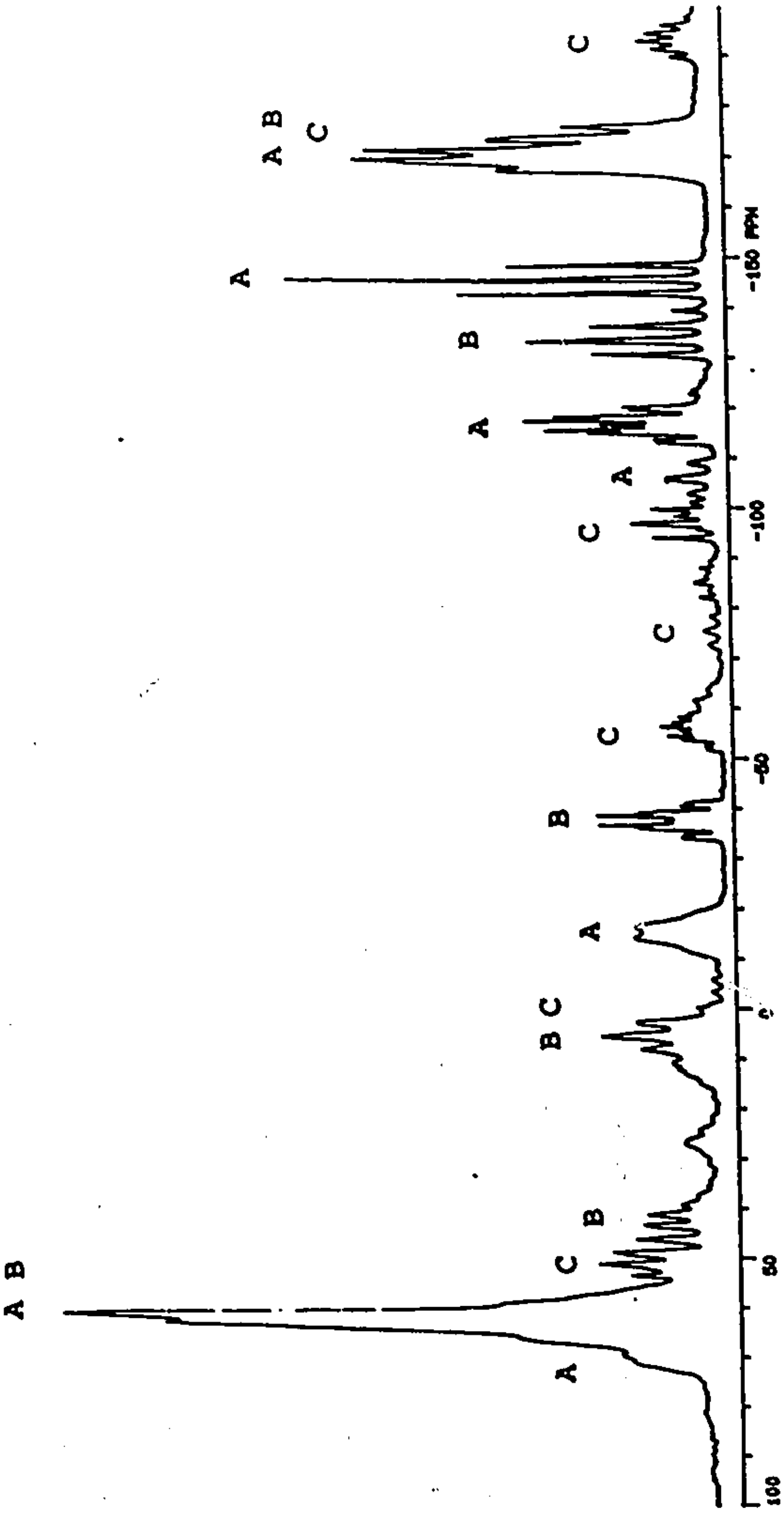
Figure 2f ^{31}P NMR spectra of the P_7^{3-} anion (ethylenediamine solution)

This suggests that the tin is not incorporated during the heating stage and remained unreacted while the sodium and phosphorus react to form the binary alloys Na/3P and Na_3P. The fact that $NaPH_2$ or KPH_2 were not formed during the extraction of the Na/2P alloy may be explained by the presence of excess sodium in the "ternary alloy" which results in the formation of a small quantity of Na_3P or K_3P. This side product then reacts, as previously noted, with the ethylenediamine to form the MPH_2.

Synthesis of K_2P_{16} and K_3P_{21}

An alternative to the extraction of binary alkali metal/phosphorus alloys for the preparation of polyphosphides may be offered by reduction of solutions of white phosphorus with alkali metals. The reactions between white phosphorus and metallic potassium were carried out by refluxing, in THF, an 8:1 stoichiometric ratio of the two elements. A dark orange colour started to form within minutes and the reaction was completed in 3 hours. Filtration of the reaction mixture gave a dark orange solution and a dark red solid. The ^{31}P NMR spectra (Figure 2g) of that solution showed the presence of three anions: K_2P_{16}, K_3P_{19} and K_3P_{21}[48]. Separation of the three anions by crystallisation was not possible.

In an effort to explore alternative solvent systems for the isolation of single polyphosphides, degassed ethanol was used to extract the red solid formed during the reaction described above. All of the solid went into solution to give a dark orange solution for which the ^{31}P NMR spectra (Figure 2h) showed only the P_{16}^{2-} dianion with a small amount of decomposition products probably due to the presence of residual oxygen. The solution was thermally stable up to the boiling point of ethanol but decomposed readily upon exposure to atmospheric oxygen.



A = P_{21}^{3-} (δ = +69, +61, -14, -107, -146, -170ppm)
B = P_{16}^{2-} (δ = +61, +43, +5, -39, -134, -170ppm)
C = P_{19}^{3-} (δ = +51, +5, -56, -76, -97, -170, -193ppm)

Figure 2g ^{31}P NMR spectra of a THF solution of P_{16}^{2-}, P_{21}^{3-} and P_{19}^{3-}

Figure 2g ^{31}P NMR spectra of a THF solution of P_{16}^{2-}, P_{21}^{3-} and P_{19}^{3-}

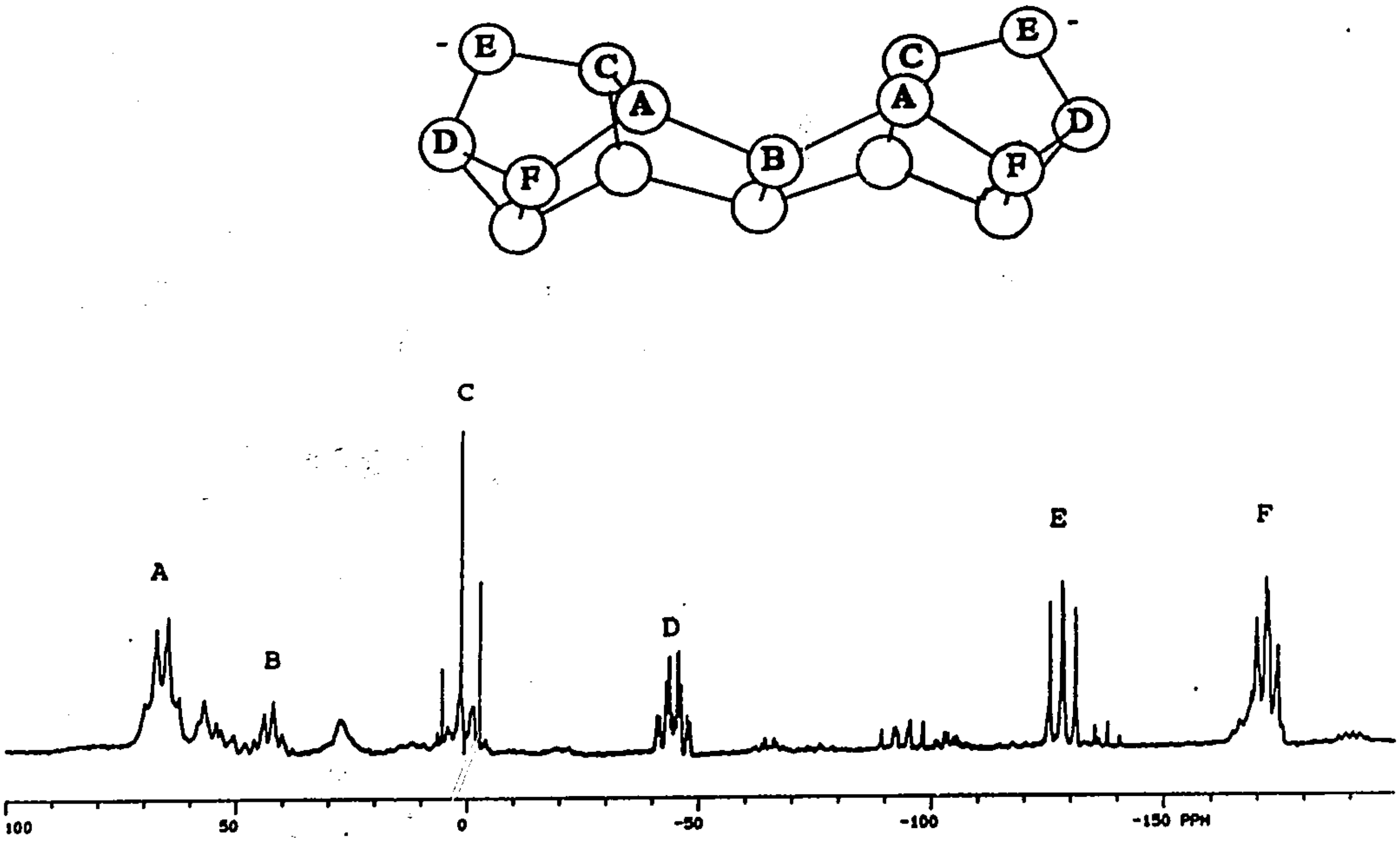


Figure 2h ^{31}P NMR spectra of P_{16}^{2-} in ethanol

Evaporation of the ethanol gave a dark solid of composition K/P=1/8. This solid extracted partially in THF to give a dark red solution with some red phosphorus. The ^{31}P NMR spectra (Figure 2i) of the THF solution showed P_{21}^{3-} as the only product.

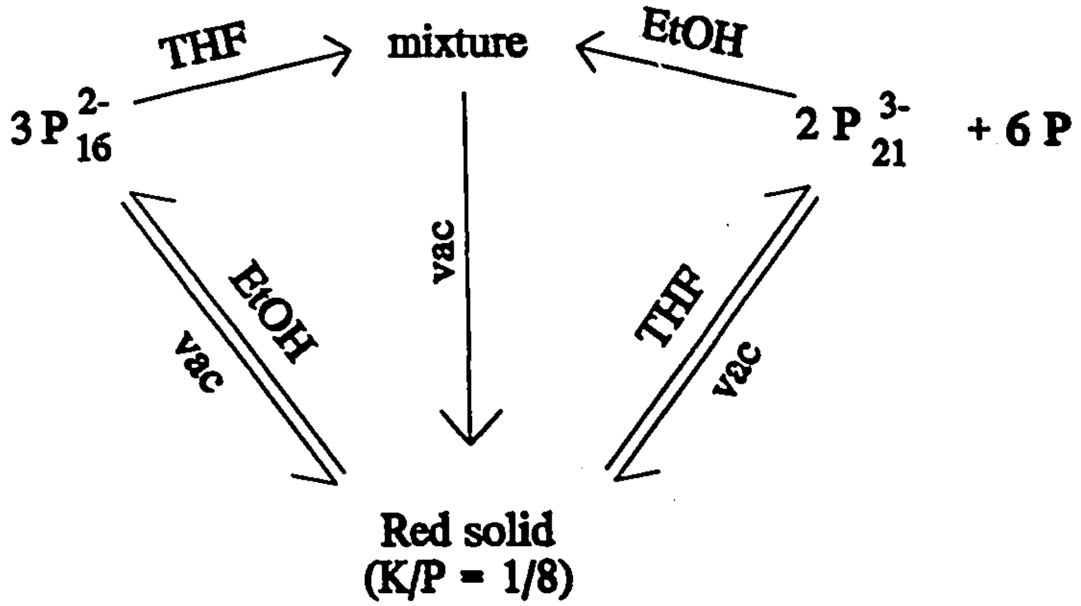


Figure 2j interconversion of P_{16}^{2-} and P_{21}^{3-}

A similar effect was also observed when THF was replaced by pyridine. One explanation for these observations is that in a coordinating solvent, such as pyridine or THF, the potassium cation is stabilised and the more reduced species, P_{21}^{3-} ($1/7^-$ per P atom) is formed. Evaporation of the cation stabilising solvent causes the oxidation of the cluster to form the less reduced anion P_{16}^{2-} ($1/8^-$ per P atom). A summary of the results of our studies of the interconversion is presented in Figure 2j. These results are the

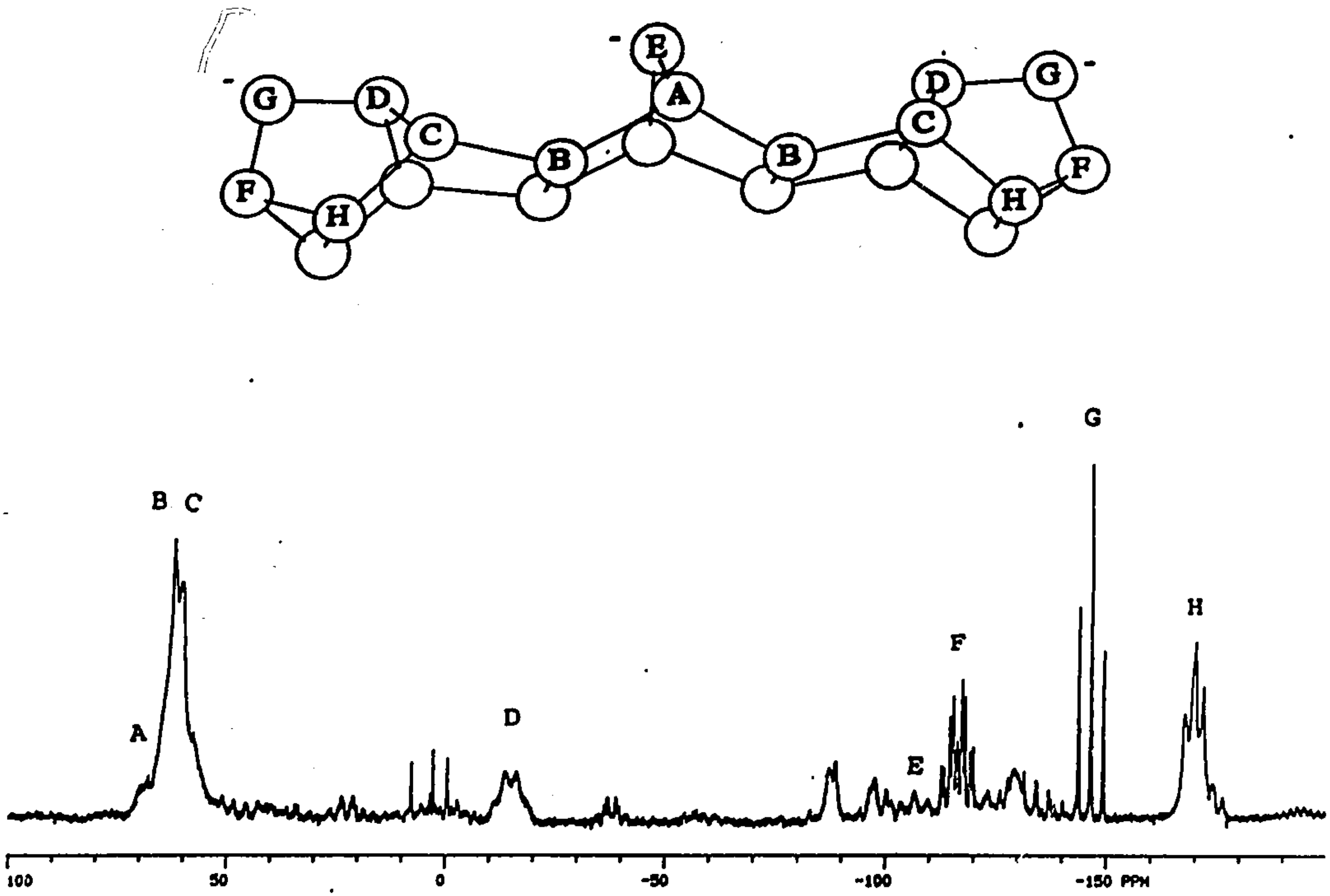


Figure 21 ^{31}P NMR spectra of P_{21}^{3-} in THF first clear evidence of the interconversion of P_{16}^{2-} to P_{21}^{3-}. They also provide a selective and efficient route for the synthesis of these two polyphosphides thus allowing further studies of their reactivity.

Reaction of K_3P_{21} with R_3ECl (R=Me,Bu,Ph;E=Si,Sn)

The reactions of K_3P_{21} with R_3ECl (R=Me,Bu,Ph;E=Si,Sn) were done by stirring, at room temperature, a solution containing stoichiometric amounts of the two components. The results of these reactions are summarised in Table 2D.

Table 2D Summary of the reaction of K_3P_{21} with R_3ECl

R_3ECl	reaction time	products
Me_3SiCl	<1 minute	insoluble
Me_3SnCl	<1 minute	insoluble
Bu_3SnCl	12 hours	P_{16}^{2-}, P_{21}^{3-}, P_{26}^{2-} (a)
Ph_3SnCl	12 hours	paramagnetic(a)

(a) from ^{31}P NMR studies

The reaction of P_{21}^{3-} with Me_3ECl (E=Si,Sn) gave only insoluble products making their characterisation difficult. Moving from alkyl substituents to aryl substituents increased the solubility of the products but the paramagnetism of the products limited the use of ^{31}P NMR for their characterisation and only broad features were observed (Figure 2k). A low temperature ^{31}P-NMR experiment was performed and no improvement was observed in the final spetra. The reaction between K_3P_{21} and Bu_3SnCl gave soluble and diamagnetic products. The results of this reaction are discussed in more detail in the next section.

Reaction of K_3P_{21} with Bu_3SnCl: formation of K_2P_{14}

The reaction of K_3P_{21} with three equivalents of Bu_3SnCl yielded, after filtration through celite, a light orange solution. The ^{31}P NMR spectra of that solution showed a mixture of clusters and successive precipitation of the THF solution by addition of hexane allowed the isolation of a yellow solid. The ^{31}P NMR spectra of a THF solution of this solid is presented in Figure 2l. It showed signals at δ=-12, -53, -68, -156 and -172ppm (intensity ratio 1:2:1:2:1) as well as small K_2P_{16} and K_3P_{21} impurities. The number, chemical shifts and intensities of the signals suggests a symmetrical P_7^{1-} unit. This hypothesis was confirmed in the 2D-^{31}P NMR spectrum (COSY) (figure 2m). All $^1J_{(P-P)}$ couplings of directly linked P atoms appear as cross-peaks. A dimeric structure in which the two P_7^{1-} unit can be trans or cis (Figure 2n **(a)** or **(b)** respectively) to each other can be proposed. This is the first evidence of the isolated unit K_2P_{14}. It is also the first example of the oxidative coupling of two P_7^{3-} unit.

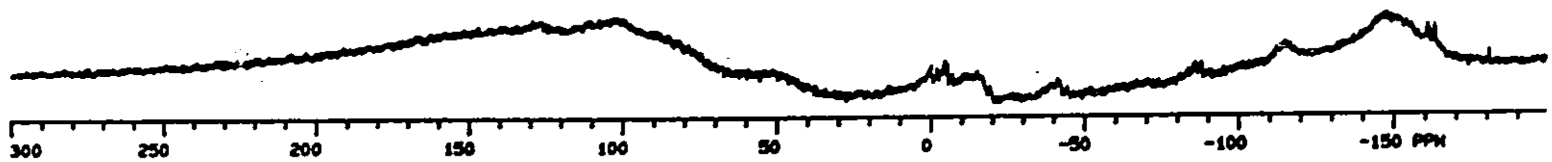


Figure 2k ^{31}P NMR spectra of the products of the reaction between K_3P_{21} and Ph_3SnCl

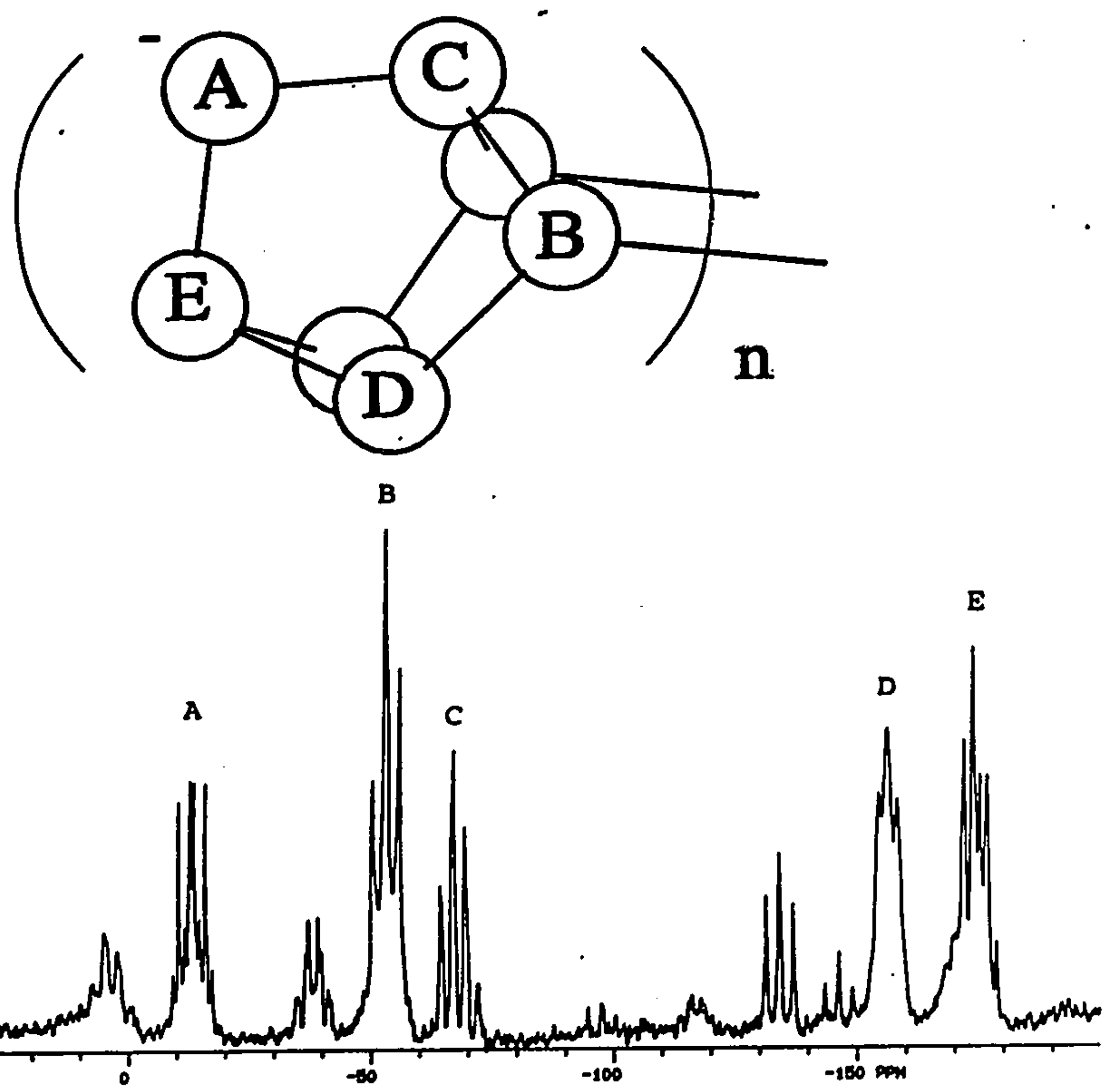


Figure 21 ^{31}P NMR spectra of K_3P_{14} in THF solution

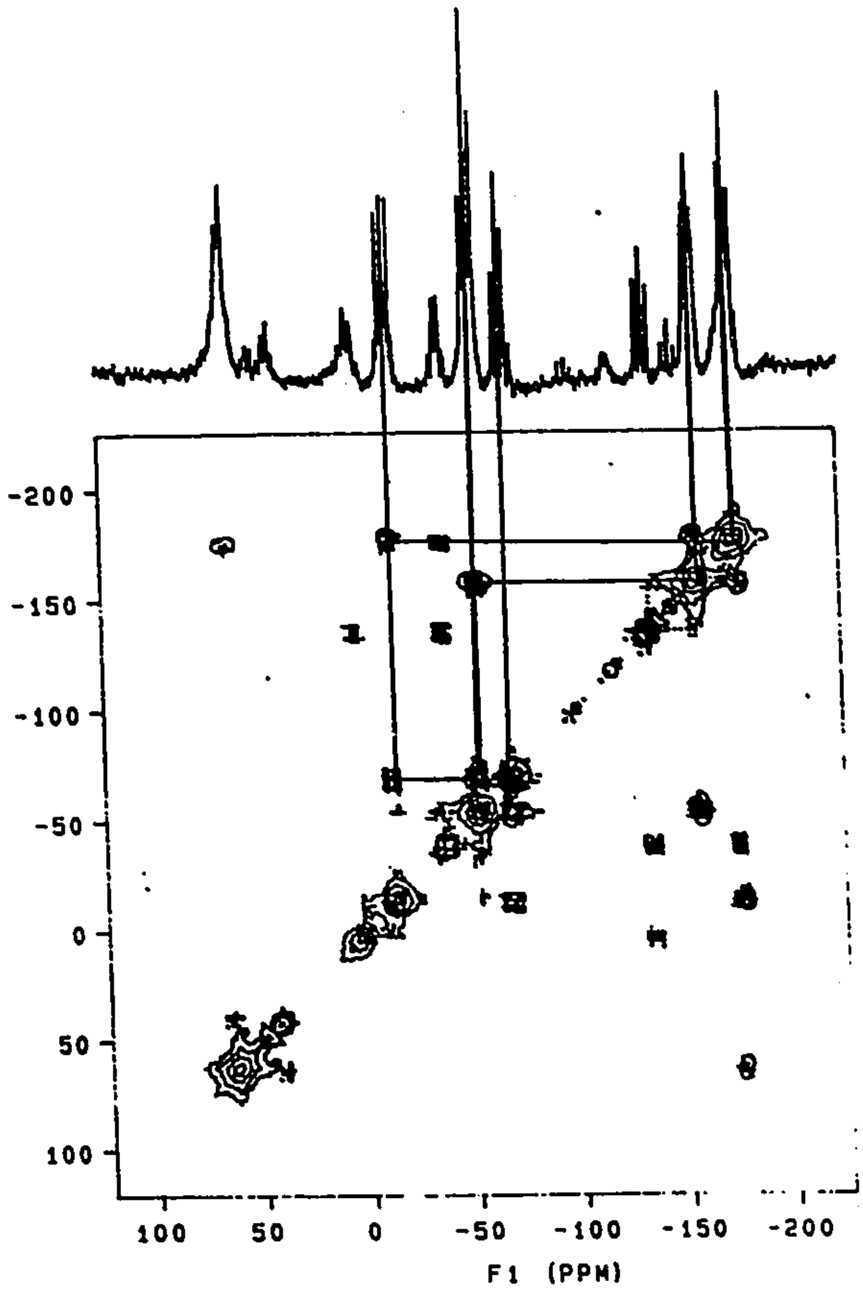


Figure 2a 2D-^{31}P NMR spectrum of the P_7^{1-} skeleton (256*256 matrix)

Other reactions attempted with P_{21}^{3-} include the reactions with inorganic halides, such as $AlCl_3$*3thf and Cp_2ZrCl_2. The products of these reactions were not fully characterised and will not be discussed here.

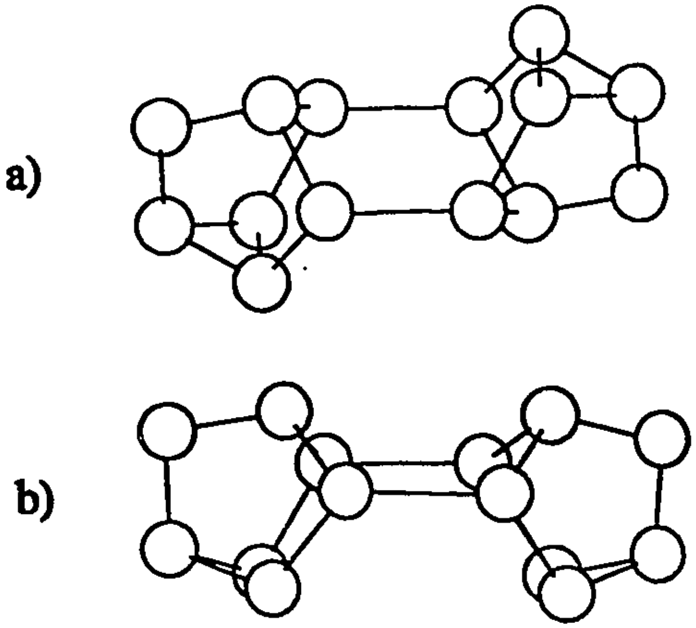


Figure 2n Possible structures of K_3P_{14} (a) trans (b) cis

CONCLUSIONS

The availability of pure polyphosphides has, until this work, limited the study of their reactivity. However, the interconversion of P_{16}^{2-} to P_{21}^{3-} provides a new synthetic route to "clean" polyphosphides thus allowing further characterisation of their chemical behaviour. Controled oxidation or metathesis reactions using inorganic halides represent the next frontier in this field. Their use as ligands in organometallic complexes may result in new species with unusual properties based on the interaction of the metal centre with the polyphosphides ligand system.

EXPERIMENTAL

GENERAL

N.B. Unless otherwise specified, the purification of the starting materials and the reactions were performed in the absence of air and water using standard Schlenk techniques.

Purification of starting materials:

The solvents

Tetrahydrofuran, hexanes, diethyl ether, pyridine, 1,2-dimethoxyethane, toluene and ethylenediamine were dried by reflux over Na/K alloy for 10 to 12 hours In the other cases, P_2O_5 (methylene chloride, carbon tetrachloride), CaH_2 (ethanol, methanol) or molecular sieves (dimethyl formamide) were used depending on the solvent.

The elements

Lithium (Aldrich,99+%), sodium (Strem,ACS) and potassium (Strem,99.99%) metals were washed with hexanes in order to remove the protective oil then dried under vacuum. The white (Aldrich,99+%) and red (Strem,99.99%) phosphorus allotropes, the metallic tin (powder and shots) (Aldrich,99.99%) and the sulphur (yellow) (Aldrich,sublimed) were used as received.

The organic cations

Tetramethyl ammonium chloride (Me_4NCl), Tetrabutyl ammonium chloride (Bu_4NCl), Tetraphenyl phosphonium bromide (Ph_4PBr) and Benzyltriethyl ammonium chloride ($BzEt_3NCl$) were dissolved in ethanol and precipitated by the addition of diethyl ether. After filtration and drying under vacuum, infrared spectroscopy was used to verify the absence of residual water or ethanol in the solid.

Benzyltrimethyl ammonium chloride ($BzMe_3NCl$) was synthesised in quantitative yield by refluxing Me_3N and BzCl in toluene overnight followed by recrystallisation from ethanol/ether.

Bis(triphenyl phosphonium) ammonium chloride (PPNCl) was synthesized using a previously reported method[57].

The organic halides

Trimethyl silyl chloride (TMSCl), Benzyl bromide (BzBr) and Phenyl bromide (PhBr) were dried using P_2O_5 followed by distillation. The purity of the distillate was monitored with ^1H NMR.

Triphenyl tin chloride (Ph_3SnCl) was purified by recrystallisation from THF and then dried under vacuum for 10 to 12 hours.

Trimethyl tin chloride (Me_3SnCl) and Tributyl tin chloride (Bu_3SnCl) were used as received from Aldrich.

The inorganic halides

Niobium pentchloride ($NbCl_5$) was purified through sublimation under vacuum.

Bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) was used as received.

Instrumentation

NMR spectroscopy

The ^1H NMR experiments were performed on a Varian Gemini 200 XL while the other nuclei ^{13}C, ^{31}P and ^{119}Sn were studied using a 300 MHz Varian spectrometer. The spectrometer frequency was set respectively to 75.43MHz, 121.42MHz, 111.75 MHz.

All ^1H NMR spectra were referenced to residual protons of the solvent. Solvent signals were also used as reference for the ^{13}C NMR spectra. 10% H_3PO_4 in H_2O and Me_4Sn or Na_4Sn_9[d] were used as external reference for the ^{31}P and ^{119}Sn NMR.

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[d] Me_4Sn was used for signals between δ=800 and -800ppm
Na_4Sn_9 was used for the more upfield signals

FTIR spectroscopy

Most IR spectra were recorded using Nujol mull between NaCl plates. Both Mattson 3000 and Bomem Michelson series 100 FTIR systems were used.

Thermal Analysis

A polymer laboratories simultaneous DSC/TGA STA1500H (Differential Scanning Calorimetry/ThermoGravimetric Analysis) was used for all thermal analysis. A heating rate of 10°C/min was found to be ideal for both speed and quality purposes. Measurements on air sensitive samples were done in sealed aluminium pans while the air stable samples were measured in an alumina pan. In both case, the samples were heated under $N_{2(g)}$ at a flow rates of 40-60 cm^3/s.

P-XRD (Powder X-Ray Diffraction)

The instruments used was a Phillips PW3710 based Xpert system. The powder patterns for the air sensitive samples were analysed using a brass air tight holder while the stable samples were done using a no background rotating Si holder. In both case the samples were collected using $Cu_{K\alpha}$ radiations (wavelength 1.54060).

<u>REACTIONS</u>

Synthesis of Na_4Sn_4

Na/Sn alloys of composition varying from 1/3 (tin rich) to 3/1 (sodium rich) were prepared by heating the elements to 300°C for 30 minutes under $N_{2(g)}$. The alloy was then ground with a mortar and pestle and extracted with ethylenediamine. The resulting suspension was then filtered to give a dark red solution.

The ^{119}Sn NMR of these solutions showed a pseudo quintet at δ=-1230ppm with $J_{Sn117-Sn119}$=258Hz. This signal was attributed to Na_4Sn9[28].

Due to the extreme sensitivity of the solution toward oxidation, attempts to isolate the compound in the solid state were unsuccessful.

Synthesis of Na_4Sn

In a typical reaction, metallic sodium (1.75g;76mmol) was heated under $N_{2(g)}$ in the presence of tin metal (2.25g;19mmol) to 300 °C for about 30 minutes. Upon cooling, a grey crystalline material is obtained in quantitative yield.

The IR spectrum of the compound showed no observable absorption band between υ=4000-500 cm^{-1}. Thermal analysis (DSC) showed only one reversible thermal event at 407 °C which can be assigned to the melting of the compound. The homogeneity of the compound was demonstrated by comparison of the experimental powder pattern with the calculated one.

Crystal structure of Na_4Sn

Data collection

A crystal of Na_4Sn having approximate dimensions of 0.4*0.3*0.3mm was mounted on a glass capillary. All the measurements were made using a Rigaku diffractometer with $Mo_{K\alpha}$ radiation.

Cell constants and an orientation matrix for data collection obtained from least-squares refinement using the setting angles of 25 reflections in the range $30<2\theta<50$ corresponded to an orthorombic cell with dimensions:

a = 9.744(3)
b = 22.751(10)
c = 5.5390(15)

For Z = 8 and FW = 210.65, the calculated density is 2.279g/cm^3. Based on the systematic absences, the space group was determined to be P*nam*.

The data were collected at a temperature of -110 °C using omega-2theta scan technique to a maximym 2θ value of 49.9 degrees.

Data reduction

A total of 1202 reflections were collected. The unique set contains only 1202 reflections. The standards were measured after every 150 reflections. No crystal decay was noticed. The data were corrected for Lorentz and polarisation effects[58]. Absorption correction was made. The minimum and maximum transmission factors are 0.06096, 0.08103.

Solution and refinement

The structure was solved by direct methods. All the atoms were refined anisotropically. The final cycle of full matrix least-squares refinemenent was based on 1052 observed reflections (I>2.5 sigma(I)) and 62 variable parameters. Weights based on counting statistics.were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.550 and -3.950 respectively, showing residual around the two tin atoms.

All calculations were performed using the NRCVAX crystallographic software package[59].

N.B. To produce the plots, the space group was transformed form P*nam* to P*nma* (#62) using the following transformation matrix.

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{vmatrix}$$

Reactions of Na_4Sn with organic cations

Reaction of Na_4Sn with Ph_4PBr

0.11g of Na_4Sn (0.5 mmol) was stirred at room temperature with 0.89g of Ph_4PBr (2.1 mmol) in THF. Within 1 hour, the solution turned dark orange and a grey precipitate formed (0.26g;94 % of NaBr + Sn). Evaporation of the solvent yielded a dark orange oil.

^1H NMR (in THF) (m) δ=7.25ppm (m), δ=7.61ppm (m) and δ=7.8ppm (Ph's ^1H); ^{31}P (s) δ=-85.1ppm (PPh_5), (s) δ=-4.8ppm (PPh_3); IR υ= 1070 and 701 cm^{-1} indicative of aromatic rings.

The pentaphenyl phosphine was isolated by recrystallisation in toluene and then thoroughly characterised through DSC/TGA and X-Ray crystallography.

Reaction of Na_4Sn with Bis(triphenylphosphine) ammonium chloride (PPNCl)

Na_4Sn (0.08g;0.4mmol) and PPNCl (0.92g;1.6mmol) were left to react at room temperature in THF for 2 hours. A dark orange solution was obtained together with a white precipitate. An oily liquid was obtained upon evaporation of the solvent.

The ^1H NMR spectra of this liquid showed three aromatic multiplets at δ=6.95ppm, 7.45ppm and 7.70ppm. The ^{31}P NMR spectra was quite complex and only PPh_3 (δ=-4.8ppm) was identified. Attempts to purify this mixture by recrystallisation using a variety solvents (such as THF, DME, hexanes and diethyl ether) were unsuccessful.

Reaction of Na_4Sn with $BzEt_3NCl$

Na_4Sn (0.19g;0.9mmol) reacts within minutes with $BzEt_3NCl$ (0.81g;3.6mmol) in both THF or diethyl ether to give a dark orange solution and a grey precipitate (Sn(0) + NaCl). An orange oil is obtained upon evaporation of the solvent.

^1H NMR ***A*** δ=0.98 ppm(dt) (J_d=16.9Hz,J_t=7.6Hz); ***B*** 1.85 ppm(q) (J_q=7.6Hz); ***C*** δ=2.15 ppm(dd) (J_d=19.8Hz,J_d=6.8Hz); ***D*** δ=7.05ppm(m); ***E*** δ=7.48 ppm(m); ***F*** δ=7.68 ppm(m).

Successive sublimations under vacuum of this oil yielded a viscous liquid for which the signal noted as ***C*** did not appear.

If the same reaction is done in benzene at reflux temperature, a colorless solution is obtained. The ^1H NMR spectra of this solution showed the three aromatic signals (*D, E & F*) and the benzylic CH_2's protons (*C*).

Reaction of Na_4Sn with Me_4NCl, Bu_4NBr, $BzMe_3NCl$

THF suspensions of Na_4Sn and 4 equivalents of the ammonium salts were refluxed overnight without any reaction.

Reactions of Na_4Sn with organic halides

Reaction of Na_4Sn with Me_3SiCl, Ph_3SnCl, PhCl, BzBr and CCl_4

In these five cases, the organic halide and the Na_4Sn were suspended in THF in a ratio 4 to 1. The suspension was then refluxed for 2 hours without any results.

Reactions of Na_4Sn with inorganic halides

N.B. Special care should be taken when reacting Na_4Sn with inorganic halides($NbCl_5$) or elements(P and S). The reactions between the two powders are violent and highly exothermic.

Reaction of Na_4Sn with $NbCl_5$

Fifteen equivalents of Na_4Sn (0.59g;2.8mmol) were mixed with 8 equivalents of $NbCl_5$ (0.41g;1.5mmol). The reaction mixture was then heated to 110 °C for 12 hours inside a TEFLON lined acid digestion bomb. Washing the solid with H_2O, EtOH and then Et_2O gave a black powder of composition Nb_7Sn_2, based on X-Ray fluorescence elemental analysis, which still contained two NaCl equivalents. The DSC done under inert atmosphere showed no thermal event before 1100°C while the one done under compressed air atmosphere showed a broad exothermic event at 500°C together with a weight increase of about 6%. The IR spectrum showed no bands and the amorphous nature of the compound was confirmed by Powder XRD.

Reaction of Na_4Sn with $GaCl_3$ or $AlCl_3$

Typically Na_4Sn (0.47g;2.2mmol) was heated with 3.0mmol of the halides (0.40g for $AlCl_3$;0.53g for $GaCl_3$) 400°C in a sealed glass tube for 10 hours.

DSC studies allowed the identification of metallic tin as one of the products.

Reactions of Na_4Sn with elements

Reaction of Na_4Sn with elemental phosphorus

Red phosphorus

One equivalent of Na_4Sn (0.23g;1.1mmol) was heated, for 12 hours, to 200°C in a sealed glass tube with 2/3 equivalent of red phosphorus (0.02g;0.7mmol).

White phosphorus

Na_4Sn (0.23g;1.1mmol) and white phosphorus (0.02g;0.7mml) were heated under reflux in toluene for 12 hours.

Both procedures gave a black solid which was then extracted with ethylenediamine. The addition of ethylenediamine resulted in a gas evolution accompanied by the formation of an orange solution. NMR, M.S. and IR spectroscopy showed the presence of $MeNH_2$, $EtNH_2$, $NaPH_2$ and Na_4Sn_9. Toepler pump experiment showed that 1.3 mmoles of gas were evolved starting with 0.1g of the powder.

^{1}H NMR {δ=0.65ppm(bs) (-NH), δ=1.95ppm(t) (Et's CH_3), δ=2.19ppm(s) (Me's CH_3), δ=2.6ppm(q) (CH_2)}

^{31}P NMR {δ=-275.2ppm(t):$^1J_{H-P}$=140Hz} and ^{119}SN NMR {δ=-1230ppm(p):$J_{Sn117-Sn119}$=258Hz}, IR {υ=3300 and 2380cm^{-1} (P-H)}.

Reaction of Na_4Sn with elemental sulfur

Typically, Na_4Sn (0.77g;3.7mmol) and S(0.23g;7.2mmol) were sealed under vacum in a glass tube and then heated to 300°C for 30 min after which heterogeneous looking solids were obtained.

Synthesis of Na_3P and K_3P

A modification of a previously reported method[40] was used for the synthesis of Na_3P. Sodium (1.38g;60.0mmol) and red phosphorus (0.62g;20.0mmol) were heated under $N_{2(g)}$ to 500°C for 3 hours. The tube was then cooled and the solid grounded with a mortar and pestle. The powder was then annealed at 500°C for 10 hours to form a black homogeneous powder. A similar procedure was used to prepare K_3P starting with potassium (1.58g;40.4mmol) and red phosphorus (0.42g;13.5mmol).

Reaction Na_3P with $NbCl_5$

Na_3P (0.48g;4.8mmol) and $NbCl_5$ (0.52g;1.9mmol) were heated under vaccum to 300°C for 12 hours. The product was then washed with water, ethanol and diethyl ether to remove any unreacted starting material and the NaCl formed during the reaction. The black powder obtained by this procedure was then grounded with an agate mortar and pestle and annealed in a quartz tube at 600°C under dynamic nitrogen for 12 hours. The powder pattern of the resulting solid showed an increased crystallinity compared to the non-annealed material.

d-value (Å) (relative intensity): 3.42(33); 2.85(24); 2.54(27); 2.42(6); 2.17(100); 1.75(21); 1.71(8); 1.67(24).

Preparation of $NaPH_2$ and KPH_2

Extraction of Na_3P (2.0g;20.0mmol) with ethylenediamine resulted in gas formation together with coloration of the solution. Evaporation of the ethylenediamine gave a yellow solid which was very soluble in ethylenediamine and pyridine, slightly soluble in THF and insoluble in diethyl ether or hexanes. The ^{31}P {^{1}H} NMR spectra of the ethylenediamine solution showed a singlet at δ=-273.2ppm while the ^1H coupled spectra showed a triplet with $^1J_{H-P}$=140Hz. The ^1H NMR spectra of the same solution showed a doublet at -1.5ppm ($^1J_{H-P}$=140Hz). The IR spectra showed bands at υ=3300(b) and 2380(s)cm^{-1} which are characteristic of $NaPH_2$[60].

^1H NMR of the gas evolved during the reaction showed a broad peak at 0.65ppm(NH), a triplet and a quartet at respectively 0.98ppm and 2.6ppm (Et's) and a singlet at 2.35ppm (Me's).

Similar reactivity was observed with K_3P to form KPH_2.

Synthesis of Na/2P alloy adn extraction to yield P_7^{3-}

Sodium (0.27g;11.7mmol) and red phosphorus (0.73g;23.4mmol) were heated to 400 °C under $N_{2(g)}$ for 30 minutes. The red-brown solid obtained from this reaction was then extracted with 25 ml of ethylenediamine resulting in the formation of a light orange solution. ^{31}P NMR showed a broad signal at δ=-122.1 ppm characteristic of P_7^{3-} in solution.

Synthesis of M/Sn/P (M=Na,K) alloys

Potassium (0.15g;3.8mmol) or sodium (0.09g;3.9mmol), tin (0.45g;3.8mmol) and red phosphorus (0.11g;3.6mmol) were heated to 400°C under $N_{2(g)}$ for 30 minutes. The solid obtained appeared to be heterogeneous and metallic tin was present.

The ^{31}P NMR spectra of the solution formed by the extraction of that solid with ethylenediamine showed a broad singlet at δ=-122.1 ppm and a triplet at δ=-273.1 ppm (J=140Hz). The first signal has been attributed to P_7^{3-} [45] and the second to MPH_2. Integration of the two signals showed that the solution contained 20 P_7^{3-} moiety for every 3 $NaPH_2$. The ^{119}Sn NMR spectra contained no signals between +1000 and -2000 ppm.

Synthesis of K_2P_{16}, K_3P_{19} and K_3P_{21}

White phosphorus (0.86g;27.8mmol) was refluxed with potassium (0.14g;3.6mmol) in THF/DME (1:1) for 3 hours. The solvent was then removed under vaccum to form a deep red solid. This technique allowed the recovery of 1.00g of crystalline K_2P_{16} solid starting form a total of 1.00 grams of material (100% yield).

The ^{31}P NMR of the orange solution obtained by extraction of the solid with degassed ethanol only showed the presence of K_2P_{16}. The solution was stable to solvolysis but decomposed rapidly to phosphoric acid when exposed to atmospheric oxygen. A red solid was obtained by vacuum evaporation of the solvent. The IR spectrum of the red solid sometimes showed bands at υ=2700, 1200, 1140 and 830 cm^{-1} which are characteristic of DME.

Reaction of K_3P_{21} with Ph_3SnCl

A small excess of Ph_3SnCl (0.37g;1.0mmol) was added to a THF solution of K_3P_{21} (0.20g;0.3mmol) and stirred at room temperature for 12 hours to yield a white solid and a bright yellow solution. The solid was then removed by filtration. Addition of hexanes to the THF solution resulted in the precipitation of a yellow solid (0,08g) which was soluble in toluene, pyridine and DME. ^{31}P NMR of the toluene solution showed the presence of paramagnetism.

Reaction of K_3P_{21} with Me_3SiCl

The Me_3SiCl (10ml;79.0mmol) was added in excess to a THF solution of K_3P_{21}(0.41g;0.5mmol). Immediate precipitation was observed leaving the solution nearly colorless. Attempts to extract the reaction products from the precipitate with a variety of solvent (THF, DME, Toluene, Et_2O, hexanes) were unsuccessful.

Reaction of K_3P_{21} with Me_3SnCl

The Me_3SnCl (0.41g;2.1mmol) was added to a THF solution of K_3P_{21} (0.41g;2.1mmol) causing the immediate precipitation of a yellowish insoluble solid.

Reaction of K_3P_{21} with nBu_3SnCl

To a THF solution of K_3P_{21} (0.40g;0.5mmol) was added (0.50g;1.6mmol) of $n$$Bu_3SnCl$. The solution was then allowed to stir at room temperature for 12 hours after which a cloudy light orange solution was obtained. Filtration of the solution over celite followed by evaporation of the solvent yieled a light brown solid which was then purified by several precipitation via addition of hexane to THF solutions. The brown solid obtained (0.36g) (88%

yield calculated for the formula $(KP_7)_n$) did not contain tin based on XRF. The ^{31}P NMR spectra of a THF solution of that solid showed signals at δ= -12, -53, -68, -156 and -172 ppm in a ratio 1:2:1:2:1 as well as K_2P_{16} and K_3P_{21} impurities.

Reaction of K_3P_{21} with Cp_2ZrCl_2 (Cp=cyclopendienyl)

K_3P_{21} (0.60g;0.8mmol) was stirred in THF with Cp_2ZrCl_2 (0.38g;1.3mmol) for 12 hours. The solution was then filtered over celite to give a red solution and a pale solid. The ^{31}P NMR was characteristic of mixture of K_2P_{16} and K_3P_{21}. The ^{13}C {^1H} NMR showed one signals at δ=106ppm and a singlet at 5.81ppm was found in the ^1H NMR. Both signals are upfield to the Cp signal in Cp_2ZrCl_2, ^{13}C δ=116.2ppm, ^1H δ=6.48ppm.

Reaction of K_3P_{21} with $AlCl_3$*3thf

A THF solution of $AlCl_3$*3thf (0.50g;1.4mmol) was added slowly to a THF solution of K_3P_{21} (0.30g;0.4mmol). Immediate precipitation of a yellowish material was observed. Due the presence of KCl in the solid and its insolubility, no characterisation was done on this product.

REFERENCES

1.**Corbett J.D.** *et al., Inorg. Chem.,* **1993,** *32,* 4349.

2. **Jung J.-S.** *et al., Eur. J. Solid State Inor. Chem.,* **1992,** *t.29,* 1055.

3. for examples see: **Corbett J.D.,** *Chem. Rev.,* **1985,** *85,* 383; **Hönle W., Von Schnering H.G.,** *Chem. Rev.,* **1988,** *88,* 243; **Eisenmann B.,** *Angew. Chem. Int. Ed. Engl.,* **1993,** *32/12,* 1693.

4. **Kaner R.B.** *et al., Inorg. Chem.,* **1993,** *32,* 2754.

5. **Johannis, A.** *C.R. Hebd. Seances Acad. Sci.,* **1891,** *113,* 795; **1892,** *114,* 587; *Ann. Chim. Phys.,* **1906,** *7,* 750. 24A; *Ann. Chim. Phys.,* **1906,** *7,* 750.

6. **Smyth, F.H.,** *J. Am. Chem. Soc.,* **1917,** *39,* 1299.

7. **Peck, E.B.,** *J. Am. Chem. Soc.,* **1918,** *40,* 335.

8. **Kraus, C.A.,** *J. Am. Chem. Soc.,* **1922,** *44,* 1216.

9. **Kraus, C.A.,** *Trans. Am. Electrochem. Soc.,* **1924,** *45,* 175.

10. **Zintl, E.; Goubeau,J.; Dullenkopf, W.Z.,** *Phys. Chem., Abt. A,* **1931,** *154,* 1.

11. **Zintl, E.; Harder, A.Z.,** *Phys. Chem., Abt. A,* **1931,** *154,* 47.

12. **Zintl, E.; Dullenkopf. W.Z.,** *Phys. Chem., Abt. B,* **1932,** *16,* 183.

13. **J. Evers, O. Oehlinger, G. Sextl,** *Angew. Chem. Int. Ed. Engl.,* **1993,** *32/10,* 1442.

14. **E. Menges, V. Hopf, H Schäfer, A.Weiß,** *Z. Naturforsch. B.,* **1969,** *24,* 1351.

15. **Schäfer H., Eisenmann B.,** *Rev. Inorg. Chem.,* **1981,** *3,* 29.

16. **Zintl E., Harder A.,** *Z. Physik. Chem.,* **1936,** *b34,* 238.

17. **Stillwell C.W., Robinson W.K.,** *J. Am. Chem. Soc.,* **1933,** *55,* 127.

18. **Mathewson C.H.,** *Z. Anorg. Chem.,* **1906,** *50,* 171.

19. **Calingaert G., Boesch W.J.,** *J. Am. Chem. Soc.,* **1923,** *45,* 1901.

20. **Shoemaker D.P., Weston N.E., Jørgen R.,** *J. Am. Chem. Soc.,* **1955,** *77,* 4226.

21. **Kummer D., Diehl L.,** *Angew. Chem.,* **1970,** *82,* 881; *Angew. Chem. Int. Ed. Engl.,* **1970,** *9,* 895; **Diehl L., Khodadesh K., Kummer D., Strähle J.,** *Z. Naturforsch B.,* **1976,** *31,* 522.

22. **Corbett, J.D.,** *Inorg. Chem.,* **1968,** *7,* 198.

23. 4,7,13,16,21,24-Hexaoxa-1,10-diaxobicyclo[8.8.8]hexacosane, $N(C_2H_4OC_2H_4)_3N$

24. **Belin C.H.E.; Corbett J.D.; Cisar A.,** *J. Am. Chem. Soc.,* **1977,** *99,* 7163.

25. **Corbett, J.D.; Edwards, P.A.,** *J. Am. Chem. Soc.,* **1977,** *99,* 3313.

26. **Critchlow S.C.; Corbett J.D.,** *J. Am. Chem. Soc.,* **1983,** *105,* 5715.

27. **Edwards P.A., Corbett J.D.,** *Inorg. Chem.,* **1977,** *16,* 903.

28. **Rudolph R.W.** *et al., J. Am. Chem. Soc.,* **1978,** *100,* 4629.

29. **Rudolph R.W., Wilson W.L.,** *J. Am. Chem. Soc.,* **1981,** *103,* 2480.

30. **Rudolph R.W., Pons B.S., Santure D.J., Taylor R.C.,** *Electrochimica Acta,* **1981,** *26,* 365.

31. **Burns R.C., Corbett J.D.,** *J. Am. Chem. Soc.,* **1982,** *104,* 2804.

32. **Haushalter R.C.** *et al., Inorg. Chem.,* **1984,** *23,* **2312.**

33. **Critchlow S.C., Corbett J.D.,** *Inorg. Chem.,* **1982,** *21,* 3286.

34. **Haushalter R.C., Eichhorn B.W., Rheingold A.L., Geib S.J.,** *J. Chem. Soc., Chem. Commun.,* **1988,** 1027.

35. **Teller R.G., Krause L.J., Haushalter R.C.,** *Inorg. Chem.,* **1983,** *22,* 1809.

36. **Huttner G., Schiemenz B.,** *Angew. Chem. Int. Ed. Engl.,* **1993,** *32/2,* 297.

37. **Hector A., Parkin I.P.,** *J. Chem. Soc., Chem. Commun.,* **1993,** 1095; **Fitzmaurice J.C., Hector A., Parkin I.P.,** *Polyhedron,* **1993,** *12/11,* 1295.

38. **Girolami G.,** *private discussion.*

39. see reference 3 and references therein

40. **Brauer G., Zintl E.,** *Z. Phys. Chem., Abt. B,* **1937,** *37,* 323; **Mansmann M.,** *Z. Kristallogr.,* 1965, *122,* 399; **Gnutzmann G., Dorn F.W., Klemm W.,** *Z. Anorg. Allg. Chem.,* **1961,** *309,* 210.

41. **Hönle W., Von Schnering H.G.,** *Angew. Chem. Int. Ed. Engl.,* **1986,** *25/4,* 352.

42. **Von Schnering H.G.** *et al., Z. Anorg. Allg. Chem.,* **1987,** *553,* 261.

43. **Dahlmann W., Von Schnering H.G.,** *Naturwissenschaften,* **1972,** *59,* 420; *ibid.,* **1973,** *60,* 429.

44. **Manriquez V., Hönle W., Von Schnering H.G.,** *Z. Anorg. Allg. Chem.,* **1986,** *539,* 95.

45. **Hönle W., Von Schnering H.G., Schmidtpeter A., Burget G.,** *Angew. Chem.,* **1984,** *96,* 796; *Angew. Chem. Int. Ed. Engl.,* **1984,** *23,* 817.

46. **Belin C.H.E.,** *J. Am. Chem. Soc.,* **1980,** *102,* 6036.

47. **Baudler M.** *et al., Angew. Chem. Int. Ed. Engl.,* **1984,** *23/4,* 317.

48. **Baudler M. Düster D., Germeshausen J.,** *Z. Anor. Allg. Chem.,* **1986,** *534,* 19.

49. **Baudler M.** *et al., Z. Anorg. Allg. Chem.,* **1984,** *518,* 7.

50. **Baudler M., Faber W.,** *Chem. Ber.,* **1980,** *113,* 3394; *Z. Anorg. Allg. Chem.,* **1985,** *529,* 7.

51. **Baudler M., Exner O.,** *Chem. Ber.,* **1983,** *116,* 1268.

52. **Von Schnering H.G.** *et al., Angew. Chem. Int. Ed. Engl.,* **1981,** *6/7,* 594.

53. **Fritz G., Hölderich W.,** *Naturwissenschafen,* **1975,** *62,* 573.

54. **Baudler M.** *et al., Naturforsch,* **1979,** *b34,* 1690.

55. **Baudler M.** *et al., Naturforsch,* **1979,** *b34,* 1690; *Z. Anorg. Allg. Chem.,* **1980,** *469,* 15.

56. **Boller, Parthe,** *Acta Crystallogr.,* **1963,** *16,* 1095.

57. **Kukushkin V.Y., Moiseev A.I.,** *Inorganica Chimica Acta,* **1990,** *176,* 79-81.

58. **Grant D.F., Gabe E.J.,** *J. appl. crystallogr.,* **1978,** *11,* 114.

59. **Gabe E.J., Lee F.L., Lepage Y.,** *J. Appl. Crystallogr.*, **1989,** *22,* 384.

60. **Knoll F., Van Wazer J.R.,** *J. Inorg. Nucl. Chem.*, **1969,** *31,* 2623.

SUPPLEMENTARY MATERIAL

Table II Structure of Na_4Sn, atomic parameters x,y,z and Biso

	x	y	z	biso
SN1	0.33613(8)	0.40520(4)	1/4	1.24(4)
SN2	0.84238(8)	0.33023(4)	3/7	1.15(4)
NA1	0.668(5)	0.3652(3)	1/4	1.82(24)
NA2	0.0091(5)	0.3700(3)	1/4	1.66(22)
NA3	0.3545(6)	0.2609(3)	1/4	1.97(23)
NA4	0.1968(6)	0.5327(3)	1/4	1.98(23)
NA5	0.1433(6)	0.2777(3)	3/4	3.2(3)
NA6	0.1539(6)	0.4178(3)	3/4	2.5(3)
NA7	0.4795(6)	0.3472(4)	3/4	3.6(3)
NA8	0.5581(7)	0.5167(4)	1/4	4.0(4)

Biso is the mean of the principal axes of the thermal ellipsoid

Estimated standard deviations refer to the last digit printed

Table III Structure of Na_4Sn, u(i,j) or U values (*100)

	u11(U)	u22	u33	u12	u13	u23
SN1	1.09(4)	2.88(6)	0.73(4)	0.28(3)	0.0	0.0
SN2	1.00(4)	2.90(6)	0.48(4)	-0.05(3)	0.0	0.0
NA1	1.9(3)	3.5(4)	1.5(3)	0.12(23)	0.0	0.0
NA2	1.9(3)	4.0(4)	0.50(24)	-0.63(24)	0.0	0.0
NA3	3.0(3)	3.3(4)	1.1(3)	-0.36(25)	0.0	0.0
NA4	2.5(3)	2.6(4)	2.4(3)	0.3(3)	0.0	0.0
NA5	3.3(3)	4.8(4)	4.0(4)	1.2(3)	0.0	0.0
NA6	3.1(3)	5.0(4)	1.3(3)	0.5(3)	0.0	0.0
NA7	2.5(3)	9.8(6)	1.3(3)	1.5(4)	0.0	0.0
NA8	3.9(4)	7.7(6)	3.4(4)	-0.9(4)	0.0	0.0

Estimated standard deviations refer to the last digit printed

Anisotropic temperature factors are of the form:

$$Temp=-2*\pi^{2}*(h^{2}*u11*(a^{*})^{2}+...+2*h*k*(a^{*})^{2}*(b^{*})^{2}+...)$$

Table IV Structure of Na$_4$Sn, atomic bond distances in Angstroms

Sn1-Na1	3.348(5)
Sn1-Na2	3.286(5)
Sn1-Na3	3.288(6)
Sn1-Na4	3.203(6)
Sn1-Na6	3.302(3)
Sn1-Na6a	3.302(3)
Sn1-Na7	3.371(4)
Sn1-Na7a	3.371(4)
Sn1-Na8	3.334(8)
Sn1-Na8b	3.448(5)
Sn1-Na8c	3.448(5)
Sn2-Na1d	3.351(3)
Sn2-Na1	3.351(3)
Sn2-Na2e	3.336(3)
Sn2-Na2f	3.336(3)
Sn2-Na3g	3.461(4)
Sn2-Na3h	3.461(4)
Sn2-Na4b	3.142(6)
Sn2-Na5f	3.166(6)
Sn2-Na5g	3.130(7)
Na1-Sn2a	3.351(3)
Na1-Na2f	3.337(7)
Na-Na3h	3.403(8)
Na1-Na7	3.342(5)
Na1-Na7a	3.342(5)
Na1-Na8	3.606(11)
Na2-Sn2i	3.336(3)
Na2-Sn2j	3.336(3)
Na2-Na1i	3.337(7)
Na2-Na3k	3.336(8)
Na2-Na5	3.713(6)
Na2-Na5a	3.713(6)
Na2-Na6	3.293(4)
Na2-Na6a	3.392(4)
Na3-Sn2l	3.461(4)
Na3-Sn2k	3.461(4)
Na3-Na1k	3.403(8)
Na3-Na2h	3.336(8)
Na3-Na5	3.471(5)
Na3-Na5a	3.471(5)
Na3-Na7	3.607(7)
Na3-Na7a	3.607(7)
Na4-Sn2b	3.142(6)
Na4-Na6m	3.598(8)
Na4-Na8	3.540(9)
Na5-Sn2i	3.166(6)
Na5-Sn2l	3.130(7)
Na5-Na2d	3.713(6)
Na5-Na3d	3.471(5)
Na5-Na6	3.189(11)
Na5-Na7	3.637(10)
Na5-Na7l	3.260(11)
Na6-Sn1d	3.302(3)
Na6-Na2d	3.293(4)
Na6-Na4m	3.598(8)
Na6-Na7	3.556(9)
Na6-Na8b	3.177(10)
Na7-Sn1d	3.371(4)
Na7-Na1d	3.342(5)
Na7-Na3d	3.607(7)
Na7-Na5g	3.260(11)
Na7-Na8b	3.118(12)
Na8-Sn1b	3.448(5)
Na8-Sn1c	3.448(5)
Na8-Na6b	3.177(10)
Na8-Na7b	3.118(12)
Na8-Na8b	3.087(7)
Na8-Na8c	3.087(7)

CLAIMS TO ORIGINAL RESEARCH

1. Na_4Sn can be synthesised by solid state reaction starting from stoichiometric of the elements. It crystallizes in the orthorhombic space group *Pnam* with a unit cell of dimensions a=9.744(3)Å, b=22.751(10)Å, c=5,5390(15)Å. The most striking features are the two different tin environments and the lack of Sn-Sn interactions.

2. The reactivity of Na_4Sn with organic and inorganic halides, elements and organic cations was investigated.

3. MPH_2 (M=Na,K) is synthesised by the reaction between M_3P and ethylenediamine. This can be used as an alternative route to the use of highly reactive phosphide, PH_3, for the synthesis of alkali metal dihydrogenephosphides.

4. The first clear evidence of the interconversion between $P_{21}{}^{3-}$ and $P_{16}{}^{2-}$ was demonstrated. The importance of the solvent on this interconversion was also shown.

5. This reaction provides a selective and high yield synthetic route to these two polyphosphides thus allowing further studies of there reactivity.

6. The oxidation of $P_{21}{}^{3-}$ in the presence of Bu_3SnCl yields the new polyphosphide: $P_{14}{}^{2-}$.