THE UNIVERSITY OF CALGARY

Preparation, Structure and Reactions of Acyclic

Phosphorus-Nitrogen-Chalcogen Anions

by

Michelle Antoinette Seay

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Preparation, Structure and Reactions of Acyclic Phosphorus-Nitrogen-Chalcogen Anions" submitted by Michelle Antoinette Seay in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

This thesis describes the preparation of the novel anions $Ph_2P(E)NSiMe_3$ (E = S,Se) by the reaction of $Ph_2P(E)N(SiMe_3)_2$ with potassium *tert*-butoxide in tetrahydrofuran (THF). These monoanions were isolated as potassium salts, characterized by infrared and NMR spectroscopy. Attempts to prepare the dianions $Ph_2P(E)N^2$ by the reaction of $Ph_2P(E)N(SiMe_3)_2$ with two molar equivalents of potassium *tert*-butoxide gave only the monoanion.

An X-ray structural determination of $K[Ph_2P(Se)NSiMe_3]$. THF revealed a dimeric, step-shaped structure in which potassium is coordinated to a nitrogen and a selenium atom of one anion, a selenium of the second anion, and a THF molecule. The crystal structure of $[Ph_4As][Ph_2P(S)NSiMe_3]$ consists of noninteracting $Ph_2P(S)NSiMe_3^-$ and Ph_4As^+ ions. The structural and infrared spectroscopic data indicate substantial charge delocalization on to chalcogen atoms of the $Ph_2P(E)NSiMe_3^-$ anions.

The reactions of $Ph_2P(E)NSiMe_3$ with iodine or chlorodiphenylphosphine sulfide occur at the chalcogen sites to give $Me_3SiNPh_2PEEPPh_2NSiMe_3$ and $Me_3SiNPh_2PEPPh_2S$, respectively, which were characterized by NMR spectroscopy.

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In memory of

George T. Seay and E. Leo Payea;

two men who have seen a world full of change.

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CHAPTER ONE

Introduction

1.1 Scope of Thesis

For years, the chemistry of cyclic phosphorus-nitrogen (P-N) compounds has interested both pure and applied scientists.¹⁻⁴ Research on these inorganic ring systems has led to the development of unique polymers whose properties have been employed in the manufacture of fuel pipes, waterproofing and flame-retarding agents, and drug delivery systems.⁵ More recently, attention has shifted to newly polymerized P-N ring systems that contain elements such as carbon⁶, sulfur⁷ or transition metals.⁸ The incorporation of metals into polymeric phosphazenes could have application for batteries, electrodes or catalysts.⁹ The insertion of a transition metal into the phosphazene ring was facilitated by a ligand capable of forming σ -bond linkages between the transition metal and the skeletal nitrogen atoms of the phosphazene unit.^{8(e)} As a result, an important aspect of this field is the development of novel ligands. These ligands can then be considered as possible "building blocks" in forming unusual heterocycles containing either transition metals or nonmetals. In examining the viability of a ligand as a "building block", the chelating or bridging properties must be assessed to determine their possible incorporation into a novel heterocycle and, possibly, a unique polymer.

Examination of monohapto ligands provides information about the chemistry of the coordinating atom of interest, prior to its incorporation into an acyclic ligand or "building block". Ligands coordinating with only one atom to another ligand or metal



centre are considered to be monohapto. With respect to main group chemistry, the monohapto ligands of the phosphorylic unit (1) and the iminophosphoranyl anion (2) help to distinguish the differences in the coordination of chalcogen atoms (sulfur or selenium) and nitrogen atoms, respectively. This can then be related to the characteristic softness or hardness of the atom, resulting from the charge to radius ratio present for the atom of interest. With the incorporation of these atoms into a symmetric ligand, it is now possible to see if only one atom will be preferred in coordinating to another "building block" or metal atom, or if the possibility of chelation or bridging exists. To examine the monohapto ligands of chalcogens and nitrogen in a symmetric unit, a review of dithiophosphinates (3) (and the selenium analogues) and bis(trimethylsilylimido)-phosphinates (4) ligand systems will be presented.



Once an understanding of the properties of a symmetric "building block" has been achieved, investigations of hybrid ligands incorporating two differing coordinating atoms provide further insight into the differences of these atoms and the versatility of the ligand. These hybrid ligands can have the two coordinating atoms either similar in nature, as with methylenethiophosphinates (5), or differing as in the case of N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide (6).



The ligand systems examined are isovalent and trends can be established by the examination of the various coordinating atoms. Adaptation of these ligands systems to form a hybrid anionic ligand containing a nitrogen-phosphorus-chalcogen (sulfur or selenium) unit seems feasible. The isolation of such a ligand could provide a novel "building block" to be incorporated into a new heterocycle, based on the phosphorus-nitrogen ring systems.

1.2 Monohapto Ligands

1.2.1 Phosphorylic Unit



The phosphorylic ligand (1) contains an electron-rich sulfur or selenium atom. It is through this centre that the ligand is considered to bond by σ -donation to various Lewis

acids, in a monohapto bonding mode. The coordination chemistry of these ligands has been discussed in a recent review by Burford.¹⁰

With coordination to Lewis acids the bond order between the phosphorus and the chalcogen atoms in **1** decreases from the double bond in the free ligand, implying that there is an electronic perturbation as a result of the coordination. The change in the bond order can be monitored in the infrared (IR) spectrum by observing the stretching frequency for the phosphorus-chalcogen double bond. A decrease of more than 50 cm⁻¹ is observed for the coordination of the thiophosphorylic unit to a Lewis acid, indicating a decrease in the bond order.¹¹ ³¹P NMR spectroscopy has proven to be a valuable tool for monitoring reactions of ligands containing phosphorus atoms, but it provides little information for correlating the phosphorus chemical shifts of the phosphorylic ligands with the decrease in the phosphorus-chalcogen bond order upon coordination. Only small changes are observed and these are attributed to the enhanced shielding of the phosphonium centre once the phosphorylic ligand is coordinated to a Lewis acid.¹²

The phosphorus-sulfur bond length in Ph_3PS is 195.0(3) pm¹³ while the average length for a phosphorus-sulfur single bond is 210.0(1) pm.¹⁴ Upon coordination of the thiophosphorylic unit, the phosphorus-sulfur bond length increases to a range of 198.4(3) pm (for $Ph_3P(S).SbBr_3^{15}$) to 204.1(1) pm (for $Ph_3P(S).MoOCl_3^{16}$).¹⁰

When the phosphorylic ligand contains a selenium atom, an additional nucleus $(^{77}$ Se, I=1/2, 7.7%) is present for monitoring by NMR spectroscopy. With bonding to a Lewis acid there is significant deshielding of the selenium centre, which is evident in a decrease of the one bond coupling constant by 100 to 350 Hz.¹⁷ This is a result of the

decreased bond order. As a guideline, triphenylphosphine selenide, Ph_3PSe , has one of the shortest phosphorus-selenium double bonds of 210.6 pm¹⁸ and a ¹J(³¹P-⁷⁷Se) of 736 Hz.¹² The cation [(Et₂N)₂PSe]₂²⁺ has significantly longer phosphorus-selenium distances of 223.8 pm, which are considered as single bonds. The coupling constant, ¹J(³¹P-⁷⁷Se), is now reduced to 341 Hz.¹⁹ Similar values of ¹J(³¹P-⁷⁷Se) are observed for other complexes containing a phosphorus-selenium single bond, e.g. Me₂PSeMe (250 Hz) and Me₂P(S)SeMe (341 Hz).¹⁷ Intermediate values of ¹J(³¹P-⁷⁷Se) observed for selenophosphorylic complexes [(Ph₃PSeH⁺ (418 Hz)²⁰; Ph₃PSe.AlCl₃ (540 Hz)¹²; (Ph₃PSe)₄Cd²⁺ (585 Hz)²¹)] are an indication of intermediate bond lengths, and the retention of part of the phosphorus-selenium multiple bonding.

Originally, the phosphorus-chalcogen bond in **1** was considered to involve a zwitterionic resonance between a single bond, with a significant degree of π -back donation from the chalcogen centre into the d orbitals of the phosphorus atom, and a polar triple phosphorus-chalcogen bond with minimal π -bonding present in the dipolar structure.¹⁰ If this was in fact the case, any coordination of the ligand to a Lewis acid would be expected to be linear, in terms of donation of the axial σ -type electron pair from the chalcogen atom. However, only "side-on" coordination is observed with the angle formed by the Lewis acid-chalcogen-phosphorus being 98° to 115°¹⁰ as depicted in complex 7. There is also a significant increase in the chalcogen-phosphorus bond length of 6 pm upon coordination,¹⁰ consistent with the lower phosphorus-chalcogen stretching frequency in the infrared spectra of these complexes.

It has been noticed that there is severe asymmetric distortion of the other



coordinated ligands in a Lewis acid bonding to a phosphorylic unit.¹⁰ Two examples are the complexes $Ph_3PS.AlCl_3$ and $Ph_3PSe.AlCl_3$ where the chlorine atoms are tilted away from the phosphonium centre to allow contact between the phosphorus and aluminum centres. The phosphorus-aluminum distance (353.8 pm) is within the sum of the Van der Waals radii (372.7 pm).¹² The phosphorus-metal interactions confirm that the observed distortions are the result of auxiliary bonding of the acid and the phosphorus centre, resulting from the "side-on" coordination of the phosphorylic ligand.¹⁰ As a result, the "side-on" coordination is envisaged as the donation of the π -type bonding pairs (π complexation), from the chalcogen atom, due to the polarization of the phosphoruschalcogen π -electron cloud onto the chalcogen. This facilitates a stronger interaction with the Lewis acid.²²

The length of the phosphorus-chalcogen bond in the phosphorylic ligand cannot be correlated with chemical shifts in the ³¹P and ⁷⁷Se NMR spectra. However, examination of the ${}^{1}J({}^{31}P-{}^{77}Se)$ coupling constant can provide information on the approximate bond order between these two atoms prior to crystallographic analysis.

1.2.2 Iminophosphoranyl Anions



The iminophosphoranyl anion, $R_3P=N$ (2), is isoelectronic with the phosphorylic ligand (1) (E=O) but has never been isolated in its free form.²³ A review by Dehnicke and Strahle covers the stable complexes this ligand forms with Lewis acidic metal halides.²³ The bonding properties of the iminophosphoranyl anion to various transition metal species is not dependent on the number of metal d electrons and, commonly, a linear bond is formed with a short nitrogen-metal distance as indicated in **8a**. A bent coordination mode has also been observed with the smallest MNP angle being approximately 130°. The bent form is best depicted by the resonance structures (**8b-c**), since the nitrogen-metal and phosphorus-nitrogen distances remain close to those of double bonds.



The phosphorus-nitrogen bond length remains independent of the nitrogen-metal distance or the angle that is assumed upon coordination of the anion to the metal centre.

The phosphorus-nitrogen bond length is typically 159 to 166 pm²³ while that of a single bond is 178 pm²⁴ and that of a double bond is 157 to 160 pm.²³ This decrease in bond order from a formal double bond indicates why the resonance structures are required for depicting the bent structure. The nitrogen-metal distances range from 171 to 190 pm but, upon examination of each individual case, the bond length is characteristic of a double bond for that particular metal.²⁵

The angle formed by the coordination of the anion to the metal centre can be deduced by IR spectroscopy. The asymmetric stretching vibration of the metal-nitrogenphosphorus unit is present in the IR spectrum at about 1100 cm⁻¹. The symmetric stretching vibration can only be assigned in a few cases and would be present at slightly less that 600 cm⁻¹. These two vibrations are maximally coupled in a linear coordinated complex (**8a**), thus having the largest difference in wavenumbers.²⁶ This coupling decreases with the decrease of the angle from 180°. By examination of the asymmetric stretch band itself, an idea of the bonding angle can also be deduced, as the wavenumber appears at a lower frequency with the decrease of the angle. For example, $[MoCl_4(NPPh_3)]_2$ forms a complex with an angle of 166° and has an asymmetric stretch band at 1128 cm^{-1 27} while $[Mo(NO)(NPMePh_2)(dttd)]$ forms an angle of 130° and the asymmetric stretch band occurs at 1050 cm^{-1,28}

Examination of the phosphonium centre by ³¹P NMR spectroscopy reveals a downfield chemical shift upon coordination to a metal centre through the nitrogen. This is due to the deshielding of the phosphorus centre by the metal atom, facilitated by the short nitrogen-metal distance.²³ The short nitrogen-metal distance permits the electron-

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withdrawing effect of the metal to interact with the phosphorus atom.

The interactions of the bonding orbitals for the linear coordination of the iminophosphoranyl anion to a transition metal have been described by Phillips and Skaski²⁹ while Mronga *et al.* have discussed the bent coordination.³⁰ In the linear form, hybridization of the d_z^2 and d_x^2 , 2 orbitals of the metal occurs to give d^2sp^3 hybridized orbitals, while the nitrogen has a sp hybridized orbital and the phosphorus orbitals are sp³. These hybrid orbitals form the σ -bonding. Interaction of the d_{zz} and d_{yz} orbitals of the metal with the p_x and p_y of the nitrogen, respectively, leads to π -interaction. The d_{yz} interaction is depicted in Figure 1.1. The d_z^2 orbital of the phosphorus atom interacts with the p_y orbital of the nitrogen. To facilitate the optimal overlap, the phosphorus atom 161°.



Figure 1.1 - *Pi* bonding of linear coordination of an iminophosphoranyl anion to a metal centre.

The nonlinear arrangement (Figure 1.2) now involves sp^2 hybridization of the nitrogen orbitals so only one p orbital is available to facilitate π -bonding with the metal

centre, rather than two as in the linear arrangement. The phosphorus atom is located at a smaller angle to the nitrogen-metal bond than in the linear arrangement, and this facilitates a better overlap of its $d_x 2_y 2$ orbital with the p_y orbital on the nitrogen.



Figure 1.2 - *Pi*-bonding of bent coordination of an iminophosphoranyl anion to a metal atom. The axes of the phosphorus atoms are rotated by 45° around the z axis with respect to the symmetry axes of the metal and nitrogen.

In both of these cases there is no strong influence of the angle assumed on the nitrogen-metal or the phosphorus-nitrogen distances. It is more likely that steric requirements of the metal complex and the anion govern the angle adopted upon coordination.

1.3 Symmetric Ligands

1.3.1 Dithiophosphinates and Diselenophosphinates

The dithiophosphinate anions (3) are versatile ligands in that they may chelate and/or bridge various metal centres. A keen interest in these ligands was apparent in the late 1960s,³¹ since the oxygen analogues were only capable of bridging various metal centres to form polymeric structures. There is also some practical interest in these



dithiophosphinate ligands as they form poly(metal phosphinates) which have a high degree of polymerization, thermal stability and plastic properties.³² The dithiophosphinates are commonly synthesized by reactions of alkali metal or ammonium salts of the ligand (or the free acids) and metal compounds.³¹ The use of the free acids is useful in the synthesis of aromatic dithiophosphinates. The selenium analogs of **3**, diselenophosphinates or the mixed ligands R_2PSSe (selenothiophosphinates) can be synthesized, but both decompose rapidly giving rise to elemental selenium.³¹ Only limited characterization has been achieved with these ligands due to their thermal instability.

Numerous investigations³³ have shown that the phosphorus-chalcogen bond in dichalcogenophosphinates has only a small π -component, therefore it is not a conventional double bond.³¹ The negative charge in the anionic ligand **3** is assumed to be delocalized through the chalcogen-P-chalcogen unit.³¹ This is facilitated by the π -type molecular orbitals of the ligand perpendicular to its plane. The empty d π orbitals on the chalcogen are used to accept from the filled p π orbitals of the phosphorus centre and to facilitate coordination to metal atoms by overlapping with the full d orbitals of the metal.³⁴

The delocalization of the negative charge through the chalcogen-P-chalcogen unit was confirmed by examination of the phosphorus-chalcogen stretching frequencies in the IR spectrum. Only two absorption bands are present as there is only one type of phosphorus-chalcogen bond if the charge is delocalized over both chelating atoms.³¹ The asymmetric stretch is in the area of 556-591 cm⁻¹ and the symmetric stretch is in the region of 475-492 cm^{-1.31}



The first structure demonstrating the chelating effect of the dithiophosphinate anion was found in nickel(II) complexes. Two structures of the type 9 were reported in dithiophosphinate ligands chelate one nickel centre, which two bis(dimethyldithiophosphinato) nickel(II)³⁵ and bis(diphenyldithiophosphinato) nickel(II).³⁶ Both structures have a square planar orientation of the nickel and four sulfur atoms while the phosphonium centre of each ligand assumes a distorted tetrahedral orientation. This is expected as a neutral nickel(II) complex is assumed to have a square planar geometry.³⁴ Both compounds crystallize in the $P2_1/c$ space group with four molecules in the unit cell. Examination of the phosphorus-sulfur bond lengths [d(P-S) = 201(1) pm] indicates that there is delocalization throughout the ligand and the angle of chelation, at phosphorus, for each of the two ligands is 101.3°.³⁶

Upon reaction of the dithiophosphinate ligand with a zinc metal centre, the first example of both chelation and bridging within the same compound was discovered.³⁷ In the dimer of bis(diethyldithiophosphinato) zinc(II) (10), the zinc centres have a distorted tetrahedral arrangement and the four-membered rings, formed by the chelating ligands,

are coplanar within 6 to 10 pm. The sulfur-zinc distances are longer when formed by the chelating ligands than by the bridging ligands (246.3 pm and 238.0 pm, respectively). The longer bond lengths facilitate the smaller angle required at the zinc centre upon chelation.



Although the structure of the analogous cobalt(II) complex was not reported, it is isomorphous to the dimer of bis(diethyldithiophosphinato) zinc(II).^{37,38} Upon subsequent examination of bis(dimethyldithiophosphinato) cobalt(II), Cavell *et al.* found a polymeric structure, depicted as **11**, rather than a dimer.³⁹ The cobalt centre remains tetrahedrally coordinated although there are no chelating ligands. The only difference between the two structures is that the alkyl groups on the phosphorus of the ligands were ethyl in the zinc dimer and methyl in the polymeric cobalt complex. It was concluded that the steric effects of the substituents on the phosphonium centre governed the structure assumed as the ligands were believed to be electronically equivalent.³⁹

Complexes of the dithiophosphinate ligand have been formed with trivalent, as well as divalent, metal centres. The degree of association with various tetrahedral metal centres is dependent upon the size of the donor atom, the radius of the metal atom and



its hybridization state. Mainly steric factors govern whether chelation and/or bridging will occur with the metal atoms. Octahedral metal centres are found only in the monomeric form with chelation of the dithiophosphinate ligands. This is due to the metal's ability to accommodate a smaller bond angle required by chelation.³¹

The dithiophosphinate complexes of palladium (II) and platinum (II) $[M(S_2PR_2)_2]$ have been investigated by Stephenson and co-workers.⁴⁰⁻⁴⁴ These neutral complexes are isomorphous with the nickel (II) complex (9). Reactions of these compounds with tertiary phosphines result in the stepwise cleavage of the metal-sulfur bonds, generating fourcoordinate adducts.⁴¹ A reaction with one molar equivalent of a tertiary phosphine cleaves a single metal-sulfur bond, causing one of the dithiophosphinate ligands to be unidentate, and the tertiary phosphine occupies the vacated site on the metal, as depicted in 12. Variable temperature ¹H NMR studies reveal that there is a rapid intramolecular exchange of the uni- and bidentate ligands in 12 at ambient temperatures.⁴² Reactions with two molar equivalents of the tertiary phosphine cleaves a dithiophosphinate ligand completely from the metal, resulting in the ionic compound 13.



Characteristic bands in the IR spectrum of the two four-coordinate adducts (12 and 13) have been assigned to the three coordination modes of the dithiophosphinate ligand. (R = Ph).⁴² The bidentate ligand is characterized by bands at 603 and 570 cm⁻¹ while the unidentate ligands have bands at 645 and 540 cm⁻¹. The ionic dithiophosphinate ligand is characterized by bands at 650 and 560 cm⁻¹. Assignment of specific vibrations to these bands has not been attempted due to the extensive coupling present, but a large contribution is attributed to the PS₂⁻ stretching modes.⁴²

Crystal structure determinations of the palladium complexes [Pd(S₂PPh₂)₂PPh₃] and [Pd(S₂PPh₂)(PPh₃)₂][S₂PPh₂] have confirmed the structures of the four-coordinate adducts 12 and 13.⁴³ In the 1:1 adduct $[Pd(S_2PPh_2)_2PPh_3]$, the bidentate ligand maintains charge delocalization through the SPS unit, evident from the phosphorus-sulfur bond lengths of 198.6(11) and 201.7(12) pm and the chelation angle, PSP, of 105.7(4)°. The SPS angle opens up to 116.3(5)° in the unidentate ligand. Delocalization of the negative charge is maintained in the SPS unit, but the phosphorus-sulfur bond lengths are no longer equal with distances 196.6(13) and 1:2 adduct of 204.7(10) pm. In the $[Pd(S_2PPh_2)(PPh_3)_2][S_2PPh_2]$, the bidentate ligand remains the same in its coordination to the metal centre. The ionic dithiophosphinate now has the negative charge located on only one sulfur atom, lengthening the phosphorus-sulfur bond (d(P-S) = 199.0(20) pm), while the other phosphorus-sulfur bond decreases to the double bond distance of 193.2(20) pm. The SPS angle opens up a little more, than observed in the unidentate ligand, to 117.9(8)°. The analogous platinum structures have been verified by NMR spectroscopy.⁴⁴ Investigations of similar reactions of dithiophosphinate ligands and tertiary phosphines have been done with osmium (II), iridium (I), rhodium (II) and ruthenium (II) and (0).⁴⁵

Due to the instability of diselenophosphinates and the mixed chalcogen ligands R_2PSSe , only a few complexes have been synthesized. The diphenyldiselenophosphinato complexes include coordination of the ligand with cobalt (II), nickel (II), copper (II), cadmium (II), zinc (II),⁴⁶ lead (II) and antimony (II).⁴⁷ The diphenylselenothiophosphinate complexes include coordination to mercury, bismuth(III), palladium (II), platinum (II) and rhodium (II).⁴⁷ Only electronic and IR spectral studies have been reported for these compounds. Two absorption bands are present in the IR spectra, indicating that there is only one type of phosphorus-chalcogen bond with the charge delocalized over both coordinating atoms. The asymmetric stretching vibration is in the region of 475-492 cm⁻¹ for the diselenophosphinates and 540-560 cm⁻¹ for the mixed ligand selenothiophosphinates.³¹ The symmetric stretch is in the regions of 449-458 cm⁻¹ and 440-454 cm⁻¹ for the diselenophosphinate and selenothiophosphinate ligands, respectively.³¹ From the limited data available, it appears that these anions are only able to form four-membered rings by chelation,⁴⁸ although no crystallographic data have been

obtained to verify this conclusion.

1.3.2 Bis(trimethylsilylimido)phosphinates



With replacement of the sulfur atoms in the dithiophosphinate ligands by trimethylsilylimido groups a different symmetric ligand (4) is obtained with hard nitrogen centres to act as the coordination sites. Much of the work done with the bis(trimethylsilylimido)phosphinate ligand system is by Edelmann and co-workers.⁴⁹ The lithium salt was synthesized from a reaction of trimethylsilylamino-trimethylsilylimino-diphenylphosphorane with an *n*-butyl-lithium in benzene (Equation 1.1).⁵⁰ Although unable to obtain initially a crystal structure of the lithium salt of the anionic ligand, Edelmann *et al.* believed that it assumed a dimeric form (14), with the two lithium atoms symmetrically bridged by two bis(trimethylsilylimido)phosphinates.





By comparison, the lithium salt of $[Me_2N(Me_3C)P(NSiMe_3)_2]^2$ assumes a dimeric form only in benzene, as evident by cryoscopic determination, although it is also soluble in ether and carbon tetrachloride in its monomer form.⁵¹ The lithium salts of sulfinamidino ligands [RNS(R')NR"] also coordinate in a similar dimeric eight-membered ring under certain conditions.⁵²

Despite the assumed bridging capabilities of the bis(trimethylsilylimido)phosphinate ligand in the lithium derivative, reactions of **14** with various anhydrous halides of lanthanides and actinides (praseodymium, neodymium, uranium, and thorium) yielded only complexes in which the bis(trimethylsilylimido)phosphinate ligand chelates to the various metal centres, giving rise to four-membered metalladiazaphosphetidine rings.⁴⁹ With the unsymmetrical coordination of the ligand to the metal centre, it was noted that the orientation of the ligand around the metal was similar to that observed for the pentamethylcyclopentadienyl and cyclopentadienyl ligands. Similar steric restrictions were assumed to be in effect.⁴⁹



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With the synthesis of the bis(trimethylsilylimido)phosphinate ligand in tetrahydrofuran (THF) rather than benzene, a crystal structure of the lithium salt (15) was

finally determined.⁵³ It revealed a monomeric structure (**15**) in which one ligand is chelated to the lithium atom, which is also coordinated to two THF molecules. The ligand is coordinated symmetrically to the lithium cation with a chelation angle of 109.4°, larger by about 8° than observed in the dithiophosphinates coordinated to metal atoms.³⁶ The phosphorus-nitrogen bond lengths of 157.9(4) and 158.0(4) pm are equivalent to those observed with the iminophosphoranyl anions,²² indicating that there is delocalization of the negative charge throughout the ligand upon coordination. The four-membered ring formed upon coordination is planar.

A recent study by Steiner and Stalke examined the crystal structures of bis(trimethylsilylimido)phosphinates with a series of alkali metals (M = Li, Na, K, Rb, Cs).⁵⁴ It was determined that the structure was dependent on the alkali metal. As with the lithium derivative **15**, the potassium derivative assumes the same monomeric structure. The phosphorus-nitrogen distances are nearly identical for both structures with a slightly larger chelation angle of 114.1(4)° in the potassium derivative. There are four THF molecules coordinated to the potassium metal. The sodium derivative forms the ionic compound [Na(THF)₆][Na((Me₃SiN)₂PPh₂)₂], with two bis(trimethylsilylimido)phosphinate ligands coordinated to one sodium atom. The negative charge is delocalized throughout the ligand with the average phosphorus-nitrogen distance of 157 pm. This is comparable to the distances observed in the iminophosphoranyl anions²². The chelation angles 111.2(3)° and 112.8(3)° are midway between those of the lithium and potassium derivatives.

A dimeric, step-shaped structure (16) occurs for the complexes with



bis(trimethylsilylimido)phosphinate ligands coordinated to rubidium and cesium.⁵⁴ The structure consists of two four-membered MNPN rings fused to a central M_2N_2 ring with the two MNPN units located above and below the central ring unit. A similar structure has been observed for alkali metal derivatives of sulfinimidamides, M[RNS(R')NR].⁵² Despite the different metallic radii of the metals, delocalization of the negative charge is maintained throughout the NPN units with average phosphorus-nitrogen distances of 157 pm. The NPN angle of 113.7(2)° is similar to that of the monomeric structures. The rubidium derivative has one THF molecule coordinated to each metal centre while the cesium derivative does not have any.



An interesting property of this ligand is observed with the reaction of two

equivalents of the lithium salt with samarium iodide (SmI_2) .⁵³ Upon reaction of bis(trimethylsilylimido)phosphinate ligands, the two iodine atoms remain attached to the metal centre (17). One lithium atom coordinates to the two iodine atoms and is stabilized by two molecules of THF. The oxidization state of samarium changes from +2 to +3 as a result of this reaction. The ligands are unsymmetrical in their coordination to the metal centre and the chelating angle decreases by approximately 3°, though they remain planar in their coordination. The changes in the ligand coordination from the lithium salt are a result of a more sterically hindered system.

1.4 Hybrid Ligands

1.4.1 Methylenethiophosphinates



Fackler Jr. *et al.* have investigated a hybrid of the dithiophosphinate ligand in which a methylene group is substituted for one of the sulfur atoms of the dithiophosphinate ligand (3). The choice of the methylene group was decided by the fact that carbon and sulfur have similar electronegativities.³⁴ The methylenethiophosphinate (5) was synthesized from triphenylphosphine sulfide and an alkyllithium reagent (Equation 1.2).^{55,56} The lithium salt was isolated from a mixture of THF and ether (2:1) but, a crystal structure of this lithium derivative has yet to be published.

(1.2)
$$Ph_3PS + RCH_2Li \xrightarrow{THF/Ether} Ph_2P(S)CH_2R + PhLi \xrightarrow{R=H} 5 + C_6H_6$$

To confirm that the reactivity of the methylenethiophosphinate ligand is similar to that of the analogous dithiophosphinate ligand, the hybrid ligand was reacted with a nickel complex, NiCl₂(PPh₃)₂, to observe if a similar coordination occurs with the nickel(II) centre.⁵⁷ The methylenethiophosphinate ligand bonded to the metal centre in a planar fashion, forming the complex (Ph₃P)NiCl(CH₂(S)PPh₂) (**18**), and the ligand maintained an identical chelation angle, of 101.3°, to that recorded for the bis(diphenyldithiophosphinato) nickel(II) complex.³⁶ With a phosphorus-sulfur bond distance of 199.9(3) pm, a delocalization of the negative charge throughout the chelating atoms is evident. This is confirmed by the phosphorus-methylene distance of 177.6 pm which is similar to those observed for ylide compounds [Me₃AuCH₂PPh₃ d(P-CH₂) = 175.5(13) pm⁵⁸]. By comparison, the phosphorus-carbon double bond is 166.1(8) pm for Ph₃PCH₂⁵⁹ and the single bond for the phenyl group attached to the phosphorus in Me₃AuCH₂PPh₃ is 181.1(12) pm.⁵⁸



With the knowledge that the hybrid ligand is capable of chelating to a metal centre, the next step was to investigate whether the ligand can bridge two metal centres.

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When the methylenethiophosphinate anion was treated with silver nitrate, a complex with a one-dimensional chain structure in the solid state resulted (depicted in 19).⁶⁰ The repeating unit consists of two silver atoms bridged by two bis(diphenyl)methylenethiophosphinate ligands (20). Each silver atom is coordinated to a sulfur and a carbon atom in a nearly linear arrangement. The orientation of the two diphenylphosphonium centres simulates a step-like structure. On the basis of low temperature ¹H NMR spectra, fluxional behaviour of the methylene group is evident in solution.⁶⁰ This is attributed to lability of the silver-ligand association either by cleavage of the methylene and/or the sulfur atom from a silver centre.



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Within the repeating unit (20), the intramolecular distance of the two silver atoms (Ag-Ag') is 299.0 pm while that of the sum of the metallic radii is smaller at 288.4 pm.⁶⁰ The intermolecular distance of the silver atoms from neighbouring units (Ag"-Ag) is even larger at 322.7 pm. However, the presence of luminescence in these compounds in the solid state indicates that there is some sort of interaction occurring between the metall centres.⁶⁰ In this polymeric structure the phosphorus-sulfur bond length (200.7(4) pm) and the phosphorus-ylide bond length (179.5(11) pm) are consistent with delocalization of the
charge throughout the ligand and a decrease in the bond order associated to the coordinating atoms.⁶⁰



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The gold complex of **5** is isomorphic with the silver complex **20** and forms an identical repeating unit with the bis(diphenyl)methylenethiophosphinate ligands.⁶¹ With the use of a bulky cation bis(triphenylphosphine)iminium, (PPN)⁺, a gold complex with two methylenethiophosphinate ligands coordinated to a single gold atom can be isolated.⁶² In this case both ligands are bonded through the methylene groups to the metal centre, leaving the sulfur atoms associated to the (PPN)⁺ cation. This provides support for the proposed explanation of the fluxional behaviour observed by ¹H NMR spectroscopy for the analogous silver complex in solution.

The reaction of the gold monomer unit with thallium(I) yields the first example of a bimetallic one dimensional polymer with short gold-thallium bonds.⁶³ The resulting polymeric structure (21) contains alternating gold and thallium centres, in an approximately linear structure (Tl'-Au-Tl = 163°), with each repeating unit consisting of one gold and one thallium centre bridged by two bis(diphenyl)methylenethiophosphinate ligands. The methylene carbons are bonded to the gold centre while the sulfur atoms are



bonded to the thallium centres. Although these thallium-sulfur bonds are considered to be weak bonds and largely ionic [d(TI-S) = 305(1) and 291(1) pm], the bond lengths are typical of other thallium-sulfur bonds.⁶⁴ Both the phosphorus-sulfur and phosphorus-methylene distances are consistent with a decrease in bond order within the ligand. The thallium-gold inter- and intramolecular distances range from 295.9 to 300.3 pm, while the sum of their metallic radii is 303.4 pm.⁶³ Luminescence is present in this compound and the metal-metal distances are short enough for interaction to occur between these atoms.

Work with this hybrid ligand system has been extended to other bimetallic systems involving gold and lead,⁶⁵ gold and mercury,⁶⁶ and gold and platinum.⁶⁷

1.4.2 N,N'-Bis(trimethylsilyl)aminodiphenylphosphine Sulfide

Another hybrid ligand based on both the dithiophosphinate and the bis(trimethylsilylimido)phosphinate ligands is N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide (6). Although it is initially a neutral ligand, one or both of the trimethylsilyl groups are lost (as Me₃SiX) upon reaction with a metal halide. This gives the ligand the required charge to facilitate bonding to a metal centre. Roesky *et al.* have reported the reaction of **6** with titanium tetrachloride to form the first complex containing a titanium-nitrogen double bond (22).⁶⁹ As found with the iminophosphoranyl anions (See Section 1.2.2), most nitrogen-metal double bonds occur with metals of groups 5 to 8 in the periodic table.⁶³



0



Strong similarities between the titanium-nitrogen bonding in and coordination of iminophosphoranyl anions (2) are evident in the coordination of the $Ph_2P(S)N^{2-}$ ligand to the metal.²² The ligand $Ph_2P(S)N^{2-}$ acts as a four electron donor, binding to the titanium centre through the nitrogen, with a bond distance of 172.0(2) pm. The titanium -nitrogen-phosphorus atoms are arranged in a nearly linear fashion with a bond angle of 172.5° and the phosphorus-nitrogen distance is 164.7(2) pm. The length of the phosphorus-sulfur bond is 195.4(1) pm, closer to that of a double bond than a single bond.



Recent work by Roesky *et al.* indicates that the reaction of N,N'bis(trimethylsilyl)aminodiphenylphosphine sulfide (6) is dependent on the nature of the metal. Bonding of 6 may not be confined to the nitrogen atom after the removal of the trimethylsilyl groups. The reaction of two equivalents of $(i-Pr)_2P(S)N(SiMe_3)_2$ with tin tetrachloride resulted in the elimination of only one trimethylsilyl group from each ligand. The $(i-Pr)_2P(S)NSiMe_3$ anions chelate with the tin atom, forming the structure 23.⁷⁰ The two four-membered rings are located in a *cis* arrangement. Delocalization of the negative charge is maintained throughout the nitrogen-phosphorus-sulfur unit. This is reflected in the phosphorus-nitrogen distances of 163.2(3) and 162.6(3) pm and the phosphorus-sulfur distances of 202.3(1) and 202.4(1) pm. The chelation angle of 103.6(1)° for the N-P-S unit is similar to those observed in metal complexes of the dithiophosphinate³⁶ and the methylenethiophosphinate ligands.⁵⁷

1.5 Objectives and Preparative Strategy

Incorporation of the coordination atom of the monohapto ligands into symmetric ligands will establish if preference of one site will occur with reactions of a "building block" or metal atom, or if the possibility of chelation or bridging exists. However, the

reactions of dithiophosphinate and bis(trimethylsilylimido)phosphinate ligands indicate that the reactions are dependent on the metal centres as well. The addition of other ligands to the metal centre can cause cleavage of bidentate ligands, as observed with the reactions of tertiary phosphines and dithiophosphinate complexes.⁴⁰⁻⁴⁴ The character of the metal can influence the coordination mode of a ligand, as illustrated with the alkali metal derivatives of bis(trimethylsilylimido)phosphinate ligands.⁵⁴

The use of hybrid ligand systems can greatly increase the versatility of a ligand as a "building block". The methylenethiophosphinates were considered to be similar to the dithiophosphinates since both the coordinating sites, sulfur and the methylene group, have similar electronegativities.³⁴ This was confirmed by the coordination of methylenethiophosphinate to a nickel (II) complex with the same (S-P-CH₂) chelation angle⁵⁷ present in the analogous dithiophosphinate system.³⁶ The ligand, however, is a valuable "building block" in the synthesis of one-dimensional chain structures by bridging two metal centres. Because of the similar electronegativities of the sulfur and the methylene group, the ligand can bridge two identical metals, as with the silver compound,⁶⁰ or two different metal centres located in close proximity in the periodic table, as with the gold and thallium compound.⁶³

Investigations with the neutral ligand N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide^{68,70} illustrate the versatility of a hybrid ligand containing two coordinating atoms which are quite different in character, i.e. the hard nitrogen and soft sulfur atoms. The reactive site is dependent on the nature of the metal combining with this ligand. The early transition metal titanium (in TiCl₄) is fairly hard in character and as a result it reacts at the nitrogen centre of the ligand.⁶⁸ By contrast, (i- $Pr)_2P(S)N(SiMe_3)_2$ reacts with the softer metal tin (in $SnCl_4$) via chelation of the ligand, releasing only one trimethylsilyl group of the ligand.⁷⁰



The objective of this thesis is to prepare the monoanions (24) and dianions (25) of the corresponding N,N'-bis(trimethylsilyl)aminodiphenylphosphine chalcogenide ligands. The anions 24 and 25 are isovalent with the symmetric and hybrid ligand systems discussed in this chapter. Once isolated, characterization of these anions by spectroscopic methods and X-ray structure determination can indicate how the negative charge is distributed through the nitrogen-phosphorus-chalcogen unit. Although removal of the trimethylsilyl groups may occur *in situ* upon coordination to a metal centre, reactions of metal or nonmetal halides with the anions 24 and 25 may occur more readily due the negative charge. Such investigations may also confirm if a preference exists for the monoanion 24 to chelate to a metal centre while unidentate coordination occurs for the dianion 25, or if the bonding mode is dependent on the characteristics of the metal atom. The reactivity of these anions will be examined to establish their applicability as synthetic "building blocks" to form novel heterocycles.

Herberhold has reviewed the chemistry of the sulfurdiimide dianion, $SN_2^{2,71}$ The potassium salt of this anion can be isolated from the reaction of bis(trimethylsilyl)sulfur

diimide with potassium *tert*-butoxide with refluxing in 1,2-dimethoxyethane (Equation 1.3).⁷² The negative charge of the SN_2^{2} anion is essentially localized on the terminal nitrogen atoms.⁷¹ The potassium salt of this dianion has been used to prepare new sulfur diimide derivatives. The successful removal of the trimethylsilyl groups from the nitrogen atoms in the sulfur diimide,⁷¹ suggests that potassium *tert*-butoxide would be an appropriate reagent for the formation of the anionic ligands 24 and 25, potassium salts, from the neutral ligand Ph₂P(S)N(SiMe₃)₂ (6) and Ph₂P(Se)N(SiMe₃)₂.



CHAPTER TWO

Preparation, X-ray Structure and Some Reactions of

the Ph₂P(Se)NSiMe₃ Anion

2.1 Introduction

Initially, the scope of this research concentrated on the selenium-containing ligand Ph₂P(Se)N(SiMe₃)₂. This ligand has three NMR active nuclei (³¹P, ⁷⁷Se and ¹H), and thus was chosen as it should provide a great deal of structural information. Many selenium-containing compounds are unstable, and are thus difficult to isolate and characterize. Examples include the diselenophosphinates and the selenothiophosphinates discussed in Section 1.3.1. With the replacement of the sulfur atoms in dithiophosphinates by selenium atoms, the resulting compounds decompose rapidly and little work has been published concerning their characterization.

(2.1) $\frac{Ph_2PN(SiMe_3)_2 + 1/8 Se_8}{65 °C / 36 hours} Ph_2P(Se)N(SiMe_3)_2}{Ph_2P(Se)N(SiMe_3)_2}$

N,N'-Bis(trimethylsilyl)aminodiphenylphosphine selenide, Ph₂P(Se)N(SiMe₃)₂, was synthesized by the method used by Roesky *et al.* for the sulfur analogue⁶⁸ and adapted by J. Michaud (Equation 2.1).⁷³ The NMR spectroscopic characterization of the product is summarized in Table 2.1. The coupling constant ${}^{1}J({}^{31}P-{}^{77}Se) = 765$ Hz is characteristic of a double bond [cf. Ph₃P=Se, ${}^{1}J({}^{31}P-{}^{77}Se) = 736$ Hz¹²]. This is supported by the value of v(P=Se) = 567 cm⁻¹ in the infrared spectrum [cf. Ph₃P=Se, v(P-Se) = 560 cm⁻¹ 74]. The chemical shift of -153 ppm reported for the doublet in the ${}^{77}Se$ NMR spectrum is

approximate (Table 2.1). The data were collected in the wrong chemical shift window (+1660 to +350 ppm). With comparison to literature values [Me₃PSe, δ (⁷⁷Se) = -235 ppm⁷⁵; (MeO)₃PSe, $\delta(^{77}Se) = -396 \text{ ppm}^{75}$; R₃PSe, $\delta(^{77}Se) = -200 \text{ to } -400 \text{ ppm}^{17}$], it was evident that the peak was folded back to give a chemical shift of +854 ppm.

	Chemical Shift (ppm)	Integration	Assignment
' <u>H NMR</u> *			
	7.97 (m)	4.00	-Ph
	7.43 (m)	6.14	-Ph
	0.18 (s)	19.88	-SiMe ₃
³¹ P NMR ^b			
•	56.2 (s)	$^{1}J(^{31}P-^{77}Se)=765$ H	Z
⁷⁷ Se NMR ^c			
	-153 (doublet)	¹ J(³¹ P- ⁷⁷ Se)=765 H	Z

^b THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert. ^c THF / D₂O insert. External reference SeO₂ / D₂O insert.



As discussed in Chapter One, the goal of this project was to synthesize both the monoanion (26) and the dianion (27) of the $Ph_2P(Se)N(SiMe_3)_2$ ligand. This may be achieved by the removal of the trimethylsilyl groups from the nitrogen. Herberhold et $al.^{72}$ have demonstrated the removal of the trimethylsilyl groups from bis(trimethylsilyl)sulfur diimide to give the potassium salt of the SN²⁻ dianion, utilizing potassium *tert*-butoxide as the nucleophile (Equation 2.2).



In this work, a similar approach has been adopted to generate the monoanion, but this method was not successful for the preparation of the dianion. Some reactions of 26 with electrophiles have also been investigated in order to determine the outcome of (a) oxidation and (b) electrophilic substitution reactions.

2.2 The Preparation and Characterization of the Ph₂P(Se)NSiMe₃⁻ Anion
2.2.1 Preparation and Spectroscopic Characterization of K[Ph₂P(Se)NSiMe₃].THF

(2.3)
$$Ph_2P(Se)N(SiMe_3)_2 + KOt Bu \frac{i)THF / -78^{\circ}C}{ii) Room temp} Ph_2P(-K^+.THF NSiMe_3)$$

It was discovered that it was unnecessary to reflux the reaction mixture in order to synthesize the monoanion, $Ph_2P(Se)NSiMe_3$. The reaction occurs easily at room temperature (Equation 2.3). A white crystalline product, identified as $K[Ph_2P(Se)NSiMe_3]$. THF (28) was isolated from a mixture of THF / hexanes. The NMR spectroscopic data are summarized in Table 2.2. A decrease in the coupling constant ${}^{1}J({}^{31}P{}^{-77}Se)$ from 765 Hz in the neutral ligand to 604 Hz for the monoanion indicates that there has been a decrease in the P-Se bond order. The coupling constant for single P-Se bonds ranges from 250 Hz (Me₂PSeMe) to 341 Hz (Me₂P(S)-SeMe).¹⁷

	Chemical	Integration	Assignment
	Shift (ppm)	mogration	<u>11001211110111</u>
H NMR ^a			
	7.99 (m)		-Ph
	7.19 (m)	10.00	-Ph
	3.54 (q)	3.39	THF
	1.45 (q)	3.47	THF
	0.06 (s)	10.58	-SiMe ₃
<u>³¹₽ NMR</u> ^b			
	22.0 (s)	$^{1}J(^{31}P-^{77}Se)=604$	Hz
<u>⁷⁷Se NMR</u> °			
	-81	$^{1}J(^{31}P-^{77}Se)=604$	Hz
	(doublet)		

^a Internal reference CDCl₃.

^b THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert.

^c THF / D₂O insert. External reference PhSeSePh / D₂O insert.

The ¹H NMR spectrum showed that one molar equivalent of THF is contained in the crystalline product. This is in agreement with the results of the elemental analysis (See Table 2.3). The infrared spectrum of **28** (Figure 2.1) confirms the decrease in the bond order of the P-Se bond. The value of v(P-Se) is shifted to 546 cm⁻¹ from 567 cm⁻¹



for $Ph_2P(Se)N(SiMe_3)_2$. Removal of one trimethylsilyl group is verified by both the ¹H NMR spectrum and the absence of v(Si-N-Si) at 918 cm⁻¹ ⁷⁶ in the infrared spectrum. Bands at 1211 cm⁻¹ and 856 cm⁻¹ show the presence of one trimethylsilyl group.⁷⁷

Table 2.3	Elemental Analysis for K	[Ph ₂ P(Se)NSiMe	3].THF (28)
	Calculated (%)	Experin	nental(%)
Carbon	49.34	48.69	48.16
Hydrogen	5.88	5.87	5.69
Nitrogen	3.03	3.14	3.07
-			

2.2.2 Crystal Structure of K[Ph₂P(Se)NSiMe₃].THF (28)

The structure of the salt in **28** was determined by X-ray crystallography by Dr. M. Parvez. The crystallographic data are summarized in Table 2.4 and selected bond lengths and bond angles are given in Table 2.5. Figure 2.2 is an ORTEP drawing of the structure. Full details of the X-ray structure are available from Dr. M. Parvez.

The structure is step-shaped and resembles that found for a number of alkali metal sulfinimidamides, M[RNS(R")NR]. A recent study of several such derivatives by Stalke *et al.*⁷⁸ revealed that this type of coordination occurs for sulfinimidamides stabilized by the alkali metals sodium, potassium, rubidium and cesium (M = Na, K, Rb, Cs). The structure (**29**) consists of two four-membered MNSN rings fused to a central M_2N_2 ring with the two MNSN units located above and below the central ring unit. The stability of **29** is attributed to the alkali metal being four-coordinate in all cases. A molecule of

<u>Table 2.4 C</u>	Cell Parameters and Crystallo or K[Ph ₂ P(Se)NSiMe ₃].THF	ographic Data (28)
MW = 462.55	C ₁₉ H ₂₇ OPNSeSiK	
monoclinic, sr	bace group P 2 ₁ /c	$beta = 91.34(2)^{\circ}$
a = 9.643(2) Å	b = 16.500(2) Å	c = 29.366(7) Å
V = 4671(1) Å ³	T = -123 °C	$D_{calc} = 1.315 \text{ g cm}^{-3}$
crystal dimensions =	0.30 x 0.43 x 0.50 mm	Z = 8
R = 0.0764	$R_{w} = 0.0811$	

for H	K[Ph ₂ P(Se)NS	SiMe ₃].THF (28)	
P(1)-Se(1)	218.1(5)	N(1)-P(1)-Se(1)	114.3(5)
P(1)-N(1)	155.6(13)	N(2)-P(2)-Se(2)	114.4(5)
N(1)-K(1)	278.9(14)	P(1)-Se(1)-K(2)	88.0(1)
Se(1)-K(1)	336.6(5)	P(2)-Se(2)-K(1)	85.7(1)
Se(1)-K(2)	341.6(4)	N(1)-K(1)-Se(2)	107.6(3)
P(2)-Se(2)	218.0(5)	N(2)-K(2)-Se(1)	97.0(3)
P(2)-N(2)	159.4(12)	Se(1)-K(2)-Se(2)	101.9(1)
N(2)-K(2)	277.0(12)	Se(1)-K(1)-Se(2)	102.4(1)
Se(2)-K(2)	338.9(4)	K(1)-Se(1)-K(2)	77.9(1)
Se(2)-K(1)	341.8(4)	K(1)-Se(2)-K(2)	77.5(1)
Ph(C1-C6)-K(2)	312.8	P(1)-N(1)-Si(1)	137.7(9)
Ph(C20-C25)-K(1)	334.1	P(2)-N(2)-Si(2)	138.8(8)

THF (not depicted in 29) occupies the fourth site. However, with this arrangement, there is a gap in the coordination sphere of the alkali metal. The π -electron system of the

phenyl substituent on the sulfur atom in sulfinimidamides (R" = Ph) interacts with the alkali metal to complete the coordination sphere.⁷⁸ The distance between the centre of the phenyl ring and the potassium metal is 369.8 pm in the crystal structure of **29** (M = K, R = SiMe₃, R" = Ph).⁷⁸ The phenyl group on the phosphorus (P(1)) in **28** is tilted towards the potassium atom (K(2)) showing a similar interaction with the π -system is occurring (Figure 2.2). Distances of 312.8 pm and 334.1 pm from the centre of the phenyl ring to the potassium metal confirm this interaction. The sulfinimidamide structures investigated had *tert*-butyl groups on the nitrogen (R = *t*-Bu), but replacement of these by trimethylsilyl groups (R = SiMe₃) had no significant effects.⁷⁸



In the potassium salt of the sulfinimidamide (29) (M = K, R = SiMe₃, R" = Ph) the shortest nitrogen-potassium distance occurs when the nitrogen is only coordinated to one alkali metal $[d(N_1-K_1) = 275.2(3) \text{ pm}]$.⁷⁸ In the structure of K[Ph₂P(Se)NSiMe₃].THF (28), comparable distances of 278.9(14) and 277.0(12) pm are observed for N(1)-K(1) and N(2)-K(2), respectively. The sides of the K₂N₂ unit in the sulfinimidamide (29) (M = K, R = SiMe₃; R" = Ph) are nearly equal $[d(N_2-K_1) = 288.0(2) \text{ pm} \text{ and } d(N_2'-K_1) = 283.4(3) \text{ pm}]^{78}$. This is also observed in the monoanion 28 with the distances K(1)-Se(1) and



Figure 2.2- ORTEP Diagram of K[Ph₂P(Se)NSiMe₃].THF (28)

K(1)-Se(2) being 336.6(5) pm and 341.8(4) pm, respectively. The M_1 - N_2 distances are directly dependent on the metallic radii of the alkali metal for the series M[RNS(R")NR] where M = Na, K, Rb and Cs.⁷⁸

Many of the ligand systems examined in the literature (cf. Chapter One) were isolated as lithium salts, however, only the bis(trimethylsilylimido)phosphinate ligands formed the step-shaped structure similar to that of **28** (M = Rb, Cs).⁵⁴ Unlike the series involving the alkali metals Na, K, Rb and Cs, it has been noted by Stalke *et al.*⁷⁸ that only systems with trimethylsilyl groups on the nitrogen of sulfinimidamides (R = SiMe₃) could be isolated as step-shaped structures when lithium was the coordinating atom (M = Li). For the lithium derivatives, replacement of these trimethylsilyl groups (R = SiMe₃) with *tert*-butyl groups (R = *t*-Bu) prevented the step-shaped structure from being formed. This is attributed to the differing electronic properties of these substituents since they are considered to be similar in steric bulkiness.⁷⁸

The specific details of the structure $K[Ph_2P(Se)NSiMe_3]$.THF (28) include the phosphorus-selenium distances of 218.1(5) pm and 218.0(5) pm correspond approximately to a bond order of 1.4. This is in comparison to a single P-Se bond distance of 223.8 pm¹⁹ and a double P-Se bond of 210.5 pm.²⁰ The phosphorus-nitrogen bond lengths of 155.6(13) and 159.4(12) pm are at the outer limits of a P-N double bond (157-160 pm)²³ with one in the lower range of P-N bond lengths in the iminophosphoranyl anions (159-166 pm).²³ The single phosphorus-nitrogen bond is typically 178 pm.²⁴ These bond lengths indicate that the negative charge is not delocalized throughout the N-P-Se unit (26) but concentrates mainly on the selenium atom, as depicted in 26a, in preference to

the nitrogen atom (26b). As a result, the soft selenium atom could be the site of electrophilic attack in reactions of the monoanion.



The angle N-P-Se is 114.3(5)°, the largest bite angle at phosphorus observed in the literature for related ligand systems which, however, were only coordinated to a single metal atom through chelation (See Chapter One). Compared to the value of 110.4(1)° observed for the N-S-N angle of the potassium salt of the sulfinimidamide **29** ($\mathbf{R} = \mathbf{SiMe}_3$, $\mathbf{R}'' = \mathbf{Ph}$), the larger angle of 114.3(5)° can be attributed to the step-shaped structure rather than the monomeric units with each ligand coordinated to only one metal atom. Similar N-P-N angles of 113.7(2)° were observed in the dimeric, step-shaped structures of bis(trimethylsilylimido)phosphinate ligands with the alkali metals rubidium and cesium.⁵⁴ The P-N-Si angles of 137.7(9)° and 138.8(8)° are larger than expected for sp² hybridization of the nitrogen atom, indicating that some sp character is involved in bonding to phosphorus and silicon.

2.3 Attempted Synthesis of the Dianion Ph₂P(Se)N²⁻

With the isolation and structural characterization of the monoanion as its potassium salt K[Ph₂P(Se)NSiMe₃].THF, the synthesis of the dianion Ph₂P(Se)N²⁻ (27) was important for the comparison of structural data (charge delocalization) and reactivity.

Delocalization of a single negative charge may indicate that the dianion would have a negative charge on each coordinating site so that both the hard and soft centres will be available for further reactions with electrophilic substrates.

(2.4)
$$Ph_2P(Se)N(SiMe_3)_2 + 2 \text{ KOt Bu}$$

ii) Room temp $Ph_2P(Se)N(SiMe_3)_2 + 2 \text{ KOt Bu}$
ii) Room temp $Ph_2P(Se)N(SiMe_3)_2 + 2 \text{ KOt Bu}$

Numerous attempts to synthesize this dianion were made. The first involved following the same procedure used for the monoanion, 28, but with two equivalents of KOtBu (Equation 2.4). The reaction, however, ceased with the production of the monoanion, as monitored by ³¹P NMR (21.5 ppm), and the excess of KOtBu caused the solution to become cloudy. Heating the reaction mixture at reflux, in THF, for 1.5 hours also produced only the monoanion (δ (³¹P) = 21.8 ppm).

The third attempt employed the higher boiling solvent 1,2-dimethoxyethane (1,2-DME) (b.p. 98 °C vs. 68 °C for THF) following the procedure of Herberhold *et al.* for the preparation of SN_2^{2} from Me₃SiNSNSiMe₃.⁷² After the slurry of KOtBu was heated at reflux for 0.5 hours, Ph₂P(Se)N(SiMe₃)₂ was added slowly and the mixture refluxed for an additional hour. Again, only a singlet at 21.3 ppm attributed to Ph₂P(Se)NSiMe₃⁻⁻ was present in the ³¹P NMR spectrum.

The final attempt involved following the procedure of Herberhold *et al.* exactly.⁷² A solution of KOtBu in 1,2-DME was refluxed with the addition of $Ph_2P(Se)N(SiMe_3)_2$ controlled at a slow rate by a dropping funnel. Again, the reaction produced only the monoanion Ph₂P(Se)NSiMe₃, 26.

It should be noted that the removal of trimethylsilyl groups from Me₃SiNSNSiMe₃ involves different nitrogen atoms, whereas the corresponding reaction of $Ph_2P(Se)N(SiMe_3)_2$ occurs at the same nitrogen atom. As a result of this structural difference, the nitrogen in the monoanion 26 carries a higher negative charge than the nitrogen attached to the trimethylsilyl group in Me₃SiNSN⁻. This greater negative charge may inhibit the removal of the second trimethylsilyl group by KOtBu.

2.4 Preparation of Ph₂P(Se)NH₂ by Hydrolysis of K[Ph₂P(Se)NSiMe₃].THF

The salt K[Ph₂P(Se)NSiMe₃].THF (28) was reacted with wash ethanol to see if hydrolysis of the monoanion occurs readily, and to determine whether the second trimethylsilyl group could be removed by hydrolysis. A white product was isolated, after a reaction time of one hour, which exhibited a singlet at 48.3 ppm in the ³¹P NMR spectrum with selenium satellites, ¹J(³¹P-⁷⁷Se) = 765 Hz (Table 2.6). This is consistent with the formation of a product with a P-Se double bond [cf. 764 Hz for Ph₂P(Se)N(SiMe₃)₂].



The ¹H NMR spectrum reveals the absence of trimethylsilyl groups while integration reveals two protons attached to the nitrogen. This is consistent with the

<u>Table 2.6</u>	Nuclear Magnetic Resonan	nce Data for Ph ₂ P(S	e)NH ₂ (30)
	Chemical Shift (ppm)	Integration	Assignment
<u>¹H NMR</u> ^a			
	7.93 (m)	4.00	-Ph
	7.48 (m)	5.85	-Ph
	2.92 (s)	2.22	-NH ₂
³¹ P NMR ^b			
<u> </u>	48.3 (s)	$^{1}J(^{31}P-^{77}Se)=765$	Hz

^a Internal reference CDCl₃.

^b THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert.

formation of Ph₂P(Se)NH₂, **30**. The infrared spectrum (See Figure 2.3) confirms the identity of the hydrolysis product, **30**. Bands attributed to asymmetric and symmetric NH₂ stretching are present at 3400 cm⁻¹ and 3200 cm⁻¹ while the Me₃Si deformation bands at ca. 1200 cm⁻¹ and 850 cm⁻¹ are absent.⁷⁷ The value of 567 cm⁻¹ for v(P-Se) is consistent with a phosphorus-selenium double bond [cf. v(P-Se) = 567 cm⁻¹ for Ph₂P(Se)N(SiMe₃)₂; v(P-Se) = 560 cm⁻¹ for Ph₃P=Se⁷⁴].

Hydrolysis of the neutral ligand, $Ph_2P(Se)N(SiMe_3)_2$, was carried out with the addition of ethanol in THF at room temperature. After 29 hours of stirring, the hydrolysis product $Ph_2P(Se)NH_2$ (27) was present in the ³¹P NMR spectrum in a 1:1 ratio with the neutral ligand. The reaction was complete after a further 85 hours. Thus it appears that the monoanion is more prone to hydrolysis than the neutral compound. Care was taken to ensure that hydrolysis was prevented in further reactions with the monoanion.



Figure 2,3-Infrared Spectrum of Ph₂P(Se)NH₂ (30)

2.5 Reactions of K[Ph₂P(Se)NSiMe₃].THF

2.5.1 Reaction of Ph₂P(Se)NSiMe₃ and Ph₂P(S)Cl



Previous investigations have led to phosphazene metallocycles $(31)^{8,79}$ and chelate rings (32) with an azadiphosphinate group attached to a metal centre by oxygen or sulfur atoms.⁴⁸ With compounds of the type 32, most work has been done with transition metals and, to a lesser extent, organometallic groups such as phenyltellurium (II) and diorganogold (III). Recent work by Haiduc *et al.* has resulted in the characterization of a complex of 33 coordinated to organotin groups, such as trimethyltin and dimethyltin chlorides.⁸⁰



It was postulated that the reaction of $Ph_2P(Se)NSiMe_3$ with chlorodiphenylphosphine sulfide could form the neutral compound 34. Removal of the trimethylsilyl group from the nitrogen would generate the anion 35 as a new chelating ligand for transition and main group metals. A further possibility is the addition of a chlorodiphenylphosphine sulfide to 34 or 35 to provide the tripod ligand 36.



(2.5) Ph₂P
$$\begin{pmatrix} -K^+ + Ph_2P(S)Cl & i \end{pmatrix}$$
 THF / reflux 1hr
NSiMe₃ $H_4P_2(S)SeNSiMe_3 + KCl$

The attempted preparation of 34 was carried out according to Equation 2.5, after discovering that reflux conditions were required to initiate the reaction. After removal of the potassium chloride, a ³¹P NMR spectrum (Figure 2.4) revealed that the monoanion and Ph₂P(S)Cl had been consumed. The major product gives rise to two mutually coupled doublets, both of which exhibit ⁷⁷Se satellites (see Table 2.8). The ²J(³¹P-³¹P) coupling of 13.5 Hz observed in the ³¹P NMR spectrum is similar to that reported for R₂P(S)-S-P(S)R₂ [²J(³¹P-³¹P)=15 Hz] (R = Me, i-Pr, t-Bu).⁸¹

The ⁷⁷Se NMR spectrum of the product consists of a doublet of doublets with ${}^{1}J({}^{31}P{}^{-77}Se)$ values consistent with those observed in the ${}^{31}P$ NMR spectrum (Figure 2.5 and Table 2.8). The observation of two approximately equal ${}^{31}P{}^{-77}Se$ coupling constants for the product is inconsistent with structure 34. Furthermore, the values of 355 and 373 Hz for this interaction are indicative of phosphorus-selenium single bonds. Hence, the

<u>Table 2.7</u>	Nuclear Magnetic Resonance	the Data for $Ph_4P_2(S)$	<u>SeNSiMe, (37)</u>
³¹ P NMR ^a	Chemical Shift (ppm)	$^{2}J(^{31}P-^{31}P)$	$^{1}J(^{31}P-^{77}Se)$
P _A .	50.2 (doublet)	13.5 Hz	373 Hz
P_{B}	3.3 (doublet)	13.5 Hz	355 Hz
⁷⁷ Se NMR ^b			
	411.9 (dd)	${}^{1}J({}^{31}P_{A}-{}^{77}Se)=373$	Hz
		${}^{1}J({}^{31}P_{B}-{}^{77}Se)=355$	Hz
	incont Enternal reference 9		

^a THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert. ^b THF / D₂O insert. External reference SeO₂ / D₂O insert.

structure 37 is proposed for the product of equation 2.4. This would account for the two significantly different phosphorus environments, assigned tentatively as P_A and P_B . This assignment is based on the ³¹P NMR chemical shifts of Ph₃PS (43 ppm, in CDCl₃)⁸² and Ph₃PNPh (0 ppm, in $C_4H_8O_2$).⁸³ Compounds of the type R_3PNR' have a range of ³¹P NMR chemical shifts from +30 ppm to -15 ppm, dependent on the substituents.⁸⁴

Unfortunately, the reaction mixture always contained other products, and various solvent combinations failed to yield a pure product. The oily nature of the product



37





Figure 2.5- ⁷⁷Se NMR Spectrum of Ph₄P₂(S)SeNSiMe₃ (37)

isolated upon the removal of the solvent is attributed to the trimethylsilyl group still attached to the nitrogen. Removal of this group could lead to a new anionic ligand **38** with both hard and soft coordination sites. However, the use of one molar equivalent of KOtBu proved unsuccessful in removing the trimethylsilyl group to form **38**. Monitoring the reaction by ³¹P and ⁷⁷Se NMR revealed a mixture of products formed at -78°C. Removal of the solvent resulted in an oily residue.

2.5.2 Reaction of Ph₂P(Se)NSiMe₃⁻ and I₂

In view of the outcome of the reaction of $Ph_2P(Se)NSiMe_3$ with $Ph_2P(S)Cl$, it was postulated that the oxidation of the monoanion, e.g. with iodine, may form a neutral compound with a selenium-selenium single bond (39).



The reaction occurred under mild conditions (Equation 2.6) and potassium iodide precipitated out upon warming to room temperature. Only one phosphorus resonance at 0.4 ppm was present in the ³¹P NMR spectrum of the product. This resonance exhibited ⁷⁷Se satellites with ¹J(³¹P-⁷⁷Se) = 354 Hz, consistent with phosphorus-selenium single bonds, and ²J(³¹P-⁷⁷Se) = 13.5 Hz (Figure 2.6 and Table 2.9). The peak at 1.2 ppm in the





Figure 2.7- ⁷⁷Se NMR Spectrum of Me₃SiNPh₂PSeSePPh₂NSiMe₃ (39)

³¹P NMR spectrum is an unidentified impurity. The natural abundance of ⁷⁷Se is only 7.7% so that the ⁷⁷Se NMR spectrum of **39** is expected to be that of an AXX' spin system (where A represents ⁷⁷Se in the most abundant isotopomer, and X and X' are the magnetically inequivalent phosphorus atoms). As illustrated in Figure 2.7, the ⁷⁷Se NMR spectrum consists of a doublet of doublets with coupling constants of 354 and 15.7 Hz consistent with one-bond and two-bond P-Se couplings, respectively, as expected for **39**. The apparent first order pattern of this spectrum suggests that the coupling between the magnetically inequivalent phosphorus nuclei is approximately zero. The differences in the values of ²J(³¹P-⁷⁷Se) observed in the ³¹P and ⁷⁷Se NMR spectra can be attributed to the poorer resolution of the ⁷⁷Se NMR spectrum (2 Hz / point).

<u>T</u>	able 2.8 Nuclear Mag Me ₃ SiNPh ₂ PSeS	anetic Resonance Data for SePPh ₂ NSiMe ₃ (39)	
	Chemical Shift (ppm	2	
³¹ P NMR ^a			
	0.37 (s)	${}^{1}J({}^{31}P-{}^{77}Se) = 354 \text{ Hz}$	
	·	${}^{2}J({}^{31}P-{}^{77}Se) = 13.5 \text{ Hz}$	
⁷⁷ Se NMR ^b			
	363 (dd)	${}^{1}J({}^{31}P_{A}-{}^{77}Se) = 354 \text{ Hz}$	
		${}^{2}J({}^{31}P_{B}-{}^{77}Se) = 15.7 \text{ Hz}$	
* THF / D ₂ O inset	rt. External reference	85% H ₂ PO ₄ / D ₂ O insert.	

^b THF / D₂O insert. External reference PhSeSePh / CDCl₃ insert.

The product **39** was isolated as an orange oil. Various attempts to obtain a pure solid product have been unsuccessful with the solvent mixtures used. This could be due

to the presence of the trimethylsilyl groups on each of the nitrogen atoms. The formation of a solid product may be possible with the conversion of the NSiMe₃ groups to NH groups by hydrolysis or upon conversion to the corresponding dianion by treatment with KOtBu.

2.5.3 Preparation of Ph₂P(Se)N(H)SiMe₃ from Me₃SiNPPh₂SeSePPh₂NSiMe₃ (39)

During repeated attempts to isolate **39** as a pure solid, various solvents were used. An orange crystalline solid was isolated from hot hexanes upon cooling. The ³¹P NMR spectrum contained a singlet at 47.2 ppm with selenium satellites, ${}^{1}J({}^{31}P-{}^{77}Se) = 762$ Hz (Table 2.9). This was initially assumed to be the hydrolysis product Ph₂P(Se)NH₂ (**30**) (See Section 2.4) since the chemical shift and coupling constants were similar [cf. Ph₂P(Se)NH₂, $\delta({}^{31}P) = 48.3$ ppm, ${}^{1}J({}^{31}P-{}^{77}Se) = 765$ Hz]. However, the ¹H NMR spectrum revealed the presence of trimethylsilyl group, as well as a proton attached to the nitrogen atom indicating the hydrolysis product **40** was formed. Elemental analysis of the solid product also confirm the compound to be **40** (Table 2.10).



40

The infrared spectrum (Figure 2.8) confirmed the presence of the trimethylsilyl groups with Me₃Si deformation bands at 1250 cm⁻¹ and 851 cm⁻¹. A N-H stretching band is present at 3170 cm⁻¹. The value of 540 cm⁻¹ for v(P-Se) is somewhat lower than



	Chemical Shift (ppm)	Integration	Assignment
<u>¹H NMR</u> ^a			
	7.83 (m)	4.10	-Ph
	7.47 (m)	5.87	-Ph
	2.41 (s)	0.77	-NH
	0.20 (s)	9.59	-SiMe ₃
³¹ P NMR ^b			
	47.2 (s)	$^{1}J(^{31}P-^{77}Se)=762$ Hz	2

Table 2.9 Nuclear Magnetic Resonance Data for Ph₂P(Se)N(H)SiMe₂ (40)

^a Internal reference CDCl₃.
^b THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert.

expected for a phosphorus-selenium double bond, as indicated by the value of the coupling constant ${}^{1}J({}^{31}P-{}^{77}Se)$ [cf. $\upsilon(P-Se) = 567 \text{ cm}^{-1}$ for $Ph_2P(Se)N(SiMe_3)_2$ and Ph₂P(Se)NH₂]. The orange colour of the crystalline product is probably due to trace amounts of excess iodine.

-	Calculated (%)	Experin	mental (%)
Carbon	51.13	51.37	51.35
Hydrogen	5.72	5.59	5.64
Nitrogen	3.98	4.04	4.05

2.5.4 Attempted Removal of SiMe₃ groups from Me₃SiNPPh₂SeSePPh₂NSiMe₃ (39) with KOtBu

Since the oily nature of $Me_3SiNPPh_2SeSePPh_2NSiMe_3$ (39) could be attributed to the presence of the trimethylsilyl groups, it was decided to attempt to remove them with KOtBu in order to isolate a pure solid potassium salt of 39 for characterization and confirmation of the presence of the selenium-selenium bond.



<u>Table 2.11</u> Nuclear Magnetic Resonance Data for the <u>Product from Me₃SiNPh₂PSeSePPhNSiMe₃ (39) and 2 KOtBu</u>

<u>(</u>	Chemical Shift (ppm)		
³¹ P NMR ^a			
	21.9 (s)	${}^{1}J({}^{31}P-{}^{77}Se) = 603 \text{ Hz}$	
⁷⁷ Se NMR ^b			
	-81 (d)	${}^{1}J({}^{31}P_{A}-{}^{77}Se) = 604 \text{ Hz}$	
* THF / D ₂ O insert.	External reference 8	5% H_3PO_4 / D_2O insert.	

^b THF / D₂O insert. External reference PhSeSePh / CDCl₃ insert.

Compound **39** was prepared according to Equation 2.6 and then two equivalents of KOtBu were added to the reaction mixture (Equation 2.7). At room temperature a single peak with selenium satellites was present in the ³¹P NMR spectrum at 21.9 ppm

(Table 2.11). From these data, it appeared that the selenium-selenium bond had been cleaved, resulting in reformation of the potassium salt $K[Ph_2P(Se)NSiMe_3]$.THF (28). This was confirmed by the ⁷⁷Se NMR spectrum as seen in Table 2.10. The product 28 was isolated as a white solid by using a mixture of THF and hexanes.

2.6 Conclusions

With the use of potassium *tert*-butoxide as a nucleophile, the monoanion $Ph_2P(Se)NSiMe_3$ (26) was isolated as the potassium salt 28 which was fully characterized. This could prove to be a vital "building block" in the synthesis of novel heterocyclic or coordination compounds. The compound K[Ph_2P(Se)NSiMe_3].THF (28) forms a dimeric, step-shaped structure in which each potassium atom is coordinated to a nitrogen and selenium atom of one anion, a selenium atom of the second anion, and a THF molecule. Repeated attempts to synthesize the dianion $Ph_2P(Se)N^{2-}$ (27) were unsuccessful, even under vigorous reaction conditions. The trimethylsilyl group in the monoanion could only be removed by hydrolysis with ethanol, forming $Ph_2P(Se)NH_2$.

In the reactions of the monoanion 26 with the electrophilic reagents chlorodiphenylphosphine sulfide and iodine, the preferred site of reaction appears to be the soft selenium centre. This is consistent with the conclusion, from structural data, that the negative charge is mainly localized on the selenium atom (26a). In contrast, the reactions of the neutral ligand N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide with TiCl₄ or SnCl₄ occur at the nitrogen atom⁶⁸ or at both the nitrogen and sulfur atoms,⁷⁰ respectively (see Section 1.4.2). This difference in behaviour may be due to the
relative softness of the electrophilic reagents $Ph_2P(S)Cl$ and I_2 compared to $TiCl_4$ or $SnCl_4$.

Difficulties were encountered in isolating pure solid products from the reactions of the monoanion with electrophiles. The presence of the NMR active nucleus ⁷⁷Se (7.7%, I=1/2) provided vital information, through its coupling to the ³¹P nuclei, in determining the plausible structures of the compounds synthesized. The use of potassium *tert*-butoxide to remove the trimethylsilyl groups in order to isolate a solid product proved unsuccessful in the case of Me₃SiNPh₂PSePPh₂S (**37**). With Me₃SiNPh₂PSeSePPh₂NSiMe₃ (**39**) potassium *tert*-butoxide reproduced the potassium salt of the monoanion, K[Ph₂P(Se)NSiMe₃].THF (**28**), presumably as a result of cleavage of the seleniumselenium bond. The hydrolysis product Ph₂P(Se)N(H)SiMe₃ (**40**) was also isolated from a solution containing Me₃SiNPh₂PSeSePPh₂NSiMe₃ (**39**).

2.7 Experimental

2.7.1 General

Due to the unknown reactivity of the compounds synthesized, all distillations and reactions were carried out under an inert atmosphere of nitrogen gas. This gas was dried by passing through a column of phosphorus pentoxide and Sicapent (E. Merck Darmstedt), a commercial drying agent of phosphorus pentoxide and a moisture indicator.

Manipulations of solids, both reagents and products, were carried out under an atmosphere of nitrogen gas, either under a cone of flowing gas or in a Vacuum Atmospheres Corporation glove box. All solutions were transferred via syringes or transfer needles, flushed with an inert gas of nitrogen or argon.

2.7.2 Instrumentation

For all nuclear magnetic resonance (NMR) spectra, three types of spectrometer were used to obtain the data. All proton (¹H) NMR spectra were carried out on a Bruker ACE 200 spectrometer. A Varian XL200 spectrometer and a Bruker AM400 spectrometer were used to obtain ³¹P NMR spectra. Both utilized an external reference of an 85% solution of H_3PO_4 with D_2O for the lock. ⁷⁷Se NMR spectra were obtained on the Bruker AM400 spectrometer with an external reference of either SeO₂ / D_2O (+1302.6 ppm relative to MeSeMe, at 0 ppm) or PhSeSePh / CDCl₃ (+461 ppm relative to MeSeMe, at 0 ppm).

Infrared spectra were obtained as Nujol mulls on KBr disks with a Mattson 4030 FT-IR spectrometer. Crystal structures were determined from data collected on a Rigaku AFC6S diffractometer, at low temperatures. Computer programs for data processing were part of TEXSAN installed on a Silicon Graphics Personal Iris 4D/35 computer.⁸⁵ The structure was solved and refined using the program SHELX.⁸⁶ It was plotted using ORTEP.⁸⁷ All chemical analyses were carried out by the Analytical Services division of the Department of Chemistry, University of Calgary.

2.7.3 Solvents

All solvents used for reactions and crystallizations were of reagent grade and refluxed over the appropriate drying agent, under an inert atmosphere of nitrogen or argon

gas. Solvents were collected after they had refluxed for a number of hours. The solvents (and drying agents) used include: acetonitrile (distilled in series from calcium hydride, phosphorus pentoxide then calcium hydride); 1,2-dimethoxyethane (1,2-DME) (sodium wire / benzophenone); dichloromethane (CH_2Cl_2) (first distilled over phosphorus pentoxide then calcium hydride); ether (sodium wire / benzophenone); hexanes (potassium metal / benzophenone); pentane (sodium wire); tetrahydrofuran (THF) (sodium wire / benzophenone) and toluene (sodium wire / benzophenone).

2.7.4 Reagents

The starting materials chlorodiphenylphosphine, hexamethyldisilazane, nbutyllithium and elemental selenium were obtained from Aldrich and used as received. Solid iodine was obtained from BDH. Celite 545 and sea sand were obtained from Fisher Scientific and dried in the oven (110°C) prior to use. Potassium tert-butoxide (KOtBu) is also available from Aldrich but needed to be purified by sublimation according to Fieser and Fieser⁸⁸ (oil bath 180-190 °C, 0.075 torr). The purity of the compound was confirmed by an infrared spectrum.

The synthesis of $Ph_2PN(SiMe_3)_2$ was based on Wilburn's method for $Me_2PN(SiMe_3)_2^{89}$ as adapted by Michaud (Equation 2.8).⁷³ After a distillation a solid product was obtained, at room temperature, in a yield of 64.3%. Purity was confirmed by the ³¹P NMR spectrum which showed a singlet at 51.5 ppm (in ether) [cf. lit $\delta(^{31}P) = 50.2$ ppm (in hexanes)⁷³].

The synthesis of the neutral ligand Ph₂P(Se)N(SiMe₃)₂ was based on the method

$$(SiMe_3)_2NH \xrightarrow{n-BuLi}_{Hexanes / 65 °C} Li[N(SiMe_3)_2] \xrightarrow{Ph_2PCl}_{Hexanes / 0°C} Ph_2PN(SiMe_3)_2$$

used by Roesky *et al.* for the sulfur analogue⁶⁸ and adapted by Michaud (Equation 2.1).⁷³ A solid product was obtained from a minimum volume of toluene in the freezer (-13 °C) in a yield of 64.8%. The compound exhibits a singlet at 56.2 ppm in the ³¹P NMR spectrum with selenium satellites [¹J(³¹P-⁷⁷Se) = 765 Hz]. The spectroscopic characterization is discussed in Section 2.1.

Chlorodiphenylphosphine sulfide was synthesized by the oxidation of chlorodiphenylphosphine with elemental sulfur in an inert solvent.⁹⁰ A pure, clear and colourless liquid was obtained after a distillation, with the ³¹P NMR spectrum showing a singlet at 80.5 ppm (in THF) (cf. lit δ (³¹P) = 79.9 ppm (in toluene)⁹⁰)

2.7.5 Synthesis of K[Ph₂P(Se)NSiMe₃].THF (28)

A clear colourless solution of $Ph_2P(Se)N(SiMe_3)_2$ (1.582 g, 3.726 mmol) in THF (25 ml) was added dropwise, over 10 minutes, to a slurry of KOtBu (0.412 g, 3.672 mmol) in THF (25 ml). The addition was done at -78 °C (dry ice / acetone bath) and the reaction mixture was maintained at this temperature for a further 15 minutes. After the reaction mixture had warmed up to room temperature (25 °C), a singlet was observed in the ³¹P NMR spectrum at 21.9 ppm. The clear pale yellow solution was reduced in volume (5 ml), layered with hexanes (45 ml) and placed in the freezer (-13 °C) to give white crystals of K[Ph_2P(Se)NSiMe_3].THF (1.560 g, 91.9 % yield). The details of the

spectroscopic characterization and analytical data for K[Ph₂P(Se)NSiMe₃].THF are given in Section 2.1.

2.7.6 Attempted Synthesis of the Dianion Ph₂P(Se)N²⁻ (27)

A solution of KOtBu (0.306 g, 2.73 mmol) was left to stir in 1,2-DME (125 ml) at room temperature for 20 hours. The solution did not become clear and so it was heated to reflux for 1 hour with an oil bath (105 °C). A clear colourless solution of $Ph_2P(Se)N(SiMe_3)_2$ (0.589 g, 1.39 mmol) in 1,2-DME (30 ml) was then added dropwise from a dropping funnel. The rate of addition was approximately 1 drop / sec. After a further three hours from the start of the addition, the solution was cooled to room temperature over 45 minutes and then the volume reduced to 20 ml. The reaction mixture was initially clear and colourless but, with the reduction in volume, the solution became cloudier and pale yellow in colour.

A ³¹P NMR spectrum of the solution revealed a singlet at 21.9 ppm due to the monoanion $Ph_2P(Se)N(SiMe_3)$. With time, the excess KOtBu settled out and a clear solution remained.

2.7.7 Synthesis of Ph₂P(Se)NH₂ (30) from K[Ph₂P(Se)NSiMe₃].THF (28)

A solution of $Ph_2P(Se)N(SiMe_3)_2$ (0.390 g, 0.92 mmol) in THF (15 ml) was added dropwise to a slurry of KOtBu (0.102 g, 0.91 mmol) in THF (25 ml). Both solutions were at -78 °C (dry ice / acetone bath) and, after the addition, the reaction mixture remained at this temperature for a further 45 minutes. Wash ethanol (20 ml) was then added to the reaction mixture over a 10 minute period and then the flask was left to warm up to room temperature. A ³¹P NMR spectrum of the solution revealed a singlet at 48.1 ppm.

Table 2.12 Elemental Analysis for Ph ₂ P(Se)NH ₂ (30)				
	Calculated (%)	Experin	nental (%)	
Carbon	51.45	49.09	49.63	
Hydrogen	4.32	3.90	4.11	
Nitrogen	5.00	4.75	4.73	

A white crystalline product was isolated from the mixture of THF and hexanes (1:1.5 solvent ratio) and identified as $Ph_2P(Se)NH_2$ (0.115 g, 44.8%). Details of the spectroscopic characterization of $Ph_2P(Se)NH_2$ are given in Section 2.4. The elemental analyses are given in Table 2.12.

2.7.8 Reaction of Ph₂P(Se)NSiMe₃ and Ph₂P(S)Cl

A clear colourless solution of $K[Ph_2P(Se)NSiMe_3]$.THF (0.619 g, 1.34 mmol) in THF (20 ml) was added over 10 minutes to a clear colourless solution of $Ph_2P(S)Cl$ (0.304 g, 1.20 mmol) in THF (20 ml). The addition was done at room temperature and then the reaction mixture was refluxed for one hour. With heating, the solution had turned slightly cloudy.

After cooling to room temperature, the volume was reduced by half and then the solution was passed through a filter stick containing layers of Celite and sea sand to

remove the KCl by-product. The filter stick was then rinsed with THF (2 x 5 ml). A ³¹P NMR spectrum of the solution revealed that the reaction had not quite gone to completion and that some minor side reactions had occurred. After stirring at room temperature for a couple of hours, removal of all solvent resulted in a white cloudy oil. The major product was identified as Me₃SiNPPh₂SePPh₂S on the basis of ³¹P and ⁷⁷Se NMR data given in Section 2.5.1. Repeated attempts to isolate a pure product with the following solvent combinations have proven unsuccessful: THF / hexanes; toluene; THF / toluene; (hot) hexanes/ THF; hot hexanes; 1,2-DME / hexanes; CH₂Cl₂ /hexanes; and CH₃CN / hexanes.

2.7.9 Reaction of Ph₂P(Se)NSiMe₃⁻ and I₂

A clear orange solution of iodine (0.121 g, 0.477 mmol) in THF (25 ml) was added dropwise to a clear colourless solution of K[Ph₂P(Se)NSiMe₃].THF (0.429 g, 0.928 mmol) in THF (25 ml). The addition was done at -78 °C (dry ice / acetone bath) over 10-15 minutes. The reaction mixture remained at -78 °C for a further 15 minutes then warmed up to room temperature over 1 hour. With warming, the clear orange solution became cloudy as a white precipitate of KI was produced.

The volume of the solution was reduced by approximately two-thirds and a ^{31}P NMR spectrum showed a singlet at 0.74 ppm. The reaction mixture was then passed through a filter stick containing layers of Celite and sea sand. The filter stick was rinsed with THF (2 x 8 ml) to give a clear orange solution. After removal of all the solvent, an orange oil remained. This product was tentatively identified as

 $Me_3SiNPPh_2SeSePPh_2NSiMe_3$ on the basis of ³¹P and ⁷⁷Se NMR data given in Section 2.5.2. Repeated attempts to isolate a pure solid product with the following solvent combinations have proven unsuccessful: THF / hexanes; ether; THF / toluene; hot hexanes; toluene / pentane; pentane; CH_2Cl_2 /hexanes; and CH_3CN / hexanes.

2.7.10 Attempted Removal of SiMe₃ groups from Me₃SiNPPh₂SeSePPh₂NSiMe₃ (39) with KO*t*Bu

A clear yellowish-orange solution of Me₃SiNPPh₂SeSePPh₂NSiMe₃ (ca. 0.22 mmol) in THF (25 ml) was added dropwise, over 15 minutes, to a slurry of KOtBu (0.065 g, 0.58 mmol) in THF (20 ml) at -78 °C (dry ice / acetone bath). The flask was then rinsed with THF (10 ml) and the washings were added to the reaction mixture, which remained at -78 °C for a further 15 minutes. After warming to room temperature, a pale pink solution resulted. A ³¹P NMR spectrum of the reaction mixture revealed a singlet (21.9 ppm) with selenium satellites present. The chemical shift and the coupling constant of 604 Hz is indicative of the formation of the monoanion **26**. A white powder was isolated from a mixture of THF / hexanes at -13 °C. The spectroscopic details are summarized in Section 2.5.3.

CHAPTER THREE

Preparation, X-ray Structure and Some Reactions of

the Ph₂P(S)NSiMe₃⁻ Anion

3.1 Introduction

As evident in Chapter Two, much of this research has concentrated on the selenium-containing ligand N,N'-bis(trimethylsilyl)aminodiphenylphosphine selenide, $Ph_2P(Se)N(SiMe_3)_2$. It was of interest to study the analogous sulfur ligand N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide, $Ph_2P(S)N(SiMe_3)_2$, to see if similar chemical reactivity exists. As illustrated with phosphinate ligands (Section 1.3.1), the sulfur-containing dithiophosphinates have proven to be more stable, thus are easily isolated and characterized, than either the diselenophosphinates or the mixed chalcogen ligands (selenothiophosphinates).³¹ This trend may be present in the hybrid ligand systems, with $Ph_2P(S)N(SiMe_3)_2$ providing more stable anions and anionic derivatives.

(3.1)
$$Ph_2PN(SiMe_3)_2 + 1/8 S_8 \xrightarrow{\text{Toluene}} Ph_2P(S)N(SiMe_3)_2$$

Room Temp / 17 hrs

N,N'-Bis(trimethylsilyl)aminodiphenylphosphine sulfide, Ph₂P(S)N(SiMe₃)₂, was synthesized by the method used by Roesky *et al.*⁶⁸ and adapted by Michaud (Equation 3.1).⁷³ The NMR spectroscopic characterization is summarized in Table 3.1. The infrared spectrum confirmed the presence of a phosphorus-sulfur double bond with v(P=S) = 628 cm⁻¹ [cf. Ph₃P=S, v(P=S) = 627 cm^{-1 74}].

Table 3.1 Nuclear Magnetic Resonance Data for Ph ₂ P(S)N(SiMe ₃) ₂					
	Chemical Shift (ppm)	Integration	Assignment		
¹ H NMR ^a	,				
	7.97 (m)	3.93	-Ph		
	7.43 (m)	6.07	-Ph		
	0.17 (s)	19.79	-SiMe ₃		
³¹ P NMR ^b					
	60.3 (s)				
	60.3 (s)				

[•] Internal reference CDCl₃.

^b THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert.



As outlined in Chapter 1, the goal to synthesize both the monoanion (41) and the dianion (42) may be achieved by the removal of trimethylsilyl groups from the nitrogen of the neutral ligand. With the use of potassium *tert*-butoxide, Herberhold *et al.*⁷² removed the trimethylsilyl groups from bis(trimethylsilyl)sulfur diimide to give the potassium salt of the SN_2^{2} dianion (Equation 3.2). Similar success in the synthesis of K[Ph₂P(Se)NSiMe₃].THF (28) with potassium *tert*-butoxide indicated that this approach was plausible for the synthesis of the monoanion 41. Although the formation of the dianion Ph₂P(Se)N² proved unsuccessful (Section 2.3), it was hoped that the sulfur analogue 42 could be prepared by this method, due to the anticipated increased stability

provided by the presence of the sulfur atom.

(3.2)
$$Me_{3}Si \bigvee_{N} = S \bigvee_{N+2 \text{ KOt Bu}} \frac{1,2\text{-DME}}{84 \text{ }^{\circ}C/4 \text{ hours}} = N \xrightarrow{K^{+}} K^{+} K^{+} K^{+} + 2 t \text{ BuOSiMe}_{3}$$

The monoanion **41** was isolated and spectroscopically characterized as the potassium salt. An X-ray structural determination of the tetraphenylarsonium salt was carried out. The reactions of **41** with electrophiles were investigated in order to determine the outcome of (a) oxidation and (b)electrophilic substitution reactions. The dianion **42** could not be prepared by the method of Herberhold *et al.*⁷²

3.2 Preparation and Characterization of the Ph₂P(S)NSiMe₃⁻ Anion

3.2.1 Preparation and Spectroscopic Characterization of K[Ph₂P(S)NSiMe₃].THF

(3.3)
$$Ph_2P(S)N(SiMe_3)_2 + KOt Bu \xrightarrow{i)THF / -78^{\circ}C} Ph_2P \xrightarrow{S} K^+.THF$$

NSiMe₃
43

The monoanion $Ph_2P(S)NSiMe_3$ was synthesized as a potassium salt under the same reaction conditions required to prepare the corresponding selenium monoanion (Section 2.2.1). The reaction occurs readily at room temperature (Equation 3.3), resulting in a singlet at 32.3 ppm in the ³¹P NMR spectrum (Table 3.2). A white crystalline product (43) was isolated from a solvent mixture of THF / hexanes, but it readily

	Chemical Shift (ppm)	Integration	Assignment
¹ H NMR ^a			
	7.93 (m)	3.66	-Ph
	7.10 (m)	6.34	-Ph
	3.54 (q)	2.03	THF
	1.44 (q)	1.77	THF
	0.02 (s)	7.19	-SiMe ₃
³¹ P NMR ^b			
	32.3 (s)		,

Table 3.2 Nuclear Magnetic Resonance Data for K[Ph₂P(S)NSiMe₃] (43)

 a Internal reference CDCl_3. b THF / D_2O insert. External reference 85% H_3PO_4 / D_2O insert.

	Calculated (%)	Experim	<u>ental (%)</u> *
Carbon	52.44	52.19	52.29
Hydrogen	5.57	5.78	5.73
Nitrogen	4.08	4.58	4.59

^a Problem evident with standards varying by 0.5%.

desolvated to yield a white powder. The presence of a small amount (approximately 0.5 molar equivalent) of THF in the crystalline product was evident in the ¹H NMR spectrum (Table 3.2). Elemental analysis indicated that the loss of solvent was complete by the time of analysis (Table 3.3).



Figure 3.1- Infrared spectrum of K[Ph₂P(S)NSiMe₃] (43)

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The ¹H NMR spectrum indicates the removal of one trimethylsilyl group from $Ph_2P(S)N(SiMe_3)_2$. The infrared spectrum of **43** (Figure 3.1) supports this with the absence of v(Si-N-Si) at 918 cm⁻¹.⁷⁶ A decrease of the phosphorus-sulfur bond order is indicated by the value of v(P-S), which is shifted from 629 cm⁻¹ for $Ph_2P(S)N(SiMe_3)_2$ to 600 cm⁻¹ for **43**. Bands at 1252 and 858 cm⁻¹ show the presence of a single trimethylsilyl group attached to the nitrogen.⁷⁷

3.2.2 Crystal Structure of [Ph₄As][Ph₂P(S)NSiMe₃].0.5THF (44)

Due to the instability of the potassium salt of $Ph_2P(S)NSiMe_3^-$ (43), with respect to the loss of THF solvent, repeated attempts at data collection for the determination of an X-ray crystal structure proved unsuccessful. Replacement of the potassium cation by the bulkier tetraphenylarsonium cation (Ph_4As^+) permitted the isolation of X-ray quality crystals (44) from a mixture of THF / toluene at -13°C. From the NMR spectroscopic data summarized in Table 3.4, the ¹H NMR spectrum reveals that tetrahydrofuran is lost from the crystalline product under vacuum. This loss of solvent contributes to inaccuracies in the elemental analysis (Table 3.5). As well, low carbon percentages are common in elemental analyses of compounds containing $Ph_4As^{+.77b}$ Examination of the infrared spectrum of 44 (Figure 3.2) reveals a value of 603 cm⁻¹ for υ (P-S), indicating a decrease in bond order compared to $Ph_2P(S)N(SiMe_3)_2$ [υ (P=S) = 629 cm⁻¹] and, hence, charge delocalization over the N-P-S unit of the monoanion.

The structure of the monoanion in 44 was determined by X-ray crystallography by Dr. Parvez. The crystallographic data are summarized in Table 3.6 and selected bond

	Table 3.4 Nuclear Magnetic Resonance Data for [Ph ₄ As][Ph ₂ P(S)NSiMe ₃].nTHF(44)		
	Chemical Shift (ppm)	Integration	Assignment
¹ H NMR ^a			
	7.96-7.29 (m)	30	-Ph
	3.74 (q)	1.02	THF
	1.84 (q)	0.93	THF
	0.19-0.05 (s) ^b	7.87	-SiMe ₃
³¹ P NMR ^c			
	26.8 (s)		

^a Internal reference CDCl₃.
^b Some reaction of the compound 44 occurs with CDCl₃ resulting in minor peaks occurring in the trimethylsilyl region. ° THF / D_2O insert. External reference 85% H_3PO_4 / D_2O insert.

Table 3.5 Elemental Analysis of [Ph ₄ As][Ph ₂ P(S)NSiMe ₃]				
Calculated (%) Experimental (%)				
Carbon	68.11	66.31	65.77	
Hydrogen	5.72	5.64	5.64	
Nitrogen	2.04	2.05	2.04	

lengths and angles are given in Table 3.7. Figure 3.3 illustrates an ORTEP drawing of the structure. Full details of the X-ray structure determination are available from Dr. Parvez.

The use of tetraphenylarsonium as the cation allows the monoanion 41 to



Figure 3.2- Infrared Spectrum of [Ph₄As][Ph₂P(S)NSiMe₃].nTHF (44)

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<u>Table 3.6 Ce</u>	Il Parameters and Crystallog	<u>caphic Data for</u> F (44)
MW = 723.84	$C_{41}H_{43}O_{0.5}PNSiAsS$	
monoclinic sp	pace group P2 ₁ /n	$beta = 112.73(2)^{\circ}$
a = 16.534(4) Å	b = 14.393(3) Å	c = 17.855(4) Å
$V = 3919(1) Å^3$	T = -73.0 °C	$D_{calc} = 1.227 \text{ g cm}^{-3}$
Crystal Dimensions =	= 0.60 x 0.50 x 0.60 mm	Z = 4
R = 0.065	$R_{w} = 0.057$	

Table 3.7 Selected Bond Lengths (pm) and Bond Angles (°) for [Ph ₄ As][Ph ₂ P(S)NSiMe ₃].0.5THF (44)				
P(1)-N(1)	155.5(8)	N(1)-P(1)-S(1)	121.2(4)	
P(1)-S(1)	198.0(4)	N(1)-P(1)-C(1)	109.9(5)	
P(1)-C(1)	184(1)	N(1)-P(1)-C(7)	106.9(5)	
P(1)-C(7)	183(1)	S(1)-P(1)-C(1)	108.3(4)	
		S(1)-P(1)-C(7)	107.1(4)	
·		P(1)-N(1)-Si(1)	136.3(5)	

crystallize as an ionic solid, with one-half of a molecule of THF. There are no bonding interactions between the monoanion (41) and Ph_4As^+ . As a result the N-P-S bite angle of 121.2(4)° is quite large. This is significantly larger than the bite angles found for the symmetric and hybrid ligand systems described in Chapter One. Since the monoanion 41 is not involved in bonding to a coordinating metal atom, the bite angle is permitted to open up. This was observed with the cleavage of a dithiophosphinate ligand when two



Figure 3.3- ORTEP Diagram of [Ph₄As][Ph₂P(S)NSiMe₃].0.5THF (44)

equivalents of triphenylphosphine were reacted with $[Pd(S_2PPh_2)_2]$.⁴³ The sulfurphosphorus-sulfur angle opens from 105.7(4)° in the bidentate coordination to 117.9(8)° for the ionic ligand in 13. The P-N-Si angle of 136.3(5)° is larger than expected for sp² hybridized orbitals present in the nitrogen atom, indicating that some sp character is involved in the bonding to phosphorus and silicon.



The phosphorus-sulfur distance of 198.0(4) pm corresponds approximately to a bond order of 1.8. This is in comparison to a single P-S bond distance of 210.0(1) pm¹⁴ and a double P-S bond of 195.0(3) pm.¹³ The phosphorus-nitrogen bond length of 155.5(8) pm is shorter than the average P-N double bond (157-160 pm).²³ Similar bond lengths are present in the ionic dithiophosphinate ligand of $[Pd(S_2PPh_2)(PPh_3)_2][S_2PPh_2]^{43}$ with one phosphorus-sulfur distance of 199.0(20) pm , with a bond order of 1.75. The second P-S distance of 193.2(20)pm is shorter than a phosphorus-sulfur double bond. These bond lengths indicate that the negative charge is delocalized over the whole N-P-S unit, as in **41**, rather than primarily localized on the sulfur atom, as depicted in **41a** and evident in K[Ph₂P(Se)NSiMe₃].THF (**28**), or localized on the nitrogen atom as in **41b**. The apparent difference in charge distribution in the monoanions Ph₂P(E)NSiMe₃⁻ may be due to the different chalcogens (E = S, Se), but it seems more likely to be attributed to the existence of **41** as a free anion, in the salt **44**, compared to the coordinated, dimeric

structure of the selenium monoanion 28.

3.3 Attempted Synthesis of the Dianion Ph₂P(S)N²⁻

(3.4)
$$Ph_2P(S)N(SiMe_3)_2 + 2 \text{ KOt Bu} \xrightarrow{i)THF / -78^{\circ}C} Ph_2P(2-2K^+ + 2 Me_3SiOt Bu)$$

ii) Room temp

The reaction of $Ph_2P(S)N(SiMe_3)_2$ with two molar equivalents of potassium *tert*butoxide was carried out according to Equation 3.4 in an attempt to generate the dianion $Ph_2P(S)N^{2-}$ (42). However, only an oily residue could be isolated from a mixture of THF / ether. The ³¹P NMR spectrum of this product had the same chemical shift, at 32.3 ppm, as the isolated potassium salt of the monoanion, 43. A ¹H NMR spectrum indicated the presence of trimethylsilyl groups at 0.06 ppm. More vigorous reaction conditions were not attempted due to the lack of success in forming the dianion of the selenium analogue, $Ph_3P(Se)N^{2-}$ (Section 2.3).

3.4 Preparation of Ph₂P(S)NH₂ by Hydrolysis of K[Ph₂P(S)NSiMe₃].THF



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The salt K[Ph₂P(S)NSiMe₃] in a THF solution was treated with ethanol to see if

hydrolysis of the monoanion occurs readily, and to determine whether the second trimethylsilyl group could be removed by hydrolysis. After a reaction time of one hour, a singlet at 53.3 ppm was observed in the ³¹P NMR spectrum and this is attributed to $Ph_2P(S)NH_2$ (45). Only a white oily residue could be isolated. While attempting to obtain a ¹H NMR spectrum of this product in CDCl₃, a reaction with the chloroform occurred, as indicated by a change to an orange colour and a pungent smell. This was confirmed the presence of unassignable peaks in the ¹H NMR spectrum and the appearance of a new peak at 19.3 ppm in the ³¹P NMR spectrum. Further attempts to isolate a pure solid product proved unsuccessful. Thus it appears that the $Ph_2P(S)NSiMe_3$ -anion is more prone to hydrolysis than its selenium analogue.

Hydrolysis of the neutral ligand, $Ph_2P(S)N(SiMe_3)_2$, was carried out with the addition of ethanol in THF at room temperature. Within 26 hours, the hydrolysis reaction was complete. A singlet representing $Ph_2P(S)NH_2$ (45) was present in the ³¹P NMR spectrum at 53.3 ppm. In comparison to the neutral ligand $Ph_2P(Se)N(SiMe_3)_2$ (Section 2.4), the sulfur compound appears to hydrolyze at a faster rate.

3.5 Reactions of the Ph₂P(S)NSiMe₃⁻ Anion

3.5.1 Reaction of Ph₂P(S)NSiMe₃ and Ph₂P(S)Cl

As discussed in Section 2.5.1, there has been recent interest in phosphazene metallocycles^{8,79} and the formation of chelate rings with azadiphosphinate groups.⁴² Recent work by Roesky *et al.* has resulted in the characterization of a complex of the monoanion 46 coordinated to trimethyltin and dimethyltin chlorides.⁸⁰ In this work it was

anticipated that the reaction of $Ph_2P(S)NSiMe_3^{-}(41)$ with chlorodiphenylphosphine sulfide could form the compound 47. Removal of the trimethylsilyl group from 47 would generate the anion 46 (R=Ph).



In the attempted synthesis of the selenium analogue of 47 (see Section 2.5.1), the ³¹P and ⁷⁷Se NMR spectra indicated that the product resulted from reaction at the selenium atom to give 37. It was envisaged that similar behaviour would be observed for the reaction of K[Ph₂P(S)NSiMe₃] with Ph₂P(S)Cl.

(3.5)
$$Ph_2P(-K^+ + Ph_2P(S)C) \xrightarrow{i)THF / reflux 1hr}_{ii) Room temp 16 hrs} Ph_4P_2S_2NSiMe_3 + KCl$$

The reaction was carried out in THF at reflux temperature (Equation 3.5). However, after one hour, the ³¹P NMR spectrum showed the presence of a substantial amount of the starting reagents. After stirring at room temperature overnight, the reaction had gone to completion, and none of the monoanion **43** was evident in the³¹P NMR spectrum (Figure 3.4). The ³¹P NMR spectrum indicated that the product **48** had been formed (Table 3.8).

The product **48** was tentatively identified on the basis of two mutually coupled doublets with ${}^{2}J({}^{31}P{}^{-31}P) = 11$ Hz. This is similar to the two bond coupling observed in the compounds $R_{2}P(S)-S-P(S)R_{2}$ [${}^{2}J({}^{31}P{}^{-31}P) = 15$ Hz] (R = Me, *i*Pr, *t*Bu).⁸¹ The two different phosphorus resonances at 57.2 and 4.8 ppm were tentatively assigned as P_A and P_B, respectively. This assignment is based on the ${}^{31}P$ NMR chemical shifts of Ph₃PS (43 ppm in CDCl₃)⁸² and Ph₃PNPh (0 ppm in C₄H₈O₂).⁸³ Compounds of the type R₃PNR' have a range of ${}^{31}P$ NMR chemical shifts from +30 ppm to -15 ppm, dependent on the substituents.⁸⁴ The ${}^{31}P$ NMR parameters for **48** are very similar to those of the selenium analogue **37** (see Table 2.7).

		а. `		
Table 3.8 Nuclear Magnetic Resonance Data for				
	<u>Me3011</u>	<u>FII₂FSFFII₂S (48)</u>		
Chemical Shift (ppm) ² J(³¹ P- ³¹ P)				
³¹ P NMR ^a				
	P _B of 48	4.8 (d)	11.2 Hz	
	P_{B} By-product	27.5 (d)	40.3 Hz	
	P _A of 48	57.2 (d)	11.3 Hz	
	P _A By-product	79.7 (d)	40.2 Hz	
	By-product	80.6 (s)		
	Ph ₂ P(S)Cl	80.3 (s)		

^a THF / D₂O insert. External reference 85% H₃PO₄ / D₂O insert.



A larger amount of by-products is formed in this reaction in comparison to the analogous selenium reaction (Section 2.5.1). The two peaks with a chemical shift of ca. 80 ppm in the ³¹P NMR spectrum are not coupled and one is identified as the reagent $Ph_2P(S)Cl$ (80.3 ppm). The second peak may be a derivative of this compound. A second set of mutually coupled doublets is also present in the ³¹P NMR spectrum, with chemical shifts of 27 ppm and 79 ppm, and ²J(³¹P.³¹P) = 40 Hz. These mutually coupled doublets are also present in minute amounts in the ³¹P NMR spectrum of the reaction of the selenium monoanion with $Ph_2P(S)Cl$ (See Section 2.5.1 and Figure 2.4). This indicates that the product is formed from the reagent $Ph_2P(S)Cl$ rather than the monoanion. This was confirmed by identical mutually coupled doublets present in the ³¹P NMR spectrum after refluxing only $Ph_2P(S)Cl$ in 1,2-DME for one hour. A possible compound may be [SPh_2P-S-PPh_2O], containing two different phosphorus environments, formed by the reaction of $Ph_2P(S)Cl$ with the hydrolysis product $Ph_2P(S)OH$.

The reaction was repeated in the higher boiling solvent 1,2-dimethoxyethane in the hope of decreasing the reaction time and reducing the amount of by-product formed. The use of 1,2-DME did decrease the reaction time as well as the intensity of the resonances at 80 ppm in the ³¹P NMR spectrum. Unfortunately, the reaction mixture always contained other products and various solvent mixtures failed to yield a pure compound. The oily nature of the residue, after removal of the solvent, was attributed to the trimethylsilyl group still attached to the nitrogen. Removal of this group could lead to a new isomer of the established ionic ligand **46**, with both hard and soft coordination sites. However, the use of one equivalent of KOtBu proved unsuccessful in removing the

trimethylsilyl group from this product. Monitoring the reaction by ³¹P NMR revealed a mixture of products formed at -78 °C.

3.5.2 Reaction of Ph₂P(S)NSiMe₃⁻ and I₂



It was postulated that the oxidation of the monoanion $Ph_2P(Se)NSiMe_3$. e.g. with iodine, may form a neutral compound with a selenium-selenium single bond (**39**). This was confirmed by the coupling constants observed between the ³¹P and ⁷⁷Se nuclei, as discussed in Section 2.5.2. A compound with a similar structure (**49**) was anticipated for the product of the reaction of iodine with K[Ph_2P(S)NSiMe_3] (Equation 3.6).



The reaction occurred under mild conditions with potassium iodide precipitating upon warming the solution to room temperature. A ³¹P NMR spectrum revealed only a

singlet at 10.2 ppm. Removal of all the solvent resulted in an orange oil and repeated attempts to isolate a pure solid product from various solvent mixtures have been unsuccessful. Consequently, further characterization of the product **49** was not possible.

3.5.3 Attempted Removal of SiMe₃ Groups from Me₃SiNPh₂PSSPPh₂NSiMe₃ (49) with KO*t*Bu

The oily nature of **49** is likely due to the presence of the trimethylsilyl groups. Consequently, it was decided to attempt to remove them with KOtBu in order to isolate a pure potassium salt of **49** for characterization and confirmation of the presence of the sulfur-sulfur bond.



Compound 49 was prepared according to Equation 3.6 and then two equivalents of KOtBu were added to the reaction mixture (Equation 3.7). At room temperature, two peaks, in a 3:1 ratio, were present in the ³¹P NMR spectrum of the reaction mixture (Figure 3.5). The major product at 32.4 ppm is attributed to the monoanion $K[Ph_2P(S)NSiMe_3]$, formed by cleavage of the sulfur-sulfur bond in 49. The minor product has a chemical shift of 7.3 ppm, which differs from the chemical shift of Me₃SiNPh₂PSSPPh₂NSiMe₃ (49) in the same solvent by approximately 3 ppm.



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The reaction (Equation 3.7) was then repeated with four equivalents of KOtBu in the hopes of increasing the amount of product at 7.3 ppm, in the ³¹P NMR spectrum, or causing it to disappear. At room temperature, the ³¹P NMR spectrum contained the same two resonances at 32.4 and 7.3 ppm in a ratio of 2:1. Only the monoanion $K[Ph_2P(S)NSiMe_3]$ was isolated from a solvent mixture of THF / hexanes. The product with a chemical shift of 7.3 ppm could not be identified, but it may be the dianion $Ph_2P(S)N^{2-}$ (42).

3.6 Conclusions

With the use of potassium *tert*-butoxide as a nucleophile, the monoanion $Ph_2P(S)NSiMe_3$ (41) was isolated as both potassium and tetraphenylarsonium salts. Both were fully characterized spectroscopically, and an X-ray crystal structure determination of the Ph_4As^+ salt was carried out. Attempts to synthesize the dianion $Ph_2P(S)N^{2-}$ (42) were unsuccessful. Hydrolysis of 41 produces $Ph_2P(S)NH_2$.

In the reactions of the potassium salt $K[Ph_2P(S)NSiMe_3]$ (43) with the electrophilic

reagents chlorodiphenylphosphine sulfide and iodine, the preferred site of attack appears to be the soft sulfur atom on the basis of the ³¹P NMR spectroscopic data for the The crystal structure of 44, however, indicates the negative charge is products. delocalized over the N-P-S unit in the anion 41. The differences in the reactive sites when compared the reactions of neutral ligand to the N.N'bis(trimethylsilyl)aminodiphenylphosphine sulfide with TiCl₄ or SnCl₄ (see Section 1.4.2) could be attributed to the softness of the electrophilic reagents when compared to the harder titanium and tin metal centres, and their determination of the reactive site on the monoanion.

Difficulties were encountered in isolating pure solid products from all reactions, including the synthesis of the monoanion. This may be attributed, in part, to the $Ph_2P(S)NSiMe_3$ being less stable than the selenium analogue. This was illustrated in the difficulties in obtaining a crystal structure of the potassium salt of **41**. The use of KOtBu to remove the trimethylsilyl groups in order to isolate solid derivatives proved unsuccessful in the case of $Me_3SiNPh_2PSPPh_2S$ (**48**). With $Me_3SiNPh_2PSSPPh_2NSiMe_3$ (**49**), the potassium *tert*-butoxide reproduced the potassium salt of the monoanion, $K[Ph_2P(S)NSiMe_3]$ (**43**), presumably the result of cleavage of the sulfur-sulfur bond, and a new product, possibly the dianion $Ph_2P(S)N^2$ (**42**). The relative yield of this product was enhanced when the amount of KOtBu was increased, as indicated by ³¹P NMR spectroscopy, but it could not be isolated.

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3.7 Experimental

3.7.1 General

Due to the unknown reactivity of the compounds synthesized, all distillations and reactions were carried out under an inert atmosphere of nitrogen gas. This gas was dried by passing through a column of phosphorus pentoxide and Sicapent (E. Merck Darmstedt), a commercial drying agent of phosphorus pentoxide and a moisture indicator.

Manipulations of solids, both reagents and products, were carried out under an inert atmosphere of nitrogen gas, either under a cone of flowing gas or in a Vacuum Atmospheres Corporation Glovebox. All solutions were transferred via syringes or transfer needles, flushed with an inert gas (nitrogen or argon).

3.7.2 Instrumentation

The collection of data for both the nuclear magnetic resonance (NMR) and infrared (IR) spectra was carried out on the instruments outlined in Section 2.7.2. An external reference of an 85% solution of H_3PO_4 with D_2O for the lock was used in the ³¹P NMR spectra.

The crystal structure was determined from data collected on a Rigaku AFC6S diffractometer, at low temperatures. The data were processed using the software outlined in Section 2.7.2.⁸⁵⁻⁸⁷ Chemical analyses were carried out by the Analytical Services of the Department of Chemistry, University of Calgary.

3.7.3 Solvents

All solvents used for reactions and crystallizations were of reagent grade and refluxed over the appropriate drying agent (See Section 2.7.3), under an inert atmosphere of nitrogen or argon gas. Solvents were collected after they had refluxed for a number of hours.

3.7.4 Reagents

The starting materials required for the following reactions were obtained from the suppliers listed and purified as outlined in Section 2.7.4. Tetraphenylarsonium chloride hydrate was obtained from Aldrich. The water was removed by heating under vacuum (oil bath 100°C, 0.075 torr) for 3 hours, according to the Merck Index.⁹¹ Confirmation of the removal of the water was provided by the infrared spectrum of the compound.

$$(3.8)(\text{SiMe}_3)_2\text{NH} \xrightarrow{\text{n-BuLi}}_{\text{Hexanes} / 65 °C} \text{Li}[\text{N}(\text{SiMe}_3)_2] \xrightarrow{\text{Ph}_2\text{PCl}}_{\text{Hexanes} / 0°C} \text{Ph}_2\text{PN}(\text{SiMe}_3)_2$$

The synthesis of $Ph_2PN(SiMe_3)_2$ was based on Wilburn's method for $Me_2PN(SiMe_3)_2^{89}$ as adapted by Michaud (Equation 3.8).⁷³ After a distillation, a solid product was obtained, at room temperature, in a yield of 64.3%. Purity was confirmed by the ³¹P NMR spectrum which displayed a singlet at 51.5 ppm (in ether) [cf. δ (³¹P) = 50.2 ppm (in hexanes)⁷³].

The synthesis of the neutral ligand $Ph_2P(S)N(SiMe_3)_2$ was based on the method used by Roesky *et al.* (Equation 3.1).⁶⁸ A solid product was obtained from a 2:1 mixture

of toluene / pentane in the freezer (-13°C) in a 81.4% yield. The compound exhibits a singlet at 60.3 ppm in the ³¹P NMR spectrum.

Chlorodiphenylphosphine sulfide was prepared according to the cited literature (see Section 2.7.4).⁹⁰

3.7.5 Synthesis of K[Ph₂P(S)NSiMe₃].THF (43)

A clear colourless solution of $Ph_2P(S)N(SiMe_3)_2$ (2.188 g, 5.79 mmol) in THF (25 ml) was added dropwise, over 10 minutes, to a slurry of KOtBu (0.635 g, 5.66 mmol) in THF (25 ml). The addition was carried out at -78°C (dry ice / acetone bath) and the reaction mixture was maintained at this temperature for 15 minutes. After the reaction mixture had warmed to room temperature over an hour period, a ³¹P NMR spectrum revealed a singlet at 32.3 ppm. The volume of the clear yellow solution was reduced to 5 ml under vacuum and then it was layered with hexanes (30 ml) and placed in the freezer. A crystalline product was isolated in a yield of 81.9% (1.593 g). The details of the spectroscopic and analytical data for K[Ph₂P(S)NSiMe₃].THF are given in Section 3.2.1.

3.7.6 Synthesis of [Ph₄As][Ph₂P(S)NSiMe₃].0.5THF (44)

A solution of K[Ph₂P(S)NSiMe₃] (0.40 g, 1.16 mmol) in THF (20 ml) was added dropwise to a slurry of Ph₄AsCl (0.515 g, 1.23 mmol) in THF (20 ml). The addition was carried out at -78°C (dry ice / acetone bath) over a 15 minute period. After a further fifteen minutes at -78°C, the reaction mixture was warmed to room temperature over an hour period.

The cloudy white solution was reduced in volume, under vacuum, and passed through a filter stick containing layers of celite and sea sand to remove KCl. After rinsing the filter stick with THF (2 x 5 ml), the volume was reduced to 7 ml. A ³¹P NMR spectrum revealed a singlet at 26.8 ppm. After layering in toluene (20 ml) and placing the solution in the freezer (-13°C), a yellowish-white crystalline product was isolated in a yield of 41.2% (0.801 g). A summary of the spectroscopic and analytical data, and the X-ray crystal structure for [Ph₄As][Ph₂P(S)NSiMe₃].0.5THF are given in Section 3.2.2.

3.7.7 Attempted Synthesis of the Dianion $Ph_2P(S)N^2$ (42)

A slurry of KOtBu (0.150 g, 1.34 mmol) in THF (10 ml) was added dropwise to a solution of $Ph_2P(S)N(SiMe_3)_2$ (0.250 g, 0.662 mmol) in THF (10 ml) over a 5 minute period. The addition occurred at -78°C (dry ice / acetone bath) and the reaction mixture remained at this temperature for a further 45 minutes. The solution was then warmed to room temperature to give a cloudy solution with a singlet at 32.5 ppm in the ³¹P NMR spectrum. As summarized in Section 3.3, the ¹H NMR spectrum revealed the presence of the trimethylsilyl group at 0.20 ppm. With time, the excess KOtBu settled out, resulting in a clear solution.

3.7.8 Synthesis of Ph₂P(S)NH₂ (45) By Hydrolysis of K[Ph₂P(S)NSiMe₃].THF

A slurry of KOtBu (0.152 g, 1.35 mmol) in THF (15 ml) was added dropwise to a solution of $Ph_2P(S)N(SiMe_3)_2$ (0.254 g, 0.673 mmol) in THF (20 ml). After the addition was carried out at -78°C (dry ice / acetone bath), the reaction mixture remained at this temperature for a further 45 minutes. Ethanol (15 ml) was then added dropwise to the reaction mixture. After a further fifteen minutes, the reaction was warmed to room temperature and a singlet at 53.4 ppm was observed in the ³¹P NMR spectrum. A solid product could not be isolated for further characterization.

3.7.9 Reaction of Ph₂P(S)NSiMe₃ and Ph₂P(S)Cl

A clear colourless solution of $Ph_2P(S)Cl$ (0.229 g, 0.906 mmol) in 1,2-DME (25 ml) was added dropwise to a solution of K[Ph_2P(S)NSiMe_3] (0.316 g, 0.920 mmol) in 1,2-DME (25 ml). At room temperature, the addition occurred over 10 minutes. The flask containing Ph_2P(S)Cl was rinsed with 1,2-DME (10 ml) and the washings were added to the reaction mixture. After 1.5 hours at reflux, the reaction mixture became cloudy. Once cooled to room temperature, the solution was reduced in volume by two-thirds and then passed through a filter stick containing layers of celite and sea sand, to remove the KCl by-product. After rinsing with 1,2-DME (2 x 4 ml), a ³¹P NMR spectrum of the clear pale yellow solution was recorded. The major product was identified as Me₃SiNPh_2PSPPh_2S by the ³¹P NMR data given in Section 3.5.1. Removal of all the solvent resulted in a white cloudy oil and attempts to isolate a pure product from THF / hexanes or 1,2-DME / hexanes proved unsuccessful.

3.7.10 Reaction of Ph₂P(S)NSiMe₃⁻ and I₂

A clear orange solution of I_2 (0.351 g, 1.38 mmol) in THF (30 ml) was added dropwise, over a 15 minute period, to a clear colourless solution of K[Ph₂P(S)NSiMe₃] (0.926 g, 2.70 mmol) in THF (30 ml). The addition was carried out at -78°C (dry ice / acetone bath). The iodine flask was rinsed with THF (10 ml) and the washings were added to the reaction mixture. After a further fifteen minutes at -78°C, the reaction mixture was warmed to room temperature, producing a white precipitate of KI.

After reducing the volume by half, under vacuum, the reaction mixture was passed through a filter stick containing layers of celite and sea sand. The filter stick was rinsed with THF (2 x 5 ml), resulting in a clear orange solution. Removal of all the solvent, under vacuum, gave an orange oil. The product was tentatively identified as $Me_3SiNPh_2PSSPPh_2NSiMe_3$, on the basis of a singlet in the ³¹P NMR spectrum at 10.2 ppm (Section 3.5.2) and comparison to the analogous selenium reaction (Section 2.5.2). Attempts to isolate a pure solid product by using the following solvent combinations have proven unsuccessful: hexanes / THF; pentane; 1,2-DME / ether; and 1,2-DME /hexanes.

3.7.11 Attempted Removal of SiMe₃ Groups from Me₃SiNPh₂PSSPPh₂NSiMe₃ (49) with KOtBu

A clear orange solution of $Me_3SiNPh_2PSSPPh_2NSiMe_3$ (0.400 mmol) in THF (25 ml) was added to a slurry of KOtBu (1.071 g, 0.632 mmol) in THF (20 ml). The addition occurred dropwise, over 10 minutes, at -78°C (dry ice / acetone bath). The flask containing $Me_3SiNPh_2PSSPPh_2NSiMe_3$ was rinsed with THF (10 ml) and the washings

were added to the reaction mixture, which remained at -78° C for 15 minutes. After warming to room temperature, a pale yellow solution resulted. A ³¹P NMR spectrum of the reaction mixture revealed two products, with K[Ph₂P(S)NSiMe₃] (32.4 ppm) as the major component, which was isolated from a mixture of THF / hexanes at -13°C. Spectroscopic details for this reaction are summarized in Section 3.5.3.
CHAPTER FOUR

Conclusions

4.1 General

Potassium *tert*-butoxide, as a nucleophile, was successful for the synthesis of the monoanions $Ph_2P(S)NSiMe_3$ and $Ph_2P(Se)NSiMe_3$ from the neutral ligands N,N'-bis(trimethylsilyl)aminodiphenylphosphine sulfide and N,N'-bis(trimethylsilyl)amino-diphenylphosphine selenide, respectively. These monoanions were isolated as potassium salts and characterized analytically and spectroscopically.

The potassium salt of Ph₂P(Se)NSiMe₃ was obtained in a crystalline form, facilitating an X-ray crystal structure determination. The dimeric, step-shaped structure of K[Ph₂P(Se)NSiMe₃].THF was interesting since most of the symmetric and hybrid ligand systems reported in the literature (see Chapter One) have monomeric structures with the ligand coordinated to a single metal atom by chelation. Although sulfinimidamides form the step-shaped structure with the alkali metals lithium, sodium, rubidium, cesium,⁷⁸ the mode of coordination of potassium, and bis(trimethylsilylimido)phosphinate ligands is dependent on the specific alkali metal centre.⁵⁴ Only with rubidium and cesium is the dimeric step-shaped structure formed. It is believed that the monoanions $Ph_2P(E)NSiMe_3$ (E = S,Se) have greater similarities with bis(trimethylsilylimido)phosphinates than the sulfinimidamides. The negative charge, as revealed by values of v(P-Se) and d(P-Se), is indicated to be primarily on the selenium atom, with double bond character for the phosphorus-nitrogen bond.

Replacement of the potassium cation with tetraphenylarsonium, Ph_4As^+ , provided X-ray quality crystals of a salt of $Ph_2P(S)NSiMe_3^-$, and a structure was determined for $[Ph_4As][Ph_2P(S)NSiMe_3].0.5THF$. The crystal structure is ionic, with no interaction between the monoanion and the coordinatively saturated cation. The ionic structure allows the nitrogen-phosphorus-sulfur bite angle to open up to the largest of the ligand systems studied. The negative charge is delocalized over the N-P-S unit, as indicated by v(P-S) and d(P-S). This is in contrast to the selenium analogue K[Ph_2P(Se)NSiMe_3].THF and may be attributed to its ionic form.

In reactions of the potassium salts of the monoanions, $[Ph_2P(E)NSiMe_3]K$ (E = S,Se), with the electrophilic reagents chlorodiphenylphosphine sulfide and iodine, the preferred reaction site is the soft chalcogen centre. Chlorodiphenylphosphine sulfide reacts with the monoanions forming Me₃SiNPh₂PEPPh₂S (E=S,Se). Difficulties were encountered in trying to isolate a pure product and the use of KOtBu to remove the trimethylsilyl group proved to be unsuccessful in forming a solid derivative. The reaction of iodine with the monoanions resulted in the formation of Me₃SiNPh₂PEEPPh₂NSiMe₃ (E = S, Se), containing a single chalcogen-chalcogen bond. The reaction of these dichalcogenides with KOtBu, in a 1:2 molar ratio, resulted in the reproduction of the potassium salts of the monoanions, K[Ph₂P(E)NSiMe₃] (E = S,Se), presumably by cleavage of the chalcogen-chalcogen bond. In the case of the disulfide, a new species was evident in the ³¹P NMR spectrum. With an increase in the amount of the KOtBu from two equivalents to four, the quantity of the unknown product also increased, although not stoichiometrically. The possibility that this product could be the dianion

 $Ph_2P(S)N^2$ is of interest, but attempts to isolate it were inconclusive.

Repeated attempts to synthesize and isolate the dianions, $Ph_2P(E)N^{2-}$ (E = S,Se), were unsuccessful. The reaction conditions were limited to those used by Herberhold *et al.* for synthesis of SN_2^{2-} from bis(trimethylsilyl)sulfur diimide.⁷² One explanation is that the negative charge located on the nitrogen of the monoanion, immediately after the removal of the first trimethylsilyl group, may inhibit the approach of the second equivalent of KOtBu. In the case of the sulfur diimide, there is only one trimethylsilyl group to be removed from each of the nitrogen atoms. The remaining trimethylsilyl group in the monoanions $Ph_2P(E)NSiMe_3$ was removed by hydrolysis with ethanol. The hydrolysis products $Ph_2P(S)N(H)SiMe_3$ and $Ph_2P(Se)NH_2$ were isolated as solids and their identities were determined by analytical and spectroscopic methods, while the hydrolysis product $Ph_2P(S)NH_2$ could only be isolated as an oil.

In contrast to the reported tendency of diselenophosphinates and selenothiophosphinates to decompose to elemental selenium, the monoanion $Ph_2P(Se)NSiMe_3$ ⁻ exhibited no signs of this decomposition. Indeed, qualitative observations on the reactions of $Ph_2P(E)NSiMe_3$ ⁻ with various reagents, including ethanol, indicate that the selenide is more stable and gives rise to cleaner reactions than the corresponding sulfide.

4.2 Future Work

Reactions of the monoanions $Ph_2P(E)NSiMe_3$ (E = S, Se) with certain electrophilic reagents have indicated that the preferred site of reaction is the soft chalcogen centre. Reactions of these monoanions with various metals centres will indicate whether the preferred coordination is through the soft chalcogen centre, the hard nitrogen atom, or through both ligand atoms via chelation or bridging as observed for the complexes of the various symmetric and hybrid ligand systems previously studied (see Chapter One). However, it must be realized that the coordination observed can be highly dependent on the metal centre. Roesky *et al.* observed that the reaction of the neutral ligand N,N'bis(trimethylsilyl)aminodiphenylphosphine sulfide with titanium tetrachloride occurs at the nitrogen, with the removal of both trimethylsilyl groups.⁶⁸ However, reaction of the analogous *iso*-propyl ligand with tin tetrachloride, in a 2:1 ratio, has resulted in the removal of one trimethylsilyl group from each of two ligands as they coordinate to the tin atom by chelation.⁷⁰ Tin is considered to be a softer metal centre than titanium. As a result, the reaction with tin tetrachloride involves the softer sulfur centre as well as the nitrogen centre. This indicates that a variety of modes of coordination are possible for the monoanions Ph₂P(E)NSiMe₃ (E = S,Se) synthesized in this thesis.

Future work should include the preparation of salts of the monoanions, $Ph_2P(E)NSiMe_3^-(E = S,Se)$, with the alkali metals lithium, sodium, rubidium and cesium to determine if the dimeric, step-shaped structure is dependent on the metal centre. This indicated by the study of alkali metal derivatives of was bis(trimethylsilylimido)phosphinate ligands, which were prepared by reaction of the protonated species $[Ph_2P(NSiMe_3)(N(H)SiMe_3)]$ with the metal hydride (M = Na, K) or the alkali metal (M = Rb, Cs). We have successfully isolated the analogous Ph₂P(Se)N(H)SiMe₃ ligand and may be able to synthesize both the selenium and sulfur compounds from the respective monoanions, under controlled reaction conditions.

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The electrophilic reagents chlorodiphenylphosphine sulfide and iodine are considered as soft reagents so reactions at the chalcogen centre are preferred. The hydrolysis products $Ph_2P(Se)N(H)SiMe_3$ and $Ph_2P(Se)NH_2$ (E = S,Se) have the hard H⁺ coordinated to the nitrogen atom. Of interest is whether or not other hard electrophilic reagents will react at the nitrogen centre, indicating that reactions are dependent on the nature of the reagents, rather than the delocalization of the negative charge in the monoanion. Methyl triflate, (CH₃CF₃SO₃), would provide a hard methyl cation as a possible electrophile.

Reactions with various hard and soft metal centres will give an indication as to the flexibility of the monoanions in their coordination behaviour. Hard metal centres to consider include calcium and the early transition metals titanium and zirconium. The softer metals palladium, platinum and silver may have a preference to attack the monoanion at the chalcogen or form chelated complexes with both the nitrogen and the chalcogen centres. With reactions of the monoanion with a hard metal centre, the possibility exists that the remaining trimethylsilyl groups will be removed *in situ* forming the coordinated dianion. Alternatively, coordination with the metal centre to give a neutral compound may facilitate the subsequent removal of the trimethylsilyl groups, by diminishing any negative charge located on the nitrogen atom. Other reagents similar to KOtBu may also be used to attempt to remove this trimethylsilyl group.

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