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^{31}P-NMR, ^{77}Se-NMR AND MASS SPECTRAL STUDIES ON SOME TRICOORDINATE P(III)-N AND TETRACOORDINATE P(V)-N SYSTEMS

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ABSTRACT. A series of aminophosphines were prepared by controlled condensation reaction between PCl_3 or $PhPCl_2$ and amines, and they were converted into the corresponding chalcogenides. ^{31}P-NMR and mass spectral data were collected for characterization of these asymmetrically substituted phosphines, and in addition, ^{77}Se-NMR data were collected for the phosphine selenides prepared. The spectral data revealed the importance of the dipolar structure for the heavier chalcogen atoms and the π-bond structure for the lighter ones. This study has also brought out the first examples of chiral tris(amino)phosphines and the corresponding selenides.

KEY WORDS: Aminophosphines, Dichlorophenylphosphine, Chiral tris(amino)phosphines, Aminophosphine chalcogenides, ^{77}Se-NMR

INTRODUCTION

Aminophosphines are important in inorganic heterocyclic chemistry and coordination chemistry. For a long time, we have been interested in a variety of aminophosphines [(chloro)aminophosphines, Cl-P(III)-N systems and aminophosphines, P(III)-N systems] which serve as effective synthons for inorganic heterocyclic compounds. These phosphines have been used for preparation of 1,5-bis(phosphinimino)cyclotetrathiazene, 1,5-$[(R_1)(R_2)(R_3)P{=}N\text{-}]_2S_4N_4$, cyclophosphadithiatriazene, $(R_1)(R_2)PS_2N_3$ and cyclodiphosphathiatriazene, $[(R_1)(R_2)P{=}N]_2NSCl$ [1-6]. The derivatives of these heterocycles are biologically important [7]. Aminophosphines are P-N bonded systems and this property enhances their versatility as they offer the possibility of manipulating substituents both on phosphorus and nitrogen besides granting nitrogen centre(s) as additional donor site(s) towards metal centres. There is also a growing interest on aminophosphine chalcogenides for their use as carriers of group VI elements (S, Se and Te) in the electronic industry [8].

^{31}P-chemical shift values for a large number of aminophosphines are compiled in the literature [9, 10]. The phosphorus chemical shifts largely depend on the nature, the electronegativity, the steric and the π-bonding effects of the substituents on phosphorus and also on the bond angles (and hence the nature of hybridization) around the central phosphorus atom. ^{31}P-chemical shift values for fully substituted aminophosphine chalcogenides [11, 12] reveal that the oxides are generally found in the upfield region (0-30 ppm, [9]) whereas those of sulfides and selenides occur over a relatively narrow and different range (60-80 ppm, [10]). Aminophosphine selenides are few in number and their ^{77}Se-NMR spectral data is even fewer [13, 14]. The coupling constants ($^1J_{P=Se}$) vary over a wide range depending upon the nature of the substituents on phosphorus and serve handy in the identification of the compounds [15, 16]. They can be measured from either of their ^{31}P-NMR or ^{77}Se-NMR spectra. The higher the electronegativity of the groups attached to phosphorus, the more are the coupling constant values affected.

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A few mass spectral studies of aminophosphines are reported in the literature [17-20] and have led to some interesting observations. Here, fairly intense molecular ion peaks and peaks from the fragment $[(R_2N)_2P]^+$ were observed in the electron impact mass spectra of compounds of the types $(R_2N)_3P$ and $(R_2N)_2PR'$. The stability of the dicoordinate fragment, $[(R_2N)_2P]^+$ has been explained on the basis of the participation of *d*-orbitals of phosphorus with the lone pair of electrons of nitrogen. Sometimes, mass spectral studies of compounds may predict the mechanistic possibilities, which are revealed by their corresponding fragmentation patterns.

In this study, we report the ^{31}P-NMR, ^{77}Se-NMR and mass spectra of some aminophosphines and aminophosphine chalcogenides along with their synthesis.

EXPERIMENTAL

All manipulations were done under inert atmosphere (dry N_2 or Ar) conditions. Solvents and amines were purified by standard methods [21]. Reported procedures were employed for synthesizing phenyldichlorophosphine, $PhPCl_2$, (*o*-phenylenedioxo)chlorophosphine, (*o*-$C_6H_4O_2$)PCl [22] and 3,5-dimethylpyrazole [23]. PCl_3 (Aldrich, 98 %), selenium (CDH), tellurium (BDH) and hydrogen peroxide solution, 30 % w/v (Qualigens) were used as received. Elemental sulfur and catechol (CDH) were recrystallized from CS_2 and hot toluene, respectively, before use. ^{31}P-NMR spectra (162 MHz) and ^{77}Se-NMR spectra (78.2 MHz) were recorded on JEOL JNM GSX-400 spectrometer in proton decoupled mode. ^{31}P-NMR and ^{77}Se-NMR spectra were obtained as dichloromethane solutions (provided with a D_2O insert) using 85 % H_3PO_4 and 1 M aqueous solution of SeO_2 as external standards, respectively. Upfield shifts are negative. Mass spectra were recorded on Finnigan MAT 8230 mass spectrometer under electron impact conditions operated at 70 eV.

Synthesis of phosphines

Synthesis of chloro(diisopropylamino)(di-n-butylamino)phosphine. To a stirred solution of PCl_3 (34.4 mmol) in hexane (80 mL) at 0 °C, diisopropylamine (68.5 mmol) in hexane (30 mL) was added dropwise during 1 h. After complete addition, the reaction mixture was brought to room temperature and stirred for 15 h and filtered to remove diisopropylamine hydrochloride (97 %). The precipitate was washed twice with hexane (2 x 30 mL) and the washings were collected along with the filtrate. This filtrate was again cooled at 0 °C while stirring and di-n-butylamine (68.8 mmol) in hexane (25 mL) was added to the filtrate as before. After 20 h of stirring, the reaction mixture was worked up as above to obtain the title phosphine, $(^iPr_2N)(^nBu_2N)PCl$ (73 % yield) as a clear pale yellow liquid which gave a singlet in its ^{31}P-NMR spectrum.

Synthesis of (diisopropylamino)(di-n-butylamino)(R$_2$N)phosphine [R$_2$N = diethylamino, morpholino, piperidino]. To a stirred solution of PCl_3 (45.8 mmol) in hexane (125 mL) at 0 °C, diisopropylamine (91.9 mmol) in hexane (25 mL) was added dropwise during 1 h. After complete addition, the reaction mixture was brought to room temperature and stirred for 15 h and filtered to remove diisopropylamine hydrochloride (95 %). The filtrate along with the hexane washings (3 x 10 mL) was further reacted at 0 °C with di-n-butylamine (91.8 mmol) in hexane (25 mL) and the resultant reaction mixture was filtered after stirring at room temperature for 20 h. This procedure was next repeated with the amine, R_2NH (91.9 mmol) in hexane (25 mL) and the final filtrate after workup was pumped off *in vacuo* to isolate the title phosphine, $(^iPr_2N)(^nBu_2N)(R_2N)P$ as a clear pale yellow liquid which gave a singlet in its ^{31}P-NMR spectrum. The yields varied from 64 to 68 %.

Synthesis of (dicyclohexylamino)(R)phenylphosphine [R = methylamino, isopropylamino, dimethylamino, diethylamino, di-n-butylamino, dimethylpyrazolyl]. Dichlorophenylphosphine (22.1 mmol) in hexane (100 mL) was kept stirred at 0 °C and a solution of dicyclohexylamine (44.2 mmol) in hexane (25 mL) was added slowly in 1 h. After 15 h of stirring at room temperature, the reaction mixture was filtered to remove dicyclohexylamine hydrochloride (96 %). The filtrate containing hexane washings (3 x 10 mL) of the precipitate was kept stirred at 0 °C and the amine, R_2NH (44.2 mmol) was added for a period of 30 min. (Methylamine and dimethylamine were generated by adding corresponding aqueous solutions to potassium hydroxide pellets). After 12 h of stirring, the reaction mixture was filtered to remove the corresponding amine hydrochloride salt and the filtrate was pumped off to dryness. The residual semisolid mass was cooled at 0 °C for a day to obtain slightly impure phosphine which was recrystallized from CH_2Cl_2-CH_3CN mixture (2:1 ratio) to isolate the title compound, $Ph[(C_6H_{11})_2N](R_2N)P$ as colourless crystals. The yields varied from 45 to 58 %.

Synthesis of (o-phenylenedioxo)(R_2N)phosphine [R_2N = diisopropylamino, dicyclohexylamino, dibenzylamino]. To (*o*-phenylenedioxo)chlorophosphine (26.1 mmol) in hexane (120 mL) kept stirred at 0 °C, the amine, R_2NH (52.2 mmol) in hexane (30 mL) was added in dropwise manner in 1 h. After complete addition, the reaction mixture was brought to room temperature, stirred for 20 h and filtered to remove the corresponding amine hydrochloride salt. The filtrate was concentrated to *ca.* 25 mL and cooled at 0 °C for a day to isolate the title phosphine, $(o\text{-}C_6H_4O_2)(R_2N)P$ as a colourless crystalline solid. The yield varied from 58 to 90 %. Dibenzylamino and morpholino derivatives are isolated as pale yellow liquids.

Synthesis of phosphine selenides. To a stirred solution of the appropriate phosphine (6.3 mmol) in benzene (25 mL), excess selenium powder (18.9 mmol) was added all at once, refluxed for 12 h and brought to room temperature. Excess selenium was removed by filtration and the filtrate was concentrated to *ca.* 10 mL. Acetonitrile (5 mL) was added and the mixture was cooled at 0 °C for a day to isolate colourless crystals of the corresponding phosphine selenide. For $Ph[(C_6H_{11})_2N](R_2N)P{=}Se$, the yields varied from 60 to 68 %, for $(o\text{-}C_6H_4O_2)(R_2N)P{=}Se$, from 61 to 69 % and for $(^iPr_2N)(^nBu_2N)(R_2N)P{=}Se$, from 72 to 78 %. The compounds $(^iPr_2N)(^nBu_2N)(R_2N)P{=}Se$ were isolated as pale yellow viscous oil.

Synthesis of phosphine sulfides. To a stirred solution of the appropriate phosphine (8.3 mmol) in benzene (25 mL) at room temperature, elemental sulfur (8.4 mmol) was added all at once. After 20 h, the clear colourless solution was concentrated to *ca.* 10 mL, acetonitrile (5 mL) added and cooled in deep freezer for a day to isolate colourless crystals of the corresponding phosphine sulfide. For $Ph[(C_6H_{11})_2N](R_2N)P{=}S$, the yields varied from 70 to 72 % and for $(o\text{-}C_6H_4O_2)(R_2N)P{=}S$, from 62 to 68 %.

Synthesis of phosphine oxides of the type ($o\text{-}C_6H_4O_2$)(R_2N)P=O [R = C_6H_{11} and $C_6H_5CH_2$]. To a stirred solution of the phosphine (3.1 mmol) in a C_6H_6-CH_3CN (1:2, 15 mL) mixture at room temperature, 30 % w/v H_2O_2 (0.8 mL) was added dropwise through a syringe and allowed to stir for 12 h during which the colour gradually turned pale pink. The clear solution was concentrated to *ca.* 5 mL and cooled at 0 °C for a day to isolate colourless crystals of the title compound. The yields varied from 40 to 50 %.

Attempted synthesis of ($o\text{-}C_6H_4O_2$)($^iPr_2N$)P=O. To a stirred solution of $(o\text{-}C_6H_4O_2)(^iPr_2N)P$ (2.1 mmol) in CH_3CN (10 mL) at room temperature, 30 % w/v H_2O_2 (0.5 mL) was added. Exothermic nature of the reaction was observed at once and the solution turned brown from which dark brown oil separated which could not be characterized. The ^{31}P-NMR spectrum of the

reaction mixture showed a singlet at 18.9 ppm and a multiplet at 2.5 ppm. No pure product could be isolated.

Attempted synthesis of phosphine tellurides of the type (o-$C_6H_4O_2$)(R_2N)P=Te

a. 1:3, 60 °C. To (o-$C_6H_4O_2$)(R_2N)P (1.4 mmol) in benzene (20 mL), was added black tellurium powder (4.2 mmol) and the mixture kept at *ca.* 60 °C (hot water bath) for 1 h. The ^{31}P-NMR spectrum of the filtrate showed only the presence of unreacted starting material.

b. 1:3, 80 °C. To a benzene solution (25 mL) of the phosphine, (o-$C_6H_4O_2$)(R_2N)P (1.6 mmol), black tellurium powder (4.8 mmol) was added all at once and refluxed for 20 h. The ^{31}P-NMR spectrum of the filtrate showed only the presence of unreacted starting material.

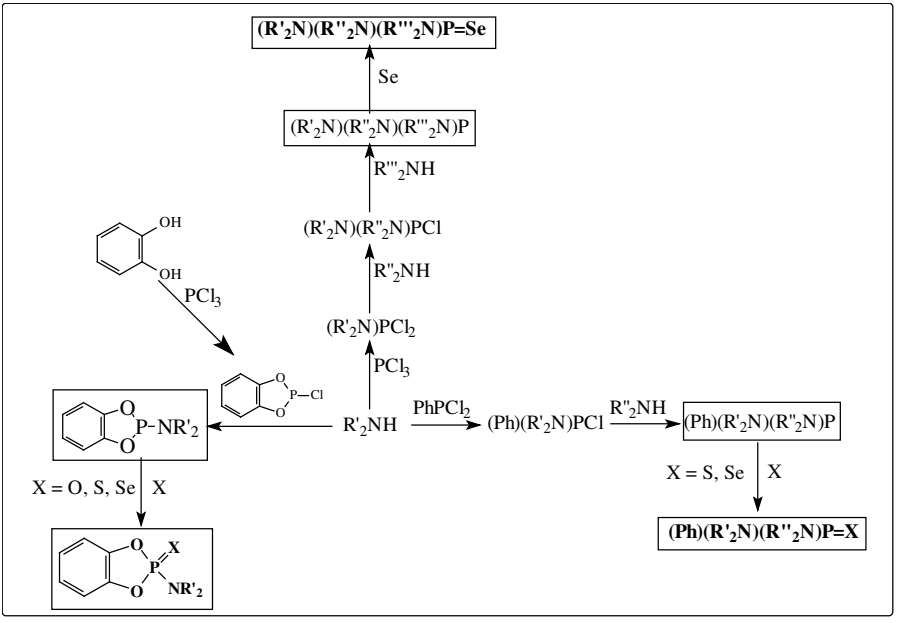
Characterization of phosphines and phosphine chalcogenides

^{1}H-NMR, ^{13}C-NMR and IR spectral data for the above phosphines and phosphine chalcogenides are given in the literature [6, 24]. Also, structures of some of the compounds like (o-$C_6H_4O_2$)[$(C_6H_{11})_2$N]P and (o-$C_6H_4O_2$)(R_2N)P=Se (R_2N = ^{i}Pr$_2$N, $(C_6H_{11})_2$N, $(PhCH_2)_2$N) were determined using single crystal X-ray diffraction [6].

RESULTS AND DISCUSSION

Synthetic aspects

The reaction scheme employed for the synthesis is given in Scheme 1. The phosphines and phosphine chalcogenides synthesized in this study are shown in Figure 1.



Scheme 1. Reaction scheme employed for synthesizing various phosphines and phosphine chalcogenides.

The phosphines reported in this study have been synthesized successfully by carrying out one/two/three step condensation reaction of PCl_3 or one/two step synthesis of $PhPCl_2$. Controlled and stepwise substitution reactions have been performed by making use of simple amine (*e.g.* Me_2NH) to sterically bulky amine [*e.g.* $(C_6H_{11})_2NH$] as well as highly reactive ones (*e.g.* $MeNH_2$). Reaction conditions were appropriately chosen to ensure smooth reactions and the overall yield realized in each case is quite good (*ca.* 45 to 90 %). Expectedly, a number of reaction parameters such as choice of solvent, reaction temperature, reaction time, molar ratio of PCl_3 to amine, mode and duration of addition of the reagents and the presence or absence of a hydrogen chloride scavenger, can affect both the formation of the desired products and their yield. The reactions (i) involving primary amines (known to give rise to complex reaction mixtures due to the possibility of inter- and intra-molecular condensation) and (ii) designed for chiral tris(amino)phosphines have led to the desired products in over 50 % yield. In the preparation of tris(amino)phosphines, the choice of amine at each step was important. Both steric bulk of the amine and the reaction conditions have been exploited for their successful preparation. In some cases, the presence of small amounts of amine hydrochloride by-product in the main product posed considerable difficulty in both isolation and purification of the target product. Despite a large success of the condensation route reported in the literature [20, 25-29], it may be mentioned that practically no report as yet is available on the use of this route for successive isolation of compounds of the kind, $(R_2N)(R'_2N)PCl$ and $(R_2N)(R'_2N)(R''_2N)P$.

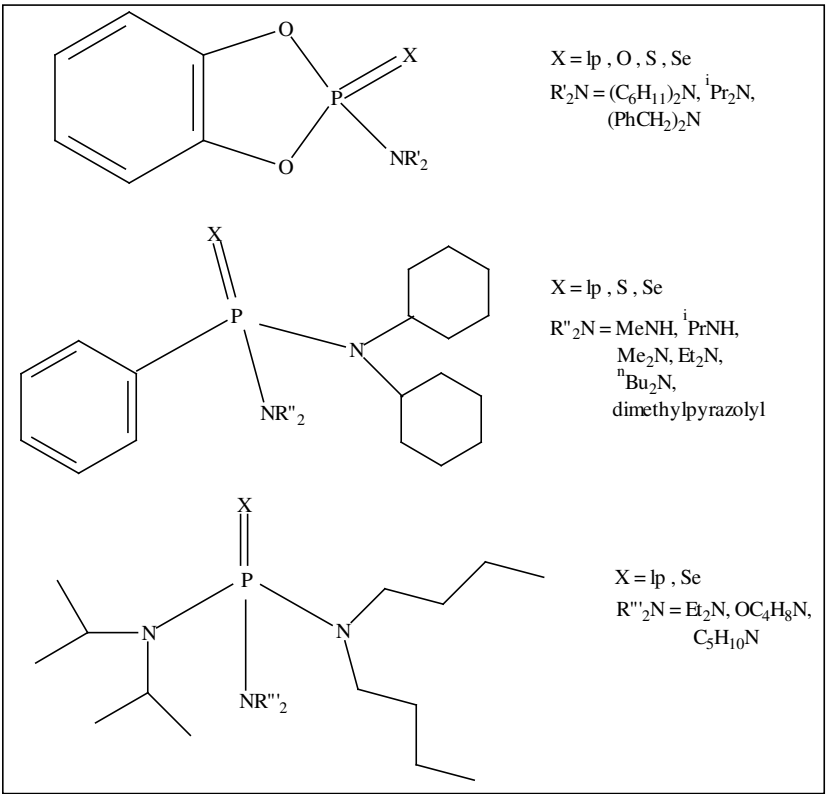


Figure 1. Phosphines and phosphine chalcogenides synthesized in this study (lp = lone pair).

In case of the preparation of phosphine chalcogenides, elemental sulfur, selenium and tellurium powder were used for sulfuration, selenation and telluration reactions, respectively. 30 % w/v hydrogen peroxide solution was used for oxygenation reactions. All the reactions were performed in non-aqueous medium (benzene and/or acetonitrile) using a slight excess of the element chalcogen reagent (particularly in case of selenation and telluration reactions). Though hetero phase in nature, the oxygenation reactions attempted were quite fast, some were even exothermic and only in a couple of cases, pure products could be isolated in moderate yields. This is because of the highly reactive and polar phosphorus(III)-nitrogen bond which gets cleaved when aqueous solution (30 % w/v) of hydrogen peroxide is used for the reactions. Elemental sulfur reacted smoothly at room temperature. Phosphine sulfides were isolated in 65-70 % yield from reactions run for ~ 15-20 h. Selenation reactions are comparatively slower and demanded fairly long refluxion times (15-20 h) in benzene or acetonitrile (*ca.* 80 °C). Telluration reactions were unsuccessful even after *ca.* 24 h of reflux in benzene (60-80 °C). Except for the three selenides of the chiral tris(amino)phosphines which are pale yellow viscous liquids, all other derivatives are isolated as colourless crystalline solids. Phosphine chalcogenides were found to be more stable to air and moisture, compared to the parent phosphines in all cases.

Characterization aspects

^{31}P-NMR data of phosphines

^{31}P-NMR data of the phosphines synthesized are given in Table 1. Proton decoupled ^{31}P-NMR spectra of the phosphines synthesized show a sharp singlet feature for the signal in all the cases. The chemical shift values span over a wide range for all the aminophosphines synthesized (*ca.* 57 - 155 ppm). The observed chemical shifts can be classified into three kinds, namely (i) phenyl(amino), (ii) (*o*-phenylenedioxo)amino and (iii) chiral aminophosphines. It is seen that the phenyl(amino)phosphines, (Ph)[$(C_6H_{11})_2$N](R$_2$N)P give rise to the most shielded signals (*ca.* 57 - 80 ppm) whereas monochloro(amino)phosphine and (*o*-phenylenedioxo)aminophosphines possess the most deshielded signals (*ca.* 131 - 144 and 144 - 154 ppm, respectively). Among the phenyl(amino)phosphines, the change in the δ-value observed provide scope to discern the substituent effect as two of the groups attached to phosphorus are same in all the cases. Accordingly, it can be said that both primary and secondary nature of the amino substituent and its steric bulk exert influence on the magnitude of the phosphorus chemical shift. The substituent steric effect is also revealed in case of monochloro and (*o*-phenylenedioxo)aminophosphines. It suggests that the increase in steric bulk of the substituent exerts a greater shielding effect (values of other such compounds depicting this relation are given in ref. [6]). It is also clear from this study that the phenyl substituent on phosphorus exerts a greater influence on shielding the phosphorus signal than that of the sterically bulky amino substituent. Interestingly, the chiral tris(amino)phosphines containing three different P-N bonds give rise to practically the same chemical shift values. All these results obtained seem to reinforce further, the known fact that the shielding mechanism of the phosphorus nucleus is more complex in nature compared to that of a proton [10, 30].

Table 2 gives the effect of amino groups on phosphorus atom when chlorine in PCl_3 is substituted stepwise by amines. As expected, when electronegative chlorine groups are gradually removed, a shielding effect is seen around phosphorus which is revealed by the δ_P values.

Table 1. ^{31}P-NMR data of the phosphines synthesized.

Serial No.	Phosphine*	δ_P (ppm)
1	PCl_3	223.0
2	$PhPCl_2$	159.8
3	$(^iPr_2N)PCl_2$	168.4
4	$Ph(Cx_2N)PCl$	131.7
5	$(o\text{-}C_6H_4O_2)PCl$	172.3
6	$(^iPr_2N)(^nBu_2N)PCl$	144.0
7	$(^iPr_2N)(^nBu_2N)(Et_2N)P$	104.3
8	$(^iPr_2N)(^nBu_2N)(OC_4H_8N)P$	103.8
9	$(^iPr_2N)(^nBu_2N)(C_5H_{10}N)P$	103.9
10	$(Ph)(Cx_2N)(MeNH)P$	67.9
11	$(Ph)(Cx_2N)(^iPrNH)P$	57.9
12	$(Ph)(Cx_2N)(Me_2N)P$	79.5
13	$(Ph)(Cx_2N)(Et_2N)P$	78.4
14	$(Ph)(Cx_2N)(^nBu_2N)P$	79.8
15	$(Ph)(Cx_2N)(DMP)P$	63.2
16	$(o\text{-}C_6H_4O_2)(^iPr_2N)P$	154.2
17	$(o\text{-}C_6H_4O_2)(Cx_2N)P$	150.7
18	$(o\text{-}C_6H_4O_2)[(PhCH_2)_2N]P$	144.4

* Serial Nos. 1-5 are reported in the literature (given here for comparison). Me – methyl, Et – ethyl, ^{i}Pr – isopropyl, ^{n}Bu – n-butyl, Cx – cyclohexyl, Ph – phenyl, DMP - dimethylpyrazolyl.

Table 2. Comparison of δ_P values for PCl_3 and its amino derivatives.

Compound	^{31}P-NMR (δ, ppm)
PCl_3	223.0
$(^iPr_2N)PCl_2$	168.4
$(^iPr_2N)(^nBu_2N)PCl$	144.0
$(^iPr_2N)(^nBu_2N)(Et_2N)P$	104.0

^{31}P-NMR data of phosphine chalcogenides

^{31}P- and ^{77}Se-NMR data of the phosphine chalcogenides synthesized are given in Table 3 and 4. All the phosphine selenides give a sharp singlet for ^{31}P nucleus with ^{77}Se-satellites on either sides which enable calculate their $^1J_{P=Se}$ values. Compared to phosphines, the δ_P values for their selenides are shielded. Also, $(o\text{-}C_6H_4O_2)(R_2N)PSe$ derivatives have more deshielded chemical shift values compared to the other two sets of compounds, namely, $(Ph)[(C_6H_{11})_2N](R_2N)PSe$ and $(^iPr_2N)(^nBu_2N)(R_2N)PSe$. This may possibly be due to the electronegativity of the *o*-phenylenedioxo moiety.

Table 3. ^{31}P-NMR data of the phosphine chalcogenides synthesized.

Sl. No.	Phosphine chalcogenides	δ_P (ppm)
1	$(Ph)[(C_6H_{11})_2N](Me_2N)P{=}S$	73.6
2	$(Ph)\ [(C_6H_{11})_2N](Et_2N)P{=}S$	72.4
3	$(Ph)\ [(C_6H_{11})_2N](^nBu_2N)P{=}S$	73.0
4	$(o\text{-}C_6H_4O_2)(^iPr_2N)P{=}S$	84.2
5	$(o\text{-}C_6H_4O_2)\ [(C_6H_{11})_2N]P{=}S$	85.2
6	$(o\text{-}C_6H_4O_2)\ [(C_6H_{11})_2N]P{=}O$	19.4
7	$(o\text{-}C_6H_4O_2)[(PhCH_2)_2N]P{=}O$	21.3

Table 4. ^{31}P- and ^{77}Se-NMR data of the phosphine selenides synthesized.

Serial No.	Phosphine selenide	δ_P (ppm)	δ_{Se} (ppm)	$^1J_{P=Se}$ (Hz)
1	(^{i}Pr$_2$N)(^{n}Bu$_2$N)(Et$_2$N)P=Se	72.0	- 207.3	785
2	(^{i}Pr$_2$N)(^{n}Bu$_2$N)(OC$_4$H$_8$N)P=Se	70.5	- 224.9	791
3	(^{i}Pr$_2$N)(^{n}Bu$_2$N)(C$_5$H$_{10}$N)P=Se	70.2	- 251.0	779
4	(Ph)[(C$_6$H$_{11}$)$_2$N](Me$_2$N)P=Se	73.3	- 275.4	771
5	(Ph) [(C$_6$H$_{11}$)$_2$N] (Et$_2$N)P=Se	70.9	- 195.4	766
6	(Ph) [(C$_6$H$_{11}$)$_2$N] (^{n}Bu$_2$N)P=Se	71.5	- 205.4	778
7	(*o*-C$_6$H$_4$O$_2$)(^{i}Pr$_2$N)P=Se	86.8	- 167.0	987
8	(*o*-C$_6$H$_4$O$_2$) [(C$_6$H$_{11}$)$_2$N]P=Se	87.9	- 169.0	978
9	(*o*-C$_6$H$_4$O$_2$)[(PhCH$_2$)$_2$N]P=Se	91.5	- 251.7	1009

Generally, the phosphine oxides seem to possess highly shielded chemical shift values (19 - 22 ppm) compared to the other chalcogenide analogues (70 - 92 ppm). This observation supports the fact that for the phosphine oxides, the π-bond form ≥P=E is important whereas for sulfides and selenides, the dipolar form ≥P$^+$-E$^-$ predominates. A similar observation was also reported in the literature stating that π-bond contribution is much less for a heavier chalcogen atom (like Se, Te) and is more for a lighter chalcogen atom (like O), based on infrared spectral studies (phosphorus-chalcogen atom stretching frequency, $\nu_{P=X}$) [30, 31]. Further, McFurlane and Rycroft in 1973 [14] have studied this aspect particularly with selenides and have concluded that in cases where phosphorus approaches along with its *3d* orbitals for π-bonding interaction with its substituents, the dipolar form predominates the phosphorus-selenium bond.

^{77}Se-NMR data of phosphine selenides

^{77}Se-NMR spectra of the phosphine selenides show a sharp doublet due to direct one bond coupling interaction of ^{77}Se with ^{31}P ($^1J_{P=Se}$). ^{77}Se signals are highly shielded (negative δ-values), clearly indicating again the existence of dipolar form, ≥P$^+$-E$^-$, where negative sign resides on the selenium atom (implying more electron density on selenium atom). In spite of similar environment that is encountered around phosphorus atom, the δ-values occur over a very wide range (*ca.* – 167 to – 275 ppm), which clearly highlights the subtle effects of the substituents on phosphorus. Among the three types of phosphine selenides synthesized in this study, a clear and readily understandable trend in both δ and J does not seem to emerge. However, it may be seen that at least six of the nine examples synthesized show a δ-range of –220 ± 30 ppm and a $^1J_{P=Se}$ range of 780 ± 15 Hz.

Mass spectral data of phosphines

Mass spectral data of the phosphines synthesized are given in Table 5. The mass spectral data have not only helped in establishing the authenticity of the various phosphines synthesized, but also have given scope to realize the relative stabilities of the phosphine molecules as such, their fragments and substituent effects. Accordingly, (*o*-phenylenedioxo)aminophosphines and phenyl(amino)phosphines are more stable compared to chloroamino and chiral tris(amino)phosphines as inferred by the observed intensities of the peak due to their molecular ions. $[M\text{-}Cl]^{+\cdot}$ and $[M\text{-}NR_2]^{+\cdot}$ peaks respectively are observed to be stronger peaks than $M^{+\cdot}$ peak in case of chloroamino and chiral tris(amino)phosphines. Another important observation made is that the dicoordinate phosphenium cation, $[R_1R_2P]^+$ is seen in considerable intensities in all the cases. This is in line with the observations reported in the literature [17 - 20]. Both in phenylbis(amino)-, Ph(R$_2$N)(R'$_2$N)P and chiral tris(amino)phosphines, (R$_2$N)(R'$_2$N)(R''$_2$N)P, the phosphenium ion arising from the loss of sterically most bulky amino group, *viz.,* (C$_6$H$_{11}$)$_2$N in

the former and $^{i}Pr_2N$ in the latter was found to be very intense compared to the other possible cleavage processes involving amino substituents. Similarly, (*o*-phenylenedioxo)phosphenium cation, $[(o\text{-}C_6H_4O_2)P]^+$ was also found to be very intense in all the cases. In general, the fragmentation pattern observed revealed that the P-N bond cleavage occurs more readily than P-C bond.

Table 5. Mass spectral data (% intensities) of the phosphines synthesized.

a. $(Ph)[(C_6H_{11})_2N](R)P$

Fragment	R					
	Me_2N	Et_2N	$^{n}Bu_2N$	DMP	MeNH	^{i}PrNH
M	27	30	48	2	70	65
M–R	20	23	53	23	10	8
M–Ph	1	1	1	--	13	14
M–Cx*	14	14	17	--	22	24
M–(R,Cx)+H	20	16	46	6	9	7
M-Cx_2N	100	100	100	6	100	100
Cx_2N	75	76	81	33	80	81
PhPH	58	56	75	4	34	37
CxNH	16	14	18	12	40	36
Ph	7	5	3	3	7	9
R	35	32	43	100	8	4

* Cx = Cyclohexyl, C_6H_{11}.

b. $(o\text{-}C_6H_4O_2)(R_2N)P$

Fragment	R		
	^{i}Pr	C_6H_{11}	$PhCH_2$
M	90	80	64
M-R	8	28	50
M-R_2N	98	100	75
R_2N	--	50	--
R	10	10	100

c. $(^{i}Pr_2N)(^{n}Bu_2N)(R)P$

Fragment	R			
	Et_2N	OC_4H_8N	$C_5H_{10}N$	Cl*
M	16	12	21	24
M-$^{i}Pr_2N$	51	47	88	60
M-$^{n}Bu_2N$	74	20	43	56
M-R	46	22	20	30
$^{i}Pr_2N$	62	28	35	50
$^{n}Bu_2N$	62	30	27	30
R	100	100	100	--
$(^{i}Pr_2N)PH$	9	7	23	--
$(^{n}Bu_2N)PH$	28	30	40	--
RPH	34	42	95	--

*$(^{i}PrNH)PCl$: 16; $(^{i}PrNH)$: 18.

Mass spectral data of phosphine chalcogenides

Mass spectral data of the phosphine chalcogenides synthesized are given in Table 6 and 7. A systematic mass spectral analysis of P-C bonded phosphines and the corresponding selenides was reported by Mirinda and coworkers in 1993 [32]. This is for the first time, mass spectra of various types of aminophosphine chalcogenides have been recorded which have provided scope to verify the effect of different chalcogen atom on the fragmentation pattern. Some of the interesting features observed are given below.

The molecular ion peak for selenides is of low intensity which reflects their poor stability. Chiral tris(amino)phosphine selenide derivatives do not give $[M\text{-}Se]^+$ fragment. In case of selenides, $[M\text{-}Se(NR_2)]^+$ peak is noticed in appreciable intensities especially when 'R' is a bulky group. Table 8 provides a comparison of mass spectral behaviour of a phosphine and its chalcogenides.

Here, it can be seen that (a) the stability of the molecular ion decreases in the order, lp > O > S > Se with increase in the steric crowding around phosphorus and (b) the intensity of $[M\text{-}X]^+$ increases in the order, O < S < Se, once again supporting the fact that the dipolar form structure, $\geq P^+\text{-}E^-$ is important for phosphine chalcogenides with heavier chalcogen atoms. The fact that the $[M\text{-}X]^+$ peak is the base peak for the selenide suggests the weak nature of the phosphorus-selenium bond. In all the (*o*-phenylenedioxo)phosphine chalcogenide derivatives, (*o*-phenylenedioxo)phosphenium cation fragment, $[(o\text{-}C_6H_4O_2)P]^+$ is quite intense. Dicyclohexylamino-containing derivatives gave the fragment $[(C_6H_{11})_2N]^+$ in appreciable intensity reflecting its stability.

Table 6. Mass spectral data (% intensities) of the phosphine chalcogenides synthesized

a. $(Ph)(Cx_2N)(R_2N)P{=}S^*$

R	M	M-S	M-Cx_2N	M-R_2N	M-Cx_2N(S)	M-R_2N(S)	Cx_2N	R_2N	CxNH
Me	24	2	26	2	20	3	100	--	10
Et	27	4	22	2	100	6	97	9	5
^{n}Bu	21	7	28	4	20	9	100	28	6

b. $(o\text{-}C_6H_4O_2)(R_2N)P{=}S$

R	M	M-S	M-SR	M-R_2N	M-R_2N(S)	M-R	R_2N	RNH
^{i}Pr	36	61	6	70	100	38	94	14
C_6H_{11}	28	58	16	40	62	15	100	65

c. $(o\text{-}C_6H_4O_2)(R_2N)P{=}O^*$

R	M	M-O	M-OR	M-R_2N	M-R_2N(O)	M-R	Cx_2N	CxNH	Cx
Cx	46	4	2	12	17	23	100	24	4

*Cx = Cyclohexyl, C_6H_{11}.

Table 7. Mass spectral data (% intensities) of the phosphine selenides synthesized

a. $(Ph)[(C_6H_{11})_2N](R_2N)P{=}Se^*$

R	M	M-Se	M-Cx_2N	M-R_2N	M-Cx_2N(Se)	M-R_2N(Se)	Ph	Cx_2N	R_2N	CxNH
Me	12	13	11	1	100	2	3	82	--	18
Et	6	2	6	1	100	12	4	98	18	7
^{n}Bu	11	6	10	1	84	28	1	100	26	6

b. (o-$C_6H_4O_2$)(R_2N)P=Se

R	M	M-Se	M-R	M-R_2N	M-SeR	M-R_2N(Se)	R_2N	RNH	R
^{i}Pr	8	42	2	8	3	100	4	5	--
C_6H_{11}	22	100	12	18	31	10	26	40	9
$PhCH_2$	15	71	9	8	12	100	8	3	85

c. (^{i}Pr_2N)(^{n}Bu_2N)(R)P=Se

Fragment	R		
	Et_2N	OC_4H_8N	$C_5H_{10}N$
M	17	10	11
M-Se	0	0	0
M-^{i}Pr_2N	10	7	7
M-^{n}Bu_2N	4	6	4
M-R	3	3	2
M-^{i}Pr_2N(Se)	100	78	100
M-^{n}Bu_2N(Se)	18	18	20
M-SeR	13	8	23
^{i}Pr_2N	65	100	57
^{n}Bu_2N	30	40	36
R	32	53	56
(^{i}Pr_2N)PH	4	4	6
(^{n}Bu_2N)PH	40	14	38
RPH	63	34	67

Table 8. Comparison of mass spectral data (% intensities) for [o-$C_6H_4O_2$)][($C_6H_{11})_2N$]PX.

X	M	M-X	M-XR	M-NR_2	M-XNR_2	M-R	Cx_2N	CxNH	Cx
lp	80	--	--	100	--	28	50	12	10
O	46	4	2	12	17	23	100	24	4
S	28	58	16	40	62	15	100	65	9
Se	22	100	81	31	20	16	26	71	33

CONCLUSIONS

Simple condensation reaction can be conveniently employed for synthesizing any complex phosphine, provided proper conditions are employed. Oxygenation reactions are too fast and sulfuration and selenation reactions are moderate and telluration reactions are too slow. A good collection of aminophosphines and the corresponding chalcogenides are used for this study along with their ^{31}P-NMR, ^{77}Se-NMR and mass spectral data. These studies indicate that the dipolar form favours the chalcogenides with heavier chalcogen atom and π-bond form favours the chalcogenides with lighter chalcogen atom.

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