Inorg. Chem. **2006**, *45*, 5893–5897

Intramolecular Amine-Induced [1,3]-Sigmatropic Rearrangement in the Reactions of Aminophosphinites or Phosphites with Elemental Sulfur or Selenium

P. Chandrasekaran,[†] Joel T. Mague,[‡] and Maravanji S. Balakrishna*[,†]

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India, and Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Received March 10, 2006

Ether- and thioether-functionalized cyclodiphosphazanes *cis*-[^{t}BuNP(OCH$_2$CH$_2$EMe)]$_2$ (E = O, **1**; E = S, **2**) react with 2 equiv of elemental sulfur or selenium to produce dichalcogenides *cis*-[^{t}BuNP(E)(OCH$_2$CH$_2$EMe)]$_2$ (**4**–**6**), whereas the similar reaction of amine-functionalized cyclodiphosphazane *cis*-[^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)]$_2$ (**3**) with elemental chalcogen results in the formation of thio- or selenophosphates *trans*-[^{t}BuNP(O)(ECH$_2$CH$_2$NMe$_2$)]$_2$ (E = S, **7**; E = Se, **8**) through [1,3]-sigmatropic rearrangement. The X-ray crystal structure of **8** confirms the rearranged product as the trans isomer with a planar P$_2$N$_2$ ring. The equimolar reaction of P(OCH$_2$CH$_2$OMe)$_3$ (**9**) with elemental sulfur or selenium produces the simple sulfide and selenide E═P(OCH$_2$CH$_2$OMe)$_3$ (E = S, **11**; E = Se, **12**) derivatives, respectively. In contrast, the reaction between P(OCH$_2$CH$_2$NMe$_2$)$_3$ (**10**) and S or Se furnishes the rearranged products (**13** and **14**). The rearrangement reaction was monitored by ^{31}PNMR spectroscopy, which confirms the formation of selenophosphinic acid as the first step of the rearrangement. The [1,3]-sigmatropic rearrangement presumably takes place through chalcogen–nitrogen interactions.

Introduction

Recently, we have reported[1] a new synthetic route for inserting carbon fragments into phosphorus−nitrogen bonds; the reactions proceed thermodynamically through the conversion of trivalent phosphorus into the corresponding phosphine-oxide derivatives. Formation of phosphine oxide (P═O) is the main driving force for many phosphorus-based reactions, such as the Wittig,[2] Michaelis−Arbuzov,[3] and Mitsunobu reactions.[4] Many sigmatropic rearrangements involving the formation of a P═O bond as the driving force are documented in the literature; significant ones are the [3,3]-rearrangement of allylic phosphorimidates to phosphoramidates,[5] [2,3]-rearrangement of allyl phosphites into allyl phosphonates,[6] and palladium-catalyzed sigmatropic rearrangement of (allyloxy)iminodiazaphospholidines.[7] Interestingly, the sigmatropic rearrangement of selenophosphinic acid leading to the formation of chalcogenophosphate is not well-known.[8] These kinds of chalcogenophosphates are prepared by reacting either R$_2$P−Cl with RSeM[9] or phosphinoselenoic halides (R$_2$P(Se)X) with sodium hydroxide followed by the addition of alkyl iodide,[10] as shown in Scheme 1.

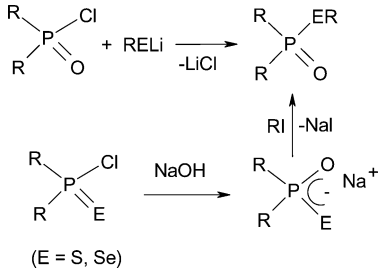
Several groups have illustrated the unique ability of cyclodiphosphazanes and their chalcogen derivatives, *cis*-[XP(E)(μ-N^{t}Bu)]$_2$ (X = NHR, E = lone pair, O, S, and Se),

* To whom correspondence should be addressed. Fax: (91) 22-2572-3480. Phone: (91) 22-2576-7181. E-mail: krishna@chem.iitb.ac.in.
† Indian Institute of Technology Bombay.
‡ Tulane University.

(1) (a) Priya, S.; Balakrishna, M. S.; Mague, J. T.; Mobin, S. M. *Inorg. Chem.* **2003**, *42*, 1272−1281. (b) Priya, S.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem. Commun.* **2001**, *4*, 437−440. (c) Priya, S.; Balakrishna, M. S.; Mobin, S. M. *Polyhedron* **2005**, *24*, 1641−1650.
(2) (a) Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1411−1416. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927.
(3) (a) Mugrage, B.; Diefenbacher, C.; Somers, J.; Parker, D. T.; Parker, T. *Tetrahedron Lett.* **2000**, *41*, 2047−2050. (b) Malachowski, W. P.; Coward, J. K. *J. Org. Chem.* **1994**, *59*, 7625−7634.
(4) (a) Dandapani, S.; Curran, D. P. *Chem.—Eur. J.* **2004**, *10*, 3130−3138. (b) Satish Kumar, N.; Praveen Kumar, K.; Pavan Kumar, K. V. P.; Kommana, P.; Vittal, J. J.; Kumara Swamy, K. C. *J. Org. Chem.* **2004**, 69, 1880−1889.
(5) (a) Chen, B.; Mapp, A. K. *J. Am. Chem. Soc.* **2004**, *126*, 5364−5365. (b) Chen, B.; Mapp, A. K. *J. Am. Chem. Soc.* **2005**, *127*, 6712−6718.
(6) Janecki, T.; Bodalski, R. *Synthesis* **1990**, 799−801.
(7) Lee, E. E.; Bately, R. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1865−1868.
(8) Nuretdinov, I. A.; Buina, N. A.; Bayandika, E. V. *Zh. Obshch. Khim.* **1978**, *48*, 1073−1078.
(9) (a) Kimura, T.; Murai, T.; Mizuhata, N. *Heteroat. Chem.* **2005**, *16*, 185−191. (b) Darmadi, A.; Haas, A.; Kaschani-Motlagh, M. *Z. Anorg. Allg. Chem.* **1979**, *448*, 35−39.
(10) (a) Kimura, T.; Murai, T. *J. Org. chem.* **2005**, *70*, 952−959. (b) Stec, W. J.; Okrusecek, A.; Lesiak, K.; Uznanski, B.; Michalski, J. *J. Org. Chem.* **1976**, *41*, 227−233.

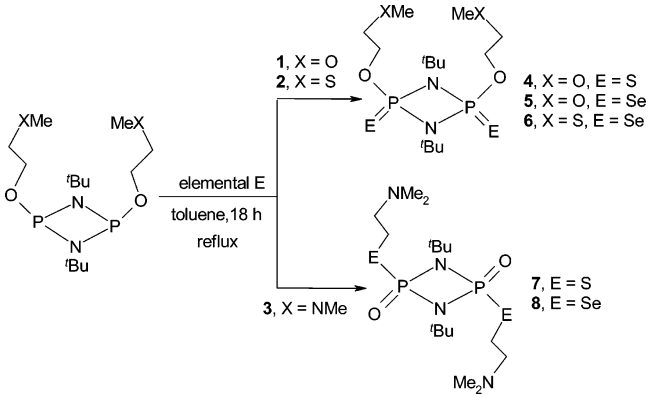
10.1021/ic060413m CCC: $33.50
Published on Web 06/30/2006

Scheme 1



to bring main-group metals into their coordination sphere;[11] these compounds also exhibit Lewis-base behavior,[12] perform ring-transformation reactions,[13] and successfully incorporate P_2N_2 rings into macrocyclic ligands.[14] We have reported the synthesis and organometallic chemistry of cyclodiphosphazanes containing ether-, thioether-, and amine-functionalized hemilabile ponytails.[15] In this paper, we describe the reactions of amine-functionalized cyclodiphosphazanes with elemental sulfur or selenium, furnishing the chalcogenophosphates via intramolecular-base-induced [1,3]-sigmatropic rearrangement, observed for the first time with cyclodiphosphazanes.

Scheme 2



Results and Discussion

The reaction of 2 equiv of S_8 or gray selenium with *cis*-[^{t}BuNP(OCH$_2$CH$_2$OMe)]$_2$ (**1**) in toluene under refluxing conditions affords the corresponding disulfide (**4**) or diselenide (**5**) derivatives, respectively, as oily liquids in good yield (Scheme 2). The ^{31}P NMR spectrum of **4** shows a single resonance at 48.6 ppm, whereas the corresponding diselenide derivative **5** exhibits a singlet at 44.6 ppm with ^{77}Se satellites attributable to the AA′X spin system typical for *cis*-selenium derivatives of cyclodiphosphazanes.[12d] The A−X ($^1J_{PSe}$) coupling constant is 953 Hz, whereas the A−A′ ($^2J_{PP}$) coupling constant is 6.7 Hz. Similarly, the reaction of thioether derivative *cis*-[^{t}BuNP(OCH$_2$CH$_2$SMe)]$_2$ (**2**) with selenium leads to the formation of diselenide **6**. The ^{31}P NMR spectrum of **6** shows a single resonance at 42.3 ppm with coupling constant values ($^1J_{PSe}$ = 954 Hz, $^2J_{PP}$ = 6.8 Hz) comparable to those of **5**. Interestingly, the reaction of 2 equiv of selenium with amine-functionalized cyclodiphosphazane *cis*-[^{t}BuNP(OCH$_2$CH$_2$−NMe$_2$)]$_2$ (**3**) under identical reaction conditions gave a white solid **8** in 72% yield. The ^{31}P NMR spectrum shows a single resonance at 4.8 ppm with a considerably lower $^1J_{PSe}$ coupling of 495 Hz. This $^1J_{PSe}$ coupling clearly indicates the absence of a P═Se bond, and the value falls in the range for P−Se bonds.[16] Further, the diselenides of cyclodiphosphazanes always show an additional $^2J_{PP}$ coupling,[12d] which was not seen in the ^{31}P NMR spectrum of **8**. Moreover, the IR spectrum shows a sharp absorption at 1072 cm^{-1}, which corresponds to the stretching vibration of the P═O bond. On the basis of elemental analysis, NMR, and mass spectral data, we assigned the structure of product **8** as a [1,3]-sigmatropic rearranged selenophosphate (**8**) and not as the usual diselenide derivative. The structure was further confirmed by low-temperature single-crystal X-ray structure determination.

The molecular structure of **8** is shown in Figure 1, along with the selected bond parameters. Single crystals of **8** were grown from toluene at −30 °C. The molecule possesses a center of symmetry, and the asymmetric unit cell consists of half of the molecule. In molecule **8**, two P═O bonds are

(11) (a) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203−250. (b) Chivers, T.; Krahn, M.; Parvez, M. *Chem. Commun.* **2000**, 463−464. (c) Chivers, T.; Fedorchuk, C.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 1936−1942. (d) Chivers, T.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 2547−2553. (e) Briand, G. G.; Chivers, T.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2003**, *42*, 525−531.

(12) (a) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; Laurent, J. C. T. R. B. S. *Coord. Chem. Rev.* **1994**, *129*, 1−90. (b) Reddy, V. S.; Krishnamurthy, S. S.; Nethaji, M. *J. Chem. Soc., Dalton Trans.* **1995**, 1933−1938. (c) Briand, G. G.; Chivers, T.; Krahn, M. *Coord. Chem. Rev.* **2002**, *233*−*234*, 237−254. (d) Chivers, T.; Krahn, M.; Parvez, M.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 2547−2553. (e) Schranz, I.; Lief, G. R.; Carrow, C. J.; Haagenson, D. C.; Grocholl, L.; Stahl, L.; Staples, R. J.; Boomishankar, R.; Steiner, A. *Dalton Trans.* **2005**, 3307−3318. (f) Lief, G. R.; Moser, D. F.; Stahl, L.; Staples, R. J. *J. Organomet. Chem.* **2004**, *689*, 1110−1121. (g) Lief, G. R.; Carrow, C. J.; Stahl, L.; Staples, R. J. *Chem. Commun.* **2001**, 1562−1563.

(13) (a) Burford, N.; Cameron, T. S.; Lam, K. C.; LeBlanc, D. J.; McDonald, C. L. B.; Philips, A. D.; Rheingold, A. L.; Stark, L.; Walsh, D. *Can. J. Chem.* **2001**, *79*, 342−348. (b) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; MacDonald, C. L. B.; Ovans, R.; Phillips, A. D.; Ragogna, P. J.; Walsh, D. *Can. J. Chem.* **2002**, *80*, 1404−1409. (c) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012−14013. (d) Burford, N.; Dyker, C. A.; Phillips, A. D.; Spinney, H. A.; Deckon, A.; McDonald, R.; Ragogna, P. J.; Rheingold, A. L. *Inorg. Chem.* **2004**, *43*, 7502−7507. (e) Burford, N.; Edelstein, E.; Landry, J. C.; Ferguson, M. J.; McDonald, R. *Chem. Commun.* **2005**, 5074−5076. (f) Burford, N.; Conroy, K. D.; Landry, J. C.; Ragogna, P. J.; Ferguson, M. J.; McDonald, R. *Inorg. Chem.* **2004**, *43*, 8245−8251. (g) Garcia, F.; Kowenicki, R. A.; Riera, L.; Wright, D. S. *Dalton Trans.* **2005**, 2495−2496.

(14) (a) Kumaravel, S. S.; Krishnamurthy, S. S.; Cameron, T. S.; Linden, A. *Inorg. Chem.* **1988**, *27*, 4546−4550. (b) Kommana, P.; Vittal, J. J.; Kumara Swamy, K. C. *Polyhedron* **2003**, *22*, 843−847. (c) Kommana, P.; Kumara Swamy, K. C. *Inorg. Chem.* **2000**, *39*, 4384−4385. (d) Dodds, F.; Garcia, F.; Kowenicki, R. A.; McPartlin, M.; Steiner, A.; Wright, D. S. *Chem. Commun.* **2005**, 3733−3735. (e) Dodds, F.; Garcia, F.; Kowenicki, R. A.; McPartlin, M.; Riera, L.; Steiner, A.; Wright, D. S. *Chem. Commun.* **2005**, 5041−5043. (f) Doyle, E. L.; Riera, L.; Wright, D. S. *Eur. J. Inorg. Chem.* **2003**, 3279−3289. (g) Doyle, E. L.; Garcia, F.; Humprey, S. M.; Kowenicki, R. A.; Riera, L.; Woods, A. D.; Wright, D. S. *Dalton Trans.* **2004**, 807−812. (h) Garcia, F.; Goodman, J. M.; Kowenicki, R. A.; McPartlin, M.; Riera, L.; Silva, M. A.; Wirsing, A.; Wright, D. S. *Dalton Trans.* **2005**, 1764−1773. (i) Garcia, F.; Kowenicki, R. A.; Kuzu, I.; Riera, L.; McPartlin, M.; Wright, D. S. *Dalton Trans.* **2004**, 2904−2909.

(15) (a) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Organometallics* **2005**, *24*, 3780−3783. (b) Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. *Inorg. Chem.* **2005**, *44*, 7925−7932.

(16) Kimura, T.; Murai, T. *J. Org. Chem.* **2005**, *70*, 5611−5617.

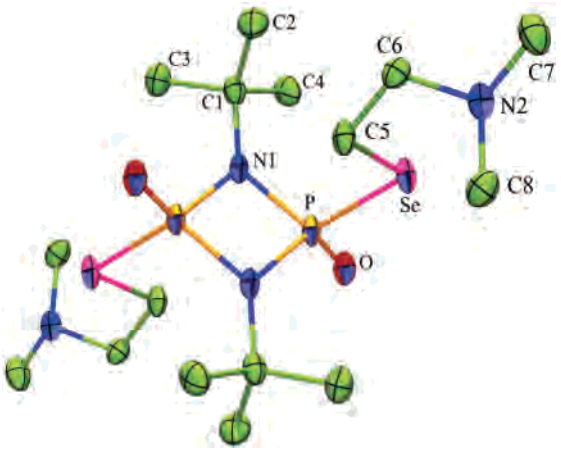


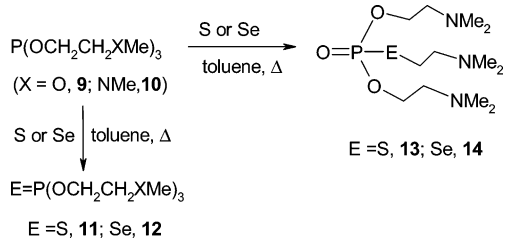
Figure 1. Molecular structure of **8** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Se−P = 2.211(2), Se−C(5) = 1.980(4), P−O = 1.476(2), P−N(1) = 1.686(2); P−Se−C(5) = 97.63(11), Se−P−O = 107.73(6), P−N(1)−P(a) = 95.79(9).

arranged in trans configuration, likewise the alkyl ($SeCH_2CH_2NMe_2$) substituents on phosphorus centers. The P═O bond distance in **8** (1.476(2) Å) is slightly longer than that in Ph_3PO (1.46(1) Å)[17] and is shorter when compared to the same in $^tBu_3PO$ (1.590(1) Å).[18] The P−Se bond distance of 2.211(2) Å is consistent with the reported literature values.[19] The bond angles around the nitrogen centers of the N_2P_2 ring sums to 360°, indicating the ring-planarity characteristic of cyclodiphosphazanes with trans conformation.[20]

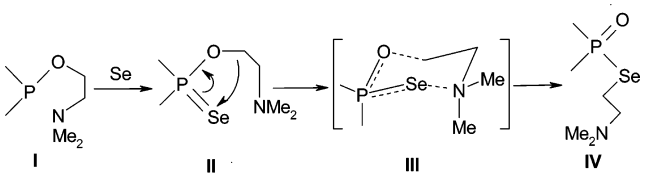
The reaction of *cis*-[^{t}BuNP($OCH_2CH_2NMe_2$)]$_2$ (**3**) with 2 equiv of elemental sulfur also leads to the formation of rearranged product **7**, as indicated by NMR spectroscopy. The ^{31}P NMR spectrum of **7** exhibits a single resonance at 17.8 ppm, which is more shielded compared to that of **4**. In the ^{1}H NMR spectrum of parent compound **3**, the peak corresponding to $POCH_2$ appeared as a multiplet at 3.96 ppm, whereas in **7**, the signal for the same methylene proton appears at 3.03 ppm. This significant change arises because of the presence of a less-electronegative sulfur atom next to the methylene group.

The ether- and amine-functionalized phosphites $P(OCH_2CH_2OMe)_3$ (**9**) and $P(OCH_2CH_2NMe)_3$ (**10**) were prepared in order to get more insight into the [1,3]-sigmatropic rearrangement of amine-functionalized cyclodiphosphazanes. Ether-functionalized phosphite **9** was synthesized by reacting PCl_3 with 3 equiv of 2-(methoxy)ethanol in diethyl ether using triethylamine, whereas amine-functionalized phosphite $P(OCH_2CH_2NMe)_3$ (**10**) was prepared by treating PCl_3 with 3 equiv of sodium salt of 2-(dimethylamino)ethanol in THF. The ^{31}P NMR spectra of **9** and **10** show single resonances at 139.8 and 137.5 ppm, respectively. The reactions of

Scheme 3



Scheme 4



$P(OCH_2CH_2XMe)_3$ (**9** and **10**) with elemental sulfur in toluene under refluxing conditions produce **11** and **13** (Scheme 3). The ^{31}P NMR spectrum of **11** shows a single resonance at 66.8 ppm, identifying the product as a sulfide derivative. The ^{31}P NMR resonance at 27.3 ppm for **13** confirms the formation of a rearranged product. Under similar reaction conditions, the reactions of **9** and **10** with 1 equiv of elemental selenium produce pale yellow oily products **12** and **14**, respectively. The ^{31}P NMR spectrum of **12** shows a singlet at 71.3 ppm with $^1J_{PSe}$ = 953 Hz, clearly indicating the existence of a P═Se bond. The ^{31}P NMR spectrum of **14** shows a single resonance at 20.5 ppm with $^1J_{PSe}$ = 495 Hz, which indicates the formation of a rearranged product.

To get further insight into the mechanism of these rearrangement reactions, we monitored the progress of the reaction using ^{31}P NMR spectroscopy. The equimolar mixture of $P(OCH_2CH_2NMe_2)_3$ (**10**) and elemental selenium were taken in C_6D_6 in a NMR tube and heated to 80 °C; ^{31}P NMR spectra were recorded at 1 h intervals. Within 1 h, the complete conversion of $P(OCH_2CH_2NMe_2)_3$ to $Se{=}P(OCH_2CH_2NMe_2)_3$ was observed, as indicated by the appearance of a peak at 74.9 ppm ($^1J_{PSe}$ = 953 Hz). The chemical shift and coupling constant values were in good agreement with similar selenide derivative **12**. At the same time, a new peak at 22.4 ppm ($^1J_{PSe}$ = 478 Hz) started appearing. As time progresses, the intensity of the peak at 74.9 decreases with a steady increase in the intensity of the peak at 22.4 ppm. After 14 h, the selenophosphinic acid derivative (**II**) was completely converted into the rearranged product (**IV**) (Scheme 4). Throughout the NMR studies, we did not observe any intermediates or the formation of any new species. In the previously reported[21] thermal conversion of phosphorylimidate to phosphorylamidate rearrangement reaction, an intermolecular mechanism was suggested on the basis of kinetic studies. In the present case, an intermolecular mechanism, in which the functional group does not play any role, can be ruled out, because only the aminophosphite or phosphite containing the NMe_2 functional group produces the rearranged product. Further, the rearrangement reactions

(17) Bandoli, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U.; Panattoni, C. *J. Chem. Soc., A* **1970**, 2778−2780.
(18) Rankin, D. W. H.; Robertson, H. E.; Seip, R.; Schmidbaur, H.; Blaschke, G. *J. Chem. Soc., Dalton Trans.* **1985**, 827−830.
(19) Sase, S.; Kano, N.; Kawashima, T. *J. Am. Chem. Soc.* **2002**, *124*, 9706−9707.
(20) (a) Silaghi-Dumitrescu, I.; Haiduc, I. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *91*, 21−36. (b) Dutasta, J. P.; Declercq, J. P.; Calderon, C. E.; Tinant, B. *J. Am. Chem. Soc.* **1989**, *111*, 7136−7144.
(21) Challis, B. C.; Challis, J. A.; Iley, J. N. *J. Chem. Soc., Perkin Trans. 2* **1978**, 813−818.

were carried out using nonpolar solvents (toluene and C_6D_6), and the products are formed in good yield. This indicates that the reaction may not involve any ionic intermediates during the rearrangement process. To assess the solvent and temperature effects on the rearrangement reaction, we carried out the reaction between $P(OCH_2CH_2NMe_2)_3$ and selenium at room temperature in toluene and THF. The reaction in toluene at room temperature (24 h) produced only diselenide whose ^{31}P NMR spectrum showed a single resonance at 70.9 ppm with $^1J_{PSe} = 945$ Hz. When the reaction was carried out in THF under reflux conditions for 18 h, only about 60% of the selenide derivative was converted into the rearranged product (selenophosphate), as calculated from the ^{31}P NMR peak intensities. These studies indicate that the polarity of the solvent does not have much effect on the rearrangement reaction and that high temperature is required for the rearrangement of selenide derivatives. From the above conclusions, we propose a tentative mechanism for the [1,3]-sigmatropic rearrangement of phosphite into the chalcogenophosphate, as shown in Scheme 4. The formation of selenophosphinic acid (**II**) is the first step, followed by the [1,3]-sigmatropic rearrangement. Here, the lone pair of electrons on the nitrogen atom plays an important role in forming the six-membered transition-state intermediate (**III**) through a N···Se interaction. These kinds of N···Se interactions[22] are well-documented in the literature compared to O···Se or S···Se interactions[23] and could be the reason for the formation of rearranged products.

Conclusions

In summary, the intramolecular amine-induced [1,3]-sigmatropic rearrangement of phosphite into chalcogenophosphates with elemental chalcogen was observed for the first time with cyclodiphosphazanes. During this rearrangement, the cyclodiphosphazane undergoes cis-to-trans isomerization. The interaction between N···E (E = S, Se) favors the rearrangement reaction by forming a six-membered transition state in amine-arm-containing phosphites. The ether- and thioether-functionalized phosphite derivatives lack corresponding strong O···E and S···E interactions for the rearrangement reactions. ^{31}PNMR spectroscopy studies confirmed that the initially formed selenophosphinic acid undergoes [1,3]-sigmatropic rearrangement to give selenophosphates. Further work to understand the effect of amine arm length and the influence of imido nitrogen substituents on the rearrangement and the possible synthetic utilities of this process is under way.

Experimental Section

All manipulations were performed under rigorously anaerobic conditions using high vacuum manifolds and Schlenk techniques. All the solvents were purified by a conventional procedure and distilled prior to use.[24] The *cis*-[^{t}BuNP(OCH_2CH_2XMe)]$_2$ (X = O, **1**; X = S, **2**; X = NMe, **3**) compounds were prepared according to published procedures.[15] 2-(Dimethylamino)ethanol was purchased from Lancaster Chemicals and used as received. 2-(Methoxy)-ethanol, PCl_3, sulfur, and selenium were purchased from SD Fine Chemicals. The ^{1}H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were recorded using a Varian 300 or 400 MHz spectrometer operating at the appropriate frequency using TMS and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield in all cases. IR spectra were recorded on a Nicolet Impact 400 FT-IR instrument in KBr disks. Microanalyses were performed on a Carlo Erba Model 1112 elemental analyzer. Mass spectra were obtained using Waters Q-Tof micromass (YA-105). Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of *cis*-[^{t}BuNP(S)(OCH_2CH_2OMe)]$_2$ (4). A mixture of *cis*-[^{t}BuNP(OCH_2CH_2OMe)]$_2$ (**1**) (0.42 g, 1.18 mmol) and elemental sulfur (0.075 g, 2.37 mmol) in 10 mL of toluene was refluxed for 18 h. The solution was cooled to room temperature and then filtered through a frit to remove unreacted sulfur. The solvent was removed under reduced pressure to afford product **4** as an oily liquid. Yield: 72% (0.35 g, 0.085 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (m, CH_2OP, 4H), 3.62 (t, CH_2, $^1J_{HH} = 4.4$ Hz, 4H), 3.37 (s, *OMe*, 6H), 1.51 (s, ^{t}Bu, 18H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 48.6 (s). FT-IR (KBr disk): $\nu_{P=S}$ 919 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{32}P_2N_2O_4S_2$: C, 40.18; H, 7.70; N, 6.69; S, 15.32. Found: C, 40.38; H, 7.91; N: 6.43; S, 15.13. MS(EI): 441.17 (m/z + Na).

Synthesis of *cis*-[^{t}BuNP(Se)(OCH_2CH_2OMe)]$_2$ (5). The synthesis was the same as that for **4**, using *cis*-[^{t}BuNP(OCH_2CH_2-OMe)]$_2$ (0.51 g, 1.44 mmol) and elemental selenium (0.22 g, 2.88 mmol) in 15 mL of toluene. Yield: 78% (0.57 g, 1.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (m, CH_2OP, 4H), 3.62 (t, CH_2, $^1J_{HH} = 4.7$ Hz, 4H), 3.37 (s, *OMe*, 6H), 1.55 (s, ^{t}Bu, 18H). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 44.6 (s, $^1J_{PSe} = 953$ Hz, $^2J_{PP} = 6.7$ Hz). FT-IR (KBr disk): $\nu_{P=Se}$ 578 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{32}P_2N_2O_4Se_2$: C, 32.82; H, 6.29; N, 5.46. Found: C, 32.97; H, 6.29; N: 5.66. MS(EI): 536.95 (m/z + Na).

Synthesis of *cis*-[^{t}BuNP(Se)(OCH_2CH_2SMe)]$_2$ (6). The synthesis was the same as that for **4**, using cis-[^{t}BuNP(OCH_2CH_2SMe)]$_2$ (**2**) (0.47 g, 1.31 mmol) and elemental selenium (0.20 g, 2.63 mmol). Yield: 68% (0.47 g, 0.88 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (m, CH_2OP, 4H), 2.67 (t, CH_2, $^1J_{HH} = 7.2$ Hz, 4H), 2.06 (s, *SMe*, 6H), 1.45 (s, ^{t}Bu, 18H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 42.3 (s, $^1J_{PSe} = 954$ Hz, $^2J_{PP} = 6.8$ Hz). FT-IR (KBr disk): $\nu_{P=Se}$ 560 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{32}P_2N_2$-$O_2S_2Se_2$: C, 30.88; H, 5.92; N, 5.14; S, 11.78. Found: C, 30.87; H, 6.07; N: 5.27; S, 11.54. MS(EI): 563.05 (m/z + Na).

Synthesis of *trans*-[^{t}BuNP(O)($SCH_2CH_2NMe_2$)]$_2$ (7). Synthesis was the same as that for **4**, using *cis*-[^{t}BuNP($OCH_2CH_2NMe_2$)]$_2$ (**3**) (0.22 g, 0.60 mmol) and elemental sulfur (0.038 g, 1.2 mmol). Yield: 78% (0.208 g, 0.47 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (m, CH_2SP, 4H), 2.62 (t, CH_2, $^1J_{HH} = 6.7$ Hz, 4H), 2.27 (s, NMe_2, 12H), 1.54 (s, ^{t}Bu, 18H). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 17.8 (s). FT-IR (KBr disk): $\nu_{P=O}$ 1089 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{38}P_2N_4O_2S_2$: C, 43.22; H, 8.61; N, 12.60; S, 14.42. Found: C, 43.65; H, 8.75; N, 12.66; S, 14.69. MS(EI): 467.43 (m/z + Na).

Synthesis of *trans*-[^{t}BuNP(O)($SeCH_2CH_2NMe_2$)]$_2$ (8). A mixture of *cis*-[^{t}BuNP($OCH_2CH_2NMe_2$)]$_2$ (0.38 g, 1.01 mmol) and

(22) (a) Kumar, S.; Kandasamy, K.; Singh, H. B.; Butcher, R. J. *Organometallics* **2004,** *23*, 4199−4208. (b) Mugesh, G.; Singh, H. B. *Chem. Soc. Rev.* **2000**, *29*, 347−357. (d) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1996**, *118*, 8077−8084.

(23) (a) Sanz, P.; Yanez, M.; Mo, O. *Chem.−Eur. J.* **2003**, *9*, 4548−4555. (b) Sanz, P.; Yanez, M.; Mo, O. *J. Phy. Chem. A* **2002**, *106*, 4661−4668. (c) Bleiholder, C.; Werz, D. B.; Koppel, H.; Gleiter, R. *J. Am. Chem. Soc.* **2006**, *128*, 2666−2674.

(24) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann Linacre House: Jordan Hill, Oxford, U.K., 1996.

elemental selenium (0.16 g, 2.03 mmol) in 15 mL of toluene was refluxed for 18 h. The solution was cooled to room temperature and filtered through Celite. The volume of the solution was reduced to 7 mL, and the solution was stored at −30 °C for 2 days to yield white crystals of **8**. Yield: 83% (0.45 g, 0.63 mmol). Mp: 140−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (m, CH_2SeP, 4H), 2.71 (t, CH_2, $^1J_{HH}$ = 6.7 Hz, 4H), 2.26 (s, NMe_2, 12H), 1.56 (s, ^{t}Bu, 18H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 4.8 (s, $^1J_{PSe}$= 495 Hz). FT-IR (KBr disk): $\nu_{P=O}$ 1072 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{38}P_2N_4O_2Se_2$: C, 35.69; H, 7.11; N, 10.40. Found: C, 36.02; H, 7.37; N, 10.56. MS(EI): 541.14 (*m*/*z* + 1).

Synthesis of P(OCH$_2$CH$_2$OMe)$_3$ (9). A solution of PCl_3 (4.72 g, 34.2 mmol) in 40 mL of diethyl ether was added dropwise to a well-stirred solution of 2-(methoxy)ethanol (7.84 g, 103 mmol) and Et_3N (10.4 g, 103 mmol), also in diethyl ether (250 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. The amine hydrochloride was removed by filtration, and the evaporation of the solvent at reduced pressure afforded compound **9** as a colorless, oily liquid. Yield: 93% (8.1 g, 31.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (m, CH_2OP, 6H), 3.50 (t, CH_2, 6H, J_{HH} = 6.2 Hz), 3.29 (s, *OMe*, 9H).^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 139.8 (s). Anal. Calcd for $C_9H_{21}O_6P$: C, 42.18; H, 8.26. Found: C, 42.47; H, 8.53. MS(EI): 279.14 (*m*/*z* + Na).

Synthesis of P(OCH$_2$CH$_2$NMe$_2$)$_3$ (10). A suspension of 2-(dimethylamino)ethanol (6.13 g, 68.7 mmol) and sodium (1.52 g, 66.0 mmol) was taken in 70 mL of THF in a two-necked flask attached with a reflux condenser and a dropping funnel. The reaction mixture was refluxed for 6 h and then allowed to cool to room temperature. The THF (30 mL) solution of PCl_3 (3.14 g, 22.0 mmol) was added to the reaction mixture at 0 °C. The reaction mixture was further stirred for 12 h at room temperature and then filtered through a frit to remove sodium chloride. The solvent was removed under reduced pressure to give **10** as an oily liquid. Yield: 85% (5.53 g, 18.7 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (m, CH_2OP, 6H), 2.53 (t, CH_2, 6H, J_{HH} = 5.8 Hz), 2.27 (s, NMe_2, 18H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 137.5 (s). Anal. Calcd for $C_{12}H_{30}N_3O_3P$: C, 48.79; H, 10.23; N, 14.22. Found: C, 48.63; H, 10.41; N, 14.12. MS(EI): 318.08 (*m*/*z* + Na).

Synthesis of S=P(OCH$_2$CH$_2$OMe)$_3$ (11). The synthesis was the same as that for **4**, using P(OCH$_2$CH$_2$OMe)$_3$ (0.937 g, 3.65 mmol) and sulfur (117 mg, 3.65 mmol). Yield: 78% (0.822 g, 2.84 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.24 (m, CH_2OP, 6H), 3.61 (t, CH_2, 6H, J_{HH} = 5.8 Hz), 3.38 (s, *OMe*, 9H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 66.8 (s). FT-IR (KBr disk): $\nu_{P=S}$ 927 (s) cm^{-1}. Anal. Calcd for $C_9H_{21}O_6S$: C, 37.49; H, 7.34; S, 11.12. Found: C, 37.68; H, 7.73; S, 11.43. MS(EI): 289.55 (*m*/*z* + 1).

Synthesis of Se=P(OCH$_2$CH$_2$OMe)$_3$ (12). The synthesis was the same as that for **5**, using P(OCH$_2$CH$_2$OMe)$_3$ (1.06 g, 4.14 mmol) and selenium (0.32 g, 4.14 mmol) in 20 mL of toluene. Yield: 79% (1.09 g, 3.25 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (m, CH_2OP, 6H), 3.62 (t, CH_2, 6H, J_{HH} = 6 Hz), 3.38 (s, *OMe*, 9H).^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 71.3 (s, $^1J_{PSe}$ = 953 Hz). FT-IR (KBr disk): $\nu_{P=Se}$ 566 (s) cm^{-1}. Anal. Calcd for $C_9H_{21}O_6$-PSe: C, 32.24; H, 6.31. Found: C, 32.07; H, 6.53. MS(EI): 359.07 (*m*/*z* + Na).

Synthesis of O=P(SCH$_2$CH$_2$NMe$_2$)(OCH$_2$CH$_2$NMe$_2$)$_2$ (13). The synthesis was the same as that for **7**, using P(OCH$_2$CH$_2$NMe$_2$)$_3$ (0.597 g, 2.02 mmol) and sulfur (0.065 g, 2.02 mmol). Yield: 66% (0.436 g, 1.33 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.16 (m, CH_2OP, 4H), 2.98 (m, CH_2SP, 2H), 2.82 (m, CH_2, 2H), 2.62 (m, CH_2, 4H), 2.28 (s, NMe_2, 12H), 2.26 (s, NMe_2, 6H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 27.5 (s). FT-IR (KBr disk): $\nu_{P=O}$ 1037 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{30}N_3O_3SP$: C, 44.01; H, 9.23; N, 12.83; S, 9.79. Found: C; 44.35; H, 9.18; N, 12.71; S, 9.63. MS(EI): 328.12 (*m*/*z* + Na).

Synthesis of O=P(SeCH$_2$CH$_2$NMe$_2$)(OCH$_2$CH$_2$NMe$_2$)$_2$ (14). The synthesis was the same as that for **8**, using P(OCH$_2$CH$_2$NMe$_2$)$_3$ (0.413 g, 1.39 mmol) and selenium (0.115 g, 1.4 mmol). Yield: 87% (0.408 g, 1.21 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.16 (m, CH_2OP, 4H), 3.03 (m, CH_2SeP, 2H), 2.67−2.58 (m, CH_2, 6H), 2.28 (s, NMe_2, 12H), 2.25 (s, NMe_2, 6H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 20.5 (s, $^1J_{PSe}$ = 486 Hz). FT-IR (KBr disk): $\nu_{P=O}$ 1041 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{30}$ N_3O_3PSe: C, 38.50; H, 8.07; N, 11.22. Found: C, 38.42; H, 8.11; N, 11.04. MS(EI): 376.07 (*m*/*z* + Na).

X-ray Crystallography. A single crystal of **8** was mounted in a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. Crystal data for **8**: $C_{16}H_{38}N_4O_2P_2Se_2$, M = 538.36, triclinic, space group $P\bar{1}$ (No. 2), a = 6.7992(8) Å, b = 9.6910(10) Å, c = 9.1660(10) Å, α = 95.505(2)°, β = 93.929(2)°, γ = 104.507(2)°, V = 579.31(11) Å^3, Z = 1, D_c = 1.543 g cm^{-3}, μ(Mo Ka) = 3.347 mm^{-1}, F(000) = 276, crystal size 0.09 × 0.12 × 0.17 mm^3, T = 100 K, R_{int} = 0.014, final R values R1 = 0.0249 and wR2 = 0.0630, GOF(F^2) = 1.08. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at φ = 0, 120, and 240°, using the SMART software package.[25] The raw data were reduced to F^2 values using the SAINT+ software,[26] and a global refinement of unit-cell parameters employing 5127 reflections chosen from the full data set was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS[27]). The structure was solved by the Patterson method and refined by full-matrix least-squares procedures using the SHELXTL program package.[28] Hydrogen atoms were placed in calculated positions and included as riding contributions, with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

Acknowledgment. We are grateful to the Department of Science and Technology (DST), New Delhi, India, for funding through Grant SR/S1/IC-05/2003. P.C. thanks CSIR for a Research Fellowship (JRF & SRF). We also thank SAIF, Mumbai, Department of Chemistry Instrumentation Facilities, Bombay, for spectral and analytical data. J.T.M. thanks the Louisiana Board of Regents through Grant LEQSF(2002-03)-ENH-TR-67 for purchase of the CCD diffractometer and the Chemistry Department of Tulane University for support of the X-ray laboratory.

Supporting Information Available: Crystallographic data for **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060413M

(25) *SMART*, version 5.625; Bruker-AXS: Madison, WI, 2000.
(26) *SAINT+*, version 6.35A; Bruker-AXS: Madison, WI, 2002.
(27) Sheldrick, G, M. *SADABS*, version 2.05; University of Göttingen: Göttingen, Germany, 2002.
(28) *SHELXTL*, version 6.10; Bruker-AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXS97* and *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.