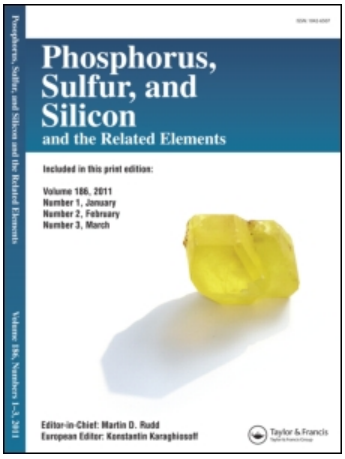

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SILYL- AND GERMYL-DIAZADIPHOSPHETIDINES

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Reaction of the 1,3,2,4-diazadiphosphetidine, *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$ with LiR (R = Me, n-Bu) followed by treatment of the resulting dianions with Me_3SiCl and Me_3GeBr produced *trans*-$[C_6H_5N(R)P(S)NC_6H_5]_2$(R = Me_3Si, **2**; Me_3Ge, **3**). Substitution occurs without cis-trans isomerization or significant cleavage of the 1,3,2,4-diazadiphosphetidine ring. **2** and **3** have been characterized by spectral (^1H and ^{31}P NMR, IR, and MS) and elemental analytical data. Analogous reactions involving Me_3SnCl yield mixtures containing $[C_6H_5N(SnMe_3)P(S)NC_6H_5]_2$ which could not be isolated or completely characterized.

Key words: 1,3,2,4-diazadiphosphetidines, silyl-, germyl-, phosphorus, polymer percursors, synthesis.

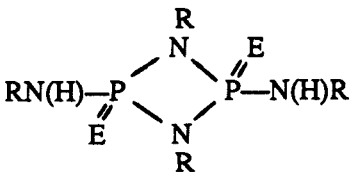
INTRODUCTION

Silyl-substituted amino phosphorus compounds have proved valuable for the synthesis of various new amino-amido phosphorus molecules. In addition to being used to protect an N—H bond,[1,2] the silyl moiety can function as a leaving[3] or migrating[4] group in phosphorus-nitrogen bond formation or rearrangement reactions as:

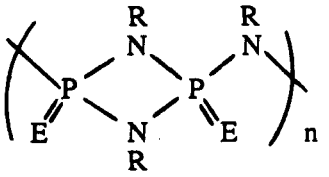
$$Me_3SiN{=}P(OCH_2CF_3)Me_2 \rightarrow Me_3SiOCH_2CF_3 + 1/n[Me_2P{=}N]_n \quad (1)$$

$$(Me_3Si)_2NPMe_2 + BrCH_2CO_2Et \rightarrow [Me_3SiNHP(Me_2)CH(SiMe_3)CO_2Et]Br \quad (2)$$

Although silylamines have been generally well studied,[1,2] only a few silylated diazadiphosphetidines, *cis*-$[(Me_3Si)MeNPN(t\text{-}Bu)]_2$,[5] $[(Me_3Si)_2NPNSiMe_3]_2$,[6a] and *trans*-$[(Me_3Si)_2NPN(t\text{-}Bu)]_2$[6b] have so far been reported. Trans isomeric monosilyl derivatives, which should be less sterically



1 (R = alkyl, aryl; E = O, S, electron pair)



2

congested and which allow potentially for more extensive further derivatization remain unstudied.

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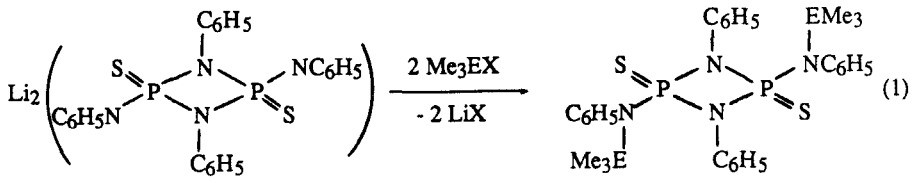
Recently, we undertook a study of 1,3,2,4-diazadiphosphetidine (**1**) amido group N—H bond reactivity in order to assess the potential for incorporation of diazadiphosphetidinyl units into high molecular weight oligomeric/polymeric poly(diazadiphosphetidines), e.g. **2**. We had determined previously that it is possible to deprotonate and subsequently alkylate the amido groups of *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$[7] [*trans*-2,4-dithio-2,4-bis(anilino)-1,3-diphenyl-1,3,2,4-diazadiphosphetidine] (**1**; $R^1 - R^4 = C_6H_5$; E = S) to form new series of N-alkylated derivatives.[8] We now report an extension of this chemistry to the preparation of new trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-derivatives.

RESULTS AND DISCUSSION

Reaction of the dilithio salt of *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$, $[C_6H_5N(Li)P(S)NC_6H_5]_2$,[8] with two equivalents of trimethyl silyl-, germyl-, or stannyl-halide (Me_3EX; E = Si, Ge, Sn) yields the *trans*-$[C_6H_5N(EMe_3)P(S)NC_6H_5]_2$(E = Si, **3**; E = Ge, **4**) in high yields. Either



(1)

3 - 5

MeLi or n-BuLi can be used to form the dilithio salt; however, reaction with MeLi is faster and cleaner. Except for the Me_3SnCl reaction, the observed products of Equation 1 appeared to be the near exclusive products of the reaction. In addition, the product in every case appears, within our detection limits, to be exclusively the trans isomer. Examination of the ^{31}P NMR spectra of reaction mixtures showed no significant resonances other than those from **3–5**. Although the resonance position of cis isomers in these P(V) phosphetidines might not be very different from that of the trans isomers,[9,10] a cis isomer should be clearly visible; the cis-trans isomer chemical shift difference ($\delta_{cis} - \delta_{trans}$) in $[Me_2NP(S)N(t\text{-}Bu)]_2$ is 9 ppm.[9] In each case, the reaction mixtures were analyzed by thin-layer chromatography in order to determine number of components; however, the results were somewhat inconclusive because of the relatively high sensitivity of **3** and **4** towards moisture.

Compounds **3** and **4** were characterized by a combination of spectral (IR, ^1H and ^{31}P NMR, MS) and elemental analytical data and the close correspondence of these spectral features to those of the previously reported *trans*-$[C_6H_5N(R)P(S)NC_6H_5]_2$(R = Me, Et)[8] whose structures were determined in x-ray single crystal analysis. **3** and **4** showed definitive MS parent ions at m/e 636 and 728, respectively, and spectral patterns as expected for diazadiphosphetidines in this class.[8,9] ^{31}P NMR resonances in the δ 40.3–43.3 region are very close to those of δ 39.0–45.0 observed for the alkylated derivatives reported earlier.[8] As expected, substitution of the

N—H hydrogen by Me_3Si or Me_3Ge groups have little effect on the ^{31}P or ^1H NMR chemical shifts.[11] Although **5** apparently formed, as indicated by the clean ^{31}P NMR resonance at δ 43.3, it could not be obtained free of impurities and therefore must be regarded as tentatively characterized.

Attempts to synthesize a monosilylated derivative of *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$, e.g. $[C_6H_5N(H)C_6H_5N(SiMe_3)][P(S)NH_6H_5]_2$, have so far been unsuccessful. Reaction of *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$ with one equivalent of RLi was shown previously to form a mixture of mono and dilithio derivatives,[8] which with alkyl halides reacted to form mixtures of mono-, and di-alkylated product along with unreacted *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$.[7] Analogous behavior was observed in reactions between Me_3SiCl and the lithiated diazadiphosphetidines obtained from 1:1 (m/m) MeLi/*trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$ reaction mixtures. ^{31}P NMR spectra of reaction mixtures showed resonances at δ 40.3 and 39.2 attributable to **3** and unreacted *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$. Resolution of these resonances was not sufficient to allow unambiguous detection of resonances between them due to the mono silylated product. Attempts to separate the reaction mixture by fractional crystallization or column chromatography were unsuccessful.

EXPERIMENTAL

Apparatus and Materials. All manipulations were carried out using standard vacuum line, glove bag, or Schlenk techniques under dry N_2.[12] Infrared, ^1H (90.0 MHz) NMR, ^{31}P NMR, and mass spectra were obtained using Perkin Elmer 337G Varian EM 390, JEOL PFT100, and Varian MAT CH-5 spectrometers, respectively. ^{31}P and ^1H chemical shifts downfield from 85% H_3PO_4 (external) and Me_4Si (internal) are reported as positive ($+\delta$). Elemental analyses were performed by Huffman Laboratories Inc., Wheatridge, Colorado.

The *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$ was prepared as reported previously.[7] Me_3SiCl (Alfa Inorganics) was distilled before use. Me_3GeBr and Me_3SnCl (Alfa Inorganics), MeLi (Alfa Inorganics, 1.4 M in diethyl ether), and n-BuLi (2.0 M in hexane) were used as obtained.

trans-$[C_6H_5N(SiMe_3)P(S)NC_6H_5]_2$ (**3**) *and trans-$[C_6H_5N(GeMe_3)$-$P(S)NC_6H_5]_2$* (**4**). Typically, to 2.00 mmole of *trans*-$[C_6H_5N(H)P(S)NC_6H_5]_2$ in tetrahydrofuran (30 mL) under N_2 at $-78°C$ in a 3-necked flask, MeLi (6–7 mmol) in Et_2O and tetrahydrofuran was added dropwise to form the $[C_6H_5N(Li)P(S)NC_6H_5]_2$ solution.[8] After reaction, the solution was stirred for 2.5 hr, recooled to $-78°C$, at which temperature Me_3SiCl, Me_3GeBr, or Me_3SnBr, (8.0–10.0 mmol) or Me_2SiCl_2 (4.5 mmol) was added dropwise. After 1 hr, the reaction mixture was warmed slowly to room temperature and stirred for 3–6 hr. The reaction mixture was filtered and the filtrate was evaporated slowly. Successive fractions of crystals were collected. Repeated recrystallization of solids from $CHCl_3$ followed by final solvent removal *in vacuo* yielded **3** (72%, m.p. dec) and **4** (57%, m.p. dec). **3**: $^{31}P\{^1H\}$ NMR (20% in $CDCl_3$): δ 40.3 (s). ^1H NMR (15% in $CDCl_3$): δ 6.48–7.78 (compl mult, area 20; C_6H_5), 0.20 [s, area 18; $(CH_3)_3Si$]. MS (rel. int.), parent and four most intense envelopes, m/e: 636 (37; $C_{30}H_{38}P_2N_4S_2{}^{28}Si_2^+$), 621 (100), 549 (79), 492 (47), 122 (77). IR (KBr pellet, major absorbtions, cm^{-1}): 1587 (vs), 1484 (vs), 1250 (vs), 1200 (s), 1070 (s), 990 (vs), 935-833 (vs), 743 (vs), 712 (s), 692 (s), 514 (s), and 487 (s). Anal. Calcd. for $C_{30}H_{38}N_4P_2S_2Si_2$: C, 56.58; H, 6.02; N, 8,80; P, 9.72. Found: C, 56.49; H, 5.97; N, 8.84; P, 9.78. **4**: $^{31}P\{^1H\}$ NMR (20% in $CDCl_3$): δ 41.5 (s). ^1H NMR (20% in $CDCl_3$): δ 6.55–7.78 (comp mult, area 20; C_6H_5), 0.40 [s, area 18; $(CH_3)_3Ge$]. MS (rel. int.), parent and four most intense envelopes, m/e: 728 (38; $C_{30}H_{38}P_2N_4S_2{}^{74}Ge_2^+$), 712 (100), 596 (26), 213 (26), 122 (76). IR (KBr pellet, major absorptions, cm^{-1}): 1577 (vs), 1478 (vs), 1256 (vs), 1198 (s), 1070 (s), 994 (vs), 930-831 (vs), 7403 (vs), 712 (s), 512 (s), and 483 (s). Anal. Calcd. for $C_{30}H_{38}N_4P_2S_2Ge_2$: C, 49.63; H, 5.28; N, 7.72; P, 8.54. Found. C, 49.10; H, 5.33; N, 7.80; P, 8.44.

Repeated recrystallization of material from the $Me_3SnCl/[C_6H_5N(Li)P(S)NC_6H_5]_2$ reaction yielded product which was tentatively characterized as $[C_6H_5N(SnMe_3)P(S)NC_6H_5]_2$ (**5**); however, neither by crystallization nor by chromatographic techniques could product which was analytically pure be obtained. $^{31}P\{^1H\}$ NMR (20% in $CDCl_3$): δ 43.3 (s). Because **5** could not be obtained pure, reliable MS, IR, and ^1H NMR and elemental analytical data were not obtained.

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