

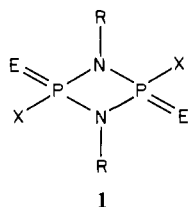
Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309Alkylation of *trans*-2,4-Dithio-2,4-dianilino-1,3-diphenyl-1,3,2,4-diazadiphosphetidineDARRELL E. COONS, VILOYA S. ALLURED, MARK D. NOIROT, R. CURTIS HALTIWANGER,
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Reaction of the 1,3,2,4-diazadiphosphetidine *trans*-[(C₆H₅NH)P(S)NC₆H₅]₂ with LiR (R = CH₃, *n*-C₄H₉) followed by treatment with CH₃I, C₂H₅I, or C₆H₅CH₂Br produces *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂, *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂, or *trans*-[C₆H₅N(CH₂C₆H₅)P(S)NC₆H₅]₂ in high yield. N-Alkylation is achieved without *trans*-*cis* isomerism or significant cleavage of the 1,3,2,4-diazadiphosphetidine ring. The structures of [C₆H₅N(CH₃)P(S)NC₆H₅]₂ and [C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ have been determined by single-crystal X-ray crystallography. *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂ crystallizes in space group *P* $\bar{1}$ with *a* = 10.131 (3) Å, *b* = 10.043 (3) Å, *c* = 13.524 (3) Å, α = 90.16 (2)°, β = 108.75 (2)°, γ = 102.86 (2)°, *V* = 1266.2 (6) Å³, and *Z* = 2. The structure, solved by direct methods, refined to *R* = 0.034 and *R*_w = 0.045 for 2611 independent reflections. The unit cell contains molecules of two slightly different conformational types, A and B. Intramolecular distances are as follows: mean P—N(ring) = 1.690 (2) Å, mean P—N(exo) = 1.636 (2) Å, and P=S = 1.914 (1) Å. Bond angles are as follows: mean \angle P—N—P(ring) = 98.3 (1)°, mean \angle N—P—N(ring) = 81.7 (1)°, \angle N—P—N(exo) = 109.6 (1)°, and mean \angle S—P—N(exo) = 113.7 (1)°. *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ crystallizes in space group *P*₁2/*n* with *a* = 10.280 (4) Å, *b* = 19.059 (4) Å, *c* = 7.531 (1) Å, β = 112.10 (2)°, *V* = 1367.0 (6) Å³, and *Z* = 2. The structure, solved by direct methods, refined to *R* = 0.033 and *R*_w = 0.043 for 1282 independent significant reflections. Intramolecular distances and angles are in close agreement with the above values. Structural generalities in the *trans*-[C₆H₅N(R)P(S)NC₆H₅]₂ (R = H, CH₃, C₂H₅) series, especially with respect to conformational properties around P—N(exo), N(exo)—C(phenyl), and N(ring)—C(phenyl) bonds, are identified and discussed.

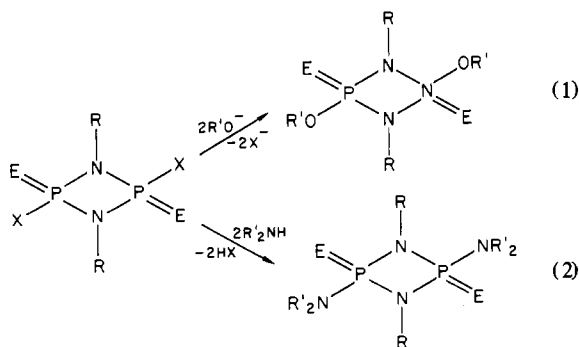
Introduction

The structural properties of four-coordinate 1,3,2,4-diazadiphosphetidines, **1**, have received considerable recent atten-



R = alkyl, aryl; E = O, S, Se, Te, RN=; X = halogen, alkyl, aryl, RNH-, R₂N-

tion.¹⁻⁴ As a result the important general structural features, the planar to near-planar P₂N₂ rings, the existence of *cis* and *trans* isomers, and the principle that the 1,3,2,4-diazadiphosphetidine ring system is a highly thermodynamically stable oligomeric assemblage of [XP(E)NR] units, are well established. In contrast, even though routes to a variety of compounds are well-known,^{1,2} there has been surprisingly little attention paid to 1,3,2,4-diazadiphosphetidine substitution and/or derivatization reactions. Reactions of 1,3-dihalo-substituted compounds (**1**, X = halogen, E = O, S, R = alkyl, aryl) with alkoxides (eq 1) or amines (eq 2) are well-established routes to alkoxy- or amido-substituted 1,3,2,4-diazadiphosphetidines^{1,5} although frequently reactions with nucleophiles result in cleavage and/or opening of the rings to acyclic products. The absence of continued development of



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four-coordinate 1,3,2,4-diazadiphosphetidine substitution chemistry is unfortunate since they could offer considerable potential to novel phosphorus-nitrogen ligand and polymer syntheses.

Recently we undertook a study of the readily available and structurally characterized *trans*-[C₆H₅N(H)P(S)NC₆H₅]₂ (**2**) (i.e., **1**, where R = C₆H₅, E = S, X = NHC₆H₅) to determine its potential for use in further reaction chemistry. Quite surprisingly we find that it is possible to deprotonate and alkylate **2** to form new series of substituted *trans*-[C₆H₅N(R)P(S)NC₆H₅]₂ products. Our results are described below.

Experimental Section

Apparatus and Materials. All manipulations requiring inert atmosphere were performed in N₂-flushed glovebags.⁶ Infrared, ¹H NMR (90.0 MHz), and mass spectra were obtained with Perkin-Elmer 337G, Varian EM 390, and Varian MAT CH-5 spectrometers, respectively. Phosphorus-31 NMR spectra were obtained with a JEOL-PFT100 spectrometer equipped with standard probe accessories. ¹H NMR chemical shifts were measured relative to internal (CH₃)₄Si; shifts downfield from the standard are given positive (+ δ) values. ³¹P NMR chemical shifts were measured relative to external H₃PO₄; downfield shifts are given negative (- δ) values. Single-crystal X-ray data were collected at ambient temperature with a Syntex P $\bar{1}$ automated diffractometer equipped with a graphite monochromator. Elemental analyses and molecular weight measurements were performed by Huffman Analytical Laboratory, Wheatridge, CO.

trans-[C₆H₅N(H)P(S)NC₆H₅]₂ (**2**) was prepared as reported previously.⁷ Methyl iodide (Fisher, Certified reagent), C₂H₅I (Fisher, Certified reagent), and C₆H₅CH₂Br (Aldrich Chemicals, 99%) were distilled onto and stored over activated 4-Å molecular sieves. Chloroform and methylene chloride were distilled from P₄O₁₀. Methylolithium (Alfa Inorganics, 1.4 M in diethyl ether) and *n*-butyllithium (Aldrich Chemicals, 2.0 M in hexane) were used as obtained.

- (1) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101 and references cited therein.
- (2) Grapov, A. F.; Mel'nikov, N. N.; Razvodovskaya, L. V. *Russ. Chem. Rev. (Engl. Transl.)* **1970**, *39*, 1.
- (3) Sherer, O. J.; Schnabl, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 486.
- (4) Chang, C. C.; Haltiwanger, R. C.; Thompson, M. L.; Chen, H. J.; Norman, A. D. *Inorg. Chem.* **1979**, *18*, 1899.
- (5) Michaelis, A. *Justus Liebig's Ann. Chem.* **1915**, *407*, 290.
- (6) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.
- (7) Buck, A. C.; Bartleson, J. D.; Lankelma, H. P. *J. Am. Chem. Soc.* **1948**, *70*, 744.

Table I. Crystal Data and Refinement Results for 3 and 4

	3	4
formula	C ₂₆ H ₂₆ N ₄ P ₂ S ₂	C ₂₈ H ₃₀ N ₄ P ₂ S ₂
M _r	520.598	548.67
space group	P1	P2 ₁ /n
a, Å	10.131 (3)	10.280 (4)
b, Å	10.043 (3)	19.059 (4)
c, Å	13.524 (3)	7.531 (1)
α, deg	90.16 (2)	90
β, deg	108.75 (2)	112.10 (2)
γ, deg	102.86 (2)	90
V, Å ³	1266.2 (6)	1367.0 (6)
d _c , g cm ⁻³	1.365	1.333
d _o , g cm ⁻³	1.365	1.325
Z	2	2
F(000)	544	576
μ(Mo Kα), cm ⁻¹	3.56	3.34
no. of variables	307	163
ratio of observns to parameters	8:1	7:1
esd of an observn of unit weight	1.524	2.012
max shift/error	0.004	0.004
final difference map	featureless	featureless
final residuals obsd data	R = 0.034, R _w = 0.045	R = 0.033, R _w = 0.043

Table II. Positional Parameters for the Atoms of 3

atom	x/a	y/b	z/c
P1A	0.50352 (8)	0.37412 (7)	0.00855 (6)
S1A	0.61548 (9)	0.27118 (8)	-0.03583 (7)
P1B	0.49876 (8)	0.12672 (7)	0.50802 (6)
S1B	0.60508 (9)	0.28317 (8)	0.46351 (7)
N1A	0.4142 (2)	0.4725 (2)	-0.0771 (2)
N2A	0.3983 (2)	0.2847 (2)	0.0667 (2)
C1A	0.3757 (4)	0.1363 (3)	0.0722 (3)
N1B	0.4141 (2)	-0.0137 (2)	0.4234 (2)
N2B	0.3909 (2)	0.1640 (2)	0.5660 (2)
C1B	0.3667 (4)	0.3007 (3)	0.5754 (3)
C11A	0.2951 (3)	0.4372 (3)	-0.1712 (2)
C12A	0.2520 (3)	0.5371 (3)	-0.2352 (2)
C13A	0.1346 (3)	0.5014 (3)	-0.3257 (2)
C14A	0.0587 (3)	0.3669 (4)	-0.3521 (2)
C15A	0.1036 (3)	0.2663 (3)	-0.2895 (2)
C16A	0.2212 (3)	0.3005 (3)	-0.1993 (2)
C21A	0.3138 (3)	0.3488 (3)	0.1122 (2)
C22A	0.3678 (3)	0.3957 (3)	0.2163 (2)
C23A	0.2832 (4)	0.4482 (4)	0.2616 (3)
C24A	0.1460 (4)	0.4518 (3)	0.2033 (3)
C25A	0.0926 (4)	0.4044 (3)	0.0992 (3)
C26A	0.1762 (3)	0.3532 (3)	0.0535 (2)
C11B	0.3002 (3)	-0.0330 (3)	0.3265 (2)
C12B	0.2639 (3)	-0.1533 (3)	0.2628 (2)
C13B	0.1536 (3)	-0.1703 (3)	0.1674 (2)
C14B	0.0801 (3)	-0.0698 (3)	0.1364 (2)
C15B	0.1162 (3)	0.0484 (3)	0.1997 (2)
C16B	0.2259 (3)	0.0681 (3)	0.2952 (2)
C21B	0.3117 (3)	0.0589 (3)	0.6119 (2)
C22B	0.3630 (3)	0.0462 (3)	0.7182 (2)
C23B	0.2839 (4)	-0.0503 (4)	0.7634 (3)
C24B	0.1554 (4)	-0.1323 (3)	0.7031 (3)
C25B	0.1051 (4)	-0.1194 (3)	0.5977 (3)
C26B	0.1830 (3)	-0.0234 (3)	0.5513 (2)

Reaction materials from reactions below were characterized by comparison of their physical and/or spectral properties with those reported in the literature or with spectra of samples prepared independently in our laboratories. Mass spectral data in the sections below give the *m/e* value for the major peak in the parent and the four most intense envelopes of the spectrum.

Syntheses of *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂ (3), *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅] (4), and *trans*-[C₆H₅N(CH₂C₆H₅)P(S)NC₆H₅] (5). Typically, to 2.00 mmol of *trans*-[C₆H₅N(H)P(S)NC₆H₅] (2) dissolved in 25–30 mL of tetrahydrofuran under N₂ at -78 °C in a three-necked flask was added dropwise a tetrahydrofuran and ether solution of CH₃Li (6–7.0 mmol). After addition, the solution was stirred for 1 h at -78 °C. The reaction mixture was warmed slowly to room temperature during 1.5 h and then recooled to -78 °C, at which temperature CH₃I, C₂H₅I, or C₆H₅CH₂Br (8.0–10.0 mmol)

Table III. Positional Parameters for the Atoms of 4

atom	x/a	y/b	z/c
S	-0.14088 (9)	-0.11897 (4)	0.2656 (1)
P	-0.08838 (8)	-0.05045 (4)	0.4659 (1)
N1	-0.0847 (2)	0.0351 (1)	0.4110 (3)
N2	-0.1703 (3)	-0.0588 (1)	0.6130 (3)
C1	-0.1460 (4)	-0.0078 (2)	0.7722 (5)
C2	-0.2733 (5)	0.0367 (2)	0.7436 (6)
C11	-0.1928 (3)	0.0803 (2)	0.2941 (4)
C12	-0.1616 (3)	0.1482 (2)	0.2574 (5)
C13	-0.2685 (4)	0.1921 (2)	0.1441 (6)
C14	-0.4049 (4)	0.1686 (2)	0.0669 (5)
C15	-0.4355 (4)	0.1017 (2)	0.1024 (5)
C16	-0.3303 (4)	0.0570 (2)	0.2168 (4)
C21	-0.2580 (3)	-0.1180 (1)	0.6138 (4)
C22	-0.2147 (3)	-0.1636 (2)	0.7666 (4)
C23	-0.3022 (4)	-0.2179 (2)	0.7755 (5)
C24	-0.4299 (4)	-0.2272 (2)	0.6302 (6)
C25	-0.4717 (4)	-0.1819 (2)	0.4766 (5)
C26	-0.3872 (3)	-0.1271 (2)	0.4684 (5)

was added dropwise. The reaction mixture was warmed slowly to room temperature and then refluxed for 6–8 h. The reaction mixture was filtered to remove solids. The solution was evaporated slowly, and successive fractions of crystals were collected. Repeated recrystallization yielded *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂ (3) (yield 60%, mp 248–249 °C), *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ (4) (yield >70%, mp 238–240 °C), and *trans*-[C₆H₅N(CH₂C₆H₅)P(S)NC₆H₅]₂ (5) (yield >80%; mp 261–263 °C).

In several experiments *n*-butyllithium was substituted for methylolithium. In all cases deprotonation occurs smoothly to form the lithiated species, which react with the alkyl halides to form products as described above.

Reaction of 2 with less than 2 equiv of alkyllithium, typically 2:CH₃Li reactant mole ratios of 2.0:0.5 to 2.0:1.2, followed by alkylation with CH₃I was carried out under the reaction conditions described above. Thin-layer chromatography (chloroform solvent) of the reaction mixture showed unreacted 2 (*R_f* = 0.07), 3 (*R_f* = 0.90), and a third component (*R_f* = 0.82). ³¹P NMR spectral analysis of the reaction mixture yielded resonances at δ -39.4 (assigned to 2), δ -45.0 (assigned to 3), and two equal-area doublets at δ -38.3 and -45.6 (²*J_{PP}* = 18.3 Hz). The last two resonances are assigned tentatively to C₆H₅N(CH₃)P₂S₂(NC₆H₅)₂N(C₆H₅N)(H) (6). 2, 3, and 6 were present in an approximately 1:3:1 molar ratio.

Characterization Data for 3. Anal. Calcd for C₂₆H₂₆N₄P₂S₂: C, 59.99; H, 5.03; N, 10.76; P, 11.90. Found: C, 59.96; H, 5.20; N, 10.71; P, 11.87. Mass spectrum (relative intensity): *m/e* 520 (22, parent), 382 (51), 168 (60), 122 (100), 106 (78). ¹H NMR spectrum (10% in THF-*d*₆): δ 7.05–7.80 (complex, C₆H₅), 3.34 (doublet, ³*J_{HP}* = 11.7 Hz, CH₃). ³¹P NMR spectrum (10% in CDCl₃): δ -45.0 (complex multiplet). Infrared absorption maxima (KBr pellet): 3190 (vs), 3040 (m), 1590 (vs), 1485 (vs), 1372 (s), 1265 (vs), 1212 (vs), 1070 (m), 1025 (s), 960 (vs), 745 (vs), 690 (vs), 640 (m), 583 (m), 500 (w), 480 (s), 452 (s), 430 (m), 320 (w) cm⁻¹.

Characterization Data for 4. Anal. Calcd for C₂₈H₃₀N₄P₂S₂: C, 61.30; H, 5.51; N, 10.21. Found: C, 61.22; H, 5.50; N, 10.13. Mass spectrum (relative intensity): *m/e* 548 (39, parent), 396 (38), 277 (20), 182 (13), 120 (100). ¹H NMR spectrum (10% in CDCl₃): δ 6.85–7.80 (complex, C₆H₅), 0.92 (triplet, ³*J_{HH}* = 7.0 Hz, CH₃). ³¹P NMR spectrum (10% in THF-C₆D₆): δ -42.9. Infrared absorption maxima (KBr pellet): 3055 (w), 3050 (w), 2970 (m), 2900 (w), 1590 (s), 1485 (vs), 1380 (w), 1335 (w), 1260 (vs), 1230 (s), 1173 (w), 1160 (m), 1060 (vs), 1027 (s), 996 (s), 970 (s), 947 (vs), 925 (vs), 748 (vs), 720 (vs), 683 (vs), 654 (s), 636 (w), 614 (w), 547 (w), 490 (m), 462 (w) cm⁻¹.

Characterization Data for 5. Anal. Calcd for C₃₈H₃₄N₄P₂S₂: C, 67.83; H, 5.09; N, 8.32. Found: C, 67.90; H, 5.15; N, 8.39. Mass spectrum (relative intensity): *m/e* 672 (<1, parent), 491 (31), 181 (36), 122 (73), 91 (100). ¹H NMR spectrum (10% in CDCl₃): δ 6.70–7.70 (complex, C₆H₅), 4.98 (doublet, ³*J_{HP}* = 12.0 Hz, CH₂). ³¹P NMR spectrum (10% in CDCl₃): δ -44.5. Infrared absorption maxima (KBr pellet): 3065 (w), 3035 (w), 3010 (w), 2980 (w), 1592 (s), 1585 (s), 1448 (w), 1382 (m), 1270 (vs), 1212 (w), 1198 (m), 1085 (w), 1060 (s), 1025 (m), 957 (s), 919 (vs), 883 (s), 778 (w), 746 (s), 720 (s), 693 (s), 657 (m), 643 (s), 610 (m), 584 (m), 555 (m), 451 (m), 429 (m) cm⁻¹.

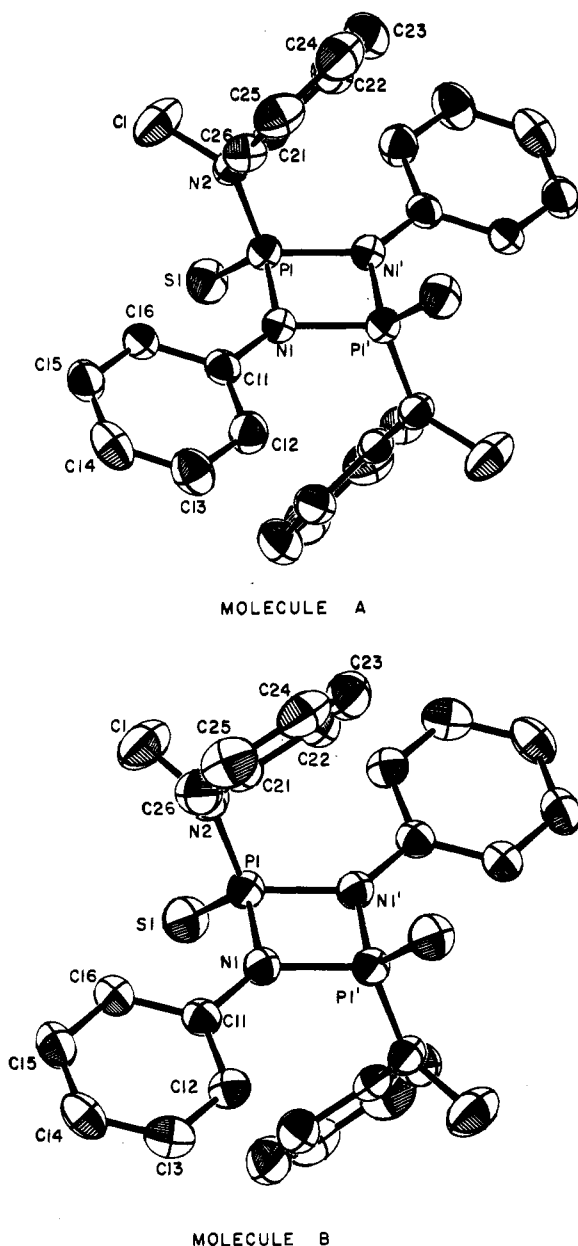


Figure 1. Structure of the A and B molecules of *trans*-[(C₆H₅N(CH₃)P(S)NC₆H₅)]₂ (3) (ORTEP diagram; 50% probability).

Data Collection and Structure Analysis for 3 and 4. Crystal data are summarized in Table I.⁸ All parameters were determined on the diffractometer and refined by least-squares fit of the parameters to 15 centered reflections. Data were collected on parallelepiped crystals of 3 (0.15 × 0.25 × 0.45 mm) and 4 (0.4 × 0.45 × 0.6 mm) at 290–295 K with use of graphite-monochromatized Mo K α ($\lambda = 0.70169$ Å) radiation. Data were corrected for Lorentz and polarization effects,⁹ but not for absorption effects. Both structures were solved by direct methods. Hydrogen atoms were located in three-dimensional difference maps and were included in the model in fixed idealized positions.¹⁰ All nonhydrogen atoms were treated anisotropically, and the models were refined to convergence. All calculations were done with only observed reflections.¹¹ The scattering factors were those for neutral atoms.¹² Final positional and thermal pa-

(8) The nonstandard setting $P2_1/n$ has the following equivalent positions: $x, y, z; \bar{x}, \bar{y}, z; 1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z$.

(9) $RLP = 1/Lp = (2.0 \sin \theta \cos \theta) / \{0.5[(\cos^2 2\theta_m + \cos^2 2\theta) / (1 + \cos^2 2\theta_m)] + 0.5[(\cos 2\theta_m + \cos^2 2\theta) / (1 + \cos 2\theta_m)]\}$ where θ and θ_m are the Bragg angles for the crystal and the monochromator ($2\theta_m = 26.60$). The fractional mosaicity of the monochromator is assumed to be 0.5.

(10) The isotropic thermal parameters for the hydrogens were set to be 1 greater than those of the atom to which they were attached.

(11) An observed reflection is defined as a reflection for which $F_o^2 > 3.0[\sigma(F_o^2)]$.

(12) Ibers, J. A.; Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

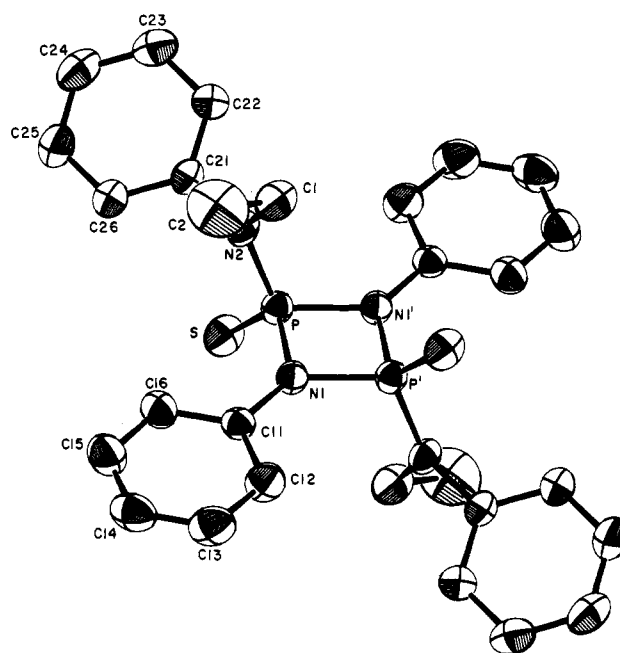
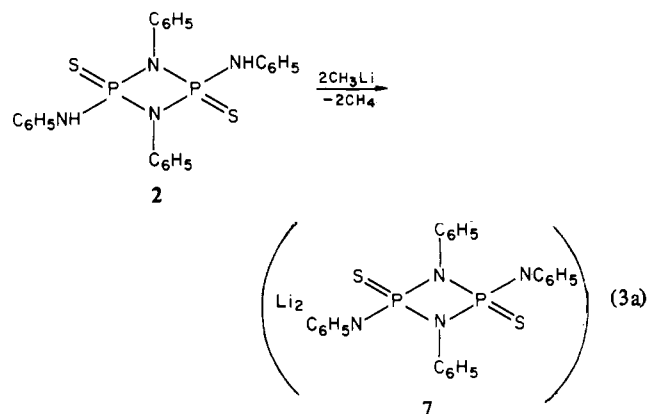


Figure 2. Structure of *trans*-[(C₆H₅N(C₂H₅)P(S)NC₆H₅)]₂ (4) (ORTEP diagram; 50% probability).

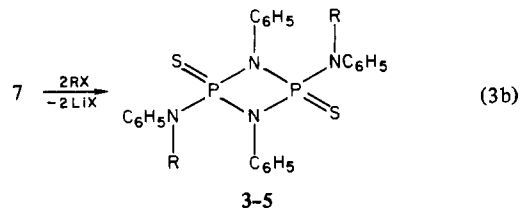
rameters are given in Tables II and III. All programs were contained in, or derived from, Syntex (now Nicolet) data reduction routines, the MULTAN 78 package,¹³ and the Northwestern University Crystallographic Computing Package of Dr. J. A. Ibers.

Results and Discussion

Alkylation Reactions. Reaction of *trans*-[(C₆H₅NH)P(S)NC₆H₅]₂ (2) with greater than 2 equiv of methyl lithium occurs smoothly according to eq 3a. Treatment of the de-



protonated product, 7, with 2 equiv of alkyl halide (RX = CH₃I, C₂H₅I, or C₆H₅CH₂Br) yields the *trans*-[(C₆H₅N(R)P(S)NC₆H₅)]₂ (R = CH₃ (3), C₂H₅ (4), or C₆H₅CH₂ (5)) products in high yields (eq 3b). Deprotonation of 2 to 7 using *n*-butyllithium occurs also; however, the reaction is slower than and less preferable to that using methyl lithium.



The products of the reactions in every case appear, within our detection limits, to be exclusively the *trans* products. The

(13) Main, P. "Multan 78, A System of Computer Programs for the Automatic Solution of Crystal Structures"; Department of Physics, University of York: York, England, March 1978; obtained from Dr. Graham J. B. Williams, Brookhaven National Laboratory, Upton, N.Y.

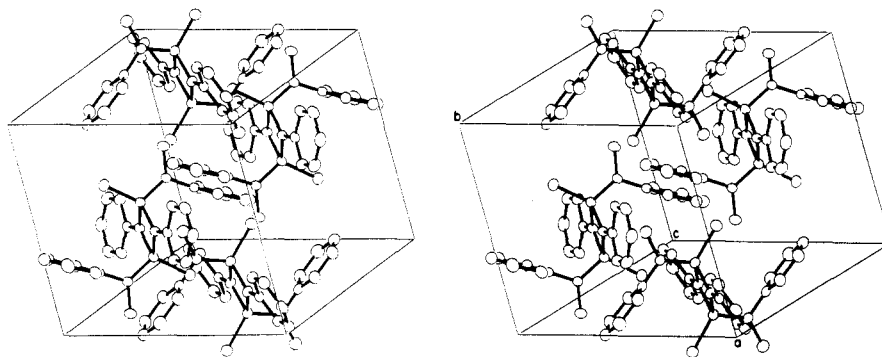


Figure 3. Unit cell of *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂.

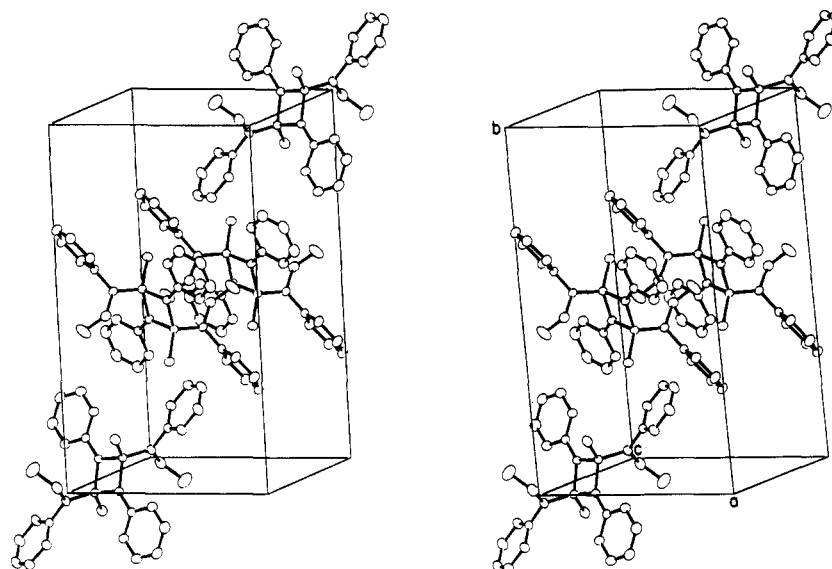
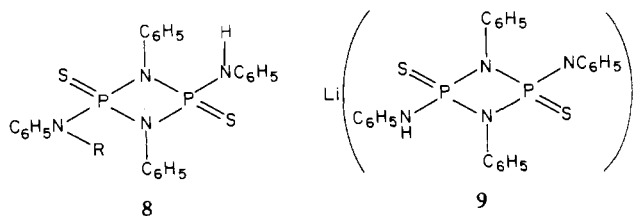


Figure 4. Unit cell of *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂.

structures of **3** and **4** were established in single-crystal X-ray analyses (see below) as was that of **2** previously.⁴ Since the ³¹P NMR chemical shifts of **2**, **3**, and **4** are all closely similar (δ -41.5 to -44.0) and in good agreement with that of **5** (δ -43.0), it is concluded that **5** also is the *trans* isomer. In each case the reaction mixture obtained after alkylation was examined by thin-layer chromatography and ³¹P NMR spectral analysis. In each system the only phosphorus-containing products detected were unreacted **2** (traces) and the products **3**–**5**. No evidence for the presence of *cis* isomeric products or partial alkylation products was obtained. Although some ring attack and subsequent degradation may occur, it appears to be insignificant overall. Thus it appears that whereas ring opening by basic species such as alkoxide ion occurs, this process can be excluded completely in favor of deprotonation through the use of the highly basic but weakly nucleophilic methyllithium reagent.

Attempts to find conditions under which monoalkylated derivatives of **2** (e.g., **8**) can be isolated have so far been



unsuccessful. Reaction of **2** with 1 equiv of methyllithium results in a mixture of **2**, **7**, and **9**, instead of only a monoalkylated product that can be subsequently alkylated to **8**. This

is inferred from the result that treatment of the 1:1 CH₃Li:**2** reaction mixture with excess CH₃I produces not only **3** but also unreacted **2** and a third species, **6**, with two chemically inequivalent phosphorus atoms. Characterization of this species is based on its ³¹P NMR spectral and thin-layer chromatographic properties. Because of the closely similar properties of unreacted **2**, **3**, and **6**, attempts to separate them by fractional crystallization have been unsuccessful. Attempts to separate them by column chromatographic techniques are currently in progress.

The results of the 1:1 CH₃Li:**2** reactions are interesting because they suggest the Brønsted acidities of **2** and the monoanion **9** are not greatly different. Thus reaction of CH₃Li with **2** produces a species that is as easily deprotonated as the parent **2**. Apparently, amido groups at opposite ends of the 1,3,2,4-diazadiphosphetidine molecule are not in close electronic communication since removal of a C₆H₅NH proton at one end does not greatly affect the acidity of the C₆H₅NH group at the other end. So far our observations of this effect are limited to *trans* isomeric systems. It remains of interest to see if similar behavior is observed for the *cis* isomers.

The work reported herein appears to represent the first example of deprotonation and realkylation of a primary amino-substituted 1,3,2,4-diazadiphosphetidine and as such opens new directions for synthetic modifications of compounds in these classes. Particularly interesting is the question of using these reactants and their N–H functionality in other substitution and possibly polymerization reactions. Along these lines, studies of reactions of **2** with acylating reagents and dihaloalkanes are being pursued currently.

Structural Analyses. Single-crystal X-ray analyses of

Table IV. Intramolecular Distances and Angles in *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂ (3) and *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ (4)

	3A	3B	4
(a) Bond Lengths (Å)			
P-N(1)	1.693 (2)	1.690 (2)	1.686 (3)
P-N(1)'	1.688 (2)	1.690 (2)	1.694 (2)
P-N(2)	1.636 (2)	1.637 (2)	1.632 (3)
P-S	1.916 (1)	1.913 (1)	1.913 (1)
N(1)-C(11)	1.422 (3)	1.418 (3)	1.421 (4)
N(2)-C(21)	1.452 (4)	1.446 (4)	1.445 (4)
N(2)-C(1)	1.463 (4)	1.460 (4)	1.490 (4)
(b) Bond Angles (Deg)			
P-N(1)-P'	98.1 (1)	98.5 (1)	98.6 (1)
N(1)-P-N(1)'	81.9 (1)	81.5 (1)	81.4 (1)
S-P-N(1)	118.8 (1)	119.3 (1)	119.5 (1)
S-P-N(1)'	119.1 (1)	119.3 (1)	118.4 (1)
N(2)-P-N(1)'	109.1 (1)	109.2 (1)	110.5 (1)
N(2)-P-N(1)	110.1 (1)	109.9 (1)	109.0 (1)
S-P-N(2)	113.8 (1)	113.6 (1)	113.8 (1)
P-N(1)-C(11)	131.4 (2)	131.0 (2)	130.9 (2)
P'-N(1)-C(11)	130.1 (2)	130.4 (2)	130.5 (2)
P-N(2)-C(21)	121.1 (2)	120.5 (2)	124.1 (2)
P-N(2)-C(1)	123.7 (2)	124.1 (2)	120.6 (2)
C(21)-N(2)-C(1)	115.1 (2)	115.4 (2)	115.0 (3)
N(1)-C(11)-C(12)	120.5 (2)	120.0 (3)	120.3 (3)
C(16)-C(11)-N(1)	119.9 (3)	120.1 (2)	120.2 (3)
N(2)-C(21)-C(22)	119.7 (3)	119.5 (3)	119.4 (2)
C(26)-C(21)-N(2)	120.3 (3)	120.4 (3)	120.7 (3)
N(2)-C(1)-C(2)			112.2 (3)

Table V. Least-Squares Plane Atoms and Deviations from Planes in *trans*-[C₆H₅N(CH₃)P(S)NC₆H₅]₂ (3) and *trans*-[C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ (4)

plane ^a	atom	dev, Å			
		3A	3B	4	
1	P* ^b	0.000 (1)	0.000 (1)	-0.000 (1)	
	N(1)*	0.000 (3)	0.000 (1)	0.000 (1)	
	P'* ^c	0.000 (1)	0.000 (1)	-0.000 (1)	
	N(1)'	0.000 (3)	0.000 (1)	-0.000 (1)	
	S	1.471	1.460	1.471	
	N(2)	-1.466	-1.469	-1.462	
2	C(11)	-0.127	-0.046	0.021	
	P*, S*, N(2)*	0 ^d	0	0	
3	P*	-0.001 (1)	-0.000 (1)	0.001 (1)	
	C(21)*	-0.007 (2)	-0.000 (2)	0.020 (3)	
	C(1)*	-0.007 (2)	-0.000 (2)	0.022 (3)	
	N(2)*	0.020 (2)	0.001 (2)	-0.035 (2)	
	4	N(1)*	-0.015 (3)	0.007 (3)	0.000 (1)
		C(11)*	0.003 (3)	-0.004 (3)	0.003 (3)
C(12)*		0.010 (3)	-0.006 (3)	0.003 (4)	
C(13)*		0.007 (3)	0.003 (3)	-0.004 (5)	
C(14)*		-0.021 (3)	0.003 (3)	-0.002 (4)	
C(15)*		0.002 (3)	0.002 (3)	0.002 (4)	
5	C(16)*	0.014 (3)	-0.005 (3)	-0.001 (4)	
	P	0.154	0.240	0.117	
	S	1.853	1.921	1.683	
	N(2)	-1.108	-1.052	-1.280	
	P'	-0.411	-0.282	-0.092	
	N(2)*	-0.041 (2)	-0.027 (3)	-0.021 (3)	
	C(21)*	0.035 (2)	0.022 (3)	0.030 (4)	
	C(22)*	0.018 (2)	0.013 (3)	0.025 (4)	
	C(23)*	-0.003 (2)	-0.004 (3)	-0.020 (4)	
	C(24)*	-0.023 (2)	-0.015 (3)	-0.026 (5)	
	C(25)*	-0.009 (2)	-0.004 (3)	-0.002 (4)	
C(26)*	0.023 (2)	0.013 (3)	0.013 (4)		
P	1.313	1.345	1.215		
C(1)	-1.396	-1.356	-1.248		

^a Planes are calculated according to Hamilton, W. C. *Acta Crystallogr.* 1961, 14, 185. For equations see the supplementary material. ^b Atoms marked with an asterisk define the plane and were used to calculate the plane. ^c Atoms marked with primes are related by the appropriate center of inversion. ^d Three atom planes, no deviations.

Table VI. Dihedral Angles (Deg) between Selected Planes in 2, 3, and 4

	1-2	1-4	2-3	2-5	3-5
[C ₆ H ₅ N(H)P(S)NC ₆ H ₅] ₂ (2) ^a					
molecule A	91.6	6.0	5.1	70.0	73.0
molecule B	91.3	28.5	18.6	34.6	44.5
[C ₆ H ₅ N(CH ₃)P(S)NC ₆ H ₅] ₂ (3)					
molecule A	89.4	14.1	6.3	86.8	90.9
molecule B	90.4	11.9	5.2	99.5	83.3
[C ₆ H ₅ N(C ₂ H ₅)P(S)NC ₆ H ₅] ₂ (4)	91.1	4.7	6.0	64.4	66.6

^a Data taken from ref 4.

crystalline samples of [C₆H₅N(CH₃)P(S)NC₆H₅]₂ (3) and [C₆H₅N(C₂H₅)P(S)NC₆H₅]₂ (4) indicate that both compounds are *N*-alkyl derivatives of the previously reported *trans*-1,3,2,4-diazadiphosphetidine 2⁴ (Figures 1 and 2). The arrangements of 3 and 4 in their unit cells are shown in Figures 3 and 4, respectively. The unit cell of 3 (Figure 3) contains two independent molecules (molecules A and B) that have different orientations and are not related by symmetry. A similar situation was observed with compound 2. Molecules 3A and 3B are located on centers of inversion symmetry at (1/2, 1/2, 0) and (1/2, 0, 1/2). For 3A, 3B, and 4, only half of each molecule is crystallographically independent. Molecules 3A and 3B differ primarily with respect to the orientation of the phenyl ring of the methylanilino moieties and the phenyl groups attached to the P₂N₂ rings. 3A and 3B conform to C_i and approximate C_{2h} symmetry point groups, respectively. 4 conforms to point group C_i.

Structural and bonding parameters for 3A, 3B, and 4 are given in Tables IV-VI. Small differences among 3A, 3B, 4, and the previously reported 2 are seen, but they appear too small to be chemically or structurally significant. The range of mean bond distances and bond angles for previously reported *trans*-dithio-1,3,2,4-diazadiphosphetidines of types [RP(S)NR']₂ (R = C₆H₅, R' = CH₃, C₂H₅, C₆H₅)¹⁴⁻¹⁸ and [(C₆H₅NH)P(S)NC₆H₅]₂ (2)⁴, e.g., P-N(ring) = 1.676-1.702 Å, P=S = 1.905-1.938 Å, ∠P-N-P(ring) = 96.3-98.2°, and ∠N-P-N(ring) = 81.8-83.7°, are consistent with those observed in 3 and 4. The P-N(exo) distances of 1.636 (2) Å in 3 and 1.632 (3) Å in 4 are closely similar to the value of 1.627 (6) Å observed in the unalkylated parent 2. Replacement of the C₆H₅NH hydrogen with CH₃ or C₂H₅ groups has minimal effects on the distances and angles in this 1,3,2,4-diazadiphosphetidine system.

The availability of structural information for compounds 2-4 leads to several interesting generalizations for the series: (i) In all cases the nitrogen atoms in the P₂N₂ rings and those of the *exo*-C₆H₅NR (R = H, CH₃, C₂H₅) groups are planar. (ii) The phenyl groups attached to the P₂N₂ rings approach coplanarity with the P₂N₂-ring planes (planes 1-4). (iii) The dihedral angle between the P, N(2), C(1), C(phenyl) plane (plane 3) and the amido phenyl ring (plane 5) appears inclined toward 90°. (iv) The planes containing the phenyl groups and *exo*-nitrogen atoms (planes 3) are closely aligned with those of the P, S, N(2) planes (planes 2). It is interesting to note also that eclipsing of the P=S bond with P-C bonds of 3 and 4 occurs just as readily as did the eclipsing of P=S with N-H bonds in 2. This argues against intramolecular N-H...S hy-

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drogen bonding being an important factor in the determination of structure in **2**, as was intimated previously.⁴ These structural generalizations above may provide insight into the bonding of four-coordinate 1,3,2,4-diazadiphosphetidine derivatives, which at this time can only be dealt with qualitatively. However, their identification can allow productive pursuit of further theoretical studies. Such studies are currently in progress in our laboratories and will be reported later.

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Registry No. **2**, 70160-66-6; **3**, 80631-62-5; **4**, 80631-63-6; **5**, 80631-64-7; C₆H₅CH₂Br, 100-39-0; CH₃I, 74-88-4; C₂H₅I, 75-03-6.

Supplementary Material Available: Tables listing structure factor amplitude data, anisotropic thermal parameters, nonessential intramolecular distances and angles, equations for least-squares planes, and data collection parameters (22 pages). Ordering information is given on any current masthead page.

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New, Systematic Syntheses of Boron Hydrides via Hydride Ion Abstraction Reactions: Preparation of B₂H₆, B₄H₁₀, B₅H₁₁, and B₁₀H₁₄

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The boron hydrides B₂H₆, B₄H₁₀, B₅H₁₁, and B₁₀H₁₄ are prepared in good yields through hydride ion abstraction reactions when the borane anions BH₄⁻, B₃H₈⁻, B₄H₉⁻, and B₉H₁₄⁻ respectively are treated with 1 molar equiv of a Lewis acid BX₃ (X = F, Cl, or Br), generally in the absence of a solvent, for reaction periods of 1-4 h. A high-yield (85-90%) method for the conversion of B₅H₉ to B₉H₁₄⁻ is presented as the precursor to the practical conversion of B₅H₉ to B₁₀H₁₄ (45-50%). Additionally, treatment of the anion BrB₃H₇⁻ with BBr₃ results in the formation of 2-BrB₄H₉ in low yield (15%). The hydride ion abstraction reactions by BBr₃ and BCl₃ lead to the new anions HBBr₃⁻ and HBCl₃⁻.

Introduction

One of the principal handicaps to the investigation of the chemistry of the intermediate boron hydrides B₄H₁₀ and B₅H₁₁ has been the absence of simple preparative procedures which would provide these materials in relatively large quantities and in good yield.^{1,2}

Traditionally, B₄H₁₀ and B₅H₁₁ have been prepared by hot-cold reactor techniques,^{3,4} thermolysis reactions,⁵⁻⁸ and more recently from the protonation of B₃H₈⁻ salts with HCl or polyphosphoric acid.⁹⁻¹² In addition, B₅H₁₁ has been prepared¹³ from the protonation of the hypoborane anion B₅H₁₂⁻.

Hot-cold reactor methods,^{3,4} although capable of providing B₄H₁₀ and B₅H₁₁ in reasonable quantities, have several experimental drawbacks. A glass hot-cold reactor requires the handling of relatively large quantities of potentially hazardous B₂H₆ at elevated temperature and high pressure. In addition,

Table I. Reactants, Conditions, and Yields (%) in the Preparation of B₂H₆ from [M][BH₄]

BX ₃	M		
	Na ⁺ ^a	N(n-C ₄ H ₉) ₄ ⁺ ^b	(CH ₃) ₃ PC(C ₆ H ₅) ₃ ⁺ ^b
BBr ₃	0	94	90
BCl ₃	0	98	94
BF ₃	95	60	60

^a No solvent, room temperature, 4-8 h (same results for 1:1 and 3:4 molar ratios of NaBH₄ and BF₃, respectively). ^b CH₂Cl₂, room temperature, 3 h.

the technique is tedious, requiring several days of operation with constant attention to produce 10-20-mmol quantities of borane products, which then require separation by low-temperature vacuum-line fractionation. In general, the hot-cold reactor method also requires greater technical skill on the part of the investigator than the simpler techniques to be discussed in this paper.

The protonation of B₃H₈⁻ salts⁹⁻¹² provides a laboratory method which eliminates the necessity of handling large quantities of B₂H₆ at high temperatures and pressures. This method, however, often requires tedious fractionation procedures before obtaining B₄H₁₀ and B₅H₁₁ in yields of 40% and 14%, respectively.⁹⁻¹² Pentaborane(11) may also be obtained in yields of up to 60% from the protonation of B₅H₁₂⁻ salts by anhydrous HCl.¹³ However, large quantities of B₅H₁₁ are difficult to prepare by this method using standard vacuum-line techniques and the overall reaction requires much time as well as an available source of B₄H₁₀.

In a preliminary communication¹⁴ we reported a new, systematic approach to boron hydride syntheses which not only

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