Heteroatom Chemistry
Volume 9, Number 2, 1998

On the Reaction of P_4S_{10} with Hexamethyldisilazane

Jiri Pinkas† and John G. Verkade*

Department of Chemistry, Iowa State University, Ames, IA 50011-3111

Received 15 April 1997

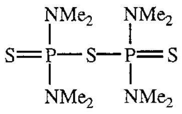
ABSTRACT

P_4S_{10} *reacts with* $(Me_3Si)_2NH$*, to give* $SP(NHSiMe_3)_x(SSiMe_3)_{3-x}$*, where* $x = 0$*–3. These species were shown by* ^{31}P *NMR spectroscopy to subsequently form cyclic and linear condensation products. The molecular structure of a linear trimer* $(Me_3SiNH)P(S)[(\mu\text{-}NH)P(S)(NHSiMe_3)_2]_2$*,* **12,** *was authenticated by an X-ray diffraction study.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:115–121, 1998

INTRODUCTION

P_4S_{10} is an aesthetically pleasing cagelike molecule [1] whose reactivity has been studied frequently. The reaction of P_4S_{10} with liquid ammonia was shown to give monomeric or cyclotrimeric products, depending on the reaction conditions [2–4]. In the presence of methylamine, P_4S_{10} affords four products, namely, $SP(NHMe)_3$, $[NH_3Me][S_2P(NHMe)_2]$, $[NH_3Me]_2[S_3PNHMe]$, and $[NH_3Me]_3[PS_4]$, as a result of a complete cleavage of the tetrahedral cage [5]. Primary aromatic amines react in two steps with P_4S_{10} ultimately providing thiophosphoric triamides [6], whereas three reaction steps were identified when secondary alkylamines were employed [7]. Tertiary amines possessing alpha hydrogens react with P_4S_{10} to form compounds of the type $[NH_2(CH_2R)_2]_2[SP(S)_2CHR]_2$ wherein the anions contain six-membered rings [8].

Silylamines, such as Me_2NSiMe_3 and Et_2NSiMe_3, cleave the P_4S_{10} cage to $SP(NR_2)_2(SSiMe_3)$, wherein R = Me, Et, and to $(Me_3Si)_2S$. As a by-product, the molecule **1** containing two phosphorus atoms was observed. Moreover, P_4S_{10} was shown to react with $(Me_3Si)_2S$ to give a high yield of $SP(SSiMe_3)_3$ [9].


$S{=}\overset{NMe_2}{\underset{NMe_2}{P}}{-}S{-}\overset{NMe_2}{\underset{NMe_2}{P}}{=}S$

1

Here we report on reactions of P_4S_{10} with hexamethyldisilazane, $(Me_3Si)_2NH$, under various stoichiometric conditions. Four primary reaction products, $SP(NHSiMe_3)_x(SSiMe_3)_{3-x}$, where $x = 0$–3, were identified by ^{31}P NMR spectroscopy. Compounds wherein $x = 2$ and 3 were isolated and characterized. In the course of the reaction, the primary products were observed to undergo intramolecular eliminations and condensations to form cyclic four-membered ring compounds or linear dimers and a trimer. The molecular structure of the trimer was established by a single-crystal X-ray study.

RESULTS AND DISCUSSION

Reactions without Solvent

P_4S_{10}, reacted with excess $(Me_3Si)_2NH$ (1:77) at reflux (bp 125°C) for 3 hours, formed three major phos-

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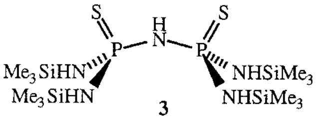
Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

†Current address: Institute of Inorganic Chemistry, Goettingen University, 37077, Goettingen, Germany.

*To whom correspondence should be addressed.

CCC 1042-7163/98/020115-07

phorus-containing species ($\delta^{31}P$ = 61.2, 55.0, and 50.5) and four minor by-products ($\delta^{31}P$ = 67.6, 66.2, 60.5, and 57.8). Additional refluxing for 12 hours led to an increase of the intensity of the 55.0 and 50.5 signals (area ratio 1:1.2) and the disappearance of the remaining signals except for those at δ 66.2 and 61.2, although their intensities diminished. Cooling of the reaction mixture to room temperature afforded one of the major products as a crystalline solid that displayed a ^{31}P chemical shift at δ 55.0 and a quartet pattern in its proton-coupled ^{31}P NMR spectrum. This suggested that the compound is $SP(NHSiMe_3)_3$, **2.** ^1H and ^{13}C NMR and IR spectra of **2** and their favorable comparison with literature data [10] confirmed our assignment. The second major product ($\delta^{31}P$ = 50.5) displayed a characteristic $AA'X_nX'_n$ signal pattern in its proton-coupled ^{31}P NMR spectrum consistent with **3,** which was previously characterized by 2D heteronuclear correlation NMR techniques in the reaction of $PSCl_3$ with $(Me_3Si)_2NH$[11]. Attempts to isolate **3** failed because of its high solubility in $(Me_3Si)_2NH$ and organic solvents.



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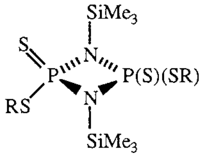
The two minor products were tentatively assigned to $SP(NHSiMe_3)(SSiMe_3)_2$, **4** (δ 66.2) and $SP(NHSiMe_3)_2(SSiMe_3)$, **5** (δ 61.2) based on the observation of a doublet (5 Hz) and a triplet (6 Hz), respectively, in their proton-coupled ^{31}P NMR spectra. A complete characterization of **5** is discussed below.

A substantial change in the reaction mixture composition was brought about by increasing the molar ratio of $P_4S_{10}/(Me_3Si)_2NH$ to 1:14. In addition to compounds **2, 3, 4,** and **5,** three ^{31}P NMR signals of low intensity at δ 65.7, 57.2, and 56.5 appeared after 24 hours of heating. These three signals remained as singlets in the proton-coupled ^{31}P NMR spectrum consistent with the absence of a $NHSiMe_3$ group bonded to phosphorus. The species with $\delta^{31}P$ = 65.7 was identified as $SP(SSiMe_3)_3$, **6,** by comparison of its chemical shift value with data in the literature [9,12]. The ^{31}P NMR signals at δ 57.2 and 56.5 (approximate ratio 1:1.5) were tentatively ascribed to the presence of *cis* and *trans* isomers of **7a,** respectively, based on a comparison with literature data for **7b** [13]. The formation of these 1,3-diaza-2,4-diphosphetidines was postulated to proceed via a [2 + 2] cycloaddition of a tricoordinate phosphorus intermediate formed by an intramolecular elimination [14]. The parallel process for the formation of **7a** is shown in Scheme 1.



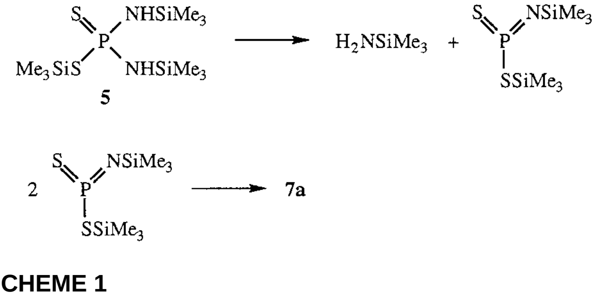
	R
7a	Me$_3$Si
7b	Me

The absence of **6** in the reaction containing a large excess of $(Me_3Si)_2NH$ and its low concentration in the reaction with a smaller excess of this reagent suggested that **6** reacts with $(Me_3Si)_2NH$ according to Equation 1:

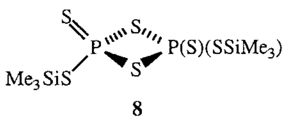
$$SP(SSiMe_3)_3 + x(Me_3Si)_2NH \rightarrow SP(NHSiMe_3)_x(SSiMe_3)_{3-x} + x(Me_3Si)_2S \quad (1)$$

As the reaction (in which the ratio of $P_4S_{10}/(Me_3Si)_2NH$ was 1:14) proceeded, compound **5** became the most abundant species, allowing it to be separated by low-temperature crystallization and characterized by ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopies, high-resolution mass spectroscopy, and elemental analysis. The number of sulfur and nitrogen substituents on the phosphorus center in **5** reflects approximately their original ratio in the starting reaction mixture.

Several new species were observed in a reaction with a relatively high $P_4S_{10}/(Me_3Si)_2NH$ ratio (1:7.6). Compound **3** and a species with $\delta^{31}P$ = 54.7 were the predominant products. The latter signal broadened in the proton-coupled ^{31}P NMR spectrum, but it revealed no P-N-H coupling information. Therefore, we suggest that the lack of $(Me_3Si)_2NH$ in the reaction mixture indicates that species such as **8** [15,16] and **9** [16] are formed that possess only sulfur ligands. The absence of a second isomer of **8** (presumably *cis*) may result from steric crowding of the $SSiMe_3$ groups. Compound **5** represents one of several minor products in this reaction.



SCHEME 1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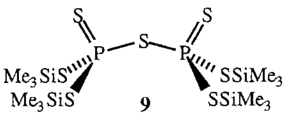
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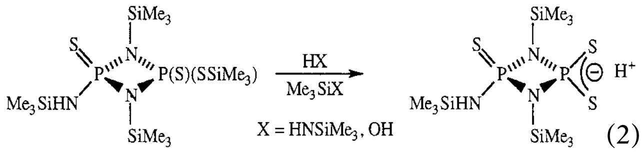
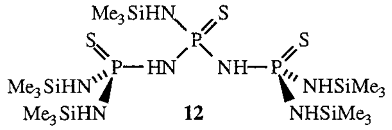
In addition, two pairs of doublets in the ratio of 2:1 were observed at $\delta^{31}P$ 55.3 and 45.1 (J_{PP} = 19 Hz) and at 53.3 and 44.9 (J_{PP} = 22 Hz). In a proton-coupled ^{31}P NMR spectrum, the upfield doublets split further into doublets of doublets with coupling constants of 9 and 10 Hz, respectively. This is consistent with the presence of a pair of *cis* and *trans* isomers of **10**.

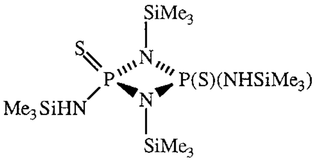


10 **11** (2)

Further support for our assignment of **10** was gained from our isolation and characterization of **11**, which displays a pair of doublets at δ 77.4 and 47.6 (J_{PP} = 17 Hz). Compound **11** precipitated from the reaction mixture upon addition of CS_2. Presumably, this compound was formed in the reaction of **10** with a proton source stemming from adventitious water or H_2NSiMe_3, according to Equation 2. Compound **11** was characterized by NMR and mass spectroscopies, and elemental analyses. Another component of the reaction mixture was a compound displaying an AX_2 spin system at $\delta^{31}P$ = 43.6 and 51.1. This species was identified by NMR and mass spectroscopies as the linear bisimidotrithiotriphosphoramide **12**. Upon standing, **12** crystallized from the CS_2 solution, and its structure was verified by a single-crystal X-ray diffraction study.


12

Compound **12** was previously detected by ^{31}P NMR techniques as one of several products in the reaction of $SPCl_2(NHSiMe_3)$ with $SP(NHSiMe_3)_2$ (1:2) [17]. Finally, a singlet at $\delta^{31}P$ = 41.1 and an overlapping group of signals centered at δ 43.3 were observed. The assignment of the former signal to *cis*-**13** was facilitated by comparison of its AA′XX′ pattern in the proton-coupled ^{31}P NMR spectrum with previously published data for this compound [11,18]. The *trans* isomer of 13 [18b] was hidden under the overlapping group of signals at δ 43.3.


13

Reactions in Solvents

The reaction of P_4S_{10} with $(Me_3Si)_2NH$ (1:4) in toluene or benzene after 20 minutes of refluxing afforded a mixture of comparable amounts of **3**, **4**, **5**, and *cis*- and *trans*-**7**, and a small amount of a compound with $\delta^{31}P$ = 37.0 (doublet, J_{PH} = 9 Hz). Further heating at reflux for 12 hours led to the disappearance of **3** and **5** and to the formation of *cis*- and *trans*-**10**. On the other hand, when the reaction was carried out at lower temperature, a slow disappearance of P_4S_{10} occurred, as was also observed in the reaction with $(Me_3Si)_2NH$ (1:12.6) in CS_2. After 24 hours at room temperature, a signal for P_4S_{10} was still noticeable in the CS_2 solution, and only two products were formed, namely, **4** and **5**. The latter species were also the final products after 10 days of stirring at room temperature.

Molecular Structure and Spectroscopic Properties of 12

Compound **12** is a rare example of a compound containing a linear P-N-P-N-P backbone [19,20]. Its molecular structure is shown in Figure 1, and important bond distances and angles are gathered in Table 1. The phosphorus atoms are in distorted tetrahedral environments. The P = S distances are in the range 1.946–1.965 Å and are comparable to the corresponding bond lengths in $Me_2P(S)(NHSiMe_3)$, **14**, (1.952(3) Å) [21], $(MePNMe)_4S_3$, **15**, (1.943(2)–1.950(2) Å) [22], $C_6H_4N_2[P(S)(NEt_2)_2]_2P(S)NEt_2$, **16**, (1.922(2)–1.938(2) Å) [20], and $[P_3S_9]^{3-}$, **17**, (1.964 Å) [23]. The P–N bond lengths clearly fall into two groups. Thus, the terminal distances are shorter (1.630(1)–1.641(1) Å) than the bridging ones (1.675(1)–1.683(1) Å). A similar trend was observed in **16** [20] and in $Me_2NP(O)[(\mu - NMe)P(O)(NMe_2)_2]_2$, **18** [19]. The N–Si distances (1.745(2)–1.763(1) Å) are similar to the terminal N–Si distances in *trans*-**13** (1.764(2) Å) [18b] and in **14** (1.741(7) Å) [21].

The $P(S)(NHSiMe_3)_2$ moieties of **12** are prochiral [24], and in solution, they are rendered diastereo-

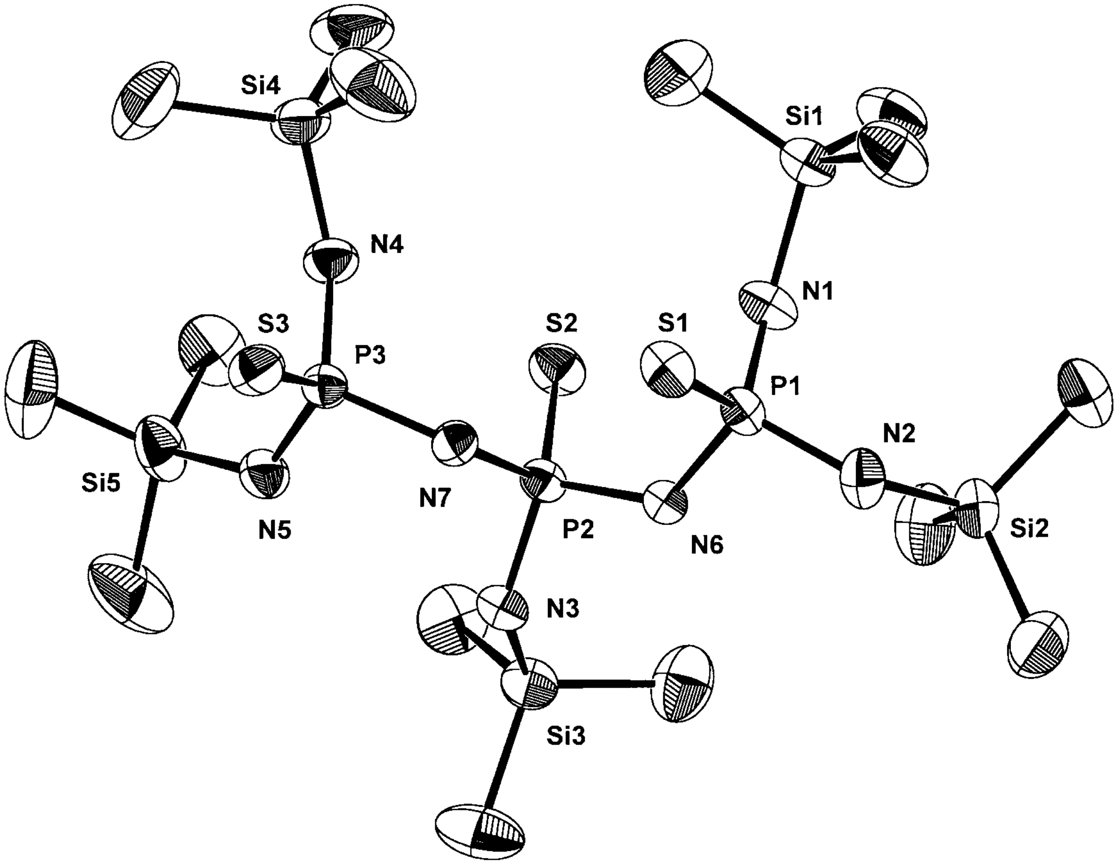


FIGURE 1 Molecular structure of $(Me_3SiNH)P(S)[(\mu\text{-}NH)P(S)(NHSiMe_3)_2]_2$, **12.**

topic by the C_s molecular symmetry. This phenomenon is nicely manifested in the pairs of signals for the NH and $SiMe_3$ end groups observed in the ^1H, ^{13}C, and ^{29}Si NMR spectra of 12 (see Experimental). Although the three phosphorus atoms are inequivalent in the solid state, only two signals were resolved in the ^{31}P solid-state NMR spectrum of 12. Their chemical shifts are nearly identical to the values obtained from solution measurements.

EXPERIMENTAL

General Procedures

All reactions were carried out under argon using Schlenk or dry-box techniques. Toluene and pentane were dried over and distilled from Na/benzophenone while P_4O_{10} was used for CS_2. P_4S_{10} was purchased from Aldrich and purified by a procedure described in the literature [25]. Its purity was checked by ^{31}P NMR and mass spectroscopies [26]. Hexamethyldisilazane was purchased from Aldrich and fractionally distilled before use. C_6D_6 was dried and distilled from CaH_2 under an argon atmosphere. ^{31}P NMR spectra were recorded on Bruker WM 200 (81.015 MHz) and Varian VXR 300 (121.421 MHz) spectrometers using 85% H_3PO_4 as an internal or an external standard, respectively. ^1H (299.949 MHz), ^{13}C (75.429 MHz), and ^{29}Si (59.591 MHz) NMR spectra were measured at room temperature in C_6D_6 on a Varian VXR 300 spectrometer and were referenced to protio impurities (7.15 ppm, ^1H), the solvent signal (126.0 ppm, ^{13}C), and Me_4Si (0.0 ppm, ^{29}Si), respectively. Mass spectra were recorded on a Finnigan 4000 low-resolution (70 eV, EI) and a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope present. IR spectra were taken on an IBM IR-98 FTIR spectrometer (4000–400 cm^{-1}) using Nujol mulls between KBr discs or KBr pellets. Elemental analyses were carried out by Galbraith Laboratories. Melting points (uncorrected) were measured in sealed capillaries. Solid-state CP/MAS ^{31}P NMR spectra (121.496 MHz) were obtained on a Bruker MSL 300 instrument and were referenced to 85% H_3PO_4. A standard single-contact spin-lock cross-polarization sequence with a contact time of 2 ms and a relaxation delay of 2 seconds was used. The sample was spun at 2.8 and 3.2 kHz. Packing of samples was carried out in a nitrogen-filled

TABLE 1 Selected Bond Distances (Å) and Bond Angles (°) for **12,** Estimated Standard Deviations in Parentheses

Distances			
P1–S1	1.9653(6)	P3–N4	1.641(1)
P2–S2	1.9455(6)	P3–N5	1.640(1)
P3–S3	1.9527(6)	P3–N7	1.683(1)
P1–N1	1.634(1)	Si1–N1	1.755(1)
P1–N2	1.639(1)	Si2–N2	1.762(2)
P1–N6	1.679(1)	Si3–N3	1.763(1)
P2–N3	1.630(1)	Si4–N4	1.745(2)
P2–N6	1.675(1)	Si5–N5	1.755(1)
P2–N7	1.688(1)		
Angles			
S1–P1–N1	116.08(6)	S3–P3–N5	118.46(6)
S1–P1–N2	110.86(6)	S3–P3–N7	109.34(5)
S1–P1–N6	112.51(5)	N4–P3–N5	105.65(8)
N1–P1–N2	108.06(8)	N4–P3–N7	110.34(7)
N1–P1–N6	103.06(7)	N5–P3–N7	101.96(7)
N2–P1–N6	105.50(7)	P2–N3–Si3	130.75(8)
S2–P2–N3	113.91(5)	P3–N4–Si4	131.65(9)
S2–P2–N6	112.85(5)	P3–N5–Si5	130.70(9)
S2–P2–N7	115.73(5)	P1–N6–P2	130.18(8)
N3–P2–N6	105.29(7)	P2–N7–P3	127.20(8)
N3–P2–N7	105.64(7)	P1–N1–Si1	130.40(9)
N6–P2–N7	102.22(7)	P1–N1–Si2	130.45(9)
S3–P3–N4	110.65(6)		

glovebox using a Teflon air-tight rotor insert that was placed in a zirconia rotor and capped with a Kel-F rotor cap.

$SP(NHSiMe_3)_3$ (**2**)

P_4S_{10} (0.181 g, 0.407 mmol) was suspended in $(Me_3Si)_2$ NH (5.0 ml, 24 mmol) and heated to reflux for 15 hours. Upon cooling of the resulting solution to −20°C, a white crystalline solid precipitated. Filtration and washing with dry pentane afforded **2** in 23% yield: ^{1}H NMR (C_6D_6) δ 0.23 (s, 9 H, $SiCH_3$, $^1J_{CH}$ = 118.8 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.8 Hz, ^{29}Si satellites), 2.25 (br d, 1 H, NH, $^2J_{PH}$ = 5.1 Hz); ^{13}C NMR (C_6D_6) δ 1.43 (d, CH_3, $^3J_{PC}$ = 2.5 Hz, $^1J_{SiC}$ = 57.8 Hz, ^{29}Si satellites, $^1J_{CH}$ = 118.8 Hz); ^{31}P NMR (C_6D_6) δ 55.0 (q, $^2J_{PH}$ = 6.7 Hz); IR (Nujol, cm^{-1}) ν 3315 s (νNH), 1261 s, 1247 vs, 1238 s, 958 m, 932 vs, 873 sh, 857 vs, 843 vs, 785 m, 771 m, 757 w, 690 m, 624 w, 607 m, 565 w, 448 w.

$SP(NHSiMe_3)_2(SSiMe_3)$ (**5**)

P_4S_{10} (1.036 g, 2.33 mmol) was suspended in $(Me_3Si)_2NH$ (7.0 mL, 33 mmol) and heated to 70–80°C with stirring for 13 hours and then to 40°C for 24 hours. Cooling of the resulting solution to −20°C afforded a white crystalline solid. Recrystallization from pentane gave **5** in 41% yield: Mp 135°C; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H, $NSiCH_3$, $^1J_{CH}$ = 118.8 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.9 Hz, ^{29}Si satellites), 0.53 (s, 9 H, $SSiCH_3$, $^1J_{CH}$ 121.5 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.6 Hz, ^{29}Si satellites), 2.72 (br d, 2 H, NH, $^2J_{PH}$ = 5 Hz); ^{13}C NMR (C_6D_6) δ 1.45 (d, $NSiCH_3$, $^3J_{PC}$ = 2.4 Hz, $^1J_{SiC}$ = 58 Hz, ^{29}Si satellites), 2.05 (d, $SSiCH_3$, $^3J_{PC}$ = 3.4 Hz); ^{29}Si NMR (C_6D_6) δ 6.3 (d, NSi, $^2J_{PSi}$ = 1.3 Hz), 18.2 (d, SSi, $^2J_{PSi}$ = 5.1 Hz); ^{31}P NMR (C_6D_6) δ 61.2 (q, $^2J_{PH}$ = 5.9 Hz); HRMS calcd for $C_9H_{29}Si_3S_2PN_2$ (M^+) *m/e* 344.08177, found *m/e* 344.08186; LRMS (EI, 70 eV) *m/e* (ion, rel. intensity) 344 (M^+, 7), 330 (20), 239 ($[M\text{-}SSiMe_3]^+$, 100), 223 ($PNS(SiMe_3)_2^+$, 20), 207 ($P(NHSiMe_3)_2^+$, 5), 191 ($PN(SiMe_3)_2^+$, 10), 163 (5), 146 ($Si_2Me_6^+$, 85), 130 (25), 106 (Me_3SiSH^+, 5), 73 ($SiMe_3^+$, 80); anal. calcd for $C_9H_{29}Si_3N_2S_2P$: C, 31.32; H, 8.49; N, 8.12; P, 8.99. Found: C, 29.28; H, 8.04; N, 7.61; P, 9.26.

$Me_3SiNHP(S)(\mu\text{-}NSiMe_3)_2P(S)SH$, (**11**)

P_4S_{10} (9.70 g, 21.8 mmol) was suspended in $(Me_3Si)_2NH$ (35.0 mL, 166 mmol) and heated to reflux for 30 minutes. All volatiles were removed under vacuum, and the resulting waxy solid was dissolved in 200 mL of CS_2. A small amount of unreacted P_4S_{10} was filtered off, and the volume of the solution was reduced to 50 mL. A white powdery solid precipitated in several batches, which, after combination, washing with 3 mL of pentane and drying in vacuum, gave **11** in 2.5% yield: Mp 122–127°C (sublimation); ^{1}H NMR (C_6D_6) δ 0.22 (s, 9 H, $NHSiMe_3$, $^1J_{CH}$ = 120 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.6 Hz, ^{29}Si satellites), 0.67 (s, 18 H, $NSiMe_3$, $^1J_{CH}$ = 120 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.9 Hz, ^{29}Si satellites), 3.03 (d, 1 H, NH, $^2J_{PH}$ = 10.5 Hz), 7.49 (br s, SH); ^{13}C NMR (C_6D_6) δ 1.36 (d, $NHSiCH_3$, $^3J_{PC}$ = 2.8 Hz), 0.85 (t, $NSiCH_3$, $^3J_{PC}$ = 2.5 Hz); ^{29}Si NMR (C_6D_6) δ 6.34, 7.80; ^{31}P NMR (C_6D_6) δ 47.6 (dd, area 1, P(S)NH, $^2J_{PP}$ = 16.8 Hz, $^2J_{PH}$ = 10.4 Hz), 77.4 (d, area 1, P(S)SH, $^2J_{PP}$ = 16.8 Hz); LRMS (EI, 70 eV) *m/e* (ion, rel. intensity) 421 (M^+, 38), 406 ($M\text{–}CH_3^+$, 12), 388 ($M\text{–}SH^+$, 51), 356 ($M\text{–}S_2H^+$, 5), 295(5), 239 ($PS(NHSiMe3)_2^+$, 3), 223 ($PSN(SiMe_3)_2^+$, 21), 191 ($PN(SiMe_3)_2^+$, 3), 178 ($(Me_3Si)_2S^+$, 7), 147(7), 130(10), 118 ($PNSiMe_3^+$, 14), 73 (Me_3Si^+, 100), 59 (Me_3SiH^+, 6), 45 ($MeSiH_2^+$, 21); LRMS (EI, 13 eV) *m/e* (ion, rel. intensity) 421 (M^+, 100), 406 ($M\text{-}CH_3^+$, 3), 388 ($M\text{-}SH^+$, 7), 147(2); anal. calcd for $C_9H_{29}N_3S_3Si_3P_2$: C, 25.63; H, 6.93; N, 9.96; S, 22.81; Si, 19.98; P, 14.69. Found: C, 26.40; H, 7.80; N, 10.98; S, 24.34; Si, 15.82; P, 14.15.

$(Me_3SiNH)P(S)[(NH)P(S)(NHSiMe_3)_2]_2$, (**12**)

Compound **12** crystallized from the CS_2 solution of the previous reaction after **11** had been completely removed. Colorless crystals of X-ray quality were filtered off, washed with 2 mL of pentane, and dried in vacuum giving **12** in 8% yield: Mp 142–144°C; ^{1}H NMR (C_6D_6) δ 0.36/0.43 (s/s, terminal (diastereotopic) Me_3Si, 18 H/18 H), 0.48 (s, middle Me_3Si, 9 H), 3.78/4.75 (d/d, terminal (diastereotopic) NH, 2 H/2 H, $^2J_{PH} = 5.1/7.8$ Hz), 4.90 (d, P(middle)NH, 1 H, $^2J_{PH} = 8.3$ Hz), 6.40 br s, $P(NHP)_2$, 2 H); ^{13}C NMR (C_6D_6) δ 1.76 (d, middle Me_3Si, $^3J_{PC} = 2.7$ Hz), 1.67/1.84 (d/d, terminal (diastereotopic) Me_3Si, $^3J_{PC} = 2.7/3.0$ Hz); ^{29}Si NMR (C_6D_6) δ 8.76 (d, middle Me_3Si, $^2J_{PSi} =$ 2.8 Hz), 6.98/6.64 (d/s, terminal (diastereotopic) Me_3Si, $^2J_{PSi} = 2.3/< 0.3$ Hz); ^{31}P NMR (C_6D_6) δ 43.6 (td, area 1, middle P, $^2J_{PP} = 11.0$ Hz, $^2J_{PH} = 8.5$ Hz), 51.1 (dt, area 2, terminal P, $^2J_{PP} = 11.0$ Hz, $^2J_{PH} =$ 6.5 Hz); HRMS calcd for $C_{15}H_{52}N_7S_3Si_5P_3$ (M^+) *m/e* 659.15058, found *m/e* 659.15094; LRMS (EI, 70 eV) *m/e* (ion, rel intensity) 659 (M^+, 62), 570 ($[M\text{-}Me_3SiNH_2]^+$, 100), 555 ($[M\text{-}Me_3SiS]^+$, 28), 537 (72), 505 (16), 481 ($[M\text{-}2Me_3SiNH_2]^+$, 30), 466 ($[M\text{-}Me_3SiNH_2\text{-}Me_3SiS]^+$, 13), 448 (13), 416 (7), 403 (12), 389 (9), 372 (7), 300 (15), 283 (9), 265 (7), 240 (12), 223 ($PSN(SiMe_3)_2^+$, 27), 206 (16), 191 ($PN(SiMe_3)_2^+$, 8), 150 (14), 146 (22), 131 (18), 118 ($PNSiMe_3^+$, 13), 73 (Me_3Si^+, 68); CP-MAS ^{31}P NMR δ 44.2 (P middle), 51.8 (P end); IR (KBr pellet, 4000–400 cm^{-1}) ν 3379 w (νNH), 3277 s, 3242 s, 3180 s, 3011 w, 2959 vs, 2901 s, 2637 w, 1420 w, 1406 w, 1308 s, 1292 s, 1252 vs, 991 vs, 982 vs, 968 vs, 930 m, 899 m, 845 vs, 787 s, 760 w, 719 w, 694 m, 633 s.

Single-Crystal X-ray Diffraction Studies of 12

Colorless crystals were grown from a CS_2 solution. A suitable single crystal (0.40 × 0.40 × 0.30 mm) was mounted on a glass fiber on an Enraf-Nonius CAD4 diffractometer for data collection. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information is given in Table 2. Lorentz and polarization corrections were applied as well as a correction based on a decay in the standard reflections of 2.6%. An absorption correction was based on a series of ψ scans. The space group $P_{\bar{1}}$ was determined by intensity statistics, and the structure was solved by direct method [27]. All nonhydrogen atoms were placed directly from the E-map and were refined with anisotropic thermal parameters. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP programs [28].

The atomic positional parameters are listed in Table 3. A copy of the crystallographic data has been deposited with the Cambridge Crystallographic Data Centre.

TABLE 2 Crystallographic Data for **12**

Formula	$P_3S_3N_7Si_5C_{15}H_{52}$
fw	660.15
a (Å)	11.933(3)
b (Å)	12.659(3)
c (Å)	13.542(2)
α (deg)	75.76(2)
β (deg)	70.51(2)
γ (deg)	82.82(2)
V (Å^3)	1867(13)
Z	2
Space group	P1 bar (No. 2)
T (°C)	−50
λ (Å)	0.71073
d_{calcd} (g cm^{-3})	1.17
μ (cm^{-1})	4.9
R^a	0.035
R_w^b	0.056

$^aR = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.
$^bR_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|)$.

TABLE 3 Positional Parameters for **12**

Atom	*x*	*y*	*z*	*B* (Å^2)
S1	0.20871(5)	0.02803(4)	0.64599(4)	3.27(1)
S2	0.46309(5)	0.35500(4)	0.52305(4)	3.11(1)
S3	0.41891(5)	0.09427(4)	0.26030(4)	3.32(1)
P1	0.27857(4)	0.10929(4)	0.71574(4)	2.50(1)
P2	0.49726(4)	0.19900(4)	0.53364(4)	2.25(1)
P3	0.47530(4)	0.19621(4)	0.31858(4)	2.45(1)
Si1	0.08088(5)	0.29131(5)	0.73345(5)	3.17(1)
Si2	0.28300(6)	0.08895(5)	0.94642(5)	3.56(1)
Si3	0.74818(5)	0.21513(5)	0.54538(5)	3.10(1)
Si4	0.28407(6)	0.35967(6)	0.25308(5)	4.01(1)
Si5	0.69497(6)	0.32360(5)	0.16713(5)	3.99(2)
N1	0.2259(2)	0.2345(1)	0.7183(2)	3.13(4)
N2	0.2660(2)	0.0440(1)	0.8393(1)	3.18(4)
N3	0.6375(1)	0.1621(1)	0.5141(1)	2.62(4)
N4	0.4044(2)	0.3156(1)	0.3013(1)	2.99(4)
N5	0.6172(2)	0.2214(1)	0.2724(1)	3.08(4)
N6	0.4250(1)	0.1244(1)	0.6542(1)	2.36(3)
N7	0.4555(1)	0.1448(1)	0.4499(1)	2.34(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(cos γ)*B(1,2) + ac(cos β)*B(1,3) + bc(cos α)*B(2,3)].

ACKNOWLEDGMENT

The authors are grateful to the Donors of the Petroleum Research Fund administered by the American Chemical Society for a grant in support of this research.

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