UV–visible spectrum is in accord with the spectra reported[1] for the other $W_3S_4^{4+}$ species.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. $[W_3S_4Cl_3(dmpe)_3]PF_6 \cdot H_2O$, 113353-42-7; $[W_3S_4Cl_3(dmpe)_3]BPh_4$, 113471-51-5.

Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Specific Syntheses of the Unsaturated Phosphorus-Nitrogen-Sulfur Rings $R_2PN_3S_2$, $1,5-(R_2P)_2N_4S_2$, and $R_2PN_5S_3$ (R = Ph, Me)

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Stephen W. Liblong, and Trenton Parks

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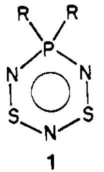
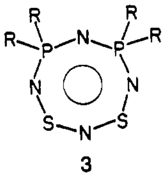
The cyclophosphathiazenes **1**–**3**[1] are aggregates of R_2PN and SN units that can be considered as hybrids of the well-known phosphazene and thiazene ring systems. The first example, **1** (R = Me_3SiNH), was prepared in 1976 by the reaction of S_4N_4 with $(Me_3Si)_2NP(NSiMe_3)_2$.[4,5] Subsequently, we obtained two other phosphadithiatriazines, **1a** (R = Ph) and **1b** (R = Me), from the reaction of S_4N_4 with R_2PPR_2.[6] Compound **1b** decomposes at room temperature to give the eight-membered ring **2b** (R = Me).[7] Further investigations of the reaction of R_2PPR_2 (or Ph_2PH) with S_4N_4 led to the isolation of both 1,3- and 1,5-diphosphadithiatetrazocines, **2a** and **3a** (R = Ph) and **2b** and **3b** (R = Me).[8] The yields of **2a** and **2b** are very low, however, and the separation and purification procedures for **1** and **3** are time-consuming. The rings **1** (R = CF_3, C_2F_5) have also been obtained in low yields (<20%) from the reaction of $R_2PN(SiMe_3)_2$ with $S_3N_2Cl_2$ and found to decompose at room temperature to give **3** (R = CF_3).[9]



1



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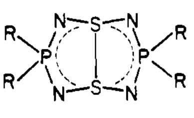

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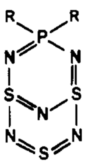

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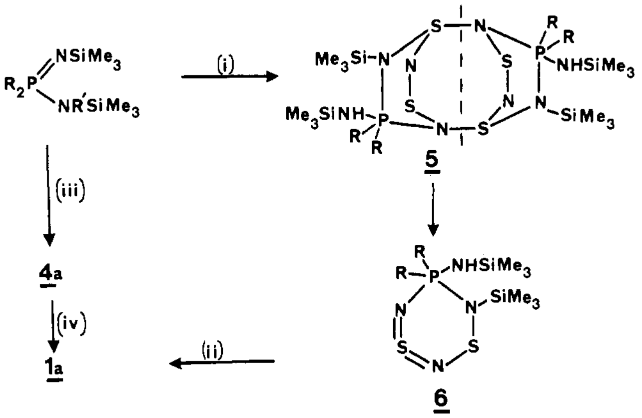

Scheme I. Synthetic routes to **1a** from the reagents $R_2P(NR'SiMe_3)(NSiMe_3)$ (R = H, $SiMe_3$)[a]

[a] Key: (i) R = H′; S_4N_4, toluene reflux; (ii) R = Ph; $-(Me_3Si)_2NH$; (iii) R = Ph, R′ = $SiMe_3$; $(NSCl)_3$, CH_2Cl_2, 0 °C; (iv) toluene, 100 °C.

Some aspects of the chemistry of **1**–**3** have been described,[6,10–12] but these investigations have been hampered by the lack of good preparative routes for individual ring systems. The synthesis of organic analogues of **1** and **2**, in which R_2P groups are replaced by RC, via cyclocondensation reactions of $RC(NR)(NR_2)$ (R = H, $SiMe_3$) with SCl_2[13] or $(NSCl)_3$,[14] suggested that a similar approach might be successful for the preparation of **1** and **2**. We have, therefore, investigated the synthesis of these PNS rings from the readily available reagents $Ph_2P(NR)(NRR')$ (R = Me_3Si; R′ = H, $SiMe_3$). The direct synthesis of the bicyclic compounds **4a** and **4b** using these reagents is also described.

Experimental Section

Reagents and General Procedures. All solvents were dried and freshly distilled before use: toluene (Na), acetonitrile (CaH_2 and P_2O_5), methylene dichloride (P_2O_5), chloroform (P_2O_5). All reactions and the manipulation of moisture-sensitive reagents were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox (oxygen scavenger, Fisher), P_2O_5, and silica gel.

Diphenylphosphine, chlorodiphenylphosphine, trimethylsilyl azide, and sulfur dichloride (all from Aldrich) were distilled before use. $Ph_2P(NHSiMe_3)(NSiMe_3)$ was prepared by heating a neat mixture of trimethylsilyl azide and diphenylphosphine (2:1 molar ratio) until nitrogen evolution ceased.[15] Literature procedures were used for the preparation of S_4N_4,[16] $(NSCl)_3$,[17] $Me_2PN(SiMe_3)_2$,[18] and $Me_2P(NSiMe_3)[N-$

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(1) The term cyclophosphathiazene refers here to unsaturated P–N–S rings containing two-coordinate sulfur in the formal oxidation state of +3. Related hybrid ring systems containing either three-coordinate sulfur in the +4 oxidation state[2] or four-coordinate sulfur in the +6 oxidation state[3] are known and are sometimes also referred to as cyclophosphathiazenes.

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Table I. ^{31}P NMR Chemical Shifts for Reagents and Products

compd^a	$\delta(^{31}P)^b$	
$Ph_2P(NHSiMe_3)(NSiMe_3)$	0.2	
$Ph_2P(NSiMe_3)[N(SiMe_3)_2]$	7.3	
$Me_2P(NSiMe_3)[N(SiMe_3)_2]$	15.2	
$Ph_2PN_3S_2$	−21.3	(−21.2)[6b]
$Me_2PN_3S_2$	5.7	(6.2)[6b]
$Ph_2PN_5S_3$	−21.4	(−21.3)[8]
$Me_2PN_5S_3$	−4.9	(−4.4)[8]
$1,5\text{-}Ph_2P(NSN)_2PPh_2$	113.8	(113.9)[11]
$1,5\text{-}Me_2P(NSN)_2PMe_2$	119.7^c	(110.0)[11]

^{a} In $CDCl_3$. ^{b} Reference: external 85% H_3PO_4; literature values are given in parentheses. ^{c} Revised value.

$(SiMe_3)_2]$.[19] *Caution! S_4N_4 may explode if subjected to heat or friction. The recommended precautions for handling S_4N_4 should be followed.*[20] $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ was prepared from $Ph_2PN(SiMe_3)_2$ and Me_3SiN_3 by using the procedure described for $Me(Ph)P(NSiMe_3)[N(SiMe_3)_2]$.[21]

The identity and purity of all products were determined by comparison of IR and ^{31}P NMR spectra with those of authentic samples: $R_2PN_3S_2$ (R = Ph, Me),[6b] $R_2PN_5S_3$ (R = Ph, Me),[11] $1,5\text{-}(R_2P)_2N_4S_2$ (R = Ph, Me).[8]

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr windows) on a Nicolet 5DX FT-IR spectrometer. ^{31}P NMR spectra were obtained by use of a Varian XL-200 instrument with external 85% H_3PO_4 as the reference. The ^{31}P NMR chemical shifts for all reagents and products are given in Table I.

Preparation of $Ph_2PN_3S_2$ (1a) from $Ph_2P(NHSiMe_3)(NSiMe_3)$. A mixture of S_4N_4 (1.0 g, 5.4 mmol) and $Ph_2P(NHSiMe_3)(NSiMe_3)$ (3.9 g, 10.8 mmol) in toluene (200 mL) was heated at reflux for 30 h. The purple solution was allowed to cool to room temperature. Solvent was removed in vacuo to give a dark purple powder, which was recrystallized twice from hot acetonitrile (50 mL) to give $Ph_2PN_3S_2$ (2.7 g, 9.3 mmol, 86%).

Preparation of $Ph_2PN_5S_3$ (4a). A solution of $Ph_2P[N(SiMe_3)_2](NSiMe_3)$ (7.88 g, 18.2 mmol) in methylene dichloride (50 mL) was added dropwise (45 min) to a stirred solution of $(NSCl)_3$ (4.52 g, 18.5 mmol) in methylene dichloride (100 mL). After 45 min at 0 °C the volume of the solution was reduced to 40 mL in vacuo and this solution was transferred slowly with vigorous stirring into a 500-mL flask containing hexanes (250 mL) at −78 °C. The orange-brown precipitate of $Ph_2PN_5S_3$ (5.63 g, 16.0 mmol, 88%) was collected by filtration.

Preparation of $Ph_2PN_3S_2$ (1a) via $Ph_2PN_5S_3$ (4a). A solution of $Ph_2P[N(SiMe_3)_2](NSiMe_3)$ (17.8 g, 41.1 mmol) in acetonitrile (60 mL)–methylene dichloride (20 mL) was added dropwise to a stirred solution of $(NSCl)_3$ (9.65 g, 39.5 mmol) in methylene dichloride (150 mL)–acetonitrile (100 mL) at 0 °C. The yellow-green solution became orange and then dark brown. Upon completion of the addition, a small amount of precipitate (0.30 g) was removed by filtration and solvents were removed from the filtrate in vacuo to give a brown oil. This product was dissolved in toluene (100 mL), and the solution was heated at reflux for 16 h. Solvent was removed in vacuo to give a purple solid, which was recrystallized from acetonitrile to produce $Ph_2PN_3S_2$ (1a) (8.46 g, 29.0 mmol). Upon removal of solvent from the filtrate and recrystallization of the purple residue from acetonitrile, a second crop of 1a (2.08 g, 7.14 mmol) was obtained. The total yield of 1a was 91%.

Preparation of $Me_2PN_5S_3$ (4b). A solution of $Me_2P[N(SiMe_3)_2](NSiMe_3)$ (4.22 g, 13.7 mmol) in methylene dichloride (30 mL) was added dropwise to a stirred solution of $(NSCl)_3$ (3.60 g, 14.7 mmol) in methylene dichloride at 0 °C. After 1 h at 0 °C the volume of the red-brown solution was reduced to ca. 20 mL under vacuum and the resulting solution was added slowly to hexanes (125 mL) at −78 °C to give an orange-brown precipitate of $Me_2PN_5S_3$ (2.10 g, 9.2 mmol, 67%).

Preparation of $Me_2PN_3S_2$ (1b) via $Me_2PN_5S_3$ (4b). A solution of $Me_2P[N(SiMe_3)_2](NSiMe_3)$ (5.42 g, 17.6 mmol) in methylene dichloride (50 mL) was added dropwise to a solution of $(NSCl)_3$ (4.24 g, 17.3 mmol) in methylene dichloride (100 mL) at 0 °C. After 2 h at 23 °C the solvent was removed from the dark orange-brown solution under vacuum and the dark red residue was dissolved in benzene (125 mL) and heated at reflux for 4 h to give a deep purple solution. Solvent was removed at 10 °C (0.1 Torr) to give a purple oil (ca. 2.5 g).

On this scale the attempted purification of $Me_2PN_3S_2$ by the literature procedure[6b] of sublimation at 23 °C (0.1 Torr) onto a cold finger at −78 °C resulted in thermal decomposition.[7] Consequently, the product was allowed to stand at 23 °C for 7 days, whereupon it was treated with hot acetonitrile. The CH_3CN-insoluble material was recrystallized from toluene to give S_4N_4 (0.46 g, 2.5 mmol). The acetonitrile filtrate yielded $1,5\text{-}Me_4P_2N_4S_2$ (0.78 g, 3.2 mmol).

Preparation of $1,5\text{-}(Ph_2P)_2N_4S_2$ (2a). A solution of SCl_2 (4.54 g, 44.1 mmol) in methylene dichloride (50 mL) was added dropwise (45 min) to a stirred solution of $Ph_2P[N(SiMe_3)_2](NSiMe_3)$ (11.8 g, 27.2 mmol) in methylene dichloride (75 mL) at 23 °C. After 16 h a ^{31}P NMR spectrum of the reaction mixture showed it to contain mainly $1,5\text{-}(Ph_2P)_2N_4S_2$ (2a) with smaller amounts of 1a, $(Ph_2P)_2N_3SCl$,[22] and two other unidentified phosphorus-containing compounds. Solvent and volatile products were removed under vacuum, and the solid residue was dissolved in hot acetonitrile (150 mL). After 1 day at 0 °C pale purple crystals of 2a (3.39 g, 6.91 mmol, 50%) were obtained by filtration. The very pale purple color is due to the presence of 1a, but this impurity is not detectable in the ^{31}P NMR spectrum of the product.

Preparation of $1,5\text{-}(Me_2P)_2N_4S_2$ (2b). A solution of sulfur dichloride (7.30 g, 70.9 mmol) in methylene dichloride (60 mL) was added dropwise ($^1/_2$ h) to a solution of $Me_2P[N(SiMe_3)_2](NSiMe_3)$ (13.7 g, 44.4 mmol) in methylene dichloride (125 mL) at −78 °C. The reaction mixture was allowed to come to room temperature during 16 h to give a dark red solution. Solvent was removed under vacuum, and the purple semisolid residue (7.2 g) was extracted with boiling acetonitrile (180 mL). After filtration to remove $c\text{-}S_8$ (0.83 g), the filtrate was cooled to −20 °C to give pale pink crystals of $1,5\text{-}(Me_2P)_2N_4S_2$ (2b) (2.68 g, 11.1 mmol). The filtrate was reduced to half-volume and cooled to −20 °C to yield a further 0.18 g of 2b. The total yield was 53%.

Results and Discussion

Synthesis of $Ph_2PN_3S_2$ (1a). The reaction of $Ph_2P(NHSiMe_3)(NSiMe_3)$ with S_4N_4 in toluene at reflux in a 2:1 molar ratio produces 1a in 86% yield. In contrast to the previous procedures for the preparation of 1a,[3,5] this reaction gives 1a exclusively and the pure compound is readily obtained by recrystallization of the crude product from acetonitrile. We propose that the reaction proceeds via a double 1,4-cycloaddition of the P=N bond of the phosphorus reagent to give the diadduct, 5, shown in Scheme I. A similar diadduct has been isolated by Appel and Halstenberg from the reaction of $(Me_3Si)_2NP(NSiMe_3)_2$ with S_4N_4, but it decomposes symmetrically to give a derivative of the six-membered ring, 6.[4] In our system the ^{31}P NMR spectra of reaction mixtures produced in either methylene dichloride or acetonitrile at reflux showed a small peak at −0.2 ppm in addition to the signals for $Ph_2P(NHSiMe_3)(NSiMe_3)$ and 1a. It is possible that this peak is due to 5 or, more likely, to 6 (R = Ph), but it has a much lower intensity than that of 1a at all stages of the reaction. Thus, it appears that the decomposition of 6 (R = Ph) into 1a occurs faster than the production of 6 under the conditions necessary for the reaction, so that the isolation of 6 is not possible. The inter- or intramolecular elimination of $(Me_3Si)_2NH$ from 6 (R = Ph) will give 1a as the exclusive product.

In principle, this route to phosphadithiatriazines could be used for a wide variety of derivatives by using reagents of the type $R_2P(NHSiMe_3)(NSiMe_3)$, but the thermal instability of other derivatives of 1 (e.g. Me,[6] CF_3,[9] F[11]) may limit its widespread application. Surprisingly, we found that the use of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ instead of $Ph_2P(NSiMe_3)(NHSiMe_3)$ in the reaction with S_4N_4 did not produce 1a. However, an alternative route to 1a using the former reagent is described below.

Synthesis of $R_2PN_5S_3$ (R = Ph (4a), Me (4b)). The reaction of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ with $(NSCl)_3$ in acetonitrile produces the bicyclic compound 4a in ca. 90% yield (Scheme I[23]). Compound 4b can be prepared in 67% yield in a similar manner. The previous synthesis of 4a or 4b involved the prior formation

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of **1a** or **1b** followed by oxidative addition of Cl_2 and treatment with $Me_3SiNSNSiMe_3$.[11] The compounds (R = R′ = F; R = F, R′ = Ph) are obtained from the reaction of PF_5 (or $PhPF_4$) with $Me_3SiNSNSiMe_3$, but that approach cannot be extended to other derivatives.[24]

If **4a** produced by this new method is heated, without isolation in boiling toluene, then **1a** is obtained in an overall yield of ca. 90% (Scheme I). In principle, this route to **1** should be applicable to other derivatives, since a variety of reagents of the type $R_2P(NSiMe_3)[N(SiMe_3)_2]$ can be prepared from the reaction of $R_2PN(SiMe_3)_2$ with trimethylsilyl azide. We have used this new procedure for the synthesis of **1b**, but the attempted purification of the crude product by sublimation resulted in the known thermal decomposition of **1b**[7] to give 1,5-$(Me_2P)_2N_4S_2$ and S_4N_4 in overall yields of 53% and 41%, respectively, based on 70% conversion of **4b** into **1b** followed by decomposition according to eq 1.

$$2Me_2PN_3S_2 \rightarrow (Me_2P)_2N_4S_2 + S_4N_4 \qquad (1)$$

Compound **1c** (R = Et) [$\delta(^{31}P) = +6.9$, *m/e* 195 (M^+)] was also prepared by this new procedure, but the thermal instability of this new derivative prevented its full characterization. It should be noted, however, that thermally unstable phosphadithiatriazines can be conveniently stored as norbornadiene adducts.[6b,11]

Synthesis of 1,5-$(R_2P)_2S_2N_4$ (R = Ph (2a), Me (2b)). The reaction of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ with SCl_2 was investigated by using a variety of solvents and reaction conditions before the optimum procedure was established. This involves the dropwise addition of SCl_2 to a solution of the phosphorus reagent in methylene dichloride using a 3:2 molar ratio of the reagents.

$$2Ph_2P(NSiMe_3)[N(SiMe_3)_2] + 3SCl_2 \rightarrow (Ph_2P)_2N_4S_2 + 6Me_3SiCl + {}^1/_8S_8 \qquad (2)$$

However, the detection of **1a**, $(Ph_2P)_2N_3SCl$,[22] and two unidentified phosphorus-containing products in the reaction mixture by ^{31}P NMR spectroscopy shows that the reaction is more complicated than indicated by eq 1. Nevertheless, pure **2a** can be isolated in 50% yield based on the amount of phosphorus reagent used by taking advantage of its low solubility, compared to that of the other products, in acetonitrile. This procedure represents a marked improvement over previous methods for the preparation of **2a**,[8] and it can also be used for the preparation of **2b** in ca. 50% yield. Similar reactions with other reagents of the type $RR'P[N(SiMe_3)_2(NSiMe_3)$[21] should lead to new derivatives of the heterocycle **2**, including those with different substituents on phosphorus.

Summary. Specific synthetic procedures have been developed for the preparation of the individual ring systems **1a**, **4a**, and **4b** in excellent yields from readily obtainable starting materials. A much improved synthesis of **2a** and **2b** that is potentially applicable to other derivatives of **2** has also been achieved. These new methods should facilitate investigations of the chemistry of these cyclophosphathiazenes.

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Registry No. **1a**, 76958-87-7; **1b**, 80126-92-7; **2a**, 85028-71-3; **2b**, 80106-10-1; **4a**, 90498-60-5; **4b**, 90498-61-6; S_4N_4, 28950-34-7; $Ph_2P(NHSiMe_3)(NSiMe_3)$, 21955-74-8; $Ph_2P[N(SiMe_3)_2](NSiMe_3)$, 61500-31-0; $(NSCl)_3$, 5964-00-1; $Me_2P[N(SiMe_3)_2](NSiMe_3)$, 21385-93-3; SCl_2, 10545-99-0.

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Effect of Pressure-Induced Freezing on the Energy of the Intervalence Electronic Absorption Band of a Binuclear Mixed-Valence Complex

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Intramolecular electron transfer (IET) is one of the most fundamental and important chemical processes.[3] Creutz and Taube[4] and Cowan and Kaufman[5] pioneered the use of binuclear transition-metal mixed-valence complexes[6] to study IET. A distinguishing characteristic of the electronic spectrum of many binuclear mixed-valence complexes is a low-energy band which cannot be attributed to either metal center alone, since it arises when electron transfer is photoinduced from one metal center to the other. This excitation is often referred to as an intervalence-transfer (or IT) band. In two previous papers we demonstrated that (1) the energy of the IT band maximum was very sensitive to concentration[7] and (2) a dielectric continuum model is not an adequate description of the energy of the IT band in solution.[8] In this paper we continue our study of the application of the dielectric continuum model to IET.

Some authors[9–11] have described the energy (λ) of the IT band as arising from two contributions: one (λ_{out}) from the reorganization of the outer-sphere coordination, i.e. the solvent structure, and the other (λ_{in}) from the reorganization of the inner sphere as indicated in eq 1. Usually a dielectric continuum model is

$$\lambda = \lambda_{out} + \lambda_{in} \qquad (1)$$

used to describe the solvent reorganizational contribution

$$\lambda_{out} = k(\Delta e)^2(D_{op}^{-1} - D_s^{-1}) \qquad (2)$$

where the proportionality factor k can be explicitly given in terms of the radii of the reactants in certain cases and in other cases can be treated with numerical techniques. In eq 2, Δe is the charge transferred, D_{op} is the optical dielectric constant (usually taken as the square of the refractive index n), and D_s is the low-frequency dielectric constant of the medium. It should be noted that eq 2 was developed by Marcus[12] for *inter*molecular electron transfer and others have applied it to interpret the energy of the IR band observed for mixed-valence complexes.[10,11] Specifically the application has been to localized mixed-valence compounds. There have been several calculations[13] carried out on the basis of eq 2.

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