

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231454845>

Preparation and molecular and electronic structures of cyclo-1 λ 5-phospha-3,5-dithia-2,4,6-triazenes and their norbornadiene adducts

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MARCH 1982

Impact Factor: 12.11 · DOI: 10.1021/ja00369a023

CITATIONS

48

READS

12

7 AUTHORS, INCLUDING:



Paul Swepston

Rigaku

28 PUBLICATIONS 576 CITATIONS

SEE PROFILE

Preparation and Molecular and Electronic Structures of Cyclo-1 λ^5 -phospha-3,5-dithia-2,4,6-triazenes and Their Norbornadiene Adducts

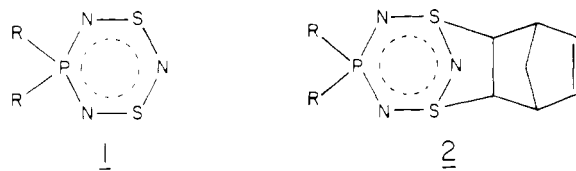
N. Burford,^{1a} T. Chivers,^{*1a} A. W. Cordes,^{1b} W. G. Laidlaw,^{1a} M. C. Noble,^{1b}
R. T. Oakley,^{1a} and P. N. Swebston^{1b}

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4 Canada, and the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. Received July 20, 1981

Abstract: The reaction of R_2PPR_2 ($R = \text{Me, Ph}$) or $(\text{PhO})_3\text{P}$ with S_4N_4 in toluene at reflux produces cyclo-1 λ^5 -phospha-3,5-dithia-2,4,6-triazenes $R_2\text{PS}_2\text{N}_3$ ($R = \text{Me, Ph, OPh}$), the cyclic structures of which have been confirmed by ^{15}N NMR spectroscopy. The crystal and molecular structure of $\text{Ph}_2\text{PS}_2\text{N}_3$ has been determined by X-ray crystallography. The crystals of $\text{Ph}_2\text{PS}_2\text{N}_3$ are monoclinic, space group $P2_1/c$, $a = 8.305$ (1) Å, $b = 13.183$ (2) Å, $c = 12.487$ (1) Å, $\beta = 105.53$ (1)°, and $Z = 4$. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares techniques, and all nonhydrogen atoms were refined anisotropically to give a final $R = 0.047$ and $R_w = 0.077$ for 1471 reflections with $I > 3\sigma(I)$. The structure consists of a 6-membered PS_2N_3 ring in which the five-atom sequence NSNSN is coplanar to within 0.05 Å, while the phosphorus atom is 0.284 (1) Å out of this plane. The S-N bond lengths are within the range 1.560 (3)–1.583 (5) Å, while the mean P-N bond length is 1.623 (4) Å. The angles at phosphorus are $\angle P_{\text{endo}} = 115.8$ (2)° and $\angle P_{\text{exo}} = 107.1$ (2)°. Ab initio Hartree-Fock-Slater SCF calculations on the model compound $\text{H}_2\text{PS}_2\text{N}_3$ show that (a) the PS_2N_3 ring contains eight π electrons largely delocalized over the NSNSN sequence, (b) contributions from 3d orbitals on phosphorus have an important stabilizing influence on the antibonding π^* MOs (c) the strong visible absorption band at 550–580 nm in $R_2\text{PS}_2\text{N}_3$ ($R = \text{Me, Ph, OPh}$) can be assigned to a $\text{HOMO}(\pi^*) \rightarrow \text{LUMO}(\pi^*)$ transition (calculated wavelength ca. 560 nm), and (d) the experimental geometry of the PS_2N_3 ring (as observed in $\text{Ph}_2\text{PS}_2\text{N}_3$) is slightly lower in energy (ca. 15 kcal mol $^{-1}$) than that of a planar PS_2N_3 ring. The phosphadithiatriazenes readily form adducts of the type $R_2\text{PS}_2\text{N}_3 \cdot \text{C}_7\text{H}_8$ with norbornadiene. The crystal and molecular structure of $\text{Ph}_2\text{PS}_2\text{N}_3 \cdot \text{C}_7\text{H}_8$ has been determined by X-ray crystallography. The crystals are triclinic, space group $P1$, $a = 9.239$ (1) Å, $b = 6.284$ (1) Å, $c = 9.314$ (1) Å, $\alpha = 76.98$ (1)°, $\beta = 118.98$ (1)°, $\gamma = 110.08$ (1)°, and $Z = 1$. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures, and all nonhydrogen atoms were refined anisotropically to give a final $R = 0.046$ and $R_w = 0.063$ for 1583 reflections with $I > 3\sigma(I)$. The structural determination confirms the ^1H and ^{13}C NMR evidence that the cycloaddition of norbornadiene to $\text{Ph}_2\text{PS}_2\text{N}_3$ occurs in a 1,3 fashion across the two sulfur atoms to give the exo- β isomer of the adduct. As a result of the addition, the central N atom of the NSNSN unit is displaced by 0.817 (6) Å from the plane of the central S_2N_2 unit, which is planar to within 0.01 Å. The S-N bond lengths are 1.61–1.64 Å, the lengthening being attributed primarily to the rupture of the π system. The cycloaddition can be regarded as a symmetry-allowed ($8_s + 2_s$) reaction, and the preference for S,S addition can be readily understood from consideration of the eigenvector coefficients of the HOMO and LUMO of the PS_2N_3 ring.

We have demonstrated that the reactions of a wide range of nucleophiles (S^{2-} , CN^- , N_3^- , NH_2^-) with tetrasulfur tetranitride result in the formation of one or both of the two binary anions S_3N_3^- and $\text{S}_4\text{N}_5^{2-}$.² More recently we have examined the reaction of triphenylphosphine with S_4N_4 and found that while the S_4N_5^- anion is formed in this reaction also, the major products are (depending on the solvent) the triphenylphosphinimino-substituted rings $\text{Ph}_3\text{P}=\text{N}-\text{S}_3\text{N}_3$ and 1,5-($\text{Ph}_3\text{P}=\text{N}$) $_2\text{S}_4\text{N}_4$.³ As a continuation of this work on the reductive degradation of S_4N_4 with phosphines, we have carried out an investigation of the reactions of diphosphines $R_2\text{PPR}_2$ ($R = \text{Me, Ph}$) and triphenyl phosphite with S_4N_4 .⁴ The products isolated from these reactions are the novel six-membered cyclo-1 λ^5 -phospha-3,5-dithia-2,4,6-triazenes, $R_2\text{PS}_2\text{N}_3$, **1** ($R = \text{Me, Ph, OPh}$). Another molecule of this type (with $R = \text{Me}_3\text{SiNH}$) was recently synthesized by Appel and Halstenberg.^{5,6} One of the most striking features of these derivatives is the intense low-energy absorption ($\lambda_{\text{max}} \sim 550$ nm, $\epsilon \sim 10^3$ M $^{-1}$ cm $^{-1}$) which they exhibit in their visible spectrum.

In our initial communication on the preparation and structure of **1** ($R = \text{Ph}$), we described its electronic structure in terms of a



cyclic delocalized eight-electron π system and suggested that a $\text{HOMO}(\pi^*) \rightarrow \text{LUMO}(\pi^*)$ excitation was responsible for its intense purple color. In order to probe more fully the electronic structure of these heterocycles, we have carried out SCF Hartree-Fock-Slater ab initio calculations on a model $\text{H}_2\text{PS}_2\text{N}_3$ system. These all-electron calculations refine the simple HMO results without contradicting their basic conclusions.⁴ In addition they provide important evidence for the role of 3d orbitals in the bonding of pentavalent tetracoordinate phosphorus compounds. We have also tested the usefulness of the MO description through the reactions of these heterocycles with olefins. The phosphadithiatriazenes **1** ($R = \text{Me, Ph, and OPh}$) all undergo a 3,5-cycloaddition reaction with norbornadiene to produce the adducts **2**. Correlation of the orbital symmetries of the reactants and products indicates that this reaction can be viewed as a novel example of an inorganic $8_s + 2_s$ process.

Herein we provide a full account of the preparation and spectral (^1H , ^{13}C , ^{15}N , and ^{31}P NMR) characterization of the phosphadithiatriazenes **1** and their norbornadiene adducts **2**. We also report the crystal and molecular structures of $\text{Ph}_2\text{PS}_2\text{N}_3$ (**1**, Ph) and $\text{Ph}_2\text{PS}_2\text{N}_3 \cdot \text{C}_7\text{H}_8$ (**2**, Ph).

(1) (a) University of Calgary; (b) University of Arkansas.

(2) (a) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668. (b) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1977**, 453. (c) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318. (d) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391.

(3) Bojes, J.; Chivers, T.; Cordes, A. W.; MacLean, G.; Oakley, R. T. *Inorg. Chem.* **1981**, *20*, 16.

(4) For a preliminary communication on a part of this work, see: Burford, N.; Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swebston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 1204.

(5) Appel, R.; Halstenberg, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 696.

(6) Weiss, J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2272.

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride,⁷ tetraphenyldiphosphine,⁸ and tetramethyldiphosphine⁹ were all prepared according to literature methods. Diphenylphosphine (Ventron), chlorodiphenylphosphine (Aldrich), tetramethyldiphosphine disulfide (Strem), triphenyl phosphite (Aldrich), iron powder (Ventron), and norbornadiene (Aldrich) were all commercial products and used as received. All the solvents employed were of reagent grade and most were dried before use, toluene by distillation from sodium, acetonitrile by double distillation from P₂O₅ and calcium hydride, and dichloromethane by distillation from P₂O₅. Anhydrous diethyl ether (Mallinckrodt) was used as received. All distillations of solvents and all reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridx and silica gel. Infrared (4000–250 cm⁻¹) spectra were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. UV-vis spectra were obtained by using a Cary 219 spectrophotometer. ¹H, ¹³C, ¹⁵N, and ³¹P NMR spectra were obtained on a Varian XL-200 NMR spectrometer operating in the FT mode. Acquisition parameters and referencing procedures for the ¹⁵N spectra were similar to those described elsewhere.¹⁰ ¹⁵N chemical shifts are reported by using the δ scale with NH₃(l) (at 25 °C) as an arbitrary zero point. Chemical shifts relative to MeNO₂ can be obtained by using the relation δ(MeNO₂) = δ(NH₃) – 380.23 ppm.¹¹ ¹⁵N-labeled S₄N₄ was prepared according to a previously described method,¹⁰ using 99% enriched ¹⁵N ammonium chloride supplied by Merck, Sharpe, and Dohme. ¹⁵N-enriched R₂PS₂N₃ derivatives were prepared as described below by use of ¹⁵N-labeled S₄N₄. Chemical analyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Preparation of Ph₂PS₂N₃ (1, R = Ph). Tetrasulfur tetranitride (1.23 g, 6.68 mmol) was added to a solution of tetraphenyldiphosphine (2.48 g, 6.70 mmol) in 40 mL of toluene, and the mixture was stirred and heated to reflux under an atmosphere of nitrogen. Within 15 min the color of the solution had turned from yellow to an intense red-purple. After 14 h the mixture was cooled and the toluene removed in vacuo to a volume of about 10 mL. The solution was then filtered and eluted down a 30 × 500 mm Bio-Beads S-X8 chromatography column, giving rise to four definite color zones: brown-orange, red, purple, and yellow. The purple band was further purified by a second elution. Evaporation of the solvent from the yellow fraction gave 0.12 g of unreacted S₄N₄ (identified by its infrared spectrum). Removal of the solvent from the purple fraction gave a solid which was recrystallized from warm acetonitrile as lustrous, deep purple plates of Ph₂PS₂N₃ (1, R = Ph): mp 93–94 °C (0.48 g, 1.65 mmol, 21%); IR (1600–250 cm⁻¹ region) 1587 (w), 1564 (w), 1480 (m), 1437 (s), 1336 (w), 1315 (w), 1276 (w), 1161 (w), 1123 (vs), 1115 (vs), 1070 (vs), 1029 (s), 1026 (m), 997 (m), 935 (vw), 840 (vw), 765 (m), 759 (m), 741 (vs), 727 (vs), 692 (vs), 621 (w), 619 (w), 526 (s), 507 (s), 447 (vw), 437 (vw), 350 (vw), 319 (vw), 282 (vw) cm⁻¹. Anal. Calcd for C₁₂H₁₀N₃PS₂: C, 49.47; H, 3.46; N, 14.42; P, 10.63; S, 22.01. Found: C, 49.26; H, 3.67; N, 14.18; P, 10.79; S, 21.84.

Preparation of Me₂PS₂N₃ (1, R = Me). Tetrasulfur tetranitride (2.38 g, 12.9 mmol) was added to an ice-cooled solution of tetramethyldiphosphine (1.58 g, 12.9 mmol) in 15 mL of toluene. The mixture was stirred at 0 °C for 30 min and allowed to warm slowly to room temperature over a period of 1 h¹² (Caution: See ref 12). The mixture was then heated under reflux for 3 h. The resulting purple solution was cooled and filtered to remove tetramethyldiphosphine disulfide, and the filtrate was then eluted down a 30 × 500 mm Bio-Beads S-X8 chromatography column, giving rise to three bands: yellow, red, and purple. The purple component was collected and the solvent removed in vacuo. The resulting oil was fractionally sublimed in vacuo onto an ice-water (0 °C) cooled finger to give deep purple crystals (with a green lustre) of Me₂PS₂N₃ 1 (R = Me, 0.25 g, 1.5 mmol, 9%): mp 16–17 °C; IR (1600–250-cm⁻¹ region) 1414 (w), 1299 (w), 1289 (m), 1224 (w), 1083 (vs), 1019 (w), 942 (m), 927 (m), 863 (m), 750 (vw), 727 (w), 688 (vs), 597 (w), 390 (w), 363 (w) cm⁻¹.

Preparation of (PhO)₂PS₂N₃ (1, R = OPh). Tetrasulfur tetranitride (1.13 g, 6.13 mmol) was added to a solution of triphenyl phosphite (3.80 g, 12.26 mmol) in 20 mL of toluene, and the mixture was heated to reflux for 1 h. The resulting black mixture was then eluted down a 20 × 200

Table I. Crystal Data

mol formula	(C ₆ H ₅) ₂ PN ₃ S ₂	(C ₆ H ₅) ₂ PN ₃ S ₂ C ₇ H ₈
mol wt	291.3	383.5
space group; mol/cell	P2 ₁ /c; 4	P1; 1
a, Å	8.305 (1)	9.239 (1)
b, Å	13.183 (2)	6.284 (1)
c, Å	12.487 (1)	9.314 (1)
α, deg	90	76.98 (1)
β, deg	105.53 (1)	118.98 (1)
γ, deg	90	110.08 (1)
V, Å ³	1317.3	441.1
reflectns in cell detn;	14; 66–85	31; 55–89
2θ range		
density (calcd), g cm ⁻³	1.37	1.44
reflectns scanned; obsd	1611; 1471	1615; 1583
(I > 3σ(I))		
2θ range scanned, deg	0–110	0–136
μ(Cu Kα), cm ⁻¹	43.3	34.74
transmission factors,	0.55–0.74	0.60–0.82
min-max		
crystal dimensions, mm	0.22 × 0.14 × 0.62	0.44 × 0.13 × 0.29
final R; R _w	0.047; 0.077	0.046; 0.063
largest shift, final cycle, σ	0.02	0.20
max peak, final diff map,	0.42	0.33
e Å ⁻³		
stand dev, obsd unit wt	0.76	0.68

mm Fluorasil column and the green-blue fraction collected and eluted down a 30 × 500 mm Bio-Beads S-X8 chromatography column. The blue fraction was collected and removal of the solvent in vacuo gave impure (PhO)₂PS₂N₃ (1, R = OPh) (0.31 g, 0.96 mmol, 12%) as a deep blue oil. It was not possible to obtain a satisfactory chemical analysis of this material; the compound was, however, characterized as its norbornadiene adduct (vide infra). The infrared spectrum of (PhO)₂PS₂N₃ (1600–250 cm⁻¹ region) shows bands at 1594 (s), 1489 (vs), 1470 (s), 1456 (s), 1335 (vw), 1308 (vw), 1290 (vw), 1215 (m), 1190 (vs), 1161 (s), 1095 (s), 1035 (s), 1010 (m), 945 (vs), 902 (m), 826 (vw), 802 (m), 773 (m), 757 (s), 717 (w), 689 (s), 656 (vw), 646 (vw), 618 (vw), 572 (w), 557 (w), 500 (m), 380 (vw), and 306 (vw) cm⁻¹.

Preparation of Norbornadiene Adducts R₂PS₂N₃·C₇H₈ (2). These compounds were all prepared by the slow addition of an excess of norbornadiene to a solution of R₂PS₂N₃ (1) in diethyl ether. Precipitation of the adduct occurred almost immediately. The crude material was filtered off and recrystallized from a mixture of acetonitrile, methylene chloride, and norbornadiene. Yields were nearly quantitative. Analytical and infrared data for the individual compounds are as follows:

Ph₂PS₂N₃·C₇H₈: colorless needles, decomposes >105 °C; IR (1600–250 cm⁻¹ region) 1588 (vw), 1569 (vw), 1436 (s), 1323 (m), 1314 (w), 1281 (w), 1258 (w), 1189 (vw), 1180 (w), 1159 (w), 1120 (s), 1111 (vs), 1036 (vs), 1023 (vs), 1013 (vs), 992 (vs), 931 (w), 907 (vw), 867 (w), 830 (vw), 797 (m), 777 (vw), 767 (w), 756 (s), 741 (m), 725 (s), 718 (vs), 699 (s), 688 (m), 661 (vw), 629 (w), 617 (vw), 550 (s), 536 (m), 518 (m), 495 (w), 457 (vw), 447 (vw), 433 (w), 355 (vw), 335 (vw) cm⁻¹. Anal. Calcd for C₁₉H₁₈N₃PS₂: C, 59.51; H, 4.73; N, 10.96. Found: C, 59.46; H, 4.59; N, 10.89.

Me₂PS₂N₃·C₇H₈: colorless blocks, decomposes >120 °C; IR (1600–250 cm⁻¹ region) 1565 (vw), 1560 (vw), 1518 (vw), 1511 (w), 1498 (vw), 1323 (m), 1299 (s), 1289 (s), 1282 (m), 1268 (w), 1258 (w), 1188 (w), 1117 (w), 1055 (vs), 1020 (s), 997 (vs), 979 (m), 952 (m), 933 (vs), 907 (m), 864 (vs), 842 (vw), 832 (vw), 787 (m), 773 (vw), 745 (s), 739 (s), 721 (vs), 694 (s), 653 (vw), 599 (m), 546 (m), 501 (w), 450 (w), 425 (w), 377 (w), 367 (w), 325 (vw), 273 (vw) cm⁻¹. Anal. Calcd for C₉H₁₄N₃PS₂: C, 41.68; H, 5.44; N, 16.20; P, 11.94; S, 24.73. Found: C, 40.85; H, 5.67; N, 16.20; P, 11.81; S, 24.95.

(PhO)₂PS₂N₃·C₇H₈: colorless blocks, decomposes >165 °C; IR (1600–250 cm⁻¹ region) 1595 (m), 1588 (m), 1492 (s), 1455 (m), 1327 (m), 1287 (w), 1269 (vw), 1261 (vw), 1225 (m), 1187 (vs), 1171 (m), 1156 (w), 1125 (w), 1116 (w), 1054 (vs), 1041 (vs), 1029 (s), 1024 (s), 1019 (s), 1006 (m), 985 (w), 961 (s), 934 (vs), 907 (m), 899 (m), 868 (m), 823 (vw), 822 (vw), 803 (s), 791 (m), 769 (m), 757 (s), 748 (s), 735 (s), 693 (m), 667 (vw), 631 (vw), 619 (vw), 610 (vw), 573 (m), 551 (m), 542 (w), 521 (m), 506 (vw), 500 (vw), 487 (w), 451 (vw), 441 (vw), 368 (w), 359 (vw) cm⁻¹. Anal. Calcd for C₁₉H₁₈O₂N₃PS₂: C, 54.93; H, 4.37; N, 10.11; P, 7.45; S, 15.43. Found: C, 54.64; H, 4.23; N, 10.09; P, 7.41; S, 15.61.

X-ray Measurements. Crystal data are given on Table I. Intensity data were collected with the use of a GE-XRD manually operated diffractometer using Ni-filtered Cu Kα (λ = 1.5418 Å) radiation, 10-s

(7) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

(8) Kuchen, W.; Buchwald, H. *Chem. Ber.* **1958**, *91*, 2871.

(9) Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 187.

(10) Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.

(11) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley-Interscience, New York, **1979**.

(12) Caution: The reaction between tetramethyldiphosphine and S₄N₄ is very vigorous in the initial stages. If the temperature is allowed to increase too quickly, there is the possibility of an explosion. Indeed, caution is recommended in all manipulations of S₄N₄.

Table II. NMR Data for Cyclophosphadithiatriazenes and Adducts^a

	Ph ₂ PS ₂ N ₃	Me ₂ PS ₂ N ₃	(PhO) ₂ PS ₂ N ₃	Ph ₂ PS ₂ N ₃ · C ₇ H ₈ ^b	Me ₂ PS ₂ N ₃ · C ₇ H ₈ ^b	(PhO) ₂ PS ₂ N ₃ · C ₇ H ₈ ^b
¹ H		1.71 (² J _{PH} = 14.4)		H _{1,4} 4.13 (d, 1.6) H _{2,3} 3.21 (t, 2.0) H _{5,6} 6.23 H ₇ 1.84, 1.18 (AB, 10.0)	4.31 (d, 1.1) 3.26 6.39 1.80, 1.20 (AB, 9.3)	3.93 (d, 1.6) 3.08 6.12 1.68, 1.09 (AB, 10.0)
				CH ₃ CH ₃	1.57 (² J _{PH} = 14.0) 1.32 (² J _{PH} = 13.4)	
¹³ C { ¹ H} ^c				C _{1,4} 81.6 C _{2,3} 43.8 C _{5,6} 139.5 C ₇ 41.9 CH ₃ CH ₃	82.2 43.7 139.6 41.4 22.4 (¹ J _{PC} = 78.6) 21.9 (¹ J _{PC} = 99.1)	84.0 43.5 139.0 41.2
³¹ P { ¹ H}	-21.2	6.2	-3.4	-17.7	1.8	-23.4
¹⁵ N	N _{2,6} 116.2 (¹ J _{PN} = 51.7) N ₄ 336.2 (³ J _{PN} = 17.2) (² J _{NN} = 2.8)	123.2 (¹ J _{PN} = 51.1) 338.9 (³ J _{PN} = 16.6) (² J _{NN} = 3.0)	135.8 (¹ J _{PN} = 38.9) 407.4 (³ J _{PN} = 20.8) (² J _{NN} = 2.7)			

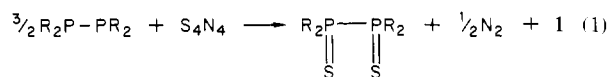
^a δ(CDCl₃, in ppm); reference: internal Me₄Si for ¹H and ¹³C, external H₃PO₄ for ³¹P and NH₃(l) at 25 °C for ¹⁵N. Coupling constants (in parentheses) are quoted in Hz and refer to H-H coupling unless otherwise stated. ^b For C and H numbering scheme, see ref 21. ^c ¹³C assignments are tentative.

stationary-crystal, stationary-counter backgrounds at each end of the scans, and θ-2θ scans at a scan rate of 2° min⁻¹. The scan range was 2° in 2θ for all data except the 120–136° data of the adduct, where a 3° scan was used. Three reflections measured periodically indicated instability/decay of a few percent in both data sets; simple linear corrections were made.

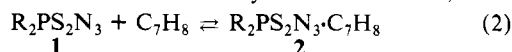
Atomic scattering factors were those of Cromer and Waber.¹³ Real and imaginary anomalous corrections were applied to all nonhydrogen elements.¹⁴ Both structures were solved by using MULTAN 80 and were refined with full-matrix least-squares methods using anisotropic thermal parameters for all nonhydrogen atoms. The least-squares weights were according to σ(F) = 2F_{min} + F + (2/F_{max})F², and no dependence of ΔF/σ on either F or θ was detected for either structure. All hydrogen atoms were located on difference maps; hydrogen atoms were included in the structure factor calculations with isotropic temperature factors (B = 5 Å²) but were constrained to idealized positions (C–H = 0.95 Å). Structure factor tables for the two structures, as well as tables giving hydrogen atom positions (SI) and thermal parameters (SII), are available as supplementary material.

Results and Discussion

Preparation of R₂PS₂N₃ and R₂PS₂N₃·C₇H₈ (1 and 2, R = Me, Ph, OPh). The reactions of tetramethyl- and tetraphenyldiphosphine and of triphenyl phosphite with tetrasulfur tetranitride all give rise to intensely colored (purple) solutions. The reactions are quite rapid, and in the case of R = Me, it is sufficiently exothermic that care must be taken in the initial stages to avoid an explosion. The yields of these preparations are not high (see Experimental Section); although the driving force is undoubtedly the formation of a phosphine sulfide [(R₂PS)₂ or (PhO)₃PS] (eq 1), the mechanism and even the stoichiometry of the reaction remain unclear. The experimental mole ratios reported are simply those that optimize the yield of product in terms of S₄N₄ consumed.



All the phosphadithiatriazenes **1** react rapidly with norbornadiene, the color of the free phosphadithiatriazenes being discharged. The products are the 1:1 adducts R₂PS₂N₃·C₇H₈ **2** (eq 2), which are obtained as colorless crystalline precipitates when the reactions are carried out in diethyl ether. However, when



the adducts are dissolved in chloroform, methylene chloride, or

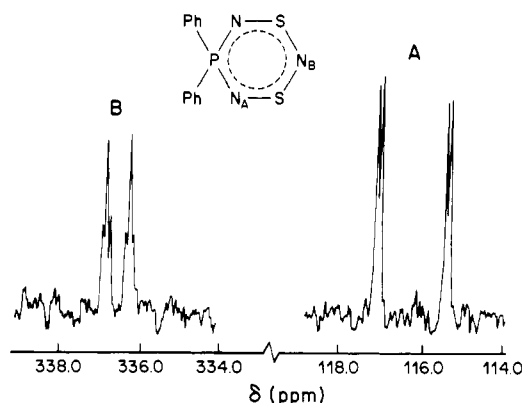


Figure 1. ¹⁵N NMR spectrum of Ph₂PS₂N₃ (99% enriched in ¹⁵N).

acetonitrile, the characteristic color of the free phosphadithiatriazene is slowly regenerated. The color can be discharged by the addition of norbornadiene to the solution. The ease of dissociation of the adducts is also observed in their mass spectra (70 eV, EI), which show no parent ion. The fragmentation patterns resemble a superposition of those found for the free R₂PS₂N₃ molecule and olefin.

NMR Spectra of R₂PS₂N₃ and R₂PS₂N₃·C₇H₈. Numerical information pertaining to the ¹H, ¹⁵N, and ³¹P NMR spectra of the cyclophosphadithiatriazenes **1** and their norbornadiene adducts **2** (R = Me, Ph, OPh) is listed in Table II. In the case of R = Ph and OPh, little structural information can be obtained from the characteristically broad multiplet associated with the proton resonances of the phenyl group. For the dimethyl compound, the ¹H chemical shift and ²J_{PH} value of the equivalent methyl protons are similar to those reported for methylphosphazenes (e.g., (NPMe₂)₃, δ(CH₃) = 1.30 ppm, ²J_{PH} = 14.0 Hz;¹⁵ N₃P₃Me₂F₄, δ(CH₃) = 1.65 ppm, ²J_{PH} = 14.0 Hz¹⁶). The ³¹P chemical shifts of all three R₂PS₂N₃ compounds are to high field of the corresponding resonances in the phosphazenes (R₂PN)₃ (δ_P (external reference H₃PO₄) = 31.9 (R = Me¹⁵), 14.3 (R = Ph¹⁷), 9 (R = OPh¹⁸) ppm). Migration of π charge toward the more electronegative sulfur atoms^{19,20} might be expected to induce a deshielding

(15) Searle, H. T.; Dyson, J.; Ranganathan, T. N.; Paddock, N. L. *J. Chem. Soc., Dalton Trans.* **1975**, 203.

(16) Cordes, A. W.; Swepston, P. N.; Oakley, R. T.; Paddock, N. L.; Ranganathan, T. N. *Can. J. Chem.* **1981**, *59*, 2364.

(17) Allen, C. W.; Faught, J. B.; Moeller, T.; Paul, I. C. *Inorg. Chem.* **1969**, *8*, 1719.

(18) Mark, V.; Dungan, C.; Crutchfield, M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227.

(13) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, **1974**; Vol. IV, p 149.

Table III. Positional and B_{eq} Thermal Parameters with esd's

atom	x/a	y/b	z/c	B_{eq}^a	x/a	y/b	z/c	B_{eq}^a
P(1)	0.5948 (1)	0.27089 (7)	0.15688 (7)	3.06 (4)	0.2454 (2)	1.0089 (3)	0.4186 (2)	3.50 (6)
N(2)	0.6779 (4)	0.3258 (2)	0.0685 (2)	4.0 (1)	0.2159 (8)	0.8353 (9)	0.2950 (6)	5.0 (3)
S(3)	0.7280 (2)	0.44009 (9)	0.0801 (1)	8.2 (7)	0.2322 (0)	0.9474 (0)	0.1280 (0)	4.70 (7)
N(4)	0.7266 (6)	0.4940 (3)	0.1928 (3)	6.4 (2)	0.3940 (7)	1.181 (1)	0.1590 (8)	5.5 (3)
S(5)	0.6683 (2)	0.44208 (8)	0.29049 (9)	5.71 (5)	0.3489 (2)	1.3657 (3)	0.2199 (2)	4.11 (6)
N(6)	0.6292 (4)	0.3252 (2)	0.2777 (2)	3.9 (1)	0.3353 (7)	1.2747 (8)	0.3895 (6)	4.4 (2)
C(7)	0.6771 (4)	0.1451 (3)	0.1794 (3)	2.7 (1)	0.3708 (7)	0.909 (1)	0.6248 (7)	3.7 (3)
C(8)	0.7281 (5)	0.1038 (3)	0.2847 (3)	3.7 (1)	0.4051 (9)	1.018 (1)	0.7550 (8)	5.0 (3)
C(9)	0.7930 (6)	0.0060 (4)	0.2978 (4)	5.0 (2)	0.510 (1)	0.949 (1)	0.9145 (9)	6.2 (4)
C(10)	0.8027 (6)	-0.0494 (3)	0.2062 (4)	4.8 (2)	0.5758 (9)	0.772 (1)	0.9425 (9)	5.5 (4)
C(11)	0.7498 (6)	-0.0094 (3)	0.1027 (4)	5.2 (2)	0.5425 (9)	0.662 (1)	0.816 (1)	5.5 (4)
C(12)	0.6837 (6)	0.0883 (3)	0.0877 (3)	4.3 (1)	0.4386 (8)	0.729 (1)	0.6545 (8)	4.6 (3)
C(13)	0.3743 (4)	0.2597 (2)	0.0953 (3)	3.1 (2)	0.0420 (8)	0.982 (1)	0.4113 (7)	3.7 (3)
C(14)	0.2761 (5)	0.2123 (3)	0.1553 (3)	3.4 (1)	-0.0212 (9)	1.166 (1)	0.3749 (7)	4.3 (3)
C(15)	0.1052 (5)	0.2011 (4)	0.1074 (4)	3.9 (1)	-0.1870 (9)	1.135 (1)	0.3607 (8)	5.3 (4)
C(16)	0.0338 (5)	0.2383 (4)	0.0028 (4)	3.7 (1)	-0.2811 (9)	0.918 (1)	0.3853 (8)	5.2 (4)
C(17)	0.1311 (6)	0.2847 (4)	-0.0557 (3)	4.0 (2)	-0.2179 (9)	0.737 (1)	0.4243 (9)	5.4 (4)
C(18)	0.3002 (5)	0.2945 (3)	-0.0117 (3)	3.6 (1)	-0.0584 (8)	0.767 (1)	0.4387 (9)	4.9 (3)
C(19)					0.0532 (8)	1.080 (1)	0.0133 (7)	3.9 (3)
C(20)					-0.0058 (9)	1.109 (1)	-0.1775 (8)	4.8 (3)
C(21)					-0.1573 (9)	1.214 (1)	-0.2437 (8)	5.2 (3)
C(22)					-0.0908 (9)	1.425 (1)	-0.2022 (9)	5.5 (4)
C(23)					0.1004 (8)	1.466 (1)	-0.1073 (7)	4.3 (3)
C(24)					0.1244 (7)	1.327 (1)	0.0610 (7)	3.6 (2)
C(25)					0.1321 (9)	1.319 (1)	-0.1922 (8)	5.3 (4)

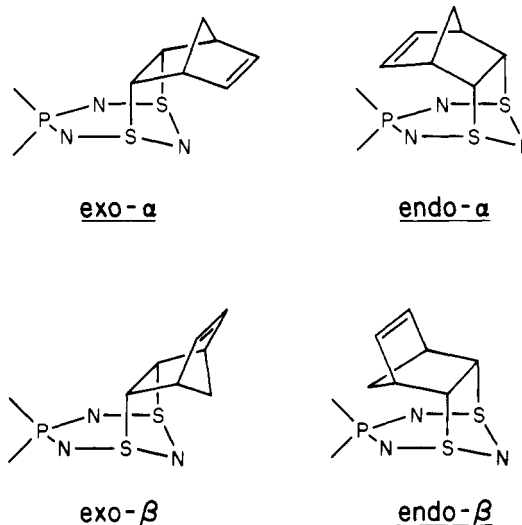
^a B_{eq} 's are the isotropic equivalents of the anisotropic parameters.

of phosphorus in the $R_2PS_2N_3$ molecules. However, the increased number of π electrons (vide infra) probably leads to an increase in π charge on phosphorus relative to the $(R_2PN)_3$ case.

The ^{15}N NMR spectra of the $R_2PS_2N_3$ compounds unambiguously confirm their proposed structures. As illustrated in Figure 1 for the diphenyl derivative, the presence of a downfield doublet of triplets and an upfield doublet of doublets is uniquely interpretable in terms of the six-membered ring (1). The $^1J_{PN}$ and $^3J_{PN}$ coupling constants appear to be quite sensitive to the nature of the R group (see Table II), and the latter values are all significantly larger than in $Ph_3P=N-S_3N_3$ and $(Ph_3P=N)_2S_4N_4$.¹⁰ The $^2J_{NN}$ coupling constants (≤ 3 Hz) are similar to those observed in other neutral conjugated SN rings.¹⁰ The origin of the relative shifts of the $N_{2,6}$ and N_4 resonances remains uncertain, but by analogy with substituted pyridines, for which there is a correspondence between ^{15}N shielding and π charge,¹¹ it is likely that the upfield position of the $N_{2,6}$ signal reflects the greater π charge expected for these nitrogens (vide infra).

The 1H and ^{13}C NMR spectra of the norbornadiene adducts $R_2PS_2N_3 \cdot C_7H_8$ establish the position of the addition, i.e., across the two sulfur atoms in the 3,5-positions. The proton assignments in Table IV differ from those of Brinkman and Allen^{21,22} and have been confirmed by homonuclear decoupling experiments. The equivalence of the 2 and 3, 5 and 6, and 1 and 4 positions in the norbornene residue of the adducts and the absence of $^2J_{PC}$ coupling establishes a symmetry that can only be attained by S,S rather than S,N or N,N addition. As well as being regiospecific, the addition appears to be stereospecific; there is no evidence for more than one stereoisomer in solution or in the solid state. The NMR spectra do not allow a differentiation between the four possible choices, i.e., endo- α , endo- β , exo- α , and exo- β , but the endo pair can be immediately rejected on steric grounds. The assignment

of an exo- α or exo- β structure has required the use of X-ray crystallography (vide infra).



Molecular Structures of $Ph_2PS_2N_3$ and $Ph_2PS_2N_3 \cdot C_7H_8$. The crystal structures of $Ph_2PS_2N_3$ and its norbornadiene adduct $Ph_2PS_2N_3 \cdot C_7H_8$ both consist of discrete molecular units (see Figure 2a,b). There are no unusual intermolecular contacts in either structure. Atom coordinates for the two structures are given in Table III, and bond lengths and intervalence angles are listed in Table IV. The molecular structure of $Ph_2PS_2N_3$ consists of a nearly planar N(2)-S(3)-N(4)-S(5)-N(6) sequence (planar to within 0.05 Å) from which the phosphorus atom is displaced by 0.284 (1) Å. Such a departure from planarity, although significant, is considerably less than is observed in the $(Me_3SiNH)_2PS_2N_3$ structure reported by Weiss.⁶ Within the PS_2N_3 ring there is little difference between the chemically inequivalent SN bonds; the mean length of S(3)-N(2) and S(5)-N(6) is 1.568 (8) Å and that of S-N(4) is 1.582 (5) Å. However, the overall mean S-N distance (1.57 (1) Å) is somewhat shorter than in $S_3N_3^-$ (1.60 Å),^{23a} indicative of the expected strengthening of the π system of the PS_2N_3 ring vs. that of $S_3N_3^-$.

- (19) Craig, D. P.; Paddock, N. L. *Nonbenzenoid Aromatics*, 1971, 2, 273.
 (20) (a) Heatley, F.; Todd, S. W. *J. Chem. Soc. A* 1966, 1152. (b) Hellwinkel, D. *Chem. Ber.* 1969, 102, 528. (c) Hellwinkel, D.; Wilfinger, H. *J. Liebigs Ann. Chem.* 1970, 742, 163. (d) Koster, R.; Simić, D.; Grassberger, A. *Ibid.* 1970, 739, 211. (e) Knunyants, I. L.; Georgiev, V. I.; Galakhov, I. V.; Ragulin, L. I.; Neimysheva, A. A. *Dokl. Chem. (Engl. Transl.)* 1971, 201, 992. (f) Van Wazer, J. R.; Letcher, J. H. *Top. Phosphorus Chem.* 1967, 5, 190.

- (21) Brinkman, M. R.; Allen, C. W. *J. Am. Chem. Soc.* 1972, 94, 1550.
 (22) The actual assignment of Brinkman and Allen, a 1,3-N,N addition, was incorrect. The S,S addition was confirmed independently by several groups: (a) Mock, W. L.; Mehrotra, I. J. *J. Chem. Soc., Chem. Commun.* 1976, 123. (b) Ertl, Von G.; Weiss, J. Z. *Anorg. Allg. Chem.* 1976, 420, 155. (c) Griffin, A. M.; Sheldrick, G. M. *Acta Crystallogr. Sect. B* 1975, B31, 895.

- (23) (a) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* 1979, 101, 4517. (b) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *Inorg. Chim. Acta* 1981, 53, L189. (c) Gimarc, B. M.; Trinajstić, N. *Pure Appl. Chem.* 1980, 52, 1443.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $\text{Ph}_2\text{PN}_3\text{S}_2$ and the Adduct $\text{Ph}_2\text{PN}_3\text{S}_2\cdot\text{C}_7\text{H}_8$

distances			angles		
	$\text{Ph}_2\text{PN}_3\text{S}_2$	adduct		$\text{Ph}_2\text{PN}_3\text{S}_2$	adduct
P(1)-N(2)	1.621 (4)	1.627 (7)	N(6)-P(1)-N(2)	115.8 (2)	117.4 (3)
P(1)-N(6)	1.625 (3)	1.617 (5)	P(1)-N(2)-S(3)	121.3 (2)	116.8 (4)
N(2)-S(3)	1.560 (3)	1.612 (7)	P(1)-N(6)-S(5)	120.3 (2)	119.4 (4)
N(6)-S(5)	1.575 (3)	1.604 (6)	N(2)-S(3)-N(4)	116.9 (2)	112.2 (3)
S(3)-N(4)	1.580 (4)	1.655 (7)	N(4)-S(5)-N(6)	116.3 (2)	111.0 (3)
S(5)-N(4)	1.583 (5)	1.644 (9)	S(3)-N(4)-S(5)	124.6 (3)	106.4 (4)
P(1)-C(7)	1.788 (4)	1.797 (5)	N(2)-P(1)-C(7)	107.9 (2)	107.4 (3)
P(1)-C(13)	1.792 (4)	1.796 (8)	N(6)-P(1)-C(7)	107.3 (2)	109.2 (3)
C(7)-C(8)	1.381 (5)	1.38 (1)	N(2)-P(1)-C(13)	108.5 (2)	108.7 (3)
C(8)-C(9)	1.389 (6)	1.39 (1)	N(6)-P(1)-C(13)	109.9 (2)	108.8 (3)
C(9)-C(10)	1.376 (7)	1.36 (1)	C(7)-P(1)-C(13)	107.1 (2)	104.6 (3)
C(10)-C(11)	1.355 (7)	1.35 (1)	C(12)-C(7)-C(8)	120.4 (3)	119.6 (6)
C(11)-C(12)	1.393 (6)	1.40 (1)	C(7)-C(8)-C(9)	119.2 (4)	119.6 (7)
C(12)-C(7)	1.381 (6)	1.39 (1)	C(8)-C(9)-C(10)	120.1 (4)	120.4 (8)
C(13)-C(14)	1.394 (6)	1.38 (1)	C(9)-C(10)-C(11)	120.6 (5)	120.7 (8)
C(14)-C(15)	1.392 (6)	1.42 (1)	C(10)-C(11)-C(12)	120.2 (4)	120.2 (8)
C(15)-C(16)	1.372 (6)	1.38 (1)	C(11)-C(12)-C(7)	119.4 (4)	119.6 (7)
C(16)-C(17)	1.370 (7)	1.36 (1)	C(18)-C(13)-C(14)	119.4 (3)	118.5 (6)
C(17)-C(18)	1.370 (6)	1.36 (1)	C(13)-C(14)-C(15)	119.5 (4)	119.8 (7)
C(18)-C(13)	1.391 (5)	1.400 (9)	C(14)-C(15)-C(16)	120.1 (4)	118.8 (7)
S(3)-C(19)		1.845 (5)	C(15)-C(16)-C(17)	120.0 (4)	121.6 (8)
S(5)-C(24)		1.843 (5)	C(16)-C(17)-C(18)	121.1 (4)	119.7 (8)
C(19)-C(24)		1.540 (8)	C(17)-C(18)-C(13)	119.8 (4)	121.6 (7)
C(19)-C(20)		1.57 (1)	S(5)-C(24)-C(19)		107.6 (4)
C(23)-C(24)		1.564 (8)	S(5)-C(24)-C(23)		115.3 (4)
C(20)-C(21)		1.54 (1)	S(3)-C(19)-C(24)		107.1 (4)
C(22)-C(23)		1.50 (1)	S(3)-C(19)-C(20)		112.9 (5)
C(21)-C(22)		1.31 (1)	C(24)-C(23)-C(25)		102.6 (6)
C(20)-C(25)		1.52 (1)	C(19)-C(20)-C(25)		101.7 (6)
C(23)-C(25)		1.52 (1)	C(24)-C(23)-C(22)		103.4 (6)
			C(19)-C(20)-C(21)		102.7 (6)
			C(21)-C(20)-C(25)		100.0 (6)
			C(22)-C(23)-C(25)		101.0 (6)
			C(20)-C(21)-C(22)		106.9 (7)
			C(23)-C(22)-C(21)		107.9 (7)
			C(20)-C(25)-C(23)		94.0 (6)

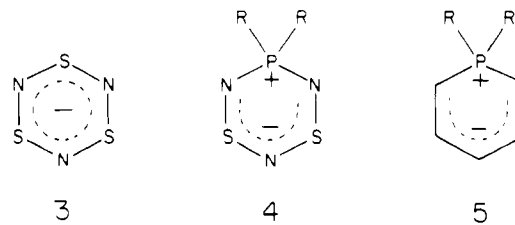
itself (vide infra). The geometry at phosphorus ($\text{P}-\text{N} = 1.623$ (4) Å, $\angle\text{P}_{\text{endo}} = 115.8$ (2)°, $\angle\text{P}_{\text{exo}} = 107.1$ (2)°) is almost identical with that found for the Ph_2P atom in $\text{Ph}_2\text{F}_4\text{P}_3\text{N}_3$ ($\text{P}-\text{N} = 1.618$ (5) Å, $\angle\text{P}_{\text{endo}} = 115.5$ (3)°, $\angle\text{P}_{\text{exo}} = 107.9$ (3)°).¹⁷ The phenyl group geometry is quite normal; both rings are planar to within 0.015 Å.

The X-ray structure determination of $\text{Ph}_2\text{PS}_2\text{N}_3\cdot\text{C}_7\text{H}_8$ confirms that addition of norbornadiene to the $\text{Ph}_2\text{PS}_2\text{N}_3$ ring occurs in a 1,3 fashion across the two sulfur atoms. Moreover, it establishes the stereochemistry of the addition; i.e., the reaction produces the *exo-β* isomer. The structure of the adduct exhibits the expected conformational changes. The N(4) atom is now displaced from the plane of the central N_2S_2 unit (which is planar to within 0.01 Å) by 0.817 (6) Å, producing a dihedral angle of 55.8 (4)°. Somewhat surprisingly (in view of steric considerations), the phosphorus atom is rotated toward the C_7H_8 group rather than away from it and lies 0.195 (2) Å away from the central S_2N_2 unit, producing a dihedral angle of 13.4 (4)° (compared to 19.8 (2)° in the parent compound). Thus the PS_2N_3 ring adopts a somewhat flattened chair conformation. There is little change in the geometry at phosphorus ($\text{P}-\text{N} = 1.622$ (5) Å, $\angle\text{P}_{\text{endo}} = 117.4$ (3)°, and $\angle\text{P}_{\text{exo}} = 104.6$ (3)°) from that found in $\text{Ph}_2\text{PS}_2\text{N}_3$ itself, but the geometry at the sulfur atoms is significantly different; both the $\text{S}-\text{N}_{2,6}$ (1.615 (3) Å) and the $\text{S}-\text{N}_4$ (1.649 (5) Å) bonds are lengthened. Such a lengthening can be attributed to the rupture of the π system, but it may also stem from the expected σ -hybridization changes at sulfur. Thus the decrease in the mean NSN angle from 116.6 (3)° in $\text{Ph}_2\text{PS}_2\text{N}_3$ to 111.6 (6)° in $\text{Ph}_2\text{PS}_2\text{N}_3\cdot\text{C}_7\text{H}_8$ would be expected to increase the p character of the σ hybrids at sulfur and lengthen the σ bonds. The S-C distance (1.844 (5) Å) is similar to that found in $\text{S}_4\text{N}_4\cdot 2\text{C}_7\text{H}_8$ (1.851 (5) Å).^{22b,c}

Electronic Structure and Bonding in Phosphadithiatriazenes 1. The electronic structures of planar binary SN rings (e.g., S_3N_3^- ,²³

$\text{S}_4\text{N}_4^{2+}$,²⁴ and $\text{S}_5\text{N}_5^{+25}$) have been the subject of much theoretical and experimental attention.²⁶ For many of these systems, all-electron calculations point to the validity of describing the valence shell in terms of separated σ and π components, the latter being composed largely of 3p orbitals on sulfur and 2p orbitals on nitrogen. Thus the S_3N_3^- anion **3** can be considered in terms of a six-center, ten- π -electron model.^{23b} Ab initio SCF Hartree-Fock-Slater calculations indicate that the 360-nm absorption of S_3N_3^- corresponds to a $\pi^* \rightarrow \pi^*$ transition from the HOMO E'' to the LUMO A_2'' ,^{23a} and the observation of a negative A term in the MCD spectrum of S_3N_3^- supports this assignment.²⁷

In developing a simple HMO description for the π bonding in the phosphadithiatriazenes reported here, we can begin by considering the $\text{X}_2\text{PS}_2\text{N}_3$ system as being derived from S_3N_3^- by replacing one sulfur atom by a phosphonium cation, e.g., **4**. As



a result of this substitution, two electrons are removed from the π system, and as an initial approximation, the π bonding can be

(24) (a) Sharma, R. D.; Aubke, F.; Paddock, N. L. *Can. J. Chem.* **1981**, *59*, 3157. (b) Gillespie, R. J.; Slim, D. R.; Tyrer, J. D. *J. Chem. Soc., Chem. Commun.* **1977**, 253. (c) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801.

(25) Bartetzko, R.; Gleiter, R. *Inorg. Chem.* **1978**, *17*, 995.

(26) Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. *J. J. Am. Chem. Soc.* **1980**, *102*, 6687.

(27) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1981**, *20*, 963.

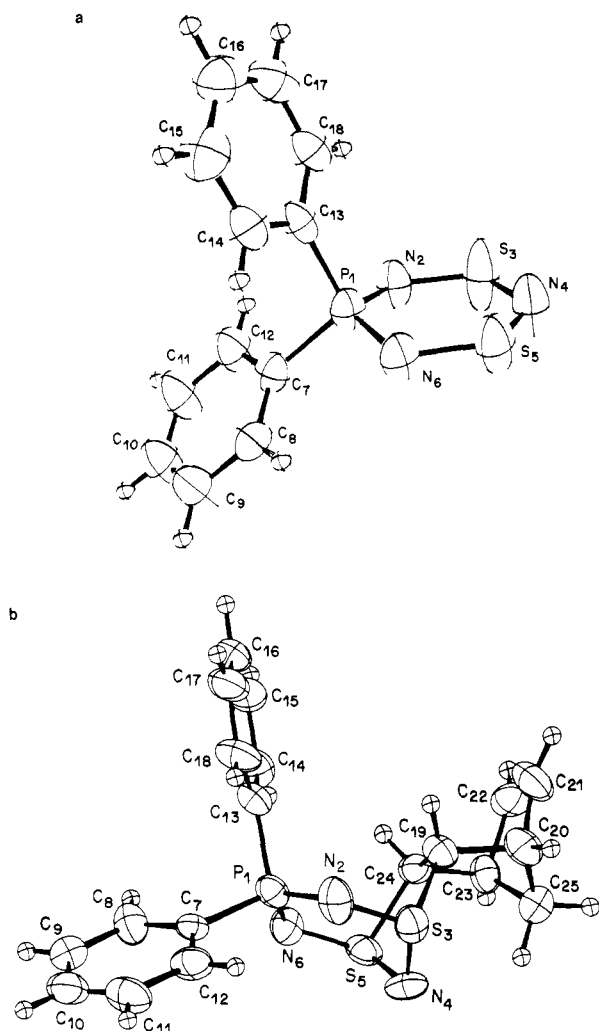


Figure 2. ORTEP drawings (50% probability ellipsoids) of Ph₂PS₂N₃ (a) and Ph₂PS₂N₃·C₇H₈ (b), showing atom numbering schemes.

considered to be confined to a five-atom sequence NSNSN. The formal analogy between **4** and λ^5 -phosphorins **5**²⁸ is then easily recognizable, the major difference between the two systems being the extent of occupancy of the π manifold (eight π electrons in **4** vs. six π electrons in **5**). For the λ^5 -phosphorins, many of the gross features of their electronic structure (photoelectron spectra, ¹³C NMR chemical shifts) can be understood in terms of the "internal salt" model in which there is no π interaction of the pentadienyl unit with phosphorus. Bond-order variations, however, require a consideration of π bonding to phosphorus. Such π bonding in both **4** and **5** can be introduced in a variety of ways. Traditionally it is assumed that the four σ bonds to phosphorus are generated from 3s and 3p orbitals exclusively, in which case 3d orbitals must be used for the π -bonding network.

In many inorganic molecules the concept of 3d–2p π bonding has been tested extensively. In phosphazenes in particular, delocalized orbitals of π symmetry are necessary to account for many properties (e.g., ionization energies,²⁹ kinetics of substitution,³⁰ and ligand–ring conjugation³¹), and generally such molecular orbitals are described in terms of 3d–2p π interactions between phosphorus and nitrogen.^{19,32} However, although the assumption

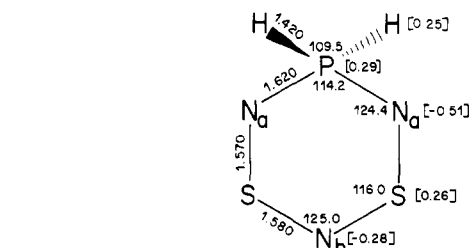


Figure 3. Molecular parameters of planar H₂PS₂N₃ model. Bond lengths are in angstroms; angles are in degrees. Calculated charges are shown in brackets.

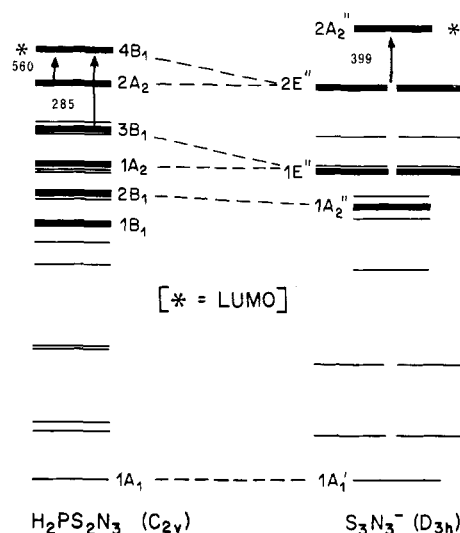


Figure 4. Orbital energy level diagram for H₂PS₂N₃ (C_{2v}) and S₃N₃[−] (D_{3h}). π levels are indicated by heavy lines.

of σ bonds being formed strictly from s and p orbitals is a useful formalism, it may be overly restrictive on the role of both p and d orbitals. If the simple sp³ hybridization for phosphorus constraints are removed, one can, in principle, generate σ bonds which employ d orbitals and π bonds which utilize p orbitals. Indeed, recent X α SW calculations on (NPF₂)_{3,4} indicate a significant contribution of phosphorus 3d orbitals to the σ bonds and of 3p orbitals to the π network.³³ Thus, although the simple (sp³) σ /(d) π analysis provides a useful qualitative picture, detailed calculations are necessary to clarify and quantify the description and to define more precisely the role of the different atomic orbitals of phosphorus and sulfur in the molecular orbital description.

We have, therefore, carried out ab initio SCF Hartree–Fock–Slater calculations on a planar model phosphadithiatriazene system H₂PS₂N₃. This hypothetical dihydride derivative was chosen to simplify an already major calculation and to minimize the number of ligand–ring interactions. It could be argued that the relatively electropositive perturbation imposed on phosphorus by the dihydride ligands would produce a chemically unrealistic model, but the inductive effects of two hydride ligands and two methyl groups (e.g., **1**, R = Me) are not likely to be radically different; indeed, monohydride derivatives of phosphazenes are known.³⁴

The ab initio SCF HFS method has been widely tested, and using comparable quality basis functions provides results equal to or better than those of the HF method. We have utilized a double- ζ basis set (as optimized by Clementi and Roetti)³⁵ and

(28) Schafer, W.; Schweig, A.; Dimroth, K.; Kanter, H. *J. Am. Chem. Soc.* **1976**, *98*, 4410.

(29) Branton, G. R.; Brion, C. E.; Frost, D. C.; Mitchell, K. A. R.; Paddock, N. L. *J. Chem. Soc. A* **1970**, 151.

(30) (a) Sowerby, D. B. *J. Chem. Soc.* **1965**, 1396. (b) Emsley, J.; Paddock, N. L. *J. Chem. Soc. A* **1968**, 2590.

(31) (a) Sharma, R. D.; Rettig, S. J.; Paddock, N. L.; Trotter, J. *Can. J. Chem.*, in press. (b) Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Sharma, R. D. *Ibid.* **1981**, *59*, 2654.

(32) Mitchell, K. A. R. *Chem. Rev.* **1969**, *69*, 157.

(33) Mitchell, K. A. R.; Noodleman, L.; Paddock, N. L. *Chem. Phys. Lett.* **1977**, *47*, 265.

(34) (a) Högel, Von J.; Schmidpeter, A. *Z. Anorg. Chem.* **1979**, *458*, 168. (b) Schmidpeter, A.; Blank, K.; Hess, H.; Riffel, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 650. (c) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

(35) Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 177.

Table V. Orbital Overlap Populations for $\text{H}_2\text{PS}_2\text{N}_3$

molecular orbital		orbital overlap populations				self-atom orbital overlap populations				
designation	ϵ , au	PH	PN _a	SN _a	SN _b	P	H	N _a	N _b	S
1A ₁	-0.916		0.007	0.033	0.052	0.01		0.08	0.20	0.10
1B ₁	-0.821		0.011	0.077	0.007	0.01		0.18	0.01	0.14
2A ₁	-0.804	0.002	0.038	0.011	0.038	0.09		0.01	0.22	0.03
3A ₁	-0.637	0.018	0.024	0.043	-0.008	0.28	0.01	0.07	0.09	0.11
2B ₂	-0.634		0.029	-0.028	0.055	0.03		0.14	0.12	0.21
3B ₂	-0.497		0.043	0.022	0.022	0.10		0.14	0.11	0.11
4A ₁	-0.454	0.049		-0.012	-0.015	0.31	0.04	0.07	0.04	0.19
1B ₁	-0.422	0.056	0.023	0.009	0.005	0.30	0.06	0.05	0.02	0.03
5A ₁	-0.369	0.013	0.008	-0.005	0.030	0.06	0.01	0.12	0.18	0.16
2B ₁	-0.364	0.024	-0.004	0.007	0.049	0.09	0.03	0.01	0.23	0.15
6A ₁	-0.316	0.002	-0.022	-0.024	-0.070	0.16		0.22	0.23	0.28
4B ₂	-0.311		0.006	0.020	-0.007	0.03		0.09	0.04	0.37
1A ₂	-0.307		0.010	0.051	0.01	0.01		0.17		0.23
7A ₁	-0.241	0.003	0.019	-0.005	-0.004	0.03		0.16	0.53	0.05
3B ₁	-0.238	0.014	0.014	0.020	0.009	0.03	0.07	0.19	0.25	0.02
5B ₂	-0.217		-0.001	-0.018	-0.010	0.03		0.36	0.09	0.13
2A ₂	-0.145		0.025	-0.054	0.03	0.03		0.23		0.35
†4B ₁	-0.079	-0.029	0.027	-0.036	-0.070	0.13	0.08	0.06	0.37	0.37
net π population		0.095	0.068	0.033	0.063		charge densities			
net population		0.180	0.230	0.149	0.153	0.29	0.25	-0.51	-0.28	0.26

† LUMO.

Table VI. Partitioned Occupations for $\text{H}_2\text{PS}_2\text{N}_3^{\text{a}}$

atom	σ (non- π)			π			total
	s	p	d	s	p	d	
H	0.534 (0.297)			0.220 (0.457)			0.754
N _a	1.649 (1.649)	2.567 (2.403)			1.296 (1.460)		5.512
N _b	1.650 (1.650)	2.455 (2.390)			1.173 (1.238)		5.278
P	1.317 (1.317)	2.433 (1.512)	0.339 (0.329)		0.176 (1.097)	0.442 (0.452)	4.707
S	1.805 (1.805)	2.009 (1.918)	0.340 (0.330)		1.399 (1.490)	0.183 (0.193)	5.736

^a Numbers not in parentheses refer to occupations for which 1B₁ has been included in the σ (non- π) system, whereas those within parentheses refer to occupations where 1B₁ is considered part of the π system.

augmented it with 3d orbitals for sulfur (exponent 1.7) and phosphorus (exponent 1.5).³⁶ The core orbitals were kept frozen throughout the SCF process.³⁷ The molecular parameters of the $\text{H}_2\text{PS}_2\text{N}_3$ model are shown in Figure 3. The initial analysis of the PS_2N_3 ring given in an earlier paragraph related its π network to that of the parent S_3N_3^- anion. Figure 4 presents the all-electron version of this analysis. Because of the inherent differences in the core of S_3N_3^- and $\text{H}_2\text{PS}_2\text{N}_3$, the lowest valence energy levels 1A₁' and 1A₁ have been aligned in order to facilitate the comparison of the two systems. Examination of the overlap populations given in Table V illustrates that of the five occupied π orbitals, 1B₁, 2B₁, 3B₁, 1A₂, and 2A₂, the lowest level, 1B₁, is primarily associated with the P-H bonds. On removing this orbital from consideration, one can clearly see that the PS_2N_3 ring possesses eight delocalized π electrons, as implied by the HMO approach. It is worth pointing out that the nature of the four occupied π orbitals 2B₁, 1A₂, 3B₁, and 2A₂ and the LUMO 4B₁ is essentially what one would expect for a delocalized open-chain five-atom sequence. Thus 2B₁ and 1A₂ are strongly bonding whereas the 2A₂ and 4B₁ are strongly antibonding in the NSNSN framework, while 3B₁ is intermediate in character. There are additional features occasioned by the availability of 3d orbitals on sulfur and phosphorus (more particularly the latter). (1) The 3B₁ orbital is mildly bonding throughout the system whereas it would be strictly nonbonding in, for example, the 5-membered pentadienyl anion. (2) Although the 2A₂ orbital is strongly antibonding to the NSNSN sequence, it is strongly bonding in the NPN region. (3) The extent of mixing (in terms of populations) of the d_{xy} on phosphorus in the 1A₂ (0.0336) and 2A₂ (0.0731) and of the d_{xz} on phosphorus in the 2B₁ (0.0280) and 3B₁ (0.0861) illustrates

the principle of increased stabilization of the upper π levels by d-orbital participation.³⁸

Insofar as there are fewer antibonding π^* levels occupied, the phosphadithiatriazene system can be viewed as less "electron-rich" than S_3N_3^- . This should result in an increase in π bonding in the NSNSN framework. As the entries in Table VI indicate, the π -overlap population certainly increases for the S-N_b-S group, but there is a slight decrease for the S-N_a bonds.³⁹ Nevertheless the net ($\sigma + \pi$) overlap population for the NSNSN frame does increase (0.59 vs. 0.52), giving rise to a strengthened SN bond. However, the very marked increase in the PN overlap population is not due so much to a decreased occupancy of the antibonding π orbitals as it is to a change in the character of the PN region of the higher lying π orbitals. Certainly 2A₂ remains antibonding for the NSNSN unit, but as Table V shows, it is strongly bonding for the P-N bonds. The same is true for the now empty 4B₁ orbital. As a result the π -overlap population of the NPN region is enhanced to the extent that the net ($\sigma + \pi$) population suggests a double bond for the P-N linkages.

We have already remarked that the concept of σ/π separability, particularly in invoking (sp³)_d π hybridization for phosphorus, is, in principle, overly restrictive. To assess this point, we have calculated the Mulliken populations for the s, p, and d atomic orbitals for each of the sulfur, phosphorus, and nitrogen centers. As the entries in Table VI indicate, the d orbitals of both sulfur and phosphorus make a small (0.3 out of 4) contribution to the non- π system. However the phosphorus 3d orbitals make a relatively large contribution to the π orbitals while the sulfur 3d

(36) The ratio of 3d exponents for sulfur and phosphorus is in the same ratio as the exponents for the 3s' orbitals of the double- ξ set.

(37) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, 2, 41.

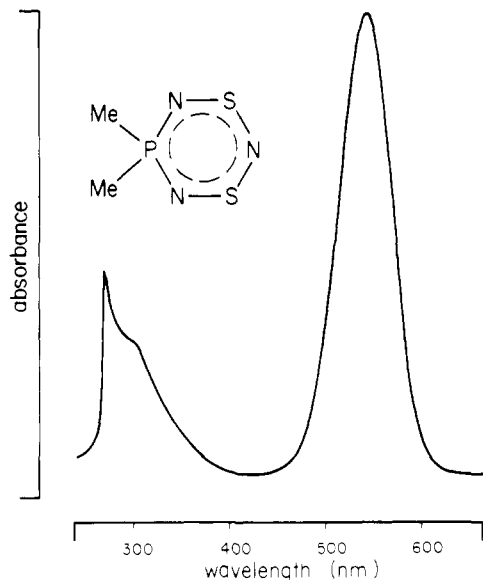
(38) The use of the d_{xy} orbital corresponds to a Möbius or heteromorphic interaction, while mixing of the d_{xz} produces a Hückel or homomorphic π system (see ref 19). The present results do not point to a clear-cut preference for one d orbital over the other.

(39) In S_3N_3^- the S-N overlap populations are 0.089 (σ) and 0.040 (π).

Table VII. UV-vis Spectra^a of R₂PS₂N₃ Derivatives

R	λ_{\max}
Me	543 (4×10^3), 295 (sh), 270 (2×10^3)
Ph	550 (5×10^3), 301 (1×10^3), ^b
OPh	583, ^c ^b
NHSiMe ₃	570 (1×10^3) ^d

^a λ_{\max} (in nm) in CH₂Cl₂; extinction coefficients (in M⁻¹ cm⁻¹) are in parentheses. ^b Obscured by $\pi \rightarrow \pi^*$ transitions on phenyl rings. ^c Not measured. ^d Data from ref 5.

Figure 5. UV-vis spectrum of Me₂PS₂N₃.

contribution to the π system remains small. Indeed, if one removes the 1B₁ orbital from the π network (insofar as it is essentially a P-H σ -bond orbital), then the phosphorus contribution to the delocalized π orbitals is dominated by the 3d contribution (0.4 of 3d vs. 0.2 of 3p) (see Table VI). Within the σ network the ratio of s and p contributions is approximately 1:1 (1.82:1.85) for sulfur, whereas for both phosphorus and nitrogen it is close to 1:2 (1.3:2.5 and 1.6:2.5, respectively). Similar ratios for the s and p contributions have been obtained by the X α SW method for the phosphorus and nitrogen atoms in (NPF₂)₃.³³

It should also be emphasized that this analysis indicates that the positive charges on sulfur (0.26) and phosphorus (0.29) represent primarily the loss of π electrons; the π population of phosphorus of 0.6 signifies a formal loss of 0.4 electron (although the classification of σ/π is imprecise because of the removal of the 1B₂ from the π network), while the π population of 1.7 for sulfur means a loss of 0.3 electron. The acquisition of electrons by nitrogen is also principally through the π system, although the σ and nonbonding electrons do carry about 25% of the charge.

Electronic Spectra of R₂PS₂N₃. The phosphadithiatrazenes **1** (R = Me, Ph, OPh) all exhibit an intense visible absorption near 550–580 nm. In the R = Me, Ph derivatives, there are other absorptions in the ultraviolet region between 250 and 300 nm (Table VII). Figure 5 illustrates the UV-vis spectrum of Me₂PS₂N₃, the appearance and analysis of which is simplified by the absence of potentially interfering $\pi \rightarrow \pi^*$ absorptions of phenyl groups (as in **1**, R = Ph, OPh). In order to establish the nature of these absorptions, particularly the low-energy one, we have calculated the energies and transition moments for all transitions between the SCF HFS orbitals of H₂PS₂N₃ that lie in the UV-vis spectrum. We find that the transitions 3B₁ \rightarrow 4B₁ and 2A₂ \rightarrow 4B₁ should be both two orders of magnitude more probable than any other transitions above 200 nm. Using experience gained with similar molecules (e.g., S₃N₃^{-23a} and S₄N⁻⁴⁰), we estimate⁴¹ a

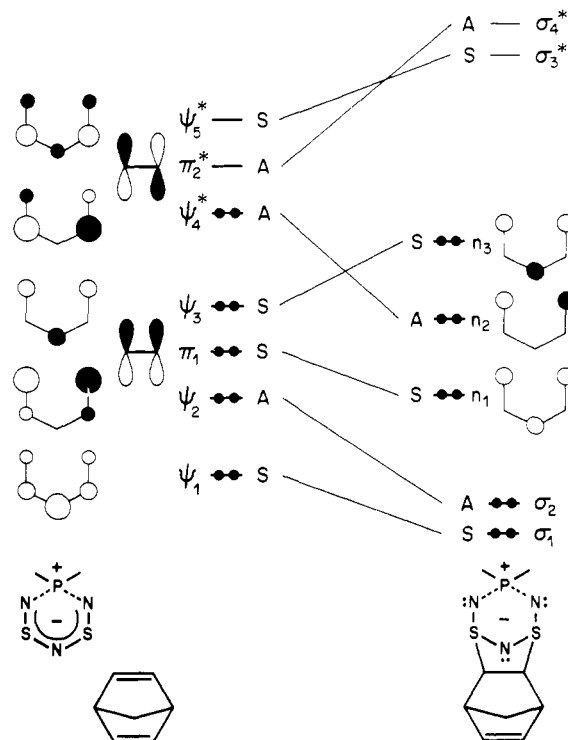


Figure 6. Qualitative orbital symmetry correlation diagram for the cycloaddition of norbornadiene to a phosphadithiatrazene ring. The designations S and A refer to the symmetry of each orbital with respect to a vertical mirror plane.

wavelength in the region of 560 nm for 2A₂ \rightarrow 4B₁ transition and a wavelength of about 280 nm for the 3B₁ \rightarrow 4B₁ transition. In the case of the low-energy transition, the correspondence between the calculated and observed energies is quite close, and we can safely assign this absorption in all the R₂PS₂N₃ derivatives to a HOMO(π^*) \rightarrow LUMO(π^*) transition, the two levels involved originating from the splitting of the degenerate HOMO of S₃N₃⁻ (see Figure 4). In addition we assign the more intense absorption in the UV region of Me₂PS₂N₃ to the $n(\pi) \rightarrow$ LUMO(π^*) (3B₁ \rightarrow 4B₁) excitation.

Symmetry Aspects of the Formation of R₂PS₂N₃·C₇H₈. The foregoing treatment of the electronic structure of the phosphadithiatrazene system reveals a π electronic structure which is identical in terms of number and composition of occupied orbitals with that obtainable by a simple HMO analysis. Insofar as the latter method is therefore justified, it is useful to extend its conclusions to the study of the cycloaddition reaction which R₂PS₂N₃ molecules undergo with norbornadiene. Although the all-electron calculations confirm the importance of conjugation to phosphorus, they indicate that the ordering of the π levels expected for an open-chain NSNSN⁻ fragment is essentially unchanged by the interaction with phosphorus; for symmetry purposes the PS₂N₃ ring can thus be considered in terms of a S₂N₃⁻ unit with eight π electrons.⁴² The concerted addition of a two-electron olefin in an S,S fashion can then be regarded as a symmetry-allowed ($8_s + 2_s$) reaction. Figure 6 illustrates the orbital symmetry correlation diagram for such a process. The preference for S,S over N,N addition is easily understandable in terms of the eigenvector coefficients of the HOMO and LUMO levels.⁴³

(41) For S₂N₃⁻, S₄N⁻, a one-electron estimate of excitation energies was consistently smaller (by about 0.4 eV) than that obtained as the difference between the estimate of the total ground and excited state energies. The estimate provided here is given by the difference in orbital energies of the ground-state calculation plus 0.4 eV.

(42) An all-valence electron ab initio HFS calculation for the relevant conformation of the isolated S₂N₃⁻ fragment indicates that there are only six π electrons. However, the LUMO is a π orbital and almost degenerate with a lone-pair HOMO. Hence any perturbation (such as the σ bonds in the system considered) will stabilize the π orbital, with the result that an eight- π -electron HMO model is a reasonable approach for the kinetic considerations.

(40) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. J. *Am. Chem. Soc.* **1980**, *102*, 5773.

Both orbitals are primarily sulfur based, so that efficient overlap in the transition state is best achieved via addition at sulfur as opposed to nitrogen. The stereospecificity of the reaction has no ready explanation on symmetry grounds. Exo- α addition would give rise to a small but positive stabilization of the transition state by the second olefin π bond, but steric factors may well be more important.

Calculations on a Nonplanar $\text{H}_2\text{PS}_2\text{N}_3$ Model. In addition to studying the planar $\text{H}_2\text{PS}_2\text{N}_3$ system described above, we have carried out an analogous calculation using a nonplanar conformation (with C_s symmetry). In this second calculation, the PS_2N_3 ring geometry was identical with that observed for the $\text{Ph}_3\text{PS}_2\text{N}_3$ molecule, with the phosphorus atom displaced by 0.28 Å from the plane of the other five atoms. We find that this model is somewhat lower in energy (by 15 kcal/mol) than the planar structure, but the ordering and spacing of the energy levels remain essentially unchanged. The PN_3 bonds have exactly the same net overlap population (of 0.230) but are slightly less polar ($q_P = 0.12$, $q_N = -0.41$) than in the planar conformation. Evidently, slight distortions from planarity lead to a more uniform charge distribution within the ring.

Conclusion

The phosphadithiatriazenes $\text{R}_2\text{PS}_2\text{N}_3$ **1** (R = Me, Ph, OPh) represent novel examples of a cyclic inorganic ring system possessing eight π electrons. SCF Hartree-Fock-Slater ab initio

calculations on the model compound $\text{H}_2\text{PS}_2\text{N}_3$ confirm the validity of the HMO method in describing the basic features of the PS_2N_3 ring system. The concept of σ/π separability has been shown to be a reasonable assumption, and the importance of 3d orbitals on phosphorus in stabilizing antibonding π levels has been demonstrated. The intense low-energy absorption which is characteristic of these molecules has been assigned to a $\text{HOMO}(\pi^*) \rightarrow \text{LUMO}(\pi^*)$ transition. The thermally allowed ($8_s + 2_s$) cycloaddition of norbornadiene to the phosphadithiatriazene ring suggests that other planar or near-planar sulfur-nitrogen heterocycles may also undergo thermally or photochemically initiated cycloaddition reactions.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the University of Calgary, and the University of Arkansas Research Committee for financial support and the NSERC for a University Research Fellowship (to RTO). We are also grateful to Dr. A. Rauk for helpful discussions and to S. Liblong and K. Wagstaff for assistance in the analysis of the HFS calculations.

Registry No. **1** (R = Ph), 80326-52-9; **1** (R = Me), 80326-53-0; **1** (R = OPh), 80326-54-1; **2** (R = Ph), 80326-55-2; **2** (R = Me), 80339-90-8; **2** (R = OPh), 80326-56-3; tetrasulfur tetranitride, 28950-34-7; tetraphenyldiphosphine, 1101-41-3; tetramethyldiphosphine, 3676-91-3; triphenyl phosphite, 101-02-0; norbornadiene, 121-46-0.

Supplementary Material Available: A listing of structure factor amplitudes and tables of hydrogen atom positions (SI) and thermal parameters (SII) for **1** (R = Ph) and **2** (R = Ph) (19 pages). Ordering information is given on any current masthead page.

(43) For a similar treatment of the S_4N_4 /norbornadiene reaction, see: Yanabe, T.; Tanaka, K.; Tachibana, A.; Fukui, K. *J. Phys. Chem.*, **1979**, *83*, 767.

$\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ (E = S, Se, and Te) as Reagents for the Preparation of Mixed-Metal Chalcogenide Clusters

Victor W. Day,^{*1a} David A. Lesch,^{1b} and Thomas B. Rauchfuss^{*1b}

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68500, and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received June 15, 1981

Abstract: The compounds $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$, where E = S, Se, and Te, react efficiently with $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$ to afford the new heterometallic clusters, $(\text{CO})_6\text{Fe}_2(\mu_3\text{-E})_2\text{Pt}(\text{PPh}_3)_2$. This reaction formally involves the homolytic cleavage of the E-E bond in the $\mu\text{-E}_2$ precursor complexes and represents a novel route to mixed-metal clusters. ^{31}P NMR of $(\text{PPh}_3)(\text{CO})_5\text{Fe}_2(\mu_3\text{-S})_2\text{Pt}(\text{PPh}_3)_2$ (prepared from $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_5(\text{PPh}_3)$) indicates that the plane of the Pt coordination sphere is perpendicular to the iron-iron vector. The structure of $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ was determined by conventional X-ray crystallographic techniques. The crystals were monoclinic with $a = 10.944$ (2) Å, $b = 16.321$ (3) Å, $c = 23.135$ (4) Å, $\beta = 94.68$ (1)°, $Z = 4$; the space group is $P2_1/n$. Conventional full-matrix least-squares refinement with nonhydrogen atoms anisotropic and fixed hydrogen atoms isotropic gave $R_1 = 0.037$ and $R_2 = 0.040$ for 7119 reflections having 2θ Mo $K\alpha < 58.7^\circ$ and $I > 3\sigma(I)$. The structure consists of an isosceles triangle of metal atoms tethered by two capping $\mu_3\text{-Se}$ moieties. The two $\text{Fe}(\text{CO})_3$ units are mutually bonded, and this fragment closely resembles $\text{Fe}_2(\mu\text{-Se}_2)(\text{CO})_6$ with an expanded Se-Se vector. We reconcile the reactivity of these $\mu\text{-E}_2$ compounds and the chemical dormancy of species such as Ph_2Te_2 and monometallic S_2 complexes as being both electronic and steric (ring strain) in origin.

The chemistry of transition-metal chalcogenides is presently expanding at a rapid rate commensurate with the structural, spectroscopic, and chemical novelty of these compounds. Recognized goals in this area of inorganic chemistry include the synthesis of models for important biological² and industrial³ catalysts and the preparation of materials for energy storage and conversion.⁴ Of particularly topical interest is the prospect that

discrete metal chalcogenide clusters may prove to be functional analogues of the catalytic sites in nitrogenase⁵⁻⁷ and hydrodesulfurization catalysts.⁸

(1) (a) University of Nebraska. (b) University of Illinois.
(2) Zimmerman, R.; Munch, E.; Brill, W. J.; Shah, V. K.; Henzl, M. T.; Rawlings, J.; Orme-Johnson, W. H. *Biochim. Biophys. Acta* **1978**, *537*, 185.
(3) Weissner, O.; Landa, S. "Sulfide Catalysts, Their Properties and Applications"; Pergamon Press: New York, 1973.

(4) Jacobson, A. J.; Whittingham, M. S.; Rich, S. M. *J. Electrochem. Soc.* **1979**, *126*, 891. Jacobson, A. J.; Chianelli, R. R.; Rich, S. M.; Whittingham, M. S. *Mater. Res. Bull.* **1979**, *14*, 1437. Kubiak, C. P.; Schneemeyer, L. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 6898.
(5) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4694, and reference therein.
(6) Coucouvanis, D.; Simhon, E. D.; Baenziger, N. C. *J. Am. Chem. Soc.* **1980**, *102*, 6646, and reference therein.
(7) Tieckelmann, R. H.; Silvis, H. C.; Kent, T. A.; Huynh, B.; Waszczak, J. V.; Tec, B.-K.; Avrill, B. A. *J. Am. Chem. Soc.* **1980**, *102*, 5550.