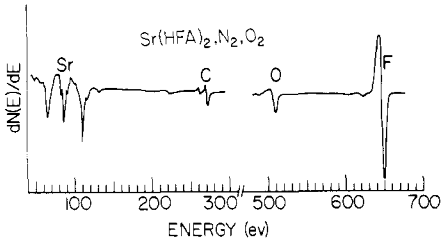

Figure 5. Auger electron spectrum of the SrF_2 film.

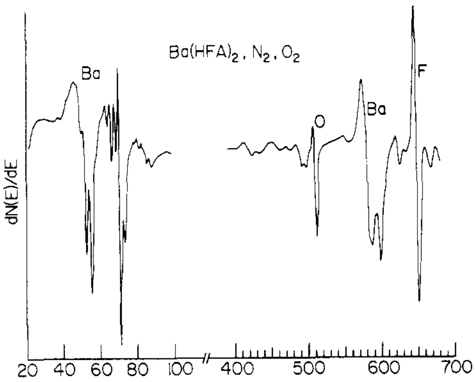

Figure 6. Auger electron spectrum of the BaF_2 film, C peak not shown (see text).

desorption.[23] For the AES spectra of our films, the F peak-to-peak height decreased rapidly with a time constant of tens of seconds. Therefore, before a spectrum was recorded, the sample was moved so that the electron beam impinged onto an unexposed area and the F line was recorded immediately. As a result, the quantitative comparison of the F peak-to-peak height with those of the metals is not meaningful.

Figure 4 shows Auger spectra for films grown from Ca[HFA]$_2$ with and without O_2 and from Ca[TFA]$_2$ with O_2. Although the C and Ca lines overlap, it is apparent that films grown with O_2 have very little C. However, the C content is large in films grown without O_2. All the Ca films contained a substantial amount of F but only several percent of O. Note that the Ca lines at 291 and 294 eV are resolved for the film grown from Ca[TFA]$_2$.

Figure 5 shows an Auger spectrum for a film grown from Sr[HFA]$_2$ with O_2. The dominant peaks are Sr and F, although there are several percent of C and O. The carbon is in the carbidic form.

Figure 6 shows an Auger spectrum from a film grown from Ba[HFA]$_2$ with O_2. The dominant peaks are Ba and F. The line shapes of the Ba lines between 40 and 80 eV indicate that the Ba is mostly elemental.[24] However, the presence of the peak near 68 eV indicates that some of the Ba was oxidized, which is commensurate with the small O line. For a fully oxidized Ba surface,[25] the ratio of the peak-to-peak heights of the Ba (584 eV) line to the O (510 eV) line would be 0.5. The peak-to-peak height of the C line (not shown) was ~4% of that of the Ba (584 eV) line. The C had a carbidic line shape.

Acknowledgment. We thank Mark Ross and John Callahan for their assistance with the mass spectral analysis.

Registry No. Ba[HFA]$_2$, 118131-57-0; Sr[HFA]$_2$, 121012-89-3; Ca[HFA]$_2$, 121012-90-6; Ba[TFA]$_2$, 84653-56-5; Sr[TFA]$_2$, 121012-91-7; Ca[TFA]$_2$, 73592-45-7; BaF_2, 7787-32-8; SrF_2, 7783-48-4; CaF_2, 7789-75-5; Si, 7440-21-3.

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Contribution from the Department of Chemistry,
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Lewis Base Properties of 1λ^5,3λ^5-Diphospha-5-thia-2,4,6-triazines: Crystal and Molecular Structures of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$

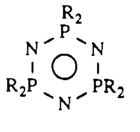
Tristram Chivers,* James Fait, and Stephen W. Liblong

Received December 28, 1988

The behavior of $Ph_4P_2N_3SPh$ (**1**) toward Lewis and Brønsted acids has been investigated, and the following adducts have been isolated: $(Ph_4P_2N_3SPh)H^+BF_4^-$ (**5**), $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (**6**), $Ph_4P_2N_3SPh{\cdot}BF_3$ (**7**), and $Ph_4P_2N_3SPh{\cdot}BCl_3$ (**8**). The ^{31}P NMR spectrum of **6** reveals inequivalent phosphorus atoms, indicating that the methyl group is coordinated to a nitrogen atom between a phosphorus and a sulfur atom of the P_2N_3S ring. An X-ray structural determination has confirmed this assignment. The crystals of **6** are monoclinic and belong to the space group $P2_1/c$, with $a = 10.317$ (2) Å, $b = 22.849$ (4) Å, $c = 14.104$ (3) Å, $\beta = 102.94$ (2)°, $V = 3241$ (1) Å^3, and $Z = 4$. The final R and R_w values were 0.046 and 0.049, respectively. The P_2N_3S ring in **6** adopts a highly distorted boat conformation. The bond lengths to the coordinated nitrogen are lengthened compared to those of the parent ring system [1.69 vs 1.62 Å for d(S–N) and 1.69 vs 1.62 Å for d(P–N)], and the adjacent S–N and P–N bonds are shortened slightly. By contrast, the ^{31}P NMR spectrum of **5** exhibits a singlet consistent with protonation at the unique nitrogen atom of the P_2N_3S ring. Compounds **7** and **8** display ^{31}P NMR spectra consistent with the formation of both symmetrical and unsymmetrical adducts. The lack of regioispecificity in the formation of adducts between the P_2N_3S ring and Lewis or Brønsted acids is discussed in terms of the electronic structure of the heterocycle.

Introduction

All four members of the series of inorganic heterocycles containing alternating phosphorus or sulfur and nitrogen atoms, **1**–**4**, are known,[1] and their π-electronic structures have been compared.[2]



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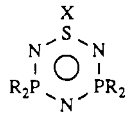

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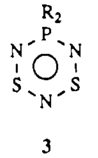

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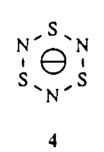

4

The Lewis base properties of **1**,[3] **3**,[4] and **4**[5] have also been investigated, and the formation of a variety of adducts with Lewis

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or protonic acids occurs via coordination to an endocyclic nitrogen atom. The limited structural information available for such adducts of **1** reveals lengthened skeletal bonds to the protonated nitrogen atoms and only minor perturbations to the conformations of the P_3N_3 ring.[6,7] By contrast, the interaction of the π-electron-rich ring $S_3N_3^-$ (**4**) with protonic acids[5] or other electrophiles[8] results in a major structural reorganization to give ring-contracted products. For the hybrid ring systems **2** and **3**, the *site* of attack is of interest in addition to the structural changes that accompany adduct formation. In the case of **3** (R = Ph) coordination occurs exclusively at a nitrogen atom between a phosphorus atom and a sulfur atom and is controlled by electrostatic effects.[4] No evidence for the formation of diadducts of **3** (R = Ph) was obtained.[4] Coordination to an electrophile also imposes a marked perturbation on both the conformation of the ring and the S–N bond lengths.[4]

The substantial structural changes that accompany adduct formation by **3** (R = Ph) and **4** have been attributed to the ready polarization of the π* electrons in these π-electron-rich systems.[4,5] In this context it was of interest to compare the Lewis base properties of the π-electron-precise ring, **2**,[1] with those of **1**, **3**, and **4**. Specifically, we set out to determine (a) the preferred coordination site, (b) the structural modifications that occur upon adduct formation, and (c) the production of diadducts in the interaction of **2** with Lewis and Brønsted acids. The phenyl derivative, **2** (X = R = Ph), was chosen because it is readily prepared,[9] is air stable, and has been structurally characterized.[2] We describe here the isolation and spectroscopic (^{31}P NMR) characterization of crystalline adducts of **2** (X = R = Ph), the X-ray structural determination of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3$ (**6**), and the formation of diadducts in solution. The apparent lack of regiospecificity in adduct formation is discussed in terms of the electronic structure of the $P_2N_3S^+$ ring.

Experimental Section

Reagents and General Procedures. All solvents were dried and distilled before use: methylene dichloride (P_2O_5), *n*-pentane, and diethyl ether (Na). All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox, P_2O_5, and silica gel. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, The University of Calgary, and by the Canadian Microanalytical Service Ltd., Vancouver, BC, Canada.

$Ph_4P_2N_3SPh$ was prepared by the literature method.[9] Other chemicals were obtained from Aldrich and used as received: $HBF_4{\cdot}Et_2O$, CF_3SO_3Me, $BF_3{\cdot}Et_2O$, and BCl_3 (1.0 M solution in hexanes).

Instrumentation. Infrared spectra were recorded as Nujol mulls (KBr windows) or KBr pellets on a Nicolet 5DX FT IR spectrometer. NMR spectra were recorded on a Varian XL-200 instrument. ^1H and ^{13}C chemical shifts are reported in ppm downfield from Me_4Si. ^{31}P chemical shifts are quoted with reference to external 85% H_3PO_4.

Preparation of $(Ph_4P_2N_3SPh)H^+BF_4^-$. A solution of $HBF_4{\cdot}Et_2O$ (0.40 g, 2.50 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $Ph_4P_2N_3SPh$ (1.00 g, 1.92 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred for 2 h at 23 °C. Addition of *n*-pentane (50 mL) with rapid stirring produced a colorless precipitate of $(Ph_4P_2N_3SPh)H^+BF_4^-$ (1.13 g, 1.85 mmol). Anal. Calcd for $C_{30}H_{26}BF_4N_3P_2S$: C, 59.13; H, 4.30; N, 6.90. Found: C, 57.60; H, 4.27; N, 6.66. IR (cm^{-1}): 3198 w, 3065 w, 1441 s, 1315 m, 1285 m, 1210 vs, 1182 vs, 1122 vs, 1074 vs, 1058 vs, 1031 s, 1023 s, 996 vs, 861 s, 816 s, 759 s, 749 s, 736 s, 726 vs, 700 s, 687 vs, 670 m, 611 m, 551 vs, 527 m, 507 vs. NMR data are given in Table I.

Preparation of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$. An excess of CF_3SO_3Me (0.36 g, 2.2 mol) was added to a solution of $Ph_4P_2N_3SPh$ (0.97 g, 1.9 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 23 °C for 1 h. This solution was then added dropwise to rapidly stirred *n*-pentane (50 mL) to give a colorless precipitate of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (1.22 g, 1.78 mmol). Anal. Calcd for $C_{32}H_{28}F_3N_3O_3P_2S_2$: C, 56.05; H, 4.12; N, 6.13. Found: C, 55.16; H, 4.16; N, 6.56. ^{13}C NMR (in $CDCl_3$): δ 39.4 (CH_3, s, $\nu_{1/2}$ = (6.5 Hz). ^1H NMR (in $CDCl_3$): δ 3.35 (3 H, d, $^3J_{PH}$ = 9.1 Hz). IR (cm^{-1}): 3058 w, 1440 s, 1283 vs, 1265 vs, 1214 vs, 1187 s, 1166 s, 1148 vs, 1121 vs, 1088 s, 1061 s, 1032 vs, 996 m, 840 m, 796 s, 746 s, 733 s, 694 s, 687 s, 636 vs, 605 m, 546 vs, 518 m, 506 s, 495 s. ^{31}P NMR data are given in Table I.

Table I. NMR Data for Lewis Acid Adducts and Protonated and Methylated Derivatives of $Ph_4P_2N_3SPh$ (**2**, X = R = Ph)

adducts[a]	$\delta(^{31}P)$[b]
2-$(Ph_4P_2N_3SPh)H^+BF_4^-$ (**5**)	17.7
4-$(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (**6**)	26.0, 20.5[c]
2-$Ph_4P_2N_3SPh{\cdot}BF_3$ (**7a**)	17.2
4-$Ph_4P_2N_3SPh{\cdot}BF_3$ (**7b**)	22.0, 18.9[d]
2-$Ph_4P_2N_3SPh{\cdot}BCl_3$ (**8a**)	17.6
4-$Ph_4P_2N_3SPh{\cdot}BCl_3$ (**8b**)	24.2, 18.5[d]
$Ph_4P_2N_3SPh$ (**2**, X = R = Ph)	10.0[e]

[a] The numerical prefixes refer to the nitrogen to which the electrophile is coordinated. The numbering scheme for the atoms of the P_2N_3S ring conforms to the rules given in ref 10; i.e., the least electronegative element is given the lowest number. [b] Chemical shifts relative to 85% H_3PO_4 as external reference. [c] $^2J_{PP}$ = 5.9 Hz. [d] $^2J_{PP}$ could not be resolved due to line broadening. [e] Data taken from ref 9.

Table II. Crystallographic Parameters

chem formula $C_{32}H_{28}F_3N_3O_3P_2S_2$	space group $P2_1/c$
fw 685.67	T = 23 °C
a = 10.319 (2) Å	λ = 0.71069 Å
b = 22.849 (4) Å	ρ_{calcd} = 1.403 g cm^{-3}
c = 14.104 (3) Å	μ = 2.68 cm^{-1}
V = 3241 (1) $Å^3$	R = 0.046
Z = 4	R_w = 0.049

Preparation of $Ph_4P_2N_3SPh{\cdot}BF_3$. An excess of $BF_3{\cdot}Et_2O$ (0.25 g, 1.8 mmol) was added by syringe to a solution of $Ph_4P_2N_3SPh$ (0.77 g, 1.5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at 23 °C for 1 day to give a small amount of white precipitate. Dropwise addition of *n*-pentane (50 mL) to the rapidly stirred solution gave $Ph_4P_2N_3SPh{\cdot}BF_3$ (0.82 g, 1.4 mmol) as a mixture of isomers (see ^{31}P NMR data in Table I). Anal. Calcd for $C_{30}H_{25}BF_3N_3P_2S$: C, 61.14; H, 4.28; N, 7.13. Found: C, 60.91; H, 4.30; N, 6.97. IR (cm^{-1}): 3058 m, 1589 m, 1440 vs, 1282 m, 1210 vs, 1180 vs, 1164 vs, 1121 vs, 1086 vs, 1072 vs, 1050 vs, 1028 vs, 1023 vs, 998 vs, 978 s, 942 vs, 926 s, 916 vs, 899 vs, 856 vs, 834 vs, 748 vs, 732 vs, 723 vs, 705 vs, 689 vs, 645 s, 619 m, 604 vs, 589 m, 559 vs, 537 vs, 520 vs, 510 vs, 498 s, 487 s, 483 s, 458 m, 437 m, 424 s, 412 m.

Preparation of $Ph_4P_2N_3SPh{\cdot}BCl_3$. A slight excess of BCl_3 (1.0 M in hexanes, 1.1 mmol) was added by syringe to a solution of $Ph_4P_2N_3SPh$ (0.52 g, 1.0 mmol) in diethyl ether/CH_2Cl_2 (10:1, 20 mL). The mixture was stirred at 23 °C for 1 day to give a colorless precipitate of $Ph_4P_2N_3SPh{\cdot}BCl_3$ (0.53 g, 0.83 mmol) as a mixture of isomers (see ^{31}P NMR data in Table I). Anal. Calcd for $C_{30}H_{25}BCl_3N_3P_3S$: C, 56.41; H, 3.95; N, 6.58. Found: C, 54.02; H, 4.05; N, 5.68. IR (cm^{-1}): 1438 vs, 1197 vs, 1176 vs, 1162 s, 1120 s, 1075 vs, 1061 vs, 1026 s, 998 s, 975 vs, 836 vs, 777 m, 750 vs, 743 s, 732 vs, 723 vs, 688 vs, 654 vs, 594 vs, 550 vs, 528 s, 507 vs, 485 s, 431 m.

X-ray Analysis of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$. A suitable transparent block-shaped crystal was wedged in a Lindemann glass capillary, and this setup was mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range 8 < θ < 12°. Reduced cell calculations did not indicate any higher metric symmetry. Crystal and instrumental instabilities were monitored through the measurement of three standard reflections every 3 h of X-ray exposure time; there was no indication of crystal decomposition. The net intensities of the data were corrected for reflection width, scale variation, Lorentz, and polarization effects. Variance ($\sigma^2(I)$) was calculated on the basis of counting statistics. Crystal data and experimental details of the structure determination are compiled in Table II.

The PNS ring was located in an *E* map with phases derived from symbolic addition.[11] The remaining non-hydrogen atoms were located in difference maps after refining the scale and thermal parameters. At

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Table III. Positional Parameters and U_{eq} for the Non-Hydrogen Atoms of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (**6**)[a]

atom	x	y	z	$1000U_{eq}$
S(1)	1.07015 (9)	0.24292 (5)	0.09652 (7)	65.5
N(2)	0.9753 (3)	0.3900 (1)	0.1435 (2)	59.9
P(3)	0.91240 (8)	0.36789 (4)	0.23820 (6)	52.8
N(4)	1.1839 (3)	0.3180 (2)	0.1811 (2)	71.7
P(5)	1.15300 (8)	0.30351 (4)	0.28726 (7)	56.9
N(6)	1.0036 (3)	0.3176 (1)	0.2937 (2)	56.4
C(2)	0.9451 (6)	0.4466 (3)	0.0913 (5)	84.7
C(111)	0.9511 (4)	0.2859 (2)	0.0532 (3)	61.4
C(112)	0.8341 (4)	0.3015 (2)	−0.0120 (3)	73.4
C(113)	0.7390 (5)	0.2603 (2)	−0.0480 (3)	86.5
C(114)	0.7616 (7)	0.2035 (3)	−0.0179 (4)	103.4
C(115)	0.8780 (8)	0.1870 (2)	0.0427 (5)	113.0
C(116)	0.9762 (5)	0.2286 (2)	0.0790 (3)	82.3
C(311)	0.9049 (3)	0.4339 (2)	0.3047 (3)	60.2
C(312)	0.7939 (5)	0.4488 (2)	0.3390 (4)	80.6
C(313)	0.7907 (5)	0.5008 (2)	0.3875 (4)	98.7
C(314)	0.8971 (6)	0.5382 (2)	0.4025 (4)	101.4
C(315)	1.0088 (5)	0.5229 (2)	0.3711 (4)	91.7
C(316)	1.0131 (4)	0.4718 (2)	0.3217 (3)	73.5
C(321)	0.7469 (3)	0.3397 (2)	0.1968 (3)	54.7
C(322)	0.6456 (4)	0.3745 (2)	0.1436 (3)	74.0
C(323)	0.5217 (4)	0.3510 (2)	0.1075 (4)	86.8
C(324)	0.4972 (4)	0.2938 (2)	0.1236 (4)	82.7
C(325)	0.5957 (4)	0.2586 (2)	0.1753 (4)	81.4
C(326)	0.7207 (4)	0.2817 (2)	0.2118 (3)	62.4
C(511)	1.2748 (3)	0.3433 (2)	0.3740 (3)	61.3
C(512)	1.2843 (5)	0.3337 (2)	0.4724 (3)	80.9
C(513)	1.3752 (6)	0.3636 (3)	0.5410 (4)	92.8
C(514)	1.4574 (5)	0.4039 (3)	0.5128 (5)	99.4
C(515)	1.4470 (5)	0.4146 (3)	0.4174 (6)	102.7
C(516)	1.3467 (4)	0.3840 (2)	0.3475 (4)	88.9
C(521)	1.1873 (3)	0.2279 (2)	0.3163 (3)	58.4
C(522)	1.0906 (4)	0.1894 (2)	0.3302 (3)	70.9
C(523)	1.1198 (5)	0.1313 (2)	0.3471 (4)	84.0
C(524)	1.2450 (5)	0.1113 (3)	0.3496 (4)	93.6
C(525)	1.3415 (5)	0.1490 (2)	0.3359 (4)	94.2
C(526)	1.3132 (4)	0.2073 (2)	0.3196 (4)	80.3
S(4)	0.2934 (1)	0.56625 (5)	0.20954 (9)	78.0
O(1)	0.3677 (4)	0.6186 (2)	0.2197 (3)	128.2
O(2)	0.2945 (4)	0.5367 (2)	0.2990 (3)	120.6
O(3)	0.1660 (3)	0.5694 (2)	0.1460 (3)	109.8
C(1)	0.3782 (5)	0.5189 (2)	0.1452 (4)	86.8
F(1)	0.3963 (4)	0.5412 (2)	0.0629 (3)	149.9
F(2)	0.3166 (4)	0.4681 (2)	0.1234 (3)	164.5
F(3)	0.5007 (3)	0.5057 (2)	0.1945 (3)	160.2

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

this stage of the refinement all of the hydrogen atoms were located in difference Fourier maps. All non-hydrogen atoms were refined anisotropically, with the hydrogens refined with independent isotropic temperature factors. Convergence was reached at $R = 0.046$ $R_w = 0.049$. The final values of the refined positional parameters are presented in Table III. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[12] All calculations were carried out on a VAX 11/780 instrument at the University of Calgary with the program package XTAL2.2.[13]

Results and Discussion

Preparation and Spectroscopic Characterization of Adducts of $Ph_4P_2N_3SPh$. The adducts of **2** (X = R = Ph) with BF_3 or BCl_3 and the protonated or methylated derivatives of **2** (X = R = Ph) were obtained by the addition of an excess of the appropriate reagent to a stirred solution of **2** (X = R = Ph) in methylene dichloride. They were isolated by precipitation upon addition of a nonpolar solvent as moisture-sensitive, colorless solids. Only the methylated derivative could be recrystallized without dissociation.[14]

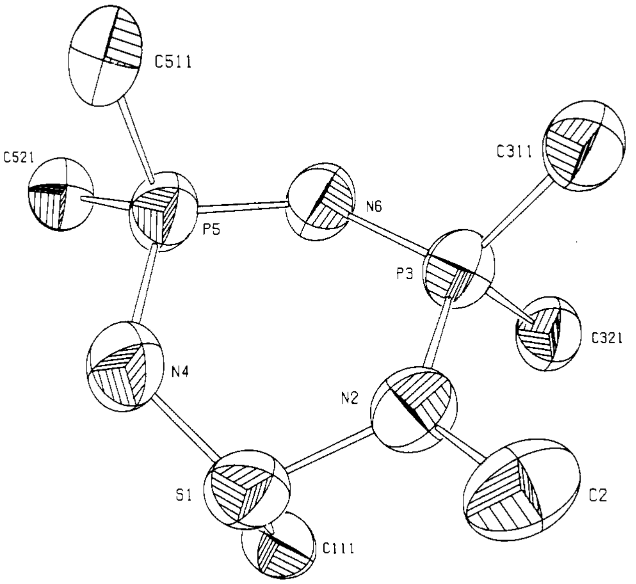

Figure 1. ORTEP plot (50% probability ellipsoids) of the $(Ph_4P_2N_3SPh)Me^+$ cation in **6**. Only α-carbon atoms of phenyl groups are shown for clarity.

The ^{31}P NMR spectra of these adducts (see Table I) reveal Lewis base properties for the P_2N_3S ring that are different from those observed for the π-electron-rich ring **3**.[2] The appearance of two doublets in the ^{31}P NMR spectrum of the methylated derivative, **6** ($^2J_{PP} = 5.9$ Hz), indicates that coordination occurs at a nitrogen atom connected to a phosphorus atom and a sulfur atom rather than at the unique nitrogen atom. This conclusion is supported by the observation of a doublet for the methyl group ($^3J_{HP} = 9.1$ Hz) in the ^1H NMR spectrum and was confirmed by the X-ray structural analysis described below. The two-bond coupling between the methyl carbon and phosphorus in the methylated derivative could not be resolved due to the broadness of the signal for the methyl group in the ^{13}C NMR spectrum.

In contrast, the ^{31}P NMR spectrum of the protonated derivative, **5**, exhibits a singlet, indicating that protonation occurs exclusively at the unique nitrogen atom. For the Lewis acids BF_3 and BCl_3 the monoadducts are obtained as a mixture of isomers, **7a**/**7b** and **8a**/**8b**, respectively, in approximately equal amounts, as indicated by the appearance of a sharp singlet and two broad signals (unresolved PP coupling) in their ^{31}P NMR spectra (Table I).

The reaction of **2** (X = R = Ph) with BCl_3 was monitored by ^{31}P NMR spectroscopy in order to investigate the formation of adducts other than those with a 1:1 stoichiometry. For molar ratios of BCl_3:**2** (X = R = Ph) in the range from 0:1 to 1:1, the ^{31}P NMR spectra show that the solution contains a mixture of monoadducts. Further addition of BCl_3 results in the disappearance of the signals due to the monoadducts and the appearance of a new singlet at 34.3 ppm. These results demonstrate that, unlike **1**, the Lewis base **2** (X = R = Ph) can coordinate more than one Lewis acid. The product so formed has not been isolated, but the ^{31}P NMR spectrum suggests that it is either the symmetrically substituted diadduct or the triadduct.

X-ray Crystal Structure of $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (6). The crystal structure of **6** consists of $(Ph_4P_2N_3SPh)Me^+$ and $CF_3SO_3^-$ ions with very weak interaction between H atoms of Ph groups and O atoms of the anion. An ORTEP drawing with the atomic numbering scheme is displayed in Figure 1, and the pertinent endocyclic and exocyclic bond lengths and bond angles are compared with the corresponding values for **2** (X = R = Ph) in Table IV. The X-ray structure of **6** confirms the conclusion based on

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(14) The combination of moisture sensitivity and dissociation upon attempted recrystallization made it extremely difficult to obtain reliable analytical data for the protonated and BCl_3 adducts. However, the ^{31}P NMR spectra of these adducts did not indicate the presence of any phosphorus-containing impurities.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for **2** (X = R = Ph) and $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (**6**)[a]

	6	**2**[b]		**6**	**2**[b]
P(3)–N(6)	1.577 (3)	1.594 (3)	N(2)–P(3)–N(6)	108.5 (2)	115.7 (1)
P(5)–N(6)	1.597 (3)	1.598 (2)	P(3)–N(6)–P(5)	126.5 (2)	120.7 (1)
P(3)–N(2)	1.688 (3)	1.621 (2)	N(4)–P(5)–N(6)	113.6 (2)	116.6 (1)
P(5)–N(4)	1.633 (4)	1.616 (2)	P(5)–N(4)–S(1)	120.0 (2)	118.8 (1)
S(1)–N(2)	1.686 (3)	1.615 (3)	N(2)–S(1)–N(4)	109.4 (2)	113.5 (1)
S(1)–N(4)	1.580 (3)	1.621 (2)	S(1)–N(2)–P(3)	118.7 (2)	118.4 (2)
N(1)–C(1)	1.463 (7)				
S(1)–C(31)	1.803 (4)	1.810 (3)			

[a] The atomic numbering scheme is given in Figure 1. [b] Data taken from ref 2.

Table V. Comparison of Mean Planes for **2** (X = R = Ph) and $(Ph_4P_2N_3SPh)Me^+CF_3SO_3^-$ (6)

	6	2 (R = Ph)[a]		6	2 (R = Ph)[a]
S(1)	−0.63	−0.55	P(5)	+0.01	+0.15
N(2)	+0.12	+0.03	N(4)	−0.18	−0.09
P(3)	−0.01	+0.03	C(2)	+0.75	
N(6)	−0.27	−0.13			

[a] Data taken from ref 5.

the ^{31}P NMR spectrum that methylation occurs at a nitrogen atom between a phosphorus atom and the sulfur atom of a P_2N_3S ring, as found for other PNS heterocycles.[4,15]

In contrast to the effects observed for π-electron-rich PNS rings,[4,15] however, coordination of a methyl group to this nitrogen results in a relatively minor perturbation in the conformation of the P_2N_3S ring (Table V). The P_2N_3S ring in **2** (X = R = Ph) adopts a distorted half-boat conformation with the S and N(6) atoms removed from the plane by +0.55 and +0.15 Å, respectively. In the methylated derivative, **6**, these distortions toward a boat conformation become +0.63 and 0.27 Å, respectively. There are short contacts (2.60 Å) between H atoms of the phenyl rings and both N(4) and N(6), which may contribute to the distortion of the heterocyclic ring.

The effect of adduct formation on the endocyclic bond lengths is more pronounced. As was found for other PNS rings,[4,15,16] the major change involves the bonds to the coordinated nitrogen. Both P(3)–N(2) and S(1)–N(2) are lengthened from ca. 1.62 Å in **2** (X = R = Ph) to ca. 1.69 Å in the methylated derivative. However, the elongation of the S–N bond (by 0.07 Å) is substantially smaller than that observed (ca. 0.13 Å) for the π-electron-rich ring **3** (R = Ph).[4] The bonds P(3)–N(6) and S(1)–N(4), adjacent to the elongated bonds in **6**, are shortened compared to their values in **2** (X = R = Ph), the effect being greater for the S–N bond. The P(5)–N(4) bond is lengthened slightly whereas P(5)–N(6) is unchanged compared to the values found for the free ligand. The observed sequence of long–short–long endocyclic bonds in **6** parallels that found for protonated cyclotriphosphazenes,[7] whereas the PN_3S_2 ring **3** (R = Ph) exhibits a long–long–short sequence of endocyclic bonds upon adduct formation.[4]

The major changes in *endocyclic* bond angles occur in the PNP unit and at sulfur. The angles at phosphorus are reduced from 115.7 (1) and 116.6 (1) to 108.5 (1) and 113.6 (2)°, respectively, while that at N(6) opens from 120.7 (1) to 126.5 (2)°. The endocyclic angle at sulfur decreases from 113.5 (1) to 109.4 (2)°. The sum of the angles at the coordinated nitrogen, N(4), is 359.8°.

In summary, the structural changes that occur upon methylation of **2** (R = X = Ph) resemble more closely those observed for protonated cyclotriphosphazenes than those found for adducts of **3** (R = Ph).

Electronic Structure of the P_2N_3S Ring and Regiospecificity of Adduct Formation. The lack of regiospecificity observed for adduct formation by **2** (R = X = Ph) is in direct contrast to the behavior of other PNS rings.[4,15] Our previous studies with **3** (R = Ph)[4] and 1,3-$Ph_4P_2N_4S_2$ have demonstrated that these interactions are controlled by electrostatic effects.[4,15] Ab initio HFS–SCF MO calculations for the model ring system $H_4P_2N_3S^+$ (**2**, R = H) have shown that the unique nitrogen carries a larger negative charge than the equivalent nitrogens, −0.51 vs −0.42, for a planar ring.[2] This difference is accentuated when the sulfur atom is lifted out of the plane of the other five atoms. It is possible that the replacement of S^+ by SPh tends to equalize the charges on the inequivalent N atoms, thus accounting for the observed lack of regiospecifity.

Conclusion. The Lewis base behavior of the π-electron-precise ring **2** differs from that of the π-electron-rich rings in several respects. For diphosphathiatriazines, (a) the interaction with Lewis or Brønsted acids is not regiospecific, being dependent on the nature of the electrophile, (b) the formation of diadducts is observed, and (c) only relatively minor changes in the conformation of the heterocyclic ring occur upon methylation. The structural changes noted for the methylated derivative of **2** (X = R = Ph) parallel those found for cyclotriphosphazenes in keeping with the isoelectronic relationship between the P_3N_3 and $P_2N_3S^+$ rings. The endocyclic bonds to the coordinated nitrogen in the methylated adduct are weakened significantly, although less than in the related π-electron-rich PN_3S_2 ring, suggesting that electrophiles might be used to promote ring transformations and/or polymerization.

Acknowledgment. We thank the NSERC (Canada) for financial support in the form of operating and infrastructure grants and Dr. K. A. Kerr for the use of the X-ray diffractometer.

Supplementary Material Available: Tables listing crystallographic parameters, thermal parameters for non-H atoms, positional and isotropic thermal parameters for H atoms, and bond lengths and bond angles for all atoms (7 pages); a table of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.

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