S,S′-Diorgano Derivatives of the 1,5-$Ph_4P_2N_4S_2$ Ring: Lithium Halide Adducts, Conformational Isomerism, and N-Methylation

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The reaction of the lithium reagents $[Li(Ph_4P_2N_4S_2R)THF]_2$ (R = Me, ᵗBu, Ph) with organic iodides R′I (R′ = Me, allyl) at 23 °C in THF produces lithium iodide adducts of the type $[Ph_4P_2N_4(SR)(SR')LiI(THF)]$, which were characterized by ^1H, ^7Li, ^{13}C and ^{31}P NMR spectroscopy. The dissolution of these adducts in CH_2Cl_2 or toluene results in the precipitation of LiI and the concomitant formation of eight-membered rings $Ph_4P_2N_4(SR)(SR')$ in the form of boat (**6B**, R = R′ = Me) or twisted boat (**10B**, R = ᵗBu, R′ = allyl) conformers with sulfur atoms in the prow and stern positions. The boat conformers ($\delta(^{31}P)$ = 14−17 ppm) are converted quantitatively to the corresponding chair conformers ($\delta(^{31}P)$ = 27−29 ppm) upon mild heating (35−40 °C) in CH_2Cl_2 or CH_3CN for 12 h. The reaction of $Na_2[Ph_4P_2N_4S_2]$ with 2 molar equiv of allyl iodide produces $Ph_4P_2N_4(Sallyl)_2$ (**11B**) in which the $P_2N_4S_2$ ring adopts a boat conformation with nitrogen atoms as the prow and stern. The treatment of $Ph_4P_2N_4(SPh)_2$ with methyl triflate yields the N-methylated adduct $[Ph_4P_2N_3(NMe)(SPh)_2][SO_3CF_3]$ (**12**). N-methylation results in elongation of the P−N and S−N bonds involving the methylated nitrogen atom by 0.074 and 0.078 Å, respectively. Crystal data: **6B**, monoclinic, space group *C*2/*c*, *a* = 34.886(12) Å, *b* = 11.870(3) Å, *c* = 12.827(8) Å, *β* = 105.97(4)°, *V* = 5106(3) Å³, *Z* = 8, *R* = 0.042, R_w = 0.040; **10B**, triclinic, space group $P\bar{1}$, *a* = 10.253(3) Å, *b* = 15.875(4) Å, *c* = 9.582(1) Å, α = 93.97(2)°, *β* = 100.75(2)°, *γ* = 84.57(2)°, *V* = 1523.3(6) Å³, *Z* = 2, *R* = 0.051, R_w = 0.028; **11B**, monoclinic, space group *C*2/*c*, *a* = 20.519(2) Å, *b* = 16.190(3) Å, *c* = 17.581(3) Å, *β* = 96.10(1)°, *V* = 5807(1) Å³, *Z* = 8, *R* = 0.051, R_w = 0.054; **12**, monoclinic, space group *Cc*, *a* = 9.949(1) Å, *b* = 20.377(4) Å, *c* = 19.376(4) Å, *β* = 100.16(1)°, *V* = 3866(1) Å³, *Z* = 4, *R* = 0.058, R_w = 0.032.

Introduction

Ring systems of the type $R_4P_2N_4S_2R'_2$ are hybrids of the well-known cyclophosphazenes $(R_2PN)_4$[1] and the tetrameric cyclothiazyl systems $(NSR')_4$, which are unknown for R′ = alkyl or aryl.[2] The preparation of the first example of this inorganic heterocycle, $Ph_4P_2N_4S_2Me_2$, which involved the use of the explosive reagent $Me_2S(NBr)_2$, was reported by Appel et al. in 1968.[3] More than 20 years later, we described the synthesis of the corresponding selenium ring system, $Ph_4P_2N_4Se_2Me_2$, and showed it to consist of an eight-membered chair with the two selenium atoms displaced on either side of the P_2N_4 plane by *ca.* 1.07 Å and methyl substituents in axial positions.[4] The *S,S′*-diphenyl derivative $Ph_4P_2N_4S_2Ph_2$, which was made by the reaction of $Ph_2PN_2(SiMe_3)_3$ with 3 molar equiv of PhSCl, adopts a similar structure.[5]

The recent discoveries of alkali metal derivatives of the anions $Ph_4P_2N_4S_2Me^-$ and $Ph_4P_2N_4S_2^{2-}$, both of which react with iodomethane to yield $Ph_4P_2N_4S_2Me_2$,[6,7] has paved the way for the synthesis of a wide range of *S,S′*-diorgano derivatives with either the same or different groups attached to the two sulfur atoms. In view of the potential applications of these inorganic ring systems as precursors for hybrid PN/SN polymers, which have been the subject of recent attention,[8] or as multidentate ligands,[9] we have prepared a variety of these eight-membered rings and structurally characterized three of them. Another incentive for a more detailed investigation of the reactions of $[Li(Ph_4P_2N_4S_2R)THF]_2$ and $Li_2[Ph_4P_2N_4S_2]$ with MeI (or other organic halides) was the observation that the ^{31}P NMR chemical shift of the initial product of these reactions differed from that of the final product by more than 10 ppm.[10] The N-methylated compound $[Ph_4P_2N_3(NMe)(SPh)_2][CF_3SO_3]$ was also prepared and structurally characterized in order to assess the possibility of using Lewis acids to promote ring-opening polymerization of the $P_2N_4S_2$ ring.

Experimental Section

Reagents and Purification Procedures. All experiments were conducted under dry argon gas in Schlenk vessels using standard air-sensitive techniques. All solvents were distilled from the appropriate drying agents under argon and deoxygenated by argon purge (15 min) prior to use. Iodomethane and allyl iodide (Aldrich) were purified by passage through a short column (5 cm) of basic alumina. The compounds 1,5-$Ph_4P_2N_4S_2$[11] and $Li[Ph_4P_2N_4S_2R]$ (R = Me, ᵗBu, Ph)[6] were prepared by the literature methods. $M_2[Ph_4P_2N_4S_2]$ (M = Li, Na) was obtained by treatment of 1,5-$Ph_4P_2N_4S_2$ with 2 molar equiv of $M[Et_3BH]$ (Aldrich) in THF at −78 °C followed by warming to 23 °C.[7] The compound 1,5-$Ph_4P_2N_4S_2Ph_2$ was prepared in 59% yield from

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Table 1. ^{7}Li{^{1}H} and ^{31}P{^{1}H} NMR Data for [$Ph_4P_2N_4$(SR)(SR′)LiI(THF)] (**1-5**) and the Boat and Chair Conformers [$Ph_4P_2N_4$(SR)(SR′)] (**6-11**)

compd[a]	$\delta(^7Li)$[b,c]	$\delta(^{31}P)$[d]	solvent
1 (R = R′ = Me)	0.61	14.7	THF
2 (R = Ph, R′ = Me)	0.64	16.4	THF
3 (R = ^{t}Bu, R′ = Me)	0.74	16.2	THF
4 (R = Ph, R′ = allyl)	0.45	16.7	THF
5 (R = ^{t}Bu, R′ = allyl)	0.66	16.5	THF
6B (R = R′ = Me)		14.1	THF
7B (R = Ph, R′ = Me)		16.3	THF
8B (R = ^{t}Bu, R′ = Me)		16.1	THF
9B (R = Ph, R′ = allyl)		16.7	THF
10B (R = ^{t}Bu, R′ = allyl)		16.4	THF
11B (R = R′ = allyl)		15.0	THF
6C (R = R′ = Me)		27.0	CH_2Cl_2
7C (R = Ph, R′ = Me)		27.6	THF
8C (R = ^{t}Bu, R′ = Me)		26.9	THF
9C (R = Ph, R′ = allyl)		27.6	THF
10C (R = ^{t}Bu, R′ = allyl)		27.2	CH_2Cl_2

[a] **B** = boat conformer; **C** = chair conformer. [b] Chemical shifts are quoted in ppm relative to 4.0 M $LiClO_4$ in D_2O, *cf.* $\delta(^7Li) = -0.11$ ppm for LiI in THF. [c] Spectra were recorded in THF with a D_2O insert. All ^{7}Li resonances listed above are singlets. [d] Chemical shifts are quoted in ppm relative to 85% H_3PO_4. The lock signal was provided by a sealed D_2O insert.

Table 2. Crystallographic Data for Compounds **6B**, **10B**, **11B** and **12**

	6B	**10B**	**11B**	**12**
formula	$C_{26}H_{26}N_4P_2S_2$	$C_{31}H_{34}N_4P_2S_2$	$C_{30}H_{30}N_4P_2S_2$	$C_{38}H_{33}N_4O_3F_3P_2S_3$
fw	520.59	588.70	572.66	808.83
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)	*Cc* (No. 9)
a, Å	34.886(2)	10.253(3)	20.519(2)	9.949(1)
b, Å	11.870(3)	15.875(4)	16.190(3)	20.377(4)
c, Å	12.827(8)	9.582(1)	17.581(3)	19.376(4)
α, deg		93.97(2)		
β, deg	105.97(4)	100.75(2)	96.10(1)	100.16(1)
γ, deg		84.57(2)		
V, Å^3	5106(3)	1523.3(6)	5807(1)	3866(1)
Z	8	2	8	4
D_{calc}, g cm^{-3}	1.354	1.283	1.310	1.389
μ(Mo Kα), cm^{-1}	3.57	3.07	3.20	3.31
λ (Å)	0.710 69	0.710 69	0.710 69	0.710 69
T (°C)	-123	23	−123	23
R,[a] R_w	0.042, 0.040	0.051, 0.028	0.051, 0.054	0.058, 0.032

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum_w\delta^2/\sum_w F_o2]^{1/2}$.

$Ph_2PN_2(SiMe_3)_3$ and 3 molar equiv of PhSCl by the literature method[5] but with CH_3CN rather than CH_2Cl_2 as solvent. The use of CH_3CN obviates the need to extract the product with pentane to remove Ph_2S_2. Methyl triflate, lithium iodide, methyllithium (1.5 M in diethyl ether), *tert*-butyllithium (1.7 M in pentane), and phenyllithium (1.8 M in cyclohexane/diethyl ether) were obtained from Aldrich and used as received. Combustion analyses were performed by the microanalytical service within the Chemistry Department at the University of Calgary.

Instrumentation. ^{31}P{^{1}H} NMR spectra were recorded on either a Varian XL-200 spectrometer (81.0 MHz) or a Bruker AM-400 spectrometer (161.978 MHz) in THF or dichloromethane with 85% H_3PO_4 as the external reference. A D_2O insert was used as the lock for the phosphorus-31 spectra. The ^{7}Li{^{1}H} NMR spectra were recorded on the AM-400 instrument at 155.508 MHz or on the Varian XL-200 instrument at 77.754 MHz, and the ^{7}Li chemical shifts are relative to 4.0 M $LiClO_4$ in D_2O. Proton NMR spectra were run on either a Bruker AM-200 spectrometer at 200.1 MHz or the Bruker AM-400 instrument at 400.1 MHz while carbon-13 spectra were run on the AM-200 instrument at 50.323 MHz. Fast atom bombardment mass spectra were recorded on a Kratos MS80 RFA instrument in a nitrobenzyl alcohol matrix using xenon as the ionizing gas.

Preparation of [$Ph_4P_2N_4$(SR)(SR′)LiI(THF)] Adducts. In a typical experiment, an equimolar quantity of either iodomethane or allyl iodide was added dropwise by syringe to a rapidly stirred yellow solution of a selected organolithium derivative, Li[$Ph_4P_2N_4S_2R$] (R = Me, ^{t}Bu, Ph), in 20 mL of THF at 23 °C. The resulting pale yellow solution was stirred for *ca.* 1 h, and then the solvent was removed under vacuum to give a buff solid. The last vestiges of free THF were removed from the product by gentle heating overnight at 40 °C under a dynamic vacuum. All of the LiI(THF) adducts described below were obtained in quantitative yield. The ^{7}Li and ^{31}P NMR data for the adducts are collected in Table 1. Selected proton and carbon-13 NMR data for the new adducts are given below along with their CHN analyses.

[$Ph_4P_2N_4(SMe)_2$LiI(THF)] (1). Anal. Calcd for $C_{30}H_{34}ON_4P_2S_2LiI$: C, 49.59; H, 4.72; N, 7.71. Found: C, 49.14; H, 4.64; N, 7.72. ^{1}H NMR (d_8-toluene): 7.05−8.15 (m, C_6H_5, 20H), 3.79 (m, THF, 4H), 2.59 (t, SCH_3, 6H, ^4J(PH) = 1.5 Hz), 1.49 (m, THF, 4H). ^{13}C{^{1}H} NMR (d_8-toluene): 137.4−127.4 (m, C_6H_5), 68.65 (s, THF), 45.40 (t, SCH_3, ^3J(PC) = 15 Hz), 25.47 (s, THF).

[$Ph_4P_2N_4$(SMe)(SPh)LiI(THF)] (2). Anal. Calcd for $C_{35}H_{36}N_4OP_2S_2LiI$: C, 53.31; H, 4.60; N, 7.10. Found: C, 53.97; H, 5.18; N, 6.45. ^{1}H NMR (d_8-toluene): 7.45−8.25 (m, C_6H_5, 25H), 3.98 (m, THF, 4H), 2.85 (t, SCH_3, 3H, ^4J(PH) = 1.5 Hz), 1.73 (m, THF, 4H). ^{13}C{^{1}H} NMR (d_8-toluene): 44.27 (t, SCH_3, ^3J(PC) = 16 Hz).

[$Ph_4P_2N_4$(SMe)(S^{t}Bu)LiI(THF)] (3). Anal. Calcd for $C_{33}H_{40}N_4OP_2S_2LiI$: C, 51.57; H, 5.25; N, 7.29. Found: C, 50.68, H, 5.85; N, 6.15. ^{1}H NMR (d_8-toluene): 6.95−8.30 (m, C_6H_5, 20H), 3.78 (m, THF, 4H), 2.70 (t, SCH_3, 3H, ^4J(PH) = 1.5 Hz), 1.48 (m, THF, 4H), 1.29 (s, $SC(CH_3)_3$, 9H).

[$Ph_4P_2N_4$(SPh)(Sallyl)LiI(THF)] (4). Anal. Calcd for $C_{37}H_{38}ON_4P_2S_2LiI$: C, 54.55; H, 4.70; N, 6.88; I, 15.58. Found: C, 54.32; H, 4.80; N, 6.65; I, 15.14. ^{1}H NMR (d_8-toluene): 6.95−8.15 (m, C_6H_5, 25H), 5.90 (ddt, $SCH_2CH_A{=}CH_BH_C$, 1H, ^3J(trans)H_A-H_B = 17.5 Hz, ^3J(cis)H_A-H_C = 10 Hz, $^3J(H_A-SCH_2)$ = 7.5 Hz), 5.08−4.97 (m, $SCH_2CH_A{=}CH_BH_C$, 2H), 3.84 (d, $SCH_2CH_A{=}CH_BH_C$, 2H, $^3J(SCH_2-H_A)$ = 7.5 Hz), 3.78 (m, THF, 4H), 1.35 (m, THF, 4H).

[$Ph_4P_2N_4$(S^{t}Bu)(Sallyl)LiI(THF)] (5). Anal. Calcd for $C_{35}H_{42}N_4OP_2S_2LiI$: C, 52.90; H, 5.33; N, 7.05. Found: C, 52.96; H, 5.92; N, 6.05. ^{1}H NMR (d_8-toluene): 6.90−8.30 (m, C_6H_5, 20H), 5.72 (ddt, $SCH_2CH_A{=}CH_BH_C$, 1H, ^3J(trans)H_A-H_B) = 17.5 Hz, ^3J((cis)H_A-H_C) = 10 Hz, $^3J(H_A-SCH_2)$ = 7.5 Hz), 4.95 (ddt, $SCH_2CH_A{=}CH_BH_C$, 1H, ^3J(trans)H_B-H_A) = 17.5 Hz, ^2J(gem)H_B-H_C) = 2 Hz, $^4J(H_B-SCH_2)$ = 1 Hz), 4.92 (dd, $SCH_2CH_A{=}CH_BH_C$, 1H, ^3J(cis)H_C-H_A) = 10 Hz, ^2J(gem)H_C-H_B) = 2 Hz), 3.93 (dd, $SCH_2CH_A{=}CH_BH_C$, 2H, $^3J(SCH_2-H_A)$ = 7.5 Hz, $^4J(SCH_2-H_B)$ = 1 Hz), 3.78 (m, THF, 4H), 1.48 (m, THF, 4H), 1.35 (s, $SC(CH_3)_3$, 9H).

Preparation of the Boat Conformers of the [$Ph_4P_2N_4$(SR)(SR′)] Rings. A typical synthesis is described as follows:

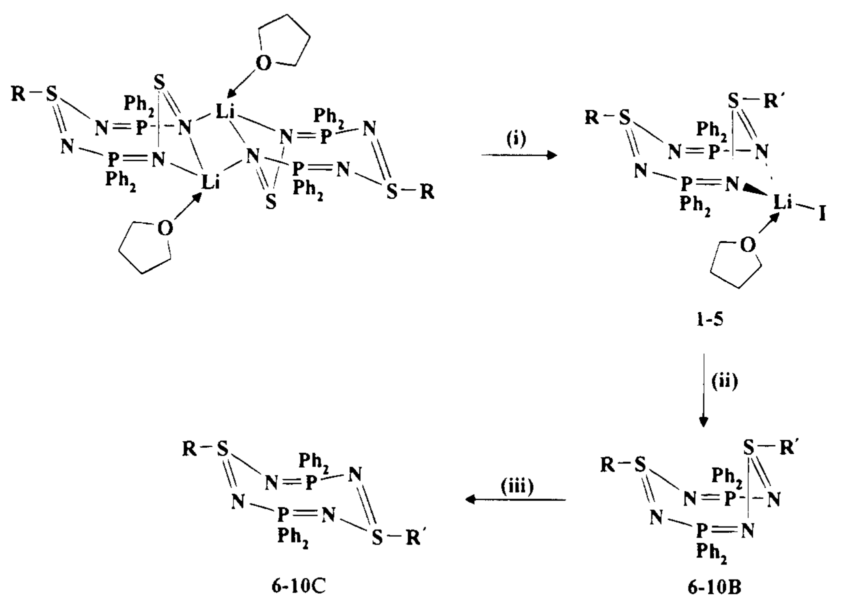
[$Ph_4P_2N_4(SMe)_2$] (6B). Dichloromethane (20 mL) was added by cannula to a flask containing solid [$Ph_4P_2N_4(SMe)_2$LiI(THF)] (0.300 g, 0.413 mmol), causing the immediate formation of a cloudy pale yellow solution. The LiI precipitate was separated from the clear yellow supernatant by filtration, and the filtrate was taken to dryness under vacuum. Recrystallization of the off-white residue from toluene (3 mL) at 0 °C afforded the boat form of [$Ph_4P_2N_4(SMe)_2$] (**6B**) (0.187 g, 0.359 mmol, 87%) as colorless crystals. Anal. Calcd for $C_{26}H_{26}P_2N_4S_2$: C, 59.98; H, 5.03; N, 10.77. Found: C, 59.40; H, 5.09; N, 10.31. FAB MS (*m*/*e*, %): M$^+$ (520, 87), M$^+$ − Me (505, 100), M$^+$ − 2Me (490, 13). ^{1}H NMR (d_8-toluene/d_6-benzene): 7.10−8.22 (m, C_6H_5, 20H), 2.55 (t, SCH_3, 6H, ^{4}J(PH) = 1 Hz). ^{13}C{^{1}H} NMR (d_8-toluene/d_6-benzene): 127.5−137.47 (m, C_6H_5), 45.41 (t, SCH_3, ^3J(PC) = 16 Hz).

All other boat conformers of the [$Ph_4P_2N_4$(SR)(SR′)] rings were obtained as colorless crystals in a similar fashion. The yields, crystallizing conditions, CHN analyses, FAB mass spectrometry data, and ^{1}H/^{13}C NMR data are summarized in the following section. The ^{31}P NMR data can be found in Table 1.

[$Ph_4P_2N_4$(SMe)(SPh)] (7B). A colorless crystalline solid was crystallized from acetonitrile at −18 °C. Yield: 56%. Anal. Calcd for $C_{31}H_{28}N_4P_2S_2$: C, 63.90; H, 4.84; N, 9.58. Found: C, 64.00; H, 4.22; N, 10.03. FAB MS (*m*/*e*, %): (M + H)$^+$ (583, 100), (M − Me + H)$^+$ (568, 79), (M$^+$ − Ph − Me) (490, 10). ^{1}H NMR (C_6D_6): 6.88−8.11 (m, C_6H_5, 25H), 2.61 (t, SCH_3, 3H), ^4J(PH) = 1 Hz).

[$Ph_4P_2N_4$(SMe)(S^{t}Bu)] (8B). A colorless crystalline solid was crystallized from acetonitrile at 23 °C. Yield: 49%. Anal. Calcd for $C_{29}H_{32}N_4P_2S_2(CH_3CN)$: C, 61.67; H, 5.84; N, 11.60. Found: C, 60.67;

Scheme 1. Formation of LiI adducts and the Boat and Chair forms of $Ph_4P_2N_4(SR)(SR')^a$



[a] Key: (i) R'I (R' = CH_3, C_3H_5), (ii) CH_2Cl_2 or toluene, −LiI; (iii) CH_3CN or CH_2Cl_2 at *ca.* 40 °C. See Table 1 for identification of **1-5** and **6-10**; **B** = Boat, **C** = Chair.

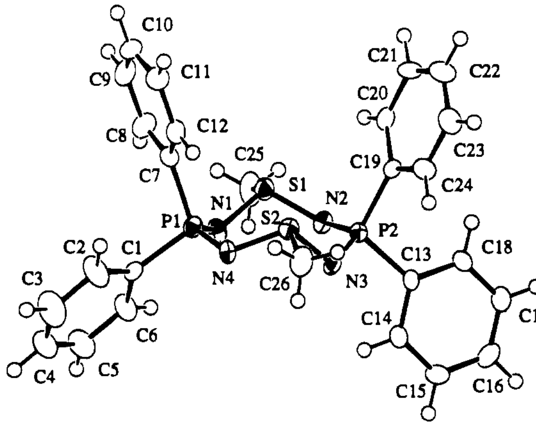


Figure 1. ORTEP drawing (50% probability ellipsoids) of $[Ph_4P_2N_4(SMe)_2]$, **6B**.

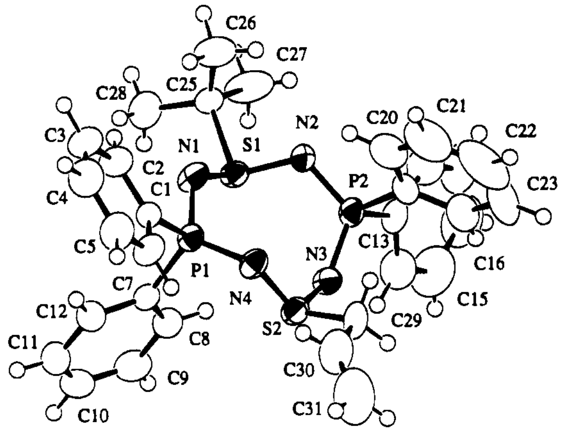


Figure 2. ORTEP drawing (50% probability ellipsoids) of $[Ph_4P_2N_4(S{}^tBu)(Sallyl)]$, **10B**.

H, 5.67; N, 11.16. FAB MS (*m/e*, %): $(M + H)^+$ (563, 45), $M^+ - {}^tBu$ (505, 100), $M^+ - {}^tBu$ - Me (490, 9). ^1H NMR ($CDCl_3$): 7.20−8.20 (m, $C_6\mathit{H}_5$, 20H), 2.89 (s, $SC\mathit{H}_3$, 3H), 2.04 (s, $C\mathit{H}_3CN$, 3H), 1.37 (s, $SC(C\mathit{H}_3)_3$, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 127.7−137.9 (m, C_6H_5), 57.12 (t, $S\mathit{C}(C\mathit{H}_3)_3$, $^3J(PC) = 15$ Hz), 44.36 (t, $S\mathit{C}H_3$, $^3J(PC) = 16$ Hz), 22.73 (s, $SC(\mathit{C}H_3)_3$).

$[Ph_4P_2N_4(SPh)(Sallyl)]$ (9B). A colorless crystalline solid was crystallized from Et_2O at 23 °C. Yield: 49%. Anal. Calcd for $C_{33}H_{30}N_4P_2S_2$: C, 65.11; H, 4.97; N, 9.21. Found: C, 64.44; H, 5.40; N, 8.79. FAB MS (*m/e*, %): $(M + H)^+$ (609, 33), $(M - C_3H_5 + H)^+$ (567, 100), $(M - C_3H_5 - Ph + H)^+$ (491, 18). ^1H NMR (C_6D_6): 7.00−8.70 (m, $C_6\mathit{H}_5$, 25H), 5.86 (ddt, $SCH_2C\mathit{H}_A{=}CH_BH_C$, 1H, $^3J((trans)\text{-}H_A{-}H_B) = 18$ Hz, $^3J((cis)H_A{-}H_C) = 10$ Hz, $^3J(H_A{-}SC\mathit{H}_2) = 7.5$ Hz), 5.00−4.91 (m, $SCH_2CH_A{=}C\mathit{H}_B\mathit{H}_C$, 2H), 3.76 (dd, $SC\mathit{H}_2CH_A{=}CH_BH_C$, 2H, $^3J(SC\mathit{H}_2{-}H_A) = 7.5$ Hz, $^4J(SC\mathit{H}_2{-}H_B) = 2$ Hz).

$[Ph_4P_2N_4(S{}^tBu)(Sallyl)]$ (10B). A colorless crystalline solid was crystallized from Et_2O at 23 °C. Yield: 32%. Anal. Calcd for $C_{31}H_{34}N_4P_2S_2$: C, 63.25; H, 5.82; N, 9.52. Found: C, 62.89; H, 5.67; N, 9.81. FAB MS (*m/e*, %): $(M + H)^+$ (589, 53), $(M - C_3H_5)^+$ (547, 83), $(M - C_3H_5 - C_4H_9{+}H)^+$ (491, 100). ^1H NMR (d_8-toluene): 6.99−8.20 (m, $C_6\mathit{H}_5$, 20H), 5.71 (ddt, $SCH_2C\mathit{H}_A{=}CH_BH_C$, 1H, $^3J((trans)\text{-}H_A{-}H_B) = 17$ Hz, $^3J((cis)H_A{-}H_C) = 10$ Hz, $^3J(H_A{-}SC\mathit{H}_2) = 7.5$ Hz), 4.96−4.87 (m, $SCH_2CH_A{=}C\mathit{H}_B\mathit{H}_C$, 2H), 3.89 (d, $SC\mathit{H}_2CH_A{=}CH_BH_C$, 2H, $^3J(SC\mathit{H}_2{-}H_A) = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (d_8-toluene): 128.8−139.0 (m, C_6H_5), 120.77 (s, $SCH_2CH{=}\mathit{C}H_2$), 62.64 (t, $S\mathit{C}H_2CH{=}CH_2$, $^3J(PC) = 11$ Hz), 57.04 (t, $S\mathit{C}(CH_3)_3$, $^3J(PC) = 15$ Hz), 22.86 (s, $SC(\mathit{C}H_3)_3$).

Conversion of $[Ph_4P_2N_4(SR)(SR')]$(Boat) to $[Ph_4P_2N_4(SR)(SR')]$(Chair). Gentle heating of the boat conformer in either dichloromethane or acetonitrile at 35−40 °C for a minimum of 12 h results in essentially quantitative conversion to the thermodynamically more favorable chair conformer. Selected proton and $^{13}C\{^1H\}$ NMR data together with FAB MS data for the chair conformers are given below. The $^{31}P\{^1H\}$ NMR data are listed in Table 1.

$[Ph_4P_2N_4(SMe)_2]$ (6C). FAB MS (*m/e*, %): M^+ (520, 6.7), $(M^+ -$ Me) (505, 100), (M^+ - 2Me) (490, 39). ^1H NMR ($CDCl_3$, 23 °C): 8.0−7.3 (m, $C_6\mathit{H}_5$, 20H), 2.80 (t, $SC\mathit{H}_3$, 6H, $^4J(PH) = 1$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 45.7 (t, $S\mathit{C}H_3$, $^3J(PC) = 21$ Hz).

$[Ph_4P_2N_4(SMe)(SPh)]$ (7C). ^1H NMR ($CDCl_3$, 23 °C): 7.91−7.28 (m, $C_6\mathit{H}_5$, 25H), 2.87 (t, $SC\mathit{H}_3$, 3H, $^4J(PH) = 1$ Hz).

$[Ph_4P_2N_4(SMe)(S{}^tBu)]$ (8C). ^1H NMR ($CDCl_3$, 23 °C): 7.97−7.32 (m, $C_6\mathit{H}_5$, 20H), 2.87 (t, $SC\mathit{H}_3$, 3H, $^4J(PH) = 1$ Hz), 1.28 (s, $C(C\mathit{H}_3)_3$, 9H).

$[Ph_4P_2N_4(SPh)(Sallyl)]$ (9C). ^1H NMR (CD_2Cl_2, 23 °C): 7.00−8.30 (m, $C_6\mathit{H}_5$, 25H), 5.76 (ddt, $SCH_2C\mathit{H}_A{=}CH_BH_C$, 1H, $^3J(trans)H_A{-}H_B) = 17$ Hz, $^3J(cis)H_A{-}H_C) = 10$ Hz, $^3J(H_A{-}SC\mathit{H}_2) = 7.5$ Hz), 5.20−5.00 (m, $SCH_2CH_A{=}C\mathit{H}_B\mathit{H}_C$, 2H), 3.48 (d, $SC\mathit{H}_2CH_A{=}CH_BH_C$, 2H, $^3J(SC\mathit{H}_2{-}H_A) = 7.5$ Hz).

$[Ph_4P_2N_4(S{}^tBu)(Sallyl)]$ (10C). FAB MS (*m/e*, %): M^+ (588. 35), $(M - C_3H_5)^+$ (547, 14), $(M - C_3H_5 - C_4H_9)^+$ (490, 24). ^1H NMR (d_8-toluene): 8.13−7.16 (m, $C_6\mathit{H}_5$, 20H), 5.83 (ddt, $SCH_2C\mathit{H}_A{=}CH_BH_C$, 1H, $^3J((trans)H_A{-}H_B) = 18$ Hz, $^3J((cis)H_A{-}H_C) = 10$ Hz, $^3J((H_A{-}SC\mathit{H}_2) = 7.5$ Hz), 5.06−4.98 (m, $SCH_2CH_A{=}C\mathit{H}_B\mathit{H}_C$, 2H), 3.63 (d,

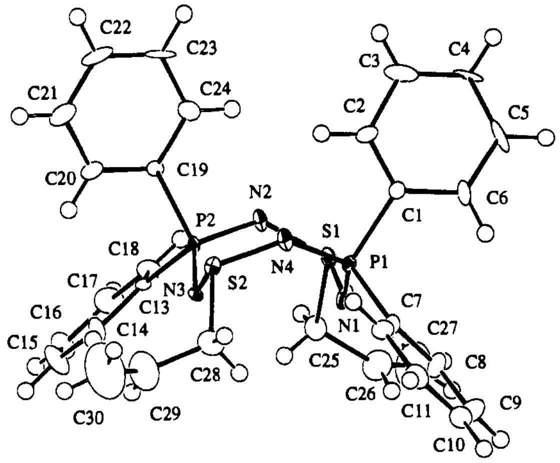


Figure 3. ORTEP drawing (50% probability ellipsoids) of [$Ph_4P_2N_4$(Sallyl)$_2$], **11B**.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $Ph_4P_2N_4(SMe)_2$, **6B**, and $Ph_4P_2N_4$(S^{t}Bu)(Sallyl), **10B**

	6B	10B		6B	10B
		Distances			
S(1)−N(1)	1.612(4)	1.616(4)	P(2)−N(3)	1.628(4)	1.611(4)
S(1)−N(2)	1.627(4)	1.619(4)	S(1)−C(25)	1.776(5)	1.844(5)
S(2)−N(3)	1.625(4)	1.610(4)	S(2)−C(26)	1.786(5)	
S(2)−N(4)	1.626(4)	1.615(4)	S(2)−C(29)		1.828(5)
P(1)−N(1)	1.610(4)	1.610(4)	C(29)−C(30)		1.453(7)
P(1)−N(4)	1.623(4)	1.618(4)	C(30)−C(31)		1.181(8)
P(2)−N(2)	1.609(4)	1.606(4)			
		Angles			
N(1)−S(1)−N(2)	110.0(2)	108.6(2)	C(25)−S(1)−N(1)	99.5(2)	99.1(2)
N(3)−S(2)−N(4)	110.6(2)	114.1(2)	C(25)−S(1)−N(2)	97.5(2)	101.1(2)
N(1)−P(1)−N(4)	120.0(2)	117.7(2)	C(26)−S(2)−N(3)	99.5(2)	
N(2)−P(2)−N(3)	120.1(2)	118.6(2)	C(26)−S(2)−N(4)	97.5(2)	
S(1)−N(1)−P(1)	121.8(2)	120.8(2)	C(29)-S(2)-N(3)		105.1(2)
S(1)−N(2)−P(2)	121.3(2)	117.8(2)	C(29)-S(2)-N(4)		97.5(2)
S(2)−N(3)−P(2)	117.3(2)	128.7(2)	C(29)-C(30)-C(31)		131.4(8)
S(2)−N(4)−P(1)	118.0(2)	121.6(3)			

$SCH_2CH_A{=}CH_BH_C$, 2H, $^3J((SCH_2{-}H_A) = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (d_8-toluene): 138.7−128.1 (m, C_6H_5), 121.19 (s, $SCH_2CH{=}CH_2$), 63.22 (t, $SCH_2CH{=}CH_2$, $^3J((PC) = 20$ Hz), 56.22 (t, $SC(CH_3)_3$, $^3J((PC) = 15$ Hz), 22.96 (s, $SC(CH_3)_3$).

Preparation of [$Ph_4P_2N_4$(Sallyl)$_2$] (11B). Neat allyl iodide (0.37 mL, 4.06 mmol) was added dropwise by syringe to a yellow slurry of $Na_2[Ph_4P_2N_4S_2]$ (1.09 g, 2.03 mmol) in THF (40 mL) at −78 °C. The mixture was warmed to room temperature and stirring was continued for 1 h until all of the $Na_2[Ph_4P_2N_4S_2]$ had dissolved. The solvent was removed under vacuum and toluene (40 mL) was added, giving a cloudy pale yellow solution. The NaI precipitate was removed by filtration, and the filtrate was taken to dryness under vacuum. Recrystallization of the pale yellow residue from CH_2Cl_2−hexane at 23 °C afforded [$Ph_4P_2N_4$(Sallyl)$_2$] (0.65 g, 1.14 mmol, 56%) as colorless crystals. Anal. Calcd for $C_{30}H_{30}N_4P_2S_2$: C, 62.92; H, 5.28; N, 9.79. Found: C, 62.70; H, 5.24; N, 9.75. FAB MS (*m/e*, %): $(M + H)^+$(573, 52), $(M - 2(C_3H_5))^+$(490, 100). $^{31}P\{^1H\}$ NMR (THF, 23 °C, D_2O lock): 15.0 (singlet). ^1H NMR (d_6-benzene): 7.08−8.28 (m, C_6H_5, 20H), 5.85 (ddt, $SCH_2CH_A{=}CH_BH_C$, 1H, ^3J((trans)$H_A{-}H_B) = 17$ Hz, ^3J((cis)$H_A{-}H_C) = 10$ Hz, $^3H(H_A{-}SCH_2) = 7.5$ Hz), 5.02−4.92 (m, $SCH_2CH_A{=}CH_BH_C$, 2H), 3.75 (d, $SCH_2CH_A{=}CH_BH_C$, 2H, $^3J(SCH_2{-}H_A) = 7.5$ Hz). $^{13}C\{^1H\}$ NMR (d_6-benzene): 132.7−128.25 (m, C_6H_5), 121.19 (s, $SCH_2CH{=}CH_2$), 63.38 (t, $SCH_2CH{=}CH_2$, $^3J(PC) = 15$ Hz).

Preparation of [$Ph_4P_2N_3$(NMe)(SPh)$_2$][CF_3SO_3] (12). Methyl trifluoromethanesulfonate (0.018 mL, 0.16 mmol) was added dropwise by syringe to a rapidly stirred, colorless solution of [$Ph_4P_2N_4(SPh)_2$] (0.100 g, 0.155 mmol) in dichloromethane (20 mL) at 23 °C. After 2 h of stirring, the solvent was removed under vacuum and the residue was recrystallized from a 1:1 mixture of CH_2Cl_2/Et_2O to give [$Ph_4P_2N_3$(NMe)(SPh)$_2$][CF_3SO_3] (0.090 g, 0.11 mmol, 72%) as colorless crystals. Anal. Calcd for $C_{38}H_{33}N_4O_3F_3P_2S_3$: C, 56.43; H, 4.11; N, 6.93. Found: C, 56.10; H, 4.17; N, 7.36. FAB MS (*m/e*, %) (M = cation of **12**): M^+ (659, 100), $(M - Ph)^+$ (582, 4). $^{31}P\{^1H\}$ (CD_2Cl_2, 23 °C): 35.97 (d, $^4J(PP) = 3$ Hz), 33.19 (d, $^4J(PP) = 3$ Hz). ^1H NMR (CD_2Cl_2, 23 °C): 7.33−8.29 (m, C_6H_5, 30H), 2.79 (d, NCH_3, 3H, $^3J(PH) = 8$ Hz).

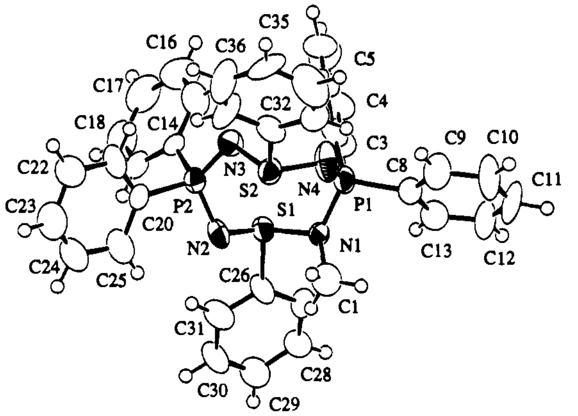


Figure 4. ORTEP drawing (50% probability ellipsoids) of [$Ph_4P_2N_3$(NMe)(SPh)$_2$][CF_3SO_3], **12**. Only the cation is shown.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for [$Ph_4P_2N_4$(Sallyl)$_2$], **11B**[a]

	Distances		
S(1)−N(1)	1.614(4)	S(2)−N(4)	1.605(4)
S(1)−N(2)	1.614(4)	S(2)−C(28)	1.815(6)
S(1)−C(25)	1.829(5)	P(2)−N(2)	1.606(4)
P(1)−N(1)	1.596(4)	P(2)−N(3)	1.615(4)
P(1)−N(4)	1.617(4)	C(28)−C(29)	1.497(8)
C(25)−C(26)	1.499(8)	C(29)−C(30a)	1.156(12)
C(26)−C(27)	1.311(8)	C(29)−C(30b)	1.176(19)
S(2)−N(3)	1.627(4)	C(30a)−C(30b)	1.322(22)
	Angles		
N(1)−S(1)−N(2)	114.0(2)	N(2)−P(2)−N(3)	120.1(2)
N(1)−P(1)−N(4)	120.1(2)	S(1)−N(2)−P(2)	127.9(3)
S(1)−N(1)−P(1)	123.8(3)	S(2)−N(4)−P(1)	129.4(3)
S(2)−N(3)−P(2)	118.5(2)	N(1)−S(1)−C(25)	97.5(2)
N(2)−S(1)−C(25)	105.2(2)	N(4)−S(2)−C(28)	105.9(2)
N(3)−S(2)−C(28)	98.0(2)	C(28)−C(29)−C(30a)	130.3(9)
C(25)−C(26)−C(27)	125.5(7)	C(28)−C(29)−C(30b)	141.1(12)
N(3)−S(2)−N(4)	113.4(2)	C(30a)−C(29)−C(30b)	69.1(12)

[a] C(30a) and C(30b) represent the two sites of the disordered C(30) atom.

X-ray Data Collection and Structure Solutions. Suitable single crystals of **6B**, **10B**, **11B**, and **12** were grown from toluene, diethyl ether, dichloromethane-hexane, and dichloromethane-diethyl ether, respectively. All intensity measurements were made on a Rigaku AFC6S diffractometer with Mo Kα radiation. Accurate cell constants along with orientation matrices were obtained from a least squares refinement of the setting angles of 25 reflections in the range $18 < 2\theta < 40°$. Intensity data were collected at either 23 °C (**10B** and **12**) or −123 °C (**6B** and **11B**) using the $\omega{-}2\theta$ scan technique. The intensities of three standard reflections were measured every 200 reflections to check for any decay. The data were corrected for Lorentz and polarization effects and for absorption (DIFABS[12]). Unit cell and other crystallographic data related to the crystal structures of **6B**, **10B**, **11B**, and **12** are reported in Table 2. All four structures were solved by direct methods[13] and expanded using Fourier techniques.[14] The non-hydrogen atoms in each structure were refined anisotropically. Hydrogen atoms were included but not refined. A phenyl group [C(1)−C(6)] and an allyl C [C(30)] in **11B** were found to be disordered and were allowed to refine over two sites; the phenyl groups were treated

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Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Ph_4P_2N_3(NMe)(SPh)_2][CF_3SO_3]$, **12**

	Distances		
S(1)−N(1)	1.700(7)	P(1)−N(1)	1.692(8)
S(1)−N(2)	1.594(8)	P(1)−N(4)	1.577(8)
S(2)−N(3)	1.633(8)	P(2)−N(2)	1.626(9)
S(2)−N(4)	1.632(9)	P(2)−N(3)	1.631(8)
S(1)−C(26)	1.79(1)	N(1)−C(1)	1.48(1)
S(2)−C(32)	1.80(1)		
	Angles		
N(1)−S(1)−N(2)	111.2(4)	P(1)−N(4)−S(2)	122.2(6)
N(3)−S(2)−N(4)	109.9(5)	P(1)−N(1)−C(1)	115.6(7)
N(4)−P(1)−N(1)	117.2(5)	S(1)−N(1)−C(1)	116.5(7)
N(3)−P(2)−N(2)	117.1(4)	N(1)−S(1)−C(26)	99.6(5)
P(2)−N(3)−S(2)	114.6(5)	N(2)−S(1)−C(26)	103.9(5)
P(2)−N(2)−S(1)	115.8(5)	N(3)−S(2)−C(32)	100.5(5)
P(1)−N(1)−S(1)	116.9(4)	N(4)−S(2)−C(32)	99.3(5)

Table 6. Atomic Coordinates and B_{eq} Values (Å^2) for $Ph_4P_2N_4(SMe)_2$, **6B**

atom	x	y	z	B_{eq}[a]
S(1)	0.40155(4)	0.0650(1)	0.64795(10)	1.96(3)
S(2)	0.35110(4)	0.1857(1)	0.38489(10)	1.77(3)
P(1)	0.42799(4)	0.2210(1)	0.51751(10)	1.69(3)
P(2)	0.33955(4)	−0.0199(1)	0.47532(10)	1.53(3)
N(1)	0.4340(1)	0.1069(3)	0.5881(3)	1.91(9)
N(2)	0.3761(1)	−0.0401(3)	0.5817(3)	1.76(9)
N(3)	0.3466(1)	0.0498(3)	0.3727(3)	1.64(9)
N(4)	0.3969(1)	0.2236(3)	0.3973(3)	1.74(9)
C(1)	0.4753(1)	0.2426(4)	0.4918(3)	1.6(1)
C(2)	0.4844(2)	0.3428(5)	0.4492(5)	3.4(1)
C(3)	0.5200(2)	0.3555(5)	0.4220(5)	4.0(2)
C(4)	0.5469(2)	0.2699(5)	0.4389(4)	3.2(1)
C(5)	0.5390(2)	0.1714(5)	0.4839(5)	3.4(1)
C(6)	0.5033(2)	0.1573(4)	0.5103(4)	2.7(1)
C(7)	0.4194(1)	0.3398(4)	0.5976(4)	1.9(1)
C(8)	0.4396(2)	0.3458(4)	0.7071(4)	2.6(1)
C(9)	0.4343(2)	0.4364(5)	0.7694(4)	3.0(1)
C(10)	0.4085(2)	0.5209(4)	0.7240(4)	2.8(1)
C(11)	0.3868(2)	0.5153(4)	0.6163(4)	2.7(1)
C(12)	0.3927(1)	0.4255(4)	0.5532(4)	2.2(1)
C(13)	0.3275(1)	−0.1596(4)	0.4228(3)	1.6(1)
C(14)	0.3503(1)	−0.2071(4)	0.3603(4)	2.2(1)
C(15)	0.3433(2)	−0.3172(4)	0.3227(4)	2.7(1)
C(16)	0.3138(2)	−0.3800(4)	0.3481(4)	2.7(1)
C(17)	0.2914(2)	−0.3342(4)	0.4105(4)	2.6(1)
C(18)	0.2982(1)	−0.2242(4)	0.4481(4)	2.2(1)
C(19)	0.2960(1)	0.0349(4)	0.5094(4)	1.6(1)
C(20)	0.2964(1)	0.0573(4)	0.6161(4)	1.9(1)
C(21)	0.2633(2)	0.1047(4)	0.6390(4)	2.3(1)
C(22)	0.2293(2)	0.1278(4)	0.5571(4)	2.6(1)
C(23)	0.2286(1)	0.1046(4)	0.4515(4)	2.6(1)
C(24)	0.2615(1)	0.0608(4)	0.4269(4)	2.2(1)
C(25)	0.4331(2)	−0.0145(5)	0.7550(4)	3.3(1)
C(26)	0.3310(1)	0.2255(4)	0.2463(4)	2.8(1)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos \alpha)$.

as regular hexagons during refinement in this structure. Neutral atom scattering factors[15] and anomalous dispersion terms[16] were taken from the usual sources. All calculations were performed using TEXSAN;[17] **11B** was refined by the program SHELX 76.[18] The most significant bond lengths and angles for **6B**, **10B**, **11B**, and **12** are given in Tables 3−5. Isotropic thermal parameters and atomic coordinates for the four structures are listed in Tables 6−9.

Table 7. Atomic Coordinates and B_{eq} Values (Å^2) for $Ph_4P_2N_4(S^tBu)(Sallyl)$, **10B**

atom	x	y	z	B_{eq}[a]
S(1)	0.7139(1)	0.32553(9)	0.2972(1)	3.09(4)
S(2)	0.6959(1)	0.22275(9)	0.6423(1)	3.34(4)
P(1)	0.8765(1)	0.32777(9)	0.5673(1)	2.81(4)
P(2)	0.6139(1)	0.17620(10)	0.3424(1)	3.03(4)
N(1)	0.8561(4)	0.3384(3)	0.3985(4)	3.5(1)
N(2)	0.7030(4)	0.2253(3)	0.2587(4)	3.6(1)
N(3)	0.5896(4)	0.2145(3)	0.4964(4)	3.2(1)
N(4)	0.8438(4)	0.2388(3)	0.6202(4)	3.2(1)
C(1)	1.0526(5)	0.3318(3)	0.6269(5)	2.7(1)
C(2)	1.1294(5)	0.3607(4)	0.5398(5)	4.0(2)
C(3)	1.2675(6)	0.3605(4)	0.5839(6)	5.0(2)
C(4)	1.3261(5)	0.3342(4)	0.7158(6)	5.0(2)
C(5)	1.2508(6)	0.3075(4)	0.8042(6)	4.6(2)
C(6)	1.1130(5)	0.3057(3)	0.7589(5)	3.8(1)
C(7)	0.7959(5)	0.4181(3)	0.6546(5)	2.8(1)
C(8)	0.6577(5)	0.4324(3)	0.6253(5)	3.6(1)
C(9)	0.5951(5)	0.5031(4)	0.6845(6)	4.3(2)
C(10)	0.6676(6)	0.5604(4)	0.7725(6)	4.8(2)
C(11)	0.8041(6)	0.5475(4)	0.8020(6)	4.8(2)
C(12)	0.8657(5)	0.4759(4)	0.7435(6)	3.9(2)
C(13)	0.4462(5)	0.1694(3)	0.2414(5)	3.4(1)
C(14)	0.3364(6)	0.1974(4)	0.2994(6)	5.1(2)
C(15)	0.2077(6)	0.1903(5)	0.2199(8)	7.3(2)
C(16)	0.1929(7)	0.1562(5)	0.0860(8)	7.5(3)
C(17)	0.3005(7)	0.1285(5)	0.0274(7)	7.1(2)
C(18)	0.4290(6)	0.1339(4)	0.1058(6)	5.6(2)
C(19)	0.6872(5)	0.0694(3)	0.3432(5)	3.3(1)
C(20)	0.8220(6)	0.0515(4)	0.3398(6)	5.0(2)
C(21)	0.8808(7)	−0.0291(6)	0.3594(8)	7.0(3)
C(22)	0.8098(9)	−0.0917(5)	0.3812(8)	8.0(3)
C(23)	0.6767(9)	−0.0782(4)	0.3817(7)	7.3(2)
C(24)	0.6159(6)	0.0042(4)	0.3635(6)	4.9(2)
C(25)	0.7494(5)	0.3608(3)	0.1298(5)	3.3(1)
C(26)	0.8732(6)	0.3127(4)	0.0948(6)	5.6(2)
C(27)	0.6280(5)	0.3441(4)	0.0158(5)	6.4(2)
C(28)	0.7591(6)	0.4548(4)	0.1514(6)	5.8(2)
C(29)	0.7337(5)	0.1147(3)	0.7015(5)	4.0(2)
C(30)	0.8206(8)	0.1101(4)	0.8397(6)	7.0(2)
C(31)	0.8067(10)	0.0820(5)	0.9464(7)	11.7(3)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos \alpha)$.

Results and Discussion

Synthesis of $[Ph_4P_2N_4(SR)(SR')LiI(THF)]$ (1, R = R' = Me; 2, R = Ph, R' = Me; 3, R = ^{t}Bu, R' = Me; 4, R = Ph, R' = allyl; 5, R = ^{t}Bu, R' = allyl). The LiI adducts **1−5** are produced in quantitative yields by the reaction of the dimers $[Li(Ph_4P_2N_4S_2R)(THF)]_2$[6] with 2 molar equiv of R'I (R' = Me, allyl) in THF at room temperature. Compounds **1-5** were isolated as hygroscopic, pale yellow crystalline solids and characterized by ^{1}H, ^{7}Li, and ^{31}P NMR spectroscopy (see Table 1). All five compounds show a singlet in the ^{7}Li NMR spectrum in the range δ 0.45−0.74 (cf. δ(^{7}Li) = −0.11 ppm for LiI in THF). This strongly supports the notion that the LiI in these adducts is bonded to the $P_2N_4S_2$ ring. The ^{31}P NMR resonances for **1-5** appear as singlets in the narrow range δ 14.7−16.7. Thus the LiI must be bonded in a symmetrical fashion to the $P_2N_4S_2$ ring. In view of the known coordination mode of lithium in the dimers $[Li(Ph_4P_2N_4S_2R)(THF)]_2$,[6] we propose that LiI is coordinated to a pair of nitrogen atoms of an NSN unit in **1-5** (see Scheme 1). We note, however, that only one S−CH_3 resonance is observed in the ^{1}H NMR spectrum of **1**. Unfortunately, however, numerous attempts to obtain crystals of one of these adducts suitable for an X-ray structural determination failed owing to the facile loss of LiI that occurs in solution.

Synthesis of $Ph_4P_2N_4(SR)(SR')$ (6−10). Dissolution of the adducts **1-5** in either CH_2Cl_2 or toluene results in the immediate precipitation of LiI and the concomitant formation of the boat

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[15] Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

[16] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[17] TEXSAN Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

[18] Sheldrick, G. M. SHELX 76. A Program for Crystal Structure Analysis, University Chemical Laboratory, Cambridge, England, 1976.

Table 8. Atomic Coordinates ($\times 10^{14}$) and U_{eq} Values (Å^2 $\times$ 10^3) for $Ph_4P_2N_4(Sallyl)_2$, **11B**[a]

atom	*x*	*y*	*z*	sof	U_{eq}
S(1)	2992(1)	933(1)	4457(1)		13(1)
S(2)	1749(1)	−1043(1)	4838(1)		12(1)
P(1)	3098(1)	−811(1)	4504(1)		10(1)
P(2)	1716(1)	670(1)	4975(1)		8(1)
N(1)	2987(2)	40(2)	4049(2)		18(2)
N(2)	2448(2)	1034(3)	5049(2)		13(2)
N(3)	1538(2)	−148(2)	4469(2)		11(2)
N(4)	2528(2)	−1175(3)	4977(3)		16(2)
C(1)	3787(2)	−771(4)	5229(3)		15(3)
C(2)	3673(2)	−689(4)	5994(3)	0.57(1)	23(4)
C(3)	4197(2)	−583(4)	6558(3)	0.57(1)	46(5)
C(4)	4837(2)	−558(4)	6358(3)	0.57(1)	42(5)
C(5)	4952(2)	−639(4)	5593(3)	0.57(1)	43(5)
C(6)	4427(2)	−745(4)	5029(3)	0.57(1)	32(5)
C(2b)*	3737(4)	−362(6)	5906(6)	0.43(1)	16(3)
C(3b)*	4271(4)	−295(6)	6464(6)	0.43(1)	36(4)
C(4b)*	4857(4)	−700(6)	6367(6)	0.43(1)	46(5)
C(5b)*	4908(4)	−1172(6)	5712(6)	0.43(1)	38(4)
C(6b)*	4374(4)	−1239(6)	5154(6)	0.43(1)	29(3)
C(7)	3300(2)	−1509(2)	3765(2)		12(3)
C(8)	3611(2)	−1210(2)	3153(2)		23(3)
C(9)	3770(2)	−1750(2)	2582(2)		33(3)
C(10)	3618(2)	−2587(2)	2624(2)		28(3)
C(11)	3307(2)	−2885(2)	3236(2)		23(3)
C(12)	3148(2)	−2346(2)	3807(2)		18(3)
C(13)	1135(2)	1418(2)	4560(2)		10(2)
C(14)	541(2)	1159(2)	4176(2)		25(3)
C(15)	87(2)	1740(2)	3864(2)		33(4)
C(16)	228(2)	2581(2)	3936(2)		33(3)
C(17)	822(2)	2841(2)	4320(2)		28(3)
C(18)	1276(2)	2260(2)	4632(2)		19(3)
C(19)	1567(1)	519(2)	5961(2)		11(3)
C(20)	940(1)	287(2)	6117(2)		24(3)
C(21)	824(1)	86(2)	6862(2)		33(3)
C(22)	1335(1)	118(2)	7452(2)		30(3)
C(23)	1962(1)	350(2)	7296(2)		28(3)
C(24)	2078(1)	551(2)	6551(2)		22(3)
C(25)	2681(3)	1533(4)	3615(3)		22(3)
C(26)	3164(3)	1531(4)	3032(4)		36(3)
C(27)	3540(4)	2152(5)	2883(5)		68(4)
C(28)	1467(3)	−1679(3)	4018(3)		24(3)
C(29)	736(3)	−1641(4)	3855(5)		48(4)
C(30)	339(7)	−2105(8)	3999(9)	0.70(1)	87(5)
C(30b)*	317(10)	−1695(13)	3347(12)	0.30(1)	28(4)

[a] Starred atoms were allowed isotropic temperature factors. Sof is the site occupancy factor. U_{eq} = $^1/_3$(trace of the orthogonalized $\mathbf{U}_{ij}$ tensors).

Table 9. Atomic Coordinates and B_{eq} Values (Å^2) for $[Ph_4P_2N_3(NMe)(SPh)_2][CF_3SO_3]$, **12**

atom	*x*	*y*	*z*	B_{eq}[a]
S(1)	0.3356	0.0717(1)	0.2237	3.59(7)
S(2)	0.5087(4)	−0.0892(1)	0.2438(2)	3.82(7)
S(3)	0.9698(5)	0.2021(2)	0.5555(3)	6.9(1)
P(1)	0.5818(4)	0.0257(2)	0.1794(2)	3.78(8)
P(2)	0.3565(4)	−0.0218(2)	0.3257(2)	3.58(8)
F(1)	1.0801(17)	0.0983(6)	0.6004(10)	20.1(7)
F(2)	1.0448(14)	0.1609(9)	0.6764(7)	22.1(7)
F(3)	1.2021(10)	0.1730(8)	0.6246(6)	16.9(6)
O(1)	0.8379(12)	0.1759(6)	0.5563(7)	12.8(5)
O(2)	0.9744(12)	0.2636(5)	0.5852(8)	14.0(5)
O(3)	1.0242(12)	0.1944(9)	0.5013(6)	21.3(7)
N(1)	0.4166(8)	0.0491(4)	0.1572(4)	3.2(2)
N(2)	0.2683(8)	0.0100(4)	0.2550(5)	4.2(2)
N(3)	0.5035(8)	−0.0544(4)	0.3192(4)	3.9(2)
N(4)	0.6100(10)	−0.0481(4)	0.2020(5)	5.6(3)
C(1)	0.3346(12)	0.0121(6)	0.0989(6)	5.8(4)
C(2)	0.6594(10)	0.0830(6)	0.2464(6)	4.2(3)
C(3)	0.6329(12)	0.1491(6)	0.2414(7)	4.9(4)
C(4)	0.7044(14)	0.1909(7)	0.2890(8)	6.4(4)
C(5)	0.8015(16)	0.1672(9)	0.3463(7)	7.0(5)
C(6)	0.8273(14)	0.0995(9)	0.3479(7)	7.2(5)
C(7)	0.7605(12)	0.0600(6)	0.2998(7)	5.4(4)
C(8)	0.6564(11)	0.0391(6)	0.1021(6)	4.4(3)
C(9)	0.7506(13)	−0.0033(6)	0.0854(7)	6.1(4)
C(10)	0.8149(15)	0.0098(8)	0.0281(8)	7.8(5)
C(11)	0.7809(17)	0.0658(8)	−0.0094(7)	7.6(5)
C(12)	0.6933(15)	0.1089(7)	0.0089(7)	6.5(5)
C(13)	0.6275(12)	0.0956(6)	0.0635(7)	5.3(4)
C(14)	0.3923(10)	0.0383(5)	0.3931(5)	3.3(3)
C(15)	0.5219(12)	0.0610(7)	0.4193(7)	5.7(4)
C(16)	0.5446(15)	0.1110(7)	0.4684(8)	7.1(5)
C(17)	0.4373(20)	0.1387(6)	0.4922(7)	6.3(4)
C(18)	0.3049(16)	0.1169(7)	0.4656(8)	6.4(5)
C(19)	0.2844(11)	0.0674(6)	0.4168(6)	4.4(3)
C(20)	0.2440(11)	−0.0789(6)	0.3570(5)	3.5(3)
C(21)	0.2947(12)	−0.1220(6)	0.4085(7)	5.4(4)
C(22)	0.2127(14)	−0.1653(7)	0.4367(7)	6.7(4)
C(23)	0.0735(16)	−0.1672(7)	0.4067(8)	6.5(5)
C(24)	0.0228(12)	−0.1215(6)	0.3601(7)	5.6(4)
C(25)	0.1043(13)	−0.0777(6)	0.3285(7)	5.9(4)
C(26)	0.1932(11)	0.1145(6)	0.1747(6)	4.3(3)
C(27)	0.2156(12)	0.1622(6)	0.1283(6)	4.8(4)
C(28)	0.1105(12)	0.2019(6)	0.1014(6)	5.2(4)
C(29)	−0.0196(12)	0.1946(7)	0.1167(7)	6.3(4)
C(30)	−0.0379(11)	0.1456(8_	0.1637(7)	6.9(5)
C(31)	0.0704(13)	0.1060(6)	0.1939(7)	6.2(4)
C(32)	0.6174(11)	−0.1582(5)	0.2719(7)	4.0(3)
C(33)	0.7169(12)	−0.1764(6)	0.2351(6)	4.7(3)
C(34)	0.7905(14)	−0.2331(7)	0.2593(9)	8.0(5)
C(35)	0.7709(15)	−0.2668(6)	0.3165(7)	5.9(4)
C(36)	0.6688(17)	−0.2473(7)	0.3510(7)	7.3(5)
C(37)	0.5949(14)	−0.1927(6)	0.3292(6)	5.6(4)
C(38)	1.0781(22)	0.1611(14)	0.6211(12)	11.0(8)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos \alpha)$.

conformers of the eight-membered rings $Ph_4P_2N_4(SR)(SR')$ **6-10B** (see Scheme 1). These heterocycles were isolated as mildly air-sensitive colorless, crystalline solids in yields ranging from 32 to 87%. They were identified by elemental analysis, FAB mass spectroscopy, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Compounds **6-10B** exhibit single ^{31}P NMR resonances with chemical shifts in the narrow range δ 14.1 − 16.7 (see Table 1), i.e. not significantly different from those of the corresponding LiI adducts, suggesting that the conformation of the eight-membered ring does not change on removal of LiI. This inference was confirmed by the X-ray structure determinations of two derivatives, **6B** and **10B**, described below.

X-ray Structures of $Ph_4P_2N_4(SMe)_2$ (6B) and $Ph_4P_2N_4$-(S^tBu)(Sallyl) (10B). ORTEP drawings of **6B** and **10B** with the appropriate atomic numbering scheme are displayed in Figures 1 and 2, respectively. The eight-membered $P_2N_4S_2$ ring in **6B** adopts a slightly distorted boat conformation in which the two sulfur atoms S(1) and S(2) serve as the prow and stern. The exocyclic methyl groups attached to sulfur are equatorial with respect to a least squares plane passing through the four nitrogen and two phosphorus atoms of the ring. The phosphorus atoms, P(1) and P(2), however, are lifted out of the best plane by *ca.* 0.3 Å. Thus the $P_2N_4S_2$ ring in **6B** can be described as intermediate between boat and crown conformations.

The unsymmetrical *S,S'*-diorgano derivative **10B** assumes a twisted boat conformation in the solid state. The envelope conformation of the P(1)N(1)S(1)N(2)P(2) segment of the ring closely resembles that of the two identical halves of **6B**, which are related by a mirror plane passing through P(1) and P(2). The ^{t}Bu group in **10B** is in an equatorial position, and the structural parameters for this half of the ring are virtually identical to those of **6B** (see Table 3−). The other half of the ring in **10B**, however, is twisted such that S(2) (the sulfur attached to the allyl group) becomes coplanar with P(1), P(2), N(1), and N(2) to within 0.06 Å, and the nitrogen atoms N(3) and N(4) are displaced on opposite sides of this plane by 0.6 and 0.79 Å, respectively. A close examination of the nonbonding contacts in **10B** reveals that the distance S(2)−C(30) is 2.75(1) Å, suggesting that a weak interaction between that sulfur atom and the olefinic carbon is responsible for the twisting of the ring.

Thermal Isomerization of the Boat Conformers $Ph_4P_2N_4(SR)(SR')$, (6−10B) into the Corresponding Chair Isomers, (6−10C). The boat conformers **6-10B** can be converted into the corresponding chair conformers **6-10C** by gentle heating at 35−40 °C for *ca.* 12 h in either acetonitrile or dichloromethane (see Scheme 1). The chair conformers exhibit a characteristic singlet in the ^{31}P NMR spectrum at δ 27−29 (see Table 1). Thus the boat → chair isomerization causes a deshielding of the heterocyclic ^{31}P resonances by 11−12 ppm. The chair conformation of these complexes has been verified previously by the X-ray structural determination of the *S,S'*-diphenyl derivative $Ph_4P_2N_4(SPh)_2$ ($\delta(^{31}P)$ 29.3 ppm in CH_2Cl_2).[5] The previous observation that the ^{31}P NMR chemical shift of the initial products of the reactions of $[Li(Ph_4P_2N_4S_2)THF]_2$ or $Li_2[Ph_4P_2N_4S_2]$ with iodoalkanes differs from that of the final product by >10 ppm[10] can now be explained by the boat → chair isomerization process. Presumably, the chair form is the thermodynamically favored isomer. Conformational flexibility is a common feature of eight-membered cyclophosphazenes.[1,19] The best known example is the existence in the solid state of both a metastable boat conformer and a centrosymmetric chair form of $N_4P_4Cl_8$.[20] The uniqueness of the present example is the ability to monitor the isomerization process in solution by ^{31}P NMR spectroscopy.

Synthesis and X-ray Structure of $[Ph_4P_2N_4(Sallyl)_2]$ (11B). In order to gain further insight into the influence of exocyclic allyl groups on ring conformation, the derivative $Ph_4P_2N_4(Sallyl)_2$ (**11**) was prepared in 56% yield by the addition of 2 molar equiv of allyl iodide to a slurry of $Na_2[Ph_4P_2N_4S_2]$ in THF. The ^1H NMR spectrum of **11** in d_6-benzene clearly shows that the two allyl groups are equivalent in solution. The ^{31}P NMR resonance consists of a singlet at δ 15.0, suggesting a boat conformer with sulfur atoms in the prow and stern positions (*vide supra*). However, an X-ray structure determination of **11** showed this assumption to be incorrect. An ORTEP drawing of **11** with the atomic numbering scheme is illustrated in Figure 3, and selected structural parameters are summarized in Table 4. The $P_2N_4S_2$ ring in **11** does indeed adopt a boat structure, but in this particular case, antipodal nitrogens rather than sulfur atoms occupy the prow and stern positions. Once again, each sulfur atom appears to be involved in a long range interaction with the attached allyl group [d(S(1)−C(26) = 2.74(1) Å) and d(S(2)−C(29) = 2.72(1) Å)]. We suggest that the ring assumes this unusual boat conformation in order to facilitate this intramolecular interaction. In distinct contrast to the behavior of the boat conformers **6-10B**, the heterocycle **11** does not isomerize to the chair conformer upon heating. In fact, rapid decomposition occurs when a solution of **11** is heated above 40 °C.

Preparation and X-ray Structure of $[Ph_4P_2N_3(NMe)(SPh)_2][CF_3SO_3]$ (12). In a previous investigation we showed that the interaction of the six-membered ring $Ph_4P_2N_3SPh$ with Lewis or Brønsted acids occurs in a regiospecific manner to give N-bonded adducts.[21] Although the four nitrogen sites are equivalent in the closely related eight-membered ring $Ph_4P_2N_4(SPh)_2$, it was of interest to determine the effect of adduct formation on the structure of the $P_2N_4S_2$ ring particularly with a view to using Lewis acids to promote ring opening and, hence, polymerization. There has been considerable interest recently in polymers based on a PNPNSN backbone,[8] but polymers with alternating PN and SN units are unknown.

The N-methylated adduct $[Ph_4P_2N_3(NMe)(SPh)_2][CF_3SO_3]$ (**12**) was prepared by the addition of a slight excess of methyl triflate to a solution of $Ph_4P_2N_4(SPh)_2$ in dichloromethane. The ^{31}P NMR spectrum of **12** showed the expected pair of mutually coupled doublets at δ 33.2 and 36.0 with $^4J(^{31}P-^{31}P) = 3$ Hz. The $N-CH_3$ resonance in the ^1H NMR spectrum appeared as a doublet [$^3J(^{31}P-^1H) = 8$ Hz]. An X-ray analysis of **12** was carried out in order to determine the structural perturbation caused by N-methylation of the $P_2N_4S_2$ ring. An ORTEP drawing with the atomic numbering scheme for the cation is shown in Figure 4, and selected bond lengths and bond angles are summarized in Table 5. The overall chair conformation of the $P_2N_4S_2$ ring is retained with some distortion arising from the movement of the methylated nitrogen out of the plane formed by the phosphorus P(2) and three other nitrogen atoms by *ca.* 0.85 Å. Phosphorus atom P(1) is 1.14 Å out of a P(2)N(2)N(3)N(4) plane on the same side as N(1). Adduct formation results in the elongation of the skeletal S−N(Me) and P−N(Me) bonds by 0.078 and 0.074 Å, respectively, and a small contraction (0.03−0.04 Å) of the adjacent P−N and S−N bonds. The other bond lengths and all the endocyclic bond angles in **12** are essentially unaffected by N-methylation. Lengthening of the skeletal bonds involved in coordination by *ca.* 0.07 Å was also observed for the six-membered ring $Ph_4P_2N_3SPh$ upon N-methylation.[21] Preliminary investigations of the thermally induced opening of $P_2N_4S_2$ rings indicated that the temperature necessary for decomposition is reduced from *ca.* 150 °C in $Ph_4P_2N_4(SPh)_2$ to <100 °C in the N-methylated adduct. However, the thermal decomposition of **12** in solution or in the solid state produced a black tar.

Conclusion. The reaction of $[Li(Ph_4P_2N_4S_2R)THF]_2$ with organolithium reagents is a versatile synthetic route to either symmetrical (R = R') or unsymmetrical *S,S'*-diorgano derivatives of the type $Ph_4P_2N_4(SR)(SR')$, which are isolated initially as lithium iodide adducts. The coordinated LiI is readily removed upon dissolution in CH_2Cl_2 or toluene to give boat conformers of the eight-membered ring. These boat conformers are readily converted into the corresponding chair conformers upon mild heating in solution with a concomitant deshielding of the ^{31}P NMR resonance for the heterocyclic phosphorus atoms by 11−13 ppm. Although conformational isomers are prevalent in cyclophosphazene chemistry, particularly for eight-membered rings, the unique feature of the hybrid derivatives **6-10** is the ability to monitor the boat → chair conformational change readily in solution by ^{31}P NMR spectroscopy.

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Supplementary Material Available: Tables listing crystallographic parameters, thermal parameters for non-H atoms, positional and isotropic thermal parameters for H atoms, bond lengths and bond angles for all atoms, torsion angles, and least squares planes (51 pages). Ordering information is given on any current masthead page.

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