

Chemistry of 1,2-Thiaphosphole 2-Sulfides. II. Reactions of 1,2-Thiaphosphole 2-Sulfides with Some Nucleophiles

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5-*t*-Butyl-1,2-thiaphosphole 2-sulfides reacted with alcohols, thiols, and amines to give the 1,4-adducts, 2-alkoxy-, 2-(*p*-tolylthio)-, and 2-alkyl(aryl)amino-1,2-thiaphosphol-3-ene 2-sulfides, respectively. However, the reactions of 5-phenyl-1,2-thiaphosphole 2-sulfides with cyclohexyl- and arylamines afforded 1,2,3-dithiaphosphorins.

Previously, we reported the synthesis of 2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides **A** and their thermolysis generating 1,2-thiaphosphole 2-sulfides **B** and α,β -unsaturated thiones **C**.¹⁾ The sulfides **B** are unique intermediates containing phosphorus and sulfur in their unsaturated heterocyclic ring, and they have been found to undergo cycloaddition reactions with various dienophiles.¹⁾ Meanwhile, interest is being shown in π -bonded phosphorus compounds such as methylenephosphine sulfides, $-(S=P=C)$, and related compounds.²⁾ Their reactions with some alcohols (as nucleophile) were also reported recently.³⁾

Accordingly, it appeared of interest to investigate further reactions of **B**. The reaction with some nucleophilic reagents is reported in the present paper.

Results and Discussion

Reactions of Phosphabicyclo Compounds **1** with Alcohols, Phenols, Thiols, and Amines.

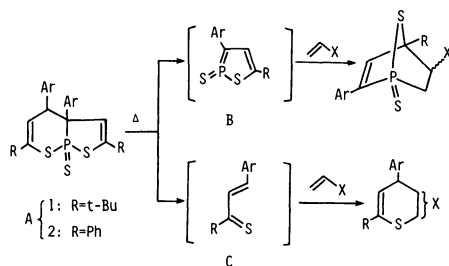
Treatment of **1** with alcohols (phenols) afforded no product on refluxing in benzene. However reactions took place readily in the presence of NEt_3 to give the 1,4-adducts (**5**) of alcohols toward **3** along with thione (**4**) dimers **6**.^{1,4)} (Scheme 2, Table 1). The reaction of **1** with cyclohexanol was carried out in refluxing xylene in the presence of NPr_3 , since the reaction was slow in refluxing benzene.

The elemental analyses and the mass spectra indicated that **5** were 1:1 adducts of **3** and the alcohols. The adducts **5** showed strong IR

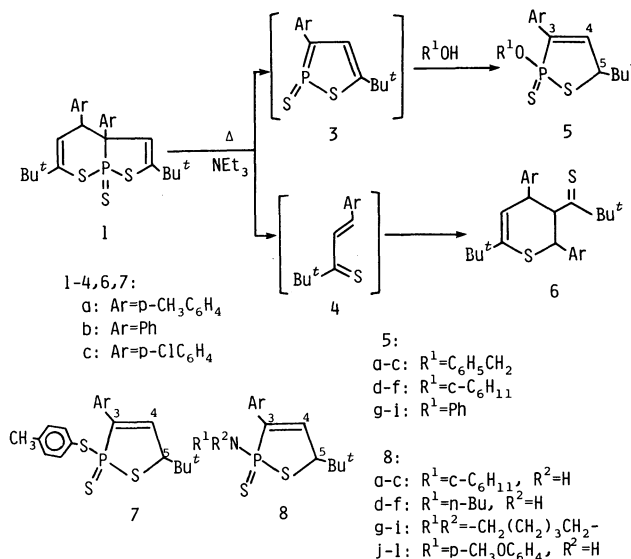
absorption due to the P–O linkage at about 1000 cm^{-1} . In the 1H NMR spectra,⁶⁾ H-4 and H-5 protons resonated at $\delta=6.8\text{--}6.9$ and $4.2\text{--}4.3$ with the coupling constant $3.0\text{--}3.5\text{ Hz}$ and the H-4 proton exhibited a large H–P coupling constant ($J_{HP}=50\text{--}55\text{ Hz}$)(Table 2). The ^{13}C NMR spectra⁷⁾ showed a signal of the C-3 olefinic carbon at $\delta=140\text{--}142$ with a large C–P coupling constant ($J_{CP}=100\text{--}107\text{ Hz}$), suggesting a direct bonding of the P–C(3). Chemical shifts of signals assigned to the C-4 and C-5 carbons and their coupling constants are summarized in Table 2.

The reactions of **1** with *p*-toluenethiol or primary and secondary amines gave similarly the 1,4-adducts **7** or **8** along with **6** (Table 1). The structures of **7** and **8** were determined as described above for **5**.^{6,7)} and the 1H and ^{13}C NMR spectral assignments are listed in Table 2.

Table 2 shows that the magnitudes of the C–P coupling constants $J_{C(3)P}$ of **5**, **7**, and **8** are in the order of $5 > 8 > 7$. This result is in accord with the observation, reported previously, that the C–P coupling constants ($^1J_{CP}$) of the structurally related phosphorus compounds, 3-phospholene 1-sulfides,



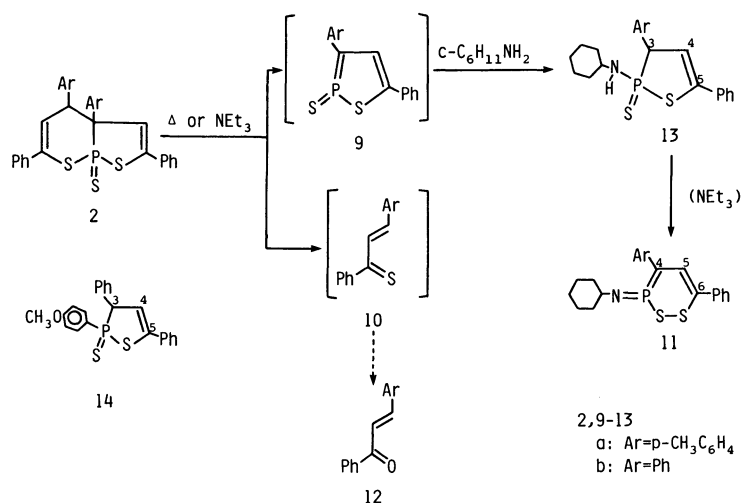
Scheme 1.



Scheme 2.

Table 1. Reactions of **1** with Alcohols, Phenols, Thiols, and Amines

Material	Reagent	Reaction time/h	Product ^a			
			Mp $\theta_m/^\circ\text{C}$	Yield/%	Yield/%	Yield/%
1a	PhCH ₂ OH	10	5a 115–118	54	6a	52
1b	PhCH ₂ OH	10	5b 107–109	36	6b	33
1c	PhCH ₂ OH	10	5c 113–116	38	6c	90
1a	<i>c</i> -C ₆ H ₁₁ OH	15 ^b	5d 129–132	53	6a	72
1b	<i>c</i> -C ₆ H ₁₁ OH	20	5e 138–141	28	6b	35
1b	<i>c</i> -C ₆ H ₁₁ OH	15 ^b	5e	40	6b	90
1c	<i>c</i> -C ₆ H ₁₁ OH	11 ^b	5f 156–159	59	6c	89
1a	PhOH	10.5	5g 155–157	76	6a	90
1b	PhOH	12	5h 151–154	48	6b	90
1c	PhOH	12	5i 161–164	29	6c	90
1a	<i>p</i> -CH ₃ C ₆ H ₄ SH	10	7a 181–183	77	6a	80
1b	<i>p</i> -CH ₃ C ₆ H ₄ SH	10	7b 150–152	68	6b	49
1c	<i>p</i> -CH ₃ C ₆ H ₄ SH	10	7c 175–177	66	6c	80
1a	<i>c</i> -C ₆ H ₁₁ NH ₂	13	8a 140–142	59	6a	61
1b	<i>c</i> -C ₆ H ₁₁ NH ₂	12	8b 136–139	62	6b	92
1c	<i>c</i> -C ₆ H ₁₁ NH ₂	12	8c 185–188	74	6c	56
1a	Bu ⁿ NH ₂	8	8d 117–119	59	6a	61
1b	Bu ⁿ NH ₂	8	8e 124–128	73	6b	82
1c	Bu ⁿ NH ₂	8	8f 118–120	59	6c	91
1a	$\overline{\text{CH}_2(\text{CH}_2)_4\text{NH}}$	7	8g 118–120	54	6a	61
1b	$\overline{\text{CH}_2(\text{CH}_2)_4\text{NH}}$	8	8h 113–116	50	6b	85
1c	$\overline{\text{CH}_2(\text{CH}_2)_4\text{NH}}$	8	8i 121–122	60	6c	98
1a	<i>p</i> -CH ₃ OC ₆ H ₄ NH ₂	14	8j 137–140	11	6a	65
1b	<i>p</i> -CH ₃ OC ₆ H ₄ NH ₂	14	8k 163–165	28	6b	65
1c	<i>p</i> -CH ₃ OC ₆ H ₄ NH ₂	14	8l 158–161	21	6c	66

a) Colorless crystals (**6**; red oil). b) NPrⁿ₃/xylene reflux.

Scheme 3.

increase with the increasing electronegativity of the exocyclic heteroatom attached to the phosphorus atom.⁹⁾

Reactions of Phosphabicyclo Compounds **2** with

Amines. Phosphabicyclo compounds **2** are more reactive than **1** and the reactions with cyclohexylamine proceeded even at room temperature by addition of NEt₃. However, the products obtained

Table 2. ^1H and ^{13}C NMR Spectral Data of **5**, **7**, and **8** (δ (J/Hz))

Compound	H(4)	H(5)	J_{HH}	$J_{\text{H(4)P}}$	$J_{\text{H(5)P}}$	C(3)	C(4)	C(5)	$J_{\text{C(3)P}}$	$J_{\text{C(4)P}}$	$J_{\text{C(5)P}}$
5a	6.85	4.29	3.4	52.0	9.5	141.8	140.6	65.9	107.2	28.1	4.9
5b	6.88	4.28	3.5	54.0	9.5	141.7	141.4	65.8	101.3	28.1	6.1
5c	6.87	4.29	3.5	55.0	10.0	141.0	141.7	65.9	102.5	28.1	4.9
5d	6.83	4.28	3.0	54.0	9.1	142.1	139.8	65.9	102.5	28.1	4.9
5e	$\approx 6.8^a$	4.29	3.2	$\approx 54^a$	9.5	140.7	140.6	65.8	102.5	28.1	4.9
5f	6.83	4.29	3.0	54.0	9.8	141.2	141.1	66.0	103.0	28.1	4.9
5g	$\approx 6.9^a$	4.35	3.2	$\approx 50^a$	9.8	141.3	140.9	66.3	100.1	28.1	6.1
5h	$\approx 6.9^a$	4.36	3.2	$\approx 50^a$	9.3	141.5	141.7	66.3	100.1	28.1	4.9
5i	$\approx 6.9^a$	4.37	3.1	$\approx 50^a$	10.0	140.3	142.2	66.4	100.1	28.1	4.9
7a	6.64	4.43	2.0	55.0	≈ 0	137.1	139.7	66.3	72.2	24.4	3.7
7b	6.65	4.44	2.5	54.5	≈ 0	141.7	140.4	66.2	72.0	23.2	2.4
7c	6.65	4.44	2.5	54.0	≈ 0	140.8	140.8	66.3	66.2	23.5	2.9
8a	6.83	4.25	2.0	52.0	≈ 0	141.1	139.8	63.4	94.0	26.9	6.1
8b	6.83	4.31	2.0	52.0	≈ 0	141.7	140.8	63.5	90.3	25.6	4.9
8c	6.86	4.30	2.5	52.2	≈ 0	140.5	141.0	63.5	90.3	25.6	4.9
8d	6.76	4.30	3.5	52.0	≈ 0	141.1	140.4	63.5	89.1	26.9	4.9
8e	6.83	4.30	2.5	51.0	≈ 0	141.2	141.2	63.6	89.1	25.6	4.9
8f	6.82	4.30	2.5	51.0	≈ 0	140.1	141.5	63.6	90.3	25.6	4.9
8g	6.81	4.33	2.5	53.5	2.5	140.7	139.2	63.2	94.0	25.6	4.9
8h	6.86	4.36	2.0	53.0	2.5	141.3	140.3	63.5	94.0	25.6	4.9
8i	6.86	4.32	2.5	48.0	1.5	140.2	140.6	63.5	95.2	24.4	4.9
8j	6.88	4.27	2.0	54.0	≈ 0	141.3	140.6	63.9	89.1	26.9	6.1
8k	6.83	4.28	3.5	54.0	≈ 0	141.4	141.5	63.9	89.1	26.9	4.9
8l	6.84	4.28	2.5	52.5	≈ 0	140.5	141.9	64.0	92.8	25.6	6.1

a) Part of the signal of the double doublet is superimposed on Ar-H.

Table 3. Reactions of **2** with Amines

Material	Reagent	Reaction Conditions			Product ^{a)}			
		Time	Solvent	Temp/°C	Mp θ_m /°C	Yield/%	Yield/%	
2a	<i>c</i> -C ₆ H ₁₁ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	11a	264—265	34	12a 99
2a	<i>c</i> -C ₆ H ₁₁ NH ₂	2 h	C ₆ H ₆	80	11a		13	12a 99
					13a	196—198 (dec.)	46	
2b	<i>c</i> -C ₆ H ₁₁ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	11b	272—274	39	12b 99
2b	<i>c</i> -C ₆ H ₁₁ NH ₂	3 h	C ₆ H ₆	80	11b		30	12b 99
					13b	190—192 (dec.)	43	
2a	<i>p</i> -CH ₃ OC ₆ H ₄ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	16a	261—263	55	17a ^{b)} 65
2b	<i>p</i> -CH ₃ OC ₆ H ₄ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	16b	227—229	33	17b ^{c)} 58
2a	<i>p</i> -CH ₃ C ₆ H ₄ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	16c	208—210	16	17c ^{d)} 97
2b	<i>p</i> -CH ₃ C ₆ H ₄ NH ₂	2 Week	NEt ₃ /C ₆ H ₆	20—25	16d	203—205	51	17d ^{e)} 70

a) **11**, **16**, and **17**; red crystals, **13**; colorless crystals. b) mp 117—120 °C. c) mp 162—164 °C (lit.¹⁰ 165 °C).d) mp 123—126 °C. e) mp 169—171 °C (lit.¹⁰ 168—169 °C).Table 4. ^1H NMR Spectral Data of **13** and **14** (δ (J/Hz))

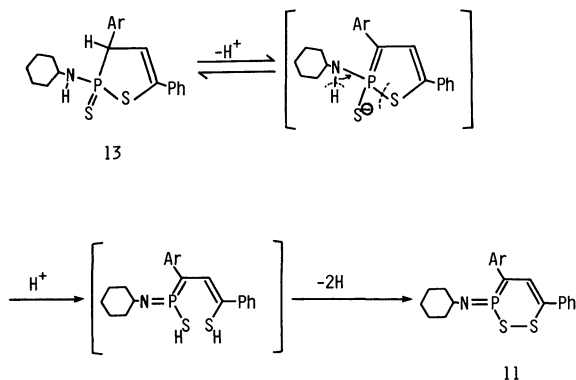
Compound	H(3)	H(4)	J_{HH}	$J_{\text{H(3)P}}$	$J_{\text{H(4)P}}$
13a	4.88	6.35	4.0	15.0	36.0
13b	4.51	6.32	4.0	15.5	36.0
14	5.17	6.32	4.0	18.0	32.0

were chalcones **12** and 1,2,3-dithiaphosphorins **11** (Scheme 3, Table 3). When the reactions were carried out in refluxing benzene without NEt₃, **11**, **12**, and 1,2-adducts **13** of cyclohexylamine toward **9** were formed.

The ^1H and ^{13}C NMR spectra of **13a** were different from those of the 1,4-adducts **8**. Namely, the

Table 5. ^1H and ^{13}C NMR Spectral Data of **11** and **16** ($\delta(\text{J/Hz})$)

Compound	H(5)	$J_{\text{H(5)P}}$	C(4)	C(5)	C(6)	$J_{\text{C(4)P}}$	$J_{\text{C(5)P}}$	$J_{\text{C(6)P}}$
11a	6.94	34.0	161.3	117.1	169.2	81.8	11.0	14.7
11b	6.94	34.0	160.9	118.1	169.1	82.4	11.8	14.7
16a	7.37	34.0	158.9	115.1	168.4	81.8	11.0	14.7
16b	7.42	34.2	160.7	116.2	167.6	81.8	11.0	14.7
16c	7.37	34.0	160.3	115.2	167.5	81.8	11.0	14.7
16d	7.42	34.0	163.0	116.3	165.9	79.4	10.3	16.2



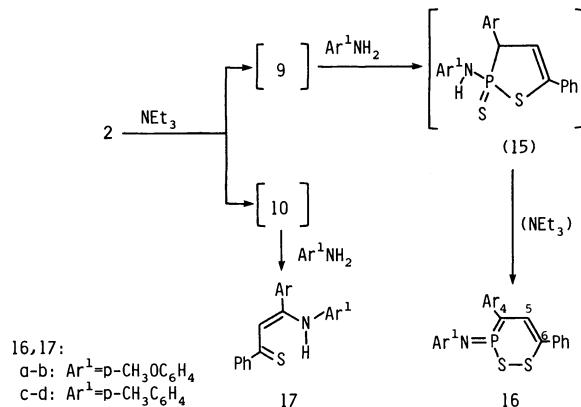
Scheme 4.

^1H NMR spectrum showed signals of the H-3 proton at $\delta=4.88$ ($J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=15.0$ Hz) and of the H-4 proton at $\delta=6.35$ ($J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=36.0$ Hz). These spectral patterns are similar to those of 1,2-thiaphosphol-4-ene 2-sulfide **14** reported previously⁹ (Table 4). In the ^{13}C NMR spectrum, the resonance at $\delta=60.7$ ($J_{\text{CP}}=61.0$ Hz) is assigned to the saturated C-3 carbon atom directly bonded to the phosphorus atom. Signals of the unsaturated carbons, C-4 and C-5, appeared at $\delta=120.4$ ($J_{\text{CP}}=4.9$ Hz) and 141.8 ($J_{\text{CP}}=11.0$ Hz), respectively.

The mass spectrum of **11a** showed a molecular ion peak at m/z 397 [M^+] and an ion peak of [$\text{M}^+ - 2\text{S}$] at m/z 333 as a base peak. The IR spectrum revealed no NH absorption band. The ^1H NMR spectrum exhibited a doublet of H-5 proton at $\delta=6.94$ ($J_{\text{HP}}=34.0$ Hz) and the ^{13}C NMR spectrum displayed three signals at $\delta=161.3$ ($J_{\text{CP}}=81.8$ Hz), 117.1 ($J_{\text{CP}}=11.0$ Hz), and 169.2 ($J_{\text{CP}}=14.7$ Hz) (Table 5).

These spectral data support the proposed structures **11** and **13**. The compounds **11** were found to be very stable, probably due to the resonance stabilization of the dithiaphosphorin ring system. Treatment of **13** with NEt_3 produced **11** instead of the corresponding 1,4-adducts. A probable pathway for the formation of **11** from **13** is illustrated in Scheme 4.

The reactions of **2** with aromatic amines (*p*-anisidine, *p*-toluidine) afforded 3-amino-2-propene-1-thiones **17**¹⁰ and 1,2,3-dithiaphosphorins **16** in contrast to the reactions with cyclohexylamine (Scheme 5, Table 3). This result is interesting but the



Scheme 5.

dehydrogenation step to form **17** is still ambiguous.¹¹⁾

The accelerating effect of NEt_3 in these reactions is remarkable and the following three rationales can be considered: (1) The amine accelerates the dissociation of **A** into **B** and **C**. (2) The amine activates the nucleophiles. (3) The amine interacts with **A** at the positive center, the phosphorus atom, to activate **A** toward the nucleophiles. When the solution of **1** and the amine in benzene was heated in the absence of the nucleophiles, the solution turned greenish-blue. A benzene solution of **2** also colored even at room temperature on adding the amine. These observations suggest the generation of the monomeric thiones **C** (or dimers) and **B**. On the other hand, previously reported cycloaddition reactions of **A** with dienophiles (Scheme 1) were also found to be accelerated on addition of the amine. On the basis of these findings, the rationale (1) is considered to be most probable. However, the possibilities of (2) and (3) still remain, especially for the reactions of **1**.

Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in CDCl_3 solution using Me_4Si as an internal standard (^1H ; at 100 MHz, ^{13}C ; at 25 MHz). ^{31}P NMR spectra were recorded at 40 MHz on a JEOL

JNM-FX 100 spectrometer using 85% H_3PO_4 as an external standard. Mass spectra were recorded on a Hitachi double focusing mass spectrometer (RMU-7M) operating at an ionizing potential of 70 eV. 2,9-Dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides **1** and **2** were prepared according to the previously described method.¹¹

General Procedure for the Reactions of the Phosphabicyclo Compounds 1 or 2 with Nucleophilic Reagents (Alcohols, Phenols, Thiols, and Amines) to Afford 1,4- or 1,2-Adducts, 5, 7, 8, and 13: A solution of **1** (3 mmol) and a nucleophilic reagent (10 mmol) in 20 cm^3 of dry benzene (xylene) and 15 cm^3 of NEt_3 (NPr^n_3) was refluxed under a nitrogen atmosphere for 2–20 h until the phosphabicyclo compound **1** was consumed, as indicated by TLC (Reaction times are shown in Tables 1 and 3). After evaporation of the solvent the residue was chromatographed on silica gel (Wakogel C-200) with benzene–hexane (1:1) as an eluent to afford the adduct. Recrystallization from ethanol gave the adduct as colorless crystals. The reaction of **2** to afford **13** was carried out without NEt_3 .

2-Benzoyloxy-5-*t*-butyl-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (5a): IR (KBr) 2970, 1375, and 1000(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.07 (s, 9H), 2.35 (s, 3H), 4.29 (dd, 1H, $J_{\text{HH}}=3.4$ Hz, $J_{\text{HP}}=9.5$ Hz), 5.06–5.28 (m, 2H), 6.85 (dd, 1H, $J_{\text{HH}}=3.4$ Hz, $J_{\text{HP}}=52.0$ Hz), and 6.93–7.54 (m, 9H); MS m/z (rel intensity) 388 (M^+ , 18), 332 (17), 282 (22), 241 (55), 225 (47), 192 (28), 91 (100), and 57 (24). Found: C, 64.68; H, 6.23%. Calcd for $\text{C}_{21}\text{H}_{25}\text{OPS}_2$: C, 64.92; H, 6.49%.

2-Benzoyloxy-5-*t*-butyl-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (5b): IR (KBr) 2970, 1370, and 990(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.04 (s, 9H), 4.28 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=9.5$ Hz), 5.06–5.28 (m, 2H), 6.88 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=54.0$ Hz), and 7.00–7.68 (m, 10H); MS m/z (rel intensity) 374 (M^+ , 16), 318 (17), 268 (25), 227 (42), 211 (30), 178 (37), 91 (100), and 57 (25). Found: C, 64.38; H, 6.40; S, 17.19%. Calcd for $\text{C}_{20}\text{H}_{23}\text{OPS}_2$: C, 64.14; H, 6.19; S, 17.12%.

2-Benzoyloxy-5-*t*-butyl-3-(*p*-chlorophenyl)-1,2-thiaphosphol-3-ene 2-Sulfide (5c): IR (KBr) 2970, 1370, and 990(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.07 (s, 9H), 4.29 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=10.0$ Hz), 5.06–5.28 (m, 2H), 6.87 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=55.0$ Hz), and 7.16–7.60 (m, 9H); MS m/z (rel intensity) 408 (M^+ , 13), 352 (18), 302 (16), 261 (44), 245 (19), 212 (29), 91 (100) and 57 (32). Found: C, 58.45; H, 5.35%. Calcd for $\text{C}_{20}\text{H}_{22}\text{OPS}_2\text{Cl}$: C, 58.74; H, 5.42%.

5-*t*-Butyl-2-cyclohexyloxy-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (5d): IR (KBr) 2960, 2940, 2860, 1370, and 980(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.10 (s, 9H), 1.14–2.18 (broad m, 10H), 2.36 (s, 3H), 4.28 (dd, 1H, $J_{\text{HH}}=3.0$ Hz, $J_{\text{HP}}=9.1$ Hz), 4.54–4.96 (broad m, 1H), 6.83 (dd, 1H, $J_{\text{HH}}=3.0$ Hz, $J_{\text{HP}}=54.0$ Hz), 7.14 (d, 2H, $J_{\text{HH}}=8.0$ Hz), and 7.48 (dd, 2H, $J_{\text{HH}}=8.0$ Hz, $J_{\text{HP}}=1.5$ Hz); MS m/z (rel intensity) 380 (M^+ , 1), 299 (100), 242 (61), 225 (17), 209 (23), and 57 (21). Found: C, 63.36; H, 7.71%. Calcd for $\text{C}_{20}\text{H}_{29}\text{OPS}_2$: C, 63.13; H, 7.68%.

5-*t*-Butyl-2-cyclohexyloxy-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (5e): IR (KBr) 2960, 2940, 2855, 1365, and 980(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.11 (s, 9H), 1.16–2.20 (broad m, 10H), 4.29 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=9.5$ Hz), 4.54–4.96 (broad m, 1H), $\approx$ 6.8 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=54$ Hz), and 6.92–7.70 (m, 5H); MS m/z (rel intensity) 366 (M^+ , 1), 285 (100), 228 (49), 211 (13), 195 (18), and 57 (56). Found: C, 62.86; H, 7.66%. Calcd for $\text{C}_{19}\text{H}_{27}\text{OPS}_2$: C,

62.26; H, 7.43%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-cyclohexyloxy-1,2-thiaphosphol-3-ene 2-Sulfide (5f): IR (KBr) 2970, 2950, 2860, 1370, and 985(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.11 (s, 9H), 1.14–2.36 (broad m, 10H), 4.29 (dd, 1H, $J_{\text{HH}}=3.0$ Hz, $J_{\text{HP}}=9.8$ Hz), 4.54–4.92 (broad m, 1H), 6.83 (dd, 1H, $J_{\text{HH}}=3.0$ Hz, $J_{\text{HP}}=54.0$ Hz), 7.28 (d, 2H, $J_{\text{HH}}=9.0$ Hz), and 7.54 (dd, 2H, $J_{\text{HH}}=9.0$ Hz, $J_{\text{HP}}=1.5$ Hz); MS m/z (rel intensity) 400 (M^+ , 2), 319 (100), 262 (45), 245 (9), 229 (14), and 57 (44). Found: C, 56.54; H, 6.12%. Calcd for $\text{C}_{19}\text{H}_{26}\text{OPS}_2\text{Cl}$: C, 56.92; H, 6.54%.

5-*t*-Butyl-2-phenoxy-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (5g): IR (KBr) 2970, 1370, and 900(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.07 (s, 9H), 2.39 (s, 3H), 4.35 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=9.8$ Hz), $\approx$ 6.9 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=50$ Hz), 6.94–7.38 (m, 7H), and 7.64 (dd, 2H, $J_{\text{HH}}=8.0$ Hz, $J_{\text{HP}}=1.5$ Hz); MS m/z (rel intensity) 374 (M^+ , 7), 318 (100), 281 (9), 225 (71), 192 (22), 161 (17), and 57 (35). Found: C, 64.13; H, 6.12%. Calcd for $\text{C}_{20}\text{H}_{23}\text{OPS}_2$: C, 64.14; H, 6.19%.

5-*t*-Butyl-2-phenoxy-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (5h): IR (KBr) 2970, 1370, and 905(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.07 (s, 9H), 4.36 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=9.3$ Hz), $\approx$ 6.9 (dd, 1H, $J_{\text{HH}}=3.2$ Hz, $J_{\text{HP}}=50$ Hz), 6.88–7.50 (m, 8H), and 7.60–7.84 (m, 2H); MS m/z (rel intensity) 360 (M^+ , 7), 304 (100), 267 (11), 211 (88), 178 (23), 147 (28), and 57 (56). Found: C, 63.62; H, 5.86; S, 17.72%. Calcd for $\text{C}_{19}\text{H}_{21}\text{OPS}_2$: C, 63.31; H, 5.87; S, 17.79%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-phenoxy-1,2-thiaphosphol-3-ene 2-Sulfide (5i): IR (KBr) 2970, 1370, 905(P-O) cm^{-1} ; ^1H NMR (CDCl_3) δ =1.08 (s, 9H), 4.37 (dd, 1H, $J_{\text{HH}}=3.1$ Hz, $J_{\text{HP}}=10.0$ Hz), $\approx$ 6.9 (dd, 1H, $J_{\text{HH}}=3.1$ Hz, $J_{\text{HP}}=50$ Hz), 6.86–7.48 (m, 7H), and 7.70 (dd, 2H, $J_{\text{HH}}=9.0$ Hz, $J_{\text{HP}}=1.7$ Hz); MS m/z (rel intensity) 394 (M^+ , 7), 338 (100), 301 (7), 245 (58), 212 (16), 181 (16), and 57 (84). Found: C, 57.88; H, 5.08%. Calcd for $\text{C}_{19}\text{H}_{20}\text{OPS}_2\text{Cl}$: C, 57.79; H, 5.10%.

5-*t*-Butyl-2-(*p*-tolylthio)-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (7a): IR (KBr) 2970 and 1375 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.81 (s, 9H), 2.29 (s, 3H), 2.41 (s, 3H), 4.43 (d, 1H, $J_{\text{HH}}=2.0$ Hz), 6.64 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=55.0$ Hz), 6.96–7.40 (m, 6H), and 7.74 (d, 2H, $J_{\text{HH}}=9.0$ Hz); MS m/z (rel intensity) 404 (M^+ , 14), 372 (2), 348 (3), 281 (60), 225 (100), 193 (61), 192 (33), 123 (11), and 57 (76). Found: C, 62.17; H, 6.04%. Calcd for $\text{C}_{21}\text{H}_{25}\text{PS}_3$: C, 62.34; H, 6.23%.

5-*t*-Butyl-3-phenyl-2-(*p*-tolylthio)-1,2-thiaphosphol-3-ene 2-Sulfide (7b): IR (KBr) 2975 and 1375 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.83 (s, 9H), 2.28 (s, 3H), 4.44 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 6.65 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=54.5$ Hz), 6.98–7.48 (m, 7H), and 7.74–7.92 (m, 2H); MS m/z (rel intensity) 390 (M^+ , 26), 358 (2), 334 (3), 267 (63), 211 (100), 178 (49), 123 (14), and 57 (91). Found: C, 61.23; H, 5.84; S, 24.55%. Calcd for $\text{C}_{20}\text{H}_{23}\text{PS}_3$: C, 61.51; H, 5.94; S, 24.63%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-(*p*-tolylthio)-1,2-thiaphosphol-3-ene 2-Sulfide (7c): IR (KBr) 2970 and 1375 cm^{-1} ; ^1H NMR (CDCl_3) δ =0.83 (s, 9H), 2.30 (s, 3H), 4.44 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 6.65 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=54.0$ Hz), 6.98–7.22 (m, 4H), 7.34 (d, 2H, $J_{\text{HH}}=9.0$ Hz), and 7.78 (d, 2H, $J_{\text{HH}}=9.0$ Hz); MS m/z (rel intensity) 424 (M^+ , 6), 392 (1), 368 (1), 301 (15), 245 (27), 212 (12), 123 (12), and 57 (100). Found: C, 56.91; H, 5.32%. Calcd for $\text{C}_{20}\text{H}_{22}\text{PS}_3\text{Cl}$: C, 56.52; H, 5.22%.

5-*t*-Butyl-2-cyclohexylamino-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (8a): IR (KBr) 3260 (NH), 2970, 2940, 2850,

and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.80\text{--}1.80$ (broad m, 9H), 1.11 (s, 9H), 1.84—2.12 (broad m, 1H), 2.35 (s, 3H), 3.02 (broad d, 2H, $J_{\text{HP}}=12.0$ Hz), 4.25 (d, 1H, $J_{\text{HH}}=2.0$ Hz), 6.83 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=52.0$ Hz), 7.11 (d, 2H, $J_{\text{HH}}=8.0$ Hz), and 7.67 (d, 2H, $J_{\text{HH}}=8.0$ Hz); MS m/z (rel intensity) 379 (M^+ , 1), 346 (4), 225 (7), 192 (5), 98 (100), and 57 (8). Found: C, 62.86; H, 8.14; N, 3.58%. Calcd for $\text{C}_{20}\text{H}_{30}\text{NPS}_2$: C, 63.29; H, 7.97; N, 3.69%.

5-*t*-Butyl-2-cyclohexylamino-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (8b): IR (KBr) 3200 (NH), 2970, 2940, 2850, and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.80\text{--}1.80$ (broad m, 9H), 1.13 (s, 9H), 1.84—2.16 (broad m, 1H), 2.93 (broad d, 2H, $J_{\text{HP}}=12.0$ Hz), 4.31 (d, 1H, $J_{\text{HH}}=2.0$ Hz), 6.83 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=52.0$ Hz), 7.12—7.40 (m, 3H), and 7.60—7.84 (m, 2H); MS m/z (rel intensity) 365 (M^+ , 1), 332 (4), 211 (6), 178 (5), 98 (100), and 57 (11). Found: C, 62.58; H, 7.84; N, 3.53%. Calcd for $\text{C}_{19}\text{H}_{28}\text{NPS}_2$: C, 62.43; H, 7.72; N, 3.83%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-cyclohexylamino-1,2-thiaphosphol-3-ene 2-Sulfide (8c): IR (KBr) 3300 (NH), 2970, 2940, 2860, and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.80\text{--}1.80$ (broad m, 9H), 1.12 (s, 9H), 1.88—2.20 (broad m, 1H), 2.96 (broad d, 2H, $J_{\text{HP}}=11.7$ Hz), 4.30 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 6.86 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=52.2$ Hz), 7.26 (d, 2H, $J_{\text{HH}}=9.0$ Hz), and 7.70 (d, 2H, $J_{\text{HH}}=9.0$ Hz); ^{31}P NMR (CDCl_3) $\delta=90.3$ (ddd, $J_{\text{PH}}=52.2$, 11.7, and 11.7 Hz); MS m/z (rel intensity) 399 (M^+ , 1), 366 (3), 300 (1), 245 (4), 212 (5), 98 (100), and 57 (18). Found: C, 57.35; H, 6.95; N, 3.48; P, 7.28; S, 16.20%. Calcd for $\text{C}_{19}\text{H}_{27}\text{NPS}_2\text{Cl}$: C, 57.06; H, 6.80; N, 3.50; P, 7.74; S, 16.03%.

2-Butylamino-5-*t*-butyl-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (8d): IR (KBr) 3270 (NH), 2960, 2850, and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.70\text{--}1.62$ (m, 7H), 1.12 (s, 9H), 2.35 (s, 3H), 2.72—3.08 (m, 3H), 4.30 (d, 1H, $J_{\text{HH}}=3.5$ Hz), 6.76 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=52.0$ Hz), 7.13 (d, 2H, $J_{\text{HH}}=9.0$ Hz), and 7.58 (d, 2H, $J_{\text{HH}}=9.0$ Hz); MS m/z (rel intensity) 353 (M^+ , 4), 320 (1), 296 (2), 281 (1), 225 (16), 192 (9), 72 (100), and 57 (13). Found: C, 61.00; H, 8.35; N, 3.81%. Calcd for $\text{C}_{18}\text{H}_{28}\text{NPS}_2$: C, 61.16; H, 7.98; N, 3.96%.

2-Butylamino-5-*t*-butyl-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (8e): IR (KBr) 3210 (NH), 2960, 2850, and 1360 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.64\text{--}1.62$ (m, 7H), 1.12 (s, 9H), 2.68—3.20 (m, 3H), 4.30 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 6.83 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=51.0$ Hz), 7.19—7.44 (m, 3H), and 7.54—7.78 (m, 2H); MS m/z (rel intensity) 339 (M^+ , 2), 306 (2), 282 (2), 267 (1), 211 (12), 178 (1), 72 (100), and 57 (17). Found: C, 60.13; H, 7.89; N, 4.27%. Calcd for $\text{C}_{17}\text{H}_{26}\text{NPS}_2$: C, 60.14; H, 7.72; N, 4.13%.

2-Butylamino-5-*t*-butyl-3-(*p*-chlorophenyl)-1,2-thiaphosphol-3-ene 2-Sulfide (8f): IR (KBr) 3280 (NH), 2960, 2860, and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.60\text{--}1.77$ (m, 7H), 1.12 (s, 9H), 2.60—3.21 (m, 3H), 4.30 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 6.82 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=51.0$ Hz), 7.28 (d, 2H, $J_{\text{HH}}=8.0$ Hz), and 7.65 (d, 1H, $J_{\text{HH}}=8.0$ Hz); MS m/z (rel intensity) 373 (M^+ , 2), 340 (1), 316 (1), 301 (1), 245 (6), 212 (6), 72 (100), and 57 (21). Found: C, 54.61; H, 6.83; N, 3.53%. Calcd for $\text{C}_{17}\text{H}_{25}\text{NPS}_2\text{Cl}$: C, 54.60; H, 6.74; N, 3.75%.

5-*t*-Butyl-2-piperidino-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (8g): IR (KBr) 2970, 2945, 2850, and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.10$ (s, 9H), 1.24—1.76 (broad m, 6H), 2.34 (s, 3H), 3.06—3.54 (broad m, 4H), 4.33 (dd, 1H,

$J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=2.5$ Hz), 6.81 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=53.5$ Hz), 7.09 (d, 2H, $J_{\text{HH}}=7.5$ Hz), and 7.55 (d, 2H, $J_{\text{HH}}=7.5$ Hz); MS m/z (rel intensity) 365 (M^+ , 2), 332 (3), 225 (8), 192 (5), 84 (100), and 57 (8). Found: C, 62.78; H, 7.85; N, 3.60%. Calcd for $\text{C}_{19}\text{H}_{28}\text{NPS}_2$: C, 62.43; H, 7.72; N, 3.83%.

5-*t*-Butyl-3-phenyl-2-piperidino-1,2-thiaphosphol-3-ene 2-Sulfide (8h): IR (KBr) 2970, 2945, 2850, and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.13$ (s, 9H), 1.20—1.83 (broad m, 6H), 2.94—3.58 (broad m, 4H), 4.36 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=2.5$ Hz), 6.86 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=53.0$ Hz), 7.18—7.50 (m, 3H), and 7.53—7.81 (m, 2H); MS m/z (rel intensity) 351 (M^+ , 1), 318 (3), 294 (1), 211 (7), 178 (7), 84 (100) and 57 (10). Found: C, 61.60; H, 7.61; N, 3.71%. Calcd for $\text{C}_{18}\text{H}_{26}\text{NPS}_2$: C, 61.51; H, 7.40; N, 3.98%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-piperidino-1,2-thiaphosphol-3-ene 2-Sulfide (8i): IR (KBr) 2970, 2945, 2850, and 1375 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.12$ (s, 9H), 1.20—1.72 (broad m, 6H), 2.96—3.52 (broad m, 4H), 4.32 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=1.5$ Hz), 6.86 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=48.0$ Hz), 7.26 (d, 2H, $J_{\text{HH}}=8.0$ Hz), and 7.64 (d, 2H, $J_{\text{HH}}=8.0$ Hz); MS m/z (rel intensity) 385 (M^+ , 1), 352 (2), 245 (3), 212 (4), 84 (100), and 57 (16). Found: C, 56.34; H, 6.66; N, 3.59; S, 16.33%. Calcd for $\text{C}_{18}\text{H}_{25}\text{NPS}_2\text{Cl}$: C, 56.02; H, 6.53; N, 3.63; S, 16.61%.

5-*t*-Butyl-2-(*p*-methoxyphenylamino)-3-(*p*-tolyl)-1,2-thiaphosphol-3-ene 2-Sulfide (8j): IR (KBr) 3150 (NH), 2960, and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.88$ (s, 9H), 2.35 (s, 3H), 3.70 (s, 3H), 4.27 (d, 1H, $J_{\text{HH}}=2.0$ Hz), 5.14 (broad d, 1H, $J_{\text{HP}}=7.0$ Hz), 6.64 (d, 2H, $J_{\text{HH}}=8.0$ Hz), 6.84 (d, 2H, $J_{\text{HH}}=8.0$ Hz), 6.88 (dd, 1H, $J_{\text{HH}}=2.0$ Hz, $J_{\text{HP}}=54.0$ Hz), 7.14 (dd, 2H, $J_{\text{HH}}=8.0$ Hz, $J_{\text{HP}}=3.0$ Hz), and 7.72 (d, 2H, $J_{\text{HH}}=8.0$ Hz); MS m/z (rel intensity) 403 (M^+ , 100), 371 (1), 346 (11), 281 (20), 250 (26), 225 (80), 192 (22), 123 (95), and 57 (40). Found: C, 62.33; H, 6.47; N, 3.45%. Calcd for $\text{C}_{21}\text{H}_{26}\text{NOPPS}_2$: C, 62.51; H, 6.49; N, 3.47%.

5-*t*-Butyl-2-(*p*-methoxyphenylamino)-3-phenyl-1,2-thiaphosphol-3-ene 2-Sulfide (8k): IR (KBr) 3210 (NH), 2960, and 1365 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.88$ (s, 9H), 3.70 (s, 3H), 4.28 (d, 1H, $J_{\text{HH}}=3.5$ Hz), 5.16 (broad d, 1H, $J_{\text{HP}}=7.0$ Hz), 6.64 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.83 (dd, 1H, $J_{\text{HH}}=3.5$ Hz, $J_{\text{HP}}=54.0$ Hz), 6.83 (dd, 2H, $J_{\text{HH}}=9.0$ Hz, $J_{\text{HP}}=2.0$ Hz), 7.20—7.36 (m, 3H), and 7.70—7.88 (m, 2H); MS m/z (rel intensity) 389 (M^+ , 68), 357 (1), 333 (6), 267 (18), 236 (15), 211 (76), 178 (17), 123 (100), and 57 (42). Found: C, 61.41; H, 6.37; N, 3.31%. Calcd for $\text{C}_{20}\text{H}_{24}\text{NOPPS}_2$: C, 61.67; H, 6.21; N, 3.60%.

5-*t*-Butyl-3-(*p*-chlorophenyl)-2-(*p*-methoxyphenylamino)-1,2-thiaphosphol-3-ene 2-Sulfide (8l): IR (KBr) 3220 (NH), 2970, and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.88$ (s, 9H), 3.72 (s, 3H), 4.28 (d, 1H, $J_{\text{HH}}=2.5$ Hz), 5.18 (broad d, 1H, $J_{\text{HP}}=8.0$ Hz), 6.66 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.84 (dd, 1H, $J_{\text{HH}}=2.5$ Hz, $J_{\text{HP}}=52.5$ Hz), 6.84 (dd, 2H, $J_{\text{HH}}=9.0$ Hz, $J_{\text{HP}}=2.0$ Hz), 7.30 (d, 2H, $J_{\text{HH}}=8.0$ Hz), and 7.78 (dd, 2H, $J_{\text{HH}}=8.0$ Hz, $J_{\text{HP}}=1.0$ Hz); MS m/z (rel intensity) 423 (M^+ , 55), 391 (2), 367 (5), 301 (9), 270 (9), 245 (35), 212 (10), 123 (100), and 57 (57). Found: C, 56.27; H, 5.48; N, 3.05; S, 15.48%. Calcd for $\text{C}_{20}\text{H}_{23}\text{NOPPS}_2\text{Cl}$: C, 56.66; H, 5.47; N, 3.30; S, 15.12%.

2-Cyclohexylamino-5-phenyl-3-(*p*-tolyl)-1,2-thiaphosphol-4-ene 2-Sulfide (13a): IR (KBr) 3200 (NH), 2950, and 2860 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.96\text{--}2.20$ (broad m, 10H),

2.36 (s, 3H), 3.08–3.64 (broad m, 2H), 4.88 (dd, 1H, $J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=15.0$ Hz), 6.35 (dd, 1H, $J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=36.0$ Hz), and 7.08–7.68 (m, 9H); MS m/z (rel intensity) 399 (M^+ , 12), 366 (12), 300 (6), 238 (25), 237 (58), 205 (19), and 98 (100). Found: C, 66.40; H, 6.55; N, 3.21%. Calcd for $\text{C}_{22}\text{H}_{26}\text{NPS}_2$: C, 66.14; H, 6.56; N, 3.51%.

2-Cyclohexylamino-3,5-diphenyl-1,2-thiaphosphol-4-ene 2-Sulfide (13b): IR (KBr) 3175 (NH), 2940, and 2850 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.96$ –2.20 (broad m, 10H), 3.08–3.64 (broad m, 2H), 4.51 (dd, 1H, $J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=15.5$ Hz), 6.32 (dd, 1H, $J_{\text{HH}}=4.0$ Hz, $J_{\text{HP}}=36.0$ Hz), and 7.08–7.60 (m, 10H); MS m/z (rel intensity) 385 (M^+ , 5), 352 (9), 286 (6), 224 (4), 223 (100), and 98 (86). Found: C, 65.34; H, 6.36; N, 3.44; S, 16.63%. Calcd for $\text{C}_{21}\text{H}_{24}\text{NPS}_2$: C, 65.43; H, 6.27; N, 3.44; S, 16.63%.

6-*t*-Butyl-3-[*t*-butyl(thiocarbonyl)]-2,4-bis(*p*-tolyl)-3,4-dihydro-2H-thiin (6a): IR (neat) 2970 and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.08$ (s, 9H), 1.24 (s, 9H), 2.18 (s, 3H), 2.30 (s, 3H), 3.73 (dd, 1H, $J_{\text{HH}}=2.4$, 6.4 Hz), 4.33 (dd, 1H, $J_{\text{HH}}=2.4$, 6.4 Hz), 4.58 (d, 1H, $J_{\text{HH}}=6.4$ Hz), 5.87 (d, 1H, $J_{\text{HH}}=6.4$ Hz), and 6.72–7.35 (m, 8H); MS m/z (rel intensity) 436 (M^+), 218 (27), 161 (100).

6-*t*-Butyl-3-[*t*-butyl(thiocarbonyl)]-2,4-diphenyl-3,4-dihydro-2H-thiin (6b): IR (neat) 2970 and 1370 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.07$ (s, 9H), 1.25 (s, 9H), 3.77 (dd, 1H, $J_{\text{HH}}=2.8$, 6.4 Hz), 4.33 (dd, 1H, $J_{\text{HH}}=2.8$, 6.8 Hz), 4.63 (d, 1H, $J_{\text{HH}}=6.8$ Hz), 5.88 (d, 1H, $J_{\text{HH}}=6.4$ Hz), and 6.40–7.33 (m, 10H); MS m/z (rel intensity) 408 (M^+ , 2), 204 (38), and 147 (100).

6-*t*-Butyl-3-[*t*-butyl(thiocarbonyl)]-2,4-bis(*p*-chlorophenyl)-3,4-dihydro-2H-thiin (6c): IR (neat) 2970, 1370, and 1100 ($\text{C}=\text{S}$) cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.08$ (s, 9H), 1.24 (s, 9H), 3.74 (dd, 1H, $J_{\text{HH}}=4.0$, 6.9 Hz), 4.43 (dd, 1H, $J_{\text{HH}}=4.0$, 11.0 Hz), 4.66 (d, 1H, $J_{\text{HH}}=11.0$ Hz), 5.87 (d, 1H, $J_{\text{HH}}=6.9$ Hz), and 6.40–7.20 (m, 8H); MS m/z (rel intensity) 476 (M^+), 238 (25), and 181 (100).

General Procedure for the Reactions of the Phosphabicyclo Compounds 2 with Amines to Afford 11, 16, and 17: A solution of **2** (3 mmol) and amine (10 mmol) in dry benzene (20 cm^3) and NEt_3 (15 cm^3) was stirred at room temperature under a nitrogen atmosphere until the phosphabicyclo compound **2** was consumed as indicated by TLC (2 weeks). The solvent was removed and the residue was chromatographed on silica gel (Wakogel C-200) with benzene–hexane (2:3) as an eluent. The solvent was evaporated and the residue was recrystallized to give the products as red crystals (**11**, **16**; from hexane–ethanol, **17**; from ethanol).

3-Cyclohexylimino-6-phenyl-4-(*p*-tolyl)-1,2,3-dithiaphosphorin (11a): IR (KBr) 2940 and 2850 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.84$ –2.56 (broad m, 9H), 2.40 (s, 3H), 4.40–4.80 (m, 2H), 6.94 (d, 1H, $J_{\text{HP}}=34.0$ Hz), 7.12–7.76 (m, 7H), and 8.06 (d, 2H, $J_{\text{HH}}=9.0$ Hz); MS m/z (rel intensity) 397 (M^+ , 9), 364 (38), 333 (100), and 251 (33). Found: C, 66.73; H, 6.10; N, 3.34%. Calcd for $\text{C}_{22}\text{H}_{24}\text{NPS}_2$: C, 66.47; H, 6.09; N, 3.52%.

3-Cyclohexylimino-4,6-diphenyl-1,2,3-dithiaphosphorin (11b): IR (KBr) 2940 and 2860 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.90$ –2.48 (broad m, 9H), 4.28–4.80 (m, 2H), 6.94 (d, 1H, $J_{\text{HP}}=34.0$ Hz), 7.20–7.84 (m, 8H), and 8.04–8.36 (m, 2H); MS m/z (rel intensity) 383 (M^+ , 15), 350 (41), 319 (57), and 237 (100). Found: C, 65.70; H, 5.92; N, 3.77%. Calcd

for $\text{C}_{21}\text{H}_{22}\text{NPS}_2$: C, 65.77; H, 5.78; N, 3.65%.

3-(*p*-Methoxyphenylimino)-6-phenyl-4-(*p*-tolyl)-1,2,3-dithiaphosphorin (16a): ^1H NMR (CDCl_3) $\delta=2.44$ (s, 3H), 3.83 (s, 3H), 6.80–7.00 (m, 2H), 7.16–7.68 (m, 9H), 7.37 (d, 1H, $J_{\text{HP}}=34.0$ Hz), and 8.20 (d, 2H, $J_{\text{HH}}=9.0$ Hz); MS m/z (rel intensity) 421 (M^+ , 21), 357 (100), and 138 (52). Found: C, 65.83; H, 4.76; N, 2.90%. Calcd for $\text{C}_{23}\text{H}_{20}\text{NOPS}_2$: C, 65.54; H, 4.78; N, 3.32%.

3-(*p*-Methoxyphenylimino)-4,6-diphenyl-1,2,3-dithiaphosphorin (16b): ^1H NMR (CDCl_3) $\delta=3.84$ (s, 3H), 6.80–7.00 (m, 2H), 7.20–7.70 (m, 10H), 7.42 (d, 1H, $J_{\text{HP}}=34.2$ Hz), and 8.12–8.40 (m, 2H); ^{31}P NMR (CDCl_3) $\delta=114.6$ (d, $J_{\text{PH}}=34.2$ Hz); MS m/z (rel intensity) 407 (M^+ , 4), 343 (100), and 138 (40). Found: C, 65.10; H, 4.41; N, 3.10; S, 15.28%. Calcd for $\text{C}_{22}\text{H}_{18}\text{NOPS}_2$: C, 64.85; H, 4.45; N, 3.44; S, 15.74%.

6-Phenyl-3-(*p*-tolylimino)-4-(*p*-tolyl)-1,2,3-dithiaphosphorin (16c): ^1H NMR (CDCl_3) $\delta=2.36$ (s, 3H), 2.40 (s, 3H), 6.96–7.64 (m, 9H), 7.37 (d, 1H, $J_{\text{HP}}=34.0$ Hz), 8.09 (d, 2H, $J_{\text{HH}}=9.0$ Hz), and 8.18 (d, 2H, $J_{\text{HH}}=8.0$ Hz); MS m/z (rel intensity) 405 (M^+ , 8), 371 (7), and 341 (100). Found: C, 68.70; H, 4.63; N, 3.10%. Calcd for $\text{C}_{23}\text{H}_{20}\text{NPS}_2$: C, 68.12; H, 4.97; N, 3.45%.

4,6-Diphenyl-3-(*p*-tolylimino)-1,2,3-dithiaphosphorin (16d): ^1H NMR (CDCl_3) $\delta=2.37$ (s, 3H), 7.04–7.76 (m, 12H), 7.42 (d, 1H, $J_{\text{HP}}=34.0$ Hz), and 8.12–8.40 (m, 2H); MS m/z (rel intensity) 391 (M^+ , 13), 357 (3), and 327 (100). Found: C, 67.49; H, 4.36; N, 3.58%. Calcd for $\text{C}_{22}\text{H}_{18}\text{NPS}_2$: C, 67.50; H, 4.63; N, 3.58%.

3-(*p*-Methoxyphenylimino)-1-phenyl-3-(*p*-tolyl)-2-propene-1-thione (17a): ^1H NMR (CDCl_3) $\delta=2.32$ (s, 3H), 3.69 (s, 3H), 6.65 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.78 (s, 1H), 6.83 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.96–7.44 (m, 7H), 7.60–7.88 (m, 2H), and 15.85 (broad s, 1H); MS m/z (rel intensity) 359 (M^+ , 61), 358 (82), 326 (9), and 252 (100). Found: C, 76.45; H, 5.90; N, 3.54%. Calcd for $\text{C}_{23}\text{H}_{21}\text{NOS}$: C, 76.85; H, 5.89; N, 3.90%.

3-(*p*-Methoxyphenylamino)-1,3-diphenyl-2-propene-1-thione (17b): ^1H NMR (CDCl_3) $\delta=3.68$ (s, 3H), 6.62 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.76 (s, 1H), 6.79 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 7.29 (m, 8H), 7.68–7.80 (m, 2H), and 15.86 (broad s, 1H); MS m/z (rel intensity) 345 (M^+ , 64), 344 (100), 312 (7), and 238 (89). Found: C, 76.51; H, 5.62; N, 3.88%. Calcd for $\text{C}_{22}\text{H}_{19}\text{NOS}$: C, 76.49; H, 5.54; N, 4.05%.

1-Phenyl-3-(*p*-tolylamino)-3-(*p*-tolyl)-2-propene-1-thione (17c): ^1H NMR (CDCl_3) $\delta=2.22$ (s, 3H), 2.32 (s, 3H), 6.64–7.36 (m, 11H), 6.76 (s, 1H), 7.60–7.80 (m, 2H), and 15.81 (broad s, 1H); MS m/z (rel intensity) 343 (M^+ , 60), 342 (96), 310 (12), and 252 (100). Found: C, 80.62; H, 6.11; N, 3.80%. Calcd for $\text{C}_{23}\text{H}_{21}\text{NS}$: C, 80.43; H, 6.16; N, 4.08%.

1,3-Diphenyl-3-(*p*-tolylamino)-2-propene-1-thione (17d): ^1H NMR (CDCl_3) $\delta=2.22$ (s, 3H), 6.72 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 6.77 (s, 1H), 6.90 (d, 2H, $J_{\text{HH}}=9.0$ Hz), 7.14–7.38 (m, 8H), 7.68–7.80 (m, 2H), and 15.83 (broad s, 1H); MS m/z (rel intensity) 329 (M^+ , 49), 328 (78), 296 (11), and 238 (100). Found: C, 79.88; H, 5.79; N, 4.07%. Calcd for $\text{C}_{22}\text{H}_{19}\text{NS}$: C, 80.20; H, 5.81; N, 4.25%. The ^1H NMR spectrum is identical with that reported by Quiniou et al.⁹

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