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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.

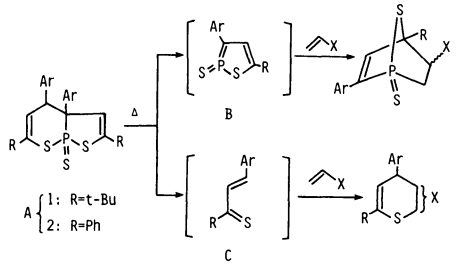
Results and Discussion

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^n_3, since the reaction was slow in refluxing benzene.

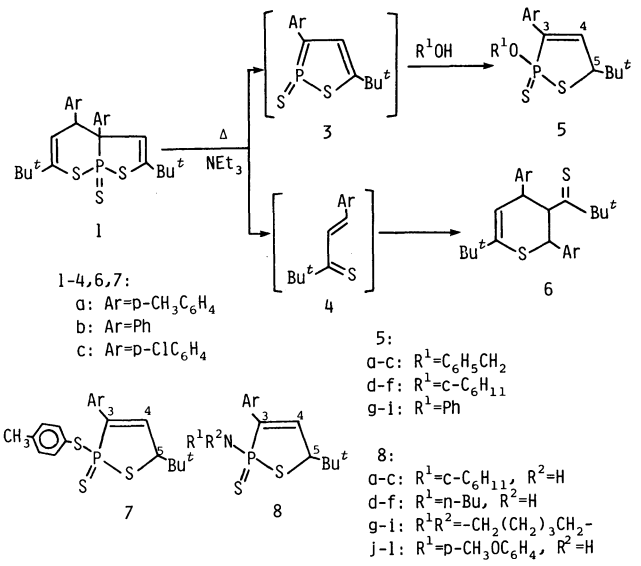
The elemental analyses and the mass spectra indicated that **5** were 1:1 adducts of **3** and the alcohols. The adducts **5** showed strong IR absorption due to the P–O linkage at about 1000 cm^{-1}. In the ^1H NMR spectra,[6] H-4 and H-5 protons resonated at δ=6.8—6.9 and 4.2—4.3 with the coupling constant 3.0—3.5 Hz and the H-4 proton exhibited a large H–P coupling constant (J_{HP}=50—55 Hz)(Table 2). The ^{13}C NMR spectra[7] showed a signal of the C-3 olefinic carbon at δ=140—142 with a large C–P coupling constant (J_{CP}=100—107 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.

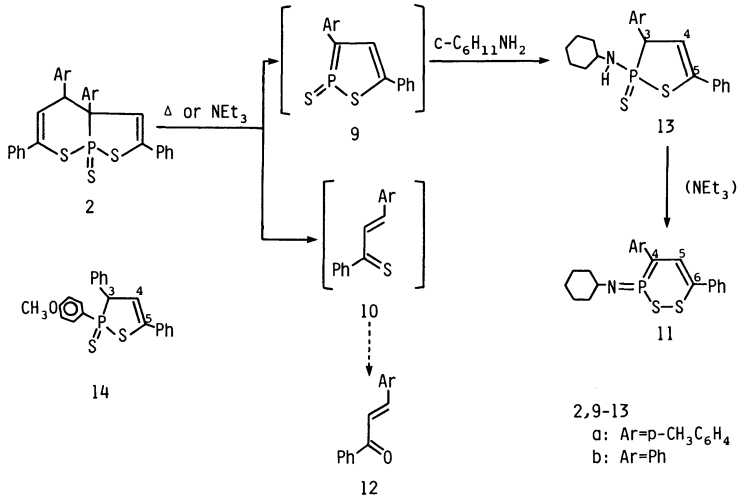


Scheme 2.

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

Material	Reagent	Reaction time/h	Product[a]				
				Mp θ_m/°C	Yield/%		Yield/%
1a	$PhCH_2OH$	10	**5a**	115—118	54	**6a**	52
1b	$PhCH_2OH$	10	**5b**	107—109	36	**6b**	33
1c	$PhCH_2OH$	10	**5c**	113—116	38	**6c**	90
1a	*c*-$C_6H_{11}OH$	15[b]	**5d**	129—132	53	**6a**	72
1b	*c*-$C_6H_{11}OH$	20	**5e**	138—141	28	**6b**	35
1b	*c*-$C_6H_{11}OH$	15[b]	**5e**		40	**6b**	90
1c	*c*-$C_6H_{11}OH$	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	*p*-$CH_3C_6H_4SH$	10	**7a**	181—183	77	**6a**	80
1b	*p*-$CH_3C_6H_4SH$	10	**7b**	150—152	68	**6b**	49
1c	*p*-$CH_3C_6H_4SH$	10	**7c**	175—177	66	**6c**	80
1a	*c*-$C_6H_{11}NH_2$	13	**8a**	140—142	59	**6a**	61
1b	*c*-$C_6H_{11}NH_2$	12	**8b**	136—139	62	**6b**	92
1c	*c*-$C_6H_{11}NH_2$	12	**8c**	185—188	74	**6c**	56
1a	Bu^nNH_2	8	**8d**	117—119	59	**6a**	61
1b	Bu^nNH_2	8	**8e**	124—128	73	**6b**	82
1c	Bu^nNH_2	8	**8f**	118—120	59	**6c**	91
1a	$\overline{CH_2(CH_2)_4NH}$	7	**8g**	118—120	54	**6a**	61
1b	$\overline{CH_2(CH_2)_4NH}$	8	**8h**	113—116	50	**6b**	85
1c	$\overline{CH_2(CH_2)_4NH}$	8	**8i**	121—122	60	**6c**	98
1a	*p*-$CH_3OC_6H_4NH_2$	14	**8j**	137—140	11	**6a**	65
1b	*p*-$CH_3OC_6H_4NH_2$	14	**8k**	163—165	28	**6b**	65
1c	*p*-$CH_3OC_6H_4NH_2$	14	**8l**	158—161	21	**6c**	66

a) Colorless crystals (**6**; red oil). b) NPr^n_3/xylene reflux.



Scheme 3.

increase with the increasing electronegativity of the exocyclic heteroatom attached to the phosphorus atom.[8]

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 NEt_3. However, the products obtained

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

Compound	H(4)	H(5)	J_{HH}	$J_{H(4)P}$	$J_{H(5)P}$	C(3)	C(4)	C(5)	$J_{C(3)P}$	$J_{C(4)P}$	$J_{C(5)P}$
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	≃6.8[a]	4.29	3.2	≃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	≃6.9[a]	4.35	3.2	≃50[a]	9.8	141.3	140.9	66.3	100.1	28.1	6.1
5h	≃6.9[a]	4.36	3.2	≃50[a]	9.3	141.5	141.7	66.3	100.1	28.1	4.9
5i	≃6.9[a]	4.37	3.1	≃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	*c*-$C_6H_{11}NH_2$	2 Week	NEt_3/C_6H_6	20—25	**11a**	264—265	34	**12a**	99
2a	*c*-$C_6H_{11}NH_2$	2 h	C_6H_6	80	**11a**		13	**12a**	99
					13a	196—198 (dec.)	46		
2b	*c*-$C_6H_{11}NH_2$	2 Week	NEt_3/C_6H_6	20—25	**11b**	272—274	39	**12b**	99
2b	*c*-$C_6H_{11}NH_2$	3 h	C_6H_6	80	**11b**		30	**12b**	99
					13b	190—192 (dec.)	43		
2a	*p*-$CH_3OC_6H_4NH_2$	2 Week	NEt_3/C_6H_6	20—25	**16a**	261—263	55	**17a**[b]	65
2b	*p*-$CH_3OC_6H_4NH_2$	2 Week	NEt_3/C_6H_6	20—25	**16b**	227—229	33	**17b**[c]	58
2a	*p*-$CH_3C_6H_4NH_2$	2 Week	NEt_3/C_6H_6	20—25	**16c**	208—210	16	**17c**[d]	97
2b	*p*-$CH_3C_6H_4NH_2$	2 Week	NEt_3/C_6H_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))

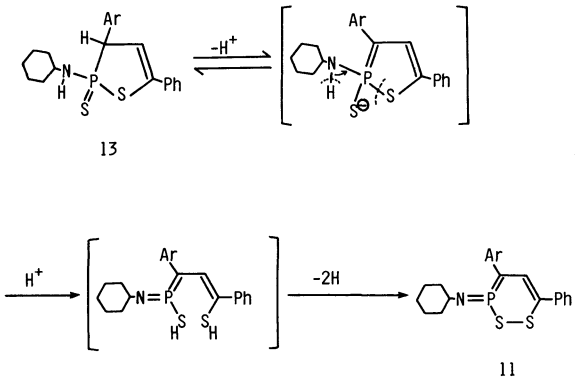
Compound	H(3)	H(4)	J_{HH}	$J_{H(3)P}$	$J_{H(4)P}$
13a	4.88	6.35	4.0	15.0	36.0
13b	4.51	6.32	4.0	15.5	36.0
14	5.17	6.32	4.0	18.0	32.0

were chalcones **12** and 1,2,3-dithiaphosphorins **11** (Scheme 3, Table 3). When the reactions were carried out in refluxing benzene without NEt_3, **11**, **12**, and 1,2-adducts **13** of cyclohexylamine toward **9** were formed.

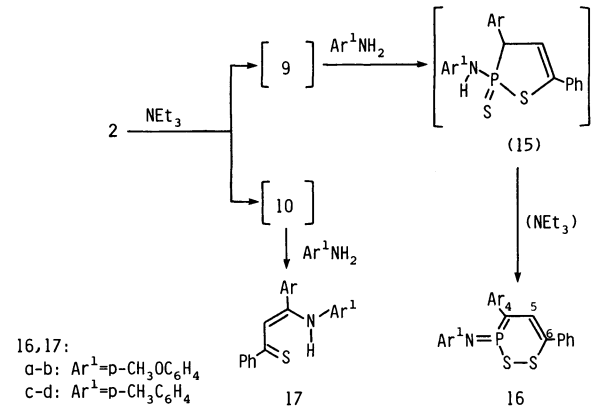
The ^1H and ^{13}C NMR spectra of **13a** were different from those of the 1,4-adducts **8**. Namely, the

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

Compound	H(5)	$J_{H(5)P}$	C(4)	C(5)	C(6)	$J_{C(4)P}$	$J_{C(5)P}$	$J_{C(6)P}$
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.



Scheme 5.

^1H NMR spectrum showed signals of the H-3 proton at δ=4.88 (J_{HH}=4.0 Hz, J_{HP}=15.0 Hz) and of the H-4 proton at δ=6.35 (J_{HH}=4.0 Hz, J_{HP}=36.0 Hz). These spectral patterns are similar to those of 1,2-thiaphosphol-4-ene 2-sulfide **14** reported previously[9] (Table 4). In the ^{13}C NMR spectrum, the resonance at δ=60.7 (J_{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 δ=120.4 (J_{CP}=4.9 Hz) and 141.8 (J_{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 [M$^+$ −2S] 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 δ=6.94 (J_{HP}=34.0 Hz) and the ^{13}C NMR spectrum displayed three signals at δ=161.3 (J_{CP}=81.8 Hz), 117.1 (J_{CP}= 11.0 Hz), and 169.2 (J_{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-ditiaphosphorins **16** in contrast to the reactions with cyclohexylamine (Scheme 5, Table 3). This result is interesting but the 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.[1]

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-Benzyloxy-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_{HH}=3.4 Hz, J_{HP}=9.5 Hz), 5.06—5.28 (m, 2H), 6.85 (dd, 1H, J_{HH}=3.4 Hz, J_{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 $C_{21}H_{25}OPS_2$: C, 64.92; H, 6.49%.

2-Benzyloxy-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_{HH}=3.5 Hz, J_{HP}=9.5 Hz), 5.06—5.28 (m, 2H), 6.88 (dd, 1H, J_{HH}=3.5 Hz, J_{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 $C_{20}H_{23}OPS_2$: C, 64.14; H, 6.19; S, 17.12%.

2-Benzyloxy-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_{HH}=3.5 Hz, J_{HP}=10.0 Hz), 5.06—5.28 (m, 2H), 6.87 (dd, 1H, J_{HH}=3.5 Hz, J_{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 $C_{20}H_{22}OPS_2Cl$: 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_{HH}=3.0 Hz, J_{HP}=9.1 Hz), 4.54—4.96 (broad m, 1H), 6.83 (dd, 1H, J_{HH}=3.0 Hz, J_{HP}=54.0 Hz), 7.14 (d, 2H, J_{HH}=8.0 Hz), and 7.48 (dd, 2H, J_{HH}=8.0 Hz, J_{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 $C_{20}H_{29}OPS_2$: 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_{HH}=3.2 Hz, J_{HP}=9.5 Hz), 4.54—4.96 (broad m, 1H), ≈6.8 (dd, 1H, J_{HH}=3.2 Hz, J_{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 $C_{19}H_{27}OPS_2$: 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_{HH}=3.0 Hz J_{HP}=9.8 Hz), 4.54—4.92 (broad m, 1H), 6.83 (dd, 1H, J_{HH}=3.0 Hz, J_{HP}=54.0 Hz), 7.28 (d, 2H, J_{HH}=9.0 Hz), and 7.54 (dd, 2H, J_{HH}=9.0 Hz, J_{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 $C_{19}H_{26}OPS_2Cl$: 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_{HH}=3.2 Hz, J_{HP}=9.8 Hz), ≈6.9 (dd, 1H, J_{HH}=3.2 Hz, J_{HP}≈50 Hz), 6.94—7.38 (m, 7H), and 7.64 (dd, 2H, J_{HH}=8.0 Hz, J_{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 $C_{20}H_{23}OPS_2$: 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_{HH}=3.2 Hz, J_{HP}=9.3 Hz), ≈6.9 (dd, 1H J_{HH}=3.2 Hz, J_{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 $C_{19}H_{21}OPS_2$: 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_{HH}=3.1 Hz, J_{HP}=10.0 Hz), ≈6.9 (dd, 1H, J_{HH}=3.1 Hz, J_{HP}≈50 Hz), 6.86—7.48 (m, 7H), and 7.70 (dd, 2H, J_{HH}=9.0 Hz, J_{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 $C_{19}H_{20}OPS_2Cl$: 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_{HH}=2.0 Hz), 6.64 (dd, 1H, J_{HH}=2.0 Hz, J_{HP}=55.0 Hz), 6.96—7.40 (m, 6H), and 7.74 (d, 2H, J_{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 $C_{21}H_{25}PS_3$: 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_{HH}=2.5 Hz), 6.65 (dd, 1H, J_{HH}=2.5 Hz, J_{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 $C_{20}H_{23}PS_3$: 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_{HH}=2.5 Hz), 6.65 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=54.0 Hz), 6.98—7.22 (m, 4H), 7.34 (d, 2H, J_{HH}=9.0 Hz), and 7.78 (d, 2H, J_{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 $C_{20}H_{22}PS_3Cl$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.80—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_{HP}=12.0 Hz), 4.25 (d, 1H, J_{HH}=2.0 Hz), 6.83 (dd, 1H, J_{HH}=2.0 Hz, J_{HP}=52.0 Hz), 7.11 (d, 2H, J_{HH}=8.0 Hz), and 7.67 (d, 2H, J_{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 $C_{20}H_{30}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.80—1.80 (broad m, 9H), 1.13 (s, 9H), 1.84—2.16 (broad m, 1H), 2.93 (broad d, 2H, J_{HP}=12.0 Hz), 4.31 (d, 1H, J_{HH}=2.0 Hz), 6.83 (dd, 1H, J_{HH}=2.0 Hz, J_{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 $C_{19}H_{28}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.80—1.80 (broad m, 9H), 1.12 (s, 9H), 1.88—2.20 (broad m, 1H), 2.96 (broad d, 2H, J_{HP}=11.7 Hz), 4.30 (d, 1H, J_{HH}=2.5 Hz), 6.86 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=52.2 Hz), 7.26 (d, 2H, J_{HH}=9.0 Hz), and 7.70 (d, 2H, J_{HH}=9.0 Hz); ^{31}P NMR ($CDCl_3$) δ=90.3 (ddd, J_{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 $C_{19}H_{27}NPS_2Cl$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.70—1.62 (m, 7H), 1.12 (s, 9H), 2.35 (s, 3H), 2.72—3.08 (m, 3H), 4.30 (d, 1H, J_{HH}=3.5 Hz), 6.76 (dd, 1H, J_{HH}=3.5 Hz, J_{HP}=52.0 Hz), 7.13 (d, 2H, J_{HH}=9.0 Hz), and 7.58 (d, 2H, J_{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 $C_{18}H_{28}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.64—1.62 (m, 7H), 1.12 (s, 9H), 2.68—3.20 (m, 3H), 4.30 (d, 1H, J_{HH}=2.5 Hz), 6.83 (dd, 1H, J_{HH}=2.5 Hz, J_{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 $C_{17}H_{26}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.60—1.77 (m, 7H), 1.12 (s, 9H), 2.60—3.21 (m, 3H), 4.30 (d, 1H, J_{HH}=2.5 Hz), 6.82 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=51.0 Hz), 7.28 (d, 2H, J_{HH}=8.0 Hz), and 7.65 (d, 1H, J_{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 $C_{17}H_{25}NPS_2Cl$: 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}; ^{1}H NMR ($CDCl_3$) δ=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_{HH}=2.5 Hz, J_{HP}=2.5 Hz), 6.81 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=53.5 Hz), 7.09 (d, 2H, J_{HH}=7.5 Hz), and 7.55 (d, 2H, J_{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 $C_{19}H_{28}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=1.13 (s, 9H), 1.20—1.83 (broad m, 6H), 2.94—3.58 (broad m, 4H), 4.36 (dd, 1H, J_{HH}=2.0 Hz, J_{HP}=2.5 Hz), 6.86 (dd, 1H, J_{HH}=2.0 Hz, J_{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 $C_{18}H_{26}NPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=1.12 (s, 9H), 1.20—1.72 (broad m, 6H), 2.96—3.52 (broad m, 4H), 4.32 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=1.5 Hz), 6.86 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=48.0 Hz), 7.26 (d, 2H, J_{HH}=8.0 Hz), and 7.64 (d, 2H, J_{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 $C_{18}H_{25}NPS_2Cl$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.88 (s, 9H), 2.35 (s, 3H), 3.70 (s, 3H), 4.27 (d, 1H, J_{HH}=2.0 Hz), 5.14 (broad d, 1H, J_{HP}=7.0 Hz), 6.64 (d, 2H, J_{HH}=8.0 Hz), 6.84 (d, 2H, J_{HH}=8.0 Hz), 6.88 (dd, 1H, J_{HH}=2.0 Hz, J_{HP}=54.0 Hz), 7.14 (dd, 2H, J_{HH}=8.0 Hz, J_{HP}=3.0 Hz), and 7.72 (d, 2H, J_{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 $C_{21}H_{26}NOPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.88 (s, 9H), 3.70 (s, 3H), 4.28 (d, 1H, J_{HH}=3.5 Hz), 5.16 (broad d, 1H, J_{HP}=7.0 Hz), 6.64 (d, 2H, J_{HH}=9.0 Hz), 6.83 (dd, 1H, J_{HH}=3.5 Hz, J_{HP}=54.0 Hz), 6.83 (dd, 2H, J_{HH}=9.0 Hz, J_{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 $C_{20}H_{24}NOPS_2$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.88 (s, 9H), 3.72 (s, 3H), 4.28 (d, 1H, J_{HH}=2.5 Hz), 5.18 (broad d, 1H, J_{HP}=8.0 Hz), 6.66 (d, 2H, J_{HH}=9.0 Hz), 6.84 (dd, 1H, J_{HH}=2.5 Hz, J_{HP}=52.5 Hz), 6.84 (dd, 2H, J_{HH}=9.0 Hz, J_{HP}=2.0 Hz), 7.30 (d, 2H, J_{HH}=8.0 Hz), and 7.78 (dd, 2H, J_{HH}=8.0 Hz, J_{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 $C_{20}H_{23}NOPS_2Cl$: 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}; ^{1}H NMR ($CDCl_3$) δ=0.96—2.20 (broad m, 10H),

2.36 (s, 3H), 3.08—3.64 (broad m, 2H), 4.88 (dd, 1H, J_{HH}=4.0 Hz, J_{HP}=15.0 Hz), 6.35 (dd, 1H, J_{HH}=4.0 Hz, J_{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 $C_{22}H_{26}NPS_2$: 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 ($CDCl_3$) δ=0.96—2.20 (broad m, 10H), 3.08—3.64 (broad m, 2H), 4.51 (dd, 1H, J_{HH}=4.0 Hz, J_{HP}=15.5 Hz), 6.32 (dd, 1H, J_{HH}=4.0 Hz, J_{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 $C_{21}H_{24}NPS_2$: 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-2*H*-thiin (6a): IR (neat) 2970 and 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (s, 9H), 1.24 (s, 9H), 2.18 (s, 3H), 2.30 (s, 3H), 3.73 (dd, 1H, J_{HH}=2.4, 6.4 Hz), 4.33 (dd, 1H, J_{HH}=2.4, 6.4 Hz), 4.58 (d, 1H, J_{HH}=6.4 Hz), 5.87 (d, 1H, J_{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-2*H*-thiin (6b): IR (neat) 2970 and 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (s, 9H), 1.25 (s, 9H), 3.77 (dd, 1H, J_{HH}=2.8, 6.4 Hz), 4.33 (dd, 1H, J_{HH}=2.8, 6.8 Hz), 4.63 (d, 1H, J_{HH}=6.8 Hz), 5.88 (d, 1H, J_{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-2*H*-thiin (6c): IR (neat) 2970, 1370, and 1100 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (s, 9H), 1.24 (s, 9H), 3.74 (dd, 1H, J_{HH}=4.0, 6.9 Hz), 4.43 (dd, 1H, J_{HH}=4.0, 11.0 Hz), 4.66 (d, 1H, J_{HH}=11.0 Hz), 5.87 (d, 1H, J_{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 ($CDCl_3$) δ=0.84—2.56 (broad m, 9H), 2.40 (s, 3H), 4.40—4.80 (m, 2H), 6.94 (d, 1H, J_{HP}=34.0 Hz), 7.12—7.76 (m, 7H), and 8.06 (d, 2H, J_{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 $C_{22}H_{24}NPS_2$: 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 ($CDCl_3$) δ=0.90—2.48 (broad m, 9H), 4.28—4.80 (m, 2H), 6.94 (d, 1H, J_{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 $C_{21}H_{22}NPS_2$: C, 65.77; H, 5.78; N, 3.65%.

3-(*p*-Methoxyphenylimino)-6-phenyl-4-(*p*-tolyl)-1,2,3-dithiaphosphorin (16a): ^1H NMR ($CDCl_3$) δ=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_{HP}=34.0 Hz), and 8.20 (d, 2H, J_{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 $C_{23}H_{20}NOPS_2$: C, 65.54; H, 4.78; N, 3.32%.

3-(*p*-Methoxyphenylimino)-4,6-diphenyl-1,2,3-dithiaphosphorin (16b): ^1H NMR ($CDCl_3$) δ=3.84 (s, 3H), 6.80—7.00 (m, 2H), 7.20—7.70 (m, 10H), 7.42 (d, 1H, J_{HP}=34.2 Hz), and 8.12—8.40 (m, 2H); ^{31}P NMR ($CDCl_3$) δ=114.6 (d, J_{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 $C_{22}H_{18}NOPS_2$: 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 ($CDCl_3$) δ=2.36 (s, 3H), 2.40 (s, 3H), 6.96—7.64 (m, 9H), 7.37 (d, 1H, J_{HP}=34.0 Hz), 8.09 (d, 2H, J_{HH}=9.0 Hz), and 8.18 (d, 2H, J_{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 $C_{23}H_{20}NPS_2$: C, 68.12; H, 4.97; N, 3.45%.

4,6-Diphenyl-3-(*p*-tolylimino)-1,2,3-dithiaphosphorin (16d): ^1H NMR ($CDCl_3$) δ=2.37 (s, 3H), 7.04—7.76 (m, 12H), 7.42 (d, 1H, J_{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 $C_{22}H_{18}NPS_2$: C, 67.50; H, 4.63; N, 3.58%.

3-(*p*-Methoxyphenylamino)-1-phenyl-3-(*p*-tolyl)-2-propene-1-thione (17a): ^1H NMR ($CDCl_3$) δ=2.32 (s, 3H), 3.69 (s, 3H), 6.65 (d, 2H, J_{HH}=9.0 Hz), 6.78 (s, 1H), 6.83 (d, 2H, J_{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 $C_{23}H_{21}NOS$: C, 76.85; H, 5.89; N, 3.90%.

3-(*p*-Methoxyphenylamino)-1,3-diphenyl-2-propene-1-thione (17b): ^1H NMR ($CDCl_3$) δ=3.68 (s, 3H), 6.62 (d, 2H, J_{HH}=9.0 Hz), 6.76 (s, 1H), 6.79 (d, 2H, J_{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 $C_{22}H_{19}NOS$: C, 76.49; H, 5.54; N, 4.05%.

1-Phenyl-3-(*p*-tolylamino)-3-(*p*-tolyl)-2-propene-1-thione (17c): ^1H NMR ($CDCl_3$) δ=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 $C_{23}H_{21}NS$: C, 80.43; H, 6.16; N, 4.08%.

1,3-Diphenyl-3-(*p*-tolylamino)-2-propene-1-thione (17d): ^1H NMR ($CDCl_3$) δ=2.22 (s, 3H), 6.72 (d, 2H, J_{HH}=9.0 Hz), 6.77 (s, 1H), 6.90 (d, 2H, J_{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 $C_{22}H_{19}NS$: 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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References

1) H. Yamaguchi, S. Kametani, T. Karakasa, T. Saito, and S. Motoki, *Tetrahedron Lett.*, **23**, 1263 (1982); T. Uchida, K. Kozawa, T. Saito, and S, Motoki, *Bull. Chem. Soc. Jpn.*, **57**, 1985, 1990 (1984); H, Tanaka, S. Kametani, T. Saito S. Motoki, ibid., **58**, 667 (1985).

2) E. Niecke and D.-A. Wildbredt, *J. Chem. Soc., Chem. Commun.*, **1981**, 72; R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, **20**, 731 (1981); R. Appel, F. Knoch, and H. Kunze, ibid., **23**, 157 (1984); M. Caira, R. H. Neilson, W. H. Watson, P. Wisian-Neilson, and Z.-M. Xie, *J. Chem. Soc., Chem. Commun.*, **1984**, 698.

3) M. Yoshifuji, J. Tagawa, and N. Inamoto, *Tetrahedron Lett.*, **1979**, 2415; B. Divisia, *Tetrahedron*, **1979**, 181; T. Kawashima, T. Tomita, and N. Inamoto, *Phosphorus and Sulfur*, **16**, 9 (1983); Th. A. van der Knaap, Th. C. Klebach, R. Lourens, M. Vos, and F. Bickelhaupt, *J. Am. Chem. Soc.*, **105**, 4026 (1983); E. Deschamps and F. Mathey, *J. Chem. Soc., Chem. Commun.*, **1984**, 1214.

4) The thione dimers **6** can not be obtained by thionation of 1-arylmethylene pinacolones under the reaction conditions as reported in the previous paper.[5]

5) T. Karakasa and S. Motoki, *J. Org. Chem.*, **43**, 4147 (1978).

6) G. Märkl and R. Potthast, *Tetrahedron Lett.*, **1968**, 1755; E. F. Moony, "Annual Reports on NMR Spectroscopy," Academic Press, New York (1973), Vol. 5B, p. 12; R. S. Macomber, G. A. Krudy, and M. Z. Amer, *J. Org. Chem.*, **48**, 1420 (1983).

7) G. A. Krudy and R. S. Macomber, *J. Org. Chem.*, **43**, 4656 (1978); K. Clausen, A. A. El-Barbary, and S.-O. Lawesson, *Tetrahedron*, **1981**, 1019; L. D. Quin, K. C. Caster, and S. B. Soloway, *J. Org. Chem.*, **49**, 2627 (1984).

8) G. W. Buchanan and V. L. Webb, *Org. Magn. Reson.*, **21**, 436 (1983).

9) S. Kametani, H. Ohmura, H. Tanaka, and S. Motoki, *Chem. Lett.*, **1982**, 793.

10) G. Duguay and H. Quiniou, *Bull. Soc. Chim. Fr.*, **1970**, 1918; E. Kleinpeter and M. Pulst, *J. Prakt. Chem.*, **322**, 575 (1980); H. Quiniou, *Phosphorus and Sulfur*, **10**, 1 (1981).

11) Treatment of thiochalcone (**10**) dimers with the aromatic amines (*p*-anisidine, *p*-toluidine) in the presence of NEt_3 also afforded 3-amino-2-propene-1-thiones **17** in low yields.