pared above was stirred rapidly for 10 min in contact with excess diamino-1,2-ethane (0.4 mL) in water (20 mL). The organic phase was then separated, washed several times with water, and dried ($MgSO_4$). The product remained as a yellow glass after removal of solvent: mp 183–185 °C; yield 1.6 g (86%); $[\alpha]_D$ −41.3° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{28}H_{30}NPPdS\cdot0.25CH_2Cl_2$: C, 59.4; H, 5.4; N, 2.5. Found: C, 59.2; H, 5.4; N, 2.3. ^1H NMR ($CDCl_3$): δ 1.87 (d, 3 H, $^3J_{HH} = 6.1$ Hz, CH*Me*), 2.24–2.98 (m, 4 H, PCH_2 and SCH_2), 2.88 (s, 3 H, NMe), 2.97 (d, 3 H, $^4J_{PH} = 3.2$ Hz, NMe), 4.40 (qn, 1 H, $^3J_{HH} = {}^4J_{PH} = 6.35$ Hz, C*H*Me), 6.74–8.11 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 64.08 (s).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-C^2,*N*][(*R*/*S*)-(2-(methylthio)ethyl)diphenylphosphine-*P*,*S*]palladium(II) Iodide. A solution of the above thiolato complex (0.8 g) in dichloromethane (15 mL) was stirred for 1 h in contact with methyl iodide (91 μL) in dichloromethane (5 mL). The product remained as an orange solid after removal of solvent: mp 197–198 °C; yield 0.9 g (90%); $[\alpha]_D$ −61.8° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{29}H_{33}INPPdS\cdot0.2CH_2Cl_2$: C, 49.5; H, 4.8; N, 2.0. Found: C, 49.8; H, 4.8; N, 2.0. ^1H NMR ($CDCl_3$): δ 2.02 (d, 3 H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.47–3.43 (m, 4 H, PCH_2 and SCH_2), 2.55 (s, 3 H, SMe), 2.88 (s, 3 H, NMe), 3.15 (d, 3 H, $^4J_{PH} = 2.8$ Hz, NMe), 4.46 (qn, 1 H, $^3J_{HH} = {}^4J_{PH} = 6.35$ Hz, C*H*Me), 6.57–8.11 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): 46.17 (s). ^1H NMR (acetone-d_6): δ 2.45–3.35 (m, 4 H, PCH_2 and SCH_2), 2.53 (s, 3 H, SMe), 2.84 (s, 3 H, NMe), 3.21 (d, 3 H, $^4J_{PH} = 2.7$ Hz, NMe), 4.47 (qn, 1 H, $^3J_{HH} = {}^4J_{PH} = 6.1$ Hz, C*H*Me), 6.65–8.30 (m, 16 H, aromatics) CH*Me* resonances obscured by the solvent signal. Treatment of the iodide with aqueous ammonium hexafluorophosphate gave the desired complex, (R_c,*R*/S_s)-**1a**, in 74% isolated yield. The physical and spectrochemical properties of this product were identical with those for the compound obtained by the direct coordination method.

Structural Analysis. Cell dimensions of $[Pd\{(R)\text{-}CH_3CH(1\text{-}C_{10}H_6)\text{-}NMe_2\text{-}C^2,N\}(R/S)\text{-}\{Ph_2PCH_2CH_2SMe\text{-}P,S\}]PF_6$ were determined from 45 reflections obtained by an automated random search routine at room temperature on a Siemens R3m/v four-circle diffractometer using graphite-monochromated Mo Kα radiation. A colorless crystal of approximate dimensions 0.25 × 0.40 × 0.60 mm was used. Data were collected for $3.0° \le 2\theta \le 50°$ and index ranges $0 \le h \le +9$, $-21 \le k \le +21$, $-25 \le l \le +25$ with a variable scan rate of 1.50–15.0° min^{-1}. A summary of the crystallographic data is given in Table II. A total of 11 526 reflections were collected, and 10 278 of these $[F > 6\sigma(F)]$ were used in the refinement. The intensities of three standard reflections were measured after every 97 reflection data were collected. Semiempirical absorption corrections were applied. The structure was solved by direct methods, and the lighter non-hydrogen atoms were located from Fourier difference maps. Non-hydrogen atoms were refined anisotropically except for methyl carbon atoms in the 1-(dimethylamino)ethylnaphthylene molecule and the disordered carbon atoms in cation IV. The function minimized during full-matrix least-squares refinement was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0004F^2$, yielding $R = 0.041$, $R_w = 0.067$, and $S = 2.34$. Phenyl rings and the hexafluorophosphate ions were refined as rigid groups. Hydrogen atoms were introduced in calculated positions only for carbons refined anisotropically and were assigned fixed thermal parameters. All calculations were performed on a Digital Equipment Corp. MicroVax II computer using the Siemens SHELXTL PLUS package.

Acknowledgment. This work was supported by grants from the National University of Singapore.

Registry No. (R_c,R_s)-**1a**, 139276-65-6; (R_c,S_s)-**1a**, 139276-67-8; (R_c,R_s)-**1b**, 139276-69-0; (R_c,S_s)-**1b**, 139402-42-9; (R_c,R_s)-**1c**, 139402-44-1; (R_c,S_s)-**1c**, 139402-46-3; (R_c,R_s)-**1a** (chloride salt), 139276-70-3; (R_c,R_s)-**1a** (iodide salt), 139276-73-6; (R_c,S_s)-**1a**, 139402-47-4; (*R*)-**2**, 80145-77-3; (*R*)-**3**, 139276-72-5; (*R*)-**4**, 139276-71-4; $Me_2AsCH_2CH_2SH$, 139276-61-2; $Me_2AsCH_2CH_2Me$, 139276-62-3; $Ph_2AsCH_2CH_2SH$, 139276-63-4; $Ph_2AsCH_2CH_2Me$, 131291-87-7; $Ph_2PCH_2CH_2SH$, 3190-79-2; $Ph_2PCH_2CH_2Me$, 20859-51-2; $NaAsMe_2$, 13787-40-1; $\overline{CH_2CH_2S}$, 420-92-8; Ph_2AsH, 829-83-4; $EtPh_2P(S)$, 1017-98-7.

Supplementary Material Available: For (R_c,*R*/S_s)-**1a**, figures showing atom-labeling schemes and tables of crystallographic data, final positional parameters and equivalent isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters (16 pages); a table of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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Photochemical Behavior of Thioxophosphoranyl Diazo Compounds: Evidence for Transient λ^5-Phosphathiirenes and for Structural Isomerizations of the Diazo Group

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Photolysis of bis[bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1**) in the presence of a slight excess of dimethyl acetylenedicarboxylate led to 1,3λ^5-thiaphosphole **5** in 95% yield. This compound was fully characterized including an X-ray diffraction study. Irradiation of (thioxophosphoranyl)(trimethylsilyl)diazomethane **2** gave rise to [bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)carbodiimide **6** in 60% yield. Photolysis of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**) quantitatively afforded 1,3,4-thiadiaza-1,6-dihydro-5λ^5-phosphinine **7** in the absence of trapping agent, while in the presence of dimethyl acetylenedicarboxylate *N*-(thioxophosphoranyl)pyrazole **8** was obtained in 70% yield. Irradiation of 1,3,4,2λ^5-thiadiazaphosphole **4** led to bis[bis(diisopropylamino)thioxophosphoranyl]carbodiimide (**9**) in 85% yield. From these results it appeared that depending on the nature of the diazo carbon substituent, the photolysis of thioxophosphoranyl diazo compounds leads to transient λ^5-phosphathiirenes with loss of nitrogen and/or to 1,3,4,2λ^5-thiadiazaphospholes which under irradiation give rise to nitrilimines which can be trapped or which rearrange into carbodiimides.

Although α-phosphoranyl diazo derivatives have been widely studied,[1] α-thioxophosphoranyl diazo compounds have attracted very little attention.[2,3] Their carbon analogues, the diazothioketones are hardly available due to their facile isomerization into 1,2,3-thiadiazoles;[4] these compounds are of special interest since they are the classical precursors of the highly unstable thiirenes A.[5] Here we report evidence for the transient formation of

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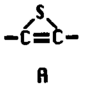
Table I. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses for Compound **5**

S(1)–C(1)	1.753 (4)	C(1)–P(1)	1.734 (4)
P(1)–C(2)	1.770 (4)	C(2)–C(3)	1.365 (6)
C(3)–S(1)	1.686 (4)	P(2)–S(2)	1.959 (2)
P(2)–C(1)	1.776 (4)		
P(1)–N(1)	1.643 (3)	P(2)–N(3)	1.683 (3)
P(1)–N(2)	1.668 (3)	P(2)–N(4)	1.677 (4)
N(1)–C(4)	1.502 (5)	N(3)–C(16)	1.466 (5)
C(4)–C(5)	1.503 (6)	C(16)–C(17)	1.512 (7)
C(4)–C(6)	1.517 (6)	C(16)–C(18)	1.505 (6)
N(1)–C(7)	1.515 (5)	N(3)–C(19)	1.504 (5)
C(7)–C(8)	1.504 (7)	C(19)–C(20)	1.512 (7)
C(7)–C(9)	1.483 (7)	C(19)–C(21)	1.496 (8)
N(2)–C(10)	1.463 (6)	N(4)–C(22)	1.479 (5)
C(10)–C(11)	1.535 (6)	C(22)–C(23)	1.532 (6)
C(10)–C(12)	1.517 (7)	C(22)–C(24)	1.526 (7)
N(2)–C(13)	1.471 (5)	N(4)–C(25)	1.485 (6)
C(13)–C(14)	1.507 (6)	C(25)–C(26)	1.531 (7)
C(13)–C(15)	1.512 (6)	C(25)–C(27)	1.492 (8)
C(2)–C(28)	1.466 (6)	C(3)–C(30)	1.523 (6)
C(28)–O(1)	1.194 (6)	C(30)–O(3)	1.164 (6)
C(28)–O(2)	1.347 (5)	C(30)–O(4)	1.347 (6)
O(2)–C(29)	1.450 (6)	O(4)–C(31)	1.440 (5)

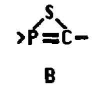
Table II. Bond Angles (deg) with Estimated Standard Deviations in Parentheses for Compound **5**

C(1)–S(1)–C(3)	97.4 (2)	C(2)–P(1)–N(1)	109.2 (2)
S(1)–C(1)–P(1)	112.4 (2)	C(2)–P(1)–N(2)	113.2 (2)
C(1)–P(1)–C(2)	95.9 (2)	N(1)–P(1)–N(2)	106.3 (2)
P(1)–C(2)–C(3)	114.9 (3)	C(1)–P(2)–S(2)	108.5 (1)
C(2)–C(3)–S(1)	117.7 (3)	C(1)–P(2)–N(3)	110.6 (2)
P(1)–C(1)–P(2)	130.8 (2)	C(1)–P(2)–N(4)	104.3 (2)
S(1)–C(1)–P(2)	116.8 (2)	S(2)–P(2)–N(3)	111.8 (1)
C(1)–P(1)–N(1)	118.2 (2)	S(2)–P(2)–N(4)	116.4 (1)
C(1)–P(1)–N(2)	113.9 (2)	N(3)–P(2)–N(4)	105.0 (2)
P(1)–N(1)–C(4)	122.4 (2)	P(2)–N(3)–C(16)	119.2 (3)
P(1)–N(1)–C(7)	123.0 (3)	P(2)–N(3)–C(19)	120.1 (3)
C(4)–N(1)–C(7)	111.7 (3)	C(16)–N(3)–C(19)	120.7 (3)
N(1)–C(4)–C(5)	112.9 (3)	N(3)–C(16)–C(17)	116.6 (4)
N(1)–C(4)–C(6)	113.4 (3)	N(3)–C(16)–C(18)	115.4 (4)
C(5)–C(4)–C(6)	109.5 (3)	C(17)–C(16)–C(18)	108.6 (4)
N(1)–C(7)–C(8)	112.2 (4)	N(3)–C(19)–C(20)	114.3 (4)
N(1)–C(7)–C(9)	116.3 (4)	N(3)–C(19)–C(21)	114.1 (4)
C(8)–C(7)–C(9)	112.9 (4)	C(20)–C(19)–C(21)	108.5 (4)
P(1)–N(2)–C(10)	122.6 (3)	P(2)–N(4)–C(22)	115.4 (3)
P(1)–N(2)–C(13)	116.5 (3)	P(2)–N(4)–C(25)	117.0 (3)
C(10)–N(2)–C(13)	119.3 (3)	C(22)–N(4)–C(25)	120.6 (3)
N(2)–C(10)–C(11)	116.6 (4)	N(4)–C(22)–C(23)	116.8 (4)
N(2)–C(10)–C(12)	115.3 (4)	N(4)–C(22)–C(24)	112.7 (4)
C(11)–C(10)–C(12)	108.9 (4)	C(23)–C(22)–C(24)	111.0 (4)
N(2)–C(13)–C(14)	114.7 (3)	N(4)–C(25)–C(26)	117.6 (4)
N(2)–C(13)–C(15)	113.3 (3)	N(4)–C(25)–C(27)	113.5 (4)
C(14)–C(13)–C(15)	111.0 (3)	C(26)–C(25)–C(27)	107.4 (4)
P(1)–C(2)–C(28)	121.9 (3)	S(1)–C(3)–C(30)	114.2 (3)
C(3)–C(2)–C(28)	122.1 (3)	C(2)–C(3)–C(30)	127.9 (4)
C(2)–C(28)–O(1)	125.7 (4)	C(3)–C(30)–O(3)	124.4 (4)
C(2)–C(28)–O(2)	111.8 (4)	C(3)–C(30)–O(4)	109.5 (4)
O(1)–C(28)–O(2)	122.3 (4)	O(3)–C(30)–O(4)	126.1 (4)
C(28)–O(2)–C(29)	116.3 (4)	C(30)–O(4)–C(31)	112.9 (3)

λ^5-phosphathiirenes B in the photolysis of α-thioxophosphoranyl diazo compounds.



A



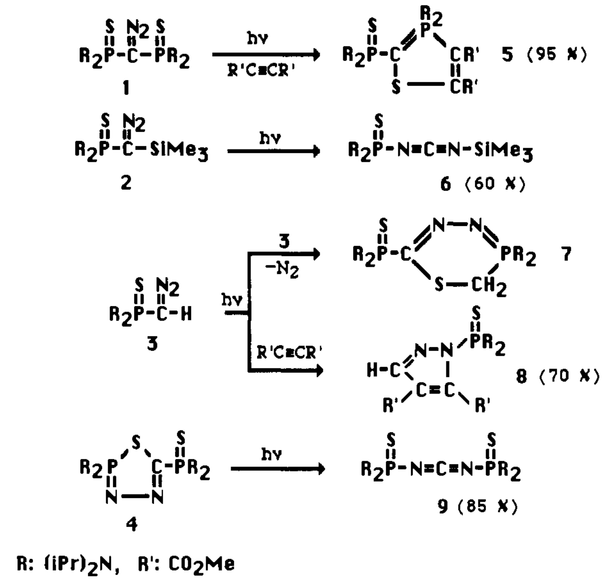
B

In the course of this study, we have never obtained the rearrangement of thioxophosphoranyl diazo compounds into 1,4,5,2λ^5-thiadiazaphospholes, expected by analogy with the carbon series, but we have observed other intriguing isomerizations of the diazo group which have never been precedented: the rearrangements into nitrilimines and into carbodiimides.

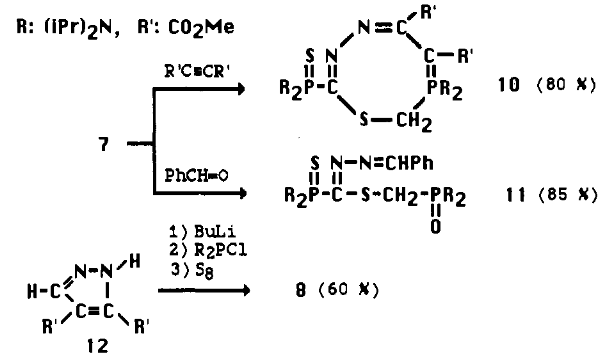
Results

The results observed in the photolysis of bis[bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1**),[2d] (thioxo-

Scheme I



Scheme II



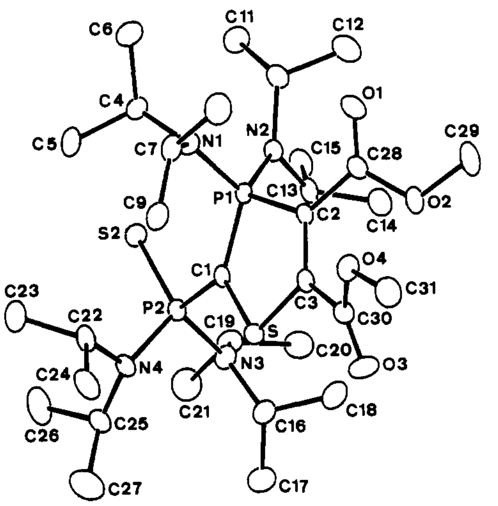


Figure 1. Molecular structure and labeling scheme of compound **5**.

Table III. Summary of Crystal and Intensity Collection Data for **5**·0.20C_6H_{12}

formula	$C_{32}H_{64.4}N_4O_4P_2S_2$	fw	695.4
cryst syst	monoclinic	space group	$P2_1/n$ (No. 14)
a, Å	15.446 (2)	temp, °C	20 ± 1
b, Å	10.505 (1)	λ, Å	0.71073
c, Å	28.737 (4)	d_{calcd}, g/cm^3	0.992
β, deg	93.49 (2)	μ, cm^{-1}	2.1
V, Å^3	4654	R^a	0.031
Z	4	$R_w{}^a$	0.034

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$; $w = [\sigma^2(F_o) + 0.0002F_o{}^2]^{-1}$.

phosphoranyl)(trimethylsilyl)diazomethane **2**,[2b] [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**),[2d] and 1,3,4,2λ^5-thiadiazaphosphole **4**,[6] in the presence or the absence of dimethyl acetylenedicarboxylate, are summarized in Scheme I. An X-ray crystal structure of **5** was done, whose results are presented in Tables I–III and in Figure 1. In order to prove the structure of compound **7**, its reactivity was studied, while pyrazole **8** was also prepared by another route as shown in Scheme II.

Experimental Section

All experiments were performed in an atmosphere of dry nitrogen. ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker AC80, AC200, WM250, or AM300 spectrometers. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported in ppm relative to $\mathrm{Me_4Si}$ as external standard. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% $\mathrm{H_3PO_4}$. IR spectra were recorded on a Perkin-Elmer 597 spectrometer, and UV spectra, on a Varian Cary 219 spectrophotometer. Mass spectra were obtained on a Ribermag R10 10E instrument. Photolysis was performed in glass and quartz tubes at 300 and 254 nm with a rayonnet photochemical reactor. Liquid chromatography was done on silica gel or neutral alumina. Melting points are uncorrected.

Synthesis of 1,3λ^5-Thiaphosphole 5. A benzene solution (5 mL) of bis[bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1**)[2d] (0.26 g, 0.46 mmol) and dimethyl acetylenedicarboxylate (0.078 g, 0.55 mmol) was irradiated at 300 nm for 20 h. After evaporation of the solvent under vacuum, **5** was isolated by column chromatography (90/10 hexane/ether; $R_f = 0.3$) and recrystallized from cold pentane as orange crystals (0.30 g; 95% yield): mp 160 °C; ^{31}P NMR ($\mathrm{CDCl_3}$) +69.5, +65.7 ($J_{\mathrm{PP}} = 48.6$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$) 1.28 (d, $J_{\mathrm{HH}} = 6.6$ Hz, 24 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 1.32 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 1.37 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 3.69 (s, 3 H, $\mathrm{CH_3O}$), 3.82 (s, 3 H, $\mathrm{CH_3O}$), 4.22 (sept d, $J_{\mathrm{HH}} = 7.0$ Hz, $J_{\mathrm{PH}} = 11.3$ Hz, 4 H, CH), 4.35 (sept d, $J_{\mathrm{HH}} = 7.0$ Hz, $J_{\mathrm{PH}} = 13.9$ Hz, 4 H, CH); ^{13}C NMR ($\mathrm{CDCl_3}$) 24.65 (d, $J_{\mathrm{PC}} = 3.6$ Hz, $\mathit{C}\mathrm{H_3CH}$), 24.78 (d, $J_{\mathrm{PC}} = 5.6$ Hz, $\mathit{C}\mathrm{H_3CH}$), 24.94 (d, $J_{\mathrm{PC}} = 4.4$ Hz, $\mathit{C}\mathrm{H_3CH}$), 25.34 (d, $J_{\mathrm{PC}} = 3.2$ Hz, $\mathit{C}\mathrm{H_3CH}$), 45.51 (d, $J_{\mathrm{PC}} = 144.9$ Hz, P=C), 47.33 (d, $J_{\mathrm{PC}} = 6.5$ Hz, CH), 48.17 (d, $J_{\mathrm{PC}} = 7.2$ Hz, CH), 51.58 (s, $\mathrm{CH_3O}$), 52.94 (s, $\mathrm{CH_3O}$), 107.0 (dd, $J_{\mathrm{PC}} = 136.6$ and 9.8 Hz, P–C), 148.13 (dd, $J_{\mathrm{PC}} = 27.2$ and 8.3 Hz, $\mathrm{PC}\mathit{C}$), 164.01 (dd, $J_{\mathrm{PC}} = 14.3$ and 1.5 Hz, CO), 164.44 (dd, $J_{\mathrm{PC}} = 16.6$ and 0.7 Hz, CO); IR ($\mathrm{CDCl_3}$) 1690 and 1725 cm^{-1} (CO); mass spectrum (EI) *m/e* 681 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{31}H_{62}N_4O_4P_2S_2}$: C, 54.68; H, 9.18; N, 8.23. Found: C, 54.85; H, 9.27; N, 8.34.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)carbodiimide (6). A benzene solution (10 mL) of [bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)diazomethane (**2**)[2b] (0.21 g, 0.56 mmol) was irradiated during 16 h at 300 nm. After evaporation of the solvent in vacuo, carbodiimide **6** was obtained as white crystals after purification on column chromatography (95/5 hexane/ether; $R_f = 0.7$) and recrystallization from acetonitrile (0.13 g; 60% yield): mp 137 °C; ^{31}P NMR ($\mathrm{C_6D_6}$) +51.0; ^{1}H NMR ($\mathrm{CDCl_3}$) 0.05 (d, $J_{\mathrm{PH}} = 0.5$ Hz, 9 H, $\mathrm{CH_3Si}$), 1.32 (d, $J(\mathrm{HH}) = 7.0$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 1.35 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 3.64 (sept d, $J_{\mathrm{HH}} = 7.0$ Hz, $J_{\mathrm{PH}} = 13.5$ Hz, 4 H, CH); ^{13}C NMR ($\mathrm{CDCl_3}$) 0.81 (s, $\mathrm{CH_3Si}$), 21.92 and 22.30 (s, $\mathit{C}\mathrm{H_3CH}$), 46.35 (d, $J_{\mathrm{PC}} = 2.9$ Hz, CH), 128.42 (d, $J_{\mathrm{PC}} = 42.2$ Hz, NCN); IR ($\mathrm{C_6H_6}$) 2161 cm^{-1} (NCN). Anal. Calcd for $\mathrm{C_{16}H_{37}N_4SiPS}$: C, 51.02; H, 9.90; N, 14.88. Found: C, 49.80; H, 9.99; N, 14.81.

Synthesis of 1,3,4-Thiadlaza-1,6-dihydro-5λ^5-phosphinine 7. A deuterated benzene solution of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**)[2d] was irradiated at 254 nm for 24 h. Compound **7** was characterized and used for further experiments without purification: ^{31}P NMR ($\mathrm{C_6D_6}$) +62.7, +4.1 ($J_{\mathrm{PP}} < 1$ Hz); ^{1}H NMR ($\mathrm{C_6D_6}$) 1.03 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 12 H, $\mathrm{CH_3}$), 1.20 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{CH_3}$), 1.44 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 12 H, $\mathrm{CH_3}$), 1.46 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 12 H, $\mathrm{CH_3}$), 2.54 (t-like, $J_{\mathrm{PH}} = 3.7$ Hz, 2 H, $\mathrm{CH_2}$), 3.41 (sep d, $J_{\mathrm{PH}} = 16.4$ Hz, $J_{\mathrm{HH}} = 7.0$ Hz, 2 H, CH), 3.45 (sep d, $J_{\mathrm{PH}} = 16.6$ Hz, $J_{\mathrm{HH}} = 6.8$ Hz, 2 H, CH), 4.05 (sep d, $J_{\mathrm{PH}} = 15.9$ Hz, $J_{\mathrm{HH}} = 6.8$ Hz, 4 H, CH); ^{13}C NMR ($\mathrm{C_6D_6}$) 20.27 (dd, $J_{\mathrm{PC}} = 3.6$ and 66.5 Hz, $\mathrm{CH_2}$), 23.28 (m, $\mathrm{CH_3}$), 47.23 (d, $J_{\mathrm{PC}} = 3.6$ Hz, CH), 48.10 (d, $J_{\mathrm{PC}} = 5.4$ Hz, CH), 132.43 (dd, $J_{\mathrm{PC}} = 45.9$ and 171.8, C=N).

Synthesis of Pyrazole 8 by Photolysis of 3. A toluene solution (10 mL) of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**)[2d] (0.48 g, 1.58 mmol) and dimethyl acetylenedicarboxylate (0.44 g, 3.10 mmol) was irradiated at 254 nm for 3 h. After evaporation of the solvent, purification on column chromatography (95/5 hexane/ether; $R_f = 0.3$), and recrystallization in a pentane/toluene solution, **8** was obtained as pale yellow crystals (0.49 g; 70% yield): mp 136 °C; ^{31}P NMR ($\mathrm{CDCl_3}$) +59.0; ^{1}H NMR ($\mathrm{CDCl_3}$) 1.16 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 1.31 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 12 H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 3.80 (sept d, $J_{\mathrm{HH}} = 6.8$ Hz, $J_{\mathrm{PH}} = 18.5$ Hz, 4 H, $\mathrm{CH_3C}\mathit{H}$), 3.83 (s, 3 H, $\mathrm{CH_3O}$), 3.98 (s, 3 H, $\mathrm{CH_3O}$), 8.96 (d, $J_{\mathrm{PH}} = 2.3$ Hz, CH=N); ^{13}C NMR ($\mathrm{CDCl_3}$) 22.51 (d, $J_{\mathrm{PC}} = 2.4$ Hz, $\mathit{C}\mathrm{H_3CH}$), 22.60 (d, $J_{\mathrm{PC}} = 3.0$ Hz, $\mathit{C}\mathrm{H_3CH}$), 48.35 (d, $J_{\mathrm{PC}} = 5.3$ Hz, $\mathrm{CH_3}\mathit{C}\mathrm{H}$), 51.86 (s, $\mathrm{CH_3O}$), 52.56 (s, $\mathrm{CH_3O}$), 114.63 (d, $J_{\mathrm{PC}} = 4.8$ Hz, $\mathrm{NC}\mathit{C}$), 141.31 (d, $J_{\mathrm{PC}} = 13.7$ Hz, C=N), 146.35 (d, $J_{\mathrm{PC}} = 8.0$ Hz, N–C=C), 162.09 (s, CO), 162.65 (s, CO); IR ($\mathrm{CDCl_3}$) 1730 cm^{-1} (CO); mass spectrum (EI) *m/e* 446 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{19}H_{35}N_4O_4PS}$: C, 51.10; H, 7.90; N, 12.55. Found: C, 50.95; H, 7.98; N, 12.51.

Synthesis of Bis[bis(diisopropylamino)thioxophosphoranyl]carbodiimide (9). A benzene solution (30 mL) of 1,3,4,2λ^5-thiadiazaphosphole **4**[6] (0.5 g, 0.85 mmol) was irradiated during 16 h at 254 nm. After evaporation of the solvent in vacuo, carbodiimide **9** was obtained as white crystals after purification on column chromatography (80/20 hexane/ether; $R_f = 0.7$) and recrystallization from cold pentane (0.42 g; 85% yield): mp 137 °C; ^{31}P NMR ($\mathrm{CDCl_3}$) +50.0; ^{1}H NMR ($\mathrm{CDCl_3}$) 1.33 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 24 H, $\mathrm{CH_3}$), 1.37 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 24 H, $\mathrm{CH_3}$), 3.68 (sept d, $J_{\mathrm{HH}} = 6.8$ Hz, $J_{\mathrm{PH}} = 19.38$ Hz, 8 H, CH); ^{13}C NMR ($\mathrm{CDCl_3}$) 21.94 and 22.33 (s, $\mathrm{CH_3}$), 46.40 (d, $J_{\mathrm{PC}} = 6$ Hz, CH), 46.45 (d, $J_{\mathrm{PC}} = 5.2$ Hz, CH), 127.43 (t, $J_{\mathrm{PC}} = 10$ Hz, NCN); IR ($\mathrm{CDCl_3}$) 2170 cm^{-1} (NCN); mass spectrum (EI) *m/e* 566 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{25}H_{56}N_6P_2S_2}$: C, 52.97; H, 9.96; N, 14.83. Found: C, 52.90; H, 10.00; N, 14.95.

Synthesis of Eight-Membered-Ring 10. To a benzene solution of **7** (1.38 mmol), prepared as mentioned above, was added neat dimethyl acetylenedicarboxylate (0.20 g, 1.41 mmol). The solution was heated for 3 h at 60 °C. After evaporation of the solvent and purification on column chromatography (50/50 hexane/ether; $R_f = 0.3$), **10** was obtained as a pale yellow oil (0.80 g; 80% yield): ^{31}P NMR ($\mathrm{CDCl_3}$) +60.3, +59.2 ($J_{\mathrm{PP}} = 2.2$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$) 1.30 (d, $J_{\mathrm{HH}} = 7.3$ Hz, 48 H, $\mathrm{CHC}\mathit{H}_3$), 3.11 (dd, $J_{\mathrm{PH}} = 7.4$ and 1.8 Hz, 2 H, $\mathrm{CH_2}$), 3.50 (s, 3 H, $\mathrm{OCH_3}$), 3.65 (s, 3 H, $\mathrm{OCH_3}$), 3.80 (m, 8 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$) 23.76 (d, $J_{\mathrm{PC}} = 2.9$ Hz, $\mathit{C}\mathrm{H_3CH}$), 23.80 (d, $J_{\mathrm{PC}} = 4.0$ Hz, $\mathit{C}\mathrm{H_3CH}$), 25.03 (d, $J_{\mathrm{PC}} = 2.8$ Hz, $\mathit{C}\mathrm{H_3CH}$), 40.92 (dd, $J_{\mathrm{PC}} = 4.0$ and 99.3 Hz, $\mathrm{CH_2}$), 48.02 (d, $J_{\mathrm{PC}} = 5.3$ Hz, CH), 48.87 (d, $J_{\mathrm{PC}} = 5.4$ Hz, CH), 49.98 (d, $J_{\mathrm{PC}} = 1.4$ Hz, $\mathrm{CH_3O}$), 51.90 (s, $\mathrm{CH_3O}$), 67.95 (dd, $J_{\mathrm{PC}} = 1.7$ and 159.5 Hz, P=C), 152.85 (dd, $J_{\mathrm{PC}} = 7.7$ and 2.4 Hz, CC=N), 156.85 (d, $J_{\mathrm{PC}} = 144.3$ Hz, PCN), 166.98 (d, $J_{\mathrm{PC}} = 9.5$ Hz, C=O), 167.63 (d, $J_{\mathrm{PC}} = 18.0$ Hz, C=O); IR ($\mathrm{CDCl_3}$) 1730 (C=O), 1650 and 1565 (CN) cm^{-1}; mass spectrum (EI) *m/e* 722 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{32}H_{64}N_6O_4P_2S_2}$: C, 53.16; H, 8.92; N, 11.63. Found: C, 53.01; H, 8.98; N, 11.63.

Synthesis of Hydrazone 11. To a benzene solution of **7** (0.52 mmol), prepared as mentioned above, was added neat benzaldehyde (0.055 g, 0.52 mmol). The solution was heated for 3 h at 60 °C. After evaporation of the solvent and purification on column chromatography (80/20 hexane/ether; $R_f = 0.7$), **11** was obtained as a yellow oil (0.30 g; 85% yield): ^{31}P NMR ($\mathrm{CDCl_3}$) +62.5, +25.6 ($J_{\mathrm{PP}} = 4.8$ Hz); ^{1}H NMR ($\mathrm{CDCl_3}$) 1.21 (d, $J_{\mathrm{HH}} = 6.7$ Hz, 24 H, $\mathrm{CH_3}$), 1.40 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{CH_3}$), 1.42 (d, $J_{\mathrm{HH}} = 7.0$ Hz, 12 H, $\mathrm{CH_3}$), 3.41 (sep d, $J_{\mathrm{PH}} = 15.8$ Hz, $J_{\mathrm{HH}} = 6.7$ Hz, 4 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 3.78 (d, $J_{\mathrm{PH}} = 12.0$ Hz, 2 H, $\mathrm{CH_2}$), 3.90 (sep d, $J_{\mathrm{PH}} = 15.8$ Hz, $J_{\mathrm{HH}} = 7.0$ Hz, 4 H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 7.40–7.77 (m, 5 H, H aromatic), 7.99 (d, $J_{\mathrm{PH}} = 1.5$ Hz, 1 H, CH=N); ^{13}C NMR ($\mathrm{CDCl_3}$) 23.13 (d, $J_{\mathrm{PC}} = 1.2$ Hz, $\mathit{C}\mathrm{H_3CH}$), 23.41 (d, $J_{\mathrm{PC}} = 1.0$ Hz, $\mathit{C}\mathrm{H_3CH}$), 23.88 (d, $J_{\mathrm{PC}} = 3.3$ Hz, $\mathit{C}\mathrm{H_3CH}$), 23.99 (d, $J_{\mathrm{PC}} = 2.4$ Hz, $\mathit{C}\mathrm{H_3CH}$), 32.26 (dd, $J_{\mathrm{PC}} = 106.0$ and 2.8 Hz, $\mathrm{CH_2}$), 46.30 (d, $J_{\mathrm{PC}} = 4.8$ Hz, $\mathit{C}\mathrm{HCH_3}$), 48.27 (d, $J_{\mathrm{PC}} = 5.1$ Hz, $\mathit{C}\mathrm{HCH_3}$), 128.21 (s, $\mathrm{C_m}$), 128.74 (s, $\mathrm{C_o}$), 131.06 (s, $\mathrm{C_p}$), 134.03 (d, $J_{\mathrm{PC}} = 1.4$ Hz, $\mathrm{C_i}$), 153.90 (d, $J_{\mathrm{PC}} = 2.6$ Hz, CH=N), 161.34 (dd, $J_{\mathrm{PC}} = 142.7$ and 6.5 Hz, C=N); IR ($\mathrm{CDCl_3}$) 1605 (C=N) cm^{-1}; mass spectrum (EI) *m/e* 686 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{33}H_{64}N_6OP_2S_2}$: C, 57.69; H, 9.39; N, 12.23. Found: C, 57.78; H, 9.51; N, 11.10.

Synthesis of Pyrazole 8 from Pyrazole 12. To a THF solution of pyrazole **12**[8] (0.37 g, 2 mmol), at −78 °C, was added dropwise the stoichiometric amount of BuLi (1.38 mL, 1.6 M in hexane). After the mixture was stirred for 10 min at −78 °C a THF solution of bis(diisopropylamino)chlorophosphane (0.53 g, 2 mmol) was added. The solution was stirred for 2 h at room temperature, and a stoichiometric amount of elemental sulfur (0.064 g) was added. After being heated at 50 °C for 5 h, the solvent was removed under vacuum and the residue was treated as mentioned above leading to **8** in 60% yield (0.53 g).

Synthesis of 15. To a toluene solution of bis(diisopropylamino)phosphane[7] (0.45 g, 1.94 mmol) and ethyldiisopropylamine (0.30 g, 2.33 mmol), at −80 °C, was added dropwise, the stoichiometric amount of *p*-tolyl chlorothionoformate (0.36 g, 1.94 mmol). After the solution was

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warmed up to room temperature and the solvent was removed, the residue was treated with pentane and filtered. After evaporation and recrystallization in a toluene/pentane solution, **15** was obtained as orange crystals (0.70 g; 95% yield): mp 76 °C; ^{31}P NMR (CDCl$_3$) +73.6; ^{1}H NMR (CDCl$_3$) 1.24 (d, J_{HH} = 6.7 Hz, 12 H, CH_3CH), 1.28 (d, J_{HH} = 6.7 Hz, 12 H, CH_3CH), 2.35 (s, 3 H, CH_3C), 3.50 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 11.6 Hz, 4 H, CH$_3$CH), 6.89 and 7.20 (d, J_{HH} = 8.4 Hz, 4 H, H aromatic); ^{13}C NMR (CDCl$_3$) 20.79 (s, CH$_3$C), 23.90 (d, J_{PC} = 6.5 Hz, CH$_3$CH), 24.17 (d, J_{PC} = 6.4 Hz, CH$_3$CH), 49.11 (d, J_{PC} = 12.17 Hz, CH$_3$$C$H), 121.52, 129.90, 135.41, 152.97 (s, C aromatic), 240.60 (d, J_{PC} = 36.3 Hz, C=S); mass spectrum (EI) m/e 382 (M$^+$). Anal. Calcd for $C_{20}H_{35}N_2OPS$: C, 62.79; H, 9.22; N, 7.32. Found: C, 62.98; H, 9.32; N, 7.16.

X-ray Crystal Structure of 5. The selected crystal was a red plate of 0.55 × 0.40 × 0.15 mm dimensions. It was glued on a glass fiber and mounted on an Enraf-Nonius CAD 4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections in the range $6° < \theta < 11°$. A summary of crystal and intensity collection data is given in Table III. A total of 8487 reflections were collected ($+h,+k,\pm l$, $2\theta_{max} = 50°$) by procedures described elsewhere.[9] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Intensity data were corrected for Lorentz-polarization.[10] No absorption corrections were made.

The structure was solved by direct methods using the SHELXS-86 program.[11] Equivalent reflections $0kl$ and $0k\bar{l}$ were merged (R_{av} = 0.025), and 3084 independent reflections, having $F_o^2 > 2\sigma(F_o^2)$ were used in following calculations. Successive Fourier maps and full-matrix least-squares refinement cycles, using the SHELX-76 program,[12] revealed the positions of all non-hydrogen atoms and the presence of crystallization solvent, i.e. hexane. Temperature factors being kept fixed, the occupancy factors of hexane's atoms were first refined and then kept fixed to 0.20. All non-hydrogen atoms were refined anisotropically, except the solvent ones. After their location on a difference-Fourier map, hydrogen atoms, except those of hexane, were introduced in calculations in constrained geometry (C–H = 0.97 Å) with general isotropic U temperature factors, first allowed to vary, and then kept fixed to 0.09 Å^2 for methyls and to 0.06 Å^2 for other ones.

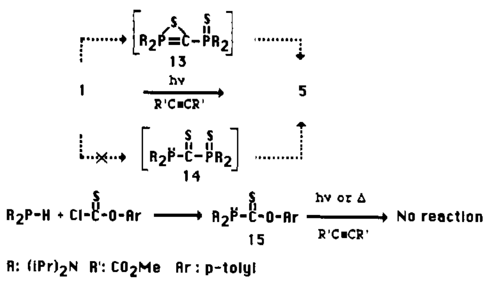
The atomic scattering factors, including anormalous dispersion effects, were taken from ref 13 and from Stewart et al.[14] for the hydrogen atoms.

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.031$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2} = 0.034$ with the weighting scheme $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n-m)]^2 = 1.47$ with n = 3084 observations and m = 408 variables. An analysis of variance showed no unusual trends. In the last cycle of refinement, the shifts for all parameters were less than 0.005σ, except for hexane parameters. A final difference Fourier map showed a residual electron density 0.33 e/Å^3. All calculations were performed on a Microvax 3400 DEC computer.

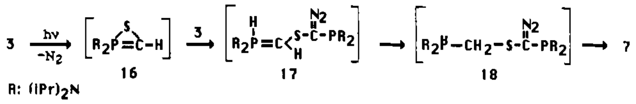
Discussion

We first chose to study the photolytic behavior of bis[bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1**)[2d] in the hope that the bulky substituents would help in kinetically stabilizing the expected phosphathiirene **13**. In fact, when the photolysis of **1** was carried out in the absence of trapping agent, a complicated mixture of unidentified products was obtained. In marked contrast, when **1** was irradiated at 300 nm, in the presence of a slight excess of dimethyl acetylenedicarboxylate, a very clean reaction occurred leading to 1,3λ^5-thiaphosphole **5** in 95% yield (Scheme I). The thermal ellipsoid diagram of this new type of phosphorus heterocycle **5** is shown in Figure 1 along with the atom-numbering scheme. Bond lengths and angles are reported in Table I and II, respectively. It is of interest to note that, in contrast with the structure of thiophenes derivatives,[15] the five-membered ring in **5** is not planar [S1C1P1C2 = 13.0 (2)°; C1P1C2C3 = −10.7 (3)°; C3S1C1P1 = −11.4 (2)°]. The most important point from this X-ray diffraction study is the demonstration that indeed the sulfur atom has migrated from phosphorus to carbon. The formation of thiaphosphole **5** formally results from an insertion of the alkyne into the phosphorus–sulfur bond of phosphathiirene **13**; this reaction is strictly analogous to that reported with thiirenes.[16] However, since N-phosphanylimines are known to undergo 3 + 2 cycloadditions with dipolarophiles,[17] an alternative mechanism could have been the transient formation of phosphanyl thioketone **14**, followed by a 2 + 3 cycloaddition. This hypothesis was easily ruled out by preparing and isolating compound **15**; no reaction occurred when **15** was irradiated or heated with dimethyl acetylenedicarboxylate (Scheme III).

Scheme III



Scheme IV



Since the phosphorus–carbon bond of phosphathiirenes should present a strong ylidic character, one could hope to decrease its reactivity in stabilizing the negative charge at carbon using a silyl substituent. Surprisingly, when the (thioxophosphoranyl)(trimethylsilyl)diazomethane **2**[2b] was irradiated at 300 nm for 15 h, [bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)carbodiimide (**6**) was obtained in 60% yield, along with several unidentified products (Scheme I). All attempts to trap any possible intermediates failed. To the best of our knowledge, such a rearrangement (diazo compound–carbodiimide) has never been observed, and at this stage, it was difficult to postulate any mechanism.

From these results, it was clear that the diazo carbon substituent was of considerable importance on the fate of the reaction. Thus, we investigated the photochemical behavior of the C-unsubstituted [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**).[2d] Irradiation of a benzene solution of **3** at 254 nm led to six-membered heterocycle **7**, in nearly quantitative yield (according to NMR spectroscopy). All attempts to isolate compound **7** failed; however, its structure was deducted from the spectroscopic data and chemical reactivity. The presence of two λ^5-phosphorus atoms, each of them substituted by two diisopropylamino groups, was shown by two quintets at +64 ($^3J_{PH}$ = 16.4 Hz) and +4 ($^3J_{PH}$ = 16.6 Hz) in the ^{31}P NMR spectrum. It was clear from ^{13}C NMR spectra (J modulation sequence) that the high-field phosphorus was directly bonded to a CH$_2$ group (20.3, dd, $^1J_{PC}$ = 66.5 Hz, $^3J_{PC}$ = 3.6 Hz) and that the low-field phosphorus atom was directly bonded to a non-hydrogen-substituted sp^2 carbon (132.4, dd, $^1J_{PC}$ = 171.8 Hz, $^3J_{PC}$ = 45.9 Hz). The CH$_2$ group appeared at 2.54 (t-like, J_{PH} = 3.7 Hz) in the ^{1}H NMR spectrum confirming the proposed structure. In order to remove all possible ambiguities, two reactions, typical of λ^5P=N double-bonded compounds were carried out. An insertion reaction was observed

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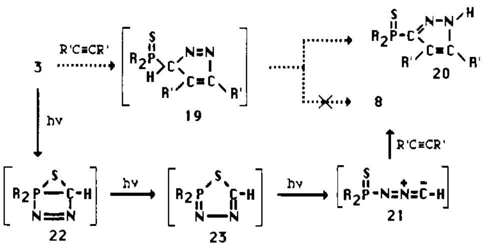
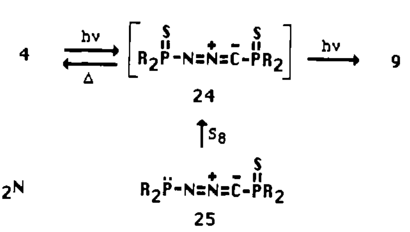
Scheme V



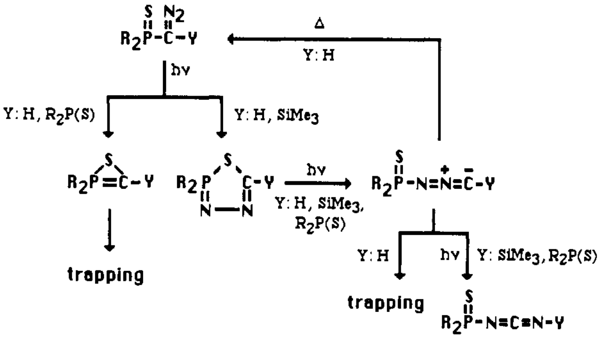
R: (iPr)$_2$N R': CO$_2$Me

Scheme VI



R: (iPr)$_2$N

Scheme VII



when dimethyl acetylenedicarboxylate was added to **7** leading to eight-membered-ring **10** in 80% yield, while a Wittig reaction occurred when benzaldehyde was used, giving rise to **11** in 85% isolated yield (Scheme II). In both cases the spectroscopic data clearly demonstrated the P–CH$_2$–S–C–P skeleton.

The most reasonable hypothesis for the formation of 1,3,4-thiadiaza-1,6-dihydro-5λ^5-phosphinine **7** is to postulate the transient formation of a phosphathiirene **16**. A CH addition of the starting material **3** to the PS bond of **16** bond would occur, leading to **17**, which would rearrange by 1,2-hydrogen shift into **18**; then an intramolecular Staudinger reaction would give rise to the observed product **7** (Scheme IV).

In the hope of trapping the transient phosphathiirene **16**, diazo compound **3** was irradiated at 254 nm in the presence of an excess of dimethyl acetylenedicarboxylate. Surprisingly, *N*-(thioxophosphoranyl)pyrazole **8** was obtained in 70% yield (Scheme I). It was clear from the spectroscopic data that the phosphorus atom was no longer directly bonded to a carbon atom and that a CH=N group was present in the molecule [^{13}C NMR (J modulation sequence) 141.31 (d, $^3J_{PC}$ = 13.7 Hz); ^{1}H NMR 8.96 (d, J_{PH} = 2.3 Hz, 1 H)]. To ascertain the structure, pyrazole **8** was synthesized by a classical route: treatment of pyrazole **12**[8] with BuLi, followed by addition of bis(diisopropylamino)chlorophosphane, and subsequent oxidation with elemental sulfur (Scheme II).

A simple way of rationalizing the formation of **8** would be to postulate a 2 + 3 cycloaddition[18] of the diazo group of **3** to the electron-poor alkyne giving 3*H*-pyrazole **19**, followed by a 1,3-shift of the bis(diisopropylamino)thioxophosphoranyl group. Indeed, 3*H*-pyrazoles are known to spontaneously rearrange into the corresponding 1*H*-pyrazoles.[19] However, the migratory ability of hydrogen is much higher than that expected for a bulky thioxophosphoranyl group and thus pyrazoline **20** should be formed instead of **8**. On the other hand, pyrazoline **8** is formally the 2 + 3 cycloadduct expected from the reaction of dimethyl acetylenedicarboxylate to nitrilimine **21**.[18] Although several examples of rearrangement of nitrilimines into the more thermodynamically stable diazo isomers have already been reported,[2b,d,20] the reverse rearrangement has never been observed. In the case of thioxophosphoranyl derivative **3**, one could think that the formation of nitrilimine **21** could occur through **22** and **23** (Scheme V).

In order to check this hypothesis, a benzene solution of a compound analogous to **23**, namely the 1,3,4,2λ^5-thiadiazaphosphole **4**,[6] was irradiated at 254 nm for 14 h. A clean reaction occurred leading to bis[bis(diisopropylamino)thioxophosphoranyl]carbodiimide (**9**) in 85% yield (Scheme I). Since nitrilimines are known to isomerize photochemically to carbodiimide,[21] this result strongly supports our hypothesis. All attempts to trap the transient bis[bis(diisopropylamino)thioxophosphoranyl]nitrilimine (**24**) by irradiating **4** in the presence of dipolarophiles failed, but we have to keep in mind that **24**, obtained by sulfurization of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**25**) was not spectroscopically observable and underwent a 1,5-electrocyclic ring closure to thiadiazaphosphole **4**[6] (Scheme VI).

The difficulty is to explain the quite different behavior of (thioxophosphoranyl)diazomethane **3** in the presence and in the absence of dimethyl acetylenedicarboxylate. The most reasonable hypothesis is to postulate that **22** is the common primary rearrangement product which can either quickly isomerize into 1,3,4,2λ^5-thiadiazaphosphole **23** and then nitrilimine **21** or slowly loose nitrogen to give phosphathiirene **16**. As mentioned above, nitrilimines easily rearrange into diazo compounds,[2b,d,20] and thus, in the absence of a nitrilimine trapping agent, **21** can isomerize into the starting diazo **3**. Although it is difficult to carried out quantitative kinetic measurements, in photolytic reactions, we observed that, in the same experimental conditions, **3** was transformed into **7** in 24 h, while the reaction giving pyrazole **8** was over in 3 h.

Conclusion

From these results it appeared that, depending on the nature of the diazo carbon substituent, the photolysis of thioxophosphoranyl diazo compounds leads to transient λ^5-phosphathiirenes with loss of nitrogen or/and to 1,3,4,2λ^5-thiadiazaphospholes, which under irradiation give rise to nitrilimines, which can be trapped or which rearrange into carbodiimides (Scheme VII). Note that, until now, the rearrangement of diazo compounds into diazirines was the only known structural isomerization of the diazo group.

Supplementary Material Available: For **5**, tables of fractional atomic coordinates, thermal parameters, all bond distances and angles, and least-squares plane equations (5 pages); a table of structure factors (15 pages). Ordering information is given on any current masthead page.

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