Evidence for α-Phosphanyl-α′-sulfinylcarbene to α-Phosphoranyl-α′-sulfanylcarbene Rearrangement. Synthesis of 2-Oxo- and 2-Thioxo-1,2λ⁵-azaphosphetanes

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[Bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane (1) reacts with *p*-toluenesulfinyl chloride and *p*-toluenesulfonyl chloride, affording the same 2-oxo-1,2λ⁵-azaphosphetane **6** in 85 and 80% yield, respectively. These results are rationalized by the transient formation of α-phosphanyl-α′-sulfinylcarbene **3**, which rearranges into α-phosphoranyl-α′-sulfanylcarbene **5** via an intramolecular Wittig-type reaction involving the multiple-bond character of phosphanylcarbenes. [Bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)diazomethane reacts with *p*-tolylsulfanyl chloride, giving 2-thioxo-1,2λ⁵-azaphosphetane **6′** in 86% yield. The same derivative **6′** is also obtained by photolysis of *C*-thioxophosphoranyl *C*-sulfanyl phosphorus ylide **13**. Derivative **6′** has been characterized by X-ray crystallography: $C_{20}H_{35}N_2PS_2$, space group $P2_1/n$, a = 26.175 (7) Å, b = 9.945 (3) Å, c = 8.966 (3) Å, V = 2332.8 Å³.

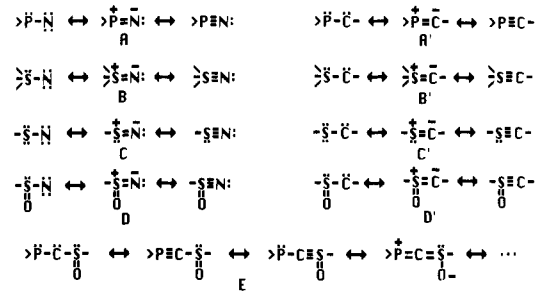
We have recently shown that nitrenes and carbenes can be stabilized[1] by the presence of a phosphanyl group directly bonded to the electron-deficient moiety, due to the delocalization of the lone pairs (n_π(P) → p_π(N or C) and to some extent n_π(N or C) → d_π(P). Thus, phosphanylnitrenes, A,[2] and phosphanylcarbenes, A′,[3] possess considerable multiple-bond character, as demonstrated by typical cycloaddition reactions. However, phosphanylcarbenes, A′, also present a "typical" carbene reactivity, giving for example, cyclopropanation reactions[3h] and CH insertions.[3f] The sulfur analogues of phosphanylnitrenes in the formal oxidation states 4 (B) and 2 (C) can be stable[4] and are usually formulated with a sulfur–nitrogen triple bond. In highly significant papers, Seppelt et al.[5] reported on the synthesis and structure, at low temperature, of (trifluoroethylidyne)sulfur trifluoride (B′), a compound with a triple-bond between sulfur and carbon. Upon warming up, it dimerizes to give the corresponding olefin, $(CF_3)(SF_3)C{=}C(CF_3)(SF_3)$, thus showing carbene reactivity. Ab initio calculations[6] predicted that α-sulfanylcarbene (C′) could present two geometric isomers (rotation barrier trans → cis of 41 kcal/mol) with a short carbon–sulfur bond length (1.67 Å) and thus will be best regarded as a sulfur–carbon double-bonded compound. However no experimental evidence[7] has corroborated these predictions so far, although α,α′-disulfanylcarbenes have been claimed to be "relatively stable".[8] Lastly, it has been shown that sulfinylnitrene (D) should be considered as oxathyazyne[9] while no multiple bond behavior has been reported for the carbene analogue (D′)[7] (Scheme I).

It was of interest to try synthesizing a carbene substituted both by a phosphanyl group and a sulfinyl group,[10] since this species should be highly stabilized due to the possible delocalization as indicated in Scheme I. Here we report evidence for the transient formation of such an electron-deficient species and its rearrangement into an α-phosphoranyl-α′-sulfanylcarbene; intramolecular trapping affords original phosphorus heterocycles, namely, 1,2λ⁵-azaphosphetanes.

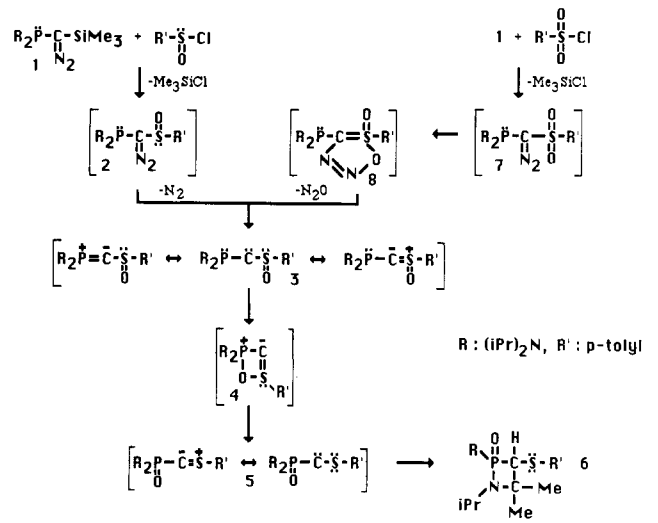
Results and Discussion

Diazo derivatives are classical precursors of carbenes.[11]

Scheme I



Scheme II



Bearing in mind the stabilizing effect of the diisopropylamino group,[2c,3f,h] we attempted to synthesize [bis(diiso-

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(1) Bis(diisopropylamino)phosphanylnitrene is stable for a few hours, in solution, at room temperature[2c] while [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene can be isolated by flash distillation at 75–85 °C/10^{-2} mmHg.[3f]

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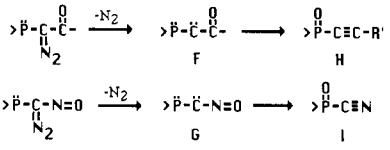
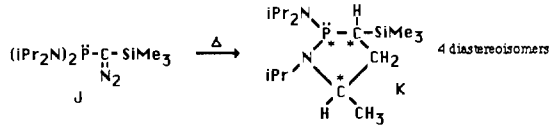
Scheme III



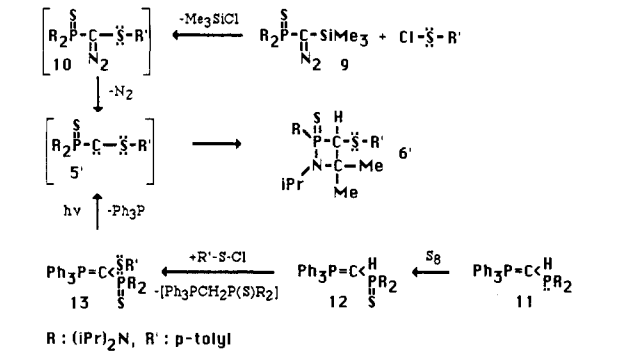
Scheme IV



propylamino)phosphanyl](*p*-tolylsulfinyl)diazomethane (**2**). We have already shown that the silylated diazo derivative **1** reacted with acyl chloride[2c] or nitrosyl chloride,[12] with elimination of trimethylchlorosilane and formation of the corresponding substituted diazo compound. When a toluene solution of **1** was treated with a stoichiometric amount of *p*-toluenesulfinyl chloride, at room temperature, evolution of nitrogen was observed and after workup 2-oxo-1,2λ⁵-azaphosphetane **6** was obtained in 85% yield along with the quantitative amount of trimethylchlorosilane (Scheme II).

It seems reasonable to postulate that under the experimental conditions used, the desired diazo derivative **2** was unstable and led to the corresponding α-phosphanyl α′-sulfinyl carbene **3**. As mentioned above, such a carbene possesses a multiple-bond character involving either the phosphorus or the sulfur atom. By analogy with the rearrangement observed with α-phosphanyl α′-keto carbene F[3] and α-phosphanyl α′-nitrosyl carbene G,[12] which give rise to phosphoranyl alkyne H and nitrile I, respectively (Scheme III), it is likely that an intramolecular Wittig-type reaction led to **5** via the four-membered ring **4**. In contrast with alkynes and nitriles, the "sulfur–carbon triple bond" reacts as a sulfanylcarbene and the formation of azaphosphetane **6** can be explained in terms of insertion of singlet carbene **5** into a carbon–hydrogen bond of an iso-

Scheme V



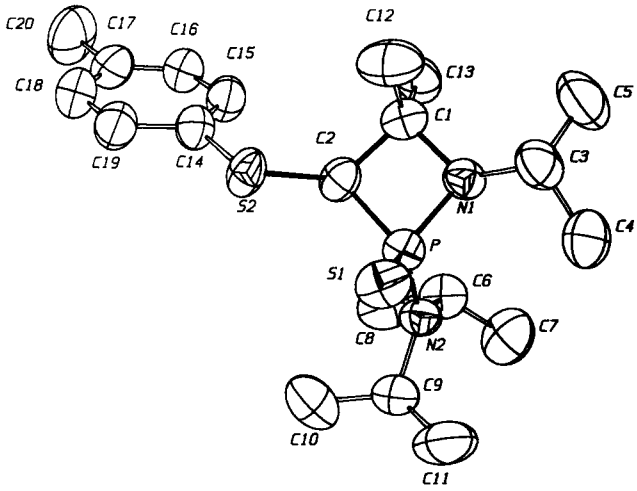


Figure 1. ORTEP plot of **6′** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for purposes of clarity.

Table I. Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

atom	*x*	*y*	*z*	*B*, Å²
S1	0.85068 (6)	0.1025 (2)	0.6550 (2)	5.06 (3)
S2	0.97877 (5)	0.1882 (2)	0.6331 (2)	4.92 (3)
P	0.88257 (4)	0.2068 (1)	0.8140 (1)	4.25 (3)
N1	0.8700 (1)	0.3718 (4)	0.8191 (4)	4.37 (8)
N2	0.8789 (1)	0.1420 (4)	0.9804 (4)	4.32 (8)
C1	0.9182 (2)	0.4155 (5)	0.7450 (5)	4.8 (1)
C2	0.9451 (2)	0.2751 (5)	0.7734 (5)	4.7 (1)
C3	0.8190 (2)	0.4296 (6)	0.7840 (6)	5.9 (1)
C4	0.7803 (2)	0.3621 (7)	0.8822 (8)	7.7 (2)
C5	0.8178 (3)	0.5800 (7)	0.8071 (9)	9.1 (2)
C6	0.8956 (2)	0.2230 (5)	1.1127 (6)	5.7 (1)
C7	0.8543 (3)	0.2232 (8)	1.2295 (7)	8.5 (2)
C8	0.9466 (3)	0.1805 (8)	1.1791 (7)	8.6 (2)
C9	0.8722 (2)	−0.0055 (5)	1.0113 (6)	5.8 (1)
C10	0.9114 (3)	−0.0907 (7)	0.9358 (9)	9.1 (2)
C11	0.8177 (3)	−0.0498 (6)	0.9857 (8)	8.2 (2)
C12	0.9110 (3)	0.4471 (7)	0.5796 (7)	8.0 (2)
C13	0.9442 (2)	0.5307 (5)	0.8288 (7)	6.6 (1)
C14	1.0429 (2)	0.2381 (5)	0.6576 (6)	5.0 (1)
C15	1.0606 (2)	0.3401 (6)	0.7505 (6)	5.6 (1)
C16	1.1126 (2)	0.3699 (6)	0.7623 (6)	5.7 (1)
C17	1.1475 (2)	0.3020 (6)	0.6828 (7)	6.3 (1)
C18	1.1300 (2)	0.1995 (6)	0.5877 (7)	7.2 (2)
C19	1.0787 (2)	0.1656 (6)	0.5772 (6)	6.1 (1)
C20	1.2036 (2)	0.3387 (9)	0.6926 (9)	9.6 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

propyl substituent. Note that the four-membered ring heterocycle **6** was formed exclusively (according to NMR data of the crude reaction mixture), in spite of the ratio

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(10) No evidence for heteroatom-substituted sulfinylcarbene has, as yet, been reported.

(11) For reviews, see: (a) Patai, S. *The chemistry of diazonium and diazo groups*; Wiley: New York, 1978. (b) Regitz, M. *Diazoalkanes*: Georg Thieme Verlag: Stuttgart, 1977. (c) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (d) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (e) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (f) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319.

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Table II. Bond Distances (Å)[a] and Angles (deg) for 6′

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
S1	P	1.932 (1)	N2	C9	1.503 (5)	C9	C11	1.504 (6)
S2	C2	1.782 (4)	C1	C2	1.581 (5)	C14	C15	1.384 (6)
S2	C14	1.758 (5)	C1	C12	1.521 (6)	C14	C19	1.399 (5)
P	N1	1.674 (3)	C1	C13	1.519 (5)	C15	C16	1.395 (5)
P	N2	1.631 (3)	C3	C4	1.519 (6)	C16	C17	1.356 (6)
P	C2	1.819 (4)	C3	C5	1.511 (6)	C17	C18	1.398 (6)
N1	C1	1.510 (4)	C6	C7	1.527 (6)	C17	C20	1.513 (6)
N1	C3	1.477 (5)	C6	C8	1.505 (7)	C18	C19	1.385 (6)
N2	C6	1.489 (5)	C9	C10	1.508 (6)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C2	S2	C14	105.4 (2)	N1	C1	C12	114.1 (3)	N2	C9	C10	112.4 (4)
S1	P	N1	117.7 (2)	N1	C1	C13	111.5 (3)	N2	C9	C11	111.9 (3)
S1	P	N2	115.2 (1)	C2	C1	C12	112.5 (3)	C10	C9	C11	115.0 (5)
S1	P	C2	115.1 (1)	C2	C1	C13	113.3 (4)	S2	C14	C15	125.6 (3)
N1	P	N2	110.3 (1)	C12	C1	C13	111.5 (4)	S2	C14	C19	116.2 (3)
N1	P	C2	79.6 (2)	S2	C2	P	115.3 (3)	C15	C14	C19	118.2 (4)
N2	P	C2	114.2 (2)	S2	C2	C1	122.8 (3)	C14	C15	C16	120.6 (4)
P	N1	C1	95.8 (2)	P	C2	C1	88.0 (2)	C15	C16	C17	121.8 (4)
P	N1	C3	123.6 (2)	N1	C3	C4	108.6 (3)	C16	C17	C18	118.0 (4)
C1	N1	C3	123.8 (3)	N1	C3	C5	112.3 (4)	C16	C17	C20	121.1 (5)
P	N2	C6	119.4 (2)	C4	C3	C5	110.0 (4)	C18	C17	C20	120.8 (4)
P	N2	C9	124.4 (2)	N2	C6	C7	110.6 (3)	C17	C18	C19	121.3 (4)
C6	N2	C9	114.5 (3)	N2	C6	C8	113.5 (4)	C14	C19	C18	120.1 (5)
N1	C1	C2	92.8 (2)	C7	C6	C8	111.4 (4)				

[a] Estimated standard deviations in parentheses. The atom-labeling scheme is shown in Figure 1.

of six methyl–CH bonds to one methine–CH bond and that only one of the possible diastereoisomers was observed. This result is in marked contrast with the exclusive formation of the five-membered ring K, as four diastereoisomers in the thermolysis of [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene (J)[3f] (Scheme IV).

We also investigated the reaction of **1** with *p*-toluenesulfonyl chloride and surprisingly the same azaphosphetane **6** was obtained in 80% yield. A possible mechanism could be an intramolecular [2 + 3] cycloaddition of the diazo moiety of **7** on a sulfur–oxygen double bond[13] leading to **8**. Then N_2O elimination would give the carbene intermediate **3**, the same one as in the previous reaction, and thus to the same final product **6** (Scheme II).

At the stage it was of interest to verify that carbene **5** was really an intermediate in these reactions and thus we tried to synthesize the corresponding diazo precursor. Actually, [bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)diazomethane (**9**) is easily available,[14] in contrast with its oxo analogue.[15] With *p*-tolylsulfanyl chloride, diazo **9** reacted instantaneously with nitrogen evolution and after workup 2-thioxo-1,2λ⁵-azaphosphetane, **6′**, was isolated in 86% yield as only one diastereoisomer (Scheme V). Compound **6′** was fully characterized by an X-ray crystal analysis. The atom-labeling scheme for **6′** is given on the ORTEP view of the molecule (Figure 1). Atomic coordinates are given in Table I, and bond lengths and angles are given in Table II. As expected, the diastereoisomer obtained possesses the diisopropylamino group and the *p*-tolylsulfanyl group in the trans position. The formation of the four-membered ring **6′** strongly supports the hypothesis of the transient formation of sulfanylcarbenes **5** and **5′**. However, since the diazo derivative **10** was not stable enough to be observed, we sought an alternative precursor. We found that the phosphorus ylide **13**, prepared by sulfuration of **11** and subsequent treatment with *p*-tolylsulfanyl chloride, undergoes a remarkably clean fragmentation into triphenylphosphane and thioxoazaphosphetane **6′**, when a 0.2 M benzene solution was irradiated (λ > 300 nm) for ca. 16 h at 0 °C (Scheme V). The cleavage of a phosphorus ylide, giving the corresponding carbene, has seldomly been observed and is strongly dependent on the nature of the ylide–carbone substituent.[16]

Conclusion

These results, as a whole, confirm the instability of α-sulfanyldiazo derivatives (such compounds have already been postulated but never spectroscopically characterized[7]), show the reluctance of the sulfur atom to be triple-bonded with carbon (while with nitrogen the multiple-bonded form is favored), and lastly confirm the ability of phosphanylcarbenes to react as multiple-bonded derivatives.

Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC80, WM250, or AM300 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR10 and a Perkin-Elmer lattice spectrometer (Mol 598), by using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used. Liquid chromatography was performed using silica gel.

Synthesis of 2-Oxo-1,2λ⁵-azaphosphetane 6 by Treatment of [Bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane, (1) with *p*-Toluenesulfinyl Chloride. To a benzene solution (10 mL) of **1**[3f] (0.5 g, 1.5 mmol) was added quickly, at room temperature, a benzene solution (10 mL) of *p*-toluenesulfinyl chloride (0.26 g, 1.5 mmol). After being stirred for 10 min, the solvent and trimethylchlorosilane were removed under vacuum, giving a white solid. Recrystallization from hexane yielded **6** (0.47 g, 85% yield) as white crystals: mp 75 °C, ^{31}P NMR (C_6D_6) +25 ppm; ^1H NMR ($CDCl_3$) 1.03 (d, J(HH) = 6.5 Hz, 3

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(15) Bis(diisopropylamino)phosphane derivatives cannot be converted into the corresponding oxides by classical reagents.
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H, CH_3CHN_{ring}), 1.13 (d, J(HH) = 6.7 Hz, 6 H, CH_3CHN), 1.17 (d, J(HH) = 6.7 Hz, 6 H, CH_3CHN), 1.21 (s, 3 H, CH_3C_{ring}), 1.24 (d, J(HH) = 6.5 Hz, 3 H, CH_3CHN_{ring}), 1.31 (s, 3 H, CH_3C_{ring}), 2.19 (s, 3 H, CH_3C_{aro}), 3.20 (sept d, J(HH) = 6.5 Hz, J(PH) = 14 Hz, 1 H, CHN_{ring}), 3.47 (m, J(HH) = 6.7 Hz, 2 H, CHN), 3.56 (d, J(PH) = 16 Hz, 1 H, PCH), 6.95, 7.17 (AB system, J_{AB} = 8.07 Hz, 4 H, H_{aro}); ^{13}C NMR ($CDCl_3$) 19.9 (s, CH_3C_{aro}), 21.63, 22.07, 22.40, 22.49 (s, CH_3CH), 23.0 (d, J(PC) = 4.6 Hz, CH_3C_{ring}), 29.11 (d, J(PC) = 19.6 Hz, CH_3C_{ring}), 43.6 (d, J(PC) = 2.6 Hz, CHN_{ring}), 45.3 (d, J(PC) = 5.3 Hz, CHN), 57.7 (d, J(PC) = 3.4 Hz, CH_3C_{ring}), 58.10 (d, J(PC) = 87.5 Hz, PCH), 128.69 (s, C_o), 129.35 (s, C_m), 132.20 (d, J(PC) = 11.3 Hz, C_i), 135.38 (s, C_p); IR (KBr) 1260 cm^{-1} (P=O); mass spectrum, m/e 382 (M^+). Anal. Calcd for $C_{20}H_{35}N_2POS$: C, 62.79; H, 9.22; N, 7.32. Found: C, 62.72; H, 9.22; N, 7.30.

Synthesis of 2-Oxo-1,2λ⁵-azaphosphetane 6 by Treatment of 1 with *p*-Toluenesulfonyl Chloride. Using the same experimental procedure described above, **6** was obtained in 80% yield.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl](*trimethylsilyl*)*diazomethane* (9). A hexane solution (20 mL) of [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane (**1**) (2 g, 5.8 mmol) and elemental sulfur (0.2 g, 6.2 mmol) was stirred at room temperature for 3 h. After filtration and evaporation of the solvent, **9** (1.6 g, 85% yield) was isolated by column chromatography (ether/hexane 10/90, R_f = 0.8) as a yellow oil: ^{31}P NMR (C_6D_6) +65ppm; ^{1}H NMR (C_6D_6) 0.55 (s, 9 H, $SiCH_3$), 1.40 (d, J(HH) = 7 Hz, 12 H, CH_3C), 1.50 (d, J(HH) = 7 Hz, 12 H, CH_3C), 3.8 (sept d, J(HH) = 7 Hz, J(PH) = 16 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) 0.31 (d, J(PC) = 0.7 Hz, $SiMe_3$), 23.61, 23.86, 24.22, 24.26 (s, CH_3C), 35.14 (d, J(PC) = 91.3 Hz, CN_2), 47.83 (d, J(PC) = 5.3 Hz, CHN), 48.10 (d, J(PC) = 3.0 Hz, CHN); IR (KBr) 2050 cm^{-1} (CN_2); mass spectrum, m/e 376 (M^+). Anal. Calcd for $C_{16}H_{37}N_4PSSi$: C, 51.03; H, 9.90; N, 14.88. Found: C, 50.86; H, 9.82; N, 14.72.

Synthesis of 2-Thioxo-1,2λ⁵-azaphosphetane 6′ by Treatment of 9 with *p*-Tolylsulfanyl Chloride. To a benzene solution (10 mL) of **9** (0.3 g, 0.8 mmol) was quickly added, at room temperature, a benzene solution (5 mL) of *p*-tolylsulfanyl chloride (0.13 g, 0.85 mmol). After being stirred for 10 min, the solvent and trimethylchlorosilane were removed under vacuum, giving a yellow residue. **6′** (0.27 g, 86% yield) was isolated by column chromatography (pentane/ether 90/10; R_f = 0.7) as white crystals: mp 88 °C; ^{31}P NMR (C_6D_6) +71 ppm; ^{1}H NMR ($CDCl_3$) 1.11 (d, J(HH) = 6.3 Hz, 3 H, CH_3CHN_{ring}), 1.29 (d, J(HH) = 7.0 Hz, 6 H, CH_3CHN), 1.30 (s, 3 H, CH_3C_{ring}), 1.35 (d, J(HH) = 7.0 Hz, 6 H, CH_3CHN), 1.38 (d, J(HH) = 6.3 Hz, 3 H, CH_3CHN_{ring}), 1.47 (d, J(PH) = 0.9 Hz, 3 H, CH_3C_{ring}), 2.29 (s, 3 H, CH_3C_{aro}), 3.38 (sept d, J(HH) = 6.3 Hz, J(PH) = 6.6 Hz, 1 H, CHN_{ring}), 3.80 (d, J(PH) = 15.5 Hz, 1 H, PCH), 3.94 (sept d, J(HH) = 7.0 Hz, J(PH) = 16.46 Hz, 2 H, CHN), 7.06, 7.33 (AB system, J_{AB} = 8 Hz, 4 H, H_{aro}); ^{13}C NMR ($CDCl_3$) 21.05 (s, CH_3C_{aro}), 21.80, 22.80, 22.89, 23.15, 23.94 (s, CH_3CH), 24.12 (d, J(PC) = 9 Hz, CH_3C_{ring}), 32.00 (d, J(PC) = 20.7 Hz, CH_3C_{ring}), 45.29 (s, CHN_{ring}), 47.33 (d, J(PC) = 3.77 Hz, CHN), 60.25 (s, CH_3C_{ring}), 61.20 (d, J(PC) = 70.2 Hz, PCH), 129.32 (s, C_o), 131.67 (s, C_m), 132.40 (d, J(PC) = 9.8 Hz, C_i), 137.00 (s, C_p); mass spectrum, m/e 398 (M^+). Anal. Calcd for $C_{20}H_{35}N_2PS_2$: C, 60.25; H, 8.85; N, 7.03. Found: C, 60.21; H, 8.84; N, 6.99.

Synthesis of *C*-Phosphanyl Phosphorus Ylide 11. To a stirred solution of methylenetriphenylphosphorane [freshly prepared from Ph_3PCH_3Br (7.14 g, 0.02 mol) in 200 mL of toluene and $NaNH_2$ (0.94 g, 0.024 mol)] was added dropwise, at 80 °C, bis(diisopropylamino)chlorophosphane (2.7 g, 0.01 mol) in 10 mL of toluene. The yellow solution turned orange and after cooling to room temperature the precipitate was filtered off and the solvent was evaporated under vacuum. The residue was recrystallized from acetonitrile to yield **11** (4.6 g, 92% yield) as bright orange crystals: mp 111 °C; ^{31}P NMR (C_6D_6) +13.3, +47.5 ppm, J(PP) = 186 Hz; ^{1}H NMR (C_6D_6) 1.24 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 1.26 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 1.87 (t-like, J(PH) = 5.6 Hz, 1 H, =CH), 3.72 (sept d, J(HH) = 6.8 Hz, J(PH) = 12.2 Hz, 4 H, CH), 7.46 (m, 15 H, CH_{aro}); ^{13}C NMR (C_6D_6) 10.6 (dd, J(PC) = 112.8 and 13.2 Hz, =C), 24.45, 24.51, 24.58, 24.62 (s, CH_3), 46.72 (d, J(PC) = 3.7 Hz, CH), 128.1 (d, J(PC) = 10.3 Hz, C_m), 130.7 (d, J(PC) = 2.9 Hz, C_p), 133.5 (dd, J(PC) = 10.3 and 2.9 Hz, C_o), 133.9 (dd, J(PC) = 85.0 and 3.0 Hz, C_i). Anal. Calcd for $C_{31}H_{44}N_2P_2$: C, 73.5; H, 8.7; N, 5.5. Found: C, 73.3; H, 8.6; N, 5.8.

Table III. Crystallographic Data for 6′

formula	$C_{20}H_{35}N_2PS_2$
mol wt	398.64
cryst system	monoclinic
a, Å	26.175 (7)
b, Å	9.945 (3)
c, Å	8.966 (3)
β, deg	91.75 (2)
V, Å^3	2332.8
Z	4
space group	$P2_1/n$
D_{calcd}	1.135
μ, cm^{-1}	27.206
cryst size, mm	0.35 × 0.30 × 0.20
radiation	Cu Kα, graphite monochromated
scan type	flying step-scan
scan speed	0.024 deg s^{-1}
scan angle	1.2 + 0.143 tg θ
octants	$\pm hkl$
θ limits	$4° < \theta < 57°$
no. of measmnts	2942
no. of reflctns with $I > 3\sigma(I)$	1830
abs min/max	0.72/1.36
$R(F)$	0.058
$R_w(F)$	0.068
GOF	1.04

Synthesis of *C*-Thioxophosphoranyl Phosphorus Ylide 12. A toluene solution (30 mL) of **11** (3.1 g, 6.1 mmol) and elemental sulfur (0.2 g, 6.2 mmol) was stirred for 1 h at room temperature. Filtration and evaporation of the solvent led to a crystalline residue, which was recrystallized from acetonitrile to give **12** (2.7 g, 85% yield) as pale yellow crystals: mp 153 °C; ^{31}P NMR ($CDCl_3$) +16.1, +70.3, J(PP) = 49.4 Hz; ^{1}H NMR ($CDCl_3$) 1.26 (d, J(HH) = 7.0 Hz, 12 H, CH_3), 1.28 (d, J(HH) = 7.0 Hz, 12 H, CH_3), H ylide not resolved, 4.19 (m, 4 H, CH), 7.56 (m, 15 H, H_{aro}); ^{13}C NMR ($CDCl_3$) 18.3 (dd, J(PC) = 151.7 and 124.5 Hz, =CH), 24.10, 24.12, 24.18, 24.20 (s, CH_3), 46.4 (d, J(PC) = 6.0 Hz, CH), 127.9 (d, J(PC) = 12.0 Hz, C_m), 130.7 (s, C_p), 131.9 (dd, J(PC) = 92.1 and 7.5 Hz, C_i), 133.6 (d, J(PC) = 9.8 Hz, C_o). Anal. Calcd for $C_{31}H_{44}N_2P_2S$: C, 69.2; H, 8.1; N, 5.2. Found: C, 68.9; H, 8.0; N, 4.9.

Synthesis of *C*-Thioxophosphoranyl *C*-Sulfanyl Phosphorus Ylide 13. To a toluene solution (20 mL) of **12** (2.7 g, 5.1 mmol) was added dropwise, at 0 °C, 0.4 g of *p*-tolylsulfanyl chloride. The reaction mixture was warmed up to room temperature and filtered. After evaporation and recrystallization from acetonitrile, **13** (1.4 g, 86% yield) was obtained as pale yellow crystals: mp 171 °C; ^{31}P NMR ($CDCl_3$) +25.9, +79.6, J(PP) = 117 Hz; ^{1}H NMR ($CDCl_3$), 1.25 (m, 25 H, CH_3CH and =CH), 2.17 (s, 3 H, CH_3C_{aro}), 4.32 (m, 4 H, CH), 6.86 (AA′BB′ system, 4 H, H_{aro}), 7.62 (m, 15 H, H_{aro}); ^{13}C NMR ($CDCl_3$) 20.5 (s, CH_3C_{aro}), 23.3 (dd, J(PC) = 146.4 and 104 Hz, =C), 24.5 (m, $CHCH_3$), 47.0 (d, J(PC) = 7.4 Hz, $CHCH_3$), 124.3 (s, C_p), 127.1 (d, J(PC) = 15.6 Hz, C_m), 128.0 (d, J(PC) = 3.1 Hz, C_o), 130.6 (d, J(PC) = 2.3 Hz, C_m), 130.7 (dd, J(PC) = 72.5 and 10.1 Hz, C_i), 132.8 (d, J(PC) = 13.6 Hz, C_p), 134.5 (d, J(PC) = 8.6 Hz, C_o), 141.5 (m, C_i); mass spectrum, m/e 660 (M^+).

Synthesis of 2-Thioxo-1,2λ⁵-azaphosphetane 6′ by Photolysis of 13. A degassed benzene solution (10 mL) of **13** (1.4 g, 2 mmol) was irradiated with a mercury high pressure lamp at 0 °C for about 16 h. The reaction was monitored by ^{31}P NMR. Then, 0.5 mL of MeI was added and the reaction mixture was stirred for 12 h at room temperature. The precipitate was filtered off and the solvent evaporated. The residue was recrystallized twice from acetonitrile, giving **4** (0.62g, 78% yield).

X-ray Study of 6′. The diffraction data were collected at room temperature on a Philips PW1100/16 diffractometer. A parallelepiped-shaped crystal was cut from a cluster and glued to a glass filament mounted on a rotation-free goniometer head. Crystal were only marginally suitable for X-ray single-crystal analysis because of asymmetric background. Data collection parameters are given in Table III. The orientation matrix was

obtained from 25 machine-centered reflections. Three standard reflections measured every hour showed no trend in intensity during data collection. The raw step-scan data were converted to intensities by using the Lehman-Larsen[17a] method and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the empirical method of Walker and Stuart[17b] since face indexating was not possible. The structure was solved by using MULTAN.[17c] After refinement of heavy atoms, difference Fourier maps revealed maxima of electron density close to the positions expected for hydrogen atoms. These atoms were introduced into structure-factor calculations by their computed coordinated (C-H = 0.95 Å) and isotropic factors such that $B(H) = 1 + B_{eqv}(C)$ Å^2. No hydrogen atom parameters was allowed to vary during full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$. The unit-weight observation in Table II is for $p = 0.08$ in $\sigma^2(F^2) = \sigma^2$ counts + $(pI)^2$. A final difference map showed no significant maxima. All computations were done on a MicroVaxII computer using the SDP/VAX[17d] package. The scattering factors were from ref 17e and 17f, respectively.

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Supplementary Material Available: Table of general displacement parameter Expression-U's and hydrogen atom parameters (3 pages); observed and calculated structure factor amplitudes for all observed reflections (*10) (8 pages). Ordering information is given on any current masthead page.

Silyl Group Transfer in the Cycloaddition Reactions of Silyl Iminium Salts Derived from Aryl-Substituted Oximes

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Reaction of the iminium salt derived from benzaldehyde oxime and (trimethylsilyl)methyl triflate with cesium fluoride gives rise to azomethine ylides. Dipolar cycloaddition proceeded with complete stereospecificity with dimethyl fumarate and maleate. In sharp contrast, reaction of the salt with alkynes produces dipolar cycloadducts derived from nitrones. The different products encountered result from the operation of several competing reactions which depend on the nature of the added dipolarophile. The initial step in all cases involves removal of the OH proton by cesium fluoride to give a nitrone intermediate. Cycloaddition occurs rapidly with activated alkynes to give isoxazolines. In the presence of the slower reacting alkene, a 1,3-silicon shift to the oxygen atom occurs, giving rise to an azomethine ylide intermediate, which subsequently cycloadds to the alkene. Supporting evidence for the postulated mechanism comes from the reaction of the iminium salt with sodium hydride and also by carrying out the cycloaddition in methanol.

Organosilicon reagents have been found to play an important role in organic synthesis.[1-4] Reports from several laboratories have disclosed that the fluoride ion induced cleavage of carbon-silicon bonds represents a useful tool for the generation of carbanion equivalents.[5-13] In light of the remarkable versatility and broad synthetic utility of silicon chemistry, it is not surprising that the desilylation reactions of α-trimethylsilyl oxonium salts are becoming an increasingly popular method for 1,3-dipole generation.[14-19] In many cases, these studies have demonstrated

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