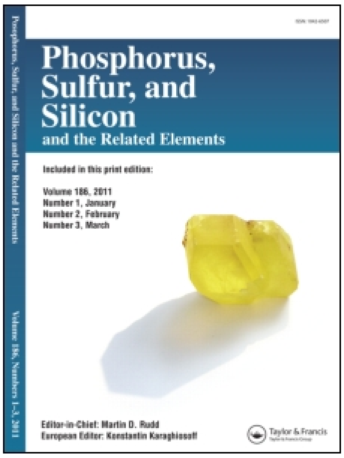


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STEREOSPECIFIC FORMATION OF A 1,2λ³ -AZAPHOSPETANE IN THE THERMOLYSIS OF BIS[BIS(DIISOPROPYLAMINO)PHOSPHANYL] DIAZOMETHANE

Marie-Joëlle Menu[a]; Yves Dartiguenave[a]; Michèle Dartiguenave[a]; Antoine Baceiredo[a]; Guy Bertrand[a]
[a] Laboratorie de Chimie de Coordination du CNRS, U8241 205, Toulouse, Cédex, France

To cite this Article Menu, Marie-Joëlle , Dartiguenave, Yves , Dartiguenave, Michèle , Baceiredo, Antoine and Bertrand, Guy(1990) 'STEREOSPECIFIC FORMATION OF A 1,2λ³ -AZAPHOSPETANE IN THE THERMOLYSIS OF BIS[BIS(DIISOPROPYLAMINO)PHOSPHANYL] DIAZOMETHANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 47: 3, 327 — 334

To link to this Article: DOI: 10.1080/10426509008037986

URL: http://dx.doi.org/10.1080/10426509008037986

Phosphorus, Sulfur, and Silicon, 1990, Vol. 47, pp. 327–334
Reprints available directly from the publisher
Photocopying permitted by license only

STEREOSPECIFIC FORMATION OF A 1,2λ³-AZAPHOSPHETANE IN THE THERMOLYSIS OF BIS[BIS(DIISOPROPYLAMINO)PHOSPHANYL] DIAZOMETHANE

MARIE-JOËLLE MENU, YVES DARTIGUENAVE, MICHÈLE DARTIGUENAVE,* ANTOINE BACEIREDO and GUY BERTRAND*
Laboratorie de Chimie de Coordination du CNRS, U8241 205, route de Narbonne 31077 Toulouse Cédex (France)

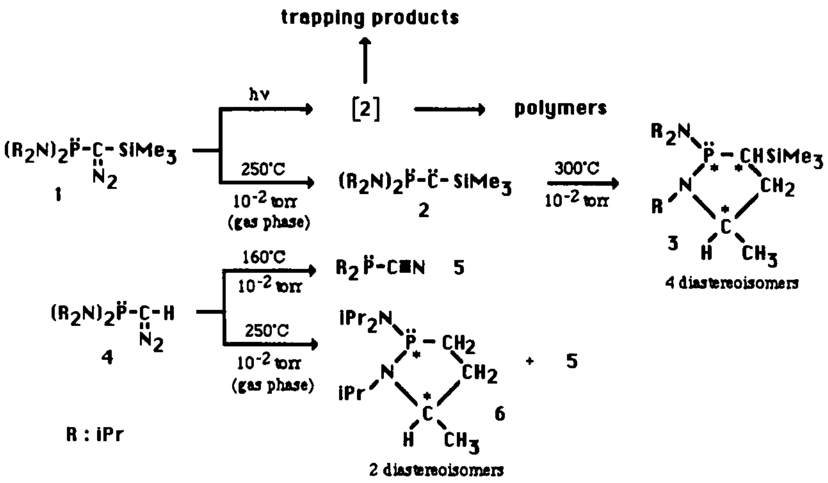
(Received May 22, 1989; in final form June 12, 1989)

Heating of bis[bis(diisopropylamino)phosphanyl]diazomethane **7**, in refluxing benzene for 48 hours, quantitatively led to the corresponding 1,2λ³-azaphosphetane **9** as only one diastereoisomer. This result is explained in terms of carbene insertion into a methin-CH bond of an isopropyl substituent. The regiospecificity and the stereospecificity of the ring closure is discussed. Treatment of **9** with elemental sulfur afforded the corresponding 1,2,2λ⁵-azathiophosphetane **10** which has been characterized by X-ray crystallography: $C_{25}H_{56}N_4P_2S_2$, space group P2(1)/*n*, $a = 13.628$ (3) Å, $b = 19.369$ (5) Å, $c = 12.485$ (4) Å, $V = 3073$ (3) Å³.

Key words: Thermolysis; carbene insertion; azaphosphetane; X-ray crystallography of azathiophosphetane.

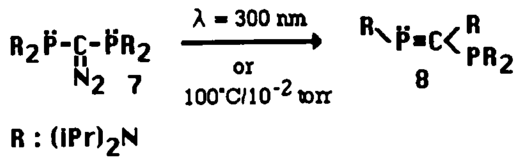
We have recently reported that both, pyrolysis and photolysis of [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane **1** led, after loss of nitrogen, to the corresponding [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene **2**.[1] When **2** was generated by pyrolysis at 250°C, under vacuum, it appeared to be stable enough to be purified by flash distillation at 75–80°C/10^{-2} mm Hg[1d]. In contrast, under photolytic conditions the carbene **2** was not isolable and decomposed into uncharacterized polymers but its transient formation has been proved by a variety of trapping reactions.[1] Pyrolysis of **2**, at 300°C under vacuum, afforded the four five-membered ring diastereoisomers **3** in 90% total yield.[1d] On the other hand, attempted distillation of [bis(diisopropylamino)phosphanyl]diazomethane **4** led to phosphinonitrile **5** in 30% yield,[1a–d] while pyrolysis of **4**, at 250°C under vacuum gave rise to the five-membered ring **6**, as a 70/30 mixture of diastereoisomers (60% yield) along with **5** (20% yield)[1d] (Scheme 1).

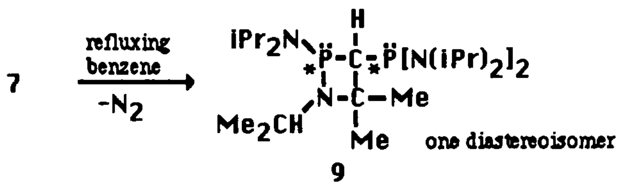
From these examples, the importance of the experimental conditions used on the fate of phosphinocarbenes is quite clear and thus it was of interest to reinvestigate the behavior of the bis[bis(diisopropylamino)phosphanyl]diazomethane **7** that we have reported[2] to afford phosphaalkene **8** by photolysis in benzene solution at 300 nm or by attempted distillation.



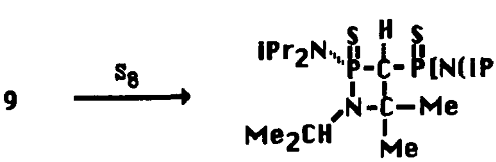
SCHEME 1

Indeed, when diazo **7** was heated in refluxing benzene for 48 hours, a clean reaction occurred affording a compound tentatively assigned to 1,2λ^3-azaphosphetane **9** as only one diastereoisomer.





The Phosphorus chemical shift [$\delta^{31}P$: +113.6(P_{ring}), +60.1] and the value of the phosphorus-phosphorus coupling constant [$J(PP) = 35.3$ Hz] were in good agreement with a λ^3P–C-λ^3P skeleton. The complexity of the signals corresponding to the methyl groups strongly suggested a cyclic product and since there were two methyl groups, at 1.54 and 1.75 ppm, non-coupled with an adjacent proton the four-membered ring structure **9** seemed quite reasonable. Homonuclear and heteronuclear decoupling experiments allowed to determine which were the protons coupled with each phosphorus atom and the CH region appeared to be of special interest. Indeed, as expected the $C\underline{H}N_{ring}$ was coupled with the P_{ring} (6.5 Hz) and 4 $C\underline{H}N$ protons were coupled with the other phosphorus (10 Hz). However, the $PC\underline{H}P$ was only coupled with the phosphorus of the ring (1.5 Hz) and more surprisingly the 2 other $C\underline{H}N$ protons tentatively assigned to the diisopropylamino group bonded to the phosphorus of the ring were coupled with both phosphorus atoms with ^4J (10 Hz) larger than ^2J (3 Hz). Since we have not been able to obtain **9** as a crystalline material, a treatment with elemental sulfur was performed giving rise to the corresponding 1,2,2λ^5-azathiophosphetane **10** in 92% isolated yield as only one diastereoisomer. This compound was fully characterized including by an X-ray crystal study.



10

Refined coordinates and anisotropic thermal parameters are given in Table I and II, respectively. Bond lengths and angles are in Table III. An ORTEP drawing of the molecule, in which the atomic labelling is displayed, is depicted in Figure 1. As expected the values of the endo- and exocyclic PCC, CPN and CNP angles are quite different: P1C1C22 = 88.2 (3) and P2C1C22 = 119.9 (3);

TABLE I

Fractional atomic coordinates with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
S(1)	0.35161(9)	0.21316(6)	0.2192(1)
P(1)	0.26122(8)	0.14532(5)	0.11673(9)
N(1)	0.3311(2)	0.0838(2)	0.0860(3)
C(11)	0.2772(3)	0.0308(2)	−0.0007(4)
C(111)	0.2903(3)	−0.0412(2)	0.0473(4)
C(112)	0.3034(4)	0.0353(2)	−0.1109(4)
C(12)	0.4486(3)	0.0782(2)	0.1281(4)
C(121)	0.5012(3)	0.1352(2)	0.0853(4)
C(122)	0.5009(3)	0.0595(3)	0.2482(4)
N(2)	0.1680(3)	0.1694(2)	−0.0036(3)
C(21)	0.1829(4)	0.2126(2)	−0.0942(4)
C(211)	0.1714(4)	0.2905(2)	−0.0736(5)
C(212)	0.1160(4)	0.1893(3)	−0.2134(4)
C(22)	0.0725(3)	0.1492(2)	0.0244(4)
C(221)	−0.0027(3)	0.1006(2)	−0.0613(5)
C(222)	0.0098(3)	0.2114(2)	0.0401(4)
C(1)	0.1391(3)	0.1128(2)	0.1387(3)
H(C1)	0.132(3)	0.0634(6)	0.129(3)
P(2)	0.09211(8)	0.11155(5)	0.2600(1)
S(2)	−0.04892(8)	0.07036(6)	0.1966(1)
N(3)	0.1775(3)	0.0634(2)	0.3621(3)
C(31)	0.1298(4)	0.0258(3)	0.4395(5)
C(311)	0.0871(4)	−0.0456(3)	0.3993(5)
C(312)	0.1950(5)	0.0268(4)	0.5634(5)
C(32)	0.2825(3)	0.0420(2)	0.3641(4)
C(321)	0.3721(4)	0.0757(3)	0.4655(4)
C(322)	0.3000(4)	−0.0345(3)	0.3617(5)
N(4)	0.0844(3)	0.1894(2)	0.3133(3)
C(41)	−0.0220(4)	0.2180(3)	0.3069(5)
C(411)	−0.0425(4)	0.2929(3)	0.2735(5)
C(412)	−0.0358(5)	0.2028(4)	0.4210(6)
C(422)	0.2070(5)	0.2315(4)	

TABLE II

Final anisotropic thermal parameters (A × 100) with estimated standard deviations in parentheses

Atom	U11	U22	U33	U12	U13	U23
S(1)	2.77(6)	3.65(7)	4.00(7)	−1.47(5)	1.27(5)	1.30(6)
P(1)	1.82(5)	2.01(6)	2.58(6)	−0.33(4)	0.47(5)	0.21(5)
N(1)	1.5(2)	2.1(2)	3.5(2)	−0.1(1)	0.6(2)	0.2(2)
C(11)	2.2(2)	2.4(2)	3.3(3)	0.3(2)	0.8(2)	0.3(2)
C(111)	3.0(3)	2.6(2)	5(3)	−0.4(2)	0.4(2)	0.4(2)
C(112)	3.9(3)	3.6(3)	4.7(3)	0.5(2)	2.3(2)	0.0(2)
C(12)	1.7(2)	3.5(3)	5.5(3)	0.0(2)	0.8(2)	0.7(2)
C(121)	2.3(2)	3.4(3)	4.9(3)	−0.2(2)	1.7(2)	−0.1(2)
C(122)	2.2(2)	6.1(4)	5.5(4)	−0.3(2)	0.5(2)	1.1(3)
N(2)	2.4(2)	1.5(2)	3.2(2)	0.1(1)	0.4(2)	−0.2(2)
C(21)	3.4(3)	2.8(2)	3.8(3)	0.3(2)	1.4(2)	0.9(2)
C(211)	5.2(3)	2.2(3)	6.8(4)	1.1(2)	2.4(3)	4.8(3)
C(22)	1.8(2)	2.3(2)	3.0(2)	−0.1(2)	0.1(2)	0.1(2)
C(221)	2.5(2)	3.6(3)	3.0(3)	−0.1(2)	0.4(2)	−0.5(2)
C(222)	2.6(2)	3.0(3)	4.1(3)	1.1(2)	1.0(2)	0.5(2)
C(1)	1.4(2)	1.7(2)	3.1(2)	−0.3(2)	0.3(2)	−0.3(2)
P(2)	1.91(5)	1.74(5)	3.27(6)	0.06(4)	0.68(5)	−0.47(5)
S(2)	2.33(5)	2.99(6)	4.91(8)	−0.70(5)	1.18(5)	−0.35(6)
N(3)	3.0(2)	4.1(2)	2.9(2)	1.6(2)	1.5(2)	0.3(2)
C(31)	4.0(3)	6.6(4)	5.5(4)	2.5(3)	1.9(3)	1.1(3)
C(311)	5.6(4)	7.2(4)	7.2(4)	1.1(3)	3.1(3)	3.3(4)
C(312)	6.5(4)	11.0(6)	5.0(4)	4.1(4)	3.4(3)	2.5(4)
C(32)	2.9(2)	3.6(3)	3.7(3)	1.2(2)	1.3(2)	1.0(2)
C(321)	3.3(3)	6.2(4)	4.7(3)	0.6(3)	0.4(2)	0.2(3)
C(322)	4.7(3)	5.4(3)	5.9(4)	2.1(3)	3.0(3)	1.5(3)
N(4)	2.8(2)	2.2(2)	5.1(3)	−0.2(2)	2.4(2)	−1.7(2)
C(41)	4.4(3)	3.7(3)	6.8(4)	0.7(2)	3.2(3)	0.6(3)
C(411)	6.3(4)	7.1(4)	6.0(4)	3.5(3)	2.9(3)	1.5(3)
C(412)	7.3(5)	11.9(6)	8.7(5)	−2.5(4)	5.1(4)	−3.7(5)
C(42)	3.7(3)	4.3(3)	4.4(3)	−0.9(2)	2.3(3)	−2.0(2)
C(421)	4.0(3)	2.4(3)	10.4(5)	−0.6(2)	2.4(3)	−2.6(3)
C(422)	9.4(5)	10.1(5)	6.5(4)	−5.8(4)	4.5(4)	−5.1(4)

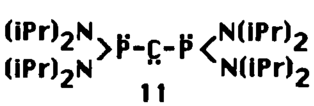
C1P1N2 = 78.4 (2) and C1P1N1 = 113.9 (2); C22N2P1 = 99.2 (3) and C21N2P1 = 125.8 (3)°. The distortion of the bond distances is less marked but noticeable: P1C1 = 1.890 (4) and P2C1 = 1.845 (5); C22N2 = 1.517 (6) and C12N2 = 1.478 (6); P1N1 = 1.656 (4) and P1N2 = 1.646 (4) Å. The sum of the angles for the ring is 359.4 (9)°. This value is consistent with a planar structure. The crystallographic equation of the average plane defined by P1C1C22N2 is $2.737\,X - 16.9197\,Y - 6.1833\,Z - 2.4138 = 0$. The distances in Å to this plane are respectively P1 = −0.0372 (10); N2 = 0.0465 (32); C22 = −0.0482 (41); C1 = 0.0389 (39). These values show clearly, that none of these atoms are in the average plane, but all are very closed. An other interesting point of this structure is due to the presence of two asymmetric centers and on the ORTEP view of the molecule it is clear that the bis(diisopropylamino)thiophosphoryl group is in trans position to the diisopropylamino substituent of the phosphorus of the ring.

The formation of $1,2\lambda^3$-azaphosphetane, **9**, can be explained in terms of insertion of singlet carbene **11** into a carbon-hydrogen bond of an isopropyl substituent.[2a]

TABLE III

Bond lengths(Å) and angles(°) with e.s.d.'s in parentheses

Bond Distances:			
S1-P1	1.934(1)	C1-P2	1.845(5)
P1-N1	1.656(4)	P2-S2	1.964(1)
P1-N2	1.646(4)	P2-N3	1.666(3)
P1-C1	1.890(4)	P2-N4	1.666(4)
N1-C11	1.479(5)	N3-C31	1.530(8)
N1-C12	1.499(6)	N3-C32	1.481(7)
C11-C111	1.503(6)	C31-C311	1.513(9)
C11-C112	1.544(8)	C31-C312	1.480(7)
C12-C121	1.515(7)	C32-C321	1.550(6)
C12-C122	1.455(7)	C32-C322	1.502(7)
N2-C21	1.478(6)	N4-C41	1.527(6)
N2-C22	1.517(6)	N4-C42	1.483(5)
C21-C211	1.459(6)	C41-C411	1.507(7)
C21-C212	1.506(6)	C41-C412	1.53(1)
C22-C221	1.512(5)	C42-C421	1.532(7)
C22-C222	1.529(6)	C42-C422	1.491(9)
C22-C1	1.556(5)		
Bond Angles:			
S1-P1-N1	111.1(1)	N2-C22-C1	93.6(3)
S1-P1-N2	120.5(1)	C221-C22-C222	108.4(4)
S1-P1-C1	120.9(1)	C221-C22-C1	112.9(3)
N1-P1-N2	108.2(2)	C222-C22-C1	114.1(4)
N1-P1-C1	113.9(2)	P1-C1-C22	88.2(3)
N2-P1-C1	78.4(2)	P1-C1-P2	135.1(3)
P1-N1-C11	119.6(3)	C22-C1-P2	119.9(3)
P1-N1-C12	127.1(3)	C1-P2-S2	104.8(1)
C11-N1-C12	113.0(3)	C1-P2-N3	106.4(2)
N1-C11-C111	113.4(3)	C1-P2-N4	114.0(3)
N1-C11-C112	113.5(4)	S2-P2-N3	113.1(1)
C111-C11-C112	112.0(4)	S2-P2-N4	109.6(1)
N1-C12-C121	114.0(3)	N3-P2-N4	109.2(2)
N1-C12-C122	116.2(4)	P2-N3-C31	114.3(3)
C121-C12-C122	115.3(4)	P2-N3-C32	124.9(3)
P1-N2-C21	125.8(3)	C31-N3-C32	119.0(3)
P1-N2-C22	99.2(3)	N3-C31-C311	115.2(5)
C21-N2-C22	133.6(3)	N3-C31-C312	115.0(4)
N2-C21-C211	112.0(4)	C311-C31-C312	111.9(5)
N2-C21-C212	112.7(4)	N3-C32-C321	111.5(4)
C211-C21-C212	113.2(4)	N3-C32-C322	115.8(4)
N2-C22-C221	114.6(4)	C321-C32-C322	110.3(4)
N2-C22-C222	113.1(3)	P2-N4-C41	120.2(3)



11

Note that the four-membered ring heterocycle **9** was formed exclusively (according to NMR data of the crude reaction mixture), in spite of the ratio of six methyl-CH bonds to one methin-CH bond, and that only one of the possible diastereoisomers was observed. This result is in marked contrast with the exclusive formation of five-membered rings **3** (as two diastereoisomers) and **5** (as

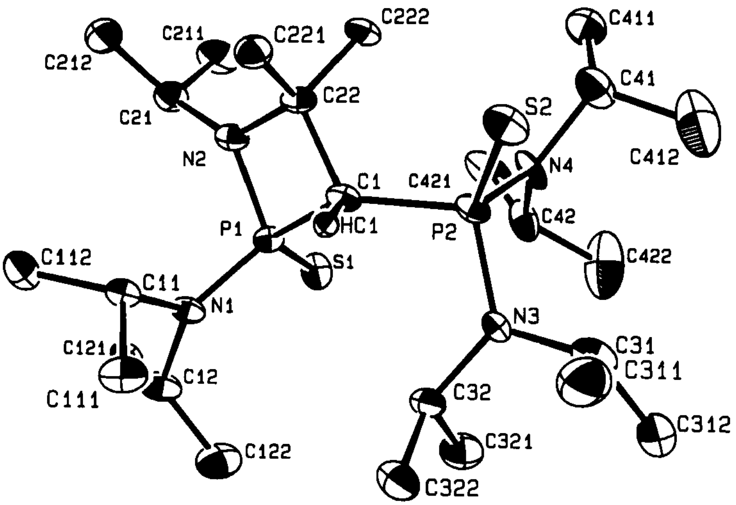
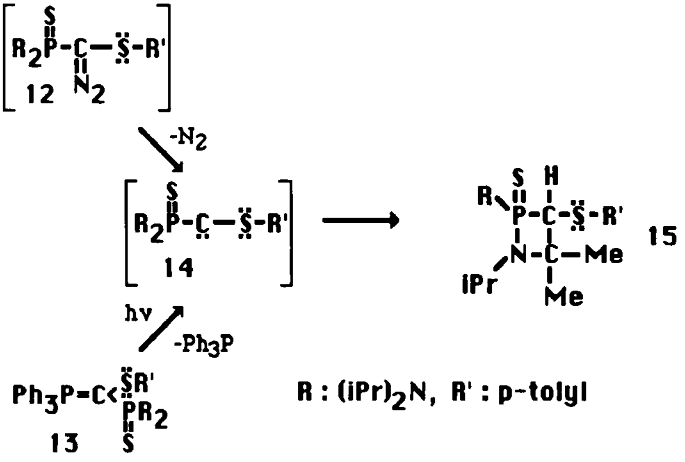


FIGURE 1 ORTEP drawing of $S_2P_2N_4C_{25}H_{56}$. The ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

four diastereoisomers) in the thermolysis of phosphinocarbene **2** and diazophosphane **4**, respectively (Scheme 1), but in good agreement with the stereospecific formation of 1,2,2λ^5-azathiophosphetane, **15**, from the corresponding diazo derivative **12** or phosphorus ylide **13**.[3]



The influence of the nature of the heteroatom (P,S) in α position of the carbene on the course of the ring closure is obvious from these examples but further work is necessary to rationalize these results.

EXPERIMENTAL SECTION

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H NMR spectra were recorded on a Bruker WM250 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR spectra were obtained on a Bruker AC80 at 32.43 MHz. Downfield shifts are expressed with a positive sign, in ppm relative to external 85% H_3PO_4. ^{13}C NMR spectra were obtained on a Bruker AM300. ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Mass spectra were obtained on a Ribermag R10 10E instrument or a Varian MAT 311A.

Synthesis of 1,2λ³-azaphosphetane **9**. A benzene solution (30 mL) of bis[bis(diisopropylamino)phosphanyl]diazomethane **7**^{2} (1.25 g, 2.5 mmol) was heated under reflux for 48 hours. After evaporation of the solvent, **9** was obtained as a colourless oil which has been used without further purification. ^{31}P NMR ($CDCl_3$) + 113.6, +60.1, $J(PP) = 35.3$ Hz; ^1H NMR ($CDCl_3$) 1.19 (d, $J(HH) = 7$ Hz, 6H, $CHC\underline{H}_3$), 1.35 (d, $J(HH) = 7$ Hz, 12H, $CHC\underline{H}_3$), 1.37 (d, $J(HH) = 7$ Hz, 12H, $CHC\underline{H}_3$), 1.44 (d, $J(HH) = 7$ Hz, 6H, $CHC\underline{H}_3$), 1.50 (d, $J(HH) = 7$ Hz, 6H, $CHC\underline{H}_3$), 1.54 (s, 3H, CH_3C), 1.75 (d, $J(PH) = 1.5$ Hz, 3H, CH_3C), 2.62 (d, $J(P_{113}H) = 1.5$ Hz, 1H, CHring), 3.25 (sept d, $J(HH) =$ 7 Hz, $J(P_{113}H) = 6.5$ Hz, 1H,CHNring), 3.50 (sept d, $J(HH) = 7$ Hz, $J(P_{60}H) = 10$ Hz, 4H, CHN), 3.68 (sept d, $J(HH) = 7$ Hz, $J(P_{60}H) = 10$ Hz, $J(P_{113}H) = 3$ Hz, 2H, CHN); mass spectrum m/e 474 (M+).

Synthesis of 1,2,2λ⁵-azathiophosphetane **10**. A benzene solution of **9** (1.18 g, 2.5 mmol) was stirred, for 3 h, at room temperature in the presence of a large excess of elemental sulfur. After filtration and evaporation of the solvent, **10** (1.23 g, 92% yield) was isolated by column chromatography on silica gel (Hexane/ether 95/5, $R_F = 0.3$) followed by recrystallization in cold pentane. mp 136–137°C; ^1H NMR ($CDCl_3$) 1.21 (d, $J(HH) = 6.5$ Hz, 3H, $CHC\underline{H}_3$), 1.28 (d, $J(HH) = 7.0$ Hz, 3H, $CHC\underline{H}_3$), 1.40 (d, $J(HH) = 6.7$ Hz, 3H, $CHC\underline{H}_3$), 1.47 (d, $J(HH) = 7.0$ Hz, 3H, $CHC\underline{H}_3$), 1.50 (d, $J(HH) =$ 7.0 Hz, 6H, $CHC\underline{H}_3$), 1.51 (d, $J(HH) = 7.0$ Hz, 12H, $CHC\underline{H}_3$), 1.57 (d, $J(HH) = 6.8$ Hz, 12H, $CHC\underline{H}_3$, 12H), 1.79 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 3.34 (sept d, $J(HH) = 7.0$ Hz, $J(PH) = 14.9$ Hz, 1H, $C\underline{H}CH_3$), 3.81 (t-like, $J(PH) = 19.7$ Hz, 1H, CH_{ring}), 4.40 (m, 6H, $C\underline{H}CH_3$); ^{13}C NMR ($CDCl_3$) 23.01, 23.10, 23.41, 24.42, 24.47, 25.05, 25.32 (s, CHÇH_3), 25.90 (d, $J(PC) = 3.24$ Hz, CÇH_3), 32.68 (d, $J(PC) = 12.15$ Hz, CÇH_3), 45.25 (s, NringCH), 47.30 (d, $J(PC) = 6.2$ Hz, ÇHCH_3), 47.50 (d, $J(PC) = 5.9$ Hz, ÇHCH_3), 48.75 (d, $J(PC) = 6.7$ Hz, ÇHCH_3), 60.92 (s, Cring), 62.73 (dd, $J(PC)$ = 85.3 and 55.5 Hz, CHring); mass spectrum m/e 538 (M^+); Anal. Calcd. for $C_{25}H_{56}N_4P_2S_2$: C, 55.72, H, 10.48; N, 10.40. Found: C, 55.80; H, 10.49; N, 10.44.

X-ray crystal study of **10**. The data were collected at −170°C using an Enraf-Nonius CAD4 Diffractometer, equipped with a graphite-monochromated MoKα. The cell parameters were

TABLE IV

Crystal data and details of data collection and structure and refinement for $S_2P_2N_4C_{25}H_{56}$

Formula	$S_2P_2N_4C_{25}H_{56}$
Cryst. sys	monoclinic
Space group	P2(1)/n
a, Å	13.628 (3)
b, Å	19.369 (5)
c, Å	12.485 (4)
β	111.19 (2)
V, Å^3	3073 (3)
Z	4
d calc, g/cm^3	1.1646
μ (Mo K α), cm^{-1}	2.54
Temp, °c	−170 C. ± 1
Scan method	ω
Data collection range (θ), deg	$1 < \theta < 25$
no. of reflections measured	5816
no. of unique data with $(1) > 3\sigma(1)$	2599
no. of parameters refined	301
R^a	0.0351
$R_w{}^b$	0.0400

[a] $R = \sum \| Fo| - |Fc\| / \sum |Fo|$.

[b] $R_w = [\sum w(|Fo| - |Fc|)^2 / \sum w\, |Fo|^2)]^{1/2}$; $w = 1/\sigma^2(|Fo|)$.

determined from a least-squares fitting of 25 centered reflections with 2θ between 17 and 30° space group determination by systematic absences was identified as $P2(1)/n$. A summary of crystal and intensity collection data is given in Table IV. Successful refinement was done in the centrosymetric space group. 5816 independent reflections, 2599 with $I > 3\sigma(I)$ measured using $\theta/2\theta$ scans for 2θ from 2 to 50°. Intensities of three reflections measured every hour during data collection varied less than 15% and thus indicated in these conditions a relative crystal stability. The data were corrected for the Lorentz effect, polarization, and absorption. Structure solved with SHEL86, refinement done by full-matrix least-squares based on $|Fo|$, by using the SHELX package.[4] After an anisotropic refinement for all non-H atoms, hydrogen atoms fixed at idealized positions ($C{-}H = 0.97$ Å, $U = 0.05$ Å^2 kept fixed) and repositioned after each least-squares cycle. Final parameters are $R = 0.0351$, $Rw = 0.0400$[5] and $S = 1.634$ for 301 variables, with shift mean $= 0.01\sigma$, max. $= 0.05\sigma$ in final cycle, largest residual electron density on final ΔF map $= 0.2$ eÅ^{-3}. Scattering factor from Cromer & Mann[6] for P, N, and C; from Stewart, Davidson and Simpson[7] for H.

Supplementary material. Hydrogen atomic positional and thermal parameters (2 pages) and observed and calculated structure factor amplitudes (13 pages) have been deposited at the Crystallographic Data Centre, University Chemical Laboratory, Cambridge.

REFERENCES

1. (a) A. Baceiredo, G. Bertrand and G. Sicard, *J. Am. Chem. Soc.* **107,** 4781 (1985); (b) A. Baceiredo and G. Bertrand, *Phosphorus Sulfur* **26,** 56 (1986); (c) G. Bertrand, A. Baceiredo, G. Sicard, M. Granier, *Phosphorus Sulfur* **30,** 353 (1987); (d) A. Igau, H. Grützmacher, A. Baceiredo and G. Bertrand, *J. Am. Chem. Soc.* **110,** 6463 (1988); (e) A. Igau, A. Baceiredo, G. Trinquier and G. Bertrand, *Angew. Chem. Int. Ed. Engl.* **28,** 621 (1989).
2. A. Baceiredo, A. Igau, G. Bertrand, M. J. Menu, Y. Dartiguenave and J. J. Bonnet, *J. Am. Chem. Soc.* **108,** 7868 (1986).
   a. References for carbene insertions of the same type are: W. Kirmse, "Carbene Chemistry"; A. T. Blomquist, H. Wasserman, Eds.; Academic Press: New York, 1971. S. Patai, "The chemistry of Diazonium and Diazo groups"; Wiley, New York, 1978.
3. G. Sicard, H. Grützmacher, A. Baceiredo, J. Fischer and G. Bertrand, *J. Org. Chem.* in press.
4. G. M. Sheldrick, 1976, SHELX76, "Program for crystal structure determination." Univ. of Cambridge, England.
5. $R = \sum ||Fo| - |Fc||/\sum |Fo|$; $R_w = [\sum w(|Fo| - |Fc|)^2/\sum w |Fo|^2]^{1/2}$; $w = 1/\sigma^2(|Fo|)$.
6. D. T. Cromer and J. B. Mann, *Acta Cryst.* **A24,** 321 (1968).
7. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* **42,** 3175, (1965).