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Reaction of Dichlorocarbene with 1-(2,4,6-Tri-*t*-butylphenyl)-1-phosphaallenes

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ABSTRACT

1-(2,4,6-Tri-t-butylphenyl)-1-phosphaallene reacted with dichlorocarbene to give 2-dichloromethylene-1-(2,4,6-tri-t-butylphenyl)-1-phosphirane. The structure was confirmed by X-ray crystal structure analysis. A similar isomerization product was obtained in the reaction of dichlorocarbene with 3-phenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaallene.

INTRODUCTION

Compounds containing heavier main group elements in low coordination states are currently of interest [1]. The kinetic stabilization technique by use of bulky substituents has turned out to be effective in the studies on such compounds. By using an extremely bulky 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) as a protecting group, we have been successful in the preparation of multiple bonded phosphorus compounds, such as diphosphenes [2], phosphaalkenes [3], and phosphacumulenes [4]. Recently, we have reported a preparative method for several phosphacumulenes via dichlorophosphiranes formed by the reaction of dichlorocarbene with the corresponding double bonded phosphorus compounds [5–8]. This method involves one carbon-atom homologation at the site of the double bond.

During the course of this research, we have found a novel isomerization reaction of the ethenylidenephosphirane **1** to the dimethylenephosphirane **2** [8,9]. A similar isomerization seemed to occur in the case of the reaction of dichlorocarbene with diphosphaallene **3** which gave the methylenediphosphirane **4** [7], whereas no isomerization of the (diphenylmethylene)phosphirane **5a** to **6a** took place, at least at room temperature or in refluxing hexane. Probably this is because the steric repulsion in **6a** is larger than that in **5a**. Thus, methylenephosphiranes with less bulky substituents at the terminal carbon, such as **5b,c**, are expected to isomerize to **6b,c**. We report here the formation of the dichloromethylenephosphiranes **6b,c** from phosphaallenes **7b,c** by the process of dichlorocarbene addition followed by rearrangement. Furthermore, the structure of **6b** was unambiguously determined by X-ray crystallographic analysis.

RESULTS AND DISCUSSION

The phosphaallene **7b** [10] was prepared using the base-induced isomerization reaction [11] of the ethynylphosphane **8** as follows. The reaction of the chlorophosphine **9** [12] with ethynylmagnesium bromide afforded **8** in 56% yield. Then **8** was treated with butyllithium at −78°C in tetrahydrofuran (THF) to give **7b** in 63% yield. The phosphaallene **7b** was also obtained by the tetrabutylammonium fluoride (TBAF)-induced isomerization reaction of the ethynylphosphine **8**. It should be noted here that **7b** was not obtained in an attempt to isomerize **8**

Dedicated to Prof. Adrian G. Brook on the occasion of his seventieth birthday.

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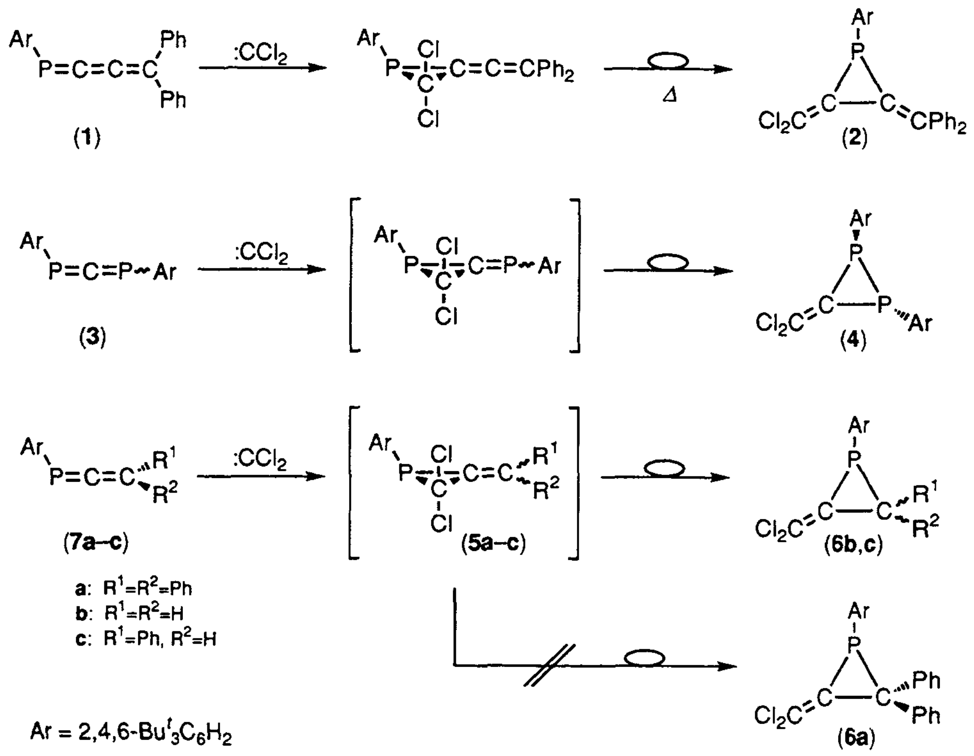
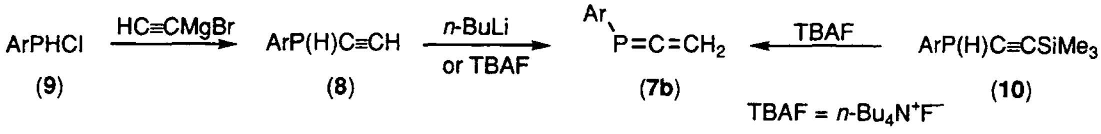


SCHEME 1



SCHEME 2

thermally in refluxing toluene for 1 hour. The reaction of the (trimethylsilylethynyl)phosphine **10** [11] with TBAF in THF also gave **7b**. The phosphaallene **7c** [10] was prepared from 2,2-dichloro-3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphirane as described previously [6].

The phosphaallenes **7b** and **7c** thus obtained were then allowed to react with dichlorocarbene by the Makosza method [13] using benzyltriethylammonium chloride as a phase-transfer catalyst: A mixture of **7b**, chloroform, and benzyltriethylammonium chloride was heated in hexane and 50% aqueous NaOH for 2 hours to give 2-dichloromethylene-1-(2,4,6-tri-*t*-butylphenyl)phosphirane **6b** in 13% yield after silica-gel chromatography. Similarly, the 3-phenyl-1-phosphaallene **7c** gave the corresponding **6c** in 18% yield.

The structure of **6b** was unambiguously determined by X-ray crystallographic analysis. Figure 1 is an ORTEP drawing [14] of **6b**. Bond lengths and bond angles are listed in Table 1. Table 2 shows fractional coordinates and temperature factors for **6b**. The atoms (C2,C3,C4,CL5,CL6) are coplanar within 0.01(1) Å, and the plane makes an angle of 16.9(5)° with the triangle plane (P1,C2,C3). The dihedral angle of C3–C2–C4–CL6 is −18(1)° and that of P1–C2–C4–CL5 is 31(1)°. Thus, the π system in the *exo*-methylene moiety is bent at C2 and twisted around the C2–C4 bond, at least partly due to the intramolecular repulsion between the *exo*-methylene and the *o*-*t*-butyl group at C8. The P1–C7 bond makes an angle of 74.6(3)° with the triangle plane (P1,C2,C3), which is roughly perpendicular to the Ar ring (C7–C12), with the dihedral angles of C3–P1–C7–C12 = −73.4(5)° and C2–P1–C7–C8 = 50.5(6)°. The bond length P1–C2 [1.794(6) Å] in **6b** is comparable to those in **4** [1.789(7) and 1.795(6) Å] but shorter than that in **2** [1.816(2) Å]. The bond angles, C2–P1–C7 [104.8(3)°] and P1–C7–C8 [124.0(4)°], are opened with the concomitant contraction of C3–P1–C7 [97.0(3)°] and P1–C7–C12 [116.2(4)°]. This reflects the large steric repulsion between the adjacent bulky groups at C7 and C8. The Ar group is deformed to a boat form as has

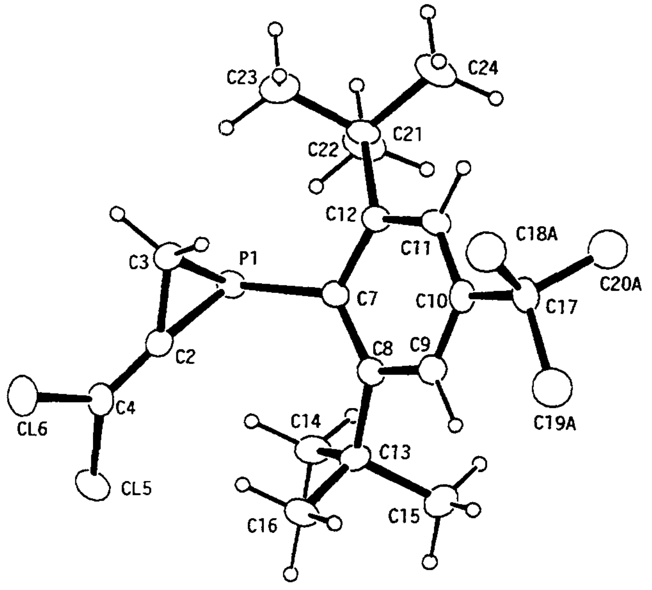


FIGURE 1 X-ray structure of **6b** showing the atom labeling scheme. The *p-t*-butyl group on the Ar ring is disordered, and one with a higher occupancy factor is shown for clarity.

been commonly observed for the Ar-containing compounds [15]. Figure 2 shows the deformations of the Ar group for **6b**, where $\alpha = 13(1)^\circ$, $\beta = 7.4(7)^\circ$, $\gamma = 5.7(8)^\circ$, $\delta = 3.4(8)^\circ$, and $d_P = 0.80(1)$ Å.

These facts indicate that steric hindrance plays an important role in the isomerization of methylenephosphiranes. Thus, in the case of **7a**, no rearrangement to **6a** was observed, whereas in either the case of **7b** or **7c**, the rearrangement of **6b** or **6c** took place, respectively, due to the steric bulk within the phosphirane system. The rearrangement might involve a phosphorus analog of the trimethylenemethane intermediate **11**, where the steric bulk is operating in determining the regiochemistry of the reaction product. We have proposed a similar reaction mechanism in the reaction of dichlorocarbene with **1** [8] and **3** [7] giving **2** and **4**, respectively. A molecular mechanics calculation also indicated that **6b** is more stable than **5b** by 2.47 kcal/mol.

EXPERIMENTAL

Instruments

All experiments were carried out under an argon atmosphere unless otherwise specified. Melting points were taken on a Yanagimoto MP-J3 micromelting points apparatus and were uncorrected. NMR spectra were recorded on either a Bruker AC-200P or AM-600 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on either a JEOL-HX-110 or a Hitachi M-2500S spectrometer. X-ray reflections were recorded on a Rigaku AFC-6A four-circle diffractometer using graphite-monochromated Mo-K_α radiation.

Ethynyl(2,4,6-tri-t-butylphenyl)phosphine (**8**)

Chloro(2,4,6-tri-*t*-butylphenyl)phosphine (**9**) was prepared from 1.13 g [4.1 mmol] of 2,4,6-tri-*t*-butylphenylphosphine as described previously [12]. The chlorophosphine **9** was then dissolved in 9 mL of THF, and the solution was added to a 0.5 M solution of ethynylmagnesium bromide (4.0 mmol) in THF at 0°C. The resulting mixture was stirred at room temperature for 1 hour, and then the solvent was removed in vacuo. Column chromatographic separation (SiO_2/pentane) of the residue

TABLE 1 Bond Distances and Bond Angles for **6b**

Bond Distance/Å		*Bond Distance/Å*		*Bond Angle/°*		*Bond Angle/°*		*Bond Angle/°*	
P1–C2	1.794(6)	C11–C12	1.362(8)	C2–P1–C3	47.1(3)	C8–C9–C10	123.1(6)	C10–C17–C20A	107.9(7)
P1–C3	1.882(8)	C12–C21	1.564(8)	C2–P1–C7	104.8(3)	C9–C10–C11	116.3(6)	C10–C17–C18B	110(1)
P1–C7	1.872(6)	C13–C14	1.545(10)	C3–P1–C7	97.0(3)	C9–C10–C17	122.4(6)	C10–C17–C19B	110(1)
C2–C3	1.472(10)	C13–C15	1.539(11)	P1–C2–C3	69.6(4)	C11–C10–C17	121.2(6)	C10–C17–C20B	109(1)
C2–C4	1.305(8)	C13–C16	1.534(9)	P1–C2–C4	148.0(6)	C10–C11–C12	124.1(6)	C18A–C17–C19A	107.8(9)
C4–CL5	1.707(8)	C17–C18A	1.515(19)	C3–C2–C4	134.8(7)	C7–C12–C11	117.6(5)	C18A–C17–C20A	111.5(9)
C4–CL6	1.729(7)	C17–C19A	1.593(16)	P1–C3–C2	63.3(4)	C7–C12–C21	124.7(5)	C19A–C17–C20A	108.1(8)
C7–C8	1.406(8)	C17–C20A	1.552(14)	C2–C4–CL5	124.9(6)	C11–C12–C21	117.5(5)	C18B–C17–C19B	109(1)
C7–C12	1.424(8)	C17–C18B	1.511(34)	C2–C4–CL6	121.9(6)	C8–C13–C14	112.1(5)	C18B–C17–C20B	110(1)
C8–C9	1.395(9)	C17–C19B	1.570(33)	CL5–C4–CL6	113.2(4)	C8–C13–C15	110.0(5)	C19B–C17–C20B	109(1)
C8–C13	1.546(10)	C17–C20B	1.552(29)	P1–C7–C8	124.0(4)	C8–C13–C16	110.9(6)	C12–C21–C22	109.9(6)
C9–C10	1.375(10)	C21–C22	1.531(10)	P1–C7–C12	116.2(4)	C14–C13–C15	105.1(6)	C12–C21–C23	113.7(5)
C10–C11	1.393(9)	C21–C23	1.551(11)	C8–C7–C12	119.2(5)	C14–C13–C16	110.2(5)	C12–C21–C24	111.0(5)
C10–C17	1.533(9)	C21–C24	1.541(9)	C7–C8–C9	117.8(6)	C15–C13–C16	108.3(6)	C22–C21–C23	108.3(6)
				C7–C8–C13	126.6(5)	C10–C17–C18A	109.4(7)	C22–C21–C24	107.1(6)
				C9–C8–C13	115.4(6)	C10–C17–C19A	112.2(7)	C23–C21–C24	106.5(6)

Numbers in parentheses are estimated standard deviations.

TABLE 2 Fractional Coordinates and Equivalent Isotropic Displacements Coefficients (Å^2) for **6b**

Atom	X^a	Y^a	Z^a	$U(eq)^{a,b}$	*Atom*	X^a	Y^a	Z^a	$U(eq)^{a,b}$
P1	0.3773(1)	−0.0049(2)	0.4943(3)	0.048(1)	C19B	0.097(2)	0.415(3)	0.138(5)	0.098(8)
C2	0.3934(3)	−0.1251(6)	0.238(1)	0.043(3)	C20B	0.078(2)	0.193(3)	−0.116(5)	0.097(8)
C3	0.4106(4)	0.0058(6)	0.212(1)	0.054(4)	H3A	0.375(4)	0.061(7)	0.100(11)	0.040(19)
C4	0.4150(3)	−0.2477(7)	0.142(1)	0.043(3)	H3B	0.468(6)	0.021(10)	0.203(16)	0.095(30)
CL5	0.4044(1)	−0.3838(2)	0.2484(3)	0.082(1)	H9	0.112(4)	0.017(8)	0.220(14)	0.066(24)
CL6	0.4562(1)	−0.2872(2)	−0.1162(3)	0.074(1)	H11	0.204(4)	0.370(7)	0.370(13)	0.055(22)
C7	0.2797(3)	0.0762(6)	0.454(1)	0.049(3)	H14A	0.259(4)	−0.106(8)	0.769(13)	0.059(23)
C8	0.2176(3)	0.0061(6)	0.384(1)	0.051(3)	H14B	0.256(4)	−0.273(8)	0.637(13)	0.059(23)
C9	0.1560(3)	0.0701(6)	0.280(1)	0.046(4)	H14C	0.323(4)	−0.185(8)	0.560(14)	0.063(23)
C10	0.1515(3)	0.2001(6)	0.257(1)	0.047(4)	H15A	0.088(4)	−0.102(8)	0.404(13)	0.063(24)
C11	0.2090(3)	0.2711(5)	0.364(1)	0.054(4)	H15B	0.124(5)	−0.225(8)	0.553(14)	0.074(26)
C12	0.2715(3)	0.2160(6)	0.467(1)	0.050(3)	H15C	0.125(5)	−0.057(8)	0.679(15)	0.080(28)
C13	0.2074(4)	−0.1322(6)	0.427(1)	0.057(4)	H16A	0.265(4)	−0.243(7)	0.133(12)	0.049(21)
C14	0.2646(4)	−0.1750(7)	0.609(1)	0.083(5)	H16B	0.205(5)	−0.334(10)	0.236(17)	0.106(34)
C15	0.1303(4)	−0.1283(8)	0.521(2)	0.070(5)	H16C	0.168(4)	−0.212(8)	0.087(13)	0.067(25)
C16	0.2124(4)	−0.2373(7)	0.207(1)	0.075(5)	H22A	0.370(4)	0.177(8)	0.827(15)	0.071(25)
C17	0.0847(4)	0.2673(7)	0.134(1)	0.051(4)	H22B	0.380(4)	0.343(7)	0.944(12)	0.044(20)
C21	0.3252(4)	0.3125(6)	0.609(1)	0.069(4)	H22C	0.293(5)	0.286(10)	0.931(17)	0.104(34)
C22	0.3443(5)	0.2766(7)	0.842(1)	0.115(7)	H23A	0.387(5)	0.343(9)	0.332(14)	0.079(27)
C23	0.3993(5)	0.3113(8)	0.495(1)	0.090(6)	H23B	0.434(6)	0.380(10)	0.601(18)	0.114(36)
C24	0.2876(5)	0.4571(7)	0.650(2)	0.105(6)	H23C	0.430(6)	0.211(10)	0.469(18)	0.111(35)
C18A	0.1115(8)	0.311(2)	−0.067(3)	0.101(4)	H24A	0.237(4)	0.462(7)	0.745(13)	0.056(22)
C19A	0.0230(8)	0.170(1)	0.041(2)	0.097(4)	H24B	0.325(4)	0.522(6)	0.753(11)	0.035(18)
C20A	0.0482(8)	0.387(1)	0.306(2)	0.096(4)	H24C	0.272(4)	0.486(8)	0.496(14)	0.070(25)
C18B	0.014(2)	0.266(3)	0.249(5)	0.101(9)	—	—	—	—	—

[a] Numbers in parentheses are estimated standard deviations.

[b] Equivalent isotropic U is defined as one-third the trace of the orthogonalized U_{ij} tensor.

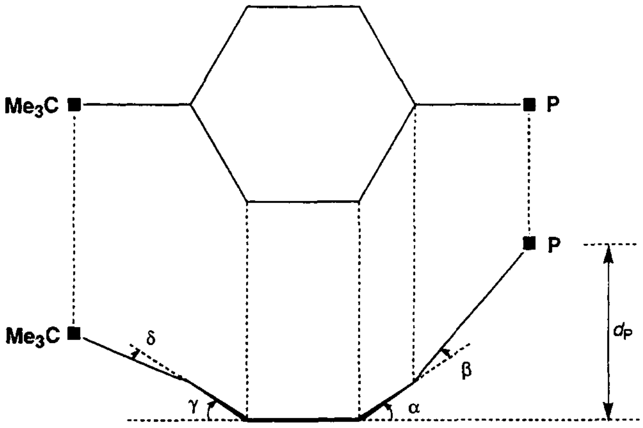
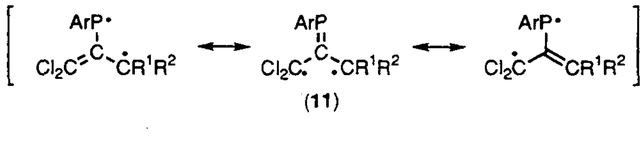


FIGURE 2 Deformation of the aromatic ring to a boat form and definitions of angles α, β, γ, and δ (°) and distance d_P (Å) in the deformed Ar ring. Hydrogen atoms and o-t-butyl groups are omitted for clarity.



SCHEME 3

afforded 682.5 mg (56%) of **8**: Colorless needles (MeOH), mp 108.5–109.5°C; ^{1}H NMR (200 MHz, CDCl$_3$) δ = 1.39 (9H, s, p-Bu^t), 1.69 (18H, s, o-Bu^t), 2.66 (1H, d, $^4J_{\mathrm{HH}}$ = 2.0 Hz, C≡CH), 5.81 (1H, dd, $^1J_{\mathrm{PH}}$ = 248.0 Hz and $^4J_{\mathrm{HH}}$ = 2.0 Hz, PH), and 7.53 (2H, d, $^4J_{\mathrm{PH}}$ = 2.0 Hz, m-Ar); ^{31}P NMR (81 MHz, CDCl$_3$) δ = −102.4 (d, $^1J_{\mathrm{PH}}$ = 247.4 Hz); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$) δ = 31.1 (s, -C$\underline{\mathrm{Me}}_3$), 33.6 (d, J_{PC} = 5.0 Hz, o-C$\underline{\mathrm{Me}}_3$), 35.0 (s, p-$\underline{\mathrm{C}}Me_3$), 39.4 (s, o-$\underline{\mathrm{C}}Me_3$), 83.5 (d, $^1J_{\mathrm{PC}}$ = 25.0 Hz, P$\underline{\mathrm{C}}$≡C), 91.0 (d, $^2J_{\mathrm{PC}}$ = 2.0 Hz, PC≡$\underline{\mathrm{C}}$), 122.7 (d, $^3J_{\mathrm{PC}}$ = 5.0 Hz, m-Ar), 125.0 (d, $^1J_{\mathrm{PC}}$ = 25.0 Hz, ipso-Ar), 150.8 (s, p-Ar), and 155.4 (d, $^2J_{\mathrm{PC}}$ = 10.0 Hz, o-Ar); UV (hexane) 249 (sh, log ϵ 3.78) and 284 nm (sh, 3.11); IR (KBr) 2402 and 2034 cm^{-1}; MS m/z (*rel* intensity) 301 (M$^+$ − 1; 100), 287 (M$^+$ − Me; 45), 245 (M$^+$ − Bu^t; 17), and 57 (t-Bu$^+$; 38); Found: m/z 302.2165. Calcd for $C_{20}H_{31}P$: M, 302.2163.

Base-Induced Isomerization of **8**

To a solution of **8** (61.0 mg, 0.20 mmol) in THF (15 mL) was added 0.21 mmol of butyllithium (1.63 M solution in hexane) at −78°C, and the mixture was stirred for 20 minutes at that temperature. To the resulting solution was added 8 μL of methanol at −78°C, and the reaction mixture was warmed to room temperature. Removal of the solvent in vacuo followed by column chromatographic separation (SiO$_2$/hexane) gave 38.7 mg (63%) of **7b** [10]. ^{1}H NMR (200 MHz, CDCl$_3$) δ = 1.32 (9H, s, *p*-Bu^t), 1.60 (18H, d, $^5J_{PH}$ = 0.6 Hz, *o*-Bu^t), 5.25 (2H, d, $^3J_{PH}$ = 29.3 Hz, C$\underline{H}_2$), and 7.42 (2H, d, $^4J_{PH}$ = 1.8 Hz, *m*-Ar); ^{31}P NMR (81 MHz, CDCl$_3$) δ = 58.7 (t, $^3J_{PH}$ = 29.2 Hz).

TBAF-Induced Isomerization of 8

TBAF (1 M solution in THF; contains <5 wt pct water) was purchased from Aldrich Chemical Company, Inc., and used as supplied. To a solution of **8** (92.6 mg, 0.307 mmol) in THF (10 mL) was added 0.030 mmol of TBAF (1 M solution in THF) at 0°C, and the mixture was stirred for 10 minutes at that temperature. The resulting THF solution was allowed to pass through a short silica-gel column without concentration. Then the solvent was removed under reduced pressure, and the residue was chromatographed (SiO$_2$/pentane) to give 82.4 mg (89%) of **7b**.

Attempted Thermal Isomerization of 8

The ethynylphosphine **8** (34.3 mg, 0.11 mmol) was dissolved in 5 mL of toluene and refluxed for 90 minutes. The solvent was concentrated in vacuo. No evidence for an isomerization could be seen in the ^{31}P NMR spectrum of the residue. The compound **8** was recovered (27.2 mg, 79%) after column chromatography.

Preparation of 7b *by the Reaction of TBAF with* 10

To a solution of **10** [11] (177 mg, 0.473 mmol) in THF (50 mL) was added 0.16 mmol of TBAF (1 M solution in THF) at −78°C, and the resulting mixture was warmed to 0°C. Removal of the solvent followed by column chromatographic separation (SiO$_2$/hexane) afforded 49.7 mg (35%) of **7b**.

2-Dichloromethylene-1-(2,4,6-tri-t-butylphenyl)phosphirane (6b)

To a solution of **7b** (97.8 mg, 0.325 mmol) and benzyltriethylammonium chloride (80.9 mg, 0.355 mmol) in hexane (5 mL) were added 5 mL of a 50% aqueous solution of sodium hydroxide and 0.4 mL (4.97 mmol) of chloroform at room temperature. The mixture was refluxed for 2 hours, and then the organic layer was separated and dried with MgSO$_4$. After evaporation of the solvent, the residue was chromatographed (SiO$_2$/pentane) to give 15.7 mg (13%) of **6b** along with 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethylene (7.9 mg, 7%) and the starting **7b** (52.8 mg, 54% recovery). **6b**: Colorless needles (MeOH), mp 119–120°C; ^{1}H NMR (200 MHz, CDCl$_3$) δ = 1.29 (9H, s, *p*-Bu^t), 1.61 (18H, s, *o*-Bu^t), 1.90 (2H, m, CH$_2$), and 7.25 (2H, d, $^4J_{PH}$ = 2.3 Hz, *m*-Ar); ^{31}P NMR (81 MHz, CDCl$_3$) δ = −126.7 (d, $^2J_{PH}$ = 21.0 Hz); ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$) δ = 25.6 (d, $^1J_{PC}$ = 23.3 Hz, CH$_2$), 31.1 (s, *p*-C$\underline{\mathrm{Me}}_3$), 33.7 (d, $^4J_{PC}$ = 8.8 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 34.5 (s, *p*-$\underline{\mathrm{C}}Me_3$), 38.9 (s, *o*-$\underline{\mathrm{C}}Me_3$), 118.5 (d, $^2J_{PC}$ = 17.8 Hz, CCl$_2$), 122.9 (s, *m*-Ar), 131 (d, $^1J_{PC}$ = 23.3 Hz, ipso-Ar), 132.3 (d, $^1J_{PC}$ = 13.6 Hz, $\underline{\mathrm{C}}$ = CCl$_2$), 148.9 (s, *p*-Ar), and 155.6 (d, $^2J_{PC}$ = 5.3 Hz, *o*-Ar); UV (hexane) 251 (sh, log ϵ 4.13) and 291 nm (sh, 3.20); IR (KBr) 1654 cm^{-1}; MS (70 eV) *m/z* (*rel* intensity) 384 (M$^+$; 1), 369 (M$^+$ − Me; 73), 349 (M$^+$ − Cl; 72), 327 (M$^+$ − Bu^t; 24), and 57 (*t*-Bu$^+$; 100); Found: *m/z* 384.1540. Calcd for C$_{21}$H$_{31}$Cl$_2$P: M, 384.1540.

2-Dichloromethylene-3-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphirane (6c)

To a solution of **7c** [6,10] (107.2 mg, 0.283 mmol) and benzyltriethylammonium chloride (62.0 mg, 0.272 mmol) in hexane (3 mL) were added 3 mL of a 50% aqueous solution of sodium hydroxide and 0.34 mL (4.25 mmol) of chloroform at room temperature. The mixture was refluxed for 2.5 hours, and then the organic layer was separated and dried with MgSO$_4$. After evaporation of the solvent, the residue was chromatographed (Al$_2$O$_3$/hexane) to give 23.7 mg (18%) of **6c**: Colorless powder, mp 105–107°C; ^{1}H NMR (200 MHz, CDCl$_3$) δ = 1.32 (9H, s, *p*-Bu^t), 1.55 (18H, s, *o*-Bu^t), 2.87 (1H, d, $^2J_{PH}$ = 4.3 Hz, C$\underline{\mathrm{H}}$Ph), 7.01 (2H, d, J = 6.8 Hz, *o*-Ph), 7.21 (1H, t, J = 6.9 Hz, *p*-Ph), and 7.26–7.30 (2H + 2H, m, *m*-Ph + *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = −99.2; ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ = 31.2 (s, *p*-C$\underline{\mathrm{Me}}_3$), 33.9 (d, $^4J_{PC}$ = 8.4 Hz, *o*-C$\underline{\mathrm{Me}}_3$), 34.6 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.0 (s, *o*-$\underline{\mathrm{C}}Me_3$), 43.4 (d, $^1J_{PC}$ = 22.1 Hz, $\underline{\mathrm{C}}$HPh), 121.8 (d, $^2J_{PC}$ = 19.0 Hz, $\underline{\mathrm{C}}$Cl$_2$), 123.1 (s, *m*-Ar), 126.1 (s, *p*-Ph), 127.1 (d, $^3J_{PC}$ = 5.9 Hz, *o*-Ph), 128.4 (s, *m*-Ph), 128.8 (d, $^1J_{PC}$ = 42.5 Hz, $\underline{\mathrm{C}}$=CCl$_2$), 135.8 (d, $^1J_{PC}$ = 59.8 Hz, ipso-Ar), 137.9 (d, $^2J_{PC}$ = 8.5 Hz, ipso-Ph), 149.3 (s, *p*-Ar), and 156.1 (d, $^2J_{PC}$ = 5.7 Hz, *o*-Ar); IR (KBr) 1730, 1635, 1362, and 877 cm^{-1}; MS (70 eV) *m/z* (*rel* intensity) 460 (M$^+$; 0.1), 425 (M$^+$ − Cl; 2), 403 (M$^+$ − Bu^t; 12), and 57 (*t*-Bu$^+$; 100); Found: *m/z* 403.1162. Calcd for C$_{23}$H$_{26}$Cl$_2$P: M$^+$ − Bu^t; 403.1149. The phosphirane **6c** decomposed in a few days at room temperature.

X-Ray Structure Determination of 6b

The compound **6b** was recrystallized from methanol. Crystal data for **6b**: C$_{21}$H$_{31}$Cl$_2$P, M_r = 385.35, triclinic, space group $P\bar{1}$, a = 18.063(6), b = 10.366(5), c = 6.050(5) Å, α = 102.01(5)°, β = 94.48(4)°, γ = 82.67(3)°, U = 1097(1) Å^3, Z = 2, D_c = 1.167 g cm^{-3}, μ = 3.68 cm^{-1}. Reflections (3867) with $2\theta \leq 50.0°$ were recorded, and 2177 of these with $F > 4\sigma(F)$ were judged as observed. The structure was solved using SHELX-86 [16]. Fullmatrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic hydrogens converged to $R = 0.076$ and $R_w = 0.126$. The disordered *p*-*t*-butyl group [site of occupancy (C18A, C19A, C20A) = 0.68 and (C18B, C19B, C20B) = 0.32] was refined isotropically [17].

Molecular Mechanics Calculation for **6b** *and* **5b**

A molecular mechanics calculation was executed for the compounds **6** and **5** by the MM2 method using the CAChe program [18] to calculate the MM energies for the optimized structures: 106.8530 kcal/mol for **6b** and 109.0320 kcal/mol for **5b**.

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of atomic coordinates, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and structure factors for **6b** (9 pages) are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

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