Preparation and Structure of Sterically Protected Diethynylphosphines and Dibutadiynylphosphines

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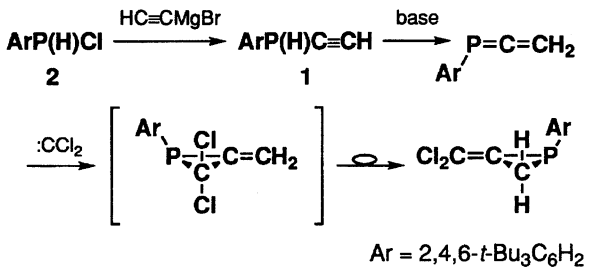
Sterically protected diethynyl(2,4,6-tri-*t*-butylphenyl)phosphines and (2,4,6-tri-*t*-butylphenyl)bis(4-trimethylsilyl-1,3-butadiynyl)phosphine were prepared and their structures were analyzed by X-ray crystallography. The aromatic rings in these molecules are distorted to boat or more likely envelope forms in the crystals. Large distortion in the –P–C≡C– moieties was also observed.

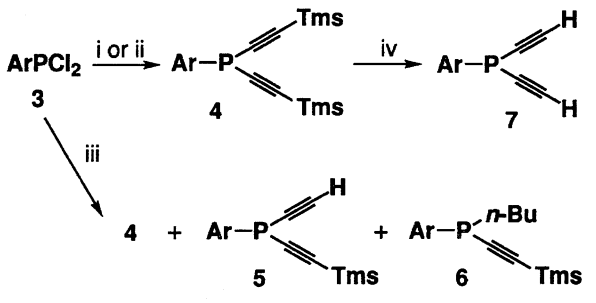
Sterically protected phosphorus compounds are currently of interest because of their unusual properties.[1] Molecular design utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) have permitted us to prepare several kinds of stabilized low-coordinated phosphorus compounds such as diphosphene,[2] phosphaallenes,[3] diphospharadialene,[4] dithioxophosphorane,[5] and diselenoxophosphorane.[6] On the other hand, structure and properties of ethynylphosphines have attracted much interest because of their interesting π bond systems and potential applications as building blocks for further interesting compounds.[7,8] However, little is known about the preparation and properties of ethynylphosphines bearing extremely bulky substituents. We have recently reported on the preparation and reaction of ethynyl(2,4,6-tri-*t*-butylphenyl)phosphine (**1**), which was prepared from chloro(2,4,6-tri-*t*-butylphenyl)phosphine (**2**) as shown in Scheme 1.[9] We now report on the preparations and structures of several sterically protected diethynylphosphines and dibutadiynylphosphines.[10]

Results and Discussion

Sterically hindered dichloro(2,4,6-tri-*t*-butylphenyl)-phosphine **3** (1.7 mmol)[2] was allowed to react with (trimethylsilylethynyl)magnesium bromide [prepared by the reaction of ethylmagnesium bromide (4.5 mmol) and trimethylsilylacetylene (4.9 mmol)] to give (2,4,6-tri-*t*-butylphenyl)bis(trimethylsilylethynyl)phosphine (**4**) in 78% yield based on **3** (Scheme 2). Similarly, the reaction of **3** (4.2 mmol) with (trimethylsilylethynyl)-lithium [prepared by the reaction of butyllithium (6.6 mmol) and trimethylsilylacetylene (7.1 mmol)] gave **4** (74% yield based on butyllithium). Either the Grignard reagent or the corresponding lithium reagent reacted with **3** to give alkylation products, but it should be noted that an excess amount of butyllithium led to the formation of ethynyl(2,4,6-tri-*t*-butylphenyl)(trimethylsilylethynyl)phosphine **5** and butyl(trimethylsilylethynyl)phosphine **6** in higher yields than expected, as well as **4** in lower yield. Thus, the reaction of **3** (5.9 mmol) with (trimethylsilylethynyl)lithium [prepared by the reaction of butyllithium (15 mmol) and trimethylsilylacetylene (12 mmol)] afforded **4** (1.4 mmol, 24% yield based on **3**), **5** (0.93 mmol, 16%), and **6** (0.61 mmol, 10%). The formation of compounds **5** and **6** seems to be due to the reaction of **4** with butyllithium, since a separate reaction of **4** with butyllithium afforded **5**, **6** and diethynyl(2,4,6-tri-*t*-butylphenyl)phosphine (**7**). But the following mechanisms cannot be ruled out: An interme-



Scheme 1.

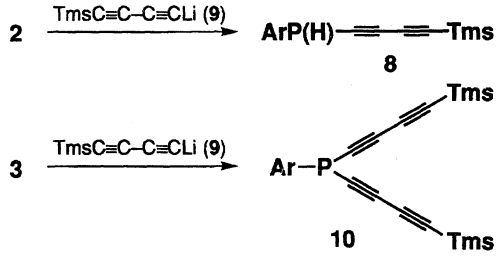


Scheme 2.

diate ArP(Cl)(C≡CSiMe$_3$) reacts with an excess amount of butyllithium to give **6**, or that an excess amount of butyllithium might first react with **3** to form ArP(Cl)-(*n*-Bu) which might then react with Me$_3$SiC≡CLi to give **6**. The diethynylphosphine **7** was also obtained by the desilylation reaction of **4** with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) (contains<5 wt% water) in 89% yield.

For a further extended diyne system, (4-trimethylsilyl-1,3-butadiynyl)(2,4,6-tri-*t*-butylphenyl)phosphine (**8**) was prepared (19% yield) by the reaction of **2** with an equimolar amount of (4-trimethylsilyl-1,3-butadiynyl)lithium (**9**)[11] (Scheme 3), whereas the reaction of **9** with the dichlorophosphine **3** afforded bis-(4-trimethylsilyl-1,3-butadiynyl)phosphine (**10**) in 53% yield. Both of the compounds **8** and **10** might serve as good starting materials for phospha[*n*]pericyclynes.

The structures of **7** and **10** were confirmed by X-ray crystallography. Figure 1 depicts the ORTEP[12] drawing of the molecular structures of **7**. Figure 2 shows the crystal structure of **10** which contains two crystallographically independent molecules per asymmetric unit. The two molecules have the mirror-image relation. The trimethylsilyl group Si(3)Me$_3$ is located between the trimethylsilyl groups Si(1)Me$_3$ and Si(2)Me$_3$. Similarly, Si(1′)Me$_3$ is located between Si(3)Me$_3$ and Si(4)-



Scheme 3.

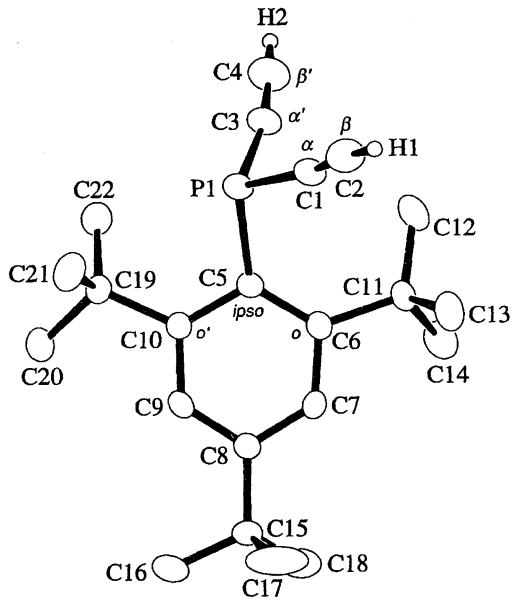


Fig. 1. Molecular structure for **7**. Hydrogen atoms, except H(1) and H(2), are omitted for clarity.

Me$_3$ (Figs. 3 and 4), forming a zipper-like arrangement of the molecules. Seemingly, the relatively rigid and long trimethylsilylbutadiynyl group causes this packing mode [Si(1)–Si(3): 6.3 Å; Si(2)–Si(3): 5.9 Å; Si(3)–Si-(1′): 6.9 Å; Si(4)–Si(1′): 5.6 Å]. Some important bond lengths and angles for **7** and **10** are listed in Table 1.

Compound **7** is suffering from steric repulsion between the ethynyl carbon(s) and the *o*-*t*-butyl group-(s), causing large distortion within the benzene ring to take a boat or more likely an envelope form. Table 2 shows the distortion of the benzene rings for **7**, where the distortion parameters are displayed in Fig. 5. Moreover, the angles P–C(*ipso*)–C(*o*) are largely distorted (127.1(2)° and 112.4(2)°, for P(1)–C-(5)–C(6) and P(1)–C(5)–C(10), respectively) in order

Table 1. Selected Bond Distances and Angles for **7** and **10**

	Bond distance/Å [a]				Bond angle/° [a]		
	7 [b]	**10** (Molecule A) [c]	**10** (Molecule B) [c]		**7** [b]	**10** (Molecule A) [c]	**10** (Molecule B) [c]
P–C(α)	1.764(4)	1.76(1)	1.76(1)	C(α)–P–C(α')	102.2(2)	101.7(6)	103.2(6)
P–C(α')	1.767(4)	1.75(2)	1.78(2)	C(α)–P–C(*ipso*)	106.1(1)	106.8(6)	107.9(6)
P–C(*ipso*)	1.852(3)	1.85(1)	1.85(1)	C(α')–P–C(*ipso*)	109.5(1)	111.2(6)	107.8(6)
C(α)–C(β)	1.168(4)	1.22(2)	1.21(2)	P–C(*ipso*)–C(o)	127.1(2)	126.6(10)	114.0(10)
C(α')–C(β')	1.166(4)	1.22(2)	1.20(2)	P–C(*ipso*)–C(o')	112.4(2)	113.5(10)	126.3(10)
C(*ipso*)–C(*o*)	1.422(4)	1.41(2)	1.42(1)	P–C(α)–C(β)	166.1(4)	168(1)	166(1)
C(*ipso*)–C(o')	1.436(4)	1.45(1)	1.43(2)	P–C(α')–C(β')	168.5(4)	170(1)	168(1)
C(β)–C(γ)	—	1.38(2)	1.38(2)	C(α)–C(β)–C(γ)	—	177(1)	179(1)
C(β')–C(γ')	—	1.38(2)	1.38(2)	C(α')–C(β')–C(γ')	—	175(1)	176(1)
C(γ)–C(δ)	—	1.16(2)	1.19(2)	C(β)–C(γ)–C(δ)	—	179(1)	178(1)
C(γ')–C(δ')	—	1.20(2)	1.21(2)	C(β')–C(γ')–C(δ')	—	177(1)	176(1)
C(δ)–Si	—	1.84(1)	1.83(2)	C(γ)–C(δ)–Si	—	179(1)	178(1)
C(δ')–Si′	—	1.83(2)	1.83(2)	C(γ')–C(δ')–Si′	—	176(1)	178(1)

a) Numbers in parentheses are estimated standard deviations. b) For atom labeling scheme, see Fig. 1. c) For atom labeling scheme, see Fig. 2.

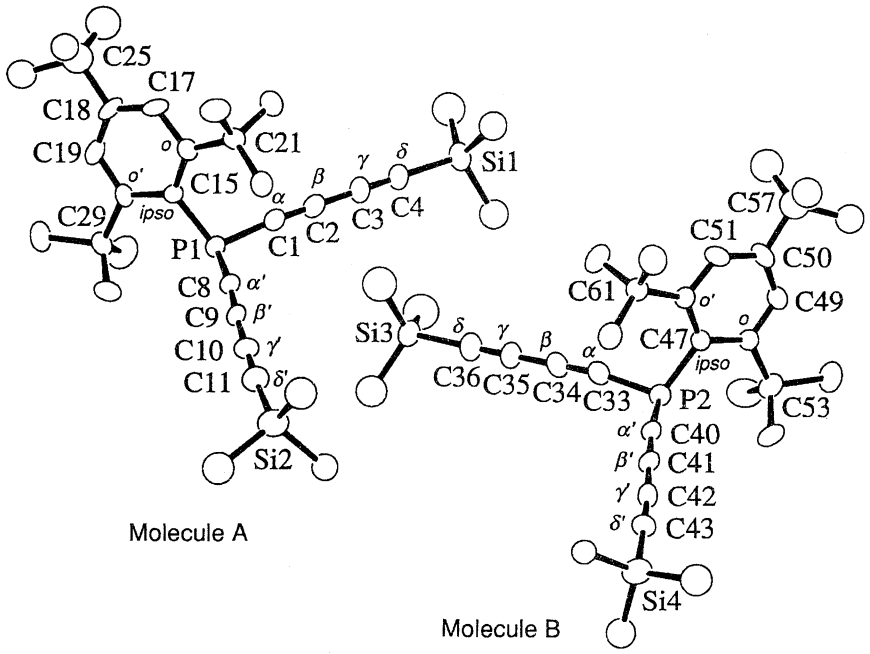


Fig. 2. Molecular structure for **10**. The structure contains two crystallographically independent molecules in each asymmetric unit. One of the Tms groups and one of the *o*-*t*-butyl groups are disordered and those with the predominant occupancy factor are displayed for clarity.

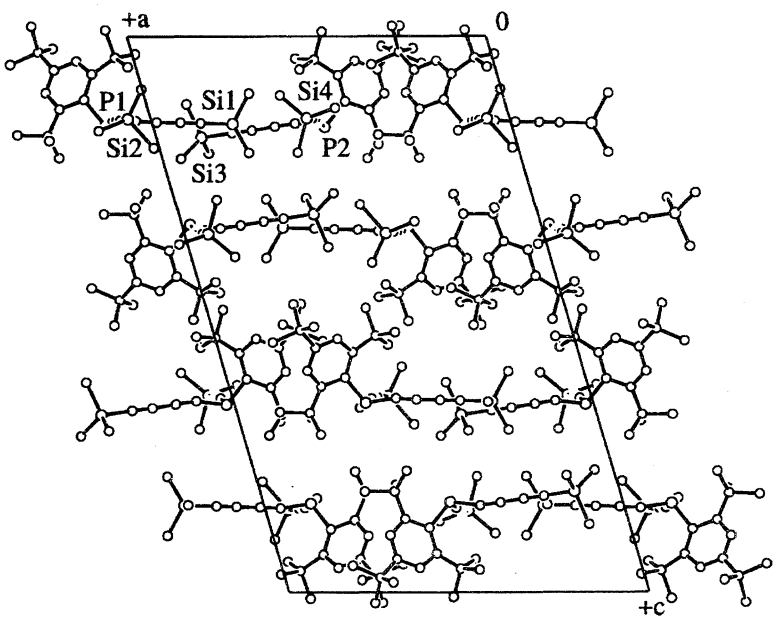


Fig. 3. Crystal structures of **10**, along the *b*-axis. Hydrogen atoms and the disordered atoms with the subordinate occupancy factor are omitted for clarity.

to reduce steric repulsion. This distortion at P–C(*ipso*)–C(*o*) moiety in **7** is comparable to those in (2,4-di-*t*-butyl-6-dimethylaminomethylphenyl)dithioxophosphorane (132.0(8)° and 109.7(8)°)[13a] and in (2,4-di-*t*-butyl-6-piperidinophenyl)diselenoxophosphorane (143.4(5)° and 96.3(4)°)[13b] in the crystals which involve intramolecular coordination of the nitrogen lone-pair to the phosphorus atom. The angles P–C(α)–C(β) for **7** are also distorted from linearity, 166.1(4)° for P(1)–C(1)–C(2) and 168.5(4)° for P(1)–C(3)–C(4). Similar distortions are also observed in the case of **10** (Tables 1 and 2). These distortions seem to be caused by steric bulk of the Ar group employed in order to increase kinetic stability of the phosphorus atom.

In summary, we have prepared some sterically protected diethynylphosphines and dibutadiynylphosphines. Large distortions around the phosphorus atoms and the benzene rings were demonstrated by X-ray crystallographic analysis. The dialkynylphosphines described above seem to be promising starting materi-

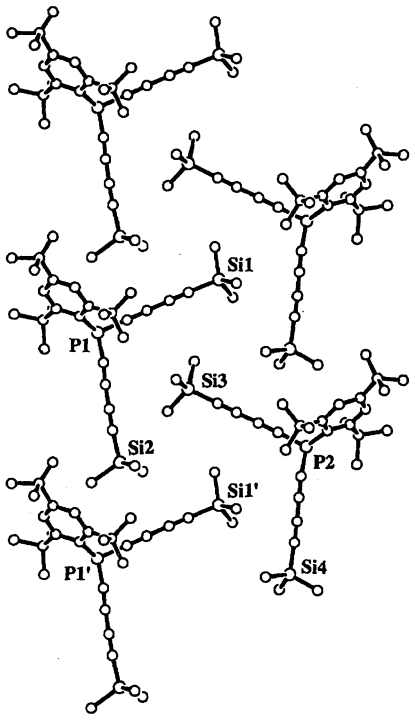


Fig. 4. Zipper like arrangement of **10**.

Table 2. Deformation of the Aromatic Rings in **7** and **10**[a)]

	7	**10** (Molecule A)	**10** (Molecule B)
α/°	7.9	6.4	3.6
β/°	11.6	10.9	8.2
γ/°	2.4	2.0	2.6
δ/°	2.0	0.2	0.5
d_P/Å	0.72	0.63	0.43

a) For the definition of the geometrical parameters, see Fig. 5.

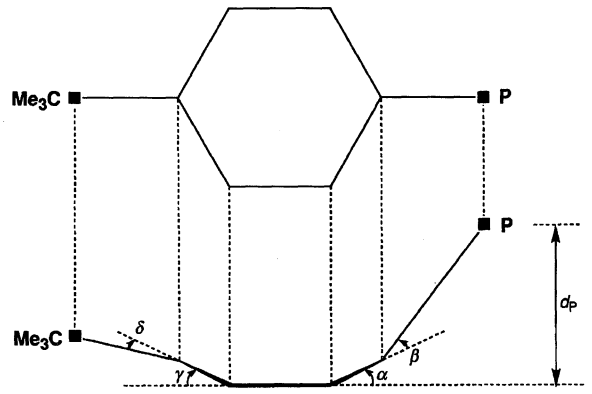


Fig. 5. Side profile of the distorted benzene ring and the distortion parameters, α, β, γ, δ, and d_P are difined as indicated, where the *o*-*t*-butyl groups are omitted for clarity.

als for preparation of interesting molecules such as phospha[*n*]pericyclynes which involve extended π-systems.

Experimental

The melting points were taken on a Yanagimoto MP-J3 micromelting-point apparatus and were uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on either a Bruker AC-200P spectrometer or a Bruker AM-600 spectrometer. ^{31}P NMR spectra were measured on a Bruker AC-200P spectrometer. UV-vis spectra were obtained on a Hitachi U-3210 spectrometer. IR spectra were recorded on a Horiba FT-300 spectrometer. MS were taken on either a JEOL HX-110 spectrometer or a Hitachi M-2500S spectrometer.

Chloro(2,4,6-tri-*t*-butylphenyl)phosphine (**2**)[14,15] and dichloro(2,4,6-tri-*t*-butylphenyl)phosphine (**3**)[2] were prepared according to the methods reported previously. (4-Trimethylsilyl-1,3-butadiynyl)lithium (**9**) was prepared according to a literature method.[11b] TBAF (1.0 mol dm^{-3} solution in THF; contains<5 wt% water) was purchased from Aldrich Chemical Company and was used as supplied.

(2, 4, 6- Tri- *t*- butylphenyl)bis(trimethylsilylethynyl)phosphine (4): To a solution of trimethylsilylacetylene (0.68 mL, 4.9 mmol) in Et_2O (6 mL) was added 4.5 mmol of ethylmagnesium bromide (0.90 M solution in THF, 1 M=1 mol dm^{-3}) at −78 °C and the resulting mixture was warmed to room temperature. This solution was added to an Et_2O (24 mL) solution of the dichlorophosphine **3** (602.6 mg, 1.7 mmol) at −78 °C. The resulting solution was warmed to room temperature and the solvent was removed under reduced pressure. The residue was extracted with pentane and dried. Removal of the solvent in vacuo, followed by column chromatographic separation (SiO_2/hexane), afforded **4** (624.6 mg, 78% yield): Pale yellow powder, mp 105.0—106.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.24 (18H, s, Tms=Me_3Si), 1.40 (9H, s, *p*-Bu^t), 1.77 (18H, s, *o*-Bu^t), and 7.55 (2H, d, $^4J_{PH}$=3.2 Hz, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=−70.3; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=−0.4 (s, Tms), 31.1 (s, *p*-C$\underline{Me_3}$), 34.1 (d, $^4J_{PC}$=7.2 Hz, *o*-C$\underline{Me_3}$), 34.9 (s, *p*-$\underline{C}Me_3$), 39.9 (d, $^3J_{PC}$=4.5 Hz, *o*-$\underline{C}Me_3$), 104.0 (d, $^1J_{PC}$=12.5 Hz, P$\underline{C}$≡C), 116.6 (d, $^2J_{PC}$=3.8 Hz, PC≡$\underline{C}$), 123.9 (d, $^3J_{PC}$=9.0 Hz, *m*-Ar), 124.4 (d, $^1J_{PC}$=22.7 Hz, *ipso*-Ar), 151.4 (d, $^4J_{PC}$=1.8 Hz, *p*-Ar), and 157.7 (d, $^2J_{PC}$=17.2 Hz, *o*-Ar); UV (hexane) 237 (sh, log ε 4.36) and 288 nm (3.62); IR (KBr) 2088, 1394, and 1249 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 471 (M^++1; 14) and 57 (Bu^{t+}; 100). Found: *m*/*z* 470.2954. Calcd for $C_{28}H_{47}PSi_2$: M, 470.2951.

Preparation of 4 by Reaction of 3 with (Trimethylsilylethynyl)lithium. To a solution of trimethylsilylacetylene (1.0 mL, 7.1 mmol) in THF (54 mL) was added 6.6 mmol of butyllithium (1.64 M solution in hexane) at −78 °C; the resulting mixture was stirred for 30 min at this temperature. To this solution was added a THF (40 mL) solution of the dichlorophosphine **3** (1.451 g, 4.2 mmol) at −78 °C. The mixture was stirred for 5 min at this temperature. The solution was then warmed to room temperature. The solvent was removed in vacuo and the residue underwent column chromatography (SiO_2/hexane) to give 1.145 g of **4** in 74% yield based on butyllithium.

Ethynyl(2, 4, 6- tri- *t*- butylphenyl)(trimethylsilylethynyl)phosphine (5) and Butyl(2,4,6-tri-*t*-butylphenyl)(trimethylsilylethynyl)phosphine (6): To a solution of trimethylsilylacetylene (1.7 mL, 12 mmol) in THF (75 mL) was added 15 mmol of butyllithium (1.62 M

solution in hexane) at −78 °C and the resulting mixture was stirred for 30 min at this temperature. To this solution was added a THF (55 mL) solution of the dichlorophosphine **3** (2.0262 g, 5.9 mmol) at −78 °C and the mixture was stirred for 5 min at this temperature. The resulting solution was warmed to room temperature and the solvent was removed under reduced pressure. Pentane was added to the residue and the insoluble substances were removed by filtration through Celite. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/hexane) afforded **4** (660.4 mg, 24% yield), **5** (371.8 mg, 16%), and **6** (260.6 mg, 10%).

5: Colorless needles, mp 44.0—45.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.20 (9H, s, Tms), 1.58 (9H, s, *p*-Bu^t), 1.71 (18H, s, *o*-Bu^t), 3.19 (1H, d, $^3J_{PH}$=0.7 Hz, C≡CH), and 7.50 (2H, d, $^4J_{PH}$=3.1 Hz, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=−71.6; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=−0.4 (d, $^4J_{PC}$=1.3 Hz, Tms), 31.6 (s, *p*-C<u>Me</u>$_3$), 34.0 (d, $^4J_{PC}$=5.6 Hz, *o*-C<u>Me</u>$_3$), 34.9 (s, *p*-<u>C</u>Me$_3$), 39.8 (d, $^3J_{PC}$=4.0 Hz, *o*-<u>C</u>Me$_3$), 82.8 (d, $^2J_{PC}$=10.0 Hz, C≡<u>C</u>H), 96.0 (d, $^1J_{PC}$=11.0 Hz, <u>C</u>≡CH), 103.1 (d, $^1J_{PC}$=12.0 Hz, <u>C</u>≡CTms), 117.4 (d, $^2J_{PC}$=4.0 Hz, C≡<u>C</u>Tms), 123.7 (d, $^1J_{PC}$=22.0 Hz, *ipso*-Ar), 123.8 (d, $^3J_{PC}$=9.0 Hz, *m*-Ar), 151.7 (d, $^4J_{PC}$=2.5 Hz, *p*-Ar), and 157.8 (d, $^2J_{PC}$=17.0 Hz, *o*-Ar); UV (hexane) 235 (sh, log ε 4.25) and 284 nm (3.57); IR (KBr) 2083, 2029, 1250, and 847 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 398 (M$^+$; 27), 383 (M$^+$−Me; 12), 325 (M$^+$−Tms; 13), 73 (Tms$^+$; 41), and 57 (Bu^{t+}; 100). Found: *m*/*z* 398.2558. Calcd for $C_{25}H_{39}PSi$: M, 398.2559.

6: Pale yellow fine needles, mp 69.0—70.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.22 (9H, s, Tms), 0.82 (3H, t, *J*= 7.0 Hz, $CH_2C\underline{H}_3$), 1.1—1.6 (4H, m, CH_2), 1.32 (9H, s, *p*-Bu^t), 1.63 (18H, s, *o*-Bu^t), 1.95 (2H, br m, PCH_2), and 7.39 (2H, d, $^4J_{PH}$=2.3 Hz, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=−51.1; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=−0.1 (d, $^4J_{PC}$=1.4 Hz, Tms), 13.8 (s, $CH_2\underline{C}H_3$), 23.6 (d, J_{PC}= 14.2 Hz, CH_2), 28.4 (d, J_{PC}=19.6 Hz, CH_2), 30.7 (d, J_{PC}= 11.5 Hz, CH_2), 31.2 (s, *p*-C<u>Me</u>$_3$), 34.2 (d, $^4J_{PC}$=7.9 Hz, *o*-C<u>Me</u>$_3$), 34.8(s, *p*-<u>C</u>Me$_3$), 39.1 (d, $^3J_{PC}$=4.5 Hz, *o*-<u>C</u>Me$_3$), 108.2 (d, $^1J_{PC}$=33.9 Hz, <u>C</u>≡CTms), 118.0 (s, C≡<u>C</u>Tms), 122.4 (d, $^3J_{PC}$=7.0 Hz, *m*-Ar), 131.5 (d, $^1J_{PC}$=34.5 Hz, *ipso*-Ar), 150.1 (d, $^4J_{PC}$=2.1 Hz, *p*-Ar), and 156.8 (d, $^2J_{PC}$= 14.1 Hz, *o*-Ar); UV (hexane) 242 (log ε 4.34) and 285 nm (sh, 3.49); IR (KBr) 2080 and 1249 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 430 (M$^+$; 23), 373 (M$^+$−Bu^t; 19), 357 (M$^+$−Tms; 18), 301 (M$^+$−Tms−Bu^t; 29), 73 (Tms$^+$; 59), and 57 (Bu^{t+}; 100). Found: *m*/*z* 430.3186. Calcd for $C_{27}H_{47}PSi$: M, 430.3184.

Diethynyl(2,4,6-tri-*t*-butylphenyl)phosphine (7): To a THF (10 mL) solution of the phosphine **4** (55.6 mg, 0.12 mmol) was added 0.01 mmol of TBAF (1.0 M solution in THF) at 0 °C and the resulting mixture was warmed to room temperature. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/hexane) afforded **7** (34.5 mg, 89% yield). **7**: Colorless needles, mp 84.0—85.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.35 (9H, s, *p*-Bu^t), 1.68 (18H, s, *o*-Bu^t), 3.24 (2H, d, $^3J_{PH}$=0.9 Hz, C≡CH), and 7.48 (2H, d, $^4J_{PH}$=3.2 Hz, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=−71.7; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=31.0 (s, *p*-C<u>Me</u>$_3$), 34.0 (d, $^4J_{PC}$=8.0 Hz, *o*-C<u>Me</u>$_3$), 34.9 (s, *p*-<u>C</u>Me$_3$), 39.7 (d, $^3J_{PC}$=4.0 Hz, *o*-<u>C</u>Me$_3$), 82.1 (d, $^2J_{PC}$= 8.0 Hz, C≡<u>C</u>H), 96.7 (d, $^1J_{PC}$=16.3 Hz, <u>C</u>≡CH), 122.9 (d, $^1J_{PC}$=20.0 Hz, *ipso*-arom.), 123.8 (d, $^3J_{PC}$=8.2 Hz, *m*-Ar), 151.9 (s, *p*-Ar), and 157.9 (d, $^2J_{PC}$=16.0 Hz, *o*-Ar); UV (hexane) 212 (log ε 4.65), 236 (sh, 4.25), and 280 nm (3.64); IR (KBr) 2030 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 327 (M$^+$+1; 13) and 57 (Bu^{t+}; 100). Found: *m*/*z* 326.2164. Calcd for $C_{22}H_{31}P$: M, 326.2163.

(2,4,6-Tri-*t*-butylphenyl)(4-trimethylsilyl-1,3-butadiynyl)phosphine (8): To a solution of (4-trimethylsilyl-1,3-butadiynyl)lithium (**9**; 1.6 mmol) in Et_2O (16 mL) was added 1.8 mmol of the chlorophosphine **2** in Et_2O (24 mL) at −78 °C and the resulting mixture was stirred for 30 min at this temperature. Then the solvent was removed under reduced pressure below 0 °C. Pentane was added to the residue and the insoluble substances were removed by filtration through Celite. Removal of the solvent in vacuo followed by column chromatographic separation (SiO_2/pentane) afforded **8** (139.3 mg, 19% yield based on **2**): Pale yellow powder, mp 106.0—107.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.18 (9H, s, Tms), 1.35 (9H, s, *p*-Bu^t), 1.65 (18H, s, *o*-Bu^t), 5.89 (1H, d, $^1J_{PH}$=250.0 Hz, PH), and 7.49 (2H, d, $^4J_{PH}$=2.7 Hz, *m*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) δ=−98.3 (d, $^1J_{PH}$=250.0 Hz); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ=−0.5 (s, Tms), 31.2 (s, *p*-C<u>Me</u>$_3$), 33.6 (d, $^4J_{PC}$=6.8 Hz, *o*-C<u>Me</u>$_3$), 35.1 (s, *p*-<u>C</u>Me$_3$), 38.3 (s, *o*-<u>C</u>Me$_3$), 78.1 (d, $^1J_{PC}$=28.9 Hz, P<u>C</u>≡C), 86.9 (s, PC≡<u>C</u>), 87.6 (d, $^4J_{PC}$=1.4 Hz, C≡<u>C</u>Tms), 88.3 (d, $^3J_{PC}$=2.3 Hz, <u>C</u>≡CTms), 122.8 (d, $^3J_{PC}$=4.9 Hz, *m*-Ar), 123.5 (d, $^1J_{PC}$=24.9 Hz, *ipso*-Ar), 151.1 (s, *p*-Ar), and 155.7 (d, $^2J_{PC}$=10.8 Hz, *o*-Ar); UV (hexane) 258 (sh, log ε 4.20), 263 (sh, 4.15), 278 (sh, 3.83), and 297 nm (3.46); IR (KBr) 2404, 2159, 2071, and 1251 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 398 (M$^+$; 34), 73 (Tms$^+$; 89), and 57 (Bu^{t+}; 100). Found: *m*/*z* 398.2556. Calcd for $C_{25}H_{39}PSi$: M, 398.2559.

(2,4,6-Tri-*t*-butylphenyl)bis(4-trimethylsilyl-1,3-butadiynyl)phosphine (10): To a solution of (4-trimethylsilyl-1,3-butadiynyl)lithium (**9**; 0.77 mmol) in Et_2O (4.5 mL) was added 117.8 mg (0.34 mmol) of the dichlorophosphine **3** in THF (3mL) at 0 °C and the resulting mixture was stirred for 10 min at this temperature. Then the solution was warmed to room temperature and the solvent was removed under reduced pressure. The residue was extracted with pentane. The organic layer was dried ($MgSO_4$) and the solvent was evaporated. Chromatographic separation (SiO_2/pentane) of the residue using chilled column afforded **10** (88.5 mg, 53% yield): Pale yellow prisms, mp 160.0 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.20 (18H, s, Tms), 1.31 (9H, s, *p*-Bu^t), 1.64 (18H, s, *o*-Bu^t), and 7.45 (2H, d, $^4J_{PH}$=3.4 Hz, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=−63.0; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=−0.5 (s, Tms), 31.0 (s, *p*-C<u>Me</u>$_3$), 34.0 (d, $^4J_{PC}$=7.2 Hz, *o*-C<u>Me</u>$_3$), 35.0 (d, $^5J_{PC}$=0.7 Hz, *p*-<u>C</u>Me$_3$), 39.6 (d, $^3J_{PC}$=5.1 Hz, *o*-<u>C</u>Me$_3$), 74.5 (d, J_{PC}=10.3 Hz, <u>C</u>≡C), 87.8 (d, J_{PC}=3.8 Hz, <u>C</u>≡C), 92.4 (d, J_{PC}=2.2 Hz, <u>C</u>≡C), 93.6 (d, $^1J_{PC}$=16.7 Hz, P<u>C</u>≡C), 121.4 (d, $^1J_{PC}$=20.6 Hz, *ipso*-Ar), 123.9 (d, $^3J_{PC}$=9.7 Hz, *m*-Ar), 152.4 (d, $^4J_{PC}$=2.2 Hz, *p*-Ar), and 158.0 (d, $^2J_{PC}$=17.9 Hz, *o*-Ar); UV (hexane) 231 (sh, log ε 4.65), 250 (4.80), 292 (3.95), and 313 nm (3.85); IR (KBr) 2159, 2065, and 1250 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 518 (M$^+$; 32) and 57 (Bu^{t+}; 100). Found: *m*/*z* 518.2952. Calcd for $C_{32}H_{47}PSi_2$: M, 518.2937.

X-Ray Structure Determination of 7 and 10. 7: $C_{22}H_{31}P$, M_r=326.46. Monoclinic, space group $P2_1/n$,

$a=10.173(2)$, $b=21.723(4)$, $c=10.321(3)$ Å; $\beta=113.49(2)°$; $V=2091.8(8)$ Å^3, $Z=4$, $\rho=1.037$ g cm^{-3}, $\mu=1.30$ cm^{-1}; 3808 unique reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochrometer). Of these, 2234 with $I>3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86.[16] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined except for H(1) and H(2). $R=0.051$, $R_w=0.052$.

10: $C_{32}H_{47}PSi_2$, $M_r=518.87$. Monoclinic, space group $P2_1/n$, $a=18.961(5)$, $b=12.618(6)$, $c=30.201(5)$ Å; $\beta=106.50(2)°$; $V=6927(3)$ Å^3, $Z=8$, $\rho=0.995$ g cm^{-3}, $\mu=1.65$ cm^{-1}; 9545 unique reflections with $2\theta \leq 45.0°$ were recorded on a four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochrometer). Of these, 4052 with $I>3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86. The methyl carbon atoms of the trimethylsilyl group (C12–C14 and C44–C46) and the *p*-*t*-butyl group (C26–C28 and C58–C60) are disordered. These disordered groups were resolved into two positions from the difference maps. The predominant occupancy factors for (C12–C14), (C44–C46), (C26–C28), and (C58–C60) were refined to be 0.57, 0.51, 0.54, and 0.57, respectively. The carbon atoms of the trimethylsilyl groups (C5–C7, C12–C14, C37–C39, and C44–C46) and those of the *p*-*t*-butyl groups (C25–C28 and C57–C60) atoms were refined isotropically, while the other non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were included but not refined. $R=0.097$, $R_w=0.120$.

Further details of the crystal structure investigations for **7** and **10** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK). The complete F_o-F_c data are also deposited as Document No. 68045 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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