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An Efficient Synthetic Method of 1-(2,4,6-Tri-*t*-butylphenyl)-3-phenyl-1-phosphaallenes [Mes*P=C=CR–Ph; R = H, $SiMe_3$] from Dibromophosphaethene [Mes*P=CBr_2] (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$)

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2-Bromo-3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-3-trimethylsiloxy-1-phospha-1-propene reacted with *t*-butyllithium and chlorotrimethylsilane to afford 3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene and/or 3-phenyl-3-trimethylsilyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene through the elimination of lithium trimethylsiloxide or hexamethyldisiloxane. The molecular structure of the latter phosphaallene was confirmed by X-ray crystallography.

Although phosphaallenes [–P=C=C<] are essentially highly reactive, we and other groups have succeeded in the synthesis, isolation, and characterization of such as 3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**1**) so far by using kinetic stabilization with the bulky 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Mes*) group.[1,2] Recently, we reported on a concise preparation method of phosphaallenes by using 1-bromo-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium (**2**);[3] moreover, we succeeded in regioselective solid state [2 + 2] dimerizations[4] and the formation of 1,4-diphosphafulvene **3** by the formal [3 + 2] dimerization of **1** (Chart 1).[5] Thus, phosphaallenes are promising compounds for the synthesis of organophosphorus compounds, since allenes have become important for organic synthesis.[6]

We report here on an alternative synthetic procedure of **1** by utilizing **2**, benzaldehyde, and chlorotrimethylsilane, which includes the preparation and isolation of a 1-phospha-1-propene derivative **5** as a precursor. In this novel procedure, the C–C bond-formation and the elimination are separated, which is expected to be a promising method to prepare a number of phosphaallene derivatives. Indeed, these procedures correspond to the Peterson olefination, which is one of the most convenient syntheses of olefins.[2c] On the other hand, Seebach and coworkers reported on the preparation of allenes from geminal dibromoethenes and aldehydes (Scheme 1).[7] Because novel synthetic method of **1** is close to the Seebach method, we examined the effects on the reaction conditions. Additionally, the structural determination of a novel phosphaallene (**6**) is described.

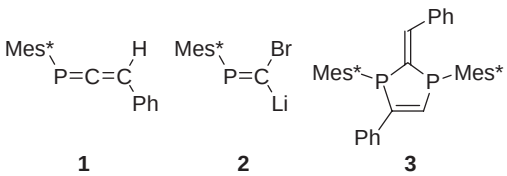
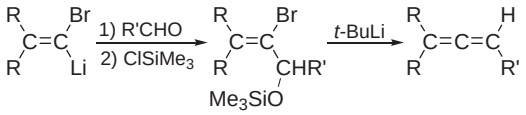
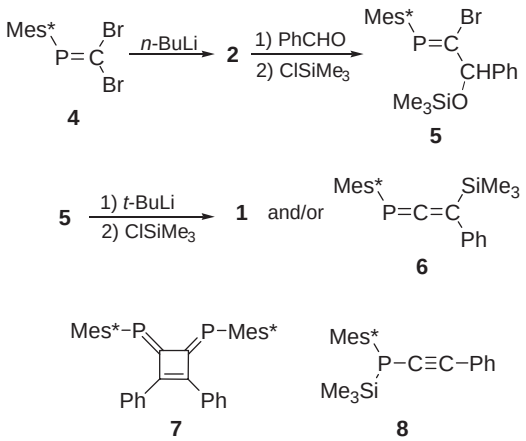


Chart 1.



Scheme 1.



Scheme 2.

Dibromophosphaethene **4**[8] was allowed to react with butyllithium to generate **2**, which was then allowed to react with benzaldehyde and chlorotrimethylsilane to afford 2-bromo-3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-3-trimethylsiloxy-1-phospha-1-propene (**5**). Compound **5** was stable to air and moisture at room temperature, and was purified by silica-gel column chromatography (Scheme 2). We next examined reactions of **5** with *t*-butyllithium and chlorotrimethylsilane: compound **5** was allowed to react with *t*-butyllithium[9] at −78 °C, and chlorotrimethylsilane was added to the reaction mixture (Scheme 2). Equimolar amounts of *t*-butyllithium and chlorotrimethylsilane were allowed to react with **5** to afford **1** in moderate yield. On the other hand, **5** was allowed to react with two molar amounts of *t*-butyllithium and two molar amounts of chlorotrimethylsilane; 3-phenyl-3-trimethylsilyl-1-phosphaallene **6** was obtained. Compound **6** was characterized by spectroscopic data, showing a higher field ^{31}P chemical shift compared with that of **1**. The structure of **6** was unambiguously confirmed by X-ray crystallography, as displayed in Fig. 1. The bond lengths and angles do not largely deviate from the previously reported phosphaallenes.[1,5]

When no chlorotrimethylsilane was employed in the reaction of **5** and *t*-butyllithium, a mixture of **1**, **3**, and 3,4-diphosphanylidenecyclobutene **7** was observed in a 10:7:1 ratio (by ^{31}P NMR spectroscopy). Additionally, **5** was allowed to react

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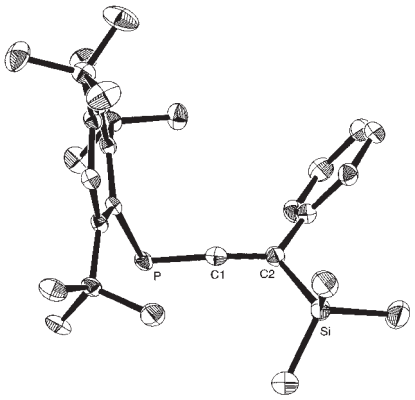
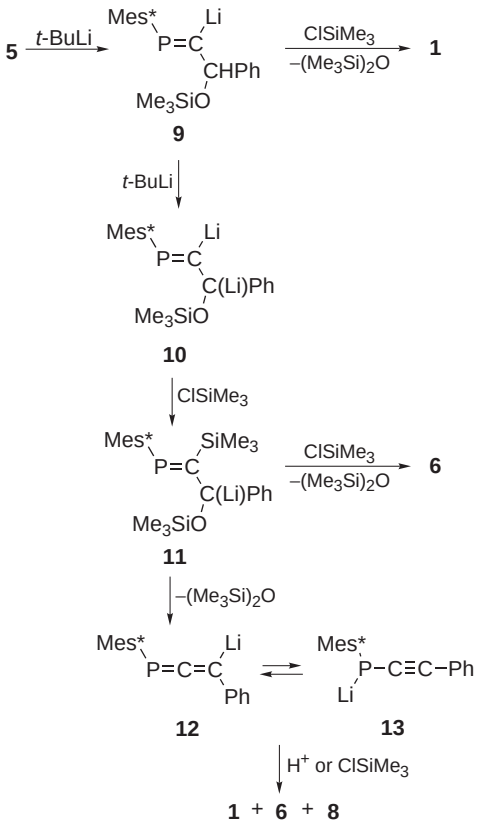


Fig. 1. Molecular structure of **6** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P–C1 1.629(2), P–C_{Mes*} 1.869(7), C1–C2 1.313(3), C2–Si 1.897(2), C2–C_{Ph} 1.495(3), C1–P–C_{Mes*} 102.81(9), P–C1–C2 170.9(2), C1–C2–Si 121.2(2), Si–C2–C_{Ph} 119.8(1), C1–C2–C_{Ph} 119.0(2).



Scheme 3.

with two molar amounts of *t*-butyllithium and one molar amount of chlorotrimethylsilane to afford a mixture of **1**, **6**, and phosphinoacetylene **8** in a 1:2:6 ratio.

By taking the results into consideration, we suggest a plausible reaction mechanism, as displayed in Scheme 3. Compound **5** reacted with *t*-butyllithium to give **9**; the elimination of $LiOSiMe_3$ gave a mixture of **1**, **3**, and **7**. This reaction is similar to the condition described in Scheme 1, and is close to the reaction of 2-bromo-3-methoxy-3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1-propene with *t*-butyllithium.[5] Thus, the reaction of **5** with one molar amount of *t*-butyllithium included formal dimerizations of **1**, and the elimination of lithium alkoxides, which might play important roles in affording **3** and **7**. Anion **9** reacted with chlorotrimethylsilane to afford **1** by the elimination of hexamethyldisiloxane, which is a modified pathway of the Peterson olefination. When two molar amounts of *t*-butyllithium reacted with **5**, probably a dilithium intermediate **10** was generated, and chlorotrimethylsilane reacted with **10** to form another intermediate **11**. The elimination of hexamethyldisiloxane follows to form anions **12** and **13**, which give **1**, **6**, and **8** upon protonation or silylation.[10] Concerning the equilibrium between **12** and **13**, we previously reported that **1** reacted with *t*-butyllithium to generate only **13**[5] and, indeed, reaction of **1** with *t*-butyllithium and iodomethane gave ethynylphosphine [Mes*P(Me)C≡CPh][11] almost quantitatively. At the same time, **11** reacted with chlorotrimethylsilane to afford **6** through the elimination of hexamethyldisiloxane. In this reaction, the formation of **6** after the generation of **1** did not seem to proceed mainly, since **1** reacted with one molar amount of *t*-butyllithium and one molar amount of chlorotrimethylsilane to afford a mixture of **1**, **6**, and **8** in a ratio of 3:1:4.

In conclusion, we have established an alternative synthetic procedure of **1** by using 2-bromo-1-phosphapropene **5**. The efficiency was comparable to that of previously reported methods.[2] The introduction of a trimethylsilyl group into the P=C=C skeleton was successful, and the structure of **6** was confirmed by X-ray analysis.

Experimental

Preparation of 5. According to our previous report,[8] **4** was prepared from a reaction of (2,4,6-tri-*t*-butylphenyl)phosphonous dichloride and bromoform in the presence of lithium diisopropylamide (LDA) at −100 °C. To a solution of **4** (1.0 g, 2.2 mmol) in THF (20 mL) was added butyllithium (2.2 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −100 °C and stirred for 10 min. The mixture was treated with benzaldehyde (2.2 mmol) and allowed to warm to room temperature. To the reaction mixture was added chlorotrimethylsilane (2.2 mmol) and stirred for 15 min. The solvent and volatile materials were removed in vacuo, and the residue was extracted with hexane. Silica-gel column chromatography (hexane) of the hexane extracts afforded 0.85 g of **5** (70% yield). Colorless needles (EtOH), mp 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (9H, s, $SiMe_3$), 1.37 (9H, s, *p*-*t*Bu), 1.47 (9H, s, *o*-*t*Bu), 1.55 (9H, s, *o*-*t*Bu), 5.76 (1H, d, $^3J_{PH}$ = 13 Hz, CH), 7.2–7.7 (7H, m, arom.); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 0.7 (s, $SiMe_3$), 31.8 (s, *p*-C*Me*$_3$), 33.0 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 33.2 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 80.6 (d, $^2J_{PC}$ = 37 Hz, CH), 122.6 (s, *m*-Mes*), 127.3 (s, *m*-Ph), 127.9 (s, *p*-Ph), 128.2 (s, *o*-Ph), 137.4 (d, $^1J_{PC}$ = 54 Hz, *ipso*-Mes*), 142.2 (d, $^3J_{PC}$ = 10 Hz, *ipso*-Ph), 151.1 (s, *p*-Mes*), 153.6 (s, *o*-Mes*), 154.0 (s, *o*-Mes*), 168.4 (d, $^1J_{PC}$ = 64 Hz, P=C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 253 (d, $^3J_{PH}$ = 13 Hz). Anal. Calcd for $C_{29}H_{44}BrOPSi$: C, 63.59; H, 8.10%. Found: C, 63.61; H, 8.08%.

Preparation of 1 from 5. To a solution of **5** (47 mg, 0.086 mmol) in THF (5 mL) was added butyllithium (0.086 mmol) at −78 °C and stirred for 15 min. The mixture was treated with chlorotrimethylsilane (0.095 mmol), and allowed to warm to room

temperature. The solvent and volatile materials were removed in vacuo and the residue was extracted with hexane. Silica-gel column chromatography (hexane) of the hexane extracts afforded 19 mg of **1** (59% yield).

Preparation of 6. To a solution of **5** (220 mg, 0.40 mmol) in THF (10 mL) was added butyllithium (0.80 mmol) at −78 °C and stirred for 15 min. The mixture was treated with chlorotrimethylsilane (0.80 mmol) and allowed to warm to room temperature. The solvent and volatile materials were removed in vacuo and the residue was extracted with hexane. Silica-gel column chromatography (hexane) of the hexane extracts afforded 119 mg of **6** (66% yield). Colorless prisms (EtOH), mp 123–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.44 (9H, s, $SiMe_3$), 1.57 (9H, s, *p*-*t*Bu), 1.80 (18H, s, *o*-*t*Bu), 7.4–7.6 (7H, m, arom.); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 0.8 (s, $SiMe_3$), 32.0 (s, *p*-C*Me*$_3$), 34.1 (d, $^{4}J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 122.3 (d, $^{3}J_{PC}$ = 12 Hz, *ipso*-Ph), 122.6 (s, *m*-Mes*), 127.0 (s, *p*-Ph), 128.6 (brs, *o*-Ph), 128.7 (s, *m*-Ph), 130.4 (d, $^{1}J_{PC}$ = 68 Hz, *ipso*-Mes*), 137.5 (d, $^{2}J_{PC}$ = 17 Hz, P=C=*C*), 150.0 (s, *p*-Mes*), 155.0 (s, *o*-Mes*), 238.4 (d, $^{1}J_{PC}$ = 37 Hz, P=*C*=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37. Anal. Calcd for $C_{29}H_{43}PSi$: C, 77.28; H, 9.62%. Found: C, 77.24; H, 9.60%.

X-ray Crystallography of 6. $C_{29}H_{43}PSi$, M = 450.72, crystal dimension 0.30 × 0.20 × 0.20 mm^3, monoclinic, $P2_1/n$ (#14), a = 10.6227(7), b = 11.316(1), c = 23.020(2) Å, β = 91.721(6)°, V = 2765.8(4) Å^3, Z = 4, $2\theta_{max}$ = 55.0°, T = 130 K, ρ(calcd) = 1.082 g cm^{-3}, μ(Mo Kα) = 0.156 mm^{-1}, F(000) = 984, 20269 collected reflections, 5925 unique reflections (R_{int} = 0.065), $R1$ = 0.049 ($I > 2\sigma(I)$), R_W = 0.069 (all data), S = 1.07 (280 parameters) (CCDC-259388).

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