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Reactions of a Sterically Protected 2,3-Dichloro-1,4-diphospha-1,3-butadiene with Some Alkyl and Hydrido Lithium Reagents

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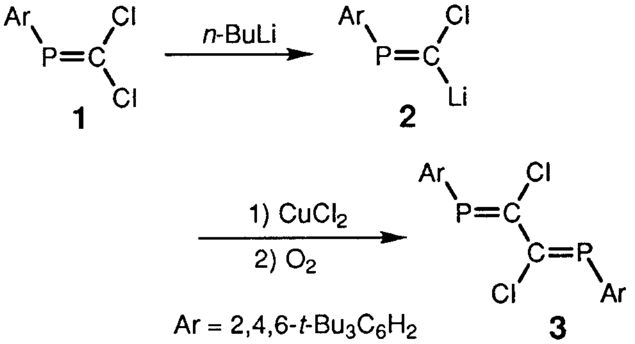
ABSTRACT: *The reactions of 2,3-dichloro-1,4-diphospha-1,3-butadiene, which is sterically protected with the 2,4,6-tri-t-butylphenyl group, with some nucleophiles, including alkyllithium reagents and lithium aluminum hydrides, afforded 1,2-diphosphinoacetylenes or 3-phosphino-1-phosphaallenes.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:171–176, 2000

INTRODUCTION

Sterically protected organophosphorus compounds are of current interest because of their unusual structures and reactivities [1]. We have recently reported the preparation of a sterically protected 2,3-dichloro-1,4-diphospha-1,3-butadiene **3** [2] with the 2,4,6-tri-*t*-butylphenyl group (abbreviated to the Ar group), starting from the coupling reaction of the 1-chloro-2-phosphaethenyllithium **2**, prepared from the 2,2-dichlorophosphaethene **1**, in the presence of copper(II) chloride and oxygen (Scheme 1). Compound **3** is the first example of a 1,4-diphosphabutadiene [3,4] carrying two chlorine atoms and two low-coordinated phosphorus atoms, and the structure was analyzed by X-ray crystallography [2]. We now report on the reaction of **3** with some alkyllithium reagents and lithium aluminum hydrides.

RESULTS AND DISCUSSION

A THF solution of the diphosphabutadiene **3** was allowed to react with 3 mol equiv. of each alkyllithium at −100°C, and the reaction was quenched with



1 **2** **3**

SCHEME 1

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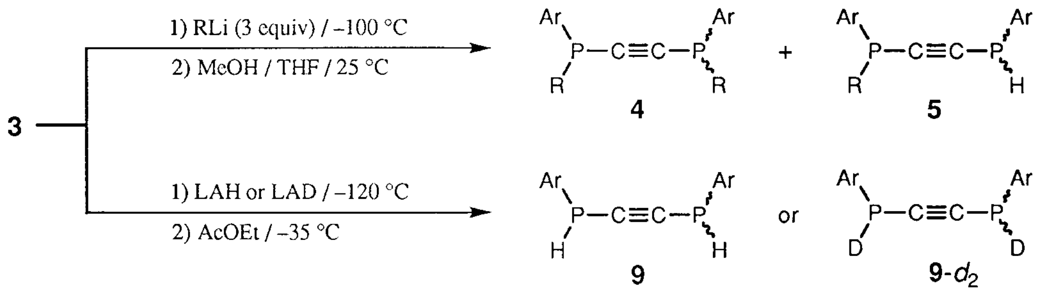
methanol at 25°C to give alkylation products **5** and/or **4** after the usual workup procedure (Scheme 2). Table 1 shows the results of the reactions of **3** with the various alkyllithium reagents. Although methyllithium gave the corresponding dialkylation product **4a** as the sole alkylation product, *s*- and *t*-butyllithium reagents gave both mono and dialkylation products (**5c,d** and **4c,d**), and *n*-butyllithium gave the 3-phosphaallenylphosphine **6b** in addition to **4b** and **5b**. Furthermore, these alkylation products were a mixture of diastereomers A and B, where A denotes the isomer of the lower ^{31}P NMR chemical shift and B denotes the isomer of the higher chemical shift as reported in this article. Table 2 lists chemical shifts and coupling constants observed in the ^{31}P NMR spectra of compounds **4** and **5**. Although attempts to separate any diastereomeric mixtures have so far not been successful by either column chromatography or recrystallization, it seems likely that *meso* isomers are the thermodynamically stable isomers. The *meso* isomers seem to be suffering from the steric hindrance less severely than the *dl* isomers according to consideration of the Newman type projections, as shown in Figure 1, where the axis stands for the P–C≡C–P bond. Furthermore, it should be mentioned that no $^3J_{PP}$ was observed for compounds **5** and **4**, while $^3J_{PP}$ was observed for tautomers of **6b** ($^3J_{PP}$ = 23.1 Hz and 29.3 Hz) as well as $^3J_{PP}$ = 30.8 and 33.9 Hz for tautomers **10**, indicating that there is little spin interaction between the two phosphorus atoms at the ends of the C≡C bond in compounds **5**.

A reaction mechanism for affording double alkylation product **4** is shown in Scheme 3, including the second nucleophilic attack of the alkyllithium [5,6] on the 3-phosphaallenylphosphine **7**. On the other hand, monoalkylation product **5** might be formed via halogen-metal exchange on **7** followed by quenching with a proton, or via formation of 1,4-diphosphabutatriene **8** [7,8], followed by nucleophilic attack with the alkyllithium [9]. Furthermore, in the case of *n*-butyllithium, **6b** with the 3-phosphaallenyl group was obtained as a tautomer of monoalkylation product **5b**, where a reaction mechanism including **8** or **7** might be operative. The compound of the type **5** seems to be far more favorable than that of the type **6**. As has been discussed previously (Table 1), methyllithium did not give the corresponding monoalkylation product **5a**, and *n*-, *s*- and *t*-butyllithiums gave monoalkylation products **4** as well as dialkylation products **5**. It is reasonable to consider that an intermediate **7** is a reactive substrate toward methyllithium, accepting it as a nucleophile to give **4a**, while the other alkyllithium reagents can operate on **7** both as a nucleophile and as a reagent of a halogen-metal exchange reaction, taking the nucleophilicity and bulkiness of alkyllithium reagents into account.

When lithium aluminum hydride (LAH; 5–8 mol equiv.) was allowed to react with **3** at −120°C, 1,2-*bis*[(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene **9** was obtained in good yield, after the reaction mixture had been treated with ethyl acetate at −52–0°C in order to destroy excess hydride. Lithium aluminum deuteride (LAD) also reacted with **3** to give the corresponding dideuteriophosphinoacetylene **9**-d_2. A reaction mechanism for affording **9** might be very similar to that for the reaction of **3** with alkyllithium reagents as shown in Scheme 3, except that no allenyl compound was observed in the case of reaction with hydrides [10].

The reaction product **9** was again a mixture of diastereoisomers, and it is interesting to note that an initial ratio of the diastereomeric isomers of **9** was changed under various conditions. For example, an initial ratio of 1:4 to 1:6 of **9** in chloroform underwent a change to a 1:1 mixture after having been allowed to stand for 18 hours at room temperature. Furthermore, the isomerization was accelerated upon heating a mixture of **9** or adding an acidic additive to **9**. In solution, this epimeric isomerization in toluene or THF slowly occurred even at 0°C over a period of two days while, in the solid state, the isomerization did not proceed within two days. As shown in Figure 1, where R equals H, steric hindrance does not seem to be serious. Therefore, it is reasonable to consider that a thermodynamic equilibrium of **9** consists of a 1:1 mixture. Furthermore, it seems likely that a major isomer at the initial stage is the *dl* isomer, taking the steric hindrance into account in the second nucleophilic attack of hydride anion, i.e., from the *si* phase of the less hindered site rather than the *re* phase, as shown in Scheme 4. However, in the presence of a proton source, an equilibrium might occur with respect to **9** to give a 1:1 mixture of *dl* and *meso* isomers, since the difference of steric hindrance between the *dl* and *meso* forms is expected not to be large.

The reaction of **9** with diethylamine gave a tautomeric isomer **10** having the phosphaallenic structure [11,12]. A 1:1 starting mixture of **9** gave a 3:1 mixture of **10** in the presence of diethylamine. The reaction of **9** with *n*-butyllithium, when quenched with methanol-*d*, gave the corresponding dideuterated product **10**-d_2, as shown in Scheme 5. Both **10** and **10**-d_2 were again mixtures of diastereoisomers. It is interesting to note that the total energy difference between the energy-optimized structures for $H_2P–C≡C–PH_2$ and $H_2P–CH=C=PH$, calculated by CAChe-MOPAC [13] using the PM3 SCF-MO method [14], is 10 kcal/mol, indicating that the diphosphi-



SCHEME 2

TABLE 1 Reaction Products of the Diphosphabutadiene **3** with Alkyllithiums RLi

		Yield/%		
Entry	*RLi/R*	**4**	**5**	**6**
a[a]	Me	46	—[c]	—[c]
b[b]	*n*-Bu	19	35	16
c[b]	*s*-Bu	25	52	—[c]
d[a]	*t*-Bu	10	40	—[c]

[a] Isolated yield.
[b] Yield determined by NMR.
[c] Not detected.

TABLE 2 δ_P Values of Compounds **4** and **5** in $CDCl_3$

		4		*5*	
Entry	*R*	δ_A	δ_B	δ_A[a]	δ_B[a]
a	Me	−60.9[b]	−60.9[b]	—[c]	—[c]
b	*n*-Bu	−47.8	−48.1	−48.8, −98.0	−49.3, −98.6
c	*s*-Bu	−36.0	−37.5	−38.4, −98.1	−38.8, −98.8
d	*t*-Bu	−20.2	−21.2	−22.0, −97.1	−23.5, −98.1

[a] No $^{3}J_{PP}$ values were observed for compounds **5** as well as **4**.
[b] By chance, $\delta_A = \delta_B$.
[c] Not formed.

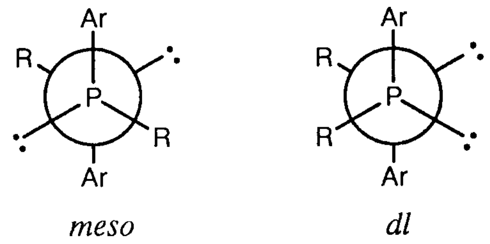


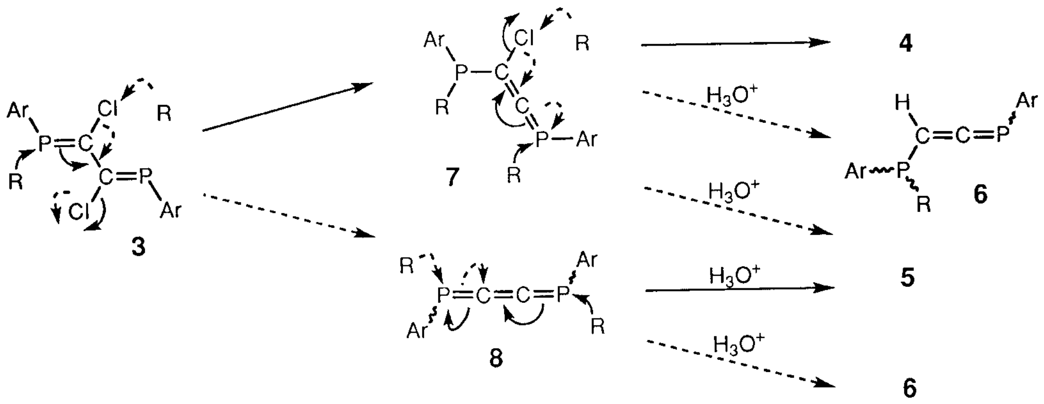
FIGURE 1 Newman projection for compounds **4** and **5**, where the axis denotes the P–C≡C–P bond.

noacetylene is much more stable than the phosphaallenylphosphine.

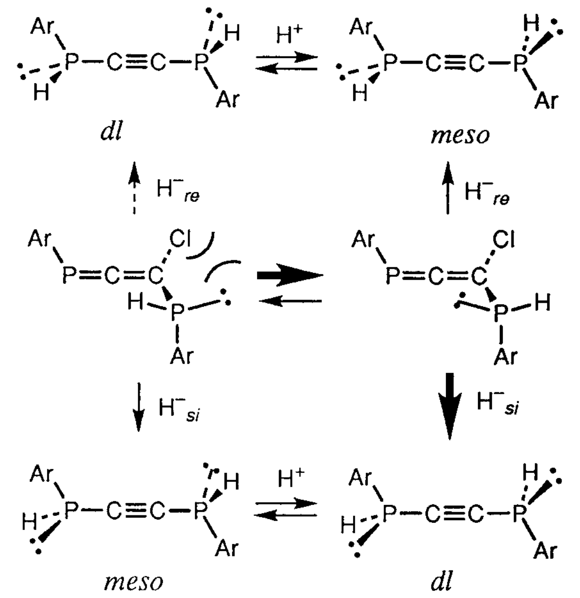
In summary, **3** reacted with some nucleophiles to give diphosphinoacetylenes as a diastereomeric mixture, and isomerization of the reaction products including tautomerization between the acetylene and the allene, as well as epimerization of diastereoisomers occurred under various conditions.

EXPERIMENTAL

All experiments were carried out under an argon atmosphere with dry solvents, unless otherwise specified. All melting points were determined with a Yan-



SCHEME 3



SCHEME 4 Nucleophilic attack of hydride on an intermediate **7** (R = H), where H–$_{si}$ and H–$_{re}$ means backside and frontside attack of the hydride from the Ar–P = C = C< system, respectively. Equilibrium between the *dl* and *meso* forms might occur under acidic conditions.

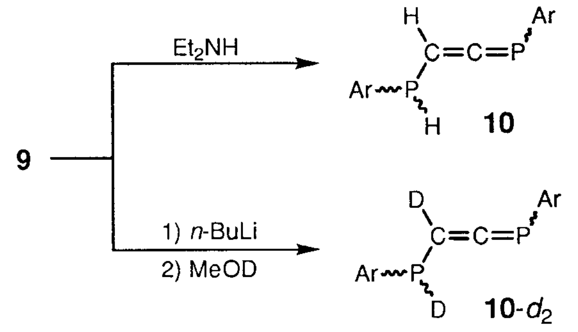
agimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were measured by either a Bruker AC-200P or AM-600 spectrometer. ^{31}P NMR spectra were obtained with a Bruker AC-200P spectrometer using 85% H$_3$PO$_4$ as an external standard. IR spectra were recorded on a Horiba FT-300 spectrometer. MS spectra were obtained with a Hitachi M-2500S or a JEOL HX-110, DX-303, or AX-500 spectrometer. UV-vis spectra were obtained with a Hitachi U-3210 spectrometer. Elemental microanalyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

Preparation of (Z,Z)*-2,3-Dichloro-1,4-bis*(*2,4,6-tri-t-butylphenyl*)*-1,4-diphospha-1,3-butadiene* (3)

(Z,Z)-2,3-Dichloro-1,4-bis(2,4,6-tri-t-butylphenyl)-1,4-diphospha-1,3-butadiene (3) was prepared according to the method described previously [2].

Reaction of 3 *with Alkyllithium Reagents*

With Methyllithium. A THF solution (20 mL) of the diphosphabutadiene **3** (35.1 mg, 0.0542 mmol) was allowed to react with methyllithium (0.168 mmol) at −100°C for 30 minutes, and the reaction was quenched with 2 mL of methanol at 25°C to give 1,2-*bis*[(2,4,6-tri-*t*-butylphenyl)methylphosphino]acetylene (**4a**) in 46% yield after the usual workup procedure including silica-gel column chromatographic separation (a mixture of pentane-ether as an eluent).



SCHEME 5

4a. A mixture of diastereomers, A:B = 1:1.4; pale yellow crystals, m.p. 45–50°C; ^{1}H NMR (200 MHz, CDCl$_3$) isomer A: δ = 1.304 (18H, s, *p*-*t*-Bu), 1.52 (6H, m, P-Me), 1.614 (36H, s, *o*-*t*-Bu), and 7.38 (4H, m, *m*-Ar); isomer B: δ = 1.309 (18H, s, *p*-*t*-Bu), 1.52 (6H, m, P-Me), 1.607 (36H, s, *o*-*t*-Bu), and 7.38 (4H, m, *m*-Ar); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) isomer A: δ_A = 113.3 (dd, $^1J_{PC}$ = 30.3 Hz, $^2J_{PC}$ = 10.0 Hz, C≡C); isomer B: δ_B = 112.7 (dd, $^1J_{PC}$ = 27.9 Hz, $^2J_{PC}$ = 10.0 Hz, C≡C); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ = −60.9; MS (70 eV, EI) *m/z* (rel intensity) 606 (M$^+$; 36), 591 (M$^+$ − Me; 26), 549 (M$^+$ − Bu; 58), 493 (M$^+$ − 2Bu + 1; 50), 361 (ArP(Me)C$_2$P$^+$; 31), 305 (ArP(Me)C$^+$; 39), 275 (ArP$^+$ − 1; 12), and 57 (*t*-Bu$^+$; 100). Found: *m/z* 606.4459; Calcd. for C$_{40}$H$_{64}$P$_2$: M, 606.4480.

With n-Butyllithium. A similar reaction of **3** with *n*-butyllithium gave 1,2-*bis*[butyl(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**4b**), 1-[butyl(2,4,6-tri-*t*-butylphenyl)phosphino]-2-[2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**5b**), and 3-[butyl(2,4,6-tri-*t*-butylphenyl)phosphino]-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**6b**) after the usual workup procedure.

4b. A mixture of diastereomers, A:B = 2:3; colorless crystals (crude); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) isomer A: δ_A = −47.8; isomer B: δ_B = −48.1.

5b. A mixture of diastereomers, A:B = 3:5; colorless crystals (crude); ^{1}H NMR (200 MHz, CDCl$_3$) isomer A: δ_A = 5.94 (1H, m, $^1J_{PH}$ = 250.0 Hz, P$\underline{H}$); isomer B: δ_B = 6.00 (1H, dd, $^1J_{PH}$ = 250.8 Hz, $^3J_{PH}$ = 25.0 Hz, P$\underline{H}$); ^{31}P NMR (81 MHz, CDCl$_3$) isomer A: δ_A = −48.8 (m), −98.0 (d, $^1J_{PH}$ = 250.0 Hz); isomer B: δ_B = −49.3 (m), −98.6 (d, $^1J_{PH}$ = 250.8 Hz).

6b. A mixture of diastereomers, A:B = 2:1; colorless crystals (crude); ^{1}H NMR (200 MHz, CDCl$_3$) isomer

A: $\delta_A = 6.34$ (1H, m, P=C=C$\underline{H}$); isomer B: $\delta_B = 6.35$ (1H, m, P=C=C$\underline{H}$); ^{31}P NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = 67.4$ (d, $^3J_{PH} = 25.0$ Hz), -23.4 (m), $^3J_{PP} = 23.1$ Hz; isomer B: $\delta_B = 59.9$ (d, $^3J_{PH} = 31.7$ Hz), -28.5 (m), $^3J_{PP} = 29.3$ Hz.

With s-Butyllithium. A similar reaction of **3** with *s*-butyllithium gave 1,2-*bis*[*s*-butyl(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**4c**) and 1-[*s*-butyl(2,4,6-tri-*t*-butylphenyl)phosphino]-2-[2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**5c**) after the usual workup procedure.

4c. A mixture of diastereomers, A:B = 2:1; colorless crystals (crude); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = -36.0$; isomer B: $\delta_B = -37.5$.

5c. A mixture of diastereomers, A:B = 2:3; colorless crystals (crude); ^{31}P NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = -38.4$ (m), -98.1 (d, $^1J_{PH} = 247.8$ Hz); isomer B: $\delta_B = -38.8$ (m), -98.8 (d, $^1J_{PH} = 250.1$ Hz).

With t-Butyllithium. A similar reaction of **3** with *t*-butyllithium gave 1,2-*bis*[*t*-butyl(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**4d**) together with **5d** [8] (ratio of 1.6:1) after the usual workup procedure.

4d. A mixture of diastereomers, A:B = 1:1.4; colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$) $\delta = 0.79$ (18H, d, $^2J_{PH} = 14.2$ Hz, P-*t*-Bu), 1.33 (18H, s, *p*-*t*-Bu), 1.55 (36H, s, *o*-*t*-Bu), and 7.26 (4H, m, *m*-Ar); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = -20.2$; isomer B: $\delta_B = -21.2$; MS (70 eV, EI) *m/z* (rel intensity) 690 (M$^+$; 6), 633 (M$^+$ − Bu; 27), 577 (M$^+$ − 2Bu + 1; 37), 275 (ArP$^+$ − 1; 22), and 57 (Bu$^+$; 100). Found: *m/z* 690.5397; Calcd. for C$_{46}$H$_{76}$P$_2$: M, 690.5418.

Reaction of **3** *with Lithium Aluminum Hydride (LAH) or Lithium Aluminum Dueteride (LAD)*

With LAH. Lithium aluminum hydride (LAH; 15.0 mg) in THF (4 mL) was allowed to react with **3** (30.0 mg, 0.0463 mmol) in THF (18 mL) with stirring at −120–−35°C for 1 hour, and the excess of LAH was destroyed by the action of ethyl acetate. The reaction mixture was concentrated, washed with ether and chloroform, the solvent was removed by evaporation, and the residue was washed with pentane to give 22.8 mg of 1,2-*bis*[(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**9**) in 85% yield. The initial diastereomeric ratio was A:B = 1:5 and changed to 1:1 on being allowed to stand in chloroform under various conditions.

9. A mixture of diastereomers, A:B= 1:1; colorless prisms (hexane), m.p. 242–244°C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$) isomer A: $\delta_A = 1.31$ (18H, s, *p*-*t*-Bu), 1.48 (36H, s, *o*-*t*-Bu), 5.73 (2H, m, $^1J_{PH} = 250.0$ Hz, PH), and 7.38 (4H, d, $^4J_{PH} = 2.0$ Hz, *m*-Ar); isomer B: $\delta_B = 1.31$ (18H, s, *p*-*t*-Bu), 1.44 (36H, s, *o*-*t*-Bu), 5.71 (2H, m, $^1J_{PH} = 251.1$ Hz, PH), and 7.36 (4H, d, $^4J_{PH} = 2.3$ Hz, *m*-Ar); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) isomer A: $\delta_A = 31.3$ (s, *p*-C($\underline{C}$H$_3$)$_3$), 33.5 (d, $^4J_{PC} = 3.7$ Hz, *o*-C($\underline{C}$H$_3$)$_3$), 35.0 (s, *p*-$\underline{C}$(CH$_3$)$_3$), 38.2 (s, *o*-$\underline{C}$(CH$_3$)$_3$), 102.8 (d, $^1J_{PC} = 30.7$ Hz, $\underline{C}$≡C), 122.4 (d, $^3J_{PC} = 2.3$ Hz, *m*-Ar), 125.7 (d, $^1J_{PCe} = 23.2$ Hz, *ipso*-Ar), 150.5 (s, *p*-Ar), and 155.3 (d, $^2J_{PC} = 10.7$ Hz, *o*-Ar); isomer B: $\delta_B = 31.3$ (s, *p*-C($\underline{C}$H$_3$)$_3$), 33.5 (d, $^4J_{PC} = 7.0$ Hz, *o*-C($\underline{C}$H$_3$)$_3$), 35.0 (s, *p*-$\underline{C}$(CH$_3$)$_3$), 38.2 (s, *o*-$\underline{C}$(CH$_3$)$_3$), 103.2 (dd, $^1J_{PC} = 25.8$ Hz, $^2J_{PC} = 5.7$ Hz, $\underline{C}$≡C), 122.3 (d, $^3J_{PC} = 4.8$ Hz, *m*-Ar), 126.0 (d, $^1J_{PC} = 25.4$ Hz, *ipso*-Ar), 150.4 (s, *p*-Ar), and 155.2 (d, $^2J_{PC} = 10.5$ Hz, *o*-Ar); ^{31}P NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = -98.7$ (d, $^1J_{PH} = 250.0$ Hz); isomer B; $\delta_B = -98.9$ (d, $^1J_{PH} = 251.1$ Hz); IR (KBr) 2395 cm^{-1}; MS (70 eV, EI) *m/z* (rel intensity) 578 (M$^+$; 29), 521 (M$^+$ − Bu; 18), 465 (M$^+$ − 2Bu + 1; 11), 333 (ArPHC$_2$PH$^+$; 28), 301 (ArPC$_2$H$^+$; 11), 277 (ArPH$^+$; 19), and 57 (Bu$^+$; 100). Found: *m/z* 578.4197. Calcd for C$_{38}$H$_{60}$P$_2$: M, 578.4170. Anal. Found: C, 78.09; H, 10.47%. Calcd for C$_{38}$H$_{60}$P$_2$: C, 78.85; H, 10.45%.

With LAD. Very similarly, lithium aluminum deuteride (LAD) also reacted with **3** to give the corresponding 1,2-*bis*[deuterio(2,4,6-tri-*t*-butylphenyl)phosphino]acetylene (**9**-*d*$_2$). **9**-*d*$_2$: a mixture of diastereomers, A:B = 1:4; colorless crystals, m.p. 218–221°C (decomp); ^{1}H NMR (200 MHz, CDCl$_3$) isomer A: $\delta_A = 1.31$ (18H, s, *p*-*t*-Bu), 1.47 (36H, s, *o*-*t*-Bu), and 7.38 (4H, d, $^4J_{PH} = 2.6$ Hz, *m*-Ar); isomer B: $\delta_B = 1.31$ (18H, s, *p*-*t*-Bu), 1.43 (36H, s, *o*-*t*-Bu), and 7.36 (4H, d, $^4J_{PH} = 2.7$ Hz, *m*-Ar); ^{31}P NMR (81 MHz, CDCl$_3$) isomer A: $\delta_A = -99.8$ (t, $^1J_{PD} = 37.0$ Hz); isomer B: $\delta_B = -99.9$ (t, $^1J_{PD} = 38.2$ Hz); IR (KBr) 1739 and 1736 cm^{-1}.

*Isomerization Reaction of 1,2-Bis(2,4,6-tri-t-butylphenylphosphino)acetylene (***9***)*

A diastereomeric mixture of 1:6 (=A:B) of **9** (1 mg) in chloroform (0.5 mL) underwent change to a 1:1 mixture after being allowed to stand for 18 hours at room temperature, and the ratio was determined by ^{1}H and ^{31}P NMR spectroscopy. The isomerization of **9** consisting of a mixture ratio of 1:4 in benzene-*d*$_6$ was allowed to stand in the dark for 28 hours to give a 1:1 mixture. A mixture of **9** (1:5) in chloroform was allowed to react with a small amount of aq. 1N HCl. After 2 hours in the dark, the ratio changed to 1:1. The solid of **9** (1:4) was allowed to stand at room temperature in the dark for 2 days to give a mixture of 2:1, but at 0°C, the ratio did not change for 2 days. A solution of **9** (1:4) in toluene was kept at 0°C for 2 weeks to give a 1:2 mixture. A solution of **9**, consisting of a 1:6 mixture in THF, was kept for 1 week at 0°C to give a 1:2 mixture.

The mixture of 8.7 mg (0.015 mmol) of **9** (1:1) with diethylamine (8 μL, 0.08 mmol) in THF (8 mL) was stirred for 1 hour and hexane was added to a mixture to give 3-[(2,4,6-tri-*t*-butylphenyl)phosphino]-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**10**) in a 1:4 mixture (A:B) almost quantitatively. The compound **10**, consisting of a mixture of 1:4 in the solid state, changed to a mixture of 1:3 at room temperature during 12 hours. The 1:3 mixture of **10** kept in chloroform for 18 hours gave a 1:1 mixture. The reaction of **9** (11.3 mg, 0.0196 mmol, 1:1 mixture) in THF (10 mL) with *n*-butyllithium (0.049 mmol) at −78°C for 30 minutes after being quenched with methanol-d_1 gave the corresponding dideuteride product **10**-d_2 as a diastereomeric mixture (A:B = 1:2). The mixture was passed through a silicagel column to give **10**-d_2 (6.2 mg, 1:1 mixture) in 55% yield. **10**. A mixture of diastereomers (A:B = 1:1), pale yellow crystals, m.p. 160–163°C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) isomer A: $\delta_A = 1.29$ (9H, s, *p-t*-Bu), 1.34 (9H, s, *p-t*-Bu), 1.41 (18H, s, *o-t*-Bu), 1.58 (18H, s, *o-t*-Bu), 5.54 (1H, ddd, $^1J_{PH} = 232.5$ Hz, $^4J_{PH} = 3.0$ Hz, $^3J_{HH} = 5.9$ Hz, PH), 5.69 (1H, ddd, $^3J_{PH} = 33.9$ Hz, $^2J_{PH} = 9.2$ Hz, $^3J_{HH} = 5.9$ Hz, $P{=}C{=}CH$), and 7.38 (4H, m, *m*-Ar); isomer B: $\delta_B = 1.30$ (9H, s, *p-t*-Bu), 1.34 (9H, s, *p-t*-Bu), 1.47 (18H, s, *o-t*-Bu), 1.57 (18H, s, *o-t*-Bu), 5.70 (1H, ddd, $^3J_{PH} = 32.8$ Hz, $^2J_{PH} = 9.2$ Hz, $^3J_{HH} = 5.9$ Hz, $P{=}C{=}CH$), 5.74 (1H, ddd, $^1J_{PH} = 232.2$ Hz, $^4J_{PH} = 3.0$ Hz, $^3J_{HH} = 5.9$ Hz, PH), and 7.38 (4H, m, *m*-Ar); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) isomer A: $\delta_A = 107.8$ (dd, $^1J_{PC} = 61.1$ Hz, $^2J_{PC} = 26.3$ Hz, $P{=}C{=}\underline{C}H$) and 235.9 (dd, $^1J_{PC} = 31.4$ Hz, $^2J_{PC} = 11.7$ Hz, $P{=}\underline{C}{=}CH$); isomer B: $\delta_B = 107.9$ (dd, $^1J_{PC} = 60.4$ Hz, $^2J_{PC} = 26.1$ Hz, $P{=}C{=}\underline{C}H$) and 237.4 (dd, $^1J_{PC} = 30.4$ Hz, $^2J_{PC} = 12.2$ Hz, $P{=}\underline{C}{=}CH$); ^{31}P NMR (81 MHz, $CDCl_3$) isomer A: $\delta_A = 58.9$ (d, $^3J_{PH} = 32.2$ Hz), −78.8 (dd, $^1J_{PH} = 232.5$ Hz, $^3J_{PH} = 9.2$ Hz), $^3J_{PP} = 33.9$ Hz; isomer B: $\delta_B = 56.3$ (d, $^3J_{PH} = 32.8$ Hz), −75.5 (dd, $^1J_{PH} = 232.2$ Hz, $^3J_{PH} = 9.2$ Hz), $^3J_{PP} = 30.8$ Hz; IR (KBr) 2375 cm^{-1}; MS (70 eV, EI) *m/z* (rel intensity) 578 (M^+; 11), 521 (M^+-Bu; 23), 465 (M^+-2Bu + 1; 22), 333 ($ArPHC_2PH^+$; 9), 301 ($ArPC_2H^+$; 7), 277 ($ArPH^+$; 17), and 57 (Bu^+; 100). Found: *m/z* 578.4161. Calcd. for $C_{38}H_{60}P_2$: M, 578.4170. **10**-d_2: pale yellow crystals (crude), a mixture of diastereoisomers, A:B = 1:1; ^{1}H NMR (200 MHz, $CDCl_3$) isomer A: $\delta_A = 1.28$ (9H, s, *p-t*-Bu), 1.33 (9H, s, *p-t*-Bu), 1.41 (18H, s, *o-t*-Bu), 1.58 (18H, s, *o-t*-Bu), and 7.34 (4H, m, *m*-Ar); isomer B: $\delta_B = 1.29$ (9H, s, *p-t*-Bu), 1.34 (9H, s, *p-t*-Bu), 1.46 (18H, s, *o-t*-Bu), 1.57 (18H, s, *o-t*-Bu), and 7.34 (4H, s, *m*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) isomer A: $\delta_A = 59.1$ (td, $^3J_{PD} = 20.4$ Hz), −78.9 (td, $^1J_{PD} = 21.2$ Hz), $^3J_{PP} = 30.7$ Hz; isomer B: $\delta_B = 56.8$ (td, $^3J_{PD} = 19.0$ Hz), −75.5 (td, $^1J_{PD} = 22.5$ Hz), $^3J_{PP} = 33.8$ Hz.

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[9] Butatriene **8** reacted with *t*-butyllithium to give **5b** in 58% yield, but **4b** was not obtained [8].

[10] Butatriene **8** (24.7 mg, 0.0428 mmol) reacted with LAH (0.216 mmol) in THF (28 mL) at 0°C for 30 minutes to give 19.2 mg of a mixture of **9** and **10** (1:4) in 78% yield.

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