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Preparation of 1,3-Diphosphabuta-1,3-dienes from Sterically Encumbered Phosphaalkyne and Phosphaethenyllithium

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ABSTRACT: *Kinetically stabilized 2-lithio-1-(2,4,6-tri-t-butylphenyl)-1-phosphapropene was allowed to react with a bulky phosphaalkyne Mes*C≡P (Mes* = 2,4,6-t-$Bu_3C_6H_2$) followed by quenching with iodomethane or benzyl bromide to give the corresponding 1,3-diphosphabuta-1,3-dienes. The presence of the bulky Mes* group on the 1-phosphorus atom prevents intramolecular [2+2] cyclization and gave the P═C─P═C skeleton, whereas Mes*C≡P reacted with half an equivalent of nucleophile to afford the PCPC four-membered ring compounds. X-ray crystallography of 4-benzyl-1,3-diphosphabuta-1,3-diene confirmed the molecular structure showing conjugation on the 1,3-diphosphabuta-1,3-diene moiety.* Heteroatom Chem 16:357–360, 2005; DOI 10.1002/hc.20104

INTRODUCTION

Substitution of the unsaturated bonds in π-conjugated systems with the double bonds of heavier main group elements has been a most attractive research topic because of the interest in the molecular structures, physical properties, and applications for novel materials. Particularly, multiple bonds of phosphorus have widely been employed for π-conjugated systems due to the similar characters to the corresponding unsaturated bonds of carbon [1,2]. Indeed, a number of compounds containing multiple phosphorus–carbon double bonds have been reported so far [1–3]. For synthesis of π-conjugated systems composed of phosphorus–carbon double bonds, phosphaethenyllithiums are promising reagents [3,4]. We have reported 1,4-diphosphabuta-1,3-dienes (**A**) [5,6] and a 1,3,6-triphosphafulvene (**B**) [7] by copper-mediated homocoupling of phosphaethenyllithiums and the unusual trimerization of a phosphanylidene carbenoid [4], respectively (see Chart 1).

Additionally, phosphorus-carbon triple bonds, phosphaalkynes, are expected to be useful for synthesis of π-conjugated systems. Indeed, cyclooligomerizations of phosphaalkynes affording heterocyclic compounds containing low-coordinated sp^2 phosphorus atoms have been established [1,2,8]. However, oligomerizations of phosphaalkynes to afford linear π-conjugated systems such as polyene-like compounds have scarcely been reported. Recently, we reported reactions of bulky phosphaalkyne Mes*C≡P (**1**) with half an equivalent of nucleophile followed by quenching with electrophile to afford 1,3-diphosphacyclobutenes (**3**) [9] or 1,3-diphosphacyclobutane-2,4-diyls (**4**) [10], indicating

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Dedicated to Prof. Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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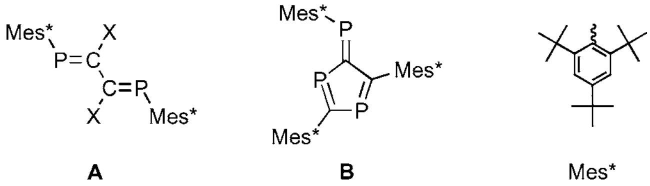


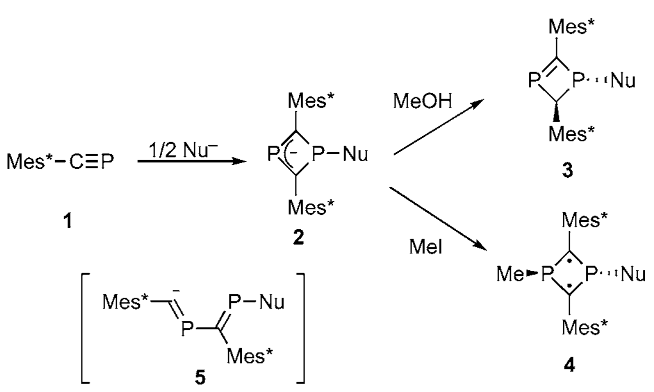
CHART 1

that the 1,3-diphosphabuta-1,3-diene intermediate (**5**) caused [2+2] cyclization to generate the anionic PCPC four-membered ring intermediate **2** (Scheme 1). Theoretical calculations have supported the lower stability of 1,3-diphosphabuta-1,3-diene compared to 1,3-diphosphacyclobutene [11].

Thus, new methods are required to synthesize oligoacetylene-type compounds such as R^1—$(P{=}CR^2)_n$—R^3. We report here preparation of novel 1,3-diphosphabuta-1,3-dienes from a bulky phosphaethenyllithium reagent [12] and **1**. Steric protection has been utilized to stabilize the 1,3-diphosphabuta-1,3-diene skeleton. X-ray crystallography of the 1,3-diphosphabuta-1,3-diene is also reported.

RESULTS AND DISCUSSION

Taking the facile [2+2] cyclization of the P=C—P=C skeleton affording **3** and **4** into consideration, the presence of a bulky substituent on the 1-phosphorus atom should prevent the cyclization. Thus, we chose 2-methyl-1-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithum (**6**) [6] and **1** as starting materials. 2-Bromo-1-phosphapropene **7** was allowed to react with butyllithium to generate **6**, and subsequently **1** was added. The anionic intermediate **8** was quenched with an electrophile such as iodomethane or benzyl bromide, and after the purification procedures, 1,3-diphosphabuta-1,3-dienes **9** were obtained as yellow crystals which are stable to air and moisture (Scheme 2). Both **9a** and **9b** were obtained as single diastereomers. In the ^{31}P NMR of **9**, the phosphorus atoms at the 1-position were observed at lower field than those of the 3-position, which are comparable to 1,3-diphosphapropenes [13]. On the other hand, attempts to obtain a 1,3-diphosphabuta-1,3-diene from 1-bromo-2-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethenyllithium [4] and **1** under similar reaction conditions for **B** [7] failed, indicating that the substituent in the phosphaethenyllithium has an effect on the synthesis.



SCHEME 1

A single crystal of **9b** suitable for X-ray crystallography was obtained, and the molecular structure was determined as shown in Fig. 1. The P=C—P=C skeleton is nearly planar [Θ(P1—C1—P2—C2) 176.9(4)°], which has been determined as the most stable conformer by theoretical calculations [14]. The benzyl group is located trans to the Mes* substituent on C2 to minimize steric repulsion. Two Mes* groups are almost perpendicular to the P1—C1—P2—C2 plane with the torsion angles of 89.5 and 86.1°. The Mes* group on the P1 atom and the benzyl group in **9b** effectively prevent [2+2] cyclization of the P=C—P=C skeleton, conforming to the stability of **9**, which also showed no [2+2] cyclization at room temperature. The P1—C1 and P2—C2 distances are close to the corresponding P=C distances

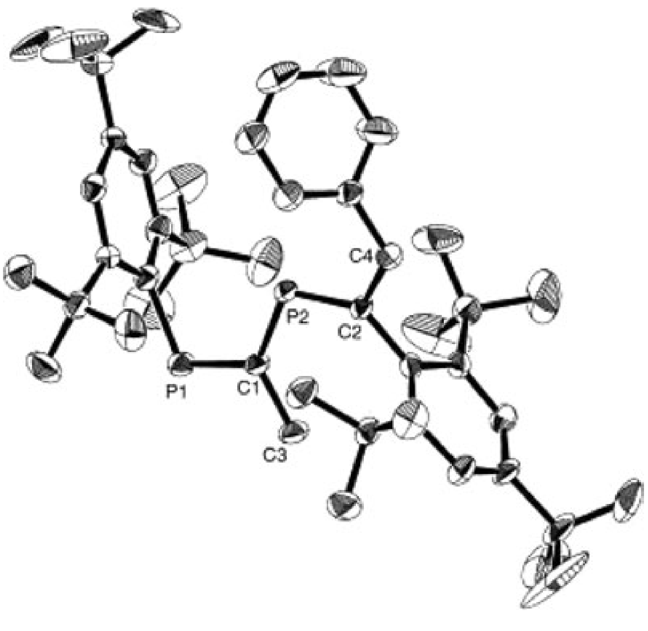
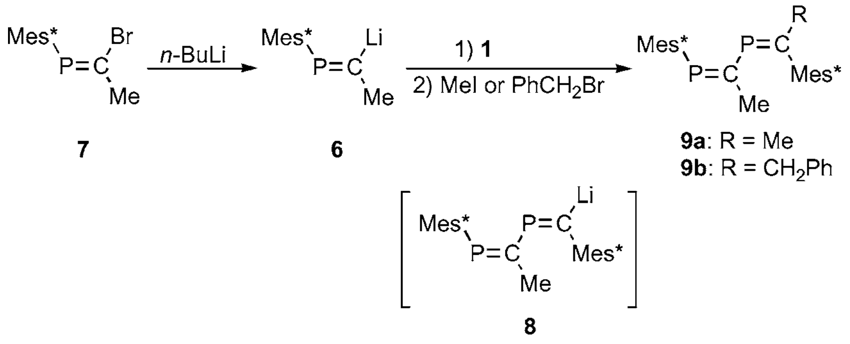


FIGURE 1 Molecular structure of **9b** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. The *p-t*-butyl group at the P1 side is disordered, and the atoms with the predominant occupancy factor (0.70) are shown.



SCHEME 2

of **10** [1.696(4), 1.696(3) Å] [15] (see Chart 2), which are slightly longer than the average P=C distance (1.67 Å) [1,2] (see Table 1). On the other hand, the P2—C1 distance indicates contraction compared with the normal P—C single bond (1.84 Å) [16]. Therefore, the structural parameters of **9b** indicate conjugation between two P=C groups.

In conclusion, we have demonstrated a novel preparation of sterically protected 1,3-diphosphabuta-1,3-dienes **9** from **1** and **6**, which is regarded as a fundamental procedure for the synthesis of polyphosphaalkynes. The molecular structure of **9b** indicated the effect of conjugation in the P=C—P=C skeleton. Properties of **9** including isomerizations and cycloadditions are currently being studied.

EXPERIMENTAL

Melting points were taken on a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University. ^{1}H NMR (400 MHz, CDCl$_3$) spectra,^{13}C NMR (101 MHz, CDCl$_3$) spectra, and ^{31}P NMR spectra were obtained on a Bruker AVANCE400 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer. Compounds **1** [10] and **7** [6] were prepared according to the procedures described in our previous reports. All reactions were carried out under argon atmosphere with dry solvents.

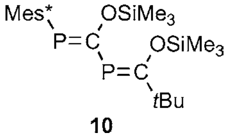


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CHART 2

Preparation of 1,3-Diphosphabuta-1,3-dienes 9

To a solution of **7** (60 mg, 0.16 mmol) in THF (2 mL) was added butyllithium (0.17 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm^{-}3) at –78°C and stirred for 5 min. The mixture was treated with a THF (2 mL) solution of **1** (0.16 mmol), and after 5 min, an excess amount of iodomethane or benzyl bromide (ca. 0.6 mmol) was added. The reaction mixture was warmed to room temperature, and the solvent was removed in vacuo. Silica gel column chromatography (hexane) and recrystallization from ethanol afforded **9**.

9a: 48% yield, yellow prisms, mp 219–220°C; ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 1.44$ (9H, s, *p*-*t*-Bu), 1.52 (27H, s, *p*-, and *o*-*t*-Bu), 1.61 (18H, s, *o*-*t*-Bu), 2.06 (3H, d, $^3J_{\mathrm{PH}} = 27$ Hz, P=C(P)Me), 2.57 (3H, dd, $^3J_{\mathrm{PH}} = 24$ Hz, $^5J_{\mathrm{PH}} = 5$ Hz, P=CMe), 7.50 (2H, s, arom), and 7.52 (2H, s, arom); ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) $\delta = 25.1$ (dd, $^2J_{\mathrm{PC}} = 45$ Hz, $^2J_{\mathrm{PC}} = 7$ Hz, P=C(P)$\underline{\mathrm{Me}}$), 32.0 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.6 (s, *o*-C$\underline{\mathrm{Me}}_3$), 35.2 (s, *p*-$\underline{\mathrm{C}}Me_3$), 35.3 (d, $^2J_{\mathrm{PC}} = 52$ Hz, P=C$\underline{\mathrm{Me}}$), 35.5 (s, *p*-$\underline{\mathrm{C}}$Me$_3$), 38.7 (s, *o*-$\underline{\mathrm{C}}$Me$_3$), 39.1 (s, *o*-$\underline{\mathrm{C}}$Me$_3$), 121.9 (s, *m*-Mes*), 124.2 (s, *m*-Mes*), 137.2 (dd, $^1J_{\mathrm{PC}} = 59$ Hz, $^3J_{\mathrm{PC}} = 18$ Hz, *ipso*-Mes*), 141.2 (d, $^2J_{\mathrm{PC}} = 16$ Hz, *ipso*-Mes*), 144.8 (d, $^2J_{\mathrm{PC}} = 6$ Hz, *o*-Mes*), 148.1 (s, *p*-Mes*), 150.7 (s, *p*-Mes*), 154.6 (s, *o*-Mes*), 182.7 (dd, $^1J_{\mathrm{PC}} = 51$ Hz,

TABLE 1 Selected Bond Distances and Angles for **9b**

Bond distance (Å)		*Bond angle (°)*	
P1–C1	1.689(7)	C1–P1–C$_{\mathrm{Mes*}}$	106.9(3)
P1–C$_{\mathrm{Mes*}}$	1.839(7)	C1–P2–C2	110.2(3)
P2–C1	1.796(7)	P1–C1–P2	121.0(4)
P2–C2	1.694(7)	P1–C1–C3	112.8(5)
C1–C3	1.540(9)	P2–C1–C3	126.0(5)
C2–C4	1.536(10)	P2–C2–C4	118.1(5)
C2–C$_{\mathrm{Mes*}}$	1.519(9)	P2–C2–C$_{\mathrm{Mes*}}$	131.7(5)
		C4–C2–C$_{\mathrm{Mes*}}$	110.2(6)

Numbers in parentheses are estimated standard deviations.

$^3J_{\mathrm{PC}} = 30$ Hz, P=*C*), and 190.4 (dd, $^1J_{\mathrm{PC}} = 88$ Hz, $^1J_{\mathrm{PC}} = 52$ Hz, P=$\underline{\mathrm{C}}$—P); ^{31}P NMR (162 MHz, $\mathrm{CDCl_3}$) $\delta = 237.9$ (dq, $^2J_{\mathrm{PP}} = 29$ Hz, $^3J_{\mathrm{PH}} = 24$ Hz, P=C) and 318.3 (dqq, $^2J_{\mathrm{PP}} = 29$ Hz, $^3J_{\mathrm{PH}} = 27$ Hz, $^5J_{\mathrm{PH}} = 5$ Hz, $\underline{\mathrm{P}}$=C—P); UV (hexanes) λ_{max} (log ε) 349 nm (4.30). EA Found: C, 79.25; H, 10.54%. Calcd for $\mathrm{C_{40}H_{64}P_2}$: C, 79.16; H, 10.63%.

9b: 40% yield, yellow prisms, mp 201–203°C; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$) $\delta = 1.29$ (9H, s, *p-t*-Bu), 1.34 (9H, s, *p-t*-Bu), 1.43 (18H, s, *o-t*-Bu), 1.46 (18H, s, *o-t*-Bu), 2.11 (3H, d, $^3J_{\mathrm{PH}} = 28$ Hz, P=C(P)Me), 3.93 (2H, dd, $^3J_{\mathrm{PH}} = 19$ Hz, $^5J_{\mathrm{PH}} = 7$ Hz, $\mathrm{CH_2}$), 7.02–7.13 (5H, m, Ph), 7.22 (2H, s, Mes*), and 7.44 (2H, s, Mes*); ^{13}C{^{1}H} NMR (151 MHz, $\mathrm{CDCl_3}$) $\delta = 26.7$ (dd, $^2J_{\mathrm{PC}} = 46$ Hz, $^2J_{\mathrm{PC}} = 6$ Hz, Me), 32.0 (s, *p*-C$\underline{\mathrm{Me}}_3$), 32.0 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.7 (s, *p*-$\underline{\mathrm{C}}$$\mathrm{Me_3}$), 34.8 (s, *p*-$\underline{\mathrm{C}}$$\mathrm{Me_3}$), 35.3 (s, *o*-C$\underline{\mathrm{Me}}_3$), 35.3 (s, *o*-C$\underline{\mathrm{Me}}_3$), 38.9 (s, *o*-$\underline{\mathrm{C}}$$\mathrm{Me_3}$), 39.6 (s, *o*-$\underline{\mathrm{C}}$$\mathrm{Me_3}$), 53.9 (d, $^2J_{\mathrm{PC}} = 37$ Hz, $\mathrm{CH_2}$), 121.9 (s, *m*-Mes*), 125.0 (s, *m*-Mes*), 127.0 (s, *p*-Ph), 128.3 (s, *m*-Ph), 130.9 (d, $^4J_{\mathrm{PC}} = 3$ Hz, *o*-Ph), 136.3 (dd, $^1J_{\mathrm{PC}} = 61$ Hz, $^3J_{\mathrm{PC}} = 18$ Hz, *ipso*-Mes*), 138.2 (d, $^3J_{\mathrm{PC}} = 11$ Hz, *ipso*-Ph), 141.6 (d, $^2J_{\mathrm{PC}} = 16$ Hz, *ipso*-Mes*), 144.9 (d, $^2J_{\mathrm{PC}} = 6$ Hz *o*-Mes*), 148.0 (s, *p*-Mes*), 150.4 (s, *p*-Mes*), 154.1 (s, *o*-Mes*), 187.3 (dd, $^1J_{\mathrm{PC}} = 89$ Hz, $^1J_{\mathrm{PC}} = 52$ Hz, P=$\underline{\mathrm{C}}$—P, and 188.3 (dd, $^1J_{\mathrm{PC}} = 53$ Hz, $^3J_{\mathrm{PC}} = 29$ Hz, P=C); ^{31}P NMR (162 MHz, $\mathrm{CDCl_3}$) $\delta = 233.7$ (dt, $^2J_{\mathrm{PP}} = 26$ Hz, $^3J_{\mathrm{PH}} = 19$ Hz, P=C) and 326.0 (dqt, $^2J_{\mathrm{PP}} = 26$ Hz, $^3J_{\mathrm{PH}} = 28$ Hz, $^5J_{\mathrm{PH}} = 7$ Hz, $\underline{\mathrm{P}}$=C—P); UV (hexanes) λ_{max} (log ε) 350 nm (4.27). EA Found: C, 81.06; H, 10.17%. Calcd for $\mathrm{C_{46}H_{68}P_2}$: C, 80.89; H, 10.04%.

X-Ray Structure Determination of 9b

$\mathrm{C_{46}H_{68}P_2}$: $M = 682.99$, pale yellow prism crystallized from ethanol. Crystal dimensions $0.40 \times 0.40 \times 0.30$ mm^3, monoclinic $P2_1/n$ (no. 14), $a = 14.1783(6)$, $b = 21.7412(9)$, $c = 14.5666(8)$ Å, $\beta = 101.95(2)$, $V = 4404.8(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.030$ g cm^{-3}, $F(000) = 1496$, $\mu = 0.126$ mm^{-1}, $T = 296$ K. A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å) was used. Of 33195 reflections measured ($2\theta_{\mathrm{max}} = 55.0°$), 9886 were observed ($R_{\mathrm{int}} = 0.090$). The structure was solved by direct methods (SIR92) [17], expanded using Fourier techniques (DIRDIF94) [18], and then refined by full-matrix least squares on F for 445 variable parameters. $R1 = 0.075$ for $I > 3.0\sigma(I)$, and $R_w = 0.114$ for all data. Structure solution, refinement, and graphical representation were carried out using the teXsan package [19]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-257070.

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