# Preparation and X-ray analyses of siloxane-bridged acyclic and 8-membered cyclic phosphaethenes

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## Abstract

Two Mes*P=C (Mes* = 2,4,6-tri-$t$-butylphenyl) parts were successfully combined with one or two disiloxane chain(s) by the reaction of 2-silyl-1-phosphaethenyllithium with dichlorotetramethyldisiloxane, and the structures of bis(1-bromo-2-phosphaethenyl)disiloxane and 3,7-diphosphinidene-2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasilacyclooctane were characterized by spectroscopic analyses and X-ray crystallography.
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## 1. Introduction

Medium- or small-size cyclic compounds bearing plural unsaturated organic groups are expected to show intriguing physicochemical properties due to through-space and through-bond π-orbital interactions, and considerable progress has been made in the chemistry of cyclophanes bearing aromatic rings [1]. π-Electron systems other than aromatic groups can be employed to construct non-conjugated π-orbital interactions as can be seen in the chemistry of pericyclynes [2]. In order to prepare such closely positioned π-orbital systems separated by non-conjugating groups, several particular chain structures have been used as tethers or spacers. Therefore, it is requisite to utilize uncommon π-electron systems and suitable tethers for novel spherically interacting π-electron systems.

A phosphorus–carbon double bond (phosphaalkene) is an isolable unsaturated bond containing a heavier main-group element and a number of phosphaalkene derivatives have been reported so far by using suitable stabilization techniques such as steric protection and electronic perturbation [3,4]. The P=C double bond displays similar nature to the corresponding carbon–carbon double bond [3b] and it will offer us novel organic molecular motives provided well-controlled chemical transformations are developed. Furthermore, low-lying LUMO of the P=C group have recently been of interest from the viewpoints of novel ligands for synthetic catalysts [5] and extraordinary chemical bond formation like a one-electron P–P linkage upon its reduction [6]. Therefore, the P=C double bond of the "carbon copy" nature is expected to show a π-electron functionality. Le Floch and Mathey et al. have established an intriguing chemistry of cyclic structures containing phosphinines [6,7] such as **A** [6a]. Scott and Unno reported medium-size pericyclyne derivatives composed of the $t$-BuPC≡C moieties (**B**) showing strong cyclic electronic interactions [8]. On the other hand, utilization of electrically less-perturbed P=C bond has not been examined extensively so far except for **C** [5], **D** [9], **E** [10], and **F** [11] (see Chart 1).

As an intriguing procedure to obtain molecules containing plural P=C groups, we have established utilization of kinetically stabilized phosphaethenyllithiums [Mes*P=C(X)Li] and analyzed several π-conjugation systems com-

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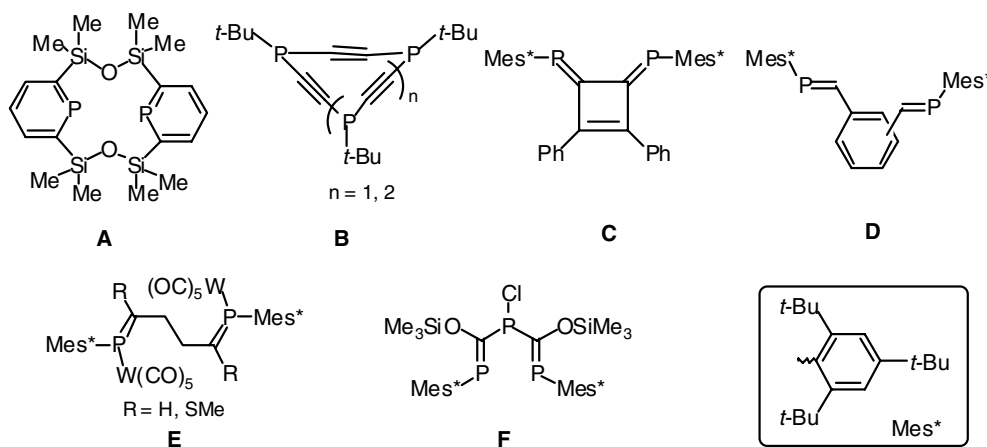
Chart 1.

posed of P=C bonds [4,12]. Nucleophilic reactivity of phosphaethenyllithiums is expected to provide us novel poly(phosphaethene) derivatives by utilizing well-controlled synthetic procedures, but such sterically encumbered P=C compounds do not seem to be suitable to accumulate plural phosphorus–carbon multiple bonds within a molecule. Nevertheless, we have found several procedures to accumulate the bulky Mes*P=C moieties that are inherently unstable [12]. Furthermore, it should be pointed out that phosphaethenyllithium [Mes*P=C(X)Li] in the case where X is halogen shows such carbenoid reactivity [12] as affording phosphaalkyne [Mes*C≡P] via the Fritsch–Buttenberg–Wiechell [1,2] rearrangement [13].

Here, we describe bond formation of two phosphaethenyl groups with the tetramethyldisiloxy chain that has been utilized to synthesize cyclophane-type molecules [14]. Indeed, binding of two unsaturated organic groups with siloxy chains are available to maintain an adequate orientation to cause interaction of interest between the two π-electron systems [6,7,14].

As for phosphaethenes bearing trialkylsilyl group at the sp² carbon atom, we reported that copper-mediated homo-coupling reaction of 2-trialkylsilyl-2-phosphaethenyllithiums [Mes*P=C(SiMe₂R)Li; R = Me, t-Bu] afford 3,4-diphosphacyclobutenes, indicating that the silyl group prompts [2 + 2] cyclization of the P=C–C=P skeleton or isomerization of phosphaethenyllithium into the phosphinocarbene structure [15]. Additionally, structure of a 2-trimethylsilyl-1,3-diphosphapropene [Mes*P=C(SiMe₃)PPh₂] suggests the effects of silyl group: presumably the group stabilizes inherently predominant C₁ symmetric P=C–P < conformation [16]. Thus, silyl groups are expected to be effective to bring out novel properties of phosphaethenes.

## 2. Results and discussion

We have utilized reactions of sterically hindered 1-halo-2-phosphaethenyllithiums [Mes*P=C(X)Li] with electrophiles such as carbonyl compounds [17] and haloalkanes

[18] to synthesize various types of organophosphorus compounds bearing the Mes*P=C(X) groups, where the halogen atoms can be transformed to other functional groups. As mentioned above, halosilanes are expected to be accessible as electrophiles.

First, we investigated the reactions with 1,1,3,3-tetra-methyl-1,3-dichlorosiloxane (ClMe₂Si)₂O, where two chlorine atoms might be substituted with the [Mes*P=CBr] groups. A dibromophosphaethene 2 [19] was allowed to react with butyllithium and phosphaethenyllithium 1 thus generated was treated with a half of equivalent amount of dichlorodisiloxane to give 3 in a moderate yield (Scheme 1). The NMR data suggested a highly symmetrical structure: ³¹P NMR spectrum showed a single peak for the Mes*P=C(Br)SiMe₂ moiety, which was also supported by ¹H and ¹³C NMR spectroscopy. The structure of 3 was unambiguously confirmed by X-ray crystallography and Fig. 1 displays that tethering of two Mes*P=CBr groups
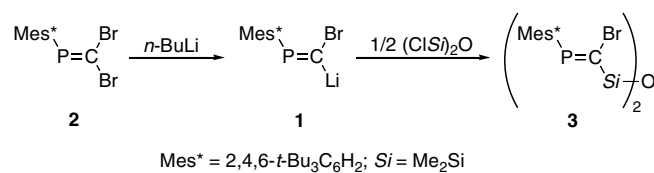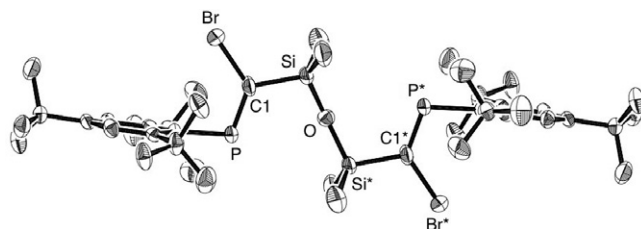


Scheme 1.



Fig. 1. An ORTEP drawing for 3 (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. The oxygen atom is disordered and one of them is displayed. Selected bond lengths (Å) and angles (°): P–C1 1.659(8), C1–Br 1.916(8), P–C_Mes* 1.847(7), C1–Si 1.885(7), Si–O 1.58(1), 1.71(1), C1–P–C_Mes* 107.0(3), P–C1–Br 126.0(4), Br–P–Si 113.4(8), P–C1–Si 120.2(4), Si–O–Si 157.8(6).

with a disiloxy chain was successful. The Mes*P=CBr moieties show a Z-configuration and the oxygen atom is disordered (isotropically assigned and analyzed in two positions). The P–C1 and C1–Si distances of **3** are comparable with that for Mes*P=C(SiMe₃)₂ [P=C: 1.665(4) Å, C($sp^2$)–Si: 1.891(4) and 1.887(4) Å] [20]. The C1–Br distance of **3** is longer than that for Mes*P=CBr₂ [1.852(10), 1.884(9) Å] [21], and comparable to that for Mes*P=CBr-CH(OMe)-*c*-Pr [1.901(3) Å] [18c]. The C1–P–C$_{Mes*}$ angle and the sum of the angles around C1 (360°) reflect one of the characteristics of phosphaalkenes [3]. Another phosphaalkene character of **3** can be referred to a planar C$_{Mes*}$–P–C1–Br(Si) skeleton [dihedral angles: −0.7(6)°, 179.8(4)°]. The abnormally large deviation of the two Si–O distances and large Si–O–Si angle are presumably due to influence of disorder and exact position of the oxygen atom should not be discussed in detail. The molecule of **3** in crystalline state shows a similar conformation of *s-trans* type to that of *meso*-[Mes*P=C(OSiMe₃)—PPh]₂ [22].

We then investigated further reaction as follows: two bromine atoms in **3** might be replaced with lithium by halogen–metal exchange reaction to generate a dilithium compound **4** that is expected to react with two equivalents of electrophile. Our idea was to combine the two anionic carbons with the (SiMe₂OSiMe₂) chain to obtain an 8-membered heterocyclic compound. Compound **3** was thus allowed to react with butyllithium (2 equiv.) to generate **4** and the resulting mixture was allowed to react with 1,1,3,3-tetramethyl-1,3-dichlorosiloxane (1 equiv.). After the work-up procedures, we isolated the desired heterocyclic compound, 2,2,4,4,6,6,8,8-octamethyl-3,7-bis(2,4,6-tri-*t*-butylphenylphosphinidene)-1,5-dioxa-2,4,6,8-tetrasila-cyclooctane **5**, together with a few non-characterized byproducts, although the yield of **5** was low (Scheme 2). Characterization of the byproducts as well as optimization of the yield for **5** is in progress. As shown in Fig. 1, the bromine atoms of **3** do not seem to locate at suitable positions for the desired reaction in the crystalline state, plausibly reflecting the low yield of **5**. Nevertheless, the (SiMe₂OSiMe₂) chain loops up the C–Si–O–Si–C chain of **4** to form the 8-membered ring **5** [6,23]. We were thus successful in incorporation of two Mes*P=C groups in an intramolecular fashion with two disiloxy chains, and the structure of the medium-size heterocyclic compound **5** was confirmed by X-ray crystallography. Fig. 2 displays a molecular structure of **5** and the molecule shows a chair-type conformation of C$_i$ symmetry, forming a sharp contrast to 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasila-3,4-*exo*-dimethylenecyclooctane of boat-type con-
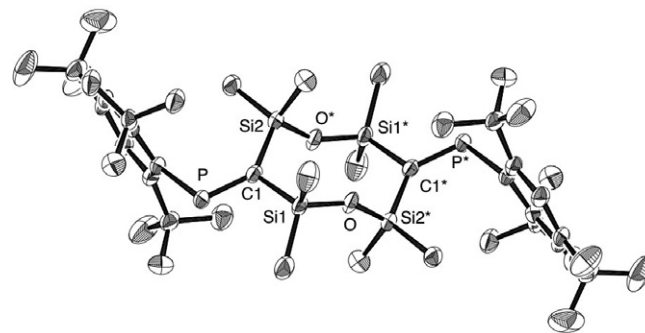


Fig. 2. An ORTEP drawing for **5** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.667(5), P1–C$_{Mes*}$ 1.856(4), C1–Si1 1.879(4), C1–Si2 1.872(5), Si1–O 1.630(3), Si2–O 1.639(3), C1–P1–C$_{Mes*}$ 108.8(2), P1–C1–Si1 110.8(3), P1–C1–Si2 134.0(3), Si1–C1–Si2 115.1(2), O–Si1–C1 109.6(2), O–Si1–C2 109.4(2), Si1–O–Si2 151.4(2).

formation [24]. The two Mes*P=C groups take a *trans* configuration in the crystalline state, presumably alleviating steric congestion. The P1–C1 and C1–Si distances of **5** are comparable to those for Mes*P=C(SiMe₃)₂ [20]. The Si–O distances of **5** are comparable to the corresponding parameters of **A** [1.642(2), 1.640(2) Å] [6a], and the Si–O–Si angle of **5**, which is larger than that for **A** [145.49(8)°], presumably suggesting the effect of the sterically crowded Mes* groups to draw the 8-membered ring into slightly narrower ring. Furthermore, the C1···C1* distance of **5** (4.77 Å) is considerably shorter than the C1···C1* distance of **3** (5.58 Å), suggesting the effect of the dual tethering. In the ³¹P NMR spectrum, one signal in a considerably lower field was observed for **5**, indicating π-electron-accepting effects of the silyl groups, as observed in Mes*P=C(SiMe₃)₂ ($\delta_P$ 393) [20]. In the ¹H and ¹³C NMR spectra (CDCl₃, 298 K), two geometrically distinct SiMe₂ moieties were observed [25], which corresponds to the character of Mes*P=C(SiMe₃)₂ [20].

## 3. Conclusion

We have succeeded in tethering two bulky Mes*P=C groups intramolecularly with two disiloxy chains in a stepwise manner to obtain a novel compound bearing two low-coordinated phosphorus atoms. The 8-membered heterocycle bearing two *exo*-P=C bonds in **5** is an intriguing molecular motif to show attractive nature due to an interaction between the reducible phosphaalkene parts and unique coordination character [6,26] supported by disiloxy chains to conform the suitable geometries [7]. Furthermore, **3** and **4** are expected to serve as a promising intermediate
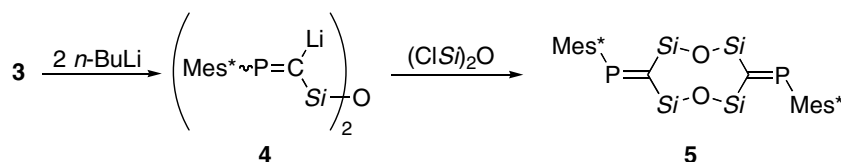


Scheme 2.

to synthesize novel organophosphorus compounds, which can be employed for coordination and supramolecular chemistry.

## 4. Experimental section

### 4.1. General procedure

All manipulations were carried out under an argon atmosphere by means of the standard Schlenk techniques. All the solvents employed were dried by appropriate methods. $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra were recorded on a Bruker AVANCE400 spectrometer in CDCl$_3$ at 298 K with Me$_4$Si ($^1$H, $^{13}$C) and H$_3$PO$_4$ ($^{31}$P), respectively, as internal or external standard. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. MS spectra were taken on a JEOL HX-110 or a Hitachi M-2500S spectrometer. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. X-ray diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SIR92) [27], expanded using Fourier techniques (DIRDIF94) [28]. Structure solution, refinement, and graphical representation were carried out using the TEXSAN package [29]. Compound **2** was prepared according to the literature [19].

### 4.2. Preparation of 3

To a solution of **2** (1.00 g, 2.23 mmol) in THF (20 mL) was added butyllithium (2.30 mmol, 1.6 M solution in hexane, 1 M = 1 mol dm$^{-3}$) at −78 °C. After 10 min, to the reaction mixture containing **1** was added 1,1,3,3-tetramethyl-1,3-dichlorosiloxane (1.12 mmol) and was stirred for an additional 10 min. The mixture was allowed to warm to room temperature, volatiles were then removed and the residual materials were purified by silica-gel column chromatography (hexane). The crude product was recrystallized from hexane to afford **3** as colorless crystals (0.38 g, 40%); m.p. 193–195 °C. $^{31}$P{$^1$H} NMR (162 MHz) δ 307.7. $^1$H NMR (400 MHz) δ 7.42 (s, 4H, arom), 1.49 (s, 36H, *o-t*-Bu), 1.37 (s, 18H, *p-t*-Bu), 0.39 (s, 12H, SiMe$_2$). $^{13}$C{$^1$H} NMR (101 MHz) δ 166.1 (d, $^1J_{PC}$ = 77.9 Hz, P=C), 153.0 (s, *o*-C of Mes*), 150.8 (s, *p*-C of Mes*), 140.5 (d, $^1J_{PC}$ = 64.5 Hz, *ipso*-C of Mes*), 122.4 (s, *m*-C of Mes*), 38.2 (s, *o*-CMe$_3$), 35.5 (s, *p*-CMe$_3$), 33.2 (d, $^4J_{PC}$ = 6.4 Hz, *o*-C*Me*$_3$), 31.9 (s, *p*-C*Me*$_3$), 1.2 (d, $^3J_{PC}$ = 6.5 Hz, SiMe$_2$). Anal. Calc. for C$_{42}$H$_{70}$Br$_2$OP$_2$Si$_2$: C 58.05, H 8.12, Br 18.39. Found: C 58.12, H 8.22, Br 18.09%.

### 4.3. Preparation of 5

To a solution of **3** (0.38 g, 0.44 mmol) in THF (20 mL) was added butyllithium (0.90 mmol) at −78 °C. After 10 min to the reaction mixture containing **4** was added 1,1,3,3-tetramethyl-1,3-dichlorosiloxane (0.45 mmol) and

was stirred for an additional 10 min. The mixture was allowed to room temperature, volatiles were then removed and the residual materials were purified by silica-gel column chromatography (hexane). The crude product was recrystallized from hexane to afford **5** as colorless crystals (26 mg, 7%); m.p. 298–300 °C. $^{31}$P{$^1$H} NMR (162 MHz) δ 379.3. $^1$H NMR (400 MHz) δ 7.36 (s, 4H, arom), 1.50 (s, 36H, *o-t*-Bu), 1.34 (s, 18H, *p-t*-Bu), 0.29 (s, 12H, *trans*-SiMe$_2$), −0.43 (s, 12H, *cis*-SiMe$_2$). $^{13}$C{$^1$H} NMR (101 MHz) δ 189.9 (d, $^1J_{PC}$ = 84.1 Hz, P=C), 152.9 (s, *o*-C of Mes*), 150.5 (s, *p*-C of Mes*), 144.1 (d, $^1J_{PC}$ = 83.3 Hz, *ipso*-C of Mes*), 122.4 (s, *m*-C of Mes*), 38.6 (s, *o*-C*Me*$_3$), 35.3 (s, *p*-C*Me*$_3$), 34.1 (d, $^4J_{PC}$ = 7.6 Hz, *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$), 4.42 (d, $^3J_{PC}$ = 12.0 Hz, *trans*-SiMe$_2$), 2.38 (s, *cis*-SiMe$_2$). ESI-MS Calc. for C$_{46}$H$_{82}$O$_2$P$_2$Si$_4$ + Na: *m/z* 863.4759, found: 863.4757.

### 4.4. X-ray crystallography for 3

C$_{42}$H$_{70}$Br$_2$OP$_2$Si$_2$, $M$ = 868.94, crystal dimensions: 0.20 × 0.10 × 0.07 mm$^3$, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 10.520(2), $b$ = 12.412(3), $c$ = 10.109(2) Å, $\alpha$ = 103.105(4), $\beta$ = 95.572(5), $\gamma$ = 110.983(3)°, $V$ = 1177.1(4) Å$^3$, $Z$ = 1, $T$ = 223 K, $2\theta_{max}$ = 55.0°, $\rho$ = 1.226 g cm$^{-3}$, $\mu$ (Mo Kα) = 1.874 mm$^{-1}$, $F_{000}$ = 458, 8361 measured reflections, 4795 unique reflections ($R_{int}$ = 0.061), $R_1$ = 0.097 ($I$ > 2.0$\sigma(I)$), $R_W$ = 0.166 (all data) (CCDC-298727).

### 4.5. X-ray crystallography for 5

C$_{46}$H$_{82}$O$_2$P$_2$Si$_4$, $M$ = 841.44, crystal dimensions: 0.15 × 0.15 × 0.10 mm$^3$, monoclinic, space group $P2_1/n$ (no. 14), $a$ = 12.1097(8), $b$ = 14.970(1), $c$ = 14.212(1) Å, $\beta$ = 94.462(3)°, $V$ = 2568.5(4) Å$^3$, $Z$ = 2, $T$ = 140 K, $2\theta_{max}$ = 55.0°, $\rho$ = 1.088 g cm$^{-3}$, $\mu$(Mo Kα) = 0.211 mm$^{-1}$, $F_{000}$ = 920, 15971 measured reflections, 5742 unique reflections ($R_{int}$ = 0.076), $R_1$ = 0.079 ($I$ > 2.0$\sigma(I)$), $R_W$ = 0.134 (all data) (CCDC-298728).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.041.

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