

# Generation, isolation, and reactivity of a kinetically stabilized diphosphene anion radical

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Dedicated to Prof. Renji Okazaki on the occasion of his 70th birthday.

## Abstract

The stable lithium diphosphene anion radical,  $[\text{Li}(\text{dme})_3]^+[\text{TbtPPTbt}]^-$  (dme: 1,2-dimethoxyethane, Tbt: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), was readily synthesized by the one-electron reduction of the corresponding neutral diphosphene ( $\text{TbtP}=\text{PTbt}$ ). The molecular structure of the diphosphene anion radical was discussed in detail on the basis of its ESR, UV–Vis and Raman spectra, and theoretical calculations. The diphosphene anion radical was found to undergo ready chalcogenation reactions using elemental sulfur and selenium to afford the corresponding thiadiphosphirane and selenadiphosphirane, respectively.

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**Keywords:** Diphosphene; Cyclic voltammetry; Reduction; Anion radical; UV–Vis spectrum; ESR spectrum

## 1. Introduction

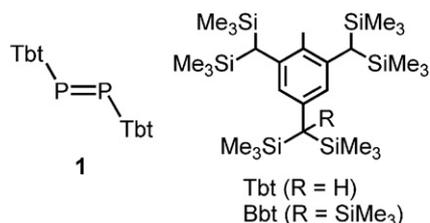
A number of kinetically stabilized dipnictenes ( $\text{ArE}=\text{EAR}$ , E; group 15 elements) have been synthesized and the intrinsic nature of the double bonds has been extensively elucidated [1] since the discovery of the first stable diphosphene ( $\text{Mes}^*\text{P}=\text{PMes}^*$ ,  $\text{Mes}^*$ ; 2,4,6-tri-*tert*-butylphenyl) by Yoshifuji et al. [2], which is a landmark in the chemistry of double-bond compounds between group 15 elements. One of the characteristic nature of diphosphenes is the low-lying LUMO level as compared with the corresponding azo-compounds due to the smaller orbital overlap between 3p orbitals of the phosphorus atoms than that between the 2p orbitals of the nitrogen atoms [2,3]. Thus, it is quite obvious that diphosphenes readily undergo electrochemical and/or

chemical reduction to afford the corresponding anion radicals. Since the first report on the generation of the persistent anion radical of  $\text{Mes}^*\text{P}=\text{PMes}^*$  in 1982 [4], there were several reports on the generation and ESR spectroscopic detection of the anion radicals of several diphosphenes bearing two same substituents (tris(trimethylsilyl)methyl [5a,5b], 2,6-dimesitylphenyl [5c], *t*-butyl [5d], cyclohexyl [5e], and phenyl groups [5e]) [6]. However, isolation and detailed characterization of diphosphene anion radicals have been unsuccessful due to their high instability and reactivity.

On the other hand, we have developed extremely bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) groups [7]. Indeed, two stable diphosphenes were synthesized by taking advantage of Tbt and Bbt groups, and their molecular structures and reactions of  $\text{BbtP}=\text{PBbt}$  with elemental sulfur or selenium were reported [7f]. Thus, it was

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demonstrated that the use of Tbt and Bbt as steric protection groups provide enough bulkiness to isolate diphosphene derivatives. Recently, the electrochemical properties of BbtP=PBbt and the physical properties of the first isolable diphosphene anion radical,  $[\text{Li}(\text{dme})_3]^+[\text{BbtPPBbt}]^-$  (dme: 1,2-dimethoxyethane), were also disclosed together with the crystalline structure of the first stable corresponding antimony-congener,  $[\text{Li}(\text{dme})_3]^+[\text{BbtSbSbBbt}]^-$  [7i,7j]. However, we could not obtain single crystals of the anion radical of BbtP=PBbt at that time [7j]. Therefore, we have decided to use Tbt-substituted diphosphene for this chemistry in the expectation of obtaining single crystals for X-ray crystallographic analysis, since it was found that the crystalline structures of BbtP=PBbt and TbtP=PTbt were largely different from each other [7f]. We present here the electrochemical behavior of the stable diphosphene **1** substituted by Tbt groups and the chemical reduction of **1** leading to the formation of the corresponding anion radical **2** which can be handled under inert atmosphere as well as the case of  $[\text{Li}(\text{dme})_3]^+[\text{BbtPPBbt}]^-$ . The physical properties of **2** were revealed by its UV–Vis, ESR, and Raman spectra in detail. The reactions of **2** with iodomethane, elemental sulfur, and selenium were found to readily proceed to afford diphosphene **1**, thiadiphosphirane **3**, and selenadiphosphirane **4**, respectively.



## 2. Results and discussion

### 2.1. Electrochemical properties of diphosphene **1**

Kinetically stabilized diphosphene **1**, TbtP=PTbt, was readily prepared via a reductive coupling reaction of the corresponding dichlorophosphine (TbtPCl<sub>2</sub>) using a magnesium metal in THF [7f]. Electrochemical properties of **1** were revealed by cyclic voltammetry in THF with *n*-Bu<sub>4</sub>NBF<sub>4</sub> as an electrolyte at room temperature in a glovebox filled with argon gas, and the voltammograms are shown in Fig. 1. The difference between cathodic and anodic potentials displayed 0.11 V, which is relatively small value under these conditions [8], though it is somewhat larger than an ideal Nernstian process (ca. 0.06 V). The current at the peak potentials of the reduction was almost equal to that of the oxidation, and a plot of the current in the cathodic peak against a square root of the scan rate displayed almost linear relationship. These results indicate that an electron transfer process for **1** should be reversible

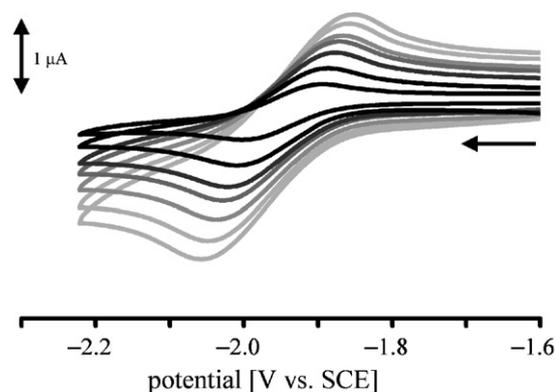


Fig. 1. Cyclic voltammograms of diphosphene **1** in THF containing 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub> at room temperature (scan rate; 10, 25, 50, 75, 100, 150, and 200 mV s<sup>-1</sup> from the inside).

Table 1  
Redox potentials (V) of diphosphenes

	$E_{pc}$	$E_{pa}$	$E_{1/2}$	Reference
TbtP=PTbt <b>1</b>	-1.96 <sup>a</sup>	-1.85 <sup>a</sup>	-1.91 <sup>a</sup>	This work
BbtP=PBbt	-1.92 <sup>a</sup>	-1.71 <sup>a</sup>	-1.82 <sup>a</sup>	[7j]
Mes*P=PMes*			-1.93 <sup>b</sup>	[5a]
TsiP=PTsi			-1.84 <sup>b</sup>	[5a]
Ar <sup>1</sup> P=PAr <sup>1</sup>			-2.08 <sup>c</sup>	[5c]

<sup>a</sup> 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in THF, V vs. SCE.

<sup>b</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub> in THF, V vs. SCE.

<sup>c</sup> 0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in THF, V vs. SCE (Ar<sup>1</sup> = 2,6-dimesitylphenyl).

under these conditions. The reductive and the corresponding oxidative waves were observed at -1.96 and -1.85 V vs. SCE (Fig. 1), respectively, and a half-wave potential of the observed reversible one-electron redox couple was -1.91 V vs. SCE, which is similar to those of the previously reported diphosphenes (Table 1) [4,5,7i,7j]. These results suggest that the electronic character of the P=P moiety of **1** is little perturbed by the  $\pi$ -electrons of the aromatic rings of the Tbt groups as in the case of the reported diphosphenes probably due to the molecular structure in solution, where the aromatic substituents might be orientated perpendicularly. Moreover, the observed reversible redox couple in the cyclic voltammogram for **1** indicates that **1** undergoes facile one-electron reduction leading to the formation of the corresponding anion radical **2**, which should be stable under these conditions.

### 2.2. Generation and isolation of the anion radical salt of diphosphene **1**

A THF solution of diphosphene **1** was reacted with lithium metal in a sealed quartz cell. The reduction reaction of **1** at room temperature was monitored by UV–Vis spectroscopy and the spectra are shown in Fig. 2, where isosbestic points were observed at 381 and 442 nm, suggesting the one-to-one reaction without metastable intermediate in this reaction. The reduction reaction of **1** was completed within 12 h, and the spectrum of the resulting solution was very

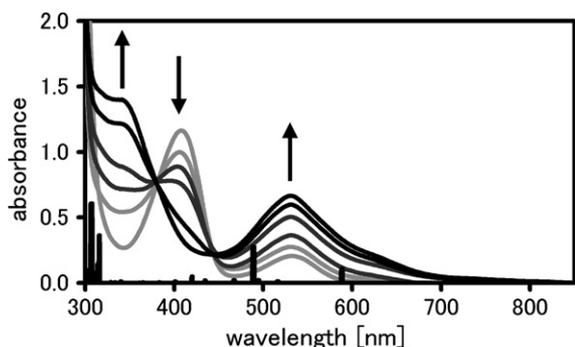
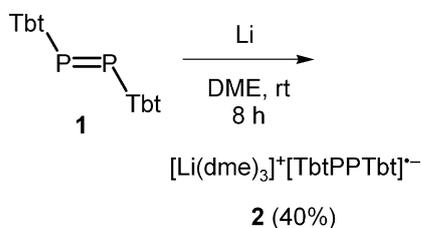


Fig. 2. UV–Vis spectra during the reaction of diphosphene **1** with lithium metal in THF at room temperature (the reaction time; 0, 2, 4, 8, 10, and 12 h). The calculated electron transitions for the excited state of [DmpPPDmp]<sup>−</sup> (black bars).



Scheme 1. Reaction of diphosphene **1** with lithium metal.

similar to that of the corresponding anion radical isolated as lithium salt (*vide infra*). At the next stage, treatment of **1** (300 mg, 0.257 mmol) with an excess amount of lithium metal (5.0 mg, 0.72 mmol) in DME at room temperature afforded the corresponding anion radical salt [Li(dme)<sub>3</sub>]<sup>+</sup>[TbtPPTbt]<sup>−</sup> (**2**, 148 mg, 0.103 mmol) as a purple powder in 40% isolated yield [9] (see Scheme 1). Although anion radical salt **2** can be isolated as a stable compound under an inert atmosphere, **2** was very sensitive toward moisture and oxygen in air. Compound **2** was thermally stable without any decomposition up to 130 °C in a degassed sealed tube, indicating the Tbt group shows sufficient performance for kinetic stabilization as well as that of the Bbt group [71].

### 2.3. ESR, UV–Vis, and Raman spectra of the anion radical salt **2**

As shown in Fig. 3, an ESR spectrum of **2** in THF displayed a characteristic triplet signal with  $a(^{31}\text{P}) = 47.6$  G at  $g = 2.010$ . This result strongly suggests that the unpaired electron of **2** occupies the P=P  $\pi^*$ -orbitals (SOMOs). The observed hyper-fine coupling constant for **2** is in the range of those for the previously reported diphosphene anion radicals (41–55 G) (Table 2) [4,5,71], which is considerably smaller than those of phosphinyl radicals R<sub>2</sub>P<sup>•</sup> (63–105 G) [10] and diphosphanyl radicals R<sub>2</sub>P–PR<sup>•</sup> (99–390 G), [11] where the unpaired electron may be localized on the central phosphorus atoms.

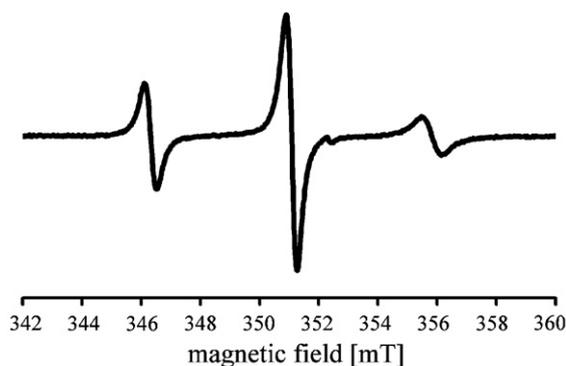


Fig. 3. ESR spectrum of lithium diphosphene anion radical **2** in THF at room temperature.

Table 2

ESR data of diphosphene anion radicals at room temperature

	$g$ value	$a(^{31}\text{P})$ (G)	$a(^{31}\text{P})$ (MHz)	Reference
Tbt <sub>2</sub> P <sub>2</sub> <sup>−a</sup>	2.010	47.6	134	This work
Bbt <sub>2</sub> P <sub>2</sub> <sup>−a</sup>	2.009	48.0	135	[71]
Mes <sub>2</sub> P <sub>2</sub> <sup>−b</sup>	2.010 <sup>b</sup> /2.013 <sup>c</sup>	55 <sup>b</sup> /55 <sup>c</sup>	155 <sup>b</sup> /155 <sup>c</sup>	[4a]/[5a]
Tsi <sub>2</sub> P <sub>2</sub> <sup>−d</sup>	2.018 <sup>c</sup> /2.0111 <sup>d</sup>	43 <sup>c</sup> /43.5 <sup>d</sup>	121 <sup>c</sup> /122 <sup>d</sup>	[5a]/[5b]
Ar <sub>2</sub> P <sub>2</sub> <sup>−e</sup>	2.008	46	129	[5c]
<i>t</i> -Bu <sub>2</sub> P <sub>2</sub> <sup>−f</sup>	2.0103	45.47	127.9	[5d]
Ph <sub>2</sub> P <sub>2</sub> <sup>−g</sup>	2.0089	40.9	115	[5e]
Cy <sub>2</sub> P <sub>2</sub> <sup>−g</sup>	2.0099	45.2	127	[5e]

<sup>a</sup> In THF solution of the isolated [Li(dme)<sub>3</sub>]<sup>+</sup>[Ar<sub>2</sub>P<sub>2</sub>]<sup>−</sup> (Ar = Tbt or Bbt).

<sup>b</sup> Generated by the reduction of neutral Mes<sub>2</sub>P<sub>2</sub> with sodium naphthalene in THF.

<sup>c</sup> Generated by the bulk electrolysis in THF (*n*-Bu<sub>4</sub>NBF<sub>4</sub>).

<sup>d</sup> Generated by the bulk electrolysis in DME (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>).

<sup>e</sup> Generated by the reduction of neutral Ar<sub>2</sub>P<sub>2</sub> (Ar<sup>1</sup> = 2,6-dimesitylphenyl) with sodium metal or potassium naphthalene in THF.

<sup>f</sup> Generated from K<sub>2</sub>[*t*-Bu<sub>2</sub>P<sub>2</sub>] in THF.

<sup>g</sup> Generated from Na<sub>2</sub>[R<sub>4</sub>P<sub>4</sub>] in THF (R = phenyl or cyclohexyl).

UV–Vis spectra of **2** in THF showed three adsorption maxima at 341 (sh,  $\epsilon = 17000$ ), 531 ( $\epsilon = 8000$ ), and 635 (sh,  $\epsilon = 2200$ ) nm, whereas the corresponding neutral diphosphene **1** showed two characteristic adsorption maxima at 408 ( $\epsilon = 14000$ ) and 532 ( $\epsilon = 2500$ ) nm attributable to the symmetry-allowed  $\pi \rightarrow \pi^*$  and symmetry-forbidden  $n \rightarrow \pi^*$  transitions of the diphosphene unit, respectively [7f]. An assignment of the absorptions was estimated based on TDDFT calculations of a model molecule, [DmpPPDmp]<sup>−</sup> (Dmp = 2,6-dimethylphenyl) (*vide infra*). As a result, the absorption maxima observed at shorter wavelength ( $\lambda_{\text{max}} = 341$  nm) can be attributed to the electron transitions from lone-pair electrons of the phosphorus atoms and the  $\pi$ -orbitals of the Tbt's aromatic ring into the  $\pi^*$ -orbitals of the Tbt's aromatic ring. The absorption bands at the middle ( $\lambda_{\text{max}} = 531$  nm) and longer wavelengths ( $\lambda_{\text{max}} = 635$  nm) are assignable to the  $\pi \rightarrow \pi^*$  and  $\pi^* \rightarrow \sigma^*$  electron transitions for the diphosphorus unit of **2**, respectively. The former is characteristically red-shifted as compared with that for diphosphene **1** ( $\lambda_{\text{max}} = 408$  nm), which indicates the diluted  $\pi$ -bond of the diphosphorus unit for **2**.

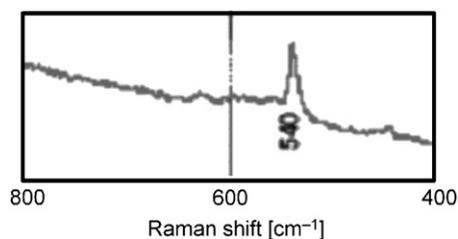


Fig. 4. Raman spectrum of **2** in the solid-state.

Since the phosphorus–phosphorus stretching vibration of diphosphene anion radicals should be symmetric, Raman spectroscopy is advantageous to obtain vibrational information on the diphosphene moiety [7i,7j]. A solid-state Raman spectrum of **2** in a sealed tube displayed a strong Raman line at  $540\text{ cm}^{-1}$  attributable to the phosphorus–phosphorus stretching vibration (Fig. 4). Thus, the observed  $\nu_{\text{P=P}}$  value of **2** was lower than those of the corresponding neutral diphosphene (e.g.,  $609\text{ cm}^{-1}$  for **1** [7f]) and higher than those of the corresponding single-bond molecules (e.g.,  $530\text{ cm}^{-1}$  for  $\text{Ph}_2\text{P-PPh}_2$  [12]), suggesting the strength of the phosphorus–phosphorus bond of **2** should be the intermediate between those of diphosphene **1** and  $\text{Ph}_2\text{P-PPh}_2$ .

#### 2.4. Theoretical calculations

In order to understand the electronic structure of diphosphene anion radicals, we performed theoretical calculations on the model compounds,  $[\text{HPPH}]^-$  **4** and  $[\text{DmpPPDmp}]^-$  **5**, where the Tbt groups of  $[\text{TbtPPTbt}]^-$  were replaced by hydrogen atoms and 2,6-dimethylphenyl groups, respectively. The optimized structures of **4** and **5** showed that the P–P bond lengths of both  $2.164\text{ \AA}$ , which was considerably longer than the phosphorus–phosphorus double-bond lengths for the corresponding neutral species (*trans*- $\text{HP=PH}$  ( $2.036\text{ \AA}$ ) and *trans*- $\text{DmpP=PDmp}$  ( $2.041\text{ \AA}$ )) and the observed ones for reported (*E*)-diaryldiphosphenes ( $1.985\text{--}2.049\text{ \AA}$ ) [1b], and shortened than reported values of the typical P–P single-bond lengths (ca.  $2.19\text{--}2.24\text{ \AA}$ ) [13]. It was also found that the H–P–P (C–P–P) bond angles of  $94.3^\circ$  and  $98.4^\circ$  for **4** and **5**, respectively, were smaller than those of the corresponding neutral species (*trans*- $\text{HP=PH}$  ( $94.3^\circ$ ) and *trans*- $\text{DmpP=PDmp}$  ( $101.0^\circ$ )). These theoretical results on **4** and **5** could be explained by one-electron introduction onto the  $\pi^*$ -orbitals of the neutral diphosphenes, *trans*- $\text{HP=PH}$  and *trans*- $\text{DmpP=PDmp}$ , leading to an elongation of the phosphorus–phosphorus bonds. The calculations indicated the KS-SOMO (Fig. 5) and the spin density of **4** and **5** were almost located on the phosphorus atoms, and their isotropic Fermi contact couplings of **4** and **5** had  $23.4$  and  $31.3\text{ G}$ , respectively, which are somewhat underestimated as compared to those of the previously reported diphosphene anion radical species ( $43\text{--}55\text{ G}$ ) [4,5,7]. The theoretical calculations for the vibrational frequencies on **4** and **5** computed at B3LYP/6-31G(d) (6-311+G(2d,p) for P) level

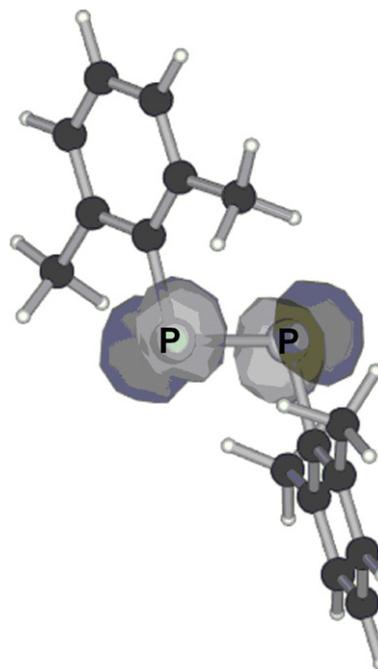


Fig. 5. KS-SOMO for **5**.

revealed that the characteristic stretching vibrations for the phosphorus–phosphorus bonds of **4** and **5** were at  $486.6$  and  $556.6\text{ cm}^{-1}$ , respectively, which are in good agreement with the experimental results obtained by the Raman spectrum of **2** ( $\nu = 540\text{ cm}^{-1}$ ).

Moreover, the excitation energies of **5** were calculated by using TDDFT calculations (the results were shown as black bars in Fig. 2). An assignment of the observed absorption maxima for lithium diphosphene anion radical **2** is reasonably supported by the TDDFT calculations for the excited states on **5** [ $307$  ( $n_{\text{PP}} \rightarrow \pi_{\text{Ar}}^*$  and  $\pi_{\text{Ar}} \rightarrow \pi_{\text{Ar}}^*$ ),  $489$  ( $\pi_{\text{PP}} \rightarrow \pi_{\text{PP}}^*$ ), and  $589$  ( $\pi_{\text{PP}}^* \rightarrow \sigma_{\text{PP}}^*$  transitions) nm] at the TD-B3LYP/6-311+G(2d,p) for P and 6-31G(d) for C and H. The calculated transition energies and oscillator strengths of the model molecule **5** allow an unambiguous assignment of the absorption spectra of lithium diphosphene anion radical **2**.

#### 2.5. Reactivity of the anion radical salt **2**

Next, we examined the reactions of diphosphene anion radical salt **2** with iodomethane, elemental sulfur, selenium, and tellurium. We have preliminarily confirmed that diphosphene **1** did not react with iodomethane in benzene at room temperature for 24 h. Moreover, no reactions of **1** were observed with elemental sulfur, selenium, and tellurium in benzene- $d_6$  at  $100\text{ }^\circ\text{C}$  for 48 h in a sealed tube. A benzene solution of **2** was reacted with an excess amount of iodomethane at room temperature, and the color of the solution immediately changed from purple to red. The  $^7\text{Li}$  NMR spectrum of the resulting red solution showed a singlet signal at  $-0.40\text{ ppm}$ , whereas that of **2** in benzene showed a sharp singlet at  $0.07\text{ ppm}$  corresponding

to the counter cation of **2**. The resulting red solution was purified to afford diphosphene **1** in 87% yield. Thus, the exclusive formation of **1** suggested that lithium anion radical **2** could likely tend to be oxidized and iodomethane could act as an oxidant for **2** in this reaction [14].

On the other hand, the reaction of **2** with elemental sulfur in benzene-*d*<sub>6</sub> proceeded at room temperature for 1 h resulting in the formation of the corresponding thiadiphosphirane **3** [1b,7f,15] and **1** in 49% and 38% yields, respectively (see Scheme 2). A plausible reaction mechanism contains the single-electron transfer process from **2** to elemental sulfur leading to the formation of **1** and the activated [S<sub>8</sub>]<sup>•-</sup>, which could readily react with **1**. It should be noted that **2** readily underwent sulfurization using elemental sulfur to give **3** in contrast to the case of sulfurization of neutral diphosphenes, Mes<sup>\*</sup>P=PMes<sup>\*</sup> [15c,16], BbtP=PBbt [7f,17], and **1** [18]. The previously reported diphosphenes bearing bulky substituents are known to undergo sulfurization to give the corresponding thiadiphosphiranes under much severe conditions [19] (See Scheme 3).

When the suspension of **2** with elemental selenium in benzene-*d*<sub>6</sub> was stood at room temperature for 2 h, the original purple color of the solution gradually changed to red. The <sup>31</sup>P NMR spectrum of the mixture displayed two singlet signals at 531.9 and -57.8 ppm, suggesting the formation of **1** and selenadiphosphirane **4** [1b,7f,20], respectively. Separation of the mixture afforded **1** and **4** in 52% and 35% yields, respectively (see Scheme 3). The formation of **4** is most likely interpreted in terms of the electron transfer from **2** to elemental selenium and the successive reaction of **1** with intermediacy of [Se]<sup>•-</sup> to afford compound **4** as in the case of the reaction of **2** with elemental sulfur. These

results should be of great interest from the viewpoint of the ready formation of **3** and **4** by the treatment of diphosphene anion radical **2** with elemental sulfur and selenium, respectively, as compared with the traditional synthetic methods for the chalcogenadiphosphiranes [21,22]. Moreover, the formation of **3** and **4** is worth of note not only as the reactivity of diphosphene anion radical species but also as the development of a new synthetic method for chalcogenadiphosphiranes. By contrast, the treatment of **2** with elemental tellurium at room temperature for 24 h resulted in the exclusive formation of **1** in 82% yield. No formation of compounds containing a tellurium might be due to its steric hindrance between the Tbt group and a tellurium atom.

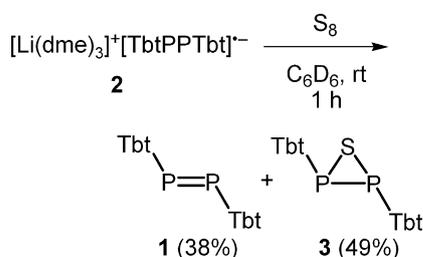
### 3. Conclusion

We reported here the reduction of a kinetically stabilized diphosphene TbtP=PTbt **1** and isolation of the corresponding anion radical species **2**. The structure of **2** was confirmed and characterized by spectroscopic analyses (ESR, UV-Vis, and Raman) and theoretical calculations. Interestingly, the reactions of **2** with elemental sulfur and selenium under ambient conditions were found to proceed under very mild conditions to afford thiadiphosphirane **3** and selenadiphosphirane **4**, respectively, in contrast to the case of sulfurization and selenization reactions of neutral diphosphenes.

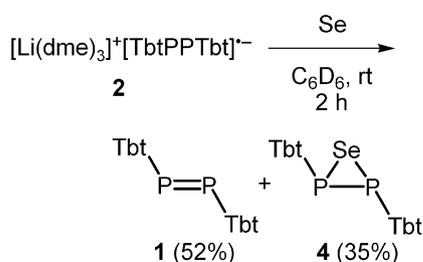
### 4. Experimental

#### 4.1. General

All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods and then dried by using an Ultimate Solvent System (Glass Contour Company) [23]. All solvents used in the reactions and spectroscopy (THF, DME, benzene, benzene-*d*<sub>6</sub>, and *n*-hexane) were dried by using a potassium mirror. Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. <sup>1</sup>H (300 MHz) and <sup>13</sup>C NMR (75 Hz) spectra were measured in C<sub>6</sub>D<sub>6</sub> with a JEOL AL-300 spectrometer using C<sub>6</sub>HD<sub>5</sub> (δ = 7.15 ppm) and C<sub>6</sub>D<sub>6</sub> (δ = 128.0 ppm) as internal standards for <sup>1</sup>H and <sup>13</sup>C NMR, respectively. <sup>7</sup>Li (116 MHz) and <sup>31</sup>P NMR (120 MHz) spectra were measured with a JEOL AL-300 spectrometer using 1 mol dm<sup>-3</sup> LiCl in D<sub>2</sub>O (δ = 0 ppm) and 85% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O (δ = 0 ppm) as external standards for <sup>7</sup>Li and <sup>31</sup>P NMR, respectively. X-Band ESR spectra were recorded on a Bruker EMX spectrometer. High-resolution FAB mass spectral data were obtained on a JEOL SX-270 mass spectrometer (matrix: 2-nitrophenyloctylether). Electronic spectra were recorded on a JASCO V-570 UV/Vis spectrometer. Raman spectra were measured on a Raman spectrometer consisting of an Spex 1877 Triplemate and an EG&G PARC 1421 intensified photodiode array detector.



Scheme 2. Reaction of lithium diphosphene anion radical **2** with elemental sulfur.



Scheme 3. Reaction of lithium diphosphene anion radical **2** with elemental selenium.

An NEC GLG 108 He–Ne laser was used for Raman excitation. Electrochemical experiments were carried out with an ALS 602A electrochemical analyzer using a glassy carbon disk working electrode, a Pt wire counter electrode, and Ag/0.01 mol dm<sup>-3</sup> AgNO<sub>3</sub> reference electrode. The measurements were carried out in THF containing 0.1 mol dm<sup>-3</sup> *n*-Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte with scan rates of 10–200 mV s<sup>-1</sup> in a glovebox filled with argon at ambient temperature. A half-wave potential of a ferrocene was observed at +0.24 V vs. Ag/Ag<sup>+</sup> in these conditions. All redox potentials were converted from vs. Ag/Ag<sup>+</sup> to vs. the aqueous saturated calomel electrode (SCE) according to the literatures [8,14]. All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Bis(2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)diphosphene **1** was prepared according to the procedures reported in the literature [7f].

#### 4.2. Synthesis of diphosphene anion radical salt **2**

To a solution of diphosphene **1** (300 mg, 0.257 mmol) in DME (5 mL) was added a lithium shot (5.0 mg, 0.72 mmol) at room temperature. After the solution was stirred at room temperature for 8 h, the color of the solution changed from red to purple. After the lithium shot and the solvent were removed, *n*-hexane (3 mL) was added to the residue. After the suspension was kept at -40 °C for 12 h, the supernatant was removed. The above-mentioned process was repeated five times to afford [Li(dme)<sub>3</sub>]<sup>+</sup>[TbtPPTbt]<sup>-</sup> **2** (148 mg, 0.103 mmol, 40%) as purple powder. **2**: M.p. 139 °C (decomp.). ESR (X-band, THF, 25 °C) *g* 2.010 (*a*<sup>31P</sup> = 47.6 G). Raman (solid-state, excitation; 632.8 nm) *v*<sub>PP</sub> 540 cm<sup>-1</sup>. UV–Vis (THF) *λ*<sub>max</sub> 341 (sh, *ε* = 17000), 531 (*ε* = 8000), 635 (sh, *ε* = 2200). <sup>7</sup>Li NMR (116 MHz, C<sub>6</sub>H<sub>6</sub>, 25 °C) *δ* 0.07 (s), (116 MHz, THF, 25 °C) *δ* 0.43 (s).

#### 4.3. Reaction of diphosphene anion radical salt **2** with iodomethane

In a glovebox filled with argon, lithium diphosphene anion radical **2** (30.0 mg, 25.6 μmol) was dissolved in benzene (0.8 mL) and the solution was transferred to an NMR tube. Iodomethane (160 μL, 2.56 mmol) was added to the solution, and the tube was evacuated and sealed. After standing at room temperature for 1 h, the signal for **2** disappeared in the <sup>7</sup>Li NMR spectrum. Then, the tube was opened and evaporated. The purification of the residue by PTLC (*n*-hexane) afforded **1** (25.8 mg, 22.2 μmol, 87%) exclusively as red crystals.

#### 4.4. Reaction of diphosphene anion radical salt **2** with elemental sulfur

In a glovebox filled with argon, the suspension of lithium diphosphene anion radical **2** (68.0 mg, 47.1 μmol)

and elemental sulfur (S<sub>8</sub>, 7.7 mg, 0.24 mmol as S) in benzene-*d*<sub>6</sub> (0.9 mL) was transferred to an NMR tube, and then the tube was evacuated and sealed. After standing at room temperature for 1 h, the color of the suspension was changed from purple to red. The signals for **1** and thiadiphosphirane **3** were observed in the <sup>1</sup>H and <sup>31</sup>P NMR spectra. After the sealed tube was opened, the separation of the mixture by PTLC (*n*-hexane) afforded **1** (21.1 mg, 18.1 μmol, 38%) as red crystals and **3** (27.5 mg, 22.9 μmol, 49%) as colorless solids. **3**: colorless crystals, M.p. 159.5 °C (dec.). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) *δ* 0.13 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.14 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.33 (brs, 72H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.43 (s, 2H, CH), 3.03 (s, 2H, CH), 3.22 (s, 2H, CH), 6.50 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 6.61 (s, 2H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 23 °C) *δ* 0.85 (s, CH<sub>3</sub>), 0.99 (s, CH<sub>3</sub>), 29.48 (brs, CH), 30.06 (brs, CH), 30.89 (s, CH), 123.41 (br, CH, *m*-C<sub>6</sub>H<sub>2</sub>), 128.10 (br, CH, *m*-C<sub>6</sub>H<sub>2</sub>), 130.62 (pseudo-triplet, *J*<sub>PC</sub> = 39.4 Hz, *ipso*-C<sub>6</sub>H<sub>2</sub>), 144.30 (s, *p*-C<sub>6</sub>H<sub>2</sub>), 148.14 (br, *o*-C<sub>6</sub>H<sub>2</sub>), 150.15 (br, *o*-C<sub>6</sub>H<sub>2</sub>). <sup>31</sup>P NMR (120 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) *δ* -72.9. HRMS (FAB) found: *m/z* 1197.5731 ([M+H]<sup>+</sup>), calcd. for C<sub>54</sub>H<sub>119</sub>P<sub>2</sub>SSi<sub>12</sub>: 1197.5676. Anal. Calc. for C<sub>54</sub>H<sub>118</sub>P<sub>2</sub>SSi<sub>12</sub>: C, 54.11; H, 9.92%. Found: C, 53.92; H, 9.64%.

#### 4.5. Reaction of diphosphene anion radical salt **2** with elemental selenium

In a glovebox filled with argon, the suspension of lithium diphosphene anion radical **2** (83.0 mg, 57.5 μmol) and elemental selenium (23.0 mg, 291 μmol) in benzene-*d*<sub>6</sub> (0.9 mL) was transferred to an NMR tube, and then the tube was evacuated and sealed. After standing at room temperature for 2 h, the color of the suspension was changed from purple to red. The signals for **1** and selenadiphosphirane **4** were observed in the <sup>1</sup>H and <sup>31</sup>P NMR spectra. After the sealed tube was opened, the separation of the mixture by PTLC (*n*-hexane) afforded **1** (34.9 mg, 29.9 μmol, 52%) as red crystals and **4** (25.1 mg, 20.1 μmol, 35%) as colorless solids. **4**: colorless crystals. M.p. 248.5–250.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 40 °C) *δ* 0.01 (s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.02 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.09 (brs, 72H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 2H, CH), 2.84 (s, 2H, CH), 2.98 (s, 2H, CH), 6.23 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 6.35 (s, 2H, C<sub>6</sub>H<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 40 °C) *δ* 0.71 (s, CH<sub>3</sub>), 0.87 (s, CH<sub>3</sub>), 1.28 (s, CH<sub>3</sub>), 29.70 (s, CH), 30.55 (s, CH), 123.10 (brs, CH, *m*-C<sub>6</sub>H<sub>2</sub>), 127.87 (brs, CH, *m*-C<sub>6</sub>H<sub>2</sub>), 143.71 (s, *p*-C<sub>6</sub>H<sub>2</sub>). In the <sup>13</sup>C NMR spectrum, the signals of *ortho*- and *ipso*-carbons of the Tbt group for **4** could not be observed due to its low solubility in common organic solvents. <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>, 40 °C) *δ* -58.5 (s with satellite signals of <sup>1</sup>*J*<sub>SeP</sub> = 123 Hz); <sup>77</sup>Se NMR (57 MHz, CDCl<sub>3</sub>, 40 °C) *δ* 2.14 (t, <sup>1</sup>*J*<sub>PSe</sub> = 123 Hz); HRMS (FAB) found: *m/z* 1244.5096 ([M]<sup>+</sup>), calc. for C<sub>54</sub>H<sub>118</sub>P<sub>2</sub><sup>80</sup>SeSi<sub>12</sub>: 1244.5115; Anal. Calc. for C<sub>54</sub>H<sub>118</sub>P<sub>2</sub>SeSi<sub>12</sub>: C, 52.08; H, 9.55. Found: C, 51.89; H, 9.71%.

#### 4.6. Reaction of diphosphene anion radical salt **2** with elemental tellurium

In a glovebox filled with argon, the suspension of diphosphene anion radical salt **2** (72.5 mg, 50.2  $\mu\text{mol}$ ) and elemental tellurium (32.0 mg, 251  $\mu\text{mol}$ ) in benzene- $d_6$  (0.9 mL) was transferred to an NMR tube, and then the tube was evacuated and sealed. After standing at room temperature for 24 h, the color of the suspension was changed from purple to red. The signals for **1** were observed in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra. After the sealed tube was opened, the suspension was filtered through Celite to remove insoluble materials. Diphosphene **1** (48.0 mg, 41.2  $\mu\text{mol}$ , 82%) was obtained as red crystals.

#### 4.7. Theoretical calculations

All theoretical calculations were carried out using the GAUSSIAN 03W program [24] with density functional theory at the B3LYP level [25]. The geometries of neutral *trans*-HP=PH and *trans*-DmpP=PDmp, and the corresponding anion radical species  $[\text{HPPH}]^-$  **4** and  $[\text{DmpPPDmp}]^-$  **5** were optimized by using the 6-31G(d) for H, C, and 6-311+G(2d,p) for P basis sets. It was confirmed that the optimized structures of *trans*-HP=PH, *trans*-DmpP=PDmp, **4**, and **5** have minimum energies by frequency calculations. The TDDFT calculations of **4** and **5** were performed at the B3LYP/[6-31G(d) for H, C, and 6-311+G(2d,p) for P] level.

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