

## 論文内容の要旨

### 論文題目 : Studies of Compounds Bearing a Bond between Two Hypervalent Atoms and Hexacoordinated Phosphorus Species Bearing Phosphorus–Hydrogen Bonds

(超原子価状態にある二つの原子が結合した化合物およびリン–水素結合を有する 6 配位リン化合物の研究)

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#### Introduction

Chemical bonds are fundamental components of every chemical compounds, and hence development of a novel type of bonding is a significant theme in chemistry. Novelty of the bonding depends on the coordination and oxidation states of the atoms that constitute the bond. When a main group element formally has more than eight electrons in its valence shell, the atom is called to be a hypervalent state. Although a hypervalent state of period 2 atoms (C, N etc.) is extremely unstable, that of silicon or phosphorus atom can be stabilized by proper ligands. In the cases of pentacoordinated phosphorus and silicon compounds, the central atom has five substituents and ten valence electrons, and compounds bearing a bond between two pentacoordinated atoms are expected to show unique structures, reactivities, and properties which are caused by severe steric and electronic congestion in the vicinity of the bond. However, it is difficult to synthesize such compounds due to aforementioned congestion and hence only few examples have been reported. The author has already synthesized the first disilicate **1** bearing a bond between two anionic pentacoordinated silicon moieties in master course (Figure 1). However, its physical property and electronic state are still unclear. In this work, the author carried out both experimental and theoretical investigations of **1** in order to elucidate its electronic state. And the author attempted to develop a bond which consists of pentacoordinated silicon and phosphorus atoms because such a bond has never been reported. Furthermore, the author also studied properties of hexacoordinated phosphorus compounds bearing P–H bonds, especially its tautomerization. In this study, an electron-withdrawing bidentate ligand that is called the Martin ligand has been used for stabilization of the hypervalent species.

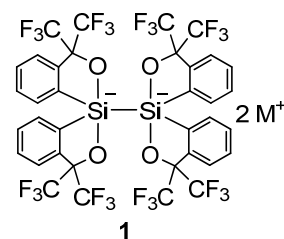


Figure 1

## Properties and electronic state of the disilicates

Electrochemical property of disilicate **1a** was studied by cyclic voltammetry and compared with those of disilanes **2** and **3** (Table 1). In the case of **1a** ( $M = (n\text{-Bu})_4\text{N}$ ), two irreversible oxidation waves were observed ( $E_{\text{pa}} = -0.22$  and  $0.83$  V vs.  $\text{Fc}/\text{Fc}^+$ ,  $0.1$  M  $(n\text{-Bu})_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$ ). This result shows **1a** has relatively higher electron donor ability than a simple disilane **3** ( $E_{\text{pa}} = 0.95$  V). On the other hand, in the case of **2**, which was obtained by protonation of **1a**, no oxidation waves were observed under the same conditions, showing that the electron donor ability was decreased by the protonation. The UV absorption spectra of **1-3** showed similar behavior to each other. The absorption maximum wavelength of **1a** ( $\lambda_{\text{max}} = 258$  nm) is longer than that of **3** ( $\lambda_{\text{max}} = 241$  nm), and the protonation of **1** was found to cause blue shift, judging from the absorption maximum of **2**. Change of the properties between **1** and **2** was reversible by protonation and deprotonation processes.

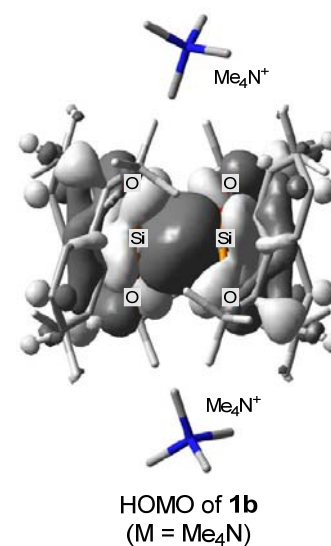
**Table 1.** Oxidation potential ( $E_{\text{pa}}$ ), UV absorption maximum ( $\lambda_{\text{max}}$ ), and calculated HOMO energy level ( $E(\text{HOMO})$ ) and LUMO–HOMO energy gap ( $\Delta E(\text{LUMO}–\text{HOMO})$ ).

	<b>1</b>	<b>2</b>	<b>3</b>
$E_{\text{pa}}/\text{V}^a$	-0.22, 0.83 <sup>d</sup>	—	0.95
$\lambda_{\text{max}}/\text{nm}^b$	258 <sup>d</sup>	237	241
$E(\text{HOMO})/\text{eV}^c$	-4.89 <sup>e</sup>	-6.81	-6.19
$\Delta E(\text{LUMO}–\text{HOMO})/\text{eV}^c$	4.94 <sup>e</sup>	5.58	5.53

<sup>a</sup>vs  $\text{Fc}/\text{Fc}^+$ ,  $0.1$  M  $(n\text{-Bu})_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup>in  $\text{CH}_2\text{Cl}_2$ . <sup>c</sup>calculated at B3PW91/6-311+G(2d)[Si]:6-31G(d)[C,H,O,F] level. <sup>d</sup> $M = (n\text{-Bu})_4\text{N}$ . <sup>e</sup> $M = \text{Me}_4\text{N}$ .

To elucidate the electronic state of the disilicate, theoretical calculation was carried out at the B3PW91/6-311+G(2d)[Si]:6-31G(d)[C,H,O,F] level. The theoretical investigation showed the high HOMO energy level and small HOMO-LUMO energy gap of **1b** ( $M = \text{Me}_4\text{N}$ ), supporting the experimental results. In general, HOMO of a Si–Si bond compound is mainly presented by the bonding  $\sigma(\text{Si}–\text{Si})$  orbital, and the HOMO of **1b** considerably contained also p orbitals of the oxygen atoms in addition to it (Figure 2). The HOMO energy level would be raised by interaction of the Si–Si bonding orbital with occupied orbitals of the oxygen atoms in the vicinity of the bond. Changing of the properties by protonation would be caused by a decrease of the interaction.

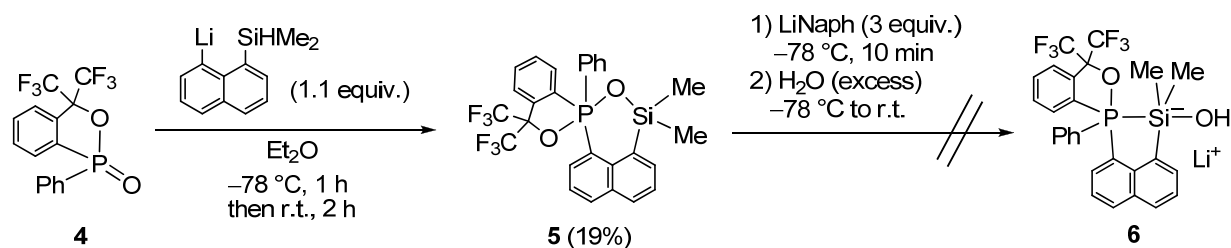
Reflecting the high HOMO energy level, addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to disilicate **1c** ( $M = \text{Li}^+$ ) afforded corresponding the hydroxysilicate. By contrast, **1c** showed high thermal stability, and it could be sublimed without decomposition at  $248$  °C.



**Figure 2**

## Construction of a bond between pentacoordinated silicon and phosphorus atoms

Considering a high reactivity of a Si–P bond, a synthesis of a compound bearing a bond between pentacoordinated silicon and phosphorus atoms would be difficult and it has been a big challenge. Therefore, phosphoranylsilicate **6** was designed as a target molecule whose phosphorus and silicon atoms are fixed at proper positions of a rigid naphthalene moiety. Phosphorane **5** was obtained by the reaction of cyclic phosphinate **4** with 8-(dimethylsilyl)naphthyllithium, but the reduction of **5** with lithium naphthalenide did not give **6** (Scheme 1). Modification of the reduction condition is expected to afford phosphoranylsilicate **6**.

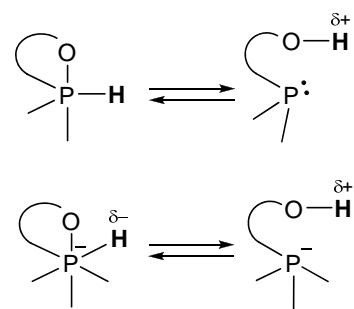


**Scheme 1.** Attempted synthesis of phosphoranylsilicate **6**

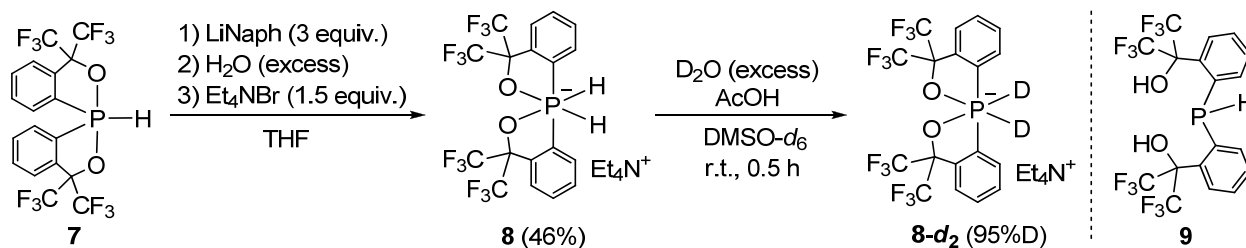
## Synthesis and properties of hexacoordinated phosphorus compounds bearing P–H bonds

A P–H bond is usually almost nonpolar because phosphorus and hydrogen has almost same electronegativity ( $\chi_{\text{P}}(\text{P}) = 2.19$ ,  $\chi_{\text{P}}(\text{H}) = 2.20$ ). However, some oxygen-substituted pentacoordinated hydrophosphoranes undergo proton exchange reaction via tautomerization to a trivalent phosphine because the hydrogen atom on the oxygen atom of the trivalent tautomer is protic. The tautomerization can interestingly change property of a hydrogen atom. Although hexacoordinated hydrophosphate with a similar framework is expected to show reversing polarity of the hydrogen atom through tautomerization, the property of such a compound has been still unclear due to difficulty of its synthesis and isolation. The author synthesized a stable hexacoordinated dihydrophosphate, which is an anionic species bearing two P–H bonds by taking advantage of the Martin ligands, and studied its tautomerization and reactivity.

Dihydrophosphate **8** was synthesized by successive treatment of hydrophosphorane **7** with lithium naphthalenide (3 equiv.), water (excess), and tetraethylammonium bromide (1.5 equiv.) (Scheme 2). The structure was determined by the X-ray crystallographic analysis, and the electronic structure was investigated by theoretical calculations. H–D (hydrogen–deuterium) exchange reaction of **8** with D<sub>2</sub>O was attempted in DMSO-*d*<sub>6</sub> in anticipation of the protic character of the O–H group in a tautomer of **8**. Although the hydrogen atoms on the phosphorus atom of **8** were hardly exchanged for the deuterium atoms of D<sub>2</sub>O under both basic and neutral conditions, the H–D exchange proceeded efficiently in the presence of AcOH (1 equiv.) to give **8-d**<sub>2</sub> bearing two P–D bonds (95%D) after 0.5 h. It is proved that hydrogen atoms on the phosphorus of **8** are exchangeable for protons of water. To clarify the exchange mechanism, the reaction of **8** with excess amount of AcOH was carried out, and formation of phosphine **9** was confirmed by <sup>31</sup>P NMR spectroscopy. Judging from these results, tautomerization would proceed after protonation of **8** under the acidic condition, and the H–D exchange would be accomplished via the generated intermediate **9**.



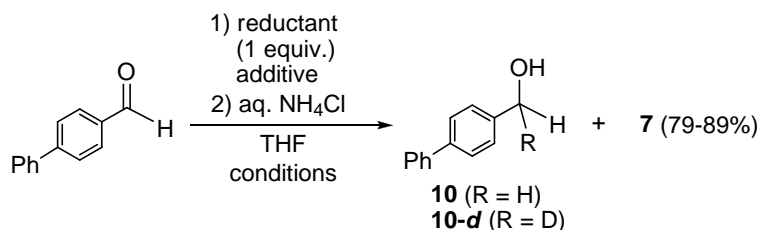
**Figure 3**



**Scheme 2.** Synthesis of dihydrophosphate **8** and the H-D exchange reaction.

Dihydrophosphate **8** is also expected to behave as a hydride donor (Table 2). The reaction of **8** with 4-phenylbenzaldehyde (1 equiv.) in refluxing THF for 10 h, followed by treatment with aqueous  $\text{NH}_4\text{Cl}$  solution, gave the corresponding alcohol **10** (85% yield) and **7**, showing the hydridic reactivity of the P–H bond of **8**. The reduction reaction was dramatically accelerated by addition of LiCl (1 equiv.) or AcOH (5 equiv.), which activated the aldehyde, and consequently the reaction was completed after 1 h at ambient

**Table 2.** Reduction of an aldehyde with phosphate **8**.



reductant	additive (equiv.)	conditions	product
<b>8</b>	none	reflux, 10 h	<b>10</b> (85%)
<b>8</b>	LiCl (1)	r.t., 1 h	<b>10</b> (90%)
<b>8</b>	AcOH (5)	r.t., 1 h	<b>10</b> (90%)
<b>8-d<sub>2</sub></b>	LiCl (1)	r.t., 1 h	<b>10-d</b> (83%, 95%D <sup>b</sup> )
<b>8<sup>a</sup></b>	AcOH (1.5) D <sub>2</sub> O (>100)	r.t., 1 h	<b>10-d</b> (82%, 97%D <sup>b</sup> )

<sup>a</sup>Stirred for 0.5 h with additives beforehand. <sup>b</sup>Estimated by <sup>1</sup>H NMR.

temperature. It is interesting that addition of AcOH can promote both the proton exchange and hydride reduction.

Compound **8-d<sub>2</sub>**, which had been prepared by the H-D exchange of **8** with  $\text{D}_2\text{O}$ , naturally reduced 4-phenylbenzaldehyde to give the deuterated alcohol, **10-d** (83% yield, 95%D) in the presence of LiCl. Furthermore, a one-pot reaction of the H-D exchange and reduction was successful. The H-D exchange from **8** using  $\text{D}_2\text{O}$  with AcOH (1.5 equiv.), followed by addition of 4- $\text{PhC}_6\text{H}_4\text{CHO}$  in THF, also gave **10-d** (82% yield, 97%D). In these reactions, the deuterium from  $\text{D}_2\text{O}$  behaves as deuteride, meaning achievement of reversing polarity from  $\text{D}^{\delta+}$  to  $\text{D}^{\delta-}$ .

## Conclusion

Properties of disilicate, which had an unprecedented chemical bond between two anionic pentacoordinated silicon moieties, were revealed. The characteristic electrochemical and optical properties could be turned off by protonation. Considering the unique properties and the high stability, such unusual Si–Si bonds are expected to be novel components to construct functional materials. The properties of hexacoordinated phosphorus compound bearing two P–H bonds were also investigated, and it could reverse the polarity of a hydrogen atom of water via the tautomerization. This method enabled reductive deuteration of carbonyl compounds using  $\text{D}_2\text{O}$  under the mild conditions without careful handling.