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# Pentacoordinate 1*H*-Phosphirenes: Reactivity, Bonding Properties, and Substituent Effects on Their Structures and Thermal Stability

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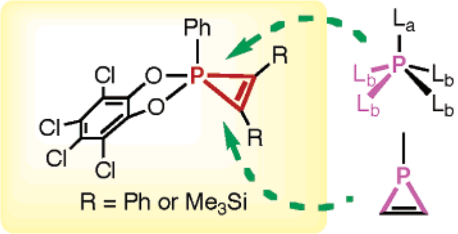

The synthesis, reactivity, and bonding properties of several pentacoordinate *P*-phenyl-substituted 1*H*-phosphirenes are discussed. X-ray crystallographic analysis of one of them reveals a highly distorted square pyramidal (SP) arrangement around the phosphorus. NMR studies confirm that they retain the SP structure in solution and demonstrate that the endocyclic P−C bonds in the three-membered ring have a very high degree of *p* character, which results from their being both basal bonds in the SP structure and endocyclic bonds of the three-membered ring. Structural parameters of the three-membered ring of the pentacoordinate phosphirenes obtained by experiment and theoretical calculations are very close to those of a tetracoordinate phosphirenium cation. Thus, by analogy with tetracoordinate phosphirenium cations, it can be considered that a $\sigma^*-\pi$ interaction between the $\sigma^*$ orbital of the apical bond and the $\pi$ orbital of the C═C bond in the three-membered ring is operative in pentacoordinate phosphirenes. The $\sigma^*-\pi$ interaction is found to lower the reactivity of the C═C bond of the three-membered ring. The reactivities of the pentacoordinate phosphirenes are also affected by the substituent on the carbon atom in the three-membered ring.

## 1. Introduction

Three-membered ring compounds have been studied for a long time both experimentally and theoretically because of their structural features and high strain energy.[1] Much attention has been paid to three-membered heterocycles,[2] and the investigation of such compounds showed that the electronic properties of the molecule are influenced by the bond angle around the heteroatom.[3] Among them, three-membered ring compounds involving one phosphorus atom, as well as those containing another additional heteroatom in the ring, have been intensively studied. Many examples of such three-membered ring compounds bearing a tri- or tetracoordinate phosphorus atom have been reported, and their structures and reactivities have been elucidated.[4,5] However, reports on three-membered ring compounds bearing a pentacoordinate phosphorus atom are limited.[6]

Pentacoordinate phosphorus compounds are among the most important hypervalent species, being intermediates of various reactions such as the Wittig reaction,[7] transphosphorylation in biological systems,[8] and so on. The typical structures of pentacoordinate phosphorus compounds are trigonal bipyramidal (TBP) and square pyramidal (SP).[9,10] A phosphorane with TBP

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[1] (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1989**, *89*, 1225.

[2] For a review of three-membered heterocycles, see: *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F., Eds.; Pergamon: Oxford, 1996; Vol. 1A.

[3] Aue, D. H.; Webb, H. M.; Davidson, W. R.; Vidal, M.; Bowers, M. T.; Goldwhite, H.; Vertal, L. E.; Douglas, J. E.; Kollman, P. A.; Kenyon, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 5151.

[4] For reviews on phosphiranes and phosphirenes, see: (a) Mathey, F. *Chem. Rev.* **1990**, *90*, 997. (b) Mathey, F.; Regitz, M. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F., Eds.; Pergamon: Amsterdam, 1996; Vol. 1A, pp 277−304. (c) Mathey, F.; Regitz, M. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Amsterdam, 2001, pp 17−55. (d) Heydt, H. *Sci. Synth.* **2002**, *9*, 85.

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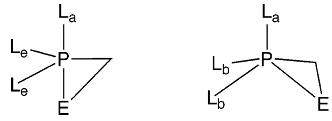
**CHART 1. Three-Membered Ring Compounds Bearing a Pentacoordinate Phosphorus Atom with TBP Structure (Left) and SP Structure (Right)[a]**



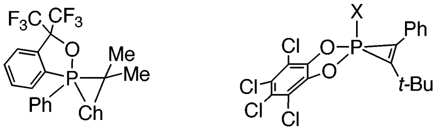
(a) TBP-like (b) SP-like

[a] $L_a$ = apical ligand; $L_e$ = equatorial ligand; $L_b$ = basal ligand; E = main group element.

geometry has three equatorial bonds and two apical bonds around the phosphorus atom, whereas a phosphorane with SP geometry has one apical bond and four basal bonds. In both geometries, the phosphoranes have electron-deficient multicenter bonds that have a high degree of *p* character and are highly polarized; the apical bonds in the TBP structure involve three-center four-electron (3c−4e) bonding, and the basal bonds in the SP structure involve five-center six-electron (5c−6e) bonding.

If three-membered ring compounds bearing a pentacoordinate phosphorus atom have a structure similar to the ideal TBP structure, one of the endocyclic bonds will form the apical bond, as theoretical calculations have predicted (Chart 1).[11] If it has a structure similar to the ideal SP structure, two ring bonds will form the basal bonds. In both cases, at least one ring bond in the three-membered ring will show electron-deficient multicenter bonding that has a high degree of *p* character and is highly polarized. Furthermore, considering that endocyclic bonds of a three-membered ring generally have a high degree of *p* character,[12] the endocyclic bonds of the three-membered ring bearing a pentacoordinate phosphorus atom should have a very high degree of *p* character. Such a three-membered ring compound is an attractive synthetic target in organophosphorus chemistry, because it is expected to show interesting properties.

**CHART 2. Pentacoordinate Chalcogenaphosphiranes 1a and 1b and Pentacoordinate Phosphirenes 2a−e**



**1a**: Ch = S
**1b**: Ch = Se

**2a**: X = CN
**2b**: X = $N_3$
**2c**: X = F
**2d**: X = Cl
**2e**: X = Br

We have been interested in the chemistry of three-membered ring compounds bearing a pentacoordinate phosphorus atom.[6e,g] We have recently reported the syntheses of pentacoordinate thiaphosphirane **1a** and selenaphosphirane **1b**, shown in Chart 2, by taking advantage of the Martin ligand and have elucidated their highly distorted TBP structures in the crystalline state, solvent-dependent change of polarization of the phosphorus−chalcogen bonds in solution, and some reactivities. Before our investigations, NMR observation of a pentacoordinate phosphirane[6b] and syntheses of pentacoordinate azaphosphirenes[6a] and thiaphosphiranes[6d] had been described, but the properties of the three-membered rings were still unknown. In addition, Regitz and co-workers reported in 1990 the synthesis of pentacoordinate 1*H*-phosphirenes **2a**−**e** and the X-ray structure of **2a**.[6c] To understand the properties of three-membered ring compounds bearing a pentacoordinate phosphorus atom, it is significant to elucidate the reactivities of pentacoordinate phosphirenes. Meanwhile, Ho and co-workers have recently reported that a pentacoordinate dioxaphosphirane, which was generated by the reaction of a phosphine with singlet oxygen at low temperature, can undergo nonradical oxygen atom-transfer reactions with olefins.[6f]

We report here some reactivities of pentacoordinate 1*H*-phosphirenes bearing a tetrachlorocatecholate ligand and the substituent effects on the structure and thermal stability obtained by experiments and theoretical calculations to elucidate the bonding properties of the three-membered ring.

## 2. Results and Discussion

**2.1. Synthesis of Pentacoordinate Phosphirenes.** Regitz et al. succeeded in synthesizing **2a**−**e**, which have halogen or pseudohalogen ligands, such as the azido group and the cyano group, on the phosphorus atom.[6c] Considering that a P−C bond is less reactive against substitution reactions than the P−X bonds, pentacoordinate phosphirenes that have a P−C bond in place of the P−X bond seem to be better for investigation of the properties of a phosphirene moiety. In this context, we chose a phenyl group as a ligand on the phosphorus atom.

Pentacoordinate phosphirenes bearing a phenyl group on the phosphorus atom were prepared according to the method reported by Regitz and co-workers.[6c,13] Treatment of tricoordinate phosphirenes **3a** and **3b**[14] with 1 equiv of *o*-chloranil in toluene at room temperature afforded pentacoordinate phosphirenes **4a** and **4b** in 58 and 52% yields, respectively, as pale orange solids (Scheme 1). The $^{31}$P NMR chemical shifts of **4a**

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**SCHEME 1. Synthesis of 4a and 4b**

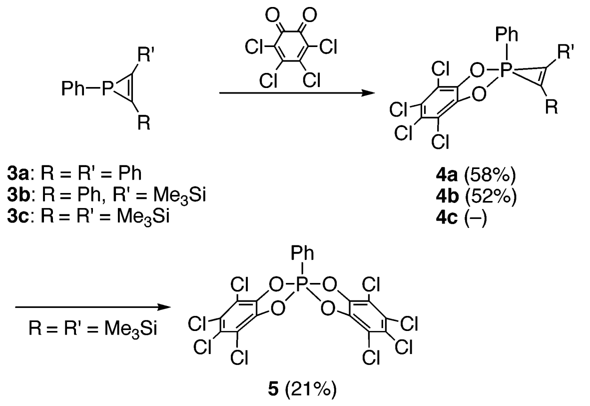
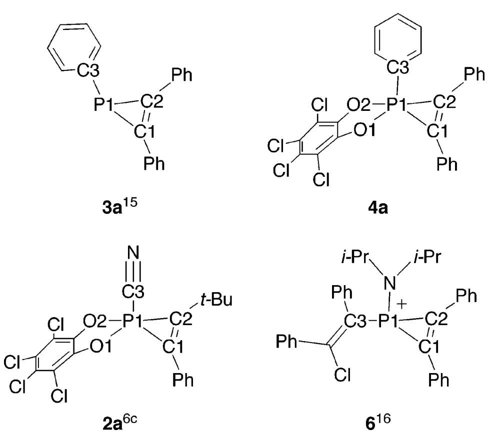


**CHART 3. Tri, Tetra-, and Pentacoordinate Phosphirenes**



and **4b**, which are close to those of **2a**−**e**, support the formation of the desired products.

Phosphirene **4a** was relatively thermally stable, whereas **4c** bearing two trimethylsilyl groups on the three-membered ring was thermally unstable. When **3c**[14] was treated with *o*-chloranil in toluene at 0 °C, a signal at $\delta_P$ −92.7 was observed in the $^{31}$P NMR spectrum, indicating the formation of **4c**. However, its isolation failed, and phosphorane **5** bearing two tetrachlorocatecholate ligands on the phosphorus was obtained in 21% yield. These results indicate that the stability of the pentacoordinate phosphirenes is influenced by substituents on the endocyclic carbon atoms and is reduced by attachment of electron-donating groups to the carbon atoms.

**2.2. X-ray Crystallographic Analysis of 4a.** The crystal structure of **4a** was established by X-ray crystallographic analysis. The selected bond lengths and angles of **4a** together with tricoordinate **3a**,[15] tetracoordinate **6** (Chart 3),[16] and pentacoordinate **2a**[6c] are summarized in Table 1. Phosphirene **4a** has a highly distorted SP arrangement at the phosphorus with two oxygen atoms of the tetrachlorocatecholate ligand and two carbon atoms in the three-membered ring at the basal positions and with the *ipso*-carbon atom of the phenyl group at the apical position, as shown in Figure 1. The endocyclic P−C and C1═C2 bond lengths in **4a** are close to those in **2a**. The C1−P1−C2 bond angle of **4a** is also similar to that in **2a**. These similarities of the structural parameters between **2a** and **4a** suggest that apical ligands on the phosphorus do not affect the structures of the three-membered ring so much. The O1−P1−O2, C3−P1−O1, and C3−P1−O2 angles of **2a** and **4a** are relatively close to those of the ideal SP structure,[9,17] whereas the angles between the apical bond and the basal bonds in the three-membered rings are somewhat wider than the value of 105° for the ideal SP structure. This deviation seems to be characteristic of a phosphorane involving a strained ring around the phosphorus.[18]

**TABLE 1. Selected Bond Lengths (Å) and Angles (deg) for the X-ray Structures of Phosphirenes 3a, 4a, 2a, and 6**

| | **3a**[a] | **4a** | **2a**[b] | **6**[c] |
|---|---|---|---|---|
| P1−C1 | 1.820(2) | 1.740(2) | 1.709(4) | 1.732(11) |
| P1−C2 | 1.821(3) | 1.7343(19) | 1.715(4) | 1.730(12) |
| C1═C2 | 1.299(3) | 1.357(9) | 1.360(6) | 1.36(2) |
| P1−C3 | 1.842(2) | 1.796(2) | 1.784(4) | 1.799(10) |
| C1−P1−C2 | 41.8(1) | 45.97(9) | 46.8(2) | 46.1(5) |
| O1−P1−O2 | | 89.53(7) | 90.3(1) | |
| P1−C1−C2 | 69.1(1) | 66.79(11) | 66.9 | 66.9(7) |
| P1−C2−C1 | 69.1(1) | 67.24(12) | 66.3 | 67.0(7) |
| C3−P1−C1 | 104.4(1) | 112.56(9) | 112.3(2) | |
| C3−P1−C2 | 104.4(1) | 115.20(9) | 108.2(2) | |
| C3−P1−O1 | | 103.90(8) | 97.3(2) | |
| C3−P1−O2 | | 100.53(8) | 102.0(2) | |

[a] Reference 15. [b] Reference 6c. [c] Reference 16.

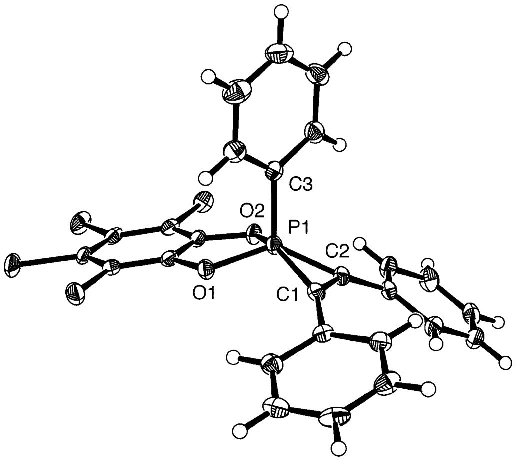


**FIGURE 1.** Crystal structure of **4a**.

As for tricoordinate **3a** and pentacoordinate **4a**, there are several differences in the structural parameters. The exocyclic P1−C3 bond length of **4a** is shorter than that of **3a**, which can be explained by a high degree of *s* character of the apical bond in the SP geometry. Also, shortening of the endocyclic P1−C1 and P1−C2 bonds, elongation of the C1═C2 bond, and enlargement of the C1−P1−C2 angle were observed in **4a** as compared with **3a**. In contrast, the structural parameters of the three-membered ring of **4a** have several similarities to those of tetracoordinate **6**. Although the ligands attached to the phosphorus are different between **4a** and **6**, these trends in the

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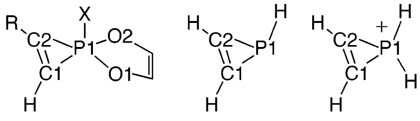
**CHART 4. Model Compounds of Phosphirenes for Theoretical Calculations**



**7a**: X = R = H
**7b**: X = H, R = $SiH_3$
**7c**: X = CN, R = H

**8**

**9**

**TABLE 2. Selected Bond Lengths (Å) and Angles (deg) for Model Compounds of Phosphirenes Optimized at B3LYP/6-31G(d)**

| | **7a**<br>(X = H) | **7b**<br>(X = H) | **7c**<br>(X = CN) | **8**<br>(X = H) | **9**<br>(X = H) |
|---|---|---|---|---|---|
| P1−C1 | 1.762 | 1.739 | 1.753 | 1.855 | 1.764 |
| P1−C2 | 1.762 | 1.795 | 1.751 | 1.855 | 1.764 |
| C1═C2 | 1.350 | 1.373 | 1.351 | 1.297 | 1.318 |
| P1−X | 1.403 | 1.402 | 1.796 | 1.444 | 1.400 |
| C1−P1−C2 | 45.0 | 45.0 | 45.4 | 40.9 | 43.9 |
| P1−C1−C2 | 67.5 | 69.6 | 67.2 | 69.5 | 68.0 |
| P1−C2−C1 | 67.5 | 65.2 | 67.4 | 69.5 | 68.0 |

structural parameters of the phosphirene rings indicate that the structures of phosphirene rings depend on the coordination number of the phosphorus atom.

**2.3. Theoretical Calculations on Tri-, Tetra-, and Pentacoordinate Phosphirenes.** Theoretical calculations on the real systems of **3a**, **4a**, and **4b** were carried out with density functional theory (B3LYP) using basis sets 6-31G(d) (see Supporting Information).[19] The calculated geometries of **3a** and **4a** roughly agreed with those of the X-ray structures. Although their calculated bond lengths were overestimated by maximum 0.05 Å (for the P−O bonds) compared to the X-ray structures, the computation reproduces reasonably the experimental results such as the shortening of the endocyclic P−C bonds and elongation of the C═C bond in the three-membered ring in **4a** compared with **3a**.

To discuss further the structure of the phosphirene rings and effects of the coordination number of the phosphorus atom on the structure, we also performed theoretical calculations on model compounds of tri-, tetra-, and pentacoordinate phosphirenes to shorten computation time. The model compounds that we chose for the theoretical calculations are shown in Chart 4. In the model compounds **7a**−**c**, the tetrachlorocatecholate ligand in the real systems was replaced by a 1,2-ethenediolate ligand (**7a**: X = R = H; **7b**: X = H, R = $SiH_3$; **7c**: X = CN, R = H). In the model compounds **8** and **9**, hydrogen was used as all the ligands of the phosphirenes. Geometry optimization on these model compounds was carried out with density functional theory (B3LYP) using basis sets 6-31G(d).[19] Table 2 shows selected bond lengths and angles of the optimized structures of **7a**−**c**, **8**, and **9**.

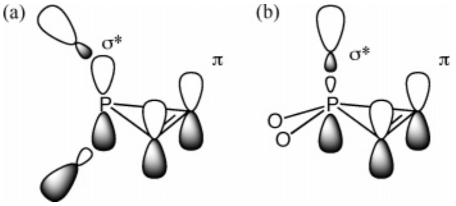
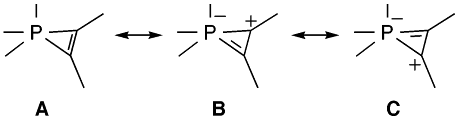


**FIGURE 2.** $\sigma^*-\pi$ interaction in (a) phosphirenium cations and (b) pentacoordinate phosphirenes.

**SCHEME 2. Electron Transfer in Pentacoordinate Phosphirene Reported by Regitz and Co-Workers**



The calculated bond angles in the three-membered rings of tricoordinate **8** and pentacoordinate **7a** are close to the crystallographically determined bond angles of **3a** and **4a**, respectively, while the calculated bond lengths of the endocyclic P−C bonds are slightly longer by about 0.03 Å than the experimental values. In the theoretical calculations of **7a** and **8**, however, a shortening of the endocyclic P−C bonds, elongation of the C═C bond, and enlargement of the C−P−C angle were observed in **7a** as compared with **8** as shown in the real systems of **3a** and **4a**. Furthermore, the theoretical calculations revealed a shortening of the apical P−H bond length in **7a** relative to the P−H bond length in **8**, supporting a higher degree of *s* character of the apical P−H bond in **7a** than that in **8**. Calculation on tetracoordinate **9** showed that the structural parameters of the three-membered ring of **9** are almost consistent with those of **7a**, although the C═C bond length in the three-membered ring of **9** is somewhat shorter than that of **7a**.

The comparable structural parameters of the phosphirene rings of the pentacoordinate phosphirenes and the tetracoordinate phosphirenium cations indicate some common characteristics in electronic structures of both the species. Theoretical study on phosphirenium cations by Clark and co-workers showed that the interaction between the $\sigma^*$ orbital of the phosphorus−ligand bond and the $\pi$ orbital of the carbon−carbon double bond in the phosphirenium cations has a weak but significant effect on the stability of the phosphirenium cations (Figure 2a).[20] By analogy with the phosphirenium cations, which exhibit delocalization of the double-bond character in the three-membered ring, such a $\sigma^*-\pi$ interaction[21] can be applicable to the pentacoordinate phosphirenes. It can be thought that the $\sigma^*$ orbital of the apical bond interacts with the $\pi$ orbital of the C═C bond, resulting in both the shortening of the endocyclic P−C bond and the elongation of the C═C bond (Figure 2b). Regitz and co-workers have reported that the contribution of the canonical structures **B** and **C**, as shown in Scheme 2, could explain the shortening of the endocyclic P−C bonds and the elongation of the C═C bond in the three-membered ring.[6c] The $\sigma^*-\pi$ interaction can be considered as an interpretation of Regitz's description from a standpoint of the molecular orbital method.

To confirm the influence of the electronic properties of the substituents on the three-membered ring, we carried out

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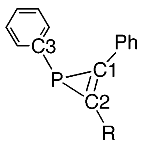
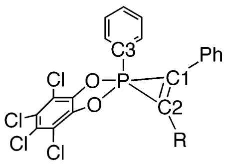
[20] Göller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840.

[21] For an investigation on $\sigma^*-\pi$ interaction in silacyclopropenes through X-ray crystallographic analysis, see: Tsutsui, S.; Sakamoto, K.; Kabuto, C.; Kira, M. *Organometallics* **1998**, *17*, 3819.

**TABLE 3. Selected NMR Data of Phosphirenes 3a,b and 4a,b in C$_6$D$_6$**



**3**



**4**

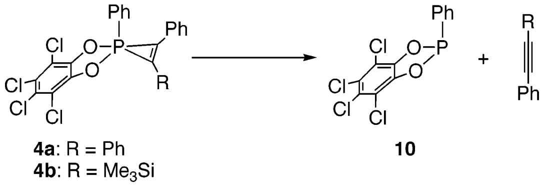
| R | 3a<br>Ph | 3b<br>Me$_3$Si | 4a<br>Ph | 4b<br>Me$_3$Si |
|---|---|---|---|---|
| $\delta_P$ | −188.1 | −204.6 | −95.2 | −91.3 |
| $\delta_C$ (C1) | 123.0 | 138.8 | 159.8 | 185.3 |
| $^{1}J$(P,C1)[a] | 44.6 | 53.6 | 17.6 | 9.2 |
| $\delta_C$ (C2) | | 123.3 | | 170.3 |
| $^{1}J$(P,C2)[a] | | 51.9 | | not obsd |
| $\delta_C$ (C3) | 142.2 | 143.8 | 134.7 | 135.4 |
| $^{1}J$(P,C3)[a] | 65.3 | 65.5 | 175.1 | 178.4 |

[a] Coupling constants are shown in Hz.

theoretical calculations on **7b** bearing a SiH$_3$ group on the carbon atom in the three-membered ring and **7c** bearing a CN group on the phosphorus atom. The structural parameters of the phosphirene ring of **7c** are very close to those of **7a**. Substitution of a CN group has little influence on the structural parameters of the phosphirene ring, as observed in the X-ray crystal structures of **2a** and **4a**, and these results suggest the small influence of the apical ligand at the phosphorus on the structures of the pentacoordinate phosphirenes. In contrast, attachment of a SiH$_3$ group to the carbon in the three-membered ring alters the structure of the phosphirene ring to some extent. In **7b**, the distance between the phosphorus and the carbon with the silyl group is elongated by about 0.03 Å compared with the basal P−C bond length of **7a**; unfortunately, the structural parameters of **4b** are not experimentally available. These results suggest that the structures of the three-membered rings in the pentacoordinate phosphirenes are influenced by the substituents on the carbon atoms in the three-membered ring rather than by the ligand on the phosphorus atom.

**2.4. NMR Studies of Phosphirenes.** The selected NMR data of tri- and pentacoordinate phosphirenes are summarized in Table 3. The $^{31}$P NMR chemical shifts of **4a** and **4b** are in the range of those of phosphirenes **2a**−**e** ($\delta_P$ −126.6 to −69.8).[6c] Compared with the $^{31}$P NMR chemical shift ($\delta_P$ −5.9) of phosphorane **5**,[17b] which has two five-membered rings involving the phosphorus atom, the $^{31}$P resonances of **4a** and **4b** appear at a much higher field, which is explained by the fact that the nuclei of a three-membered ring resonate upfield relative to the less strained compound.[22] The $^{31}$P NMR chemical shifts of **4a** and **4b** lie at a relatively low field compared with those of **3a** and **3b**. Large upfield shifts of **3a** and **3b** in $^{31}$P NMR spectroscopy are a typical feature of tricoordinate phosphirenes.[4a,b] Considering that the upfield shifts in $^{31}$P NMR spectroscopy are correlated with the degree of *s* character of the phosphorus lone pair,[4a,23] such upfield shifts of the tricoordinate phosphirenes are due to both high *s* character of the phosphorus lone pairs and the three-membered ring effect. Hence, the downfield shifts of **4a** and **4b** in $^{31}$P NMR spectroscopy relative to **3a** and **3b** are attributable to the absence of a lone pair in the pentacoordinate phosphirenes.

**SCHEME 3. Thermolysis of 4a and 4b**



In the $^{13}$C NMR spectra, the signals of the $^{13}$C nuclei of the three-membered ring of **4a** and **4b** lie at lower fields relative to the chemical shifts of **3a** and **3b**.[24] In both cases, the coupling constants, $^{1}J$(P,C), of the endocyclic P−C bonds in **4a** and **4b** are smaller than those of **3a** and **3b**. It is worth noting that the signal of C2 in **4b**, to which a trimethylsilyl group is attached, was observed as a singlet at $\delta_C$ 170.3, and no coupling between the phosphorus and carbon nuclei was detected. Considering that the coupling constant increases as the *s* character of each bond increases,[25] the endocyclic P−C bonds in **4a** and **4b** have a high degree of *p* character, which reflects their being both basal bonds in an SP structure and endocyclic bonds in three-membered ring. The endocyclic P−C2 bond in **4b**, in particular, has a considerably high degree of *p* character. In contrast, coupling constants of the exocyclic bonds between the phosphorus atom and the *ipso*-carbon atom of the phenyl group in **4a** and **4b** are larger than those of **3a** and **3b**, indicating a high degree of *s* character of the exocyclic P−C bond in **4a** and **4b**. Such a high degree of *s* character is a characteristic of apical bonds in SP. These NMR studies show that **4a** and **4b** have an SP arrangement around the phosphorus in the solution state, which is consistent with the fact that the structures of pentacoordinate phosphorus compounds in the solid and the solution states do not differ substantially.[26]

**2.5. Reactivities of Pentacoordinate Phosphirenes: Thermolyses of 4a and 4b.** It has been reported that a pentacoordinate phosphirane with a saturated three-membered ring synthesized by Denney et al. is thermally unstable and detectable only at −80 °C, decomposing to give the corresponding phosphonite and ethylene at room temperature.[6b] In contrast, **4a** is thermally stable; no decomposition of **4a** was observed in the NMR spectra after being heated at 60 °C for 40 h. Upon heating at 80 °C for 36 days, **4a** underwent a reductive elimination reaction to give the corresponding phosphonite **10** and diphenylacetylene, although some of **4a** still remained in the solution (Scheme 3).

Phosphirene **4b** is thermally less stable, and it decomposed at room temperature to give **10** and phenyl(trimethylsilyl)-acetylene. These results indicate that attachment of a trimethylsilyl group to the endocyclic carbon lowers the thermal stability of the pentacoordinate phosphirenes. Considering that a phosphorane with an SP structure is stabilized when an

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(22) (a) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870. (b) Seyferth, D.; Lambert, R. L. J.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *122*, 311. (c) Crimaldi, K.; Lichter, R. L. *J. Org. Chem.* **1980**, *45*, 1277.

(23) Chesnut, D. B.; Quin, L. D.; Wild, S. B. *Heteroatom Chem.* **1997**, *8*, 451.

(24) One of the reviewers suggested that the NMR data of Table 3 fit the description of Me$_3$Si as an accepting group, because C1 is more deshielded when R is Me$_3$Si than when R is Ph. We think that the Me$_3$Si groups behave as an electron-accepting group, but their electron-donating nature is not negligible in the α-carbon, considering that C2 is more shielded than C1 in **3b** and **4b**.

(25) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; Chapter 4.

(26) Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230.

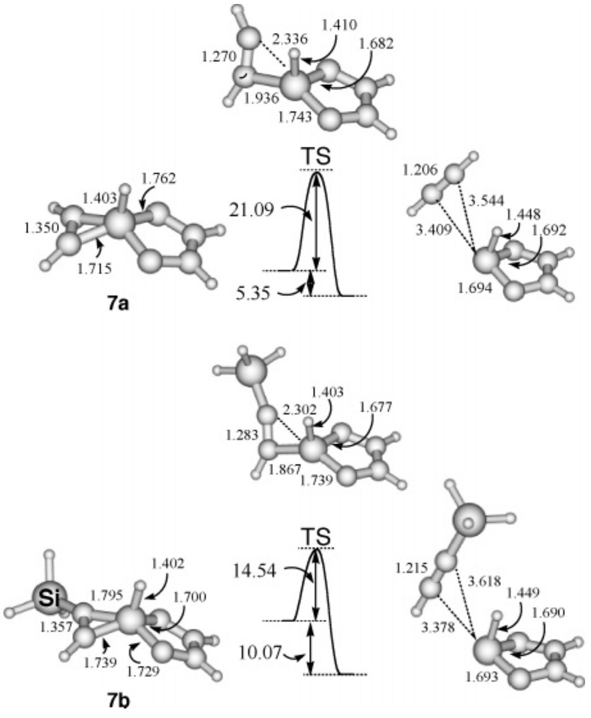
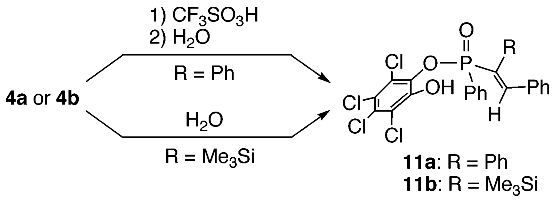
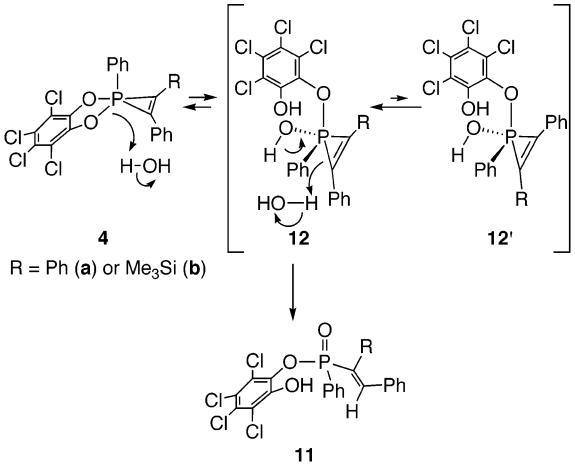


**FIGURE 3.** Calculated reaction profile of decomposition of **7a** (top) and **7b** (bottom). Bond lengths are shown in Å. Energies calculated at the B3LYP/6-311+G(2d,p)// B3LYP/6-31G(d) level, zero-point energy corrected, are in kcal/mol.

**SCHEME 4. Reaction of 4a and 4b with Proton Sources**



**SCHEME 5. Plausible Mechanism of Hydrolysis of 4**



electron-withdrawing ligand occupies the basal position,[10] **4b** is destabilized by a trimethylsilyl group, which is more electron-donating than a phenyl group.

These results are supported by theoretical calculations on **7a** and **7b**. They were used to examine activation energies for the reductive elimination reaction of the pentacoordinate phosphirenes. Both the optimized geometries and calculated energies of **7a** and **7b** are summarized in Figure 3. In both cases, the decomposition reactions are exothermic, releasing 5.35 and 10.07 kcal/mol for **7a** and **7b** at the B3LYP/6-311+G(2d,p)// B3LYP/6-31G(d) level, respectively. The calculated activation barrier for reductive elimination in **7b** (14.54 kcal/mol) is lower than that in **7a** (21.09 kcal/mol), supporting the experiment results. The lower activation energy for **7b** than that for **7a** is attributable to destabilization of the starting molecule that results from attachment of an electron-donating silyl group to the carbon at the basal position.[27]

**Reactions of 4a and 4b with Proton Sources.** Reactions of the pentacoordinate phosphirenes with some reagents that provide protons were examined. Phosphirene **4a** reacted neither with excess amount of water in $CDCl_3$ nor with hydrogen chloride in $Et_2O$/THF at room temperature. Cleavage of the endocyclic P−C bond, however, took place when much stronger acid was used; treatment of **4a** with trifluoromethanesulfonic acid followed by aqueous workup gave vinylphosphinate **11a** in 89% yield (Scheme 4). The (*E*)-configuration of the olefin moiety of **11a** was determined by differential NOE experiments. Although **4a** was not hydrolyzed by water, silyl-substituted **4b** was hydrolyzed immediately in wet $C_6D_6$ to give **11b** quantitatively. The stereochemistry of the alkene moiety of **11b** was determined to be the (*E*)-isomer by X-ray crystallographic analysis, which revealed that the P−C(Ph) bond was cleaved regioselectively in this reaction. The reaction rate for the hydrolysis of **4b** was considerably faster than that for **4a**, showing that attachment of the silyl group to the carbon in the phosphirene ring also affects the reactivity of pentacoordinate phosphirenes toward proton sources.

A possible mechanism for the reactions of **4a** and **4b** with reagents affording protons is shown in Scheme 5. The first step is thought to be protonation to the oxygen of **4**, followed by P−O bond cleavage to afford phosphorane intermediates **12** or **12′** with distorted TBP structures. In the case of unsymmetrical **4b** (R = $Me_3Si$), **12b** should be more stable than **12b′** because the electron-donating silyl substituent on the carbon atom at the equatorial position enhances the stability of the phosphorane with the TBP arrangement.[28] Considering that apical bonds in a phosphorane with the TBP arrangement are weaker and more reactive than equatorial bonds, further hydrolysis of **12b** should occur with cleavage of the apical P−C bond, resulting in formation of **11b**, which is consistent with the experimental results. In the case of **4a** (R = Ph), an electron-withdrawing phenyl group at the equatorial position should destabilize **12a**, thereby the initial protonation of **4a** should be slower relative to that of **4b**. Thus, the difference of the reactivity between **4a** and **4b** can be explained by comparison of the stability of the phosphorane intermediates.

**Reaction of 4a with Bromine.** When **4a** reacted with bromine at room temperature, cleavage of the P−C bond in the three-membered ring took place and vinylphosphinate **14** was obtained in 97% yield (Scheme 6). The regiochemistry of **14** was determined by X-ray crystallographic analysis, and the olefin moiety was found to have the (*Z*)-configuration.[29] Although a weak signal of an intermediate at $\delta_P$ −5 together

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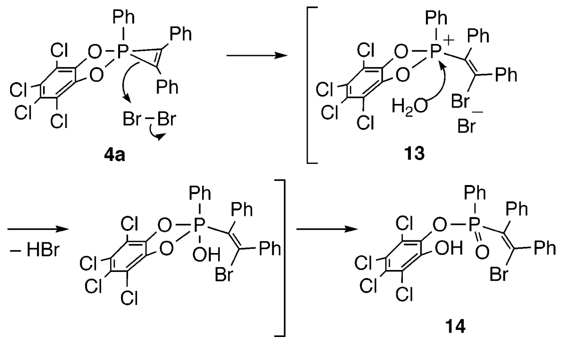
(27) NBO analyses on **4a** and **4b** at the B3LYP/6-31G(d) level show the electron-donating nature of the $SiMe_3$ group (**4a**: −0.324 and −0.325 for C1 and C2, respectively, **4b**: −0.312 for C1 and −0.792 for C2).

(28) For a methyl group as an electron-donating substituent, see: Kawashima, T.; Okazaki, R.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2500.

**SCHEME 6. Plausible Mechanism of Reaction of 4a with Bromine**



with a strong signal due to **14** was observed in the $^{31}P$ NMR spectra, the intermediate could not be identified.

A plausible mechanism for this reaction is illustrated in Scheme 6. Bromine electrophilically attacks the exocyclic P−C bond, resulting in formation of phosphonium bromide **13**. Then, water, which exists in the solution as impurity, attacks the phosphorus of **13** to afford the hydroxyphosphorane intermediate, which is immediately converted to **14**. Because there was a possibility of electrophilic attack of bromine on the carbon−carbon double bond in the three-membered ring, the molecular orbitals of model compound **15** were examined. Selected MOs of **15** are shown in Figure 4. The MO pictures show that the endocyclic P−C $\sigma$ bonds are involved in HOMO-2, while a $\pi$-type orbital of the C═C bond is involved in HOMO-3, which lies at lower energy. This is a strong indication that the electrophilic attack of bromine on the P−C bond is more favorable than that on the C═C double bond.

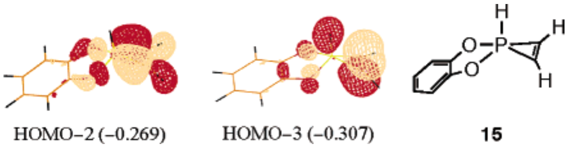
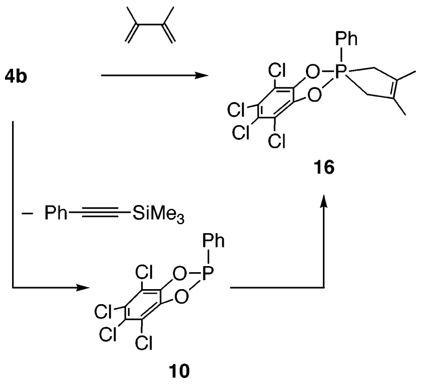

HOMO−2 (−0.269) HOMO−3 (−0.307) **15**

**FIGURE 4.** Kohn−Sham orbitals of **15**. Energies (in hartree) are shown in parentheses.

**Reactions of 4a and 4b with 1,3-Dienes.** Because a trivalent phosphirene tungsten complex has been reported to undergo a [4 + 2]-cycloaddition reaction with 2,3-dimethyl-1,3-butadiene,[30] reactions of **4a** and **4b** with 1,3-butadienes were performed to examine the reactivity of the C═C double bond in the three-membered ring of the pentacoordinate phosphirenes. On one hand, treatment of a toluene solution of **4a** with 2,3-dimethyl-1,3-butadiene at 60 °C and Danishefsky's diene[31] at 100 °C resulted in no reaction. On the other hand, reaction of **4b** with 2,3-dimethyl-1,3-butadiene gave phosphorane **16** in 79% yield (Scheme 7). In the course of the reaction of **4b** with the diene, a signal attributable to **10** that was formed from the thermolysis of **4b** was detected by $^{31}P$ NMR spectroscopy, indicating that **16** was produced by a [4 + 1]-cycloaddition reaction of **10** with the diene.[32] Formation of **16** by the reaction of **10** with the diene was independently confirmed by a control experiment. These results indicate that the alkene moieties of **4a** and **4b** are inert toward Diels−Alder reactions, and decomposition overcomes the cycloaddition of **4b**. The $\sigma^*-\pi$ interaction seems to lower the reactivity of the C═C bond in the three-membered rings.

**SCHEME 7. Reaction of 4b with 2,3-Dimethyl-1,3-butadiene**



## 3. Conclusion

Several pentacoordinate *P*-phenyl-substituted 1*H*-phosphirenes were successfully synthesized. X-ray crystallographic analysis of one of them revealed its distorted SP arrangement around the phosphorus. NMR studies on the pentacoordinate phosphirenes revealed that they persist in an SP arrangement around the phosphorus in the solution state and that the endocyclic P−C bonds in the three-membered ring have a very high degree of *p* character. Such a high degree of *p* character of the endocyclic P−C bonds resulted from their being both basal bonds in the SP structure and endocyclic bonds of the three-membered ring.

Crystallographically determined structural parameters of the three-membered ring of the pentacoordinate phosphirenes are very close to those of a tetracoordinate phosphirenium cation, but they are considerably different from those of the tricoordinate phosphirenes. Theoretical calculations on the phosphirenes reproduced these experimental results. Such a similarity of the structural parameters of the three-membered ring between tetra- and pentacoordinate phosphirenes is explained in terms of a $\sigma^*-\pi$ interaction, where the $\sigma^*$ orbital of the apical bond interacts with the $\pi$ orbital of the C═C bond of the three-membered ring.

The $\sigma^*-\pi$ interaction seems to lower the reactivity of the C═C bond in the three-membered ring; Diels−Alder reactions of the pentacoordinate phosphirenes with 1,3-butadienes did not proceed. In contrast, the endocyclic P−C bond in the three-membered ring was more reactive than the endocyclic C═C bond, and hence P−C bond cleavage took place even in the reaction with bromine. The reactivity of pentacoordinate phosphirenes is also affected by the substituent attached to the carbon atom in the three-membered ring. Their thermal stability and reactivity toward water are dramatically changed when an electron-donating trimethylsilyl group is attached to the basal carbon atom in the three-membered ring.

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(29) Because a single crystal of **14** was of low quality, the details of the structural parameters could not be discussed, but the regiochemistry of the olefin moiety of **14** was determined to be the (*Z*)-configuration by X-ray crystallographic analysis. The crystallographic data for **14** (CCDC-285444) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(30) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700.

(31) (a) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807. (b) Danishefsky, S. J.; Larson, E.; Askin, D.; Kato, N. *J. Am. Chem. Soc.* **1985**, *107*, 1246.

(32) Hasserodt, U.; Hunger, K.; Korte, F. *Tetrahedron* **1963**, *19*, 1563.

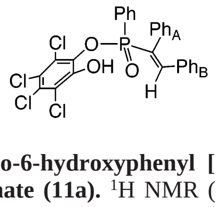
## 4. Experimental Section

**4,5,6,7-Tetrachloro-1′,2′,3′-triphenylspiro[1,3,2-benzodioxaphosphole-2,1′$\lambda^5$-[1*H*]-phosphirene] (4a).** A toluene solution (1.5 mL) of **3a** (68 mg, 0.24 mmol) and *o*-chloranil (57 mg, 0.23 mmol) was stirred for 2 h at room temperature, and the solvent was evaporated. In a glovebox under an argon atmosphere, the resulting orange solid was washed with hexane (2 mL) to give **4a** as pale orange solid (57 mg, 58%). Pale orange solid; mp 143.5 °C (dec); $^{1}$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 6.94−7.01 (m, 3H; para and meta of P−Ph), 7.10−7.14 (m, 2H; para of C−Ph), 7.20 (t, $^{3}J$(H,H) = 7.9 Hz, 4H; meta of C−Ph), 7.88−7.91 (m, 2H; ortho of P−Ph), 7.98 (d, $^{3}J$(H,H) = 7.9 Hz, 4H; ortho of C−Ph); $^{13}$C{$^{1}$H} NMR (126 MHz, C$_6$D$_6$, 25 °C) $\delta$ 115.0 (d, $^{2}J$(P,C) = 12.5 Hz), 124.5 (s), 129.0 (d, $^{3}J$(P,C) = 10.5 Hz; ortho of C−Ph), 129.2 (s; meta of C−Ph), 129.5 (s; meta of P−Ph), 130.6 (s; para of C−Ph), 130.8 (d, $^{2}J$(P,C) = 12.5 Hz; ipso of C−Ph), 131.1 (d, $^{2}J$(P,C) = 7.3 Hz; ortho of P−Ph), 131.8 (d, $^{4}J$(P,C) = 3.5 Hz; para of P−Ph), 134.7 (d, $^{1}J$(P,C) = 175.1 Hz; ipso of P−Ph), 143.5 (s), 159.8 (d, $^{1}J$(P,C) = 17.6 Hz, P−*C*(Ph)); $^{31}$P{$^{1}$H} NMR (202 MHz, C$_6$D$_6$, 25 °C) $\delta$ −95.2. LRMS (FAB): *m*/*z* 530 (M$^+$); Anal. Calcd for $C_{26}H_{15}Cl_4O_2P$: C, 58.68; H, 2.84. Found: C, 58.62; H, 3.06.

**4,5,6,7-Tetrachloro-1′,2′-diphenyl-3′-trimethylsilylspiro[1,3,2-benzodioxaphosphole-2,1′$\lambda^5$-[1*H*]-phosphirene] (4b).** Similarly, reaction of **3b** (207 mg, 0.73 mmol) with *o*-chloranil (170 mg, 0.73 mmol) at room temperature for 30 min gave **4b** as pale orange solid (196 mg, 52%). Pale orange solid; $^{1}$H NMR (500 MHz, C$_6$D$_6$, 25 °C) $\delta$ 0.35 (s, 9H; (C*H*$_3$)$_3$Si), 6.98−7.10 (m, 3H; para of P−Ph and meta of P−Ph), 7.11−7.15 (m, 1H; para of Ph), 7.21−7.24 (m, 2H; meta of Ph), 7.81−7.89 (m, 4H; ortho of Ph−P and ortho of Ph); $^{13}$C{$^{1}$H} NMR (126 MHz, C$_6$D$_6$, 25 °C) $\delta$ −0.93 (d, $^{3}J$(P,C) = 2.6 Hz; (*C*H$_3$)$_3$Si), 114.7 (d, $^{2}J$(P,C) = 11.7 Hz), 115.0 (d, $^{2}J$(P,C) = 14.0 Hz), 124.0 (s), 124.6 (s), 129.0 (d, $^{3}J$(P,C) = 10.7 Hz; meta of Ph−P), 129.1 (d, $^{3}J$(P,C) = 2.1 Hz; ortho of Ph), 129.2 (s; meta of Ph), 130.8 (d, $^{2}J$(P,C) = 13.0 Hz; ortho of Ph−P), 131.2 (s; para of Ph), 131.7 (d, $^{4}J$(P,C) = 3.7 Hz; para of Ph−P), 132.2 (d, $^{2}J$(P,C) = 9.1 Hz; ipso of Ph), 135.4 (d, $^{1}J$(P,C) = 178.4 Hz; ipso of Ph−P), 142.6 (s), 144.4 (s), 170.3 (s; C(Ph)=*C*(TMS)), 185.3 (d, $^{1}J$(P,C) = 9.2 Hz; *C*(Ph)=C(TMS)); $^{31}$P{$^{1}$H} NMR (202 MHz, C$_6$D$_6$, 25 °C) $\delta$ −91.3; HRMS−FAB (*m*/*z*): [M + H]$^+$ calcd for $C_{23}H_{20}O_2{}^{35}Cl_4SiP$, 526.9724; found, 526.9718.

**Thermolysis of 4b.** Pentacoordinate phosphirene **4b** (11 mg, 21 $\mu$mol) and a drop of 2,4,6-tri(*t*-butyl)benzene as an internal standard were dissolved in C$_6$D$_6$ (0.5 mL), and the solution was degassed and sealed in an NMR tube. After the solution was allowed to stand at room temperature for 5 d, a signal at $\delta_P$ −91.3 due to phosphirene **4b** disappeared, and the signal at $\delta_P$ 196.1 due to phosphonite **10** was observed in the $^{31}$P NMR spectrum. The $^{1}$H NMR spectrum showed a signal at $\delta_H$ 0.29 due to the trimethylsilyl group of phenyl(trimethylsilyl)acetylene. The yield of trimethylsilyl(phenyl)acetylene was estimated as 99% from the integral of the $^{1}$H NMR spectrum.

**Reaction of 4a with Trifluoromethanesulfonic Acid.** To a CDCl$_3$ solution (0.6 mL) of **4a** (20 mg, 38 mol) was added trifluoromethanesulfonic acid (5 $\mu$L, 0.06 mmol). After the reaction mixture was allowed to stand at room temperature for 10 min, the reaction mixture was opened in air. After being washed with water, the resulting organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure to give **11a** (19 mg, 89%) as colorless solid.



**2,3,4,5-Tetrachloro-6-hydroxyphenyl [(*E*)-1,2-Diphenylethenyl]phenylphosphinate (11a).** $^{1}$H NMR (500 MHz, CDCl$_3$, 25 °C) $\delta$ 7.04 (d, $^{3}J$(H,H) = 7.7 Hz, 2H; ortho of Ph$_B$), 7.10 (d, $^{3}J$(H,H) = 7.3 Hz, 2H; ortho of Ph$_A$), 7.15 (d, $^{3}J$(H,H) = 7.7 Hz, 2H; meta of Ph$_B$), 7.23 (d, $^{3}J$(H,H) = 7.1 Hz, 1H; para of Ph$_B$), 7.30 (t, $^{3}J$(H,H) = 7.3 Hz, 2H; meta of Ph$_A$), 7.32−7.35 (m, 1H; para of Ph$_A$), 7.44−7.48 (m, 2H; meta of Ph−P), 7.59−7.62 (m, 1H; para of Ph−P), 7.73 (d, $^{3}J$(P,H) = 24.1 Hz, 1H; C=C(Ph)*H*), 7.80−7.85 (m, 2H; ortho of Ph−P), 11.0 (br, 1H; OH); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ 122.7 (d, *J* = 35.2 Hz), 123.9 (s), 125.1 (d, *J* = 5.2 Hz), 126.8 (d, $^{1}J$(P,C) = 134.7 Hz; ipso of Ph−P), 128.4 (s; meta of Ph$_B$), 128.7 (d, $^{3}J$(P,C) = 13.4 Hz; meta of Ph−P), 128.7 (s; para of Ph$_A$), 129.0 (s), 129.2 (d, $^{1}J$(P,C) = 75.6 Hz; *C*=C(Ph)(H)), 129.96 (s), 130.03 (s), 130.7 (d, $^{1}J$(P,C) = 129.9 Hz; ipso of Ph$_B$), 130.7 (s), 132.7 (d, $^{3}J$(P,C) = 10.3 Hz; ortho of Ph−P), 133.0 (d; *J* = 9.3 Hz), 133.7 (d; *J* = 20.8 Hz), 133.9 (s), 136.2 (d; *J* = 10.5 Hz), 145.3 (s), 146.0 (d, $^{2}J$(P,C) = 13.5 Hz; C=*C*(Ph)(H)); $^{31}$P{$^{1}$H} NMR (109 MHz, CDCl$_3$, 25 °C) $\delta$ 41.8; HRMS−FAB (*m*/*z*): [M + H]$^+$ calcd for $C_{26}H_{18}O_3{}^{35}Cl_4P$, 548.9747; found, 548.9739.

**Reaction of 4b with Water.** Pentacoordinate phosphirene **4b** was dissolved to wet C$_6$D$_6$ (0.5 mL). After the solution was allowed to stand at room temperature for 5 min, only a signal due to **11b** was observed in the $^{31}$P NMR spectrum, and signals due to **11b** were observed in the $^{1}$H NMR spectrum.

**2,3,4,5-Tetrachloro-6-hydroxyphenylphenyl [(*E*)-2-Phenyl-1-trimethylsilylethenyl]phosphinate (11b):** Colorless solid; mp 176.3 °C; $^{1}$H NMR (500 MHz, CDCl$_3$, 25 °C) $\delta$ 0.11 (s, 9H; (C*H*$_3$)$_3$Si), 7.28−7.30 (m, 2H; ortho of Ph), 7.37−7.40 (m, 3H; meta and para of Ph), 7.45−7.50 (m, 2H; meta of Ph−P), 7.56−7.59 (m, 1H; para of Ph−P), 7.88−7.93 (m, 2H; ortho of Ph−P), 8.23 (d, $^{3}J$(P,H) = 36.4 Hz; P−C(TMS)=C*H*(Ph)), 11.3 (br, 1H; OH); $^{13}$C{$^{1}$H} NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ 1.11 (d, $^{4}J$(P,C) = 6.7 Hz; (*C*H$_3$)$_3$Si), 122.7 (d, *J* = 5.5 Hz), 124.9 (d, *J* = 5.4 Hz), 126.9 (d, $^{1}J$(P,C) = 123.5 Hz; ipso of Ph−P), 128.0 (s; ortho of Ph), 128.3 (s; meta of Ph), 128.8 (d, $^{3}J$(P,C) = 13.4 Hz; meta of Ph−P), 129.3 (s; para of Ph), 129.5 (s), 132.7 (d, $^{2}J$(P,C) = 11.0 Hz; ortho of Ph−P), 133.3 (d, $^{1}J$(P,C) = 87.7 Hz; P−*C*(TMS)=CH(Ph)), 133.8 (d, $^{4}J$(P,C) = 2.6 Hz; para of Ph−P), 136.2 (d, *J* = 9.8 Hz), 137.7 (d, $^{3}J$(P,C) = 28.9 Hz; ipso of Ph), 145.8 (d, *J* = 2.9 Hz), 161.8 (d, $^{2}J$(P,C) = 1.3 Hz; P−C=*C*H(Ph)), a signal due to a quaternary carbon could not be found; $^{31}$P{$^{1}$H} NMR (109 MHz, CDCl$_3$, 25 °C) $\delta$ 53.2; LRMS (FAB) *m*/*z* = 547 ([M + H]$^+$); Anal. Calcd for $C_{23}H_{21}Cl_4O_3PSi$: C, 50.57; H, 3.87. Found: C, 50.31; H, 4.05.

**Reaction of 4a with Bromine.** To a dichloromethane solution (1 mL) of **4a** (18 mg, 33 $\mu$mol) was added a dichloromethane solution of bromine (0.39 M, 0.13 mL, 51 $\mu$mol) at room temperature. After the reaction mixture was stirred for 30 min at room temperature, the solvent was evaporated and the resulting brown solid was exposed to air. The crude mixture was purified by GPLC (CHCl$_3$) to give **14** (20 mg, 97%) as a colorless solid.

**2,3,4,5-Tetrachloro-6-hydroxyphenyl [(*Z*)-2-Bromo-1,2-diphenylethenyl]phenylphosphinate (14):** $^{1}$H NMR (500 MHz, CDCl$_3$, 25 °C) $\delta$ 7.05−7.23 (m, 10H), 7.47−7.53 (m, 2H: meta of Ph−P), 7.62 (t, $^{3}J$(H,H) = 7.5 Hz, 1H; para of Ph−P), 8.00 (dd, $^{3}J$(P,H) = 13.6 Hz, $^{3}J$(H,H) = 7.7 Hz, 2H; ortho of Ph−P), 10.8 (s; O*H*); $^{13}$C{$^{1}$H} NMR (126 MHz, CDCl$_3$, 25 °C) $\delta$ 122.5 (s), 122.9 (s), 124.9 (d, *J* = 5.2 Hz), 127.4 (d, $^{1}J$(P,C) = 134.7 Hz; ipso of P−Ph), 127.9 (s), 128.2 (s; para of Ph−C), 128.3 (s), 128.8 (d, $^{3}J$(P,C) = 14.5 Hz; meta of P−Ph), 129.0 (s), 129.3 (s), 129.5 (s), 130.4 (br), 132.0 (d, $^{2}J$(P,C) = 11.5 Hz; ortho of P−Ph), 133.9 (d, $^{4}J$(P,C) = 2.6 Hz; para of Ph), 135.1 (d, $^{1}J$(P,C) = 141.0 Hz; P*C*(Ph)=C), 135.9 (d, *J* = 9.3 Hz), 136.1 (d, *J* = 5.2 Hz), 139.4 (d, $^{2}J$(P,C) = 13.5 Hz; ipso of P−C−*Ph*), 141.5 (d, $^{3}J$(P,C) = 7.3 Hz; ipso of P−C=C(*Ph*)), 145.3 (s); $^{31}$P{$^{1}$H} NMR (109 MHz, CDCl$_3$, 25 °C) $\delta$ 38.7; HRMS−FAB (*m*/*z*); [M + H]$^+$ calcd for $C_{26}H_{17}O_3{}^{35}Cl_4{}^{79}BrP$, 626.8853; found, 626.8824.

**Reaction of 4b with 2,3-Dimethyl-1,3-butadiene.** To a C$_6$D$_6$ solution (0.5 mL) of **4b** (20 mg, 38 $\mu$mol) in an NMR tube was added 2,3-dimethyl-1,3-butadiene (30 $\mu$L, 0.26 mmol), and the solution was degassed and sealed. After the reaction mixture was allowed to stand at room temperature for 6 d, a signal at $\delta_P$ 14.0 due to **16** was observed. The sealed tube was opened in a glovebox under an argon atmosphere, and the solvent was evaporated to give red solid (22 mg) containing **16**. Yield of **16** was estimated to be 79% from the integral of the $^1$H NMR spectrum.

**Theoretical Calculation.** Theoretical calculations reported here were performed with the Gaussian 98 (revision A.11.4).[19] Full geometry optimizations of the stable structures and the transition states were performed with the density functional theory (B3LYP) using basis sets 6-31G(d), where no symmetry constraints were imposed in any case. The stationary points were identified exactly by the curvature of the potential energy surface at these points corresponding to the eigenvalues of the Hessian. All reported stable structures exhibit exclusively positive Hessian eigenvalues, while all transition states have exactly one negative Hessian eigenvalue. The stationary points shown in Figure 3 are connected with each other on the potential surface as confirmed by intrinsic reaction coordinate (IRC) analysis.[33] For decomposition of **7a** and **7b**, the electronic energies of the B3LYP/ 6-31G(d) geometries at the B3LYP/6-311+G(2d,p) level were corrected by nonscaled zero-point energies.

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**Supporting Information Available:** General experimental methods, ORTEP drawings of **11b** and **14**, details of theoretical calculation (Cartesian coordinates and computed total energies), and X-ray crystallographic data for **4a**, **11b**, and **14** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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