JOC Article

Synthesis, Structure, and Reactivity of Novel 3,4-Diphosphacyclobutenes Bearing Silyl Groups

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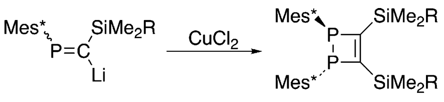


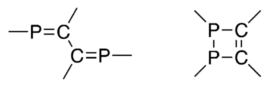
R = Me, *t*Bu; Mes* = $2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$

Copper-mediated homocoupling of sterically hindered 2-(2,4,6-tri-*tert*-butylphenyl)-1-trialkylsilyl-2-phosphaethenyllithiums afforded 1,2-bis(trialkylsilyl)-3,4-diphosphacyclobutenes (1,2-dihydrodiphosphetenes) through a formal electrocyclic [2+2] cyclization in the P═C—C═P skeleton as well as 2-trimethylsilyl-1,4-diphosphabuta-1,3-diene. Reduction of 1,2-bis(trimethylsilyl)-3,4-diphosphacyclobutenes followed by quenching with electrophiles afforded ring-opened products, (*E*)-1,2-bis(phosphino)-1,2-bis(trimethylsilyl)ethene and (*Z*)-2,3-bis(trimethylsilyl)-1,4-diphosphabut-1-ene. The structures of the ring-opened products indicated *E*/*Z* isomerization around the C═C bond after P—P bond cleavage of **5**, and the isomerization of the P—C═C skeleton. Ring opening of 1,2-bis(trimethylsilyl)-3,4-diphosphacyclobutenes affording (*E*,*E*)- and (*Z*,*Z*)-1,4-diphosphabuta-1,3-dienes was observed upon desilylation.

Introduction

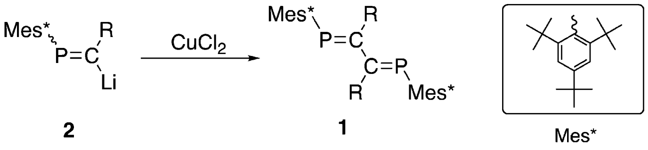
The 1,4-diphosphabuta-1,3-diene skeleton (**A**) is one of the simplest π-electron systems composed of phosphorus−carbon multiple bonds. Basically, **A** is energetically disfavored compared to the 3,4-diphosphacyclobutene system (**B**), which has been suggested by theoretical calculations[1] as well as experimental investigations (Chart 1).[2] Although the strain energy in the unsaturated four-membered-ring system is released, the stability of the phosphorus−carbon double bond is inferior to that of a carbon−carbon double bond, causing **B** to be more stable than **A**.[1a]

CHART 1



A **B**

SCHEME 1



R = H, Me, Cl, Br, SMe, SPh, STol

Despite this, kinetic stabilization has been utilized to synthesize various stable low-coordinated phosphorus compounds bearing multiple bonds of phosphorus.[3] We have synthesized several kinetically stabilized 1,4-diphosphabuta-1,3-dienes **1** by using copper-mediated homocoupling of bulky phosphaethenyllithiums **2** bearing the 2,4,6-tri-*tert*-butylphenyl group (hereafter abbreviated as Mes*) (Scheme 1).[4] The stable 1,4-diphosphabuta-1,3-dienes **1**, which we have reported to date, have displayed no cyclization upon irradiation or heating, probably due to steric hindrance around the phosphorus atoms.

Since we established preparation protocols for the 1,4-diphosphabuta-1,3-dienes from the corresponding phosphaethenyllithiums, we have been interested in the homocoupling of 1-phosphaethenyllithiums bearing silyl groups such as **4**. Contrary to our prediction, 3,4-diphosphacyclobutenes **5**, which are the formal result of

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(1) (a) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040. (b) Schoeller, W. W.; Tubbesing, U. *Chem. Ber.* **1996**, *129*, 419.

(2) Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, *21*, 1923.

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10.1021/jo050195z CCC: $30.25

SCHEME 2

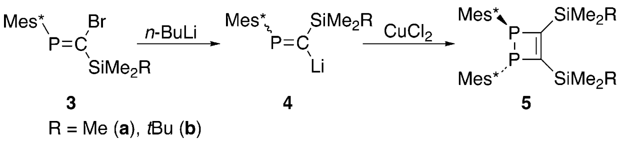
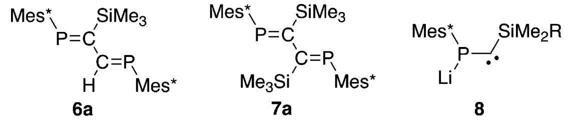


CHART 2



[2+2] cyclization, were obtained as the major product, whereas the desired 2,3-bis(trialkylsilyl)-1,4-diphosphabuta-1,3-diene (**7**) was not isolated. In this paper, we report the isolation and structural determination of **5**. Moreover, we report here reduction with sodium naphthalenide to give the corresponding ring-opened products through P—P bond cleavage. Although 3,4-diphosphacyclobutenes have been reported,[5] the study of **5** revealed novel findings concerning the properties of 3,4-diphosphacyclobutene.

Results and Discussion

Preparation and Structure of Diphosphacyclobutene. (*Z*)-2-Bromo-2-trialkylsilyl-1-phosphaethenes **3**[6] were prepared from 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [Mes*P=CBr$_2$].[7] Compound **3a** was allowed to react with butyllithium to generate the corresponding phosphaethenyllithium **4a**[6a] followed by the addition of copper(II) chloride. After the usual workup procedures, 1,2-bis(trimethylsilyl)-3,4-diphosphacyclobutene **5a** was obtained together with the protonated adduct, 2-trimethylsilyl-1-phosphaethene [Mes*P=C(H)-SiMe$_3$][6] (Scheme 2).

The desired 2,3-bis(trimethylsilyl)-1,4-diphosphabuta-1,3-diene (**7**; Chart 2) was not isolated in this reaction,[8] whereas a trace amount of 2-trimethylsilyl-1,4-diphosphabuta-1,3-diene **6a**[9] was isolated after purification indicating partial desilylation on the silica gel column. Neither irradiation ($\lambda > 300$ nm) nor heating (110 °C) of **5a** gave the ring-opened product **7a**. Similarly, phosphaethenyllithium **4b**, generated from **3b**, afforded the corresponding 3,4-diphosphacyclobutene **5b** but in a low yield. In the ^{31}P NMR of **5**, only one signal was observed, indicating that **5** exists as a single diastereomer. Indeed, compounds **5a**,**b** were recrystallized from hexane and the structure was confirmed by X-ray crystallography as shown in Figure 1 (the molecular structure of **5b** is displayed in the Supporting Information). Four independent molecules of **5a** have been identified and one of them is displayed in Figure 1 together with the bond lengths and angles. The four-membered ring is not planar and the dihedral angle of the P—C=C—P is 23.3° (**5a**) or 21.4° (**5b**). The bulky Mes* groups take a trans configuration to avoid steric congestion. The average bond lengths of the four-membered ring are comparable to the corresponding parameters of the previously reported 3,4-diphosphacyclobutenes [P—P 2.214−2.248 Å; P—C 1.814−1.830 Å; C=C 1.356−1.358 Å].[5b,9,10] The Si—C(sp^2) bond length of **5a** is close to that of **6a** [1.897(2) Å].[9]

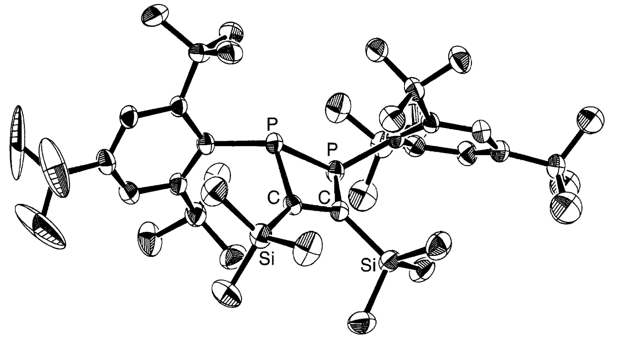


FIGURE 1. An ORTEP drawing of the molecular structure of **5a**. One of the four independent molecules is displayed. Hydrogen atoms are omitted for clarity. One of the *p-tert*-butyl groups (right) is disordered and the atoms with the predominant occupancy factor (0.60) are displayed. Selected average bond lengths (Å) and angles (deg): P—P 2.259, P—C$_{\mathrm{Mes^*}}$ 1.871, P—C 1.817, C=C 1.374, C—Si 1.882, P—P—C 74.8, P—C=C 102.2.

Theoretical calculations have suggested that 3,4-diphosphacyclobutene is energetically favored over 1,4-diphosphabuta-1,3-diene.[1] However, the 1,4-diphosphabuta-1,3-dienes bearing Mes*-P moieties (**1**) have not shown [2+2] cyclization affording the corresponding 3,4-diphosphacyclobutenes, because of the steric congestion around the phosphorus atoms. Thus, the formation of **5** would involve a reaction mechanism other than the [2+2] cyclization of the P=C—C=P skeleton. As an alternative formation mechanism of **5** from **4**, we propose an intermediate containing a phosphinocarbene[11,12] skeleton such as **8**, which affords the homocoupled product **5** in the presence of copper(II) chloride (Chart 2). Indeed **8** is one of the "stable" phosphinosilylcarbenes in which the phosphorus donates a π-electron to the carbene center whereas the silyl group behaves as a π-electron acceptor.[12c] Efforts to prove the presence of intermediate **8** are in progress.

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(5) (a) Tirla, C.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Inorg. Chem.* **2002**, *41*, 6032. (b) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3. (c) Appel, R.; Barth, V.; Knoch, F. *Chem. Ber.* **1983**, *116*, 938.

(6) (a) van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174. (b) van der Sluis, M.; Klootwijk, A.; Wit, J. B. M.; Bickelhaupt, F.; Veldman, N.; Spek, A. L.; Jolly, P. W. *J. Organomet. Chem.* **1997**, *529*, 107. (c) Appel, R.; Casser, C.; Immenkeppel, M. *Tetrahedron Lett.* **1985**, *26*, 3551.

(7) Synthesis of Mes*P=CBr$_2$: Sugiyama, S.; Ito, S.; Yoshifuji, M. *Chem. Eur. J.* **2004**, *10*, 2700. See also: Goede, S. J.; Dam, M. A.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 278.

(8) A ^{31}P NMR signal of δ_P 317, which seemed to be of **7a**, was observed in the reaction mixture.

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(10) (a) Cénac, N.; Chrostowsk, A.; Sotirpoulos, J.-M.; Donnadieu, B.; Igau, A.; Pfister-Guillouzo, G.; Majoral, J. P. *Organometallics* **1997**, *16*, 4551. (b) Schmidt, O.; Fuch, A.; Gudat, D.; Nieger, M.; Hoffbauer, E.; Niecke, E.; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1998**, *38*, 3028. (c) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365. (d) Heinemann, F. W.; Kummer, S.; Seiss-Brandl, U.; Zenneck, U. *Orgnometallics* **1999**, *18*, 2021. (e) Mackewitz, T. W.; Peters, C.; Bergsträsser, U.; Leininger, S.; Regitz, M. *J. Org. Chem.* **1997**, *62*, 7605. (f) Jones, C.; Richards, A. F. *Organometallics* **2002**, *21*, 438. (g) Mackewitz, T. W.; Peters, C.; Bergsträsser, U.; Leininger, S.; Regitz, M. *J. Org. Chem.* **1997**, *62*, 7605.

(11) (a) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781. (b) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (c) Bourissou, D.; Guerret, O.; Gabbäi, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 58.

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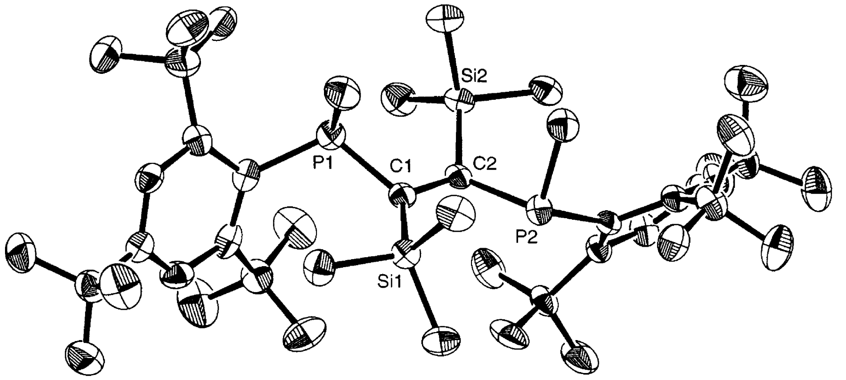


FIGURE 2. An ORTEP drawing of the molecular structure of **9**. Hydrogen atoms are omitted for clarity. The P2 atom disordered and the atom with the predominant occupancy factor (0.89) is displayed. Typical bond lengths (Å) and angles (deg): P1−C1 1.871(3), P2−C2 1.868(3), P1−Me 1.867(3), P1−C_{Mes*} 1.870(2), P2−Me 1.867(3), P2−C_{Mes*} 1.886(3), C1−C2 1.375(3), C1−Si1 1.944(3), C2−Si2 1.949(3), P1−C1−Si1 121.6(1), P1−C1−C2 110.6(2), Si1−C1−C2 124.2(2), P2−C2−Si2 121.1(1), P2−C2−C1 109.8(2), Si2−C2−C1 124.8(2), Θ(P1−C1−C2−P2) 154.4(1), Θ(Si1−C1−C2−Si2) 161.0(1), Θ(P1−C1−C2−Si2) 2.3(3), Θ(Si1−C1−C2−P2) 4.2(3).

SCHEME 3

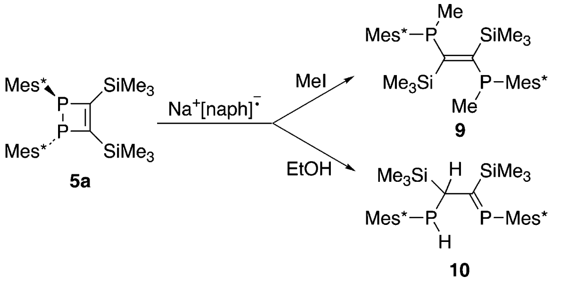
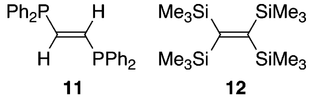


CHART 3



Reduction and Ring-Opening of 3,4-Diphosphacyclobutene. Reduction of 3,4-diphosphacyclobutenes with alkaline metals has been established and used for the synthesis of various heterocyclic compounds[5,13] and thus we are interested in the reactivity of **5a**. Compound **5a** was allowed to react with sodium naphthalenide (ca. 3 equiv) to afford the corresponding anionic intermediate as a deep-purple solution, which was stable at −78 °C but afforded **5a** at ca. −40 °C. The anionic intermediate was quenched with iodomethane or ethanol at −78 °C to give 1,2-diphosphinoethylene **9** or 1,4-diphosphabut-1-ene **10** (Scheme 3).[14] Similarly to the tetraphenyl-3,4-diphosphacyclobutene reported by Mathey et al.,[5,13] **5a** revealed P−P bond cleavage upon reduction.

In contrast to the reduction of tetraphenyl-3,4-diphosphacyclobutene, **5a** afforded ring-opened products indicating *E*/*Z* isomerization during the formation of **9**. Additionally, **9** was obtained as a mixture of *dl* isomers. Although the structure was not identified, a trace amount of another diastereomer ($\delta_P = 14.1$) was observed in the reaction mixture. Compound *dl*-**9** was recrystallized from hexane and the structure was determined by X-ray crystallography (Figure 2). The C1 and C2 atoms locate above the P1−Si1−P2−Si2 plane (the distances between the C1 and C2 atoms from the P1−P2−Si1−Si2 plane are 0.325 and 0.334 Å, respectively). Accordingly, the C1 and C2 atoms slightly pyramidalize [sums of the bond angles: ∑(C1) 356.4°, ∑(C2) 355.7°]. The P1−C1 and P2−C2 distances are longer than the corresponding P−C distances in (*E*)-1,2-bis(diphenylphosphino)ethane (**11**) [1.807(3) and 1.808(3) Å].[15] Moreover, the Si1−C1 and Si2−C2 distances are longer than the corresponding distances of tetrakis(trimethylsilyl)ethane (**12**) [1.909−1.918 Å], which is one of the most crowded olefins.[16] The C=C distance of **9** is close to that of **12** [1.368(3) Å].[16] These structural properties of **9** indicate that the steric congestion is relieved mainly by elongation of the bond lengths, whereas **12** displays a twisted conformation due to the repulsion between the trimethylsilyl groups.[16]

When **5a** was allowed to react with sodium naphthalenide and ethanol, a diastereoisomer of **10** was observed in the reaction mixture ($\delta_P = 355.7$, -35.9, $J_{PP} = 146.1$ Hz). The first observed diastereomer was completely isomerized to afford **10** during silica gel column chromatography. The isolated single diastereomer of **10** was analyzed by X-ray crystallography as displayed in the Supporting Information. The determined molecular structure shows an *RS* configuration at the P2 and C2 atoms. The P=C−C−P skeleton twists with a torsion angle of 71.6(6)° probably as a result of steric interaction. Compound **10** shows an isomerization involving a [1,3] hydrogen shift, which is similar to the isomerization of vinylphosphines to afford phosphapropenes.[17]

Ring-Opening of 3,4-Diphosphacyclobutene Affording 1,4-Diphosphabuta-1,3-dienes. To understand whether the trimethylsilyl groups in **5a** can be removed or replaced with other substituents, reaction of **5a** with tetrabutylammonium fluoride (TBAF) was carried out. Desilylation took place when **5a** was mixed with 2 equiv

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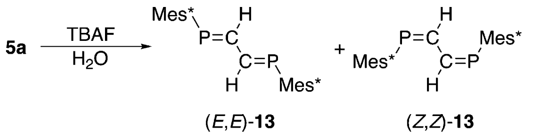
[13] (a) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 950. (b) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534. (c) Charrier, C.; Maigrot, N.; Mathey, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623.

[14] Reaction of the anionic species from **5a** with either iodine, bis(cyclopentadienyl)zirconium dichloride, or 1,2-dibromoethane gave **5a**.

[15] Schmidbaur, H.; Reber, G.; Wagner, F. E.; Müller, G. *Inorg. Chim. Acta* **1988**, *147*, 143.

[16] Sakurai, H.; Nakadaira, Y.; Tobita, H. *J. Am. Chem. Soc.* **1982**, *104*, 300.

SCHEME 4



of TBAF in wet THF. In contrast to our prediction, the products were mainly 1,4-diphosphabuta-1,3-dienes **13** and no 3,4-diphosphacyclobutene derivative was observed (Scheme 4). This result indicates that the 3,4-diphosphacyclobutene skeleton underwent thermal conrotatory [π2s+σ2a] ring-opening, and thus, the (*E*,*E*) and (*Z*,*Z*) isomers of **13**[18] were produced. It seems that silyl groups sufficiently stabilize the sterically encumbered 3,4-diphosphacyclobutene skeletons to avoid ring-openings.[19]

Conclusion

It has been established that copper-mediated coupling of the 1-silyl-2-phosphaethenyllithiums (**4**) afforded 3,4-diphosphacyclobutenes (**5**) through formal [2+2] cyclization of 1,4-diphosphabuta-1,3-diene. The structures of **5** showed a butterfly conformation. Reduction of **5a** with sodium naphthalenide gave the anionic intermediate that was allowed to react with iodomethane and ethanol to furnish **9** and **10**, respectively, indicating P—P bond cleavage. Particularly, the structure of **9** indicated *E*/*Z* isomerization during the reaction, which had not been known in the previous studies on 3,4-diphosphacyclobutenes. The isolated **9** and **10** are useful as novel bulky P2-ligands.[20] Furthermore, it has been clear that silyl groups affect the molecular structures and reactivity of phosphaethenyllithiums and 3,4-diphosphacyclobutenes.

Experimental Section

Preparation of 3b. To a solution of 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (Mes*P=CBr$_2$; 1.00 g, 2.23 mmol)[7] in THF (20 mL) was added butyllithium (2.3 mmol, 1.5 M solution in hexane) at -78 °C and the mixture was stirred for 10 min. The solution was mixed with a THF (5 mL) solution of *tert*-butyldimethylsilyl chloride (2.45 mmol) at -78 °C and the resulting mixture was stirred for 10 min. After the reaction mixture was allowed to warm to room temperature the solvent was removed in vacuo. The crude residue was purified by silica gel column chromatography (hexane) and recrystallized from ethanol to give 0.85 g of **3b** (78% yield). Colorless needles (EtOH), mp 72−74 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 314.4; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.34 (d, J = 0.8 Hz, 6H), 1.06 (s, 9H), 1.39 (s, 9H), 1.52 (s, 18H), 7.45 (d, J = 0.9 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ -3.2 (d, J_{CP} = 10.7 Hz), 19.0 (d, J_{CP} = 4.1 Hz), 27.8, 32.0, 33.4 (d, J_{CP} = 6.6 Hz), 35.6, 38.3, 122.5, 141.2 (d, J_{CP} = 65.7 Hz), 150.9, 153.0, 165.3 (d, J_{CP} = 79.4 Hz). Anal. Calcd for $C_{25}H_{44}BrPSi$: C, 62.09; H, 9.17; Br, 16.52. Found: C, 62.37; H, 9.26; Br, 16.82.

Preparation of 5a. To a solution of **3a** (200 mg, 0.45 mmol) in THF (15 mL) was added butyllithium (0.50 mmol) and the mixture was stirred at -78 °C for 5 min. Copper(II) chloride (0.50 mmol) was added to the reaction mixture and the solution was then stirred for 1 h at -78 °C. The reaction mixture was allowed to warm to room temperature, treated with ammonia (10% NH_3 in sat. NH_4Cl_{aq}) and extracted with ether (200 mL). The organic layer was washed with water then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and silica gel column chromatography of the residue (hexane) afforded crude **5a** together with a trace amount of **6a**. The crude **5a** was recrystallized from hexane at -18 °C; 49 mg, 30%. Pale yellow prisms (hexane), mp 227−229 °C dec; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 11.8; ^{1}H NMR (400 MHz, CDCl$_3$) δ -0.30 (s, 18H), 1.33 (s, 18H), 1.60 (s, 36H), 7.39 (s, 4H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 0.8, 31.6, 34.3 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 5.5 Hz), 35.3, 39.6, 122.0, 138.1 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{PC}})/2$ = 49.6 Hz), 151.7, 159.0 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 6.6 Hz), 168.0 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 8.5 Hz); UV (hexanes) $\lambda_{\max}$ (log ϵ) 208 (3.68), 254 (3.51), 285 (3.43), 335 (sh, 2.85). Anal. Calcd for $C_{44}H_{76}P_2Si_2$: C, 73.06; H, 10.60. Found: C, 72.90; H 10.87.

Preparation of 5b. To a solution of **3b** (850 mg, 1.8 mmol) in THF (20 mL) was added butyllithium (1.8 mmol) and the mixture was stirred at -78 °C for 5 min. Copper(II) chloride (1.8 mmol) was added to the reaction mixture and the solution was then stirred for 1 h at -78 °C. The reaction mixture was allowed to warm to room temperature, treated with ammonia (10% NH_3 in sat. NH_4Cl_{aq}), and extracted with ether (300 mL). The organic layer was washed with water then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and silica gel column chromatography followed by GPC of the residue (hexane) afforded 12 mg of **5b** (2% yield). Yellow prisms (hexane), mp 186−188 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 3.7; ^{1}H NMR (400 MHz, CDCl$_3$) δ -0.94 (s, 6H), 0.13 (s, 6H), 0.86 (s, 18H), 1.33 (s, 18H), 1.50 (s, 18H), 1.67 (s, 18H), 7.28 (s, 2H) 7.37 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ -4.6, -1.7, 20.1, 28.8, 31.5, 34.8, 35.2, 40.0, 123.3, 136.0 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 47.8 Hz), 151.4, 161.4 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 17.9 Hz), 167.5 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 11.9 Hz). Anal. Calcd for $C_{50}H_{88}P_2Si_2$: C, 74.38; H, 10.99. Found: C, 74.38; H, 11.05.

Reduction of 5a. To a solution of **5a** (20 mg, 0.028 mmol) in THF (1 mL) was added sodium naphthalenide (ca. 0.084 mmol) in THF (1 mL) at -78 °C and the mixture, colored deep purple, was stirred for 5 min. An excess amount of iodomethane or ethanol in THF was added to the reaction mixture at -78 °C and the mixture, colored pale yellow, was allowed to warm to room temperature. The solvent was removed in vacuo and the residue was dissolved in hexane. The insoluble materials were filtered off and the solution was concentrated. Recrystallization from hexane afforded **9**: 43% yield, mp 166−168 °C; ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ 17.4; ^{1}H NMR (400 MHz, CDCl$_3$) δ -0.01 (br s, 18H), 1.30 (s, 18H), 1.37 (s, 18H), 1.45 (s, 18H), 1.60 (br s, 6H), 7.07 (br s, 1H), 7.17 (br s, 1H), 7.28 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 6.7, 22.4 (pt, $(J_{\mathrm{CP}}+J_{\mathrm{CP}})/2$ = 8.7 Hz), 31.7, 34.2, 34.4, 35.2, 38.8, 40.5, 121.6, 123.3, 138.3 (dd, J_{CP} = 33.5 Hz, 26.5 Hz), 146.6, 154.2, 155.5, 180.6 (dd, J_{CP} = 15.6 Hz, 9.0 Hz). EA Calcd for $C_{46}H_{82}P_2Si_2\cdot H_2O$: C, 71.63; H, 10.97. Found: C, 71.77; H, 10.85. When the reaction mixture of **5a** and sodium naphthalenide in ethanol was concentrated in vacuo, a diastereoisomer of **10** was observed in the ^{31}P NMR spectrum (δ_{P} = 355.7, -35.9, J_{PP} = 146.1 Hz). Silica gel column chromatography caused isomerization of the product to afford **10**. **10**: 82% yield,

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(19) One of the Reviewers pointed out that, as a result of theoretical calculation, the substitution effect on energy difference between 1,2-disilyl-3,4-diphosphacyclobutene and 2,3-disilyl-1,4-diphosphabutadiene is large, indicating the silyl groups effectively stabilize the diphosphacyclobutene structure. On the other hand, no ring-closure of 1,4-diphosphabutadiene has been directly observed so far. It also would be difficult to confirm that **5a** is formed via ring-closure of **7a** even if the process is thermodynamically favorable. The substitution effect on low-coordinated phosphorus compounds is described by: Nyulászi, L. *J. Organomet. Chem.* on line 26 Nov. 2004.

(20) Compound **11** was used for the preparation of several gold(I) complexes as described in ref 15. See also: Brandys, M.-C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 4839.

mp 155−158 °C; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ −27.4, 347.2 (dd, $J_{PP} = 110.8$ Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.25 (s, 9H), −0.23 (s, 9H), 1.31 (s, 9H), 1.35 (s, 9H), 1.54 (s, 9H), 1.57 (s, 9H), 1.60 (s, 9H), 1.68 (s, 9H), 2.93 (dd, $J = 36.0$ Hz, $J = 11.1$ Hz, 1H), 5.33 (dd, $J = 241.0$ Hz, $J = 10.8$ Hz, 1H), 7.23−7.40 (br s, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 0.8, 1.8, 31.7, 33.8 (d, $J_{CP} = 6.7$ Hz), 34.1 (d, $J_{CP} = 5.9$ Hz), 34.3 (d, $J_{CP} = 10.3$ Hz), 34.9, 35.3, 38.8, 39.1, 121.8, 122.1, 123.0, 133.4 (dd, $J_{CP} = 56.1$ Hz, 6.3 Hz), 139.8 (d, $J_{CP} = 69.2$ Hz), 148.3, 150.3, 154.0, 154.1, 155.1, 155.7, 194.6 (dd, $J_{CP} = 66.0$ Hz, 4.4 Hz); MS (ESI) *m/z* 725.5190 [M + H]; calcd for $C_{44}H_{79}P_2Si_2$ 725.5195.

Reaction of 5a with TBAF. A mixture of **5a** (60 mg, 0.083 mmol) and TBAF (tetrabutylammonium fluoride, 0.17 mmol) in wet THF (5 mL) was stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue was extracted with hexane. The hexane solution was concentrated and purified by silica gel column chromatography (hexane) to afford (*E*,*E*)- and (*Z*,*Z*)-**13**[18] as a 1:1 mixture (14 mg, 30% yield).

X-ray Crystallography for 5a. A Rigaku MSC Mercury CCD detector with graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) was used. The structure was solved by direct methods (SIR92),[21] expanded with Fourier techniques (DIRDIF94),[22] and then refined by full-matrix least squares. Structuresolution, refinement, and graphical representation were carried out with the teXsan package.[23] $C_{44}H_{76}P_2Si_2$, $M = 723.20$, crystal dimensions 0.20 × 0.20 × 0.20 mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 13.963(1)$ Å, $b = 22.947(4)$ Å, $c = 31.616(5)$ Å, $\alpha = 70.01(2)°$, $\beta = 87.85(2)°$, $\gamma = 83.46(2)°$, $V = 9458(3)$ Å^3, $Z = 8$, $T = 296$ K, $2\theta_{max} = 132.7°$, $\rho_{calc} = 1.016$ g cm^{-3}, μ(CuKα) = 0.150 mm^{-1}, 200 692 observed reflections, 26 573 unique reflections ($R_{int} = 0.033$), $R1 = 0.093$ ($I > 3\sigma(I)$), $R_W = 0.088$ (all data) (CCDC-255489).

X-ray Crystallography for 9. A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) was used. The structure was solved by direct methods (SIR92),[21] expanded using Fourier techniques (DIRDIF94),[22] and then refined by full-matrix least squares. Structure solution, refinement, and graphical representation were carried out with the teXsan package.[23] $C_{46}H_{82}P_2Si_2$, $M = 753.27$, crystal dimensions 0.30 × 0.20 × 0.20 mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 10.650(1)$ Å, $b = 16.920(2)$ Å, $c = 27.253(1)$ Å, $\beta = 100.309(3)°$, $V = 4831.7(7)$ Å^3, $Z = 4$, $T = 130$ K, $2\theta_{max} = 55.0°$, $\rho_{calc} = 1.035$ g cm^{-3}, μ(MoKα) = 0.167 mm^{-1}, 36 384 observed reflections, 19 266 unique reflections ($R_{int} = 0.030$), $R1 = 0.065$ ($I > 3\sigma(I)$), $R_W = 0.088$ (all data) (CCDC-255488).

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Supporting Information Available: ORTEP drawings of molecular structures of **5b** and **10**, and X-ray crystallographic data for **5a**, **5b**, **9** and **10** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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