Preparation and Isomerization of 3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutenes[1)]

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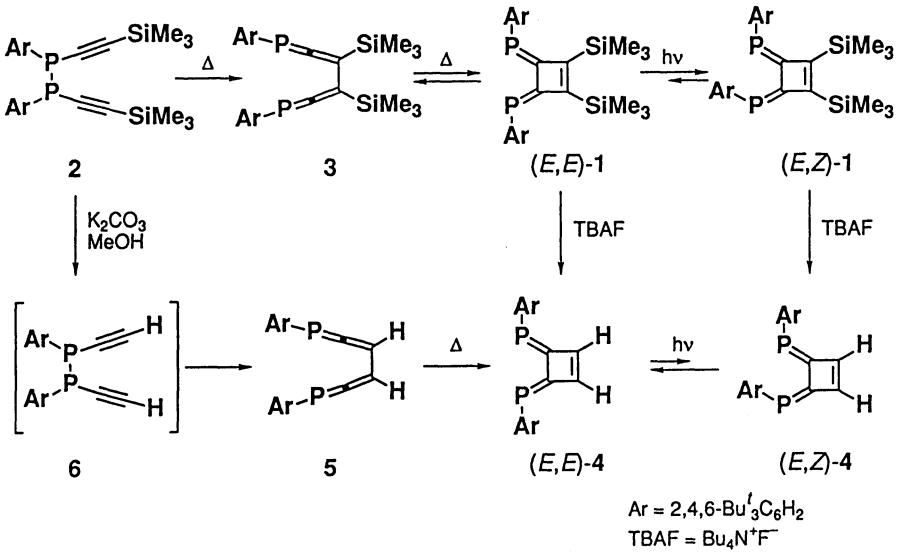
Synopsis. (*E,E*)- and (*E,Z*)-3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutenes were prepared by desilylation reaction of the corresponding 1,2-bis(trimethylsilyl)cyclobutenes or by thermal isomerization reaction of 1,6-bis(2,4,6-tri-*t*-butylphenyl)-1,6-diphospha-1,2,4,5-hexatetraene. Optimized structures and total energies of various parent compounds $C_4H_4P_2$ were calculated by ab initio method and the effect of steric congestion on the valence isomerization is discussed.

Phosphorus compounds in low coordination states are of current interest.[2)] By utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl moiety (hereafter abbreviated to Ar) as a protecting group, we and others have been successful in preparing various types of low-coordinated phosphorus compounds such as diphosphenes,[3)] phosphaalkenes,[4)] phosphaalkynes,[5)] and phosphacumulenes[6)] as stable chemical species. Recently, we have reported the preparation of (*E,E*)- and (*E,Z*)-3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutenes (**1**) via the corresponding bis(trimethylsilylethynyl)diphosphane **2** and 1,6-diphospha-1,2,4,5-hexatetraene **3**.[7)] The complex formation reactions of **1** with some group-6 metal(0) carbonyls have also been reported.[8)] Since **1** has a unique π-system containing phosphorus–carbon pπ–pπ double bonding, the physicochemical properties of **1** and their analogues are of interest. We report here the desilylation reaction of **1** and **2** as well as the photoisomerization and thermal isomerization among the desilylated products (Scheme 1).

Results and Discussion

The desilylation of (*E,E*)-**1** was successfully performed by addition of a solution of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) (contains <5 wt% water) at ambient temperature to give (*E,E*)-**4** in 69% yield. Similarly, (*E,Z*)-**1** afforded the desilylated product (*E,Z*)-**4** in the reaction with TBAF in 74% yield. Similarly to the case of (*E,E*)-**1**, the *E,Z*-isomerization of (*E,E*)-**4** was easily performed by irradiation of (*E,E*)-**4** using a medium pressure mercury lamp. Thus, irradiation of (*E,E*)-**4** in C_6D_6 for 5 h lead to an equilibrium mixture of (*E,E*)-**4** and (*E,Z*)-**4** (3 : 1 ratio; determined by ^{1}H NMR). Furthermore, the equilibrium mixture of approximately the same ratio was obtained by irradiation of (*E,Z*)-**4** in C_6D_6 for 4 h. It should be noted here that the *E,Z*-isomerization did not take place during the desilylation process of either (*E,E*)-**1** or (*E,Z*)-**1** performed in the dark.

Contrary to the case of **1**, the desilylation reactions of either the diphosphane **2** or the 1,6-diphospha-1,2,4,5-hexatetraene **3** with TBAF at room temperature resulted in the formation of mixtures of unidentified compounds. However, by treatment with potassium carbonate in methanol, **2** was slowly desilylated and the ^{31}P NMR spectrum of the solution showed two signals due to **2** and the 1,6-diphospha-1,2,4,5-hexatetraene **5** in 2 : 5 ratio after 96 h. During this reaction, the desilylated diphosphane **6** may first be formed as an intermediate. The compound **5** was isolated by flash column



Scheme 1.

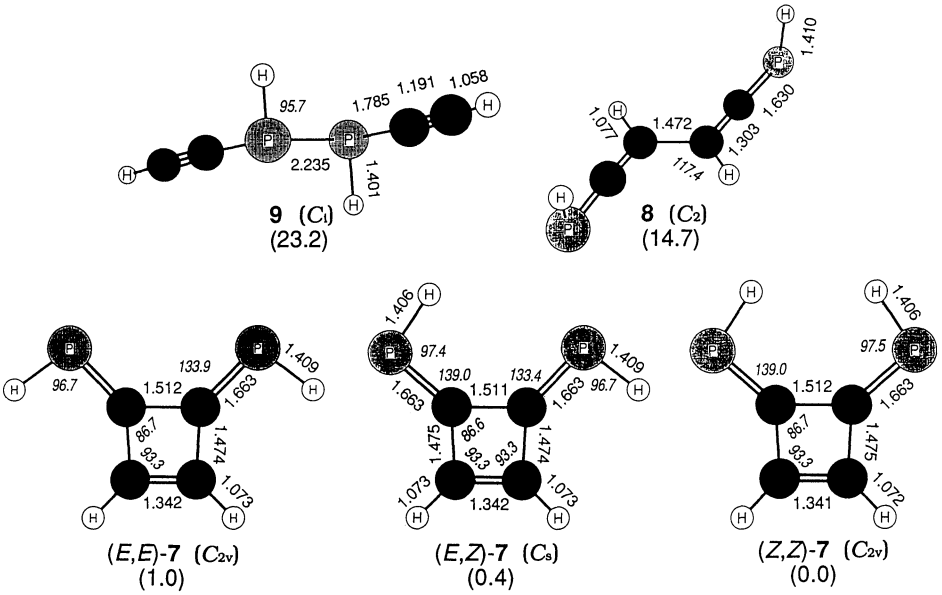


Fig. 1. Some important bond lengths (Å) and *bond angles* (°) of optimized structures of $C_4H_4P_2$ **7**—**9** with molecular symmetry and the relative energies (in parentheses/kcal mol^{-1}).

chromatography followed by gel permeation chromatography, although the isolated yield (6%) was low probably because of some decomposition during the chromatographic treatment.

We have previously reported the thermal equilibrium between (*E,E*)-**1** and **3**,[7,9] however, it seems likely that the rearrangement of the desilylated 1,6-diphospha-1,2,4,5-hexatetraene **5** to (*E,E*)-**4** is irreversible or that the equilibrium balance is largely in favor of the latter, as (*E,E*)-**4** was obtained almost quantitatively by heating of **5** in refluxing toluene for 1 h in the dark. In addition, no remarkable change was observed in the ^{31}P NMR spectra of (*E,E*)-**4** in toluene after refluxing for 1 h. These experimental results indicate that the steric repulsion between the 2,4,6-tri-*t*-butylphenyl groups and the trimethylsilyl groups at the cyclobutene ring in (*E,E*)-**1** is large enough to permit equilibration to **3** whereas (*E,E*)-**4** is stable enough because it is free from such steric repulsion. Ab initio calculation (GAUSSIAN 88, MP2/6-31G*//HF/6-31G*) of the mythical compounds $C_4H_4P_2$ (**7**—**9**) indicated that (*E,E*)-diphosphinidenecyclobutene [(*E,E*)-**7**] is more favorable than 1,6-diphospha-1,2,4,5-hexatetraene **8** by 13.7 kcal mol^{-1} (Fig. 1). The isomer (*Z,Z*)-**7** is the most stable among those isomers **7**—**9**, though the energies of (*E,Z*)- or (*E,E*)-**7** are close to that of (*Z,Z*)-**7**. Apparently, the bulky 2,4,6-tri-*t*-butylphenyl group suppresses the formation of (*Z,Z*)-**1** or (*Z,Z*)-**4**. 3,4-Diphospha-1,5-hexadiyne **9** has the highest energy among those, which is consistent with the experimental results. The preference of diphosphinidenecyclobutenes **7** may be due to the better π-bond conjugation (including phosphorus–carbon π-bond) than those of **8** or **9**.

Experimental

All experiments were carried out under argon unless specified otherwise. Melting points were taken on a Yanagimoto MP-S3 micromelting points apparatus and were uncorrected. NMR spectra were recorded on a Bruker AC-200P spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on either JEOL HX-110 or Hitachi M-2500 spectrometers.

Materials. (*E,E*)- and (*E,Z*)-3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutenes (**1**), 1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-bis(trimethylsilylethynyl)-diphosphane (**2**), and 1,6-bis(2,4,6-tri-*t*-butylphenyl)-3,4-bis-(trimethylsilyl)-1,6-diphospha-1,2,4,5-hexatetraene (**3**) were prepared as described previously.[7] Tetrabutylammonium fluoride (1.0 mol dm^{-3} solution in THF; contains <5 wt% water) was purchased from Aldrich Chemical Company, Inc.

(*E,E*)-3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutene (*E,E*)-4. To a solution of (*E,E*)-diphosphinidenecyclobutene (*E,E*)-**1** (30.0 mg, 0.040 mmol) in 5 ml of THF was added 40 μl (0.040 mmol) of TBAF (1.0 M solution in THF, 1 M=1 mol dm^{-3}) and stirred at room temperature for 30 min in the dark. The solvent was evaporated and the residue was submitted to column chromatography (SiO_2: pentane/CH_2Cl_2) to give 16.5 mg (69% yield) of (*E,E*)-**4** as colorless crystals: Mp 192.5—195 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.31 (18H, s, *p*-Bu^t), 1.49 (36H, s, *o*-Bu^t), 5.82 (2H, pseudo t, J_{PH}=1.4 Hz, P=C-CH), and 7.34 (4H, s, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=170.5; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.3 (s, *p*-C$\underline{Me}_3$), 33.1 (pseudo t, J_{PC}=3.5 Hz, *o*-C$\underline{Me}_3$), 34.9 (s, *p*-$\underline{C}$Me$_3$), 37.8 (s, *o*-$\underline{C}$Me$_3$), 120.8 (s, *m*-arom.), 136.0 (dd, $^1J_{PC}$=60.0 Hz and $^4J_{PC}$=5.3 Hz, *ipso*-arom.), 146.7 (dd, $^2J_{PC}$=44.0 Hz and $^3J_{PC}$=26.4 Hz, P=C-$\underline{C}$), 149.3 (s, *p*-arom.), 154.7 (s, *o*-arom.), 182.0 (dd, $^1J_{PC}$=50.0 Hz and $^2J_{PC}$=25.0 Hz, P=$\underline{C}$-C); UV (hexane) 238 (log ε 4.4), 296 (4.5), and ca. 350 nm (sh, 3.7); IR (KBr) 1303 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 603 (MH^+; 100). Found: *m/z* 602.4185. Calcd for $C_{40}H_{60}P_2$: M, 602.4170.

(*E,Z*)-3,4-Bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutene (*E,Z*)-4. To a THF (5 ml) solution of (*E,Z*)-diphosphinidenecyclobutene (*E,Z*)-**1** (71.7 mg, 0.096 mmol) was added 140 μl (0.14 mmol) of TBAF (1.0 M solution in THF) and stirred at room temperature for 30 min in the dark. The solvent was removed in vacuo and the residue was submitted to column chromatography (SiO_2: pentane) to give 42.8 mg (74%) of (*E,Z*)-**4** as pale yellow solid: Mp 149—152 °C

(decomp); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.29 (9H, s, *p*-Bu^t), 1.34 (9H, s, *p'*-Bu^t), 1.36 (18H, s, *o*-Bu^t), 1.59 (18H s *o'*-Bu^t), 5.94 (1H, dd, $^3J_{PH}$=3.6 Hz and $^4J_{PH}$=2.2 Hz, P=C-CH), 7.12 (1H, pseudo t, J_{PH}=2.5 Hz, P=C-CH), 7.30 (2H, s, arom.), and 7.38 (2H, d, $^4J_{PH}$=1.2 Hz, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=177.3 and 188.9 (ABq, $^3J_{PP}$= 11.5 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.3 (s, *p*-CMe_3), 31.5 (s, *p,'*-CMe_3), 32.7 (d, $^4J_{PC}$=7.6 Hz, *o*-CMe_3), 33.8 (d, $^4J_{PC}$=7.1 Hz, *o'*-CMe_3), 34.8 (s, *p,p'*-CMe_3), 37.9 (s, *o,o'*-CMe_3), 121.0 (s, *m*-arom.), 121.2 (s, *m'*-arom.), 135.0 (d, $^1J_{PC}$=52.4 Hz, *ipso*-arom.), 137.1 (d, $^1J_{PC}$=59.6 Hz, *ipso'*-arom.), 147.4 (dd, $^2J_{PC}$=41.1 Hz and $^3J_{PC}$=21.2 Hz, P=C-C), 147.4 (dd, $^2J_{PC}$=36.3 Hz and $^3J_{PC}$=23.6 Hz, P=C-C), 149.0 (s, *p*-arom.), 150.4 (s *p'*-arom.), 154.1 (s, *o*-arom.), 155.1 (d, $^2J_{PC}$=2.3 Hz, *o'*-arom.), 178.9 (dd, $^1J_{PC}$=48.0 Hz and $^2J_{PC}$=18.3 Hz, P=C), and 181.0 (dd, $^1J_{PC}$=47.1 Hz and $^2J_{PC}$=19.1 Hz, P=C); UV (hexane) 242 (log ε 4.3), 280 (sh, 4.3), and 295 nm (4.3); IR (KBr) 1589, 1477, 1465, and 1459 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 603 (MH^+; 100), 545 (M^+−Bu^t; 67), and 489 (MH^+−2Bu^t; 82). Found: *m/z* 602.4186. Calcd for $C_{40}H_{60}P_2$: M, 602.4170.

Photoisomerization Reaction of (*E,E*)- and (*E,Z*)-4. A solution of (*E,E*)-**4** (24.5 mg, 0.041 mmol) in 0.5 ml of C_6D_6 in an NMR sample tube of 5 mm ϕ was irradiated by a medium pressure mercury lamp for 5 h at 0 °C. ^{31}P NMR spectra of the resulting solution showed signals due to (*E,E*)- and (*E,Z*)-**4** in 3 : 1 ratio. Similarly, 42.0 mg (0.070 mmol) of (*E,Z*)-**4** in C_6D_6 (0.5 ml) was irradiated for 4 h at 0 °C, which resulted in the formation of a mixture of (*E,E*)- and (*E,Z*)-**4** in 3 : 1 ratio (determined by ^{1}H NMR spectroscopy).

1,6-Bis(2,4,6-tri-*t*-butylphenyl)-1,6-diphospha-1,2,4,5-hexatetraene (5). To a mixture of the diethynyldiphosphane **2** (141.1 mg, 0.18 mmol) and anhydrous potassium carbonate (155.6 mg, 1.1 mmol) was added 15 ml of methanol and stirred at room temperature for 96 h. After evaporation of the solvent the residue was submitted to flash column chromatography (SiO_2: pentane) and successively to recycling preparative HPLC over gel permeation columns (Japan Analytical Industry, Co., Ltd., JAIGEL Hl+H2: THF) to give 6.0 mg (6%) of **5** together with **2** in 4.2 mg (3% of recovery). **5**: Mp 75—76 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.30 (18H, s, *p*-Bu^t), 1.58 (36H, s, *o*-Bu^t), 6.25 (2H, dd, $^3J_{PH}$=21.8 Hz and $^4J_{PH}$=4.9 Hz, P=C=CH), and 7.38 (4H, s, arom.); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=70.4; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ=31.2 (s, *p*-CMe_3), 33.1 (d, $^4J_{PC}$=7.4 Hz, *o*-CMe_3), 34.9 (s, *p*-CMe_3), 38.0 (s, *o*-CMe_3), 106.6 (dd, $^2J_{PC}$=14.9 Hz and $^3J_{PC}$=11.8 Hz, P=C=C), 122.2 (s, *m*-arom.), 130.1 (d, $^1J_{PC}$= 63.8 Hz, *ipso*-arom.), 149.9 (s, *p*-arom.), 153.4 (s, *o*-arom.), 241.4 (dd, $^1J_{PC}$=25.2 Hz and $^4J_{PC}$=4.5 Hz, P=C=C); UV (hexane) 265 nm (log ε 4.6); IR (KBr) 1592, 1479, 1455, 1392, and 1361 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 602 (M^+; 15), 545 (M^+−Bu^t; 29), 489 (MH^+−2Bu^t; 41), 327 (MH^+−ArP; 32), 275 (ArP^+−1; 32), 246 (ArH^+; 28), and 231 (ArH^+−Me; 100). Found: *m/z* 602.4169. Calcd for $C_{40}H_{60}P_2$: M, 602.4170.

Thermal Isomerization of 5. The 1,6-diphospha-1,2,4,5-hexatetraene **5** (28.7 mg, 0.048 mmol) was dissolved in 3 ml of toluene and refluxed for 30 min. Then the solvent was removed in vacuo and the residue was submitted to column chromatography (SiO_2: pentane) to give 24.5 mg of (*E,E*)-**4** (85%).

Thermal Isomerization of (*E,E*)-4. A solution of (*E,E*)-**4** (30.6 mg, 0.051 mmol) in toluene (5 ml) was refluxed for 1 h. No peak except (*E,E*)-**4** was observed in the ^{31}P NMR spectra of the resulting solution.

Ab initio Calculations. The structures of each parent compound $C_4H_4P_2$ were optimized by the ab initio method at the HF/6-31G* level using the GAUSSIAN 88 program.[10] The relative energies were calculated at MP2/6-31G*//HF/6-31G*.

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9) On the contrary, (*E,Z*)-**1** in dark did not afford **3** in refluxing toluene for 3 h, which may indicate that the ring opening/closure reaction proceeds in a concerted manner. It should be noted that the compounds **2**, **3**, and **5** appear to consist of a single diastereomeric isomer, respectively, since each ^{31}P NMR spectrum (81 MHz) shows only one single peak. The compound **3** was also desilylated with K_2CO_3/MeOH to give **5** almost quantitatively.

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