

## Preparation and X-Ray Analysis of 2,2',3,3'-Tetraphosphinidene-1,1'-bicyclobutyl<sup>#</sup>

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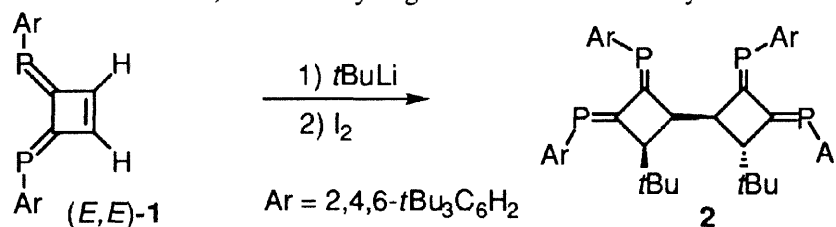
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**Abstract:** A sterically protected diphosphinidenecyclobutene with the 2,4,6-tri-*tert*-butylphenyl group was allowed to react with *tert*-butyllithium and iodine, successively, to give 2,2',3,3'-tetraphosphinidene-1,1'-bicyclobutyl derivative, and the structure was confirmed by X-ray analysis, showing unusual short contact between the C=P moieties at the 2 and 2' positions. A strong through-space interaction between them appears to play an important role in rationalization of the <sup>31</sup>P NMR and UV/Vis.

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Sterically protected phosphorus-containing multiple bonded compounds with bulky substituents such as the 2,4,6-tri-*tert*-butylphenyl group (abbreviated to Ar) are currently of interest. We have been interested in the cumulated and conjugated systems<sup>1–4</sup> involving phosphorus atom(s) in low coordination states, as well as diphosphenes<sup>5</sup> and phosphathenes.<sup>6</sup> Recently, Appel,<sup>7</sup> Märkl,<sup>8</sup> and we<sup>9–11</sup> have reported the preparation and isolation of diphosphinidenecyclobutenes, as well as their *E/Z* isomerization about the C=P bonds<sup>9,12</sup> and their transition-metal complex formation.<sup>10,13–16</sup> We now report on the coupling reaction of diphosphinidenecyclobutene and its structure analysis, where the two cyclobutane rings strongly interact with each other beyond the isolated conjugation system.

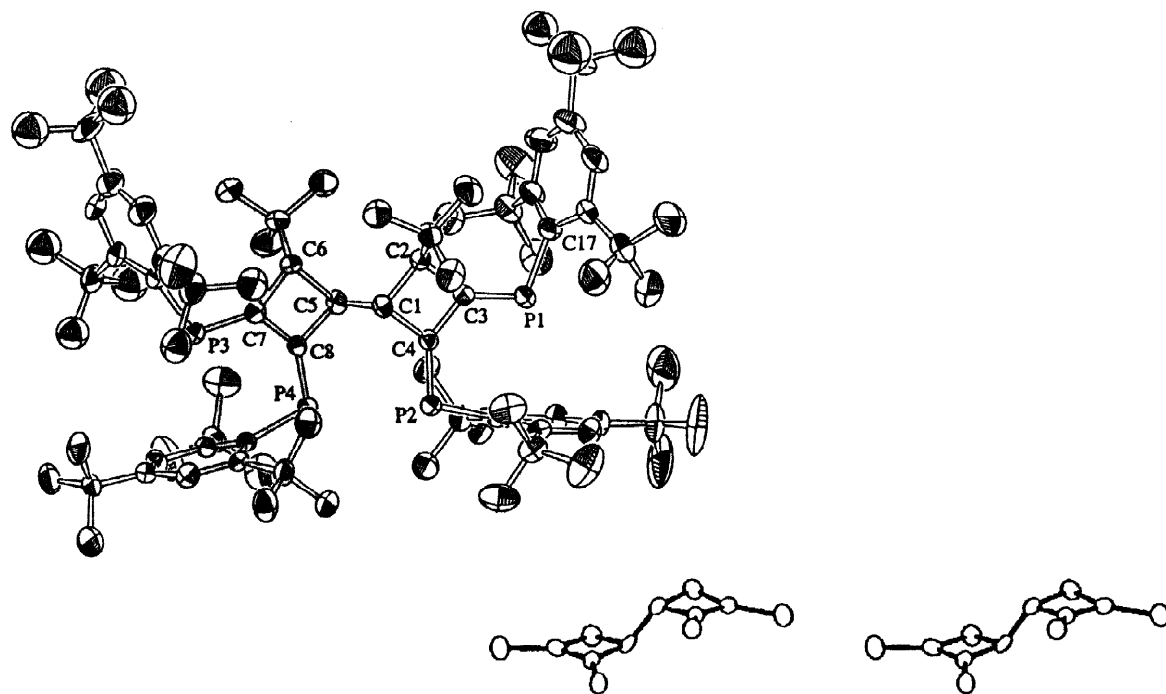
The starting diphosphinidenecyclobutene (*E,E*)-**1** was prepared as reported previously<sup>11</sup> and was allowed to react with *tert*-butyllithium and iodine, successively to give the dimer **2** in 47% yield.<sup>17</sup>



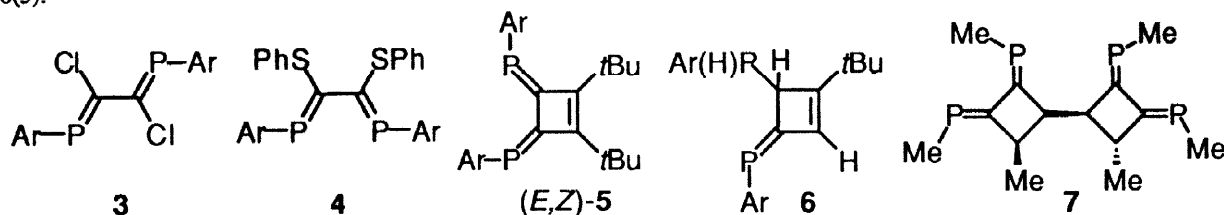
In the <sup>31</sup>P NMR spectrum in THF-*d*<sub>8</sub>, **2** showed a typical AA'XX' pattern and the simulated spectrum, with calculated parameters,<sup>17</sup> was superimposable on the observed one. The coupling constant between P(2) and P(4) was calculated to be extraordinarily large, indicating a strong interaction between the two *exo* C=P moieties at the 2 and 2' positions. The fact might be explained by the unusually short contact between P(2) and P(4). Furthermore, it seems likely that *E/Z* isomerization occurred during the reaction, probably in the presence of iodine, where facile isomerization is known for **1**.<sup>12</sup>

The structure of **2** was unambiguously confirmed by the X-ray analysis<sup>18</sup> to reveal an interesting feature. Figure 1 depicts an ORTEP drawing of the molecular structure for **2** with a stereo side view of the framework. Some selected bond lengths and bond angles are listed in the caption to Figure 1. The two cyclobutane rings with

*exo E*- and *Z*-C=P bonds are almost coplanar within 0.05 Å and are parallel (dihedral angle of the two planes is 3.05°) with a distance of about 1.3 Å, causing the P(2) and P(4) to get closer (3.31 Å), compared to that of P(1) and P(2) or P(3) and P(4) of 3.74 or 3.75 Å, respectively.



**Figure 1.** Molecular structure of tetraphosphinidenebicyclobutyl 2 showing the atomic labeling scheme. Three of the twelve *tert*-butyl groups are disordered but only atoms with a dominant occupancy factor are displayed. A stereo side view of the selected framework is also depicted; four atoms attached to the cyclobutane rings denote the low-coordinated phosphorus atoms. Some selected bond lengths [Å] and bond angles [°]: P(1)–C(3) 1.698(7), P(2)–C(4) 1.684(7), P(3)–C(7) 1.707(7), P(4)–C(8) 1.689(7), C(1)–C(2) 1.553(9), C(2)–C(3) 1.548(9), C(3)–C(4) 1.464(9), C(4)–C(1) 1.526(9), C(5)–C(6) 1.564(9), C(6)–C(7) 1.553(10), C(7)–C(8) 1.451(9), C(8)–C(5) 1.521(9); P(1)–C(3)–C(2) 144.0(5), P(1)–C(3)–C(4) 124.6(5), P(2)–C(4)–C(1) 128.6(5), P(2)–C(4)–C(3) 139.8(5), C(3)–P(1)–C(17) 107.9(3), C(1)–C(2)–C(3) 87.5(5), C(2)–C(3)–C(4) 91.3(5), C(3)–C(4)–C(1) 91.6(5), C(4)–C(1)–C(2) 88.8(5).



The C=P bond lengths of **2** [1.698(7), 1.684(7), 1.707(7), and 1.689(7) Å] are similar to those for 1,4-bis(2,4,6-tri-*tert*-butylphenyl)-2,3-dichloro-1,4-diphosphabutadiene **3**<sup>3</sup> [1.691(4) and Å] or its phenylthio derivative **4**<sup>4</sup> [1.70(1) and 1.72(1) Å] but rather longer than those for (*E,Z*)-**1**<sup>9</sup> [1.665(7) and 1.662(7) Å] or those for (*E,E*)-**1**<sup>14</sup> [1.678(6) and 1.676(5) Å]. On the other hand, the bond lengths of C(3)–C(4) and C(7)–C(8) for **2** [1.464(9) and 1.451(9) Å] are much shorter than the corresponding bond length between the two C=P moieties for (*E,Z*)-**1** [1.523(9) Å], and rather similar to the corresponding bond length for **3** [1.445(7) Å] or **4** [1.49(2) Å], indicating that the steric factor is no so serious in **2** as that observed for **1**.

Figure 2 depicts the UV/Vis spectrum of **2**. Compared to (*E,Z*)-1,2-di-*tert*-butyldiphosphinidenecyclobutene, (*E,Z*)-**5** [UV/Vis (hexane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 291 (4.46), 345 nm (3.82, sh)],<sup>12</sup> **2** showed an enormous red shift by more than 100 nm, in spite of the isolated 4 $\pi$  system. A ZINDO calculation for a model compound **7**,

bearing a fixed framework with the observed bond lengths and angles for **2**, which includes short contact between the two P=C moieties, showed  $\lambda_{\max}(\log \epsilon) = 320$  (4.66), 374 nm (4.61), while a conformational isomer of **7**, being calculated as an energy-minimum conformer by the MOPAC-PM3 method of less congestion with the P–P distance of longer than 4.0 Å, showed  $\lambda_{\max}(\log \epsilon) = 300$  (4.94).<sup>19</sup> Again, a reasonable explanation for this phenomenon might be the strong through-space interaction between the two 4 $\pi$  systems, as observed in the X-ray and <sup>31</sup>P NMR analyses.

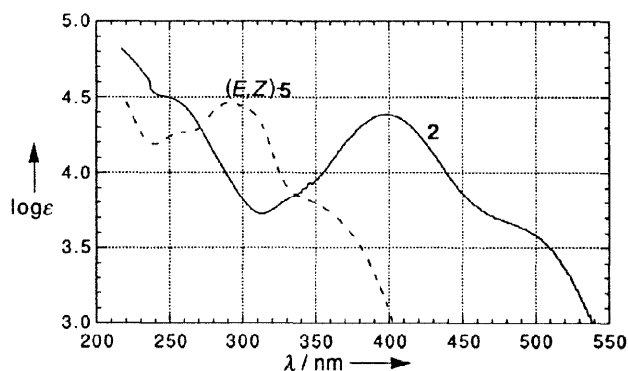


Figure 2. UV/Vis spectrum of **2** together with (*E,Z*)-**5** in hexane.

The reaction of (*E,E*)-**1** with *tert*-butyllithium followed by quenching with water gave a diastereomeric mixture of 1-*tert*-butyl-3-(2,4,6-tri-*tert*-butylphenylphosphinidene)-4-(2,4,6-tri-*tert*-butylphenylphosphino)-cyclobutene (**6**) in 41% yield,<sup>20</sup> suggesting that a nucleophilic attack of the *tert*-butyl group proceeded on the C=C bond under the reaction conditions. On the other hand, attempted reactions of (*E,E*)-**1** with methyllithium or phenyllithium, followed by quenching with iodine, failed to give a similar reaction product.

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17. Preparation of **2**: Under argon, a solution of 3,4-diphosphinidenecyclobutene (*E,E*)-**1** (49.9 mg, 82.8  $\mu$ mol) in THF (30 mL) was cooled at  $-78^{\circ}\text{C}$  and was allowed to react with *tert*-butyllithium (492  $\mu$ mol) for 10 min and the mixture was warmed to  $25^{\circ}\text{C}$  to give a dark-green solution. Into this solution was added iodine (30 mg) to give an orange solution. After removal of the solvent, the residue was chromatographed over silica-gel (hexane - ethyl acetate) to give 23.5 mg of **2** in 43% yield. **2**: Red plates; M.p.  $273.5\text{--}274^{\circ}\text{C}$  (decomp.); elemental analysis calcd for  $\text{C}_{88}\text{H}_{138}\text{P}_4$ : C 80.14, H 10.55; found: C, 79.60; H, 10.24%;  $^1\text{H}$  NMR (600 MHz,  $\text{THF-}d_8$ ,  $25^{\circ}\text{C}$ , TMS)  $\delta$  = 0.43 (s, 18H; 4,4'-*t*Bu), 1.29 (s, 18H; (*E*)-*p*-*t*Bu), 1.39 (s, 18H; (*Z*)-*p*-*t*Bu), 1.44 (s, 18H; (*E*)-*o*-*t*Bu), 1.50 (s, 18H; (*E*)-*o'*-*t*Bu), 1.73 (s, 18H; (*Z*)-*o*-*t*Bu), 1.81 (s, 18H; (*Z*)-*o'*-*t*Bu), 2.81 (d,  $^3J(\text{P,H})$  = 14.1 Hz, 2H; 1,1'-H), 3.43 (s, 2H; 4,4'-H), 7.27 (broad s, 4H; (*E*)-*m*-arom), 7.51 (d,  $^4J(\text{H,H})$  = 1.67 Hz, 2H; (*Z*)-*m*-arom), 7.56 (d,  $^4J(\text{H,H})$  = 1.64 Hz, 2H; (*Z*)-*m'*-arom);  $^{13}\text{C}$  NMR (150 Hz,  $\text{THF-}d_8$ ,  $25^{\circ}\text{C}$ , TMS)  $\delta$  = 29.9 (4,4'-CMe<sub>3</sub>), 32.7 ((*E*)-*p*-CMe<sub>3</sub>), 33.1 ((*Z*)-*p*-CMe<sub>3</sub>), 34.6 ((*Z*)-*o'*-CMe<sub>3</sub>), 35.0 ((*E*)-*o*-CMe<sub>3</sub>, (*Z*)-*o*-CMe<sub>3</sub>), 36.0 (4,4'-CMe<sub>3</sub>), 36.2 (d,  $^4J(\text{P,C})$  = 7.6 Hz; (*E*)-*o'*-CMe<sub>3</sub>), 36.5 ((*E*)-*p*-CMe<sub>3</sub>), 36.8 ((*Z*)-*p*-CMe<sub>3</sub>), 40.0 ((*Z*)-*o*-CMe<sub>3</sub>), 40.2 ((*E*)-*o*-CMe<sub>3</sub>), 40.3 ((*E*)-*o'*-CMe<sub>3</sub>, (*Z*)-*o'*-CMe<sub>3</sub>), 54.6 (d,  $^2J(\text{P,C})$  = 12.5 Hz; 4,4'-C), 66.0 (broad s; 1,1'-C), 123.48 ((*E*)-*m*-arom), 123.51 ((*E*)-*m'*-arom), 124.2 ((*Z*)-*m*-arom), 126.0 ((*Z*)-*m'*-arom), 140.0 (d,  $^1J(\text{P,C})$  = 37.7 Hz; (*Z*)-*ipso*-arom), 140.3 (d,  $^1J(\text{P,C})$  = 71.2 Hz; (*E*)-*ipso*-arom), 151.3 ((*E*)-*p*-arom), 151.7 ((*Z*)-*p*-arom), 154.7 (d,  $^2J(\text{P,C})$  = 4.6 Hz; (*Z*)-*o'*-arom), 155.1 (d,  $^2J(\text{P,C})$  = 4.6 Hz; (*Z*)-*o*-arom), 156.1 ((*E*)-*o*-arom), 156.3 ((*E*)-*o'*-arom), 183.7 (m, P=C), 189.7 (m, P=C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ , ext. 85%  $\text{H}_3\text{PO}_4$ ) (AA'XX')  $\delta_{\text{P}}\text{X} = \delta_{\text{P}}\text{X}' = 231.3$ ,  $\delta_{\text{P}}\text{A} = \delta_{\text{P}}\text{A}' = 277.8$ ,  $J(\text{A,A}') = 146.6$  Hz,  $J(\text{A,X}) = 149.2$  Hz,  $J(\text{A,X}') = 10.8$  Hz; UV/Vis (hexane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 253 (5.49, sh), 399 (5.38), 500 nm (3.59, sh); IR (KBr):  $\tilde{\nu}$  = 2956, 2904, 2870, 1591, 1475, 1394, 1362, 1240, 1209, 1126, 876, 750  $\text{cm}^{-1}$ ; FAB-MS:  $m/z$  (%) 1318 (61) [ $\text{M}^+$ ], 1 073 (84) [ $\text{M}^+ - \text{Ar}$ ], 684 (100) [ $\text{M}^+ - 2\text{Ar} - 2\text{tBu} - \text{P}$ ], 603 (52) [ $\text{Ar}_2\text{P}_2\text{C}_4\text{H}_2$ ].
18. Crystal data for **2**: Recrystallized from  $\text{CH}_2\text{Cl}_2$ .  $\text{C}_{88}\text{H}_{138}\text{P}_4$ ,  $M = 1319.95$ , triclinic,  $a = 16.165(3)$  Å,  $b = 25.516(4)$  Å,  $c = 10.995(5)$  Å,  $\alpha = 100.48(2)^{\circ}$ ,  $\beta = 91.67(3)^{\circ}$ ,  $\gamma = 101.53(1)^{\circ}$ ,  $V = 4359(2)$  Å<sup>3</sup>,  $P\bar{1}$ ,  $Z = 2$ ,  $T = 223$  K,  $D_c = 1.006$  g  $\text{cm}^{-3}$ ; 16366 reflections with  $2\theta \leq 50.0^{\circ}$  were recorded on a four-circle diffractometer using graphite-monochromated Mo-K $\alpha$  radiation. Of these, 7037 with  $I > 3\sigma(I)$  were judged as observed. The structure was solved using SIR92. The nonhydrogen atoms were refined anisotropically. The *p*-*t*Bu group of the Ar at P1 and that of the Ar at P3 and one of the two *o*-*t*Bu groups of the Ar at P3 were disordered and refined isotropically (occupancy factor for the dominants: 0.69, 0.70, and 0.79, respectively). Hydrogen atoms except for those on the disordered carbon atoms were included, but their positions were not refined.  $R = 0.080$ ,  $R_w = 0.096$ . Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EW, UK.
19. UV/Vis spectra were calculated with the ZINDO (Ver. 3.8) and the PM3 calculations were performed using the CAChe program package available from CAChe Scientific, Co. Ltd.
20. Preparation of **6**: To a THF (5 mL) solution of (*E,E*)-**1** (90 mg, 149  $\mu$ mol) was added 372  $\mu$ mol of *tert*-butyllithium at  $25^{\circ}\text{C}$ . The resulting green solution was stirred for 15 min, and then it was quenched with water. After the usual workup, **6** (41 mg) was obtained in 42% yield as a mixture of diastereomers in a ratio of 3 : 2. **6**: Pale yellow solid; M.p.  $140\text{--}145^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) major product:  $\delta$  = 0.22 (s, 9H; *t*Bu), 2.85 (d,  $^2J(\text{P,H})$  = 18 Hz, 1H; PHCH), 5.78 (d,  $^3J(\text{P,H})$  = 5 Hz, 1H; P=CCH), and 5.94 (d,  $^1J(\text{P,H})$  = 235 Hz, 1H; PH); minor product:  $\delta$  = 0.18 (s, 9H; *t*Bu), 2.87 (br s, 1H; PHCH), 5.72 (d,  $^3J(\text{P,H})$  = 5 Hz, 1H; P=CCH), and 5.79 (d,  $^1J(\text{P,H})$  = 234 Hz, 1H; PH);  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ) major product:  $\delta$  = 185.0 and  $-84.3$  (pseudo dd,  $^1J(\text{P,H})$  = 235 Hz,  $^2J(\text{P,H})$  = 18 Hz), AB,  $^3J(\text{P,P})$  = 16 Hz; minor product:  $\delta$  = 185.8 and  $-84.4$  (pseudo dd,  $^1J(\text{P,H})$  = 234 Hz,  $^2J(\text{P,H})$  = 19 Hz), AB,  $^3J(\text{P,P})$  = 37 Hz; MS (70 eV)  $m/z$  (%) 660 (21) [ $\text{M}^+$ ], 603 (25) [ $\text{M}^+ - \text{tBu}$ ], 547 (25) [ $\text{M}^+ - 2\text{tBu} + 1$ ], 415 (26) [ $\text{M}^+ - \text{Ar}$ ], 383 (27) [ $\text{M}^+ - \text{ArPH}$ ], 277 (16) [ $\text{ArPH}^+$ ], 275 (24) [ $\text{ArP}^+ - 1$ ], 261 (12) [ $\text{ArP}^+ - \text{Me}$ ], and 57 (100) [*t*Bu<sup>+</sup>]. Found:  $m/z$  660.4956. Calcd for  $\text{C}_{44}\text{H}_{70}\text{P}_2$ :  $M$ , 660.4952.