

The Existence of Two Short-Bond Isomers for Bicyclo[1.1.0]butane Derivatives Based on Boron and Phosphorus**

Vincent Gandon, Jean-Baptiste Bourg, Fook S. Tham, Wolfgang W. Schoeller,* and Guy Bertrand*

Inorganic bicyclo[1.1.0]butane^[1] derivatives have attracted considerable interest, particularly because they were identified as candidates for a very rare type of isomerism, namely bond-stretch isomerism.^[2,3] The existence of long- and short-bond isomers has been predicted by calculations for silicon-containing bicyclo[1.1.0]butanes,^[4] depending on the number of silicon centers, either the long-bond^[5] isomer **A** or short-bond^[6] isomer **A'** was isolated (Figure 1). The extreme case

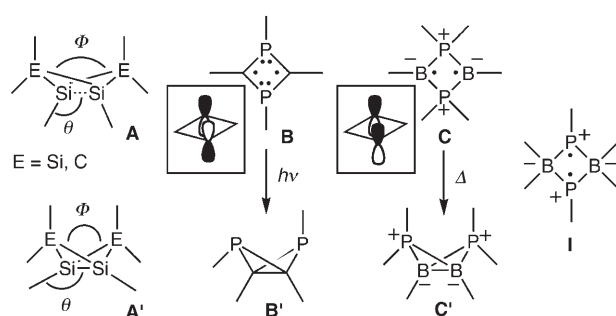


Figure 1. Schematic representation of long-bond isomers **A–C** and short-bond isomers **A'–C'**, and target diradical **I**.

for bond-stretch isomerism is reached when the long-bond isomer is a singlet diradical. In the carbon series, cyclobutane-2,4-diyls are predicted to be only transition states in the inversion of bicyclo[1.1.0]butanes.^[7,8] However, inorganic four-membered heterocyclic diradicals,^[9,10] which include structures **B**^[11] and **C**^[12] (Figure 1) have been isolated. Compounds of the form **B** have a transannular antibonding π overlap, which prevents the thermal disrotatory ring closure to the bicyclo[1.1.0]butane isomers **B'**; the latter can however be obtained by photolytic excitation.^[11c] Derivatives of type **C** feature a transannular bonding π overlap, and depending on

the nature of the phosphorus and boron substituents, **C** and **C'** can either coexist in solution,^[12d] or one of them can be isolated.^[12] Although the bond-stretch isomerism relationship **C/C'** is not arguable, the diradical nature of **C** has been questioned.^[13] In particular, for compound **C1** (*t*Bu at B, and *i*Pr at P), the HOMO and LUMO occupation numbers were calculated to be 1.83 and 0.17, respectively, leading Head-Gordon et al.^[13c] to conclude that **C1** should only be considered a “diradicaloid”.

This comment prompted us to design compounds with two unpaired electrons, each of which occupies two degenerate or nearly degenerate molecular orbitals. Herein we report our calculations concerning the parent diradical of type **I**, which is related to **C** by inverting the role played by the phosphorus and boron moieties. We show that **I** is a true diradical, and consequently should not have one but two short-bond isomers **I'** and **I''**. We also describe the synthesis, single crystal X-ray diffraction data, and reactivity of the first representative of a bicyclo[1.1.0]butane derivative of type **I'**.

We computationally studied the parent (H_2BPH)₂ diradical **I** at the CAS(10,10)/6-311++g** level of theory.^[14] Diradical **I** is planar with a very long P...P distance of 2.637 Å, which indicates the absence of a bonding interaction (Figure 2). In contrast to the parent diradical **C** (ΔE_{ST} =

	I	I'	I''	II
P–P [Å]	2.637	2.355	2.334	2.216
Φ [°]	180	147	180	—
Θ [°]	180	94	95	—
E [kcal. mol ^{−1}]	0	−58.3	−49.4	−48.1

Figure 2. Optimized geometry and relative energy of the parent diradical **I**, *cis*- and *trans*-bicyclo[1.1.0]butanes **I'** and **I''**, and 1,2-diboryldiphosphane **II** (B black, P gray, H white).

−21.7 kcal mol^{−1}), **I** has a negligible singlet–triplet energy gap (1.2 kcal mol^{−1} in favor of the singlet state). This implies that the occupation number of both the HOMO and the LUMO is almost 1, and therefore **I** would be a perfect diradical. However, as in the case of the parent diradical **C**, **I** is not an energy minimum on the potential energy surface, and ring closures can occur with no energy barriers. This is mainly due to the phosphorus atoms, which exert strong pyramidalization forces. Since **I** is a perfect diradical, two different bicyclo[1.1.0]butane derivatives **I'** and **I''** can be formed by disrotatory and conrotatory ring closures. Compound **I'** refers

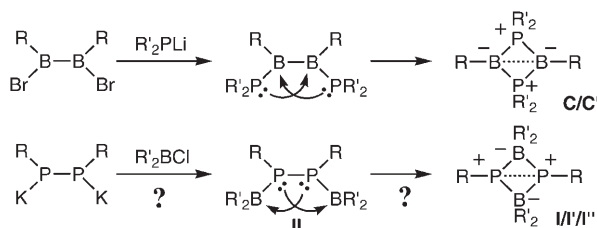
[*] Dr. V. Gandon, Dr. J.-B. Bourg, Dr. F. S. Tham, Prof. W. W. Schoeller, Prof. G. Bertrand
UCR–CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: wolfgang.schoeller@ucr.edu
guy.bertrand@ucr.edu
Homepage: <http://research.chem.ucr.edu/groups/bertrand/guy-bertrandwebpage/>

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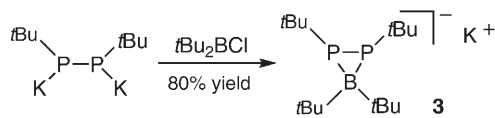
to the *cis* isomer and is folded, as expected for a bicyclo-[1.1.0]butane structure; it was found to be 58.3 kcal mol⁻¹ lower in energy than **I**. More surprising is the geometry of the *trans* isomer **I'**, which adopts a *C*_{2h} symmetry with a very unusual planar PBPB skeleton. The latter resembles diradical **I**, but the phosphorus atoms are strongly pyramidalized, and the phosphorus–phosphorus distance is in the usual range for a P–P single bond (2.355 Å). Derivative **I'** was calculated to be 8.9 kcal mol⁻¹ higher in energy than the *cis* isomer **I**. To complete our study, we also investigated the 1,2-diboryldiphosphane **II**, and found that it was the least stable isomer. The geometric parameters show no interaction between the phosphorus lone pairs and the boron vacant orbitals; the phosphorus atoms are strongly pyramidalized and the phosphorus–boron distances long.

As derivatives **C/C'** were prepared by valence isomerization of 1,2-diphosphino-1,2-diboranes,^[12] and as the butadiene valence isomer **II** was calculated to be higher in energy than **I/I'**, it seemed reasonable to expect that 1,2-diboryl-1,2-diphosphanes would similarly undergo an isomerization into the target compounds (Scheme 1). Aiming at introducing



Scheme 1. Valence isomerization as a synthetic strategy.

bulky groups around the BPBP core, 1,2-dipotassium-1,2-di(*tert*-butyl)diphosphane^[15] was chosen as a starting material, and was treated with two equivalents of chlorodi(*tert*-butyl)borane. A clean reaction occurred, but the spectroscopic data of the resulting compound **3** revealed the presence of two equivalent phosphorus and only one boron nucleus (Scheme 2). The upfield ³¹P ($\delta = -73$ ppm) and ¹¹B NMR



Scheme 2. Reaction of a bulky chloroborane with a sterically hindered diphosphide leading to **3**.

($\delta = +14$ ppm) chemical shifts were consistent with a three-membered-ring structure with a tetracoordinated boron atom. A single-crystal X-ray diffraction study^[16] of compound **3** confirmed our hypothesis; noteworthy is the extremely long phosphorus–boron distance (2.04 Å) (Figure 3).

Even under forcing conditions, we have not been able to introduce a second di(*tert*-butyl)boryl group to **3**. As the excessive steric bulk seemed to be the obstacle, we gradually decreased the size of the substituents at boron, then at

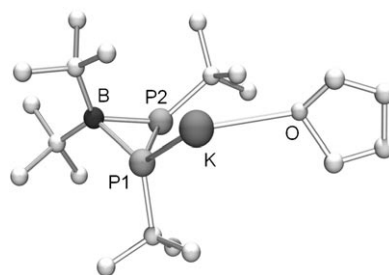
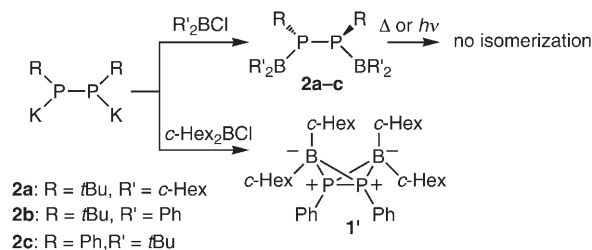


Figure 3. Molecular structure of **3** in the solid state (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.1467(7), P2–B 2.044(2), B–P1 2.042(2), P1–K 3.3039(7); P1–B–P2 63.39(7), P2–P1–B 58.35(6), P1–P2–B 58.26(6).

phosphorus. The addition of dicyclohexyl- and chlorodiphenylborane to 1,2-dipotassium-1,2-di(*tert*-butyl)diphosphane, and of chlorodi(*tert*-butyl)borane to 1,2-dipotassium-1,2-diphenyldiphosphane,^[17] led to **2a**, **2b**, and **2c**, which were isolated in 59, 60, and 55 % yield, respectively, as extremely air-sensitive but thermally stable crystals (Scheme 3). The



Scheme 3. Preparation of 1,2-diboryl-1,2-diphosphanes **2a–c**, and 2,4-diborata-1,3-diphosphonio[1.1.0]bicyclobutane **1'**. *c*-Hex = cyclohexyl.

³¹P NMR (**2a**: $\delta = -3.6$; **2b**: -5.4 ; **2c**: -23.7 ppm) and ¹¹B NMR (**2a**: $\delta = +77$; **2b**: $+77$; **2c**: $+87$ ppm) chemical shifts are found relatively downfield, which suggests the formation of 1,2-diphosphino-1,2-diboranes. In marked contrast with the related derivatives reported by Power et al,^[18] with mesityl groups at boron and a 1-adamantyl or a mesityl substituent at phosphorus, X-ray diffraction studies showed that compounds **2a–c** do not have butadiene-like structures (Figure 4).

Interestingly, along the series **2a–2b–2c**, there is a lengthening of phosphorus–boron distances (1.89–1.90–1.93 Å), and a pyramidalization of the phosphorus centers ($\Sigma^{\circ}_{\text{P}} = 341$ –335–328°), which indicate decreasing interactions between the phosphorus and boron in the α position. Consequently, the phosphorus and boron centers should be more nucleophilic and electrophilic, respectively, which should favor the desired 1,3-interactions and thus the formation of compounds of types **I/I'**. However, all attempts to thermally (benzene, reflux, 12 h) and photochemically (254 nm) induce the rearrangement of these compounds failed. The size of the boron substituents was decreased further, and when two equivalents of chlorodicyclohexylborane were added to 1,2-dipotassium-1,2-diphenyldiphosphane, a new compound **1'** was isolated in 54 % yield (Scheme 3). The 2,4-diborata-1,3-diphosphonio-

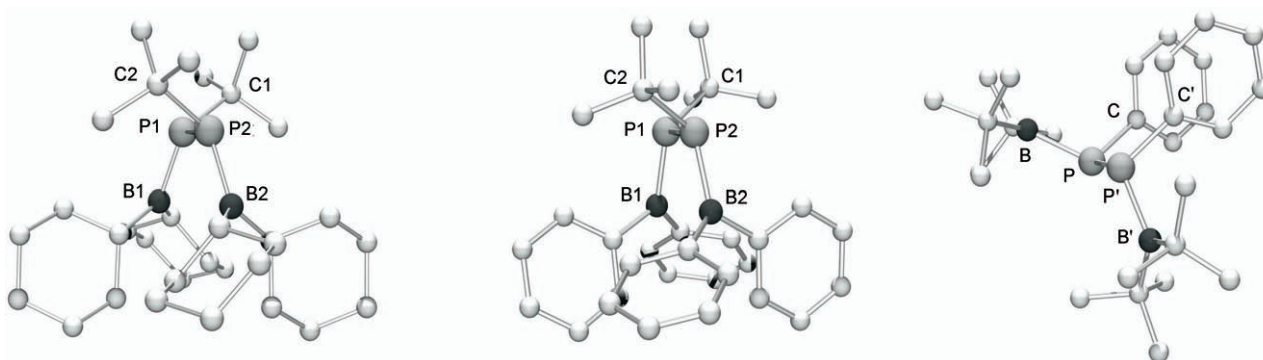


Figure 4. Molecular structures of **2a** (left), **2b** (center), and **2c** (right) in the solid state (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: **2a** P1-B1 1.886(2), P1-P2 2.1462(8), P2-B2 1.883(2); B1-P1-C1 117.88(10); B1-P1-P2 114.90(7), P2-P1-C1 108.47(7). **2b** P1-B1 1.8980(15), P1-P2 2.1641(5), P2-B2 1.9023(15); B1-P1-C1 117.23(6); B1-P1-P2 107.95(5), P2-P1-C1 110.14(5). **2c** P-B 1.9252(15), P-P' 2.2088(6); B-P-C 107.79(6); B-P-P' 116.14(5); P'-P-C 104.34(5).

[1.1.0]bicyclobutane structure with bridging phosphorus atoms and tetracoordinated boron centers was suggested by the upfield ^{31}P ($\delta = -106$ ppm) and ^{11}B NMR chemical shifts ($\delta = +37$ ppm), respectively. A single crystal X-ray diffraction study confirmed this hypothesis and revealed a *cis* butterfly structure (Figure 5).

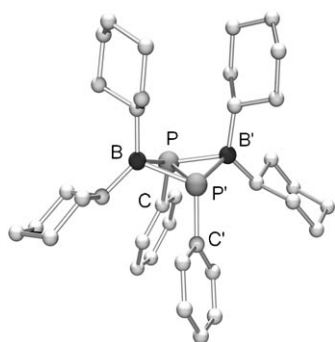
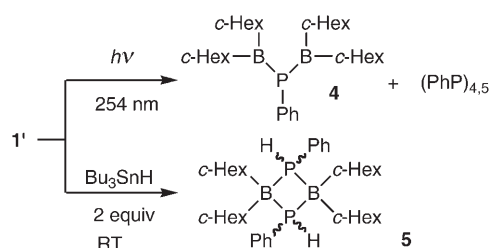


Figure 5. Molecular structure of **1'** in the solid state (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P-B 2.0273(18), P-B' 2.0625(19), P-P' 2.2817(9); P-B-P' 67.81(6); B-P-B' 104.83(7), B-P-C 120.35(7), B'-P-C 111.50(7), P'-P-C 111.81(5).

The bridging phosphorus–phosphorus bond length observed for **1'** (2.28 Å) is not very much longer than usual phosphorus–phosphorus single bonds. In that respect, this compound is similar to the short-bond isomers of type **A'**^[6] (where the central bond is only about 0.05 Å longer than a standard silicon–silicon bond). However, in contrast to the short-bond isomers **A'** (Θ : 137–150°; Φ : 128–134°) but similar to the long-bond isomers **A** (Θ : 92–110°; Φ : 142–145°)^[5] (Figure 1), derivative **1'** features a small Θ angle (112°) and a large interflap angle ($\Phi = 145^\circ$). These geometric parameters are very similar to those calculated for the parent derivative **I'**, showing that they are inherent to the B_2P_2 core and not due to substituent effects.

Interestingly, in the ^{13}C NMR spectra, the signals corresponding to the cyclohexyl carbon atoms bonded to boron coalesce at about -30°C , which corresponds to a free energy of activation for the inversion of the bicyclo[1.1.0]butane **1'** of 11.6 kcal mol $^{-1}$. This value is about one fourth that of the all-carbon analogue.^[7] Since the transition state for the ring flip is obviously the corresponding diradical of type **I**, these data suggested that **1'** might behave as a diradical under thermal or photochemical excitation. We found that under UV irradiation, **1'** undergoes a fragmentation into a phosphinodiborane **4** and phenylphosphinidene, which oligomerizes into $(\text{PhP})_{4,5}$. More striking is the spontaneous formation at room temperature of the four-membered heterocycle **5** as a mixture of *cis* and *trans* isomers upon addition of two equivalents of tributyltin hydride (Scheme 4).



Scheme 4. Photolytic fragmentation, and reaction of **1'** with tributyltin hydride. *c*-Hex = cyclohexyl.

These results show that compound **I**, which is related to **C** by simply inverting the role played by the phosphorus and boron moieties, is a true diradical. Consequently, two different bicyclo[1.1.0]butane derivatives **I'** and **I''** can be formed by disrotatory and conrotatory ring closures. The *cis* isomer was experimentally obtained by valence isomerization of a 1,2-diboryl-1,2-diphosphane. We are currently investigating the possibility of synthesizing the second short-bond stretch isomer, namely the *trans* bicyclo[1.1.0] butane of type **I''**,

which is predicted to feature a very unusual planar geometry, with a short phosphorus–phosphorus bond.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Complete spectroscopic data for all new compounds are available in the Supporting Information.

3: Neat chlorodi(*tert*-butyl)borane (4 mmol) was added dropwise at -78°C to a suspension of 1,2-dipotassium-1,2-di(*tert*-butyl)diphosphane (4 mmol) in THF (40 mL). The mixture was stirred at room temperature for 2 h, and the solvent was removed under vacuum. Addition of hexane to the resulting dark oil led to a precipitate, which was washed several times with hexane. The resulting white solid was extracted into diethyl ether. Addition of hexane to the ether solution resulted in an oil that crystallizes within 5 min at room temperature, affording **3** as colorless crystals in 80% yield. M.p. 220°C (decomp).

General procedure for **2a–c**: A hexane solution of chlorodialkylborane (1M, 4 mL) was added dropwise at room temperature to a suspension of diphosphide (2 mmol) in 30 mL of hexane. The mixture was stirred for 1 h. The solids were removed by filtration and washed with hexane (3×5 mL). The filtrate was concentrated to about 4 mL and the product crystallized at -20°C . **2a**: Colorless needles (59% yield); m.p. 164 – 166°C . **2b**: Yellow crystals (60% yield); m.p. 152°C . **2c**: Yellow prisms (55% yield); m.p. 128 – 136°C . Synthesis of **1'**: Using the same procedure as for **2a–c**, **1'** was obtained as colorless prisms in 54% yield. m.p. 118 – 120°C ; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): $\delta = 105.8$ ppm; ^{11}B NMR (160.5 MHz, C_6D_6): $\delta = 37$ ppm; ^1H NMR (300.1 MHz, C_6D_6): $\delta = 1.10$ – 1.90 (m, 22H), 6.88–7.05 (m, 6H), 7.15–7.20 ppm (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, C_6D_6): $\delta = 27.9$, 29.7, 34.6 (broad), 35.7 (broad), 130.4, 131.3 (t, $J_{\text{PC}} = 15.0$ Hz), 136.6 ppm.

Photolysis of **1'**: Compound **1'** (570 mg, 1 mmol) was dissolved in hexane (40 mL) in a quartz Schlenk tube. The solution was photolyzed (254 nm) at room temperature overnight. $(\text{PhP})_{4,5}$ were characterized in solution by ^{31}P NMR spectroscopy. The solution was then filtered and concentrated to 3 mL. After one week at -20°C , colorless needles of **4** were obtained (65% yield). M.p. 146 – 152°C .

5: Tributyltin hydride (2 mmol) was added dropwise at -20°C to a solution of **1'** (570 mg, 1 mmol) in hexane (10 mL). The mixture was then stirred at room temperature for 4 h. The white precipitate was collected by filtration, washed with hexane, and dried under vacuum, affording **5** (1:4 mixture of *cis* and *trans* isomers) as a white powder in 80% yield.

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