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Thermal Valence Isomerization of 2,3-Diborata-1,4-diphosphoniabuta-1,3-dienes to Bicyclo[1.1.0]butanes and Cyclobutane-1,3-diyls**

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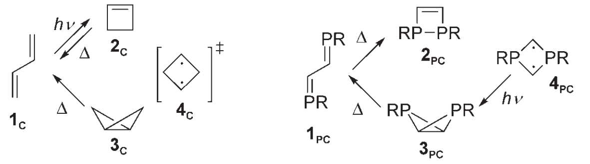
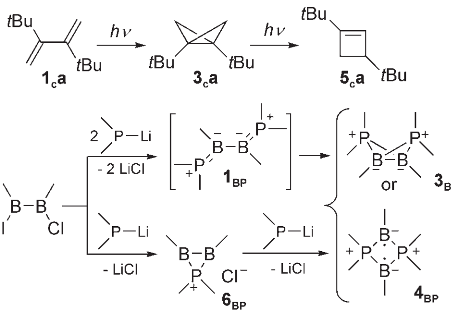
In his Nobel lecture entitled "Bridges between Inorganic and Organic Chemistry", Hoffmann concluded: "The isolobal analogy is a model. It is the duty of our scientific craft to push it to its extremes, and being only a model it is certain to fail somewhere".[1] Comparison of the relative stabilities and the interconversions of the different valence isomers of butadiene (C_4H_6) with those of its isolobal analogues provides a good demonstration of Hoffmann's conclusions. In carbon chemistry, s-*trans*-buta-1,3-diene ($\mathbf{1_C}$) is the most stable valence isomer, cyclobutene ($\mathbf{2_C}$) and bicyclo[1.1.0]butane ($\mathbf{3_C}$) being 14.8 and 31.1 kcal mol^{-1} higher in energy, respectively (Scheme 1, left).[2] The singlet cyclobutane-1,3-diyl ($\mathbf{4_C}$) was predicted only as a transition state for the inversion of $\mathbf{3_C}$.[3,4] The interconversion of these different valence isomers $\mathbf{1_C}$–$\mathbf{4_C}$ has been studied extensively, both experimentally and theoretically.[5] It has been found that the thermolyses of both $\mathbf{2_C}$[5a–c] and $\mathbf{3_C}$[5d,e] lead to butadiene $\mathbf{1_C}$, the photolysis of which gives back $\mathbf{2_C}$.[5f–h] When some or all of the carbon atoms of the backbone are replaced by heavier elements, the order of stability of the valence isomers and their modes of interconversion may be either similar or very different.[6] For example, it has been shown that 1,4-diphosphabutadienes $\mathbf{1_{PC}}$ can undergo a ring closure to form $\mathbf{2_{PC}}$,[7] but only thermally (Scheme 1, right). Moreover, diradicals $\mathbf{4_{PC}}$ are not only a minimum on the potential energy surface, but can even be isolated, provided they have the right set of substituents.[8] Photolysis of $\mathbf{4_{PC}}$ affords the bicyclic derivatives $\mathbf{3_{PC}}$, from which subsequent thermolysis gives butadienes $\mathbf{1_{PC}}$.[8c]



Scheme 1. Known valence isomerizations of singlet C_4H_6 (left) and of $P_2C_2R_4$ derivatives (right).

Most of the possible interconversions between isomers **1**–**4** have been observed for systems with various heteroatoms.[5–8] However, there is only one example of a photochemical isomerization of a butadiene ($\mathbf{1_Ca}$) into a bicyclo[1.1.0]butane ($\mathbf{3_Ca}$; Scheme 2, top)[9,10] and no definitive evidence for this process under thermal conditions.[11] This situation prompted us to study in detail the mechanism of formation of 1,3-diborata-2,4-diphosphoniabicyclo-[1.1.0]butanes $\mathbf{3_{BP}}$ and 1,3-diborata-2,4-diphosphoniacyclobutane-1,3-diyls $\mathbf{4_{BP}}$.[12,13] We postulated the involvement of transient 2,3-diborata-1,4-diphosphoniabuta-1,3-dienes $\mathbf{1_{BP}}$ (Scheme 2, bottom). However, a second pathway via a cationic three-membered heterocycle $\mathbf{6_{BP}}$ could also explain the formation of $\mathbf{3_{BP}}$ and $\mathbf{4_{BP}}$.



Scheme 2. Photochemical isomerizations of butadiene $\mathbf{1_Ca}$ (top), and two possible mechanisms for the formation of bicyclo[1.1.0]butanes $\mathbf{3_{BP}}$ and/or butane-1,3-diyls $\mathbf{4_{BP}}$ (bottom).

Herein, we report the synthesis and single-crystal X-ray diffraction study of a derivative of type $\mathbf{1_{BP}}$, and its thermal valence isomerization into the corresponding bicyclic derivative $\mathbf{3_{BP}}$. Strong evidence that butadienes $\mathbf{1_{BP}}$ can also isomerize thermally into diradicals $\mathbf{4_{BP}}$ is presented. Moreover, it is shown that, under photolytic activation, heterobicyclo[1.1.0]butanes $\mathbf{3_{BP}}$ undergo a ring-opening reaction accompanied by a 1,2-shift, a process similar to that observed for the all-carbon analogue $\mathbf{3_Ca}$.[9]

To probe the putative formation of a three-membered BBP heterocycle of type $\mathbf{6_{BP}}$, we first treated 1,2-di-*tert*-butyl-1,2-dichlorodiborane with one equivalent of lithium diphe-

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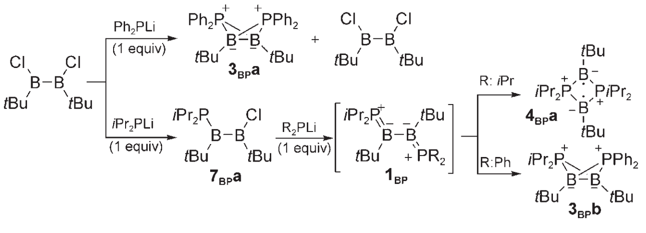
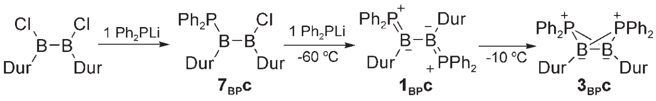
nylphosphide at −60 °C (Scheme 3). However, only the bicyclic compound $\mathbf{3_{BP}a}$ was formed,[12b] and an equimolar amount of the starting diborane remained. In the hope of preventing the addition of the second phosphide group, the bulkier diisopropylphosphide was used. A clean reaction occurred, and derivative $\mathbf{7_{BP}a}$ was isolated as a yellow oil in 93 % yield. The nonsymmetrical and acyclic structure of $\mathbf{7_{BP}a}$ was apparent from the presence of two signals in the ^{11}B NMR spectrum ($\delta = 93$, 63 ppm) and from the rather low-field position of the signal in the ^{31}P NMR spectrum ($\delta =$ 50 ppm).[14] Addition of one equivalent of lithium diisopropylphosphide to $\mathbf{7_{BP}a}$ gives rise to the known diradical $\mathbf{4_{BP}a}$ (68 % yield).[12a] Monitoring the reaction by ^{31}P NMR spectroscopy did not allow the observation of any intermediate. Hypothesizing that the presence of a less basic phosphine fragment might slow down the valence isomerization of the putative butadiene intermediate of type $\mathbf{1_{BP}}$, we added lithium diphenylphosphide to $\mathbf{7_{BP}a}$. This experiment also did not allow the detection any intermediate and led to the unsymmetrically substituted bicyclic compound $\mathbf{3_{BP}b}$ (69 % yield).



Scheme 3. Synthesis of bicyclo[1.1.0]butane $\mathbf{3_{BP}a}$, and syntheses of butane-1,3-diyl $\mathbf{4_{BP}a}$ and bicyclo[1.1.0]butane $\mathbf{3_{BP}b}$ via transient butadienes of type $\mathbf{1_{BP}}$.

In the hope of crystallizing a phosphinodiborane of type $\mathbf{7_{BP}}$, we replaced the *tert*-butyl groups by duryl groups (Dur = 2,3,5,6-tetramethylphenyl). One equivalent of lithium diphenylphosphide was added to 1,2-diduryl-1,2-dichlorodiborane at −78 °C, and 1-chloro-2-phosphinodiborane $\mathbf{7_{BP}c}$ was isolated as yellow crystals in 62 % yield (Scheme 4). An X-ray diffraction analysis[15] showed that the phosphorus center has a slightly pyramidalized environment (sum of the angles = 343.1°) and that the B1–P1 distance (1.845(2) Å) is halfway between those of a single and a double bond (Figure 1, left).[16] This geometry indicates that the lone pair of the phosphorus atom interacts to some extent with the vacant orbital of the adjacent boron atom. The phosphorus lone pair is therefore not available to attack the second boron center to induce ring closure into a three-membered heterocycle of type $\mathbf{6_{BP}}$.



Scheme 4. Synthesis of diborane $\mathbf{7_{BP}c}$ and butadiene $\mathbf{1_{BP}c}$, and valence isomerization of $\mathbf{1_{BP}c}$ into bicyclo[1.1.0]butane $\mathbf{3_{BP}c}$.

Monitoring the reaction of one equivalent of lithium diphenylphosphide with $\mathbf{7_{BP}c}$ at −60 °C, or of two equivalents with the dichlorodiborane at −60 °C, we observed the formation of a new species. Importantly, only one signal was observed both in the ^{31}P NMR ($\delta = 12$ ppm) and the ^{11}B NMR ($\delta = 76$ ppm) spectra, suggesting a symmetrical structure. These signals disappeared in a few minutes at −10 °C and were replaced by ^{31}P NMR ($\delta = -51$ ppm) and ^{11}B NMR ($\delta =$ −13 ppm) signals in the range expected for the bicyclic derivative $\mathbf{3_{BP}c}$. After work up, $\mathbf{3_{BP}c}$ was obtained as yellow crystals in 66 % yield and was characterized by X-ray diffraction (Figure 1, right).[15] These results prompted us to further investigate the structure of the intermediate detected by NMR spectroscopy, and we were fortunate to obtain single crystals by recrystallization at −40 °C. The X-ray diffraction

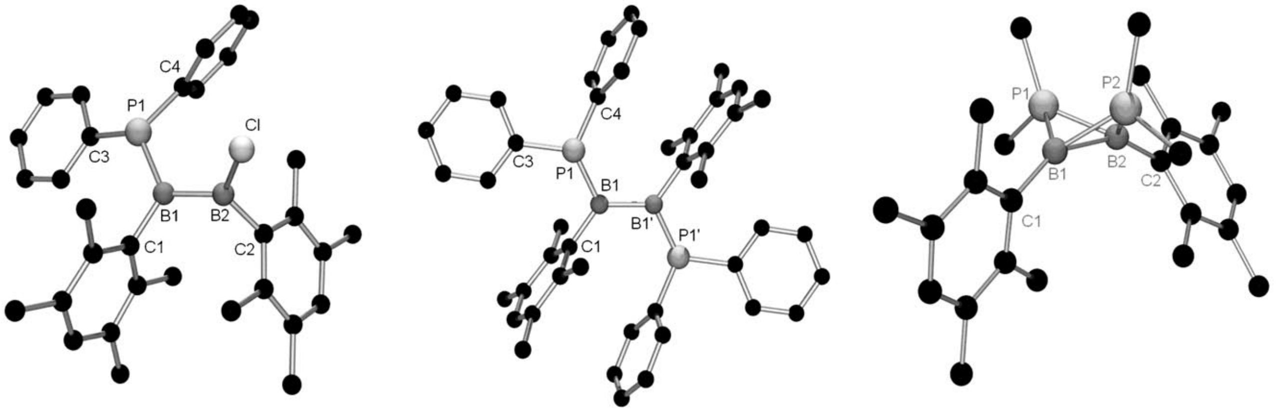
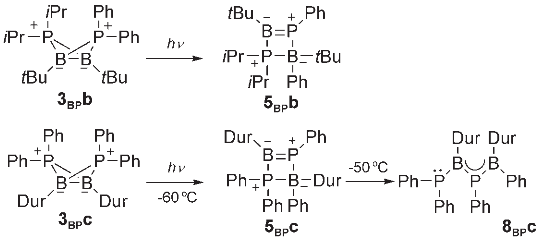


Figure 1. Molecular structure of $\mathbf{7_{BP}c}$ in the solid state (left; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–B1 1.845(2), B1–B2 1.687(3); B1-P1-C4 115.78(9), B1-P1-C3 119.83(10), C4-P1-C3 107.48(9), P1-B1-B2 119.85(15), P1-B1-C1 121.21(14), B2-B1-C1 118.65(16), B1-B2-Cl 119.86(15), B1-B2-C2 121.57(17), Cl-B2-C2 118.50(15). Molecular structure of $\mathbf{1_{BP}c}$ in the solid state (center; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–B1 1.8346(16), B1–B1′ 1.712 (3); B1-P1-C4 121.73(6), B1-P1-C3 121.69(7), C4-P1-C3 107.15(7), P1-B1-B1′ 117.03(12), P1-B1-C1 116.08(9), B1′-B1-C1 126.44(15). Molecular structure of $\mathbf{3_{BP}c}$ in the solid state (right; hydrogen atoms and noncoordinated atoms of the phenyl groups on the phosphorus atoms are omitted for clarity). Selected bond lengths [Å]: B1–B2 1.971(2), B1–P1 1.8874(15), B1–P2 1.8858(15), B2–P1 1.8819(16), B2–P2 1.8870(16).

analysis[15] showed that the intermediate corresponds to the planar butadiene $\mathbf{1_{BP}c}$ with an s-*trans* conformation (Figure 1, center).[17,18] The B1–P1 bond length (1.8346(16) Å) and the environment around the phosphorus centers (sum of the angles: 350.1°) are similar to those observed for $\mathbf{7_{BP}c}$.

The thermal rearrangement of $\mathbf{1_{BP}c} \rightarrow \mathbf{3_{BP}c}$ (Scheme 4), is opposite to that observed for the parent hydrocarbon ($\mathbf{3_C} \rightarrow \mathbf{1_C}$) and the PCPC system ($\mathbf{3_{PC}} \rightarrow \mathbf{1_{PC}}$; Scheme 1). However, the rearrangement is analogous to that reported for sterically hindered carbon skeletons ($\mathbf{1_C a} \rightarrow \mathbf{3_C a}$; Scheme 2, top), in which case it was photochemically induced. To extend these comparisons, we investigated the photochemical behavior of $\mathbf{3_{BP}b}$ and $\mathbf{3_{BP}c}$.

Upon irradiation at $\lambda = 254$ nm, $\mathbf{3_{BP}b}$ was quantitatively converted into $\mathbf{5_{BP}b}$ after 2 h at room temperature in toluene solution (Scheme 5). The cleavage of the B–B bond and the 1,2-shift of a phenyl group from phosphorus to boron were indicated by the spectroscopic data and confirmed by an X-ray diffraction analysis (Figure 2).[15] Notably, $\mathbf{5_{BP}b}$ is obtained as a single regioisomer; the migration selectively involves a phenyl ring rather than an isopropyl group. The four-membered ring of $\mathbf{5_{BP}b}$ is perfectly planar. The short P2–B1 bond length (1.795(8) Å) and the planar environment at P2 (sum of the angles = 360°) are indicative of a double bond. These geometric parameters suggest that $\mathbf{5_{BP}b}$ is a hetero analogue of $\mathbf{5_C a}$. A similar rearrangement was observed upon irradiation of $\mathbf{3_{BP}c}$, but the resulting four-membered ring $\mathbf{5_{BP}c}$ could only be characterized at low temperature. It quickly rearranges into the acyclic product $\mathbf{8_{BP}c}$, which features an allylic 2-π-electron, rather than a butadiene 4-π-electron structure. Indeed, as shown by X-ray diffraction,[15] the internal phosphorus atom P1 has a planar environment (sum of the angles = 359°), while the environment of the terminal phosphorus atom P2 is strongly pyramidalized (sum of the angles = 317°; Figure 3). The instability of $\mathbf{5_{BP}c}$ relative to $\mathbf{5_{BP}b}$ probably results from the weaker basicity of the diphenylphosphine fragment relative to the diisopropylphosphine fragment.



Scheme 5. Photochemical isomerizations of bicyclo[1.1.0]butanes $\mathbf{3_{BP}b}$ and $\mathbf{3_{BP}c}$.

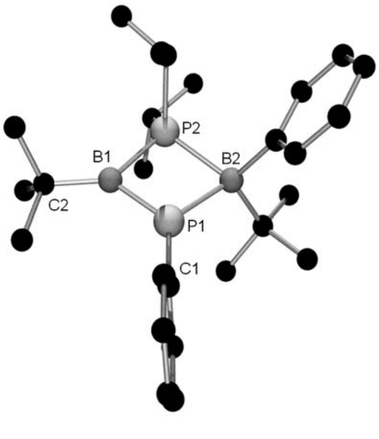


Figure 2. Molecular structure of $\mathbf{5_{BP}b}$ in the solid state (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–B1 1.795(8), P1–B2 2.014(7), P2–B1 1.949(8), P2–B2 2.053(7); B1-P1-B2 99.8(3), B1-P1-C1 128.4(3), B2-P1-C1 131.8(3), P1-B1-P2 87.2 (4), P1-B1-C2 136.1(5), P2-B1-C2 136.7(5), B1-P2-B2 93.6(3), P1-B2-P2 87.2(4).

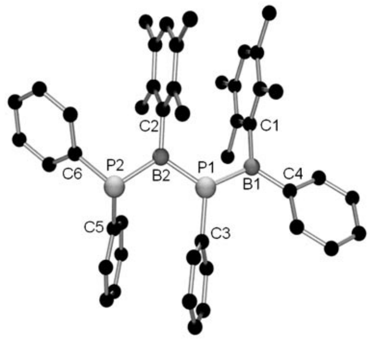


Figure 3. Molecular structure of $\mathbf{8_{BP}c}$ in the solid state (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–B1 1.863(7), P1–B2 1.866(7), P2–B2 1.911(8); B1-P1-B2 124.5(3), B1-P1-C3 118.6(3), B2-P1-C3 116.8(3), B2-P2-C5 106.7(3), B2-P2-C6 105.8(3), C5-P2-C6 104.5(3), P1-B1-C4 124.2(5), P1-B1-C1 115.7(5), C4-B1-C1 120.0(6), P1-B2-P2 116.1(4), P1-B2-C2 120.3(5), P2-B2-C2 122.2(5).

These results as a whole highlight the analogies and dichotomies in the interconversion between the valence isomers of various butadienes and heterobutadienes. Surprisingly, the closest analogue of the inorganic PBPB system is an all-carbon butadiene bearing bulky substituents. These are the only known systems in which an isolated butadiene valence isomerizes into a bicyclo[1.1.0]butane, although in the all-carbon case, the rearrangement is photochemically induced. Both bicyclo[1.1.0]butane systems rearrange under photolytic conditions into a cyclobutene isomer. Note also that, unlike for most known stable diradicals,[19,20] but as for cyclobutane-1,3-diyls, the ring closure of BPBP diradicals $\mathbf{4_{BP}}$ into their bicyclic isomers $\mathbf{3_{BP}}$ is thermally allowed. Accordingly, the substituents at the phosphorus and boron atoms strongly influence the ground-state structure of these compounds. Thus, the diradical $\mathbf{4_{BP}a}$ or the bicyclic compound $\mathbf{3_{BP}b}$ are formed depending on the phosphide used (Scheme 3).[12b] This result suggests that the BPBP diradical $\mathbf{4_{BP}a}$ results from the thermal rearrangement of the corresponding transient butadiene $\mathbf{1_{BP}}$, which is a type of valence isomerization that has no precedent.

Experimental Section

$\mathbf{7_{BP}c}$: A solution of Ph_2PLi (0.53 g, 2.8 mmol) in THF (10 mL) was added to a solution of 1,2-diduryl-1,2-dichlorodiborane (1.0 g, 2.8 mmol) in toluene (10 mL) at −78 °C. The volatiles were removed under vacuum at 0 °C, the residue was dissolved in hexane, and the salts were removed by filtration. Yellow crystals of $\mathbf{7_{BP}c}$ were obtained from a concentrated hexane solution at −30 °C (0.88 g, 62 % yield). M.p. 127–128 °C (dec.); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ = 17.2 ppm; ^{11}B{^{1}H} NMR (96.3 MHz, CDCl$_3$): δ = 81, 56 ppm.

$\mathbf{1_{BP}c}$: A solution of Ph$_2$PLi (0.11 g, 0.56 mmol) in [D$_8$]THF (0.8 mL) was added to 1,2-diduryl-1,2-dichlorodiborane (0.10 g, 0.28 mmol) at −78 °C. The reaction mixture was stirred for 10 min at −78 °C. Multinuclear NMR spectroscopy indicated the quantitative formation of $\mathbf{1_{BP}c}$. Red crystals suitable for a single-crystal X-ray diffraction study were obtained from a concentrated THF solution at −40 °C. ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF): δ = 12 ppm; ^{11}B{^{1}H} NMR (96.3 MHz, [D$_8$]THF): δ = 76 ppm.

$\mathbf{3_{BP}c}$: When a [D$_8$]THF solution of $\mathbf{1_{BP}c}$, prepared as described above, was warmed to −10 °C, the color changed from red to yellow. The volatiles were removed under reduced pressure, and toluene (30 mL) was added. After filtration and reduction of the volume, cooling at −30 °C gave $\mathbf{3_{BP}c}$ as yellow crystals (0.12 g, 66 % yield). ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF): δ = −51 ppm; ^{11}B{^{1}H} NMR (96.3 MHz, [D$_8$]THF): δ = −13 ppm.

Photolysis of $\mathbf{3_{BP}b}$: A solution of $\mathbf{3_{BP}b}$ (0.10 g, 0.22 mmol) in [D$_8$]toluene (0.8 mL) was irradiated at λ = 254 nm for 2 h at room temperature. ^{31}P NMR spectroscopy indicated the quantitative conversion of $\mathbf{3_{BP}b}$ into $\mathbf{5_{BP}b}$. Colorless crystals of $\mathbf{5_{BP}b}$ were obtained from [D$_8$]toluene solution at −30 °C. M.p. 124–127 °C; ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$): δ = 65 (d, J_{PP} = 301 Hz), 5 ppm (d, J_{PP} = 301 Hz); ^{11}B{^{1}H} NMR (96.3 MHz, C$_6$D$_6$): δ = 56, 7 ppm.

Photolysis of $\mathbf{3_{BP}c}$: When the irradiation at λ = 254 nm of a solution of $\mathbf{3_{BP}c}$ (0.10 g, 0.20 mmol) in [D$_8$]toluene at −60 °C was monitored by ^{31}P NMR spectroscopy (121.5 MHz), signals corresponding to $\mathbf{5_{BP}c}$ were observed at δ = 80 (d, J_{PP} = 324 Hz) and −12 ppm (d, J_{PP} = 324 Hz). Upon warming to −50 °C, $\mathbf{5_{BP}c}$ quantitatively isomerized into $\mathbf{8_{BP}c}$, which was obtained as colorless crystals. ^{31}P{^{1}H} NMR (121.5 MHz, C$_7$D$_8$): δ = 31 (d, J_{PP} = 48 Hz), −3 ppm (d, $^2J_{PP}$ = 48 Hz); ^{11}B{^{1}H} NMR (96.3 MHz, C$_7$D$_8$): δ = 80 ppm.

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