Main-Group Chemistry

σ-Bond Stretching: A Static Approach for a Dynamic Process[**]

*David Scheschkewitz, Hideki Amii, Heinz Gornitzka, Wolfgang W. Schoeller, Didier Bourissou, and Guy Bertrand**

The understanding of chemical transformations has been considerably improved by the direct observation of short-lived intermediates or through the synthesis of stable versions of these species.[1–5] However, since chemical bonds form, break, and change geometrically with awesome rapidity, only femtosecond spectroscopic techniques[6] can give a "motion picture" of chemical transformations by "freezing" molecular structures as reactions unfold and pass through their transition states. Herein, we demonstrate that it is possible to mimic the dynamic process corresponding to one of the simplest chemical reaction: the stretching and eventual rupture of a σ bond to afford two single-electron species, together with the reverse bond-forming process.

One of the archetypal examples of this type of reaction is the inversion of bicyclo[1.1.0]butanes **A**,[7] which occurs via singlet cyclobutane-1,3-diyls **B** in the transition state (Figure 1).[8] Two different types of 1,3-diradicals, related to **A**, have been recently isolated by taking advantages of the unique properties of the heteroelements.[9] The groups of Niecke and Yoshifuji have reported the synthesis of 2,4-diphosphacyclobutane-1,3-diyls **D**,[10,11] confined by a trans-annular antibonding π overlap, which makes the thermal ring closure into **C** forbidden. In marked contrast, 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls **F**[12,13] feature a transannular bonding π overlap, which allows for the thermal ring closure into **E** (Figure 2). Therefore, a variation of the phosphorus and boron substituents was expected to strongly influence the ground-state structure of compounds **E** and **F** and thus offered an opportunity not only to isolate the structural extremes, as reported for **C** and **D**,[14] but also to mimic the whole reaction profile for the inversion of **E**.

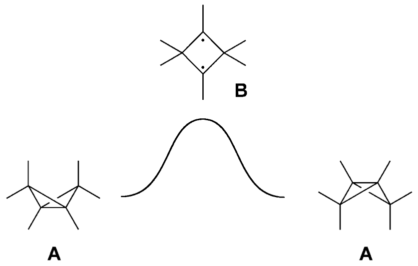


Figure 1. Schematic representation for the reaction profile between bicyclo[1.1.0]butanes **A**, and cyclobutane-1,3-diyls **B**.

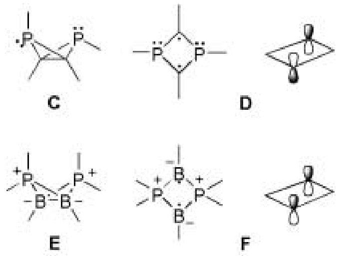
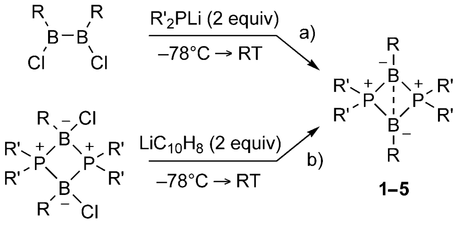


Figure 2. Structure of the heteroatom-containing analogues **C**, **D**, **E**, and **F** and schematic representations of the HOMO orbitals for **D** and **F**.

Compounds **2**–**4** were obtained by the synthetic route used previously for the preparation of **1**[12]: the reaction of the appropriate lithium phosphide (two equiv) with 1,2-dichlorodiborane. As the 1,2-diphenyl-1,2-dichlorodiborane is known to be highly unstable,[15] derivative **5** was synthesized by the reduction of the corresponding 1,3-dichloro-1,3-diborata-2,4-diphosphoniocyclobutane[16] with two equivalents of lithium naphthalenide in toluene solution. The compounds **2**–**5** were isolated in moderate to good yields as very air-sensitive, but thermally highly stable crystalline materials (Scheme 1).



1: R=*t*Bu, R'=*i*Pr, 68% yield; mp = 212°C; yellow (a)
2: R=Dur, R'=*i*Pr, 72% yield; mp = 224°C; colorless (a)
3: R=*t*Bu, R'=Ph, 71% yield; mp = 228°C; colorless (a)
4: R=Dur, R'=Et, 58% yield; mp = 213°C; colorless (a)
5: R=Ph, R'=Ph, 47% yield; mp = 181°C; colorless (b)

Scheme 1. Synthesis and physical properties of derivatives **1**–**5**.

---

[*] Dr. D. Scheschkewitz, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMR 2282)
Department of Chemistry
University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 909-787-2725
E-mail: gbertran@mail.ucr.edu

Dr. D. Scheschkewitz, Dr. H. Amii, Dr. H. Gornitzka,
Dr. D. Bourissou, Prof. G. Bertrand
Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069)
Université Paul Sabatier
118, route de Narbonne, 31062 Toulouse Cedex 04 (France)

Prof. W. W. Schoeller
Fakultät für Chemie
Universität Bielefeld
Postfach 10 01 31, 33615 Bielefeld (Germany)

[**] We are grateful to the NSF (CHE 0213510), the CNRS, the DFG and RHODIA for financial support of this work, and to the Alexander von Humboldt Foundation for a grant to D.S. We thank Mr. Christian Pradel for his help in generating the cover illustration.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352944

The impact of the substituents on the boron atoms upon structure was first investigated by replacing the *tert*-butyl groups of **1** by duryl rings (duryl = 2,3,5,6-tetramethylphenyl), while retaining the *iso*-propyl groups on the phosphorus atoms. Single-crystal X-ray diffraction analysis[17] (Figure 3) revealed that **2** adopts a very different structure to that observed for **1**. The BPBP core deviates from planarity (interplanar angle between the two PBB units 130°), the B–B distance is significantly shortened (2.24 Å). Steric hindrance probably does not favor a coplanar arrangement of the duryl rings and BPBP core of **2**, thereby preventing efficient stabilization of the radical centers through π delocalization.[18]

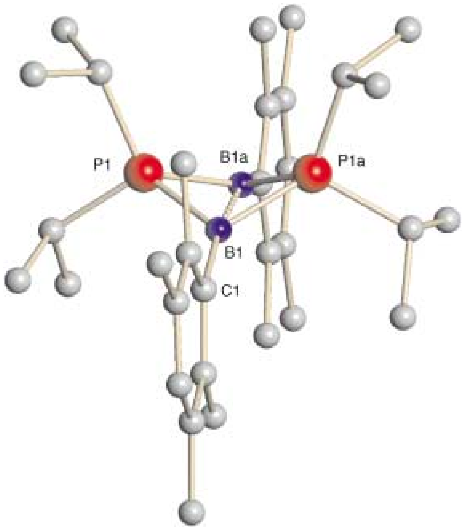


Figure 3. Molecular view of **2** in the solid state. Selected bond lengths and angles are as follows: P1-B1, 1.8879 ± 10 Å; P1-B1a, 1.8891 ± 11 Å; B1-C1, 1.5984 ± 13 Å; B1-P1-B1a, 72.77 ± 5°, P1-B1-P1a, 95.35 ± 5°, P1-B1-C1, 132.33 ± 7°; P1a-B1-C1, 130.83 ± 7°.

The influence of the substituents on the phosphorus atoms was then studied by replacing the *iso*-propyl substituents of **1** by phenyl rings. The B–B distance of **3** is noticeably shortened again (1.99 Å), while the BPBP core deviates further from planarity (interplanar angle 118°) (Figure 4). This result suggests that the less sterically demanding substituents on the phosphorus atoms favor the folded structure by decreasing the 1,3-diaxial interactions. This hypothesis was confirmed by comparing the solid-state structures of compounds **4** (B–B = 1.89 Å; interplanar angle 115°) and **2**, both featuring duryl groups on the boron atoms, but ethyl (**4**) and *iso*-propyl (**2**) substituents on the phosphorus atoms.

Lastly, the most folded structure (interplanar angle 114°) was obtained for the perphenylated derivative **5**, for which the B–B distance (1.83 Å) is in the range typical for B–B single bonds, and about 40 % shorter than in **1**. The geometric parameters observed for **5** are very similar to those calculated for the parent bicyclic compound **E*** (hydrogen atom on the boron and phosphorus and phosphorus atoms), while the data for **1** are very close to those predicted for the parent diradical **F***, which is the transition state for the inversion of **E***.[12] Therefore, in the solid state, derivatives **2**–**4** adopt intermediate structures between those of **E** and **F**.

Variable-temperature NMR studies give some information on the dynamic behavior of each of the individual derivatives **2**–**5** (Figure 4). All of these compounds invert rapidly at room temperature as shown by the magnetic equivalence of the axial and equatorial phosphorus substituents. The shortening of the B–B bond from **2** to **5** was

compound	1	2	3	4	5
	$(i\mathrm{Pr_2PB}t\mathrm{Bu})_2$	$(i\mathrm{Pr_2PBDur})_2$	$(\mathrm{Ph_2PB}t\mathrm{Bu})_2$	$(\mathrm{Et_2PBDur})_2$	$(\mathrm{Ph_2PBPh})_2$
δ ^{31}P (ppm)[a]	+3	−26	−56	−55	−54
δ ^{11}B (ppm)[a]	+25	−13	−12	−19	−13
B–B (Å)	2.57	2.24	1.99	1.89	1.83
τ (°)	180	130	118	115	114

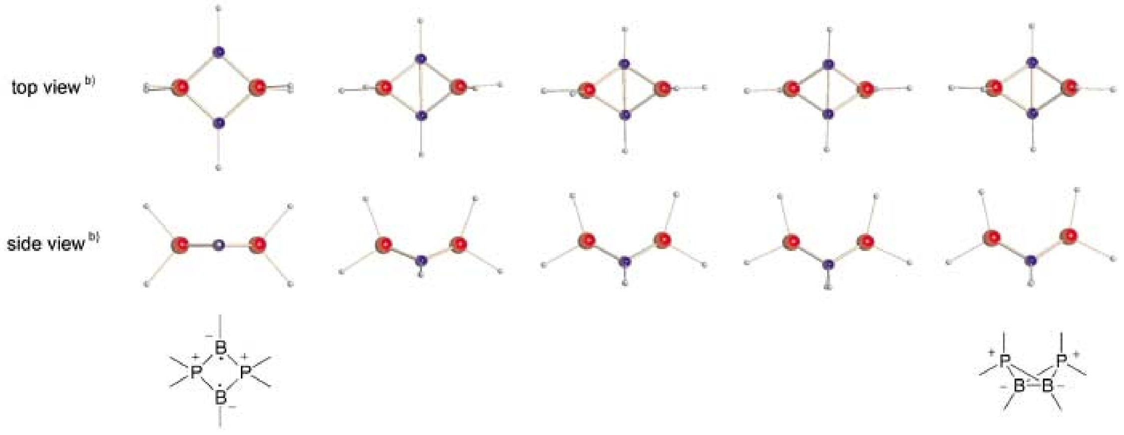


Figure 4. ^{11}B and ^{31}P NMR chemical shifts at room temperature in solution, X-ray data and molecular structure of compounds **1**–**5**. a) ^{11}B and ^{31}P NMR chemical downfield chemical shifts are expressed with a positive sign, in parts per million, relative to external $\mathrm{BF_3.OEt_2}$ and 85 % $\mathrm{H_3PO_4}$, respectively. b) For clarity the substituents are omitted.

expected to strengthen the inversion barrier of the bicyclic form **E** via the diradical **F**. Indeed, the inversion process could be frozen at low temperature for **4**, but not for the less folded derivative **2** even at −95 °C. The coalescence temperature ($T_c = -81$ °C) observed in solution for the ^{13}C NMR signal of the CH_2 ethyl group of **4** corresponds to an inversion barrier $\Delta G^{\neq}$ of about 8.5 kcal mol^{-1}, which is about half of that predicted for the parent derivative **E*** (16.4 kcal mol^{-1}).[12]

Snapshots on the reaction profile between **E** and **F** are obtained by varying the substituents around the BPBP framework. Besides this static approach that makes use of different derivatives, the characterization of bond-stretch isomers for a single compound remains a challenging project.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon by using standard Schlenk techniques.

Route a: A solution of R'_2PLi, which was prepared by adding *n*BuLi (3.75 mL, 1.6 M, hexane) to R'_2PH (6 mmol) in diethyl ether (10 mL) at −80 °C and subsequent stirring at room temperature for 2 h, was added dropwise to 3 mmol of the desired 1,2-dichlorodiborane in diethyl ether (20 mL) at −80 °C. The reaction mixture was warmed to room temperature within 1 h and the solvents were removed under vacuum. Toluene (20 mL) was added, the salts were removed by filtration and the remaining product was washed with toluene (2 × 3 mL). Crystals of compounds **2**–**4** were obtained by cooling saturated boiling toluene solutions to room temperature.

Route b: A freshly prepared solution of lithium naphthalenide (6.4 mL, 0.8 M, THF) was added dropwise to the desired 1,3-dichloro-2,4-diphospha-1,3-diboretane (2.5 mmol) in toluene (15 mL) at −80 °C. The reaction mixture was warmed to room temperature and stirring was maintained for about 30 minutes. The solvents were removed in vacuo and the residue was dissolved in pentane (30 mL). The salts were removed by filtration and the pentane was removed in vacuo. Naphtalene was sublimed by heating to 80 °C in vacuo for 30 minutes. Crystals of compound **5** were obtained by cooling saturated pentane solutions to −30 °C.

Received: September 24, 2003 [Z52944]

Keywords: boron · heterocycles · phosphorus · radicals · substituent effects

---

[1] For example, stable versions of carbocations,[2] radicals,[3] triplet[4] and singlet carbenes[5] have been described and reviewed.

[2] G. A. Olah, *Angew. Chem.* **1995**, *107*, 1517; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1393.

[3] C-Radikale in *Methoden der Organischen Chemie (Houben-Weyl)*, *Vol. E19a* (Eds.: M. Regitz, B. Giese), Thieme, Stuttgart, **1989**.

[4] H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315.

[5] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

[6] A. H. Zewail, *Angew. Chem.* **2000**, *112*, 2688; *Angew. Chem. Int. Ed.* **2000**, *39*, 2587.

[7] For recent work on carbon-based 1,3-diradicals, see: M. Abe, W. Adam, T. Minamoto, Y. Ino, M. Nojima, *J. Org. Chem.* **2003**, *68*, 1796, and references therein.

[8] K. A. Nguyen, M. S. Gordon, J. A. Boatz, *J. Am. Chem. Soc.* **1994**, *116*, 9241.

[9] H. Grützmacher, F. Breher, *Angew. Chem.* **2002**, *114*, 4178; *Angew. Chem. Int. Ed.* **2002**, *41*, 4006.

[10] a) E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem.* **1995**, *107*, 640; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 555; b) O. Schmidt, A. Fuchs, D. Gudat, M. Nieger, W. Hoffbauer, E. Niecke, W. W. Schoeller, *Angew. Chem.* **1998**, *110*, 995; *Angew. Chem. Int. Ed.* **1998**, *37*, 949; c) W. W. Schoeller, C. Begemann, E. Niecke, D. Gudat, *J. Phys. Chem. A* **2001**, *105*, 10731.

[11] H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem.* **2003**, *115*, 3932; *Angew. Chem. Int. Ed.* **2003**, *42*, 3802.

[12] D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880.

[13] a) M. Seierstad, C. R. Kinsinger, C. J. Cramer, *Angew. Chem.* **2002**, *114*, 4050; *Angew. Chem. Int. Ed.* **2002**, *41*, 3894; b) W. W. Schoeller, A. Rozhenko, D. Bourissou, G. Bertrand, *Chem. Eur. J.* **2003**, *9*, 3611; c) Y. Jung, M. Head-Gordon, *ChemPhysChem* **2003**, *4*, 522; d) M. J. Cheng, C. H. Hu, *Mol. Phys.* **2003**, *101*, 1319.

[14] E. Niecke, A. Fuchs, M. Nieger, *Angew. Chem.* **1999**, *111*, 3213; *Angew. Chem. Int. Ed.* **1999**, *38*, 3028.

[15] H. Hommer, H. Nöth, J. Knizek, W. Ponikwar, H. Schwenk-Kircher, *Eur. J. Inorg. Chem.* **1998**, 1519.

[16] M. S. Lube, R. L. Wells, P. S. White, *Inorg. Chem.* **1996**, *35*, 5007.

[17] Crystal data for **2**: $C_{32}H_{54}B_2P_2$, $M_r = 522.31$, monoclinic, space group $C2/c$, $a = 21.8891(4)$, $b = 8.8609(2)$, $c = 16.9297(3)$ Å, $\beta = 107.800(1)°$, $V = 3126.45(11)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.158$ mm^{-1}, crystal size 0.5 × 0.6 × 0.8 mm^3, 21139 reflections collected (5525 independent, $R_{int} = 0.0210$), 171 parameters, $R1$ $[I > 2\sigma(I)] = 0.0392$, $wR2$ [all data] = 0.1140, largest electron density residue: 0.549 e Å^{-3}. **3**: $C_{16}H_{19}BP$, $M_r = 253.09$, orthorhombic, space group $Pccn$, $a = 10.2223(6)$, $b = 13.7704(8)$, $c = 21.0047(13)$ Å, $V = 2956.7(3)$ Å^3, $Z = 8$, $\mu(Mo_{K\alpha}) = 0.166$ mm^{-1}, crystal size 0.1 × 0.4 × 0.5 mm^3, 16514 reflections collected (3026 independent, $R_{int} = 0.0386$), 166 parameters, $R1$ $[I > 2\sigma(I)] = 0.0360$, $wR2$ [all data] = 0.0995, largest electron density residue: 0.281 e Å^{-3}. **4**: $C_{14}H_{23}BP$, $M_r = 233.10$, tetragonal, space group $P4_32_12$, $a = 8.5915(5)$, $b = 8.5915(5)$, $c = 37.445(3)$ Å, $V = 2764.0(3)$ Å^3, $Z = 8$, $\mu(Mo_{K\alpha}) = 0.171$ mm^{-1}, crystal size 0.4 × 0.6 × 0.8 mm^3, 17302 reflections collected (3571 independent, $R_{int} = 0.0625$), 151 parameters, $R1$ $[I > 2\sigma(I)] = 0.0410$, $wR2$ [all data] = 0.1054, largest electron density residue: 0.277 e Å^{-3}. **5**: $C_{18}H_{15}BP$, $M = 273.08$, triclinic, space group $P\bar{1}$, $a = 10.180(3)$, $b = 10.846(3)$, $c = 15.558(5)$ Å, $\alpha = 90.628(6)°$, $\beta = 108.642(5)°$, $\gamma = 113.071(6)°$, $V = 1479.0(8)$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.171$ mm^{-1}, crystal size 0.1 × 0.4 × 0.5 mm^3, 8522 reflections collected (4251 independent, $R_{int} = 0.0714$), 361 parameters, $R1$ $[I > 2\sigma(I)] = 0.0514$, $wR2$ [all data] = 0.0951, largest electron density residue: 0.360 e Å^{-3}. Data for all structures were collected at 193(2) K using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were employed.[19] The structures were solved by direct methods (SHELXS-97),[20] and refined by using the least-squares method on F^2.[21] CCDC-224340 (**2**), 224341 (**3**), 224342 (**4**) and 224343 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[18] A. C. Goren, D. A. Hrovat, M. Seefelder, H. Quast, W. T. Borden, *J. Am. Chem. Soc.* **2002**, *124*, 3469.

[19] SADABS, Program for data correction, Bruker-AXS.

[20] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[21] SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, **1997**.