# Homoconjugation in 7-Boranorbornene and 7-Boranorbornadiene: Comparison with the Isoelectronic 7-Norbornenyl and 7-Norbornadienyl Cations

**Jerome M. Schulman,*,[†] Raymond L. Disch,[†] Paul von Ragué Schleyer,*,[‡] Michael Bühl,[‡] Matthias Bremer,[‡] and Wolfram Koch[§]**

*Contribution from the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367, the Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Germany, and the Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17 Juni 135, D-1000 Berlin 12, Germany. Received March 27, 1992*

**Abstract:** Ab initio calculations on 7-boranorbornadiene (**1**) and 7-boranorbornene (**2**) provide evidence of homoconjugative (three-center, two-electron) interaction between the boron atom and a C–C double bond. The geometries of **1** and **2**, optimized at HF/6-31G* and MP2(FU)/6-31G*, show pronounced tilting of the boron bridge toward the double bond, in agreement with recent X-ray structures of derivatives of **1** and **2**. The use of homodesmotic reactions based upon MP2(FC)/6-31G* energies indicates that the homoconjugative stabilizations of **1** and **2** are comparable to, and possibly greater than, those of the isoelectronic 7-norbornadienyl (**4**) and 7-norbornenyl (**5**) carbocations. The calculated [11]B chemical shifts and molecular electric dipole moments provide further evidence of these interactions.

This study is concerned with the boron compounds **1–3**, analogues of the carbocations **4–6**. In particular, it deals with the extent to which the three-center, two-electron (nonclassical) bonding found in cations **4** and **5**[1] is also found in the neutral compounds **1** and **2**. An early indication of nonclassical bonding in the isoelectronic boron compounds was obtained by ab initio calculation in a minimal basis, which showed that **1** is more stable than the symmetrical structure **1a**: the boron bridge was found



1      1a      2      3
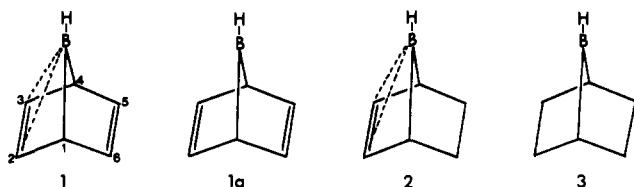
to be significantly canted toward a somewhat lengthened C–C double bond.[2] The present work is a detailed investigation of this homoconjugative interaction. Calculations of molecular energy are carried out in larger basis sets with inclusion of electron correlation for both **1–3** and relevant model compounds; homoconjugation in **1** and **2** is also studied from the viewpoint of its effect upon the [11]B chemical shift.

Before we describe our study of **1–3**, it is useful to review briefly what is now known of the analogous carbocations **4–6**. Evidence for the exceptional stabilities of **4** and **5** was first obtained by Winstein and his associates[3,4] in their studies of the enhanced rate of solvolysis of 7-*anti*-norbornenyl tosylate, leading to **5**,[3] and of 7-norbornadienyl chloride, leading to **4**,[4] both relative to the rates



4      4a      5      6
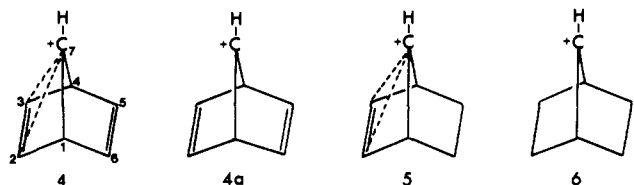
of the corresponding saturated 7-norbornyl derivatives, which yield **6**. These rate-enhancements, among the most impressive examples of neighboring-group participation (anchimeric assistance) yet discovered, correspond to decreases in activation energy of ca. 15–20 kcal/mol. In contrast, the saturated norbornyl cation (**6**)

has unusual thermodynamic instability; solvolysis rates leading to this species are much lower than those of typical secondary derivatives.[1,5]

The 7-norbornadienyl cation was one of the first nonclassical carbonium ions studied by NMR spectroscopy.[6] The number of proton signals is consistent with a structure of $C_s$ (**4**) rather than $C_{2v}$ (**4a**) symmetry, implying three-center bonding involving the formally charged center C(7) with primarily one double bond. Indeed, the 7-norbornenyl cation (**5**) has NMR characteristics similar to those of **4**. That there is no NMR evidence below the decomposition temperature for "bridge flipping" between the two equivalent $C_s$ forms **4**, presumably via **4a**, suggests that the barrier is at least 19.6 kcal/mol.[6b]

While the literature on these and related carbocations is extensive,[1] detailed information on their structures is only now becoming available. Experimentally, the canting of the C(7)[+] bridge toward the C(2)–C(3) double bond in **4** and **5**, first inferred from the NMR observations,[6] can be seen in Laube's recent X-ray structure of the 7-phenyl-2,3-dimethyl-7-norbornenyl cation **7**.[7]



7
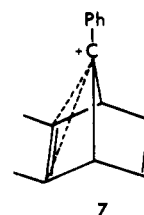
This result is important in that the NMR study of the 7-phenylnorbornadienyl cation indicated that replacement of hydrogen by phenyl lowers the activation energy for bridge flipping via rapid interconversion of the canted forms to ≤7.6 kcal/mol.[6b]

---

(1) Reviews: (a) Winstein, S. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; John Wiley: New York, 1972; Vol. III, p 965. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (c) Lenoir, D.; Siehl, H.-U. In *Houben-Weyl*; Hanack, M., Ed.; Thieme Verlag: Stuttgart, 1990; Vol. 19c.

(2) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863.

(3) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183.

(4) Winstein, S.; Ordronneau, C. *J. Am. Chem. Soc.* **1960**, *82*, 2084.

(5) Hoffmann, R.; Mollère, P. D.; Heilbronner, E. *J. Am. Chem. Soc.* **1973**, *95*, 4860.

(6) (a) Story, P. R.; Saunders, M. *J. Am. Chem. Soc.* **1962**, *84*, 4876. (b) Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352.

(7) Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224.

† City University of New York, Queens College.
‡ Friedrich-Alexander Universität Erlangen-Nürnberg.
§ Technische Universität Berlin.

**Table I.** Total Energies (-au)

| species | 6-31G*//6-31G* | MP2(FC)/6-31G*//6-31G* | MP2(FC)/6-31G*//MP2(FU)/6-31G* |
|---|---|---|---|
| 1 ($C_s$) | 255.898 12 (255.894 70)[a] | 256.750 50 | 256.754 18 (256.789 72)[b] |
| 1a ($C_{2v}$) | 255.885 51 | 256.725 35 | |
| 2 ($C_s$) | 257.091 44 (257.088 08)[a] | 257.949 09 | 257.953 19 (257.988 52)[b] |
| 3 ($C_{2v}$) | 258.268 76 | 259.121 69 | |
| 4 ($C_s$) | 268.820 76 (268.818 49)[a] | 269.696 86 | 269.699 15 (269.734 07)[b] |
| 4a ($C_{2v}$) | 268.786 76 | 269.654 53 | |
| 5 ($C_s$) | 270.020 99 | 270.904 79 | |
| 6 ($C_{2v}$)[c] | 271.176 76 | 272.088 61 | |
| 8 ($C_{2v}$) | 269.652 51 | 270.550 95 | |
| 9 ($C_s$) | 270.861 84 | 271.767 37 | |
| 10 ($C_{2v}$) | 272.061 20 | 272.975 04 | |

[a] Energy at HF/6-31G*//MP2(FU)/6-31G*. [b] Energy at MP2(FU)/6-31G*//MP2(FU)/6-31G*. [c] The $C_{2v}$ data for the 7-norbornyl cation have been taken for energy comparisons, although lower symmetries are favored (see ref 5).

A high-level ab initio study[8] of the cations **4–6** and the corresponding hydrocarbons, norbornadiene (**8**), norbornene (**9**), and norbornane (**10**), provided evidence for the interaction of the
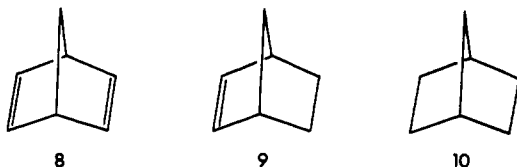
double bond of **5** and one of the double bonds of **4** with the cationic center, C(7): at HF/6-31G*, the "nonbonded" C(2)–C(7) distances are only 1.745 and 1.719 Å, respectively; the C(2)–C(3) bond lengths increase from ca. 1.32 Å, typical of C=C distances, to 1.38 Å (near the value for benzene). The electron-correlated (MP2(FU)/6-31G*) geometry of **4** exhibits these features to an even greater degree, having nonbonded and C=C distances of 1.701 and 1.400 Å, respectively.

## Computational Methods

This work was carried out using Gaussian 90,[9] CADPAC,[10] and programs developed by us. Gaussian 90 was adapted to IBM 3090 computers for the MP2(FU)/6-31G* optimizations, which were carried out by finite-difference methods. Results are reported here using the notations of Pople: "//" means "at the geometry of," "/" means "in the basis," "FU" means that correlation of all electrons is included, and "FC" indicates that the frozen-core approximation is used in the calculation of electron-correlation energy at the second-order Møller–Plesset (MP2) level. We have not included differential zero-point and thermal effects in the calculated energies of homodesmotic reactions, as they are expected to be very small.

IGLO (individual gauge for localized orbitals)[11] calculations of chemical shifts were carried out on the designated geometries using the standard double-zeta (DZ) and II' basis sets. The latter is of triple-zeta + polarization quality for B and C, and DZ for H. A typical designation is DZ(IGLO)//MP2(FU)/6-31G*.

## Energies

The 6-31G*//6-31G* and MP2(FC)/6-31G*//6-31G* energies of **1**, **1a**, **2**, and **3** are given in Table I, together with those of **4–6** and **8–10** reported previously.[8] The MP2(FU)/6-31G* and MP2(FC)/6-31G* energies of **1**, **2**, and **4** at their MP2-(FU)/6-31G* geometries are also given in Table I. The MP2-(FC)/6-31G* energies decrease by 1.4 to 3.3 kcal/mol in passing from the 6-31G* geometries to those computed at MP2(FU)/6-

(8) Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1042.

(9) *GAUSSIAN 90*: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1990.

(10) Amos, R. D.; Rice, J. E. *CADPAC: The Cambridge Analytic Derivatives Package*, Issue 4.0, Cambridge, 1987.

(11) (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (b) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (c) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (d) Kutzelnigg, W.; Schindler, M.; Fleischer, U. In *NMR, Basic Principles and Progress*; Springer Verlag: Berlin, Heidelberg, 1990; Vol. 23, p 165.

31G*. Unless otherwise indicated, the following evaluations employ MP2(FC)/6-31G*//6-31G* for uniformity, and all values of $\Delta H$ are in kcal/mol.
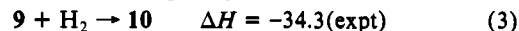
Consider first the formal hydrogen-transfer reaction, eq 1, whose

$$3 + 9 \rightarrow 2 + 10 \qquad \Delta H = -22.0 \qquad (1)$$

calculated enthalpy change is -22.0 kcal/mol. Because of the homoaromatic effect in 7-boranorbornene (**2**), its heat of hydrogenation to 7-boranorbornane (eq 2) is less exothermic than

$$2 + H_2 \rightarrow 3 \qquad \Delta H = -12.3 \qquad (2)$$
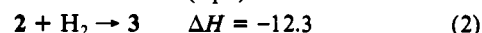
that of norbornene to **10** (eq 3) by this amount.

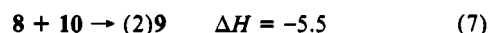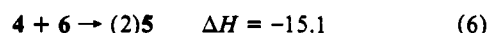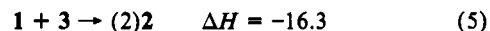$$9 + H_2 \rightarrow 10 \qquad \Delta H = -34.3(\text{expt}) \qquad (3)$$

The enthalpy change for the hydrogenation **2** → **3**, eq 2, is estimated to be -12.3 kcal/mol, based upon the calculated heat of reaction 1 and the experimental enthalpy change of reaction 3, -34.3 kcal/mol.[12] A computed value of the heat of hydrogenation can be obtained from the MP2(FC)/6-31G* energies of **2** and **3** by the group-equivalent method of Ibrahim et al.[13] This yields -8.5 kcal/mol.

The effect of a second double bond, present in 7-boranorbornadiene (**1**), can be assessed by means of eq 4, which involves

$$3 + 8 \rightarrow 1 + 10 \qquad \Delta H = -33.2 \qquad (4)$$

$$3 + 8 \rightarrow 1a + 10 \qquad \Delta H = -17.4 \qquad (4a)$$

the formal transfer of four hydrogens. This reaction is exothermic by 33.2 kcal/mol, compared to 22.0 kcal/mol for reaction 1, indicating a significant additional stabilizing effect of the second double bond in **1**. The energy of the $C_{2v}$ structure **1a** is higher than that of **1** by 15.8 kcal/mol (the SCF barrier is somewhat smaller, 7.9 kcal/mol). When **1a** replaces **1** in reaction 4, the exothermic heat is reduced from -33.2 to -17.4 kcal/mol, smaller in magnitude than that of reaction 1. These results demonstrate strong homoaromatic effects in **1** and **2**, which persist, to some extent, in **1a**.

An alternative assessment of the stabilizing effect of the second double bond in 7-boranorbornadiene (**1**) is provided by the disproportionation reaction 5, whose energy change, -16.3 kcal/mol, is equal to the difference in the hydrogenation energies of **1** → **2** and **2** → **3**. Reaction 6, involving the 7-norbornadienyl cation (**4**), is exothermic by a similar amount, 15.1 kcal/mol. In contrast to eqs 5 and 6, the disproportionation energy of the hydrocarbons norbornadiene (**8**) and norbornane (**10**) with norbornene (**9**, 2 mol) is quite modest, -5.5 kcal/mol (eq 7). An experimentally derived value is -2.6.[12]

$$1 + 3 \rightarrow (2)2 \qquad \Delta H = -16.3 \qquad (5)$$

$$4 + 6 \rightarrow (2)5 \qquad \Delta H = -15.1 \qquad (6)$$

$$8 + 10 \rightarrow (2)9 \qquad \Delta H = -5.5 \qquad (7)$$

We have estimated the energy change for the hydrogenation **2** → **3** to be -12.3 kcal/mol (eq 2). From the energy change of

(12) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(13) Ibrahim, M. R.; Fataftah, Z. A.; Schleyer, P. v. R.; Stout, P. D. *J. Comput. Chem.* **1987**, *8*, 1131.

**Table II.** Selected Geometrical Parameters[a] of 7-Boranorbornadiene (**1** and **1a**), 7-Boranorbornene (**2**) and 7-Boranorbornane (**3**)

|  | geometry | C(2)–C(3) | C(5)–C(6) | C(1)–B | C(2)–B | C(5)–B | $\alpha$ | $\beta$ |
|---|---|---|---|---|---|---|---|---|
| **1** | HF/6-31G* | 1.358 | 1.321 | 1.617 | 1.844 | 2.497 | 149.1 | 85.7 |
|  | MP2(FU)/6-31G* | 1.392 | 1.344 | 1.629 | 1.759 | 2.515 | 153.7 | 79.8 |
| **1a** | HF/6-31G* | 1.329 | 1.329 | 1.600 | 2.293 | 2.293 | 119.8 | 119.8 |
| **2** | HF/6-31G* | 1.357 | 1.547 | 1.604 | 1.898 | 2.545 | 145.1 | 91.2 |
|  | MP2(FU)/6-31G* | 1.396 | 1.540 | 1.622 | 1.775 | 2.572 | 149.7 | 82.6 |
| **3** | HF/6-31G* | 1.563 | 1.563 | 1.589 | 2.391 | 2.391 | 123.4 | 123.4 |

[a] Units in angstroms and degrees. $\alpha$ is the dihedral angle C(6)–C(1)–C(4)–B; $\beta$ is C(2)–C(1)–C(4)–B.

reaction 5, the heat of hydrogenation for **1** → **2** is estimated to be −28.6 kcal/mol. A similar value, −24.8 kcal/mol, is obtained from the ab initio energies of **1** and **2** using the method of Ibrahim et al.[13]

The difference between the homoaromatic stabilization energy of 7-boranorbornene (**2**) and that of the 7-norbornenyl cation (**5**) can be estimated by means of reaction 8. Surprisingly, the

$$3 + 5 \rightarrow 2 + 6 \qquad \Delta H = -7.0 \qquad (8)$$

reaction is exothermic by 7.0 kcal/mol, indicating that stabilization of the electron-deficient center by the double bond is somewhat greater in the boron compound.

Similarly, eq 9 compares the homoaromatic stabilization of 7-boranorbornadiene (**1**) with that of the 7-norbornadienyl cation (**4**). This reaction is exothermic by 12.9 kcal/mol (versus 7.0

$$3 + 4 \rightarrow 1 + 6 \qquad \Delta H = -12.9 \qquad (9)$$
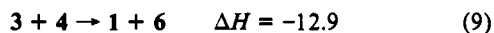
for reaction 8), again implying greater homoaromatic stabilization of the boron compound. From eqs 8 and 9, the extra stabilizing effect of the second double bond in **1**, relative to that in the cation **4**, is 5.9 kcal/mol. (The enthalpy changes of reactions 8 and 9 are positive at the HF/6-31G* level, 13.5 and 9.2 kcal/mol, respectively.)

Bridge flipping in 7-boranorbornadiene between the two equivalent forms (**1** via **1a**) requires 15.8 kcal/mol, as noted above. Fagan has obtained an experimental bridge-flipping barrier, $\Delta G^{\ddagger}$, in 7-phenylbora-1,2,3,4,5,6-hexamethylboranorbornadiene (**11**)

**11**
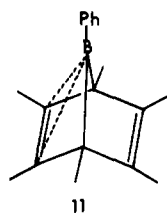
which is somewhat smaller, 9.6 kcal/mol at −65 °C.[14] The reduced barrier to bridge flipping in the phenyl derivative **11** relative to **1** is consistent with the analogous effect in 7-substituted 7-norbornadienyl cations.[1,6b] In both **1** and **4** the phenyl substituent decreases the barrier because its stabilizing interaction with C+ or B is greater in the $C_{2v}$ transition state than in the $C_s$ form.

The calculated barrier for bridge flipping in **1**, 15.8 kcal/mol, is smaller than that of **4**, 26.6 kcal/mol. Thus, while reaction 4a is exothermic, reaction 10 is endothermic. (Both of these reactions involve the $C_{2v}$ forms.)

$$6 + 8 \rightarrow 4a + 10 \qquad \Delta H = 6.3 \qquad (10)$$

## Geometries

Selected geometrical parameters for **1**, **1a**, **2**, and **3** are given in Table II. The boron bridge in **1** and **2** is canted toward the C(2)–C(3) double bond; the C(2)–C(1)–C(4)–B dihedral angles, $\beta$, are 85.7° and 91.2°, respectively, in the 6-31G* geometries. An earlier STO-3G study found $\beta$ = 87.8° in **1**.[2] As shown in Figure 1, tilting of the bridge in **1** and **2** is quite pronounced. The C(2)-B distances in **1** are 1.844 Å at 6-31G* and 1.759 Å at MP2(FU)/6-31G*. The corresponding values for **2** are 1.898 and 1.775 Å. .
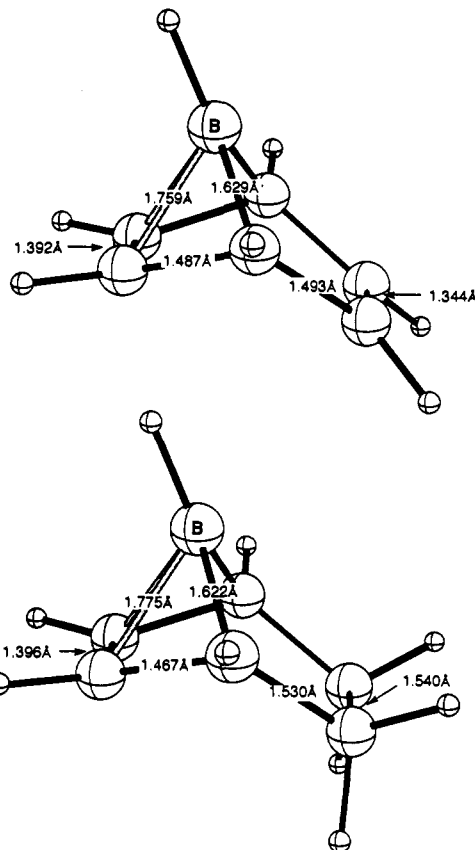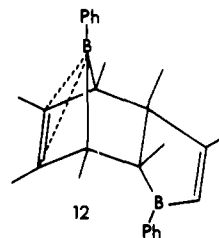
**Figure 1.** MP2(FU)/6-31G* optimized geometry of 7-boranorbornadiene (**1**) and 7-boranorbornene (**2**).

Recently, Fagan and co-workers have obtained X-ray structures for **11** and **12**, which are derivatives of **1** and **2**, respectively.[14,15] The bridge canting found by calculation is clearly seen in these

**12**

X-ray structures. For **11**, $\beta$ and the C(2)–B distance are respectively 83.5° and 1.814 Å, compared to 85.7° (79.8°, MP2) and 1.844 Å (1.759 Å, MP2) in **1**. For **12**, these quantities are 90.1° and 1.864 Å, compared to 91.2° (82.6°, MP2) and 1.898 Å (1.775 Å, MP2) in **2**. The X-ray values of the C(2)-B distances in **11**[14] and **12**[15] are in somewhat better agreement with the SCF than the MP2 geometries of **1** and **2**. However, the former compounds are much more heavily substituted, and probably have smaller degrees of delocalization.

The C(2)–C(3) bond lengths in **1** and **2**, 1.358 and 1.357 Å, respectively, are greater than the C=C length in norbornene, 1.322

(14) Fagan, P. J. Private communication.

(15) Fagan, P. J.; Burns, E. G.; Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 1979.

**Table III.** Calculated (IGLO) Chemical Shifts $\delta^{11}B$ and $\delta^{13}C$ for 1–3

| species | level of theory[a] | B | C(1,4) | C(2,3) | C(5,6) |
|---|---|---|---|---|---|
| **1** ($C_s$) | DZ//expt | −23.6 | 49.5 | 126.6 | 134.3 |
| | DZ//6-31G* | −21.7 | 47.0 | 123.5 | 133.2 |
| | DZ//MP2/6-31G*[b] | −31.2 | 51.9 | 123.5 | 136.0 |
| expt on **11**, ref 14 | | −11.6 | 60.8 | 126.6 | |
| **1a** ($C_{2v}$) | DZ//6-31G* | 41.7 | 34.8 | 138.8 | |
| **2** ($C_s$) | DZ//6-31G* | −22.6 | 35.4 | 129.8 | 21.6 |
| | DZ//MP2/6-31G* | −40.6 | 44.1 | 128.1 | 24.0 |
| expt on **12**, ref 14 | | −14.3 | 51.4 | 127.3 | 37.5 |
| **3** ($C_{2v}$) | DZ//6-31G* | 72.5 | 16.6 | 19.0 | |

[a] DZ is a 7s3p[4111,21] Huzinaga basis for C, and 3s[21] for H. [b] The IGLO values with a larger basis set (denoted II'//MP2/6-31G*) are the following: B(−27.1), C(1,4) (43.9), C(2,3) (115.5), and C(5,6) (133.2) ppm. The contraction is 9s5p1d[51111,2111,1] for C and B, but the same as DZ for H.

Å (all at 6-31G*), but are not as great as the C(2)–C(3) distances in **4** and **5** (both 1.380 Å at 6-31G*).[8] Another comparison is provided by the bond lengths, 1.349 and 1.351 Å, of the formal C–C double bonds in borepin, a resonance-stabilized (RE = 12.7 kcal/mol) heterocyclic aromatic compound isoelectronic with the tropylium cation ($r_{CC} = 1.389$ Å at 6-31G*, essentially the benzene distance).[16] The $C_{2v}$ structure **1a**, which lacks the three-center bonding of **1**, affords a direct comparison. Not surprisingly, **1a** has normal C(2)–C(3) (and C(5)–C(6)) lengths of 1.329 Å, essentially the same as the length of the non-interacting C(5)–C(6) double bond (1.321 Å) in the $C_s$ form, **1**.

Electron correlation is known to favor three-center bonding; this is well demonstrated by the changes in geometry found here (Table II). The C(2)–C(3) double-bond length in **1** increases from 1.358 at 6-31G* to 1.392 Å at MP2(FU)/6-31G*, and in **2** from 1.357 to 1.396 Å. Interestingly, the length of the more weakly interacting C(5)–C(6) double bond in **1** increases nearly as much, from 1.321 to 1.344 Å. The experimental C(2)–C(3) distances are 1.388 Å in **11** and 1.375 Å in **12**; the C(5)–C(6) value is 1.327 Å in **11**.[14,15]

### Chemical Shifts and Electric Dipole Moments

The hypercoordinate character of the boron bonding in **1** and **2**, as well as in **11** and **12**, is clearly manifested in their $^{11}$B chemical shifts relative to that of BF$_3$·OEt$_2$. The calculated (IGLO) boron chemical shifts of the parent compounds **1** and **2** are ca. −30 and −40 ppm, respectively (Table III). The computed values are quite sensitive to geometry: the shorter C(2)–B distances of the MP2 geometries result in increased boron shielding.

The experimental $\delta^{11}$B values[14] for **11** and **12** are −11.6 and −14.3 ppm, respectively. The phenyl substituent in **11** reduces the magnitude of the three-center bonding. This is shown by the somewhat greater C(2)–B distance (relative to the MP2/6-31G* value in **1**), as well as by an IGLO calculation employing the experimental geometry of **11** (with the substituents changed to hydrogen atoms): the computed $\delta^{11}$B value (DZ//expt in Table III) is ca. 8 ppm downfield from the DZ//MP2/6-31G* value.

The IGLO $\delta^{11}$B value of the saturated "purely classical" compound **3**, 72.5 ppm (DZ//6-31G*), differs substantially from the values calculated for **1** and **2**. It is similar to those of other three-coordinate boron compounds such as B-phenyl-3-borolene (**13**), for which $\delta^{11}$B is 86.2 ppm.[17]
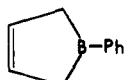


13

In the transition structure **1a** ($C_{2v}$ symmetry), there is still some interaction of the "vacant" boron p orbital with the double bonds. This is reflected in the IGLO $\delta^{11}$B of ca. 40 ppm, which lies between the values for **1** and **3**. Note that the radial extension of the B p orbital is greater than that of the contracted C⁺ p
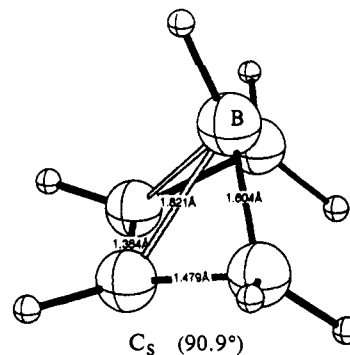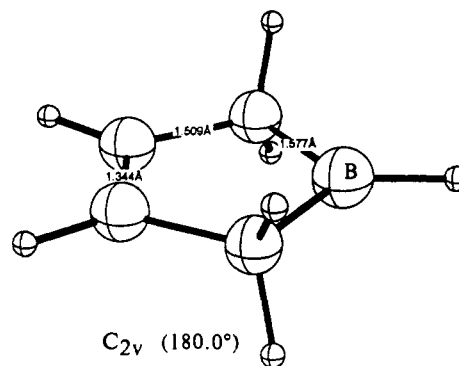
(16) Schulman, J. M.; Disch, R. L., *Organometallics* **1989**, *8*, 733.
(17) Herberich, G. E.; Boveleth, W.; Heßner, B.; Höstalek, M.; Köffer, D. P. J.; Ohst, H.; Söhnen, D. *Chem. Ber.* **1986**, *119*, 420.

$C_{2v}$ (180.0°)

$C_s$ (90.9°)

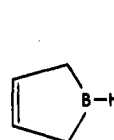**Figure 2.** MP2(FU)/6-31G* optimized geometry of $C_{2v}$ borolene (**14a**) and $C_s$ borolene (**14b**).

orbital. (The chemical shifts of the carbocations **4** and **5** are discussed in ref 8. The $\delta^{13}$C value for C(7) in **4a** differs appreciably from its value in **4**.)

The calculated chemical shifts $\delta^{13}$C of **1**–**3** are less informative. For example, despite considerable differences in the 6-31G* and MP2/6-31G* geometries of **1** (Table II), the DZ IGLO values for C(2,3)—atoms which participate in the three-center arrangement—are identical. Agreement with the experimental chemical shifts is not expected, because of the alkyl (and phenyl) substituents in **11** and **12**.

The homoconjugative interaction between the boron atom and a ring double bond produces a large change in the electric dipole moment as well as in the boron chemical shift. The dipole moments of **1** and **2** are 1.64 and 1.82 D, respectively, at the HF/6-31G* level. The direction of the moments is consistent with increased electronic population on the boron atom. The saturated compounds **3** and **10** have dipole moments of only 0.16 and 0.19 D, respectively. Compound **1a** has the intermediate value 0.26 D, much closer to that of **3** than to that of **1**. The increased proximity of B to a C–C double bond in the MP2(FU)/6-31G* geometry of **1** increases its dipole moment to 1.83 D.

### Discussion

The striking homoconjugative stabilizations of **1** and **2**, also present in their B-phenyl derivatives **11** and **12**, led us to search for such effects in model compounds. One such case is borolene (Figure 2), the parent of B-phenyl-3-borolene, previously invoked as having a normal trigonal boron atom. The MP2(FU)/6-31G* potential energy surface for conversion of **14a** into a folded ($C_s$)



14a                                         14b

form is quite flat. A shallow minimum for **14b** is found at a dihedral angle C(3)–C(2)–C(5)–B equal to 90.9°; the energy of

**Table IV.** Total Energies of Model Compounds (–au)

| species | 6-31G* //6-31G* | 6-31G** //6-31G* | MP2(FC) /6-31G* //6-31G* | MP2(FC) /6-31G** //6-31G* |
|---|---|---|---|---|
| 14b (*C_s*) | 180.18361 | 180.19520 | 180.78377 | 180.84006 |
| 15 (*C_{2v}*) | 181.38399 | 181.39807 | 181.97456 | 182.04736 |
| 16b (*C_s*) | 193.10120 | 193.11353 | 193.72499 | 193.77878 |
| 17 (*C_{2v}*) | 194.28868 | 194.30375 | 194.90696 | 194.97604 |
| 17 (*C_2*) | 194.29284 | | 194.91237 | |

this structure is less than 1 kcal/mol lower than that of **14a**. The "nonbonded" B–C(3) distance in **14b** is 1.821 Å, comparable to the values computed for **1** and **2**, 1.759 and 1.775 Å, respectively (Table II).

It appears that the homoconjugative stabilization favoring $C_s$ borolene is almost completely counteracted by the increase in strain energy, by loss of some hyperconjugative stabilization from its geminal C–H bonds upon folding, and perhaps by other effects as well. Thus reaction 11, in which *both* **2** and **3** are "folded,"

$$2 + 15 \rightarrow 3 + 14b \qquad \Delta H = 11.4 \qquad (11)$$

has a positive enthalpy change, 11.4 kcal/mol (Tables I and IV). (The geometry of boracyclopentane (**15**) was optimized at HF/6-31G* in $C_{2v}$ symmetry.)
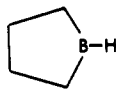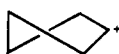


15

The flat potential energy surface linking **14a** to **14b** is in strong contrast with that of the cyclopenten-4-yl cation, in which the energy of the planar form (**16a**) is 18.9 kcal/mol higher than that of the bridged form (**16b**) at the MP2(FC)/6-31G*//6-31G*



level.[18] It is therefore of interest to compare the homoconjugative effects of B and C⁺ by means of reaction 12, in which strain energy

$$16b + 15 \rightarrow 17 + 14b \qquad \Delta H = 2.1 \qquad (12)$$

should be approximately balanced. (The cyclopentyl cation (**17**) has $C_2$ symmetry, a structure ca. 3.4 kcal/mol lower in energy than the $C_{2v}$ form;[19] we find no evidence of energetically significant twisting effects in boracyclopentane.) This reaction, the analogue of reaction 8, has an enthalpy change of ca. 2 kcal/mol. Thus, in the monocyclic case, the homoconjugative stabilization appears to be slightly greater for C⁺ than for boron.

It is worth noting that in $C_s$ boretane, the transannular interaction of B with C(2) leads to ring puckering and a small barrier, ca. 2.5 kcal/mol, for interconversion of $C_s$ boretanes through a $C_{2v}$ transition state.[20] The same effect is found in the isoelectronic bicyclobutonium ion; however, the barrier to interconversion is much larger, 16.1 kcal/mol.

It would appear, then, that the pronounced stabilizations of **1** and **2** relative to their carbocation analogues are not necessarily found in other systems.

(18) Schleyer, P. v. R.; Bentley, T. W.; Koch, W.; Kos, A. J.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 6953.

(19) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475.

(20) Bühl, M.; Schleyer, P. v. R.; Ibrahim, M. A.; Clark, T. *J. Am. Chem. Soc.* **1991**, *113*, 2466.

# Communications to the Editor

## Catalysis of H₂–D₂ Equilibration by Platinum–Gold Cluster Compounds

Mark A. Aubart and Louis H. Pignolet*

*Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455*

*Received February 14, 1992*
*Revised Manuscript Received June 8, 1992*

The catalysis of H₂–D₂ equilibration ($H_2 + D_2 = 2HD$) has been studied for a series of phosphine-stabilized Pt–Au cluster compounds under homogeneous conditions in the solution phase and under heterogeneous conditions as molecular solids at 30 °C and 760 Torr total pressure. The cluster compounds, **1–4**, shown in Table I are excellent catalysts for this reaction and have turnover frequencies which are orders of magnitude greater than those of most homogeneous catalysts reported to date. Previous homogeneous studies have included monometallic compounds such as *trans*-IrCl(CO)(PPh₃)₂,[1] Pt(O₂)(PPh₃)₂,[1] NiI₂(PPh₃)₂,[2] RhCl-

**Table I.** H₂–D₂ Equilibration Kinetic Data under Homogeneous Conditions[a]

| cluster compound | amount of cluster (μmol)[b] | 10⁵k at 30 °C (s⁻¹)[c] | 10²(turnover freq) (s⁻¹)[d] |
|---|---|---|---|
| [Pt(AuPPh₃)₈](NO₃)₂ (**1**) | 2.5 | 12.9 | 6.5 ± 0.5 |
| [(PPh₃)Pt(AuPPh₃)₆](NO₃)₂ (**2**) | 1.5 | 2.5 | 2.0 ± 0.1 |
| [(PPh₃)₂Pt(AuPPh₃)₄](NO₃)₂ (**3**) | 2.2 | 5.6[e] | 3.0 ± 0.1 |
| [(PPh₃)₂Pt(AuPPh₃)₃](NO₃) (**4**) | 2.3 | 8.2 | 4.6 ± 0.2 |
| [Au(AuPPh₃)₈](NO₃)₃ (**5**) | 1.3 | 0[f] | 0 |
| (C₂H₄)Pt(PPh₃)₂ (**6**) | 7.2 | 6.5 | 0.11 ± 0.01 |

[a] The initial gas mixture consisted of ca. 0.5 atm of H₂ and 0.5 atm of D₂. Reactions were typically run for ca. 4 h or until at least 70% equilibrated. [b] Each catalyst was dissolved in 6 mL of nitrobenzene. [c] First-order rate constants were determined by plotting the equation, $\ln \{[HD]_e/([HD]_e - [HD]_t)\} = kt$, where $[HD]_e$ and $[HD]_t$ are the mole fractions of HD at equilibrium and at time $t$, respectively. $[HD]_e$ was calculated from initial H₂ and D₂ concentrations and $K_e = 3.2$ at 30 °C. [d] Turnover frequency is equal to $k[mol(H_2 + D_2 + HD)]/(mol\ cluster)$ where mol(H₂ + D₂ + HD) = $1.21 \times 10^{-3}$ for all experiments. [e] Initial rate data reported for the first 75 min where the ln plot was linear. The rate increased nonlinearly after this time due to decomposition (see text). [f] No HD observed after 2 days.

(1) Tadros, M. E.; Vaska, L. *J. Colloid Interface Sci.* **1982**, *85*, 389.
(2) Ando, N.; Maruya, K.-I.; Mizoroki, T.; Ozaki, A. *J. Catal.* **1971**, *20*, 299.

(PPh₃)₃,[3] RuH₂(PPh₃)₄,[4] and RuHCl(PPh₃)₃.[4] No cluster compounds have been previously studied. The Pt–Au cluster com-