Table II. Relative Intensities of Prominent Ions in the Mass Spectra of β-Diketonate–Beryllium Complexes

R	R′	$M^{\bullet+}$	$M^{\bullet+} - R'$	$M^{\bullet+} - L$	$FBe(RCOCHCO)^+$	RCO^+	R^+	R'^+
CH_3	CF_3	31	100	30	69	96		97
C_6H_5	CF_3	36	69	55	59	100	68	43
C_4H_3S	CF_3	32	54	62	59	100	11	44
C_4H_3O	CF_3	37	71	47	100	59	4	42
C_6H_5	C_2F_5	13	37	13	29	100	48	15
C_4H_3S	C_2F_5	11	28	20	35	100	6	22
C_6H_5	C_3F_7	5	23	2	6	100	30	7
C_4H_3S	C_3F_7	6	21	4	5	100	4	12

Table III. ^{9}Be NMR Chemical Shift Data for $Be(RCOCHCOR')_2$

R	R′	δ(^{9}Be)	R	R′	δ(^{9}Be)
CH_3	CF_3	3.14	C_4H_3S	C_2F_5	3.66
C_6H_5	CF_3	3.74	C_6H_5	C_3F_7	3.14
C_4H_3S	CF_3	3.22	C_4H_3S	C_3F_7	3.15
C_4H_3O	CF_3	3.26	CH_3	CH_3	2.97
C_6H_5	C_2F_5	3.64	CF_3	CF_3	3.58

of β-diketones and their metal complexes, especially for fluorinated or partially fluorinated β-diketones and their complexes. For the beryllium complexes in this study, formation of the even-electron BeL^+ ion is followed by transfer of a fluorine atom to beryllium and loss of a fluorine-containing even-electron neutral species. When R′ is CF_3, $:CF_2$ is lost, giving the ion $[FBe(RCOCHCO)]^+$. When R′ is C_2F_5, C_2F_4 is lost, generating the same ion. Minute peaks for $:CF_2$ loss are observed, leading to the $[FBe(RCOCHCOCF_2)]^+$ ion, but these are understandably of very low intensity in view of the stability of the alkene C_2F_4 over the neutral carbene CF_2. When R′ is C_3F_7, C_3F_6 is lost, with no or only trace peaks observed for $:CF_2$ and C_2F_4 losses.

The migration of a fluorine atom from the ligand to the metal has precedent in the metal complexes of fluorinated β-diketonates of some transition metals[3,6] beryllium,[4] alkaline earths,[7a] group 13 metals,[7a] lanthanides,[5,7b] tin,[7a] and zinc[6]. Other transition metals, such as copper,[6] do not show fluorine migration in their fluorinated β-diketonate complexes. Hard–soft acid–base theory, and class a and class b metal designations have been invoked[5,7] to explain these observations. It is not unexpected then to find the "hard" fluoride migrating to the "hard" Be^{2+}.

The base peak in most of the spectra examined corresponds to RCO^+, as seen in Table II. The formation of RCO^+ can be explained by loss of the neutral even-electron species FBe(COCH) from $[FBe(RCOCHCO)]^+$ as shown in Figure 2. The RCO^+ ion is particularly stable when R is phenyl or thienyl, due to resonance stabilization of the charge over the ion fragment framework. RCO^+ further degrades by loss of CO. The intensities of the resulting R^+ ion are given in Table II. One notes that the intensity of R^+ is generally less than that of R'^+, except when R is phenyl, again due to the resonance stability of the phenyl cation. Contributions to the intensity of the R^+ peak would certainly include R^+ formation from decomposition of RCO^+, and from cleavage of the nonfluorinated substituent on the ligand from $M^{\bullet+}$ to generate R^+ and $LBe(R'COCHCO)\cdot$.

The ^{9}Be NMR spectra of these complexes are characterized by a single sharp resonance. The chemical shifts are given in Table III. The width at half-height is ca. 6 Hz when R′ is CF_3 or CH_3. When R′ is C_2F_5 or C_3F_7, the half-height line width increases to ca. 10 Hz. The cause of this change is uncertain but it may be due to minor through-space interactions with the fluorine atoms on the ends of R′ with beryllium.

The range of measured chemical shifts for the β-diketonate complexes (+2.96 to +3.66 ppm) fit into the range for four-coordinate ^{9}Be centers as previously established (ca. −2 to +6 ppm).[10] These data agree with the crystallographically established 4-coordinate tetrahedral geometry at beryllium.[9]

The ^{9}Be NMR chemical shift for $Be(acac)_2$ is 2.97 ppm and it has the most shielded resonance of the beryllium–β-diketonate complexes studied. Due to a total chemical shift range of only 0.77 ppm for the compounds observed, care must be taken in interpreting the chemical shift data in terms of any definite trends. Substitution of a CF_3 group for a CH_3 group results in an upfield shift of the beryllium resonance for $Be(tfac)_2$. A futher upfield shift is noted for $Be(hfac)_2$. This deshielding trend at beryllium is consistent with the electron-withdrawing ability of the CF_3 groups. Keeping the R group constant and varying the R′ group from CF_3 to C_2F_5 to C_3F_7, one observes a reversal of this trend when R is phenyl. Likewise when R is 2′-thienyl the ^{9}Be NMR resonance increases from 3.22 to 3.66 ppm when R′ is CF_3 and C_2F_5, respectively, but decreases when R′ is C_3F_7 to 3.15 ppm. This latter chemical shift variation indicates that the electronegativity of the substituent is not always the primary effect in determining the direction of the chemical shift. For example, the electronegativity of the X group in a series of C_5H_5BeX compounds has a small effect on the deshielding at the beryllium atom as compared to the paramagnetic ring current of the η^5-C_5H_5 ring.[10a] An explanation of these possible trends reported here must await further study with theoretical calculations.

Experimental Section

The β-diketonates and their beryllium complexes listed in Table I were prepared as previously described.[9] $Be(acac)_2$ was obtained from Alfa Products, and $Be(hfac)_2$ was a gift from Professor Gaines. Mass spectra were obtained on a Finnegann 4000 gas chromatograph/EI-CI. ^{9}Be NMR spectra were recorded in $CDCl_3$ at ambient temperature at approximately 0.1 M concentration on a Bruker AM-500 at 70.278 MHz using a 5.0-μs pulse width and a pulse delay of 111.3 μs between scans over a 5600-Hz window. Chemical shifts were referenced to $Be(H_2O)_4^{2+}$(aq).

Acknowledgment. The authors thank W. Schulze, of Miller Brewing Co., Inc., for the mass spectral data. The authors also thank Professor D. Gaines, Drs. T. Hill and B. Adams, and G. Edvenson at the University of Wisconsin—Madison for the ^{9}Be NMR spectra.

Registry No. **1**, 13939-10-1; **2**, 14052-07-4; **3**, 13928-05-7; **4**, 13928-06-8; **5**, 93595-66-5; **6**, 93595-67-6; **7**, 93595-68-7; **8**, 93595-69-8; Be, 7440-41-7.

---

(10) (a) Gaines, D. F.; Coleson, K. M.; Hillenbrand, D. F. *J. Magn. Reson.* **1981**, *44*, 84. (b) Lindman, B.; Forsen, S. *in NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849

Can the Bis(diboranyl) Structure of B_4H_{10} Be Observed?

Michael L. McKee

Received February 18, 1986

Two recent theoretical studies[1,2] have appeared on the relative stability of the known "butterfly" C_{2v} structure of B_4H_{10} (**2**) and the unknown bis(diboranyl) C_2 structure of B_4H_{10} (**1**). Given the prediction of nearly equal stability, it is perhaps unusual that the bis(diboranyl) structure has not been observed. The purpose of the present note is to explore theoretically the potential energy

---

(1) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1981**, *20*, 4452.

(2) Morris-Sherwood, B. J.; Hall, M. B. *Chem. Phys. Lett.* **1981**, *84*, 194.

0020-1669/86/1325-3545$01.50/0

Table I. Energies (kcal/mol) of B_4H_{10} Structures Relative to the "Butterfly" C_{2v} Structure

molecule	no.	3-21G	6-31G	MP2/6-31G	6-31G*	[MP2/6-31G*][a]	MP2/6-31G*
bis(diboranyl)	**1**	−6.12	−6.92	5.81	−8.22	4.51	8.99
"butterfly"	**2**	0.0	0.0	0.0	0.0	0.0	0.0
$BH_3 + B_3H_7$[b]	**8**	13.55	10.18	30.46	12.18	32.46	39.37
path a	**3**	120.08	118.34	122.31	130.23	134.20	138.66
path b	**4**	42.44	42.78	56.96	43.89	58.07	62.25
path c	**5**	7.70	5.99	29.27	10.57	33.85	41.60
path c	**6**	28.71	28.78	33.83	29.38	34.43	38.50
$2B_2H_5$	**9**	77.43	74.07	104.27	71.26	98.10	111.20

[a] Additivity approximation: McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 762. [b] The reference is the 2102 *styx* structure (**8**).

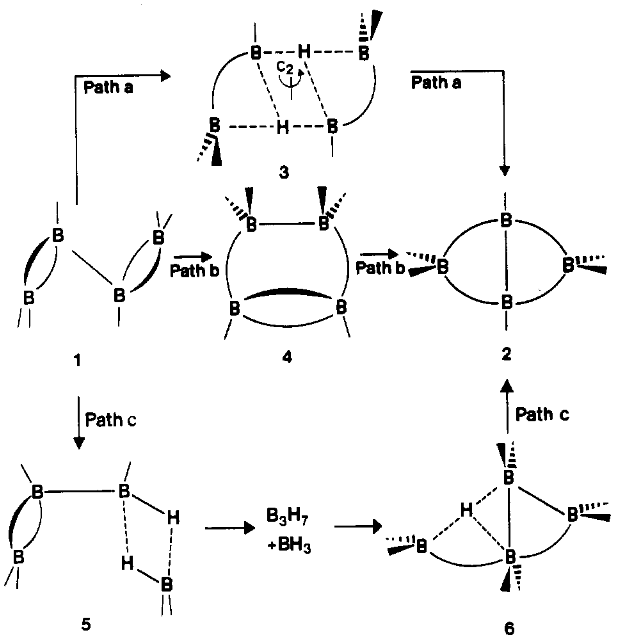


Figure 1. Three possible pathways for interconversion of the bis(diboranyl) structure (**1**) and the known structure of B_4H_{10} (**2**). Path c is the lowest energy pathway.

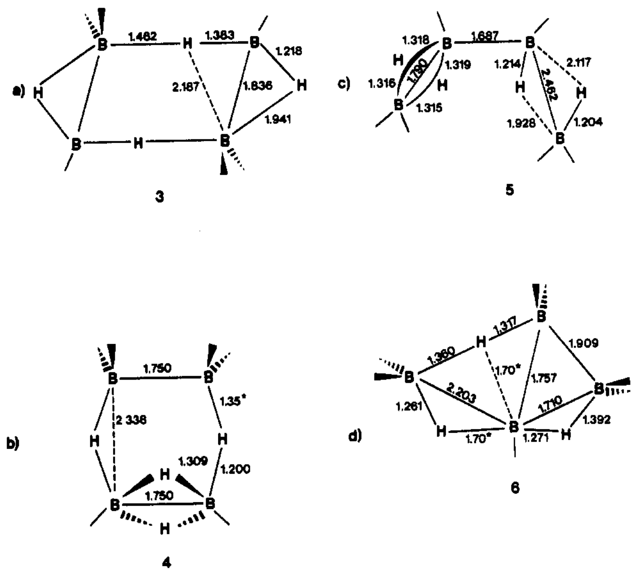


Figure 2. Selected geometric parameters for structures on the B_4H_{10} potential energy surface at the 3-21G level. An asterisk indicates a parameter that was held constant during optimization.

surface connecting the two structures.

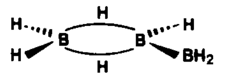
At least three pathways can be envisioned (Figure 1). In one (path a), the symmetry of the transition state preserves the C_2 axis common to **1** and **2**. The second pathway (path b) involves the interchange of bridge and terminal hydrogens, while the third pathway (path c) involves the stepwise elimination of borane (BH_3) from **1** to form B_3H_7 and BH_3 followed by the addition of borane to B_3H_7 to form **2**.

Optimizations were carried out by using the 3-21G basis set with no constraints within the assumed point group except those mentioned specifically below. For the 3-21G geometries, polarization effects (6-31G*) and correlation effects (MP2/6-31G) were combined to determine relative energies ([MP2/6-31G*]). In addition, the full calculations at the MP2/6-31G* level were also carried out. Relative energies at various levels are presented in Table I.

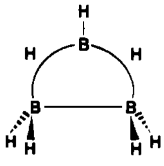
When C_2 symmetry was enforced, a stationary point on path a and intermediate to **1** and **2** was located (Figure 2a). A vibrational frequency calculation of **3** revealed four imaginary frequencies, proving that it is not a transition state but rather a stationary state of order 4. In fact, the largest negative mode ($-2154\ cm^{-1}$) corresponds to a degenerate rearrangement ($B_2H_6 + B_2H_4 \rightarrow B_2H_4 + B_2H_6$) instead of **1** → **2**. The high energy of **3** relative to **2** (138.7 kcal/mol) strongly suggests that the C_2 pathway (path a) is very unfavorable.

The second pathway (path b) involves the conversion of two bridge hydrogens to terminal hydrogens and the exchange of two bridging interactions. If **4** is assumed to lie on path b, then a lower limit of the activation barrier can be determined by comparing **1** and **4**. The optimization of **4** in the C_{2v} point group without constraint led to $B_2H_6 + B_2H_4$. Therefore, the optimization was carried out with the constraint that two bridging interactions be fixed at 1.35 Å (Figure 2b). Since a least motion path is not readily apparent between **4** and **2** and the energy of **4** is already 62.5 kcal/mol higher than that of **2**, consideration of reaction along path b can be eliminated.

The third pathway (path c) from **1** to **2** involves as the first step the dissociation to B_3H_7 plus borane. The donation-back-donation aspects of this step have been discussed[3] in the context of the analogous $B_2H_6 \rightarrow 2BH_3$ dissociation. The two bridging interactions involving the departing borane (Figure 2c) are broken to a different extent in the transition state (1.928 vs. 2.177 Å, Figure 2c) due to the steric influence of the adjacent diborane moiety. The product of dissociation is the 2012 (*styx* notation) B_3H_7 structure (**7**), which is calculated[4] to be 7.4 kcal/mol less stable than the 2102 form (**8**). The activation barrier is calculated to be 32.6 kcal/mol, which is similar to the known dissociation barrier of B_2H_6 (35 kcal/mol).[5]



7



8

The transition state (**6**, Figure 2d) for addition of BH_3 to B_3H_7 (2102) could not be located with an unconstrained optimization at the 3-21G level, the key feature of which is a triple-bridging

---

(3) Lipscomb, W. N. *Science* (*Washington, D.C.*) **1977**, *196*, 1047.
(4) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1982**, *21*, 2846.
(5) Fehlner, T. P. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed., Academic: New York, 1967; Chapter 7.

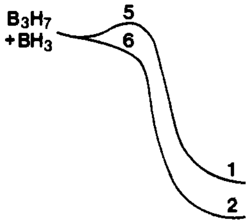


Figure 3. Minimum energy reaction profile (MERP) for the reaction of $BH_3 + B_3H_7$ to form structure **1** or **2**. The transition state **5** is 3.1 kcal/mol higher in energy than **6** at the MP2/6-31G* level.

hydrogen that is underestimated at the 3-21G level.[6] The structure in Figure 2d was completely optimized subject to the constraint that the two forming bridge interactions are 1.70 Å from the more distant boron.[7] The constraint is not necessary if geometries are optimized at the MP2/3-21G level, as shown recently[6] for the reaction $B_3H_9 \rightarrow B_2H_6 + BH_3$. For that reaction the geometry from the constrained optimization leads to an energy only 1 kcal/mol higher than that of the fully optimized MP2/3-21G geometry when both were calculated at a higher level of theory.[6] The lowest pathway for decomposition of **2** is not to $B_3H_7 + BH_3$ but rather to $B_4H_8 + H_2$, which has an experimental activation barrier of 24 kcal/mol.[8,9] Thus, the bis(diboranyl) structure is not likely formed in a direct conversion but could be formed from B_3H_7 and BH_3, which are present in steady-state concentrations from other pyrolytic reactions. The minimum energy reaction profile (MERP) is shown in Figure 3 for reaction of $B_3H_7 + BH_3$ to form **1** and **2** over transition states **5** and **6**, respectively. The reaction to form **1** proceeds with a 2.2 kcal/mol barrier while the reaction to form **2** proceeds with a negative enthalpic barrier (−0.9 kcal/mol).[10]

During pyrolysis of diborane (100–150 °C), the product ratio should be determined by the difference in activation barriers corresponding to the two paths for reaction of $B_3H_7 + BH_3$ (3.1 kcal/mol) if under kinetic control, while the ratio should be determined by the difference in stabilities of products (9.0 kcal/mol) if under thermodynamic control. It should be considered that although the barriers for reaction of $B_3H_7 + BH_3$ are low, the concentrations of the two transient boron hydrides will be very small. More likely, the reaction will be between B_3H_7 and a stable boron hydride such as B_2H_6, where the borane is delivered bound as the dimer. The mechanism of reaction, however, will be unchanged, and the difference in activation barriers will be similar even though the barriers themselves will be higher.[6]

The product ratio (**2**:**1**) can be estimated by determining the ratio of rates for the two reactions. The entropy of activation (which is required to compute the *A* factor) for the reaction $BH_3 + B_3H_7 \rightarrow$ **2** can be estimated as the entropy of activation for a closely related reaction, $BH_3 + B_2H_6 \rightarrow B_3H_9$, which is −28.4 cal deg^{-1} mol^{-1} at the MP2/STO-3G level.[6] For the reaction $BH_3 + B_3H_7 \rightarrow$ **1**, the entropy of activation is calculated by using the 3-21G vibrational frequencies for the reactants and the transition state (−29.6 cal deg^{-1} mol^{-1}). The entropies of activation for both reactions are negative, which is reasonable for a bimolecular reaction, and similar in magnitude. Calculation of rates using the above approximations leads to a 100:1 product ratio at 100 °C. If the reaction is under thermodynamic control, the ratio would be much greater, 10^6:1. However, the high reverse barriers (32.6 and 39.4 kcal/mol) should slow the approach to equilibrium concentrations.

Thus, it may be possible to use IR spectroscopy to detect bis(diboranyl) as a minor component under pyrolysis conditions that favor B_4H_{10} formation. It is suggested to look for the asymmetric bridge stretching frequencies, which are predicted to be about 300 cm^{-1} lower in **2** compared to **1**. The calculated asymmetric BHB stretches in the "butterfly" structure (**2**) are 1378, 1514, 1584, and 1611 cm^{-1} (obsd 1308, 1324, 1388, and 1444 cm^{-1})[11] compared to 1748, 1826, 1861, and 1878 cm^{-1} in the bis(diboranyl) structure (**1**) at the 3-21G level. At the same level of computation the calculated asymmetric bridge stretches in B_2H_6 are 1820 and 1915 cm^{-1} (obsd 1602 and 1768 cm^{-1}).[12]

There are two relevant reactions that may actually go through **1** while yielding only **2** as an observable product. In one, mercury-sensitized photolysis of diborane yielded B_4H_{10} in good yield.[13] Initial formation of $B_2H_5^{\bullet}$ (**9**) could form **1** with sufficient excess energy (102.2 kcal/mol) to rearrange to **2**. The second reaction, carried out in the early days of boron chemistry by Stock,[14,15] involved the conversion of B_2H_5I in the presence of sodium amalgam to B_4H_{10} in low yields using a Wurtz-type coupling reaction.[16]

Acknowledgment. M.L.M. thanks the Auburn University Computation Center for a generous allotment of computer time, Dr. Peter Livant for helpful suggestions, and Professor William N. Lipscomb for helpful conversations. The reviewers are acknowledged for pointing out the two reactions that might initially proceed via a bis(diboranyl) intermediate.

Registry No. B_4H_{10}, 18283-93-7.

---

(6) McKee, M. L.; Lipscomb, W. N., to be submitted for publication.
(7) Ortiz, J. V.; Lipscomb, W. N. *Chem. Phys. Lett.* **1983**, *103*, 59.
(8) Greatrex, R.; Greenwood, N. N.; Potter, C. D. *J. Chem. Soc., Dalton Trans.* **1984**, 2435.
(9) Brennan, G. L.; Schaeffer, R. *J. Inorg. Nucl. Chem.* **1961**, *20*, 205.
(10) At the 3-21G level the activation barrier is 15.2 kcal/mol; however, inclusion of correlation and polarization stabilizes the transition state (**6**) more than $BH_3 + B_3H_7$ resulting in a negative barrier at the MP2/6-31G* level. Since the entropy of activation will be negative for a recombination reaction, the free energy of activation will probably be positive.
(11) Dahl, A. J.; Taylor, R. C. *Inorg. Chem.* **1971**, *10*, 2508.
(12) Ramaswany, K.; Shannugam, G. *Acta Phys. Pol., A* **1973**, *44*, 349.
(13) Plotkin, J. S.; Astheimer, R. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 4155–4163.
(14) *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Interscience: New York, 1968; Vol. 5, p 66.
(15) Stock, A. E. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1933.
(16) Garst, J. F. In *Free Radicals*; Kochi, J. K., Ed.,; Wiley: New York, 1973; Vol. 1, pp 539–541.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Formation of a Binuclear Complex by Reaction of $(H_2O)_5CrCH_2CN^{2+}$ with Mercury(II)

Margaret J. Sisley and Robert B. Jordan*

Received October 28, 1985

The carbon–chromium bond in organochromium complexes of the type $(H_2O)_5Cr{-}R^{2+}$ is cleaved readily by electrophiles such as mercury(II). The rate constants for a large number of these reactions with Hg^{2+} and varying –R groups have been determined.[1] There have been two kinetic studies of reaction 1 which confirmed the rate law given in eq 2. There is satisfactory agreement on the value of k_{Hg} of 9.8[2] and 8.7[3] M^{-1} s^{-1} (25 °C, 1 M $LiClO_4/HClO_4$).

$$(H_2O)_5CrCH_2CN^{2+} + Hg^{2+} + H_2O \rightarrow Cr(OH_2)_6^{3+} + HgCH_2CN^+ \quad (1)$$

$$\text{rate} = k_{Hg}[CrCH_2CN^{2+}][Hg^{2+}] \quad (2)$$

In this note it is shown that eq 1 is not a complete representation of the reaction in that the true products are not just those shown. The present observations have implications for other such reactions, especially if the organic group has substituents that can coordinate to chromium(III).

---

(1) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.
(2) Funke, L. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 897.
(3) Kupferschmidt, W. C.; Jordan, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 991.