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# Possible Mechanisms for the Isomerization of $B_9H_9^{2-}$ and $C_2B_7H_9$

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Lipscomb proposed the diamond–square–diamond (DSD) mechanism as a general scheme for framework rearrangements of boranes and carboranes. In our paper we analyze these processes for $B_9H_9^{2-}$ and the isoelectronic carborane $C_2B_7H_9$. We can show that a mechanism involving a single DSD rearrangement is forbidden by the principle of conservation of orbital symmetry, but a double DSD process is allowed. Qualitative considerations and the results of ab initio MO calculations suggest that the three carborane isomers of lowest energy are separated from each other by activation barriers that might be large enough to permit isolation of these low-energy isomers if indeed rearrangement takes place by the double DSD process. There is no experimental evidence of structural rearrangements for $B_9H_9^{2-}$ or the isomerization of $C_2B_7H_9$, only one isomer of which has been prepared and characterized.

Introduction

Twenty years ago Lipscomb[1] proposed a general mechanism for the framework reorganization or isomerization of *closo*-boranes and -carboranes, $B_nH_n^{2-}$ and $C_2B_{n-2}H_n$. These molecules and ions have structures that are polyhedra with triangular faces.[2] A hydrogen substituent is in the exo position on each carbon or boron. In his classic review Lipscomb suggested that rearrangements take place through a diamond–square–diamond (DSD) process in which a bond or edge shared by two triangular faces breaks as a new bond forms perpendicular to the breaking bond.[1]
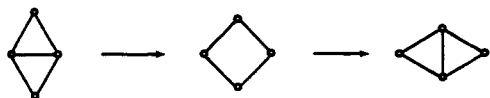
The proposal of this mechanism as a general scheme was based on earlier considerations of specific systems.[3-5]

$B_9H_9^{2-}$ and $C_2B_7H_9$ have structures that have been described as tricapped trigonal prisms (1).[6,7] The symmetry is idealized
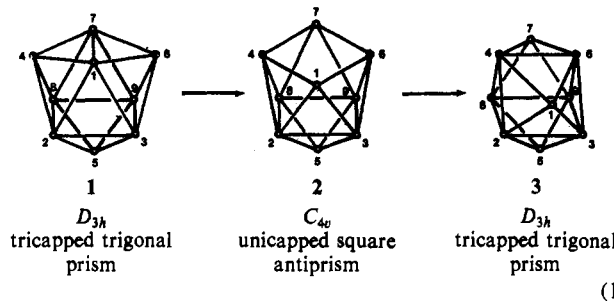

1
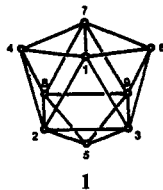
D_{3h}. Although six isomers of $C_2B_7H_9$ are possible, only the 4,5-isomer has been prepared. Empirical valence theory,[2] the rule of topological charge stabilization,[8] and the results of ab initio SCF MO calculations[9] predict that the 4,5-isomer has the lowest energy. The six carborane isomers, each labeled with typical vertices that locate the two carbon heteroatoms, are as follows: cap–cap (4,5); cap–near vertex (1,4); cap–far vertex (3,4); triangular edge (1,2); rectangular edge (1,7); rectangular diagonal (1,8).

Although $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$, for example, are known to be fluxional,[10-13] all available experimental evidence suggests that $B_9H_9^{2-}$ is structurally rigid.[14-16] $B_9H_9^{2-}$ does not show structural

ambivalence in solution[15] nor evidence of structural rearrangements that are fast on the NMR time scale.[16] An analysis of crystallographic results for $B_9H_9^{2-}$ with various counterions does not reveal the polyhedral framework distorted toward structures that might approximate a rearrangement intermediate.[14] Only one of the six possible isomers of $C_2B_7H_9$ is known to exist.[7] Apparently the nine-atom polyhedron does not rearrange. Nevertheless, there has been much speculation concerning whether these systems can rearrange, and if not, why not. From the fact that only a single isomer of $C_2B_7H_9$ is known, Williams[17] concluded that polyhedral rearrangements in this system must be easy, allowing higher energy isomers to rearrange to the most stable 4,5-form. Other carboranes, for which two or more isomers exist, must rearrange with difficulty, leaving higher energy forms trapped behind activation barriers and permitting their identification. Muetterties[14,16] pointed out that it is easy to visualize rearrangement mechanisms that require minimal atomic motion during reorganization, suggesting possible isomerizations. On the basis of connectivity arguments, King[18] concluded that $B_9H_9^{2-}$ should be inherently fluxional.

Single DSD Process

Equation 1 describes a single DSD process that can convert one isomer of $C_2B_7H_9$ into another through an intermediate structure of idealized C_{4v} symmetry. This process was one of two

1	2	3
D_{3h}	C_{4v}	D_{3h}
tricapped trigonal prism	unicapped square antiprism	tricapped trigonal prism

(1)

proposed by Guggenberger and Muetterties.[14] Imagine the 1,7 bond in **1** breaking with the simultaneous formation of a new bond between vertices 4 and 6 to give **3**. The new 4,6 bond in **3** is perpendicular to the 1,7 bond that was broken in **1**. If all the vertices in **1** are occupied by the same kind of atom (as they would be in $B_9H_9^{2-}$, except for isotopic substitution), then the new structure **3** is identical with **1**, except for labeling. King has called such a process a degenerate process.[18] The situation is related to Berry pseudorotation.[19] However, if carbon heteroatoms (indicated by •) are at positions 4 and 6, then the DSD process (1) converts a cap–cap isomer (equivalent to 4,5) into an isomer in which the heteroatoms are related by a rectangular or parallel prism edge (equivalent to 1,7). Thus, we can say that eq 1 converts

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(2) (a) Williams, R. E.; Gerhert, F. J. *J. Am. Chem. Soc.* **1965**, *87*, 3513–3515. (b) Williams, R. E. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon: Oxford, England, 1970; Vol. 2, p 37.
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(6) Guggenberger, L. J. *Inorg. Chem.* **1968**, *7*, 2260–2264.
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(11) Berry, T. E.; Tebbe, F. N.; Hawthorne, M. F. *Tetrahedron Lett.* **1965**, 715–720.
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(13) Muetterties, E. L. *Tetrahedron* **1974**, *30*, 1595–1604.
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(15) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1966**, *5*, 1955–1960.
(16) Muetterties, E. L.; Hoel, E. L.; Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1975**, *14*, 950–951.
(17) Reference 2b, p 70.
(18) King, R. B. *Inorg. Chim. Acta* **1981**, *49*, 237–240.
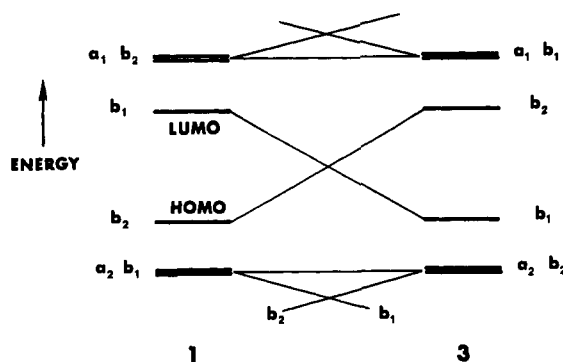(19) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.

Figure 1. MO energy level correlation diagram for the single DSD process of eq 1. Only those levels around the HOMO–LUMO gap are shown. Orbitals are classified according to C_{2v}, the minimum symmetry maintained during the rearrangement. Crossing of filled b_2 and vacant b_1 orbitals indicates a symmetry-disallowed process.

the 4,5-isomer into the 1,7-isomer. By starting with pairs of carbon atoms at different positions in **1**, it is possible to generate all six isomers starting with any given isomer. The six isomers are related by the chain

$$1,4 \rightleftharpoons 1,2 \rightleftharpoons 1,7 \rightleftharpoons 4,5 \rightleftharpoons 3,4 \rightleftharpoons 1,8$$
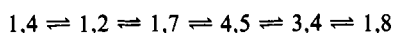
4

For example, the 4,5-isomer can convert by a single DSD process into either the 1,7- or 3,4-isomer but the 1,4-isomer can become the 1,8-isomer only by a series of DSD processes passing through each of the other four isomers.

It is worth looking a little more closely at what happens in eq 1. In **1** and **3** each cap is four-coordinate (not counting the bond to the exo hydrogen) and each prism vertex is five-coordinate. To preserve the same degree of connectivity in initial and final structures, for each cap that becomes a prism vertex there must be a prism vertex that becomes a cap. The tricapped trigonal prism has three different kinds of edges: rectangular or parallel prism edges, triangular face edges, and cap edges. A single switch of one of these edges must perserve the degree of connectivity of the polyhedron. King calls such an edge a switching edge.[18] Only the rectangular edges can act as switching edges because only they preserve the appropriate degree of coordination at the vertices. Therefore, only eq 1 (and equivalent processes involving edges 2,8 and 3,9) can regenerate the polyhedron through a single DSD process.

Notice that the 3-fold rotational axis in **1** (perpendicular to the plane of the page) is lost during eq 1, reappearing in **3** (in plane of page) as rotated by 90°. The two planes of symmetry are maintained during the process and the C_3 axis shifts from one plane to the other. This shift may give rise to an orbital symmetry disallowed process[20] as it does in the DSD rearrangement proposed for $B_5H_5^{2-}$ and $C_2B_3H_5$.[21] To see if this occurs for the nine-atom polyhedron, we performed extended Hückel calculations[22] for $B_9H_9^{2-}$. Figure 1 is a molecular orbital energy level correlation diagram for eq 1, showing orbitals around the HOMO–LUMO gap. Although the end points **1** and **3** have D_{3h} symmetry and the intermediate structure **2** has C_{4v} symmetry, the intervening structures are C_{2v}. Therefore, we have classified the orbitals as a_1, a_2, b_1, or b_2 using the C_2 axis that is preserved and the plane of symmetry of the page. The a_1,b_2 and a_2,b_1 degenerate pairs for **1** would be classified as e′ and e″, respectively, under the full D_{3h} symmetry of this structure. The crossing of occupied b_2 and vacant b_1 levels indicates that eq 1 is forbidden by the principle of conservation of orbital symmetry or, in more general terms, that this process probably faces a large activation energy barrier
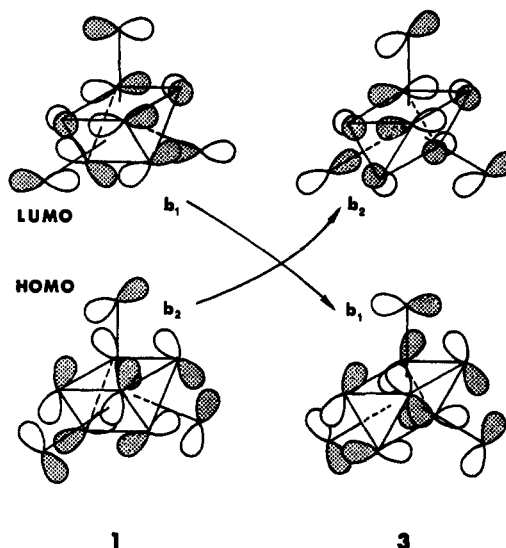

Figure 2. Schematic AO composition diagrams for HOMO and LUMO of $B_9H_9^{2-}$ undergoing eq 1. The orbitals of **1** and **3** are identical except for a 90° rotation of the polyhedron, but orbitals are classified according to their symmetry with respect to the plane of the page. Connecting orbitals of like symmetry requires a crossing of occupied and vacant orbitals.

that prevents its occurrence. The crossing of filled and empty energy levels for eq 1 was at least anticipated by Guggenberger,[6] who reported that an extended Hückel calculation for the C_{4v} intermediate **2** of $B_9H_9^{2-}$ gave an open-shell electron configuration, with two electrons to go into a degenerate pair of orbitals at high energy, while the D_{3h} form had a closed-shell configuration.[23]

Structures **1** and **3** differ only by a rotation of 90° in space (following the 3-fold axis) so their orbital energies are identical. But the rotation changes the symmetry classification of the b orbitals, which must be either symmetric with respect to the plane of the page (subscript 1) or antisymmetric (subscript 2). The effect of the 90° rotation is to change each b_1 to b_2 and vice versa. No such reversal in symmetry is required for a_1 and a_2 orbitals. Figure 2 shows atomic orbital composition diagrams[24] of the filled b_2 and vacant b_1 orbitals at the crossing and provides a pictorial explanation for the crossing shown in Figure 1. The reversal of b_1 and b_2 classifications does not guarantee that an orbital crossing will occur at the HOMO–LUMO gap. The calculations for **1** reveal five b_2 orbitals at or below the HOMO and only four occupied b_1 orbitals. Consequently, the occupied MO's of **3** must include five of b_1 symmetry and four of b_2. Therefore, a crossing of filled b_2 and vacant b_1 must occur during eq 1.

If eq 1 is not allowed for $B_9H_9^{2-}$, what about the related but less symmetric carboranes? Closer analysis of Figure 2 reveals that the essential property governing the allowed or forbidden nature of the process is the symmetry of the orbitals with respect to the plane of the page. If the starting carborane isomer (**1**) has C_s symmetry, then a_1 and b_1 orbitals under C_{2v} become a′ (symmetric with respect to the plane of the page) under C_s and a_2 and b_2 orbitals become a″ (antisymmetric). From the extended Hückel results for **1** there are 12 filled orbitals of a′ symmetry and only 7 of a″. As before, the symmetry of the former b_1 and b_2 orbitals reverses as **1** rotates to **3**, giving 13 filled orbitals of a′ and 6 of a″. Since the numbers of orbitals of a′ and a″ symmetries are not the same for **1** and **3**, crossings of filled and empty orbitals are assured. The process is symmetry-forbidden.

Only the 4,5- and 1,7-$C_2B_7H_9$ isomers meet the minimum requirement for C_s symmetry. The structurally possible isomerizations involving these two isomers are a subset of **4**:

$$1,2 \rightleftharpoons 1,7 \rightleftharpoons 4,5 \rightleftharpoons 3,4$$
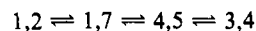
(20) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, FRG, 1970.
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(24) Gimarc, B. M. *Molecular Structure and Bonding*; Academic: New York, 1979.

For example, the 2,8-isomer of **1** is equivalent to 1,7. In eq 1 2,8 is converted into a triangular edge isomer (equivalent to 1,2), so we can say that the interconversion of 1,7 and 1,2 is structurally possible. None of these conversions is symmetry-allowed however. The argument that this process will also have a high energy barrier for less symmetric carborane isomers is less compelling but generally follows the reasoning usually invoked for organic reaction mechanisms.[25] The MO's of the less symmetric isomers will have nodal properties that are similar to those of $B_9H_9{}^{2-}$. These will produce intended correlations that may produce an activation barrier large enough to block rearrangement in the less symmetric cases.

Double DSD Processes

Another structural reorganization process proposed by Guggenberger and Muetterties[14] is shown in eq 2. This one involves two simultaneous DSD processes. Imagine the 1,7 and 2,3 bonds

(2)
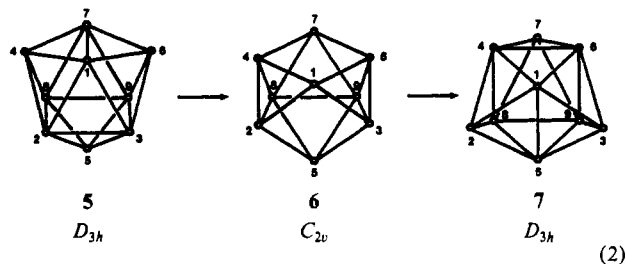
in **5** breaking and two new bonds forming between 4 and 6 and between 1 and 5 to give **7**. For the particular rearrangement described in eq 2, the 4,6-isomer (or its equivalent 4,5) is converted into an isomer equivalent to 1,2. By starting with a pair of carbon heteroatoms in other positions and following the rearrangements, one can determine that interconversion of all isomers is possible through the closed cycle

8
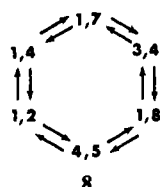
Equation 2 can include processes that are degenerate in the sense mentioned by King. For example, starting from the 2,5-isomer (equivalent to 1,4) eq 2 leads to a structure that is also equivalent to 1,4.

Although intermediate **6** is of C_{2v} symmetry, only a single symmetry element is maintained throughout this double DSD rearrangement: the vertical plane of symmetry perpendicular to the plane of the page. The C_3 axis of **5** (perpendicular to the page) is lost, to reappear in **7** (vertical, in plane of page). Although 90° apart, the C_3 axes of **5** and **7** both lie in the plane of symmetry that is maintained during the rearrangement. The rotation of the structure does not require a reclassification of orbitals with respect to the symmetry plane and therefore eq 2 is symmetry-allowed even in the cases of the most symmetric structures: $B_9H_9{}^{2-}$ and the 4,5- and 1,7-isomers of $C_2B_7H_9$.

Muetterties[16] argued that two considerations should govern the ease of structural rearrangements: energetics and dynamics. Intermediate structures along the pathway should be energetically low, and the atomic motions necessary to achieve the new conformation should be minimal. In eq 1 the atomic motions are easy enough but orbital symmetry considerations suggest a formidable energy barrier. In eq 2 orbital symmetry does not interpose an energy barrier but the atomic motions required to carry the process through are much more complicated. Furthermore, bond energy considerations suggest that the energy barrier might be high in eq 2, which starts with the simultaneous breaking of two bonds.
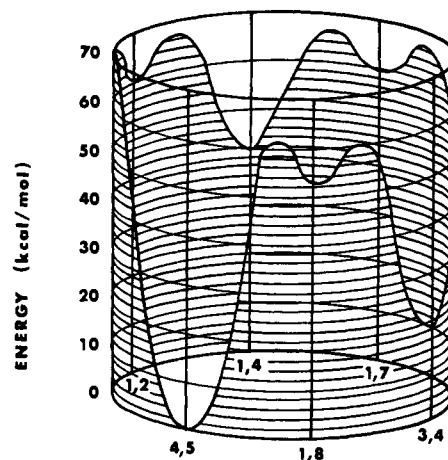
**Figure 3.** Schematic representation of the potential surface around the cycle **8** for the double DSD process, eq 2.

We do have information that allows us to make some limited statements about the barriers separating isomers in eq 2. Qualitative considerations[8,2] have given us the following order of stabilities for the six isomers of $C_2B_7H_9$:

$$4,5 > 3,4 > 1,4 > 1,8 > 1,2 > 1,7$$
$$0 \quad 19.9 \quad 42.6 \quad 53.1$$

9

The numbers below the isomer vertices in **9** are the relative energies (in kcal/mol) obtained from geometry-optimized ab initio SCF–MO calculations at the STO-3G level.[9] It is interesting that in the loop or cycle (**8**) relating the interconversion of isomers by the double DSD process, eq 2, the three lower energy isomers are separated by the three higher energy isomers. Although we can say nothing qualitatively about energy barriers between pairs of isomers that are adjacent to each other in the loop and we do not know the energies of the two least stable isomers, we do have estimated lower bounds for the barriers between the three most stable isomers. The tops of these barriers must be at least as high as the energy of the 1,8-isomer. Figure 3 shows a cylindrical slice through a schematic potential surface around the loop (**8**) connecting isomers by eq 2. From these results we conclude that it should be possible to isolate the 3,4- and 1,4-isomers, if the process governing the interconversion of isomers is indeed eq 2. We emphasize once more that only the 4,5-isomer has been prepared and characterized.

Other Rearrangements

The process described by eq 2 is related to the framework rearrangement that Lipscomb[1,26] originally proposed for $B_9H_9{}^{2-}$ involving an intermediate structure **10**, which, like **6**, has C_{2v}

10
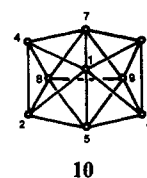
symmetry. Notice that structure **10** contains a 6-coordinate atom at vertex 1. Such structures are known in borane and carborane chemistry. For example, both $B_{11}H_{11}{}^{2-}$ and $C_2B_9H_{11}$ each have a single 6-coordinate boron atom.[7,27] The rearrangement of **5** to **10** requires one DSD step, and the subsequent conversion of **10** to **7** takes still another. Therefore, the rearrangement involving **10** can be said to follow two sequential DSD processes. However, exactly the same symmetry arguments we used in connection with eq 2 can be recycled to show that the rearrangement passing through **10** is symmetry-allowed and the various carborane isomers produced by such rearrangements are related by the same loop

(25) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, England, 1984; p 357.

(26) Muetterties, E. L.; Storr, A. T. *J. Am. Chem. Soc.* **1969**, *91*, 3098–3099.
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(8). We are carrying out ab initio SCF–MO calculations to compare total energies of **6** and **10**.

In the double DSD process, eq 2, the degree of coordination at the vertices is preserved because the two switching edges are perpendicular to each other and involve a common vertex, in this case vertex 1. Switching edge 1,7 to 4,6 creates new caps at 1 and 7 and converts old caps at 4 and 6 into prism vertices. Simultaneously, the switch of the perpendicular edge from 2,3 to 1,5 forms new caps at 2 and 3 and turns the former cap at 5 and the incipient cap at 1 into prism vertices, preserving three caps and six prism vertices. For a double DSD process, one vertex must be common to both bond breaking and bond forming at the two switching edges. As a counterexample consider the process in which bonds 2,8 and 3,9 break in **1** to form two squares faces sharing the common vertex 5. The resulting structure (**11**) has

1   **11**
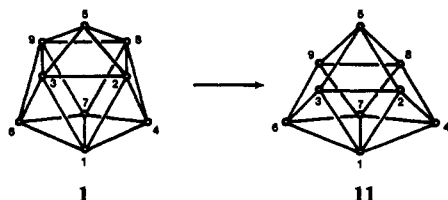
C_{2v} symmetry and is identical, except for labeling, with **6**. But as Guggenberger and Muetterties pointed out,[14] formation of new bonds in [1]**1** will not carry this structure into a tricapped trigonal prism, and therefore this process will not lead to a DSD isomerization. Equations 1 and 2 appear to be the only DSD processes that regenerate the starting polyhedron with an exchange of vertex labels.[28]

Conclusions

We have shown that for $B_9H_9^{2-}$ and $C_2B_7H_9$ the single DSD process, eq 1, is forbidden by orbital symmetry while the double

DSD mechanism, eq 2, is allowed. On the basis of qualitative considerations, we can conclude that energy barriers must separate the three lowest energy $C_2B_7H_9$ isomers on the loop or cycle connecting rearrangements that follow eq 2. The results of ab initio SCF–MO calculations suggest that these barriers might be large enough to allow isolation of the lowest energy isomers, if indeed rearrangement takes place by eq 2. Only a single isomer is known experimentally.

Theoretical analyses of DSD framework reorganizations have previously been reported for B_4H_4 (symmetry-forbidden but unknown experimentally),[29,30] for $B_5H_5^{2-}$ (symmetry-forbidden; experimentally known to be rigid),[24] and for $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ (symmetry-allowed; experimentally fluxional).[31,32] PRDDO–MO calculations have been reported for possible mechanisms for the observed interconversion of the two $C_2B_4H_6$ isomers.[33] There is experimental evidence for DSD rearrangements in $C_2B_5H_7$.[34] Lipscomb has suggested that polyhedral rearrangements occurring at high temperature might involve symmetry crossings of molecular orbitals.[35]

The DSD framework rearrangement proposal has stimulated productive research for 20 years. We now know that such rearrangements very likely occur in some systems but not in others. As in all mechanistic processes, Nature does not always allow reactants to follow the paths that chemists find most appealing and most readily visualized.

(28) One of the reviewers pointed out that, to be absolutely certain on this point, one would have to examine each of the 2606 combinatorially distinct 9-atom polyhedra. See: Duijvestijn, A. J. W.; Federico, P. J. *Math. Comput.* **1981**, *37*, 523.

(29) Kleier, D. A.; Bicerano, J.; Lipscomb, W. N. *Inorg. Chem.* **1980**, *19*, 216–218.
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On the Electronic Structure of Metal Tetrahydroborates: Quasi-Relativistic Xα–SW Study of M(BH₄)₄ (M = Zr, Hf, Th, U)

D. Hohl and N. Rösch*

Quasi-relativistic SCF-Xα scattered-wave calculations are presented for the series of metal tetrakis(tetrahydroborates) M(BH₄)₄ (M = Zr, Hf, Th, U). The bonding in the transition-metal compounds is that of tetrahedral d⁰ complexes with strong covalent contributions from π bonding ligand group orbitals. In the actinide complexes, 5f orbitals of the central atom are found to be important to covalent ligand–metal bonding but less than in the corresponding di-π-[8]annulene compounds. The ligand field manifold of U(BH₄)₄ and the corresponding spin–orbit constant agree well with experimental data. Photoelectron spectra are reproduced satisfactorily with the exception of a uniform shift. An explanation is presented why the first ligand-derived band in the spectra of the actinide complexes is narrower than that in the transition-metal compounds. The difference between the zirconium and hafnium complexes in the splitting of the second band is found to be a relativistic effect due to a more effective covalent mixing of the Hf 6s orbital.

Introduction

Recent molecular orbital studies[1,2] have shown that f orbitals of actinides and lanthanides contribute to covalent bonding in complexes containing the [8]annulene ligand. Fairly sizable f

covalency effects have been identified for uranocene ((di-π-[8]annulene)uranium(IV)),[1,2] and somewhat smaller effects for thorocene and cerocene.[2,3] It is of considerable interest whether such bonding is unique to this type of molecule or whether it may

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