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Tetracoordinate Carbon as a Nucleophile? Interconversion of Carbenium Ions with Carbonium Ions Possessing Nearly Square-Pyramidal Pentacoordinate Carbons

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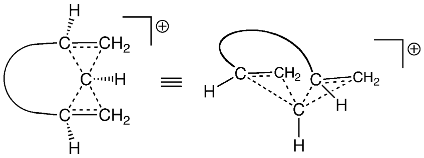
Received September 29, 2005



Quantum chemical calculations (B3LYP and Moeller−Plesset second-order perturbation theory) on carbonium ions containing hypercoordinated carbon atoms in distorted square-pyramidal geometries are described. The importance of overall charge (in addition to the delocalization of a certain number of electrons) for the stability of such structures is explored through calculations on isoelectronic systems containing boron atoms. The effects of alkyl substitution as well as variations in the structure of the linker attached to the C_5 core substructure are explored systematically for a variety of structures that do not have severe geometric constraints that rigidly enforce unusual geometries. In addition, transition structures for reactions involving the intramolecular attack of tetracoordinate carbons on carbenium ion centers were located; in some cases, such carbenium-to-carbonium rearrangement processes (in which tetracoordinate carbon centers act as nucleophiles) are actually both exothermic and accompanied by low activation barriers.

Introduction

One of the greatest crimes an undergraduate chemistry student can commit is to draw a carbon atom connected to five other atoms, but what is rarely taught in our undergraduate curricula, albeit for good reason, is that carbon does occasionally associate with more than four neighbors.[1] Energy minima with five-coordinate carbons are comparatively rare (although many such species have now been described) but are nonetheless important in several respects. First and foremost, they have stood as challenges to our models of bonding and to our conceptions of what organic molecular architectures are possible. One of the greatest debates in the history of organic chemistry, the so-called “nonclassical ion problem”, concerned the feasibility of hypercoordination and its relevance to the rates of various reactions.[2] In addition, hypercoordinate carbocations (carbonium ions) may actually be utilized by nature in the biosynthesis of complicated natural products; although more work is required to confirm this contention, there is evidence for the involvement of such species in some biosynthetic carbocation rearrangements.[3]

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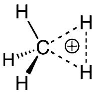
[1] For leading references, see: (a) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, S. G. K. *Onium Ions*; Wiley-Interscience: New York, 1998. (b) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Y. A. *Nonclassical Structures of Organic Compounds*; MIR Publishers: Moscow, 1987. (c) Minkin, V. I.; Minyaev, R. M. *Mendeleev Commun.* **2004**, 43−46.

[2] For leading references, see: (a) Issue 12 of *Acc. Chem. Res.* **1983**, *16*, 6. (b) Brown, H. C. *The Nonclassical Ion Problem*; Plenum: New York, 1977 (with comments by Schleyer, P. v. R.).

[3] For leading references on proposed carbonium ion intermediates in terpenoid biosynthesis, see: (a) Wessjohann, L. A.; Brandt, W. *Chem. Rev.* **2003**, *103*, 1625−1647. (b) Giner, J.-L.; Buzek, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 12871−12872. (c) Erickson, H. K.; Poulter, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 6886−6888. (d) He, X.; Cane, D. E. *J. Am. Chem. Soc.* **2004**, *126*, 2678−2679. (e) Dewar, M. J. S.; Ruiz, J. M. *Tetrahedron* **1987**, *43*, 2661−2674. (f) Gutta, P.; Tantillo, D. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2719−2723. (g) For leading references to older proposals by Djerassi, Arigoni, and Eschenmoser, see: Giner, J.-L. *Chem. Res.* **1993**, *93*, 1735−1752. (h) For a discussion of the possibility of carbonium ion formation in antibody-catalyzed reactions, see: Lee, J. K.; Houk, K. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1003−1005. (i) Ma, L.; Sweet, E. H.; Schultz, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 10227−10228 and references therein. (j) Protonated cyclopropanes have also been proposed as intermediates in the biosynthesis of cyclopropane fatty acids. See, for example: Iwig, D. F.; Grippe, A. T.; McIntyre, T. A.; Booker, S. J. *Biochemistry* **2004**, *43*, 13510−13524.

10.1021/jo052053a CCC: $33.50 © 2006 American Chemical Society
Published on Web 12/17/2005

Several geometric arrangements are possible for a five-coordinate carbon. The parent carbonium ion is protonated methane (methonium), CH_5^+. Quantum chemical calculations and experimental observations have shown that a C_s symmetric structure (**1**) is very slightly preferred for this ion, although pseudorotation leading to other conformations is extremely rapid (making CH_5^+ a fluxional molecule).[1,4] This species can be thought of as a complex of CH_3^+ with H_2 in which the empty orbital on the CH_3^+ interacts with the H—H σ-bonding orbital leading to a cyclic, delocalized, three-center, two-electron bonding array. Most carbonium ions can be described in a similar way, as complexes between CR_3^+ and H—H σ-, C—C σ-, or C═C π-bonds (e.g., **2**).[1,2] Five-coordinate carbons with different geometries have also been described. For example, a trigonal bipyramidal arrangement is only slightly less stable than the preferred geometry for **1** and is itself preferred outright in ions such as **3** (in which the R groups are interconnected, thus encouraging hypercoordination to occur).[5] As suggested by the pictures of **1**−**3**, hypercoordination does not require carbon to break the octet rule but rather to delocalize some of its electrons over several partial (i.e., less than 2-electron) “bonds”.



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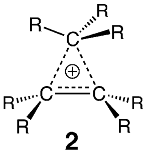

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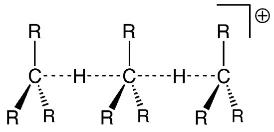

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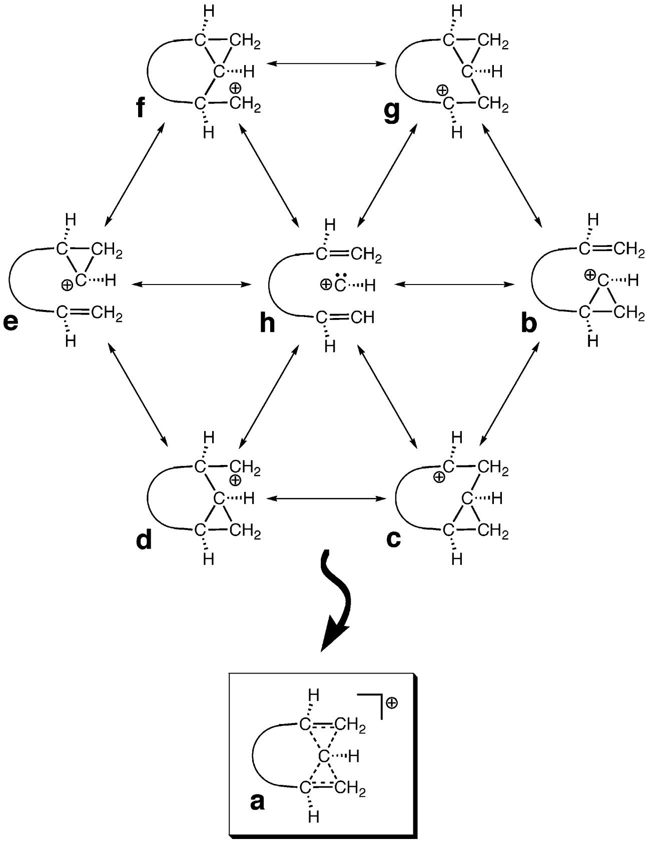
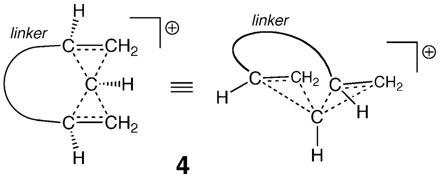
Herein, we discuss a different family of carbonium ions (**4**) containing hypercoordinated carbon atoms in distorted square-pyramidal geometries.[6,7] These carbocations can be thought of as hybrids of the various resonance structures shown in Scheme 1 and, therefore, contain more highly delocalized bonding arrays than species such as **2**.[6] Closely related species (Chart 1) have been described previously, experimentally and theoretically.[7] Of particular relevance to the work described herein are the studies of Cremer and co-workers on cation **4** with an ethylene linker (we discuss this cation below as well, calling it structure **6**).[7e,f] In the studies of Cremer and co-workers (MP4(SDQ)/6-31G(d)//MP2/6-31G(d) calculations), the geometry of this carbonium ion was described, along with its racemization and, interestingly, its interconversion with the bicyclohept[3.2.0]-3-yl and 2-norbornyl cations.

SCHEME 1



In the study described herein, we explore a different reaction mode of carbonium ions **4**: their interconversion with carbenium ions via the elongation of one of their four partial single bonds. In the reverse (i.e., carbenium-to-carbonium) direction, these reactions can be thought of as nucleophilic attacks by tetracoordinate carbons. We describe, to our knowledge, for the first time, transition structures for such processes and show that in some cases carbonium ion formation is both exothermic and accompanied by a low activation barrier. By systematically varying the linker attached to the C_5 core of cations **4**, we explore the effects of linker length and rigidity on this reactivity. We also probe the effects of substitution and charge by examining alkyl-substituted derivatives and isoelectronic relatives with the various carbon atoms of the C_5 core replaced by boron.



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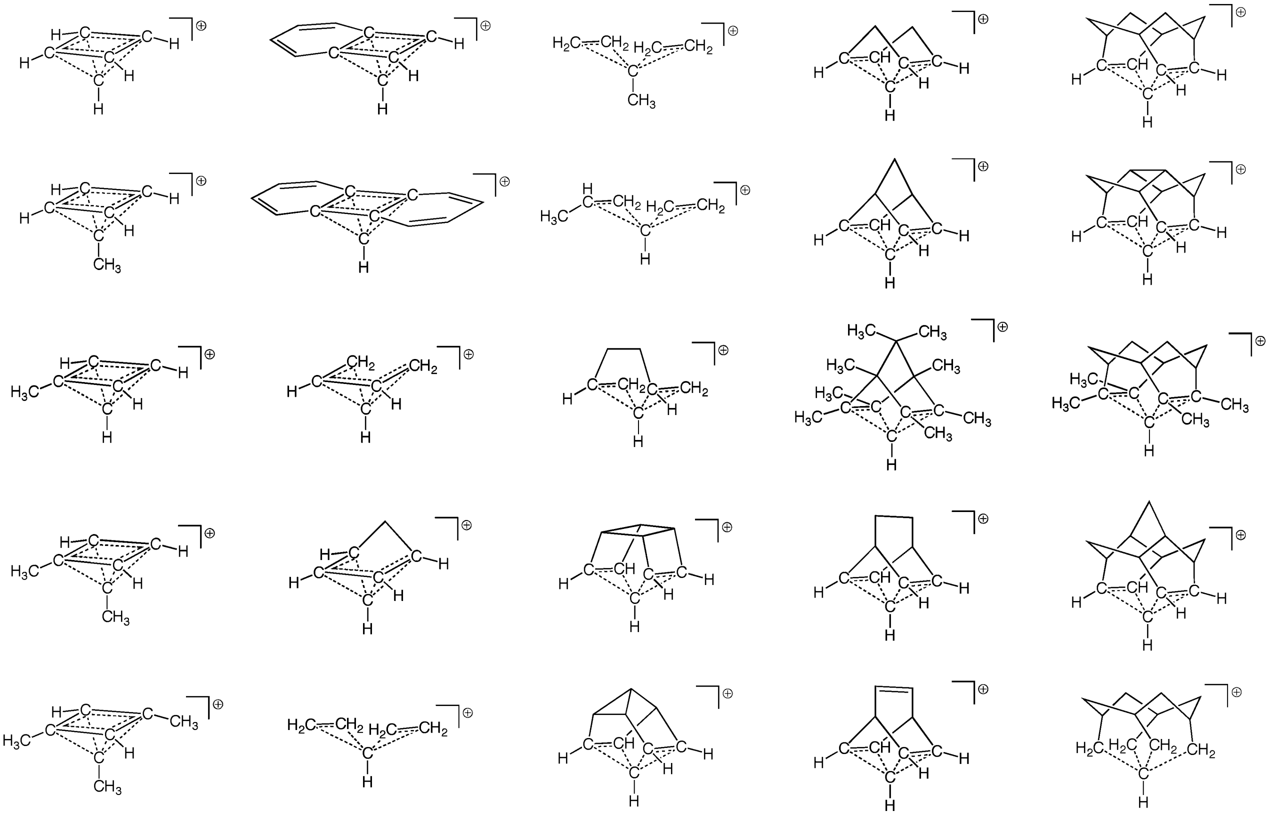
(4) For leading references, see: (a) McCoy, A. B.; Braams, B. J.; Brown, A.; Huang, X.; Jin, Z.; Bowman, J. M. *J. Phys. Chem. A* **2004**, *23*, 4991−4994. (b) Thompson, K. C.; Crittenden, D. L.; Jordan, M. J. T. *J. Am. Chem. Soc.* **2005**, *127*, 4954−4958. (c) Asvany, O.; Kumar, P.; Redlich, B.; Hegemann, I.; Schlemmer, S.; Marx, D. *Science* **2005**, *309*, 1219−1222. (d) See also: Merino, G.; Vela, A. Hypercoordination: a topological point of view. In *Reviews of Modern Quantum Chemistry. A Celebration of the Contributions of Robert G. Parr*; Sen, K. D., Ed.; Work Scientific: Singapore, 2002.

(5) (a) Tantillo, D. J.; Hoffmann, R. *J. Am. Chem. Soc.* **2003**, *125*, 4042−4043. (b) Ponec, R.; Yuzhakov, G. *J. Org. Chem.* **2003**, *68*, 8284−8286. (c) Related structures: Yamashita, M.; Yamamoto, Y.; Akiba, K.; Hashizume, D.; Iwasaki, F.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 4354−4371 and references therein.

(6) Related cations, which can be thought of as analogues with central protons rather than CH^+ groups, have recently been described. See ref 3f.

(7) (a) Reviews on pyramidal carbonium ions: Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 991−1066. See also: ref 1b. (b) See (for a seminal report): Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661−1668. For recent computations, see: (c) Rasmussen, D. R.; Radom, L. *Chem.—Eur. J.* **2000**, *6*, 2470−2483. (d) Jemmis, E. D.; Subramanian, G.; Prasad, B. V.; Tsuzuki, S.; Tanabe, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 865−867. (e) Szabo, K. J.; Kraka, E.; Cremer, D. *J. Org. Chem.* **1996**, *61*, 2783−2800. (f) Szabo, K. J.; Cremer, D. *J. Org. Chem.* **1995**, *60*, 2257−2259. (g) Prakash, G. K. S.; Rasul, G.; Olah, G. A. *J. Phys. Chem. A* **1998**, *102*, 2579−2583.

CHART 1



Computational Methods

All calculations were performed with Gaussian 03.[8] Geometries were optimized without symmetry constraints at the B3LYP/6-31G(d)[9] and MP2/6-31G(d)[10] levels of theory. All structures were characterized by frequency analysis, and the reported energies include zero-point energy corrections scaled by 0.9806 for the B3LYP/6-31G(d) level and by 0.9661 for the MP2/6-31G(d) level.[11] Intrinsic reaction coordinate (IRC)[12] calculations were also used to verify the identity of various transition structures (see Supporting Information). Comparisons of the performance of the B3LYP and MP2 methods for computing geometries, relative energies, and electronic properties of three-center, two-electron, and other delocalized cations have been reported.[3f,13] These methods often produce comparable results as to the relative energy ordering of related isomeric structures but occasionally disagree, most often when flat potential energy surfaces are involved. In such cases, MP2 tends to favor more delocalized structures than does B3LYP. As described below, this tendency was observed for the cations explored herein as well. For some neutral species, geometries from X-ray crystal structures were used to test the validity of the predicted structures.[14−16] Structures **5**, **5**‡, and **5b** were also re-examined at the B3LYP/6-31+G(d,p) level; only minor changes to the geometries (most changes, <0.01 Å; maximum change, 0.04 Å) and the relative energies (maximum change, 0.05 kcal/mol) were observed compared to B3LYP/6-31G(d). Wiberg bond indices were used in some cases to determine effective bond orders.[17] Charges were also computed using the CHelpG method.[18] Structural drawings were produced using Ball & Stick.[19]

Results and Discussion

Representative Example. The first cation of type **4** that we explored contains a cyclopropane linker (**5**, Figure 1). This structure is C_s-symmetric and contains a five-coordinate carbon at the center of a distorted square pyramid. Of particular note are the C−C bond lengths (1.60−1.67 Å) in the C_5 core, all of which are in the range of long C−C single bonds typical of highly strained systems.[20] The C−H bond to the central carbon is also not unusual, being 1.08 Å long (with both B3LYP and MP2). The symmetry of this structure is most likely due to the

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[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2004.

[9] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Solid State* **1988**, *37*, 785−789. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

[10] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

[11] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

[12] (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523−5527. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363−368.

[13] See the following and references therein: (a) Vrcek, I. V.; Vrcek, V.; Siehl, H.-U. *J. Phys. Chem. A* **2002**, *106*, 1604−1611. (b) Farcasiu, D.; Lukinskas, P.; Pamidighantam, S. V. *J. Phys. Chem. A* **2002**, *106*, 11672−11675.

[14] Boese, R.; Blaser, D.; Gomann, K.; Brinker, U. H. *J. Am. Chem. Soc.* **1989**, *111*, 1501−1503.

presence of the rigid cyclopropane ring (see below for unsymmetrical examples), which locks the central five-membered ring into an envelope conformation with the five-coordinate carbon bent out of plane. CHelpG charge computations[18] indicate that the positive charge is distributed throughout the molecule, and the Wiberg bond indices[17] for the two longer and two shorter C—C bonds attached to the central carbon, the other two C—C bonds of the C_5 core (1.43 Å long), and the C—H bond are respectively 0.68 and 0.78, 1.12, and 0.88 (B3LYP/6-31G(d)). These values and the corresponding distances indicate that there is significant bonding between the central carbon and all five atoms attached to it. Taking all of these factors into account, we feel that **5** is best represented by the resonance hybrid **a** (Scheme 1).

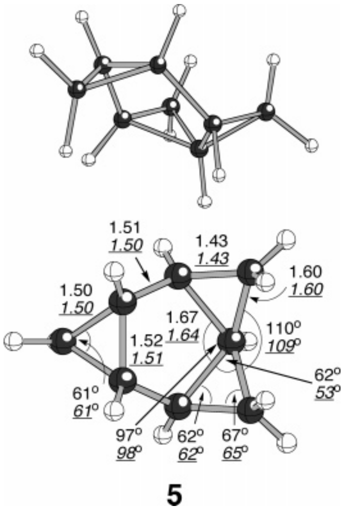


FIGURE 1. Two views of C_s-symmetric cation **5** (corresponding to the two views drawn above for generic structure **4**). Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

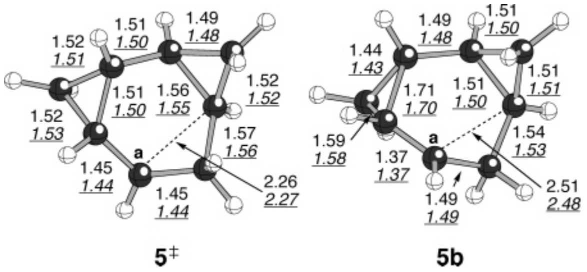
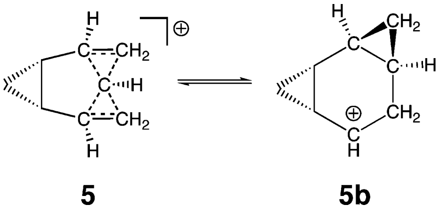


FIGURE 2. Structures of cation **5b** and transition structure $\mathbf{5}^{\ddagger}$. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

SCHEME 2



By lengthening an interior "bond" in the C_5 array of **5**, the classical isomer **5b** can be produced (Scheme 2 and Figure 2). Structures **5** and **5b** are connected by transition structure $\mathbf{5}^{\ddagger}$ (Figure 2). Structure **5b** is 13.4 (B3LYP; 8.2, MP2) kcal/mol lower in energy than **5**, and $\mathbf{5}^{\ddagger}$ is 8.5 (B3LYP; 16.8, MP2) kcal/mol above **5**. It might appear that transition structure $\mathbf{5}^{\ddagger}$ is unusually late in terms of its geometry, but C_a is reorienting itself during the **5** → **5b** reaction to allow for hyperconjugation with one of the C—C bonds in the adjacent cyclopropane ring (note the 1.71 and 1.37 Å distances, Figure 2). MP2 predicts a significantly higher barrier for this rearrangement than does B3LYP, but this is in line with MP2 tending to favor more delocalized cations; note that $\mathbf{5}^{\ddagger}$ is actually less delocalized than either **5** or **5b**.

Isoelectronic Relatives. The sensitivity of structures such as **5** to changes in overall charge was examined by substituting the various carbons of the C_5 core with borons and then subjecting the new structures to geometry optimization. The

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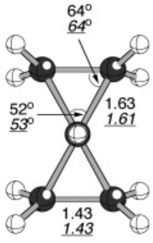
(15) We have also computed the structures of the following previously reported[7,14,16] species (selected distances in Å; B3LYP/6-31G(d) in normal text, MP2/6-31G(d) in underlined italics, and X-ray crystallography data[14] shown in bold, underlined text). The energy difference between structures **A** and **B** is 202 (B3LYP; 199, MP2) kcal/mol, while the energy difference between structures **D** and **E** is 214 (B3LYP; 211, MP2) kcal/mol. Structure **D**, with its bridgehead hydrogens disposed trans, is 37 (B3LYP; 38, MP2) kcal/mol lower in energy than **6′**, while **E** is 9.8 (B3LYP; 9.1, MP2) kcal/mol *higher* in energy than **6**.



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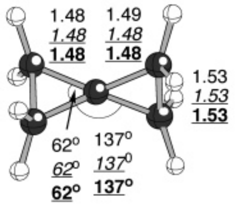

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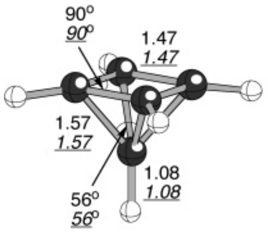

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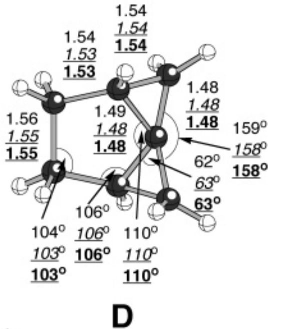

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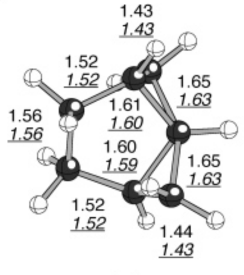


E

(16) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. *J. Org. Chem.* **1995**, *60*, 6860−6863.

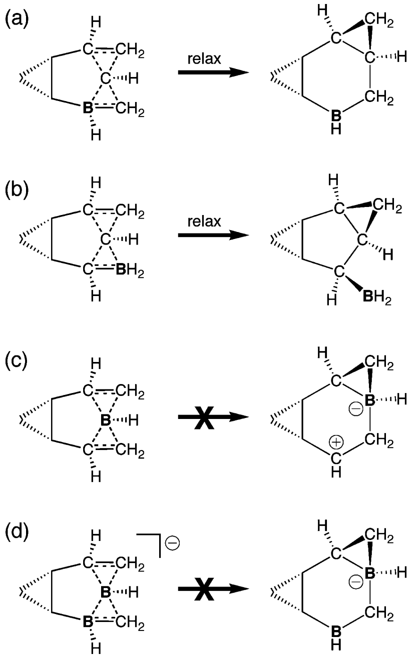
(17) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

(18) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361−373.

(19) Müller, N.; Falk, A. *Ball & Stick*, V.3.7.6; molecular graphics application for MacOS computers; Johannes Kepler University: Linz, Austria, 2000.

(20) Zavitsas, A. A. *J. Phys. Chem. A* **2003**, *107*, 897−898.

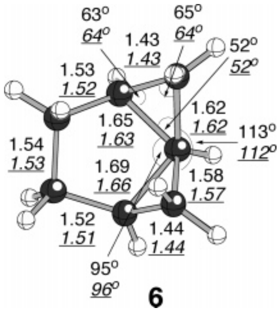
SCHEME 3



replacement of any single carbon by boron changes the overall charge from +1 to 0, and the replacement of two carbons by two borons will further reduce the charge to −1. Scheme 3 summarizes the various substitutions made and the consequences of each.

The substitution of any of the perimeter carbon atoms by boron leads to ring opening (a and b). This makes sense in that ring opening produces four neutral four-coordinate carbons and a neutral three-coordinate boron. The substitution of the central carbon by boron does not lead to ring opening, however (c). If ring opening were to have occurred, a structure with a formally negative four-coordinate boron and a formally positive three-coordinate carbon would have resulted. Similarly, when both the central carbon and a perimeter carbon are exchanged for borons, ring opening does not occur because it would lead in this case to a formally negative four-coordinate boron near a neutral three-coordinate boron (d). It seems that, in general, ring opening occurs if it leads to structures with no formal charges. If ring opening results in the localization of charge, then it does not occur. Thus, it is not merely the delocalization of a particular number of electrons that affords structures such as **4** their stability.[21]

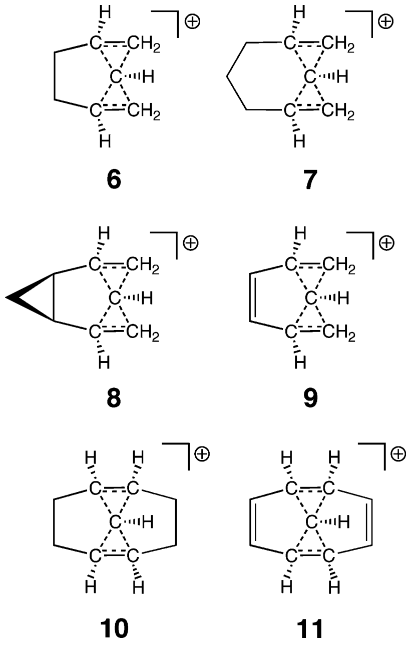
Linker Variants. Several simple linker structures were also examined (Chart 2). First, the cyclopropane bridge of **5** was truncated to a simple ethylene linker to produce **6** (Figure 3). Unlike **5**, **6** no longer possesses a plane of symmetry. Once the cyclopropane group is removed, the linker relaxes into a geometry that allows its hydrogens to be staggered. Nonetheless, the C_5 core still remains delocalized.[22]



6

FIGURE 3. Structure of C_1-symmetric cation **6**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).[22]

CHART 2



Although some of the potential energy surface for **6** was described previously (at the MP4(SDQ)/6-31G(d)//MP2/6-31G(d) level),[7e,f] the ring-opening reaction equivalent to that described in Scheme 2 was not. The structures of ring-opened **6b** and the transition structure for its formation, **6**‡, are shown in Figure 4. In this case, the delocalized carbonium ion **6** is 5.7 (B3LYP; 14.8, MP2) kcal/mol *lower* in energy than the classical carbenium ion **6b**, indicating that ring *closure* to the nonclassical cation is thermodynamically favorable! In addition, the barrier

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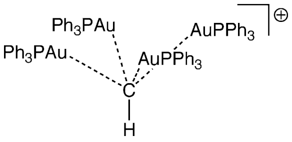
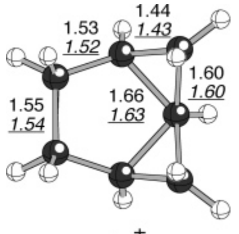
[21] A related gold-containing cation with a distorted square-pyramidal five-coordinate carbon is also known. See: Schmidbauer, H.; Gabbaï, F. P.; Schier, A.; Riede, J. *Organometallics* **1995**, *14*, 4969−4971.



[22] (a) The MP2/6-31G(d) geometry of this structure was reported previously.[7e,f] (b) Structure **6** and its mirror image can be interconverted through a conformational change involving C_s symmetric transition structure **F**‡. The barrier for this process is 1.4 (B3LYP; 2.2, MP2) kcal/mol. These values are in accordance with the previously reported value of 1.9 kcal/mol computed at the MP4(SDQ)//MP2/6-31G(d) level.[7e,f]



F‡

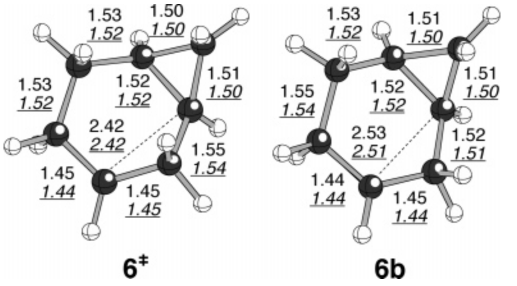


FIGURE 4. Structures of cation **6b** and transition structure **6‡**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

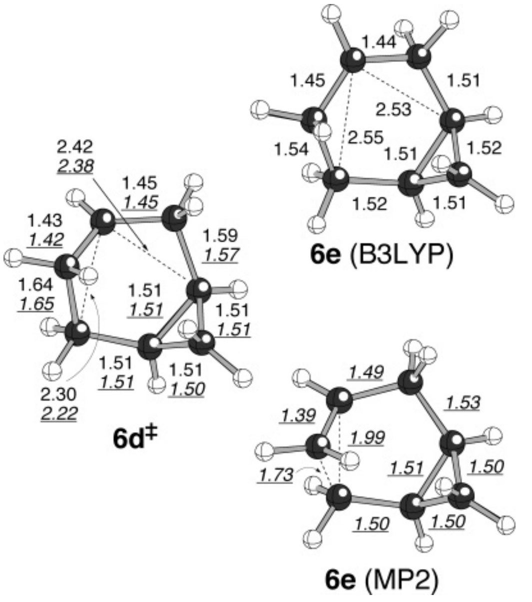


FIGURE 5. Structures of cation **6e** and transition structure **6d‡**. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

for this ring closure is only 1.4 (B3LYP; 0.8, MP2) kcal/mol. Thus, in this system, nucleophilic attack of a four-coordinate carbon onto a carbenium ion is predicted to occur instantaneously.

Since **6** is not symmetrical, breaking the other (shorter) internal bond of its C_5 core is distinct from the process shown in Figure 4. The transition structure (**6d‡**) and product (**6e**) for this ring opening are shown in Figure 5. Structure **6d‡** is 2.2 (B3LYP; 0.6, MP2) kcal/mol higher in energy than **6‡**, while **6e** is 1.8 (B3LYP; 0.7, MP2) kcal/mol lower in energy than **6b**. Note that MP2 predicts a structure for **6e** that resembles a traditional three-center, two-electron nonclassical ion. Thus, at the MP2/6-31G(d) level, **6d‡** is a transition structure resembling a carbenium ion that connects two carbonium ions whose five-coordinate carbon atoms are involved in distinctly different delocalized bonding arrays. This is the reverse of the more common situation in which two carbenium ions are connected by a transition structure resembling a carbonium ion (e.g., for a [1,2] alkyl shift).[23]

The addition of another methylene to the linker of **6** leads to **7** (Chart 2, Figure 6). In this structure, C_s symmetry is restored for both boatlike (**7**) and chairlike (**7a**) conformers. These two conformers are close in energy: **7a** lies only 1.1 (B3LYP; −0.7, MP2) kcal/mol above **7**.[24]

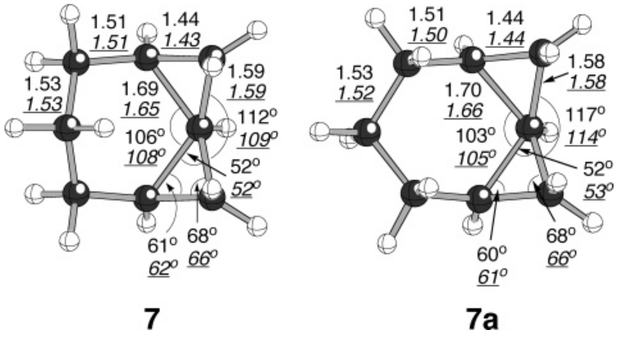


FIGURE 6. Structures of cations **7** and **7a**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

Cation **7** can also undergo ring opening. The product of this ring opening (**7b**, Figure 7), however, is 11.9 (B3LYP; −2.8, MP2) kcal/mol higher in energy than the delocalized cation **7**. Structure **7‡** is 14.3 (B3LYP; 23.2, MP2) kcal/mol higher in energy than **7**. Interestingly, while the ring opening proceeds as expected with B3LYP, with MP2 it appears to be coupled with a [1,2] hydrogen shift to give **7b** (MP2) directly. IRC

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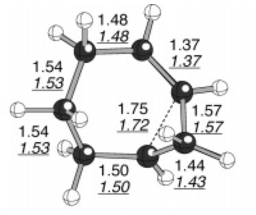
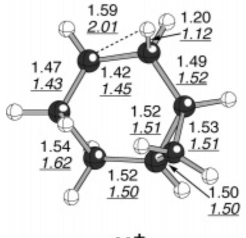
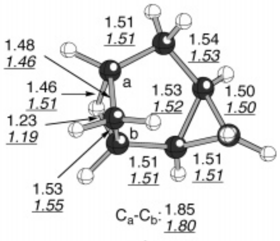
[23] Cation **6e** can also open to carbenium ion **G** via hydrogen shifts. A [1,2]-H shift via transition structure **H‡** leads directly to **G**. A [1,3]-H shift via transition structure **I‡** leads to the mirror image of **G**. Cation **G** is 20.3 (B3LYP; 25.6, MP2) kcal/mol lower in energy than **6e**. Transition structure **H‡** is 0.8 (B3LYP; 0.8, MP2) kcal/mol above **6e**, while transition structure **I‡** is 14.3 (B3LYP; 5.4, MP2) kcal/mol above **6e**.



G

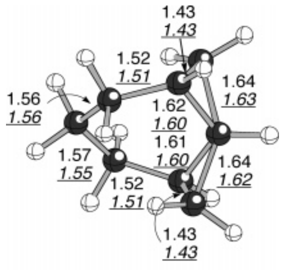


H‡

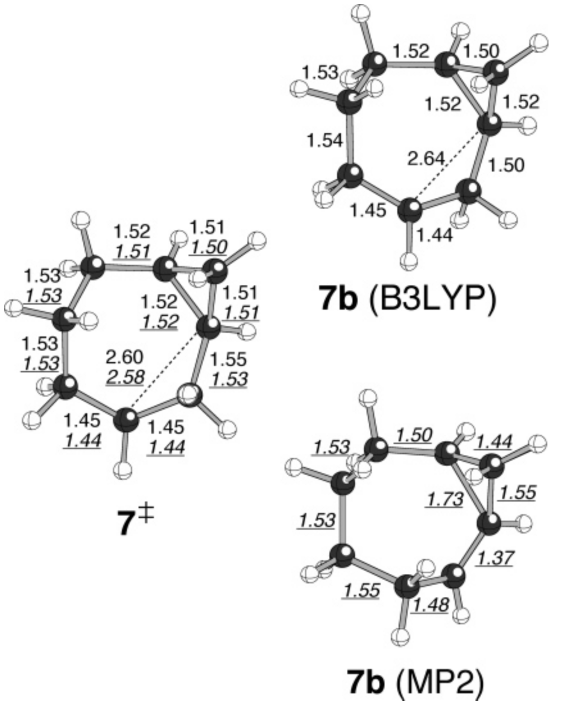


I‡

[24] An isomer of this structure (**J**), in which the bridgehead hydrogens on the perimeter of the C_5 core are trans relative to each other rather than cis, was also examined (below, selected distances in Å). This structure is more strained than its cis isomers, being 12.8 (B3LYP; 12.1, MP2) kcal/mol higher in energy than **7**.



J

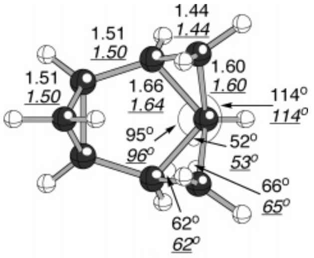


7‡

7b (B3LYP)

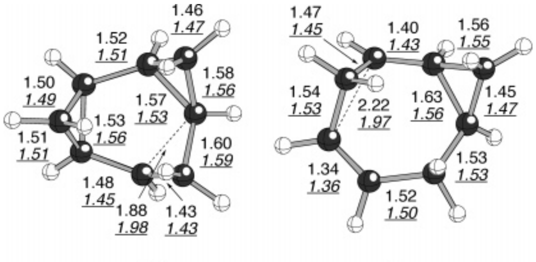
7b (MP2)

FIGURE 7. Structures of **7b** and transition structure **7**‡. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).



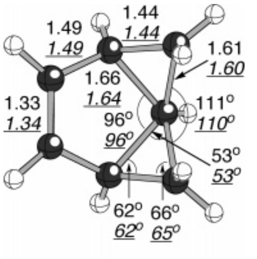
8

FIGURE 8. Structure of cation **8**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).



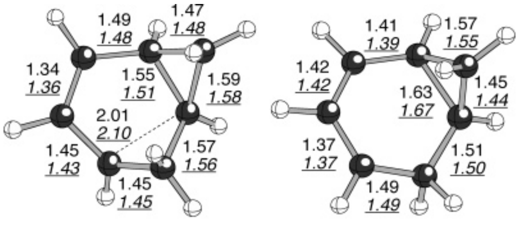
8‡ **8b**

FIGURE 9. Structures of cation **8b** and transition structure **8**‡. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).



9

FIGURE 10. Structure of cation **9**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).



9‡ **9b**

FIGURE 11. Structures of cation **9b** and transition structure **9**‡. Selected distances (Å) and angles are shown (B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

calculations (see Supporting Information) indicate that these two events are asynchronous but still concerted.

If the methylene of the cyclopropane in **5** is moved to the other face of the molecule, cation **8** results (Chart 2, Figure 8). The C—C bond lengths in **8** are extremely similar to those in **5**, but **5** is 4.0 kcal/mol (B3LYP; 4.3, MP2) lower in energy than **8**, most likely primarily a result of the steric interactions associated with placing the methylene group of the cyclopropane on the same face of the molecule as the other two methylene groups.

The ring opening of **8** is expected to occur in a fashion similar to that of **5** (Scheme 2). In this case, classical ion **8b** is 21.3 (B3LYP; 13.3, MP2) kcal/mol lower in energy than the nonclassical ion **8** (Figure 9). Structure **8**‡ is 0.3 (B3LYP; 3.0, MP2) kcal/mol above **8**. Note that the syn arrangement of the cyclopropane rings in the expected product allows for extreme hyperconjugation.

The replacement of the cyclopropane ring in either **5** or **8** with a C=C double bond results in cation **9** (Chart 2, Figure 10). Structure **9** is extremely similar to **5** and **8**, having comparable C—C distances in its C_5 core and again possessing a plane of symmetry. Not surprisingly, the cyclopropanes and the C=C double bond impose similar geometric constraints on the system.

The ring opening of **9** produces **9b** (Figure 11). In this case, the delocalized carbonium ion **9** is 28.3 (B3LYP; 18.8, MP2) kcal/mol higher in energy than the classical carbenium ion **9b** (Figure 11) as a result of the fact that ring opening leads here to an allylic cation that also interacts with the adjacent cyclopropane ring (note the long C—C distance of 1.63 (1.67) Å in **9b**; Figure 9). The barrier for ring opening from **9** is 2.5 (B3LYP; 9.6, MP2) kcal/mol.

The addition of linkers to both sides of the C_5 core was also considered. Structures **10** and **11** (Chart 2, Figure 12) are representative examples of such architectures. Cation **10** is C_2 symmetric, again twisting to avoid eclipsing in its ethylene bridges, and cation **11** is C_{2v} symmetric.[25a] Like structures **6**−**9**, both **10** and **11** contain highly delocalized C_5 cores, demonstrating the robustness of this architecture.[15]

Methyl Substituents. Cation **6** was used as a framework upon which to test the effects of alkyl substitution. Methyl groups

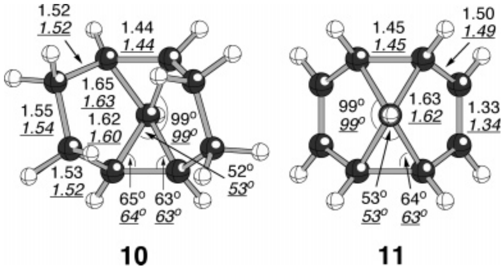
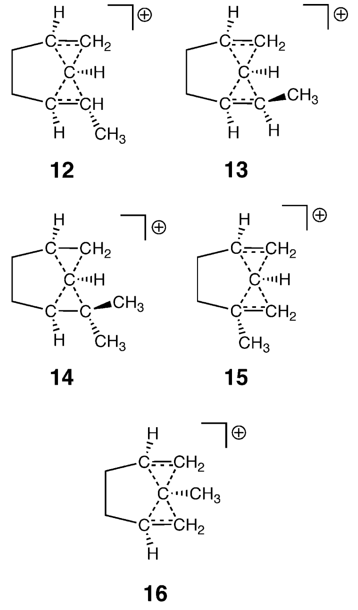


FIGURE 12. Structures of cations **10** and **11**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics). To make the hydrogen that is attached to the five-coordinate carbon of **11** visible, this structure has been reoriented so that it is facing out of the page.

CHART 3



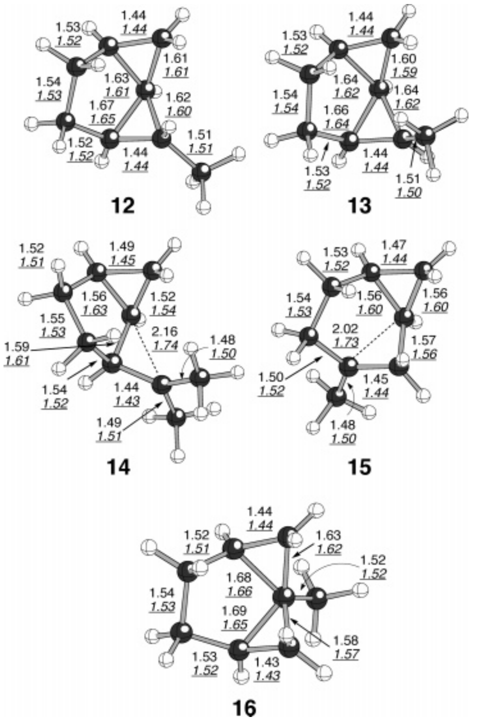


FIGURE 13. Structures of cations **12**−**16**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

were added at various positions (Chart 3), and the resulting structures were optimized. The geometries of cations **12**−**16** are shown in Figure 13. The addition of a single methyl group to one of the CH_2 groups of **6** (to produce **12** or **13**) leaves the C_5 core intact, although the length of the C−C bond from the five-coordinate carbon to the site of substitution lengthens slightly (compare Figures 3 and 13). This is a result of the ability of the methyl group to stabilize the cationic character on an attached carbon through hyperconjugation. In conjunction with the lengthening of this bond, the other three C−C bonds of the C_5 core shorten slightly. Adding a pair of geminal methyl groups (**14**) or adding one methyl group to a bridgehead carbon (**15**) leads to the destruction of the C_5 core, at least with B3LYP. Apparently, ring opening to structures with neutral four-coordinate carbons and tertiary cationic carbons is favored over more extensive delocalization. However, the MP2 method here again produces more delocalized structures with much shorter C···C contacts. The replacement of the hydrogen on the central carbon with a methyl group, leading to **16**, has only a minor effect on the geometry of the C_5 core, consistent with the delocalized pictures of cations **4** described above, in which the bond to the apical group is not involved in the delocalization to any appreciable extent. In this interesting structure a carbon is bonded directly to five other carbons and all five bonds are less than 1.7 Å long.

Deprotonation. Because deprotonation of cations **5**−**11** should lead to very strained structures, we decided to examine their gas-phase acidities. The optimized geometries of the structures produced on deprotonation of **5**−**11** are shown in Figure 14 (**5′**−**11′**). The computed geometries for **6′** and **10′** (at the HF/3-21G level) have been reported previously.[26] Cations **5**, **7**, **8**, and **9** are C_s symmetric; however, when they are deprotonated, their symmetry is reduced as the cores of these molecules torque and they attempt to produce central carbons with tetrahedral geometries.[27] Deprotonation also, of course, leads to the shortening of the long bonds in the C_5 array. Interestingly, cations **10** and **11** do not relax to pseudotetrahedral spiropentane geometries upon deprotonation,[25b] retaining the

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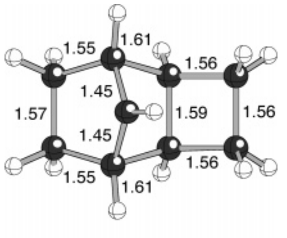
(25) (a) Attempts to optimize a geometrical isomer of **10** with its bridges disposed trans to each other led to isomers with different ring systems, such as that shown below (**K**, B3LYP/6-31G(d), selected distances in Å).



K

(b) For calculations regarding isomers of **10′**, see: Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285−5291.

(26) The **10′** interior bond distances previously reported were substantially longer than those reported herein; see ref 25b for previous reports on **6′** and **10′**. The following reference describes a need for *d*-polarization functions in describing highly strained molecules, including cyclopropane rings: Wiberg, K. B.; Snoonian, J. R. *J. Org. Chem.* **1998**, *63*, 1390−1401.

TABLE 1. Proton Affinities (PA) of Cations 5−11 and Several Amines[a]

conjugate base	theoretical PA [kcal/mol]	experimental PA[28] [kcal/mol]
5′	271.3 (268.8)	
6′	260.5 (258.0)	
7′	241.7 (237.7)	
8′	272.9 (271.6)	
9′	267.9 (267.5)	
10′	284.6 (282.2)	
11′	282.1 (278.6)	
pyridine	224.7 (221.3)	222
trimethylamine	226.7 (227.2)	226.8
aniline	213.3 (213.3)	213.3

[a] B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in parentheses.

roughly square-pyramidal geometries present in the cations. For structure **11**, deprotonation actually leads to the lengthening of the central C−C bonds.

It has been reported previously that the highest occupied molecular orbital of neutral hydrocarbons possessing square-pyramidal C_5 units (e.g., **10′** and **11′**) is localized on the central carbon atom.[7c] That this lone pair could be readily protonated has also been suggested.[7c] Structures such as **5′−9′** are also very strained, and some of the strain they possess might also be dissipated upon protonation. The proton affinities of **5′−11′** (i.e., the differences in energy between **5′−11′** and **5−11**) are shown in Table 1 along with those of several amines, for comparison.[28] Like more geometrically complicated hemialkaplanes and hemispiroalkaplanes,[7c] structures **5′−11′** are indeed very basic, considerably more basic than typical amines. Note that the least basic of these hydrocarbons is **7′**, which is also the most geometrically flexible.[29,30]

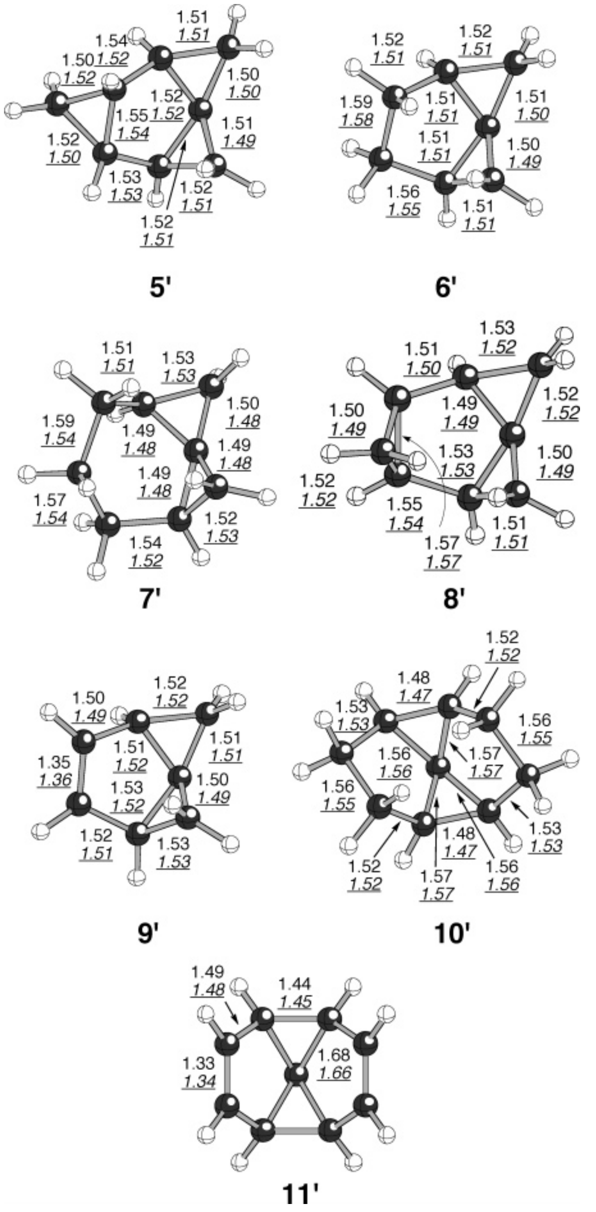


FIGURE 14. Structures of **5′−11′** produced upon deprotonation[27] of cations **5−11**. Selected distances are shown (Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics).

Conclusions

Perturbations to the C_5 core of cations **4** have shown that this structural unit is quite robust. Many variations of linker length and structure are accommodated with little distortion to the bond lengths in the C_5 core. We have located transition structures for the formation of carbonium ions **4** from carbenium ions, and in some cases, this process is exothermic and bears only a small activation barrier. Ring closure can be discouraged, however, by including groups that will selectively stabilize the classical cation form (e.g., an alkene to make an allyl cation or enough alkyl groups to make a 3° cation). The importance of delocalization of both charge and electron density have also been explored with analogues for which carbons of the C_5 core were replaced with borons; if ring opening can lead to a neutral three-coordinate boron, then it occurs, but if it leads to charge separation, it does not occur. The unusually weak acidities of cations **4** have also been described and provide a different

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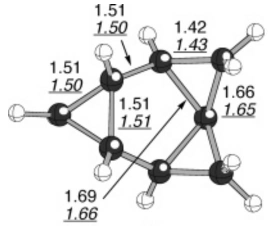
(27) (a) An interesting structure, **L** (selected distances shown in Å; B3LYP/6-31G(d) in normal text and MP2/6-31G(d) in underlined italics), was also obtained from the deprotonation of **5**. At the B3LYP/6-31G(d) level, **L** is a transition structure whose imaginary frequency corresponds to twisting about the formerly five-coordinate carbon. At the MP2/6-31G(d) level, **L** is a minimum. See ref 7 for related structures. (b) For leading references on discussions of spiropentadiene-based structures, some of which have planar four-coordinate carbons, see: Esteves, P. M.; Ferreira, N. B. P.; Corrêa, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 8680−8685. (c) Perez, N.; Heine, T.; Barthel, R.; Seifert, G.; Vela, A.; Mendez-Rojas, M. A.; Merino, G. *Org. Lett.* **2005**, *7*, 1509−1512 (this paper also discusses ring-opening reactions related to those discussed in the text). (d) Merino, G.; Mendez-Rojas, M. A.; Beltran, H. I.; Corminboeuf, C.; Heine, T.; Vela, A. *J. Am. Chem. Soc.* **2004**, *126*, 16160−16169.



L

(28) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413−656.

(29) Successful syntheses of the C_2-symmetric isomers of **6′** and **7′** were achieved several years ago.[15,30a,d] Photoelectron spectra, X-ray crystallographic data, and NMR data on the C_2-symmetric isomer of **6′** are available.[14,26b,30b,c]

(30) (a) Skattebol, L. *J. Org. Chem.* **1966**, *31*, 2789−2794. (b) Gleiter, R.; Krennrich, G.; Brinker, U. H. *J. Org. Chem.* **1986**, *51*, 2899−2901. (c) Wiberg, K. B.; Chavez, A. *J. Am. Chem. Soc.* **1989**, *111*, 8052−8053. (d) Miebach, T.; Brinker, U. H. *J. Org. Chem.* **1993**, *58*, 6524−6525.

measure of their stability. Both the propensities of some ring-opened structures to close to structures with five-coordinate carbons and the high proton affinities of the deprotonated versions of cations **4** highlight the inclination of some four-coordinate carbons toward nucleophilicity.

Acknowledgment. We gratefully acknowledge the University of California—Davis, the donors of the American Chemical Society Petroleum Research Fund, the National Science Foundation CAREER program, and the National Science Foundation's Partnership for Advanced Computational Infrastructure (Pittsburgh Supercomputer Center) for support.

Supporting Information Available: Coordinates and energies for all computed structures and information on IRC calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052053A