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Selective Stabilization of Transition State Structures for Cope Rearrangements of Semibullvalene and Barbaralane through Interactions with Halogens

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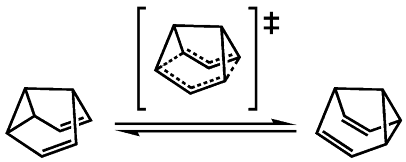
A new means—discovered through quantum chemical studies (B3LYP/6-31G(d))—of selectively stabilizing the delocalized forms of unsubstituted semibullvalene and barbaralane is described. Calculations indicate that complexation of delocalized semibullvalene and barbaralane Cope rearrangement transition structures by halogen-containing molecules (homo- and heteronuclear diatomics and Lewis acids) can reduce the barrier significantly, in many cases causing it to disappear entirely.

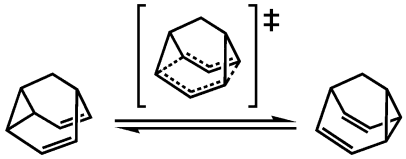
Semibullvalene and barbaralane hold honored positions in the history of physical organic chemistry.[1] The chemistry of these molecules and their derivatives provides classic examples of various physical organic principles. For example, the manipulation of substitution patterns, reactant strain, and preorganization have all been employed in the "quest" for semibullvalene and barbaralane derivatives with "stable transition states" (for Cope rearrangements) that exhibit neutral homoaromaticity.[1,2] Along these lines, substituents and solvents were shown to work in concert for substituted barbaralane **1**, allowing the delocalized form to exist as a minimum in *N*,*N*′-dimethylpropylene urea (DMPU), due in part to particularly favorable interactions between the solvent and the delocalized structure arising from its increased polarizability.[3] Replacing some carbon atoms of the hexadiene substructures of semibullvalene and barbaralane with certain heteroatoms was also predicted to lead to delocalized minima (e.g., **2**; note that formal charges are not shown here).[4] By appending small rings to semibullvalene (e.g., **3**), localized forms were selectively destabilized, allowing delocalized forms—in which strain is relieved to some extent—to again become minima for some systems.[5] Fusing multiple barbaralanes together also led to structures, so-called "σ-polyacenes" (e.g., **4**), for which delocalized minima were predicted.[6] The delocalized form of unsubstituted semibullvalene itself was also predicted to be a minimum when complexed to Li^+ in the gas phase (**5**), and the selective stabilization of the delocalized form in this case was suggested to result primarily from improved electrostatic interactions between Li^+ and the charge distribution of the delocalized (rather than localized) form of semibullvalene.[7]

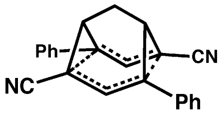
In this report, we describe another means, discovered through quantum chemical studies, of selectively stabilizing the delocalized forms of unsubstituted semibullvalene and barbaralane. Interactions between these structures and halogen-containing molecules (to form complexes **6**, X = halogen, Y = halogen, AlX_2, BX_2) consistently lower the barriers for Cope rearrangement, in many cases abolishing them completely.

semibullvalene



barbaralane





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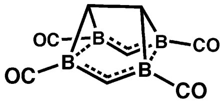

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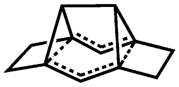

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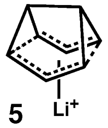

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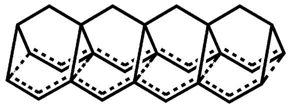

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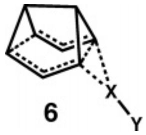

6

In the course of theoretical studies on semibullvalene bromination,[8] we discovered that, among the various semi-

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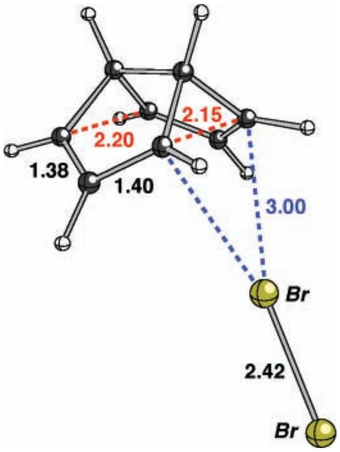


Figure 1. Computed geometry (B3LYP/6-31G(d); distances in Å) of **6** (X = Y = Br).

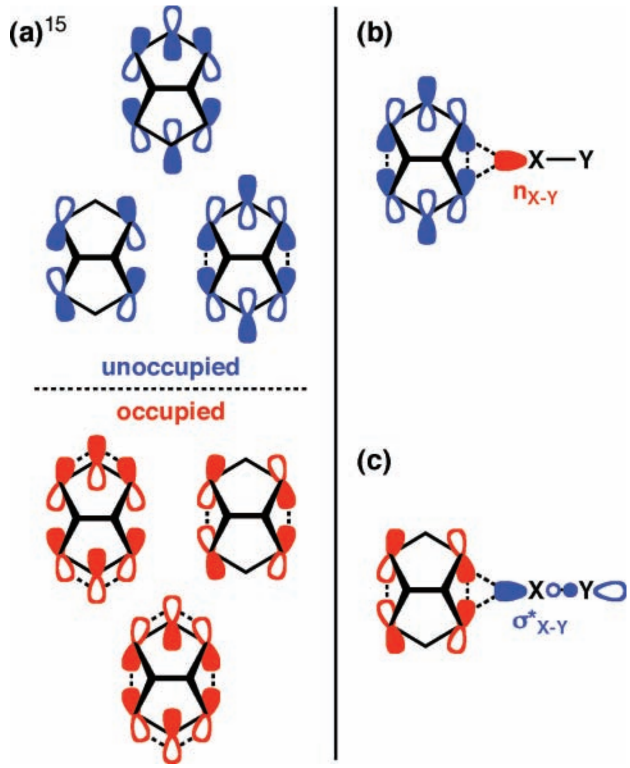
bullvalene$-$Br$_2$ complexes (minima) that we could locate with the B3LYP/6-31G(d) method,[9] one resembled the delocalized form of semibullvalene—usually the transition structure for Cope rearrangement—complexed to Br$_2$. This structure is shown in Figure 1.[10] Note that although the Br$_2$ interacts directly with only one side of the semibullvalene, the semibullvalene is highly delocalized (e.g., the two terminal interallyl distances are 2.20 and 2.15 Å).

Intrigued by this structure, we proceeded to examine complexes of both semibullvalene and barbaralane with various halogens (**6** with X$-$Y = Br$_2$, Cl$_2$, F$_2$, BrCl, ClBr, BrF, FBr, ClF, FCl).[11,12] Let us first consider the semibullvalene$-$Br$_2$ complex. Interestingly, in addition to the minimum shown in Figure 1, we also located the more localized minima shown in Figure 2a,b,[13] along with transition state structures that connect the three minima (Figure 2c,d). At first glance, this appears to be a very unusual situation, in that either localized or delocalized semibullvalenes—and not both—are expected to be minima. However, the energies of all five species in Figures 1 and 2 are within 2 kcal/mol of each other, indicating that the region of the semibullvalene + Br$_2$ energy surface that they inhabit is actually quite flat. Nonetheless, the barrier for Cope rearrangement (4.5 kcal/mol for uncomplexed semibullvalene at the same level of theory[9a]) has been effectively removed by selective complexation of the delocalized form of semibullvalene.[14]

Unlike the previously described semibullvalene$-$Li$^+$ complex,[7] in the Br$_2$-bound case, semibullvalene's complexation partner is both neutral and not centered under semibullvalene's bis-allyl substructure. Both of these characteristics are consistent with covalent interactions contributing significantly to semibullvalene$-$Br$_2$ binding. Although Br$_2$ is somewhat polarizable, its lack of a net charge would likely make any electrostatic interactions with the (also somewhat polarizable) delocalized semibullvalene less significant than for Li$^+$. It is also unlikely that predominantly electrostatic binding would lead to complexation of Br$_2$ with only one end of semibullvalene.

Simple orbital arguments can be used to rationalize the end-on complexation on covalent grounds. The molecular orbitals derived from σ-interaction of the two allyl substructures in delocalized semibullvalene[6] are shown in Chart 1a.[15] In Chart 1b-c are shown the donor$-$acceptor interactions expected to be most important for semibullvalene$-$Br$_2$ binding. Note that for the orbital interaction shown in Chart 1c, the occupied orbital of semibullvalene can donate electron density to the $\sigma^*_{\mathrm{Br-Br}}$ orbital only if the Br$_2$ is not centered over the bis-allyl substructure, since a nodal plane bisects the semibullvalene donor orbital in that region. The computed Kohn$-$Sham molecular orbital corresponding to the orbital cartoon in Chart 1c is shown in Figure 3. Note also that the Br$-$Br bond in the complex is lengthened compared to the distance in uncomplexed Br$_2$ (2.32 Å) and that the longest Br$-$Br distance is observed for the delocalized complex in Figure 1 (2.42 Å; compare with the structures in Figure 2), consistent with this orbital interaction, which will lengthen the Br$-$Br bond as its antibonding orbital is populated, playing a key role in selective stabilization of the delocalized structure upon complexation. Fragment analysis[9b] on the semibullvalene$-$Br$_2$ interaction suggests that the contributions from electrostatic and orbital effects to the interaction energy are comparable.[16a] Complexation of semibullvalene with F$_2$ and Cl$_2$ is similar to that with Br$_2$, both in terms of complex geometries and relative energies of localized and delocalized species (see Supporting Information for details).[16b]

CHART 1



The mixed halogens BrCl, BrF, and ClF were also examined. BrCl, for example, again behaved similarly to Br$_2$, having three minima spread over an energy window of ~2 kcal/mol for both possible orientations (Br or Cl near to semibullvalene). However, the three minima with Br near to semibullvalene were each ~5$-$6 kcal/mol lower in energy than the corresponding minima with Cl near to semibullvalene, most likely due primarily to polarization of the $\sigma^*_{\mathrm{Br-Cl}}$ orbital toward the less electronegative and larger Br.[17]

Complexes with two X$-$Y groups (both homo- and heteronuclear diatomics) were examined as well. For complexes with two identical homonuclear diatomics (e.g., Figure 4a)[18] or two different homonuclear diatomics (e.g., Figure 4b), flat energy surfaces were again observed, sporting delocalized structures in shallow wells. Note that elongation of the halogen$-$halogen bonds is less when two halogen molecules are bound simultaneously (e.g., compare Figures 1 and 4).

The situation with heteronuclear diatomics is slightly more complex than with homonuclear diatomics. Take, as a representative example, the semibullvalene$-$2BrCl system. In this

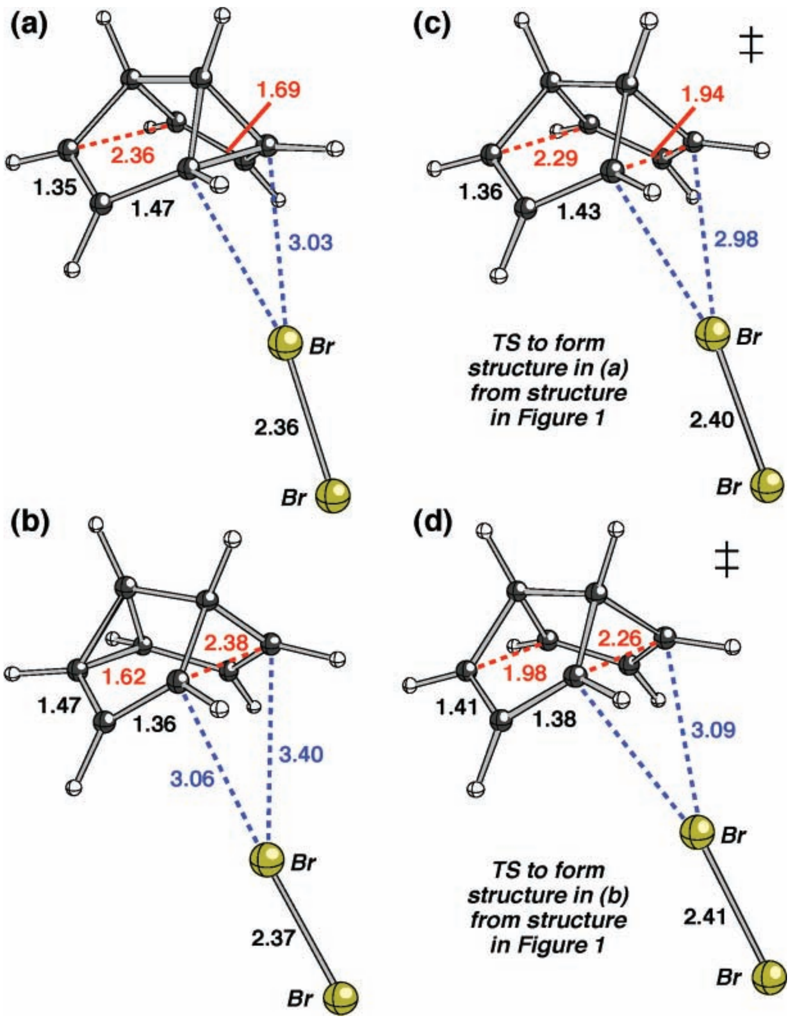


Figure 2. Computed geometries (B3LYP/6-31G(d); distances in Å) of other minima and transition structures on the energy surface for **6** (X = Y = Br). The energies (kcal/mol) of these four structures, relative to that of structure **6** (X = Y = Br) as shown in Figure 1, are (a) −0.1, (b) −1.7, (c) +0.1, (d) +0.2.

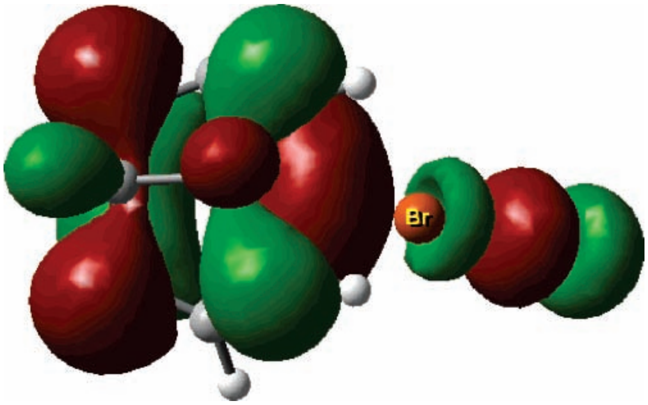


Figure 3. Computed (B3LYP/6-31G(d)) Kohn−Sham molecular orbital corresponding to Chart 1c.

case, three different complexation motifs are possible (**A**−**C**, Chart 2). For all three binding modes, both localized and delocalized minima with small barriers for their interconversion are found (delocalized minima for each binding mode are shown in Figure 5). However, the structures found for binding mode **A** are ~4−5 kcal/mol lower in energy than those for **B**, which are ~4−5 kcal/mol lower in energy than those for **C**. Thus, reorienting each BrCl such that its Br end, rather than its Cl end, is close to semibullvalene is favorable by ~4−5 kcal/mol, which is consistent with our calculations for the semibullvalene−

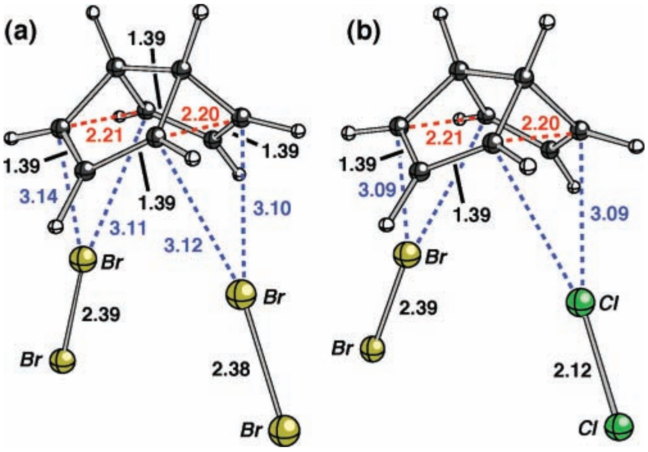


Figure 4. Computed geometries (B3LYP/6-31G(d); distances in Å) of delocalized semibullvalene complexes with (a) two Br_2 molecules and (b) one Br_2 and one Cl_2 molecule.

BrCl complexes described above. The energies of the Br_2−semibullvalene−Cl_2 complexes (e.g., Figure 4b) fall between those of **B** and **C**. Similar situations are observed for other mixed halogens (see Supporting Information for details).

As described above, a key factor in delocalized semibullvalene−halogen binding is the donation of electrons

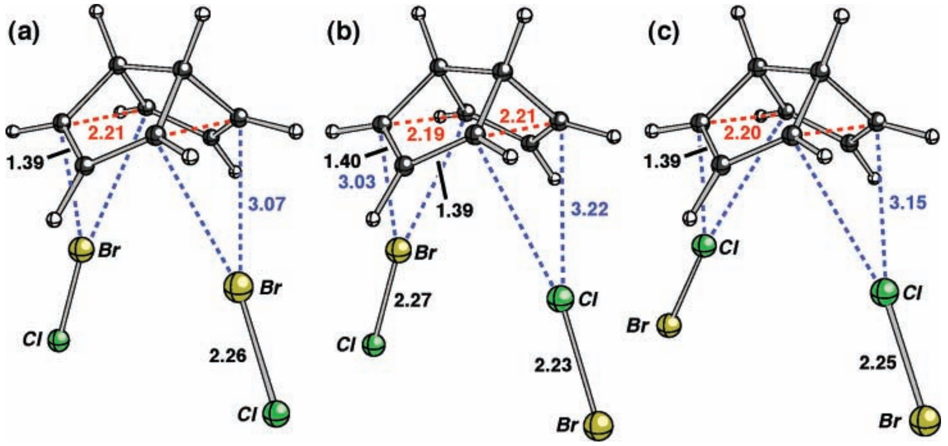


Figure 5. Computed geometries (B3LYP/6-31G(d); distances in Å) of delocalized minima A−C. The energies (kcal/mol) of these three structures, relative to that of the Br_2−semibullvalene−Cl_2 structure shown in Figure 4b, are (a) −7.3, (b) −2.0, (c) +3.5.

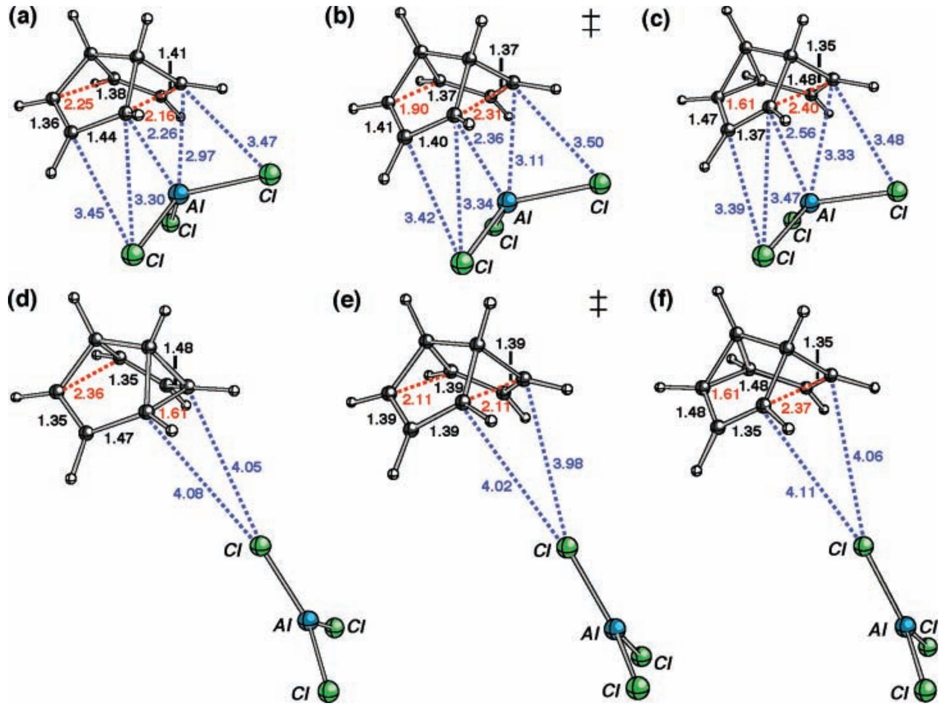
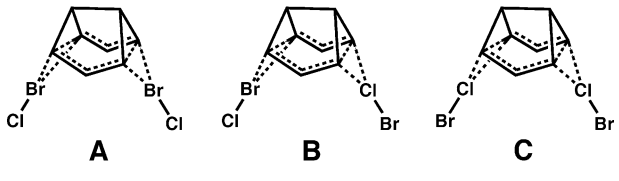


Figure 6. Computed geometries (B3LYP/6-31G(d); distances in Å) of minima (a, c, d, f) and transition structures (b, e) on the energy surface for semibullvalene + $AlCl_3$. The relative energies (kcal/mol) of these structures are (a) [0.00], (b) +1.5, (c) +0.2, (d) +9.2, (e) +13.5, and (f) +9.0.

CHART 2



from semibullvalene to an acceptor orbital on the halogen. Are other groups with good acceptor orbitals capable of forming similar complexes? In this regard, complexes of semibullvalene with several common Lewis acids ($AlCl_3$, BF_3, BCl_3) were also explored. For each of these three systems, two families of complexes are observed—one in which the semibullvalene interacts with the empty orbital at the central atom of the Lewis acid and another in which the semibullvalene interacts with a halogen−central atom σ^* orbital (see Figure 6 for representative examples using $AlCl_3$; complexes with BF_3 and BCl_3 can be found in the Supporting Information). For all three Lewis acids examined, no minima with fully delocalized semibullvalene structures were located. Nonetheless, the barriers for Cope rearrangements in such complexes were lower than for free semibullvalene (e.g., only 1.5 kcal/mol for complexes with the central atom of $AlCl_3$ and 4.3 kcal/mol for complexes with the Cl−Al bond, which is only slightly lower than that for uncomplexed semibullvalene).[19]

Complexes involving barbaralane (with Br_2, Cl_2, F_2, BrF, $2Br_2$, $2Cl_2$, $2F_2$, and 2BrF) were also examined. In these cases, no minima with delocalized barbaralane substructures were located, but barriers for Cope rearrangements were generally lowered upon complexation (the rearrangement barrier for uncomplexed barbaralane with B3LYP/6-31G(d) is 6.6 kcal/mol[9a] and the barriers for the complexes ranged from 3.7 to 6.7 kcal/mol; see Supporting Information for details).

Thus, we find that complexation of delocalized semibullvalene and barbaralane transition structures by halogens and halogen-containing species can lower the associated barriers for Cope rearrangement. For many semibullvalene complexes the barrier disappears entirely and delocalized structures become minima. To our knowledge, these are the first uncharged species described theoretically or experimentally with minima that contain delocalized unsubstituted semibullvalenes.

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Supporting Information Available: Additional details on calculations, including coordinates and energies for all structures, binding data, fragment analysis data, and NICS data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(4) (a) using boron: Wu, H. S.; Jiao, H.; Wang, Z.-X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2003**, *125*, 10524−10525. (b) using phosphorous (for barbaralane): Reiher, M.; Kirchner, B. *Angew. Chem., Int. Ed.* **2002**, *41*, 3429−3433. (c) Note also that removing an electron from semibullvalene appears to lead to a delocalized radical cation with C_{2v} symmetry: Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2835−2837.

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(7) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1760−1763.

(8) Wang, S. C.; Tantillo, D. J. *Eur. J. Org. Chem.* **2006**, 738−745 (note, in particular, reference 15 therein).

(9) (a) All geometries were optimized using B3LYP/6-31G(d) (Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652; Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627) as implemented in *GAUSSIAN03* (Frisch, M. J.; et al. Gaussian, Inc.: Pittsburgh, PA, 2003; see Supporting Information for full reference). This level of theory has been shown to perform well in studies of Cope rearrangements, including those involving semibullvalenes and barbaralanes (see, e.g., refs 3, 5, 6, and Hrovat, D. A.; Brown, E. C.; Williams, R. V.; Quast, H.; Borden, W. T. *J. Org. Chem.* **2005**, *70*, 2627−2632 and references therein). For comparison, computed binding energies for halogen complexes with C_2H_4, C_2H_2, NH_3, H_2O, and HCN can be found in the Supporting Information; in general, it appears that B3LYP/6-31G(d) slightly overestimates absolute binding energies for these species. All stationary points were characterized as minima or transition structures by analyzing their vibrational frequencies. All reported energies include zero-point energy corrections from frequency calculations, scaled by 0.9806 (Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513). In some cases, the effects of solvent were modeled using CPCM calculations (with UAKS radii), a self-consistent reaction field (SCRF) method (Barone, V.; Cossi, M. J. *J. Phys. Chem. A* **1998**, *102*, 1995−2001. Barone, B.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404−417). Structural drawings were produced using *Ball & Stick* (Müller, N., Falk, A. *Ball & Stick V.3.7.6*, *Molecular Graphics Application for MacOS Computers*; Johannes Kepler University: Linz, Austria, 2000.). (b) The Amsterdam Density Functional (ADF) Program was also used to calculate and analyze the binding energies between semibullvalene and various halogens. The B3LYP functional with the triple-zeta doubly polarized (TZ2P) basis set was used as implemented in ADF2006 (Scientific Computing & Modeling, NV, Amersterdam). See Supporting Information for further details. For a general description of ADF, see: Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1−86.

(10) The delocalized semibullvalene−Br_2 complex is also a minimum at the B3LYP/6-31+G(d,p) level. At the MP2/6-31G(d) level, the delocalized semibullvalene−Br_2 complex is a transition structure for Cope rearrangement, but the barrier for this rearrangement is only 2 kcal/mol (the barrier for uncomplexed semibullvalene at this level is 4 kcal/mol). For Cl_2, a barrier of 3 kcal/mol was computed with MP2/6-31G(d), while for F_2, the delocalized structure is a minimum with MP2/6-31G(d). See Supporting Information for further details.

(11) We also examined complexes of semibullvalene with one or two molecules of $BrCH_3$, $ClCH_3$, FCH_3, BrOH, and ClOH, in the hopes that, if delocalized minima could be located for such species, halogen atoms could be covalently tethered to the semibullvalene framework to produce delocalized species stabilized through intramolecular interactions. Unfortunately, no delocalized minima were located for these species. Barrier-lowering upon complexation was still observed, however. See Supporting Information for details.

(12) Absolute gas phase complexation energies (with and without BSSE) can be found in the Supporting Information. Binding energies (both enthalpies and free energies) were generally small, but in some cases were larger than 5 kcal/mol. For example, the localized structures in Figure 2a,b are not predicted to be bound based on computed free energies of binding at 300 K, but the more delocalized structures in Figures 1 and 2c,d are predicted to be bound by 2.4, 0.7, and 1.2 kcal/mol, respectively; i.e. more delocalized structures are more tightly bound.

(13) The structure shown in Figure 2b is much less symmetrical than those in Figures 1 and 2a,c,d; yet this structure corresponds to a minimum even with tightened convergence criteria. Constraining the C−Br distances to 3.1 Å and allowing the rest of the structure to relax leads to a (non-minimum) structure that is only 0.4 kcal/mol higher in energy than the optimized structure, however, suggesting that the energy surface in this area is very flat.

(14) Single-point calculations (and some optimizations) were performed on the structures in Figures 1 and 2 in CH_2Cl_2, H_2O, and DMSO. In general, the energies of these structures remained within a couple kcal/mol of each other, with the biggest changes being observed, not surprisingly, for H_2O. See Supporting Information for details.

(15) Note that the computed HOMO (resembling the structure at the right of Chart 1a) and HOMO-1 (left in Chart 1a) for uncomplexed semibullvalene are close in energy (−0.179 and −0.235 eV, respectively, at the B3LYP/6-31G(d) level). The LUMO (left in Chart 1a) and LUMO-1 (right in Chart 1a) for uncomplexed semibullvalene are also close in energy (−0.006 and +0.029 eV, respectively).

(16) (a) The electrostatic contribution is computed to be 15.2 kcal/mol while the orbital interaction contribution is computed to be 17.2 kcal/mol. Details on complexes with other halogens can be found in the Supporting Information. (b) Nucleus-independent chemical shift (NICS) values (Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842−3888) for the various complexes with delocalized semibullvalene can also be found in the Supporting Information; these values are almost always close to −18 (GIAO-B3LYP/6-31G(d)), indicating that the aromaticity of uncomplexed delocalized semibullvalene (NICS value of −14 at same level) is not disrupted upon complexation.

(17) With FBr and FCl, in addition to complexes like those shown for BrCl, complexes were located with these mixed halogens pointing "up" rather than "down" (as in the structures shown in the text). See Supporting Information for further details.

(18) The complex shown in Figure 4a does not have perfect C_{2v} symmetry; yet this structure appears to be a minimum. Constraining all four C−Br distances to 3.1 Å and allowing the rest of the structure to relax leads to a structure that is only 0.04 kcal/mol higher in energy than the optimized structure, however.

(19) (a) All minima and transition state structures for the semibullvalene−$AlCl_3$ complexes shown in Figure 6 were also optimized in dichloromethane; in this case, the barriers were found to be 5.5 and 4.2 kcal/mol. (b) Minima and transition state structures for semibullvalene−BF_3 complexes analogous to those shown in Figure 6 were also located; in this case, the barriers were 4.2 and 4.5 kcal/mol in the gas phase. (c) Likewise, minima and transition state structures for semibullvalene−BCl_3 complexes analogous to those shown in Figure 6 were also located; in this case, the barriers were 4.2 and 4.2 kcal/mol in the gas phase. See Supporting Information for additional details.