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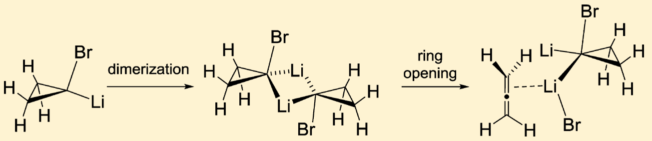
Computational Studies on a Carbenoid Mechanism for the Doering−Moore−Skattebøl Reaction

Alicia C. Voukides, Katharine J. Cahill, and Richard P. Johnson*

Department of Chemistry University of New Hampshire, Durham, New Hampshire 03824, United States

Ⓢ *Supporting Information*

ABSTRACT: The reaction of geminal dihalocyclopropanes with metals or alkyllithiums affords carbenoids which undergo low-temperature ring opening to allenes; this is known as the Doering−Moore−Skattebøl reaction. DFT and CCSD(T)//DFT computations have been used to model the structure, coordination state, and ring opening of 1-bromo-1-lithiocyclopropane as a model for cyclopropylcarbenoid chemistry. Both implicit (PCM) and explicit solvation models have been applied. Carbenoid ring opening is similar to the process predicted in earlier studies on cyclopropylidene. The initial disrotatory stereochemistry becomes conrotatory en route to the allene−LiBr complex. Predissociation of the carbenoid to cyclopropylidene + LiBr is not supported by computations. DFT computations predict modestly exergonic dimerization of the carbenoid, with or without solvation, and the dimer appears to be the most likely reactive species in solution. Predicted barriers to ring opening are only modestly affected by solvation or by dimer formation, remaining in the range of 9−12 kcal/mol throughout.



INTRODUCTION

In 1958, Doering and LaFlamme reported that the reaction of *gem*-dibromocyclopropanes such as **1** with magnesium or sodium on alumina (Scheme 1) yields the allene **2**.[1] The authors favored a mechanism in which two-electron reduction leads to successive loss of the halogens, followed by ring opening, perhaps proceeding through an intermediate cyclopropylidene. Soon afterward, Moore and Ward described a similar result with alkyllithiums.[2] Skattebøl quickly reported much greater detail on the dibromocyclopropane−alkyllithium reaction, showing how both acyclic and cyclic allenes such as **4** can be easily prepared.[3] Following these seminal papers, the Doering−Moore−Skattebøl reaction has been widely applied in the synthesis of allenes and higher cumulenes.[4] This reaction offers a superb route to strained cyclic allenes[5] and butatrienes.[6] In the presence of chiral complexation agents, a modest level of asymmetric allene synthesis has been achieved.[7]

Although it has long been recognized that this transformation must initially proceed through a carbenoid, the existence of free cyclopropylidenes remains a point of contention; indeed, the Doering−Moore−Skattebøl reaction still seems to be synonymous with cyclopropylidene chemistry, even though the timing of events is unknown.[4] At the extremes of a mechanistic continuum, the intermediate generated by initial lithium−halogen exchange, represented as **6** in Scheme 2, can either lose LiBr to make the free cyclopropylidene **7**, which opens to **9**, or proceed directly to **8**, followed by loss of LiBr. It is known from both experiment[8] and theory[9] that cyclopropylidenes should have barriers of <10 kcal/mol to ring opening. Among many studies, Valtazanos and Ruedenberg most clearly demonstrated the complexity of the cyclopropylidene energy surface, which initially traces a disrotatory ring-opening pathway and then becomes conrotatory after passage through a valley−ridge inflection point.[9d,e] Many other examples of this type of potential energy surface are now known.[10] More recent work has shown that bicyclic cyclopropylidenes, ideal precursors to small-ring cyclic allenes, also will have low barriers to ring opening.[9f,g] Alternatively, the carbenoid **6** might dimerize to **6-d**; sequential ring opening would then yield **6** plus **8**. Of course, higher oligomers of **6** are possible.

Carbenoids are unusual species, caught between organometallic and hydrocarbon chemistry.[11] In 1964, Closs and Moss described "carbenoids" as "intermediates which exhibit reactions qualitatively similar to those of carbenes without necessarily being free divalent species".[11a] Common carbene reactions such as cyclopropanation and C−H insertion occur frequently with carbenoids. Carbenoids prepared with diverse metals have been widely applied in synthetic chemistry.[11] A recent review by Capriati and Florio nicely summarizes advances in this broad field.[11g] Computational studies on simple lithium carbenoids (X = halogen) predict the existence of two monomeric minima, corresponding (Figure 1) to **10** or **11**.[11e,12] The bent structure **10** is usually of slightly lower energy. There have also been a number of studies on carbenoid dimers (**10d**) in which lithium bridges the two structures.[12a−c] Dimerization is predicted to be modestly exergonic.

Portions of the cyclopropylcarbenoid surface have been studied previously by several groups. In 1989, Wang and coworkers used HF/6-31G(d)//HF/3-21G calculations to predict a bent structure for lithium fluorocarbenoid **12a** and a disrotatory transition state for ring opening which is 16.4 kcal/mol higher in energy.[13] The authors suggested a more complex reversal of rotation after this point in the process but did not

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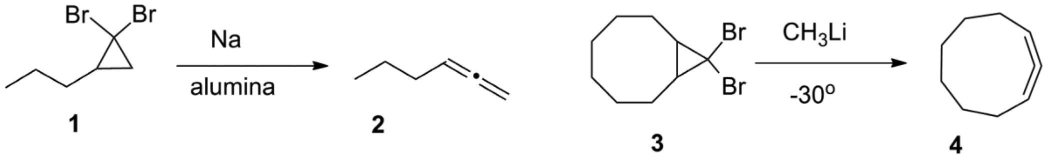
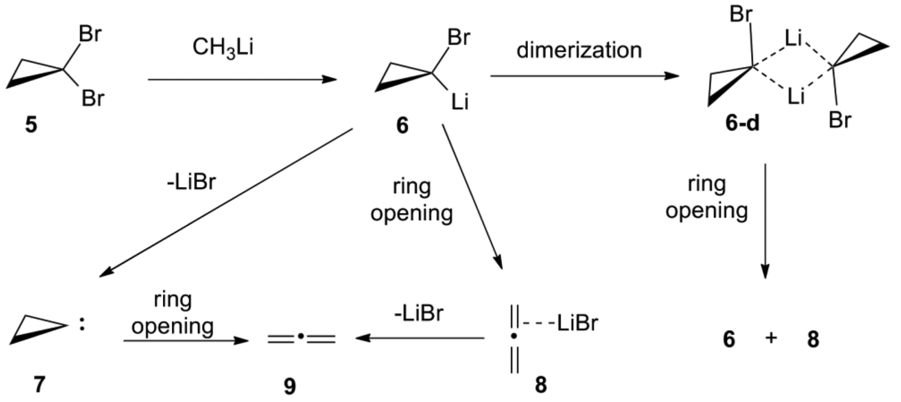
Scheme 1. Examples of the Doering−Moore−Skattebøl Reaction



Scheme 2. Potential Reaction Pathways



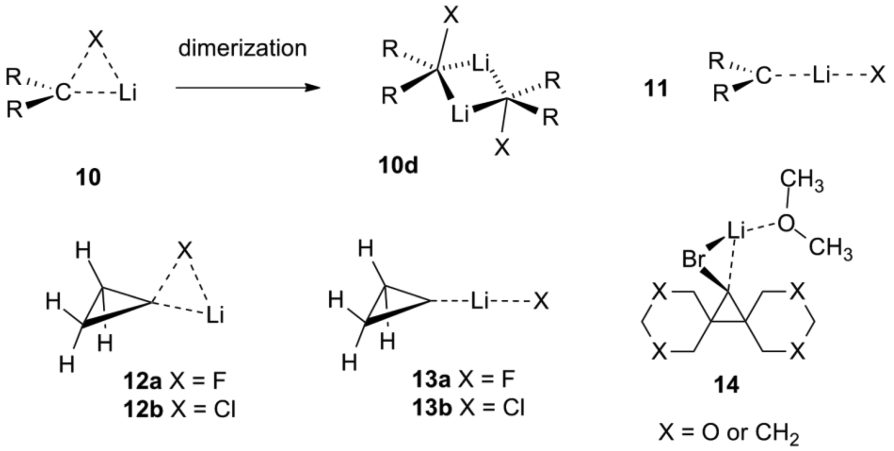
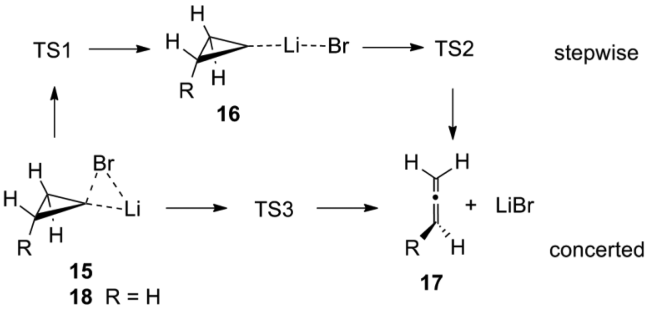


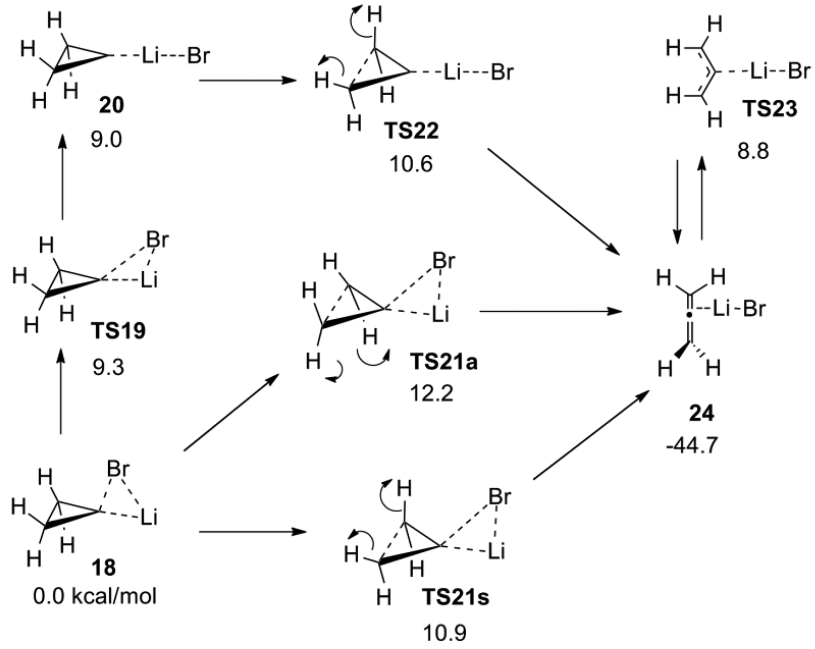
Figure 1. Carbenoid structures.

Scheme 3. Stepwise vs Concerted Mechanisms



locate any stationary points along this path. In a 2001 study, Sigal and Apeloig examined the structure and ring opening of chlorolithiocarbenoid **12b** using MP2/6-31G(d) theory.[14] They located **12b** and **13b** as minimized structures for the carbenoid but only considered a LiCl dissociation pathway for ring opening. This was predicted to have a 42.5 kcal/mol activation energy, far above the barrier expected for a reaction that occurs readily below 0 °C. Boche and Lorenz reported HF/6-311++G(d,p) structural data on a collection of cyclopropyl carbenoids, again supporting a bent structure (as in **12**) as the lowest energy geometry.[11e] Kaszynski and co-workers studied the structures and energetics of carbenoid ether complexes **14** and the parent carbenoid **6**.[15] Using B3LYP calculations, they again predicted bent-carbenoid structures and showed that several schemes for LiBr dissociation to free cyclopropylidenes were both endothermic and endergonic. In the most recent studies, Azizoglu and co-workers have employed DFT and MP2 methods to study cyclopropylcarbenoids (**15**; Scheme 3) bearing electron-donating and -withdrawing substituents[16a] in addition to analogues with silicon and germanium.[16b−d] They concurred with earlier reports, predicting a bent-carbenoid geometry (**15**). Two mechanisms were proposed for ring opening of lithium cyclopropylcarbenoids to the allene.[16a] A "concerted" reaction proceeds directly from **15** through **TS3** to **17** + LiBr, whereas a stepwise mechanism passes through rearrangement via **TS1** to the linear carbenoid intermediate **16**, as described earlier by Wang.[13] Electron-donating substituents lead to lower predicted activation energies, consistent with cyclopropyl cation character

Scheme 4. CCSD(T)/6-311+G(d,p)//B3LYP + ZPVE Energetics (kcal/mol)



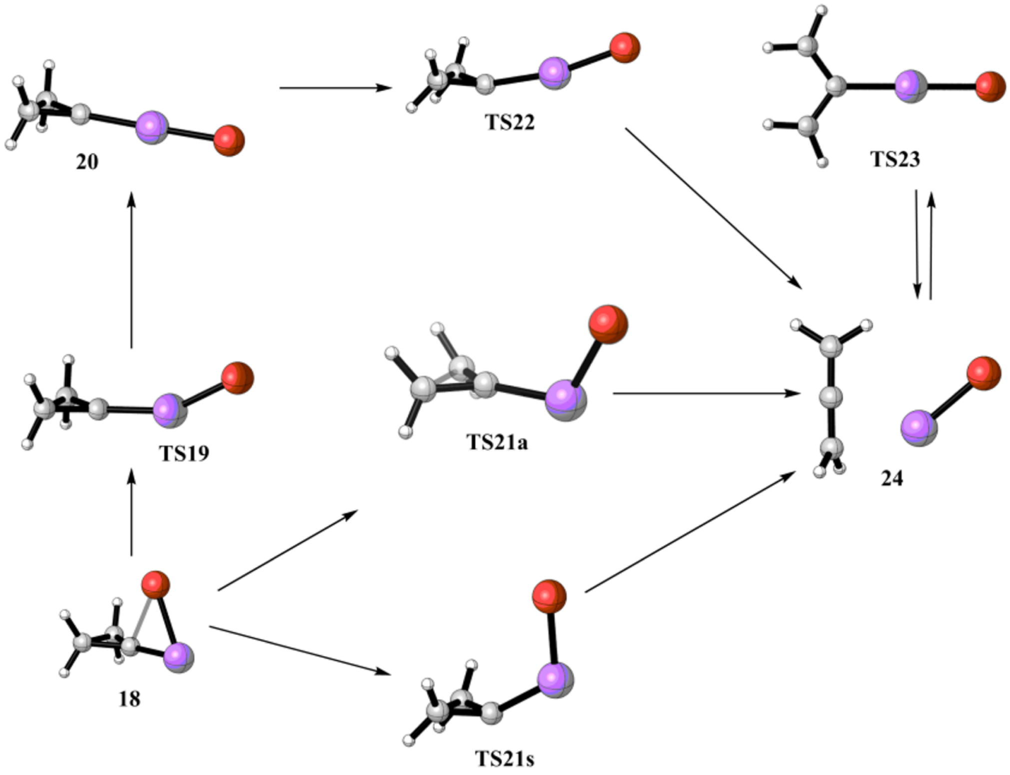


Figure 2. Structures for stationary points.

in the transition state. For the parent carbenoid **18, TS3** was not located.[16a]

The importance of aggregation in Doering–Moore–Skattebøl chemistry is unknown. Low-temperature NMR studies have been reported by Seebach and co-workers for lithium cyclopropylcarbenoids, but no conclusions could be made about geometry or aggregation state.[17]

We report here results of our studies on cyclopropylcarbenoids and the Doering–Moore–Skattebøl reaction which include (a) location of *two* diastereomeric transition states for direct ring opening of monomeric carbenoid **18** and intrinsic reaction coordinate (IRC) calculations showing the novel features of this path, (b) calculations for monomeric carbenoids at the CCSD(T)/6-311+G(d,p) level of theory to more accurately predict reaction energetics and assess the reliability of DFT methods, (c) assessment of the effects of solvation on carbenoid structures and transition states, (d) optimization of dimeric carbenoid structures and energetic estimates for dimerization with and without solvent effects, and (e) location of transition states for ring opening of the dimeric carbenoid.

■ COMPUTATIONAL METHODOLOGY

All calculations were carried out with Spartan[18] or Gaussian.[19] Geometries were optimized with the well-documented B3LYP functional,[20] followed in some cases by single-point CCSD(T) calculation. Optimized structures and other data are compiled in the Supporting Information. Solvation models employed either the PCM method[21] with diethyl ether as solvent or explicit solvation through lithium complexation with two molecules of dimethyl ether.[22]

■ RESULTS AND DISCUSSION

Monomeric Carbenoid Models. We initially examined the structure and reactions of the lithium bromocarbenoid **6**. Energetics from CCSD(T)//B3LYP computations are summarized in Scheme 4. In agreement with previous studies,[13,14,16] we located bent and linear minima for the carbenoid structure, represented as **18** and **20**, respectively. These are separated by a low barrier through **TS19**. Our results agree with all earlier studies on cyclopropylcarbenoids, showing the linear structure to be of significantly higher energy.

Pathways were studied for ring opening of each carbenoid structure. The most easily located transition state, **TS22**, lies only slightly above the linear structure **20** and is similar to that described earlier by Wang and co-workers[13] and more recently by Azizoglu and co-workers.[16] This has a nearly linear C−Li−Br arrangement. For the lower energy bent carbenoid **18**, we initially located **TS21s**, in which hydrogens *syn* to the bromine rotate outward. Azizoglu et al. postulated the existence of this transition state (**TS3** in Scheme 3) but only reported it for substituted structures.[16] Because there appeared to be no compelling reason for this exclusive stereochemistry, we explored the opposite sense of rotation and, with much greater effort, located the diastereomeric **TS21a**, in which hydrogens *anti* to the bromine rotate outward. All three ring-opening barriers of 10.6−12.2 kcal/mol are in the range expected for this low-temperature reaction and are also consistent with the well-documented ability to carry out other carbenoid reactions such as alkylation, protonation, and addition to carbonyl compounds in competition with ring opening.[11] The slight difference between **TS21s** and **TS21a** suggests that the counterion location plays only a small role.

On the product side, we optimized the allene−LiBr complex **24**, in which the metal is coordinated with a single π bond rather than a delocalized arrangement. Because previous work suggested a disrotatory ring opening, we also examined the planar geometry **TS23**, which might lie at the end of a symmetrical disrotatory pathway. This structure was found to have modest open-shell character ($S^2 > 0$) and displays a single imaginary mode. Inspection of this vibrational mode and IRC calculations showed **TS23** to be the transition state for π bond rotation in complex **24**. This is similar to π bond rotation in uncomplexed allenes.[5,9f,g] Figure 2 provides images of stationary point geometries.

Energetics of these stationary points were assessed with DFT, MP2, and CCSDT(T)//DFT theories. Scheme 4 summarizes CCSD(T)//DFT results; a more complete listing is given Table 1. Predicted energetics are surprisingly consistent across different methods and basis sets. Even the simplest method used, B3LYP/6-31+G(d), provides relative energies only slightly different from those of CCSD(T). Pratt and coworkers have reported extensive computations on similar comparisons of basis sets and functionals for lithium carbenoid calculations.[12a,23]

Table 1. Reaction Energetics Compared over Several Computational Methods (ZPVE Corrected; kcal/mol)

structure	B3LYP/6-31+G(d)	B3LYP/6-311+G(d,p)	CCSD(T)//B3LYP/6-311+G(d)	MP2/6-31+G(d)
18	0.00	0.00	0.00	0.00
TS19	9.17	7.39	9.29	13.29
20	8.50	7.31	9.01	12.12
TS22	10.63	9.14	10.63	13.31
TS23	6.84	5.51	8.83	9.41
24	−44.71	−48.27	−44.69	−44.23
TS21S	11.75	9.45	10.86	13.80
TS21A	12.89	10.24	12.21	14.59

The intrinsic reaction coordinate (IRC) for ring opening of **18** through the lower energy **TS21s** is reproduced in Figure 3. In contrast, we were unable to optimize an IRC from linear **TS22**. The pathway from **18** initially traces disrotatory stereochemistry, with two groups rotating outward on the same side as bromine. This portion is relatively flat. Midway through the reaction, the path becomes conrotatory, proceeding more steeply downward toward the product. The change occurs at a bifurcation point which is very similar to that reported earlier for the parent cyclopropylidene.[9]

Carbenoids can act as either nucleophiles or electrophiles.[11d,g] This ambivalent behavior is easily explained from the two structural minima shown in Figure 4. On the basis of its pyramidal carbon bonding, **18** would be expected to behave as a cyclopropyl anion. This structure is consistent with the facile alkylation of cyclopropyl carbenoids, their addition to carbonyl groups, and their behavior as strong bases.[4a,11] In contrast, the higher energy **20** might be expected to have cyclopropyl cation character. Natural charge densities of the two carbenoid minima support this simple analysis. This striking charge reversal at carbon along the reaction coordinate has been noted earlier by Brinker.[11c] Both carbenoid structures lead to transition states in which the hydrogen motion is disrotatory. Several groups have noted that the initial disrotatory ring opening of cyclopropylidenes is similar to that for a cyclopropyl cation.[9d−g] Warner and Sutherland showed experimentally that this is also true for carbenoids.[8f] Ring opening along the **20**−**TS22** pathway has a smaller additional barrier because the carbenoid carbon already bears the requisite cation character. In contrast, **18** requires a charge reversal, which occurs as the C−Li−Br bond becomes more linear. As will be shown below, structure **18** best represents components in the carbenoid dimer.

Reaction Models with Implicit Solvation. The role of solvent was explored next using both implicit and explicit solvation models. Models for implicit solvation describe the solute in a bulk solvent cavity, while explicit solvation models consider a molecular complex of solute and solvent molecules. To create an implicit solvation model, stationary points were located at the B3LYP/6-311+G(d,p) level of theory, with inclusion of the polarized continuum model (PCM)[19] and diethyl ether as solvent. Energies are summarized in Scheme 5. The triangular carbenoid structure **18-PCM** optimized easily to a structure that was little changed from the unsolvated model and showed only a modest decrease in the barrier for ring opening. However, the linear carbenoid **20-PCM** repeatedly optimized back to **18-PCM**; not surprisingly, repeated attempts to locate **TS22-PCM** failed to locate a stationary point, instead

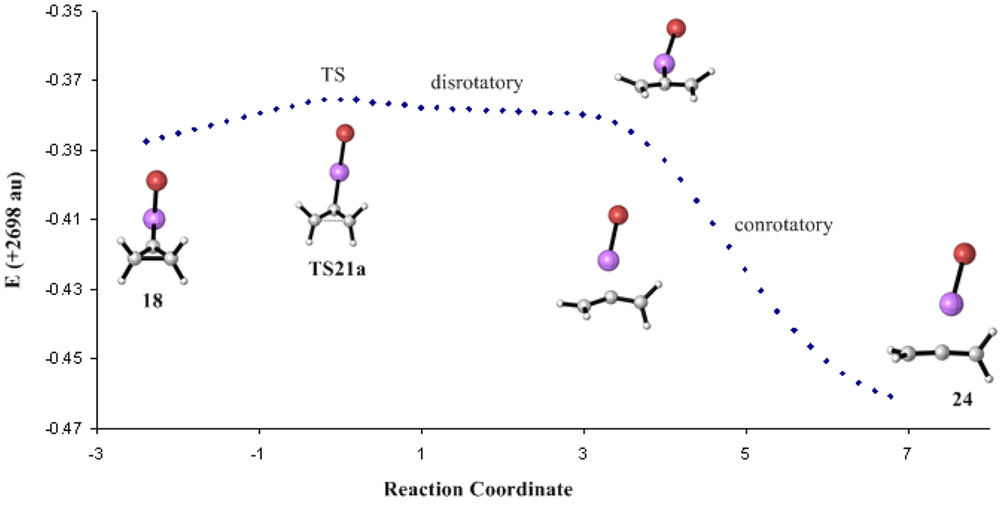


Figure 3. Intrinsic reaction coordinate for carbenoid ring opening (**18** → **24**).

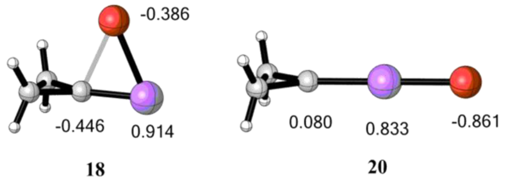


Figure 4. B3LYP/6-311+G(d,p) natural charge densities.

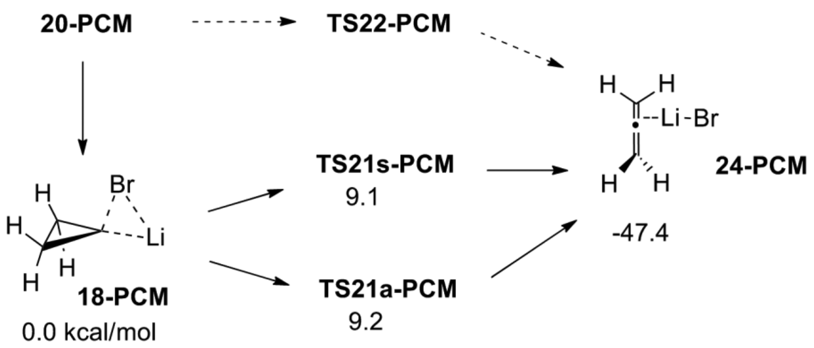
optimizing toward product. *syn* and *anti* transition states for opening of **18-PCM** are nearly isoenergetic. Thus, our model with implicit solvation in diethyl ether predicts the single minimum energy carbenoid structure **18-PCM**, which opens through transition states similar in structure and energetics to those described above without solvent.

Reaction Models with Explicit Solvation. Explicit solvation of organolithium compounds has long been recognized as important for predicting reactivity.[22] Our models were constructed by adding two molecules of dimethyl ether (**DME**) complexed to lithium in the carbenoid. The energetics of optimized structures are summarized in Scheme 6. Although both carbenoid structures could be optimized, the linear structure **20-DME$_2$** is now 20.6 kcal/mol higher in energy; no transition state corresponding to **TS22-DME$_2$** could be located. Only one mode of ring opening for **18-DME$_2$** was found. The barrier for ring opening through **TS21-DME$_2$** is only slightly higher than that without solvation. We conclude that both implicit and explicit solvation models favor triangular carbenoid **18**, and ring opening occurs from this structure. Inclusion of solvation does not significantly alter the predicted barriers.

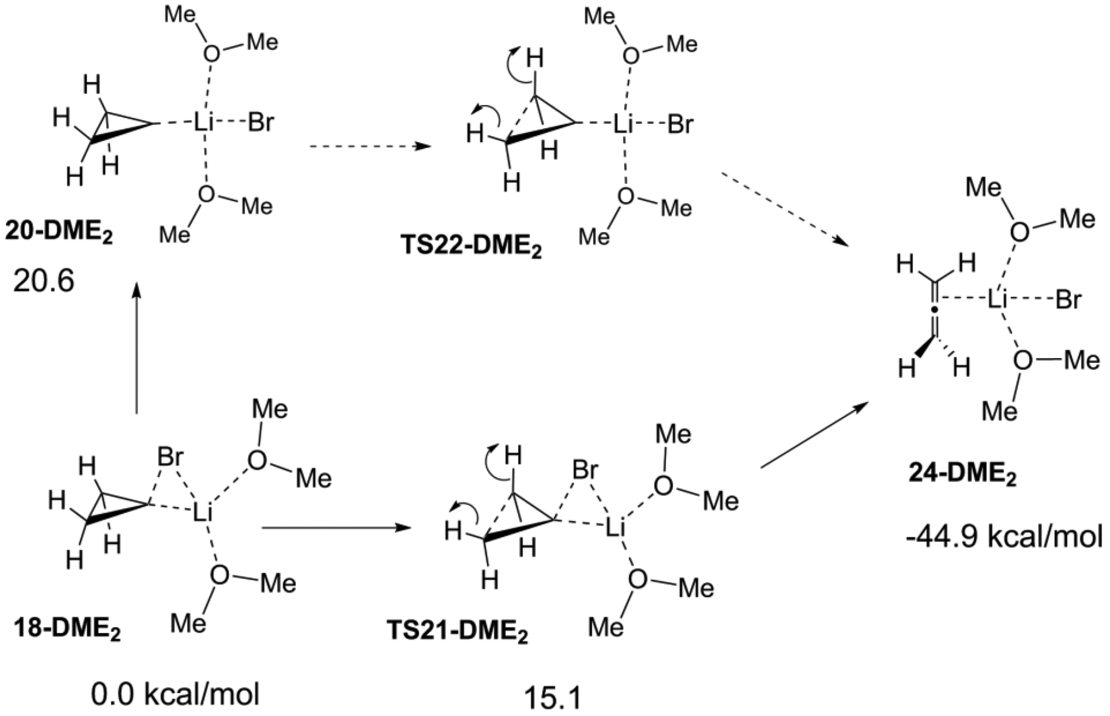
LiBr Dissociation Models. We assessed the energetics of complete LiBr dissociation at each stage during ring opening of the carbenoid **18-PCM**. Scheme 7 summarizes energy and free energy changes calculated at the B3LYP/6-311+G(d,p) level of theory, with PCM solvation in diethyl ether. Free energy calculations model the energetics at −30 °C, a typical reaction temperature. As noted above, solvation favors the bent structure **18**, and so the linear carbenoid structure **20** is not included here. For the carbenoid, dissociation of LiBr at −30 °C is endothermic and modestly endergonic. However, dissociation becomes more favorable upon progression to the transition state, and more so at the allene product, which is predicted to be dissociated. These results support a mechanism in which the carbenoid is initially stabilized by cyclopropylidene−LiBr association but then *dissociates along the ring-opening path* rather than at the end. Thus, what begins as a carbenoid finishes as a free hydrocarbon. Of course, this conclusion describes only a monomeric carbenoid and depends upon how well the B3LYP + PCM model represents these species and their energetics in solution. Explicit solvation with two dimethyl ether molecules bound to lithium does not change these trends; see the Supporting Information for complete results.

Dimeric Carbenoid Models. We next explored the structure, energetics, and ring-opening pathways for carbenoid dimers which are expected to be in equilibrium with the

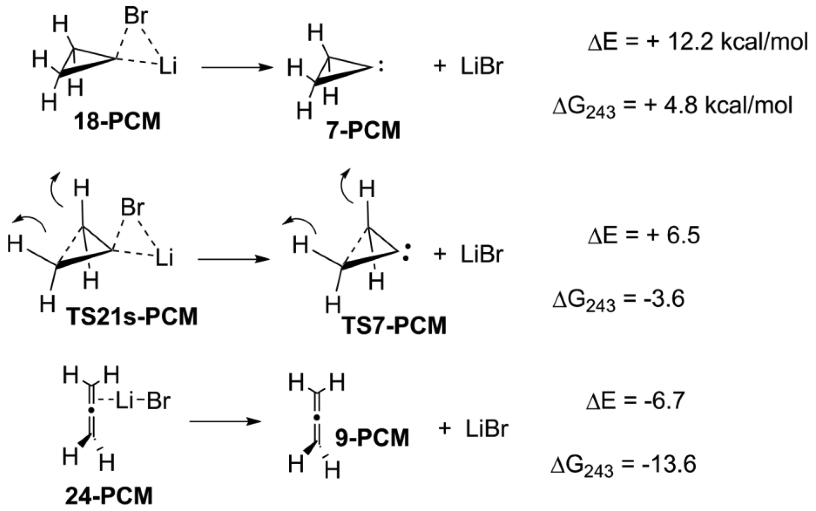
Scheme 5. Energetics for Implicit Solvation Reaction Models



Scheme 6. Explicit Solvation Models



Scheme 7. B3LYP/6-311+G(d,p) Free Energies of LiBr Dissociation with PCM Solvation (Diethyl Ether, −30 °C)

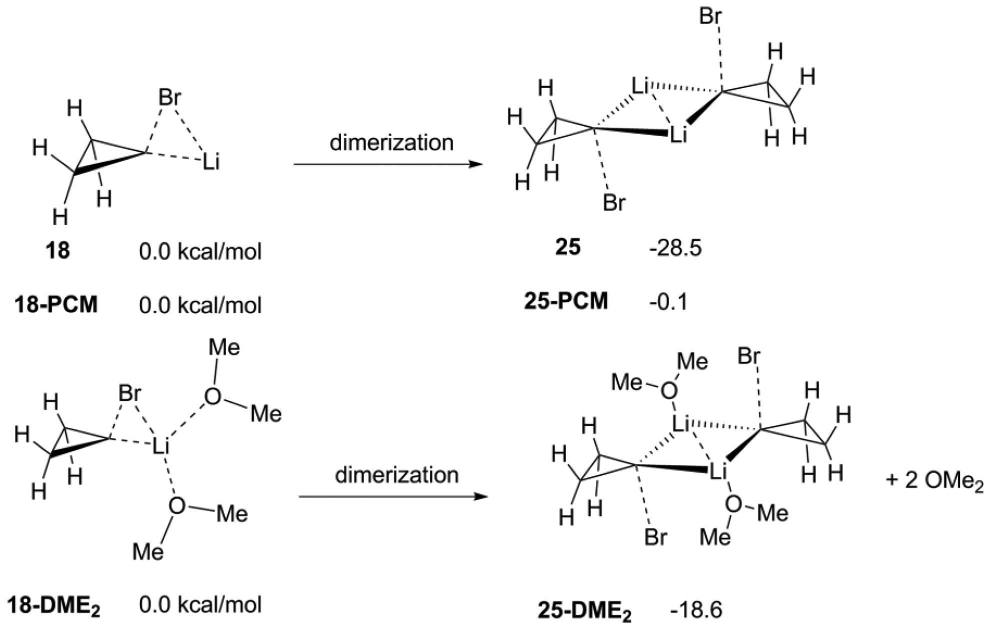


monomers. Although higher oligomers are possible, these seem less likely on the basis of steric and bonding requirements. Various trial structures for the dimer **6-d** optimized to a near-C_2-symmetric geometry (**25**) in which lithium atoms bridge the two carbenoid centers. This structure is best described as a side-by-side dimer of **18**. With inclusion of PCM solvation, a similar structure (**25-PCM**) was optimized but the geometry was somewhat more compact. We also optimized a C_i-symmetric top−bottom dimeric structure in which bromines and lithiums are coplanar; this proved to be a first-order transition state for lithium atoms exchanging relative positions.

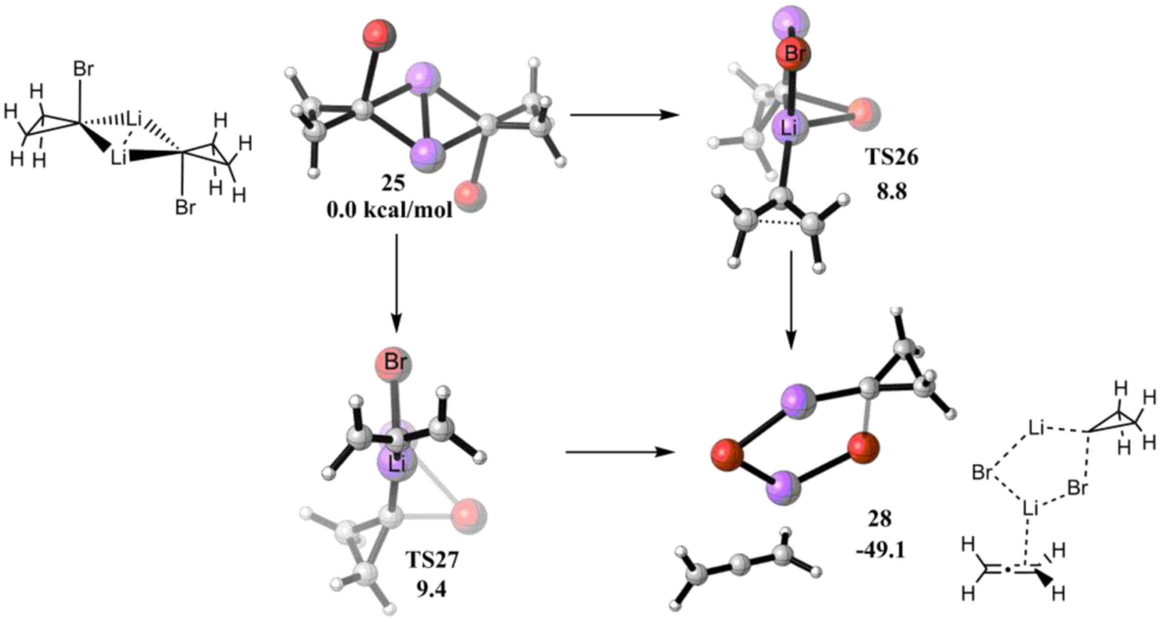
Scheme 8 summarizes the energetics of dimerization with and without solvation. Dimerization in silico is predicted to be exothermic by 28.5 kcal/mol; however, with PCM solvation in diethyl ether this diminishes to 0.1 kcal/mol, presumably because of decreased polar surface area in the dimer. Explicit solvation with two molecules of dimethyl ether predicts that dimerization is exergonic by 18.6 kcal/mol. Our calculations thus predict a dimeric carbenoid structure (**25**) at equilibrium. However, given the close energetics and similar ring-opening barriers, the observed chemistry might be due to either monomer or dimer.

Dimer Ring Opening. We explored ring-opening pathways in which one of the carbenoids in a dimeric pair undergoes ring opening. Scheme 9 summarizes the results without solvation. As with the monomer, dimer **25** displayed two diastereomeric transition states for ring opening. The slightly lower energy transition state has the same mode of disrotatory ring opening as the monomer **18**, in which hydrogens *syn* to the bromine rotate outward. Attempts to locate IRCs for these ring openings were only partially successful but showed initial disrotatory stereochemistry.

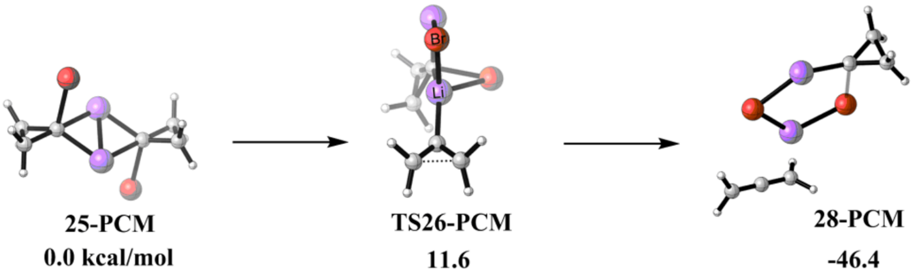
Scheme 8. B3LYP/6-31+G(d) Dimerization Free Energies



Scheme 9. Unsolvated Model (B3LYP/6-31+G(d)-PCM) for Ring Opening of the Carbenoid Dimer



Scheme 10. Solvated Model (B3LYP/6-31+G(d)-PCM) for Ring Opening of the Carbenoid Dimer



Implicit solvation models were next implemented for the dimer **25-PCM**, with results shown in Scheme 10. The predicted reaction barrier is only slightly higher than that for the in silico reaction, but only one of the two disrotatory modes could be optimized. We did not explore transition state models for dimers with explicit solvation.

CONCLUSIONS

The reaction of dihalocyclopropanes with metals or alkyllithiums, commonly known as the Doering−Moore−Skattebøl reaction, was discovered over 50 years ago.[1−3] Many mechanistic features of this important synthetic transformation have remained obscure and may be resolved by theory. Central to our understanding of this reaction are the questions of carbenoids vs free cyclopropylidenes, reaction stereochemistry, and coordination states of the carbenoid. Solvation plays a role in answering all of these questions.

As noted in earlier computational studies,[11,13,14] two minima exist on the cyclopropyl carbenoid surface, one with a triangular C−Li−Br arrangement (**18**) and one nearly linear (**20**). We find three low-energy transition states connecting both structures to a much lower energy LiBr−allene complex. IRC calculations for the lowest transition state show that ring opening is initially disrotatory but then becomes conrotatory after passing through a bifurcation point, precisely the behavior noted earlier for ring opening of cyclopropylidenes.[8,9] Our results indicate that an economical computational method for studying this reaction may be B3LYP/6-31+G(d) theory, since this yields stationary point energies very similar to those of CCSD(T).

The effects of solvation are critical. The higher energy in silico minimum (**20**) for the carbenoid, which has a linear C−Li−Br arrangement, *disappears* with the inclusion of implicit solvation and lies at higher relative energy with explicit solvation, probably because of poor coordination geometry around lithium. Thus, the more accurate model for a monomeric structure in solution should be the triangular carbenoid **18**, which has carbanionic character; this observation is consistent with other known reactions of this carbenoid such as nucleophilic alkylation with alkyl halides.[11] During ring opening, the negative charge shifts to bromine and this carbon acquires more cationic character. This explains the initial disrotatory stereochemistry for ring opening.

Our computations predict modestly exergonic dimerization of the carbenoid, with or without solvation, and the dimer **25** appears to be the most likely reactive species in solution. Predicted barriers to ring opening are only slightly affected by solvation or by dimer formation, remaining in the range of 9−12 kcal/mol. This is consistent with the low temperature required for the Doering−Moore−Skattebøl reaction.

Dissociation of the carbenoid to cyclopropylidene + LiBr is endergonic by 12.2 kcal/mol for the monomer but becomes increasingly favorable as the reaction proceeds and may occur as early as the ring-opening transition state. The true nature of the Doering−Moore−Skattebøl reaction probably lies somewhere between the extremes of free carbene and carbenoid mechanisms, with the initially stabilizing LiBr being jettisoned along the reaction coordinate, perhaps as early as the ring-opening transition state. It is not surprising that these lithium carbenoids behave like diazo compounds and diazirines in showing character that is remarkably similar to that of free carbenes.[25]

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving Cartesian coordinates, summary energetics for stationary points, structures of stationary points, and the full ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for R.P.J.: rpj@cisunix.unh.edu.

Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to the memory of Professor William von Eggers Doering, one of the great pioneers in synthetic and mechanistic organic chemistry.[24]

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