

# Origins of Stereoselective Carbene 1,2-Shifts and Cycloadditions of 1,2-Dichloroethylidene: A Theoretical Model Based on CBS-Q and B3LYP Calculations

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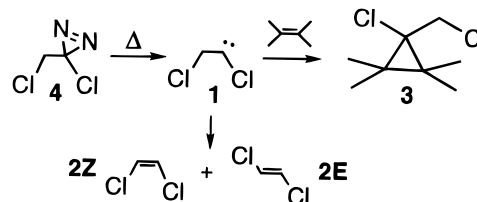
**Abstract:** Bonneau *et al.* (*J. Am. Chem. Soc.* **1996**, *118*, 3829–3827) have proposed that carbene–olefin  $\pi$ -complexes can mediate the stereoselectivity of 1,2-dichloroethylidene (**1**) rearrangements. Computational studies at MP2 and CBS-Q theoretical levels confirm the experimentally observed preference for rearrangement of **1** to give (*Z*)-1,2-dichloroethylene. Studies of this and related rearrangements have led to a model to explain the origin of this stereoselectivity. Density functional calculations using Becke3LYP/6-31G\* theory suggest that carbene–olefin complexes do not exist as intermediates in the cycloadditions of **1** to ethylene or to tetramethylethylene. The experimental results can be explained by an alternative model in which 18.7% of the diazirine precursor produces alkene product without intervention of the carbene. Becke3LYP/6-31G\* calculations on the 1,2-shift of hydrogen concerted with loss of nitrogen and on rearrangement of the diazirine to a diazo intermediate show that these processes are not likely to be the alternative pathways.

## Introduction

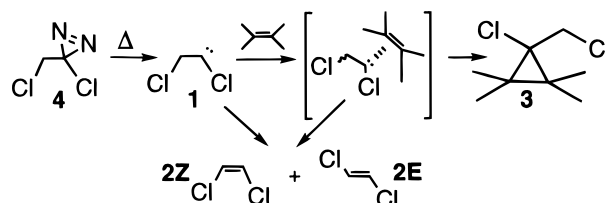
Several central tenets of carbene chemistry have been challenged by recent claims that carbene–alkene complexes are intermediates in cycloadditions and can also mediate 1,2-shift stereoselectivity.<sup>1</sup> Bonneau *et al.* recently reported that the *Z*:*E* ratio of ethylene products formed from photolysis or thermolysis of certain diazirine precursors is sensitive to the presence of a carbene-trapping alkene such as tetramethylethylene (TME). For example, the thermolysis of **4** gives (*E*)- and (*Z*)-dichloroethylene (**2**), presumably via carbene **1**, in a **2Z**:**2E** ratio of about 16:1.<sup>1</sup> In the presence of TME, the expected cyclopropane adducts from carbene cycloaddition are also formed (**3**, Scheme 1).

The selectivity of the reaction (**2Z**:**2E**) decreases to as little as 2.4:1 when TME is present in large excess. Such an observation indicates that Scheme 1 is incomplete, since it predicts that the **2Z**:**2E** product ratio will be independent of TME concentration. Bonneau *et al.* have proposed that a carbene–olefin complex, shown in brackets in Scheme 2, can account for the experimental observations. They suggest that the carbene–alkene complex can give not only cyclopropane, but also 1,2-shift products with selectivity altered from that of the free carbene.<sup>1</sup> Carbene–alkene complex intermediates have previously been invoked to explain cycloaddition kinetics,<sup>2</sup> but computational results cast doubt on the existence of such stable complexes;<sup>3,4</sup> alternative explanations have been suggested for these phenomena.<sup>5–7</sup>

## Scheme 1



## Scheme 2



We have carried out a density functional theory (DFT) and Complete Basis Set (CBS) study of the rearrangement and cycloaddition behavior of carbene **1**. Our results provide further strong evidence that carbene–alkene complexes do not exist as intermediates in cycloadditions of **1** to TME and also explain the origin of the high stereoselectivity observed for the unimolecular 1,2-H shift reaction. We present an alternative kinetic scheme which can explain a variation of the ratio **2Z**:**2E** with TME concentration ( $[TME]$ ), and we evaluate its plausibility with a fit of rate constants to the experimental data as well as a computational study of the thermal reactivity of **4**.

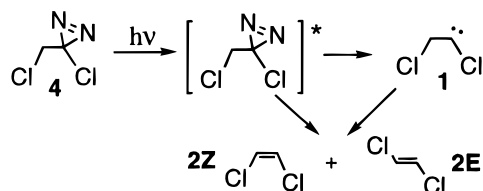
## Background

In addition to the unexpected dependence of the ratio **2Z**:**2E** on  $[TME]$ , the photolysis or thermolysis of **4** also leads to more rearrangement products relative to cycloaddition products (**2**:**3**) at higher concentrations of TME than would be expected on the basis of Scheme 1. Similar results have been obtained with

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## Scheme 3



3-chloro-3-propyldiazirine, 3-chloro-3-(*p*-chlorobenzyl)diazirine and 3-chloro-3-(*p*-methylbenzyl)diazirine, and these have been interpreted in terms of carbene-alkene complex formation by Liu and co-workers.<sup>8,9</sup> It has been elegantly demonstrated, especially by Platz's group, that an alternative photochemical path from precursor to olefin (presumably involving an excited state of the diazirine, as shown in Scheme 3) can account for the observation of such excess rearrangement products in photochemical reactions.<sup>7,10–12</sup> In particular, White and Platz have shown that carbene-alkene complexes are not necessary to explain the photoreactivity of benzylchlorocarbene.<sup>7</sup>

In the case of 4, Bonneau and Liu have performed both thermal and photochemical experiments to quantify the contribution of such excited state precursor reactivity. Their findings that thermolysis and photolysis give more 2 than predicted and that the 2Z:2E ratio under both types of conditions is sensitive to the concentration of TME support their hypothesis of a carbene-alkene intermediate. Such a complex, as shown in Scheme 2, can provide the non-carbene route to 2 needed to explain the data in the absence of excited state species. The variation of 2Z:2E with [TME] can also be explained by this scheme if the Z:E selectivity of the free carbene rearrangement is 15.7:1 and that from the intermediate complex is 1.5:1.

Theoretical studies have shown no evidence for stable carbene-alkene complexes. In 1984 Houk *et al.* investigated the reactions of  $\text{CF}_2$  and  $\text{CCl}_2$  with ethylene and found intermediate complexes, at the RHF/3-21G level, at carbene-olefin separations of 2.694 and 3.283 Å, respectively.<sup>3,6</sup> However, with the inclusion of electron correlation (MP4/3-21G//RHF/3-21G), the stability of the  $\text{CF}_2$ -olefin complex is reduced and the complex of  $\text{CCl}_2$  with ethylene disappears altogether. It was shown that entropy further disfavors these "complexes", implying that they are not free energy minima. Kinetic phenomena previously attributed to carbene-alkene complexes have been explained by consideration of free energies.<sup>5,6</sup> These results were confirmed by Jorgensen *et al.* in 1989, in a calculation including electron correlation and a larger basis set; MP2/6-31G\* trajectories for the addition of dichlorocarbene to ethylene gave a  $\pi$ -complex stabilized enthalpically by 2.0 kcal/mol with respect to the reactants, but this complex disappeared with inclusion of the entropy of reaction.<sup>4</sup> Computational evidence, therefore, suggests that carbene-alkene complexes with ethylene are not likely to exist, even in the gas phase. Increases in computer speed and the availability of density functional methods now make it feasible to investigate directly complex formation between carbenes and substituted alkenes such as TME.

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## Computational Methods

Unimolecular rearrangements of 1 and of the 1,2-dichloroethyl cation (5) were examined with MP2/6-31Gd<sup>+</sup> theory, supplemented for 1 by complete basis set (CBS-Q)<sup>13,14</sup> energy calculations, and compared with results from density functional theory (DFT) using the hybrid DFT/Hartree-Fock method Becke3LYP<sup>15–17</sup> with the 6-31G\* and cc-pVDZ<sup>18–20</sup> basis sets. The reactivity of (chloromethyl)chlorodiazirine was examined using B3LYP/6-31G\* theory. This method was also used to compute cycloaddition pathways. All *ab initio* and density functional calculations were performed using GAUSSIAN 94.<sup>21</sup>

Energies reported in the text represent electronic energies with zero-point energy (ZPE) correction made at the B3LYP/6-31G\* (for all DFT calculations) or MP2/6-31G<sup>+</sup> (for MP2 calculations) level. CBS-Q energies reported include both zero-point energies and thermal corrections to give the electronic energy at 298 K. All CBS-Q energy calculations were performed at MP2/6-31G<sup>+</sup>-optimized stationary points. Free energies were determined using GAUSSIAN 94, which treats low-energy normal mode frequencies as vibrations for the computation of entropies. Frequencies were scaled by 0.9806 for B3LYP/6-31G\* calculations, 0.9670 for MP2/6-31G<sup>+</sup> calculations, and 0.9135 for CBS-Q calculations.<sup>22</sup>

Tunneling probabilities for the 1,2-H shift in 1a and 1b were computed using TheRate 96.<sup>23</sup> The program uses a direct dynamics approach to estimate tunneling along the so-called Marcus-Coltrin path, which includes a small amount of corner-cutting.<sup>24–26</sup> Tunneling calculations were done on the basis of an intrinsic reaction path computed at the B3LYP/6-31G\* level with GAUSSIAN 94.<sup>27,28</sup> The energy along this path was improved by carrying out a series of 38 B3LYP/cc-pVDZ single point calculations.

## Results and Discussion

**Unimolecular Reactivity.** Figure 1 shows the MP2/6-31G<sup>+</sup> geometries for the *cis* (1a) and *trans* (1b) conformations of 1 and the corresponding transition states leading to (Z)- and (E)-dichloroethylene. The B3LYP/6-31G\* geometries are very similar and are reported in the Supporting Information.<sup>29</sup> The *cis*-conformer (1a) of the carbene is predicted to be 2.6, 3.5, or 3.3 kcal/mol more stable than the *trans* (1b) with MP2/6-31G<sup>+</sup>, B3LYP/6-31G\*, and B3LYP/cc-pVDZ calculations. With the basis-set extrapolation and improved correlation treatments in the CBS-Q method, this difference is reduced to 1.9 kcal/mol. The *trans*-isomer 1b is less stable because of electrostatic repulsions between  $\text{Cl}_2$  and the lone pair of electrons on C1

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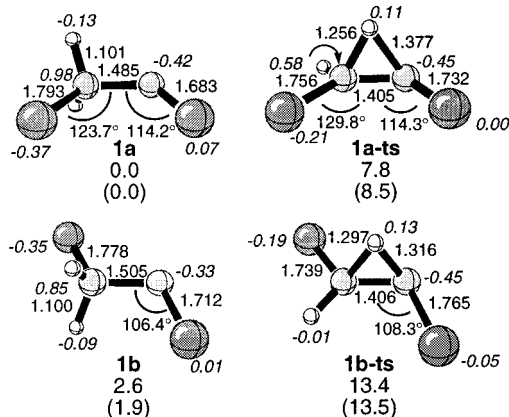
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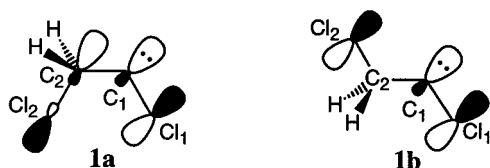
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**Figure 1.** MP2/6-31G<sup>+</sup> geometries of **1a**, **1b**, and transition states to form **2Z** (**1a-ts**) and **2E** (**1b-ts**). CHELPG charges are given in italics.<sup>32</sup> MP2/6-31G<sup>+</sup> and CBS-Q energies (in parentheses) are given below the structures. B3LYP/6-31G\* energies relative to **1a** (0.0) are 3.5 (**1b**), 9.9 (**1a-ts**), and 16.2 (**1b-ts**) kcal/mol while B3LYP/cc-pVDZ gives 3.3 (**1b**), 8.2 (**1a-ts**), and 14.0 (**1b-ts**) kcal/mol.



**Figure 2.** Orbitals involved in stabilization of *cis*-carbene **1a** and destabilization of **1b** and **1b-ts**.

(atom labels in Figure 2) and because the *cis*-conformer (**1a**) is stabilized by carbene lone-pair,  $\sigma^*_{C-Cl}$  negative hyperconjugation.<sup>30,31</sup> The resulting dipole moments of the *cis*- and *trans*-isomers, respectively, are 1.00 and 2.45 D.

The free energy barrier to the *cis*–*trans* isomerization of **1** is high using density functional or MP2/6-31G<sup>+</sup> methods (5.8–7.0 kcal/mol). Similar results using B3LYP/6-31G\* were reported during the course of our studies by Rauk and co-workers.<sup>33</sup> This barrier is reduced considerably at the CBS-Q level, to 3.9 kcal/mol. The activation energies at the CBS-Q level for 1,2 shifts are computed to be 8.5 (**1a**) and 11.6 kcal/mol (**1b**), and the free energy barriers are 9.3 and 12.6 kcal/mol, respectively, at 298 K. The *cis*-transition state is 5.0 kcal/mol more stable than the *trans*, whereas product alkene **2Z** is only 0.5 kcal/mol more stable than **2E**.

The exceptional difference in conformational energies in the transition state is a consequence of the charge separation which accompanies hydrogen migration.<sup>34–36</sup> A shift of electron density away from the migration origin and into the previously empty carbene p orbital raises the energy of orbitals on C<sub>1</sub> and Cl<sub>1</sub> while lowering those centered on C<sub>2</sub> and Cl<sub>2</sub> (Figure 2). As a result, a filled–filled orbital interaction between the C<sub>1</sub> lone pair and the filled in-plane p orbitals on Cl<sub>1</sub> and Cl<sub>2</sub> destabilizes the *trans*-transition state. In the *cis*-isomer the carbene lone pair is stabilized by the C<sub>2</sub>–Cl<sub>2</sub>  $\sigma^*$  orbital, which becomes a

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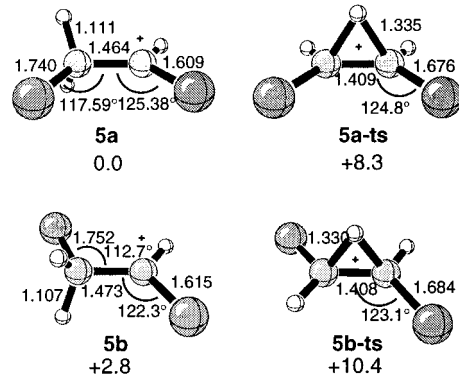
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**Figure 3.** MP2/6-31G<sup>+</sup> structures for the dichloroethyl cation (**5a**). **5b** is the transition structure for rotation around the C–C bond, which we use as a model for the C<sub>s</sub> planar carbene. MP2/6-31G<sup>+</sup> electronic energies are given for the cation and for the transition structures for 1,2-hydride shifts (**5a-ts** and **5b-ts**). The corresponding energies of *cis*- and *trans*-carbenes and their 1,2-H shift transition states are 0.0 (**1a**), 2.6 (**1b**), 7.8 (**1a-ts**), and 13.4 (**1b-ts**) kcal/mol at the same level.

better acceptor in the transition state and relieves the filled–filled interaction. The high degree of selectivity exhibited in this system is therefore a consequence of the attractive and repulsive interactions of the carbene lone pair in the two transition states.

This explanation is supported by studies of the 1,2-hydride shifts in the *cis*- and *trans*-1,2-dichloroethyl cations (**5**) which result from protonation of the carbene lone pair. Figure 3 shows the cation and transition structures for the *cis* and *trans* 1,2-hydride shifts which have activation energies of 8.3 and 7.6 kcal/mol, respectively, at the MP2/6-31G<sup>+</sup> level. A comparison of the relative energies of the carbene rearrangement at the same level shows a much larger difference in energy between **1a-ts** and **1b-ts** (5.6 kcal/mol) than between the cation structures **5a-ts** and **5b-ts** (2.1 kcal/mol). This further implicates the carbene lone pair in the destabilization of transition structure **1b-ts** relative to **1a-ts**.

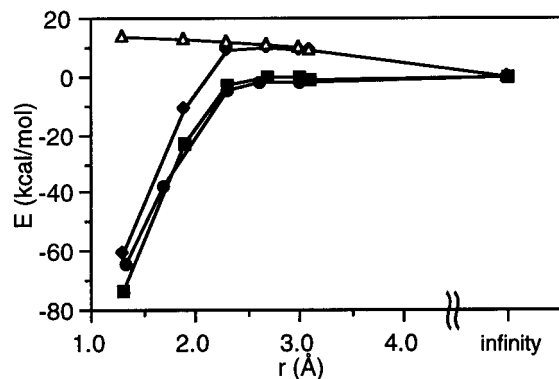
The CBS-Q free energy of activation for the *cis* 1,2-shift of **1a** is 9.3 kcal/mol at 298 K. This corresponds to a rate of  $1.0 \times 10^6 \text{ s}^{-1}$  at room temperature, as compared to the experimental value of  $2 \times 10^7 \text{ s}^{-1}$  obtained using photoacoustic calorimetry.<sup>1</sup> High-temperature quantum mechanical tunneling has been implicated for the 1,2-H shift in methylchlorocarbene,<sup>37,38</sup> and we have investigated whether tunneling is involved in the 1,2-shift in dichloroethylidene. Calculations of the tunneling probability with direct dynamics techniques using a small-curvature model<sup>26,39</sup> applied to the B3LYP/cc-pVDZ//B3LYP/6-31G\* surface (with  $\Delta G^\ddagger = 8.5$  kcal/mol) predict rate enhancement by a factor of only 5.8 for the *cis*-isomer and 4.1 for the *trans* at 298 K.<sup>23</sup> The calculation predicts a rate of  $4.7 \times 10^7 \text{ s}^{-1}$  for the *cis*-rearrangement, and a similar correction applied to the CBS-Q rate gives  $\sim 6 \times 10^6 \text{ s}^{-1}$ , improving agreement with experimental data. The tunneling contribution reduces the Arrhenius activation energy,  $E_a$ , from 8.5 to 5.9 kcal/mol at 298 K for **1a** and from 10.9 to 8.7 kcal/mol for **1b**. This change is similar to that previously observed in calculations done on the 1,2-hydrogen shift in methylchlorocarbene, in which  $E_a$  was reduced from 10.9 to 7.7 kcal/mol.<sup>37</sup>

The **2Z**:**2E** product ratio predicted by density functional and CBS-Q calculations, however, is quite far from that found

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**Figure 4.** Electronic energies (with ZPE correction) for the addition of **1a** to ethylene (■) and to TME (●).  $-T\Delta S$  and  $\Delta G$  at 298 K for the reaction of **1a** with ethylene are shown as  $\triangle$  and  $\diamond$ , respectively. The additions of **1b** to ethylene and to TME show very similar reaction profiles.

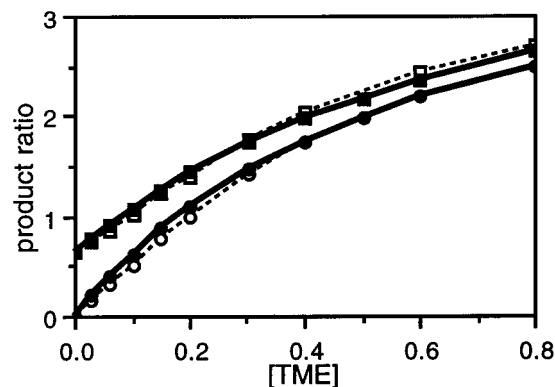
experimentally. Bonneau *et al.* report a **2Z**:**2E** ratio of 16:1 in the absence of TME, corresponding to a free energy difference of 2.0 kcal/mol for the two barriers; CBS-Q predicts 860:1 ( $\Delta\Delta G^\ddagger = 5.0$  kcal/mol) at the experimental temperature of 100 °C. Thus theory predicts that only the *cis*-product, **2Z**, should be observable by the direct carbene 1,2-shift.

**Bimolecular Cycloadditions.** The cycloadditions of **1a** and **1b** to ethylene and to TME were simulated using a reaction coordinate defined by the distance between the carbene carbon  $C_1$  and the midpoint of the olefin double bond ( $r$ ). For each constrained value of  $r$ , the geometry was optimized; energies were obtained at a series of constrained geometries. Neither the addition to ethylene nor the addition to TME showed any indication of a complex. Optimizations begun at separations of 2.9 Å or more led directly to cyclopropane products for additions of both **1a** and **1b** to ethylene and to TME. Virtually no selectivity between the addition of **1a** and **1b** was observed, although this is difficult to quantify without variational optimization of the transition states.<sup>26,39</sup> Figure 4 shows reaction profiles obtained by optimizations with constrained values of  $r$ . Frequencies calculated at the B3LYP/6-31G\* level were used to compute entropies for the addition of **1a** to ethylene.<sup>40</sup> This cycloaddition is predicted to have a free-energy barrier of approximately 10.3 kcal/mol ( $\Delta H^\ddagger = -0.5$  kcal/mol,  $\Delta S^\ddagger = -36.4$  eu) at 298 K.<sup>26,39</sup>

**Alternative Reaction Paths.** Calculations at a higher level than previously available still give no evidence for the existence of stable complexes of **1** with TME. We have searched for an alternative explanation for the variation in the ratio of **2Z**:**2E** with [TME] that is observed experimentally. A key observation is the prediction by high levels of theory that the *cis*-carbene rearrangement product should be preferred to the exclusion of the *trans* in the absence of TME; calculations predict that **2E** will not be formed in detectable quantities, although 6% is measured experimentally. If the theoretical prediction is correct, there must be an alternative reaction path leading to the formation of **2E**, or a mixture of **2E** and **2Z**, which does not involve the free carbene as a precursor. Assuming the existence of such a path, we can estimate to what extent and with what selectivity it must operate.

We have employed the simple kinetics shown in Scheme 1, with the additional assumptions that (1) the carbene gives only **2Z** (no **2E**) by 1,2-H shift rearrangement and (2) there is an alternative, non-carbene source of **2**, presumably originating

(40) Frequency calculations on this reaction path gave one imaginary frequency (corresponding to cycloaddition), which was neglected when computing entropies.



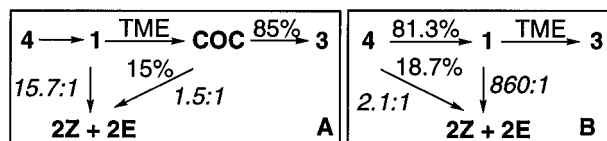
**Figure 5.** Comparison of experimental data with a simple model which assumes that 18.7% of the reaction products are **2Z** and **2E** formed from a non-carbene route in a 2.1:1 ratio. Squares (■) represent the ratio **2E**:**2Z**, circles (●) represent 10 times the ratio **3**:**2**. Experimental data from ref 1 are shown with open symbols and dashed lines.

from the diazirine. To compute product ratios for a number of possible scenarios, we have assigned the rate of 1,2-H shift to be  $1.8 \times 10^8$  s<sup>-1</sup>, based on experimental data,<sup>41</sup> and we have varied the rate of cyclopropanation along with the amount of **2E** and **2Z** produced from another reaction path as needed to fit both (1) the ratio **2Z**:**2E** in the absence of TME and (2) the ratio **3**:**2** at 0.8 M TME. The data in Figure 5 shows the results of our best fit. This variation of **3**:**2** and **2Z**:**2E** with [TME] results from a cyclopropanation rate constant of  $1.62 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, along with a non-carbene source of **2** contributing 18.7% of the reaction products. The **2Z**:**2E** selectivity of the alternative path, which is independent of [TME], is 2.1:1. The cycloaddition rate which results from this fit is in good agreement with the rates of cycloaddition of methylchlorocarbene ( $1.32 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>)<sup>42</sup> and benzylchlorocarbene ( $6 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>)<sup>9</sup> to TME measured by Liu and Bonneau. The close approximation of the predictions of this model to experiment, emphasized in Figure 5, demonstrate that a carbene-olefin complex is not necessary to explain the experimental variation of **2Z**:**2E** with [TME]. Clearly a second competing pathway from the diazirine precursor to the alkene could account for the data.

The model we have presented here implies that approximately 18.7% of rearrangement products are derived from some source other than the free carbene; this alternative source gives a **2Z**:**2E** selectivity of 2.1:1. The contribution of this route and the selectivity of the non-carbene rearrangement are very similar to the contribution and selectivity of the "carbene-olefin complex" reaction path as determined by Bonneau *et al.* A comparison is shown in Figure 6. Despite apparent similarities, however, the two models are different in several ways. In the absence of TME, the complex model (Figure 6A) predicts that the **2Z**:**2E** selectivity observed upon thermolysis of (chloromethyl)chlorodiazirine will be that of the free carbene, while a model based on Figure 6B suggests that the **2Z**:**2E** ratio under these conditions includes the contributions of an alternative thermal path. In addition, the complex model A predicts that a change in the concentration of TME will directly affect the rate and selectivity of paths leading to the formation of **2**. This is not a requirement of model B. These two possible kinetic schemes could be distinguished experimentally by investigating

(41) The lifetime of **1** has been reported as 50 ns, at an unspecified temperature.<sup>1</sup> If we assume that the value refers to 298 K, then we can use the results of the direct dynamics calculations (which give Arrhenius plots which include the effects of tunneling) to estimate the rate at 368 K, which is a representative temperature for the thermolysis experiments. This leads to an estimate of  $k_{1,2-H} = 1.8 \times 10^8$  s<sup>-1</sup> for unimolecular rearrangement.

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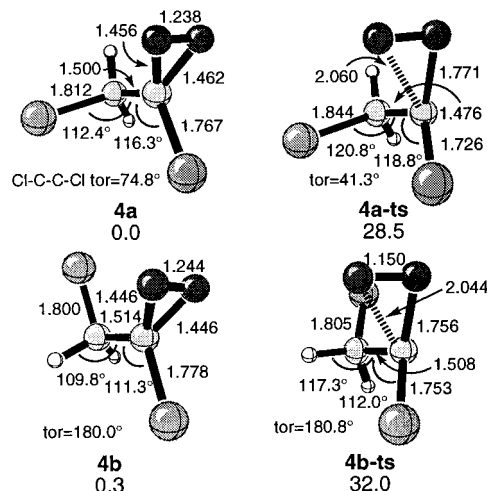


**Figure 6.** Model proposed by Bonneau *et al.* involving a carbene–olefin complex (COC) (A) compared to an alternative scheme fit to experimental data (B). Relative contributions of competing paths are indicated as percentages while the ratios **2Z**:**2E** for each path are indicated in italics.

product ratios resulting from the reaction of “true carbenes” generated without the use of nitrogenous precursors.<sup>43</sup>

Our hypothesis that the thermolysis of (chloromethyl)-chlorodiazirine may give rise to olefins **2Z** and **2E** via non-carbene paths is reminiscent of Platz’s proposal that excited state diazirine reactivity in photolysis experiments contributes to the formation of rearrangement products.<sup>7</sup> In the case of dichloroethylidene, however, the thermal reaction conditions require that any alternative path must occur on a ground state surface. The thermal rearrangement of nitrogenous precursors to carbenes has been proposed previously as an alternative source of 1,2-shift products,<sup>44,45</sup> and the reaction of **4** to give **2** directly might provide such a path. Rearrangement of the diazirine to diazoalkane followed by loss of nitrogen and 1,2-shift is another alternative discussed by Bonneau *et al.*<sup>1</sup> Additionally, an acid-catalyzed route might operate, as might a radical mechanism facilitated by the presence of radicals generated from abstraction of Cl<sup>•</sup> from **4**, **1**, **2**, or **3**.<sup>46,47</sup>

In an attempt to identify a thermal path that may generate **2Z** and **2E** by a non-carbene route, we have considered the possibility that a concerted ground-state rearrangement of **4** might lead to **2**. This mechanism has been previously investigated by Miller *et al.*, who examined the denitrogenation of methyl diazirine and diazoethane using coupled cluster theory.<sup>48</sup> They could find only stepwise paths to rearrangement products involving initial formation of the carbene; the barriers for carbene formation were predicted to be 30.2 and 26.9 kcal/mol, respectively, at the CCSD(T)/TZP//CISD/TZP level. We have investigated the potential surface for **4** and have similarly failed to locate a concerted path for H-migration and loss of N<sub>2</sub>. Using B3LYP/6-31G\* theory we have located transition states for the loss of N<sub>2</sub> to give carbene for the gauche (**4a**) and anti (**4b**) conformers of **4** (Figure 7). These give activation energies of 28.5 and 32.0 kcal/mol, similar to the results of Miller *et al.* The *cis*-preference of the forming carbene is felt to a large extent in the transition state. We have also searched for pathways by



**Figure 7.** B3LYP/6-31G\* structures for gauche (**4a**) and anti (**4b**) diazirines and transition states (**4a-ts**, **4b-ts**) to lose N<sub>2</sub>, forming *cis*- and *trans*-1,2-dichloroethylidene. B3LYP/6-31G\* energies are given below the structures.

which the diazirine might rearrange to the diazo compound, but have again found only paths to carbene formation.

## Conclusions

We have investigated the intra- and intermolecular reactivity of 1,2-dichloroethylidene and its diazirine precursor using both *ab initio* and density functional theoretical methods. We reproduce a high experimental *Z*-selectivity for the unimolecular carbene rearrangement and have explained this on the basis of the electronic structures of the reactants and transition states. We have also carried out quantum mechanical tunneling calculations which improve the agreement between experimental and theoretical rates for the 1,2-H shift in **1a**.

Theoretical study of the potential surfaces for the cycloadditions of **1** to ethylene and to TME show that barriers are produced by entropy control, in good agreement with previous calculations of the cycloaddition of dichlorocarbene to ethylene.<sup>4</sup> No carbene–olefin complexes were found on the cycloaddition surfaces. An alternative kinetic scheme which invokes a non-carbene route to alkene products can explain the experimental results. Density functional calculations, however, suggest that concerted thermal rearrangement of the diazirine precursor is not the source of this reactivity, and so the source of the anomalous *E* product remains unknown.

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**Supporting Information Available:** B3LYP/6-31G\* stationary point geometries for **1** and energetics for reactions of **1**, **4**, and **5** at all levels mentioned in the text (2 pages). See any current masthead page for ordering and Internet access instructions.

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