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Density Functional Theory Investigation of the Remarkable Reactivity of Geminal Dizinc Carbenoids $(RZn)_2CHI$ (R = Et or I) as Cyclopropanation Reagents with Olefins Compared to Mono Zinc Carbenoids $RZnCHI_2$, EtCHIZnR (R = Et or I)

Cunyuan Zhao,[†] Dongqi Wang, and David Lee Phillips*

Contribution from the Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

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Abstract: Density functional theory calculations for the cyclopropanation reactions of several mono zinc carbenoids and their corresponding *gem*-dizinc carbenoids with ethylene are reported. The mono zinc carbenoids react with ethylene via an asynchronous attack on one CH_2 group of ethylene with a relatively high barrier to reaction in the 20−25 kcal/mol range similar to other Simmons−Smith type carbenoids previously studied. In contrast, the *gem*-dizinc carbenoids react with ethylene via a synchronous attack on both CH_2 groups of ethylene and substantially lower barriers to reaction (about 15 kcal/mol) compared to their corresponding mono zinc carbenoid. Both mono zinc and *gem*-dizinc carbenoid reactions can be accelerated by the addition of ZnI_2 groups as a Lewis acid, and this lowers the barrier by another 1.0−5.1 kcal/mol and 0.0−5.5 kcal/mol, respectively, for addition of one ZnI_2 group. Our results indicate that *gem*-dizinc carbenoids react with C═C bonds with significantly lower barriers to reaction and in a noticeably different manner than Simmons−Smith type mono zinc carbenoids. The three *gem*-dizinc carbenoids have a substantially larger positive charge distribution than those in the mono zinc carbenoids and, hence, a stronger electrophilic character for the *gem*-dizinc carbenoids.

Introduction

Cyclopropane groups are observed in many natural and unnatural products possessing important biological activities and in a number of compounds used as starting materials and intermediates in organic synthesis.[1−30] Therefore, many research groups have discovered novel and diverse methods to make cyclopropanated products.[1−50] For instance, the reactions between diazoalkane and olefinic substrates assisted by transition

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* To whom correspondence should be addressed. E-mail: phillips@hkucc.hku.hk.

[†] Permanent address: Department of Chemistry, Northwest Normal University, Lanzhou 730070, People's Republic of China.

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metal complexes[13,18−20,30] give useful methods for cyclopropanation of electron-deficient and electron-rich double bonds. A variety of the Norrish−Yang reaction was recently found to be useful to produce cyclopropane products for some molecules.[34] Ultraviolet photolysis of diiodomethane in solutions containing olefins has also been found to make cyclopropanated products with high stereospecificity at room temperature.[31−33] These are only a few examples of the various methods that have been developed over the years to produce cyclopropanated products.[1−50]

The Simmons−Smith reaction is a commonly used method for synthesizing cyclopropanated products from olefins, and the reactive species is produced from diiodomethane and a Zn−Cu couple.[35] Following the ground-breaking work of Simmons and Smith,[35] many efforts were invested to develop improvements and alternative techniques to form active reagents similar to the Simmons−Smith reagent that are able to make cyclopropanated products from olefins with high efficiency and stereoselectivity.[36−50] A procedure that involves alkyl group exchange between diethylzinc and diiodomethane to make a carbenoid species was developed by Furukawa.[42] An alternative method to produce the Simmons−Smith reagent that uses the addition of CH_2I_2 to freshly prepared EtZnI was developed by Charette and Marcoux.[39] Some reagents with the general structure "$ROZnCH_2I$" (R = alkyl or allyl) are unreactive toward olefins in the absence of a Lewis acid.[45] However, one reagent (likely with a $RCOOZnCH_2I$ structure and made by mixing stoichiometric amounts of Et_2Zn, trifluoroacetic acid and CH_2I_2) converted styrene to its corresponding cyclopropane in higher yield than when the classic Simmons−Smith reagent is used.[46] A new family of iodomethylzinc aryloxide cyclopropanating reagents based on an "$ArOZnCH_2I$" structure (where Ar is an aromatic group) were observed to be very effective for the cyclopropanation of unfunctionalized olefins by Charette and co-workers.[47]

There are not as many theoretical studies of the Simmons−Smith type carbenoids compared to the large number of experimental investigations for their cyclopropanation reactions with olefins.[51−57] Several theoretical studies of the Simmons−Smith reaction of $XZnCH_2X$ (X= Cl and I) with CH_2CH_2 have been reported. The potential energy surface for the reaction between ethylene and (chloromethyl)zinc chloride (a model system for the Simmons−Smith cyclopropanation reaction) using the B3LYP/6-311G** method was examined by Bernardi and co-workers.[51] A relativistic core potential approach[52] was used to study the Simmons−Smith cyclopropanation reaction and predicted it to be exothermic by 33.5−37.8 kcal/mol with a barrier height of about 14.3 kcal/mol. Density function theory (B3LYP) calculations have been used to examine the effects of a Lewis acid like $ZnCl_2$ molecules on the Simmons−Smith reaction by Nakamura and co-workers.[53,54] Boche and co-workers[55,56] also employed density functional theory calculations to examine the Simmons−Smith reaction and found a barrier height of ∼17 kcal/mol for the $IZnCH_2I$ reagent cyclopropanation reaction. We have recently employed density functional theory calculations to study the Simmons−Smith reaction with a view to comparing it to the closely related but much more reactive $CH_2I{-}I$ species.[57]

A number of isopolyhalomethane species such as isodiiodomethane ($CH_2I{-}I$) have been observed and identified in room-temperature liquids using nanosecond and picosecond time-resolved resonance Raman spectroscopy[58−62] and in low-temperature matrixes[63,64] using infrared spectroscopy. The reaction of isodihalomethanes ($CH_2X{-}X$, where X = I, Br, Cl) with ethylene have been examined using density functional theory calculations[65,66] and showed that the $CH_2I{-}I$ photoproduct species easily reacted with a barrier of only 2.9 kcal/mol with ethylene via a one-step mechanism similar to that found for Simmons−Smith carbenoids ($XZnCH_2X$).[51−57] Recent nanosecond time-resolved resonance Raman experiments showed that $CH_2I{-}I$ reacts with cyclohexene solvent to form an I_2 molecule leaving group on the 5−10 ns time scale.[67] Both experimental and theoretical results indicate that $CH_2I{-}I$ is most likely the methylene transfer agent for the cyclopropanation reaction of olefins via ultraviolet photoexcitation of diiodomethane, and a reaction mechanism was proposed.[65,66] The very reactive $CH_2I{-}I$ carbenoid species has only one atom less than the classical Simmons−Smith carbenoid ($IZnCH_2I$) and presents an intriguing prototype for comparison to Simmons−Smith type carbenoids.

Charette and co-workers recently reported the first evidence for the formation of a geminal dizinc carbenoid that was found to be very reactive and able to compete successfully with mono zinc carbenoids to undergo cyclopropanation reactions with olefins.[50] The *gem*-dizinc carbenoid(s) displayed remarkable reactivity toward several different olefins with the cyclopropanation reaction being very rapid (<15 min) and providing

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excellent yields at 0 °C.[50] This indicates the *gem*-dizinc carbenoid(s) are significantly more reactive than typical Simmons−Smith reagents. In this paper, density functional theory calculations are presented for several mono zinc carbenoids and their corresponding *gem*-dizinc carbenoids and their cyclopropanation reactions with ethylene in order to better understand the chemical reactivity of the *gem*-dizinc carbenoids compared to the traditional Simmons−Smith type mono zinc carbenoid species. To our knowledge, this is the first theoretical study of the cyclopropanation reactions of a *gem*-dizinc carbenoid species. The cyclopropanation reactions of mono zinc carbenoids $RZnCHI_2$, EtCHIZnR (where R = Et or I) with ethylene were found to proceed asynchronously via a preferential attack on one CH_2 group of ethylene with barriers to reaction in the 20−24.6 kcal/mol range. The changes in the structures of the transition state relative to the parent carbenoid for these mono zinc carbenoids were found to be similar to those previously obtained for related Simmons−Smith carbenoids[51−57] and isopolyhalomethane carbenoids.[57,65,66] However, the *gem*-dizinc carbenoids were found to have substantially lower barriers to reaction compared to their analogous mono zinc carbenoid compound when the second ZnR (R═I or Et) group is introduced to form the *gem*-dizinc carbenoid. This appears to be due to the synchronous attack of the carbenoid carbon atom toward both CH_2 groups of ethylene as well as to the small structural changes that take place in the $Zn^1-Zn^2-I^1-C^1$ moiety as the reactions proceed from the reactants to the transition structures. The effect of the addition of ZnI_2 as a Lewis acid was also explored for both mono zinc and *gem*-dizinc cyclopropanation reactions and found to lower the barrier further by about 1−5.1 kcal/mol and 0−5.5 kcal/mol respectively for addition of one ZnI_2 group. The Lewis acid effect becomes smaller as the number of ZnI_2 become larger and appears to be described as an exponential decay as the number of ZnI_2 goes from $n = 0$ to $n = 3$. The *gem*-dizinc carbenoids with one to three ZnI_2 groups were found to give very efficient cyclopropanation reactions with ethylene on the order 8.7 kcal/mol to 7.3 kcal/mol. These results are consistent with Charette and coworkers experimental observation that very efficient cyclopropanation of olefins by *gem*-dizinc carbenoids are observed at 0 °C and supplant the competition reactions of the corresponding mono zinc carbenoids.[50]

Computational Details

The B3LYP density functional method[68−72] was employed to examine the cyclopropanation reaction mechanisms of the $RZnCHI_2$ and EtCHIZnR (R = Et or I) mono zinc carbenoids and the $(RZn)_2CHI$ (R = Et or I) geminal dizinc carbenoids with ethylene. The cyclopropanation reaction mechanism of addition of one or more ZnI_2 species and EtZnI to the carbenoids have also been investigated and compared with those of the pure carbenoids. The stationary structures of the potential energy surfaces were fully optimized using C_1 symmetry at the B3LYP level of theory although some of the stationary structures have pseudo C_s symmetry. Analytical frequency calculations were done in order to confirm the optimized structures to be either a minimum or a first-order saddle-point as well as to obtain the zero-point energy correction. IRC calculations[73] were performed to confirm the transition states connected the relevant reactants and products. Geometry optimization for all reactants, transition states and products as well as the frequency calculations were carried out with the 6-311G** basis set for all the pure carbenoid cyclopropanation reactions with ethylene. This basis set is denoted as BS1 hereafter. For the cyclopropanation reactions of the carbenoids with addition of ZnI_2 with ethylene, the geometry optimization and frequency calculations were done with the 6-311G** basis set for all C, H, Zn atoms and one I leaving atom (the atom denoted as I′ in the figures). The lanl2dz basis set[74] (which combines the Hay−Wadt relativistic core-potential) was used for all the other I atoms. The hybrid basis set is denoted as BS2 hereafter and contains 440 basis functions contracted from 730 primitive Gaussian functions for the $(IZn)_2CHI + 3ZnI_2 + C_2H_4$ system. All of the calculations were done using the Gaussian 98 program suite.[75]

Results and Discussion

The optimized stationary structures (minima, saddle points) on the potential energy surfaces of the reactions are depicted schematically in Figs. 1, 2, 3, and 4. Selected key geometry parameters (bond lengths and bond angles) are also shown in Figures 1−4. The detailed structural parameters and energies for the structures determined in this study are collected in the Supporting Information. The relative energies including zero-point energies (ZPE) are shown graphically in Figure 5.

A. Cyclopropanation Reactions of Mono Zinc Carbenoids $RZnCHI_2$, EtCHIZnR (where R = Et or I) with Ethylene. Figure 1 displays the optimized geometry found for the mono zinc carbenoids $RZnCHI_2$, EtCHIZnR (where R = Et or I) and their transition states (TS1 to TS4) for reactions with ethylene to produce c-C_3H_5I, c-C_3H_5Et, EtZnI, and ZnI_2. All four carbenoids approach ethylene (C_2H_4) in an asymmetric manner and react with one of the CH_2 groups from above the molecular plane. A weak complex may be formed when the two molecules move toward one another, but this has little effect on the chemical reaction and will not be discussed further. A transition state (TS1) was found on the way to c-C_3H_5I and EtZnI products for the reaction of the carbenoid $EtZnCHI_2$ with C_2H_4, whereas another transition state (TS2) was observed for the reaction of the carbenoid $IZnCHI_2$ with C_2H_4. A transition state (TS3) was found on the way to the c-C_3H_5Et and ZnI_2 products for the reaction of the EtCHIZnI carbenoid with C_2H_4. The EtCHIZnI carbenoid is one of the isomers of the $EtZnCHI_2$ carbenoid. A transition state (TS4) was found for the reaction of EtCHIZnEt with C_2H_4.

Examination of Figure 1 shows the molecule $EtZnCHI_2$ approaches CH_2CH_2 in an asynchronous manner. The C^1-C^2 distance in TS1 is 2.204 Å, and this is 0.36 Å shorter than the

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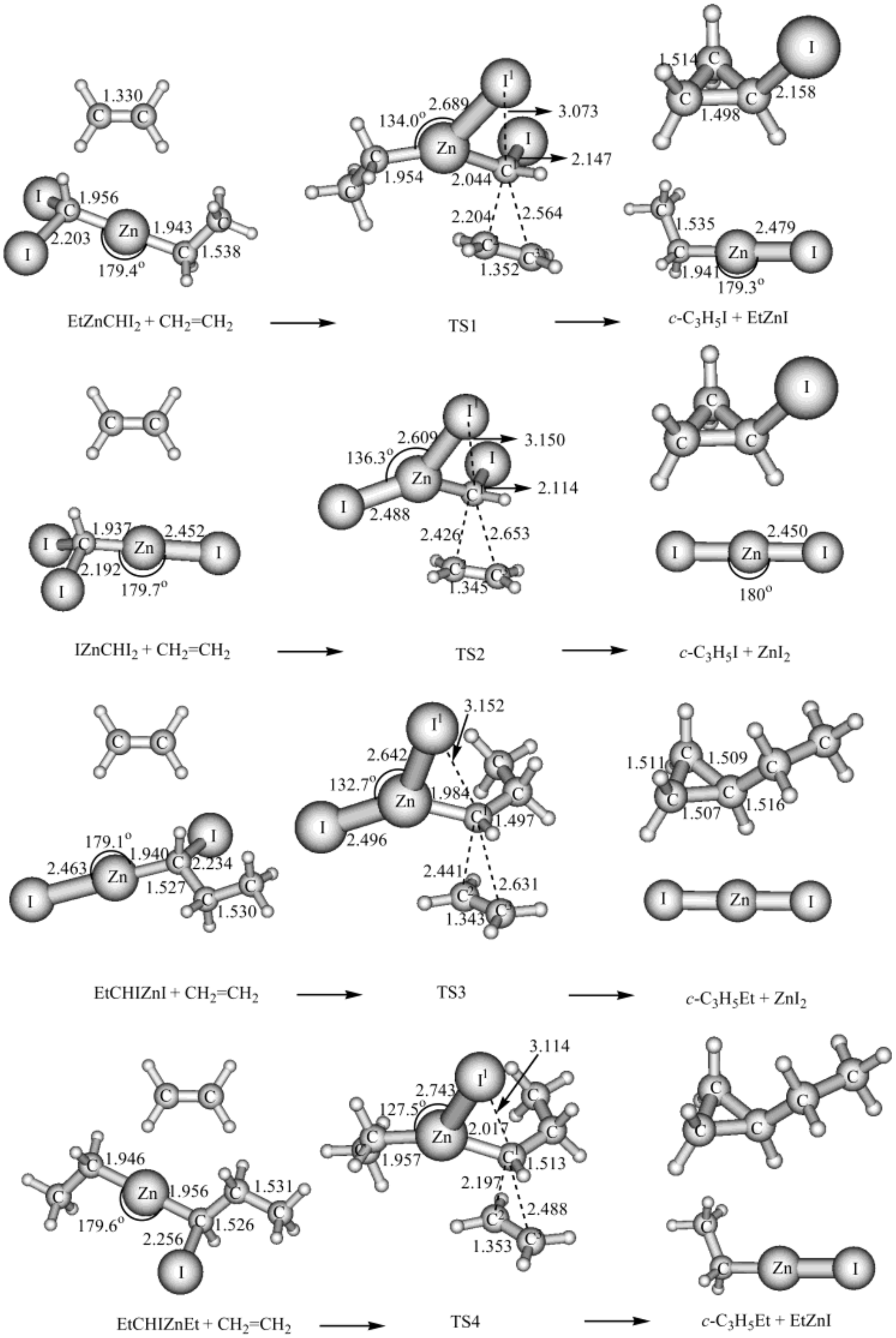

Figure 1. Schematic diagrams of the optimized geometry from the B3LYP/BS1 computations for the mono zinc carbenoids RZnCHIR′ (R, R′ = Et or I) as well as the transition states for the cyclopropanation of these species with ethylene. TS1 = transition state for reaction of $EtZnCHI_2$ with ethylene. TS2 = transition state for reaction of $IZnCHI_2$ with ethylene. TS3 = transition state for reaction of EtCHIZnI with ethylene. TS4 = transition state for reaction of EtCHIZnEt with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in degrees.

$C^1{-}C^3$ distance. The planar ethylene molecule has a significant pyramidalization of about 15° at C^2 in the TS1 structure that indicates the onset of the $sp^2 \rightarrow sp^3$ rehybridization required for cyclopropane formation, while the pyramidalization is only 2° for the C^3. This reflects the asynchronous approaching of CH_2CH_2 for the cyclopropanation reaction. The $C^2{=}C^3$ and $C^1{-}Zn$ bond lengths are increased by 0.022 and 0.088 Å, respectively, in going from the reactants to the transition state. The interaction of the $EtZnCHI_2$ moiety with the π olefin orbitals are mainly responsible for the slight lengthening of the $C^2{=}C^3$ and $C^1{-}Zn$ bonds. Relatively large changes are associated with the $C^1{-}Zn{-}C$ angle, $C^1{-}I^1$ and $Zn{-}I^1$ distances that vary from 179.4°, 2.203, and 3.406 Å in $EtZnCHI_2$ to 146.3°, 3.073, and 2.689 Å in TS1. Meanwhile, the $C^1{-}I^1$ bond (3.073 Å) is nearly broken and the $Zn{-}I^1$ bond (2.689 Å) is almost formed in TS1. These changes in the bond lengths and angles are attributed to the EtZnI molecule being partially formed in the transition state. It is evident that TS1 is the transition state of the concerted

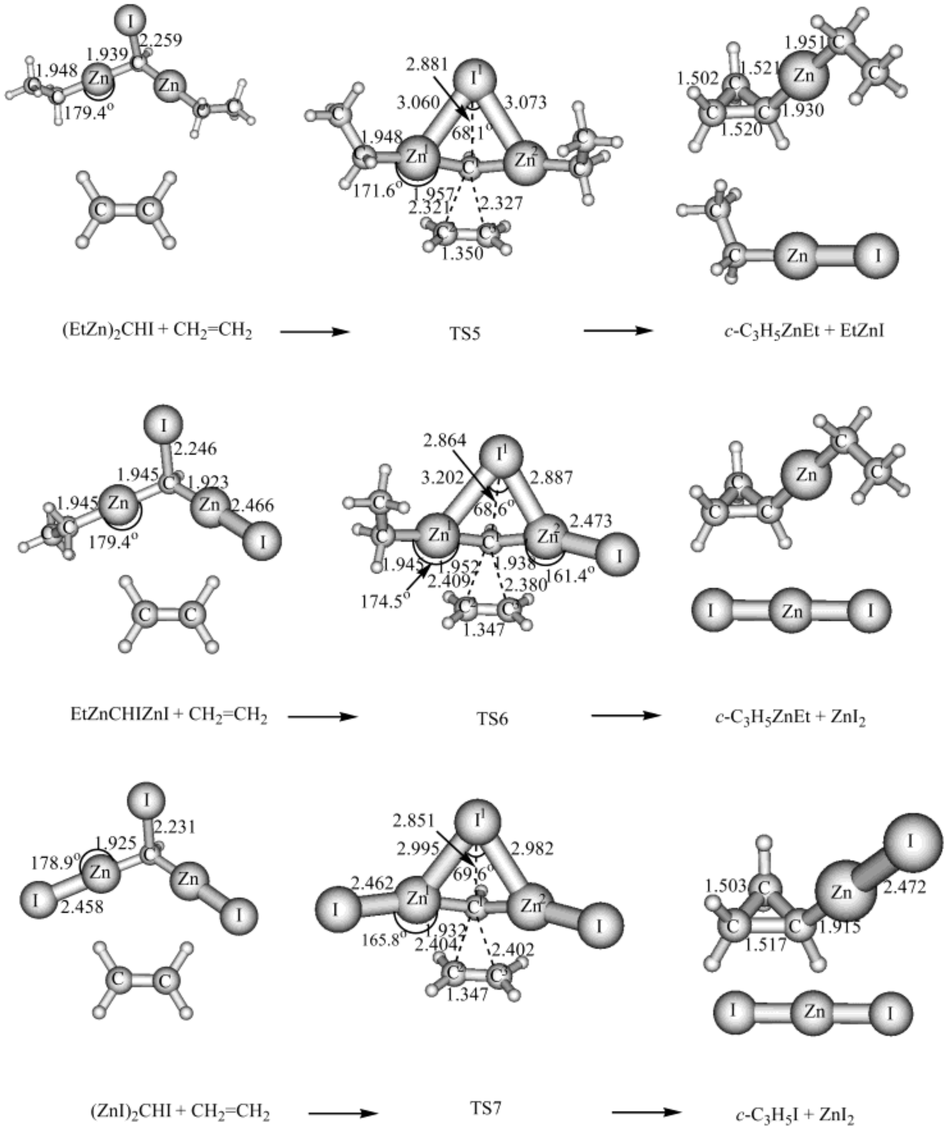

Figure 2. Schematic diagram of the optimized geometry from the B3LYP/BS1 computations for the *gem*-dizinc carbenoids $(EtZn)_2CHI$, EtZnCHIZnI, and $(IZn)_2CHI$ as well as the transition states for the cyclopropanation of these species with ethylene. TS5 = transition state for the reaction of $(EtZn)_2CHI$ with ethylene. TS6 = transition state for reaction of EtZnCHIZnI with ethylene. TS7 = transition state for reaction of $(IZn)_2CHI$ with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in degrees.

reaction from $EtZnCHI_2 + CH_2CH_2$ reactants to $c\text{-}C_3H_5I$ + EtZnI products. Vibrational analysis shows that the optimized TS1 structure has one imaginary frequencies of 302i cm^{-1} and the transition structure was confirmed to be the first-order saddle point connecting the corresponding reactants and products by IRC calculations.

Relative to the separated reactants of $EtZnCHI_2$ and CH_2CH_2, the reaction has a barrier of 24.5 kcal/mol and is exothermic by about 27.7 kcal/mol at the B3LYP/BS1 level, including the ZPE correction, as shown in Figure 5a. The barrier height of 24.5 kcal/mol predicts that the reaction does not occur easily under room-temperature conditions and cannot explain the experimental results of Charette and co-workers[50] that found that appreciable reaction could occur at a temperature of only 0 °C. This suggests the reaction could take place at a relatively low temperature and they proposed that geminal dizinc carbenoids could be the more reactive species for the cyclopropanation reaction observed experimentally.[50] To obtain evidence for the formation of *gem*-dizinc carbenoid species, the reagents were mixed and aliquots were quenched with D_2O. The relative percentages of the CHI_3, $CDHI_2$, and CHD_2I produced confirmed the existence of mono zinc and *gem*-dizinc carbenoids in the experimental reaction system.[50] We shall discuss more details of the *gem*-dizinc carbenoids reaction mechanism in the following sections.

Replacement of the ethyl group with iodine atom in $EtZnCHI_2$ produces the $IZnCHI_2$ carbenoid. The transition state (TS2) was found for the reaction of $IZnCHI_2$ with CH_2CH_2 on the way to $c\text{-}C_3H_5I$ and ZnI_2. The geometry of TS2 is very similar to that of TS1. The reaction has a barrier height of 20.0 kcal/mol and is exothermic by about 24.8 kcal/mol at the B3LYP/BS1 level, including the ZPE correction, as shown in Figure 5 (a). Compared to the reaction of $EtZnCHI_2 + CH_2CH_2$, the reaction barrier of $IZnCHI_2 + CH_2CH_2$ was lowered by 4.5 kcal/mol while the exothermicity of the reaction became smaller by 2.9 kcal/mol. This suggests that $IZnCHI_2$ is a more reactive carbenoid than $EtZnCHI_2$. The reaction barrier is even smaller by 1.0 kcal/mol than that of Simmons−Smith cyclopropanation

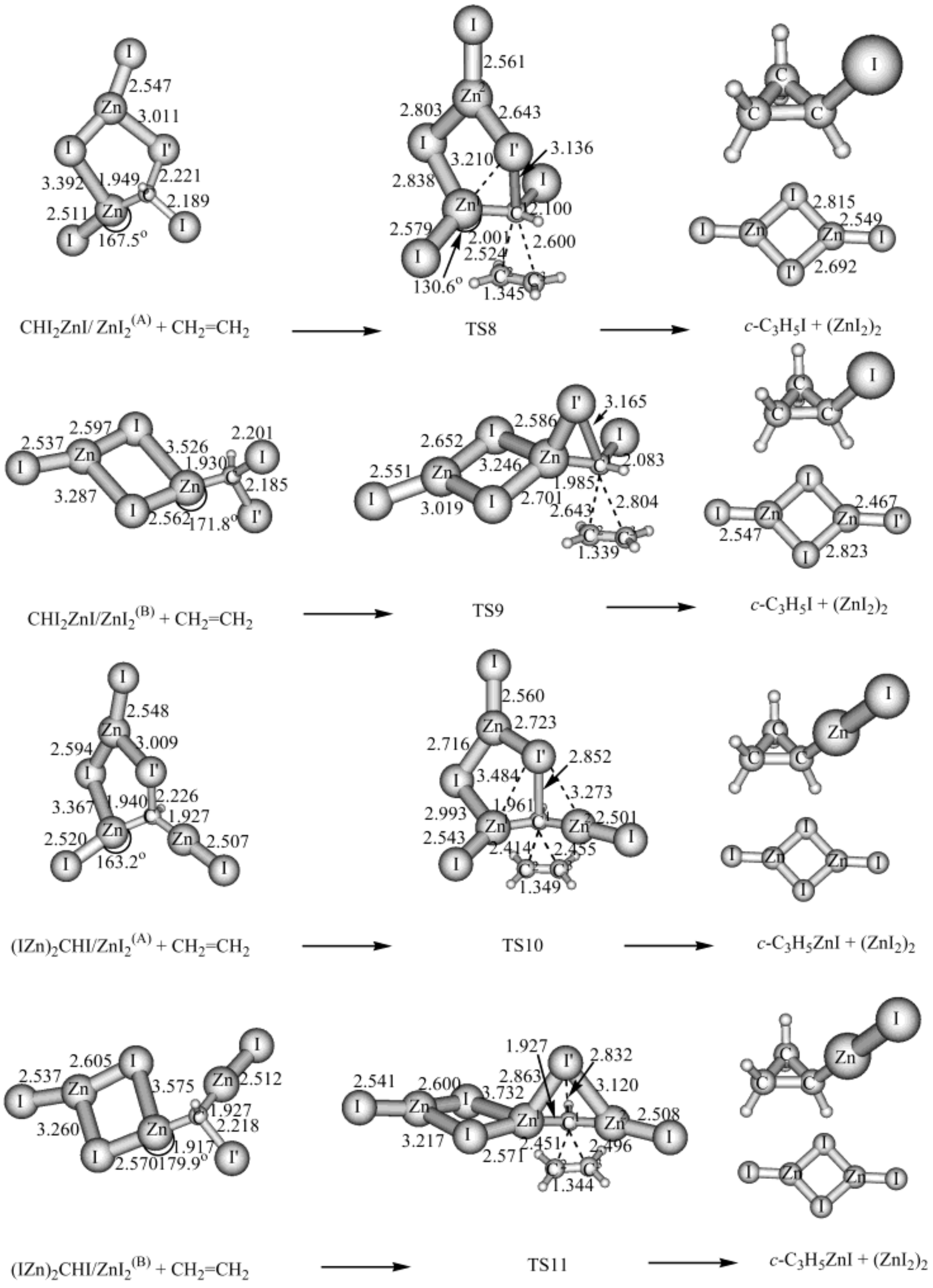

Figure 3. Schematic diagram of the optimized geometry from the B3LYP/BS2 computations for the carbenoids species $IZnCHI_2/ZnI_2$ and $(IZn)_2CHI/ZnI_2$ as well as the transition states for the cyclopropanation of these species with ethylene. Two possible pathways are indicated in the figure. In path A, the leaving I′ atom is directly coordinated to the Zn^2 atom in ZnI_2, whereas one of the I atoms in ZnI_2 is coordinated to the Zn^1 in the carbenoid to form a five-center complex. In path B, the Zn and I atoms in ZnI_2 are coordinated to the I and Zn atoms in the IZn group of carbenoid species respectively to form a four-center complex. TS8 = transition state for the reaction of $IZnCHI_2/ZnI_2$ with ethylene along path A. TS9 = transition state for reaction of $IZnCHI_2/ZnI_2$ with ethylene along path B. TS10 = transition state for reaction of $(IZn)_2CHI/ZnI_2$ with ethylene along path A. TS11 = transition state for reaction of $(IZn)_2CHI/ZnI_2$ with ethylene along path B. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in degrees.

reaction of $IZnCH_2I + CH_2CH_2$ at the same level of theory with ZPE correction.[57]

The carbenoid EtCHIZnI is one of the isomers of the $EtZnCHI_2$ carbeonoid. Isomerization of $EtZnCHI_2$ to EtCHIZnI is exothermic by as much as 36.8 kcal/mol at the B3LYP/BS1 level with ZPE correction. A transition state (TS3) was found for the cyclopropanation reaction of EtCHIZnI with C_2H_4 on the way to the products c-C_3H_5Et and ZnI_2. The barrier height was calculated to be 21.1 kcal/mol and the reaction to be exothermic by 21.8 kcal/mol at the B3LYP/BS1 level, including the ZPE correction, as shown in Figure 5b. There was no evidence for the formation of the very stable carbenoid EtCHIZnI from the recent experiments.[50] Therefore, this carbenoid can be ruled out from the current reaction system though the reaction barrier of 21.1 kcal/mol for the cyclopropanation reaction is similar to that for the other mono zinc carbenoids.

Changing the iodine atom to an ethyl group in the EtCHIZnI leads to formation of the EtCHIZnEt carbenoid. A transition state (TS4) was found for the reaction of EtCHIZnEtwith CH_2-CH_2 on the way to c-C_3H_5Et and EtZnI. The geometry of TS4

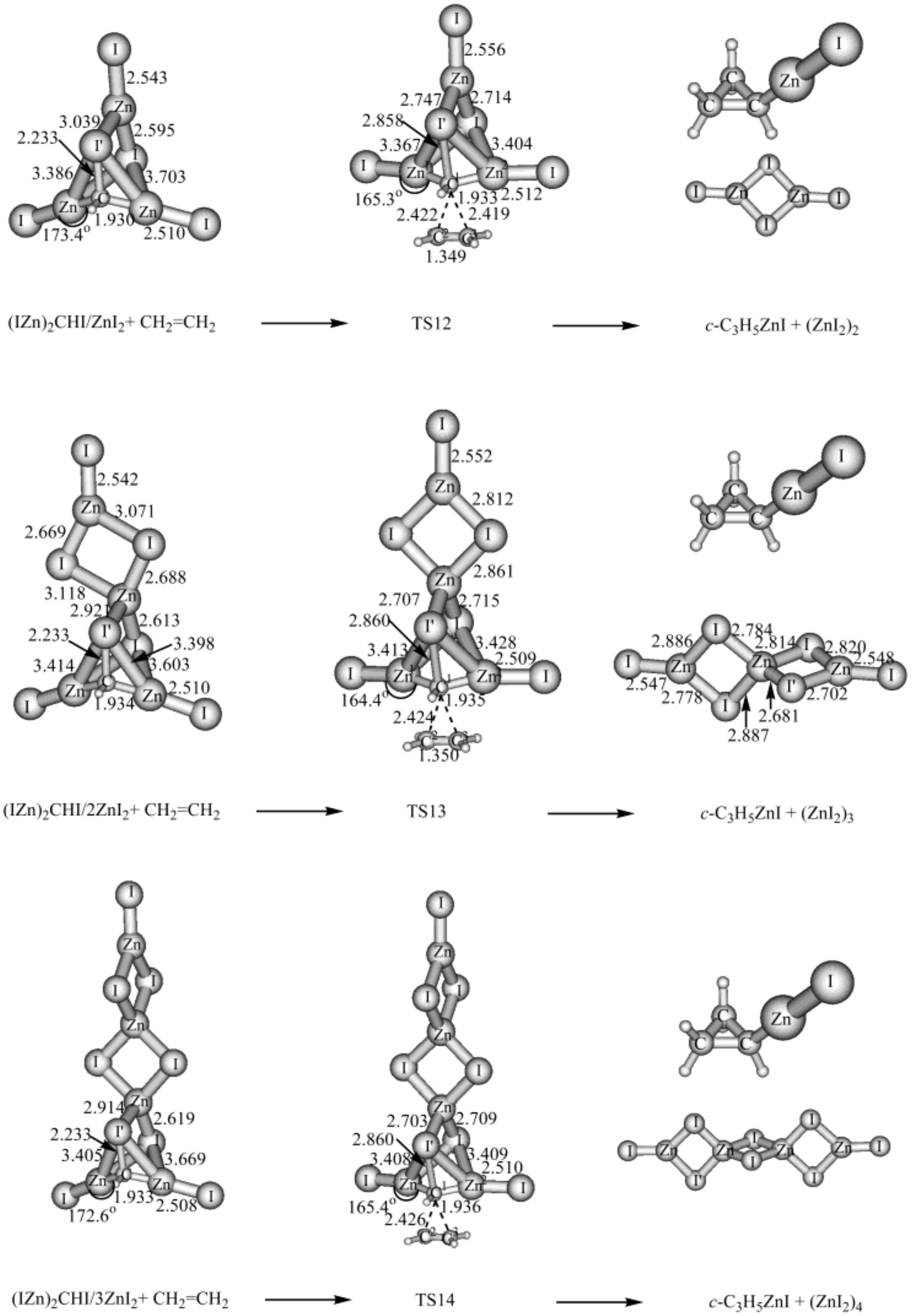

Figure 4. Schematic diagram of the optimized geometry from the B3LYP/BS2 computations for the carbenoid species $(IZn)_2CHI/(ZnI_2)_n$ (n=1, 2, 3) as well as the transition states for the cyclopropanation of these species with ethylene. TS12 = transition state for the reaction of $IZnCHI_2/ZnI_2$ with ethylene. TS13 = transition state for reaction of $IZnCHI_2/(ZnI_2)_2$ with ethylene. TS14 = transition state for reaction of $(IZn)_2CHI/(ZnI_2)_3$ with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in degrees.

is similar to that of TS3. The reaction has a barrier height of 24.6 kcal/mol and is exothermic by 27.9 kcal/mol at the B3LYP/BS1 level, including the ZPE correction, as depicted in Figure 5 (b).

There are several common features of the four transition states (TS1−TS4). First, the C^1-I^1 bond is mostly broken in TS1, TS2, TS3 and TS4. Second, the C^1-Zn bond is only slightly elongated compared with those of the parent carbenoid. Third, the ZnI_2 or the EtZnI molecules are nearly formed in the transition states. There also exist some differences in structures of the four transition states TS1−TS4. For instance, the C−I^1 bond is elongated by 39.5%, 43.7%, 41.1%, and 38.0% more for the TS1, TS2, TS3, and TS4, respectively, compared to the corresponding parent carbenoid. The C^1−Zn bonds in TS1−TS4 are elongated 0.088 Å, 0.073, 0.044, and 0.061 Å, respectively, compared to the corresponding carbenoid. The I^1−Zn−C angles or I^1−Zn−I angles are 134.0°, 136.3°, 132.7°, and 127.5° for TS1−TS4, respectively. The formation of I^1-Zn bond in TS1−TS4 is only elongated by 0.21, 0.16, 0.192, 0.26 Å, respectively, compared to the byproduct ZnI_2 or EtZnI. It is interesting to note that there exist a good correlation between the structural parameters of the transition states and the

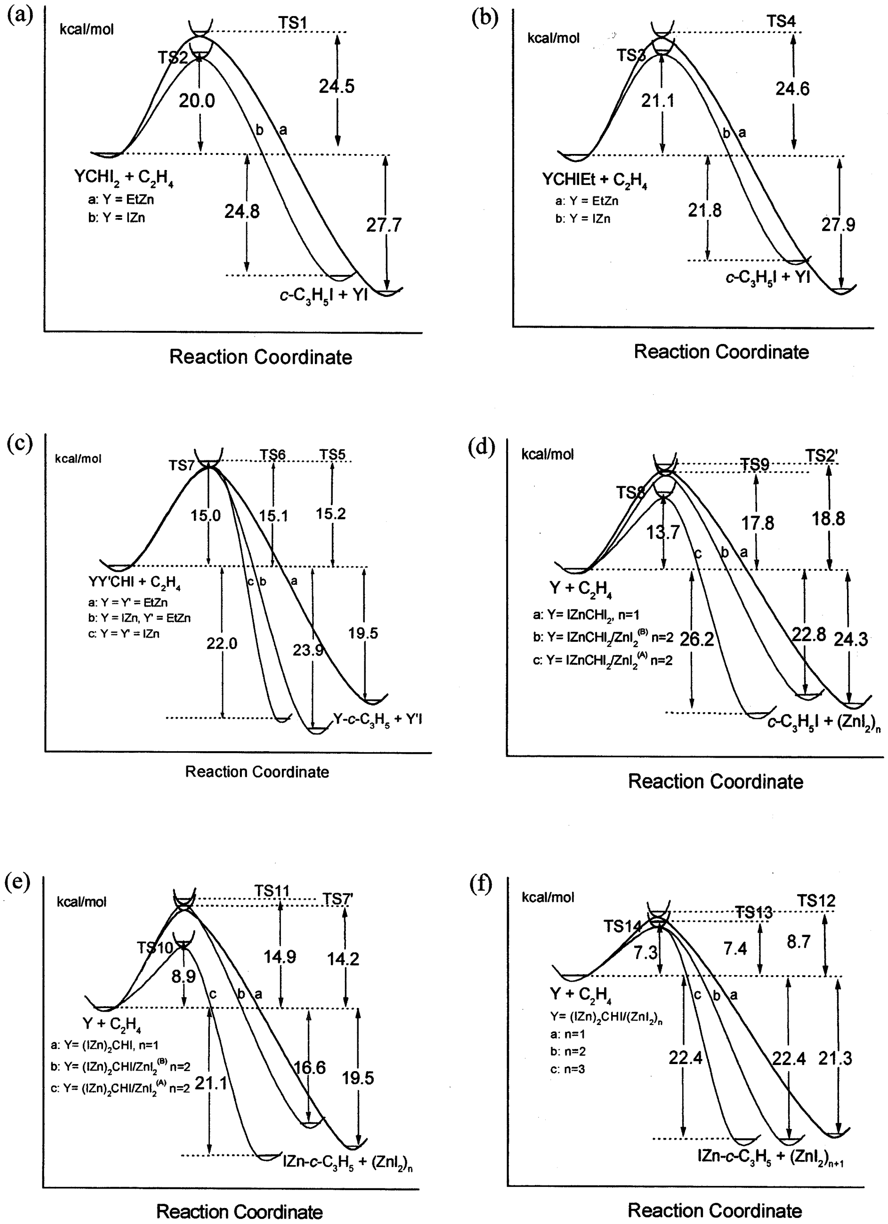

Figure 5. Schematic diagram showing the computed relative energies (in kcal/mol) for reactions of the mono zinc carbenoids RZnCHI$_2$ (R = Et or I) (a), EtCHIZnR (R = Et or I) (b), the *gem*-dizinc carbenoids (EtZn)$_2$CHI, EtZnCHIZnI, and (IZn)$_2$CHI (c), IZnCHI$_2$ and IZnCHI$_2$/ZnI$_2$ (d), (IZn)$_2$CHI and (IZn)$_2$CHI/ZnI$_2$ (e), and (IZn)$_2$CHI/(ZnI$_2$)$_n$ (f) with ethylene with the transition states and products energies given relative to the separated reactants. Values for Figure 5a−c are from B3LYP/BS1 calculations and values for Figure 5d−f are from B3LYP/BS2 calculations of this work.

corresponding cyclopropanation reaction barriers. For instance, the degree of elongation (39.5%, 43.7%, 41.1%, and 38.0%) of the C^1−I bond for TS1−TS4 correlates with the barrier height (24.5, 20.0, 21.1, 24.6 kcal mol^{-1} for TS1−TS4) of the reactions. The more elongated the C^1−I^1 bond is, the lower the barrier. The bond lengths of I^1−Zn and the I^1−Zn−C or I^1−Zn−I bond angles in TS1−TS4 have a similar correlation with the reaction barrier. The smaller the I^1−Zn bond, the lower the barrier; the larger the I^1−Zn−C or I^1−Zn−I bond angles, the lower the barrier. The cyclopropanation reactions for these mono zinc carbenoids are similar to those for related Simmons−Smith carbenoids[51−57] and isopolyhalomethane carbenoids.[57,]

B. Cyclopropanation Reactions of Geminal Dizinc Carbenoids (RZn)$_2$CHI (R = Et or I) with Ethylene. A recent study reported the first experimental evidence for the formation of a geminal dizinc carbenoid species.[50] To better understand the properties and chemical reactivity of the *gem*-dizinc cabenoids (RZn)$_2$CHI (R = Et or I), we have theoretically investigated their cyclopropanation reactions with ethylene and compare them with the reactivities of the corresponding mono zinc carbenoids. To our knowledge, this is the first theoretical study of *gem*-dizinc cabenoids and their cyclopropanation reactions.

Figure 2 displays the optimized geometry found for the *gem*-dizinc carbenoids (EtZn)$_2$CHI, EtZnCHIZnI, and (IZn)$_2$CHI and their transition states (TS5, TS6, and TS7) for reactions with ethylene to produce EtZn-*c*-C$_3$H$_5$, IZn-*c*-C$_3$H$_5$, EtZnI, and ZnI$_2$. All three *gem*-dizinc carbenoids approach ethylene in a symmetric or nearly symmetric manner and synchronically attack both of the CH$_2$ groups from above the molecular plane. A transition state (TS5) was found on the way to the products EtZn-*c*-C$_3$H$_5$ and EtZnI for the reaction of the *gem*-dizinc carbenoid $(EtZn)_2CHI$ with CH_2CH_2, whereas another transition state (TS6) was observed for the reaction of the *gem*-dizinc carbenoid EtZnCHIZnI with C_2H_4. A transition state (TS7) was found on the way to the products *c*-C_3H_5I and ZnI_2 for the reaction of the *gem*-dizinc carbenoid $(IZn)_2CHI$ with C_2H_4.

As shown in Figure 2, the molecule $(EtZn)_2CHI$ approaches CH_2CH_2 in a synchronous way. The TS5 structure approximately possesses C_s symmetry if the two ethyl groups are not concerned. The C_s mirror is along with the C^1HI^1 plane and divides the $C^2{=}C^3$ bond into two equivalent CH_2 groups. The C^1-C^2 distance in TS5 is 2.321 Å, and this is only 0.006 Å shorter than the C^1-C^3 distance. The planar ethylene molecule has a significant pyramidalization of about 8° at both C^2 and C^3 in the TS5 structure that indicates the onset of the $sp^2 \rightarrow sp^3$ rehybridization required for the substituted cyclopropane formation. This reflects the synchronous approach toward CH_2CH_2 for the reaction. The $C^2{=}C^3$ and C^1-Zn bonds in the TS5 structure are increased by 0.02 and 0.018 Å, respectively, compared to those found for the reactants. The largest change is associated with the $I^1-C^1-Zn^1$ bond angle that varies from 104.6° to 75.8° in the TS5 structure. Meanwhile, the C^1-I^1 bond (2.881 Å) is nearly broken and the $Zn-I^1$ bond (3.060 Å) is almost formed in TS5. These changes in the bond lengths and angles are attributed to the EtZnI molecule being partially formed in the transition state. Another structural feature is that the Zn^1-Zn^2 distance is only slightly elongated in going from reactant (3.328 Å) to transition state (3.434 Å). The Zn−Zn distance is in the range of related binuclear zinc crystal structures.[76] It is interesting to note that both the parent *gem*-dizinc carbenoid and TS5 structures look like a flattened tetrahedron for the mainframework of $Zn^1-Zn^2-I^1-C^1$. When the reactant molecules approach the CH_2CH_2, it looks like the C^1H group move closer above the ethylene plane while the Zn^1 and Zn^2 move slightly closer to I^1 atom to form the EtZnI molecule. The bridged I^1 atom, which partially connects both zinc atoms, could significantly stabilize the transition state. It should be noted that the elongation degree of the C^1-Zn^1 and C^1-I^1 bonds in TS5 is much smaller than those in the mono zinc TS1. For instance, the elongation of 0.088 and 0.87 Å for the C^1-Zn^1 and C^1-I^1 bonds in TS1 is decreased to 0.018 and 0.622 Å in TS5. This suggests that, in contrast to the mono zinc analogous TS1, there are relatively small changes in the structure of the whole tetrahedral framework $Zn^1-Zn^2-I^1-C^1$ as it goes from the reactant to the transition state TS5. It is anticipated that the two strongly Lewis acidic zinc atoms in TS5 can stabilize the leaving iodine atom while for those single zinc carbenoids only one Lewis acidic zinc atom in TS1 can stabilize the leaving iodine atom. That is to say, the leaving byproduct EtZnI can be stabilized by an $EtZn^1-I^1-Zn^2Et$ moiety. As for the formation of the cyclopropane ring, the averaged C^1-C^2 and C^1-C^3 distance in TS5 is only 2.324 Å, which is much shorter than those (2.384 Å) in TS1. The relatively small changes in structure predict that the barrier to reaction will be fairly low for the $(EtZn)_2CHI + C_2H_4$ reaction.

Vibrational analysis shows that the optimized TS5 structure has one imaginary frequency of 364i cm^{-1}. The eigenvector corresponding to the negative eigenvalue of the force constant matrixes shows the internal coordinate reaction vectors are made up mostly of changes in the C^1-C^2, C^1-Zn^1, C^1-I^1 bond lengths and $I^1-C^1-Zn^1$ and $C^3-C^2-C^1$ bond angles. The reaction vector with ethylene is $0.66R_{C1-C2} + 0.12A_{I1-C1-Zn1} + 0.25A_{C3-C2-C1} - 0.06R_{C1-Zn1} - 0.43R_{C1-I1}$. Further IRC computations were done to confirm the TS5 transition state smoothly connects the corresponding reactants and products. Our computations indicate that the reaction of $(EtZn)_2CHI$ with ethylene proceeds essentially via a concerted process (i.e., an elementary reaction).

Figure 5c schematically displays the potential energy profiles for the *gem*-dizinc cyclopropanation reactions. The barrier height for the reaction of $(EtZn)_2CHI + C_2H_4$ was calculated to be 15.2 kcal/mol and exothermic by about 19.5 kcal/mol at the B3LYP/BS1 level of theory with the ZPE correction included. The reaction barrier of $(EtZn)_2CHI + C_2H_4$ is lowered by as much as 9.3 kcal/mol whereas the exothermicity of the reaction of $(EtZn)_2CHI + C_2H_4$ is lowered by 8.5 kcal/molcompared to the corresponding mono zinc carbenoid with ethylene. The relatively small barrier of the *gem*-dizinc carbenoid with ethylene is consistent with the small structural changes as it goes from the reactant to the transition state TS5. The reaction barrier is also in reasonable agreement with the experimental reaction conditions that show the cyclopropanation reaction can take place at a temperature of 0 °C.[50]

We can obtain two more carbenoids: $(IZn)_2CHI$ and EtZnCHIZnI by replacement of the ethyl groups with iodine atoms in the carbenoid $(EtZn)_2CHI$. The transition state (TS7) was found for the reaction of $(IZn)_2CHI$ with CH_2CH_2 on the way to IZn-*c*-C_3H_5 and ZnI_2. TS7 is very similar to TS5 in structure. The TS7 structure approximately possesses C_s symmetry. The C_s mirror is along the C^1I^1H plane and divides the $C^2{=}C^3$ bond into two equivalent CH_2 groups. The reaction has a barrier height of 15.0 kcal/mol at the B3LYP/BS1 level, including the ZPE correction (shown in Figure 5c). The barrier height is lowered to 14.2 kcal/mol when the B3LYP method combined with the hybridized BS2 basis set is used and the ZPE correction is included. This is only 0.8 kcal/mol smaller than the barrier with B3LYP/BS1, indicating the smaller BS2 basis set does not change the barrier height significantly. The reaction is exothermic by 22.0 kcal/mol at B3LYP/BS1 level with ZPE correction. Compared to the reaction of $(EtZn)_2CHI + CH_2CH_2$, the reaction barrier of $(IZn)_2CHI + CH_2CH_2$ is lowered by only 0.2 kcal/mol, whereas the exothermicity of the reaction is larger by 2.5 kcal/mol. The small barrier difference between TS5 and TS7 indicate that the reactivities of *gem*-dizinc carbeonoids ($(RZn)_2CHI$, where R = Et or I) would not change too much by changing R substitutes in that the electrophilicity of the central carbonate carbon has been saturated in *gem*-dizinc carbenoids due to the introduction of the second zinc atoms. This character is also subject to the hybridized *gem*-dizinc carbenoid.

The reaction of hybridized *gem*-dizinc carbenoid $EtZn_2$-CHIZnI with ethylene possesses a similar transition state TS6 on the way to IZn-*c*-C_3H_5 and EtZnI. In contrast to TS5 and TS7, the transition state TS6 has no symmetry and the molecule EtZnCHIZnI approaches CH_2CH_2 in an asynchronous manner. The C^1-C^2 distance in TS6 is 2.404 Å, and this is 0.029 Å shorter than the C^1-C^3 distance. Compared to the larger shortening (0.36 Å) from C^1-C^3 to C^1-C^2 for the reaction of the mono zinc carbenoid $EtZnCHI_2$ with C_2H_4, the small

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(76) Kaminskaia, N. V.; Spingler, B.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 6411−6422.

difference between the C^1-C^3 and C^1-C^2 distance for the reaction system EtZnCHIZnI with C_2H_4 indicate that essentially it can be approximately regarded as an synchronous attack. The barrier height for this reaction is calculated to be 15.1 kcal/mol and to be exothermic by 23.9 kcal/mol at the B3LYP/BS1 level of theory with the ZPE correction included.

There are some common structural features of the three transition states (TS5−TS7) that are worth noting. The C^1-Zn^1-C (Et) or C^1-Zn^1-I bond is linear or nearly linear (179.4°, 177.7°, 178.9° for $(EtZn)_2CHI$, EtZnCHIZnI, and $(IZn)_2CHI$, respectively) in the reactants (i.e., favored geometry for a Zn(II) species) is slightly bent (171.6°, 174.5°, 165.8°, for TS5, TS6, and TS7, respectively) in the TSs. However, the C^1-Zn^1-C (Et) or C^1-Zn^1-I bonds in the reactions of the single zinc carbenoids with ethylene are bent significantly as they go from the reactants to the transition states. Other structural features in TS5−TS7 in general exhibit comparatively smaller changes relative to their reactants than the transition states TS1−TS4 relative to their mono zinc carbenoid reactants.

In summary, the reactivity of the three *gem*-dizinc carbenoids studied here are similar to one another and there is not much difference for the three reaction barriers. The barrier height for the cyclopropanation reactions follow $(IZn)_2CHI + C_2H_4 <$ EtZnCHIZnI $+ C_2H_4 < (EtZn)_2CHI + C_2H_4$. However, compared to the reactions of the corresponding mono zinc carbenoids with ethylene, the barriers are significantly lowered by introducing the second ZnR (R═I or Et) group. The main reason for the large lowering is due to the increase of the electrophilicity by introducing the second zinc atom. Natural population analysis shows that the natural group charges in the groups of $ZnCHI_2$ for the mono zinc carbenoids $EtZnCHI_2$ and $IZnCHI_2$ are 0.56 and 0.59 respectively and the groups of Zn_2CHI for the three *gem*-dizinc carbenoids $(EtZn)_2CHI$, EtZnCHIZnI, and $(IZn)_2CHI$ are 1.19, 1.20, and 1.21, respectively. It is evident that the three *gem*-dizinc carbenoids possess a substantially larger positive charge distribution than those in the mono zinc carbenoids, indicating the strong electrophilic character for the *gem*-dizinc carbenoids. This is consistent with the fact that the *gem*-dizinc carbenoids have much lower barriers than those of mono zinc carbenoids to the cyclopropanation reactions. Furthermore, the group charges qualitatively correlate with the ordering of the electrophilic degree of the carbenoids. For instance, the $IZnCHI_2 + C_2H_4$ reaction has a smaller barrier than those of $EtZnCHI_2 + C_2H_4$, qualitatively consistent with the positive charge distribution of the group $ZnCHI_2$ in $IZnCHI_2$ being larger than that in $EtZnCHI_2$. The charge distributions of the group Zn_2CHI in the three *gem*-dizinc carbenoinds have similar correlation with the reaction barriers. Another reason for the large lowering of the barrier is due to the small structural changes as the structures of the moiety $Zn^1-Zn^2-I^1-C^1$ as the reaction goes from the reactants to the transition states. A third reason is that formation of the cyclopropyl ring occurs synchronously and the reactions of the *gem*-dizinc carbenoids $+ C_2H_4$ have much later transition states than those of mono-zinc carbenoids $+ C_2H_4$.

C. Additive Effect of the ZnI_2 on the Cyclopropanation Reactions of Mono Zinc $IZnCHI_2$ and Geminal Dizinc $(IZn)_2CHI$ Carbenoids with Ethylene. It has been known for a number of years that an added Lewis acid can dramatically accelerate cyclopropanation reactions. Several experimental groups have extensively investigated the aggregation effect of the Lewis acid ZnI_2 on some Simmons−Smith type cyclopropanation reactions.[49,77,78] Nakamura and co-workers have also theoretically investigated Lewis acid acceleration in the Simmons−Smith reaction.[53,54]

Before discussing the additive effect of the Lewis acid ZnI_2, we make a comparison of the basis sets BS1 and BS2 mentioned in the computational details. To help assess the accuracy of the smaller BS2 [the 6-311G** basis set for all C, H, Zn atoms and one leaving iodine atom (which is referred to I′ in the figures and is expected to affect reaction barriers more than the other iodine atoms) and the lanl2dz basis set with Hay−Wadt relativistic effective core potential for all other iodine atoms], we performed B3LYP/BS2 optimizations for the reactions of $IZnCHI_2 + C_2H_4$ and $(IZn)_2CHI + C_2H_4$. As shown in Figure 5d,e, the reaction barriers (referred to as TS2′ and TS7′ in Figure 5d,e) are calculated to be 18.8 and 14.2 kcal/mol, respectively, at the B3LYP/BS2 level with ZPE corrections. These values are lowered by only 1.2 and 0.8 kcal/mol respectively compared to the corresponding results at B3LYP/BS1 level of theory. The CCSD(T)//B3LYP/BS2 single point calculations for the reaction of $IZnCHI_2 + C_2H_4$ is found to be 20.0 kcal/mol without ZPE correction. This value becomes 20.2 kcal/mol with ZPE correction. The above values are in excellent agreement with those calculated at the B3LYP/BS1 level and confirm the results at the B3LYP/BS2 level of theory should be reliable for further calculations of larger systems. All calculations for the cyclopropanation reactions of carbenoids with addition of ZnI_2 with ethylene were done at the B3LYP/BS2 level of theory so as to be tractable within our available computational resources.

There are two possible pathways for complexation of ZnI_2 to the mono zinc carbenoids $IZnCHI_2$. One path is to have the leaving I′ atom directly coordinated to the Zn^2 atom in ZnI_2, whereas one of I atoms in ZnI_2 is coordinated to the Zn^1 in the carbenoid to form a five-centered complex and is denoted as $IZnCHI_2/ZnI_2^{(A)}$ hereafter and in the figures. The other path is to have the Zn and I atoms in ZnI_2 coordinated to the I and Zn atoms in the IZn group of $IZnCHI_2$ to form a four-centered complex and is denoted as $IZnCHI_2/ZnI_2^{(B)}$ hereafter and in the figures. The two complexes are essentially the same in energy with ZPE corrections although they have different coordination modes. A five-centered transition state (TS8, Path A) was found on the way to the products c-C_3H_5I and the dimer $(ZnI_2)_2$ for the reaction of the carbenoid $IZnCHI_2$ with CH_2CH_2, whereas a four-centered transition state (TS9, Path B) was observed for the reaction of the carbenoid $IZnCHI_2$ with CH_2CH_2. Examination of the TS8 structures shown in Figure 4 finds that the C^1-I' bond is almost broken and elongated by 41.2% more than in complex $IZnCHI_2/ZnI_2^{(A)}$, but C^1-Zn^1 is not cleaved yet and elongated by only 2.7% more than in complex $IZnCHI_2/ZnI_2^{(A)}$. Although the molecules $IZnCHI_2$ approach CH_2CH_2 in an asynchronous manner, similar to the analogous mono zinc carbenoid, the differences between the C^1-C^3 and C^1-C^2 distances for TS8 and TS9 are only 0.076 and 0.161 Å, respectively, smaller than in TS2 (0.227 Å). This suggests the reaction process becomes more and more symmetric as one goes from TS2 and TS9 to TS8.

Figure 5d schematically displays the potential energy profiles for the cyclopropanation reactions for the addition of ZnI_2. It

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(77) Denmark, S. E.; O′Connor, S. P. *J. Org. Chem.* **1997**, *62*, 584−594.
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was shown that the path A is more feasible than path B. The barrier height for path A for the reaction of $IZnCHI_2/ZnI_2^{(A)}$ + C_2H_4 was calculated to be 13.7 kcal/mol and the reaction is exothermic by 26.2 kcal/mol at the B3LYP/BS2 level of theory with the ZPE correction included The reaction barrier of $IZnCHI_2/ZnI_2^{(A)} + C_2H_4$ is lowered by 5.1 kcal/mol compared to the corresponding mono zinc carbenoid with ethylene. The barrier height for path B for the reaction of $IZnCHI_2/ZnI_2^{(B)}$ $+C_2H_4$ was calculated to be 17.8 kcal/mol and the reaction to be exothermic by 22.8 kcal/mol at the B3LYP/BS2 level with the ZPE correction. The reaction barrier of $IZnCHI_2/ZnI_2^{(B)}$ + C_2H_4 is lowered by only 1.0 kcal/mol compared to the corresponding mono zinc carbenoid with ethylene. It is interesting to note that the barriers become noticeably lower as the reaction process becomes more symmetric.

Similarly, two possible pathways were found for the reaction of $(IZn)_2CHI + C_2H_4$ on the way to the products IZn-*c*-C_3H_5 and dimer $(ZnI_2)_2$. Path A involves a five-centered complex $(IZn)_2CHI/ZnI_2^{(A)}$ and a corresponding transition state, whereas path B involves a popular 1,2-iodine migration. It was shown in Figure 5 (e) that the barrier height for path A for the reaction of $(IZn)_2CHI/ZnI_2^{(A)}$ $+C_2H_4$ was calculated to be 8.9 kcal/mol and to be exothermic by 21.1 kcal/mol at the B3LYP/BS2 level of theory with the ZPE correction included. The reaction barrier of $(IZn)_2CHI/ZnI_2^{(A)} + C_2H_4$ is lowered by 5.3 kcal/mol compared to the corresponding pure *gem*-dizinc carbenoid reaction system $(IZn)_2CHI + C_2H_4$, in which no Lewis acid ZnI_2 is involved. The barrier height for path B for the reaction of $(IZn)_2CHI/ZnI_2^{(B)}$ $+C_2H_4$ was calculated to be 14.9 kcal/mol the reaction to be exothermic by 16.6 kcal/mol at the B3LYP/BS2 level with the ZPE correction. Surprisingly, the reaction barrier of $(IZn)_2CHI/ZnI_2^{(B)} + C_2H_4$ is deactivated by 0.7 kcal/mol compared to the corresponding to the *gem*-dizinc carbenoid with ethylene. The reason for such deactivation could possibly be due to the effect Lewis acidity has on a saturated Zn^1 atom of the *gem*-dizinc carbenoids due to the ineffective coordination mode. The structural changes for the *gem*-dizinc carbenoids have similar trends for the ZnI_2 added to the mono zinc carbenoid systems.

In addition to the two pathways mentioned above, a symmetric approach process was also found for the reaction system $(IZn)_2CHI/ZnI_2 + C_2H_4$. In this approach mode, one of the I atoms in ZnI_2 is symmetrically coordinated to the two zinc atoms opposite of the H atom of the carbenoid $(IZn)_2CHI$, whereas the Zn atom in ZnI_2 is directly coordinated to the leaving I′ atom. This then produces a cage-like complex and the leaving I′ atom bond is elongated compared to the uncoordinated I atom. This kind of cage-like transition state could stabilize the I′ atom leaving group as a whole. Examination of the structure TS12 finds that the degree of elongation of C^1-I' and C^1-Zn^1 or C^1-Zn^2 is smaller than that in TS10 and TS11. For instance, the C^1-Zn^1 bond is elongated by only 0.03 Å (0.2%) more than in the parent carbenoid complex. The C^1-I' bond is almost broken and elongated by 0.625 Å (28.0%) more than in the parent carbenoid complex. The largest change is associated with the $I'-C^1-Zn^1$ bond angle that varies from 108.7° to 87.1° in the TS5 structure. Another structural feature for TS12 is noteworthy. The C^1-Zn^1-I bond that is nearly linear (173.4°) in the reactant complex is now slightly bent (165.3°). These changes in the bond lengths and angles are attributed to the dimer $(ZnI_2)_2$ molecule being partially formed in the transition state.

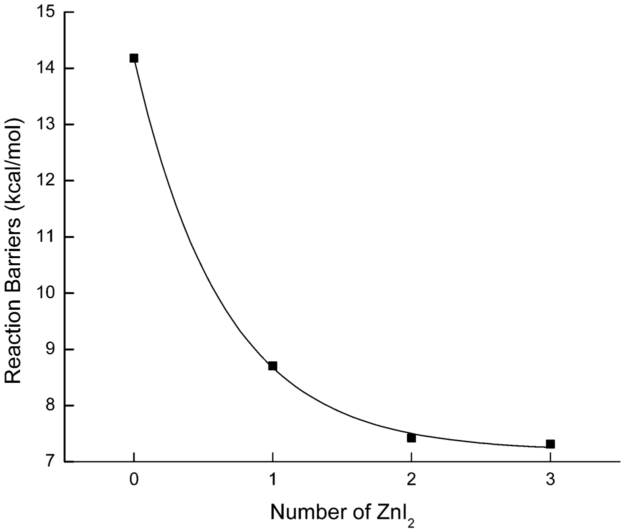

Figure 6. Energy barriers to the cyclopropanation of $(IZn)_2CHI/(ZnI_2)_n$ (n = 0 ~3)with ethylene plotted versus the number of ZnI_2 combined to the carbenoid. Values are from B3LYP/BS2 calculations of this work.

Figure 5f schematically displays the potential energy profiles for the addition of ZnI_2 in *gem*-dizinc cyclopropanation reactions. It was shown that the symmetric approach process is the most feasible among the three pathways for the reaction of ZnI_2 added *gem*-dizinc with ethylene. The barrier height for the reaction of $(IZn)_2CHI/ZnI_2 + C_2H_4$ was calculated to be 8.7 kcal/mol and the reaction to be exothermic by 21.3 kcal/mol at the B3LYP/BS2 with ZPE correction. The reaction barrier of $(IZn)_2CHI/ZnI_2 + C_2H_4$ is lowered by 5.5 kcal/mol compared to the pure *gem*-dizinc carbenoid with ethylene, but this is only 0.2 lower than in path A. The relatively small barrier of the *gem*-dizinc carbenoid with ethylene is consistent with the small structural changes as it goes from the reactant to transition state TS12. The reaction barrier is also in excellent agreement with the experimental reaction conditions where the cyclopropanation reaction can take place at a temperature of 0 °C.

To investigate the aggregation effect of ZnI_2, two and three ZnI_2 were added to the reaction system symmetrically as shown in Figure 4. The dimer and trimer $(ZnI_2)_n$ ($n = 2, 3$) were symmetrically coordinated to the pure *gem*-dizinc carbenoids. Similar to the TS12, TS13, and TS14 were found as the transition states for the reaction systems $(IZn)_2CHI/(ZnI_2)_n$ ($n = 2,3$) + C_2H_4 on the way to the products IZn-*c*-C_3H_5 + $(ZnI_2)_n$ ($n = 3, 4$). The barrier height for the reaction of $(IZn)_2CHI/(ZnI_2)_2 + C_2H_4$ was calculated to be 7.4 kcal/mol at the B3LYP/BS2 with ZPE correction. This is 1.3 kcal/mol smaller than the system $(IZn)_2CHI/ZnI_2 + C_2H_4$. The barrier height for the reaction of $(IZn)_2CHI/(ZnI_2)_3 + C_2H_4$ was calculated to be 7.3 kcal/mol at the B3LYP/BS2 with ZPE correction. This is only 0.1 kcal/mol smaller than the system $(IZn)_2CHI/(ZnI_2)_2 + C_2H_4$. It is apparent that the Lewis acid effect becomes smaller and smaller as the number of ZnI_2 become larger and larger. This appears to be described as an exponential decay process as the number of ZnI_2 goes from $n = 0$ to $n = 3$ as shown in Figure 6.

D. Brief Comparison of Cyclopropanation Reactions of Mono Zinc Carbenoids $RZnCHI_2$, EtCHIZnR (where R = Et or I) and Geminal Dizinc Carbenoids $(RZn)_2CHI$ (R =

Et or I) to Those of $LiCH_2I$ and CH_2I-I Carbenoids. It is interesting to note that theoretical studies of the very reactive $LiCH_2X$ (where X = F, Cl, Br, and I) and CH_2I-I carbenoid species have found these carbenoids react in an asynchronously and preferentially attack one CH_2 group of ethylene[51,54,57,65] in a manner very similar to the Simmons−Smith mono zinc reactions.[51−57] The $LiCH_2X$ species are known to be very reactive carbenoids and react with olefins even at low temperatures[79−81] and a quantum chemical study found the barrier for the cyclopropanation reaction of $LiCH_2I$ with ethylene to be about 7.4 kcal/mol.[55] The $LiCH_2I$ carbenoid undergoes relatively small changes in its structure as it proceeds from reactants to the transition state compared to the Simmons−Smith carbenoids.[51−57] This is similar to the behavior of the *gem*-dizinc carbenoids examined here and is consistent with the small barriers to reaction found for both the $LiCH_2I$ and *gem*-dizinc carbenoids. The CH_2I-I carbenoid has an even lower barrier to reaction with ethylene (about 2.9 kcal/mol)[65] than either the $LiCH_2I$ or the *gem*-dizinc carbenoids. The CH_2I-I species has a charge distribution for the CH_2I moiety that is similar to a CH_2I^+ cation[58,65] and thus CH_2I-I exhibits noticeable electrophilic behavior and a chemical reactivity not much greater than singlet methylene toward C═C bonds.[58,65] The metal ions in the organometallic carbenoids also influence the charge distribution of the carbenoid and appear to help bring the CH_2 moiety near the C═C bond, so that the cyclopropanation reaction can occur. It is interesting to note that there is usually an asymmetric character for the atoms attached and adjacent to the carbon atom to be transferred in the cyclopropanation reaction of the $LiCH_2X$, $RZnCHI_2$, and EtCHIZnR (R = Et or I) mono zinc carbenoids as well as the Simmons−Smith (ICH_2ZnI) carbenoid and all of these carbenoids react in an asynchronous manner preferentially attacking one CH_2 group of ethylene.[51−57] The very reactive CH_2I-I carbenoid also displays this asymmetry and reacts in a manner similar to the Simmons−Smith type carbenoid species. In contrast, the $(RZn)_2CHI$ (R = Et or I) *gem*-dizinc carbenoids have a high degree of symmetry about the C atom to be transferred to the C═C bond during the cyclopropanation reactions and this appears to correlate with the synchronous attack of both CH_2 groups of ethylene for these *gem*-dizinc carbenoids. Inspection of the structures of TS5, TS6, and TS7 provide support for the synchronous reaction being correlated to the symmetry of the carbenoid species about the C atom to be transferred during the cyclopropanation reaction. The $(IZn)_2CHI$ carbenoid is very symmetric and has C−C bonds of about 2.404 and 2.402 Å in TS7. The $(EtZn)_2CHI$ carbenoid is also symmetric and the C−C bonds being formed in TS5 are also about the same (2.321 and 2.327 Å). However, the EtZnCHIZnI carbenoid has somewhat less symmetry and the C−C bonds being formed in TS6 are noticeably more different (2.409 and 2.380 Å) than those in TS5 and TS7 associated with the more symmetric *gem*-dizinc carbenoids. Comparison of our results for the *gem*-dizinc carbenoids to those previously found for $LiCH_2X$, CH_2I-I, and mono zinc Simmons−Smith type carbenoids indicate that the more synchronous reaction and the smaller changes in the carbenoid structure as one goes from the reactant to the transition state both contribute significantly to the enhanced reactivity of the *gem*-dizinc carbenoids relative to their corresponding mono zinc carbenoids.

Conclusion

Density functional theory calculations have been presented for the cyclopropanation reactions with ethylene for several mono zinc carbenoids and their corresponding *gem*-dizinc carbenoids. The mono zinc carbenoids $RZnCHI_2$, EtCHIZnR (where R = Et or I) react with ethylene by preferentially attacking one CH_2 group of ethylene in an asynchronous manner with barriers to reaction in the 20−24.5 kcal/mol range. The changes in the structures of the transition states relative to the parent carbenoid for these mono zinc carbenoids were found to be relatively large and similar to those previously obtained for related Simmons−Smith carbenoids[51−57] and isopolyhalomethane carbenoids.[57,65,66] The *gem*-dizinc carbenoids were observed to have significantly lower barriers to reaction of about 15 kcal/mol. This indicates that when the second ZnR (R═I or Et) group is introduced to form the *gem*-dizinc carbenoid the barrier to reaction becomes substantially lower. This lower barrier for the *gem*-dizinc carbenoids is mainly due to the following: an increase of the electrophilicity by introducing the second zinc atom, the synchronous reaction of the carbenoid carbon atom toward both CH_2 groups of ethylene and to the small structural changes that occur in the $Zn^1-Zn^2-I^1-C^1$ moiety as the reactions go from the reactants to the transition states. Both mono zinc and *gem*-dizinc cyclopropanation reactions were investigated for the effect of addition of ZnI_2 as a Lewis acid. Addition of one ZnI_2 group was found to lower the barrier further by about 1−5.1 kcal/mol and 0−5.5 kcal/mol, respectively, for the mono zinc and *gem*-dizinc cyclopropanation reactions. As the number of ZnI_2 become larger, the Lewis acid effect becomes smaller and can approximately be described by an exponential decay as the number of ZnI_2 goes from $n = 0$ to $n = 3$. The *gem*-dizinc carbenoids with one to three ZnI_2 groups were found to give facile cyclopropanation reaction with ethylene with barriers to reaction of only 8.7 kcal/mol to 7.3 kcal/mol. Our results indicate that the gem-dizinc carbenoids are substantially more reactive than their mono zinc carbenoids. This is consistent with and can help explain the recent experimental results of Charette and co-workers that found *gem*-dizinc carbenoids can undergo efficient cyclopropanation reactions with olefins at 0 °C and compete effectively with their corresponding mono zinc carbenoids.[50]

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Note Added after ASAP Posting. Due to a production error, the version published on the Web 10/1/2002 did not include the final corrections to the paper. The version published on the Web 10/3/2002 and the print version are correct.

Supporting Information Available: Selected output from the density functional theory calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies for the mono zinc and gem-dizinc carbenoid reactants, transition states, and products for the cyclopropanation reactions investigated here and shown in Figures 1−6. This material is available free of charge via the Internet at http://pubs.acs.org.

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