Organometallics **2002,** *21,* 5901−5910

Density Functional Theory Investigation of the Reactivity of $LiCH_2I$ and Iodomethylzinc Phenoxide Cyclopropanation Reagents with Olefins

Dongqi Wang and David Lee Phillips*

Department of Chemistry, University of Hong Kong, Pokfulam Road,
Hong Kong, People's Republic of China

Wei-Hai Fang*

Department of Chemistry, Beijing Normal University,
Beijing 100875, People's Republic of China

Received August 19, 2002

We report a systematic density functional theory investigation for the reactions of $LiCH_2I$, $IZnCH_2I$, iodomethylzinc phenoxide ($PhOZnCH_2I$), 2,4,6-F_3-$PhOZnCH_2I$, and 2,4,6-Cl_3-$PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. All of the reactions examined displayed similar concerted mechanisms for the cyclopropanation of these reagents. The zinc carbenoids had similar barriers for the cyclopropanation reaction (in the 17−21 kcal/mol range), while the $LiCH_2I$ carbenoid had a much lower barrier for the cyclopropanation reactions (in the 6−7 kcal/mol range). The properties and chemical reactivity of the carbenoids investigated here were compared to each other and to recent results for the isodiiodomethane (CH_2I−I) species.

Introduction

The cyclopropane moiety has been found in many natural and unnatural products possessing important biological activities, and cyclopropane derivatives are also widely used as starting materials and intermediates in organic synthesis.[1−30] This has led to a great deal of recent research to discover novel and diverse approaches to the synthesis of cyclopropanes.[1−47] For example, the reactions between diazoalkane and olefinic

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* To whom correspondence should be addressed.

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substrates assisted by transition-metal complexes[13,18−20,30] provide important methods for the cyclopropanation of electron-deficient and electron-rich double bonds. Diiodomethane activated by ultraviolet photolysis in solutions containing olefins has also been found to produce cyclopropanated products with high stereospecificity.[31−33] The Norrish−Yang reaction was recently demonstrated to be useful to synthesize cyclopropane products for some molecules.[34] These are only a few examples of the diverse range of methods that have been used for cyclopropanation reactions.

The Simmons−Smith reaction[35] is a powerful and commonly used method for synthesizing cyclopropanes from olefins, where the reactive species is generated from diiodomethane (CH_2I_2) and a Zn−Cu couple.[35] After the pioneering study of Simmons and Smith,[35] much work has been done to develop improvements and alternative methods to prepare active reagents similar to the Simmons−Smith reagent that are capable of converting olefins into cyclopropanes with high efficiency and stereoselectivity.[36−47] For instance, Furukawa[42] has developed a procedure that involves alkyl group exchange between diethylzinc and CH_2I_2 to form a cyclopropanating agent. Charette and Marcoux[39] have developed an alternative procedure to prepare the Simmons−Smith reagent that uses the addition of CH_2I_2 to freshly prepared EtZnI. Although zinc carbenoids have been studied extensively, relatively little work has been done to modify the character of the R group of the zinc reagent "$RZnCH_2I$" and to compare the reactivity of this reagent to the classical Simmons−Smith (using R = I) reagent.[35] Charette and Brochu[45] found that some reagents with the general structure "$ROZnCH_2I$" (R = alkyl, allyl) are unreactive toward olefins in the absence of a Lewis acid. The Shi and Charette groups observed that some reagents (likely having a $RCOOZnCH_2I$ structure and made by mixing stoichiometric amounts of Et_2Zn, trifluoroacetic acid, and CH_2I_2) exhibited an increase in reactivity toward stilbene, which is relatively unreactive with the classic Simmons−Smith reagent. Charette and co-workers[47] have recently reported a new family of (iodomethyl)zinc phenoxide cyclopropanating reagents based on an "$ArOZnCH_2I$" structure (where Ar is an aromatic group) and observed these new carbenoids to be very reactive species for the cyclopropanation of unfunctionalized olefins. The reactivity of these new "$ArOZnCH_2I$" reagents was found to depend highly on the position and nature of the substituents on the aromatic ring.[47]

In comparison to the number of experimental studies that have been done for Simmons−Smith type carbenoids, there have been fewer reports of theoretical work for their cyclopropanation reaction with olefins.[48−52] Several theoretical calculations have focused on the initial Simmons−Smith reaction of $XZnCH_2X$ (X = Cl, I) with CH_2CH_2. For example, Bernardi and co-workers[48] have studied the potential energy surface for the reaction between ethylene and (chloromethyl)zinc chloride (which represents a model system for the Simmons-Smith cyclopropanation reaction) using the B3LYP/6-311G** method. A relativistic core potential approach[49] has also been used to investigate the Simmons−Smith cyclopropanation reaction, and the reaction was predicted to be exothermic by 33.5−37.8 kcal/mol with a barrier height of about 14.3 kcal/mol. Nakamura and co-workers used density functional theory (B3LYP) calculations to examine the effects of Lewis acid like $ZnCl_2$ molecules on the Simmons−Smith reaction.[50] Boche and co-workers[51,52] have used 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.

Isopolyhalomethane species such as isodiiodomethane ($CH_2I{-}I$) have recently been observed and identified in room-temperature liquids using nanosecond and picosecond time-resolved resonance Raman (TR^3) spectroscopy.[53−57] Isopolyhalomethane species have also been previously observed in low-temperature matrixes,[58,59] but there has not been much characterization of their chemical reactivity. We recently examined the reaction of isodihalomethanes ($CH_2X{-}X$, where X = I, Br, Cl) with ethylene using density functional theory calculations (DFT).[60,61] The $CH_2I{-}I$ photoproduct species reacted readily with ethylene via a one-step mechanism similar to that found for Simmons−Smith carbenoids ($XZnCH_2X$).[48−51] However, the $CH_2I{-}I$ species reacted with ethylene to give a cyclopropane product and I_2 leaving group with a much smaller barrier height of about 2.9 kcal/mol[60,61] compared to the analogous barrier height of about 17 kcal/mol for the Simmons-Smith reaction using $IZnCH_2I$.[51] The DFT results for the $CH_2I{-}I$ reaction with ethylene suggest 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.[60,61] Recent nanosecond TR^3 experiments have shown that the $CH_2I{-}I$ species reacts with cyclo-

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hexene solvent to produce an I_2 molecule leaving group on the 5−10 ns time scale, which then almost immediately forms a I_2−cyclohexene complex.[62] This provides further support for the carbenoid behavior of the CH_2I−I species and its role in the cyclopropanation reactions using ultraviolet photolysis of diiodomethane in the presence of olefins. The CH_2I−I carbenoid species has only one atom less (the Zn atom is absent) than the classical Simmons−Smith carbenoid ($IZnCH_2I$) and provides an interesting prototype for comparison to Simmons−Smith type carbenoids.

It has been found experimentally that the cyclopropanation reactions of $RMCH_2X$ (M = metal atom) with olefins are highly dependent on the nature of M, X, the R group, and the bond character between them. The rate of the cyclopropanation reaction would also depend on the structure and the nature of olefins. In addition, the aggregation states of the reagents, solvent, concentration of substrate, and Lewis acid catalysis may also influence the rate and direction of cyclopropanation reactions. The mechanism responsible for the reactions is essential for explaining the differences in reactivity of different reagents toward olefins and for a more complete understanding of the factors that influence chemical reactivity. In this paper, we present a systematic density functional theory investigation for the reactions of $LiCH_2I$, $IZnCH_2I$, iodomethylzinc phenoxide ($PhOZnCH_2I$), 2,4,6-F_3-$PhOZnCH_2I$, and 2,4,6-Cl_3-$PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. Similar concerted mechanisms were found for the cyclopropanation reactions for these reagents. We compare the structural features of the carbenoids and their transition states and attempt to obtain a better understanding of the relationship between structure and reactivity for these carbenoids.

Computational Details

The B3LYP density functional method has been used to investigate the reaction mechanisms of $LiCH_2I$ and $PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. For comparison purposes, the reaction pathways of $IZnCH_2I$, 2,4,6-F_3-$PhOZnCH_2I$, and 2,4,6-Cl_3-$PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$ are also investigated at the same level of theory. The stationary structures in the potential energy surfaces are optimized at the B3LYP level without symmetry constraint. The analytic frequency calculations have been performed in order to confirm that the optimized structures are either at a minimum or at a first-order saddle point and to carry out zero-point energy corrections. Geometry optimization and frequency calculations were carried out with the 6-311G** basis set[63] for the C, H, O, and Zn atoms and the DZVP basis set for the I atom. The 6-311G** basis set corresponds to the McLean−Chandler (12s,9p)[64,65] basis sets for second-row atoms[66,67] and the Wachters−Hay[68,69] all-electron basis set for the first transition row augmented with f polarization functions using the scaling factors of Raghavachari and Trucks.[70] These calculations are referred to as "B3LYP/6-311G**" hereafter in the paper. The basis set used here contained 460 basis functions contracted from 827 primitive Gaussian functions for the $PhOZnCH_2I$ + $PhCHCH_2$ system. To examine the dependence of the calculated energy on the size of the basis set, single-point energy calculations were performed with the hybridized basis set (denoted by pVTZ hereafter) composed of the cc-pVTZ basis set[71] for the C, H, and O atoms, the TZV basis set for the Zn atom and the Sadlej-pVTZ basis set[72] for the I atom. All calculations were carried out using the Gaussian 98 program suite.[73]

The 6-311G** basis set was used for the cyclopropanation of $ClZnCH_2Cl$ with CH_2CH_2 by Bernardi and co-workers and appeared to give reliable results.[48] We note many efforts have been made to develop better basis sets for the first-row transition metals, including Zn.[74,75] For example, Hall and co-workers[74] formulated optimal $(n + 1)$p functions for the valence orbitals on the ECP derived by Hurley et al.[75] We performed additional calculations for the reactions of $IZnCH_2I$ with CH_2CH_2 and $CH_3CHCHCH_3$ by adding diffuse functions to Zn (6-311+G**) and obtained barriers of 15.8 and 14.2 kcal/mol, respectively, compared to 19.8 and 17.6 kcal/mol for calculations using the 6-311G** basis set. This indicates using diffuse functions can moderately change the barrier for the cyclopropanation reactions to be lower by about 4.0−3.4 kcal. This appears to be a systematic effect, so that one can obtain reliable trends in the relative barriers to reaction as long as the same method and basis set is used in calculations for different reaction systems.

Results

The optimized stationary structures (minima and saddle points) on the potential energy surfaces of the reactions are displayed in Figures 1−3, respectively. Selected key geometry parameters (bond lengths and bond angles) are also given in Figures 1−3. The detailed structural parameters and energies for the structures determined in this study are collected in the Supporting Information. The relative energies are given in Table 1.

A. Cyclopropanation Reactions of $PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. The structure of (iodomethyl)zinc phenoxide ($PhOZnCH_2I$) was optimized with C_1 symmetry. The C−C bond lengths in the aromatic ring were predicted to be in the range of 1.39−1.40 Å by the B3LYP/6-311G** calculations and indicate the conjugation character of the aromatic ring is described well by the present

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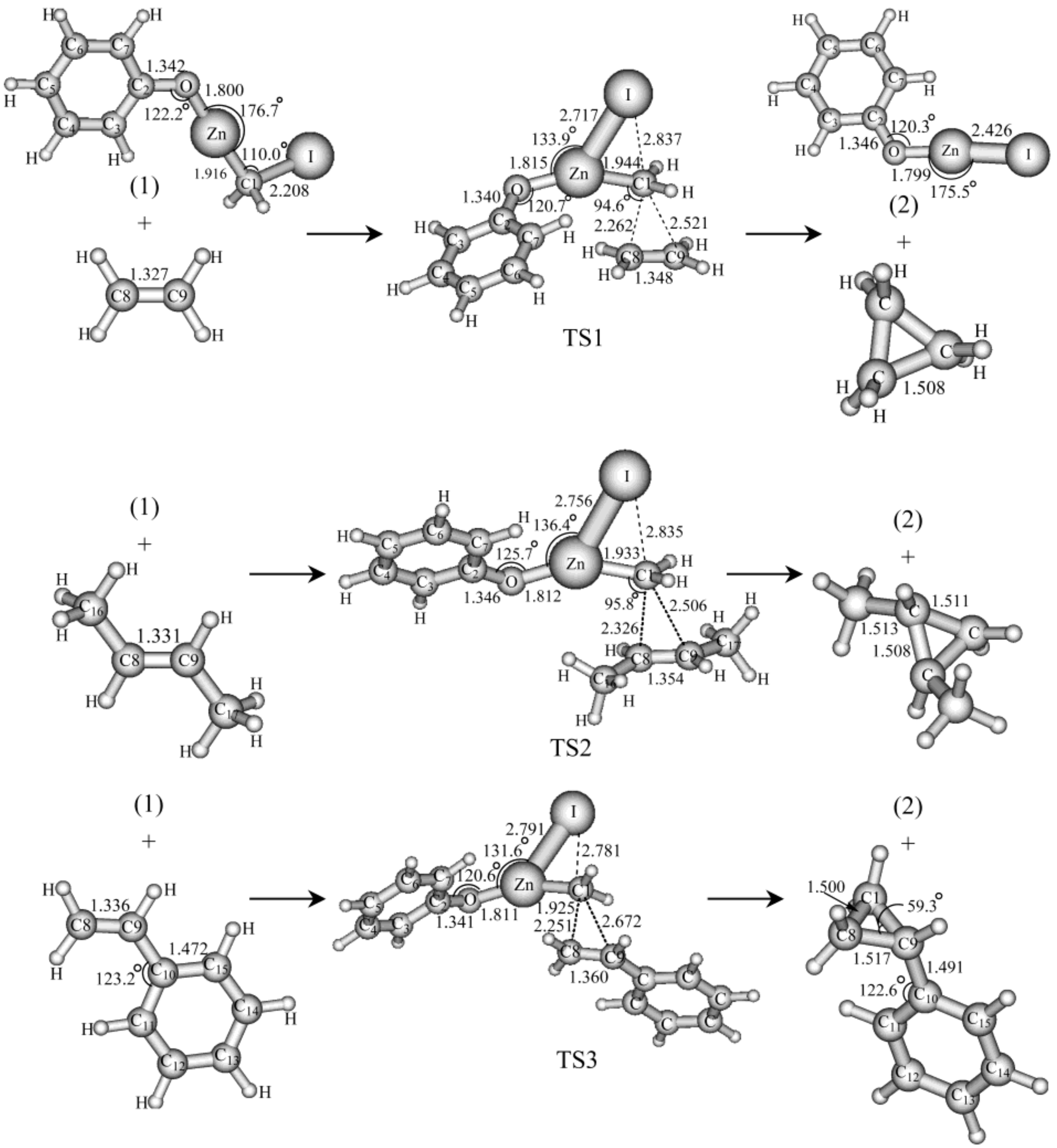

Figure 1. Minimum-energy structures from B3LYP/6-311G** calculations (see text for more details), schematically plotted for the reactions of iodomethylzinc phenoxide ($PhOZnCH_2I$) with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. Selected key bond parameters (bond lengths are given in angstroms, and the bond angles are given in degrees) are indicated for each minimum energy structure, and the atoms are numbered.

calculations. A transition state, TS1, was found on the way from $PhOZnCH_2I$ and CH_2CH_2 to the products of cyclopropane (c-C_3H_6) and PhOZnI. The C1−C8 distance in TS1 is 2.262 Å, and this is 0.259 Å shorter than the C1−C9 distance. This indicates a concerted asynchronous pathway for the cyclopropanation reaction of $PhOZnCH_2I$ with CH_2CH_2. The relatively large C1−C8 and C1−C9 distances predict that TS1 is closer to the reactants in structure than the products. This structural feature agrees with Hammond's postulate:[76] the exothermic reaction has a transition-state geometry close to that of the reactant. The planar ethylene molecule has a significant pyramidalization of about 5° at C8 in the TS1 structure that indicates the onset of the $sp^2 \rightarrow sp^3$ rehybridization required for cyclopropane formation. The C8═C9 and C1−Zn bond lengths are increased by 0.021 and 0.027 Å, respectively, in going from the reactants to the transition state. The interaction of the $PhOZnCH_2I$ moiety with the π olefin orbitals are mainly responsible for the slight lengthening of the C8═C9 and C1−Zn bonds. Relatively large changes are associated with the O−Zn−C1 and Zn−C1−I angles that vary from 176.7 and 110.0° in $PhOZnCH_2I$ to 133.9 and 66.2° in TS1. Meanwhile, the C1−I bond (2.837 Å) is nearly broken and the Zn−I bond (2.717 Å) is almost formed in TS1. These changes in the bond lengths and angles

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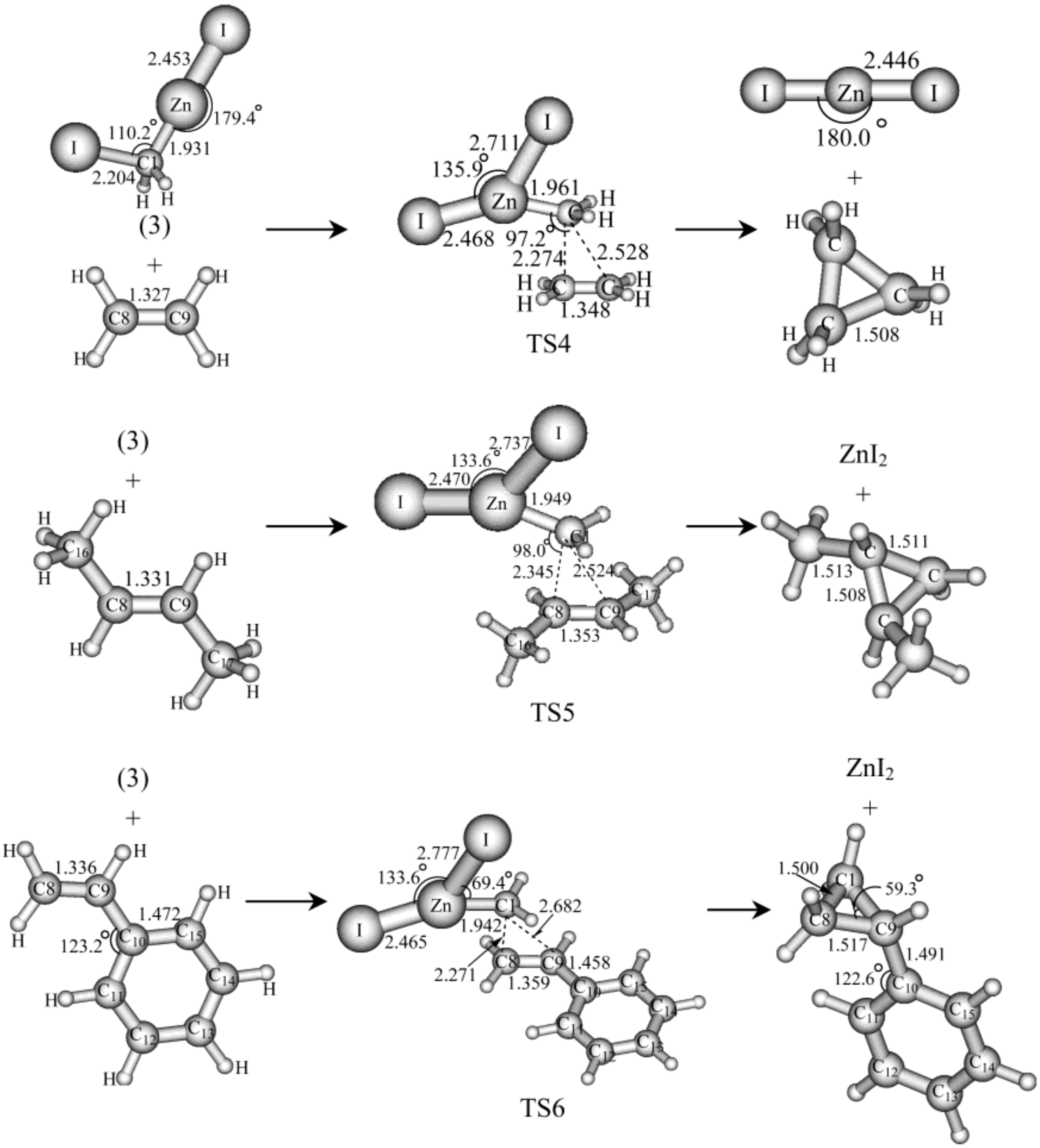

Figure 2. Minimum-energy structures from B3LYP/6-311G** calculations (see text for more details), schematically plotted for the reactions of $IZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. Selected key bond parameters (bond lengths are given in angstroms, and the bond angles are given in degrees) are indicated for each minimum energy structure, and the atoms are numbered.

are attributed to the PhOZnI leaving group being partially formed in TS1. Vibrational analysis shows that the optimized TS1 structure has one imaginary frequency of 338i cm^{-1} with a reaction vector $0.10R_{C1-Zn} - 0.36R_{I-Zn} + 0.62R_{C1-I} - 0.45R_{C8-C1} + 0.10A_{O-Zn-I}$. This indicates that TS1 is the transition state for the reaction from $PhOZnCH_2I + CH_2CH_2$ reactants to $c\text{-}C_3H_6$ + PhOZnI products.

Relative to the separated reactants of $PhOZnCH_2I$ and CH_2CH_2, the reaction has a barrier of 20.2 kcal/mol at the B3LYP/6-311G** level of theory (with the zero-point energy correction). Using the B3LYP/6-311G** optimized structures, the single-point energy calculations with the pVTZ basis set predict the barrier height to be 20.3 kcal/mol and becomes 20.8 kcal/mol with the B3LYP/6-311G** zero-point energy correction. Increasing the size of the basis set from 6-311G** to pVTZ does not have a significant influence on the relative energies of the reaction. The reaction is exothermic by 23.2 kcal/mol at the same level of theory. Similarly, the exothermicity of the reaction is only slightly influenced by the single-point energy calculations with the pVTZ basis set.

Similar transition states of TS2 and TS3 were found for the reactions of $PhOZnCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$, respectively. The common features of the three transition states (TS1−3) are the following: (1) the C1−I bond is mostly broken in TS1, TS2, and TS3; (2) the C1−Zn bond is only slightly elongated, as compared with that in $PhOZnCH_2I$; (3) the PhOZnI molecule is nearly formed in the transition states. However, there are also some differences in the structures of the three transition states. The conjugation interaction of the phenyl group and the C8═C9 double bond in styrene results in a polarization of the HOMO that has a more important coefficient in C8. This in turn

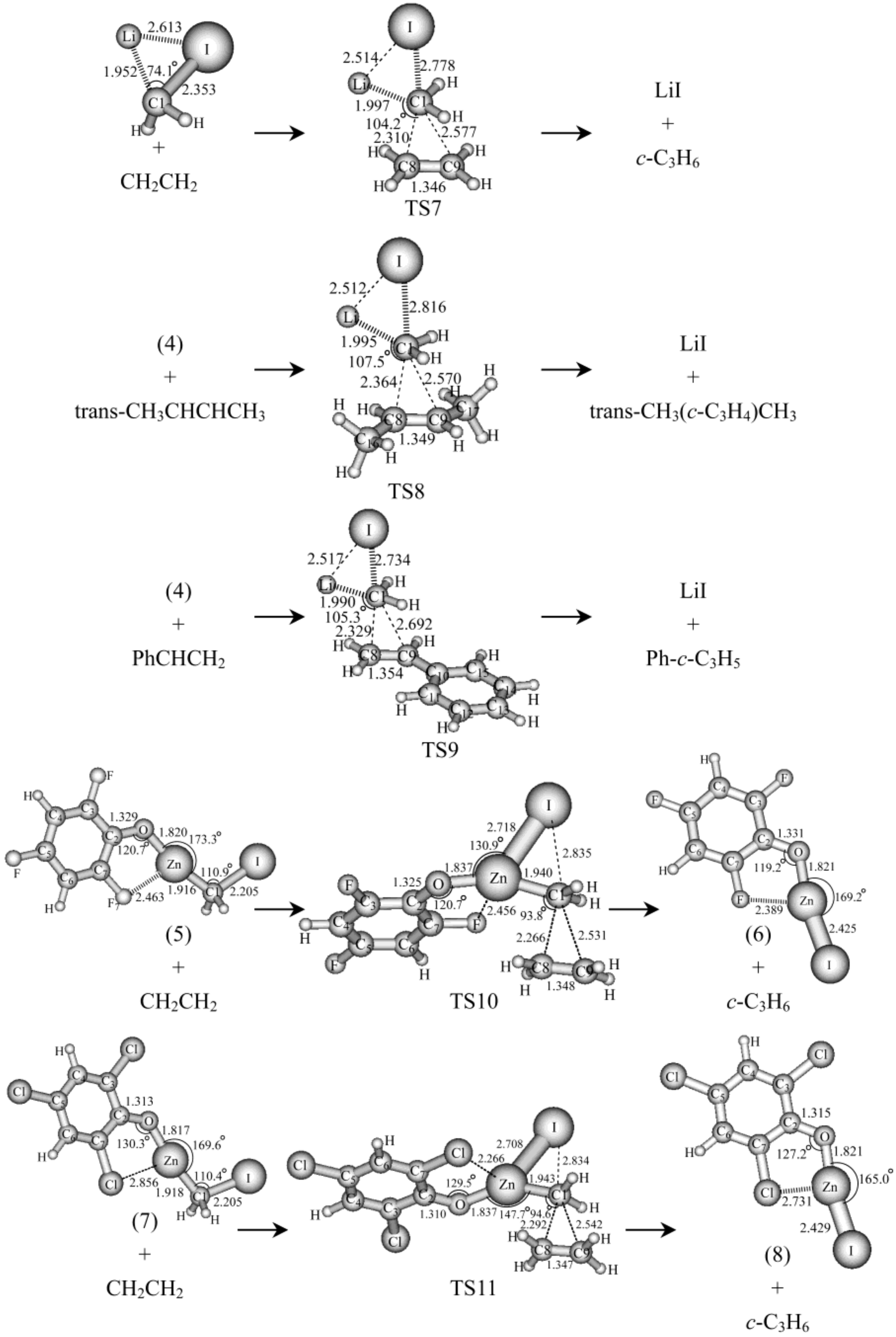

Figure 3. Minimum-energy structures from B3LYP/6-311G** calculations (see text for more details), schematically plotted for the reactions of $LiCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$ and reactions of 2,4,6-F_3-$PhOZnCH_2I$ and 2,4,6-Cl_3-$PhOZnCH_2I$ with CH_2CH_2. Selected key bond parameters (bond lengths are given in angstroms, and the bond angles are given in degrees) are indicated for each minimum energy structure, and the atoms are numbered.

Table 1. Relative Energies (Δ*E*) and Enthalpies (Δ*H*) in kcal mol^{-1} for the Cyclopropanation Reactions of $PhOZnCH_2I$, $IZnCH_2I$, and $LiCH_2I$ Carbenoids with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$ and of $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$ with CH_2CH_2 Computed from the B3LYP/6-311G Calculations**[a]

carbenoid species	olefin reactant species					
	CH_2CH_2		*trans*-$CH_3CHCHCH_3$		PhC_2H_3	
	Δ*E*	Δ*H*	Δ*E*	Δ*H*	Δ*E*	Δ*H*
$PhOZnCH_2I$	20.2	23.2	16.8	20.3	16.9	19.9
$IZnCH_2I$	19.8	23.5	17.6	20.7	16.4	20.5
ICH_2Li	6.6	46.5	6.9	43.6	5.3	43.2
$F_3PhOZnCH_2I$	19.1	22.8				
$Cl_3PhOZnCH_2I$	19.6	23.1				

[a] Note that the reaction products are c-C_3H_6, CH_3(c-C_3H_4)CH_3, and Ph(c-C_3H_5)).

leads to a more asynchronous reaction pathway and a stronger C1−C8 primary orbital interaction. The methyl groups in *trans*-2-butene increase electron density in the C═C region with respect to ethylene, which is the main reason that *trans*-2-butene has greater reactivity than ethylene.

The reaction of $PhOZnCH_2I$ with CH_2CH_2 is exothermic by 23.2 kcal/mol. The exothermic character of the reaction is unchanged by substitution of hydrogen with methyl or phenyl groups. However, substituents have a significant influence on the barriers of the cyclopropanation reactions. For the reaction of $PhOZnCH_2I$ with CH_2CH_2, the barrier height is 20.2 kcal/mol at the B3LYP/6-311G** level of theory with the corresponding zero-point energy correction. It becomes 16.8 and 16.9 kcal/mol for the reaction of $PhOZnCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$, respectively. The decrease of the barrier height for the cyclopropanation reaction is related to structural changes of the reactants CH_2CH_2 to *trans*-$CH_3CHCHCH_3$ or $PhCHCH_2$ and their different interactions with $PhOZnCH_2I$, and this will be detailed in the Discussion.

B. Cyclopropanation Reactions of $IZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. Previously reported BP calculations with effective core potentials[49] for Zn and I atoms predicted the $IZnCH_2I$ + CH_2CH_2 reaction to be exothermic by 34.0 kcal/mol with an about 15 kcal/mol barrier height. Another DFT study found a barrier of 17 kcal/mol with the reaction being 40 kcal/mol exothermic.[51] The transition state for the $IZnCH_2I$ + CH_2CH_2 reaction found in previous studies[49,51] is structurally similar to those for the reactions of $PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. The transition state has been confirmed to be the first-order saddle point connecting the corresponding reactants ($IZnCH_2CI$ + CH_2CH_2) and products (c-C_3H_6 + ZnI_2) by the IRC calculations.[49] The optimized structure of TS4 and the calculated potential energy profile are shown in Figure 2 and Table 1, respectively, for the reaction from $IZnCH_2I$ + CH_2CH_2 to c-C_3H_6 + ZnI_2. The Simmons−Smith cyclopropanation reaction takes place with appreciable efficiency only at room temperature or above,[39] and this indicates that a barrier of about 20 kcal/mol for the reaction is reasonable.

TS5 and TS6 were optimized and confirmed to be the first-order saddle points on the corresponding reaction pathways of $IZnCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$ to give CH_3−(c-C_3H_4)−CH_3 and Ph−(c-C_3H_5) cyclopropanated products and ZnI_2 leaving groups. The systematic differences in the C1−Zn and C1−I bond lengths predict that TS6 has a structure slightly closer to the reactants than TS5, while TS5 has a structure slightly closer to reactants than TS4. Inspection of the transition-state structures in Figure 2 reveals that the C9═C8 bond length and the C9−C1 distance are systematically elongated upon going from TS4 to TS5 and TS6. This mainly originates from the structural differences of the corresponding olefins and the interaction between the C═C double bond and the $ZnCH_2I$ moiety in the transition states. The C8−C1 distance in TS5 is significantly longer than that in TS4 or TS6 and the C9−C1 distance is slightly shorter than that in TS4 or TS6, due to the steric effect from one methyl group that is close to the I−Zn−I moiety. The relative energies for the three reactions are shown in Table 1. The exothermic character is less influenced with the different olefins as the reactant. However, there is a significant change in the barrier heights, which are computed to be 19.8, 17.6, and 16.4 kcal/mol for the reactions of $IZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$, respectively. A similar situation was found for the analogous reactions of $PhOZnCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$.

C. Cyclopropanation Reactions of $LiCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$. Carbenoids of $LiCH_2X$ (X = F, Cl, Br, I) are synthetically useful reactive intermediates.[77−79] Experiments found that $LiCH_2X$ is a “stronger carbenoid” than $XZnCH_2X$, and the cyclopropanation reaction of $LiCH_2X$ with CH_2CH_2 is fast even at very low temperature.[77−79] Hermann, Lohrenz, Kühn, and Boche[51] have performed a quantum-chemical investigation of the reaction between $LiCH_2X$ and CH_2CH_2 in order to understand the influence of the leaving group X on the nature of the lithium carbenoid. Structures and energies were discussed in that study. Here we have extended our investigation to investigate the structures and energies of $LiCH_2I$ in order to compare them to those for the related Simmons−Smith and new $ArOZnCH_2I$ cyclopropanation reactions. The $LiCH_2I$ molecule has a triangular geometry with C−Li, C−I, and Li−I distances of 1.952, 2.353, and 2.613 Å, respectively, in Figure 3. The C−I bond is significantly elongated, and the Li−I bond is partially formed in the $LiCH_2I$ molecule. This helps provide a good chance for addition of a CH_2 group into CH_2CH_2 to form cyclopropane molecules. There is one transition state (TS7) on the way from $LiCH_2I$ + CH_2CH_2 to LiI + c-C_3H_6. In contrast to the Simmons−Smith reaction process with the reactants $IZnCH_2I$ + CH_2CH_2, there are relatively small changes in the structure of the $LiCH_2I$ moiety as it goes from the reactant to TS7, and this predicts the barrier to reaction will be fairly low for the $LiCH_2I$ + CH_2CH_2 reaction. With respect to the separated reactants, the barrier height is only 6.6 kcal/mol at the B3LYP/6-311G** level of theory with the zero-point energy correction included and is in good agreement with the value of 7.4 kcal/mol found in previous calcula-

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tions.[51] This indicates that the cyclopropanation reaction of $LiCH_2I$ with CH_2CH_2 proceeds much more easily (with a barrier of 6.6 kcal/mol) than the $IZnCH_2I + CH_2CH_2$ reaction does (with a barrier of 19.8 kcal/mol), and this is consistent with both previous theoretical studies[51] and experiments[77–79] that show $LiCH_2I$ is a more reactive carbenoid than the $IZnCH_2I$ carbenoid.

The reactions of $LiCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$ have transition states of TS8 and TS9, respectively, and are similar to TS7 in structure. The structure of the Li−C−I moiety is almost unchanged upon going from TS7 to TS8 or TS9. Vibrational analyses show that there is only one imaginary frequency for the transition states (they are 291.1i, 281.8i, and 275.8i cm^{-1} for TS7, TS8, and TS9, respectively). The reaction vector associated with TS7 has been identified as $0.49R_{C8-C1} + 0.39R_{C9-C1} - 0.10R_{Li-C1} - 0.18A_{I-Li-C1}$, and similar reaction vectors for TS8 and TS9 were obtained. The IRC calculations were performed at the B3LYP/6-311G** level of theory for TS7, which was confirmed to be the transition state connecting the reactants of $LiCH_2I + CH_2CH_2$ and the products of c-C_3H_6 + LiI. The IRC calculations are time consuming and were not done for the very similar TS8 and TS9 transition states. The similar structural features and reaction vectors of the three transition states suggest that TS8 and TS9 are the corresponding transition states of the concerted reactions of $LiCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$. The reactions of $LiCH_2I$ with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$ have barrier heights of 6.9 and 5.3 kcal/mol, respectively, at the B3LYP/6-311G** level of theory with the zero-point energy correction included. The reactions of $LiCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$ are respectively exothermic by 46.5, 43.6, and 43.2 kcal/mol. The very low barrier heights and high exothermic character predict that the cyclopropanation reactions of $LiCH_2I$ with olefins proceed very easily even at low temperatures, in good agreement with experiment.

D. Cyclopropanation Reactions of CH_2CH_2 with 2,4,6-(halo)$_3$PhOZnCH$_2$I. We have done additional calculations to begin to study the dependence of reactivity upon changing the substituents on the aromatic ring of $PhOZnCH_2I$. The structures of 2,4,6-F_3-$PhOZnCH_2I$ ($F_3PhOZnCH_2I$) and 2,4,6-Cl_3-$PhOZnCH_2I$ ($Cl_3PhOZnCH_2I$) were optimized at the B3LYP/6-311G** level of theory with a C_s symmetry constraint. The resulting geometries for $Cl_3PhOZnCH_2I$ and $F_3PhOZnCH_2I$ were confirmed to be minima. It appears that $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$ are modestly stabilized with respect to $PhOZnCH_2I$, especially for $F_3PhOZnCH_2I$. This can be seen from the structures in Figure 3 that show the *o*-F−Zn and *o*-Cl−Zn distances are 2.463 and 2.856 Å in $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$, respectively. Overall, the transition states of TS10 and TS11 are similar to TS1 in structure. The interaction between the halogen and zinc atoms stabilizes $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$ to a moderate degree, and this interaction is somewhat stronger in TS10 and TS11, since the *o*-F−Zn and *o*-Cl−Zn distances are shorter in the transition states relative to $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$. The stronger stabilization interaction in TS10 and TS11 predicts that the aromatic hydrogen atoms substituted by the halogen atoms will decrease the barrier height of the reaction moderately. As depicted in Table 1, the reactions of $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$ with CH_2CH_2 have barriers of 19.1 and 19.6 kcal/mol, respectively. These values are about 0.5−1.1 kcal/mol lower than that for the reaction of $PhOZnCH_2I$ with CH_2CH_2. The reactivity of the zinc phenoxide reagents is dependent on the stability of the reagents and transition states as well as the position and nature of the substituents on the aromatic ring. This is discussed further in the following section.

Discussion

The reactions investigated here can be divided into four categories with respect to their differences in barrier heights in order to facilitate discussion of change in structural and other properties with chemical reactivity. The first category includes the reactions of $IZnCH_2I$ and $PhOZnCH_2I$ with CH_2CH_2, which have potential barriers to reaction of around 20 kcal/mol. The substitution of fluorine and chlorine atoms on the aromatic ring stabilizes the reactant of $PhOZnCH_2I$ less than the transition state, and this decreases the potential barrier of the reaction by about 0.5−1.1 kcal/mol. The aromatic halogen-substituted species $PhOZnCH_2I$ are considered as the second kind of cyclopropanation reaction with CH_2CH_2. The third category is the reactions of the zinc reagents with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$. The barrier to this category of reactions is significantly reduced with olefinic hydrogen substituted by the methyl or phenyl group. The reactions of $LiCH_2I$ with CH_2CH_2, *trans*-$CH_3CHCHCH_3$, and $PhCHCH_2$ are assigned to the fourth category of reactions discussed here. For comparison purposes, we will include a fifth category in our discussion for the CH_2I−I carbenoid and its reaction with CH_2CH_2 that we have previously investigated.[60,61]

In the reaction processes of $RZnCH_2I$ (R = I, C_6H_5O, $C_6F_3H_2O$, and $C_6Cl_3H_2O$) and CH_2CH_2, the C−C π orbital of CH_2CH_2 and the C−I and C−Zn σ bonds are broken. According to simple frontier molecular orbital theory, the occupied C−C π orbital of CH_2CH_2 can interact with either the empty C−I or C−Zn σ^* orbital. However, the overlap interaction between the occupied C−I or C−Zn σ orbital and the C−C π^* orbital of CH_2CH_2 takes place with less probability, due to a different phase relation. The B3LYP/6-311G** calculations show that the C−I σ^* orbital is lower in energy than the C−Zn σ^* orbital for $IZnCH_2I$. As a result, the interaction between the C−C π and C−I σ^* orbitals has more preference over the interaction between the C−C π and C−Zn σ^* orbitals. The above orbital correlation analysis suggests that there is a relatively large change in the C1−I bond and less change in the C1−Zn bond from the reactant to the transition state. This is in agreement with the B3LYP optimized structures of TS1−6, TS10, and TS11 in Figures 1−3.

The C1−I bond is almost broken and the Zn−I bond is nearly formed in the transition states, while the olefinic C=C double bond is only slightly increased with respect to that in CH_2CH_2. When $RZnCH_2I$ and CH_2CH_2 approach each other, the olefinic π electrons transfer toward the C1−I bond. As a consequence, the negative charges on the I atom are increased and strengthen the interaction between the I and Zn atoms.

Table 2. Atomic Charges for Selected Elements in the Carbenoid Species Investigated Obtained from Mulliken Population Analysis in the B3LYP/6-311G Calculations**

carbenoid species	atomic charges			
	I (attached to CH_2 group)	C1	Zn	Li
CH_2I-I	0.3	−0.3		
$IZnCH_2I$	−0.1	−0.9	1.1	
$PhOZnCH_2I$	−0.1	−0.9	1.2	
ICH_2Li	−0.2	−0.5		0.5

This strong interaction is mainly responsible for breaking the C1−I bond and forming the Zn−I bond in the transition states. The small increase in the C═C bond length is due to the weak interaction between the $CH_2{=}CH_2$ and $RZnCH_2I$ moieties in the transition states.

The interaction between the ortho F or Cl atom and the Zn atom stabilizes $F_3PhOZnCH_2I$ or $Cl_3PhOZnCH_2I$ and TS10 and their transition states (TS10 and TS11, respectively). This is consistent with the experimental observation that the ortho substituents on the aromatic ring can achieve relatively high conversion into cyclopropyl derivatives. The electron-withdrawing substituents on the aromatic ring could result in a decrease in the nucleophilicity of the aromatic ring, thus preventing the rapid decomposition of the carbenoid. With respect to $PhOZnCH_2I$, the somewhat higher stability of $F_3PhOZnCH_2I$ or $Cl_3PhOZnCH_2I$ is likely one of the reasons $F_3PhOZnCH_2I$ or $Cl_3PhOZnCH_2I$ appears experimentally to have a higher reactivity toward CH_2CH_2 than does $PhOZnCH_2I$. In fact, the $PhOZnCH_2I$ reagent was not characterized by NMR spectroscopy.[47] However, a solution of $Cl_3PhOZnCH_2I$ in CH_2Cl_2 was observed to be stable for about 1 h at 0 °C. Thus, the higher experimentally observed efficiency of the aromatic halogen substitution carbenoids such as $F_3PhOZnCH_2I$ and $Cl_3PhOZnCH_2I$ to react with olefins compared to $PhOZnCH_2I$ is probably mostly due to the greater stability and longer lifetimes of the aromatic halogen-substituted reagents as well as some lowering of the barrier height for the cyclopropanation reaction. It should be noted that solvent and aggregation effects are not considered here and could have significant influence on the stability of reactants and may also significantly change the barrier heights of the reactions. These issues will be explored in future work.

The cyclopropanation reactions of the zinc reagents with *trans*-$CH_3CHCHCH_3$ and $PhCHCH_2$ have barriers that are lower than for the reactions with CH_2CH_2. The methyl substitution results in an increase in the nucleophilicity of the olefins. An increase in electron density of the double bond by the methyl substitution leads to the reaction of the zinc reagents with *trans*-$CH_3CHCHCH_3$ to proceed more easily compared to the reaction with CH_2CH_2. In styrene the conjugation interaction slightly reduces the densities of the π electrons in the region of the C8═C9 double bond. In practice, the whole conjugation π system in styrene interacts with the C1−I σ^* orbital and is stronger than that found between reactants in the reaction of $YZnCH_2I + CH_2CH_2$.

The olefin molecule has π electrons, and electrophilic reagents are expected to react with the olefin relatively easily. Table 2 shows the atomic charges for some elements in the CH_2I-I, $IZnCH_2I$, $PhOZnCH_2I$, and $LiCH_2I$ carbenoids obtained from Mulliken population analysis of the B3LYP/6-311G** calculations. There is more than +1 atomic charge distributed onto the Zn atom of the zinc reagents, and the initial static electricity interaction between the zinc reagent and olefin results in formation of a complex[49] with Zn bonded by the π electron cloud. However, the cyclopropanation reaction is induced by the $\pi-\sigma^*$ interaction in the C1−I region, and formation of the complex does not significantly accelerate the reaction of the zinc reagents with olefins. Therefore, the zinc reagents do not reveal considerable electrophilicity in the cyclopropanation reactions, although a large amount of positive charge is distributed on the Zn atom. The reaction of CH_2I-I with CH_2CH_2 was predicted to proceed very easily in our previous work.[60,61] The C atom has a atomic charge of −0.3 in the CH_2I-I molecule, and the CH_2I moiety has a charge distribution similar to the CH_2I^+ cation species due to the I−I interaction.[53] Once a complex is formed between the olefin and CH_2I-I, the cyclopropanation reaction takes place very quickly.[60,61] There is about +0.5 atomic charge on the Li atom in the $LiCH_2I$ molecule. When the $LiCH_2I$ and CH_2CH_2 molecules approach each other, a complex is first formed via interaction of the Li atom with the CH_2CH_2 π electrons[51] and the reactions of $LiCH_2I$ with olefins are induced by the $\pi-\pi^*$ interaction in the C1−Li region. This is similar to the case of the cyclopropanation reactions of CH_2I-I with olefins, and the cyclopropanation reaction proceeds quickly after complexation of $LiCH_2I$ with the olefin.

Significantly different chemical reactivity toward the two different types of C═C bonds found in limonene is observed in the Simmons−Smith reaction and the photochemical reaction of diiodomethane in the presence of olefins.[33,80] The Simmons−Smith $IZnCH_2I$ carbenoid reacts mainly with the less highly substituted isopropenyl double bond, while the photochemical reaction of diiodomethane (via the CH_2I-I carbenoid) reacts mostly with the more highly substituted cyclohexenyl double bond. This significantly different chemical reactivity between the $IZnCH_2I$ and CH_2I-I carbenoids can be explained by a combination of different electrophilic and steric properties. The zinc reagents do not have much electrophilicity in the cyclopropanation reactions, although a large amount of positive charge is distributed on the Zn atom. In contrast, the CH_2I-I carbenoid displays considerable electrophilic behavior and a greater reactivity toward more highly substituted C═C double bonds. Inspection of the structures of $IZnCH_2I$ (in Figure 1) and CH_2I-I (see Figure 1 of ref 60) shows that the CH_2I-I species has a much more open structure about the CH_2 moiety than the $IZnCH_2I$ species and thus much less steric interaction when approaching highly substituted C═C bonds. Both the steric effect and electrophilic properties reinforce each other in the $IZnCH_2I$ and CH_2I-I carbenoids to give their very different chemical reactivities toward more highly substituted carbon double bonds. The $LiCH_2I$ carbenoid also has a noticeably more open structure for the CH_2 group than the $IZnCH_2I$ carbenoid, and this suggests that

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$LiCH_2I$ will have less steric interaction with highly substituted C═C bonds than the $IZnCH_2I$ carbenoid. This suggests that $LiCH_2I$ may display chemical reactivity toward highly substituted carbon double bonds similar to that of the CH_2I-I species.

The cation-like nature of the CH_2I moiety (similar to the charge distribution of the CH_2I^+ species)[53,60] in the CH_2I-I carbenoid appears to be an important factor in its low barrier for cyclopropanation (~2.9 kcal/mol) compared to the zinc carbenoids (in the 17−21 kcal/mol range). It is important to note that the CH_2I-I and $LiCH_2I$ carbenoids are not very stable and are thus very short-lived species. Although they are very reactive, their short lifetimes limit their practical usefulness for synthetic applications. We note the recent elegant work done by Charette and co-workers[47] to improve the stability and robustness of Simmons−Smith type zinc carbenoids in the new family of $ArOZnCH_2X$ carbenoids has increased the synthetic utility of Simmons−Smith type Zn carbenoids. This suggests that it may be worthwhile to attempt to increase the stability (through use of novel substituents or modification) of Li or other metal-based carbenoids in $RMCH_2X$ type molecules that are relatively unstable but are substantially more reactive than the Zn-based Simmons−Smith carbenoids.

Acknowledgment. This research has been supported by grants from the Research Grants Council of Hong Kong (HKU/7087/01P) to D.L.P. and the National Natural Science Foundation of China (Grant Nos. 20073005 and 29873008) to W.-H.F.

Supporting Information Available: Tables of Cartesian coordinates, total energies (in au), and vibrational zero-point energies for all stationary structures reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020679A