A Density Functional Theory Study of Aluminum Carbenoid $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) Promoted Cyclopropanation Reactions Compared to $IMCH_2I$ (M = Li, Sm, Zn) Carbenoids

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Density functional theory calculations are reported for the cyclopropanation reactions of selected aluminum carbenoids with ethylene for two reaction channels: methylene transfer and carbometalation. The aluminum carbenoids react with ethylene via an asynchronous attack on one CH_2 group of ethylene with a relatively high barrier (11−15 kcal/mol). In contrast, the reaction barriers for cyclopropanation via the carbometalation are much higher (about 30 kcal/mol). These computational results are in good agreement with experimental results, and this suggests that the methylene transfer process is favored and the competition from the carbometalation pathway is negligible. The $(CH_3)_2AlCH_2Cl$ carbenoid (reaction barrier of 11.3 kcal/mol) is found to be the most reactive carbenoid in the $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) series of carbenoids, and the $(CH_3)_2AlCH_2I$ carbenoid is the least reactive one. The present computational results are briefly compared with previously reported results for related lithium, samarium, and zinc carbenoids. The trend of the cyclopropanation reaction barrier of the carbenoids compared is $LiCH_2I$ (6.8 kcal/mol) ≈ $ISmCH_2I$ (5.5 kcal /mol) < $(CH_3)_2AlCH_2I$ (12.8 kcal/mol) < $IZnCH_2I$ (21.2 kcal/mol). These results are qualitatively consistent with the agreement between carbenoid character and experimental conditions needed for efficient reaction.

Introduction

Cyclopropane-containing molecules are found in a wide range of natural and unnatural compounds that display important biological activities and in many substances used as starting materials and intermediates in organic synthesis.[1−14] Since the reported use of diiodomethane and a Zn/Cu couple to react with olefins to form cyclopropane units by Simmons and Smith,[15] much research has been done to develop improvements or alternative techniques to form active reagents similar to the Simmons−Smith reagent that can make cyclopropane-containing products from olefins with high efficiency and stereoselectivity.[16−23] In addition to zinc carbenoids (such as the Simmons−Smith reagents, the Furukawa reagents,[18] and the Wittig−Denmark reagentss[19,20]), other powerful cyclopropanating carbenoid reagents have also been developed. For example, in 1964, Closs and Moss[21] discovered a lithium carbenoid that can give the expected arylcyclopropanes in the presence of olefins at −10 °C with fair to good yields. In 1987, Molander[22,23] first reported

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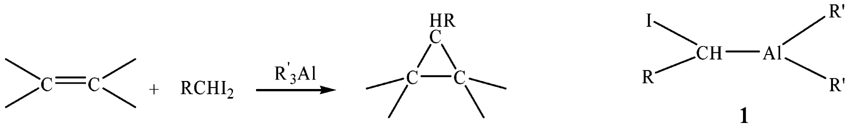
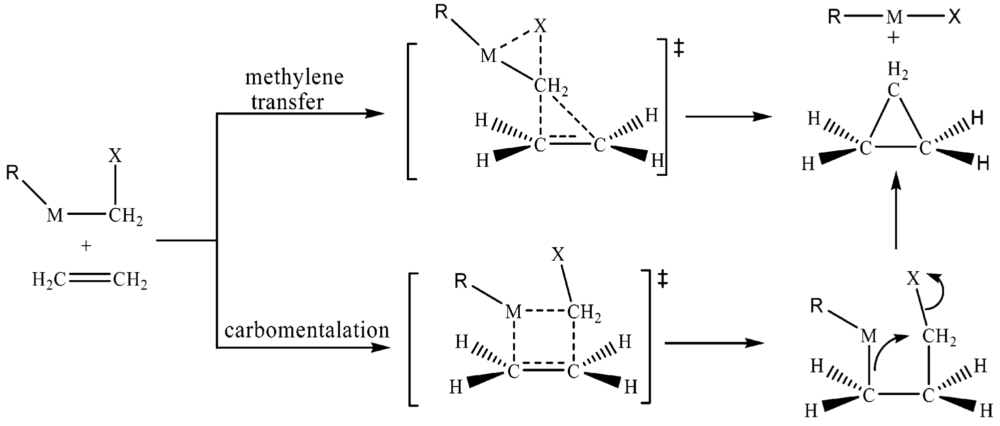
Scheme 1



Scheme 2



X=halogen or OR, M=Zn, Al, Li or Sm

the generation of samarium carbenoids by using a samarium/mercury amalgam in conjunction with CH_2I_2, and these carbenoids are believed to be one of the most efficient and highly diastereoselective cyclopropanating reagents. In 1985, Yamamoto and co-workers[24] discovered the dialkyl(α-iodoalkyl)-aluminum carbenoids (see species **1** in Scheme 1). The cyclopropanation reactions with these aluminum carbenoids are usually performed by addition of a solution of olefin and 1−2 equiv of CH_2I_2 in CH_2Cl_2 solvent at −40 °C, and high yields of cyclopropanated products can be produced.[24] Furthermore, the aluminum carbenoid has a different character in chemoselectivity from other analogous carbenoids.[22−25] Because of this unusual character of aluminum carbenoids, it is important to better understand the chemical reactivity of the aluminum carbenoid species and their cyclopropanation mechanism(s).

It has been proposed that the carbenoid-promoted cyclopropanation reactions of interest proceed through two likely reaction pathways: methylene transfer and carbometalation (see Scheme 2). The reaction mechanism is system-dependent. For zinc carbenoids, it is thought that the methylene transfer mechanism represents the reaction reality.[26−30] Samarium carbenoid cyclopropanation reactions are believed to have some competition between the methylene transfer mechanism and the carbometalation mechanism.[31,32] As for lithium carbenoids, Hoffmann[31] reported a possible alternative carbometalation/methylene transfer pathway. In this paper, several aluminum carbenoid promoted cyclopropanation reactions are investigated using theoretical methods for the first time. We found that these aluminum carbenoids have a carbenoid character similar to the classical Simmons−Smith carbenoids previously investigated using density functional theory calculations, while they are more reactive than Simmons−Smith carbenoids. These aluminum carbenoids are noticeably different from lithium and samarium carbenoids that have a “metal carbene complex” character.[32a] Our result for the aluminum carbenoids shows that the methylene transfer pathway is favored and competition from the carbometalation pathway is very small. This is in good agreement with experiments.[24,26] We briefly compare our present results for the aluminum carbenoid promoted cyclopropanation reactions to those related Zn, Li, and Sm carbenoids to better understand the factors that determine the reactivity of the carbenoids and the reaction pathways of metal carbenoid promoted cyclopropanation reactions.

Computational Details

The hybrid B3LYP density functional method[33,34] was used to investigate the cyclopropanation reaction mechanisms of the aluminum carbenoids with ethylene. The stationary structures of the potential energy surfaces were fully optimized at the B3LYP level of theory. Analytical frequency calculations at the same level of theory were performed in order to confirm the optimized structures to either a minimum or a first-order saddle point as well as to obtain the zero-point energy correction. Furthermore, intrinsic reaction coordinate (IRC) calculations[35] were performed to confirm that the optimized transition states correctly connect the relevant reactants and products. Geometry optimization for all of the

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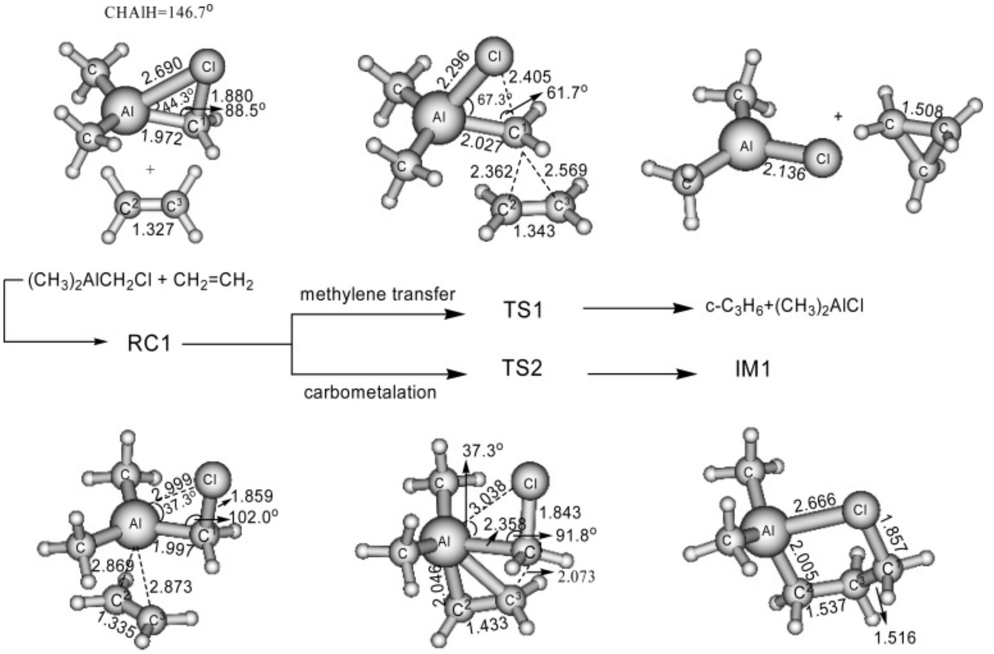

Figure 1. Schematic diagrams of the optimized geometry from the B3LYP/6-311G** computations for the aluminum carbenoid $(CH_3)_2$-$AlCH_2Cl$, reactant complex RC1, the intermediate IM1, and the transition state for the cyclopropanation with ethylene. TS1 = transition state for the methylene transfer for reaction of $(CH_3)_2AlCH_2Cl$ with ethylene. TS2 = transition state for carbometalation for reaction of $(CH_3)_2AlCH_2Cl$ with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and the bond angles in deg.

reactants, intermediates, transition states, and products as well as the frequency calculations were carried out with the 6-311G** basis set for all atoms of the reactions investigated except that the 6-311G** basis set for iodine atom is taken from ref 36. To consider solvent effects on the reactions of interest, the polarized continuum model (PCM) was applied to the calculations. Single-point energy calculations were done at the B3LYP/PCM/6311G** level of theory. All of the calculations were carried out using the Gaussian 98 and Gaussian 03 program suites.[37]

Results and Discussion

The optimized stationary structures (minima, saddle points) on the potential energy surfaces of the reactions investigated in this work are depicted schematically in Figures 1−5. Selected key geometry parameters (bond lengths and bond angles) for these structures are also shown in Figures 1−5 and Tables 1 and 2. The relative energies for the different reaction channels are shown graphically in Figures 4 and 5.

Cyclopropanation Reaction of the Al Carbenoid $(CH_3)_2Al$-CH_2Cl with Ethylene. The optimized geometry for the Al carbenoid $(CH_3)_2AlCH_2Cl$ is shown in Figure 1 along with the optimized geometry of the reactant complex (RC1) and the transition states (TS1, TS2) for cyclopropanations of ethylene through two different pathways to produce cyclopropane (c-C_3H_6) and $(CH_3)_2AlCl$. The methylene transfer pathway involves a concerted [2+1] addition through a transition state, TS1, in which the pseudotrigonal methylene group of the carbenoid adds to the ethylene π-bond to form new C−C bonds asynchronously. This process is accompanied by a 1,2-migration of the Cl anion from the carbon atom to the aluminum atom. According to the transition state proposed by Simmons[15a] and Moser,[38] this "butterfly" transition structure can explain the stereochemical features of this type of reaction. Another pathway named a carbometalation process involves a [2+2] addition of ethylene to the Al−C bond to form an intermediate (IM1) through a four-centered transition state (TS2). A subsequent intramolecular substitution reaction of this intermediate produces the final cyclopropane product. In the methylene transfer pathway, the Al carbenoid $(CH_3)_2AlCH_2Cl$ approaches ethylene from above the molecular plane in an asymmetric manner, while in the carbometalation process, the ethylene molecule simultaneously moves to the Al carbenoid to form a π-complex, which can be regarded as the reactant complex for both reaction pathways. In the transition structure TS1, the ethylene molecule has changed its planar structure with a significant pyramidalization of about 7.3° for C^2, which indicates that the $sp^2 \rightarrow sp^3$ rehybridization is necessary for cyclopropane formation, whereas the pyramidalization of C^3 is only 0.8°. There is another significant piece of evidence for an asynchronous approach of the CH_2CH_2 molecule in the methylene transfer mechanism. The C^1−C^2 distance in TS1 is 2.362 Å, which is 0.207 Å shorter than the C^1−C^3 distance. The interactions of the $(CH_3)_2AlCH_2$-Cl moiety with the π-olefin orbital are mainly responsible for the slight lengthening of $C^2{=}C^3$ bond and C^1−Al bond from the reactant complex (RC1) to the transition state (TS1), where the $C^2{=}C^3$ bond length is elongated by 0.016 Å and the C^1−Al bond length is elongated by 0.029 Å, respectively. Relatively large changes are associated with the Cl−C^1−Al and Cl−Al−C^1 angles and the C^1−Cl and Al−C^1 distances, which vary from

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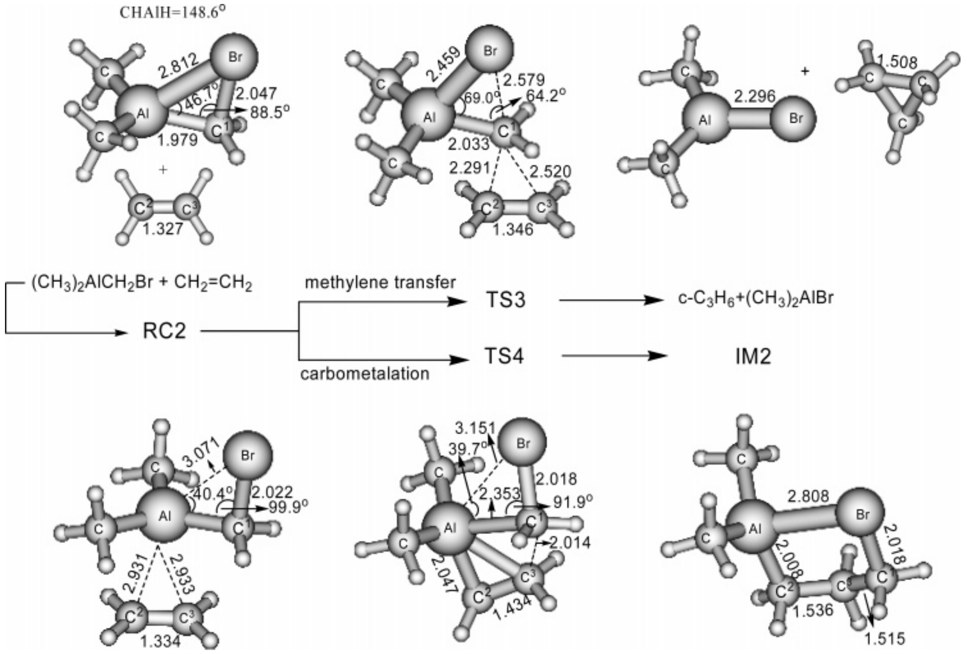

Figure 2. Schematic diagrams of the optimized geometry from B3LYP/6-311G** level computations for the aluminum carbenoid $(CH_3)_2$-$AlCH_2Br$, reactant complex RC2, the intermediate IM2, and the transition state for the cyclopropanation with ethylene. TS3 = transition state for the methylene transfer for reaction of $(CH_3)_2AlCH_2Br$ with ethylene. TS4 = transition state for carbometalation for reaction of $(CH_3)_2AlCH_2Br$ with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and bond angles in deg.

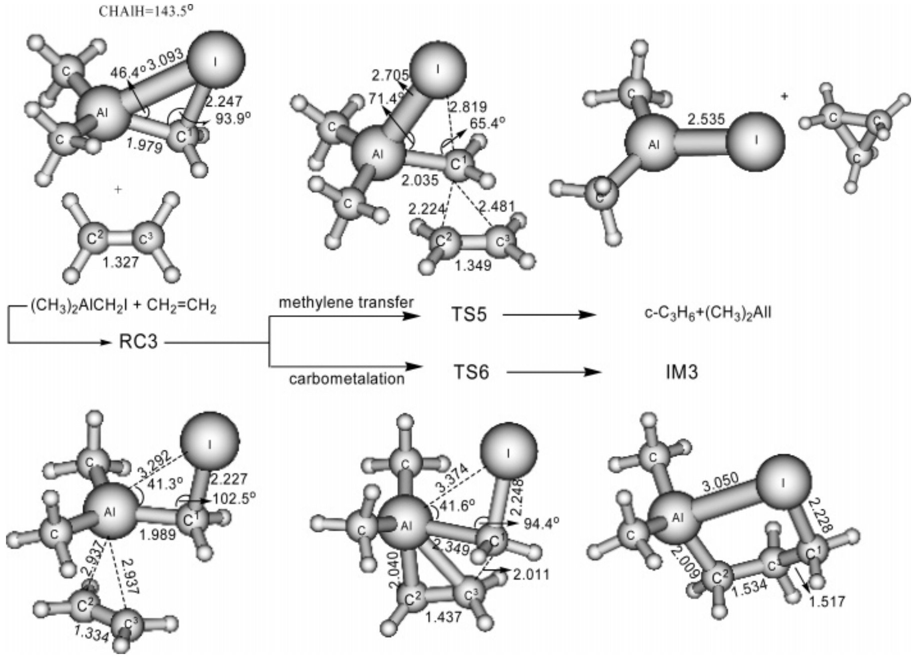

Figure 3. Schematic diagrams of the optimized geometry from the B3LYP/6-311G** level computations for the aluminum carbenoid $(CH_3)_2AlCH_2I$, reactant complex RC3, the intermediate IM3, and the transition state for the cyclopropanation with ethylene. TS5 = transition state for the methylene transfer for reaction of $(CH_3)_2AlCH_2I$ with ethylene. TS6 = transition state for carbometalation for reaction of $(CH_3)_2AlCH_2I$ with ethylene. Selected structural parameters are shown for each species with the bond lengths in Å and bond angles in deg.

102.0°, 37.3°, 1.859 Å, and 1.997 Å in RC1 to 61.7°, 67.3°, 2.405 Å, and 2.027 Å in TS1, respectively, as shown in Figure 1. Notably, in the transition state TS1, the C^1-Cl bond becomes nearly broken and the electron-rich Cl atom is attracted by the metal center to result in an almost complete Al−Cl bond. These changes in the bond lengths and angles are attributed to partial formation of the $(CH_3)_2AlCl$ byproduct in the transition state. The Al−Cl interaction is believed to give a sufficient compensation for the weakening of the $Al-C^1$ bond from RC1 to TS1. As shown in Figure 5, the methylene transfer pathway has a barrier of 11.3 kcal/mol in $(CH_3)_2AlCH_2Cl$ and is exothermic by about 38.9 kcal/mol at the B3LYP level of theory, indicating that the cyclopropanation reaction of $(CH_3)_2AlCH_2Cl$ with ethylene proceeds less easily (with a barrier of 11.3 kcal/mol) than the reaction of $LiCH_2Cl$ with CH_2CH_2, which has a barrier of 6.8 kcal/mol, as shown in Table 2, but much more easily than the reaction of $ClZnCH_2Cl + CH_2CH_2 + CH_2CH_2$, which has a barrier of 21.2 kcal/mol, as shown in Table 2. Vibrational analysis shows that the TS1 structure is a first-order saddle point with only one imaginary frequency of 289i cm^{-1}, and the IRC

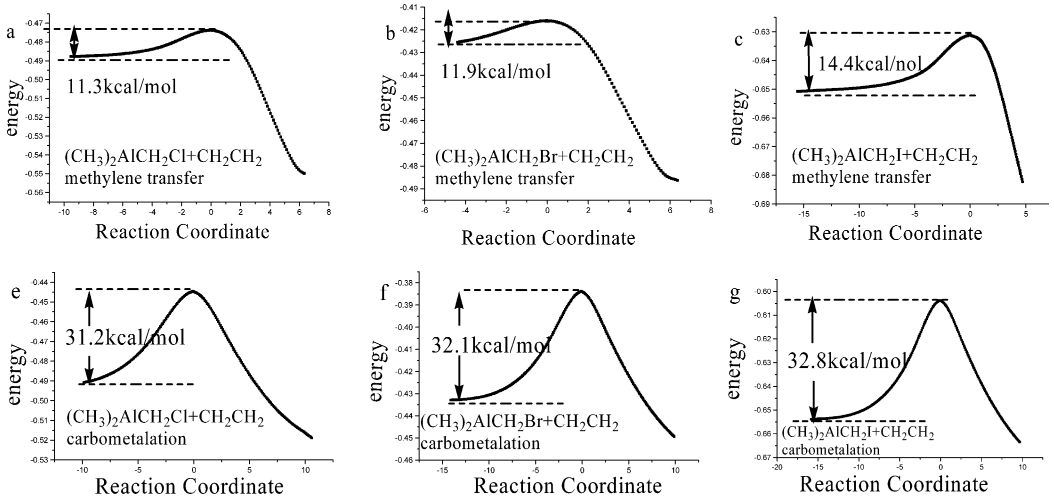

Figure 4. Potential energy profiles along the reaction coordinate.

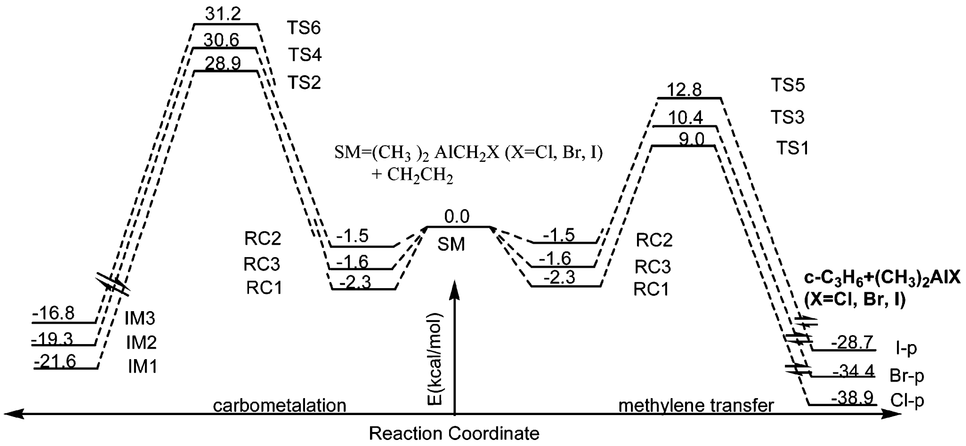

Figure 5. Schematic diagram showing the computed relative energy (in kcal/mol) at the B3LYP/6-311G** level for reactions of $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) + CH_2CH_2 with the transition states and products energy given relative to the separated reactants.

Table 1. Calculated Bond Lengths and Bond Elongation in the TS*n* (*n* = 1, 3, 5) as Compared to the Bond Lengths of the RC*n* (*n* = 1, 2, 3), Respectively

	C^1-Al		C^1-X		$Al-X$	
X	*r* [Å]	elong. [%]	*r* [Å]	elong. [%]	*r* [Å]	elong. [%]
I	2.035	2.31	2.819	26.58	2.705	−17.83
Br	2.032	2.11	2.579	27.54	2.459	−19.92
Cl	2.027	1.50	2.405	29.37	2.296	−23.44

Table 2. Activation Energies and Experimental Conditions for the Reactions of Various Carbenoids with Ethylene

	barrier (kcal/mol)		
reactive species	methylene transfer	carbometalation	experimental condition (*T*)
$LiCH_2I$	6.8 (7.5)[a]	7.7 (8.5)[a]	−78 °C[c]
$ISmCH_2I$	5.5[b]	9.7[b]	−78 °C[d]
$(CH_3)_2AlCH_2I$	12.8	31.2	−40 °C[e]
$IZnCH_2I$	21.2	36.5	≈25 °C[f]

[a] Values in parentheses are from single-point energies computed at the CCSD(T) level using the structures optimized with the B3LYP/6-311G** method, corrected by ZPE energies from frequency analysis at B3LYP/6-311G**. [b] Values from ref 32. [c] Value from refs 21, 29. [d] Value from ref 40. [e] Value from ref 24. [f] Value from refs 15, 41[41].

calculations (see Figure 4a) confirmed that TS1 connects the corresponding reactant RC1 and products c-C_3H_6 and $(CH_3)_2AlCl$. Thus, it is evident that TS1 is the transition state of the concerted reaction of $(CH_3)_2AlCH_2Cl$ with ethylene through the methylene transfer pathway.

With regard to the carbometalation pathway, there is an insertion reaction of the ethylene to the $Al-C^1$ bond to produce the intermediate IM1 through a four-centered TS2 transition state. Compared with the methylene transfer pathway, the carbometalation pathway has larger changes in the geometry from the reaction complex to the transition state. The $Al-C^2$ interaction increases significantly from 2.869 Å in RC1 to 2.046 Å in TS2. The C^1-C^3 goes from a distance of 3.296 Å in RC1 to 2.073 Å in TS2. This is accompanied by the weakening of the C^1-Al bonds from 1.997 Å in RC1 to 2.358 Å in TS2. It

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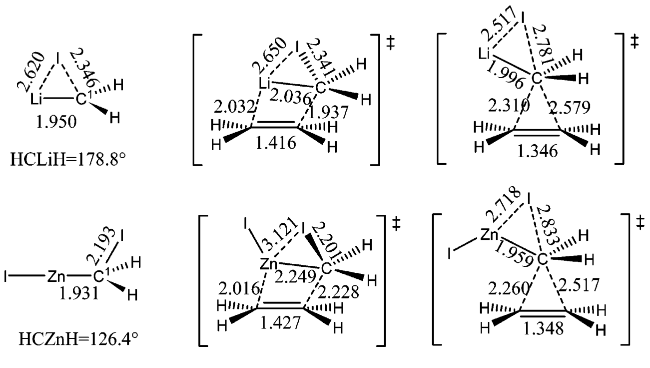
(39) Cyclopropanation of ethylene with $LiCH_2I$ and $IZnCH_2I$ at the B3LYP/6-311G** level of theory. The optimized structures obtained shown below are virtually similar to the structures reported previously.[28]



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is interesting that the C^1-Cl bond length and the Al−Cl interaction change only very slightly during the process from RC1 to TS2. This is different from the methylene transfer pathway and indicates that the Al−Cl interaction contributes little to the weakening of the C^1-Al bonds of TS2 in the carbometalation process. Thus, more energy is needed to overcome the barrier of the carbometalation pathway from RC1 to TS2. The reaction barrier height at the B3LYP/6-311G** level of theory for the reaction system of $(CH_3)_2AlCH_2Cl + CH_2CH_2$ is calculated to be 31.2 kcal/mol, as shown in Figure 5. The barrier height of 31.2 kcal/mol predicts that the reaction does not occur easily under room-temperature conditions. Vibrational analysis found that the optimized TS2 structure had one imaginary frequency of 381i cm^{-1} and was confirmed to connect the corresponding reactants and products by IRC calculations (see Figure 4e). To examine bulk solvation effects on the reactions of interest, the polarized continuum model (PCM) was utilized for dichloromethane solvent ($\epsilon = 8.93$). All of the single-point energy calculations were done at the B3LYP/PCM/6-311G** level of theory for the reaction systems (RC, TS). The reaction barriers from RC to TS were computed with the ZPE corrections included. The barriers decrease by 0.5 and 0.3 kcal/mol for the methylene transfer and the carbometalation pathways, respectively, indicating that the dichloromethane solvent has a slightly positive effect on the chemical reactivity.

B. Cyclopropanation Reaction of the Al Carbenoid $(CH_3)_2AlCH_2Br$ with Ethylene. The $(CH_3)_2AlCH_2Br$ carbenoid is produced by replacing the Cl atom with a Br atom in $(CH_3)_2AlCH_2Cl$. The transition state (TS3) (299i cm^{-1}) was found for the reaction of $(CH_3)_2AlCH_2Br$ with CH_2CH_2 on the methylene transfer pathway to c-C_3H_6 and $(CH_3)_2AlBr$ products. The geometry of TS3 is very similar to that of TS1. The reaction has a barrier of 11.9 kcal/mol and is exothermic by about 34.4 kcal/mol at the B3LYP/6-311G** level of theory, as shown in Figure 5. Compared to the reaction of $(CH_3)_2AlCH_2Cl + CH_2CH_2$, the reaction barrier of $(CH_3)_2AlCH_2Br + CH_2CH_2$ becomes higher by 0.6 kcal/mol while the exothermicity of the reaction becomes smaller by 4.5 kcal/mol. This suggests that $(CH_3)_2AlCH_2Br$ is slightly less reactive than $(CH_3)_2AlCH_2Cl$. We found that the cyclopropanation reaction of $(CH_3)_2AlCH_2Br$ with ethylene proceeds less easily (with a barrier of 11.9 kcal/mol) than the reaction of $LiCH_2Br$ with CH_2CH_2 (this has a barrier of 6.5 kcal/mol),[26] but much more easily than reaction of $BrZnCH_2Br + CH_2CH_2$ (this has a barrier of 19.2 kcal/mol).[26]

As for the carbometalation pathway, the geometry of TS4 (381i cm^{-1}) is very similar to that of TS2. This reaction has a barrier of 32.1 kcal/mol and is exothermic by about 19.3 kcal/mol at the B3LYP level of theory, as shown in Figure 5. The barrier of the reaction of $(CH_3)_2AlCH_2Br$ is a little higher than that of $(CH_3)_2AlCH_2Cl$, probably due to less interaction between the metal and halogen in the transition state. The TS3 and TS4 transition states were also confirmed to connect the corresponding reactants and products by IRC calculations (see Figure 4b,f). Taking the solvation effect into account, we found that the dichloromethane solvent helps to enhance the chemical reactivity of the reaction of $(CH_3)_2AlCH_2Br$ with ethylene. The barriers decrease by 1.1 and 0.6 kcal/mol for the methylene transfer and the carbometalation pathways, respectively.

C. Cyclopropanation Reaction of the Al Carbenoid $(CH_3)_2AlCH_2I$ with Ethylene. Changing the Br atom to an I atom in the $(CH_3)_2AlCH_2Br$ carbenoid leads to formation of the $(CH_3)_2AlCH_2I$ carbenoid. A transition state (TS5) (330i cm^{-1}) was found for the reaction of $(CH_3)_2AlCH_2I$ with CH_2 on the methylene transfer route to c-C_3H_6 and $(CH_3)_2AlI$ products. The geometry of TS5 is similar to that of TS1 and TS3. The reaction has a barrier height of 14.4 kcal/mol and is exothermic by 28.7 kcal/mol at the B3LYP/6-311G** level of theory, which is slightly higher than the barriers of $(CH_3)_2AlCH_2Cl$ and $(CH_3)_2AlCH_2Br$ carbenoids, as shown in Figure 5. This indicates that $(CH_3)_2AlCH_2I$ is the least reactive one among the $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) series of carbenoids. We found that the cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with ethylene (this has a barrier of 14.4 kcal/mol) proceeds much less easily than the reaction of $LiCH_2I + CH_2CH_2$ (with a barrier of 6.8 kcal/mol),[28,39] but much more easily than the reaction of $IZnCH_2I + CH_2CH_2$ (this has a barrier of 21.2 kcal/mol, see Table 2). In the carbometalation pathway, the geometry of TS6 (391i cm^{-1}) is very similar to that of TS2 and TS4. The reaction has a barrier of 32.8 kcal/mol and is exothermic by about 16.8 kcal/mol at the B3LYP/6-311G** level of theory, as shown in Figure 5. The TS5 and TS6 were confirmed to connect the corresponding reactants and products by IRC calculations (see Figure 4c,g). The barriers calculated with the PCM method (to take into account the solvent effect of CH_2Cl_2) are 12.9 and 32.1 kcal/mol for the methylene transfer and carbometalation pathways, respectively. These results also suggest a helpful enhancement for the reactivity of the carbenoid $(CH_3)_2AlCH_2I$ toward ethylene.

There are several common features of the three transition states (TS1, TS3, and TS5). First, the C^1-X (X = Cl, Br, I) bonds are mostly broken in TS1, TS3, and TS5. Second, the C^1-Al bonds are only slightly elongated compared with those of the reactant complexes. There also exist some differences in the structures of the three transition states (TS1, TS3, and TS5). For instance, the C^1-X (X = Cl, Br, I) bonds are elongated by 29.37%, 27.54%, and 26.58% from RC1, RC2, and RC3 to TS1, TS3, and TS5, respectively. Similarly, the $Al-C^1$ bonds are elongated by 1.5%, 2.11%, and 2.31% from RC1, RC2, and RC3 to TS1, TS3, and TS5, respectively (as shown in Table 1). It is worth noting that there exists a good correlation between the structural parameters of the transition states and the corresponding cyclopropanation reaction barriers. For example, the more elongated the C^1-X (X = Cl, Br, I) bond, the lower the barrier. This behavior is also associated with a lesser elongation of the C^1-Al bond and a greater shortening of the Al−X bond. As discussed above, the stronger Al−X interaction can give more sufficient compensation for the weakening of the $Al-C^1$ bond from RC to TS. These results help explain why the $(CH_3)_2AlCH_2Cl$ carbenoid is the most reactive one of the $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) carbenoids. Evidence can also be found from the natural charge distributions obtained by natural bond orbital (NBO) analysis. The natural charge of C^1 is −0.881, −0.942, and −1.070 for the $(CH_3)_2AlCH_2Cl$, $(CH_3)_2AlCH_2Br$, and $(CH_3)_2AlCH_2I$ carbenoids, respectively. The least negative nature charge of C^1 makes the $(CH_3)_2AlCH_2Cl$ carbenoid the most electrophilic, indicating that the $(CH_3)_2AlCH_2Cl$ carbenoid is the most reactive one in the $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) series of carbenoids.

D. Comparison of Cyclopropanation Reactions of $LiCH_2I$, $ISmCH_2I$, $(CH_3)_2AlCH_2I$, and $IZnCH_2I$ Carbenoids. In recent years, many research groups have reported theoretical investigations for the reaction mechanisms of carbenoid-promoted cyclopropanation reactions. It is interesting that the reaction mechanism is system-dependent. For zinc carbenoids, it is widely accepted that the methylene transfer mechanism represents the reaction reality.[26−30] For samarium carbenoids, Zhao et al.[32] reported that samarium carbenoid promoted cyclopropanation reactions are thought to have competition between the methylene transfer and the carbometalation pathways to a certain extent. As for lithium carbenoids, Hoffmann observed that either the carbometalation pathway or the methylene transfer pathway is feasible,[31] which is also supported by Nakamura and co-workers[28] using computational methods. The metal center of the carbenoid is the most important factor to determine the reaction mechanism for the cyclopropanation reaction. Lithium carbenoid has almost completely ionic bond character in the Li−C bond, which makes the process of carbometalation easier, with a barrier height of about 7.7 kcal/mol. The samarium carbenoid has a similar ionic bond nature in the Sm−C bond, so it is also believed to have some competition between the methylene transfer mechanism (with a barrier of about 5.5 kcal/mol) and the carbometalation mechanism (with a barrier of about 9.7 kcal/mol). The aluminum carbenoid and the zinc carbenoid favor the methylene transfer pathway over carbometalation pathway, because of the more covalent nature of the M−C bond. As shown in Table 2, the reaction barriers of the carbometalation pathways are much higher than those of the methylene transfer pathways for both aluminum carbenoid and zinc carbenoid.

Holger Hermann et al.[29] studied the potential energy surface for the reaction between ethylene and $LiCH_2I$ and found a barrier height of about 6.6 kcal/mol. Zhao et al.[32] used density functional theory calculations to examine the Simmons−Smith reaction and found a barrier height of ∼20.0 kcal/mol for the $IZnCHI_2$ reagent cyclopropanation reaction. The $ISmCH_2I$ and $(ZnI)_2CHI$ carbenoids were also studied by Zhao et al.[32] The barrier energies for selected Li, Zn, Sm, and Al carbenoids computed at the same level of theory are given in Table 2. From Table 2 we observed that the barrier heights for the reactions increase in the following order, with computed barrier heights given in parentheses: $LiCH_2I$ (6.8 kcal/mol) ≈ $ISmCH_2I$ (5.5 kcal /mol) < $(CH_3)_2AlCH_2I$ (12.8 kcal/mol) < $IZnCH_2I$ (21.2 kcal/mol). Lithium and samarium carbenoids are the most reactive cyclopropanation reagents, and they can cyclopropanate olefins at −78 °C. The aluminum carbenoid can also promote cyclopropanation reactions at relatively low temperatures because of their relatively low activation energies. However, the zinc carbenoid reacts with olefins at relatively high temperatures since it has noticeably higher activation energies. As shown above, the reactivity of the Li, Sm, Al, and Zn carbenoids of interest is mainly determined by the carbenoid character attributed to the metal−carbon bond. The more ionic bond character the metal−carbon bond has, the more reactive the carbenoid, and the less advantage the methylene transfer pathway has in its competition with the carbometalation pathway. Although the lithium carbenoid has the lowest activation energy, it can react with olefins through both the methylene transfer and carbometalation mechanisms. Thus, the aluminum carbenoids are thought to be potential cyclopropanation reagents with good reactivity and are able to undergo efficient cyclopropanation reactions with olefins at about −40 °C. Evidence can also be seen from the hybridization character of the C orbital in the C−I bond obtained by NBO analysis (M = Li, Sm, Al, Zn hybridization values of $sp^{16.7}$, $sp^{15.5}$, $sp^{9.7}$, and $sp^{3.7}$, respectively) and the H−C−M−H dihedral angles of the various carbenoids (M = Li, Sm, Al, Zn values of 178.8°, 164.7°,[32] 146.9°, and 126.4°, respectively). With a H−C−M−H dihedral angle value of 178.8°, the carbon atom is almost completely sp^2 hybridized in the lithium carbenoid, accompanied with the highest p-character of the C orbital in the C−I bond, of which the hybridization value is $sp^{16.7}$. The higher p-character of the C orbital in the C−I bond corresponds to a σ_{C-X} orbital of higher energy and a σ^*_{C-X} bond of lower energy, indicating a stronger electrophilic character of the carbenoids.[29b] Therefore the lithium carbenoid has the strongest carbenoid character and reacts with olefins most efficiently. With the H−C−M−H dihedral angle value of 164.7° and a C orbital hybridization value in the C−I bond of $sp^{15.5}$, the samarium carbenoid can be considered to have a carbenoid character similar to the lithium carbenoid and can also promote cyclopropanation very efficiently. However, the aluminum carbenoid has a lesser sp^2-hybridized carbon atom (the H−C−M−H dihedral angle value is 146.9°) and a lower p-character of the C orbital in the C−I bond (the hybridization value is $sp^{9.7}$) so that it undergoes a relatively large structural change from the reactant complex to the methylene transfer transition state, implying that it needs to overcome a relatively higher reaction barrier. For the zinc carbenoid, the carbon atom in it has almost sp^3 character (the H−C−M−H dihedral angle value is 126.4°). Furthermore it has the lowest p-character of the C orbital in the C−I bond with a hybridization value of $sp^{3.7}$. This indicates that the zinc carbenoid is the least reactive cyclopropanation reagent among these four kinds of carbenoids. The above comparison is qualitatively consistent with the experimental reaction conditions as shown in Table 2 and helps to provide a reasonable explanation for understanding some basic factors that determine the reactivity of these types of carbenoids and their reaction pathways for metal carbenoid promoted cyclopropanation reactions.

Conclusion

In this paper we have studied the potential energy surfaces for the reactions between ethylene and $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) carbenoids. The results from these calculations are compared to results for other related carbenoids (i.e., $LiCH_2I$, $ISmCH_2I$, and $IZnCH_2I$). This DFT approach represented model systems for aluminum carbenoid promoted cyclopropanation reactions. Two reaction channels were investigated: methylene transfer and carbometalation. The energy barriers for the methylene transfer pathway (11−15 kcal/mol) are significantly smaller than those of the carbometalation pathway (about 30 kcal/mol). The methylene transfer process is favored and the competition from the carbometalation process is very small, and this is consistent with experimental results. We have also demonstrated that the methylene transfer transition state corresponds to a three-centered structure similar to that originally suggested by Simmons[15a] and Moser.[38] Reactant complexes located on the reaction surface appear to form without any barrier. Among the $(CH_3)_2AlCH_2X$ (X = Cl, Br, I) series of carbenoids, the $(CH_3)_2AlCH_2Cl$ carbenoid is the most reactive (with a barrier of about 11.3 kcal/mol), while the $(CH_3)_2AlCH_2I$ carbenoid is the least reactive. The relatively lower barrier for the $(CH_3)_2AlCH_2Cl$ carbenoid is mainly due to the following: an increase of its electrophilicity by the halogen and the smaller structural changes that occur in the $(CH_3)_2AlCH_2Cl$ carbenoid as the reaction goes from the reactant to the transition state. Our results are consistent with and can help explain the experimental observation that Al carbenoids can undergo efficient cyclopropanation reactions with olefins at −40 °C. The comparison of the cyclopropanation reactions of $LiCH_2I$, $ISmCH_2I$, $(CH_3)_2AlCH_2I$, and $IZnCH_2I$ carbenoids shows that the more carbenoid character there is, the more reactive the carbenoid is, and the less advantage the methylene transfer has in its competition with the carbometalation mechanism. The trend of the carbenoid reaction reactivity is $LiCH_2I$ (6.8 kcal/mol) ≈ $ISmCH_2I$ (5.5 kcal /mol) < $(CH_3)_2AlCH_2I$ (12.8 kcal/

mol) < $IZnCH_2I$ (21.2 kcal/mol), which is consistent with experimental results.

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Supporting Information Available: Selected output from the ab initio calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies for the reactants, transition states, and products for the reactions investigated here. This material is available free of charge via the Internet at http://pubs.acs.org.

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