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Samarium(III) Carbenoid as a Competing Reactive Species in Samarium-Promoted Cyclopropanation Reactions

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

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China, and Department of Chemistry, Northwest Normal University, Lanzhou 730070, P.R. China

phillips@hkucc.hku.hk

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Abstract: The trivalent samarium carbenoid I_2SmCH_2I-promoted cyclopropanation reactions with ethylene have been investigated and are predicted to be highly reactive, similarly to the divalent samarium carbenoid $ISmCH_2I$. The methylene transfer and carbometalation pathways were explored and compared with and without coordination of THF solvent molecules to the carbenoid. The methylene transfer was found to be favored, with the barrier to reaction going from 12.9 to 9.2 kcal/mol compared to barriers of 15.4–17.5 kcal/mol for the carbometalation pathway upon the addition of one THF molecule.

As an important building block in natural and unnatural products, the cyclopropyl group plays a crucial role in bioactive compounds. Thus, the preparation of cyclopropyl groups is an important topic in organic synthesis.[1] Among the various protocols for the preparation of cyclopropane derivatives, methylene insertion by a carbenoid species into the C=C bond is one of the most widely used methods since the recognition of the Simmons–Smith reaction.[2–5]

Previous studies proposed the formation of a reactive carbenoid species as a key step in the carbenoid-promoted cyclopropanation reaction.[2,6–11] Theoretical investigations[12–16] confirmed the existence of these carbenoid species for a wide range of Simmons–Smith-type reagents that work as methylene transfer reagents. These types of carbenoids are thought to be formed from the reaction of CH_2I_2 with a metal atom and to typically have a $RMCH_2X$ structure (where R is a halogen atom or (substituted) alkyl group; M is a metal atom such as Zn, Li, or Sm; and X is halogen atom Cl, Br, or I).

We reported a density functional theory (DFT) investigation on the divalent samarium(II) carbenoid promoted cyclopropanation reaction.[16d] The $ISmCH_2I$ carbenoid was found to possess a structure characterized as a samarium carbene complex and appeared to have a much higher reactivity in the cyclopropanation toward ethylene, with a barrier to reaction of 5.5 kcal/mol for the methylene transfer pathway compared to 9.7 kcal/mol for the carbometalation pathway relative to the separate reactants. The THF solvent molecule was found to help enhance the reactivity of $ISmCH_2I$ toward ethylene for the methylene transfer pathway but not for the carbometalation pathway.[16d]

To further improve our understanding of the samarium-promoted reactions, we carried out the calculations on a samarium(III) carbenoid promoted cyclopropanation with ethylene reaction. The samarium(III) carbenoid I_2SmCH_2I was proposed by Molander and Harring[9d] and Imamoto and Takiyama[8] to be generated from the reaction of $SmI_2 + ClCH_2I$, and it was reported that the reactivity and selectivity of the probable I_2SmCH_2I carbenoid from $SmI_2/ClCH_2I$ is similar to that of $ISm^{(II)}CH_2I$, which is derived from $Sm(Hg)/CH_2X_2$.[9d] The present DFT study starts the reactions with the separated reactants of $I_2SmCH_2I + CH_2CH_2$. The transition states, probable reactant complexes (RC) for the relevant reactions, were located. To study the additive effect of THF, the THF molecule was complexed to the

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[†] University of Hong Kong.

[‡] Northwest Normal University.

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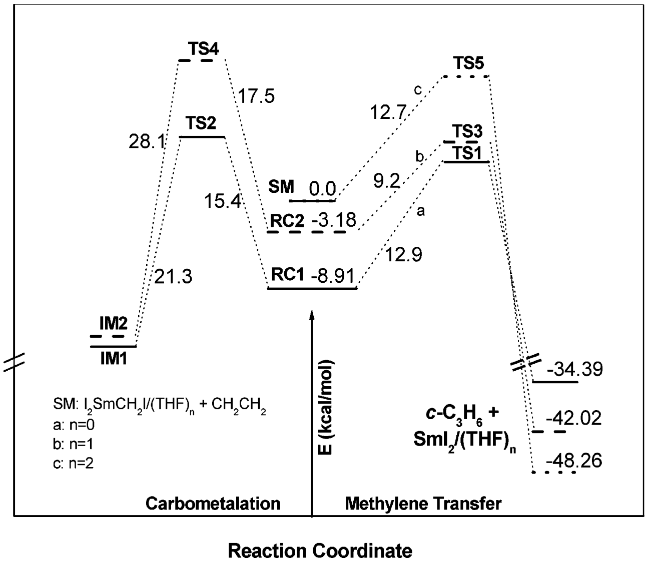
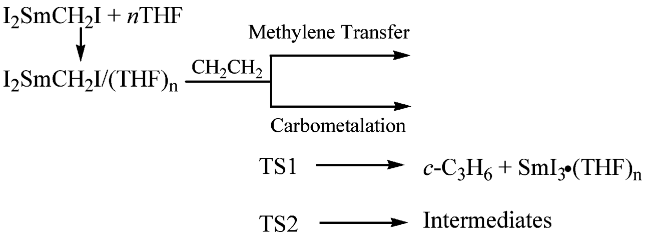


FIGURE 1. Schematic diagram showing the computed relative energies (in kcal/mol) from the B3LYP calculations for the reactions of $I_2SmCH_2I/(THF)_n$ ($n = 0, 1, 2$) with C_2H_4 with the energies given relative to the starting materials (SM = $I_2SmCH_2I/(THF)_n + C_2H_4$ ($n = 0, 1, 2$)).

SCHEME 1



Sm atom through a Sm···O dative bond. These processes are shown in Scheme 1. The optimized geometries of the stationary points are collected in Supporting Information together with the total energies and zero-point energies. The potential energy surfaces of the reactions are depicted in Figure 1. A simple comparison of the structure of the Sm(III) and Sm(II) carbenoid species is shown in Table 1.

Similar to the divalent samarium carbenoid (Scheme 2), the samarium(III) carbenoid I_2SmCH_2I was found to have a "samarium carbene complex" character and to be noticeably different from the closely related classical Simmons−Smith ($IZnCH_2I$) carbenoid in structure with more electrophilic character and higher chemical reactivity.

Examination of Table 1 indicates that the interaction among Sm, C, and I becomes stronger systematically. These changes are related the oxidation state of Sm varying from +2 to +3, which results in the stronger electrophilicity of the Sm center. The stronger interaction of the Sm···I′ (leaving group) benefits the methylene insertion reaction, and the samarium(III) carbenoid $I_2Sm^{(III)}CH_2I$ can be expected to have a reactivity toward olefins in cyclopropanation reactions similar to that of the $ISm^{(II)}CH_2I$ carbenoid. The character of the carbenoid as a complex of samarium iodide and carbene stays essentially unchanged with the dihedral angle of $D_{H-C-Sm-H}$ becoming a little smaller (159.5° in $I_2Sm^{(III)}CH_2I$ compared to 164.7° in $ISm^{(II)}CH_2I$).

TABLE 1. Selected Key Structural Parameters for the Sm(III) and Sm(II) Carbenoids

	Sm−C	C−I′	Sm−I′	Sm−I	$D_{H-C-Sm-H}$
$I_2Sm^{(III)}CH_2I$	2.440	2.296	3.132	2.948	159.5°
$ISm^{(II)}CH_2I^{a}$	2.589	2.335	3.280	3.082	164.7°
SmI_2^{a}/SmI_3			3.056/2.922		

[a] From ref 16d.

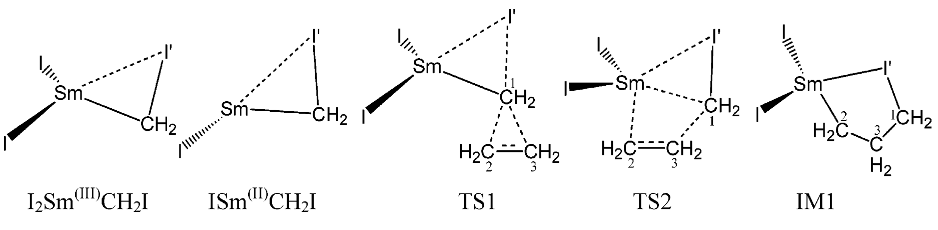
Two transition states, TS1 and TS2 (Scheme 2), were found for the reactions of $I_2Sm^{(III)}CH_2I$ with CH_2CH_2 and are located on the methylene transfer and carbometalation pathways, respectively. The geometries of TS1 and TS2 have approximate symmetry of C_s, with C^1, Sm, I′, and $C^2{=}C^3$ staying in the symmetric planar and the other two I and hydrogen atoms on either side. A π-complex, RC1, was observed prior to the transition states.

In the methylene transfer pathway, the carbenoid approaches the ethylene substrate in an asynchronous manner similar to the observations in the cyclopropanation reaction of $ISm^{(II)}CH_2I$ with CH_2CH_2 and the difference between the distance of $C^1\cdots C^2$ and $C^1\cdots C^3$ is predicted to be about 0.181 Å. The activation energy predicted for this reaction was about 12.9 kcal/mol relative to RC1 with ZPE correction included and this suggests that the $I_2Sm^{(III)}CH_2I$ is an active species in the methylene insertion reaction toward ethylene similar to the Sm(II) carbenoid.

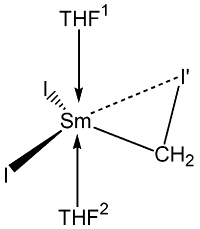
The carbometalation pathway is a reaction for CH_2CH_2 to be inserted into the Sm−C^1 bond to produce a five-membered ring intermediate IM1 (Scheme 2) similar to the carbometalation of $ISm^{(II)}CH_2I$ with CH_2CH_2.[16d] The barrier to reaction was calculated to be 6.5 kcal/mol relative to separate reactants and 15.4 kcal/mol relative to RC1 with the ZPE correction included. This indicates it is a little more difficult for the olefin reaction to proceed along the carbometalation pathway compared to the methylene transfer protocol.

Calculations using small core ECPs treatment on the Sm atom were also carried out for the methylene transfer reactions of $I_2Sm^{(III)}CH_2I$ with CH_2CH_2 to estimate the

SCHEME 2. Schematic Elucidation of Selected Typical Stationary Points for Sm-Promoted Reactions with Ethylene



SCHEME 3. Schematic Elucidation of the Addition Manner of THF Solvent Molecule to Sm(III) Carbenoid



quality of the large core ECPs treatment on Sm, and the calculations with small core ECPs treatment gave the barriers to reactions to be 13.8 kcal/mol relative to the corresponding reactant complex RC1. This confirms that the predictions from calculations using the large core ECPs treatment on Sm atom can give reasonable predictions for the reactions of $I_2Sm^{(III)}CH_2I$ with CH_2CH_2.

In an attempt to explore the additive effect of THF solvent molecules, we investigated the reactivity of I_2SmCH_2I/nTHF ($n = 1, 2$) toward ethylene. Based on the I_2SmCH_2I geometry that the dihedral angles of $D_{I-Sm-I-I'}$ and $D_{I-Sm-I-C}$ are 172.6° and 136.2°, respectively, it is possible for THF molecules to complex with Sm from above or below the planar of I−Sm−I (Scheme 3).

The first THF molecule was added to the carbenoid substrate from above the I−Sm−I plane in the manner with least steric hindering (Scheme 3). The strong interaction between the Sm and the O atom of THF weakens the Sm−C and Sm−I bonds to a noticeable degree, with their bond lengths increasing by 0.02−0.03 Å. The interaction between Sm and I′ (leaving group) is also weakened significantly, and the distance between Sm and I′ goes from 3.132 to 3.263 Å upon the addition of the THF molecule. This change disfavors the following cyclopropanation reactions, and it can be observed from the relative energies of TS1 as 4.0 kcal/mol and TS3 as 6.0 kcal/mol relative to corresponding starting materials. However, from the viewpoint of the trans effect coming from the ligand, the electron donor THF will decrease the ability of the Sm to coordinate with another ligand, e.g., ethylene, from the opposite position of THF, and this makes the reactant complex less stable. This hypothesis is supported by the stabilization energy of the reactant complexes, which are −8.9 kcal/mol for RC1 but only −3.2 kcal/mol for RC2 relative to corresponding starting materials. The overall effect leads to the lowering of the reaction barrier, which goes from 12.9 to 9.2 kcal/mol relative to the corresponding reactant complex upon the addition of the THF molecule.

The addition of the second THF molecule results in the coordination number of Sm being 6 and saturates the coordination ability of this lanthanide atom. This blocks the interaction between Sm and ethylene and so decreases the possibility of the formation of reaction complexes. In our current study, we could not find the existence of the reactant complex of $I_2SmCH_2I/2$THF with CH_2CH_2, and the starting materials appear to react directly without experiencing the formation of a significant complex. Thus, a barrier of 12.7 kcal/mol was found for the methylene transfer pathway.

For the carbometalation pathway, the addition of THF solvent molecule was found to significantly prevent the reaction from proceeding along this way, and a barrier to reaction of 17.5 kcal/mol is predicted relative to RC2 with the ZPE correction included. This suggests there is some difficulty in the formation of Sm−C (C═C) bond after the coordination of Sm with THF. Furthermore, no transition state could be located upon the addition of a second THF solvent molecule, and it appears the carbometalaton pathway is blocked.

In conclusion, the present DFT study describes the Sm(III) carbenoid as a reactive species toward ethylene. Methylene transfer and carbometalation are two competitive pathways in the reactions with ethylene with barriers to reactions of 12.9 and 15.4 kcal/mol, respectively, relative to corresponding reactant complex. The incorporation of THF solvent molecules was found to modify the mechanism of the reactions to a noticeable degree through the strong interaction of Sm···O. The behavior of THF in enhancing the cyclopropanation reactions can be outlined in the following two points:

1. Addition of THF helps stabilize the carbenoid species.
2. Addition of THF helps block the carbometalation pathway.

The addition of THF to samarium atom decreases the interaction between Sm and I′ (leaving group), which plays a negative role in the methylene insertion reaction, but it is even more significant that the incorporation of THF prevents Sm from binding with the ethylene substrate, which is the key step for the carbometalation pathway, and so blocks its progress. This benefits the reaction to move forward along the methylene transfer pathway.

Computational Details

The hybrid B3LYP density functional method[18] was used to investigate the reaction mechanisms of the I_2SmCH_2I carbenoid with ethylene. The stationary structures of the potential energy surfaces were fully optimized with C_1 symmetry at the B3LYP level of theory. Analytical frequency calculations were performed in order to confirm the character of the optimized structures and to obtain the zero-point energy correction. All of the calculations were carried out using the Gaussian 98 program suite.[21]

Hybridized basis sets were used to carry out geometry optimization and vibrational analysis. The composite basis set is composed of the 6-311G** basis set for the $CH_2{=}CH_2$ and the CH_2 group in the Sm carbenoid moiety, the 6-31G* basis set for the THF solvent molecule, the Lanl2DZ basis set[19] for the iodide atom, and the relativistic large core potentials (RECPs) for the Sm(III) atom, which is optimized by the Stuttgart−Dresden group.[20] The large core RECP treatment for Sm handles 5s, 5p, 5d, and 6s electrons as "valence" electrons, with the remaining electrons replaced by the RECP.[20] Thus, 11 valence electrons RECP was used for the Sm(III) center. In addition, in this large

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core RECP, the partially filled $4f^5$ electrons, which do not participate actively in the bonding, were also included in the core for a total of 51 electrons. The RECPs were used in combination with their optimized basis set with an additional f polarization function with an exponent of 0.2776.

For comparison purposes, a small core treatment on Sm was also employed for the reactions of $I_2SmCH_2I + CH_2CH_2$. The small core RECPs explicitly treat the 4f shell as a valence shell.

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Supporting Information Available: Selected output from the DFT calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies for the $I_2SmCH_2I/(THF)_n$ ($n = 0, 1, 2$) carbenoid reactants, transition states, and products for the cyclopropanation reactions investigated here. This material is available free of charge via the Internet at http://pubs.acs.org.

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