

The [2+1] Cycloadditions of Dichlorocarbene, Silylene, Germylene, and Oxycarbonylnitrene onto the Sidewall of Armchair (5,5) Single-Wall Carbon Nanotube

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The [2+1] cycloadditions of dichlorocarbene, silylene, germylene, and oxycarbonylnitrene onto the sidewall of an armchair (5,5) single-wall carbon nanotube (SWNT) have been investigated by means of a two-layered ONIOM (MO:MO) approach. It is shown that (i) the [2+1] cycloaddition on the nanotube sidewall is site-selective, the 1,2-pair site being favored, giving rise to the formation of three-membered ring species, (ii) the additions of dichlorocarbene and oxycarbonylnitrenes require small activation energies, whereas the additions of silylene and germylene are barrierless, (iii) thermal stability of the as-formed SWNT derivatives follows the order oxycarbonylnitrene \gg dichlorocarbene $>$ silylene $>$ germylene, and (iv) among the four reagents concerned, silylene is the best to be used for the functionalization and purification of SWNTs. Finally, we propose that the [2+1] cycloaddition products of SWNTs can be good starting points for further functionalization of SWNTs because the three-membered rings in these SWNT derivatives (e.g., silacyclopropano-SWNTs and aziridino-SWNTs) would be subject to a great deal of ring-opening reactions that have been well-established for the transformation of their organic analogues (e.g., aziridines and silacyclopropanes) in synthetic organic chemistry.

Introduction

Chemical functionalization of carbon nanotubes has recently attracted considerable attention^{1–3} in the research field of carbon nanotubes as a result of the appeal to make use of their fascinating structural, mechanical, electrical, and electromechanical properties for practical applications.^{4–9} Bearing a curved graphene-like structure, the sidewalls of carbon nanotubes were believed to be quite chemically stable. Hence, it is difficult to approach covalent functionalization of the sidewalls of carbon nanotubes. However, the curvatures of the sidewalls of carbon nanotubes furnish them higher chemical reactivity than that of flat graphenes,^{10–12} as evidenced by the progress recently made on this subject.^{1–3} It has been shown experimentally that covalent sidewall functionalization of single-wall carbon nanotubes (SWNTs) can be reached by means of, for example, fluorination,^{13,14} radical-addition-like alkylation,¹⁵ [2+1] cycloaddition,^{15–17} birch reduction,¹⁶ radical-addition-like arylation,^{18,19} 1,3-dipolar cycloaddition,^{20,21} ozonolysis,²² and amination.²³ In the meantime, theoretical predictions have been reported by us that it is viable to covalently functionalize the sidewalls of SWNTs by ozonation,²⁴ 1,3-dipolar cycloadditions (1,3-DCs),^{24,25} [4+2] cycloaddition of quinodimethane,²⁶ [2+3] cycloaddition of OsO₄,²⁷ and hydroboration.²⁸ In this paper, we report the results of our theoretical calculations concerning the [2+1] cycloadditions of dichlorocarbene (CCl₂), silylene (SiH₂), germylene (GeH₂), and oxycarbonylnitrene (CH₃OC(O)N) on the sidewall of an armchair (5,5)-SWNT.

So far there have been several reports regarding the addition of carbene^{16,17,29,30} and nitrene¹⁵ onto the sidewalls of SWNTs. The addition of oxycarbonylnitrenes (produced by thermal decomposition of alkyl azidoformate precursors) to SWNTs was

found to produce oxycarbonylaziridino-SWNTs.¹⁵ Haddon et al.^{16,17,29} found that dichlorocarbene can be added onto the sidewalls of SWNTs with about 2% of the carbon atoms in the SWNTs being involved in the cycloaddition reaction.^{16,17} A recent semiempirical quantum chemical study suggested that the addition of dichlorocarbene can form two isomers, that is, “horizontal-open” (i.e., CCl₂ is adsorbed on the 1,2-pair site shown in Figure 1) and “sloping-closed” (i.e., CCl₂ is adsorbed on the 2,3-pair site shown in Figure 1) isomers, on the sidewalls of armchair SWNTs, the former being more stable in energy.³⁰ No details of the addition mechanism have been reported so far. Our previous quantum chemical study revealed that the 1,3-DC onto the sidewall of armchair (5,5)-SWNT is site-selective, occurring preferentially on the 1,2-pair site.²⁴ This implies that the 1,2-pair site is more ene-like than the 2,3-pair site in the sidewalls of armchair SWNTs. Accordingly, we envision that the [2+1] cycloadditions would be more favorable on the 1,2-pair site than on the 2,3-pair site of the armchair (*n,n*) SWNTs. The purpose of the present theoretical work is twofold: (i) to explore the reaction pathway and site selectivity for the [2+1] cycloadditions of dichlorocarbene and oxycarbonylnitrene onto the sidewalls of SWNTs and (ii) to predict whether such [2+1] cycloaddition chemistry can be extended to other reactants, such as silylenes and germylenes, on the sidewalls of SWNTs.

Computational Details

A two-layered ONIOM (MO:MO) approach was used.^{31,32} The semiempirical AM1 method³³ and the hybrid density functional B3LYP method^{34,35} together with the standard 6-31G* basis set were employed for the low-level and high-level treatments, respectively. Geometry optimizations were performed within such two-layered ONIOM (B3LYP/6-31G*: AM1) approach using the Gaussian 98 program.³⁶ As depicted in Figure 1, the armchair (5,5)-SWNT was taken as an example

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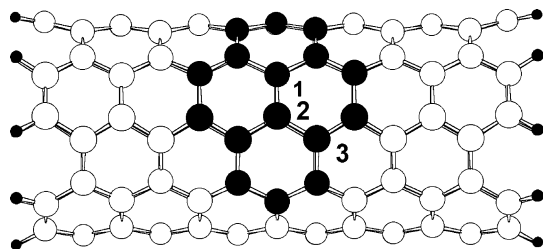


Figure 1. A $C_{130}H_{20}$ model tube representing an armchair (5,5)-SWNT, in which the sixteen shaded atoms are used for the high-level treatment in the two-layered ONIOM (B3LYP/6-31G**/AM1) calculations.

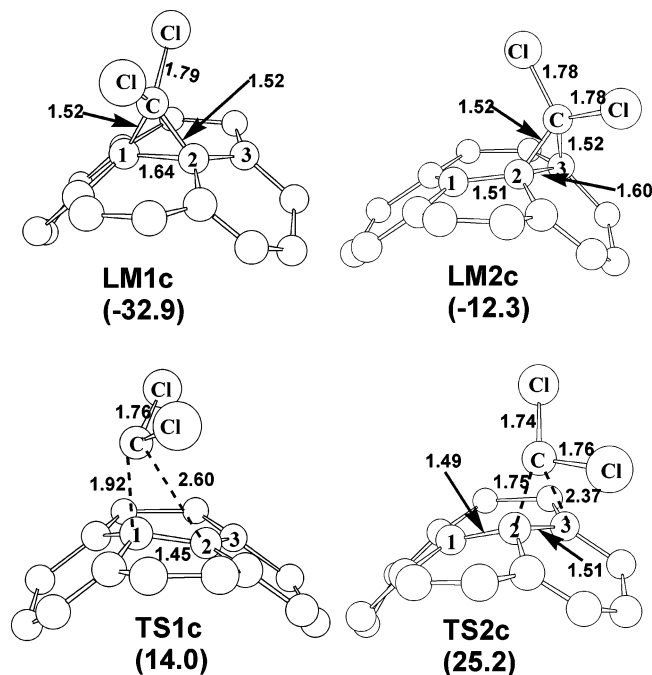


Figure 2. Optimized geometries (local view, bond length in Å) of products (**LM1c** and **LM2c**) and transition states (**TS1c** and **TS2c**) for the [2+1] cycloaddition of dichlorocarbene on the sidewall of (5,5)-SWNT. Energies (kcal/mol) relative to free reactants are given in parentheses.

and was represented by a $C_{130}H_{20}$ model tube (optimal diameter ≈ 6.8 Å), in which the high-level part is a C_{16} cluster (see the shaded atoms in Figure 1) in together with ten H atoms as boundary atoms (not shown in Figure 1). Such a modeling scheme was employed in our previous study of the 1,3-DCs and Diels–Alder addition of quinodimethane onto the sidewall of (5,5)-SWNT.^{24–26} Similar ONIOM modeling schemes were used in our theoretical investigation of the basis-catalyzed [2+3] cycloaddition of transition metal oxide (OsO_4) on (5,5)-SWNT²⁷ and by other groups in the theoretical studies of carbon nanotube chemistry.^{37–44}

Results and Discussion

A. Addition of Dichlorocarbene. As shown in Figure 1, there are two inequivalent C–C pair sites on the sidewall of armchair (5,5)-SWNT, denoted as 1,2-pair site and 2,3-pair site. The [2+1] additions of CCl_2 onto the 1,2-pair site and 2,3-pair site give rise to two cyclic products, **LM1c** and **LM2c**, respectively, as depicted in Figure 2. The formation energies predicted at the ONIOM (B3LYP/6-31G**/AM1) level are -32.9 kcal/mol for **LM1c** and -12.3 kcal/mol and for **LM2c**, indicating that the [2+1] cycloadditions of CCl_2 are exothermic on both sites with the addition on the 1,2-pair site being favored thermodynamically. In either case, the cycloaddition product is a three-

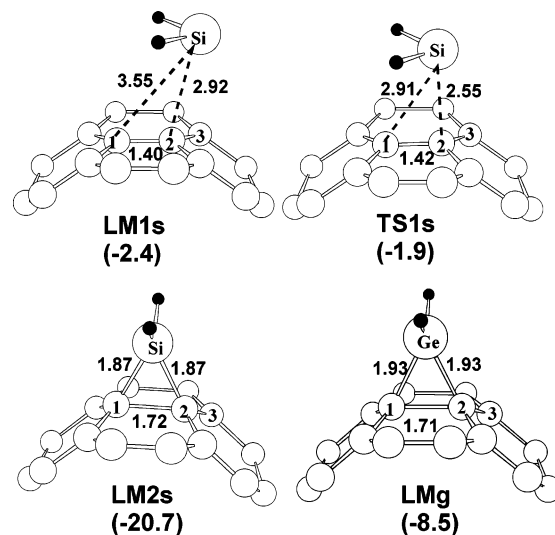


Figure 3. Optimized geometries (local view, bond length in Å) of precursor (**LM1s**), transition state (**TS1s**), and product (**LM2s**) for the [2+1] cycloaddition of silylene on the sidewall of (5,5)-SWNT and optimized geometry (local view, bond length in Å) of product (**LMg**) for the [2+1] cycloaddition of germylene. Energies (kcal/mol) relative to free reactants are given in parentheses.

membered ring species with the substrate C–C bond unbroken but elongated by ~ 0.2 Å. This is reasonable because the two substrate carbon atoms that are involved in the cycloaddition reaction adopt sp^2 hybridization/ sp^3 hybridization before/after cycloaddition.

The predicted transition states for the [2+1] cycloadditions of CCl_2 on the 1,2-pair and 2,3-pair sites are depicted as **TS1c** and **TS2c** in Figure 2, respectively. In **TS1c**, the nearest CCl_2 –SWNT distance is 1.92 Å, whereas in **TS2c** the nearest CCl_2 –SWNT distance is 1.75 Å. This clearly indicates that **TS1c** is earlier than **TS2c**. In accordance with the Hammond postulate,⁴⁵ the earlier transition state **TS1c** gives rise to a lower barrier height, that is, 14.0 kcal/mol for the [2+1] cycloaddition on the 1,2-pair site vs 25.2 kcal/mol for the addition on the 2,3-pair site. As such, the 1,2-pair site is kinetically much favored in the [2+1] cycloaddition of dichlorocarbene.

The above analysis clearly demonstrates that the [2+1] cycloaddition of dichlorocarbene on the sidewall of an armchair (5,5)-SWNT is highly site-selective and should preferentially take place over the 1,2-pair site. On account of the resemblance in reaction mechanism, similar site selectivity should be followed in the [2+1] cycloadditions of silylene, germylene, and nitrene on the sidewall of (5,5)-SWNT. Therefore only the 1,2-pair site has been considered in our calculations of the [2+1] additions of silylene, germylene, and oxycarbonylnitrene given below.

B. Addition of Silylene. As shown in Figure 3, the [2+1] cycloaddition of silylene onto the 1,2-pair site of (5,5)-SWNT also results in a three-member ring surface species, **LM2s**. The predicted formation energy for **LM2s** is -20.7 kcal/mol at the ONIOM (B3LYP/6-31G**/AM1) level of theory, showing that the cycloaddition process is exothermic and the silylene–SWNT bonding is weaker than the dichlorocarbene–SWNT bonding concerned above. In addition to the cycloaddition product **LM2s**, a precursor complex **LM1s** and a transition state **TS1s** have been located for the [2+1] cycloaddition process of silylene (see in Figure 3). The silylene–SWNT bonding energy in the precursor complex **LM1s** is predicted to be at a value of only 2.4 kcal/mol, along with a large silylene–SWNT distance of 2.92 Å. Hence, this precursor state is a van der Waals complex

in nature. The transition state **TS1s**, which has a silylene–SWNT distance of 2.55 Å, is predicted to be higher than **LM1s** in energy by only 0.5 kcal/mol. Therefore, the [2+1] addition of silylene onto (5,5)-SWNT is overall barrierless and would readily occur at low temperatures. This is similar to its molecular analogue, that is, the [2+1] cycloaddition of silylene with simple alkenes, which was found to be barrierless and highly exothermic.^{46–49} Previous *ab initio* calculations^{47–49} predicted exothermicities higher than 40 kcal/mol for the barrierless [2+1] cycloaddition of silylene with ethylene. The much lower exothermicity for the cycloaddition of silylene onto the sidewall of SWNT can be ascribed to the much higher stability of the SWNT sidewall induced by the high π -conjugation.

The prediction given above strongly suggests that the formation of SWNT silirane derivatives is plausible. In practice, silylenes can be produced, for example, by photolyzing trisilanes.⁵⁰ The as-produced silylenes can be readily added onto the sidewalls of pristine SWNTs or solubilized SWNTs in organic solutions. It is note-worthy that a similar technique was successfully employed to synthesize fullerene silirane derivatives.⁵¹ Furthermore, the moderate silylene–SWNT bonding in the SWNT silirane derivative suggests the following: (i) the as-formed SWNT silirane derivatives can be thermally decomposed, leading to a functionalization–defunctionalization process that can be used to purify SWNTs; (ii) the three-membered ring silacyclopropane-like surface species would be subject to further chemical manipulations, such as ring opening accompanied by the attachment of other chemical functional groups.⁵²

C. Addition of Germylene. The [2+1] addition of germylene onto the 1,2-pair site of (5,5)-SWNT gives rise to the formation of SWNT germirane derivative, **LMg**, as depicted in Figure 3. This process is predicted to be exothermic by only 8.5 kcal/mol, far less exothermic than the [2+1] cycloadditions of dichlorocarbene and silylene on the sidewall of (5,5)-SWNT. It is also less exothermic than the [2+1] cycloaddition of germylene with ethylene, for which an exothermicity of 25 kcal/mol was predicted in previous B3LYP/6-31G* calculations.⁵³ The instability of germylene adduct compared with the silylene and carbene adducts can be attributed to the weakness of Ge–C bonds compared with Si–C bonds and C–C bonds, as it was estimated that a germirane skeleton has a slightly lower strain energy than does a silirane skeleton.⁵³

No transition state has been located in our calculations for the [2+1] cycloaddition of germylene onto (5,5)-SWNT. This is different from its molecular analogue ($\text{GeH}_2 + \text{C}_2\text{H}_4$), for which previous B3LYP/6-31G* calculations predicted a π -complex precursor and a transition state, both lower than free reactants in energy.⁵³ Though the addition of germylene is barrierless on the SWNT, the rather weak germylene–SWNT bonding in the as-formed SWNT germirane derivative suggests that germylene might not be a good candidate to be used in the sidewall functionalization of SWNTs.

D. Addition of Nitrene. The [2+1] addition of oxycarbonylnitrene on the sidewall of (5,5)-SWNT is predicted to be exothermic by 66.2 kcal/mol at the ONIOM (B3LYP/6-31G*:AM1) level of theory. The product **LM1n** is the oxycarbonyl-aziridino-(5,5)-SWNT containing a three-membered C–C–N ring, as depicted in Figure 4. A transition state **TS1n** (see in Figure 4) has been located, which gives rise to an activation barrier of 7.2 kcal/mol for such a [2+1] cycloaddition process. This clearly demonstrates the facileness of the [2+1] addition of nitrene onto the sidewall of (5,5)-SWNT. Analogous [2+1] addition of nitrenes onto [60]-fullerene was reported

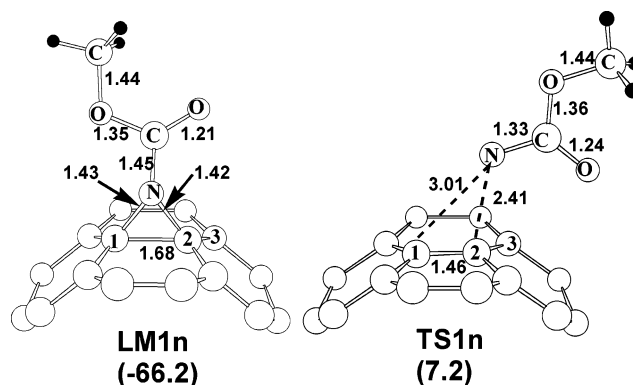


Figure 4. Optimized geometries (local view, bond length in Å) of product (**LM1n**) and transition state (**TS1n**) for the [2+1] cycloaddition of oxycarbonylnitrene on the sidewall of (5,5)-SWNT. Energies (kcal/mol) relative to free reactants are given in parentheses.

previously,^{54–56} for which an activation energy of 3.6 kcal/mol was predicted at the B3LYP/6-31G**/AM1 level of theory.⁵⁶

It should be noted that for the four [2+1] addition processes concerned above the addition of oxycarbonylnitrene is the most exothermic. On the other hand, for the corresponding retro-[2+1] addition processes, the oxycarbonylnitrene case demands the largest activation energy (73.4 kcal/mol), whereas the germylene case requires the lowest activation energy (8.5 kcal/mol). This means that the as-formed oxycarbonyl-aziridino-SWNT is the most stable among the four SWNT derivatives concerned. With a too-high activation energy, the retro-[2+1] cycloaddition of oxycarbonylnitrene can hardly occur even at elevated temperature. However, the aziridino-SWNTs that have three-membered ring species would be subject to nucleophilic ring-opening accompanied by the attachment of other organic functional groups.⁵⁷ In this regard, the well-established synthetic methods for aziridine ring-opening⁵⁷ can be used.

E. [2+1] Cycloadditions on the (5,5)-SWNT and C₆₀-Fullerene: Similarities and Differences. It is interesting to compare the as-concerned [2+1] cycloaddition chemistry on the sidewall (5,5)-SWNT with the known fullerene chemistry. C₆₀-Fullerene displayed high regioselectivity in various cycloaddition reactions.^{58,59} For example, direct [2+1] cycloaddition of carbenes occurs preferentially onto the fullerene 6–6 ring fusions, affording exclusively closed [6,6]-adducts with the reacted C–C bond intact.⁵⁸ Yet, open [5,6]-adducts of carbenes, in which the 5–6 ring fusion C–C bond is broken, can be obtained in a much more indirect way, for example, by 1,3-dipolar cycloaddition of diazo compounds followed by thermal elimination of N₂.^{58,59} It is “the bent structure of the carbon network C₆₀ and the filling of its molecular orbital with 60 π -electrons” that dictates such intriguing regiochemistry.⁵⁹ Empirically, C₆₀ can be regarded as an assembly of C=C double bonds (at 6–6 ring fusions) connected by C–C single bonds (at 5–6 ring fusions).⁶⁰ This accounts for the regioselectivity of C₆₀ in the direct [2+1] cycloaddition reactions. As alluded to above, the [2+1] cycloadditions on the (5,5)-SWNT also display a regioselectivity with the addition onto the 1,2-pair site being favored. Differing from the adducts of C₆₀, the [2+1] additions on both the 1,2-pair and 2,3-pair sites of the (5,5)-SWNT give rise to cycloaddition products with reacted C–C bonds being preserved, despite that the direct [2+1] addition on the 2,3-pair site is disfavored. Furthermore, the much higher stability of the 1,2-pair adducts compared with the 2,3-pair adducts⁶¹ suggests that the 2,3-pair adducts, if formed, could be readily isomerized into the 1,2-pair adducts.

Concluding Remarks

We have performed ONIOM (MO:MO) calculations on the [2+1] cycloadditions of dichlorocarbene, silylene, germylene, and oxycarbonylnitrene onto the sidewall of an armchair (5,5) single-wall carbon nanotube. The calculations revealed that the [2+1] cycloaddition is site-selective on the nanotube sidewall, the 1,2-pair site being favored. The thermal stability of the as-formed SWNT derivatives follows the order oxycarbonylnitrene \gg dichlorocarbene $>$ silylene $>$ germylene. Our calculations suggest that besides the experimentally known [2+1] cycloadditions of oxycarbonylnitrene and dichlorocarbene, the [2+1] addition of silylene can be used for the functionalization and purification of SWNTs. Furthermore, it is interesting to note that the [2+1] cycloaddition products all contain three-membered rings in which the substrate C–C bonds are retained but severely elongated because of rehybridization induced by the addition reactions. These cyclic derivatives would be subject to a great deal of ring-opening reactions that have been well-established for the transformation of their organic analogues (e.g., aziridines and silacyclopropanes) in synthetic organic chemistry.^{52,57} Because various organic functional groups can be introduced onto the sidewalls of SWNTs in these ring-opening reactions,^{52,57} the [2+1] cycloaddition products of SWNTs can be good starting points for further functionalization of SWNTs. This work indicates further routes for routine chemical manipulation of SWNTs.

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