Addition of Carbenes to the Sidewalls of Single-Walled Carbon Nanotubes

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Abstract: The addition of carbenes CX_2 (X=H, Cl) to single-walled carbon nanotubes (SWNTs) was investigated by density functional theory and finite, hydrogen-terminated nanotube clusters or periodic boundary conditions in conjunction with basis sets of up to polarized triple-ζ quality. For armchair [(3,3) to (12,12)] and zigzag tubes [(3,0) to (18,0)], reaction of CH_2 with the C−C bond oriented along the tube axis (A) is less exothermic than with those C−C bonds having circumferential (C) orientation. This preference decreases monotonically with in-creasing tube diameter for armchair, but not for zigzag tubes; here, tubes with small band gaps have a very low preference for circumferential addition. Axial addition results in cyclopropane products, while circumferential addition produces "open" structures for both armchair and zigzag tubes. The barriers for addition of dichlorocarbene to a (5,5) SWNT, studied for a finite $C_{90}H_{20}$ cluster, are higher than that for addition to C_{60}, in spite of similar diameters of the carbon materials. Whereas addition of CCl_2 to [60]fullerene proceeds in a concerted fashion, addition to a (5,5) armchair SWNT is predicted to occur stepwise and involve a diradi-caloid intermediate according to B3LYP, PBE, and GVB-PP computations. Addition to C bonds of (5,5) armchair tubes resulting in the thermodynamically more stable insertion products is kinetically less favorable than that to A bonds yielding cyclopropane derivatives.

Keywords: carbenes · carbon · density functional calculations · nanotubes · reaction mechanisms

Introduction

The reaction of carbenes, molecules having divalent carbon atoms,[1,2] with organic π systems has widely been applied for the synthesis of cyclopropanes and has received much attention, both experimentally and theoretically.[3,4] An unusual but highly interesting organic π system is provided by the surface of carbon nanotubes (CNTs), whose extended π systems give rise to metallic or semiconducting electronic properties depending on the structure of the tubule (see Figure 1). These π systems can also be used for chemical functionalization of the CNT sidewalls, and a wide range of derivatization protocols have been developed. These were recently reviewed by Hirsch and Vostrowsky,[5] while Lu and Chen have given a thorough account of the theoretical aspects of nanotube functionalization.[6] Haddon et al. pioneered the addition of carbenes to the sidewalls of single-

walled carbon nanotubes (SWNTs).[7–10] Using Seyferth's phenyl(bromodichloromethyl)mercury reagent, a precursor for free dichlorocarbene CCl_2,[11] Haddon et al. could add this electrophilic carbene and extensively characterize the resulting functionalized CNT.[8–10] Nitrenes, a related class of
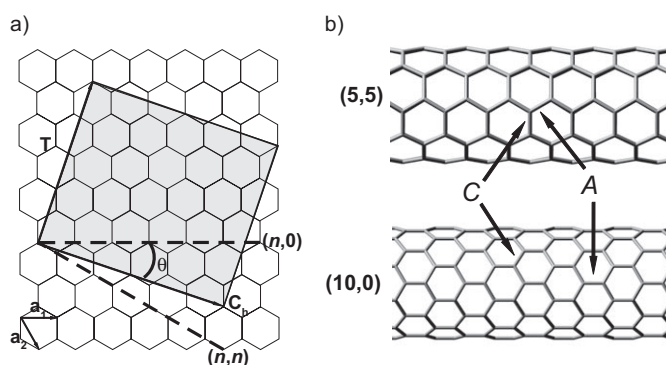
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Figure 1. a) Rolling of graphene sheet results in nanotubes with zigzag [(n,0), θ=0°] and armchair [(n,n), θ=30°] structures having limiting chiral angles θ. b) The two symmetry-unique C−C bonds in armchair (top) and zigzag (bottom) carbon nanotubes, labeled as "circumferential" C and "axial" A.

subvalent neutral reactive intermediates, could also be successfully added to the CNT sidewalls.[12,13]

Theoretical investigations of the addition of carbenes to SWNTs, although initially treated with skepticism,[14] are in support of the experimental observations.[15–19] Computations with various density functionals on a number of CNT model systems arrive at high exothermicities of around $-90\ kcal\,mol^{-1}$ for the addition of triplet methylene to the CNT sidewalls.[16,17] Infinitely long zigzag and armchair SWNTs, the two types of tubules with extreme chiral angles θ (0° and 30°), only have two symmetry-unique types of C–C bonds (Figure 1). The computations suggest that in both types of tubes one of these bonds, the "axial" bond A, reacts with a carbene, or more generally also with nitrenes, oxygen, and sulfur atoms, with formation of the usual three-membered ring.[16] The other bond, termed "circumferential" C in the remainder of this paper, undergoes carbene insertion into the C–C bond, and opening of the sidewalls was predicted based on computations. This latter mode of reaction was found to be more favorable than cyclopropane formation by $29\ kcal\,mol^{-1}$ for a (5,5) armchair nanotube.[16,17]

Systematic investigations of carbene reactivity towards SWNTs taking into account different chiral angles and tube diameters, though highly desirable for understanding SWNT chemistry, are not available today. Similarly, available mechanistic investigations are of rather limited scope.[15,19] The present paper attempts to address these aspects of carbene and carbon nanotube chemistry by using DFT methods in conjunction with finite and infinite CNT models. The paper is structured in the following way: 1) The smallest model for studying carbene addition to infinitely long CNTs is established; 2) the models are used to determine the CH_2 binding energies as a function of tube diameter and limiting chiral angles $\theta = 0°$, 30° (zigzag and armchair); and 3) the reaction pathway for addition of dichlorocarbene CCl_2 to the (5,5) armchair CNT is mapped out.

Results and Discussion

Evaluation of models for studying CNT chemistry: lengths of finite clusters and unit cells in periodic calculations: The interaction of a single molecule with an infinitely long SWNT can be simulated computationally either by using a finite-length fragment of the nanotube or by imposing periodic boundary conditions (PBC). In each case it is necessary to determine the minimum length of the SWNT model for deriving the binding energy of a single addend molecule to the sidewall of a SWNT [Eqs. (1) and (2)].
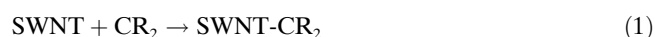
$$SWNT + CR_2 \rightarrow SWNT\text{-}CR_2 \qquad (1)$$

$$E_{rxn} = E(SWNT\text{-}CR_2) - E(SWNT) - E(CR_2) \qquad (2)$$

In other words, the reaction energy must be converged with respect to the size of SWNT model if intrinsic properties are sought. This convergence guarantees the elimination of effects from edges in finite cluster computations or addends in neighboring unit cells in PBC calculations. The previous study on carbene addition focused on the open (5,5) armchair tube by using finite clusters of various lengths, $C_{30+10n}H_{20}$, and on the circumferential C–C bond C.[17] It concluded that a fully benzenoid[20,21] model system should be used, and that $C_{90}H_{20}$ would be the minimal model for studying the chemistry of the (5,5) armchair tube.[17] Consequently, this $C_{90}H_{20}$ model was used to study the reaction mechanism.

Application of the cluster approach to zigzag nanotubes is problematic, as their electronic structure differs from that of armchair tubes. The latter have a band crossing, which is located at $2/3\mathbf{k}$ within the zone-folding approximation. Consequently for finite-length clusters studied earlier, the band gaps decrease with increasing SWNT length, but remain large enough for spin-restricted Kohn–Sham wave functions to be stable. In contrast, the bands of zigzag tubes have the smallest (or vanishing) gaps at the center Γ of the Brillouin zone. Finite models consequently also have very small HOMO–LUMO gaps that result in triplet instabilities of the KS wave functions.[22] The spin-unrestricted solutions are significantly lower in energy, but are plagued by very large $\langle S^2 \rangle$ values (e.g., 2.91 for the (10,0) tube fragment $C_{100}H_{20}$ at the PBE/3-21G level).

I therefore prefer to study these zigzag systems, and for comparison also the armchair tubules, using periodic boundary conditions. The dependence of the addition energy E_{rxn} of $CH_2(^3B_1)$ with respect to the lengths of the unit cells, given in multiples of the minimum unit cell of pristine tubes, is shown in Figure 2. For both (5,5) and (10,0) tubes a smooth convergence of the addition energy with respect to the length of the unit cell is obtained for bonds A and C (see Figure 2).

Based on these results, two unit cells for armchair and three unit cells for zigzag tubes were used for further study of the dependence on diameter of E_{rxn}. Note that the binding energy of $CH_2(^3B_1)$ to bond A of the (5,5) SWNT derived from the PBC approach, $-98.0\ kcal\,mol^{-1}$, is in very good agreement with that derived from the $C_{90}H_{20}$ finite cluster, $-98.5\ kcal\,mol^{-1}$ at the PBE/6-31G*//PBE/3-21G level of theory.

Addition energies of CH_2: dependence on addition site, nanotube chiral angle, and diameter: As expected from the previous investigation of the addition of CH_2 to (5,5) armchair nanotubes,[17] for all armchair tubes between (3,3) and (12,12) reaction with the circumferential C–C bonds yields the insertion products throughout, while the reaction with axial C–C bonds results in formation of a three-membered ring. The corresponding C–C distances range from 2.15 to 2.26 Å [(12,12) to (3,3)] for insertion and are around 1.57 Å for cyclopropanation products. The long C–C distance resulting from circumferential addition of CH_2 to the (12,12) CNT is in contrast to recent results of Lu et al.,[23] possibly due to the larger basis set and more accurate reciprocal space integration in the present work. Insertion is more fa-
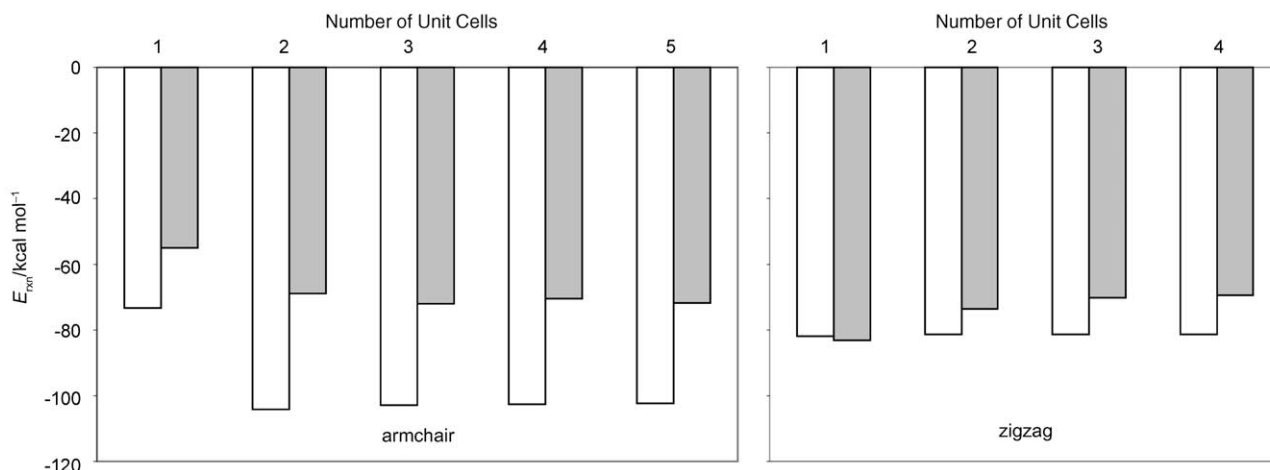
Figure 2. Dependence of the binding energy of $CH_2(^3B_1)$ to the circumferential (white) or axial (gray) C−C bonds in (5,5) armchair and (10,0) zigzag carbon nanotubes on the number of unit cells at the PBC-PBE/3-21G level of theory.

vorable than cyclopropanation for all armchair tubes considered (Figure 3). For both types of reactions the exothermicity decreases monotonically with increasing tube diameter. Also the preference for the circumferential mode, $\Delta E_{rxn} = (E_{rxn}^A - E_{rxn}^C) > 0$, decreases with increasing diameter; in the limit of a planar graphene sheet, the two modes are degenerate due to symmetry.

For (3,0) to (18,0) zigzag tubes the reaction with circumferential bonds also results in insertion products (C−C 2.10–2.29 Å), while that with axial bonds yields cyclopropane derivatives (C−C 1.50–1.56 Å). For both modes of reaction the binding energies also decrease with increasing SWNT diam-

eter, and insertion into circumferential C−C bonds is more favorable than cyclopropanation of axial bonds. However, the energy difference ΔE_{rxn} between axial and circumferential modes is significantly smaller than for armchair tubes. More importantly, however, ΔE_{rxn} does not decrease monotonically with tube diameter as found for armchair tubes. Rather, an oscillatory behavior of ΔE_{rxn} with a period of three is observed. This seems to be related to the electronic nature of the zigzag tubes. Within the zone-folding approximation (ZFA), zigzag $(n,0)$ tubes are metallic for $n = 3k$ $(k = 1, 2, 3,...)$ and, with exception of the highly strained (3,0) tube, these tubes show the least preference for circum-
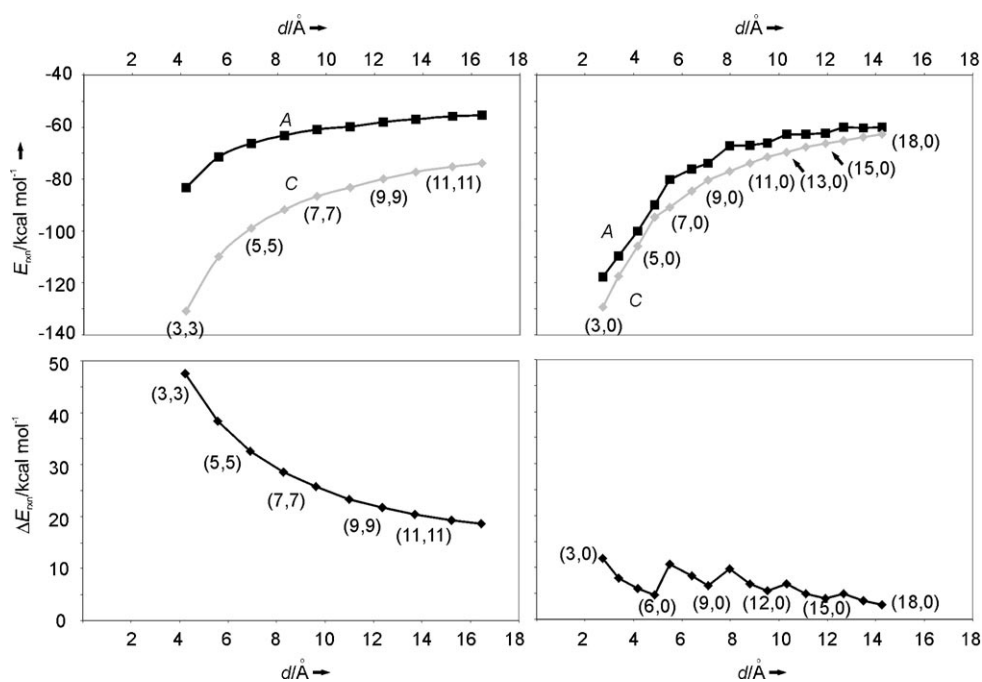

Figure 3. Top: Binding energies of $CH_2(^3B_1)$ to circumferential (C) and axial (A) C−C bonds in armchair (left) [(3,3) to (12,12)] and zigzag (right) [(3,0) to (18,0)] nanotubes as obtained at the PBC/6-31G*//PBC/3-21G level by imposing periodic boundary conditions. Bottom: Dependence on diameter of the preference of addition to circumferential C−C bonds in armchair (left) and zigzag (right) tubes. The solid lines are intended to guide the eye.

ferential binding. Note that deviations of the band gaps from predictions based on the ZFA are well documented for small-diameter zigzag tubes,[24–26] and that the DFT computations give vanishing band gaps for $n = 3, 4, 5$, and 6, and finite band gaps (0.02–0.14 eV) for (9,0), (12,0), (15,0), and (18,0) tubes, in agreement with these studies. However, the actual finite band gaps of the "metallic" tubes ($n = 6, 9, 12, 15, 18$) are much smaller than those that are semiconducting within the ZFA. Hence, zigzag tubes $(n,0)$ ($n = 6, 9, 12, 15, 18$) with very small band gaps show only small preference for addition of methylene to axial bonds.

The preference for insertion versus cyclopropanation on reaction with carbenes discussed above for CNTs is related to the well-known valence tautomerization of an aromatic 1,6-methano[10]annulene (**1**) and the cyclopropane derivative bisnorcaradiene (**2**), which can result from carbene addition to the central bond of naphthalene.[27]
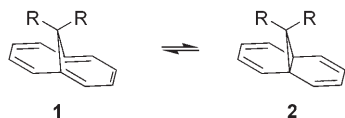
Experimental and computational data agree that the preference for closed versus open structures depends on the substituent R at the methano bridge $-CR_2-$; for R = H, F the "open" 1,6-methano[10]annulene is preferred.[28–30] As the naphthalene unit is also embedded in the SWNT sidewall, open structures might be expected to form irrespective of the addition site and tube chiral angle. However, a balance between strain in the pristine tube and in the reaction products on the one hand and homoconjugative stabilization on the other appears to determine the structure. The *C* bonds hold the tubular structure and are strained, more so in armchair than in zigzag tubes. Therefore, the *C* bonds readily break on bridging to give open products, which can additionally enjoy homoconjugative stabilization. This mechanical argument is in agreement with the monotonic decrease of E_{rxn} for *C* bonds with increasing diameter for both armchair and zigzag tubes. By the same mechanical argument, the axial bonds *A* are only slightly (armchair) or not at all (zigzag) strained, while their breaking would result in significant strain and ultimately cause a kink in the entire CNT backbone. This appears to be too costly energetically to be counterbalanced by homoconjugative stabilization.

Energy profiles for the addition of CCl₂ to [60]fullerene and to (5,5) SWNT: As the addition of carbenes to the circumferential *C* bonds in armchair tubes is always more exothermic than addition to an axial bond, a selective reaction of carbenes with *C* bonds of armchair tubes might be possible. Such an assumption, based on the Bell–Evans–Polyani principle, requires a study of the corresponding transition states for verification. Therefore, a detailed investigation of the re-

action path of CCl₂ addition, the carbene experimentally employed by Haddon et al.,[8–10] is worthwhile as significant insight into the properties of CNT is expected to be gained. Hence, the energy profile for CCl₂ addition using the finite $C_{90}H_{20}$ model of a (5,5) armchair tube is investigated here. The cluster approach was chosen due to the need to characterize transition states by computation of the Hessian eigenvalues, a task too demanding with PBC. For comparison and evaluation of the theoretical approach the $C_2H_4 + CF_2$ and $C_{60} + CCl_2$ addition reactions are also considered.

Carbon nanotubes and fullerenes can ultimately be considered to be alkenes. The addition of singlet carbenes to alkenes is well known to proceed in a single step[31–33] and in a non-least-motion fashion,[4,34–36] as the least-motion mechanism is symmetry-forbidden in the sense of the Woodward–Hoffmann rules.[37] The reaction is generally considered to proceed in two phases: in the first the carbene approaches suprafacially to the π system and thereby maximizes the electrophilic carbene–alkene interaction, that is, the HOMO(olefin)–LUMO(carbene) interaction in terms of frontier orbital theory. In the second phase the nonbonding electron pair of the carbene participates in nucleophilic interaction with the LUMO of the alkene. Depending on the natures of the carbene and the olefin, the addition reaction involves a single transition state on the potential energy surface or none at all in the case of $CH_2(a^1A_1) + C_2H_4$.[38] The structure of the TS is intimately related to the electronic structures of the carbene and the olefin.[39–43] For the reaction of dichlorocarbene with the prototypical ethene a transition state is found at the B3LYP and MP2 levels of theory, and the classical barrier for the reaction is computed to be 1.7 kcal mol⁻¹ at the B3LYP/6-311G**//B3LYP/6-31G* level.[44]

[60]Fullerene is a strongly electrophilic substrate and as such reacts with electrophilic and nucleophilic carbenes at the [6,6] bonds. Computations on $C_{60}CH_2$ showed that the [6,6] adduct, methanofullerene (**1**), is more stable thermodynamically than the [5,6] adduct, methanohomofullerene (**2**), which is characterized by a long C–C distance beyond 2 Å between the bridgehead carbons.[29,45–47] The addition of CCl₂ ($^1A_1$ state) to both the [6,6] and [6,5] bonds of the C_{60} molecule proceeds as outlined above for a typical alkene: there is one transition state for each addition site (**TS[6,6]** and **TS[5,6]**), which lie 1.6 and 3.9 kcal mol⁻¹, respectively, above the separated reactants $C_{60} + CCl_2$. Correction for ZPVE gives 1.8 and 4.1 kcal mol⁻¹ (Figure 4 and Figure 5).

Computation of the intrinsic reaction coordinate (IRC) confirms that **TS[6,6]** connects to the cyclopropanation product, the methano[60]fullerene $C_{61}H_2$. Both **TS[6,6]** and **TS[5,6]** are similar in geometry and share the structural features typical for the TSs of carbene–olefin reactions (Figure 4). In accord with its higher energy, **TS[5,6]** is located "later" along the reaction coordinate, as judged from the distance between the carbene carbon atom and the fullerene. The relative energies of the two transition states are in agreement with the Bell–Evans–Polyani principle: the more exothermic reaction has a lower barrier.
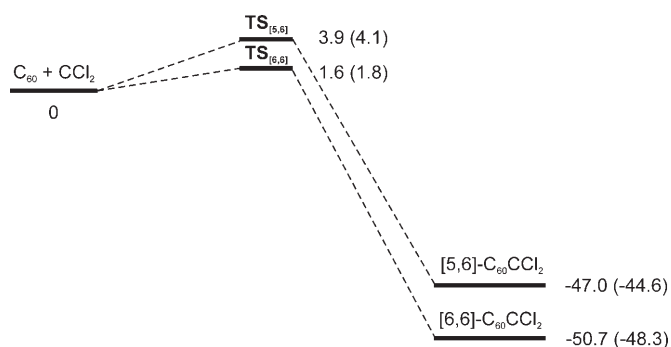
Figure 4. Schematic energy profile [kcal mol^{-1}] for the reaction of [60]fullerene with singlet dichlorocarbene as computed at the B3LYP/6-311G**//B3LYP/6-31G* level of theory. Zero-point-corrected data are given in parentheses.

Figure 6. Schematic energy profile [kcal mol^{-1}] for the addition of singlet dichlorocarbene to the central circumferential (C) and axial (A) bonds of a finite (5,5)-CNT slab of $C_{90}H_{20}$ stoichiometry at the B3LYP/6-311G**//B3LYP/6-31G* (regular print), PBE/6-311G**//PBE/6-31G* (italic), and GVB(1)-PP/6-31G*//B3LYP/6-31G* (bold) levels of theory.
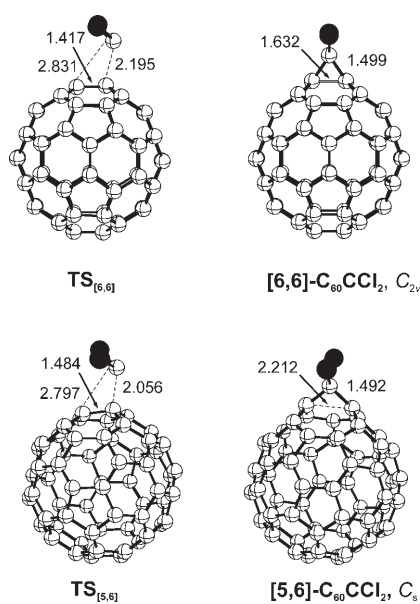

Figure 5. Transition structures and products computed for the addition of singlet dichlorocarbene (chlorine: black spheres) to the [6,6] and [6,5] bonds of [60]fullerene at the B3LYP/6-31G* level of theory. Bond lengths are given in ångstrom.

Figure 7. Transition structures and diradicaloid intermediate **D** computed for the addition of dichlorobenzene (chlorine: black spheres) to the axial (A) and circumferential (C) bonds of a (5,5)-$C_{90}H_{20}$ model as computed at the UB3LYP/6-31G* level of theory. Important distances are given in ångstrom.

While [60]fullerene is an excellent electron acceptor (low-lying LUMO) and a good π donor (high-lying HOMO), carbon nanotubes are even better Lewis acids and Lewis bases by virtue of their small or vanishing band gap. For example, the Fermi level (crossing of highest and lowest crystal orbital bands, HOCO and LUCO) of the (5,5) armchair tube is at −4.03 eV, while C_{60} has HOMO and LUMO at −5.50 and −3.83 eV, respectively (PBE/6-31G* data). This change in electronic structure has a pronounced effect on addition with CCl_2: it turns into a two-step reaction involving a diradicaloid intermediate.

On approach of CCl_2 to the circumferential and axial C−C bonds of the (5,5) SWNT the transition states **TS1c** and **TS1a** are encountered (Figures 6 and 7). In contrast to the
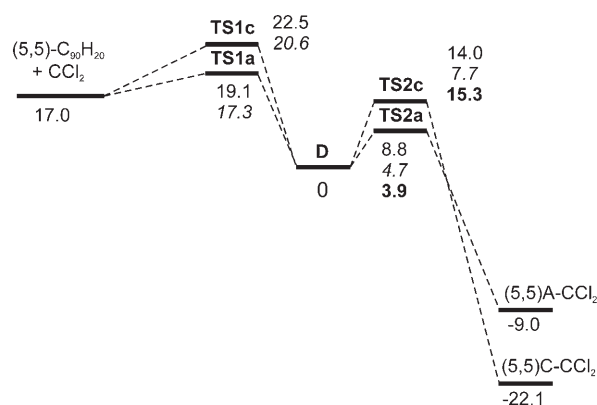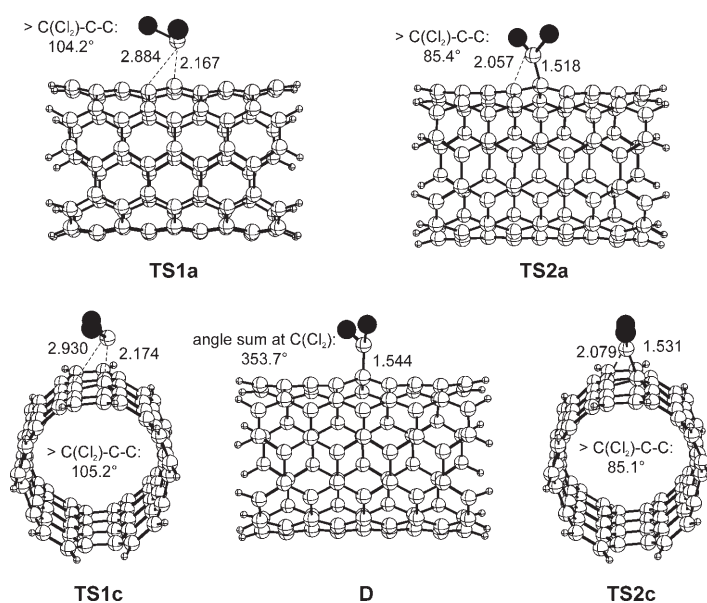
transition states for the $C_{60}+CCl_2$ reaction, the RB3YLP solutions have triplet instabilities; the $\langle S^2 \rangle$ expectation values in UB3LYP optimized structures of 1.01 and 0.42 are indicative of some diradical character. The transition structures **TS1c** and **TS1a** are very similar in geometry to those for addition to C_{60} (Figure 5), and are somewhat higher in energy: 5.5 and 2.1 kcal mol^{-1} with respect to the separated reactants. The axial bond A in (5,5) SWNT is more easily attacked than the circumferential bond C, in spite of the higher exothermicity of the addition to C.

The next stationary point along the reaction path is diradicaloid **D** (see Figure 7), which is bound by 17 kcal mol^{-1} with respect to the reactants. It is characterized by a short C−C bond of 1.544 Å and a pyramidalized CCl$_2$ moiety. Upon exploration of the potential energy surface for rotation about the C−CCl$_2$ bond another higher lying isomer was found at the UB3LYP/3-21G level of theory. This rotamer, however, converges to **D** on geometry optimization at the UB3LYP/6-31G* level.

Two additional transition states were located: in one the CCl$_2$ moiety is bent towards the adjacent carbon atom in circumferential direction (**TS2c**), and in the other in axial direction (**TS2a**) (see Figure 7). Both of these TSs describe ring-closure reactions and are early compared to the reaction products. The barrier heights for these two reaction channels emanating from the diradicaloid intermediate **D** are sizeable, 14.0 and 8.8 kcal mol^{-1}, respectively, at the UB3LYP/6-311G**//UB3LYP/6-31G* level of theory.

Qualitative agreement with the hybrid Hartree–Fock DFT data provided by UB3LYP is obtained with the gradient-corrected UPBE functional. However, the barriers for the ring-closure reaction via **TS2c** and **TS2a** are significantly lower. In particular, the relative energy of **TS2a**, decisive for the existence of a diradicaloid intermediate on the potential energy surface, is only 4.7 kcal mol^{-1}. Therefore the study was extended to the GVB(1)-PP/6-31G* level of theory, which provides an adequate zeroth-order description of diradicaloid species. While the barrier of 15.3 kcal mol^{-1} via **TS2c** at GVB is similar to UB3LYP data, it is smaller (3.9 kcal mol^{-1}) for the reaction through **TS2a** than at UB3LYP, but in reasonably good agreement with UPBE.

All available computational data are thus in favor of a nonconcerted mechanism for addition of CCl$_2$ to a (5,5) armchair CNT. Two-step mechanisms for carbene addition to olefins were discussed previously by Jones and Moss.[4] While the recent computational investigation of Merrer and Rablen[48] does not lend support to the existence of intermediates in the reaction of CCl$_2$ with cyclopropenes,[49–52] the rearrangements of vinyl-substituted cyclopropylcarbenes are best rationalized by a diradicaloid intermediate.[53,54] The computational analysis of the ethylene+CF$_2$ reaction by Bernardi et al.[55] at the (4,4)-CASSCF/6-31G* level suggested a two-step mechanism with a diradical intermediate having a barrier to ring closure of only 0.2 kcal mol^{-1}. This barrier was found to disappear on inclusion of multireference second-order perturbation theory single-point energy corrections.

From comparison with the C$_2$H$_4$+CF$_2$ reaction (see Supporting Information) it is concluded that UB3LYP overestimates the stability of a potential diradicaloid intermediate in the C$_2$H$_4$+CF$_2$ reaction, while the concerted mechanism obtained at the PBE level is in agreement with more elaborate multireference configuration interaction results. Based on this comparison, the UB3LYP level possibly overestimates the stability of **D**. The lower barrier obtained for ring closure via **TS2a** at the UPBE and GVB levels, 4–5 kcal mol^{-1}, appears to be a more reasonable estimate for this

process. While desirable for further evaluation of the stability of the diradicaloid intermediate, higher level computations cannot be performed at this time. However, from a chemical point of view, its existence appears possible due to the good stabilization the diradicaloid can enjoy from the presence of the extended π system. This special stabilization by an adjacent π system was already invoked by Jones et al. in rearrangements of vinyl-substituted cyclopropylcarbenes.[4,53,54] Similarly, Schreiner et al.[56,57] concluded in a recent investigation of the Cope and related rearrangements that two-step mechanisms become competitive with conventional concerted pathways if diradicaloid intermediates can be stabilized by delocalization, be it allylic or aromatic.

The finding of a nonconcerted reaction mechanism for addition of singlet CCl$_2$ to a (5,5) armchair tube is at variance with a recent study on carbene addition to this nanotube using the B3LYP functional.[58] Su identified one transition state for addition of singlet dimethylcarbene and thus describes the reaction as a concerted process.[58] However, these computations did not probe for spin-unrestricted solutions of the Kohn–Sham equations and were thus inappropriate for locating diradicaloid structures. Note that the investigation described here is restricted to singlet dichlorocarbene, while the influence of substituents bound to the carbene center on the reaction mechanism has not been investigated. Addition of dimethylcarbene to a (5,5) CNT may not involve an intermediate, but more computational investigations are needed to clarify this interesting point.

Finally, at all levels of theory employed here, formation of the higher energy addition product (5,5)A-CCl$_2$ is kinetically more favorable than formation of the ring-opened product (5,5)C-CCl$_2$. This is an apparent violation of the Bell–Evans–Polyani principle, and might be due to the nonexistence of the putative cyclopropane product of circumferential addition. This "hidden" intermediate[59] might be so highly strained that it its three-membered ring spontaneously opens in later phases of the reaction, which are, however, not involved in determining the reaction barriers.

Conclusion

The results reported here give significant insight into the chemical properties of single-walled carbon nanotubes with respect to the reaction with carbenes, a prototypical class of neutral reactive intermediates. The following conclusions can be drawn:

1) In armchair tubes ranging from (3,3) to (12,12) insertion into the circumferential bond C to form a "methano-homonanotube" is always more exothermic than cyclopropanation of the axial bond A. The preference for reaction with A decreases monotonically with increasing tube diameter, and in the planar limit the two modes are degenerate.

2) Circumferential C−C bonds in zigzag SWNTs also undergo insertion of carbenes, while the axial C−C bonds un-

dergo cyclopropanation. The energetic preference of the reaction with circumferential bonds is less pronounced for metallic zigzag tubes than for semiconducting ones.

3) At a given diameter, addition to the circumferential bond of armchair tubes is more exothermic than to any bond in zigzag tubes.

4) The reaction mechanism for dichlorocarbene addition to a (5,5) SWNT is unusual: it does not proceed according to the typical one-step mechanism, but rather involves a diradicaloid intermediate. The very good delocalization of the nonbonding electron can provide sufficient stabilization to turn the diradicaloid into a minimum on the potential energy surface. The barrier separating this diradicaloid intermediate from the products is estimated to be about 4 kcal mol^{-1}. Formation of the thermodynamically more favorable open CCl_2 addition product is kinetically less favorable than formation of traditional cyclopropane derivatives, at least for the (5,5) armchair tube studied here.[71]

Computational Details

Density functional computations employed the gradient corrected functional due to Perdew, Burke, and Ernzerhof (PBE)[60,61] and the three-parameter hybrid functional due to Becke[62] as implemented in the Gaussian 03[63] program suite in conjunction with the exchange-correlation functional of Lee, Yang, and Parr[64] (B3LYP). In this study, three different basis sets were used: 3-21G,[65] 6-31G*,[66] and 6-311G**.[67]

Infinite carbon nanotubes were modeled by imposing periodic boundary conditions (PBC) as implemented[68,69] in Gaussian 03. In PBC computations, geometries were optimized at the PBE/3-21G level of theory, while final energies were obtained by single-point computations with the 6-31G* basis set. The largest PBC computations for the (18,0) tube involved 3259 basis functions and 52 **k** points.

Finite carbon nanotube models were terminated with hydrogen atoms to avoid dangling bonds. For the study of these models, the B3LYP and PBE functionals were employed. Geometries were obtained with the 6-31G* basis set, while single-point energies were computed with the 6-311G** basis set. Triplet states of carbenes were computed by using the spin-unrestricted formalism. The spin-restricted Kohn–Sham wave functions of singlet states were checked for instabilities, and the transition states and intermediates involved in the reaction of CCl_2 with the (5,5) SWNT were found to have triplet instabilities and were thus described by using the spin-unrestricted formalism.[22] For comparison the perfect-pairing generalized valence bond (GVB-PP) approach with one pair of electrons and two orbitals in conjunction with the 6-31G* basis set at the geometries obtained at the UB3LYP/6-31G* level of theory (GVB(1)/6–31G*//UB3LYP/6–31G*) was also employed. While the resulting wave function is the minimal requirement for a theoretically sound description of diradicaloid species, it does not include the effects of dynamic correlation, which are expected to be important for a more reliable treatment. However, due to the size of the systems (1443 basis functions for $C_{90}H_{20}+CCl_2$ when using the 6-31G* basis set) the GVB wavefunction could not be corrected by a perturbation treatment. The GVB computations were performed with the GAMESS-US program.[70]

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[71] Note added in proof (13.3.2006): Geometry optimizations at the GVB(1)-PP/6-31G* level of theory confirm the existence of the diradicaloid intermediate D, while no such diradical could be located at this level for the addition of CCl₂ to [60]fullerene.