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Theoretical Study of Cycloaddition Reactions of Heavy Carbenes with C_{60}

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The potential energy surfaces for the cycloaddition reaction $Me_2X: + C_{60} \rightarrow Me_2X(C_{60})$ (X = C, Si, Ge, Sn, and Pb) have been studied at the B3LYP/LANL2DZ level of theory. It has been found that there are two competing pathways in these reactions, which can be classified as a [6,5]-attack (path 1) and a [6,6]-attack (path 2). It was found that, given the same reaction conditions, the cycloaddition reaction of C_{60} via a [6,6]-attack is more favorable than that via a [6,5]-attack, both kinetically and thermodynamically. A qualitative model that is based on the theory of Pross and Shaik has been used to develop an explanation for the reaction barrier heights. As a result, our theoretical investigations suggest that the singlet−triplet splitting $\Delta E_{st}(=E_{triplet} - E_{singlet})$ of the 6 valence electron $Me_2X:$ and C_{60} species can be used as a guide to predict their reactivity toward cycloaddition reactions. Our model results demonstrate that the reactivity of heavy carbene cycloaddition to C_{60} decreases in the order $Me_2C: > Me_2Si: > Me_2Ge \gg Me_2Sn: > Me_2Pb:$. As a consequence, we show that electronic effects play a decisive role in determining the energy barriers as well as the reaction enthalpy.

I. Introduction

During the last two decades, owing to the synthesis of buckminsterfullerene (C_{60})[1,2] in macroscopic quantities, chemistry aimed at modifying or manipulating C_{60} has become increasingly facile.[3] In fact, the derivatives of C_{60} have attracted much attention due to their interesting properties and possibilities of application.[4] Functionalization by cycloaddition reactions represents a powerful route to C_{60} derivatives.[5] With 12 five-membered rings, 20 six-membered rings, and 30 double bonds in contiguous conjugation, buckminsterfullerene possesses the potential for varied main group chemistry. For instance, in spite of the relative short history of C_{60} science, the aza-, methano-, oxo-, and sila-bridged C_{60} fullerenes have already been the subject of intensive studies.[6−9]

An important reaction in the main group chemistry of buckminsterfullerenes is the addition of carbene to a carbon−carbon bond. Indeed, the reaction of C_{60} with carbenes and carbene equivalents has been studied since the earliest days of buckminsterfullerene chemistry.[10] It was found that, for instance, addition of a carbene such as $Br_2C:$ to C_{60} results in the formation of a cyclopropane.[11] Besides this, the study of the chemical reactivity of carbenes and C_{60} has also led to the synthesis of many intriguing molecules.[12−14] Nevertheless, the detailed reaction mechanisms for such addition reactions have not yet been firmly established by either experimental or theoretical studies, and many key questions remain open. In addition, despite the considerable experimental interest that has been shown in carbene addition chemistry with C_{60} in the past 20 years, the addition chemistry with other heavy carbenes (such as silylene,[15] germylene,[16] stannylene, and plumbylene) has not been similarly investigated.

As a result, this prompted us to investigate systematically the mechanism of addition of heavy carbenes to buckminsterfullerenes. We feel that if we could understand the basic factors governing the chemical reactivity of a variety of heavy carbenes with buckminsterfullerenes, this would help to design systems, which can facilitate these synthetically useful, but presently unattainable, reactions. Our aim is therefore to search for a general theory of reactivity for carbene and its heavier analogues and to delineate the significant role played by their singlet−triplet energy separations (vide infra). We have thus calculated the potential energy surfaces of the following reactions:

$$Me_2X: + C_{60} \rightarrow Me_2X{-}C_{60} \text{ (6−6 attack)} \tag{1}$$

$$Me_2X: + C_{60} \rightarrow Me_2X{-}C_{60} \text{ (6−5 attack)} \tag{2}$$

where X = C, Si, Ge, Sn, and Pb.

No systematic theoretical study has yet, to our knowledge, been published on the potential energy surfaces and reaction mechanisms of such cycloaddition reactions. In this work, we have thus attempted to study the heavier carbene reactions using density functional theory (DFT). On the back of these computational results, we will show that the singlet−triplet splitting of the carbene analogues can be used as a diagnostic tool for the prediction of their reactivity.

II. Computational Details

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structures showed various elements of symmetry. DFT was employed with the three-parameter hybrid exchange functional of Becke[17] and the Lee, Yang, and Parr correlation functional.[18] This functional is commonly known as B3LYP. Computations were carried out with use of relativistic effective core potentials on group 14 elements modeled using the double-ζ (DZ) basis sets.[19] Thus, the model compounds $Me_2X{\cdot}C_{60}$ have 578 (382 electrons) basis functions for M = C, Si, Ge, Sn, and Pb. Moreover, the restricted B3LYP approach was used in this work to describe all the stationary points, except for the triplet states of the reactants, which were described by unrestricted wave functions. Hence, all the singlet B3LYP calculations are denoted by B3LYP/LANL2DZ. The spin-unrestricted (UB3LYP) for-

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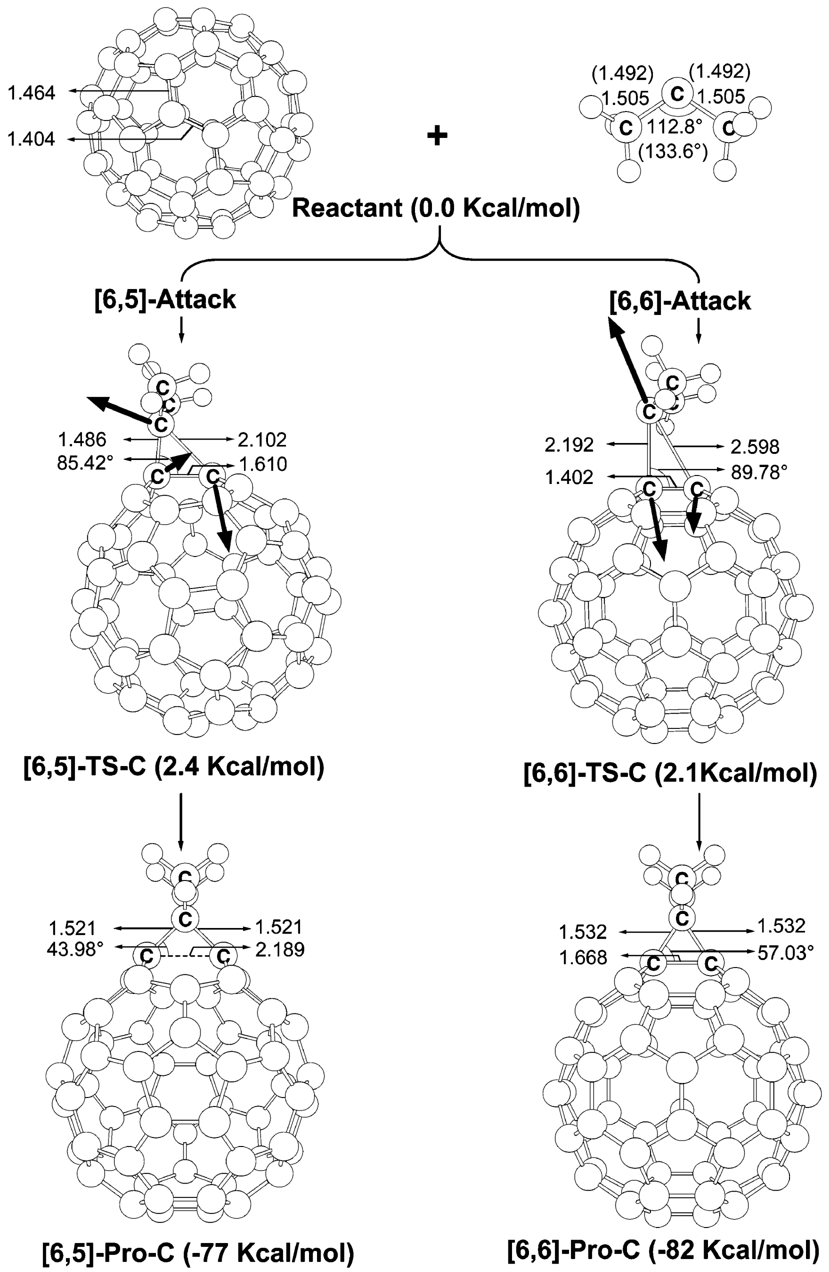

Figure 1. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants, transition states, and products of the Me_2C: case. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

malism was used for the open-shell (triplet) species. The S^2 expectation values of the triplet state for these species all showed an ideal value (2.00) after spin annihilation, so that their geometries and energetics are reliable for this study. Vibrational frequency calculations at the RHF/LANL2DZ level were used to characterize all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). These stationary points were further calculated at the B3LYP/LANL2DZ level with the opt=readfc keyword. Due to limitations of both CPU time and memory size, the B3LYP zero-point energy (ZPE) could not be applied for all of the $Me_2X{\cdot}C_{60}$ systems in the present work. That is, because frequencies were not calculated for all the species at the B3LYP/LANL2DZ level of theory, ZPE corrections were not performed. Nevertheless, the addition of these corrections would not change our conclusions. All the calculations were performed with the GAUSSIAN 03 package of programs.[19]

III. The Geometries and Energetics of Heavy Carbenes + C_{60}

In this section the computational results for three regions on the potential energy surfaces will be presented: 6-valence-electron Me_2X: (X = C, Si, Ge, Sn, and Pb) plus free C_{60} (**Rea**), the transition state (**TS**), and the cycloaddition product (**Pro**). The fully optimized geometries for those stationary points calculated at the B3LYP/LANL2DZ level are collected in Figures 1−5, respectively. To simplify the comparisons and to emphasize the trends, we have also given the energies relative to the two reactant molecules, i.e., Me_2X: + C_{60}, which are summarized in Table 1. Cartesian coordinates calculated for the stationary points at the B3LYP level are available as Supporting Information.

(1) The Heavy Carbene Systems and C_{60}. It is well-known that the two lowest states of heavier carbene analogues Me_2X: (X = C, Si, Ge, Sb, and Pb) are $^1A_1$ and $^3B_1$. These states are

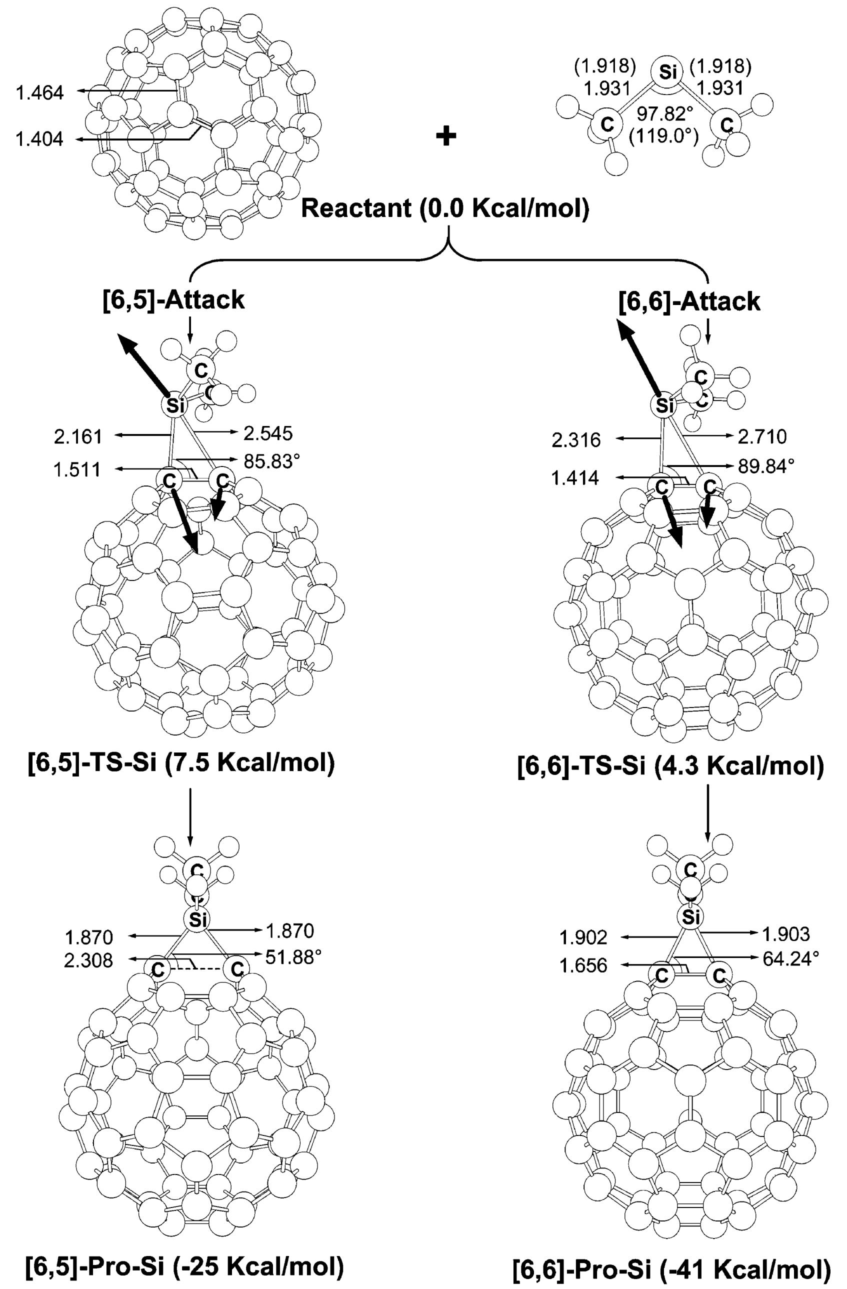

Figure 2. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants, transition states, and products of the Me_2Si: case. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

derived from the ground state HOMO, an essentially nonbonding σ orbital (a_1 symmetry) based on the X atom, and the LUMO, an effectively nonbonding $\pi-\pi$ orbital (b_1 symmetry) on the X atom. As seen in Figures 1−5, the triplet state of Me_2X: has significantly wider bond angles (∠CXC) and shorter bond distances (X−C) than its closed shell singlet state. In fact, this is usually the case in group 14 divalent compounds, in accordance with expectations of the Walsh rules.[20] Besides this, as expected, no matter what multiplicity the Group 14 carbene adopts, our computations suggest that the C−X bond distance shows a monotonic increase down the group from C to Pb. The reason for this is mainly due to the increase of the atomic radius of X. Additionally, our theoretical investigations also point out that, irrespective of its multiplicity, the bond angle ∠CXC decreases uniformly as the central atom, X, is changed from C to Pb. It hence appears that, as the X atom becomes heavier, a more acute bond angle ∠CXC in singlet Me_2X: is preferred. For instance, the singlet ∠CXC bond angles at the C, Si, Ge, Sn, and Pb centers in Me_2C, Me_2Si, Me_2Ge, Me_2Sn, and Me_2Pb, respectively, decrease in the following order: 113° > 97.8° > 95.6° > 93.6° > 92.9°. The reason for this may be due to the relativistic effect.[21] When X changes from carbon to lead, the valence s orbital is more strongly contracted than the corresponding p orbitals.[21] Namely, the size difference between the valence s and p orbitals increases from C to Pb. In consequence, the valence s and p orbitals of the heavier members of the group overlap less to form strong hybrid orbitals.[21] It is thus expected that a Me_2X: compound with a heavier X center favors a smaller bond angle ∠CXC.

Moreover, the other intriguing feature is the singlet−triplet splitting ($\Delta E_{st} = E_{triplet} - E_{singlet}$). As one can see in Table 1, our theoretical calculations indicate that the singlet−triplet splittings for carbon, silicon, germanium, tin, and lead are −5.5, 21, 27, 29, and 37 kcal/mol, respectively, i.e., as usual,[22] ΔE_{st} increases in the order C < Si < Ge < Sn < Pb. Again, as mentioned earlier, the reason for such a difference can be traced

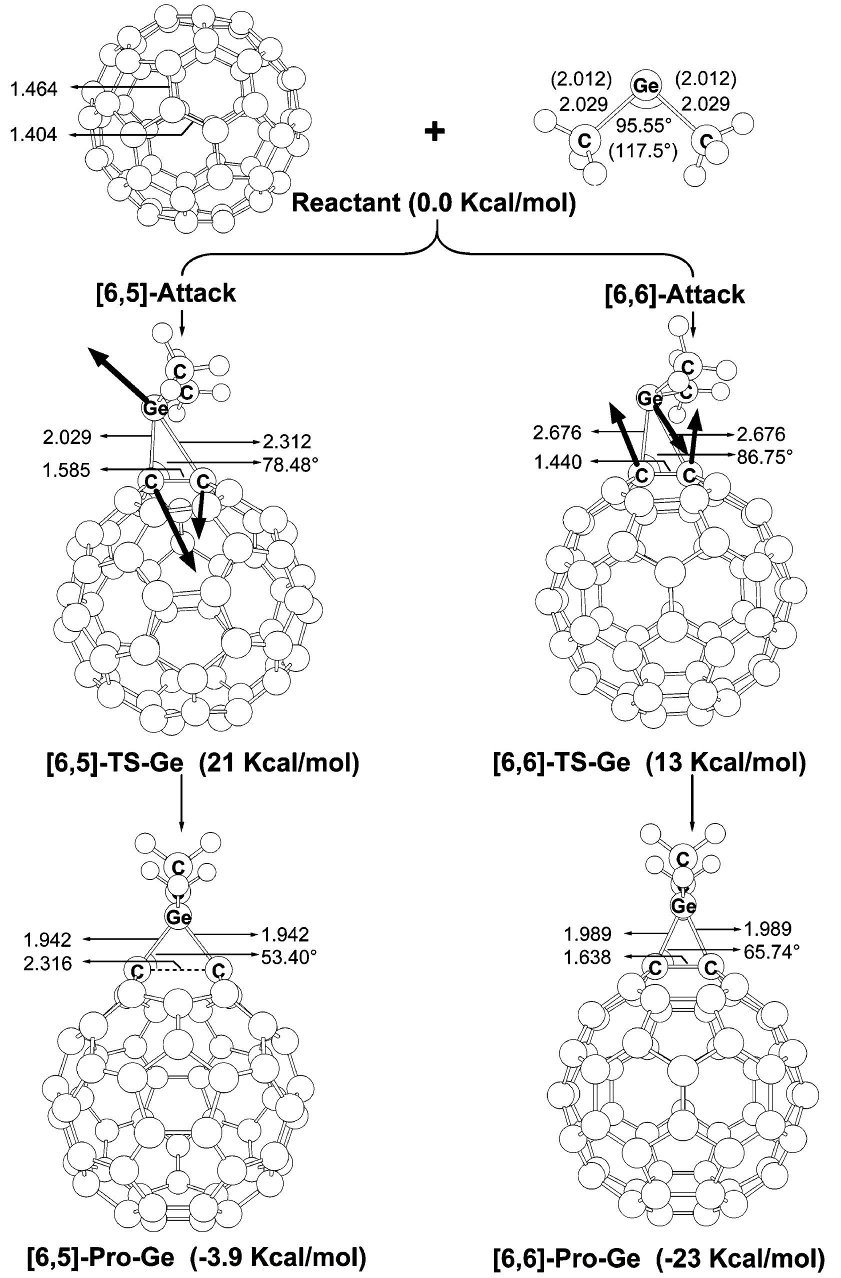

Figure 3. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants, transition states, and products of the Me_2Ge: case. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

directly to electronic factors. As observed previously,[22] it is apparent that the magnitude of the energy difference between HOMO and LUMO for the methyl-substituted carbene systems becomes larger as one proceeds along the series from C to Pb. We shall use the above results to explain the origin of barrier heights for their addition reactions with C_{60} in a later section.

Furthermore, although every carbon atom in C_{60} is chemically equivalent, there are two different types of C−C bonds within buckminsterfullerene.[8b, 23] One type occurs at the six−six ring fusion (i.e., [6,6] bond), while the other occurs at the six−five ring fusion (i.e., [6,5] bond). See Figure 6. Accordingly, two crystalline derivatives of C_{60} would be obtained by addition of heavy carbenes to buckminsterfullerene (vide infra). We thus performed a geometry optimization on the free buckminsterfullerene molecule under I_h symmetry constraints. The computed values of 1.404 and 1.464 Å, respectively, for the [6,6] and [6,5] bonds are very close to the experimental values of 1.401 and 1.458 Å from electron diffraction[24] and of 1.391 and 1.455 Å from neutron powder diffraction.[25] Due to the good agreement between B3LYP and the available experimental data on the known buckminsterfullerene features, we are confident that the computational methods used in this study are reliable.

Besides this, there could be generally four kinds of synthetic results for the addition of carbene to C_{60}.[26] However, it has been found that all 6−6-bridged monoadducts of C_{60} possess a closed trans-annular bond, while all 5−6-bridged compounds have an open trans-annular structure. In addition, there are two other structural possibilities for the monoadducts of C_{60}; these are the 6−6-bridged compound with an open trans-annular structure and the 5−6-bridged compound with a closed trans-annular bond. We shall see that the computational results confirm the above predictions in a later section.

As stated above, our DFT results suggest that the carbene (Me_2C:) should adopt a triplet ground state as shown in Table 1. This implies that Me_2C: may add to the C=C double bond of C_{60} via a diradical-type mechanism. However, the B3LYP

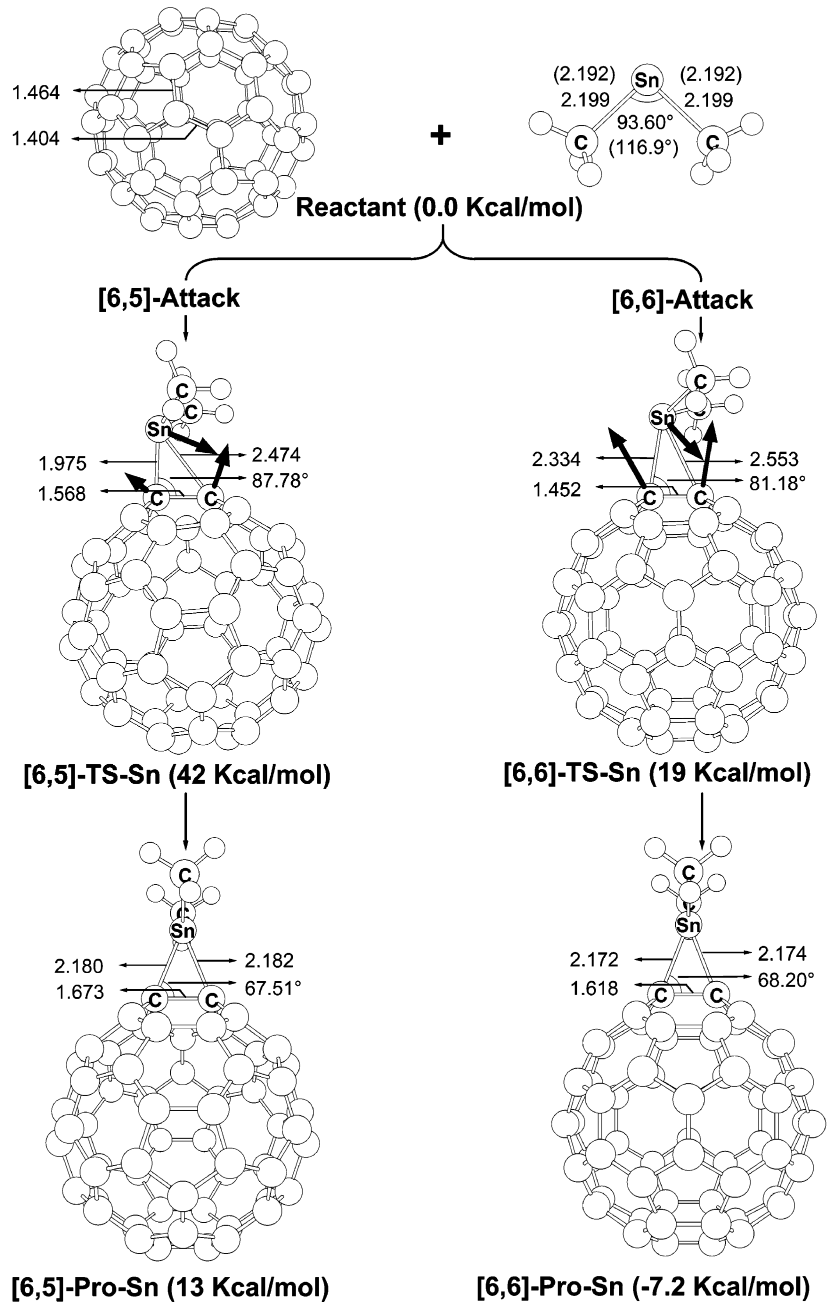

Figure 4. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants, transition states, and products of the Me_2Sn: case. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

results in Table 1 also indicate that the Me_2C: species with a triplet ground state has a small excitation energy to the first singlet state, i.e., $\Delta E_{st} = -5.5$ kcal/mol. In consequence, due to the fact that Me_2C: has such a small singlet−triplet splitting ΔE_{st} and that the other heavy carbene species adopt a singlet ground state, it could well be that the cycloaddition of heavy carbenes (Me_2X:) to C_{60} proceeds on the singlet surface, even if the reactants start from the triplet state. We shall thus focus on the singlet surface from now on.

(2) Transition State. The transition state geometries for the additions of heavy carbene Me_2X: ($X = C$, Si, Ge, Sb, and Pb) to buckminsterfullerene are given in Figures 1−5, respectively. As discussed earlier, since C_{60} has two different types of chemical bonds, the approaching heavy carbene may attack either of these two kinds of bonds. That is, it rearranges further either into a [6,5] cycloadduct via a [6,5] attack (i.e., path 1) or into a [6,6] cycloproduct via a [6,6] attack (i.e., path 2).

For reaction path 1, we have located the transition state **([6,5]-TS-C, [6,5]-TS-Si, [6,5]-TS-Ge, [6,5]-TS-Sn**, and **[6,5]-TS-Pb**) for each heavy carbene species at the B3LYP/LANL2DZ level of theory, along with the imaginary frequency eigenvector (see Figures 1−5). We have been able to locate only one transition state for each reaction and have confirmed that it is a true transition state on the basis of frequency analysis. The RHF/LANL2DZ frequency calculations for the transition states **[6,5]-TS-C, [6,5]-TS-Si, [6,5]-TS-Ge, [6,5]-TS-Sn**, and **[6,5]-TS-Pb** suggest that the single imaginary frequency values are 277*i*, 343*i*, 241*i*, 237*i*, and 233*i* cm^{-1}, respectively. As can be seen in Figures 1−5, the major component of the [6,5]-TS vibrational mode is located at the group 14 atom and two connected carbon atoms on C_{60}.

For reaction path 2, the transition state geometries for the [6,6] attack are depicted in Figures 1−5, respectively. All these transition states possess one imaginary frequency and are true

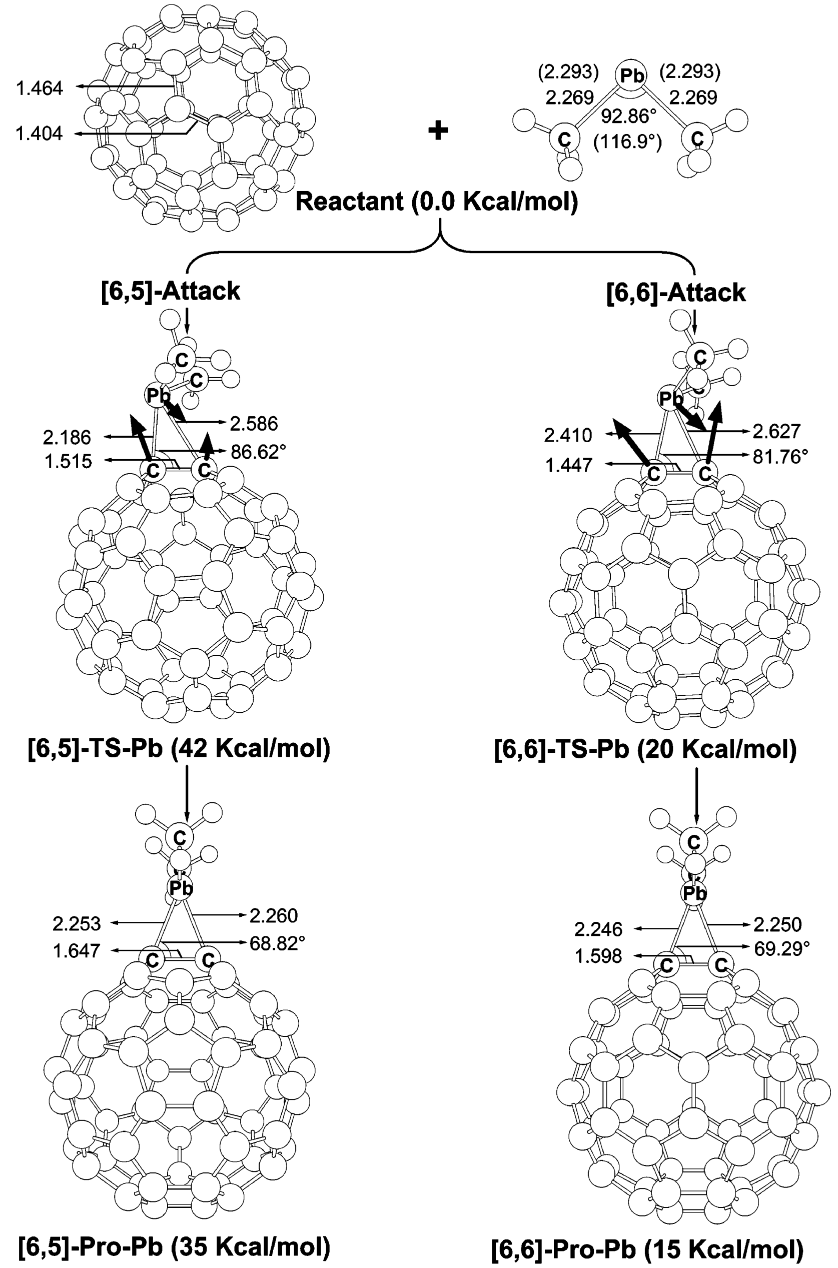

Figure 5. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants, transition states, and products of the Me_2Pb: case. The heavy arrows indicate the main atomic motions in the transition state eigenvector.

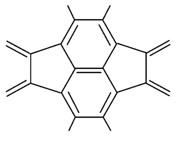

Figure 6. The carbon atoms present in the cyclohexatrienyl unit in C_{60}.

first-order saddle points. Our RHF/LANL2DZ frequency calculations indicate that the single imaginary frequency values are 248*i*, 206*i*, 190*i*, 196*i*, and 151*i* cm^{-1} for **[6,6]-TS-C, [6,6]-TS-Si, [6,6]-TS-Ge, [6,6]-TS-Sn**, and **[6,6]-TS-Pb**, respectively. As shown in Figures 1−5, the main components of the **[6,6]-TS** vibrational mode correspond to the displacement of the heavy carbene toward a double bond in the C_{60} and formation of a three-membered-ring cycloadduct.

From the earlier discussion, one can easily see that, of the two possible routes, the most promising one is [6,6] attack (path 2), which has a lower activation energy than [6,5] attack (path 1). For example, at the B3LYP level of theory, comparing the barrier heights between path 1 and path 2, we find the following trend: **[6,6]-TS-C** (2.1 kcal/mol) < **[6,5]-TS-C** (2.4 kcal/mol), **[6,6]-TS-Si** (4.3 kcal/mol) < **[6,5]-TS-Si** (7.5 kcal/mol), **[6,6]-TS-Ge** (13 kcal/mol) < **[6,5]-TS-Ge** (21 kcal/mol), **[6,6]-TS-Sn** (19 kcal/mol) < **[6,5]-TS-Sn** (42 kcal/mol), and **[6,6]-TS-Pb** (20 kcal/mol) < **[6,5]-TS-Pb** (42 kcal/mol). Consequently, our model calculations strongly suggest that the cycloadditions of heavy carbenes to C_{60} should produce the [6,6] cycloadduct via a [6,6] attack as the major product, with the [6,5] cycloproduct via a [6,5] attack being the minor product. Indeed, after many experimental as well as theoretical investigations, it was observed that buckminsterfullerene invariably shows a preference for 6−6 over 6−5 ring junction attack.[27]

Considering the nature of the group 14 atom center, the B3LYP/LANL2DZ calculations suggest that the barrier to cycloaddition for the lighter group 14 systems is lower than that for the heavier group 14 systems. For instance, the barrier energies increase in the following order: **[6,6]-TS-C** (2.1 kcal/

TABLE 1: Relative Energies for Singlet and Triplet Heavy Carbene Analogues with C_{60} and for the Process $Me_2X + C_{60} \rightarrow$ Transition State $\rightarrow$ Cycloadduct[a]

systems	ΔE_{st}[b] (kcal/mol)	ΔE_{act}[c] (kcal/mol)	ΔH[d] (kcal/mol)
$(CH_3)_2C$			
[6,5]-attack	−5.482	+2.404	−76.61
[6,6]-attack	−5.482	+2.110	−82.10
$(CH_3)_2Si$			
[6,5]-attack	+20.87	+7.480	−24.76
[6,6]-attack	+20.87	+4.338	−40.76
$(CH_3)_2Ge$			
[6,5]-attack	+26.95	+20.62	−3.845
[6,6]-attack	+26.95	+13.04	−22.90
$(CH_3)_2Sn$			
[6,5]-attack	+28.80	+41.95	+12.83
[6,6]-attack	+28.80	+19.17	−7.257
$(CH_3)_2Pb$			
[6,5]-attack	+36.68	+42.33	+35.04
[6,6]-attack	+36.68	+20.16	+15.13

[a] At the B3LYP/LANL2DZ level. See the text. [b] Energy relative to the corresponding singlet state. A negative value means the triplet is the ground state. [c] The activation energy of the transition state, relative to the corresponding reactants. [d] The reaction enthalpy of the product, relative to the corresponding reactants.

mol) < **[6,6]-TS-Si** (4.3 kcal/mol) < **[6,6]-TS-Ge** (13 kcal/mol) < **[6,6]-TS-Sn** (19 kcal/mol) < **[6,6]-TS-Pb** (20 kcal/mol). Likewise, the barrier for the [6,5] attack follows the same trend as the [6,6] attack: **[6,5]-TS-C** (2.4 kcal/mol) < **[6,5]-TS-Si** (7.5 kcal/mol) < **[6,5]-TS-Ge** (21 kcal/mol) < **[6,5]-TS-Sn** (42 kcal/mol) ≈ **[6,5]-TS-Pb** (42 kcal/mol). Accordingly, our theoretical calculations strongly suggest that carbene, silylene, and germylene cycloaddition reactions with C_{60} are much more favorable than those with stannylene and plumbylene. Our theoretical conclusions are consistent with the experimental observations.[10−16]

In addition, we note that at the[6,5]-TSs in Figures 1−5, the forming X−C bond is stretched by an average 56%, 35%, 32%, 13%, and 12% for **[6,5]-TS-C**, **[6,5]-TS-Si**, **[6,5]-TS-Ge**, **[6,5]-TS-Sn**, and **[6,5]-TS-Pb**, respectively, relative to in its corresponding three-membered-ring cycloadduct. Similarly, the forming X−C bond is stretched by an average 26%, 20%, 12%, 11%, and 8.7% relative to its equilibrium value as the heavy carbene changes from **[6,6]-TS-C**, **[6,6]-TS-Si**, **[6,6]-TS-Ge**, **[6,6]-TS-Sn**, and **[6,6]-TS-Pb**, respectively. Namely, the barrier is encountered earlier in the reactions with Me_2C:, Me_2Si:, and Me_2Ge: than for the reactions with Me_2Sn: and Me_2Pb:. In other words, a heavy carbene with a less massive but more elecronegative central atom reaches the transition state relatively early, whereas a heavy carbene with a more massive and less electronegative central atom arrives relatively late. The former is thus predicted to undergo a more exothermic addition, which is borne out by our DFT calculations (vide infra).

(3) Cycloadduct. The optimized product structures for the two kinds of addition products (**[6,5]-Pro-C**, **[6,6]-Pro-C**; **[6,5]-Pro-Si**, **[6,6]-Pro-Si**; **[6,5]-Pro-Ge**, **[6,6]-Pro-Ge**; **[6,5]-Pro-Sn**, **[6,6]-Pro-Sn**; and **[6,5]-Pro-Pb**, **[6,6]-Pro-Pb**) are collected in Figures 1−5. To simplify comparisons and to emphasize the trends, the calculated reaction enthalpies are also summarized in Table 1.

From Table 1 and Figures 1−5, one may readily see that the monocycloadduct from the [6,6] attack (path 2) forms a 6−6-bridged compound with a closed trans-annular structure. Amazingly, the C−C bond length in the [6,6] cycloadduct decreases in the order 1.668 Å (**[6,6]-Pro-C**) > 1.656 Å (**[6,6]-Pro-Si**) > 1.638 Å (**[6,6]-Pro-Ge**) > 1.618 Å (**[6,6]-Pro-Sn**) > 1.598 Å (**[6,6]-Pro-Pb**). On the other hand, in the [6,5] attack (path 1) the structure of the monocycloadduct appears to form a 5−6-bridged compound with an open trans-annular bond. For example, the C−C bond length in the [6,5] cycloadduct decreases in the order 2.316 Å (**[6,5]-Pro-Ge**) > 2.308 Å (-**[6,5]-Pro-Si**) > 2.198 Å (**[6,5]-Pro-C**) > 1.673 Å ([6,5]-Pro-Sn) > 1.647 Å (**[6,5]-Pro-Pb**).

Also, it is apparent that the order of the reaction enthalpy follows a similar trend to that of the activation energy. For instance, the enthalpy for path 1 (i.e., [6,5] attack) increases in the following order: **[6,5]-Pro-C** (−77 kcal/mol) < **[6,5]-Pro-Si** (−25 kcal/mol) < **[6,5]-Pro-Ge** (−3.9 kcal/mol) < **[6,5]-Pro-Sn** (+13 kcal/mol) < **[6,5]-Pro-Pb** (+35 kcal/mol). Similarly, for path 2 (i.e., [6,6] attack) the reaction enthalpy increases in the following order: **[6,6]-Pro-C** (−82 kcal/mol) < **[6,6]-Pro-Si** (−41 kcal/mol) < **[6,6]-Pro-Ge** (−23 kcal/mol) < **[6,6]-Pro-Sn** (−7.3 kcal/mol) < **[6,6]-Pro-Pb** (+15 kcal/mol). Three interesting points follow readily from the above. First, our theoretical results again indicate that the reaction enthalpy of the [6,6] attack (path 2) should be more exothermic than that of the [6,6] attack (path 1). Indeed, buckminsterfullerene shows a strong preference for 6−6 over 6−5 ring junction attack.[27] Second, it is obvious that, from both a kinetic and a thermodynamic viewpoint, the chemical reactivity for C_{60} cycloadditions decreases in the following order: Me_2C: > Me_2Si: > Me_2Ge: ≫ Me_2Sn: > Me_2Pb:. Third, we note that the energies of **[6,6]-Pro-Pb** and **[6,5]-Pro-Pb** are above those of their corresponding starting materials. Accordingly, we expect Me_2Pb: to be much more stable with respect to cycloaddition to a buckminsterfullerene than Me_2C:, Me_2Si:, Me_2Ge:, and Me_2Sn:.

IV. Overview of C_{60} Cycloaddition Reactions with Heavy Carbenes

Taking all five heavy carbene systems studied in this paper together, one can obtain the following conclusions:

1. A precursor complex for the cycloaddition of C_{60} to a heavy carbene (Me_2X:) should not exist. This conclusion is based on the present computational results.
2. The barriers for Me_2C:, Me_2Si:, and Me_2Ge: cycloaddition with C_{60} are low. This strongly implies that such cycloadditions with C_{60} should be facile processes at room temperature.
3. Cycloaddition of C_{60} to a heavy carbene should produce a three-membered-ring cycloadduct compound in a single step (i.e., in a concerted manner), thus stereospecifically. Namely, such cycloaddition reactions should be favored for producing stereoretention products.
4. For a given heavy carbene species, the activation barrier for the [6,6] attack is smaller than that for the [6,5] attack, indicating that the former is kinetically more favorable than the latter. Accordingly, the yield of product produced from the [6,6] attack should be much larger than that from the [6,5] attack.
5. Given identical reaction conditions, the [6,6] attack should be more exothermic than the [6,5] attack. Consequently, the production of $Me_2X(C_{60})$ compounds from the former pathway is clearly more thermodynamically favored than the latter.
6. Considering both the activation barrier and reaction enthalpy based on the model calculations presented here, we may conclude that the heavy carbenic reactivity order is as follows: Me_2C: > Me_2Si: > Me_2Ge: ≫ Me_2Sn: > Me_2Pb:. In other words, a heavy carbene with a less massive but highly electronegative central atom will accelerate the cycloaddition reaction with C_{60}, whereas a heavy carbene with a more massive and less electronegative central atom will retard the reaction.

7. Electronic as well as steric factors should play an important role in determining the chemical reactivity of the heavy carbene species with C_{60} from both a kinetic and thermodynamic viewpoint.

V. The Configuration Mixing Model

To understand the key factors that determine the general features of these addition reactions, a configuration mixing (CM) model, which was developed by Pross and Shaik,[28,29] has been used to gain a better understanding of the reactivity of the various reactants. According to the conclusions of this model, the energy barriers governing processes as well as the reaction enthalpies should be proportional to the energy gaps for both heavy carbene and C_{60}, that is, ΔE_{st} ($=E_{triplet} - E_{singlet}$ for heavy carbene) + $\Delta E_{st}(C_{60})$ ($=E_{triplet} - E_{singlet}$ for C_{60}). We therefore conclude that both the order of the singlet and triplet states and their energy separation are responsible for the existence and the height of the energy barrier.[28,29] Bearing these analyses in mind, we shall now explain the origin of the following observed trends:

(1) Why are the C, Si, and Ge reactions more favorable than the Sn and Pb reactions in the cycloaddition of C_{60} to heavy carbene?

The reason for this can be traced back to the singlet−triplet energy gap (ΔE_{st}) of a 6 valence-electron carbene. As discussed above, a smaller ΔE_{st} of a heavy carbene will facilitate the cycloaddition reaction with C_{60}. It is well-established that a carbene with a more electronegative central atom possesses a smaller singlet−triplet splitting than one containing a less electronegative central atom.[22] In contrast to the carbene (Me_2C:), the silylene (Me_2Si:), germylene (Me_2Ge:), stannylene (Me_2Sn:), and plumbylene (Me_2Pb:) characterized have exclusively singlet ground states, with the magnitude of the singlet−triplet energy separation increasing with increasing atomic mass of the group 14 element,[22] which has been confirmed by our DFT calculations as given in Table 1. Furthermore, this result is in accordance with the trends in activation energy and enthalpy (ΔE_{act}, ΔH) for heavy carbine [6,6] addition reactions which are Me_2C: (+2.4, −77) kcal/mol, Me_2Si: (+7.5, −25) kcal/mol, Me_2Ge: (+21, −3.9) kcal/mol, Me_2Sn: (+42, +13) kcal/mol, and Me_2Pb: (+42, +35) kcal/mol. Similarly, for heavy carbine [6,6] addition reactions it was found that the trend was Me_2C: (+2.1, −82) kcal/mol, Me_2Si: (+4.3, −41) kcal/mol, Me_2Ge: (+13, −23) kcal/mol, Me_2Sn: (+19, −7.3) kcal/mol, and Me_2Pb: (+20, +15) kcal/mol. Consequently, our model calculations provide strong evidence that an electronic factor resulting from the group 14 element should play a decisive role in determining the reactivity of a heavy carbene.

(2) Given identical reaction conditions, why is the cycloaddition reaction of C_{60} via [6,6]-attack more favorable than that via [6,5]-attack both kinetically and thermodynamically?

Again, the driving force for this may be traced to the singlet−triplet energy gap (ΔE_{st}) of C_{60}. According to the CM model mentioned earlier, we know that a smaller ΔE_{st} for the fused two-ring system results in a lower barrier height and a larger exothermicity. We do not discuss further details about these coordination structures, because the comparison of two coordination structures (i.e., [6,5] attack and [6,6] attack) has been previously discussed in theoretical work.[30]

VI. Conclusion

In summary, this observation makes it quite obvious that, in order to find a good model for the facile cycloaddition of a 6 valence electron heavy carbene (L_2X:) to buckminsterfullerene (C_{60}), an understanding of its singlet−triplet splitting ΔE_{st} is crucial. In other words, the efficiency of cycloaddition depends markedly upon the ancillary ligand L as well as on the central group 14 atom X. Our theoretical findings therefore predict that for heavy carbene L_2X systems, choosing a less massive but highly electronegative central atom X, which leads to a smaller ΔE_{st}, will facilitate the cycloaddition reactions with C_{60}. On the contrary, a heavy carbene with a more massive and less electronegative central atom, which leads to a larger ΔE_{st}, will hinder the cycloaddition reactions with C_{60}. The predictions may be useful as a diagnostic tool to future synthetic efforts and to indicate problems that merit further study by both theory and experiment. Despite the fact that the estimated magnitude of the barrier and reaction enthalpy for such cycloadditions appear to be dependent on the calculational level applied, our qualitative predictions from the present work are in good agreement with the experimental evidence.

It is hoped that the present work can stimulate further research into this subject.

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Supporting Information Available: Tables of geometries calculated at B3LYP/LANL2DZ and frequencies calculated at RHF/LANL2DZ. This material is available free of charge via the Internet at http://pubs.acs.org.

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