

Formation of Heterofullerenes by Direct Exposure of C_{60} to Boron Vapor**

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An intriguing way to modify the properties of fullerenes is by replacing a carbon atom in the caged network with a heteroatom.^[1–6] The resulting molecule, a heterofullerene, acquires electronic structure that is distinct from its all-carbon precursor. Therefore, modification of electronic and optical properties by heteroatom doping is a promising route toward devising, for example, fullerene-based molecular electronics, solar cells, and hydrogen-storage technologies, as well as exploring new fullerene chemistry.^[7–14] Preferred elements for fullerene doping are trivalent heteroatoms that most closely resemble carbon in size and electronegativity, because such elements are most likely to exhibit covalent bonding in a fullerene. Thus, nitrogen and boron are the most attractive candidates to form closed-cage heterofullerenes.

Nitrogen-containing heterofullerenes have received much attention and investigation because rational syntheses have been devised. Hirsch and co-workers first reported formation of $C_{59}N^+$ by gas-phase rearrangement of N-containing C_{60} derivatives, and subsequently succeeded in obtaining macroscopic quantities of azafullerenes.^[15,16] Wudl and co-workers first realized a solution-based procedure to produce its dimer, $(C_{59}N)_2$, also using synthetically prepared N-containing C_{60} derivatives.^[17] Since then, many advances in azafullerene chemistry have been achieved, including synthesis of the $C_{59}N^+$ carborane salt and $C_{59}NH$.^[18–20] In contrast, hetero-

fullerenes that incorporate boron have received little experimental investigation.^[21–23] The primary reason for this discrepancy is that a strategy to form borafullerenes directly from C_{60} has not been discovered. Furthermore, heterofullerenes that are isoelectronic to C_{60} , such as $C_{59}N^+$, are some of the most attractive synthetic targets because these species should be quite stable. Accordingly, the boron-doped isoelectronic equivalent, $C_{59}B^-$, should be a rewarding heterofullerene synthetic target.

We have recently reported that fullerenes and endohedral metallofullerenes grow by a closed network growth mechanism, in which smaller cages incorporate atomic carbon and C_2 to form larger fullerenes.^[24] Along with fullerene cage growth by C and C_2 uptake, atom exchange events are also observed as a significant process upon exposure of fullerenes to carbon vapor. That realization led us to investigate exposure of fullerenes to heteroatom vapor as a route toward heterofullerene synthesis. In particular, our interest was to devise a method to prepare $C_{59}B$ directly from C_{60} .

Herein, we report facile gas-phase formation of $C_{59}B$ by atom exchange resulting from exposure of C_{60} to boron vapor. The processes are elucidated by means of a pulsed laser vaporization cluster source,^[25] which was analyzed by state-of-the-art Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry.^[26,27] This procedure, or other vaporization setups, such as arc discharge, for $C_{59}B$ formation may be scaled up to be used as a preparative method. Further, the technique is convenient because synthetic preparation of boron-containing C_{60} derivative precursors is not necessary; it is the first report of borafullerene formation directly from pristine C_{60} . The method is also applicable to other fullerenes; for example, we find that $C_{69}B$ is directly generated from C_{70} . Thus, many new borafullerenes and endohedral borafullerenes may be synthesized by exposure of various pre-existing fullerenes to boron vapor. The atom exchange process is efficient even when using low-cost, commercially available grades of boron (90 % B). Thus, the gas-phase synthetic route reported in this work is also an economical approach to access heterofullerenes.

Figure 1 shows gas-phase reaction products formed by exposure of pure C_{60} to boron vapor. It is demonstrated that $C_{59}B^-$ forms from the C_{60} precursor by atom exchange (unreacted C_{60} is also present). The high mass accuracy and resolution afforded by the present 9.4T FT-ICR mass spectrometer permits conclusive identification of the reaction products; for example, mass accuracy for $^{12}C_{59}^{11}B$ is 600 parts per billion, and all 7–13 milliDalton mass differences between reaction product heterofullerenes and fullerenes ($C_{59}B$, $C_{58}B_2$, and C_{60}) are unambiguously resolved, as shown in the insets of

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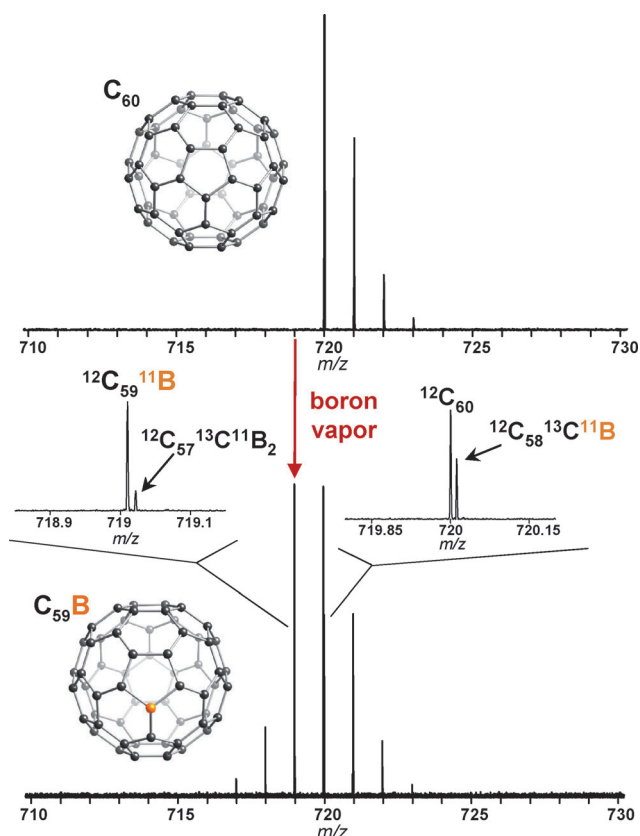


Figure 1. FT-ICR mass spectra (negative ions) of C_{60} without boron vapor (top), and after exposure to boron vapor (bottom).

Figure 1. The mono-doped fullerene anion, $C_{59}B^-$, exhibits high relative abundance, indicating the atom exchange process is facile. The corresponding $C_{59}B^+$ species, however, is not observed after direct exposure of C_{60} to B vapor, whereas it is possible to detect C_{60}^+ . That observation indicates an altered electronic structure resulting from covalent bonding of the B atom in the $C_{59}B$ caged network. $B_{58}B_2^-$ is also formed, but in much lower relative abundance.

Substitution of one C atom by one B atom reduces the symmetry of the fullerene to C_s . Consequently, the five degenerate HOMO (h_u) and the three degenerate LUMO (t_{1u}) orbitals for icosahedral C_{60} are broken into two sets of non-degenerate orbitals. Molecular orbital energy diagrams (computed at the BP86/TZP level; see the Experimental Section) are shown in Figure 2. $C_{59}B$ exhibits an open-shell electronic structure because it possesses one less electron than C_{60} . The singly occupied molecular orbital (SOMO) of $C_{59}B$ appears at -5.93 eV, which is only 0.32 eV above the HOMO of C_{60} . The LUMO also shows a rather low energy (-5.60 eV). Conversely, the SOMO of the related molecule $C_{59}N$, with one more electron than C_{60} , correlates with the LUMOs of C_{60} and appears at much higher energy (-5.02 eV). It follows that $C_{59}B$ should be a good electron acceptor, while $C_{59}N$ is a good electron donor. Accordingly, $C_{59}B^-$ and $C_{59}N^+$ are closed-shell molecules with rather large HOMO–LUMO gaps. Furthermore, several interesting studies have shown that charging fullerenes induces only small structural changes.^[28,29]

The unpaired electron in neutral $C_{59}B$ is distributed over a large area of the cage, as shown by the spin-density diagram in Figure 2. The topology of the HOMO for the closed-shell $C_{59}B^-$ anion (Figure 2) is closely related to the spin density of $C_{59}B$, with small differences owing to spin polarization. The computed ionization energies (IE) and electron affinities (EA) for $C_{59}B$, C_{60} , and $C_{59}N$ are shown in Table 1. From these

Table 1: Ionization energies (IE) and electron affinities (EA), along with energies of the HOMO and LUMO, for I_h-C_{60} , $C_{59}B$, and $C_{59}N$ ^[a].

	I_h-C_{60}	$C_{59}B$	$C_{59}N$
IE	7.470	7.160	6.307
EA	2.934	3.874	3.133
ϵ_{HOMO}	-6.247	-5.903	-5.023
ϵ_{LUMO}	-4.592	-5.597	-4.814

[a] Energy in eV.

results, it is clearly shown that: 1) the $C_{59}B$ molecule possesses the largest electron affinity, in agreement with its low-energy LUMO; and 2) the $C_{59}N$ molecule has the lowest ionization energy, in accordance with its high-energy HOMO. These factors further explain why $C_{59}B^-$ is found in high relative abundance, yet $C_{59}B^+$ is not observed. It is noteworthy that the most electronically stable form of $C_{59}B$ is generated directly from C_{60} in our experiments, which may facilitate isolation of this borafullerene. In fact, a mono-anionic form of the $La@C_{82}$ metallofullerene, in which the SOMO of $La@C_{82}$ accepts an electron to become a closed-shell orbital, has been isolated as a stable species.^[30]

To obtain strong evidence that the B atom in $C_{59}B$ is not an adatom or other unstable species, collision-induced dissociation (CID) experiments were performed. $C_{59}B^-$ is determined to be very robust in the gas phase and does not exhibit B loss when highly thermally excited, indicating that the B atom has, as expected, replaced a C atom in the fullerene cage network. Smaller C_2 loss (“shrink-wrapping”) fullerene fragmentation products cannot be observed in negative-ion mode by CID. However, $C_{59}B^+$ was able to be generated by a different route to detect molecular fragmentation products: vaporization of a boron-doped graphite rod (without a fullerene precursor). Subsequent CID investigations on the $C_{59}B^+$ cation clearly show successive C_2 loss events with retention of the B atom.

Although the $C_{59}B^+$ cation was not generated directly from C_{60} , and is thus not necessarily the same $C_{59}B$ substitutional isomer formed from I_h-C_{60} , the fragmentation behavior confirms the ability of a single boron atom to bond in a caged carbon network. Interestingly, $C_{59}B^-$ is not readily observed by simple vaporization of graphite/boron without a fullerene precursor. Thus, the two routes may generate charged borafullerenes by different growth mechanisms. Exposing I_h-C_{60} to B vapor clearly generates $C_{59}B^-$ (and possibly the less stable neutral species) by atom exchange, as shown in Figure 1. In contrast, the $C_{59}B^+$ and neutral species that are produced by simple vaporization of graphite and boron may form from smaller boron-containing fullerenes, such as $C_{57}B$,

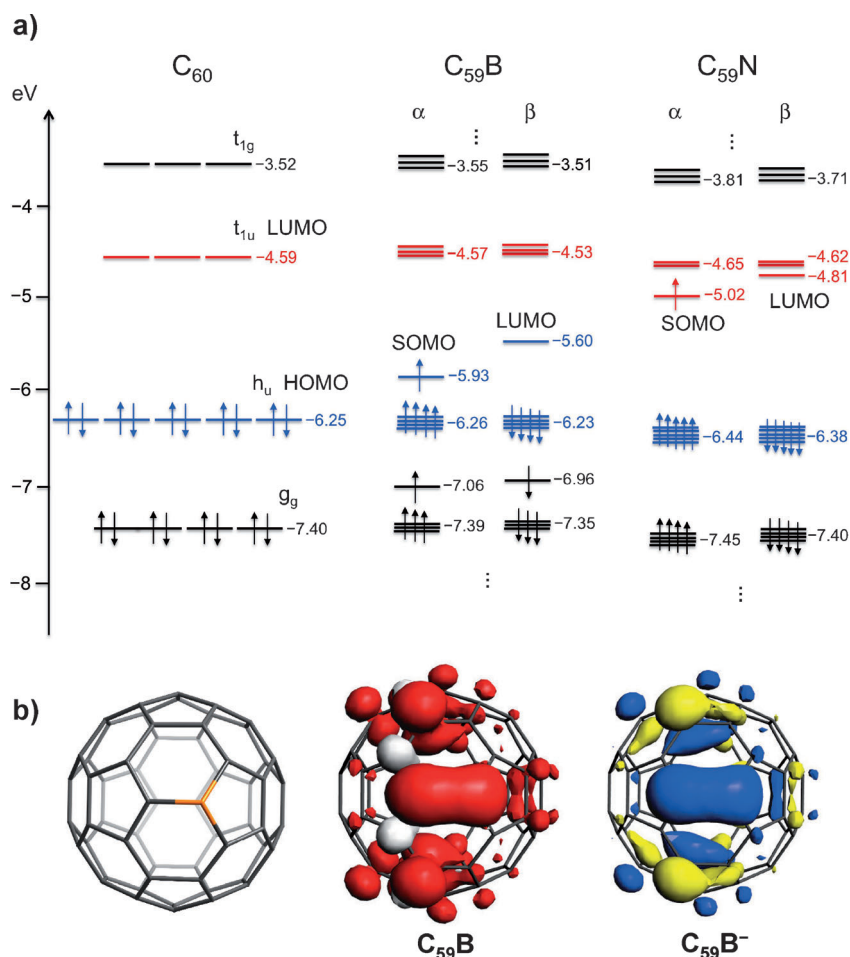


Figure 2. a) Molecular-orbital energy diagrams near the HOMO and LUMO of $C_{59}B$ compared to I_h-C_{60} and $C_{59}N$. The HOMOs and LUMOs of I_h-C_{60} are broken into five (blue) and three (red) non-degenerate orbitals for $C_s-C_{59}X$ ($X=B$ and N) heterofullerenes. b) Representations of spin density for neutral $C_{59}B$ (red and white), and the topology of the HOMO for $C_{59}B^-$ (yellow and blue).

through the recently elucidated closed network growth (CNG) mechanism by incorporation of C and C_2 .^[24,31]

Under certain conditions (high He pressure and laser fluence), although $C_{59}B$ is still the major reaction product, vaporization of boron rods with lower concentrations of C_{60} show higher relative abundances of doubly and triply doped molecules, as well as $C_{56}B_4$ and higher doped fullerenes at lower abundance. The results suggest that the number of atom exchange events is dependent on exposure time and the amount of B available for reaction. Therefore, longer exposure times of C_{60} to boron vapor should generate more atom exchange events to form higher doped borafullerenes, $C_{n-m}B_m$ ($m > 1$). In contrast to carbon, boron does not self-assemble to form large clusters,^[32] although smaller boron clusters that exhibit intriguing electronic properties and structures have been studied.^[33–35] Indeed, we find no evidence for self-assembly of large all-boron clusters in our investigations. Experimental set-ups that permit exposure of fullerenes to sufficient amounts of boron vapor may permit gas-phase formation of highly doped clusters to provide insight into large boron species.

Importantly, we find that exposure of $D_{5h}-C_{70}$ to B vapor generates $C_{69}B^-$, which is isoelectronic with C_{70} , as an abundant heterofullerene product (Figure 3). It should therefore be possible to create borafullerenes from additional pristine fullerenes through atom exchange by exposure to B vapor, and it is also likely that endohedral heterofullerenes can be synthesized in the same way. Recently, several fascinating endohedral heterofullerenes have been characterized: namely, $Gd_2@C_{79}N$, $Y_2@C_{79}N$, and $Tb_2@C_{79}N$.^[36,37] Still, the small amount of endohedral heterofullerene material produced under known parameters by conventional methods (arc discharge of doped graphite rods) is a challenge to further study of these exciting nanomaterials. Exposure of pre-formed metallofullerenes to heteroatom vapor may be a more efficient avenue to produce endohedral heterofullerenes. Investigations are under way to synthesize additional doped fullerenes and endohedral heterofullerenes. Future studies with samples of borafullerenes produced by this formation method should also confirm the isomeric structure of $C_{59}B$ formed from I_h-C_{60} , which we predict to be the substitutional isomer.

In summary, borafullerene formation directly from a pristine fullerene has been accomplished for the first time. In particular, C_{60} undergoes facile atom-exchange processes in the gas phase to produce $C_{59}B$. The species is observed as $C_{59}B^-$, and this anion yields an electronically closed-shell molecule that is isoelectronic to C_{60} . The

formation should be convenient and economical to scale up for use as a preparative method to open up study on borafullerenes, which should exhibit distinct chemical and physical properties from previously studied heterofullerenes. $C_{69}B$ is also directly generated from C_{70} by atom exchange. Thus, it is likely that additional pristine fullerenes or metallofullerenes may be exposed to boron vapor to produce B-doped analogues. Furthermore, atom-exchange reactions with fullerene carbon networks demonstrated in this study should be applicable to other carbon nanostructures. For example, conversion of carbon nanotubes or graphene into their B-doped analogues may be accomplished by exposure of the pre-existing carbon nanostructures to boron vapor.

Experimental Section

C_{60} or C_{70} was exposed to boron vapor by use of a supersonic cluster source,^[24] which was achieved through vaporization of fullerene-containing boron rods by a single pulse of a Nd:YAG laser (532 nm, 5 mJ/pulse) under a flow of helium. The composite rods are comprised of thoroughly mixed fullerene (10 mg, > 99% I_h-C_{60} or $D_{5h}-C_{70}$) and

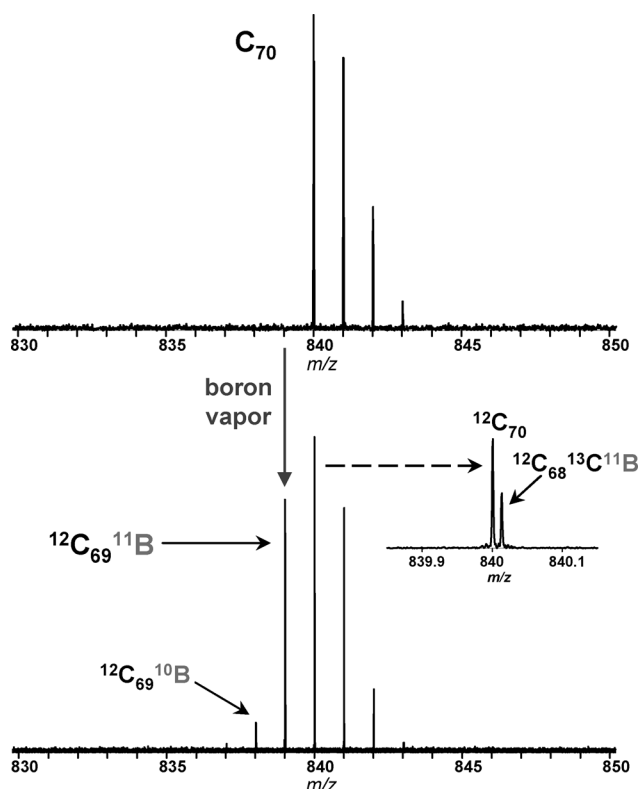


Figure 3. $C_{69}B^-$ observed to form in high abundance after exposure of $D_{5h}-C_{70}$ to boron vapor.

amorphous and crystalline boron powder (2 g, 99% or 90% purity B). Gas-phase reaction products were analyzed by a custom-built 9.7 FT-ICR mass spectrometer directly coupled to the cluster source. Ions produced by 5–10 individual laser and helium-pulse events were accumulated, and then transferred by octopoles to an open cylindrical trap. The ions were then accelerated to a detectable radius by a broadband frequency sweep excitation, and subsequently detected as the differential current induced between two opposed electrodes of the ICR cell. Up to three time-domain acquisitions were averaged. $C_{59}B^+$ is generated by vaporization of a graphite rod doped with boron powder (5% B). Fragmentation experiments were performed by sustained off-resonance irradiation (SORI-CID). The calculations were carried out using DFT methodology with the ADF 2010 program.^[38] The exchange-correlation functionals of Becke^[39] and Perdew^[40] were used. Relativistic corrections were included by means of the ZORA formalism. Slater triple-zeta plus polarization basis sets were employed to describe the valence electrons of C and N. Frozen cores consisting of the 1s shell for C and N were described by means of single Slater functions.

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