# Structures and Formation of Small LaC$_n^+$ Metallofullerenes

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*Received: June 17, 1994; In Final Form: October 18, 1994*[®]

Injected ion drift tube techniques have been used to probe LaC$_n^+$ clusters in the size range around LaC$_{36}^+$ where the fullerene cage becomes too small to accommodate a La atom. Mobility measurements show that as the fullerene cage shrinks, the La atom moves out of the cage into the carbon network, stabilizing clusters with an odd number of carbon atoms. Annealing studies demonstrate that in this size range the presence of the La atom dramatically enhances the efficiency of conversion of bicyclic and monocyclic LaC$_n^+$ rings into fullerenes and graphite sheets.

Endohedral metallofullerenes (fullerene cages encapsulating metal atoms) are currently an object of widespread experimental and theoretical research.[1] The interest in these species is driven by the expectation that they will be useful materials with properties that can be controlled by the nature of the encapsulated atom. So far, bulk quantities of metallofullerenes are only available for a few specific M@C$_n$ compounds (such as La@C$_{82}$).[2,3] However, a wide range of metallofullerenes can be generated and studied in gas phase experiments. In their laser "shrink-wrapping" experiments (the sequential reduction of a fullerene cage by loss of C$_2$ units[4]), Smalley and co-workers found that below a certain critical size (LaC$_{36}^+$ for La-containing fullerenes[5]) the cage becomes too small to encapsulate a metal atom and disintegrates. To examine in more detail what happens with metallofullerenes in this size regime, we have used injected ion drift tube techniques to study LaC$_n^+$ clusters with 29−40 carbon atoms. We find that LaC$_n^+$ metallofullerenes are endohedral for $n = 36$ and $n > 37$ and nonendohedral for $n < 34$ and $n = 35$. For LaC$_{34}^+$ and LaC$_{37}^+$ we observe both endohedral and nonendohedral isomers. Formation of nonendohedral metallofullerenes occurs more readily for clusters with an odd number of carbon atoms, where the La atom can occupy a defect site in the carbon network. Other isomers present are assigned to La-containing monocyclic and bicyclic rings and graphite sheets. Annealing studies show that in this size regime conversion of ring isomers into fullerenes and graphite sheets is much more efficient for LaC$_n^+$ than for C$_n^+$ clusters.

The experimental apparatus used in these studies is described in detail elsewhere.[6,7] La-containing carbon clusters are generated by laser vaporization of a composite La$_2$O$_3$−, LaBr−, or LaC$_2$−graphite rod. Short (50 $\mu$s) pulses of mass-selected clusters are injected into a drift tube containing helium buffer gas. The clusters become collisionally excited and undergo a transient heating cycle as they enter the drift tube, and if the injection energy is high enough, they may anneal or fragment. The clusters then travel across the drift tube under the influence of a weak electric field. Isomers with different shapes have different mobilities and are separated in the drift tube.[8] The resulting drift time distribution provides information about the structural isomers that are present and their relative abundances.

Figure 1a shows the drift time distribution for LaC$_{36}^+$ recorded at a low injection energy. This distribution is typical for LaC$_n^+$ clusters in the $n = 29−40$ size range. Four isomers (labeled **I, II, III,** and **IV**) are present. For each of these isomers an analogue exists in drift time distributions of pure carbon
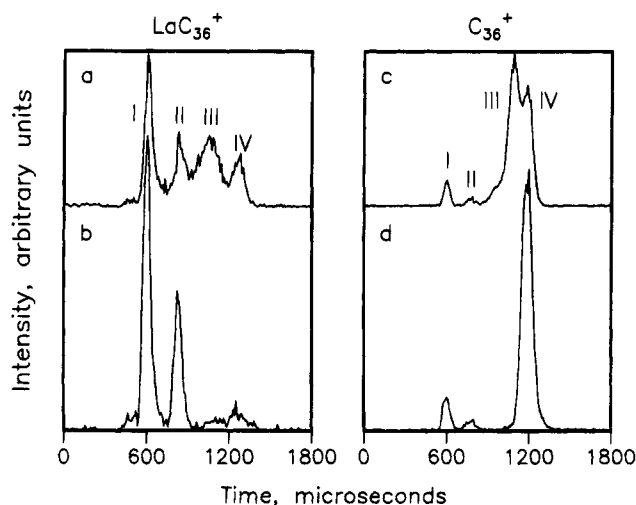
**Figure 1.** Drift time distributions for LaC$_{36}^+$ at injection energies of 50 eV (a) and 225 eV (b) and for C$_{36}^+$ at injection energies of 50 eV (c) and 200 eV (d). (The data for the pure carbon clusters are taken from ref 17.)

clusters,[9] as shown in Figure 1c. Isomers **III** and **IV**, which dominate for clusters with fewer than 30 carbon atoms, have been previously assigned to bicyclic and monocyclic La-containing carbon rings, respectively.[10] Their structures will not be discussed further here.

Figure 2 shows the inverse mobilities of isomers **I** and **II** plotted against cluster size. Overall, the mobility of each isomer systematically decreases as the cluster size increases. However, there is an abrupt change in mobility of isomer **I** around LaC$_{36}^+$, which indicates the presence of two distinct substructures of this isomer. For $n = 36$ and all $n > 37$ the mobility of isomer **I** of LaC$_n^+$ differs from the mobilities of pure C$_n^+$ fullerenes (plotted as a dashed line in Figure 2)[11] by no more than 1.5%. If the metal atom was outside the fullerene cage, the mobility of the metallofullerene would be expected to be smaller than the mobility of a pure fullerene by at least 6%.[12] We therefore assign the more compact structure of isomer **I** to endohedral metallofullerenes La@C$_n^+$. Endohedral La@C$_n^+$ exists for $n = 34$ and all $n > 35$ and is the dominant isomer for LaC$_{36}^+$ and larger clusters.

The mobility of the other substructure of isomer **I**, which exists for $n = 29−35$ and $n = 37$, is 9−12% smaller than the mobility of C$_n^+$ fullerenes of the same size. In this size range a fullerene cage becomes too small to readily encapsulate the metal atom.[4,5] The observed decrease in the mobility of isomer
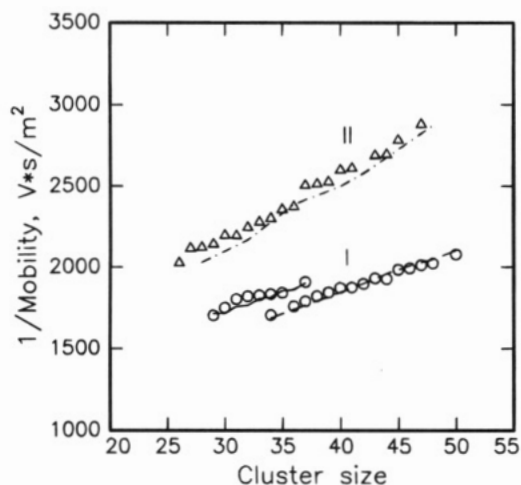
**Figure 2.** Plot of the inverse mobilities of isomers **I** and **II** against cluster size. The points are the experimental data for $LaC_n^+$ clusters. The dashed line shows the measured mobilities of $C_n^+$ fullerenes (ref 11); the solid line shows the simulated mobilities of networked $LaC_n^+$ fullerenes (see text); and the dash-dotted line shows the simulated mobilities of $LaC_n^+$ graphite sheets (see text).

**I** can be attributed either to the opening of the cage of an endohedral metallofullerene or to formation of nonendohedral species. The first explanation seems unlikely because for $LaC_{34}^+$ and $LaC_{37}^+$, both substructures of isomer **I** coexist, and we observe no significant decrease in mobility of the endohedral metallofullerene (see Figure 2). Therefore, we assign the less compact substructure of isomer **I** to nonendohedral metallofullerenes. Nonendohedral $LaC_n^+$ fullerenes with an odd number of carbon atoms are substantially more abundant in the isomer distributions and substantially more stable toward fragmentation at high injection energies[13] than nonendohedral metallofullerenes with an even number of carbon atoms. Pure fullerenes with an odd number of carbon atoms have a cage defect (due to the missing atom). In $LaC_{2n+1}^+$ metallofullerenes the $La^+$ ion can occupy this defect site and become a part of the carbon network. It seems likely that such "networking" is responsible for stabilization of small metallofullerenes with an odd number of carbon atoms.

In order to obtain more information about such networked structures, we have performed *ab initio* quantum chemical calculations[14] for $LaC_{29}^+$ where the $La^+$ ion replaces a carbon atom at a junction of three five-membered rings of the $D_{5h}$ isomer of $C_{30}$ fullerene (Figure 3). In the equilibrium geometry the $La^+$ ion forms three almost equivalent bonds with the nearest carbon atoms with the average bond length of 2.53 Å. The analysis of energy-localized molecular orbitals shows that these three $\sigma$-bonds have Mulliken populations around 0.3 on La and around 1.7 on C. The additional electron required to form three La–C bonds comes from the $\pi$-system of the fullerene, converting the cluster to a closed-shell configuration. Since the La sits out of the cage, its atomic orbitals make no significant contribution to the $\pi$-system of the fullerene. The Mulliken charge on La is 1.82, and the La is bound to the cage by 6.2 eV.

The mobility of the calculated structure of networked $LaC_{29}^+$ estimated using a simple hard-sphere collision model[15] is in a good agreement with the measured mobility. Mobilities of other networked fullerenes calculated using a similar structural model[16] (plotted as a solid line in Figure 2) deviate from experimental values by no more than 3%. In this calculation networked $LaC_{2n}^+$ fullerenes are simulated as $C_{2n+2}$ cages with two adjacent carbon atoms missing and the $La^+$ occupying the defect position. Alternatively, nonendohedral metallofullerenes
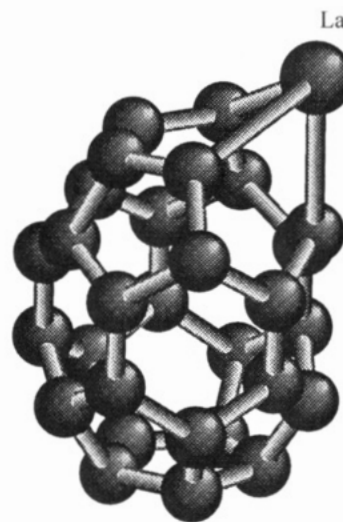


**Figure 3.** Calculated structure of networked $LaC_{29}^+$ metallofullerene.

with an even number of carbon atoms can be viewed as intact fullerene cages with the metal atom attached externally. The estimated difference in mobilities of these two structures is too small to be resolved in our experiments.

Isomer **II** of $LaC_n^+$ exists over a wide size range ($n = 24–50$) and is most abundant at $n = 32$. Its analogue for pure carbon clusters has been tentatively assigned to roughly planar graphite sheet fragments.[17] The mobility of isomer **II** for $LaC_n^+$ is 9–14% smaller than for $C_n^+$ clusters. This difference can be accounted for by a La atom coordinated to dangling bonds on the edge of a graphite sheet. The dash-dotted line in Figure 2 shows the mobilities calculated for this structural model.[16] They are in a reasonable agreement with the measured mobilities of isomer **II** over the entire size range. For pure carbon clusters the relative abundance of isomer **II** never exceeds a few percent.[7,9] However, for $LaC_n^+$ the relative abundance of this isomer in the isomer distribution for annealed clusters can reach 75%. Clearly, the La atom plays a role in stabilizing isomer **II** or catalyzing its formation.

The structural interconversions of the various isomers can be examined by increasing the energy at which the cluster ions are injected into the drift tube. The lower half of Figure 1 shows the drift time distributions recorded with injection energies around 200 eV, where the clusters become collisionally excited and anneal as they enter the drift tube. The amount of fragmentation at these injection energies does not exceed 5%, so that the changes observed in drift time distributions result primarily from isomer interconversions. For $C_{36}^+$ the main annealing product is the monocyclic ring (isomer **IV** in Figure 1d), and only a small fraction of $C_{36}^+$ rings converts into the fullerene.[7] At higher injection energies the rings dissociate. Conversion of rings into fullerenes becomes more efficient for larger pure carbon clusters.[18] In contrast to $C_{36}^+$, annealing of $LaC_{36}^+$ results in the formation of the metallofullerene and the graphite sheet (Figure 1b). Figure 4 shows the efficiency of the conversion of ring isomers into more compact structures for $C_n^+$ and $LaC_n^+$. In the size range $n = 29–35$ annealing into metallofullerenes occurs more readily for $LaC_n^+$ clusters with an odd number of carbon atoms. This is consistent with the assignment of small $LaC_{2n+1}^+$ metallofullerenes to networked structures (see above). The overall efficiency for conversion of $LaC_n^+$ rings into fullerenes far exceeds that for pure carbon clusters (compare solid and dash-dotted lines in Figure 4). For small $LaC_n^+$ clusters, metallofullerenes are less favored because they are highly strained, and the graphite sheets are the primary annealing product. Up to 50% of $LaC_n^+$ rings
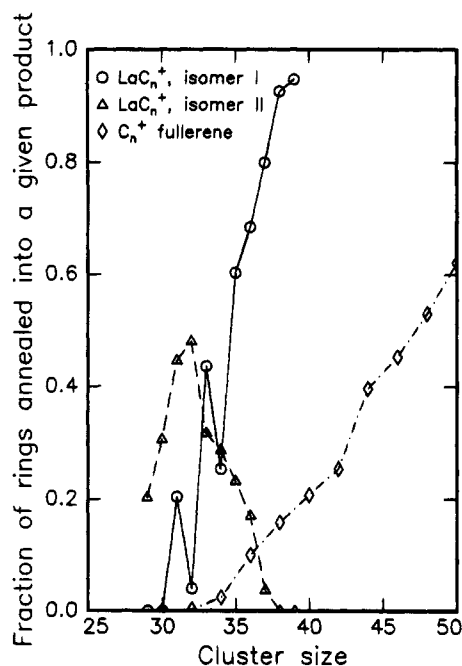
**Figure 4.** Fraction of the ring isomers annealed into fullerenes and graphite sheets plotted against cluster size. Results are given for both $LaC_n^+$ and $C_n^+$ (taken from ref 18). For $LaC_{34}^+$ and $LaC_{37}^+$ the fractions annealed into endohedral and networked metallofullerenes are summed. The absolute uncertainty in $LaC_n^+$ data is around $\pm 0.05$. No conversion of $C_n^+$ rings into graphite sheets has been observed.

can anneal to form the graphite sheets (dashed line in Figure 4), while this process has almost zero efficiency for $C_n^+$ clusters.[7,17]

The most plausible explanations for the dramatic effect a metal atom has on the conversion of rings into fullerenes and graphite sheets are as follows. First, a metal atom can activate C−C bonds in carbon rings, lowering activation barriers for their rearrangement and cross-linking. Second, the isomerization products (fullerenes and graphite sheets) or critical intermediates involved in their formation may be stabilized with respect to the reagents (ring isomers) by a metal atom. This will shift microcanonical equilibria involved in the isomerization process toward the products. Estimates of the activation energies for isomerization of rings into fullerenes in $LaC_n^+$ system show that they are similar to those for pure carbon clusters.[19] We therefore are inclined to think that the observed enhancement of fullerene and graphite sheet formation is due to an increase in the thermochemical stability of reaction products and/or intermediates relative to ring isomers. The first few critical steps in conversion of rings into fullerenes (or rings into graphite sheets) are expected to involve several cyclization processes necessary to form an initial network of hexagons and pentagons.[18] A metal atom incorporated into a carbon cluster can relieve the strain energy in intermediates formed in these cyclizations. The relative stabilization of fullerenes and graphite sheets can be achieved, for example, by reduction of the differences in ionization energies between various isomers due to the presence of a metal atom with a low ionization potential

(IP(La) = 5.58 eV[20]). The isomerization of metal-containing carbon rings into metallofullerenes and graphite sheets is a complicated multi-step process, so a combination of these and other factors is probably involved in the mechanism of its enhancement by metal atoms.

**References and Notes**

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(13) The dominant fragmentation product observed for all $LaC_n^+$ clusters in this study is $LaC_4^+$. Other fragmentation products include $LaC_{2n}^+$ ($n = 0–5$).

(14) The calculations were performed at the Hartree−Fock level with double-zeta quality basis sets and 11-electron relativistic effective core potential on La (Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; LaJohn, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654) using the Gaussian 92 program (Frisch, M. J.; *et al. Gaussian 92, Revision E.1*; Gaussian, Inc.: Pittsburgh, PA, 1992). Only a singlet configuration has been considered.

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(16) The calculated mobilities reported here are for MNDO-optimized carbon cluster geometries. Lanthanum−carbon bond lengths were determined in Hartree−Fock calculations for small model systems. The mobility estimates require two empirical parameters:. He-C and He−La hard-sphere collision radii. He−C collision radii (2.81 Å for isomer I and 2.66 Å for isomer II) were determined by fitting mobility data for pure carbon clusters. The He−La collision radius employed (3.07 Å) was determined from experimentally measured mobilities of $La^+$ and $La_2^+$ in He buffer gas, and the same value was used for both isomers.

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(19) This conclusion is specific to the $La^+–C_n$ system, where both valence electrons of $La^+$ are normally consumed by existing La−C bonds and no electrons are available for activation of other bonds. Our recent studies of $ZrC_n^+$ system similar to those described in the present paper show that Zr, which has one more valence electron than La, does lower the activation barrier for isomerization of metal-containing carbon rings into fullerenes.

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