Bonding of Metals to Carbon Rings: LaC_n^+ Isomers with La^+ Inserted and Attached to the Ring

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Doping carbon clusters with metal atoms provides an intriguing way to modify their properties and generate new materials. The metallofullerenes[1,2] and metallocarbohedranes[3,4] are good examples. Despite the intense interest in these systems, there is virtually no experimental information about how a metal atom binds to a carbon cluster, even in simple model systems. In this communication we describe studies of small ($n = 12$–40) LaC_n^+ clusters and report the observation of two families of LaC_n^+ monocyclic rings. For clusters with an even number of carbon atoms, an isomer where the lanthanum atom appears to be inserted into the ring dominates, while for odd-numbered clusters, only isomers where the lanthanum appears to be attached to the outside (or inside) of the carbon ring are observed. The odd/even fluctuations in the relative abundances of the two isomers provide an important clue about the nature of the chemical bonding in these clusters. This information is necessary to unravel the mechanism of endohedral metallofullerene synthesis, since recent studies have shown that LaC_{60}^+ polycyclic rings can be annealed into the endohedral metallofullerene with near unit efficiency.[5]

The apparatus and experimental techniques have been described in detail previously.[6] LaC_n^+ ions generated by pulsed laser vaporization of a La_2O_3/graphite composite rod[1] were size selected with a quadrupole mass spectrometer. Fifty-microsecond pulses of mass-selected ions were then injected into a drift tube containing ~5 Torr of helium. When the ions enter the drift tube they experience a rapid transient heating cycle as their injection energy is thermalized by collisions with the buffer gas. At high injection energies, the clusters may be heated to the point where they anneal or even fragment.[7] Further collisions with the buffer gas rapidly cool the clusters. They then travel across the drift tube under the influence of a weak electric field. The drift time depends on the structure of the cluster, such that clusters with compact geometries have shorter drift times than clusters with less compact geometries.[8] After exiting the drift tube the ions are focused into a second quadrupole mass spectrometer that is used to monitor the fragmentation pattern and transmit only the ion of interest.

The results presented here were recorded with an injection energy of 150 eV. At this energy a considerable amount of annealing and some fragmentation (usually less than 10%) occurs as the ions enter the drift tube. Thus, the drift time distributions of the surviving parent ions are dominated by relatively stable isomers.[9] Figure 1 shows drift time distributions recorded for LaC_{20}^+, LaC_{21}^+, LaC_{22}^+, and LaC_{23}^+.[10] Clusters containing even numbers of carbon atoms (LaC_{2n}^+) show two relatively large peaks, while odd-numbered clusters (LaC_{2n+1}^+) show only one. As the number of carbon atoms increases, the drift times become systematically larger because of the increase in the physical size of the cluster. The results in Figure 1 show that the smaller peak at shorter drift times for the LaC_{2n}^+ clusters correlates with the single peak observed for LaC_{2n+1}^+ clusters, while the larger peak at longer times for LaC_{2n}^+ clusters is not present in the data for the LaC_{2n+1}^+ clusters.

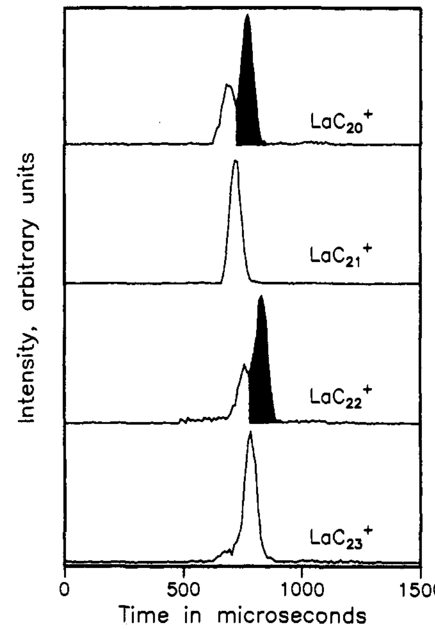

Figure 1. Drift time distributions recorded for LaC_{20}^+, LaC_{21}^+, LaC_{22}^+, and LaC_{23}^+ at an injection energy of 150 eV. Clusters containing an even number of carbon atoms display two peaks while the odd-numbered clusters show only one. The shaded peak for the even clusters corresponds to the isomers assigned in the text to slow rings. The other nonshaded peaks correspond to isomers that we assign to fast rings. See the text for a discussion of the geometries. The small feature at shorter times in the drift time distribution for LaC_{23}^+ is assigned to a bicyclic ring. The bicyclic rings appear to anneal into monocyclic rings as the injection energy is increased.

The basic patterns displayed in Figure 1 for the even- and odd-numbered clusters are observed over the entire 12-40-atom size range, although for even-numbered clusters above LaC_{26}^+ the relative intensity of the shorter-time peak is too small to clearly distinguish it from the larger peak at longer times. As discussed below, we assign these two sets of peaks to fast and slow monocyclic rings. Slow rings are observed only for LaC_{2n}^+ clusters, while fast rings are observed for both LaC_{2n}^+ and LaC_{2n+1}^+ clusters, but dominate for LaC_{2n+1}^+. For LaC_{12}^+–LaC_{24}^+ clusters, the fast and slow rings are the only isomers present in significant abundance. For larger clusters additional peaks appear at shorter times. These include peaks that we attribute to bicyclic rings and metallofullerenes. The metallofullerenes dominate the isomer distribution for clusters larger than LaC_{34}^+. We have studied these small metallofullerenes in some detail and will discuss them elsewhere.[11] The bicyclic rings first emerge at around LaC_{23}^+ (which is roughly the size that this isomer emerges for pure carbon clusters[8]). The bicyclic rings appear to anneal into monocyclic rings, as has been observed for the pure carbon clusters.[12,13]

Figure 2 shows the inverse mobilities determined for the two components in the drift time distributions plotted against cluster

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(9) Although the drift time distributions vary with cluster size, in general at low injection energies a larger abundance of isomers that we attribute to LaC_n^+ bicyclic rings is observed.
(10) Several other peaks in addition to those shown in Figure 1 were often apparent in the measured drift time distributions. These additional peaks are assigned to doubly charged ions and/or ions that do not have the elemental composition LaC_n^+ (as deduced from studies performed as a function of the LaC_n^+ isotope distribution). For clarity we have removed the peaks in the drift time distributions shown in Figure 1 that do not result from LaC_n^+ ions.
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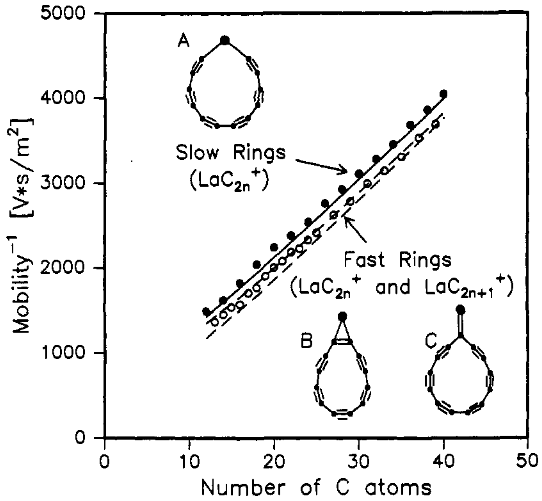

Figure 2. The points show the inverse of the measured mobilities plotted against the number of carbon atoms in the cluster. The solid circles correspond to the slow rings (see text) that dominate the drift time distributions for LaC_{2n}^+ clusters (as shown in Figure 1). The open circles are due to fast rings that dominate for LaC_{2n+1}^+. The inset in the upper-left portion of the figure shows a structural model for a typical slow ring (LaC_{12}^+). The inset in the bottom-right portion of the figure shows structural models for both even (LaC_{12}^+) and odd (LaC_{13}^+) clusters. The solid line shows the mobilities calculated for the isomer with La^+ inserted into the ring. The upper dashed line shows the nearly identical mobilities calculated for isomers **B** and **C** where the La^+ is not inserted and sits outside of the ring. The lower dashed line shows the mobilities calculated for isomers where La^+ sits inside the ring.

size. Clearly there are two distinct families of isomers. For pure unannealed carbon clusters in this size regime the main isomers present are monocyclic and bicyclic rings (along with tricyclic rings and fullerenes for the larger clusters with $n > 30$).[8] When the pure carbon clusters containing 10–40 atoms are annealed, the monocyclic ring becomes the dominant isomer.[12,13] Thus, a reasonable place to begin assigning the features observed for the LaC_n^+ clusters is with a monocyclic ring. If we assume that La^+ (which is divalent) retains the charge and bonds covalently, as demonstrated for La^+ attached to small hydrocarbon fragments,[14] then two basic types of geometry are plausible: one with La^+ inserted into the ring and the other with La^+ bound to the outside (or inside) of the ring. In the former case, La^+ is a part of the ring, forming what are effectively two single covalent bonds to produce C–La–C (isomer **A** in Figure 2). In the latter case, several isomers are possible, including La^+ bridging across a C–C bond (isomer **B** in Figure 2), La^+ forming a double bond with a single carbon atom in the ring (isomer **C**), and finally a structure where the La^+ sits inside the ring, possibly bound by electrostatic interactions.

In order proceed further with the structural assignments, it is necessary to generate model geometries and calculate their mobilities for comparison to our experimental data. Bond length estimates of 2.43 and 2.11 Å, for La—C single and La═C double bonds, respectively, were obtained from molecular orbital studies of La^+ attached to small hydrocarbon fragments.[15] These studies also gave force constants for bending and stretching of the pertinent La–C bonds, which when combined with C–C bond distances and force constants[16] were used to estimate the general shapes of the metal–carbon rings by minimizing their strain energies. This approach cannot be expected to give geometries that are as accurate as those provided by sophisticated theoretical techniques. However, the approximate geometry is sufficient for our purpose because the mobilities are not sensitive to minor structural differences. Mobilities were calculated for the optimized geometries assuming hard sphere interactions between the cluster and the helium buffer gas.[17] The calculated mobilities for the two isomers with the La^+ bound to the outside of the ring (labeled **B** and **C** in Figure 2) are essentially indistinguishable. For isomers where La^+ sits inside of the ring, the calculated mobilities are slightly larger. These results provide upper and lower limits for the mobilities of isomers where the La^+ is not inserted. The calculated mobilities for the isomers with La^+ inserted into the ring are smaller because the two relatively long La–C bonds increase the physical size of the ring.

Comparisons of the calculated mobilities to the experimental data are shown in Figure 2. From the excellent agreement between the calculated and measured mobilities we assign the slow rings observed for the LaC_{2n}^+ clusters to isomers with the lanthanum inserted into the ring (isomer **A**). The fast rings are assigned to isomers where the La^+ is not inserted.[18] The measured mobilities for the fast rings are in best agreement with the mobilities calculated for the isomers where La^+ is attached to the outside of the ring (isomers **B** and **C**). However, the agreement is also reasonably good for the isomer where La^+ sits inside the ring, so these geometries cannot be ruled out.

High-level *ab initio* calculations for pure carbon clusters show that polyacetylene (—C≡C—C≡C—) and cumulene (═C═C═C═C═) bonding schemes are close in energy, and the bonding scheme may fluctuate with cluster size.[19] Inserting a divalent La^+ into a carbon ring directs the bonding in the remaining portion of the ring to become polyacetylenic (as shown for isomer **A** in Figure 2). However, an even number of carbon atoms is required for the polyacetylene bonding scheme to propagate completely around the ring. Thus, the isomer with La^+ inserted into the ring is expected to be substantially more stable for clusters with an even number of carbon atoms. Experimentally, this isomer is observed only for clusters containing an even number of carbon atoms. So, the assignment of the slow rings to an isomer with La^+ inserted into a polyacetylene ring is compelling.

When the La^+ is bound to the outside of the ring, two polyacetylenic structures are possible. Isomer **B** should be more stable for clusters with an even number of carbon atoms while odd-numbered clusters should favor isomer **C**. Isomers consisting of La^+ in a bridging configuration with a cumulene ring are plausible for all cluster sizes, as are isomers where the La^+ is inside the ring. It seems reasonable that the fast rings, that dominate for LaC_{2n+1}^+ clusters, are due to isomer **B**. This suggestion is consistent with all of our experimental results, but this assignment is not definitive. Detailed theoretical calculations might help to resolve the remaining uncertainty about the geometries of the fast rings and provide further insight into the nature of the chemical bonding in these novel systems.

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(17) Mobilities were calculated from momentum transfer theory using a hard sphere collision model; see: Mason, E. A.; McDaniel, E. W. *Transport Properties of Ions in Gases*; Wiley: New York, 1988. For LaC_n^+–He, the hard sphere collision radius for He–C was taken to be 2.875 Å, a value that fits our measured data for the monocyclic rings of pure carbon clusters containing 10–60 carbon atoms; see ref 12. The He–La collision radius used was 3.2 Å.

(18) We have calculated model structures and mobilities for a variety of other possible isomers including LaC_n^+ chains and bicyclic rings. These models do not reproduce the experimental mobilities. Short chains attached to monocyclic rings were also considered. The mobilities of these species are almost identical to those for the isomers with the La^+ outside of the ring. However, the strain energy for these isomers is larger, and therefore they will be less stable than the monocyclic rings.

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