

## Structure and Stability of Palladium–Carbon Cations

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A theoretical study has been carried out to explore various isomers of palladium–carbon cations,  $\text{PdC}_x^+$ . By using the B3LYP density functional method, the geometries have been optimized for linear  $\text{PdC}_x^+$  as well as several classes of cyclic, bicyclic, and graphitic isomers. Linear clusters are shown to be the most stable isomers for  $x < 10$ , which is contrary to the previously studied behavior of lanthanum, an early transition metal. For larger systems, several classes of ring-containing structures are more stable than the linear isomers. Experimental ion mobility studies of the  $\text{PdC}_x^+$  clustering process reveal monocyclic rings for  $x > 10$ , a result consistent with the B3LYP prediction of rings as the most stable isomer. The ion mobility experiments did not produce any results for  $x < 10$ , which may be due to the reactivity of the linear  $\text{PdC}_x^+$ , which are predicted by B3LYP to be the most stable isomers at those sizes. Bicyclic  $\text{PdC}_{20}^+$  is shown to be less stable than the monocyclic rings, but the appearance of bicyclic  $\text{PdC}_{20}^+$  in the ion mobility experiments is explained as the result of binary collisions since it is stable with respect to  $\text{PdC}_{10}^+$  and  $\text{C}_{10}$  rings. Graphitic  $\text{PdC}_{20}^+$  is shown to be more stable than either monocyclic or bicyclic rings, although the graphitic sheets do not appear in the ion mobility experiments until  $\text{PdC}_{26}^+$ .

### Introduction

Ion mobility spectrometry<sup>1</sup> is a technique that has been used to elucidate the clustering process which ultimately leads to fullerenes<sup>2–4</sup> and their metal-containing counterparts, the metallofullerenes.<sup>5–8</sup> This experimental technique provides gross structural information concerning the molecules that are produced during the clustering process, and these molecules may, in fact, be intermediates along the path to fullerene formation. However, ion mobility spectrometry has limitations in distinguishing between isomers which are very structurally similar. The use of theoretical methods to supplement the experiments can narrow down a list of structurally similar isomers by determining which candidates are more energetically stable than others. The power of theory to serve in this way has been previously demonstrated for lanthanum–carbon clusters  $\text{LaC}_x^+$ .<sup>9</sup>

Recent ion mobility experiments<sup>8</sup> have elucidated the clustering process for palladium–carbon clusters  $\text{PdC}_x^+$ . No results were reported for  $x < 10$  because the clusters were not sufficiently abundant for ion mobility measurements to be made.<sup>10</sup> However, for  $x \geq 10$ , monocyclic rings are observed, bicyclic rings appear for  $x \geq 20$ , and graphitic sheets are seen for  $x \geq 26$ . The palladium–carbon ion mobility results for  $x > 10$  qualitatively resemble the results of all-carbon<sup>2</sup> and lanthanum–carbon<sup>5</sup> clusters in regard to the appearance of the various isomers, although the appearance of graphitic sheets at  $x = 26$  is earlier than for lanthanum–carbon and all-carbon results, which do not show graphitic sheets until  $x = 30$ .

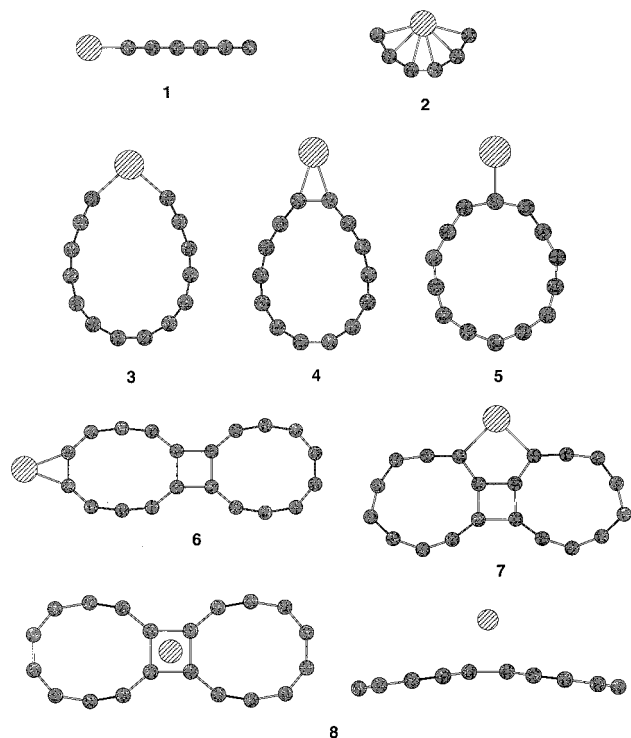
In the present work, theoretical calculations are carried out on a wide range of  $\text{PdC}_x^+$  clusters with the goal of elucidating the relative energetic stability of the various isomers of  $\text{PdC}_x^+$ . Are cyclic clusters more stable than linear ones at small cluster sizes, as is the case for all-carbon and lanthanum–carbon molecules? How do the various classes of cyclic isomers compare with each other? These questions are addressed over a range of sizes from  $x = 3$  to 24.

### Computational Methods

The calculations in this work have been carried out using the Gaussian 94 program.<sup>11</sup> Energy calculations and geometry optimizations have been performed using the B3LYP density functional method, which employs the Becke three-parameter (B3) exchange functional<sup>12</sup> and the Lee–Yang–Parr (LYP) correlation functional,<sup>13</sup> as implemented in Gaussian 94. Effective core potentials from Hay and Wadt<sup>14</sup> are used for the palladium atoms, and the palladium basis set is derived from the Hay and Wadt basis<sup>14</sup> using the LANL2DZ contraction scheme from Gaussian 94, with the two outermost p-functions replaced by a (41) split of the optimized outer p-function from Couty and Hall.<sup>15</sup> Further splitting gives the [4s4p3d] basis that is used for the palladium atom, and the carbon atoms each have a 6-31G\* basis set. All calculations in this work were performed with this basis set. For the  $^2\text{D}(4d^9)$  to  $^4\text{F}(4d^85s^1)$  energy difference of the  $\text{Pd}^+$  ion, this basis yields 2.55 eV, while the experimental value (properly averaged to remove the spin–orbit splitting) is 3.1 eV. Doublet states and quartet states of  $\text{PdC}_x^+$  have been considered, and the results reflect the energy of each molecule in its own ground state. Most of the ring isomers have doublet ground states, and the linear  $\text{PdC}_x^+$  alternate between even-numbered  $x$ , which have quartet states, and odd-numbered  $x$ , which have doublet states.

### Results and Discussion

Representative clusters from each class in this work are shown in Figure 1 and are similar in structure to many of the isomers from a previous lanthanum–carbon study (ref 9): (1) linear, (2) fan rings, (3) open rings, (4) closed rings, (5) “one-carbon” rings, (6) 2 + 2 cycloadducts with side-on attachment of the palladium atom (denoted “2 + 2-side”), (7) 2 + 2 cycloadducts with end-on attachment of the palladium atom (“2 + 2-end”), and (8) 2 + 2 cycloadducts with the palladium atom out of the plane on top of the four-membered ring (“2 + 2-top”). Also,



**Figure 1.** Examples of  $\text{PdC}_x^+$  classes in this study: (1) linear; (2) fan ring; (3) open ring; (4) closed ring; (5) one-carbon ring; (6) 2 + 2-side; (7) 2 + 2-end; (8) two views of 2 + 2 top.

**TABLE 1: B3LYP Relative Energies of  $\text{PdC}_x^+$  Clusters (Energies in eV)**

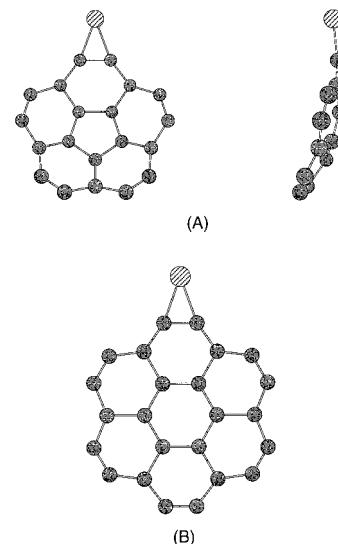
$x$	linear 1	fan ring 2	open ring 3	closed ring 4	one-carbon ring 5
3	0.00	1.54			1.03
4	0.00	1.60			2.62
5	0.00	2.60	1.24	4.95	4.34
6	0.00	2.53	1.13	1.59	1.05
7	0.00		0.59	1.19	1.09
8	0.00		0.44	1.77	1.37
9	0.00		0.48	1.12	1.86
10	0.00		0.38	-0.55	-0.78
11	0.00		-0.12	-0.35	-0.60
12	0.00		-0.36	-0.34	-0.15
14	0.00		-0.26	-1.58	-1.08
16	0.00		-0.84	-1.33	-0.94
18	0.00		-0.70	-2.01	-1.77

**TABLE 2: B3LYP Relative Energies (in eV) for  $\text{PdC}_x^+$  ( $x = 20, 24$ )**

	$x = 20$	$x = 24$
open ring	1.03	
closed ring	0.86	
one-carbon ring	0.86	
2 + 2-side	1.74	3.07
2 + 2-end	2.14	3.33
2 + 2-top	2.94	
graphitic	0.00	0.00

for large values of  $x$ , graphitic sheets are examined. The B3LYP relative energies of 1–5 for  $x = 3$ –18 are shown in Table 1. The relative energies of the rings (3–5), 2 + 2 adducts (6–8), and the graphitic sheets for  $x = 20$  and 24 are shown in Table 2. The results address a variety of questions regarding the stability of  $\text{PdC}_x^+$  clusters.

**Small Clusters ( $x = 2$ –10).** Table 1 shows that linear clusters are the most stable isomers for  $x < 10$ , with the fan rings and the other ring isomers higher in energy. In the fan



**Figure 2.** Graphitic  $\text{PdC}_x^+$ : (A) two views of  $x = 20$  corannulene-like; (B)  $x = 24$  coronene-like.

ring (2), the two competing energetic forces are the destabilizing strain of bending the linear chain to form the fan and the stabilizing influence of the increased coordination of the chain to the metal. However, the d-orbitals of palladium are nearly full ( $\text{Pd}^+$  has a  $d^9$  ground state), so that there is very little benefit to the higher degree of coordination, and the fan ring is unstable. This effect may also account for the fact that endohedral  $\text{PdC}_x^+$  fullerenes are not seen for larger clusters. The small open rings (3), closed rings (4), and one-carbon rings (5) also all suffer from carbon ring strain which counteracts any stabilization which comes from metal–carbon bonding or additional carbon–carbon bonds.

**Intermediate Clusters ( $x = 10$ –18).** The data in Table 1 reveal that the closed ring and one-carbon ring are both more stable than the linear cluster for  $x = 10$ . For  $x = 11$  and all higher values, all three rings are more stable than linear clusters since, for these large sizes, the ring strain has been reduced sufficiently such that it is no longer the dominant factor in the ring energetics. Since the closed rings and one-carbon rings have a complete carbon ring and the open rings do not, closed rings and one-carbon rings are more likely to incur an energetic penalty for having a carbon cycle of  $4n$  atoms versus  $4n + 2$  atoms. This  $4n/4n + 2$  stability pattern is clearly reflected in the  $x = 12, 14, 16,$  and 18 data.

**Large Clusters ( $x = 20, 24$ ).** For  $x = 20$  and 24, 2 + 2 cycloadducts and graphitic sheets have been considered in addition to the classes of monocyclic rings. The 2 + 2 cycloadducts are included because they are reasonable structures for the bicyclic rings seen in the ion mobility experiments. Also, the 2 + 2 cycloadduct is a reasonable product of binary collisions which occur between the smaller monocyclic rings. The energies from Table 2 illustrate the basic features of the cycloadducts. The 2 + 2 cycloadducts are less stable than monocyclic rings because of the added ring strain of grouping the carbon atoms in two smaller rings rather than one large ring. The 2 + 2 cycloadducts prefer a metal atom placement in the plane of the carbon cluster because a nonplanar placement would break the planarity of the carbon structure and disrupt its  $\pi$ -system.

The  $x = 20$  and  $x = 24$  graphitic sheets are shown in Figure 2 and are corannulene-like and coronene-like, respectively. Relative energy data for the  $x = 20$  and  $x = 24$  clusters are shown in Table 2. The graphitic sheets are more stable than

any of the other isomers, and in fact, the extent to which the graphitic sheets are more stable is very likely underestimated by B3LYP. The tendency of gradient-corrected density functional methods (such as B3LYP) to underestimate the stability of graphitic clusters has been established previously.<sup>9,16</sup>

**Ion Mobility Interpretations.** The ion mobility study<sup>8</sup> of palladium–carbon clusters reports no clusters for  $x < 10$ . The clusters at those small sizes were insufficiently abundant for ion mobility measurements. This result is possibly due to a shift in the nature of the dominant isomer at the  $x = 10$  threshold, which is predicted by the B3LYP results in Table 1. Perhaps the linear clusters, which would be expected to dominate the distribution of clusters for  $x < 10$  because of their stability, are more difficult to accumulate in quantity than the various ring isomers, which would be expected to be the largest fraction of the  $x > 10$  clusters. Linear clusters are less compact than ring structures and have a higher collision cross section, which may result in such rapid addition of carbon atoms during the clustering process that the linear chains grow into the rings quickly and have a correspondingly low abundance. Although linear carbon chains have been observed in all-carbon ion mobility experiments,<sup>2</sup> the palladium atom may be mediating cluster growth in such a way as to preclude detection of the linear  $\text{PdC}_x^+$  clusters. Alternatively, the inability to detect linear  $\text{PdC}_x^+$  could also be accounted for if the palladium atom is somehow detached from the linear clusters in a dissociation process which does not occur in the rings.

Over the range  $x = 10$ –18, monocyclic rings are the only isomers seen in the ion mobility experiments, an observation which correlates well with the energetic stability of monocyclic rings of those sizes as shown by the B3LYP results in Table 1. At  $x = 20$ , bicyclic rings appear in the ion mobility distributions, but the B3LYP results in Table 2 show that the 2 + 2 cycloadducts are much less stable than their monocyclic counterparts. The appearance of the bicyclic rings can be explained with respect to plausible reactants that undergo the cycloaddition. For example, taking as hypothetical reactants the  $\text{PdC}_{10}^+$  one-carbon ring (5, the most stable monocyclic ring for  $x = 10$ ) and an all-carbon  $\text{C}_{10}$  ring, the process of forming any of the  $\text{PdC}_{20}^+$  2 + 2 cycloadducts listed in Table 2 would be exothermic by at least 3.4 eV at the B3LYP level of theory. Therefore, it is reasonable that bicyclic rings should be observed for  $x = 20$  but not for smaller  $x$  because of the lack of plausible reactants, since  $x = 10$  is the smallest  $\text{PdC}_x^+$  for which the most stable isomer is cyclic. The results in Table 2 also imply that transforming bicyclic rings to monocyclic rings would be exothermic, and in fact, some of the bicyclic rings have been shown to become monocyclic rings at sufficiently high injection energies in the  $\text{PdC}_x^+$  ion mobility experiments.<sup>8</sup> On the other hand, graphitic  $\text{PdC}_{20}^+$  is more stable than either monocyclic rings or 2 + 2 adducts and is not seen experimentally. Clearly the process of forming a graphitic sheet is more complex than a binary collision of rings, and some intermediate step in graphite sheet formation may be kinetically or energetically unfavorable for  $x = 20$ .

**Palladium vs Lanthanum.** The energetics of  $\text{PdC}_x^+$  differ substantially from the previously studied energetics of lanthanum–carbon clusters.<sup>9</sup> For the smallest clusters in the lanthanum–carbon case, fan rings are more stable than linear clusters. This is because the electron-deficient lanthanum atom can effectively coordinate to each atom in a linear chain, with the stabilizing energy of metal–carbon interactions, such as  $\pi$ -donation from the C–C  $\pi$ -bonds to the metal atom, overcoming the strain of bending an otherwise linear all-carbon chain. The

**TABLE 3: Pd–C Bond Length (in Å) and Average C–C Bond Alternation (in Å) for Monocyclic  $\text{PdC}_x^+$  (Results at B3LYP Level of Theory)**

$x$	open ring 3	closed ring 4	one-carbon ring 5
10	1.87 0.04	1.97 0.05	1.99 0.04
12	1.86 0.02	1.98 0.10	1.88 0.03
14	1.91 0.02	2.01 0.02	1.91 0.01
16	1.86 0.02	1.99 0.09	1.88 0.03
18	1.87 0.04	2.00 0.05	1.90 0.03

electron-rich palladium atom is not sufficiently stabilized by donation from the carbon chain, so the relative energies of small  $\text{PdC}_x^+$  are governed by the carbon atoms, which are most stable in a linear chain at small sizes. At larger sizes, such as the range  $x = 10$ –18, palladium–carbon and lanthanum–carbon clusters are qualitatively similar in that the various monocyclic rings are lowest in energy.

The one major difference over  $x = 10$ –18 is in the one-carbon rings, which are high-energy transition states for lanthanum but energy minima for palladium. Table 3 shows the Pd–C bond lengths and average C–C bond alternation of the open ring (3), closed ring (4), and one-carbon ring (5) over the range  $x = 10$ –18. The open rings have very short Pd–C bonds and very little bond alternation, which implies that the palladium atom is simply another member of a cumulenic carbon ring with Pd–C double bonds. The closed rings have much longer Pd–C bonds, which are likely Pd–C single bonds attaching the Pd atom to a carbon ring whose degree of bond alternation varies between rings with  $x = 4n$  and rings with  $x = 4n + 2$ . The one-carbon rings have Pd–C bonds which are shorter than those of the closed rings and, therefore, have a higher degree of double bond character. The stability of the one-carbon rings is likely the result of palladium's ability to form a metal–carbon double bond of sufficient strength that there is not a significant energetic driving force to break the double bond and form two single bonds instead.

## Conclusions

Several conclusions can be drawn from the B3LYP results: (1) Small palladium–carbon clusters prefer linear arrangements, because palladium is electron-rich and does not need the high coordination of the fan rings favored by early metals. (2) The three classes of monocyclic rings are qualitatively close to each other in energy and all more stable than linear clusters beginning at  $x = 11$  with some rings more stable than linear as early as  $x = 10$ . (3) Carbon 2 + 2 cycloadducts prefer palladium attachment in the plane of the adduct and side-on, in proximity to the four-membered ring.

In regard to the ion mobility study of  $\text{PdC}_x^+$ , the B3LYP calculations predict a shift in the nature of the dominant isomer at the  $x = 10$  threshold. Monocyclic rings are experimentally observed for  $x > 10$ , which is consistent with the B3LYP results, which show monocyclic rings to be most stable. The absence of experimental data for  $x < 10$  may be the result of linear clusters, predicted by B3LYP to be most stable, growing to larger clusters too rapidly to be accumulated in sufficient quantity for ion mobility measurements.

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