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Cage Shrinkage of Fullerene via a C_2 Loss: from IPR $C_{90}(28)Cl_{24}$ to Nonclassical, Heptagon-Containing $C_{88}Cl_{22/24}$

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Supporting Information

ABSTRACT: A new case of chlorination-promoted fullerene cage shrinkage is reported. Chlorination of C_{90} (isolated pentagon rule isomer no. 28) with VCl_4 afforded $C_{88}Cl_{22}$ with a nonclassic carbon cage (NCC) containing 1 heptagon and 13 pentagons including 2 fused pairs flanking the heptagon. The pathway of C_2 abstraction from the C_{90} cage is suggested on the basis of density functional theory calculations.

The classical fullerene cages composed of pentagons and hexagons demonstrate considerable stability toward skeletal transformations. This is especially true of the lowest-energy isomers that satisfy the isolated pentagon rule (IPR), i.e., have no adjacent pentagons.[1] Accordingly, most of the fullerene reactions under nonextremal conditions consist in exohedral functionalization.[2] Notable exclusions comprise the formation of derivatized C_{62} from C_{60},[3] oxidative cage opening, and its reductive restoration.[4] The pristine fullerene cages also show remarkable thermal stability. Certain higher fullerenes (C_{76}, C_{78}, and C_{84}) were reported to degrade to the lower ones only above 1000 °C.[5]

Documented observations of skeletal transformations in fullerenes are rare. Recently, conversion of IPR to non-IPR isomers via chlorination-promoted Stone−Wales (SW) rearrangements (rotations of C−C bonds by 90°)[1] was reported for $C_{76}(1)$,[6] $C_{82}(3)$,[7] and $C_{102}(19)$[8] fullerenes (isomer numbering according to the spiral algorithm[1]). Another type of skeletal transformation in fullerenes is C_2 abstraction. The first example of cage shrinkage upon chemical modification was due to fluorination of C_{60} with cesium−lead oxyfluorides at 550 °C.[9] In addition to the main reaction product, $C_{60}F_{18}$, two byproducts, $C_{58}F_{18}$ and $C_{58}F_{17}(CF_3)$, were isolated. The ^{19}F NMR data suggested that they comprise a heptagon with adjacent triples of pentagons. More recently, C_2 abstraction was observed under much milder conditions: upon chlorination with VCl_4 at ca. 300 °C.[10] Normally, this protocol affords fullerene chlorides with intact IPR cages, e.g., $C_{60}Cl_{30}$, $C_{70}Cl_{28}$, $C_{78}(2)Cl_{30}$, $C_{90}(46)Cl_{32}$, etc.,[11] but its application to the IPR isomer $C_{86}(16)$ gave $C_{84}Cl_{32}$ with a heptagon in the carbon cage.[10] Hereinafter we will use the term "nonclassical carbon cage" (NCC) for the heptagon-containing structures.

Even though the possible role of heptagons and C_2 abstraction in the high-temperature fullerene formation pathways has been widely discussed in the literature,[12−14] it is commonly accepted that NCC fullerenes are too unstable to survive as terminal products of the synthesis of pristine fullerenes. The aforementioned instances of heptagon formation in the halogenated fullerenes involve stable preformed IPR cages. In the arc-discharge synthesis, only in situ functionalization can stabilize an NCC compound. So far, the only example is the heptagon-containing $C_{68}Cl_6$ obtained via the addition of a source of chlorine, namely, CCl_4, in the reactor.[14]

Here, we report a new observation of cage shrinkage in higher fullerenes. Chlorination of $C_{90}(28)$ provides $C_{88}Cl_{22}$ with a heptagonal ring and two pairs of fused pentagons. The structures of both the initial (IPR) and final (NCC) chlorinated compounds were unambiguously determined by means of single-crystal X-ray diffraction (XRD).

Three C_{90} fractions (I−III) were isolated by multistep high-performance liquid chromatography from the fullerene soot as described elsewhere.[15] The mass spectrometric analyses, as well as our previous chlorination experiments at 280−300 °C, followed by single-crystal XRD studies, demonstrated that all three fractions contain only the isomeric mixtures of C_{90}.[15] In particular, fraction III was observed to contain at least three C_{90} isomers, nos. 30, 28, and 34. The present experiments involved ampule chlorination of fraction III with VCl_4 at higher temperatures in the range of 340−360 °C over the course of several weeks. X-ray crystallography of the isolated tiny orange crystals with the use of synchrotron radiation revealed two closely related molecular structures, $C_{88}Cl_{22}$ (Figure 1), which was obtained in three different crystalline modifications, and $C_{88}Cl_{24}$.[16]

The remarkable property of the new molecules is that they have two C atoms less than in the starting C_{90} and feature a heptagonal ring flanked by two fused pairs of pentagons. These pairs likely play a vital role in stabilizing the heptagon with its increased valence angles.

The distribution of 22 Cl atoms on the carbon cage of the $C_{88}(NCC)Cl_{22}$ (**6**) molecule is far from uniform (Figure 2). A total of 11 Cl atoms on one hemisphere form para contacts in

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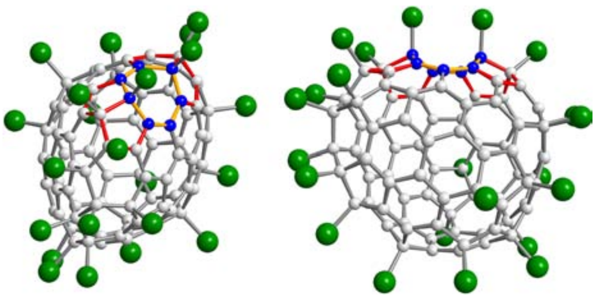

Figure 1. Two projections of the molecule **6**. Color code: C, gray except for a seven-membered ring (blue); Cl, green; fused pentagonal rings, red; bonds of the heptagonal ring, yellow.

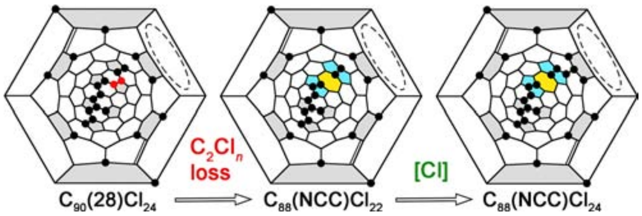

Figure 2. Schlegel diagram presentation of a C_2 loss from IPR $C_{90}(28)Cl_{24}$ under formation of **6** and further chlorination to $C_{88}(NCC)Cl_{24}$. In the diagram of $C_{90}(28)Cl_{24}$, the two Cl atoms attached to the leaving C_2 unit are shown in red. Heptagons and fused pentagons are highlighted, respectively, with yellow and cyan. Benzenoid rings and isolated double C−C bonds on fullerene cages are also indicated.

hexagons and 1,3 contacts in pentagons, while on the opposite hemisphere, which comprises the heptagon and the fused pentagons, most of the addends are attached adjacently, forming an "ortho chain" including one Cl atom with three close Cl···Cl contacts. Both addition motifs have been already observed in higher fullerene chlorides.[11] The addition to **6** of two extra Cl atoms produces $C_{88}(NCC)Cl_{24}$ with one more triple Cl···Cl contact (see Figure 2).

Similar to many previously reported cases, the chlorine addends cut the spherical π system of the fullerene into smaller conjugated domains with conventional planar aromaticity. They include one isolated benzenoid ring and two much larger assemblies: one of five hexagons with vinyl appendixes and the other of seven hexagons. Besides, two isolated C−C double bonds are formed. Yet another similarity with the known higher fullerene chlorides consists in considerable elongation of the sp^3−sp^3 C−C distances within the "ortho chains", up to 1.58−1.60 Å for the 5:5 bonds and 1.64−1.65 Å for some of the 5:6 bonds and the bonds at the triple Cl···Cl contacts. The lengths of the C−Cl bonds in the molecule **6** range between 1.77 and 1.84 Å, which reflects a certain dispersion in the binding energy. The shortest C−Cl bonds are found at the pentagon−pentagon junctions and in the central position of the triple Cl···Cl contacts (1.77−1.78 Å), where pyramidalization of the carbon sites is highest. All other C−Cl bond lengths fall within the usual range of 1.79−1.84 Å, with average values of 1.804 Å for the ortho chain and 1.819 Å for the para attachments.

To rationalize the mechanism of C_2 loss, one first needs to determine the starting IPR fullerene compound. Reconstructive analysis to identify the possible C_{90} IPR precursors reveals that only the C_2-symmetric IPR isomer $C_{90}(28)$ can give the observed $C_{88}(NCC)$ via a single act of C_2 abstraction. Furthermore, formal abstraction of a C_2Cl_2 unit from its nonsymmetric chloride $C_{90}(28)Cl_{24}$, one of the previously reported products of chlorination of C_{90},[15] directly gives the reported **6** (see Figure 2). Thus, $C_{90}(28)Cl_{24}$ may confidently be viewed as a precursor of **6**.

In our previous work on C_2 abstraction from the chlorides of C_{86}, we have not identified any reaction mechanism limited to fullerene, chlorine, and vanadium chlorides with activation energy below 3 eV. Although loss of C_2 in a form of, e.g., C_2Cl_4, from the initial $C_{86}Cl_{28}$ molecule was thermodynamically favorable, the C_2 fragment in question belonged to its rather stable corannulene substructure. Consequently, any relatively stable intermediates on the possible C_2 abstraction pathways were accessible only upon cleavage of at least two C−C bonds in $C_{86}Cl_{28}$. In the present case, however, the C_2 fragment in the starting $C_{90}(28)Cl_{24}$ is already chlorinated and is located in the rather highly curved region of the carbon cage, which has a large effect on the energetics of skeletal transformations.

The branched pathway discovered in our density functional theory (DFT; PBE/TZ2p) computations using the *PRIRODA* software[17] is sketched in Figure 3. For simplicity, we omit the intermediate minima and transition states due to chlorine transfer between VCl_4/VCl_5 and the carbon sites. Such transfer precedes and follows each act of rearrangement of the C−C bonds, but the barriers of these C−C rearrangement substeps shown in Figure 3 always dominate.

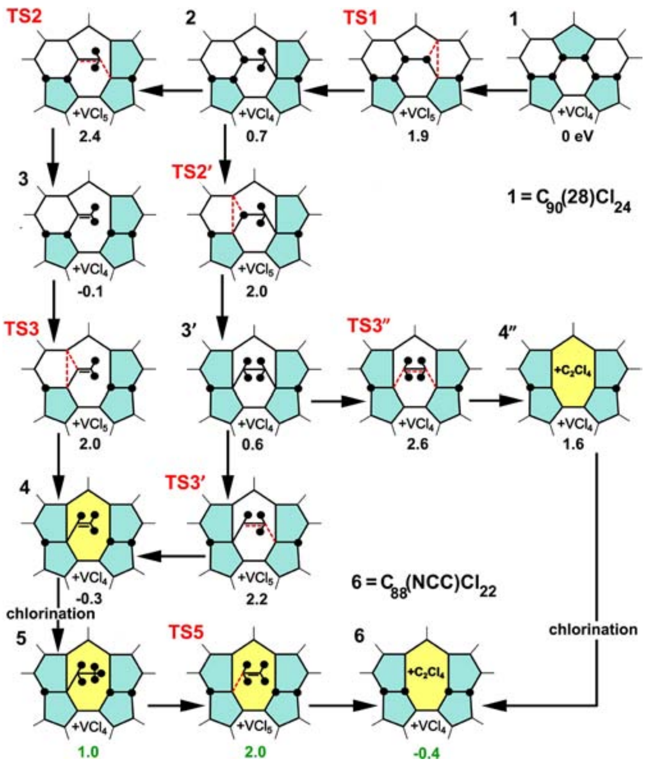

Figure 3. Calculated pathways of C_2 abstraction. The structures with black numbers represent the PES minima; the TS structures are transition states where the forming and cleaving bonds are shown with red dashes. The energy in electronvolts is given relative to $C_{90}(28)Cl_{24}$ + VCl_4 (**1**); see the text for an explanation of the values for **5**, **TS5**, and **6** with two extra Cl atoms.

The first stages of the pathway resemble, in certain aspects, the mechanism of the SW rearrangements promoted by $SbCl_5$.[6] Initially, one of the Cl atoms adjacent to the C_2 unit in question is being transferred to a VCl_4 molecule that acts as a catalyst and transiently forms VCl_5. Unlike formation of the $SbCl_6^-$ anion in the course of $SbCl_5$-promoted SW rearrangements, charge transfer to VCl_5 does not exceed 0.3e because of its moderate electron affinity. Chlorine transfer is followed by rearrangement of the C−C bonds (**TS1**) and then reverse chlorine transfer to give the intermediate structure **2**, where one of the atoms of the abstracted C_2 unit forms a CCl_2 bridge. Because of the global asymmetry of the starting chloride, the reaction profile depends on which of the atoms of the C_2 unit is being initially involved. Here we present the results for the alternative characterized by 0.2−0.3 eV more stable intermediate structures.

Compound **2** is a possible branching point of the pathway. One route leads to structure **3** with a $=CCl_2$ moiety, which is slightly more stable than the parent chloride **1**. The other possibility is to repeat the first stage of the pathway with the second atom of the abstracted C_2 unit to form a C_2Cl_4 bridge in **3′**. Although the sterically strained **3′** is less stable, here we observe a somewhat lower activation barrier of 2.0 eV. Single-stage retro-Diels−Alder abstraction of C_2Cl_4 from **3′** already affords the final C_{88}(NCC) cage in **4″**, and highly exothermic chlorination of the freed pentagon−pentagon junctions completes **6**. However, the calculated barrier of 2.6 eV for abstraction of C_2Cl_4 may be slightly too high for a reaction below 400 °C. A more likely route starting from both **3′** and **3** involves the initial formation of an intermediate compound **4** with the C_{88}(NCC) cage and a $-C_2Cl_3$ moiety.

Chlorination of the $-C_2Cl_3$ group yields $-C_2Cl_5$ in compound **5**. In fact, this chlorination is rather unfavorable because of high steric repulsion with the adjacent chlorine addends, and **5** can hence be viewed only as an intermediate. Because the calculated energy of chlorination of **4** is ca. 1.3 eV lower that the averaged chlorination energy per two addends in the typical IPR fullerene chlorides accessible by chlorination with VCl_4, we assign to **5** the effective relative energy of 1.0 eV. The highly exothermic final transformation of **5** to **6** is characterized by an activation barrier **TS5** comparable to those of the previous stages. Chlorination of the released C_2Cl_4 to C_2Cl_6 will ensure irreversibility of the process.

The calculated pathway may be rather common for a board group of higher fullerene cages, given that certain structural prerequisites are being fulfilled. In particular, there must be a chlorinated (5:6) bond belonging to a hexagon that has three adjacent pentagons. In this case, abstraction of such bond will lead to stabilization of the emerging heptagon by the pentagon−pentagon junctions at its sides. Also, it may be important that the fragment in question is located in a highly curved region of the carbon cage. However, our present findings still leave the open question about the possible C_2 abstraction pathways in the above-mentioned case of C_{86}. In view of that, further studies of carbon cage shrinkage in higher fullerenes remain of considerable fundamental interest.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF, Berlin, Germany) using a MAR225 CCD detector, $\lambda = 0.8551-0.9050$ Å. $C_{88}Cl_{22.05}$ (modification I): triclinic, $P\bar{1}$, $a = 12.5461(9)$ Å, $b = 14.583(1)$ Å, $c = 19.408(1)$ Å, $\alpha = 106.232(4)$, $\beta = 93.548(5)°$, $\gamma = 112.024(5)°$, $V = 3104.6(3)$ Å^3, $Z = 2$, R1(F)/wR2(F^2) = 0.055/0.143 for 11710/13530 reflections and 1027 parameters. $C_{88}Cl_{22.05}$ (II): monoclinic, $P2_1/c$, $a = 12.777(1)$ Å, $b = 23.0058(8)$ Å, $c = 21.095(1)$ Å, $\beta = 98.35(1)°$, $V = 6135.0(6)$ Å^3, $Z = 4$, R1(F)/wR2(F^2) = 0.053/0.135 for 10647/14881 reflections and 1020 parameters. $C_{88}Cl_{22.55}$ (III): monoclinic, $C2/c$, $a = 24.327(2)$ Å, $b = 14.4721(6)$ Å, $c = 36.516(1)$ Å, $\beta = 101.652(9)°$, $V = 12591.0(12)$ Å^3, $Z = 8$, R1/wR2 = 0.094/0.232 for 11836/13752 reflections and 1139 parameters. $C_{88}Cl_{24.21}$: monoclinic, $P2_1/c$, $a = 36.778(3)$ Å, $b = 14.428(1)$ Å, $c = 24.192(2)$ Å, $\beta = 98.894(9)°$, $V = 12682.7(17)$ Å^3, $Z = 8$, R1/wR2 = 0.114/0.281 for 14975/25632 reflections and 2074 parameters.

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