J|A|C|S
COMMUNICATIONS

Disclosure of the Elusive C_{2v}-C_{72} Carbon Cage

Karolin Ziegler, Andreas Mueller, Konstantin Yu. Amsharov, and Martin Jansen*

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

Received September 20, 2010; E-mail: M.Jansen@fkf.mpg.de

Abstract: The stability of all fullerenes (closed carbon cages composed of pentagons and hexagons) can be explained by a simple empirical rule that forbids direct pentagon pentagon junctions (the isolated pentagon rule). Among thousands of possible fullerene structures, only one was predicted to violate this rule, namely, C_{2v}-symmetric $^{\#11188}C_{72}$. In this work, we present the synthesis and isolation of this elusive fullerene cage for the first time. The C_{2v}-C_{72} cage was captured by in situ chlorination to form $C_{72}Cl_4$, whose structure was unambiguously determined by single-crystal X-ray analysis. The chlorination pattern and resulting stability of $C_{72}Cl_4$ are discussed.

The stabilities of fullerenes can be explained in terms of the so-called isolated pentagon rule (IPR), which states that all pentagons must be completely surrounded by hexagons because the pentagon junction results in very high local strain.[1] Indeed, all known pristine fullerenes obtained by conventional synthesis obey this rule without exception. The IPR-violating fullerenes nevertheless can be stabilized by either endohedral encapsulation of metal clusters or exohedral derivatization.[2] In situ chlorination using CCl_4 or Cl_2 as an additional reagent in conventional fullerene synthesis has been found to be an effective method for stabilizing non-IPR fullerene cages.[3] Several unconventional fullerenes have been obtained using this approach, including $C_{50}Cl_{10}$,[3a] $C_{54}Cl_8$,[3e] $C_{56}Cl_{10}$,[3b] $C_{56}Cl_{12}$,[3e] $C_{60}Cl_8$,[3c] $C_{60}Cl_{12}$,[3c] $C_{64}Cl_4$,[3d] $C_{66}Cl_6$,[3e] $C_{66}Cl_{10}$,[3e] and $C_{78}Cl_{10}$.[3f] In addition to these, two examples of chlorinated non-IPR fullerenes, $C_{76}Cl_{24}$ and $C_{84}Cl_{32}$, have been realized by elegant Stone−Wales rearrangement of higher IPR fullerenes into non-IPR cages under strong chlorination conditions.[4]

Among the numerous fullerene species, $^{\#11188}C_{72}$ is a peculiar one since it represents the only known example where a non-IPR cage is expected to be more stable than its IPR isomer, D_{6d}-C_{72}.[5] Despite the fact that $^{\#11188}C_{72}$ was predicted as long as 13 years ago[5a] to be the most stable cage for 72 carbon atoms, no convincing evidence of its existence has been reported to date. All attempts to stabilize the C_{72} fullerene by endohedral elements have resulted in the formation of less stable cages.[6] This can be explained by the fact that the stabilization of endofullerenes is mostly related to the stability of the corresponding negatively charged cages, irrespective of the stability of the neutral cage itself.[2,7] In contrast, exohedral stabilization, where the stability of the parent empty pristine fullerene cage is assumed to play a major role,[2,3b,e] seems to be a key to catching the mysterious $^{\#11188}C_{72}$.

In this communication, we report the synthesis, isolation, and structural characterization of the elusive C_{2v}-C_{72} fullerene cage stabilized by exohedral derivatization through in situ chlorination.

The chlorofullerene-containing soot was prepared using CCl_4 as a chlorinating agent by applying the high-frequency furnace technique, which has been found to be exceptionally suitable for the synthesis of higher chlorinated fullerenes.[8] The soot obtained was extracted with cold toluene, from which $C_{72}Cl_4$ was separated by means of multistage high-performance liquid chromatography (HPLC). Notably, the separation protocol developed avoids a time-consuming recycling process and thus is more suitable for preparative separation (for details, see the Supporting Information). The HPLC profile and UV−vis spectrum of the purified sample are presented in Figure 1. The compound was found to be stable in toluene solution as well as in the solid state under an air atmosphere, as neither degradation nor formation of any products were observed over several weeks according to HPLC data. Under laser desorption ionization (LDI) mass analysis conditions, the chlorofullerene easily loses all of its chlorine atoms, which is a typical phenomenon for chlorinated fullerenes,[9] and only a single peak at *m*/*z* 864.0 corresponding to the C_{72} carbon cage could be observed. In contrast, in matrix-assisted LDI (MALDI) mode with 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as a matrix, the chlorinated species $C_{72}Cl^+$, $C_{72}Cl_2^+$, $C_{72}Cl_3^+$, and (with a low-intensity signal) $C_{72}Cl_4^+$ could be detected (Figure 1). The isotopic distribution can be found in the Supporting Information.

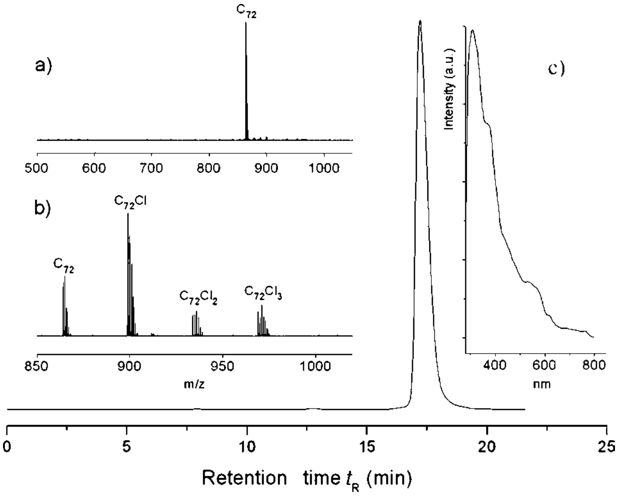

Figure 1. HPLC profile of purified $^{\#11188}C_{72}Cl_4$ (Buckyprep 4.6 × 250, toluene as eluent, 1 mL min^{-1}, 25 °C). (a) LDI mass spectrum showing a single signal at *m*/*z* 864.0, implying that the newly isolated compound has a C_{72} cage. (b) MALDI mass spectrum using DCTB as a matrix, displaying that at least four chlorine atoms are attached to the C_{72} cage. (c) UV−vis spectrum of pure $C_{72}Cl_4$ in toluene.

Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a CS_2 solution. The structure determination and refinement revealed that the $^{\#11188}C_{72}$ cage is stabilized by four chlorine atoms.[10] All of them are attached to carbon atoms that belong to the fused pentagon fragment, as shown in Figure 2. Such an addition reduces the symmetry of the parent C_{72} from C_{2v} to C_2, resulting in two stereoisomers of $C_{72}Cl_4$. Despite the fact that halogenated chiral fullerenes tend to form highly ordered structures,[11,3e] in the crystal under discussion, both stereoisomers were found to occupy the same crystallographic site. Fortunately, the quality of

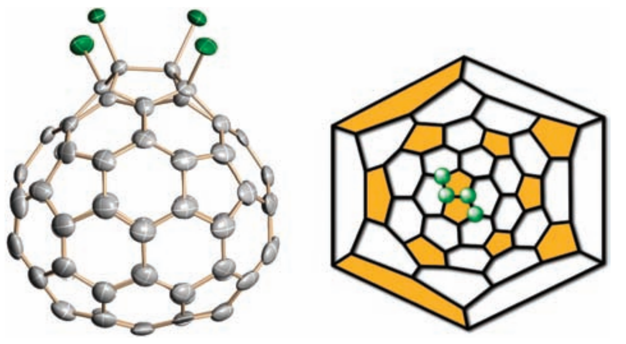

Figure 2. (left) ORTEP plot of the molecular structure of $C_{72}Cl_4$ in the crystal. Thermal ellipsoids are set at 50% probability. Carbon and chlorine atoms are coded by gray and green colors, respectively. (right) Schlegel diagram showing the connectivity and chlorination pattern (green circles) of the experimentally observed C_2-symmetric $C_{72}Cl_4$ (only one stereoisomer is presented).

the crystal allowed refinement of all carbon positions without any restraints, providing reliable data. The $C_{72}Cl_4$ molecules crystallize in the hexagonal close packing motif with typical short C···C and C···Cl contacts of 3.2−3.3 Å, while CS_2 molecules occupy the octahedral voids. A more detailed analysis revealed that molecules in the crystal are not statistically disordered but instead form fully ordered "chains" consisting of only one isomer each. As can be seen from the crystal packing (Figure 3), two $C_{72}Cl_4$ cages of the same enantiomer (coded by the blue color) are separated by a CS_2 molecule (yellow stick) with typical van der Waals distances (Cl···S, 3.6−3.8 Å; C···S, 3.5−3.6 Å). Replacement of one molecule by its stereoisomer in the crystal lattice is not possible, as this would cause overlapping of chlorine atoms with the CS_2 molecule. These contacts are extended along the *b* axis, forming the above-mentioned "chain". Because of the high similarity in shape, the "chains" can be randomly packed in the crystal. Thus, the crystal under discussion represents a case of a racemic twin, although the twin treatment cannot be applied because of the small size of the domains (for details, see the Supporting Information).

The chlorination pattern of C_{72} can be understood considering cage relaxation caused by chlorine addition. The inherent strain of fullerenes originates mainly from deviations from the ideal sp^2 hybridization which can be quantitatively described using π-orbital axis vector (POAV) analysis.[12] For graphite, the pyramidalization angle θ_p of the carbon atoms ($\theta_p = \theta_{\sigma\pi} - 90°$, where $\theta_{\sigma\pi}$ is the angle between the σ and π orbitals of the sp^2-hybridized carbon atoms) is 0°, representing the fully relaxed carbon lattice, while it is ~11.64° for all of the carbon atoms in C_{60}.[12] Fused pentagons introduce much larger pyramidalization angles of ~16° at the carbon atoms of the junction, and thus, these carbon atoms are considered to have partial sp^3 character, which explains their increased reactivity and the need for stabilization.[13] Chlorine addition to these carbon atoms results in a change from sp^2 to sp^3 hybridization, thus releasing strain energy.[14]

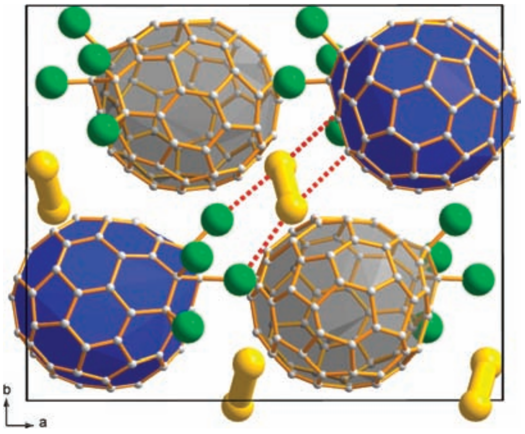

Figure 3. Projection of the structure of $C_{72}Cl_4 \cdot CS_2$ onto the (110) plane. For clarity, only one orientation of $C_{72}Cl_4$ is given. The dotted lines display the van der Waals contacts between $C_{72}Cl_4$ and CS_2 (yellow sticks). Such packing can only be realized if the blue-coded fullerenes involved in the $C_{72}Cl_4 \cdots CS_2 \cdots C_{72}Cl_4$ contacts represent the same stereoisomer.

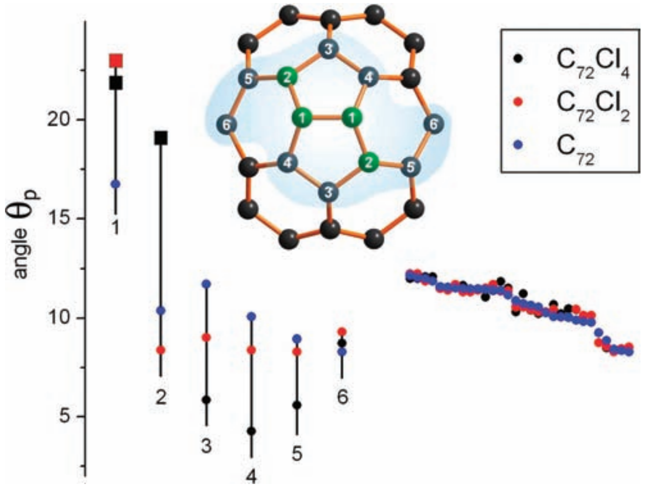

Figure 4. Representation of changes in the pyramidalization angle θ_p for C_{72} after addition of two chlorine atoms (to carbons 1) and four chlorine atoms (to carbons 1 and 2) based on the DFT-optimized structures. Only the fullerene fragment including the doubly fused pentagons where angle alternation occurs (highlighted with blue shading) is shown. The symbols ● and ■ represent sp^2 and sp^3 hybridization, respectively.

The presented $C_{72}Cl_4$ shows as expected two chlorine atoms at the pentagon−pentagon junction (the carbons labeled 1 in Figure 4) as well as two additional chlorines at neighboring positions (carbons 2 in Figure 4). In order to elucidate the role of those additional two chlorine atoms, density functional theory (DFT) analysis at the 6-311G level was performed for C_{72}, $C_{72}Cl_2$ [with the two chlorines attached to the fused-pentagon (5:5) bond], and $C_{72}Cl_4$.

POAV analysis showed that chlorine addition induces alterations in the pyramidalization angle only in the region surrounding the 5:5 bond (shaded blue in Figure 4), whereas the rest of the carbon cage remains insensitive. The first chlorination step induces a change from sp^2 to sp^3 hybridization for carbon 1, reflected by the large increase in θ_p from 16.7 to 22.9°; a slight increase in θ_p for carbon 6 and decreases in θ_p for carbons 2, 3, 4, and 5 also occur. Further chlorination leads to a change in hybridization from sp^2 to sp^3 for carbon 2, and accordingly, θ_p increases to 19.1°, which is very close to 19.48°, the ideal pyramidalization angle for sp^3-hybridized carbon. θ_p for carbon 1 decreases slightly as well, approaching the ideal tetrahedral angle of 19.48°. Furthermore, the θ_p values for carbon atoms 3, 4, 5, and 6 decrease considerably, thus relieving further local strain.

Despite unfavorable 1,2-addition of chlorine because of the chlorine−chlorine repulsion, the first and second steps of chlorination result in a large energy gain of ~40 kcal mol^{-1} each, which is more typical for addition to olefins rather than to fullerenes.[15] The large gain in energy results from local release of strain in the carbon cage in the region around the pentagon−pentagon junction, as represented by the changes in the pyramidalization angles of the carbon atoms.

Importantly, the first chlorination step decreases the HOMO−LUMO gap from 1.42 to 1.3 eV, whereas the second one leads to a huge increase to 2.25 eV, which is just slightly less than the HOMO−LUMO gaps of C_{60} (2.76 eV) and C_{70} (2.69 eV). In combination with the more efficient strain release by addition of four chlorine atoms, this also explains why $C_{72}Cl_4$ shows a high abundance in the fullerene extract.

In summary, the most stable C_{72} fullerene, namely, the non-IPR $^{\#11188}C_{72}$ cage, has been synthesized as the chlorinated derivative $C_{72}Cl_4$, which was separated and unambiguously characterized by X-ray analysis. The low degree of chlorination makes the title compound a very promising candidate for further derivatization. Moreover, it seems to be possible to strip off the chlorine atoms in order to access the pristine empty C_{72} cage in bulk amounts, as already indicated by the LDI mass spectrometry analysis. The relatively high yield, which is comparable to that for the most abundant higher fullerenes (C_{76}, C_{78}), and the simplicity of separation make this C_{72} cage not just an example of an exotic carbon cage but a fullerene available for further investigation.

Acknowledgment. The authors are grateful to Dr. Jurgen Nuss and Dr. Ivan Halasz for helpful discussions on crystallography issues.

Supporting Information Available: Chromatograms of separation, UV−vis spectrum, LDI and MALDI mass spectra (positive and negative modes), Schlegel diagrams of the two stereoisomers, illustrations of crystal packing, and Cartesian coordinates for the DFT-optimized structure of $C_{72}Cl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kroto, H. W. *Nature* **1987**, *329*, 529–531. (b) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Oxford University Press: Oxford, U.K., 1995.
(2) Tan, Y. Z.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *Nat. Chem.* **2009**, *1*, 450–460, and references cited therein.
(3) (a) Xie, S. Y.; Gao, F.; Lu, X.; Huang, R. B.; Wang, C. R.; Zhang, X.; Liu, M. L.; Deng, S. L.; Zheng, L. S. *Science* **2004**, *304*, 699. (b) Tan, Y. Z.; Han, X.; Wu, X.; Meng, Y. Y.; Zhu, F.; Qian, Z. Z.; Liao, Z. J.; Chen, M. H.; Lu, X.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *J. Am. Chem. Soc.* **2008**, *130*, 15240–15241. (c) Tan, Y. Z.; Liao, Z. J.; Qian, Z. Z.; Chen, R. T.; Wu, X.; Liang, H.; Han, X.; Zhu, F.; Zhou, S. J.; Zheng, Z. P.; Lu, X.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *Nat. Mater.* **2008**, *7*, 790–794. (d) Han, X.; Zhou, S. J.; Tan, Y. Z.; Wu, X.; Gao, F.; Liao, Z. J.; Huang, R. B.; Feng, Y. Q.; Lu, X.; Xie, S. Y.; Zheng, L. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5340–5343. (e) Tan, Y. Z.; Li, J.; Zhu, F.; Han, X.; Jiang, W. S.; Huang, R. B.; Zheng, Z. P.; Qian, Z. Z.; Chen, R. T.; Liao, Z. T.; Xie, S. Y.; Lu, X.; Zheng, L. S. *Nat. Chem.* **2010**, *2*, 269–273. (f) Tan, Y. Z.; Lu, J.; Zhou, T.; Feng, Y. Q.; Lin, S. C.; Lu, X.; Zhan, Z. P.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *J. Am. Chem. Soc.* **2010**, *132*, 12648–12652.
(4) (a) Ioffe, I. N.; Goryunkov, A. A.; Tamm, N. B.; Sidorov, L. N.; Kemnitz, E.; Troyanov, S. I. *Angew. Chem., Int. Ed.* **2009**, *48*, 5904–5907. (b) Ioffe, I. N.; Chuanbao, C.; Shangfeng, Y.; Lev, N. S.; Kemnitz, E.; Troyanov, S. I. *Angew. Chem.* **2010**, *122*, 4894–4897.
(5) (a) Kobayashi, K.; Nagase, S.; Yoshida, M.; Ōsawa, E. *J. Am. Chem. Soc.* **1997**, *119*, 12693–12694. (b) Slanina, Z.; Ishimura, K.; Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **2004**, *384*, 114–118. (c) Nagase, S.; Kobayashi, K.; Akasaka, T. *THEOCHEM* **1999**, *461*, 97–104.
(6) (a) Kato, H.; Taninaka, A.; Sugai, T.; Shinohara, H. *J. Am. Chem. Soc.* **2003**, *125*, 7782–7783. (b) Wakahara, T.; Nikawa, H.; Kikuchi, T.; Nakahodo, T.; Rahman, G. M. A.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Yamamoto, K.; Mizorogi, N.; Slanina, Z.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 14228–14229. (c) Lu, X.; Nikawa, H.; Tsuchiya, T.; Maeda, Y.; Ishitsuka, M. O.; Akasaka, T.; Toki, M.; Sawa, H.; Slanina, Z.; Mizorogi, N.; Nagase, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 8642–8645. (d) Lu, X.; Nikawa, H.; Nakahodo, T.; Tsuchiya, T.; Ishitsuka, M. O.; Maeda, Y.; Akasaka, T.; Toki, M.; Sawa, H.; Slanina, Z.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2008**, *130*, 9129–9136. (e) Yamada, M.; Wakahara, T.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Mizorogi, N.; Nagase, S. *J. Phys. Chem. A* **2008**, *112*, 7627–7631.
(7) Campanera, J. M.; Bo, C.; Poblet, J. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7230–7233.
(8) (a) Peters, G.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 223–224. (b) Jansen, M.; Peters, G.; Wagner, N. *Z. Anorg. Allg. Chem.* **1995**, *621*, 689–693. (c) Mueller, A.; Ziegler, K.; Amsharov, K. Yu.; Jansen, M. *Eur. J. Inorg. Chem.*, in press.
(9) (a) Kuvychko, I. V.; Streletskii, A. V.; Popov, A. A.; Kotsiris, S. G.; Drewello, T.; Strauss, S. H.; Boltalina, O. V. *Chem.−Eur. J.* **2005**, *11*, 5426–5436. (b) Kuvychko, I. V.; Streletskii, A. V.; Shustova, N. B.; Seppelt, K.; Drewello, T.; Popov, A. A.; Strauss, S. H.; Boltalina, O. V. *J. Am. Chem. Soc.* **2010**, *132*, 6443–6462. (c) Rogner, I.; Birkett, P.; Campbell, E. E. B. *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 103–108. (d) Streletskiy, A. V.; Kouvitchko, I. V.; Esipov, S. E.; Boltalina, O. V. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 99–102. (e) Vasil'ev, Yu. V.; Streletskiy, A. V.; Kouvitchko, I. V.; Boltalina, O. V.; Birkett, P. R.; Campbell, E. E. B.; Korobov, M. V.; Drewello, T. *Int. J. Mass Spectrom.* **2003**, *228*, 979–984.
(10) Crystal data: orthorhombic; space group *Pnma*; $a = 20.376(6)$ Å, $b = 16.900(5)$ Å, $c = 10.960(3)$ Å; $V = 3774.1$ Å^3, $Z = 4$; $2\theta_{max} = 48.34°$; $-23 < h < 23$, $-19 < k < 19$, $-12 < l < 12$; $\lambda = 0.71073$ Å; $T = 100(2)$ K; final R value $= 0.0834$ ($R_w = 0.2761$). All atomic positions were refined freely. Anisotropic parameters for overlapping carbons were refined using the constraint SIMU.
(11) (a) Simeonov, K. S.; Amsharov, K. Yu.; Jansen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8419–8421. (b) Simeonov, K. S.; Amsharov, K. Yu.; Jansen, M. *Chem.−Eur. J.* **2009**, *15*, 1812–1815.
(12) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.
(13) (a) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 1113–1127. (b) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *Chem. Phys. Lett.* **1986**, *130*, 203–207.
(14) (a) Lu, X.; Chen, Z. F.; Thiel, W.; Schleyer, P. v. R.; Huang, R. B.; Zheng, L. S. *J. Am. Chem. Soc.* **2004**, *126*, 14871–14878. (b) Xie, S. Y.; Gao, F.; Lu, X.; Huang, R. B.; Wang, C. R.; Zhang, X.; Liu, M. L.; Deng, S. L.; Zheng, L. S. *Science* **2004**, *304*, 699–699.
(15) The model reactions of 1,2-addition of Cl_2 to double bonds in C_2H_4, I_h-C_{60}, C_{2v}-C_{72}, and $C_{72}Cl_2$ were considered using DFT calculations with the 6-311G basis set. While the reaction enthalpy for Cl_2 addition to C_2H_4 is about−46 kcal mol^{-1}, that for Cl_2 addition to C_{60} is only−18 kcal mol^{-1}. In contrast, the reaction enthalpy for Cl_2 addition to C_{72} is−41 kcal mol^{-1}, and a second addition of Cl_2 to afford $C_{72}Cl_4$ has a reaction enthalpy of −36 kcal mol^{-1}.

JA108470P