Partial Separation and Structural Characterization of C_{84} Isomers by Crystallization of $(\eta^2\text{-}C_{84})Ir(CO)Cl(P(C_6H_5)_3)_2$

Alan L. Balch,* Arwa S. Ginwalla, Joong W. Lee,
Bruce C. Noll, and Marilyn M. Olmstead

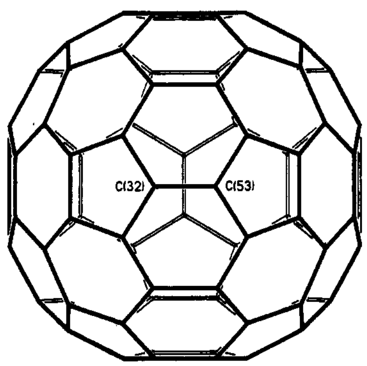
Department of Chemistry
University of California, Davis
Davis, California 95616

Received October 21, 1993

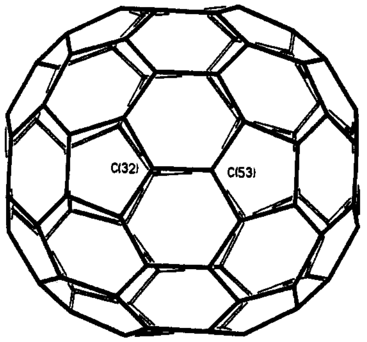
Experimental work to probe the structures of the higher fullerenes is impeded by the low yields that are available in current synthetic methods and the occurrence of a multiplicity of isomers.[1] C_{84} is one of the more abundant higher fullerenes, and its structure has been the subject of extensive theoretical treatment.[2–7] The 24 isolated-pentagon structures that can be drawn for it[4] have been shown to fall into two disjoint families[6] which can be interrelated through the pyracylene or Stone–Wales transformation.[8] Calculations indicate that the D_2 (22) and D_{2d} (23) isomers, which are shown in Figure 1, are lowest in energy.[2,3,5] ^{13}C NMR studies of C_{84} have concluded that the 32-line pattern can be explained by the presence of a 2:1 mixture of the D_2 (22) and D_{2d} (23) isomers.[9–11] However, to date no effective separation of these has been achieved.

In previous studies we have shown that $Ir(CO)Cl(PPh_3)_2$ readily and reversibly reacts with C_{60} and C_{70} to give crystalline adducts $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2$[12] and $(\eta^2\text{-}C_{70})Ir(CO)Cl(PPh_3)_2$,[13] whose structures have been determined from X-ray diffraction studies. Here we describe the results of reacting $Ir(CO)Cl(PPh_3)_2$ with C_{84}. In this case not only is there the question of regioselectivity of addition, which was also a factor in the $Ir(CO)Cl(PPh_3)_2/C_{70}$ reaction, but there is also the question of selectivity between the isomeric forms of C_{84} itself.

C_{84} was prepared by the contact arc process[14] and separated from other fullerenes by high-pressure liquid chromatography.[15] Treatment of a saturated benzene solution of a triply chromatographed sample of C_{84} with a 21-fold molar excess of $Ir(CO)Cl(PPh_3)_2$ produced a green-brown solution, from which black crystals of $(\eta^2\text{-}C_{84})Ir(CO)Cl(PPh_3)_2{\cdot}4C_6H_6$ were obtained by slow diffusion of diethyl ether into the mixture.



D2d (23)



D2 (22)

Figure 1. Computed geometries of the lowest energy C_{84} isomers: D_{2d} (23) and D_2 (22). These views look down C_2 axes of each isomer. The C(32)–C(53) bond in the D_{2d} (23) isomer is the iridium binding site. Note the similar external shapes of the two isomers.

The structure of the complex as determined by a single-crystal X-ray diffraction study[16] is shown in Figure 2. While the complex itself has no crystallographically imposed symmetry, the geometry of the C_{84} moiety does correspond to that of the D_{2d} (23) isomer. The distance along the principal axis that bisects the C(32)–C(53) and C(42)–C(43) bonds is 8.61 Å, while the distance across the two axes that are perpendicular to this is 8.34 Å. Within D_{2d} symmetry, there are 19 different sets of C–C bonds for C_{84}.[17] For the iridium adduct, the average values within each of the 19 sets along with their standard deviations are given in the following compilation. (Each set of bonds is identified by the smallest numbered C–C pair in that set.) The average lengths of the C–C bonds at the 6:6 ring junctions fall into three groups. Those bonds that join two pentagons are the shortest: C(42)–C(43), 1.332(11) Å; C(9)–C(10), 1.336(20) Å; C(5)–C(6), 1.340(15) Å. Those that connect a pentagon and a hexagon also span a small range: C(7)–C(22), 1.406(14) Å; C(1)–C(2), 1.410(10)

---

(1) Diederich, F.; Whetten, R. L. *Acc. Chem. Res.* **1992**, *25*, 119.

(2) Raghavachari, K. *Chem. Phys. Lett.* **1992**, *190*, 397.

(3) Zhang, B. L.; Wang, C. Z.; Ho, K. M. *J. Chem. Phys.* **1992**, *96*, 7183. Wang, X.-Q.; Wang, C. Z.; Zhang, B. L.; Ho, K. M. *Phys. Rev. Lett.* **1992**, *69*, 69. Wang, X.-Q.; Wang, C. Z.; Zhang, B. L.; Ho, K. M. *Chem. Phys. Lett.* **1993**, *207*, 349.

(4) Manolopoulos, D. E.; Fowler, P. W. *J. Chem. Phys.* **1992**, *96*, 7603. The 24 C_{84} isolated-pentagon isomers are numbered in this article, and those numbers are given in parentheses after the symmetry of the isomer. There are two D_{2d} and four D_2 isomers.

(5) Bakowies, D.; Kolb, M.; Thiel, W.; Richard, S.; Ahlrichs, R.; Kappes, M. M. *Chem. Phys. Lett.* **1992**, *200*, 411.

(6) Fowler, P. W.; Manolopoulos, D. E.; Ryan, R. P. *J. Chem. Soc., Chem. Commun.* **1992**, 408.

(7) Schneider, U.; Richard, S.; Kappes, M. M.; Ahlrichs, R. *Chem. Phys. Lett.* **1993**, *210*, 165.

(8) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501.

(9) Kikuchi, K.; Wakabayashi, T.; Nakahara, N.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature (London)* **1992**, *357*, 142.

(10) Manolopoulos, D. E.; Fowler, P. W.; Taylor, R.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3117.

(11) Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J. S.; Kroto, H. W.; Walton, D. M. R. *J. Chem. Soc., Perkins Trans. 2* **1993**, 1029.

(12) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980.

(13) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953.

(14) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(15) Welch, C. J.; Pirkle, W. H. *J. Chromatogr.* **1992**, *609*, 89.

(16) Black $(\eta^2\text{-}C_{84})Ir(CO)Cl(P(C_6H_5)_3)_2{\cdot}4C_6H_6$ crystallizes in the triclinic space group $P\bar{1}$, $a = 15.549(2)$ Å, $b = 18.017(3)$ Å, $c = 19.065(3)$ Å, $\alpha = 108.728(11)°$, $\beta = 111.001(10)°$, $\gamma = 103.353(11)°$, $V = 4345.5(11)$ Å^3, $Z = 2$. Refinement of 11 373 reflections with 1334 parameters (including anisotropic parameters for all non-hydrogen atoms) and 21 restraints yielded a conventional $R_1 = 0.036$ (based on F) for 10 274 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.091$ (based on F^2 with all 11 373 reflections). In addition to the disorder in the fullerene, there is disorder observed for one benzene molecule and for the carbonyl and chloride groups, as is common for such complexes.[11,12] Six of the 21 restraints involved fixing the Ir–Cl, Ir–C(85), and C(85)–O distances, while the other 15 involved the distances to the low-occupancy carbon atoms that are shown in Figure 3. The benzene molecules were refined as rigid hexagons.

(17) Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813. Our numbering scheme for the D_2 (22) and D_{2d} (23) isomers of C_{84} follows that outlined in this article.

(18) We thank the National Science Foundation (Grant CHE 9022909) for support, Johnson Matthey Inc. for a loan of iridium chloride, and Prof. K. M. Ho for providing computed coordinates for the 24 C_{84} isomers.

0002-7863/94/1516-2227$04.50/0

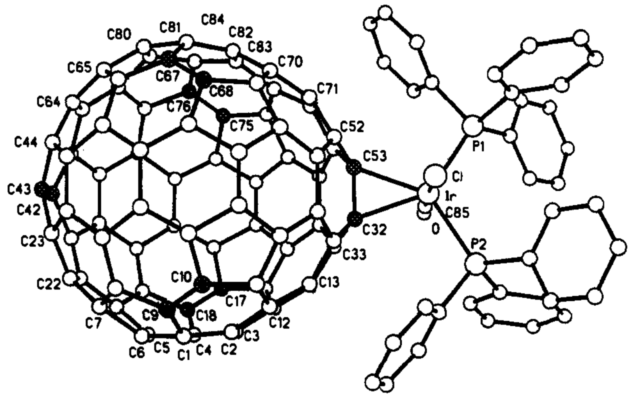


Figure 2. A view of (η^2-C_{84})Ir(CO)Cl(PPh_3)$_2$ with uniform spheres to represent all atoms. In idealized D_{2d} symmetry, the principle 2-fold axis bisects the C(32)–C(53) and C(42)–C(43) bonds and the other 2-fold axes pass through the midpoints of the C–C bonds between the other hatched carbon atoms.

Å; C(11)–C(12), 1.410(14) Å; C(21)–C(41), 1.412(10) Å; C(12)–C(13), 1.416(8) Å. Those that connect two hexagons are the longest: C(2)–C(3), 1.447(3) Å; C(2)–C(12), 1.459(7) Å; C(21)–C(22), 1.473(8) Å. In contrast, the C–C bonds at 5:6 ring junctions (all of which connect two hexagons) show a wider variation than that found in the three preceding groups: C(13)–C(31), 1.410(10) Å; C(7)–C(8), 1.423(16) Å; C(1)–C(6), 1.440(22) Å; C(13)–C(14), 1.449(12) Å; C(1)–C(9), 1.451(13) Å; C(8)–C(9), 1.457(11) Å; C(5)–C(20), 1.462(22) Å; C(23)–C(43), 1.475(14) Å.

The iridium ion is coordinated to the C(32)–C(53) bond. Hückel calculations indicate that this is the bond in C_{84} that has the highest π-bond order, and therefore it should be the most reactive.[17] As a consequence of coordination, the C(32)–C(53) bond length (1.455(6) Å) is considerably longer than that of its counterpart, the C(42)–C(43) bond (1.332(11) Å) at the opposite pole of the fullerene.

Careful examination of the fullerene portion of the structure reveals the presence of a degree of disorder. During refinement, difference maps revealed electron density in the hexagons that were adjacent to three bonds: C(17)–C(18), C(42)–C(43), and C(67)–C(68). These were refined as carbon atoms with a fixed isotropic thermal parameter and populations tied to those of the adjacent carbons. Thus the populations of C(17) and C(18) were each $1 - x$, and those of the additional carbon atoms, C(17a) and C(18a), were each x. Figure 3 shows the location of these additional carbon atoms after refinement. The pattern in each case is a superposition of that given by the Stone–Wales transformation. The population at each site is not the same: $x = 0.104(13)$ for the site at C(17a) and C(18a), 0.204(15) at C(42a) and C(43a), and 0.197(14) at C(67a) and C(68a). We have found no other orientation of the D_{2d} (23) isomer of C_{84} which would produce such a set of minor carbon atom sites. On the other hand, the presence of small amounts of other isomers could produce these features. In particular, the presence of the D_2 (22) isomer with the iridium bound to the C(32)–C(53) bond, the bond which is predicted to have the second highest π-bond order in the molecule,[17] does produce a C_{84} moiety which overlays that shown in Figure 2 very closely but places carbon atoms in the minor "a" sites in faces A–C of Figure 3. This simple interpretation requires that the population of the three minor sites be equivalent, but that is not the case. Consequently other orientations of the D_2 (22) moiety or other isomers of C_{84} may be present. Nevertheless, these other isomers are present in small amounts in the crystal, and adduct formation and crystallization has produced a sample consisting of predominantly the D_{2d} (23) isomer, whose structure has now been solved. The selective crystallization of the D_{2d} (23) isomer, which is suspected to be less abundant than the D_2 (22) isomer, may result from a stronger tendency of that isomer to form adducts. Hückel calculations show that the D_{2d} (23) isomer has the most localized π-bonding of the fullerenes that have been isolated, and it has been suggested that it will be the most reactive toward addition reactions.[17] Further work that uses iridium-based reagents to effect separations of the higher fullerenes is in progress.

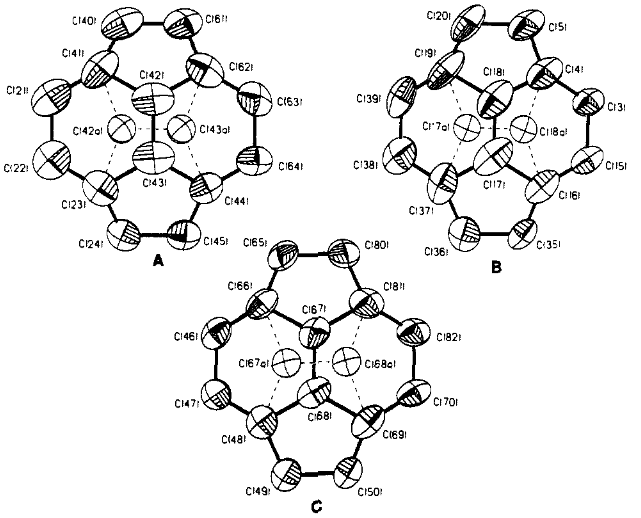


Figure 3. Views of faces of the C_{84} moiety in (η^2-C_{84})Ir(CO)Cl(PPh_3)$_2$ that show the locations of the six low-occupancy carbon atoms C(17a), C(18a), C(42a), C(43a), C(67a), and C(68a).

Supplementary Material Available: Details of data collection and structure refinement, tables and atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for (η^2-C_{84})Ir(CO)Cl(PPh_3)$_2$·4C_6H_6 (22 pages); tables of observed and calculated structure factors for (η^2-C_{84})Ir(CO)Cl(PPh_3)$_2$·4C_6H_6 (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.