

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231340164>

Directing Effects in a Fullerene Epoxide Addition. Formation and Structural Characterization of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$

ARTICLE in INORGANIC CHEMISTRY · MAY 1994

Impact Factor: 4.76 · DOI: 10.1021/ic00088a002

CITATIONS

44

READS

20

5 AUTHORS, INCLUDING:



Alan Balch

University of California, Davis

597 PUBLICATIONS 18,708 CITATIONS

SEE PROFILE



David A Costa

Los Alamos National Laboratory

27 PUBLICATIONS 1,028 CITATIONS

SEE PROFILE



Bruce C Noll

Bruker AXS Inc.

286 PUBLICATIONS 6,644 CITATIONS

SEE PROFILE



Marilyn M. Olmstead

University of California, Davis

951 PUBLICATIONS 25,945 CITATIONS

SEE PROFILE

Directing Effects in a Fullerene Epoxide Addition. Formation and Structural Characterization of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$

Alan L. Balch,* David A. Costa, Joong W. Lee, Bruce C. Noll, and Marilyn M. Olmstead

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

Received February 17, 1994

The fullerene monoxide, C_{60}O , has been detected as a byproduct of fullerene synthesis.^{1,2} It can also be formed by electrochemical oxidation of C_{60} ,³ by photo-oxygenation of C_{60} ,² and through the addition of dimethyldioxirane to C_{60} .⁴ The latter two procedures have allowed this monoxide to be obtained in macroscopic quantities. ¹³C NMR spectroscopic analysis provides strong evidence for the presence of an epoxide structure with an oxygen atom placed above a 6:6 ring junction rather than the isomeric 1,6-oxido[10]annulene structure.^{2,4} However theoretical studies have suggested that an isomer with an oxygen atom inserted into a 5:6 ring junction has lower energy than the experimentally observed epoxide structure and that there is a significant energy barrier which separates these two isomers.⁵ In the solid state, C_{60}O is orientationally disordered.⁶

In previous studies we have shown that $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$, **1**, readily and reversibly reacts with C_{60} and C_{70} to give crystalline adducts (e.g., $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ and $(\eta^2\text{-C}_{70})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$) whose structures have been determined from X-ray diffraction studies.⁷ In these adducts, the iridium atom binds to an olefinic bond at a 6:6 ring junction, and because of the reversibility of the adduct formation, the products are formed under thermodynamic control. Here we report on the reaction between **1** and C_{60}O . This reaction was studied in order to obtain further information on the structure of C_{60}O , to assess its reactivity, and to examine the ability of the oxygen atom to direct the addition of an organometallic reagent. In the context of reactivity, it is important to note that epoxides have been observed to undergo ring opening when treated with **1** and other low valent metal complexes.⁸

C_{60}O was prepared by the oxidation of C_{60} (0.28 mmolar) with *m*-chloroperoxybenzoic acid (16.8 mmolar) in a 3/1 toluene/dichloromethane solution for 60 h. This procedure forms C_{60}O along with five other products in relative amounts which are different from that seen in the photochemical oxygenation. The C_{60}O was isolated in 20% yield by evaporation of the mixture, washing with ethanol, and chromatography with a "Bucky-clutcher" column.⁹ The fullerene oxide was identified by comparison of its ¹³C NMR and electronic spectra with those of

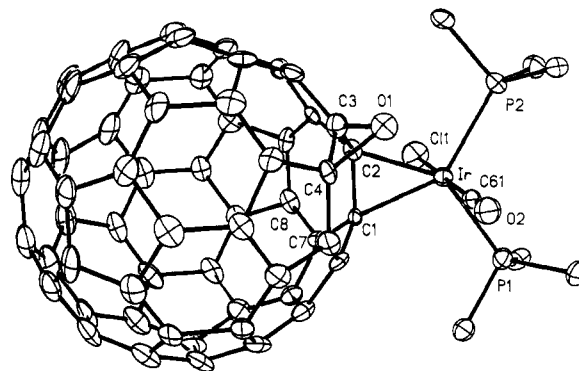


Figure 1. View of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ with 50% thermal contours for all atoms. For clarity only the ipso carbon atoms of each phenyl ring are shown. Selected bond distances (Å): O(1)–C(3), 1.445(12); O(1)–C(4), 1.462(12); C(3)–C(4), 1.480(11); Ir–C(1), 2.168(7); Ir–C(2), 2.174(7); C(1)–C(2), 1.500(11). Selected bond angles (deg): C(3)–O(1)–C(4), 61.2(6); O(1)–C(3)–C(4), 59.9(6); O(1)–C(4)–C(3), 58.8(6); C(1)–Ir–C(2), 40.4(3); P(1)–Ir–P(2), 113.44(8).

authentic samples prepared by photooxygenation.² A saturated benzene solution of triply chromatographed sample of C_{60}O was layered over a saturated chloroform solution of $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. Deep purple crystals of the product, $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot 0.53 \text{CHCl}_3 \cdot 4.47 \text{C}_6\text{H}_6$, **2**, grew at the interface of the two solutions within 48 h. The infrared spectrum of the product showed the iridium-bound carbon monoxide stretching vibration at 2022 cm^{-1} , which is consistent with adduct formation.⁷

The structure of complex **2** as determined by an X-ray diffraction study¹⁰ is shown in Figure 1. The epoxide functionality is clearly present. The O(1)–C(3)–C(4) unit forms a nearly equilateral triangle, and the C–O distances (1.445(12), 1.462(12) Å) and C–C distance (1.480(11) Å) are within the range of distances expected for an epoxide unit.¹¹ The iridium complex has added to the carbon–carbon bond at one of the 6:6 ring junctions that is immediately adjacent to the epoxide unit. The nonbonded Ir–O(1) separation is large (3.463(7) Å), and it is clear that there is no insertion of the iridium complex into the epoxide unit.

Careful examination of the fullerene portion of the structure reveals the presence of a second site (O(1')) for the oxygen atom. The location of that site relative to the other atoms is shown in Figure 2. The geometric parameters at the second site are similar to those at the primary site, and the iridium complex is again bound to an immediately adjacent 6:6 ring junction. The refined occupancy of O(1) was 0.644(19) while that of O(1') was 0.25(2). Since the sum of these occupancies is only 0.89, it is likely that the crystal also contains a small amount of $(\eta^2\text{-C}_{60})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. It is well-known that C_{60}O readily loses its oxygen

- (1) Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarne, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.
- (2) Creagan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.
- (3) Millar, J. M.; Creagan, K. M.; Robbins, J. L.; Robbins, W. K.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M. *Synth. Met.* **1993**, *59*, 317.
- (4) Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363.
- (5) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.
- (6) Raghavachari, K. *Chem. Phys. Lett.* **1992**, *195*, 221. Raghavachari, K.; Sosa, C. *Chem. Phys. Lett.* **1993**, *209*, 223.
- (7) Vaughan, G. B. M.; Heiney, P. A.; Cox, D. E.; McGhie, A. R.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III. *Chem. Phys.* **1992**, *168*, 185.
- (8) (a) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980. (b) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953. (c) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 5455. (d) Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1356. (e) Balch, A. L.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 10984.
- (9) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178. Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893.
- (10) Welch, C. J.; Pirkle, W. H. *J. Chromatogr.* **1992**, *609*, 89.

(10) Deep purple plates of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot 0.53 \text{CHCl}_3 \cdot 4.47 \text{C}_6\text{H}_6$ form in the monoclinic space group $\text{P}2_1/\text{n}$ with $a = 14.5880(10)$ Å, $b = 19.745(2)$ Å, $c = 28.319(3)$ Å, $\beta = 100.089(7)^\circ$, $V = 8030.8(13)$ Å³, $Z = 4$. Refinement of 10484 reflections with 1204 parameters and 21 restraints yielded $R = 0.057$, $wR2 = 0.133$. In addition to the disorder in the fullerene oxide, there is disorder at one solvate site which is shared by 0.53 molecule of chloroform and 0.47 molecule of benzene.

(11) Matthews, D. A.; Swanson, J.; Mueller, M. H.; Stucky, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 5945.

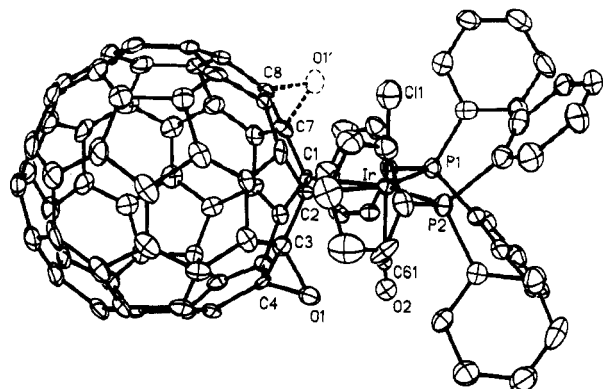


Figure 2. View of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ which indicates the locations of both the major oxygen atom site (O(1) with 0.644(19) occupancy) and the minor oxygen site (O(1') with 0.25(2) occupancy).

atom to re-form C_{60} .^{2,4} We have shown through chromatographic studies that while a benzene solution of C_{60}O itself is stable during the time period necessary for crystal growth, a similar solution when exposed to $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ or triphenylphosphine slowly undergoes oxygen atom transfer to produce some C_{60} . This reaction with triphenylphosphine is faster, and it is likely that the deoxygenation that is observed with the iridium complex is a result of a small degree of ligand dissociation from the complex.

Compound **2** is the first double addition product of C_{60} with two different addenda to receive thorough structural characterization. The relative orientations of the oxygen and iridium atoms on the surface of the C_{60} moiety differ from the orientations found in double addition products that involve the addition of two metal complexes to the fullerene surface. Addition of $\text{Ir}(\text{CO})\text{Cl}(\text{PPhMe}_2)_2$ to C_{60} yields two different crystalline forms of a double addition product. Both of these have the added iridium complexes bound to opposite ends of the fullerene.^{7e} With the addition of osmium tetroxide, which proceeds under kinetic

control, five double addition products have been observed to form.¹² The structural analysis of these osmylation products proceeded under the assumption that steric effects precluded addition to the hemisphere that received the initial osmylation. Addition of $\{\text{Ir}_2\text{Cl}_2(\eta^4\text{-C}_8\text{H}_{12})_2\}_2$ to C_{60} does yield a product, $\text{C}_{60}\{\text{Ir}_2\text{Cl}_2(\eta^4\text{-C}_8\text{H}_{12})_2\}_2\cdot 2\text{C}_6\text{H}_6$, in which two iridium atoms are bound to two C–C bonds on a common hexagonal face of the fullerene, but the presence of chloro bridges between the two iridium atoms in that structure may play a decisive role in the positioning of the iridium atoms.¹³ Additionally in $\text{C}_{60}\{\text{Ir}_2\text{Cl}_2(\eta^4\text{-C}_8\text{H}_{12})_2\}_2\cdot 2\text{C}_6\text{H}_6$, notice that the two dinuclear iridium complexes are bound to opposite ends of the fullerene and are as far apart as possible. In the case of addition of a metal complex to C_{60}O , the epoxide presents minimal steric interference to addition, and it is likely that electronic effects are responsible for directing the regioselectivity of the iridium complex addition. $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ reacts only with electron-deficient olefins, and metal-to-olefin back-bonding in the Dewar–Chatt model is a major contributor to the stability of these adducts. In the case of C_{60}O , it is likely that those double bonds that are adjacent to the epoxide function will be affected most strongly by the electron withdrawal of the epoxide. Consequently, it is reasonable that the thermodynamic preference for binding of **1** to C_{60}O involves placement of the two groups in the closest possible proximity. Further studies of the other products obtained by peroxyacid oxidation of C_{60} are in progress.

Acknowledgment. We thank the National Science Foundation (Grant CHE9022909) for support and Johnson Matthey Inc. for a loan of iridium chloride.

Supplementary Material Available: Tables giving details of the data collection and structure refinement, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2\cdot 0.53\text{CHCl}_3\cdot 4.47\text{C}_6\text{H}_6$ (16 pages). Ordering information is given on any current masthead page.

- (12) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Bunz, U.; Nunlist, R.; Ball, G. E.; Ebbesen, T. W.; Tanigaki, K. *J. Am. Chem. Soc.* **1992**, *114*, 7954.
- (13) Rasinkangas, M.; Pakkanen, T. T.; Pakkanen, T. A.; Ahlgrén, M.; Rouvinen, J. *J. Am. Chem. Soc.* **1993**, *115*, 4901.