Structural characterization of $C_{70}O$. Remarkable disorder in crystalline $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]\cdot5C_6H_6$

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X-Ray diffraction data on $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]$ show that the epoxide structure is present with the oxygen atom disordered over two sites, the C_{70} portion is also disordered with two different orientations of the long fullerene axis; the results are consistent with the presence of two isomers of $C_{70}O$ which have been separated by high-pressure liquid chromatography.

Fullerene oxides are likely products of atmospheric degradation of fullerenes[1] and precursors to the formation of redox-active, electrochemically generated films.[2] Three oxides of C_{60}, $C_{60}O$,[3] $C_{60}O_2$,[4] and $C_{120}O$,[5] have been identified and there are several reports on the formation of $C_{70}O$.[6,7] While theoretical calculations have indicated that the fullerene addition products with the oxygen atom added across a 5:6 ring junction rather than to a 6:6 ring junction are thermodynamically more stable,[8] both $C_{60}O$ and $C_{60}O_2$ have epoxide structures with addition to a 6:6 ring junction. The fullerene C_{70} has a more complex structure than C_{60} as shown in Fig. 1. This figure also shows diagrams of the four $C_{70}O$ isomers that can be formed by addition of an oxygen atom to the 6:6 ring junctions of C_{70}. Calculations indicate that the most stable structure is clearly **4** with an oxygen atom inserted into what was essentially a C_e–C_e single bond at the central belt of the fullerene.[9] Here we report on a structural study of $C_{70}O$ in which we use coordination of the organometallic complex, $[Ir(CO)Cl(PPh_3)_2]$, to produce a crystalline sample suitable for analysis by single-crystal X-ray diffraction.[10,11]

Treatment of C_{70} with *m*-chloroperoxybenzoic acid with the procedure developed for C_{60} oxidation[4] yielded a mixture from which $C_{70}O$ was separated in a single, symmetrical peak by preparative high-pressure liquid chromatography using a 'Bucky-clutcher' column and elution with toluene–hexane (6:4) as shown in trace A of Fig. 2. A saturated benzene solution of $C_{70}O$ was carefully layered over a solution of $[Ir(CO)Cl(PPh_3)_2]$ in chloroform. The two solutions gradually mixed as they stood, and black crystals of the adduct grew. The IR spectrum of the black crystals showed a new carbon monoxide stretching vibration at 2028 cm^{-1}

The results of X-ray crystallographic study of $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]\cdot5C_6H_6$ are shown in Fig. 3.† The structural analysis has been complicated by disorder in the orientation of the basic C_{70} skeleton, the location of the oxygen atom of the epoxide function, the position of the carbon monoxide and chloride ligands, and the orientation of one of the five benzene solvate molecules. Despite this disorder, valuable information in regard to the structure of $C_{70}O$ can be gleaned from the structural results.

Remarkably, two orientations of the fullerene framework are present at a common site within the unit cell as shown in parts **A** and **B** of Fig. 3. These two pictures are drawn from the same perspective, and the structural features of the $Ir(CO)Cl(PPh_3)_2$ portion are identical in each drawing. In **A** and **B**, however, the long axes of the C_{70} units have markedly different orientations which differ by 59.2°. In Fig. 1 the pentagons at the opposite poles of the fullerene are differentiated by the use of solid lines, and the long axis of the fullerene runs through the centre of each of these pentagons. In orientation **A** the long axis runs horizontally, while in orientation **B** it is tilted from horizontal by about 60°. The two C_{70} units have been treated as rigid groups which have refined occupancies of 0.464(9) for the orientation

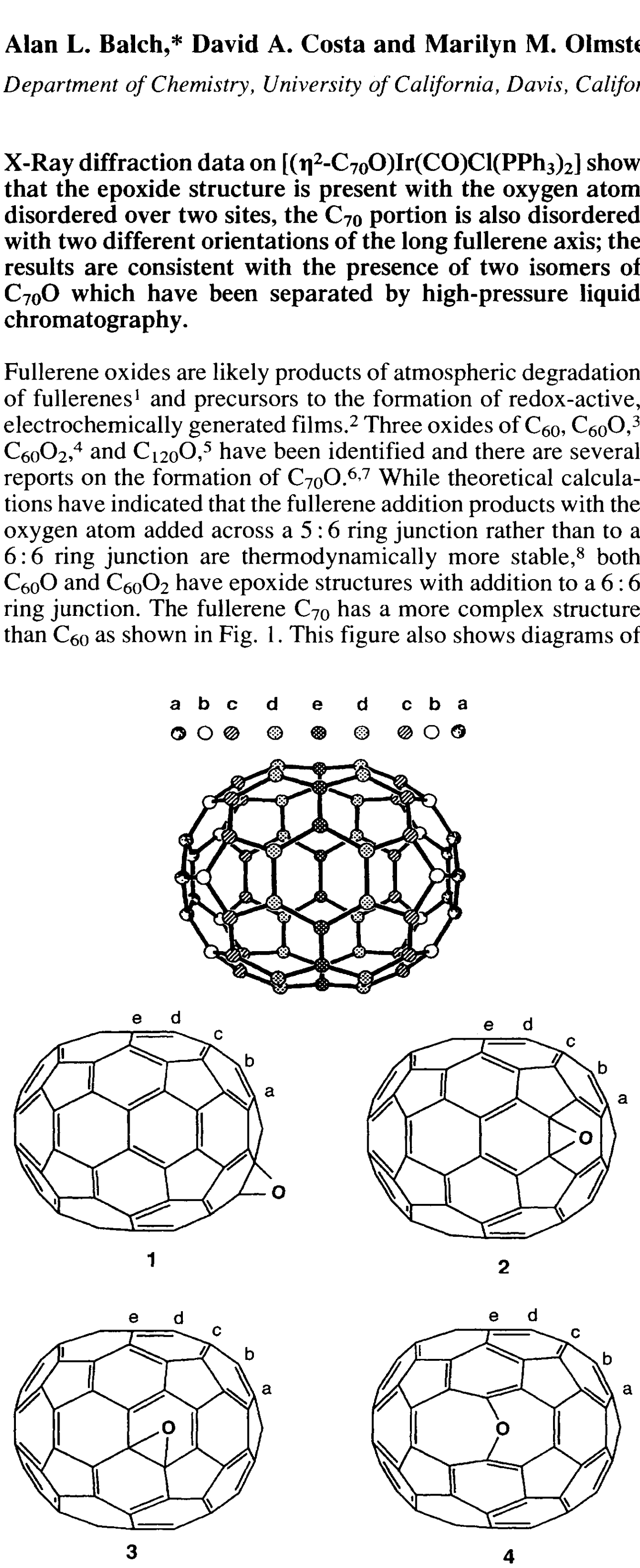

Fig. 1 Top, a drawing of C_{70} which emphasizes the layers of five types of carbon atoms, C_a–C_e. Bottom, the four possible $C_{70}O$ isomers, **1–4**, with oxygen atoms spanning 6:6 ring junctions.

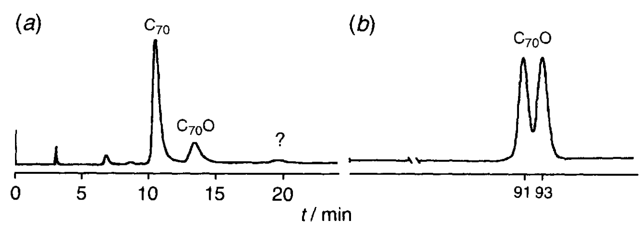

Fig. 2 High-pressure liquid chromatograms for: (*a*) a sample of C_{70} after oxidation with *m*-chloroperoxybenzoic acid on a 'Bucky-clutcher' column with elution with toluene–hexane (6:4); (*b*) the sample of $C_{70}O$ in (*a*) after isolation rerun on a Cosmocil Buckyprep column (4.6 × 250 mm, available from JM Science, Grand Island, NY) with elution by toluene–dichloromethane (7:3) and a flow rate of 1.2 ml min^{-1} at 800 psi

in **A** and 0.536(9) for the orientation in **B**. In both orientations the $Ir(CO)Cl(PPh_3)_2$ portion is bonded to a 6 : 6 ring junction at a C_a–C_b bond. This is the same position that is involved in bonding one or two $Ir(CO)Cl(PR_3)_2$ units to C_{70} itself.[10] Notice that the portions of the fullerene that are in close proximity to the iridium complex are very similar in **A** and **B**.

There are also two sites on the fullerene that are occupied by oxygen atoms. Site O(1A) has a refined occupancy of 0.41(2), while site O(1B) has a refined occupancy of 0.59(2). Both sites span 6 : 6 ring junctions and both have geometrical features that are characteristic of epoxide groups. In orientation **A**, site O(1A) spans a C_a–C_b bond, while site O(1B) spans a C_c–C_c bond. In orientation **B**, site O(1A) lies over a C_c–C_c bond while site O(1B) lies over a C_a–C_b bond. In all situations, the iridium is bound to a 6 : 6 ring junction that is immediately adjacent to the epoxide group. The relative orientation of the iridium complex and the epoxide is analogous to that found in $[(\eta^2\text{-}C_{60}O)Ir(CO)Cl(PPh_3)_2]$.[11] Moreover, the disorder in the epoxide location is also similar to that seen in $[(\eta^2\text{-}C_{60}O)Ir(CO)Cl(PPh_3)_2]$.

As is typical for iridium complexes with a *trans* Cl–Ir–CO group, there is interchange disorder in chloride and carbonyl groups.[12] The site, Cl(A), has a refined occupancy of 0.464(10), while site Cl(B) has an occupancy of 0.536(10).

Since the populations of the sites for the fullerene, the epoxide oxygen, and the carbonyl/chloride positions are close to statistical expectations, it is difficult to draw conclusions from a correlation of their occupancies. However, it is clear that the structural data show epoxide units that span 6 : 6 ring junctions and are consistent with the presence of only two of the possible isomeric forms of $C_{70}O$ (**1** and **2**). These are the same two isomers that have been identified by A. B. Smith, III *et al.* in their spectroscopic investigation of $C_{70}O$.[7]

Careful additional high-pressure liquid chromatography with a Cosmocil column and elution with toluene–dichloromethane (7 : 3) does lead to an effective separation of the two isomers (trace B of Fig. 2). All samples that we have examined contain nearly equal amounts of the two components. Analysis of samples collected from each fraction by MALDI mass spectrometry shows an intense peak at 856 due to $C_{70}O$. Note that work utilizing ^{3}He NMR spectroscopy on endohedral ^{3}He doped $C_{70}O$ and ^{13}C NMR spectroscopy also indicated that the two $C_{70}O$ isomers occur in a 1 : 1 ratio.[7] The UV–VIS absorption spectra of these fractions are similar: **a** (λ_{max}/nm) 318, 354, 372, 446, 580 (sh), 670; **b** (λ_{max}/nm) 318, 354, 370, 454,668.

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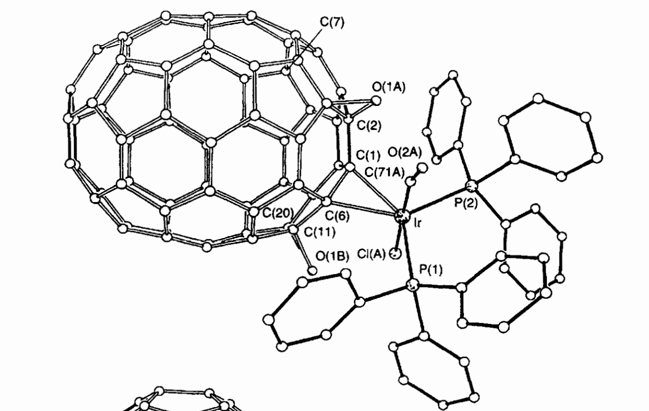

Fig. 3 Views of $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]$ with uniform, arbitrarily sized circles for all atoms. The two orientations, **A** and **B**, that occupy a common site are shown from the same perspective. Both locations of the epoxide oxygen atoms are shown in each drawing, but only one, arbitrarily chosen orientation of the carbon monoxide and chloride ligands is given in each view.

Footnote

† *Crystal data*: black needles of $[(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2]\cdot 5C_6H_6$, $C_{137}H_{54}ClIrO_2P_2$, {obtained by diffusion of a benzene solution of $C_{70}O$ into a chloroform solution of $[Ir(CO)Cl(PPh_3)_2]$} form in the triclinic space group $P\bar{1}$ with a = 15.475(5), b = 18.153(4), c = 18.464(5) Å, α = 95.80(2), β = 114.72(2), γ = 110.39(2)° at 125(2) K with Z = 2. Data collection employed Cu-Kα (λ = 1.54178 Å) Ni-filtered radiation. Refinement (based on F^2) of 10 744 reflections and 773 parameters yielded wR_2 = 0.285 for all data and a conventional R_1 = 0.099 [based on observed data with $I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/222.

References

1 M. Wohlers, H. Werner, D. Herein, T. Schedel-Niedrig, A. Bauer and R. Schlogl, *Synth. Met.*, 1996, **77**, 299.
2 M. Fedurco, D. A. Costa, A. L. Balch and W. R. Fawcett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 194; K. Winkler, D. A. Costa, A. L. Balch and W. R. Fawcett, *J. Phys. Chem.*, 1995, **99**, 17431.
3 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, III, J. P. McCauley, Jr., D. R. Jones and R. T. Gallagher, *J. Am. Chem. Soc.*, 1992, **114**, 1103.
4 A. L. Balch, D. A. Costa, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1995, **117**, 8926.
5 S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor and W. Krätschmer, *Tetrahedron Lett.*, 1995, **36**, 4971; A. B. Smith, III, H. Toyuyama, R. M. Strongin, G. T. Furst, W. J. Romanow, B. T. Chait, U. A. Mirza and I. Haller, *J. Am. Chem. Soc.*, 1995, **117**, 9359; A. L. Balch, D. A. Costa, W. R. Fawcett and K. Winkler, *J. Phys. Chem.*, 1996, **100**, 4823.
6 F. Diederich, R. Ettl, Y. Rubin, R. L. Whetton, R. Beck, M. Alvarez, S. Anz, D. Sehsharma, F. Wudl, K. C. Khemani and A. Koch, *Science*, 1991, **252**, 548; J. B. Howard, A. L. LaFleur, Y. Makarovsky, S. Mitra, C. J. Pope and T. K. Yadov, *Carbon*, 1992, **30**, 1183; D. Heyman and L. P. F. Chibante, *Chem. Phys. Lett.*, 1993, **207**, 339; D. Heyman and L. P. F. Chibante, *Recl. Trav. Chim. Pays-Bas*, 1993, **112**, 531.
7 A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Furst, J. H. Atkins, W. J. Romanow, M. Saunders, H. A. Jiménez-Vázquez, K. G. Owens and R. J. Goldschmidt, *J. Org. Chem.*, 1996, **61**, 1904.
8 K. Raghavachari, *Chem. Phys. Lett.*, 1992, **195**, 221.
9 K. Raghavachari and C. M. Rohlfing, *Chem. Phys. Lett.*, 1992, **197**, 495; K. Raghavachari, *Int. J. Modern Phys. B*, 1992, **6**, 3821.
10 A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, **113**, 8953; A. L. Balch, J. W. Lee and M. M. Olmstead, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1358.
11 A. L. Balch, D. A. Costa, J. W. Lee, B. C. Noll and M. M. Olmstead, *Inorg. Chem.*, 1994, **33**, 2071.
12 M. R. Churchill, J. C. Fettinger, L. A. Buttrey, M. D. Barkan and J. S. Thomson, *J. Organomet. Chem.*, 1988, **340**, 257.

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