

Developing Reagents To Orient Fullerene Derivatives. Formation and Structural Characterization of (η^2 -C₆₀O)Ir(CO)Cl(As(C₆H₅)₃)₂

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

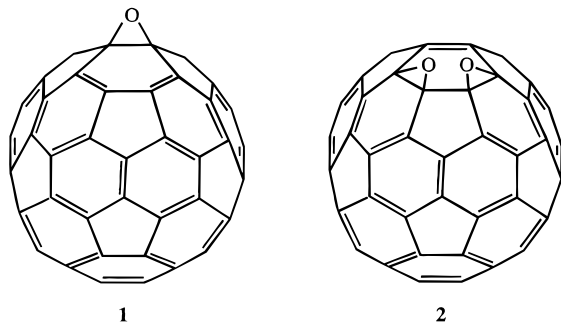
Department of Chemistry, University of California, Davis, California 95616

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In order to obtain crystals of fullerene oxides that are suitable for single-crystal X-ray diffraction, the reactions between C₆₀O and Vaska type iridium complexes have been examined. While reaction with Ir(CO)Cl(P(C₆H₅)₃)₂ (and with triphenylphosphine but not triphenylarsine) results in partial deoxygenation of the fullerene epoxide, reaction with Ir(CO)Cl(As(C₆H₅)₃)₂ produces crystalline (η^2 -C₆₀O)Ir(CO)Cl(AsPh₃)₂·4.82C₆H₆·0.18CHCl₃. Black triangular prisms of (η^2 -C₆₀O)Ir(CO)Cl(AsPh₃)₂·4.82C₆H₆·0.18CHCl₃ form in the monoclinic space group *P*2₁/*n* with *a* = 14.662(2) Å, *b* = 19.836(2) Å, *c* = 28.462(5) Å, and β = 100.318(12)° at 123 (2) K with *Z* = 4. Refinement (on *F*²) of 10 472 reflections and 1095 parameters with 10 restraints yielded *w*R₂ = 0.152 and a conventional *R* = 0.066 (for 7218 reflections with *I* > 2.0σ(*I*)). The structure shows that the iridium complex is bound to a 6:6 ring junction of the fullerene with four partially occupied sites for the epoxide oxygen atom. Thus, while deoxygenation of the fullerene does not occur upon reaction with Ir(CO)Cl(AsPh₃)₂, there is a greater degree of disorder in (η^2 -C₆₀O)Ir(CO)Cl(AsPh₃)₂ than previously reported for (η^2 -C₆₀O)Ir(CO)Cl(PPh₃)₂.

Introduction

The fullerene monoxide, **1**, C₆₀O, has been extensively characterized and shown to have an epoxide structure in which the oxygen atom is positioned over a 6:6 ring junction.^{1–3}



Recently, this monomer was shown to be a precursor to the formation of tough, redox-active films that can be deposited electrochemically on a variety of electrodes, including platinum, gold, glassy carbon, and conducting tin oxide.⁴ In order to further understand the nature of these insoluble films and to prepare new variants with other related fullerene derivatives, we have been exploring the chemistry of the higher oxides of C₆₀⁵ and the oxides of C₇₀.⁶ In this work we have been able to

isolate the diepoxide, **2**, and structurally characterize it.⁵ For adequate structural characterization of these oxides, it has been beneficial to utilize the addition reactions with Vaska's compound, Ir(CO)Cl(PPh₃)₂. The fullerene adducts formed from Vaska's compound readily form crystals that are small but still suitable for single-crystal X-ray diffraction.^{3,7–10} Crystals of C₆₀O, like those of C₆₀ itself, suffer from orientational disorder.^{11,12} This disorder is a consequence of the high symmetry of these molecules and the fact that, even with an epoxide unit bound on the outside, the surface features of C₆₀O are relatively uniform. In the adducts of fullerenes with Vaska's complex, the fullerene portion is generally ordered although in crystalline (η^2 -C₆₀O)Ir(CO)Cl(P(C₆H₅)₃)₂ there are two sites that are partially occupied by the epoxide group. Additionally, during the growth of crystals of (η^2 -C₆₀O)Ir(CO)Cl(P(C₆H₅)₃)₂, a significant amount of the epoxide was converted back into C₆₀.³ Because (η^2 -C₆₀O)Ir(CO)Cl(P(C₆H₅)₃)₂ and (η^2 -C₆₀)Ir(CO)Cl(P(C₆H₅)₃)₂ have very similar external shapes, they are able to cocrystallize. The sample that was previously examined by X-ray diffraction was found to contain a 89:11 mixture of the fullerene epoxide and the fullerene itself.³ Here we report an attempt to overcome the problem of deoxygenation of C₆₀O during its reactions with Vaska type complexes.

Results

The reaction of C₆₀O with triphenylphosphine and Ir(CO)Cl(PPh₃)₂ has been monitored by high-pressure liquid chromatography (HPLC) with the use of a "Buckyclutcher 1" column.¹³ Representative results are shown in Figure 1, which shows

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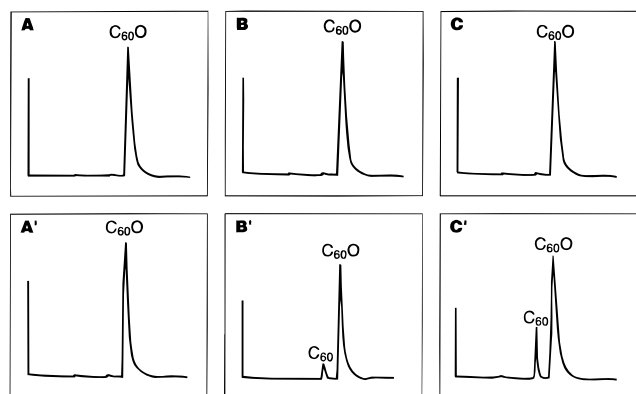


Figure 1. High-pressure liquid chromatograms of samples of C₆₀O alone, 0.22 mM in 5 mL of a 60:40 toluene:*n*-hexane solution (A), with Vaska's complex, 1.0 mM (B), and with triphenylphosphine, 3.0 mM (C), immediately after preparation, and after 12 h (traces A', B', and C').

chromatograms of 60:40 toluene:*n*-hexane solutions of C₆₀O alone (trace A), C₆₀O in the presence of triphenylphosphine- (trace C), and C₆₀O in the presence of Vaska's compound (trace B) immediately after preparation. These chromatograms show the region where C₆₀O and C₆₀ elute, and in each case there is a prominent peak due to C₆₀O. Traces A', B', and C' show the chromatograms of the same solutions after they had stood for 12 h. The sample of C₆₀O alone has retained its purity as seen by comparison of traces A and A'. However with triphenylphosphine present, the chromatograms (traces C and C') show that a considerable quantity of C₆₀ is formed due to deoxygenation of the fullerene epoxide. With Vaska's complex present, there is also a significant amount of C₆₀ formed as well, as shown in traces B and B'. This may arise from a reaction with Vaska's complex itself but may also be a result of some degree of triphenylphosphine dissociation from the complex, with the free triphenylphosphine acting as the deoxygenating agent. Triphenylphosphine is also capable of effecting the stepwise deoxygenation of the diepoxide, C₆₀O₂. Chromatograms which show this are presented in Figure 2. Trace A shows a sample of C₆₀O₂ immediately after it was mixed with triphenylphosphine. Only a single peak due to C₆₀O₂ is present. Traces B and C of that figure show the same sample after 12 and 24 h, respectively. During that time period, significant quantities of C₆₀O and C₆₀ form. On further standing, eventually only C₆₀ is left in the sample. In order to avoid the problem with deoxygenation of C₆₀O by triphenylphosphine, the reactivity of C₆₀O with triphenylarsine and with Ir(CO)Cl(AsPh₃)₂ was also examined. In these cases, no deoxygenation of the epoxide was observed under conditions that were similar to those used to obtain the data in Figure 1.

Treatment of C₆₀O with Ir(CO)Cl(AsPh₃)₂ in benzene results in formation of a black crystalline solid which can be isolated in 48% yield. The infrared spectrum of the crystalline solid showed a carbon monoxide stretching vibration at 2013 cm⁻¹. The increase in this value over that of the parent, Ir(CO)Cl(AsPh₃)₂ at 1993 cm⁻¹, is indicative of adduct formation.^{7-10,14}

Crystallographic Characterization of (η²-C₆₀O)Ir(CO)Cl(AsPh₃)₂·4.82 C₆H₆·0.18CHCl₃. Crystals of (η²-C₆₀O)Ir(CO)Cl(AsPh₃)₂·4.82C₆H₆·0.18CHCl₃ are isomorphous with those of (η²-C₆₀)Ir(CO)Cl(PPh₃)₂·5C₆H₆,⁶ (η²-C₆₀O)Ir(CO)Cl(PPh₃)₂·0.53CHCl₃·4.47C₆H₆,³ and (η²-C₆₀O₂)Ir(CO)Cl(PPh₃)₂·5C₆H₆.⁵ Figure 3 shows a drawing of the fullerene adduct in (η²-C₆₀O)Ir(CO)Cl(AsPh₃)₂·4.82C₆H₆·0.18CHCl₃. Atomic coordinates

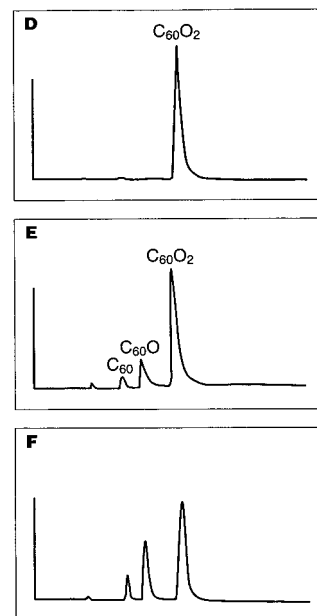


Figure 2. High-pressure liquid chromatograms of a sample of C₆₀O₂, 0.22 mM in a 60:40 toluene:*n*-hexane solution and triphenylphosphine, 3.0 mM, immediately after preparation (D), after 12 h (E), and after 24 h (F).

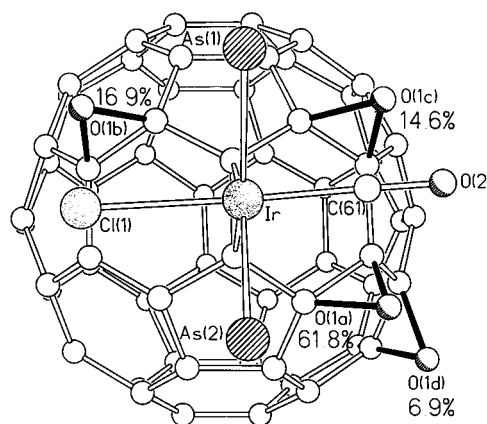


Figure 3. View of (η²-C₆₀O)Ir(CO)Cl(AsPh₃)₂. For clarity only the ipso carbon atoms of each phenyl ring are shown. The four epoxide oxygen sites and their percent occupancies are shown. Only the major sites for the chloride and carbon monoxide ligands are shown.

are given in Table 1, and some selected interatomic distances and angles are given in Table 2. As in the fullerene adducts of Ir(CO)Cl(PPh₃)₂, the iridium atom is coordinated to the fullerene through the olefinic carbon-carbon bond at a 6:6 ring junction. The orientations of the carbonyl, chloride, and arsine ligands on the iridium have the expected arrangements. Bond distances and angles within this unit are in the expected ranges. However, there is some disorder in the locations of the oxygen atoms and in the positions of the carbon monoxide and chloride ligands. The chloride and carbon monoxide ligands bound to iridium show exchange disorder, which is a common feature in the structures of complexes where these nearly equally sized groups are trans to each other.^{7,9,10,15}

There are four sites on the fullerene where oxygen atoms reside. The refined occupancies indicate that O(1A) is the major site with an occupancy of 0.62(2) but that there are three other sites with occupancies of 0.169(15) for O(1B), 0.146(15) for O(1C), and 0.069(15) for O(1D). The geometry about each site

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$

atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a	atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
O(1A)	2059(9)	848(6)	364(4)	25(4)	C(62)	-606(9)	3128(6)	-290(4)	27(3)
O(1B)	436(29)	2314(24)	1754(15)	25(4)	C(63)	-1546(9)	3183(6)	-513(4)	33(3)
O(1C)	-176(36)	911(26)	358(18)	25(4)	C(64)	-1719(10)	3264(6)	-1010(4)	36(3)
O(1D)	2647	-151	462	25(4)	C(65)	-1016(10)	3264(6)	-1272(4)	33(3)
C(1)	738(8)	1521(6)	1102(4)	20(3)	C(66)	-118(10)	3195(6)	-1049(4)	38(3)
C(2)	1769(7)	1503(5)	1102(4)	15(2)	C(67)	92(9)	3123(5)	-550(4)	28(3)
C(3)	2171(8)	914(5)	886(4)	18(3)	C(68)	-1333(8)	2455(5)	507(4)	23(3)
C(4)	1548(8)	387(5)	633(3)	17(3)	C(69)	-1851(9)	2597(7)	860(4)	40(3)
C(5)	532(8)	404(6)	649(4)	21(3)	C(70)	-2536(10)	2169(7)	950(6)	52(4)
C(6)	175(8)	940(6)	892(4)	21(3)	C(71)	-2755(10)	1607(7)	671(5)	47(4)
C(7)	429(8)	1636(5)	1574(4)	21(3)	C(72)	-2271(10)	1456(7)	309(5)	46(4)
C(8)	1068(9)	1762(5)	1988(4)	24(3)	C(73)	-1565(9)	1879(6)	233(4)	30(3)
C(9)	2059(9)	1729(5)	1996(4)	25(3)	C(74)	-484(8)	3868(6)	667(4)	30(3)
C(10)	2377(8)	1572(6)	1580(4)	26(3)	C(75)	-400(9)	3928(7)	1168(4)	39(4)
C(11)	3147(8)	1102(6)	1608(4)	24(3)	C(76)	-528(10)	4552(7)	1352(5)	47(4)
C(12)	3002(8)	693(6)	1182(4)	24(3)	C(77)	-669(11)	5105(7)	1062(5)	55(5)
C(13)	3281(8)	25(6)	1216(4)	25(3)	C(78)	-733(12)	5050(7)	579(5)	58(5)
C(14)	2676(8)	-491(6)	963(4)	25(3)	C(79)	-655(9)	4428(6)	378(5)	37(3)
C(15)	1832(8)	-322(6)	699(4)	21(3)	C(80)	2574(8)	2775(6)	-235(4)	27(3)
C(16)	1021(9)	-717(6)	723(4)	27(3)	C(81)	2604(9)	2120(6)	-415(4)	33(3)
C(17)	218(8)	-277(6)	691(4)	22(3)	C(82)	2626(9)	2004(7)	-886(5)	40(3)
C(18)	-457(8)	-403(6)	960(4)	22(3)	C(83)	2603(9)	2532(7)	-1198(5)	44(4)
C(19)	-846(8)	117(6)	1196(4)	26(3)	C(84)	2549(10)	3181(7)	-1028(5)	44(4)
C(20)	-516(7)	773(6)	1173(4)	21(3)	C(85)	2547(9)	3316(6)	-549(4)	35(3)
C(21)	-357(8)	1206(6)	1593(4)	25(3)	C(86)	3620(8)	2537(6)	793(4)	25(3)
C(22)	-523(9)	954(6)	2030(4)	28(3)	C(87)	4133(8)	2055(7)	623(4)	35(3)
C(23)	104(10)	1109(6)	2464(4)	35(3)	C(88)	4868(9)	1745(8)	927(5)	45(4)
C(24)	885(8)	1498(6)	2440(4)	23(3)	C(89)	5107(8)	1958(7)	1394(5)	37(3)
C(25)	1774(10)	1311(6)	2719(4)	33(3)	C(90)	4608(8)	2460(6)	1565(4)	31(3)
C(26)	2485(9)	1459(6)	2445(4)	29(3)	C(91)	3859(8)	2742(6)	1266(4)	29(3)
C(27)	3255(8)	1036(6)	2470(4)	25(3)	C(92)	2672(9)	3871(6)	528(4)	32(3)
C(28)	3589(8)	858(6)	2045(5)	31(3)	C(93)	3550(10)	4135(6)	510(5)	40(3)
C(29)	3873(8)	152(6)	2073(5)	32(3)	C(94)	3700(10)	4818(6)	590(4)	37(3)
C(30)	3734(8)	-249(6)	1672(5)	32(3)	C(95)	3003(10)	5237(7)	683(4)	37(3)
C(31)	3396(9)	-930(6)	1707(5)	35(3)	C(96)	2136(10)	4960(6)	700(4)	33(3)
C(32)	2748(9)	-1086(6)	1271(4)	29(3)	C(97)	1975(8)	4294(6)	628(4)	29(3)
C(33)	1970(9)	-1486(6)	1288(4)	30(3)	C(101)	-4860(14)	3251(12)	-453(8)	91(7)
C(34)	1094(9)	-1297(6)	1010(4)	31(3)	C(102)	-5029(11)	3472(9)	-926(8)	77(6)
C(35)	377(9)	-1445(6)	1283(4)	27(3)	C(103)	-4673(11)	3131(8)	-1265(5)	52(4)
C(36)	-374(9)	-1010(6)	1260(4)	29(3)	C(104)	-4108(10)	2602(9)	-1148(6)	59(4)
C(37)	-172(8)	-831(6)	1692(4)	28(3)	C(105)	-3912(11)	2376(9)	-684(7)	72(5)
C(38)	-1020(8)	-128(6)	1653(4)	27(3)	C(106)	-4301(13)	2687(12)	-347(7)	86(6)
C(39)	-859(8)	270(6)	2062(4)	28(3)	C(107)	7265(10)	8797(7)	2579(5)	44(4)
C(40)	-399(9)	4(7)	2526(4)	34(3)	C(108)	6926(12)	8454(10)	2930(5)	71(5)
C(41)	201(10)	528(7)	2768(4)	36(3)	C(109)	6132(12)	8070(8)	2803(6)	58(5)
C(42)	1049(11)	344(7)	3035(4)	40(4)	C(110)	5675(10)	8049(9)	2336(6)	62(5)
C(43)	1848(9)	744(6)	3021(4)	30(3)	C(111)	6018(12)	8412(9)	1997(5)	62(5)
C(44)	2660(9)	305(7)	3041(5)	36(3)	C(112)	6822(11)	8786(8)	2116(5)	58(4)
C(45)	3336(9)	438(6)	2774(4)	31(3)	C(113)	4630(13)	7799	-292(6)	74(5)
C(46)	3728(10)	-112(6)	2533(4)	38(4)	C(114)	3783(11)	527(8)	-178(6)	56(4)
C(47)	3394(10)	-772(6)	2554(4)	37(4)	C(115)	3191(12)	223(8)	-497(6)	60(5)
C(48)	3244(9)	-1189(6)	2132(4)	32(3)	C(116)	3402(11)	84(7)	-948(5)	50(4)
C(49)	2423(10)	-1595(6)	2161(5)	37(3)	C(117)	4215(11)	253(8)	-1075(6)	55(4)
C(50)	1790(10)	-1733(6)	1742(5)	34(3)	C(118)	4831(12)	646(8)	-734(6)	65(5)
C(51)	812(9)	-1723(6)	1747(4)	30(3)	C(119)	2300(14)	3456(10)	-2571(6)	79(6)
C(52)	478(10)	-1548(6)	2158(4)	33(3)	C(120)	2068(15)	4140(11)	-2559(7)	97(7)
C(53)	-308(10)	-1100(7)	2125(5)	39(3)	C(121)	1329(13)	4336(10)	-2358(6)	81(6)
C(54)	-146(10)	-664(7)	2546(4)	39(4)	C(122)	769(10)	3873(7)	-2221(5)	46(4)
C(55)	741(11)	-851(6)	2833(4)	41(4)	C(123)	939(11)	3206(8)	-2259(5)	56(4)
C(56)	1327(12)	-357(7)	3073(4)	44(4)	C(124)	1717(11)	2988(9)	-2433(6)	64(5)
C(57)	2303(10)	-384(6)	3070(4)	37(3)	C(125)	8125(14)	9906(11)	3933(7)	62(6)
C(58)	2679(10)	-895(6)	2845(4)	36(3)	C(126)	8024(15)	9528(10)	4342(7)	58(5)
C(59)	2088(9)	-1429(6)	2588(5)	33(3)	C(127)	8450(13)	8942(10)	4410(7)	59(6)
C(60)	1155(9)	-1397(7)	2593(5)	36(3)	C(128)	8999(12)	8678(9)	4106(7)	48(5)
Ir	1143(1)	2347(1)	687(1)	20(1)	C(129)	9169(14)	9077(11)	3733(7)	59(6)
Cl(1)	1484(2)	3049(2)	1381(1)	31(1)	C(130)	8712(13)	9690(9)	3638(6)	47(5)
Cl(1B)	802(12)	1656(7)	-15(4)	6(5)	Cl(2)	8295(15)	10033(9)	3483(6)	51(7)
O(2)	664(8)	1600(5)	-228(3)	47(3)	Cl(3)	8518(17)	9736(10)	4485(5)	57(7)
As(1)	-295(1)	2985(1)	399(1)	23(1)	Cl(4)	9028(16)	8751(9)	3834(8)	54(7)
As(2)	2472(1)	2908(1)	429(1)	25(1)	C(131)	8221(15)	9389(9)	3905(7)	28(17)
C(61)	835(10)	1876(7)	121(3)	28(3)					

^a U_{eq} is defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

Table 2. Bond Lengths (Å) and Angles (deg) for $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$

Bond Lengths			
Ir—C(1)	2.165(11)	Ir—C(2)	2.158(10)
Ir—Cl(1)	2.396(3)	Ir—Cl(1B)	2.402(5)
Ir—As(1)	2.4695(14)	Ir—As(2)	2.466(2)
Ir—C(61)	1.847(5)	C(61)—O(2)	1.123(5)
C(1)—C(2)	1.512(14)	C(3)—C(4)	1.487(14)
C(7)—C(8)	1.39(2)	C(5)—C(6)	1.42(2)
C(14)—C(15)	1.37(2)		
O(1A)—C(3)	1.47(2)	O(1A)—C(4)	1.48(2)
O(1B)—C(7)	1.44(5)	O(1B)—C(8)	1.51(4)
O(1C)—C(6)	1.52(5)	O(1C)—C(5)	1.57(5)
O(1D)—C(15)	1.51	O(1D)—C(14)	1.57

Bond Angles			
C(2)—Ir—C(1)	40.9(4)	C(61)—Ir—Cl(1)	174.7(5)
C(61)—Ir—C(2)	95.7(5)	C(61)—Ir—Cl(1)	92.6(5)
C(2)—Ir—Cl(1)	89.6(3)	C(1)—Ir—Cl(1)	91.5(3)
C(2)—Ir—Cl(1B)	91.0(5)	C(1)—Ir—Cl(1B)	89.2(5)
C(61)—Ir—As(2)	92.9(5)	C(2)—Ir—As(2)	103.4(3)
C(1)—Ir—As(2)	144.3(3)	C(61)—Ir—As(1)	84.8(5)
C(2)—Ir—As(1)	146.4(3)	C(1)—Ir—As(1)	105.5(3)
Cl(1)—Ir—As(1)	90.89(9)	Cl(1B)—Ir—As(1)	88.8(4)
Cl(1)—Ir—As(2)	85.69(9)	Cl(1B)—Ir—As(2)	93.9(4)
As(2)—Ir—As(1)	110.08(5)		
C(3)—O(1A)—C(4)	60.5(7)	C(7)—O(1B)—C(8)	56(2)
C(6)—O(1C)—C(5)	55(2)	C(15)—O(1D)—C(14)	53
C(12)—C(3)—O(1A)	119.9(10)	O(1A)—C(3)—C(4)	59.9(7)
O(1A)—C(3)—C(2)	120.4(10)	C(15)—C(4)—O(1A)	120.0(10)
O(1A)—C(4)—C(3)	59.5(7)	O(1A)—C(4)—C(5)	126.9(10)
C(6)—C(5)—O(1C)	61(2)	C(17)—C(5)—O(1C)	117(2)
C(4)—C(5)—O(1C)	124(2)	C(5)—C(6)—O(1C)	65(2)
C(20)—C(6)—O(1C)	114(2)	C(1)—C(6)—O(1C)	120(2)
C(8)—C(7)—O(1B)	65(2)	O(1B)—C(7)—C(21)	120(2)
O(1B)—C(7)—C(1)	118(2)	C(7)—C(8)—O(1B)	59(2)
C(9)—C(8)—O(1B)	125(2)	C(24)—C(8)—O(1B)	117(2)
C(15)—C(14)—O(1D)	61	C(13)—C(14)—O(1D)	94
C(32)—C(14)—O(1D)	151	C(14)—C(15)—O(1D)	66
C(16)—C(15)—O(1D)	151	C(4)—C(15)—O(1D)	88

is consistent with the presence of an epoxide group, and in each case, the oxygen atom is situated above a 6:6 ring junction. While the disorder problems limit the accuracy of the metric details of the geometry, it should be noted that in the major site the O(1A)—C(3)—C(4) unit forms a nearly equilateral triangle and the C—O distances (1.47(2), 1.48(2) Å) and C—C distance (1.487(14) Å) are within the ranges expected for an epoxide unit.¹² The nonbonded Ir—O separations are large (the shortest being 3.38 Å), and it is clear that there is no insertion of the iridium complex into the epoxide unit.

Discussion

Some low-oxidation-state transition metal complexes are capable of insertion into epoxides.^{16,17} Although Ir(CO)Cl(AsPh₃)₂ is somewhat more reactive than Ir(CO)Cl(PPh₃)₂ in oxidative-addition reactions,¹⁸ the arsine complex still is not sufficiently reactive to insert into the C—O bonds of the epoxide portion of the fullerene. The results presented here show that Ir(CO)Cl(AsPh₃)₂ reacts with C₆₀O to form a crystalline adduct without deoxygenation of the fullerene. However, in the resulting crystalline adduct, the disorder in the location of the epoxide function is more pronounced than it was in $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2 \cdot 0.53\text{CHCl}_3 \cdot 4.47\text{C}_6\text{H}_6$.³ In this adduct, three of the four fullerene oxygen atom sites are positioned over 6:6 ring junctions that are immediately adjacent to the 6:6 ring

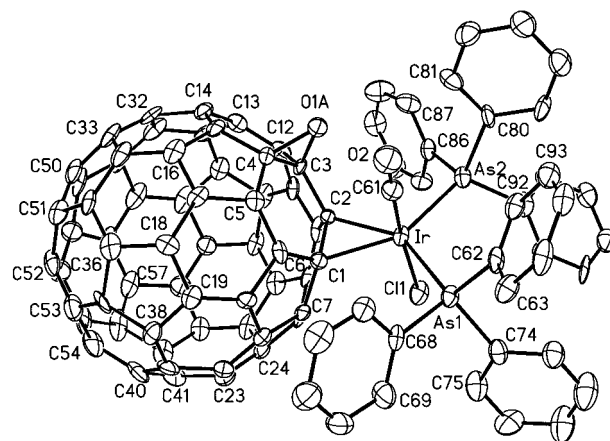


Figure 4. View of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2$, with 50% thermal contours for all atoms, showing the geometry of the major form that is present in the solid.

junction that is bound to the iridium atom of the Vaska's complex analog. The fourth site, while still involving a 6:6 ring junction, is slightly more remote from the location of the iridium atom. This is also the least populated of the four sites. The positional exchange disorder that affects the carbonyl and chloride ligands may be correlated with the disorder in the locations of the fullerene epoxide units. Steric effects are greatest between nonbonded units when the chloride unit is adjacent to an epoxide, but this orientation can be avoided by exchanging the locations of the carbon monoxide and chloride ligands. Thus the high occupancy of the Cl(1) site avoids contact with the high-occupancy oxygen atom site O(1A) and as well as site O(1C), while placing the chloride ligand in the lower occupancy site, Cl(1B), avoids contact with the low-occupancy oxygen atom site, O(1B). Clearly, entropic considerations, along with the reversible nature of this sort of adduct formation, play a major role in the production of this disorder. Nevertheless, it is clear that the double bonds in the vicinity of the epoxide function in C₆₀O are the most reactive toward adduct formation with Vaska type complexes.

Other strategies will be required to obtain more highly ordered forms of the fullerene oxides for structural characterization. One possibility is complex formation with Lewis acids that bind directly to the epoxide unit but do not induce ring opening. For example (tetraarylporphyrinato)carbonylruthenium(II)¹⁹ and soluble cadmium carboxylates²⁰ form isolable complexes with epoxides and might be useful in orienting fullerene oxides.

Experimental Section

Preparation of Compounds. C₆₀O and C₆₀O₂ were prepared by the oxidation of C₆₀ with *m*-chloroperoxybenzoic acid as described previously.⁵

$(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$. Under a dioxygen-free atmosphere of dinitrogen, a filtered solution of 3 mg (4 μmol) of C₆₀O in 1.5 mL of benzene was carefully layered over a filtered solution of 4 mg (5 μmol) of Ir(CO)Cl(AsPh₃)₂ in 1 mL of benzene. The mixture was allowed to stand undisturbed for 7 days. The purple-black crystals that formed at the interface between the two solutions were collected by filtration and washed with cold benzene: yield 3 mg, 48% based on C₆₀O. Under microscopic examination, the product appeared homogeneous, and crystals suitable for X-ray crystallography were obtained.

X-ray Data Collection. A suitable crystal of $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$ was coated with a light hydrocarbon oil

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Table 3. Crystal Structure Data for $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$

formula	$\text{C}_{126.10}\text{H}_{59.10}\text{As}_2\text{Cl}_{1.55}\text{Ir}_2\text{O}_2$
fw	2003.02
system; space group	monoclinic; $P2_1/n$
a , Å	14.662(2)
b , Å	19.836(2)
c , Å	28.462(5)
β , deg	100.318(12)
V , Å ³	8144(2)
Z	4
T , K	123(2)
radiation; λ , Å	Cu K α ; 1.541 78
μ , mm ⁻¹	5.041
d_{calc} , Mg/m ³	1.634
transm factors	0.29–0.71
no. of reflns	10473
no. of reflns ($I > 2\sigma(I)$)	7218
no. of params; no. of restraints	1095; 10
R^a	0.066
wR2 ^b	0.1520

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, for $I > 2\sigma(I)$. ^b $wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

and mounted in the 130(2) K dinitrogen stream of a Siemens P4/RA diffractometer which was equipped with a locally modified LT-2 low-temperature device. Intensity data were collected with nickel-filtered Cu K α radiation from a Siemens rotating-anode X-ray generator that operated at 15 kW. Crystal data are given in Table 3. No decay (<2%) in the intensities of two standard reflections was observed during data collection. The data were corrected for Lorentz and polarization effects. Further details are given in the Supporting Information.

Structure Solution and Refinement. Calculations were performed with SHELXTL Plus (Sheldrick, Siemens, 1990) and SHELXL-93 (Sheldrick, 1993). Scattering factors and corrections for anomalous dispersion were taken from a standard source.²¹ An absorption correction was applied to the structures with the program XABS2 which calculates 24 coefficients from a least-squares fit of $1/A$ vs $\sin^2(\theta)$ to a cubic

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equation in $\sin^2(\theta)$ by minimization of F_o^2 and F_c^2 differences.²² The structure was solved in the space group $P2_1/n$ with the use of direct and difference Fourier methods. Four oxygen atom sites on the fullerene were identified. During the refinement, the thermal parameters for these four atoms were tied together and a final U value of 0.025(4) Å² resulted. In addition, the positional parameters for O(1D), the oxygen site with the smallest occupancy, were fixed at the values obtained from a difference Fourier map. The refined occupancies of the four oxygen atom sites on the fullerene were as follows: O(1A), 0.62(2); O(1B), 0.169(15); O(1C), 0.146(15); O(1D), 0.069(15). No additional restraints influenced the refined occupancies, and since the average thermal parameter for the complex approximates the value found for the oxygen atoms, it can be assumed that all of the sites of oxygen atom occupancy have been identified. The chloride and carbon monoxide ligands bound to iridium show exchange disorder. The relative occupancies were allowed to refine and converged to 0.860(8) for the major site, Cl(1), and 0.14(1) for the minor site, Cl(1B). The carbon and oxygen atoms of the minor orientation were not located. One of the solvate sites is disordered with occupancy by both a benzene molecule and a molecule of chloroform. The occupancies of the two groups were refined and converged at 0.82(1) for the benzene molecule and 0.18(1) for the chloroform molecule. Hydrogen atoms were fixed to appropriate carbon atoms through the use of a riding model and isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameters of the adjacent carbon atoms. Refinement involved full-matrix, least-squares methods based on F^2 and the use of all data. Anisotropic thermal parameters were used for all non-hydrogen atoms with the exclusion of the disordered epoxide oxygen atoms, the disordered carbon monoxide ligand, the disordered benzene molecule, and the minor site of the chloride ligand. The largest peak on the final difference map had a magnitude of 1.1 e Å⁻³. There are no unusually short intermolecular contacts in the structure.

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Supporting Information Available: Tables giving details of data collection and structure refinement, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for $(\eta^2\text{-C}_{60}\text{O})\text{Ir}(\text{CO})\text{Cl}(\text{AsPh}_3)_2 \cdot 4.82\text{C}_6\text{H}_6 \cdot 0.18\text{CHCl}_3$ (13 pages). Ordering information is given on any current masthead page.

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