

atom. The indium lies almost at the center of gravity of the ring spanned by the five manganese atoms (distance 8.5 pm; deviation from the best plane 4.6 pm). Its coordination is approximately pentagonal planar. This unusual coordination form in **3** is exclusively due to the sterically rigid  $[\text{Mn}_5(\text{CO})_{20}]$  "ligand".

### Experimental Procedure

All manipulations were conducted under an inert atmosphere (argon) in the absence of moisture and air. All glass apparatus was evacuated several times on an oil vacuum line and flushed with argon before use. The solvents were dried under argon and freshly distilled.

**1**: Prepared by published methods [8, 9], this compound contains 30% KOH. For the preparation of **2** and **3**, **1** was freed of KOH by dissolution in acetone and filtration, followed by evaporation of the acetone. KOH-free **1** is pyrophoric.

**2** and **3**: THF (8.5 mL) was added to a mixture of **1** (0.58 g, 0.94 mmol) and dry  $\text{InCl}_3$  (0.87 g, 4.10 mmol). The color changed immediately from green to blue. The solution was stirred for 5 min, methanol (1.5 mL) was added, and the mixture was separated on a chromatography column (MPLC column  $46 \times 2.6$  cm, silica gel 40–63  $\mu$ , eluent THF/methanol 10/1). A yellow and a blue fraction that have not yet been able to be characterized were eluted first in low yields. The third violet fraction was treated with  $\text{AsPh}_4\text{Cl}$  monohydrate (100 mg, 0.229 mmol), the solvent removed at  $10^{-1}$  mbar, and the residue taken up in a mixture of *n*-hexane, ethyl acetate, and acetone (5:20:15 mL). The violet mother liquor was filtered off through a G3 Schlenk filter; at  $+4^\circ\text{C}$   $2\text{-(AsPh}_4)_2 \cdot (\text{CH}_3)_2\text{CO}$  precipitates as red-brown crystals. They are separated from the mother liquor by decantation, washed three times with diethyl ether, and dried in vacuum. Yield: 90 mg (8%, calculated on initial amount of **1**), correct elemental analyses.

The fourth, brown fraction was treated with  $\text{AsPh}_4\text{Cl}$  monohydrate (50 mg, 0.115 mmol), the solvent removed at  $10^{-1}$  mbar, and the residue taken up in ethyl acetate. Excess  $\text{AsPh}_4\text{Cl}$  and KCl remained undissolved. The brown mother liquor was filtered through a G-3 Schlenk filter. At  $+4^\circ\text{C}$ ,  $3\text{-(AsPh}_4)_2$  precipitated in the form of dark brown crystals, which were separated by decantation from the mother liquor, washed three times with diethyl ether, and dried at  $10^{-1}$  mbar. Yield: 15 mg (2%, calculated on initial amount of **1**), correct elemental analyses. A light brown residue which cannot be eluted remains on the column.

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CAS Registry numbers:

**1**, 130934-60-0; **2-(AsPh}\_4)\_2 \cdot (\text{CH}\_3)\_2\text{CO}, 138407-41-7; **3-(AsPh}\_4)\_2, 138407-43-9; In, 7440-74-6; Mn, 7439-96-5.****

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[10] Spectroscopic data of **2** and **3**:  $2\text{-(AsPh}_4)_2 \cdot (\text{CH}_3)_2\text{CO}$ : UV/VIS ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  [nm] ( $\epsilon$ ) = 264 (39000), 270 (36800), 320 (23300), 570 (8800);  $^1\text{H NMR}$  (300 MHz,  $[\text{D}_6]\text{acetone}$ , internal standard  $[\text{D}_6]\text{acetone}$ , room temperature):  $\delta$  = 7.82–7.95 (m, phenyl-H);  $^{13}\text{C NMR}$  (75 MHz,  $[\text{D}_6]\text{acetone}$ , internal standard  $[\text{D}_6]\text{acetone}$ , room temperature):  $\delta$  = 230.6 (s, carbonyl-C); 135.5, 134.3, 132.0, 122.1 (phenyl-C); IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 2064 st, 2030 st, 1979 sst, 1950 sst, 1887 st, 1869 st (C=O). **3-(AsPh}\_4)\_2: UV/VIS ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  [nm] ( $\epsilon$ ) = 264 (43900), 270 (38300), 342 (22400), 490 (12300);  $^1\text{H NMR}$  (300 MHz,  $[\text{D}_6]\text{acetone}$ , internal standard  $[\text{D}_6]\text{acetone}$ , room temperature):  $\delta$  = 7.82–7.95 (m, phenyl-H); IR (KBr):  $\nu$  [ $\text{cm}^{-1}$ ] = 1988 sst, 1968 sst, 1947 st, 1938 st, 1926 st, 1912 st, 1902 st, 1887 m, 1880 m, 1864 m (C=O).  
[11] Crystal structure of **2** and **3**:  $2\text{-(AsPh}_4)_2 \cdot (\text{CH}_3)_2\text{CO}$ :  $\text{C}_{60}\text{H}_{46}\text{O}_{19}\text{As}_2\text{In}_2\text{Cl}_2\text{Mn}_4$ ,  $M = 1849.29$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 2462.8(8)$ ,  $b = 1521.0(9)$ ,  $c = 2221.1(8)$  pm,  $\beta = 117.72(2)^\circ$ ,  $V = 7365(1) \times 10^6$  pm $^3$ ,  $Z = 4$ ,  $T = 298$  K,  $\theta$  range  $3.0^\circ < 2\theta < 52.5^\circ$ , 7908 measured reflections, 4416 observed reflections ( $I > 2\sigma(I)$ ), 3850 independent reflections ( $I > 2.5\sigma(I)$ ), 396 refined parameters,  $R(R_w) = 0.064$  (0.052). **3-(AsPh}\_4)\_2:  $\text{C}_{60}\text{H}_{44}\text{O}_{20}\text{As}_2\text{InMn}_5$ ,  $M = 1716.44$ , rhombic,****

space group *Pbca* (no. 61),  $a = 1930(1)$ ,  $b = 2403(1)$ ,  $c = 2922(1)$  pm,  $V = 1355(1) \times 10^7$  pm $^3$ ,  $Z = 8$ ,  $T = 298$  K,  $\theta$  range  $3.0^\circ < 2\theta < 50.0^\circ$ , 12515 measured reflections, 6410 observed reflections ( $I > 2\sigma(I)$ ), 5652 independent reflections ( $I > 2.5\sigma(I)$ ), 530 refined parameters,  $R(R_w) = 0.070$  (0.056). Measurement on a Siemens (Nicolet-Syntex) R3 four circle diffractometer,  $\text{MoK}\alpha$  radiation, graphite monochromator. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-55887, the names of the authors, and the journal citation.

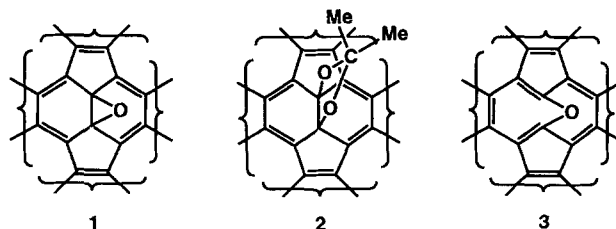
- [12] Selected distances [pm] and angles [ $^\circ$ ] for **2**: In 1-Mn 1 272.5(3), In 1-Mn 2a 269.2(2), In 1-Mn 2 265.0(2), In 1-Cl 1 248.8(4), Mn 2-Mn 2a 316.4(2); In 1-Mn 2-Mn 2a 54.3(1), In 1a-Mn 2-Mn 2a 53.1(1), Mn 2-In 1-Mn 2a 72.6(1), Mn 1-In 1-Cl 1 100.9(1), Mn 1-In 1-Mn 2 128.8(1), Mn 1-In 1-Mn 2a 130.4(1), Cl 1-In 1-Mn 2a 108.7(1), Cl 1-In 1-M 2 113.9(1).  
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## Reaction of $\text{C}_{60}$ with Dimethyldioxirane— Formation of an Epoxide and a 1,3-Dioxolane Derivative\*\*

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Since their discovery,<sup>[1]</sup> the fullerenes have attracted much attention.<sup>[2–4]</sup> Although gram quantities of  $\text{C}_{60}$  and  $\text{C}_{70}$  can now be produced,<sup>[5, 6]</sup> the chemical reactivity of these new compounds is just beginning to be explored, and few products have been completely characterized. Among these are adducts to  $\text{C}_{60}$  of  $\text{OsO}_4$ ,<sup>[7, 8]</sup> other metal-complex fragments,<sup>[9–11]</sup> and diphenylcarbene.<sup>[12]</sup>

Although  $\text{C}_{60}$  is easy to reduce and reacts readily with nucleophiles, it is very difficult to oxidize.<sup>[13–17]</sup> Dioxiranes have been used to make epoxides that are difficult to prepare by other routes.<sup>[18–26]</sup> We now report that  $\text{C}_{60}$  reacts with dimethyldioxirane to give an epoxide  $\text{C}_{60}\text{O}$  and a 1,3-dioxolane derivative.



$\text{C}_{60}$  reacts with dimethyldioxirane to give two products, **1** and **2**, which in the solid state are stable dark crystals. Solutions of **2** in toluene are yellow, those of **1**, purple (similar to solutions of  $\text{C}_{60}$ ). The UV/VIS spectra of **1** and **2** are shown in Figures 1a and 1b. The FTIR spectrum of **1** is shown in Figure 2a. The  $^{13}\text{C NMR}$  spectrum of **1** (Fig. 3a) consists of 17 signals, of which four correspond to two carbon atoms and

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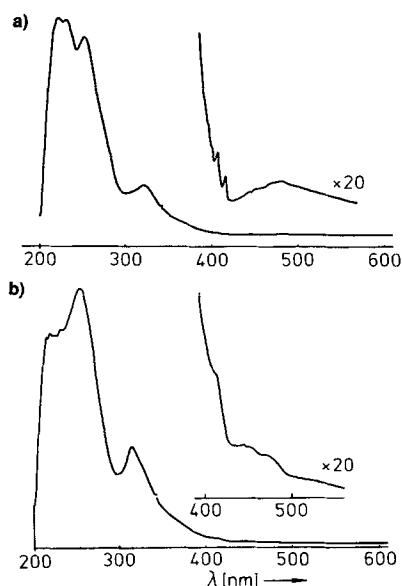


Fig. 1. UV/VIS spectra of a)  $C_{60}O$  **1** and b)  $C_{60}$ -1,3-dioxolane **2** in *n*-hexane.

thirteen correspond to four carbon atoms. This is the correct number and ratio of peak intensities for a  $C_{60}$  adduct of  $C_{2v}$  symmetry. The osmium-tetraoxide adduct, of which a detailed NMR study has recently appeared,<sup>[27]</sup> has the same symmetry.

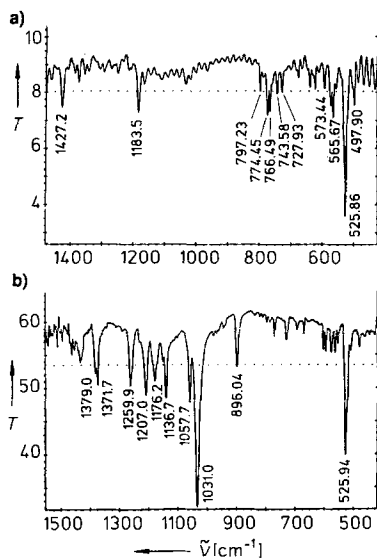


Fig. 2. FTIR spectra (KBr pellets) of a)  $C_{60}O$  **1** and b)  $C_{60}$ -1,3-dioxolane **2**.

The LD-TOF mass spectrum (laser desorption time-of-flight)<sup>[28, 29]</sup> of **1** displays a peak for  $C_{60}O$  ( $m/z$   $736 \pm 2$ ,  $M^+$ ) as well as for  $C_{60}$ , which arises from loss of one oxygen atom. The FAB mass spectrum (not shown) shows a weak peak at  $m/z$  736, but the loss of an oxygen atom is much more pronounced here. There is no  $C_{60}O$  in the starting material, as shown by the LD-TOF spectrum, and the isolated **1** is not contaminated by  $C_{60}$  according to HPLC. Based on the above data, **1** is a monoepoxide of  $C_{60}$  with the oxygen bridging the bond connecting two six-membered rings, a bonding situation also found in other  $C_{60}$  adducts.<sup>[27]</sup>

After much of this work had been completed, we received a manuscript from chemists at Exxon and the University of Pennsylvania reporting the preparation of  $C_{60}O$  by a photo-

chemical route and by isolation from soot.<sup>[30]</sup> The properties of their material are in excellent agreement with those reported above. The infrared bands differ slightly in relative intensities, which we attribute to the difference in medium (KBr pellet vs. film). The  $^{13}C$  NMR shifts are quite similar, although the solvents used are different ( $CS_2$  vs.  $C_6D_6$ ). Both  $C_{60}O$  and  $C_{70}O$  have also been detected in the gas phase.<sup>[31]</sup> An oxide of  $C_{70}$  is formed in the soot with other fullerenes and has been characterized only by mass and UV/VIS spectrometry.<sup>[6]</sup> Recent electrochemical studies reported that the dianion of  $C_{60}$  reacts with  $O_2$  to form a series of  $C_{60}$  oxides which were detected by FAB mass spectrometry but were not otherwise characterized.<sup>[32]</sup>

Our product is clearly the epoxide **1** rather than the annulene<sup>[33]</sup> **3**, as shown by the  $^{13}C$  NMR signal at  $\delta = 90.92$ ; an  $sp^2$  C–O should give rise to a signal below  $\delta = 140$ .<sup>[34, 35]</sup> Substituted epoxide carbons typically resonate at  $\delta = 52$ – $70$ .<sup>[36]</sup> Although the resonance at  $\delta = 90.92$  is at low field for epoxide carbons, the downfield shift is probably caused by the anisotropy of the partially broken fullerene, which was also reported in the diphenylcarbene adduct.<sup>[12]</sup> The similarity of the UV/VIS spectrum of the diphenylcarbene adduct to that of  $C_{60}$  was taken as indirect evidence for the open annulene structure, which is clearly implied by the long C–C bond.<sup>[37]</sup> The UV/VIS spectra of **1** and  $C_{60}$  are also quite similar, but the NMR spectrum of **1** provides definitive proof of its epoxide character.

Based on spectral data we identify the second product of the reaction of dimethyldioxirane and  $C_{60}$  as 1,3-dioxolane **2**. The FTIR spectrum of compound **2** (Fig. 2b) shows a very strong  $sp^3$  C–O absorption band at  $1031\text{ cm}^{-1}$  and a C–H absorption band at  $2900\text{ cm}^{-1}$ . The LD-TOF mass spectrum has a molecular ion ( $m/z$  795,  $M^+$ , corresponding to  $C_{60}$  + dimethyldioxirane) and signals of greater intensity for fragmentation to  $C_{60}O$  (loss of acetone) and to  $C_{60}$ . The exact molecular mass of  $M^+$  (794) was obtained from the FAB mass spectrum but here, as with **1**, the signal of the  $C_{60}$  ion is dominant. The  $^{13}C$  NMR spectrum of **2** (Fig. 3b) also has 17 signals for the  $C_{60}$  skeleton, of which 13 correspond to four carbon atoms, and four correspond to two carbon atoms. The resonance at  $\delta = 96$  (at lower field than the related signal in **1**) is assigned to the O-bound carbon atoms. The signals at  $\delta = 113.04$  (1 C) and  $28.92$  (2 C) are assigned to the

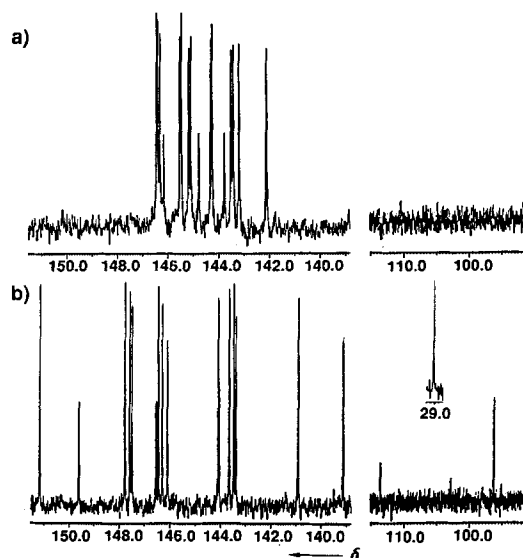


Fig. 3.  $^{13}C$  NMR spectra of a)  $C_{60}O$  **1** and b)  $C_{60}$ -1,3-dioxolane **2** in  $CS_2$  with  $[D_6]$ acetone as internal lock and  $[Cr(acac)_3]$  as relaxation agent.

ketal and methyl C atoms, respectively. In the  $^1\text{H}$  NMR spectrum (in  $\text{CS}_2$ ) the methyl hydrogens give rise to a sharp singlet at  $\delta = 1.56$ .

The 1,3-dioxolane structure can be deduced from the number of signals in the  $^{13}\text{C}$  NMR spectrum; the 1,2-isomer would have only a single mirror plane. The same reasons advanced in favor of the epoxide structure for **1** lead us to conclude that adduct **2** also has the closed structure. The fullerene regions of the  $^{13}\text{C}$  NMR spectra of the  $\text{OsO}_4$  adduct of  $\text{C}_{60}$ <sup>[27]</sup> and of **2** are strikingly similar (Fig. 3b), confirming their structural similarity. Hydrolysis of this ketal and oxidation of the resulting diol may offer an attractive and specific route to ring-opened fullerenes.

The determination of the mechanism for the formation of **1** and **2** will require further study. It is particularly surprising that the O–O bond of the dimethyldioxirane opens. To our knowledge, this is the first reported dimethyldioxirane adduct of this type. Small amounts of a 1,3-dioxolane were formed during the epoxidation of *cis*-3-hexene,<sup>[38]</sup> but this resulted from addition of acetone to the epoxide under the acidic conditions used. When a solution of **1** in acetone/toluene was stirred at 50 °C for 12 h, no change was observed (HPLC). Solutions of **1** in toluene heated at 110 °C for 24 h showed gradual decomposition of **1** to  $\text{C}_{60}$ . The 1:1 dimethyldioxirane– $\text{C}_{60}$  adduct **2** could give epoxide **1** by loss of acetone, or **1** and **2** could be formed in competitive reactions. But no change was observed (HPLC) for solutions of **2** in toluene after they had been heated at 110 °C for 24 h. Thus, the two compounds do not interconvert under more extreme conditions than those required for their formation (and isolation), and the competitive pathway seems likely.

Addition of dimethyldioxirane to  $\text{C}_{60}$  could proceed by either homolytic or heterolytic cleavage of the O–O bond. Although Wudl et al. report reactions of  $\text{C}_{60}$  with 1,3-dipoles,<sup>[12]</sup> the path via diradicals seems more likely in our case.

### Experimental Procedure

A solution of  $\text{C}_{60}$  (200 mg, 0.28 mmol)<sup>[39]</sup> in toluene (400 mL) was treated with 2.5 mL of a solution of dimethyldioxirane [19] in acetone (0.11 M) at room temperature. After 12 h a brown insoluble material was removed by filtration. The elemental analysis (C 84.97, H 0.94, O 14.09) corresponds to  $\text{C}_{60}\text{H}_{10}\text{O}_{7-8}$ ; FTIR (KBr):  $\nu[\text{cm}^{-1}] = 527, 1041 (\text{s}), 1208, 1174, 2940 (\text{w}), 2989 (\text{w})$ . The products were separated by preparative HPLC ( $\text{C}_{18}$  reverse-phase, acetonitrile/toluene, 55:45 (v:v), detection at 340 nm, 9.5 mL min<sup>-1</sup>). Baseline peak separation allowed isolation of 12 mg of **2**, 8 mg of **1**, and 66 mg of unreacted  $\text{C}_{60}$ . Chromatography on alumina also led to separation of **1** and **2**. UV/VIS (*n*-hexane): **1**:  $\lambda_{\text{max}} [\text{nm}] = 228, 249, 319 (\text{s}), 405, 416 (\text{w}), 478 (\text{br., w})$ ; **2**:  $\lambda_{\text{max}} [\text{nm}] = 253, 313 (\text{s}), 412, 444, 471 (\text{vw})$ . FTIR (KBr): **1**:  $\nu[\text{cm}^{-1}] = 1427, 1184, 774, 766, 566, 526$ , and others; **2**: three weak bands at 2900  $\text{cm}^{-1}$ , others at 1379, 1207, 1176, 1138, 1058, 1031 (s), 896, 526 (s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CS}_2$ , [ $\text{D}_6$ ]acetone as internal lock,  $[\text{Cr}(\text{acac})_3$ ] as relaxation agent, 42 000 scans, 25 °C): **1**:  $\delta$ (number of carbon atoms) = 146.32(4), 146.29(4), 146.20(4), 146.04(2), 145.40(4), 145.34(4), 145.05(4), 144.97(4), 144.64(2), 144.18(4), 144.14(4), 143.64(2), 143.38(4), 143.30(4), 143.07(4), 141.99(4), 90.92(2); **2** (same conditions as for **1** except 38 000 scans):  $\delta = 151.04(4), 149.47(2), 147.64(4), 147.45(4), 147.36(4), 146.40(2), 146.31(4), 146.17(4), 145.96(4), 143.96(4), 143.93(2), 143.53(4), 143.35(4), 143.26(4), 140.79(4), 139.02(4), 113.04(1), 96.15(2), 28.92(2)$ .

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### Ab Initio Investigations of Structure and Stability of $[\text{R}_3\text{SiAl}]_4$ , R = H, Me, *t*Bu\*\*

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The synthesis of metastable Al<sup>I</sup> compounds, for example, AlCl in toluene/ether by Schnöckel et al.,<sup>[1]</sup> opened new routes in aluminium chemistry.<sup>[2]</sup> Thus,  $\text{Cp}^*_4\text{Al}_4$ ,

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