Sulphur Dioxide as an Unsupported Bridging Ligand: Synthesis and *X*-Ray Crystallographic Characterization of μ-(Sulphur dioxide)-bis-(π-cyclopentadienyldicarbonyliron)

By Melvyn R. Churchill,* Barry G. DeBoer, and Krishan L. Kalra
(*Department of Chemistry, University of Illinois at Chicago Circle, Box* 4348, *Chicago, Illinois* 60680)

and P. Reich-Rohrwig and A. Wojcicki
(*Department of Chemistry, Ohio State University, Columbus, Ohio* 43210)

Summary $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$ has been prepared from $\pi\text{-}C_5H_5Fe(CO)_2Na$ and SO_2 and its molecular stereochemistry determined from a single-crystal *X*-ray diffraction study; this complex represents the first known molecule in which SO_2 alone bridges two transition metal atoms.

Sulphur dioxide has been shown to "insert" into metal-carbon bonds[1] and the structures of selected products have been determined crystallographically.[2] In the course of investigations of electrophilic interactions between SO_2 and organometallic species, we have discovered a new type of reaction which extends the range of SO_2 containing complexes. Reported below is the synthesis, chemical and crystallographic characterization, and some chemical properties of $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$.† This molecule represents the first fully characterized complex in which SO_2 alone bridges two transition metal atoms.

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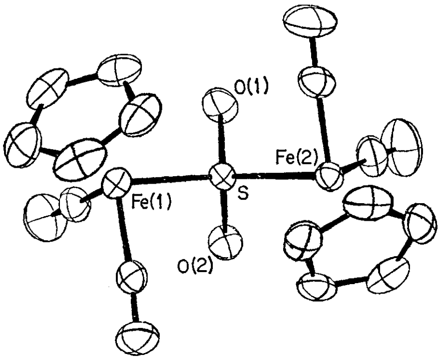
† Note that the direct reaction of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and SO_2 yields only isomers of $(\pi\text{-}C_5H_5)_4Fe_4(CO)_4(SO_2)_3$ and not this simple "insertion product" (see ref. 3).

A solution of π-$C_5H_5Fe(CO)_2Na$ in tetrahydrofuran (THF) was treated with a 30-fold molar excess of SO_2 at –75°C and allowed to warm to room temperature over 45—60 min. Chromatography on Florisil yielded $[\pi$-C_5H_5-$Fe(CO)_2]_2$, $[\pi$-$C_5H_5Fe(CO)_2]_2SO_2$ (red crystals, 12–30%, decomp. 142°) and a trace of a polynuclear red complex which analyses approximately for $(\pi$-$C_5H_5)_2Fe_2(CO)_3SO_2$ $[\pi$-$C_5H_5Fe(CO)_2]_2SO_2$ is soluble in benzene, chloroform and acetone, but decomposes rapidly in solution. Its i.r. spectrum (Nujol mull) shows ν_{CO} at 2027s, 2015vs, 1965s, and 1953vs cm^{-1} and ν_{SO} at 1135 and 993 cm^{-1}. Attempted sublimation or photolysis of $[\pi$-$C_5H_5Fe(CO)_2]_2SO_2$ in THF each result in loss of SO_2 to afford $[\pi$-$C_5H_5Fe(CO)_2]_2$ in good yield. By way of contrast, only one Fe–S bond is broken upon reaction with neat MeI) [equation (1)].



FIGURE

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2 + MeI \rightarrow \pi\text{-}C_5H_5Fe(CO)_2SO_2Me + \pi\text{-}C_5H_5Fe(CO)_2I \qquad (1)$$

The formation of $[\pi$-$C_5H_5Fe(CO)_2]_2SO_2$ may involve oxidation of the π-$C_5H_5Fe(CO)_2SO_2^-$ ion (see ref. 4), but cannot involve direct reaction of $[\pi$-$C_5H_5Fe(CO)_2]_2$ and SO_2, which affords different products.†

The molecular structure of $[\pi$-$C_5H_5Fe(CO)_2]_2SO_2$ has been unambiguously determined *via* a single-crystal *X*-ray diffraction study.

Crystal Data: $C_{14}H_{10}Fe_2O_6S$, $M = 417\cdot99$, monoclinic, $a = 7\cdot7028(17)$, $b = 17\cdot1559(45)$, $c = 12\cdot8488(27)$ Å, $\beta = 117\cdot48(1)°$, $U = 1506\cdot0$ Å^3, $D_c = 1\cdot844$, $Z = 4$, space group $P2_1/c$ (C_{2h}^5; No. 14).

Diffraction data complete to $2\theta = 55°$ (Mo-K_α radiation) were collected on a Picker FACS-1 diffractometer and were corrected for Lorentz, polarization, and absorption ($\mu = 21\cdot36$ cm^{-1}) effects. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been accurately located, the final discrepancy index being R 3·0% for the 3472 independent reflections.

As shown in the Figure, the SO_2 molecule is "inserted" symmetrically between two iron atoms and is *S*-bonded to both, with Fe(1)–S = 2·2790(6) and Fe(2)–S = 2·2814(6) Å; the Fe(1) · · · Fe(2) distance of 3·9090(8) Å is essentially non-bonding. The central sulphur atom has a distorted tetrahedral stereochemistry, with Fe(1)–S–Fe(2) = 118·00(2), O(1)–S–O(2) = 112·91(8), Fe(1)–S–O(1) = 106·51(6), Fe(1)–S–O(2) = 106·54(6), Fe(2)–S–O(1) = 107·04(6), Fe(2)–S–O(2) = 106·06(6)°; S–O(1) = 1·4797(14), and S–O(2) = 1·4764(14) Å.

The mean iron–sulphur distance of 2·2802 Å is intermediate between that observed in π-$C_5Me_5Fe(CO)_2SO_2 \cdot CH_2 \cdot$-CH:CHPh [Fe–S = 2·218(2) Å][2a] and that expected for an iron–sulphur bond of unit bond order [2·38 Å, using Pauling's value of 1·04 Å for the covalent radius of sulphur[5] and Churchill's value of 1·34 Å for the radius of iron(II) in π-$C_5H_5Fe(CO)_2X$ species[6]]. This, in conjunction with S–O stretching frequencies in the present complex being lower by 50 cm^{-1} than those in π-$C_5H_5Fe(CO)_2SO_2R$[7] species, provides excellent evidence for multiple bond character in these iron-sulphur linkages.

Other distances and angles are as expected for a π-C_5H_5-$Fe(CO_2)$ derivative, *viz.*, Fe–C(π-C_5H_5) = 2·086(2)—2·122(2), Fe–CO = 1·763(2)—1·775(2), C–O = 1·137(3)—1·141(3), C–C(π-C_5H_5) = 1·373(5)—1·411(4), and C–H = 0·83(4)—0·97(4) Å.

We acknowledge computing time supplied by the Computer Center, University of Illinois at Chicago Circle and financial support from the National Science Foundation.

(*Received, 3rd July* 1972; *Com.* 1161.)

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