

Preliminary communication

SYNTHESIS OF A TRANSITION METAL-DITHIONITE COMPLEX, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-S(O)}_2\text{S(O)}_2\text{-Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$

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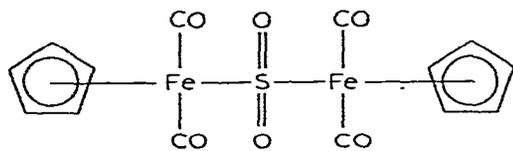
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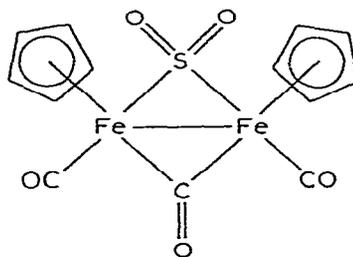
Summary

The reaction of $\text{Na}[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]$ with large excess of SO_2 in THF at -78°C followed by warming to room temperature affords an iron-dithionite complex, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe-S(O)}_2\text{S(O)}_2\text{-Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$.

It has been previously established [1] that the reaction of SO_2 with $\text{Na}[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]$ in THF solution yields two isolable crystalline complexes, I and II. In each case a sulfur dioxide molecule bridges two $\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2$ units and the molecular structures of these compounds have been confirmed by X-ray diffraction studies [2,3].



(I)

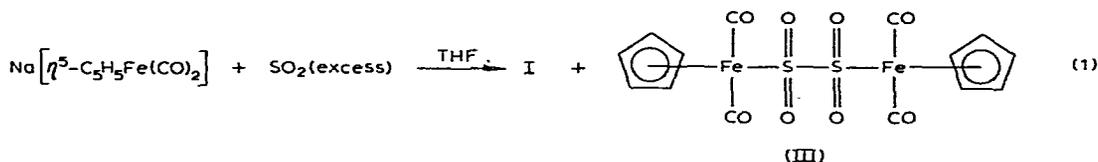


(II)

The interaction of SO_2 and $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$ at elevated temperatures is also documented [4], but in that case no simple products of this type were reported. The isolated complexes were formulated as isomers of the polynuclear species $(\eta^5\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4(\text{SO}_2)_3$ where the SO_2 molecule again acts in a bridging capacity.

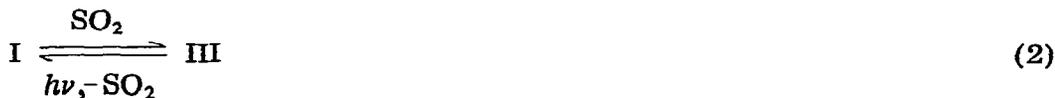
We find that the reaction of SO_2 with $\text{Na}[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]$ in THF solution is sensitive to the relative concentrations of these reagents, and we

now report that when a large excess of SO₂ is employed* an additional product results. Thus, treatment of a solution of Na[η⁵-C₅H₅Fe(CO)₂] (10 mmol) in THF at -78°C with an 11-fold molar excess of SO₂ for 5 min followed by slow (1 h) warming to room temperature and chromatography of the reaction mixture on Florisil affords [η⁵-C₅H₅Fe(CO)₂]₂ (1 mmol), I, and a new orange crystalline material III, m.p. 140-146°C (dec.) (0.8 mmol, 16% yield).



We formulate III as a novel type of binuclear transition metal complex in which two iron atoms are bridged by a dithionite linkage. Support for this formulation is provided by elemental analysis and osmometric molecular weight determination**, and spectroscopic data are entirely compatible with the proposed structure. The proton NMR spectrum at 25°C (CDCl₃ soln.) shows a single resonance at τ 4.64 ppm which does not broaden down to -40°C in (CD₃)₂CO solution, and the ¹³C NMR spectrum at 25°C (CDCl₃ soln.) exhibits signals at 208.381 due to CO and 86.176 ppm from TMS due to C₅H₅; the latter signal remaining sharp down to -70°C in (CD₃)₂CO solution. The infrared spectrum contains ν(CO) bands (CDCl₃ soln.) at 2070m, 2059m-s, and 2024-s(br) and ν(SO) bands (Nujol mull) at 1223s and 1040s cm⁻¹. Both sets of infrared absorptions show a substantial shift to higher energy compared to the corresponding bands of I. This would be consistent with an increase in positive charge on the iron in the η⁵-C₅H₅Fe(CO)₂ moiety on going from I to III, thus resulting in a reduction in Fe-to-S π-bonding.

It appears likely that III arises from subsequent interaction of SO₂ with I generated in reaction I. Our observation that III is in fact formed by treatment of I with SO₂ (eq. 2) not only supports this suggestion but further adds credence to the dithionite structural assignment. The insertion of SO₂



into I proceeds either in THF solution under conditions which mirror those of reaction 1 or in neat sulfur dioxide at reflux. The reverse process, SO₂ extrusion from III, has also been achieved, in 26% yield, under photolytic conditions in THF, though the reaction is accompanied by formation of some [η⁵-C₅H₅Fe(CO)₂]₂ and extensive decomposition.

*The reaction that afforded I and II utilized a 1.5-fold excess of SO₂, not a 30-fold excess as reported incorrectly in ref. 1.

**Found: C, 35.08; H, 2.10; S, 13.20; mol.wt. (CHCl₃ soln.), 501. C₁₄H₁₀S₂O₈Fe₂ calcd.: C, 34.88; H, 2.09; S, 13.30%; mol.wt., 482. No satisfactory mass spectrum was obtained because of decomposition.

Cleavage of III by CH_3I in THF solution at reflux yields $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-S}(\text{O})_2\text{CH}_3$ and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ in a 1/1.8 ratio (62% total yield). No evidence was obtained for the formation of the species $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$. The same two products were isolated earlier [1] from the reaction between I and CH_3I .

The range of this class of dithionite complexes and their mode of formation are under investigation.

Acknowledgements

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References

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