

Preliminary communication

Reversible insertion of SO<sub>2</sub> into the N–N bond  
of [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-Ph<sub>2</sub>N<sub>2</sub>)]<sup>1</sup>

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Abstract

The unusual lability of the N–N bond of the azobenzene ligand in [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-Ph<sub>2</sub>N<sub>2</sub>)] (**1**) has allowed the insertion of SO<sub>2</sub> under normal conditions. The resulting complex [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-PhN–SO<sub>2</sub>–NPh)] (**2**) has been shown by structure determination to be a labilized sulphamide derivative. Thermolysis of **2** leads to elimination of SO<sub>2</sub> and isolation of [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-PhN–CO–NPh)] (**3**), which is also a thermolysis product of **1**.

*Keywords:* Iron; Azobenzene; Sulphur dioxide; Insertion reactions

1. Introduction

The synthesis and reactivity of polynuclear complexes containing organic azo compounds as bridging ligands can provide insights into the behaviour of N–N units under the conditions of technical catalysis, including the Haber–Bosch process. We, among others, have provided examples for this in the form of azoalkane bridged iron and ruthenium clusters [1–3] which contain labile N–N or C–H bonds respectively. We observed an even higher reactivity at the N–N bond in the azobenzene bridged dinuclear iron complex **1** [4,5] which, owing to this property, had eluded synthesis in reasonable quantities before [6,7]. The accessibility of **1** has enabled us to start a systematic investigation of its reactions at the Fe–Fe, Fe–N, and N–N bonds. This paper reports one of the findings of this investigation, the cleavage of the N–N bond of **1** by insertion of SO<sub>2</sub>.

2. Results and discussion

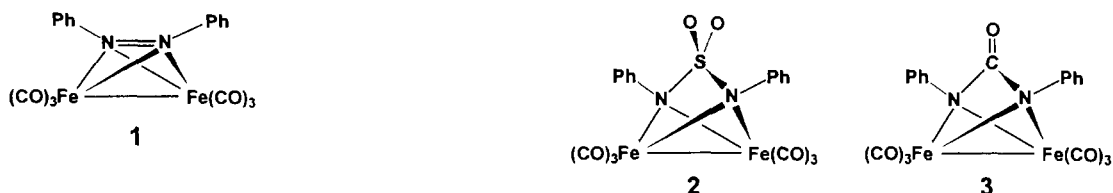
SO<sub>2</sub> was chosen as one of the substrates for the reactivity of **1** because it is polyfunctional, being able to

act as a donor ligand as well as an unsaturated species susceptible to insertions into X–Y units at the sulphur atom alone or across the S–O bond [8]. Of these possibilities, only one was realized exclusively and quantitatively here: at normal temperature and pressure in hexane the conversion of **1** to **2** was complete within a few minutes, and **2** was isolated in 95% yield. This, to our knowledge, is the first reported example of SO<sub>2</sub> insertion into an N–N bond, and one of the rare examples of SO<sub>2</sub> insertion into an intra-ligand bond. In contrast, SO<sub>2</sub> additions across metal–metal bonds or insertions into metal–ligand bonds are commonplace [8,9,10]. Complex **2** was identified by its structure determination (see below). Of its spectral data (see the Experimental section) the <sup>1</sup>H-NMR resonances are inconclusive while the three ν(CO) IR bands are typical for Fe<sub>2</sub>(CO)<sub>6</sub>(μ-X)<sub>2</sub> complexes and the two ν(SO) IR bands are in the expected range.

The SO<sub>2</sub> insertion to form **2** was found to be reversible by heating a toluene solution of **2** to reflux. SO<sub>2</sub> was eliminated, but instead of the starting compound **1** its CO insertion product **3** [4] was isolated. We assume that this reaction involves the reversion of **2** to **1** as an intermediate step. This assumption is based on the observation that **2** does not react with CO in solution at temperatures up to the boiling point of cyclohexane, at which temperature the thermolysis of **1** occurs with formation of **3** even in the absence of a CO atmosphere

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<sup>1</sup> Dedicated to Professor Marv Rausch on the occasion of his 65th birthday.



[4]. The latter conversion involves the consumption of CO generated from partial decomposition of **1** for the insertion reaction  $1 \rightarrow 3$ . Hence, we conclude that there is no direct reaction path from **2** to **3**, but instead the reversion of **2** to **1** makes the formation of **3** possible.

The structure determination of **2** (for details see the Experimental section) has shown the molecules to be highly symmetrical, being bisected by mirror planes containing the iron, sulphur, and oxygen atoms and the sulphur and nitrogen atoms respectively. Fig. 1 gives a view of the molecules and lists some bonding parameters. **2** belongs to the large group of  $\text{Fe}_2(\text{CO})_6(\mu\text{-X})_2$  compounds with very similar atomic arrangements, some of which are listed in Ref. [4].

The Fe–Fe and Fe–N bond lengths in **2** correspond closely to those in **3** (2.40 and 1.99–2.01 Å) [11], but the Fe–Fe distance is markedly shorter and the Fe–N distance is markedly longer than that in **1** (2.49 and 1.89–1.92 Å respectively). This may reflect a general relation between the hinge angle and the lengths of the edges in such butterfly shaped  $\text{Fe}_2\text{N}_2$  bicyclobutane frames. This hinge angle (i.e. the dihedral angle  $\text{NFeFe}/\text{N}'\text{FeFe}$ ) is  $59^\circ$  in **1**,  $84^\circ$  in **3**, and  $87^\circ$  in **2**.

The  $\mu_2$  ligand in **2** is derived from diphenyl sulphamide, and its atomic arrangement can be compared with that in the parent compound sulphamide [12]. In the complexed form the N–S–N angle is severely compressed, compared with the nearly ideal value of  $112^\circ$  in free sulphamide, and both the S–O and S–N bond

lengths (1.39 and 1.60 Å in free sulphamide) are significantly lengthened. However, the S–O bond distance in **2** is virtually identical to that in gaseous  $\text{SO}_2$  (1.432 Å) [13]. These two observations make us call the complex **2** a labilized sulphamide derivative, i.e. one with weaker S–O and S–N bonds. In other words, the bonding parameters of the  $\text{SO}_2(\text{NR})_2$  ligand in **2** are closer to those of  $\text{SO}_2$  than to those of  $\text{SO}_2(\text{NH}_2)_2$ , in agreement with the tendency of **2** to liberate  $\text{SO}_2$  upon heating.

### 3. Conclusion

Both the formation of **2** and the observed deinsertion of  $\text{SO}_2$  are striking examples of polymetallic activation. **1** can be called an  $\text{Fe}_2(\text{CO})_6$  derivative of diphenyl hydrazine, and **2** one of sulphuric acid bis-anilide. While neither the  $\text{SO}_2$  insertion into hydrazines nor the  $\text{SO}_2$  liberation from sulphamides are known to occur, the attachment of the  $\text{Fe}_2(\text{CO})_6$  units has changed the energetics and activation barriers for both reactions such that they take place in a convenient range of time and temperature. The reversibility of the  $\text{SO}_2$  insertion makes the  $1 \rightarrow 2$  interconversion eligible for the list of reactions which are discussed for the recovery of  $\text{SO}_2$  from gaseous pollutants.

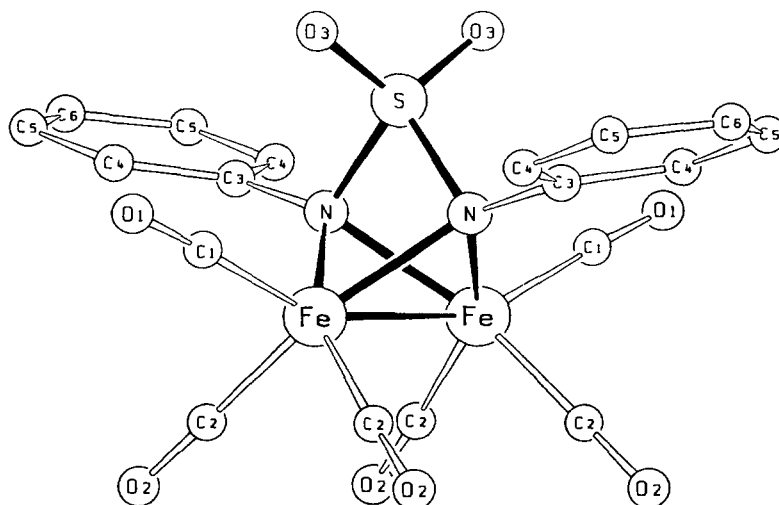


Fig. 1. Molecular structure of **2**. Selected bond lengths: Fe–Fe 2.378(1), Fe–N 2.005(3), S–N 1.672(4), S–O 1.431(3) Å; bond angles N–Fe–N 67.1(2), Fe–N–Fe 72.7(1), N–S–N 83.0(2), N–S–O 113.7(1), O–S–O 115.1(3) $^\circ$ .

#### 4. Experimental details

The general experimental techniques were as described previously [14]. The starting compound **1** was prepared according to the published procedure [4]. SO<sub>2</sub> gas was purified by bubbling through concentrated H<sub>2</sub>SO<sub>4</sub> and then passed through columns filled with CaCl<sub>2</sub> and P<sub>4</sub>O<sub>10</sub>.

##### 4.1. Preparation of **2**

SO<sub>2</sub> gas was bubbled through a hexane solution (40 ml) of compound **1** (0.075 g, 0.162 mmol) for 5 min. An immediate reaction took place resulting in the formation of an orange precipitate. The reaction mixture was allowed to stir for an additional 10 min and then cooled to –15 °C to complete precipitation. The precipitate was separated from the clean solution by decantation and washed twice with cold hexane. Recrystallization of the residue from hexane/CH<sub>2</sub>Cl<sub>2</sub> at –5 °C gave 0.081 g (95%) of **2** as orange crystals with m.p. 165 °C (dec.).

Anal. Found: C, 41.16; H, 1.88; N, 5.33. C<sub>18</sub>H<sub>10</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>8</sub>S (526.1). Calc.: C, 41.10; H, 1.92; N, 5.33.

IR (CH<sub>2</sub>Cl<sub>2</sub>, νCO): 2091 m, 2058 vs, 2017 s cm<sup>-1</sup>; IR (KBr, νSO): 1298 m, 1154 m cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.30–7.52 ppm (m).

##### 4.2. Thermolysis of **2**

A toluene solution (20 ml) of **2** (0.025 g, 0.048 mmol) was heated to reflux under nitrogen for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH<sub>2</sub>Cl<sub>2</sub> (3:2, v/v) gave two orange bands. The faster moving band gave unconsumed **2** (0.003 g), while the second band afforded 0.015 g (65%) of **3**.

##### 4.3. Structure determination [15]

Crystals of **2** (0.15 × 0.15 × 0.15 mm<sup>3</sup>) were obtained from hexane/CH<sub>2</sub>Cl<sub>2</sub>. They belong to the space group *Cmcm* with  $a = 11.705(2)$ ,  $b = 10.816(2)$ ,  $c = 15.950(3)$  Å,  $Z = 4$ ,  $V = 2019.3(6)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.73$  g cm<sup>-3</sup>,  $\mu = 15.9$  cm<sup>-1</sup>. 1863 reflections were collected with an Enraf-Nonius CAD4 diffractometer using Mo K $\alpha$  radiation and the  $\omega/2\theta$  scan technique at  $2\theta = 5$ – $49^\circ$  for the indices  $\pm h$ ,  $\pm k$ ,  $-l$ . 936 independent reflections with  $I \geq 2\sigma(I)$  were used for the structure solution with direct methods and the full-matrix least-squares refinement with anisotropic temperature factors using the SHELX program system [16]. No absorption correction was applied. Hydrogen atoms were included

with a common isotropic temperature factor and a fixed C–H distance of 0.96 Å. The final unweighted  $R$  value was 0.029 for 94 variables. The difference electron density maxima were +0.3 and –0.3 eÅ<sup>-3</sup>. The drawing was produced with the SCHAKAL program [17]. Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions have been deposited [15].

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