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Insertion of SO_2 into the P–P bond of $Fe_2(CO)_6(\mu\text{-}P_2{}^tBu_2)$☆

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Abstract

The P–P bond in the dinuclear iron complex $Fe_2(CO)_6(\mu\text{-}P_2{}^tBu_2)$ was found to be labile towards SO_2 insertion, yielding $Fe_2(CO)_6(\mu\text{-}{}^tBuP\text{–}SO_2\text{–}P^tBu)$, which was characterized by a structure determination. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metal carbonyls; Dinuclear complex; Iron; Sulfur dioxide; Insertion; P–P bond

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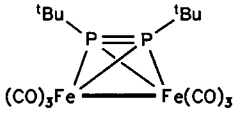
1. Introduction

The labilization of azo compounds bound to iron carbonyls is a good example of the cluster/surface analogy, in that it mirrors the activation of dinitrogen by metallic iron during ammonia synthesis. We could contribute several examples for this, e.g. the spontaneous thermal cleavage of the N=N bond [1] or insertions of various substrates into it [2,3]. In both the complex types $Fe_2(CO)_6(\mu\text{-}N_2R_2)$ and $Fe_3(CO)_9(\mu\text{-}N_2R_2)$ the N–N bond lengths which are close to the single bond values are a clue to the weakening of the N–N interaction due to multicenter attachment [2,3].

In contrast, in the analogous diphosphene complex $Fe_2(CO)_6(P_2{}^tBu_2)$ (**1**) the P–P bond length of 2.06 Å corresponding to a double bond indicates a strong P–P interaction [4]. Nevertheless this complex too loses the P–P bond upon insertion of hydrogen, ethylene, or CO [4]. It seems that the relief of steric strain in the Fe_2P_2 tetrahedrane framework provides some of the driving force for these reactions.

As a test for this assumption we investigated the reaction of **1** with SO_2. We had previously observed that SO_2 is quickly inserted at room temperature and ordinary pressure into the N–N bond of $Fe_2(CO)_6(\mu\text{-}N_2Ph_2)$ yielding **2** [5]. The $SO_2(NRFe)_2$ part of **2** is a sulphamide derivative, e.g. a member of an easily accessible and stable class of compounds. In contrast complex **3**, the product of SO_2 insertion into the P–P bond of **1**, would be a sulfuric acid bis-phosphide, a rather unusual representative of the compound class $SO_2(PR_2)_2$ which seems to be non-existent due to the preference of other bonding alternatives, e.g. $S(PR_2O)_2$ [6].



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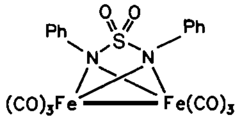

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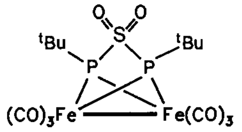

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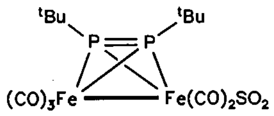

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2. Results and discussion

Experiment showed that SO_2 is inserted into the P–P bond, though less facile than into the N–N bond. In refluxing acetone through which SO_2 was bubbled complex **1** was transformed in 6 h with a conversion of 66%. Two reaction products were isolated in yields of 25–30%. They are the SO_2 insertion product **3** and the

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☆ Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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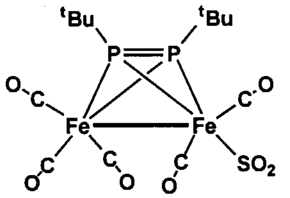
presumed complex **4** resulting from CO substitution by SO_2. We found no experimental evidence indicating that one of the two complexes is the precursor of the other one.

In both cases the constitutions of the complexes could be deduced from the spectra. **3** shows single resonances in the ^{1}H- as well as in the ^{31}P-NMR spectra (see Section 3). Its two IR bands for the SO_2 unit correspond to those of **2** [5], and the ν(CO) IR bands show the simple pattern typical for $Fe_2(CO)_6(\mu\text{-}L)_2$ complexes. **4** contains SO_2 in a different bonding mode as evident from the IR bands. A comparison with literature data [7] allows a tentative assignment as a η^1-bound ligand at one of the two iron atoms. Both the ^{1}H- and the ^{31}P-NMR spectrum indicate that the two P^tBu groups in **4** are in different chemical environments. This can be explained by attachment of the SO_2 ligand *cis* to the Fe–Fe bond. This in turn is borne out by the ν(CO) IR bands which show a pattern quite similar to that of $Fe_2(CO)_5P(OMe)_3(\mu\text{-}PhN\text{-}CO\text{-}NPh)$ [3] which also has the $P(OMe)_3$ ligand in the *cis* position. Thus the proposed structure of **4** is as follows:



The structure of **3** was confirmed by a X-ray analysis (see Fig. 1). The molecules have crystallographic mm symmetry. Their Fe–Fe and Fe–P bond lengths are in the normal range and correspond to those in the only other representative of the $Fe_2(\mu\text{-}P\text{–}X\text{–}P)$ complex type, $Fe_2(CO)_6(\mu\text{-}^tBuP\text{–}CO\text{–}P^tBu)$ [4]. The P–S bonds (2.22 Å) are rather long when compared to those in $Fe_2(CO)_6(\mu\text{-}^tBuP\text{–}S\text{–}S\text{–}P^tBu)$ (2.12 Å) [8] or $Fe_2(CO)_6(\mu\text{-}MeP\text{–}S\text{–}CH_2\text{–}CH_2\text{–}S)$ (2.07 Å) [9]. The P–S–P angle (72°) is unusually small, even when compared to the corresponding N–S–N [3] or P–C(O)–P [4] angles, while the O–S–O angle (116°) is similar to those of the $Fe_2(\mu\text{–}N\text{–}SO_2\text{–}N)$ complexes [3]. The dihedral angle FePFe/FeP′Fe (95°) on the other side is quite large when compared to those in the reference compounds mentioned above, and actually resembles that in $Fe_2(CO)_6(\mu\text{-}^tBuP\text{–}CH_2\text{–}CH_2\text{–}P^tBu)$ [4]. This implies that the tendency of the P–S–P unit to spread the wings of the Fe_2P_2 butterfly is out-balanced by the repulsive forces between the tertiary butyl groups and the carbonyl ligands. The tetrahedral symmetry both at phosphorus and sulfur is severely distorted due to the angular constraints in the cage-like molecule.

The description of the bonding situation of the P–SO_2–P unit is non-trivial. The S–O bond length and the O–S–O angle are so close to those in free SO_2 (1.43 Å and 119°) that it is tempting to consider complex **3** a weak adduct of the Lewis base SO_2 to two electron-deficient phosphinidene units $RPFe_{2/2}(CO)_{6/2}$. This would conform to the weak S–P bonds and the narrow P–S–P angle. On the other hand, as mentioned above, the latter two are also a result of intramolecular strain, as observed before for $Fe_2(CO)_6(\mu\text{-}^tBuP\text{–}CO\text{–}P^tBu)$ [4]. Thus the alternative description of the $SO_2(PRFe)_2$ unit as a stabilized sulfuric acid bis-phosphide is also viable. In this case the bonding of the PR functions to two iron atoms would render them sufficiently electronegative to be stable as phosphide units in the presence of hexavalent sulfur, while the dismutation by oxygen transfer to a RP(O)–S–P(O)R derivative is hampered by the fact that the phosphorus atoms are already four-coordinate in the complex.

Yet another bonding description would be that of a bis–phosphine adduct of the Lewis acid SO_2. This would conform to the existence of the only other structurally characterized compound with a RP-SO atomic arrangement the $Ph_3P\text{–}SO_3$ adduct [10]. This description would have the advantage of yielding the closest agreement between the P–S bond lengths (2.18 Å for $Ph_3P{\cdot}SO_3$). However, both the lack of precedence in the form of bis-adducts of SO_2 and the difficulty in finding an electron count that makes the two ^{t}BuPFe$_2$ units equivalent to PR_3 ligands render this description an unrealistic one. Thus it remains to be stated that both the formation and the bonding situation of complex **3** are unusual in terms of phosphorus-sulfur chemistry, but that they are typical examples for the ability of polynuclear metal carbonyls to stabilize nonclassical molecular fragments.

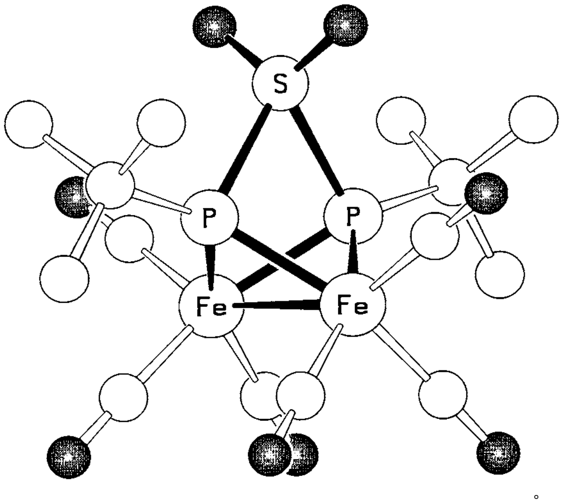


Fig. 1. Molecular structure of **3**. Pertinent bond lengths (Å) and angles (°): Fe–Fe 2.646(1), Fe–P 2.205(1), P–C 1.858(3), P–S 2.216(1), S–O 1.448(3), P···P 2.602(2); P–Fe–P 72.35(4), Fe–P–Fe 73.76(3), Fe–P–C 134.68(6), Fe–P–S 95.19(3), S–P–C 111,07(10), P–S–P 71.92(5), P–S–O 115.38(9), O–S–O 116.0(2).

3. Experimental

3.1. General

The general experimental and measuring techniques were as described previously [11], as was the purification of SO_2 [5]. Complex **1** was prepared according to the published procedure [4]. Silica gel plates (Merck, silica gel 60, F_{254}, thickness 0.2 mm) were used for thin-layer chromatography.

3.2. Preparation

A solution of 0.15 g (0.33 mmol) of **1** in 40 ml of acetone was heated to reflux, and SO_2 gas was bubbled through it for 6 h. After evaporation to dryness the residue was picked up in hexane/CH_2Cl_2 (1:1) and subjected to thin layer chromatography. The first, red band afforded 50 mg (33%) of unreacted **1**. From the second, yellow band after crystallization from hexane/CH_2Cl_2 at 0°C 41 mg (25%) of yellow, crystalline **4** were obtained. Anal. Found: C, 32.25; H, 3.92. $C_{13}H_{18}Fe_2O_7P_2S$ (492.0) Calc.: C, 31.74; H, 3.69. ^{1}H-NMR ($CDCl_3$): $\delta = 1.78$ (d, $J = 17.4$ Hz, 9H, ^{t}Bu), 1.62 (d, $J = 17.4$ Hz, 9H, ^{t}Bu). ^{31}P-NMR ($CDCl_3$): $\delta = 319.9$ (d, $J = 132.1$ Hz, 1P), 263.6 (d, $J = 132.1$ Hz, 1P). IR (CH_2Cl_2): ν(CO) = 2063s, 2029vs, 1993vs, 1975sh. IR(KBr): $\nu(SO_2)$ = 1245m, 1098m.

From the third, yellow band resulted after crystallization from hexane/CH_2Cl_2 at −20°C 50 mg (29%) of yellow, crystalline **3**. Anal. Found: C, 32.55; H, 3.57. $C_{14}H_{18}Fe_2O_8P_2S$ (520.0) Calc.: C, 32.34; H, 3.49. ^{1}H-NMR ($CDCl_3$): $\delta = 1.53$ (d, $J = 17.7$ Hz). ^{31}P-NMR ($CDCl_3$): $\delta = 359.9$ (s). IR (CH_2Cl_2): ν(CO) = 2070s, 2037vs, 2000vs. IR (KBr): $\nu(SO_2)$ = 1250m, 1168m.

3.3. Structure determination

Crystals of **3** were used as obtained. Data were obtained on a Nonius CAD4 diffractometer with Mo–K_α radiation. Crystal data: $C_{14}H_{18}Fe_2O_8P_2S$ (520.00), $0.40 \times 0.20 \times 0.10$ mm^3, orthorhombic, *Cmcm*, $Z = 4$, $a = 11.400(1)$, $b = 12.888(1)$, $c = 14.617(1)$ Å, $V = 2147.6(2)$ Å^3, $d_{calc} = 1.61$ g cm^{-3}, $\mu = 1.63$ mm^{-1}, $2\theta_{max} = 52°$, 1152 reflections, 941 reflections with $I > 2\sigma(I)$, 74 parameters, $R_1 = 0.024$ (941 reflections), $wR_2 = 0.068$ (all reflections). The structure was solved with direct methods and refined anisotropically using the SHELX program suite [12]. The drawing was produced with SCHAKAL [13]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as 'supplementary publication no. 113640'. Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 IEZ (fax: +44-1223-336-033; e-mail: teched@chemcrys.cam.ac.uk).

Acknowledgements

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