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Crystal and molecular structures of dppm-bridged diiron dithiolate complexes $[Fe_2(CO)_4(\mu\text{-}SAr)_2(\mu\text{-}dppm)]$ (Ar = Ph, *p*-tol; Ar_2 = C=N–*p*-tol)

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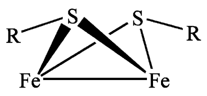
Abstract

Crystallographic studies have been carried out on three bis(diphenylphosphino)methane (dppm) bridged diiron dithiolate complexes. Both $[Fe_2(CO)_4(\mu\text{-}SAr)_2(\mu\text{-}dppm)]$ (Ar = Ph, *p*-tol) adopt the expected *anti* configuration, while $[Fe_2(CO)_4\{\mu\text{-}SC(=N\text{–}p\text{-}tol)S\}(\mu\text{-}dppm)]$ is constrained to be *syn*. In each the diphosphine lies *trans* to one of the bridging sulfurs but this has no significant effect on the iron–sulfur bond lengths.

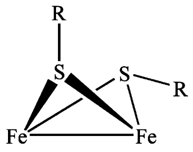
Keywords: Iron; Dithiolate; Diphosphine; Carbonyl

1. Introduction

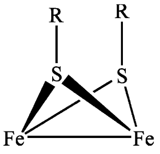
As a result of the realisation that the iron-only hydrogenases contain a low valent dithiolate-bridged diiron unit supported by carbonyl ligands [1–3], interest in the chemistry and properties of complexes of this type have been extensively revived [4–11]. Simple iron(I) hexacarbonyl complexes $[Fe_2(CO)_6(\mu\text{-}SR)_2]$ have been known for many years, with interest centring on the bonding between the iron atoms [12], their role as electron-transfer catalysts [13] and conformational preferences at sulfur [14]. With regard to the latter, three conformations are possible, namely *syn* (I), *anti* (II) and *syn′* (III). Due to adverse steric effects, the *syn′* conformation (III) is generally unfavourable in non-constrained systems, however, it is found exclusively in sulfur-bridged complexes such as the iron-only hydrogenases, in which the two sulfur atoms are linked by a trimethylene unit [1–3].



syn (I)



anti (II)



syn′ (III)

In some instances more than one isomer can be isolated. King first separated *syn* (I) and *anti* (II) forms of $[Fe_2(CO)_6(\mu\text{-}SMe)_2]$ by chromatography [15] and more recently a number of studies have focussed on the interconversion of *syn* and *anti* isomers in solution [16]. The *anti* isomer (II) is generally preferred thermodynamically, and this is reflected in a number of crystallographic studies with this conformation [17,18]. Interestingly, for $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$ both *anti* (II) and *syn* (I) isomers have been crystallographically characterised [18,19], the latter resulting from a rapid crystallisation procedure.

A number of phosphine derivatives have also been prepared, but few have been crystallographically characterised [5,6,19,20]. Of these with unlinked dithiolate-

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bridges, all have the phosphine(s) lying approximately *trans* to the iron–iron vector and adopt the *anti* configuration [20], although one example of a *syn* complex, namely [Fe$_2$(CO)$_4$(PMe$_3$)$_2$(μ-SMe)$_2$], has been reported [21]. The diphosphine bis(diphenylphosphino)methane (dppm) has a strong propensity to bridge metal–metal bonds [22], thus precluding a *trans* orientation of the phosphorus centres with respect to the metal–metal bond. While dppm-bridged diiron complexes are very common, we were somewhat surprised to find little reference to complexes of the type [Fe$_2$(CO)$_4$(μ-SR)$_2$(μ-dppm)] in the literature, except an early report in which a *syn* (I) configuration is proposed [23]. This seemed unlikely and in order to investigate further we have prepared and crystallographically characterised [Fe$_2$(CO)$_4$(μ-dppm)(μ-SAr)$_2$] (Ar = Ph, *p*-tol) (**1**–**2**). As a comparison, we also report the X-ray structure of [Fe$_2$(CO)$_4${μ-SC(=N–*p*-tol)S}(μ-dppm)] (**3**), which contains a constrained *syn′* (III) dithiolate unit. We have previously prepared **3** from the reaction of [Fe$_2$(CO)$_7$(μ-dppm)] with *p*-tolylNCS, but erroneously characterised it as [Fe$_2$(CO)$_4${μ-SC(O)C(=N–*p*-tol)S}(μ-dppm)], primarily on the basis of IR data [24].

2. Results and discussion

Complexes [Fe$_2$(CO)$_4$(μ-SAr)$_2$(μ-dppm)] (Ar = Ph, *p*-tol) (**1**–**2**) were prepared in high yield upon thermolysis of the parent hexacarbonyl complexes with dppm in toluene, while [Fe$_2$(CO)$_4${μ-SC(=N–*p*-tol)S}(μ-dppm)] (**3**) was the major product of the photochemical reaction of [Fe$_2$(CO)$_7$(μ-dppm)] and *p*-tolylNCS [24]. X-ray quality crystals of each were grown from the slow diffusion of methanol into dichloromethane solutions and the results are summarised in Figs. 1–3 and Table 1.

In all three complexes, the dppm ligand bridges the diiron centre approximately symmetrically, lying *trans* to one dithiolate and *cis* to the second. Coordination of

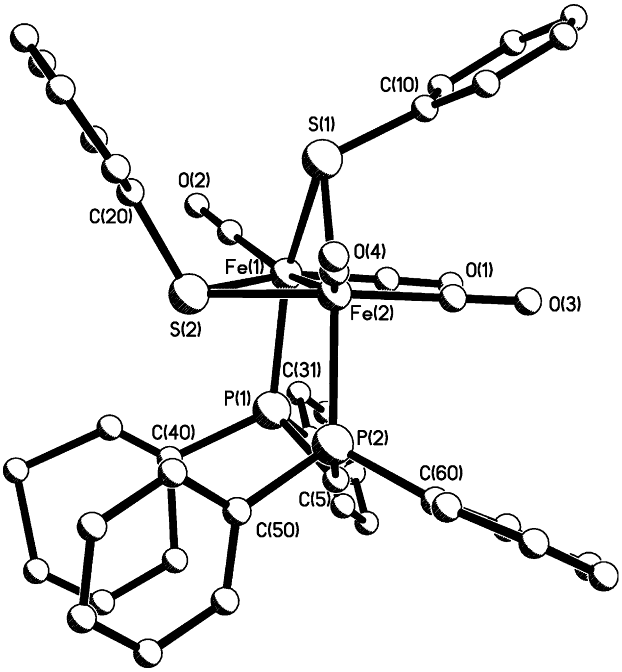


Fig. 1. Molecular structure of [Fe$_2$(CO)$_4$(μ-SPh)$_2$(μ-dppm)] (**1**).

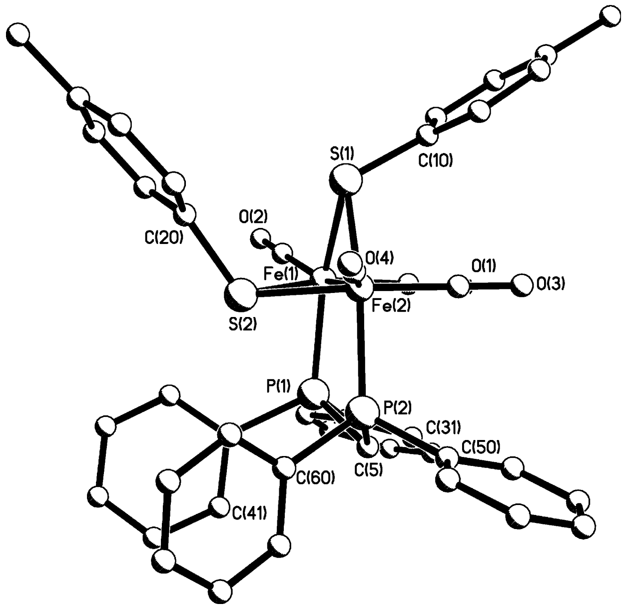


Fig. 2. Molecular structure of [Fe$_2$(CO)$_4$(μ-S–*p*-tol)$_2$(μ-dppm)] (**2**).

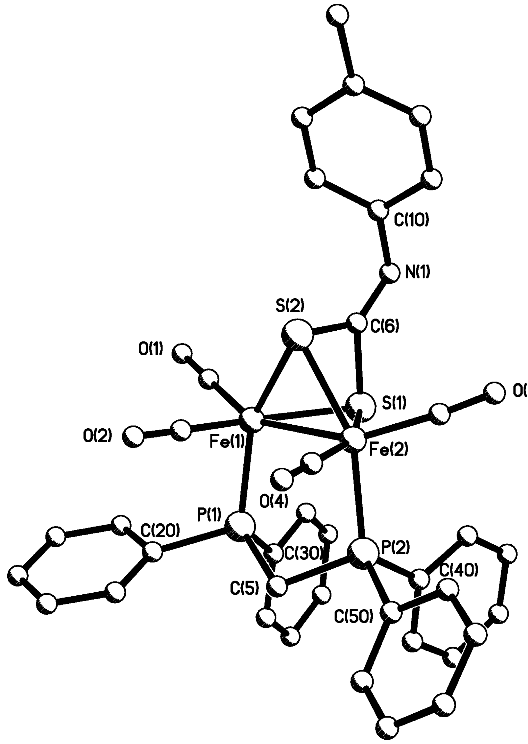
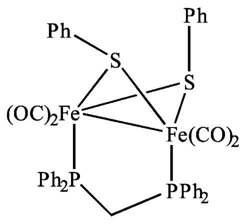
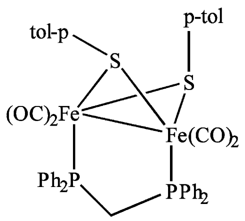


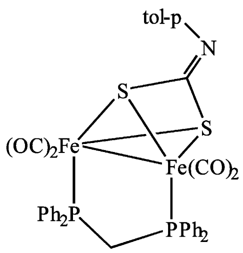
Fig. 3. Molecular structure of [Fe$_2$(CO)$_4${μ-SC(=N–*p*-tol)S}(μ-dppm)] (**3**).



1



2



3

the diphosphine has little effect upon the iron–sulfur bond lengths, differing by less than 0.03 Å. Similarly, the iron–iron bond remains essentially unaffected, the value of 2.5025(8) Å in **1** being comparable with those of 2.516(2) and 2.495(3) Å found in *anti* and *syn*-$[Fe_2(CO)_6(\mu\text{-}SPh)_2]$ respectively [18,19]. The *anti* configuration of the dithiolate ligands in **1**–**2** is in line with the expectation that this is the thermodynamic product. The conformation at the *cis* thiolate, S(2), clearly results from the minimisation of adverse steric interactions between the aryl group and those on the diphosphine, and this in turn dictates the conformation at the *trans* ligand, S(1). Thus, it is easy to see why addition of dppm constrains the conformation to be *anti*, a *syn* conformation being ruled out on steric grounds. The angles subtended at sulfur of around 67° also vary little from those in related complexes [17–19], while fold angles about the iron–iron bond of 81.4 and 81.6° for **1** and **2** respectively are as expected.

Gross structural features of **3**, which has a constrained *syn′* (III) configuration, are generally similar to those of **1** and **2,** the most significant difference being the increased fold angle of 93.8° between the two Fe_2S planes. This must be a consequence of the single atom bridge linking the two sulfurs, and is significantly different from the trimethylene-linked dithiolate complexes considered as models for iron-only hydrogenase; for example in $[Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**4**) the dihedral angle is 109.2° [7]. The iron–iron bond of 2.4817(11) Å is also somewhat shorter than that found in most other dithiolate-bridged diiron complexes [7], however, it is comparable to that found in those with a single atom bridge, such as $[Fe_2(CO)_6\{\mu\text{-}SCH(CH_2COMe)S\}]$ [Fe–Fe 2.485(1) Å; dihedral angle between Fe_2S planes 89.3°] [25].

In the dithiolate backbone of **3**, the two sulfur–carbon bonds are equivalent [S(1)–C(6) 1.789(5), S(2)–C(6) 1.791(5) Å] and the carbon–nitrogen interaction

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **1**–**3** (this work), $[Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**4**) [6,7] and *syn*-$[Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SEt)_2]$ (**5**) [6]

	1	**2**	**3**	**4**	**5**
Fe–Fe	2.5025(8)	2.5104(6)	2.4817(11)	2.555(2)	2.5097(7)
Fe–P	2.2270(13)	2.2127(9)	2.2148(15)	2.234(3)	2.2163(10)
	2.2149(13)	2.2170(9)	2.2222(15)		2.2216(9)
$Fe–S_{trans}$	2.2771(12)	2.2702(9)	2.2643(15)	2.252(2)	
	2.2609(12)	2.2902(9)	2.2715(15)		
$Fe–S_{cis}$	2.2630(11)	2.2630(8)	2.2959(14)	2.256(2)	2.2733(9)
	2.2640(12)	2.2612(9)	2.2952(14)		2.2795(10)
$Fe–S_{trans}–Fe$	66.93(4)	66.80(3)	66.34(4)	69.06(8)	67.01(3)
$Fe–S_{cis}–Fe$	67.12(3)	67.41(2)	65.44(4)		66.56(3)
$P–Fe–S_{trans}$	153.03(5)	154.55(3)	152.43(6)	160.87(11)	
	154.09(5)	152.00(4)	153.37(6)		
$P–Fe–S_{cis}$	88.05(4)	87.38(3)	97.32(5)	89.59(11)	94.80(4)
	89.46(4)	88.62(3)	96.08(5)		98.34(3)
Fe–Fe–P	96.85(4)	95.90(3)	96.03(4)	106.49(9)	145.95(3)
	97.40(4)	97.56(3)	96.93(4)		149.20(3)
Dihedral [a]	81.4	81.6	93.8	109.2	94.6
Dihedral [b]	2.4	1.8	5.0		
Dihedral [c]	83.7	83.1	88.9		

The *cis* and *trans* notation relates to the relative orientation of phosphorus and sulfur atoms and applies strictly only to complexes **1**–**3**.

[a] Defined by the angle between the two Fe_2S planes.

[b] Defined by the angle between the Fe_2P_2 and Fe_2S_{trans} planes.

[c] Defined by the angle between the Fe_2P_2 and Fe_2S_{cis} planes.

[C(6)–N(1) 1.259(5) Å] shows the expected double bond character. This is confirmed by the bond angle at nitrogen of 115.2(4)°, while the *para*-tolyl group is orientated towards the *trans* thiolate-bridge. In our original report of **3**, we erroneously assigned a structure $[Fe_2(CO)_4\{\mu\text{-}SC(O)C(=N\text{-}p\text{-}tol)S\}(\mu\text{-}dppm)]$ in which the two sulfur atoms were linked via both a carbonyl and an imine group. This was primarily on the observation of two IR bands at 1605 and 1483 cm^{-1} in the solid state [24]. Now it is clear that both bands are probably due to C=N vibrations, and result from the mixture of isomers (ca. 5:1) seen by NMR. These isomers arise from the different orientation of the *para*-tolyl group and we assume that the configuration seen in the solid state relates to that which is most abundant in solution. This orientation reduces unfavourable steric interactions, in the second form the *para*-tolyl substituent would lie in close proximity to two of the phenyl substituents on the diphopshine.

In all three complexes **1**–**3**, the diphosphine as expected is constrained to lying *cis* to the metal–metal bond [Fe–Fe–P ca. 96–97°] and its orientation renders the thiolate-bridges inequivalent A *cis* orientation is found in $[Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**4**) [7] [Fe–Fe–P 106.49(9)°], although the phosphines are now not constrained to lie on the same side of the molecule, and consequently the thiolate-bridges are equivalent. In contrast, for *syn*-$[Fe_2(CO)_4(PMe_3)_2(\mu\text{-}SEt)_2]$ (**5**) [7] the phosphines lie approximately *trans* to the metal–metal bond [Fe–Fe–P 145–149°] a situation which is allowed due to the *syn* orientation of the thiolate-bridges reducing otherwise adverse steric interactions. As far as we are aware the dppm derivatives of $[Fe_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ and $[Fe_2(CO)_6(\mu\text{-}SEt)_2]$ have not been reported, and it will be interesting to see what the effect of making the dithiolate-bridges inequivalent will have on the structural and reaction chemistry in these systems.

2.1. Experimental

All reactions were carried out under nitrogen using standard vacuum line techniques and dried and degassed solvents. Chromatography was carried out on deactivated alumina (6% w/w distilled water) wet packed with light-petroleum unless otherwise stated. The solution to be separated was added to alumina (3–5 g) and the solvent removed under reduced pressure. The resulting solids were then deposited on top of the prepared column and separation effected by elution with progressively more polar solvents. IR spectra were recorded on a Nicolet 205 FTIR spectrometer. NMR spectra were recorded on Bruker AMX400 and Avance500 spectrometers and internally referenced to residual solvent peaks (^1H, ^{13}C) or externally to $P(OMe)_3$ (^{31}P). Mass spectra were recorded on VG 7070 high resolution and VG Analytical ZAB2F spectrometers and elemental analyses were performed in house. Complexes **1** and **2** were prepared from the reaction of a slight excess of dppm with $[Fe_2(CO)_6(\mu\text{-}SAr)_2]$ in refluxing toluene, and **3** by literature methods [24].

2.2. X-ray data collection and solution

A single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K for **1** and **2** and 150 ± 2 K for **3**. Data reduction was carried out with SAINT+ and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were generally placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package.

Crystallographic data for **1**: red block, dimensions $0.24 \times 0.16 \times 0.15$ mm^3, monoclinic, space group $P2_1/n$, $a = 11.1991(8)$, $b = 19.0141(13)$, $c = 17.9770(13)$ Å, $\beta = 91.256(1)°$, $V = 3827.1(5)$ $Å^3$, $Z = 4$, $F(000) = 1696$, $D_{calc} = 1.434$ g cm^{-3}, $\mu = 0.991$ mm^{-1}, $T_{max}/T_{min} = 0.865/0.797$. A total of 24 124 reflections were collected, 8960 unique [$R_{int} = 0.0437$] of which 4924 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0589$, $wR_2 = 0.1458$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1179$, $wR_2 = 0.1730$ (all data), for 505 parameters.

Crystallographic data for **2**: red block, dimensions $0.16 \times 0.12 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $a = 11.3382(7)$, $b = 17.0442(10)$, $c = 22.8902(13)$ Å, $\beta = 103.515(1)°$, $V = 4301.0(4)$ $Å^3$, $Z = 4$, $F(000) = 1800$, $D_{calc} = 1.347$ g cm^{-3}, $\mu = 0.888$ mm^{-1}, $T_{max}/T_{min} = 0.917/0.871$. A total of 26 894 reflections were collected, 10 105 unique [$R_{int} = 0.0316$] of which 6598 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0528$, $wR_2 = 0.1463$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0852$, $wR_2 = 0.1644$ (all data), for 492 parameters.

Crystallographic data for **3**: orange needle, dimensions $0.08 \times 0.02 \times 0.01$ mm^3, monoclinic, space group $P2_1/c$, $a = 14.319(3)$, $b = 14.777(3)$, $c = 16.643(3)$ Å, $\beta = 92.836(4)°$, $V = 3517.3(11)$ $Å^3$, $Z = 4$, $F(000) = 1616$, $D_{calc} = 1.491$ g cm^{-3}, $\mu = 1.075$ mm^{-1}, $T_{max}/T_{min} = 0.989/0.919$. A total of 29 858 reflections were collected, 8407 unique [$R_{int} = 0.1628$] of which 4046 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0626$, $wR_2 = 0.1011$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1570$, $wR_2 = 0.1281$ (all data), for 433 parameters.

3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 200869, 200868 and 200870 for **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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