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Insertion of CO and SO_2 into the N–N bond of $[Fe_2(CO)_6(\mu\text{-}Ph_2N_2)]$

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Abstract

The N–N bond of the azobenzene ligand in $[Fe_2(CO)_6(\mu\text{-}Ph_2N_2)]$ (**1**) is unusually labile. In addition to being cleaved by incorporation of CO or H_2, it also inserts CO resulting from phosphine substitution at the iron atoms. Complexes $[Fe_2(CO)_5(PR_3)(\mu\text{-}PhN{-}CO{-}NPh)]$ (**2a,b**) and $[Fe_2(CO)_4\{P(OMe)_3\}_2(\mu\text{-}PhN{-}CO{-}NPh)]$ (**2c**) are formed with PPh_3 and $P(OMe)_3$. Bis(diphenylphosphino)methane produces $[Fe_2(CO)_4(\eta^1\text{-dppm})_2(\mu\text{-}PhN{-}CO{-}NPh)]$ (**2d**). All these complexes also result from $[Fe_2(CO)_6(\mu\text{-}PhN{-}CO{-}NPh)]$ (**2**) and the corresponding phosphine. Reaction of **1** with SO_2 yields the insertion product $[Fe_2(CO)_6(\mu\text{-}PhN{-}SO_2{-}NPh)]$ (**4**). Complex **4** does not react with CO at temperatures up to its decomposition point. Its thermal degradation in the absence of CO, however, produces the CO insertion product **2**, which involves SO_2 elimination with intermediate re-formation of **1**. Treatment of **4** with phosphines results only in CO displacement, producing $[Fe_2(CO)_5P(OMe)_3(\mu\text{-}PhN{-}SO_2{-}NPh)]$ (**4b**), $[Fe_2(CO)_4(PR_3)_2(\mu\text{-}PhN{-}SO_2{-}NPh)]$ (**4a,c**, $PR_3 = PPh_3$ or $P(OMe)_3$), and $[Fe_2(CO)_4(\mu\text{-dppm})(\mu\text{-}PhN{-}SO_2{-}NPh)]$ (**4d**). For comparison with the basic structures of **1**, **2** and **4** two CO insertion products and two SO_2 insertion products were characterized by crystal structure determinations. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Azobenzene; Carbon monoxide insertion; Sulfur dioxide insertion; Phosphine substitution

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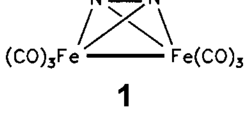
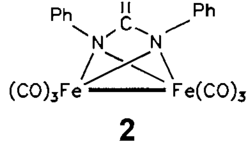
1. Introduction

Overcoming the inertness of the dinitrogen molecule in order to convert it into ammonia derivatives is of great scientific as well as technical interest. The most feasible way to do this seems to be via attachment of the N_2 unit to several iron atoms, as demonstrated by the biological (nitrogenase enzymes) as well as the technical (Haber–Bosch process) ammonia synthesis. Similarly, in model systems from coordination chemistry the fixation of the N–N containing reaction intermediates to two iron atoms was one of the best approaches [1].

By using oligonuclear iron carbonyls we could show that multicenter attachment to organometallic complexes also leads to an unusual weakening of N–N multiple bonds [2,3] which is not the case when the same N–N containing substrates are attached to ruthenium clusters [4,5]. It seemed that the weakening was most pronounced in the Fe_2N_2 system **1** which prior to our work had eluded synthesis in reasonable quantities by rearrangements due to N–N cleavage [6,7]. We found an efficient preparation of the azobenzene complex **1** [3] which has enabled us to utilize the lability of its N–N bond, and we reported the reactions with CO and H_2 under very mild conditions leading to the insertion products **2** and **3** [3].



1



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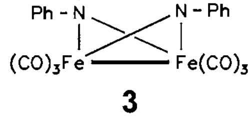

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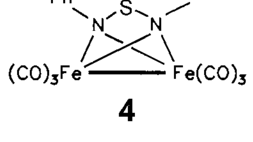

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This paper presents further investigations on the reactivity of **1** versus CO, specifically under the influence of phosphine ligands. Secondly the reactivity towards SO_2, whose insertion leading to **4** was briefly communicated [8], is detailed and some phosphine derivatives of the SO_2 insertion product are described.

2. Results and discussion

2.1. CO insertion products

As already reported [3], CO is inserted in the N–N bond of **1** quite easily. It therefore seemed to be of interest to find out whether this insertion tendency can be modified by ligand substitution at the iron atoms. Compound **1** was thus subjected to reactions with phosphine ligands. To our surprise no simple phosphine derivative of **1** could be obtained that way. Instead the CO liberated was incorporated by insertion in the N–N bond in all cases, and the resulting products were phophine derivatives of **2**. Triphenylphosphine produced the monosubstituted product **2a**. Trimethylphosphite gave a mixture of monosubstituted **2b** and disubstituted **2c**. The chelating phosphine dppm was attached twice in a monodentate fashion in product **2d**.

$Fe_2(CO)_5PPh_3(\mu-PhN-CO-NPh)$ **2a**

$Fe_2(CO)_5[P(OMe)_3](\mu-PhN-CO-NPh)$ **2b**

$Fe_2(CO)_4[P(OMe)_3]_2(\mu-PhN-CO-NPh)$ **2c**

$Fe_2(CO)_4(\eta^1-dppm)_2(\mu-PhN-CO-NPh)$ **2d**

All four complexes were also obtained by reacting the basic CO insertion product **2** with the corresponding phosphine under the same conditions. This indicates that the phosphine substitutions do not occur on **1** at all. Support for this assumption comes from the observation [3,8] that thermolysis of **1** yields considerable amounts of **2**. On the other hand phosphine substitution sets in only at temperatures close to the thermolysis temperature of **1**.

2.2. SO_2 insertion products

Like CO, SO_2 is also inserted in the N–N bond of **1**, yielding **4** quickly at room temperature and ordinary pressure [8]. However, unlike CO, SO_2 can be eliminated from **4** again by thermal treatment. The product of this elimination reaction was again found to be a CO insertion product, namely **2**. The experimental evidence indicates that this reaction involves the re-formation of **1** as an intermediate step. The major observation in this context is that **4** does not react with CO up to its decomposition point, while at temperatures below this decomposition point **1** is being converted to **2** [3,8].

Table 1
IR data for the CO ligands (CH_2Cl_2, cm^{-1})

2a	2056 vs	1993 vs	1993m	
2b	2053 m	2001 s	1983 vs	1945 s
2c	2012 vs	1976 vs	1944 vs	1925 sh
2d	2005 s	1970 vs	1939 vs	
4a	2005 vs	1962 s	1939 s	
4b	2064 s	2014 s	1993 vs	1953 w
4c	2017 s	1988 vs	1948 vs	
4d	2008 s	1981 vs	1943 vs	

In order to find out whether phosphine substitution can also induce such a replacement of SO_2 by CO under milder conditions, we treated complex **4** with the same phosphines as complex **1**. The only reactions observed, however, were phosphine substitutions leading to PR_3 derivatives of **4**. PPh_3 was incorporated twice yielding **4a** while $P(OMe)_3$ replaced one or two CO ligands with formation of **4b** and **4c**. The reaction with dppm seems to have taken a course different from that with **1**: replacement of one CO on each iron atom results in **4d** with a symmetrically bridging dppm ligand.

$Fe_2(CO)_4(PPh_3)_2(\mu-PhN-SO_2-NPh)$ **4a**

$Fe_2(CO)_5[P(OMe)_3](\mu-PhN-SO_2-NPh)$ **4b**

$Fe_2(CO)_4[P(OMe)_3]_2(\mu-PhN-SO_2-NPh)$ **4c**

$Fe_2(CO)_4(\eta^1-dppm)(\mu-PhN-SO_2-NPh)$ **4d**

Further heating of complexes **4a**–**4d** or the reaction mixtures leading to them did not result in SO_2 elimination prior to thermal decomposition. This indicates that phosphine substitution stabilizes the complexes with respect to SO_2 elimination and reduces the likelihood of CO liberation, thereby suppressing both reaction steps occurring in the conversion of **4** to **2**.

2.3. Product identifications

All complexes **2** show the presence of their μ-PhN–CO–NPh ligand by a medium-intensity ν(CO) band at 1720–1725 cm^{-1} in the IR. Similarly the μ-PhN–SO_2–NPh ligand in all complexes **4** gives rise to two medium-intensity ν(SO) bands at 1280–1290 and 1150–1155 cm^{-1}, respectively. The ν(CO) bands of the terminal CO ligands (see Table 1) are in accord with the presence of either $Fe_2(CO)_5$ or symmetrical $Fe_2(CO)_4$ units. In the ^1H-NMR spectra the dominant features

Table 2
^{31}P-NMR data ($CDCl_3$, δ/J) for the complexes

2a	46.8/s	4a	42.6/s
2b	164.3/s	4b	166.2/s
2c	164.8/s	4c	162.1/s
2d	5.2/28.2 60.5/28.2	4d	53.8/s

are the phenyl multiplets, complemented for complexes **b**, **c**, and **d** by the $P(OMe)_3$ doublets or the $P–CH_2–P$ multiplets. Relevant information is contained in the $^{31}P\{^1H\}$-NMR spectra (Table 2). They display the typical chemical shifts for the iron-bound phosphorus nuclei of PPh_3, $P(OMe)_3$, and dppm. This way the bonding situations in **2d** and **4d** are clearly differentiated: **4d** has both phosphorus atoms attached to iron while in **2d** one phosphorus atom of each dppm ligand is uncoordinated.

Crystal structure determinations of **2a** and **2b** as well as of **4a** and **4c** rounded off the product identifications. The molecular structures are displayed schematically in Figs. 1–4, and the pertinent bond lengths and angles are listed in Table 3 and Table 4. For reference purposes, the data of the parent complexes **2** and **4** are included.

Tables 3 and 4 show that for both types of compounds there is a very high similarity within the groups of three complexes each. The metal-ligand bonds vary only by ± 0.03 Å, the angles by ± 1°. The most significant, yet still minor, variation is that of the Fe–Fe bond lengths from 2.38 in **4** to 2.43 Å in **4c**. Thus neither the type or degree of phosphine substitution nor the character of the species inserted in the N–N bond have a noteworthy influence on the bonding parameters of the Fe_2N_2 molecular skeleton.

Complexes **2**, **2a** and **2b** can be considered derivatives of diphenylurea. They show this relation by having a coplanar arrangement of their C–N–CO–N–C constituents. In comparison to free urea [9] or diphenylurea [10] which observe the sp^2 requirements of the central carbon atom by showing valence angles very close to 120°, the N–C–N angle in the three complexes is severely narrowed and the N–C–O angles widened accordingly. The C–O bond is unusually short (cf. the standard value of 1.23 in esters and amides or the value of 1.26 Å in urea), and concomitantly the C–N bonds are unusually long (cf. the C–N bond length of 1.32 in amides and the value of 1.33 Å in urea). Thus the CO insertion products look structurally more like lightly stabilized CO (cf. the C–O bond length of 1.13 Å in free CO) than like derivatives of urea.

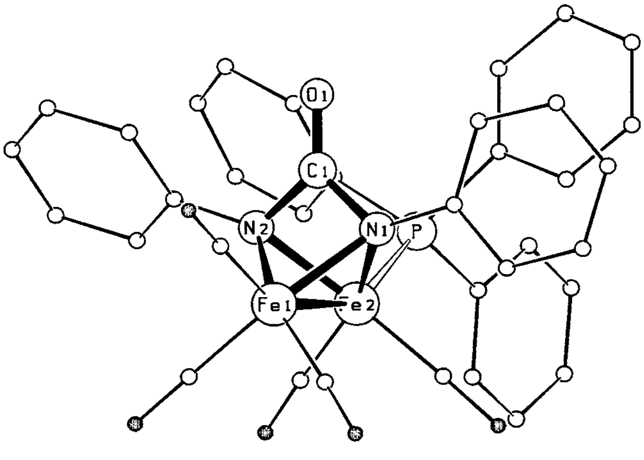

Fig. 1. Molecular structure of **2a**.

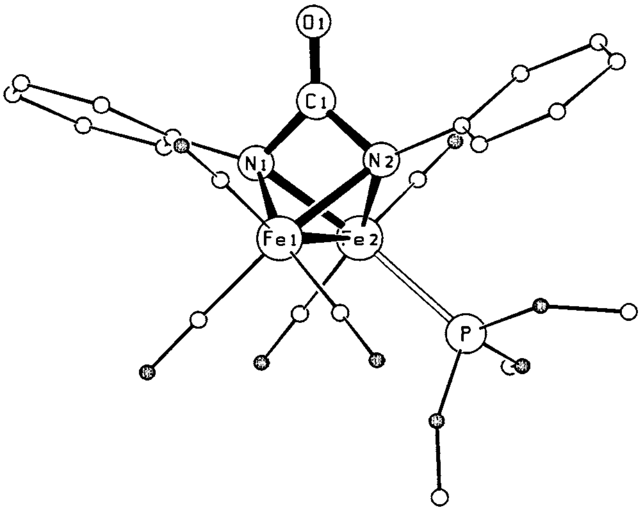

Fig. 2. Molecular structure of **2b**.

The bridging ligand in complexes **4**, **4a** and **4c** is derived from diphenyl sulphamide, and the structural data of sulphamide are available for comparison [11]. Again in the complexed form the N–S–N angle is severely compressed, when compared to the 'free' value of 112°, and both the S–O and S–N bond lengths are significantly lengthened in comparison to those in free sulphamide (1.39 and 1.60 Å, respectively). Actually the S–O bond lengths are virtually identical to those in free SO_2 (1.432 Å) [12]. This may indicate that the partly anionic nature of the sulphamide ligands results in a lengthening of all their bonds or that the inserted substrate has partly maintained its SO_2 character, as is also evident from the reversibility of the SO_2 insertion in the N–N bond of **1** [8].

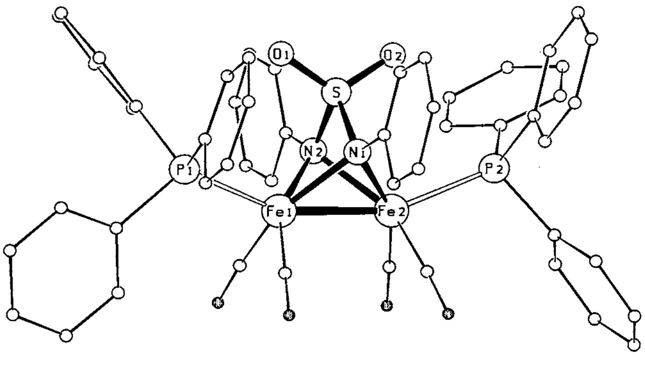

Fig. 3. Molecular structure of **4a**.

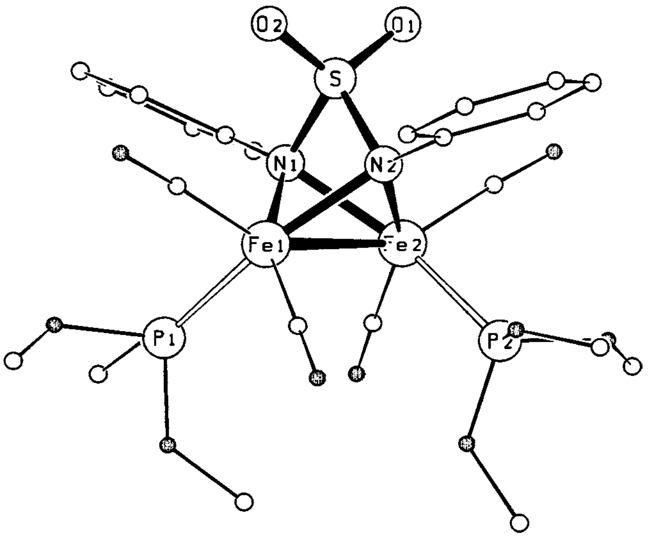

Fig. 4. Molecular structure of **4c**.

The most visible difference within the two pairs of complexes **2a/2b** and **4a/4c** concerns the attachment of the phosphine ligands. In both cases the triphenylphosphine ligands are attached axially, i.e. *trans* to the Fe–Fe bonds, while the trimethyl phosphite ligands are located equatorially, i.e. *cis* to the Fe–Fe bonds. This may be explained by steric as well as electronic reasons. The sterically more demanding PPh_3 ligands prefer the sterically less crowded axial positions. The better π-accepting $P(OMe)_3$ ligands prefer the positions *trans* to the more electron-releasing nitrogen donors. Similar phenomena have been observed for phosphine substitutions of donor ligand capped clusters [13,14]. The noticeably different Fe–P bond lengths for Fe–PPh_3 versus Fe–$P(OMe)_3$ support this argument.

Table 3
Bond lengths (Å) and angles (°) in complex **2** and its phosphine derivatives

	2	**2a**	**2b**
Bond length (Å)			
Fe1–Fe2	2.400(1)	2.415(1)	2.416(1)
Fe1–N1	1.982(2)	2.008(2)	1.996(2)
Fe1–N2	1.996(2)	1.994(2)	1.987(3)
Fe2–N1	1.991(2)	2.022(2)	1.984(2)
Fe2–N2	1.986(2)	2.007(3)	2.011(2)
Fe2–P	—	2.273(1)	2.160(1)
N1–C1	1.413(4)	1.408(4)	1.403(4)
N2–C1	1.410(4)	1.414(4)	1.421(4)
C1–O1	1.194(4)	1.194(4)	1.195(4)
Bond angle (°)			
Fe1–N1–Fe2	74.3(1)	73.6(1)	74.8(1)
Fe1–N2–Fe2	74.1(1)	74.3(1)	74.4(1)
N1–Fe1–N2	64.7(1)	64.3(1)	64.6(1)
N1–Fe2–N2	64.7(1)	63.9(1)	64.3(1)
N1–C1–N2	97.8(2)	98.1(2)	97.7(2)

Table 4
Bond lengths (Å) and angles (°) in complex **4** and its bis(phosphine) derivatives

	4 [8]	**4a**	**4c**
Bond length (Å)			
Fe1–Fe2	2.378(1)	2.391(1)	2.431(1)
Fe1–N1	2.005(3)	2.056(2)	2.023(3)
Fe1–N2	2.005(3)	2.042(2)	2.025(3)
Fe2–N1	2.005(3)	2.035(2)	2.023(3)
Fe2–N2	2.005(3)	2.058(2)	2.019(3)
Fe1–P1	—	2.297(1)	2.173(1)
Fe2–P2	—	2.293(1)	2.160(1)
N1–S	1.672(4)	1.662(2)	1.667(3)
N2–S	1.672(4)	1.653(2)	1.665(3)
S–O1	1.431(3)	1.431(2)	1.439(3)
S–O2	1.431(3)	1.434(2)	1.438(3)
Bond angle (°)			
Fe1–N1–Fe2	72.7(1)	71.6(1)	73.8(1)
Fe1–N2–Fe2	72.7(1)	71.4(1)	73.9(1)
N1–Fe1–N2	67.1(2)	66.4(1)	66.9(1)
N1–Fe2–N2	67.1(2)	66.5(1)	67.0(1)
N1–S–N2	83.0(2)	85.2(1)	84.1(2)
O1–S–O2	115.1(3)	114.7(1)	114.0(2)

3. Conclusions

This work has underlined the labilization of the N=N bond of azobenzene by its attachment to the $Fe_2(CO)_6$ fragment. Neither CO nor SO_2 insertions are known to occur in free azoarenes. Complex **1**, in contrast, undergoes these insertions under rather mild conditions, and the resulting products are of considerable stability. They can be derivatized easily by phosphine substitution. The molecular backbones Fe_2N_2CO and $Fe_2N_2SO_2$ show a strong conservation of their structural and bonding features irrespective of the number and kind of phosphine ligands present. It seems worthwhile to exploit the insertion reactions in terms of converting CO or SO_2 into organic compounds.

4. Experimental details

The general experimental techniques were as described previously [15], as was the purification of SO_2 [8]. Complexes **1** and **2** were prepared according to the published procedure [3]. Phosphines were obtained commercially. Silica gel plates (Merck, silica gel 60, F_{254}, thickness 0.2 mm) were used for thin layer chromatography.

4.1. Preparations

Complex **2a**: (a) A hexane solution (50 ml) of **1** (0.075 g, 0.162 mmol) and PPh_3 (0.045 g, 0.172 mmol) was heated to reflux for 1 h. The solvent was removed under reduced pressure and the residue was subjected to

TLC. Hexane/CH_2Cl_2 (1:1) eluted one major band which afforded 0.083 g (70%) of red, crystalline **2a**. Anal. Found: C, 59.41; H, 3.53; N, 3.92. $C_{36}H_{25}Fe_2N_2O_6P$ (724.3). Calc.: C, 59.70; H, 3.48; N, 3.87.

(b) A hexane solution (50 ml) of **2** (0.065 g, 0.133 mmol) and PPh_3 (0.035 g, 0.133 mmol) was heated to reflux for 1 h. The solvent was removed in vacuo and the residue recrystallized from hexane/CH_2Cl_2 (1:1) to give 0.094 g (92%) of **2a**.

Complexes **2b** and **2c**: (a) A hexane solution (60 ml) of **1** (0.202 g, 0.437 mmol) and $P(OMe)_3$ (0.081 g, 0.653 mmol) was heated to reflux for 1 h. The solvent was removed in vacuo. TLC with hexane/CH_2Cl_2 (2:1) afforded first an orange band yielding 0.115 g (45%) of orange, crystalline **2b**. Anal. Found: C, 42.95; H, 3.23; N, 4.78. $C_{21}H_{19}Fe_2N_2O_9P$ (586.1). Calc.: C, 43.04; H, 3.27; N, 4.78. Next, a red band was eluted, yielding 0.119 g (40%) of red, crystalline **2c**. Anal. Found: C, 40.65; H, 4.36; N, 4.15. $C_{23}H_{28}Fe_2N_2O_{11}P_2$ (682.1). Calc.: C, 40.50; H, 4.14; N, 4.11.

(b) A hexane solution (30 ml) of **2** (0.075 g, 0.153 mmol) and $P(OMe)_3$ (0.032 g, 0.258 mmol) was refluxed and worked up as before to yield 0.045 g (50%) of **2b** and 0.042 g (40%) of **2c**.

Complex **2d**: (a) A hexane solution (60 ml) of **1** (0.075 g, 0.162 mmol) and dppm (0.130 g, 0.338 mmol) was refluxed for 1 h. The solvent was removed in vacuo. TLC with hexane/CH_2Cl_2 (1:1) gave several minor bands followed by one major orange band which afforded 0.059 g (30%) of orange, amorphous **2d**. Anal. Found: C, 66.43; H, 4.61; N, 2.29. $C_{67}H_{54}Fe_2N_2O_5P_4$ (1202.8). Calc.: C, 66.90; H, 4.53; N, 2.32.

(b) **2** (0.075 g, 0.153 mmol) and dppm (0.118 g, 0.307 mmol) by the same procedure as before yielded 0.129 g (70%) of **2d**.

Complex **4**: SO_2 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_2Cl_2 at − 5°C gave 0.081 g (95%) of **2** as orange crystals. Anal. Found: C, 41.16; H, 1.88; N, 5.33. $C_{18}H_{10}Fe_2N_2O_8S$ (526.1). Calc.: C, 41.10; H, 1.92; N, 5.33.

Complex **4a**: A toluene solution (20 ml) of **4** (0.050 g, 0.095 mmol) and PPh_3 (0.050 g, 0.191 mmol) was heated at 60°C for 8 h. The solvent was removed under reduced pressure and the residue washed several times with cold hexane to remove unreacted PPh_3. TLC with hexane/CH_2Cl_2 (2:1) gave a single orange band which yielded 0.085 g (90%) of orange, crystalline **4a**. Anal. Found: C, 62.51; H, 3.94; N, 2.89. $C_{52}H_{40}Fe_2N_2O_6P_2S$ (994.6). Calc.: C, 62.79; H, 4.05; N, 2.82.

Complexes **4b** and **4c**: A toluene solution (25 ml) of **4** (0.085 g, 0.162 mmol) and $P(OMe)_3$ (0.040 g, 0.322 mmol) was heated at 50°C for 10 h. The solvent was removed in vacuo. TLC with hexane/CH_2Cl_2 (1:1) eluted first 0.005 g of unreacted **4**, then an orange band yielding 0.030 g (30%) of orange, crystalline **4b**. Anal. Found: C, 37.95; H, 2.89; N, 4.25. $C_{20}H_{19}Fe_2N_2O_{10}PS$ (622.1). Calc.: C, 38.61; H, 3.08; N, 4.50. The third, orange, band afforded 0.064 g (55%) of orange, crystalline **4c**. Anal. Found: C, 36.65; H, 3.79; N, 3.86. $C_{22}H_{28}Fe_2N_2O_{12}P_2S$ (718.2). Calc.: C, 36.79; H, 3.93; N, 3.90.

Complex **4d**: A toluene solution (30 ml) of **4** (0.085 g, 0.152 mmol) and dppm (0.073 g, 0.190 mmol) was heated at 60°C for 8 h. After removal of the solvent in vacuo, TLC with hexane/CH_2Cl_2 (3:1) gave one major band which yielded 0.104 g (80%) of orange, crystalline **4b**. Anal. Found: C, 57.29; H, 3.63; N, 3.21. $C_{41}H_{32}Fe_2N_2O_6P_2S$ (854.4). Calc.: C, 57.63; H, 3.78; N, 3.28.

*4.2. Thermolysis of **4***

A toluene solution of **4** (0.025 g, 0.048 mmol) was heated to reflux for 3 h. The solvent was removed in vacuo. TLC with hexane/CH_2Cl_2 (3:2) gave two orange bands. From the first band traces of unreacted **4** were recovered. The second band yielded 0.015 g (65%) of **2**.

4.3. Structure determinations [16]

Crystals were obtained directly from the isolated compounds. The data sets were obtained with an Enraf-Nonius CAD4 diffractometer using Mo–K_α radiation and the $\omega/2\Theta$ scan technique at $2\Theta = 4$–52°. Absorption corrections based on psi scans were applied. The structures were solved by direct methods and refined anisotropically using the SHELX program suite [17]. Hydrogen atoms were included with a common isotropic temperature factor and a fixed C–H distance of 0.96 Å. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$. The structure of **2** [18] was redetermined for the purpose of precision and comparability. Drawings were produced with SCHAKAL [19]. Table 5 lists the crystallographic details.

Acknowledgements

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Table 5
Crystallographic details

	2a	**2b**	**4a**	**4c**
Crystal size (mm)	0.4 × 0.3 × 0.3	0.6 × 0.6 × 0.4	0.7 × 0.4 × 0.3	0.8 × 0.5 × 0.1
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.308(1)	15.210(1)	11.507(1)	10.900(1)
b (Å)	11.791(1)	9.373(1)	26.785(2)	16.052(1)
c (Å)	13.453(1)	18.658(2)	15.173(1)	18.113(2)
α (Å)	80.44(4)	90	90	90
β (Å)	82.99(5)	109.33(6)	99.60(5)	105.87(5)
γ (Å)	66.37(4)	90	90	90
Z	2	4	4	4
V (Å^3)	1617.5(2)	2510.0(3)	4611.1(5)	3048.4(4)
$D_{\text{calc.}}$ (g cm^{-3})	1.49	1.55	1.43	1.57
μ (mm^{-1})	1.00	1.27	0.80	1.19
Reflections collected	6610	5072	9392	6175
Independant reflections [$I \geq 2\sigma(I)$]	4672	4201	6615	4173
Variables	424	316	586	370
R_1	0.039	0.042	0.035	0.042
wR_2	0.118	0.119	0.110	0.118
Res. El. densities (e Å^3)	+0.6 −0.6	+0.8 −0.7	+0.4 −0.3	+0.6 −0.4

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[16] The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre under the reference numbers 101734 (for **2**), 101735 (for **2a**), 101738 (for **2b**), 101736 (for **4a**) and 101737 (for **4c**). Copies of the data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telefax: + 12 23/3 36 0 33; e-mail: teched@chemcrys.cam.ac.uk).

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