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## The synthesis of phosphine derivatives of $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ : crystal structures of $[\text{Fe}_4\text{N}(\text{CO})_9(\text{NO})(\text{PPh}_3)_2]$ , $[\text{HFe}_4\text{N}(\text{CO})_{11}(\text{PPh}_3)]$ and $[(\text{PPh}_3)_2\text{N}][\text{Fe}_4\text{N}(\text{CO})_{11}(\text{PMe}_2\text{Ph})]$

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### Abstract

Phosphines react with butterfly tetranuclear nitrido-iron clusters,  $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$  and  $[\text{Fe}_4\text{N}(\text{CO})_{11}(\text{NO})]$ , to give mono- and di-substituted complexes. X-Ray analyses of the title compounds showed that the phosphine ligands are bound to the wing-tip atoms.

### Introduction

The exposed carbido-carbon atom in  $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$  is known to react with alkylating reagents to give *C*-alkylated complexes [1].  $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$  also reacts with unsaturated mononuclear complexes, which allows selective syntheses of heteronuclear metal carbido-clusters [2]. No similar reaction occurs with butterfly nitrido-iron clusters. This lack of reactivity is due to two main factors: (a) *2s* and *2p* nitrogen orbitals are at lower energy than *2s* and *2p* carbon orbitals, so that bonding molecular orbitals involving the heteroatom are at lower energy in nitrido-clusters than in carbido-clusters [3]; (b) the lower charge on nitrido-iron clusters. Muetterties and co-workers [4] have shown that polyhedral expansions based on exposed carbide carbon atoms could not be achieved with clusters having a single negative charge, probably because these species lack sufficient electron density to exhibit reactivity towards electrophilic reagents. Our investigations of the influence of CO substitution in square pyramidal pentanuclear iron-clusters [5] have shown that an increase in the cluster electron density led to a shift of the carbide carbon out of the basal plane and a partial localization of this supplementary electron density on the heteroatom. A similar effect can be expected for butterfly tetranuclear clusters.

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Substitution of some carbonyl groups in these complexes by less good  $\pi$  acceptor ligands such as phosphines leads to a destabilization of the  $\text{Fe}_4\text{L}_{13}$  fragment, which increases the energy separation between the metallic fragment and the exposed heteroatom, and therefore weakens the interaction between these two fragments. Part of the excess of electron density is then shifted to the exposed heteroatom. Consistent with this proposal, Bradley [6] has shown that although  $[\text{Fe}_4\text{C}(\text{CO})_{13}]$  reacts readily at the carbide with MeOH, substituting carbon monoxide for  $\text{PMe}_3$  prevents this reaction; this indicates that the charge on the carbido-carbon atom is highly sensitive to CO substitution. Attempts to increase the reactivity of iron nitrido-clusters towards electrophiles led us to investigate the substitution of carbonyl groups by phosphine ligands in these complexes.

## Results and discussion

Carbonyl substitution of nitrido-nitrosyl clusters has recently been studied by Gladfelter [7], who has shown that  $[\text{FeRu}_3\text{N}(\text{NO})(\text{CO})_{11}]$  reacts readily with phosphines to give mono-, di-, and in some cases tri-substituted clusters. We have prepared  $[\text{Fe}_4\text{N}(\text{NO})(\text{CO})_9(\text{PPh}_3)_2]$  (**1**) similarly by reaction of  $[\text{Fe}_4\text{N}(\text{NO})(\text{CO})_{11}]$  with an excess of  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.

The substituted anions  $[\text{Fe}_4\text{N}(\text{CO})_{11}(\text{PR}_3)]^-$  can be prepared by reaction of the parent  $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$  with the corresponding phosphine ( $\text{PPh}_3$  or  $\text{PMe}_2\text{Ph}$ ) in refluxing THF. Prolonged reaction with an excess of phosphine did not lead to the disubstituted clusters but to decomposition products. These monosubstituted clusters can be readily protonated in  $\text{CH}_2\text{Cl}_2$  to give the corresponding hydridonitrido-cluster. In contrast to the heteronuclear clusters  $[\text{HFeRu}_3\text{N}(\text{CO})_{12-x}(\text{P}(\text{OMe})_3)_x]$  ( $x = 1-3$ ), which can be obtained from  $[\text{HFeRu}_3\text{N}(\text{CO})_{12}]$  and  $\text{P}(\text{OMe})_3$ , these compounds cannot be prepared from  $[\text{HFe}_4\text{N}(\text{CO})_{12}]$ ; even the mildly basic phosphine  $\text{PPh}_3$  deprotonates  $[\text{HFe}_4\text{N}(\text{CO})_{12}]$ .

The molecular structures of **1**,  $[\text{HFe}_4\text{N}(\text{CO})_{11}(\text{PPh}_3)]$  (**2**), and  $[\text{Fe}_4\text{N}(\text{CO})_{11}(\text{PMe}_2\text{Ph})]^-$  (**3**) are shown in Figs. 1-3, together with the atom-numbering schemes adopted. In all three clusters, the metallic skeletons retain the butterfly geometry common to the parent compound  $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$  and related tetranuclear nitrides [8]. As for the pentanuclear clusters,  $[\text{Ru}_5\text{C}(\text{CO})_{15-x}(\text{PPh}_3)_x]$  ( $x = 1, 2$ ) [9] and  $[\text{Fe}_5\text{C}(\text{CO})_{12}(\text{PMe}_2\text{Ph})_3]$  [5], the phosphine ligands are located on the iron atoms with the lowest connectivity, the electron poorer metal atoms, the wing-tip atoms. The  $^{31}\text{P}$  NMR spectra consist of singlets which indicates that this geometry may be kept in solution at room temperature.

The asymmetric unit of **1** contains two independent but similar molecules, each with a pseudo  $C_2$  symmetry. In one of these molecules, the nitrosyl group is clearly disordered over the two positions *trans* to the Fe-Fe hinge bond. This geometry is very similar to that of  $[\text{Fe}_4\text{N}(\text{NO})(\text{CO})_{10}(\text{P}(\text{OMe})_3)]$  [10]. In the second molecule, the nitrosyl ligand could not be distinguished from carbonyl ligands without any ambiguity. This ligand has been refined as evenly distributed over five positions: three wing-tip positions (11, 12 and 22) and two hinge positions (31 and 41). It is not clear from the X-ray data that this disposition reflects exactly the actual nitrosyl location in this molecule. Indeed a disorder of the nitrosyl group over more than two positions destroys any confidence in carbonyl/nitrosyl distinction. Furthermore, the broadness of the infrared stretching nitrosyl absorption prevents

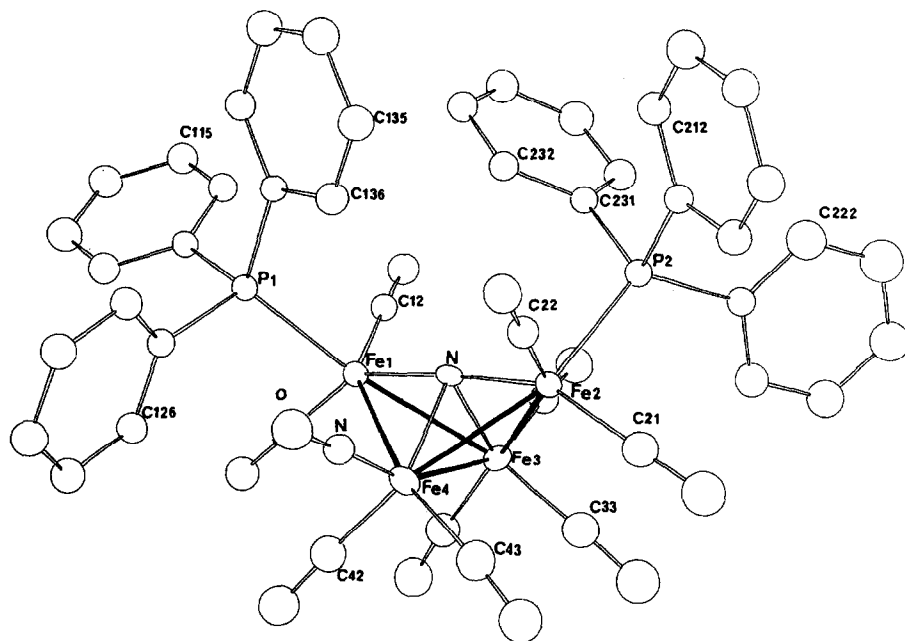


Fig. 1. The molecular structure of  $[\text{Fe}_4\text{N}(\text{CO})_9(\text{NO})(\text{PPh}_3)_2]$  (1); the nitrosyl ligand is represented in one of the possible positions.

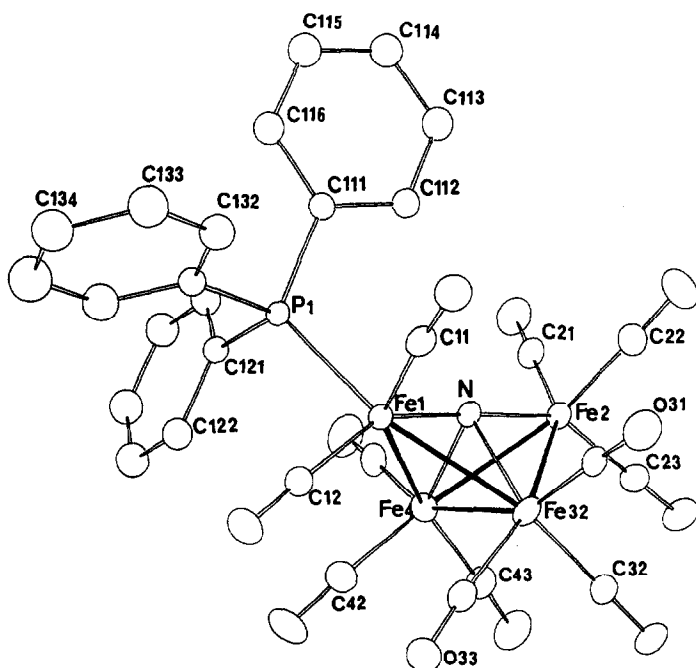


Fig. 2. The structure of  $[\text{HFe}_4\text{N}(\text{CO})_{11}(\text{PPh}_3)]$  (2) showing the atom numbering scheme.

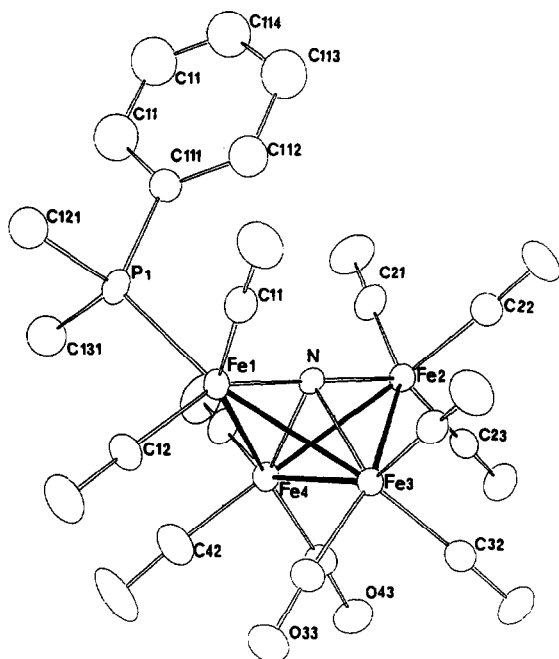


Fig. 3. The structure of the anion  $[\text{Fe}_4\text{N}(\text{CO})_{11}(\text{PMe}_2\text{Ph})]^-$  (**3**).

any distinction between frequencies corresponding to chemically different environments for the nitrosyl group, in particular between hinge and wing-tip positions.

In the monosubstituted clusters, **1** and **2**, the Fe–Fe bond distances between the wing-tip atom Fe(1) which bears the phosphine ligand and the hinge atoms Fe(3) and Fe(4) are slightly longer (0.03–0.05 Å, e.s.d. *ca.* 0.002 Å) than the corresponding Fe(2)–Fe(3) and Fe(2)–Fe(4) bond distances. The substitution of a carbonyl group by a less  $\pi$ -acidic phosphine ligand destabilizes this  $\text{Fe}(\text{CO})_2\text{PR}_3$  fragment, which decreases the bonding interaction with the remaining cluster fragment.

In **2**, the hydrido-hydrogen atom has not been located by X-ray crystallography. However, comparison of the NMR hydride resonance at –30.58 ppm with other  $\text{HM}_4\text{N}$  [11] clusters suggests that the hydride bridges the hinge Fe(3)–Fe(4) bond of the butterfly core. This is consistent with the lengthening of this bond (2.552(1) Å) with respect to the equivalent bond in **3** (2.504(1) Å) and in  $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$  (2.512(1) Å) [8].

As in other butterfly clusters, the distances between the wing-tip metal atoms and the exposed heteroatom are *ca.* 0.10–0.15 Å shorter than those between the hinge atoms and this heteroatom.

The Fe(1)–N–Fe(2) angle is 175.8(3)° and 175.1(3)° in **1**, 175.2(3)° in **2**, and 179.3(4)° in **3**. The dihedral angle of the butterfly wings is 105.1° and 106.1° in **1**, 104.3° in **2** and 102.0° in **3**.

In conclusion, these values show that, in contrast to square pyramidal iron carbido-clusters, there is no distortion towards trigonal bipyramids as the clusters become electron richer from **1** to **3**. Such an increase of the cluster core electron density by carbonyl substitution is not sufficient to significantly modify the cluster

geometry from butterfly to trigonal bipyramidal. In agreement with this observation, all our attempts to methylate the nitrido-nitrogen atom have been unsuccessful.

## Experimental

PPN[Fe<sub>4</sub>N(CO)<sub>12</sub>] [12] (PPN = bis(triphenylphosphine)nitrogen (1 +) cation) was prepared according to the published procedure. Other reagents were used as purchased. All reactions were carried out under argon using dry, distilled solvents [13]. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer. <sup>1</sup>H NMR data were obtained using CDCl<sub>3</sub> as solvent at -20°C and <sup>31</sup>P spectra using CDCl<sub>3</sub> as solvent and H<sub>3</sub>PO<sub>4</sub> as reference on a Bruker WM 250 spectrometer. Mass spectra were obtained with a Nermag R10-10 spectrometer.

### Syntheses

*Preparation of [Fe<sub>4</sub>N(CO)<sub>9</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] (1).* [Fe<sub>4</sub>N(CO)<sub>11</sub>(NO)] was prepared from PPN[Fe<sub>4</sub>N(CO)<sub>12</sub>] and NOBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> [12] and purified by chromatography with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (1:2) mixture as eluent.

To a solution of [Fe<sub>4</sub>N(CO)<sub>11</sub>(NO)] (500 mg, 0.87 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was added a two-fold excess of PPh<sub>3</sub> (920 mg, 3.5 mmol). After stirring overnight at room temperature, the solution was then concentrated and chromatographed using a hexane/dichloromethane/acetone mixture as eluent. The red brown fraction was then evaporated and the residue was dissolved in a hexane/dichloromethane (5:1, v:v) mixture. Slow partial evaporation of the solution led to 115 mg of crystalline [Fe<sub>4</sub>N(CO)<sub>9</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] (yield 12%).

Anal. Found: C, 21.11; H, 3.33; N, 2.50; P, 6.01. C<sub>45</sub>Fe<sub>4</sub>H<sub>30</sub>N<sub>2</sub>O<sub>10</sub>P<sub>2</sub> calc.: C, 21.40; H, 2.90; N, 2.68; P, 5.93%. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2050s, 2005vs, 1965w sh, 1930w sh; ν(NO) 1760 cm<sup>-1</sup>. <sup>31</sup>P NMR: δ 62.94 ppm.

*Preparation of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)].* To PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>] (1.0 g, 0.9 mmol) and PPh<sub>3</sub> (240.0 mg, 1.1 mmol) was added freshly distilled THF via a syringe. The suspension was stirred for 16 h at reflux temperature. After partial evaporation under vacuum, the crude product was precipitated with hexane, filtered and washed with hexane. After washing with MeOH (50 ml), the precipitate was dried under vacuum and extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 ml). After addition of EtOH (60 ml), the solution was allowed to stand overnight at -25°C to give black crystals of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)] (420 mg, yield 35%).

Anal. Found: C, 57.99; H, 3.30; N, 2.17; P, 6.90. C<sub>65</sub>Fe<sub>4</sub>H<sub>45</sub>N<sub>2</sub>O<sub>11</sub>P<sub>3</sub> calc.: C, 57.99; H, 3.37; N, 2.08; P 6.90%. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2040m, 2005vw, 1960vs, 1965sh, 1925w, 1880w, cm<sup>-1</sup>. <sup>31</sup>P NMR: δ 67.65 and 21.59 ppm (relative intensity 1:2).

*Protonation of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)].* To a 10 ml solution of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)] (170 mg, 0.126 mmol) was added 13 μl of CF<sub>3</sub>SO<sub>3</sub>H. After stirring for 30 min, the green-brown solution turned red and the solvent was evaporated under vacuum. The residue was extracted with warm (35°C) hexane (2 × 50 ml). The solution was then concentrated under vacuum and left in a freezer (-20°C) to give 60 mg of [HFe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)] (2) (yield 59%).

Anal. Found: C, 43.22; H, 2.29; N, 1.69; P, 4.12. C<sub>29</sub>Fe<sub>4</sub>H<sub>16</sub>N<sub>1</sub>O<sub>11</sub>P<sub>1</sub> · 0.5C<sub>6</sub>H<sub>14</sub> calc.: C, 45.2; H, 2.72; N, 1.64; P, 3.64%. C<sub>29</sub>Fe<sub>4</sub>H<sub>16</sub>N<sub>1</sub>O<sub>11</sub>P<sub>1</sub> calc.: C, 43.07; H,

1.99; N, 1.73; P, 3.83%. Mass spectrum: ( $M + 1$ ) 810. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2080w, 2045vs, 2030vs, 2015vs, 1970w br, 1940w br  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  -30.58 ppm;  $^{31}\text{P}$  NMR:  $\delta$  65.44 ppm.

*Preparation of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PMe<sub>2</sub>Ph)] (3).* A solution of PPN [Fe<sub>4</sub>N(CO)<sub>12</sub>] (1 g, 0.9 mmol) and PMe<sub>2</sub>Ph (140  $\mu\text{l}$ , 0.98 mmol) in THF (150 ml) was heated under reflux overnight. After partial evaporation under vacuum, addition of hexane gave an oily precipitate which was washed with hexane (50 ml) and EtOH (20 ml). The solid residue was then extracted with dichloromethane; to this solution was added EtOH; the mixture was then concentrated under vacuum and cooled to -25°C giving 310 mg (yield 28%) of PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PMe<sub>2</sub>Ph)].

Anal. Found: C, 54.42; H, 3.44; N, 2.14; P, 7.60. C<sub>55</sub>Fe<sub>4</sub>H<sub>41</sub>N<sub>2</sub>O<sub>11</sub>P<sub>3</sub> calc.: C, 54.05; H, 3.38; N, 2.29; P, 7.60%. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2040m, 2005vw, 1960vs, 1965sh, 1925w, 1880w  $\text{cm}^{-1}$ .  $^{31}\text{P}$  NMR:  $\delta$  35.03 and 21.59 ppm (relative intensity 1:2).

*Molecular structure determinations of [Fe<sub>4</sub>N(CO)<sub>9</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] (1), [HFe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)] (2) and PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PMe<sub>2</sub>Ph)] (3)*

Suitable crystals of the three compounds were mounted in Lindemann tubes under argon. After survey photography by precession methods, selected crystals were set up on an Enraf-Nonius, CAD-4F diffractometer (Mo- $K_\alpha$  radiation,

Table 1

Crystal data and refinement parameters for [Fe<sub>4</sub>N(CO)<sub>9</sub>(NO)(PPh<sub>3</sub>)<sub>2</sub>] (1), [HFe<sub>4</sub>N(CO)<sub>11</sub>(PPh<sub>3</sub>)] (2), PPN[Fe<sub>4</sub>N(CO)<sub>11</sub>(PMe<sub>2</sub>Ph)] (3)

|   | 1   | 2  | 3   |
|---|---|--|---|
| Formula                                     | C <sub>45</sub> Fe <sub>4</sub> H <sub>30</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub> | C <sub>29</sub> Fe <sub>4</sub> H <sub>16</sub> N <sub>1</sub> O <sub>11</sub> P <sub>1</sub><br>-0.5 C <sub>6</sub> H <sub>14</sub> | C <sub>55</sub> Fe <sub>4</sub> H <sub>41</sub> N <sub>2</sub> O <sub>11</sub> P <sub>3</sub> |
| M   | 1044.07   | 808.81; 43.89  | 1224.24   |
| Crystal dimensions (mm)                     | 0.3 × 0.3 × 0.4   | 0.15 × 0.2 × 0.6   | 0.5 × 0.2 × 0.1   |
| Crystal system                              | Triclinic   | Triclinic  | Orthorhombic  |
| <i>a</i> (Å)                                | 14.813(4)   | 9.118(7)   | 18.179(5)   |
| <i>b</i> (Å)                                | 15.140(5)   | 11.856(2)  | 34.034(5)   |
| <i>c</i> (Å)                                | 21.391(6)   | 17.814(3)  | 17.606(3)   |
| $\alpha$ (°)                                | 80.98(3)  | 75.65(2)   | 90  |
| $\beta$ (°)                                 | 87.62(2)  | 81.11(4)   | 90  |
| $\gamma$ (°)                                | 69.00(3)  | 69.94(4)   | 90  |
| <i>U</i> (Å <sup>3</sup> )                  | 4423  | 1747   | 10893   |
| <i>D<sub>c</sub></i> (g cm <sup>-3</sup> )  | 1.57  | 1.62   | 1.49  |
| <i>Z</i>                                    | 4   | 2  | 8   |
| <i>F</i> (000)                              | 2112  | 888  | 4976  |
| Space group                                 | $P\bar{1}$  | $P\bar{1}$   | <i>Pbca</i>   |
| $\mu$ (Mo- $K_\alpha$ ) (cm <sup>-1</sup> ) | 14.15   | 17.30  | 11.90   |
| 2 $\theta$ limits                           | 3 ≤ 2 $\theta$ ≤ 46   | 8 ≤ 2 $\theta$ ≤ 50  | 4 ≤ 2 $\theta$ ≤ 48   |
| No. of parameters refined                   | 777   | 351  | 471   |
| Reflections used                            | 6814  | 4138   | 4645  |
| refinements                                 |   |  |   |
| <i>R</i> (%)                                | 3.92  | 4.46   | 5.13  |
| <i>R'</i> (%)                               | 4.02  | 4.77   | 5.63  |

Table 2a

Fractional atomic coordinates for **1**, the nitrosyl nitrogen atom is disordered over the positions of carbon atoms 11, 12, 22, 31, 41

| Atom   | x          | y          | z          | $U_{\text{iso}}$ |
|--------|------------|------------|------------|------------------|
| Fe(1)  | 0.29228(7) | 0.64060(7) | 0.52752(4) | 0.0404           |
| Fe(2)  | 0.23636(8) | 0.88534(7) | 0.45759(4) | 0.0437           |
| Fe(3)  | 0.38293(8) | 0.75778(8) | 0.52168(5) | 0.0557           |
| Fe(4)  | 0.21617(9) | 0.80347(8) | 0.56981(5) | 0.0548           |
| N(1)   | 0.2613(4)  | 0.7624(4)  | 0.4907(2)  | 0.0383           |
| C(11)  | 0.3427(5)  | 0.5545(5)  | 0.5947(3)  | 0.0498           |
| O(11)  | 0.3785(4)  | 0.5003(4)  | 0.6387(3)  | 0.0684           |
| C(12)  | 0.3694(5)  | 0.5734(5)  | 0.4743(3)  | 0.0480           |
| O(12)  | 0.4249(4)  | 0.5288(4)  | 0.4419(3)  | 0.0637           |
| C(21)  | 0.2429(6)  | 0.9986(6)  | 0.4610(4)  | 0.0637           |
| O(21)  | 0.2455(6)  | 1.0734(4)  | 0.4630(3)  | 0.0908           |
| C(22)  | 0.1125(6)  | 0.9308(5)  | 0.4383(4)  | 0.0549           |
| O(22)  | 0.0312(4)  | 0.9587(4)  | 0.4270(3)  | 0.0744           |
| C(31)  | 0.4694(6)  | 0.7120(6)  | 0.4654(4)  | 0.0561           |
| O(31)  | 0.5272(5)  | 0.6837(5)  | 0.4306(3)  | 0.0859           |
| C(32)  | 0.4471(6)  | 0.6867(6)  | 0.5915(4)  | 0.0674           |
| O(32)  | 0.4923(5)  | 0.6446(5)  | 0.6351(3)  | 0.0886           |
| C(33)  | 0.4081(7)  | 0.8598(7)  | 0.5319(4)  | 0.0745           |
| O(33)  | 0.4344(6)  | 0.9195(5)  | 0.5412(3)  | 0.0995           |
| C(41)  | 0.0930(7)  | 0.8231(5)  | 0.5726(3)  | 0.0514           |
| O(41)  | 0.0136(5)  | 0.8355(4)  | 0.5782(3)  | 0.0814           |
| C(42)  | 0.2518(6)  | 0.7344(6)  | 0.6459(4)  | 0.0662           |
| O(42)  | 0.2699(5)  | 0.6950(5)  | 0.6964(3)  | 0.0868           |
| C(43)  | 0.2136(7)  | 0.9150(6)  | 0.5878(4)  | 0.0723           |
| O(43)  | 0.2094(6)  | 0.9857(5)  | 0.6035(3)  | 0.0903           |
| P(1)   | 0.1718(1)  | 0.5858(1)  | 0.51836(8) | 0.0404           |
| C(111) | 0.2176(5)  | 0.4570(5)  | 0.5165(3)  | 0.044(2)         |
| C(112) | 0.2700(5)  | 0.4222(5)  | 0.4653(3)  | 0.056(2)         |
| C(113) | 0.3077(6)  | 0.3242(6)  | 0.4622(4)  | 0.066(2)         |
| C(114) | 0.2923(6)  | 0.2631(6)  | 0.5105(4)  | 0.073(2)         |
| C(115) | 0.2418(6)  | 0.2937(6)  | 0.5620(4)  | 0.080(3)         |
| C(116) | 0.2035(6)  | 0.3929(6)  | 0.5655(4)  | 0.064(2)         |
| C(121) | 0.0843(5)  | 0.6030(5)  | 0.5823(3)  | 0.045(2)         |
| C(122) | -0.0145(5) | 0.6365(5)  | 0.5709(3)  | 0.055(2)         |
| C(123) | -0.0787(6) | 0.6528(6)  | 0.6205(4)  | 0.065(2)         |
| C(124) | -0.0453(6) | 0.6346(6)  | 0.6811(4)  | 0.070(2)         |
| C(125) | 0.0519(6)  | 0.6020(6)  | 0.6939(4)  | 0.065(2)         |
| C(126) | 0.1163(5)  | 0.5865(5)  | 0.6441(3)  | 0.056(2)         |
| C(131) | 0.0928(5)  | 0.6354(5)  | 0.4482(3)  | 0.043(2)         |
| C(132) | 0.0694(5)  | 0.5804(5)  | 0.4108(4)  | 0.057(2)         |
| C(133) | 0.0070(6)  | 0.6236(6)  | 0.3589(4)  | 0.069(2)         |
| C(134) | -0.0323(6) | 0.7202(6)  | 0.3463(4)  | 0.069(2)         |
| C(135) | -0.0118(6) | 0.7765(6)  | 0.3826(4)  | 0.066(2)         |
| C(136) | 0.0525(5)  | 0.7342(5)  | 0.4336(3)  | 0.055(2)         |
| P(2)   | 0.2823(1)  | 0.8869(1)  | 0.35678(8) | 0.0440           |
| C(211) | 0.1835(5)  | 0.9652(5)  | 0.3036(3)  | 0.047(2)         |
| C(212) | 0.1410(5)  | 0.9334(5)  | 0.2609(4)  | 0.059(2)         |
| C(213) | 0.0617(6)  | 0.9968(6)  | 0.2234(4)  | 0.072(2)         |
| C(214) | 0.0255(6)  | 1.0911(6)  | 0.2308(4)  | 0.070(2)         |
| C(215) | 0.0671(6)  | 1.1232(6)  | 0.2728(4)  | 0.072(2)         |
| C(216) | 0.1458(6)  | 1.0614(6)  | 0.3092(4)  | 0.066(2)         |

Table 2a (continued)

| Atom   | x          | y          | z           | $U_{iso}$ |
|--------|------------|------------|-------------|-----------|
| C(221) | 0.3798(5)  | 0.9299(5)  | 0.3312(3)   | 0.051(2)  |
| C(222) | 0.3883(7)  | 0.9608(7)  | 0.2677(5)   | 0.093(3)  |
| C(223) | 0.4649(9)  | 0.9921(8)  | 0.2477(5)   | 0.113(4)  |
| C(224) | 0.5294(7)  | 0.9929(7)  | 0.2903(5)   | 0.096(3)  |
| C(225) | 0.5455(7)  | 0.9588(7)  | 0.3517(5)   | 0.090(3)  |
| C(226) | 0.4492(6)  | 0.9278(6)  | 0.3719(4)   | 0.073(2)  |
| C(231) | 0.3172(5)  | 0.7717(5)  | 0.3293(3)   | 0.045(2)  |
| C(232) | 0.2557(5)  | 0.7219(5)  | 0.3420(3)   | 0.053(2)  |
| C(233) | 0.2718(5)  | 0.6359(5)  | 0.3195(4)   | 0.060(2)  |
| C(234) | 0.3526(6)  | 0.6010(6)  | 0.2858(4)   | 0.070(2)  |
| C(235) | 0.4152(6)  | 0.6465(6)  | 0.2741(4)   | 0.078(2)  |
| C(236) | 0.3996(6)  | 0.7332(6)  | 0.2952(4)   | 0.065(2)  |
| Fe(5)  | 0.23338(7) | 0.13125(6) | -0.02183(4) | 0.0356    |
| Fe(6)  | 0.20229(6) | 0.34838(6) | 0.03883(4)  | 0.0365    |
| Fe(7)  | 0.09903(7) | 0.24279(7) | 0.04064(5)  | 0.0443    |
| Fe(8)  | 0.26995(8) | 0.16833(7) | 0.08558(4)  | 0.0440    |
| N(2)   | 0.2192(3)  | 0.2422(3)  | 0.0053(2)   | 0.0331    |
| O(51)  | 0.3554(6)  | 0.0911(5)  | -0.0432(3)  | 0.0446    |
| O(51)  | 0.4352(4)  | 0.0660(4)  | -0.0562(3)  | 0.0642    |
| O(52)  | 0.2194(5)  | 0.0189(5)  | -0.0087(3)  | 0.0448    |
| O(52)  | 0.2096(4)  | -0.0548(4) | 0.0002(2)   | 0.0663    |
| O(61)  | 0.1632(5)  | 0.4105(5)  | 0.1050(4)   | 0.0476    |
| O(61)  | 0.1375(4)  | 0.4474(4)  | 0.1483(3)   | 0.0698    |
| O(62)  | 0.1332(5)  | 0.4419(4)  | -0.0186(3)  | 0.0381    |
| O(62)  | 0.0872(4)  | 0.5010(3)  | -0.0566(2)  | 0.0557    |
| O(71)  | 0.0581(5)  | 0.1439(5)  | 0.0515(3)   | 0.0485    |
| O(71)  | 0.0239(4)  | 0.0867(4)  | 0.0596(3)   | 0.0692    |
| O(72)  | 0.0420(5)  | 0.2904(5)  | 0.1098(3)   | 0.0450    |
| O(72)  | 0.0022(4)  | 0.3192(4)  | 0.1530(3)   | 0.0637    |
| O(73)  | 0.0156(5)  | 0.3209(5)  | -0.0170(3)  | 0.0481    |
| O(73)  | -0.0379(4) | 0.3738(4)  | -0.0537(3)  | 0.0632    |
| O(81)  | 0.2395(5)  | 0.2079(5)  | 0.1606(4)   | 0.0514    |
| O(81)  | 0.2263(4)  | 0.2279(4)  | 0.2107(3)   | 0.0720    |
| O(82)  | 0.2630(5)  | 0.0524(6)  | 0.1107(3)   | 0.0525    |
| O(82)  | 0.2624(4)  | -0.0221(4) | 0.1308(3)   | 0.0708    |
| O(83)  | 0.3930(5)  | 0.1441(4)  | 0.0840(3)   | 0.0441    |
| O(83)  | 0.4738(4)  | 0.1279(4)  | 0.0872(3)   | 0.0726    |
| P(3)   | 0.1815(1)  | 0.1561(1)  | -0.12179(8) | 0.0395    |
| C(311) | 0.2218(5)  | 0.2414(5)  | -0.1736(3)  | 0.049(2)  |
| C(312) | 0.1936(5)  | 0.3332(5)  | -0.1592(4)  | 0.061(2)  |
| C(313) | 0.2256(7)  | 0.4018(7)  | -0.1967(4)  | 0.085(3)  |
| C(314) | 0.2842(7)  | 0.3730(7)  | -0.2447(5)  | 0.097(3)  |
| C(315) | 0.3127(7)  | 0.2877(8)  | -0.2609(5)  | 0.096(3)  |
| C(316) | 0.2814(6)  | 0.2163(6)  | -0.2240(4)  | 0.074(2)  |
| C(321) | 0.0509(5)  | 0.1993(5)  | -0.1350(3)  | 0.043(2)  |
| C(322) | 0.0005(5)  | 0.1458(5)  | -0.1041(3)  | 0.054(2)  |
| C(323) | -0.0997(6) | 0.1748(6)  | -0.1140(4)  | 0.067(2)  |
| C(324) | -0.1472(6) | 0.2566(6)  | -0.1541(4)  | 0.071(2)  |
| C(325) | -0.0982(6) | 0.3101(6)  | -0.1847(4)  | 0.068(2)  |
| C(326) | 0.0017(5)  | 0.2825(5)  | -0.1762(3)  | 0.053(2)  |
| C(331) | 0.2207(5)  | 0.0490(5)  | -0.1615(3)  | 0.043(2)  |
| C(332) | 0.1667(6)  | 0.0463(6)  | -0.2119(4)  | 0.066(2)  |
| C(333) | 0.1965(6)  | -0.0353(6) | -0.2413(4)  | 0.078(3)  |
| C(334) | 0.2763(6)  | -0.1110(6) | -0.2203(4)  | 0.074(2)  |



Table 2a (continued)

| Atom   | x         | y          | z          | $U_{iso}$ |
|--------|-----------|------------|------------|-----------|
| C(335) | 0.3298(6) | -0.1098(6) | -0.1715(4) | 0.068(2)  |
| C(336) | 0.3021(5) | -0.0281(5) | -0.1414(3) | 0.054(2)  |
| P(4)   | 0.3301(1) | 0.3957(1)  | 0.02540(8) | 0.0393    |
| C(411) | 0.4295(5) | 0.3272(4)  | -0.0201(3) | 0.042(2)  |
| C(412) | 0.5254(5) | 0.3108(5)  | -0.0069(3) | 0.054(2)  |
| C(413) | 0.5969(6) | 0.2626(6)  | -0.0468(4) | 0.070(2)  |
| C(414) | 0.5738(6) | 0.2328(6)  | -0.0986(4) | 0.071(2)  |
| C(415) | 0.4797(6) | 0.2484(6)  | -0.1116(4) | 0.065(2)  |
| C(416) | 0.4076(5) | 0.2941(5)  | -0.0717(3) | 0.053(2)  |
| C(421) | 0.3903(5) | 0.4038(5)  | 0.0962(3)  | 0.043(2)  |
| C(422) | 0.4002(5) | 0.3372(5)  | 0.1494(4)  | 0.059(2)  |
| C(423) | 0.4498(6) | 0.3391(6)  | 0.2026(4)  | 0.072(2)  |
| C(424) | 0.4896(6) | 0.4080(6)  | 0.2019(4)  | 0.070(2)  |
| C(425) | 0.4800(6) | 0.4738(6)  | 0.1505(4)  | 0.068(2)  |
| C(426) | 0.4314(5) | 0.4738(5)  | 0.0963(3)  | 0.057(2)  |
| C(431) | 0.2933(5) | 0.5179(5)  | -0.0183(3) | 0.044(2)  |
| C(432) | 0.3058(6) | 0.5336(6)  | -0.0827(4) | 0.065(2)  |
| C(433) | 0.2682(6) | 0.6276(6)  | -0.1168(4) | 0.078(3)  |
| C(434) | 0.2202(6) | 0.7011(6)  | -0.0847(4) | 0.074(2)  |
| C(435) | 0.2063(5) | 0.6869(5)  | -0.0226(4) | 0.062(2)  |
| C(436) | 0.2427(5) | 0.5947(5)  | 0.0117(3)  | 0.052(2)  |

$\lambda = 0.71069 \text{ \AA}$ ). Unit cell dimensions and orientation matrices were obtained by least-squares from the setting angles of 25 reflections in the range  $24^\circ < 2\theta < 30^\circ$ . Crystal data and experimental details of data collections are summarized in Table 1. Two standard reflections were measured at regular intervals throughout the data collections and showed no significant variations. The intensities were corrected for Lorentz, polarization and absorption [14]. All structures were determined by direct methods and electron density difference syntheses. They were refined by least squares with a large block approximation of the normal matrix.

For **1**, in a first step, CO and NO ligands were refined as carbonyl groups. Analyses of isotropic temperature factors and bonding distances showed that, for the two molecules in the asymmetric unit, the nitrosyl groups were partially disordered. In one of the molecules, the nitrosyl group is clearly statistically disordered over two positions, one on each of the two hinge iron atoms Fe(3) and Fe(4). To these positions was assigned the carbon atomic vibration factor and an occupation factor of  $1/2 \times 1/6(7+6) = 1.08333$  which takes into account the statistical distribution. For the second molecule in the asymmetric unit, nitrosyl group distinction was not straightforward. The nitrosyl group was considered as evenly distributed over the five positions with the smallest isotropic temperature factors and the shortest Fe–C distances. These positions were refined as carbon atoms with an occupation factor of  $1/5(7/6 + 4 \times 6/6) = 1.0333$ .

For **2**, difference Fourier maps indicated the presence of hexane disordered about the origin. In a first stage, the occupation factors of the two positions found for this molecule refined to 0.25 and were then fixed at these values in subsequent refinements. Slack constraints [15] were applied to the geometry of these molecules. The phenyl group H atoms were positioned geometrically, and their positions recalculated after each refinement cycle.

Table 2b  
Positional parameters for 2

| Atom   | x          | y          | z          | $U_{iso}$ |
|--------|------------|------------|------------|-----------|
| Fe(1)  | 0.99551(9) | 0.20864(7) | 0.79290(4) | 0.0339    |
| Fe(2)  | 0.73532(9) | 0.42342(7) | 0.90083(5) | 0.0384    |
| Fe(3)  | 1.0329(1)  | 0.35177(8) | 0.87217(6) | 0.0448    |
| Fe(4)  | 0.8561(1)  | 0.44827(8) | 0.75977(5) | 0.0494    |
| N(1)   | 0.8596(5)  | 0.3164(4)  | 0.8443(2)  | 0.0354    |
| C(11)  | 1.0513(6)  | 0.0783(6)  | 0.8683(4)  | 0.0439    |
| O(11)  | 1.0854(6)  | -0.0023(4) | 0.9202(3)  | 0.0638    |
| C(12)  | 1.1649(7)  | 0.1667(5)  | 0.7283(3)  | 0.0453    |
| O(12)  | 1.2749(5)  | 0.1418(5)  | 0.6870(3)  | 0.0655    |
| P(1)   | 0.8685(2)  | 0.1213(1)  | 0.73875(8) | 0.0346    |
| C(111) | 0.7119(6)  | 0.0753(5)  | 0.8015(3)  | 0.040(1)  |
| C(112) | 0.6417(7)  | 0.1330(5)  | 0.8618(3)  | 0.047(1)  |
| C(113) | 0.5170(8)  | 0.1034(6)  | 0.9080(4)  | 0.061(2)  |
| C(114) | 0.4668(8)  | 0.0158(7)  | 0.8927(4)  | 0.066(2)  |
| C(115) | 0.5336(8)  | -0.0416(6) | 0.8345(4)  | 0.066(2)  |
| C(116) | 0.6595(7)  | -0.0130(6) | 0.7868(4)  | 0.055(2)  |
| C(121) | 0.7774(6)  | 0.2151(5)  | 0.6505(3)  | 0.040(1)  |
| C(122) | 0.8661(7)  | 0.2711(6)  | 0.5919(4)  | 0.055(2)  |
| C(123) | 0.7990(9)  | 0.3434(7)  | 0.5236(4)  | 0.068(2)  |
| C(124) | 0.6490(9)  | 0.3590(7)  | 0.5143(4)  | 0.073(2)  |
| C(125) | 0.5594(9)  | 0.3074(7)  | 0.5710(4)  | 0.071(2)  |
| C(126) | 0.6222(7)  | 0.2344(6)  | 0.6394(4)  | 0.055(2)  |
| C(131) | 0.9956(6)  | -0.0205(5) | 0.7097(3)  | 0.039(1)  |
| C(132) | 1.0256(9)  | -0.0318(7) | 0.6338(4)  | 0.068(2)  |
| C(133) | 1.130(1)   | -0.1412(8) | 0.6149(5)  | 0.091(3)  |
| C(134) | 1.1977(9)  | -0.2365(7) | 0.6710(5)  | 0.079(2)  |
| C(135) | 1.1662(9)  | -0.2273(7) | 0.7462(5)  | 0.074(2)  |
| C(136) | 1.0638(8)  | -0.1195(6) | 0.7655(4)  | 0.062(2)  |
| C(21)  | 0.5382(7)  | 0.4516(6)  | 0.8809(4)  | 0.0508    |
| O(21)  | 0.4138(5)  | 0.4698(5)  | 0.8681(3)  | 0.0736    |
| C(22)  | 0.7270(7)  | 0.3331(6)  | 0.9958(4)  | 0.0507    |
| O(22)  | 0.7211(6)  | 0.2738(5)  | 1.0567(3)  | 0.0779    |
| C(23)  | 0.6923(7)  | 0.5667(6)  | 0.9310(4)  | 0.0513    |
| O(23)  | 0.6651(6)  | 0.6564(5)  | 0.9507(3)  | 0.0718    |
| C(31)  | 1.0964(6)  | 0.2495(6)  | 0.9571(4)  | 0.0394    |
| O(31)  | 1.1421(6)  | 0.1855(5)  | 1.0122(3)  | 0.0758    |
| C(32)  | 1.0299(7)  | 0.4916(6)  | 0.8964(4)  | 0.0490    |
| O(32)  | 1.0373(6)  | 0.5758(4)  | 0.9126(3)  | 0.0646    |
| C(33)  | 1.2085(8)  | 0.3386(6)  | 0.8077(4)  | 0.0536    |
| O(33)  | 1.3201(5)  | 0.3357(5)  | 0.7688(3)  | 0.0670    |
| C(41)  | 0.6878(8)  | 0.4784(5)  | 0.7118(4)  | 0.0505    |
| O(41)  | 0.5795(7)  | 0.5067(5)  | 0.6799(3)  | 0.0858    |
| C(42)  | 1.0005(9)  | 0.4357(6)  | 0.6797(4)  | 0.0606    |
| O(42)  | 1.0875(7)  | 0.4383(5)  | 0.6260(3)  | 0.0823    |
| C(43)  | 0.8307(9)  | 0.6022(7)  | 0.7643(4)  | 0.0666    |
| O(43)  | 0.8137(8)  | 0.7023(5)  | 0.7636(4)  | 0.0876    |
| C(1)   | 0.258(4)   | 0.258(3)   | 0.448(2)   | 0.08(1)   |
| C(2)   | 0.320(4)   | 0.122(3)   | 0.447(2)   | 0.10(1)   |
| C(3)   | 0.465(3)   | 0.068(1)   | 0.495(2)   | 0.09(1)   |
| C(4)   | 0.237(4)   | 0.214(3)   | 0.445(2)   | 0.09(1)   |
| C(5)   | 0.401(4)   | 0.150(3)   | 0.425(2)   | 0.12(1)   |
| C(6)   | 0.440(4)   | 0.016(2)   | 0.471(2)   | 0.14(2)   |

Table 2c

## Fractional atomic coordinates for 3

| Atom   | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>iso</sub> |
|--------|------------|------------|------------|-------------------------|
| Fe(1)  | 0.67582(6) | 0.36434(3) | 0.16868(6) | 0.0400                  |
| Fe(2)  | 0.55254(6) | 0.43218(3) | 0.25365(7) | 0.0420                  |
| Fe(3)  | 0.57381(6) | 0.35743(3) | 0.27200(6) | 0.0386                  |
| Fe(4)  | 0.67739(6) | 0.40416(4) | 0.29696(7) | 0.0453                  |
| N(1)   | 0.6149(3)  | 0.3983(2)  | 0.2107(3)  | 0.0343                  |
| C(11)  | 0.6300(5)  | 0.3446(3)  | 0.0909(5)  | 0.0518                  |
| O(11)  | 0.5982(4)  | 0.3326(2)  | 0.0387(4)  | 0.0765                  |
| C(12)  | 0.7402(5)  | 0.3252(2)  | 0.1773(5)  | 0.0497                  |
| O(12)  | 0.7811(4)  | 0.2997(2)  | 0.1828(5)  | 0.0853                  |
| P(1)   | 0.7504(1)  | 0.39933(7) | 0.0977(1)  | 0.0473                  |
| C(111) | 0.7080(5)  | 0.4409(3)  | 0.0510(5)  | 0.058(2)                |
| C(112) | 0.6352(7)  | 0.4437(3)  | 0.0428(6)  | 0.084(3)                |
| C(113) | 0.6003(8)  | 0.4741(5)  | -0.0015(8) | 0.118(5)                |
| C(114) | 0.6477(9)  | 0.5022(4)  | -0.0292(8) | 0.113(5)                |
| C(115) | 0.7175(9)  | 0.5020(5)  | -0.0202(9) | 0.124(5)                |
| C(116) | 0.7528(8)  | 0.4713(4)  | 0.0202(8)  | 0.114(5)                |
| C(121) | 0.8322(6)  | 0.4181(3)  | 0.1427(7)  | 0.087(4)                |
| C(131) | 0.7882(6)  | 0.3729(3)  | 0.0176(6)  | 0.073(3)                |
| C(21)  | 0.5780(6)  | 0.4785(3)  | 0.2174(6)  | 0.0648                  |
| O(21)  | 0.5936(5)  | 0.5084(2)  | 0.1930(5)  | 0.0888                  |
| C(22)  | 0.4683(5)  | 0.4287(3)  | 0.2030(5)  | 0.0553                  |
| O(22)  | 0.4155(4)  | 0.4265(3)  | 0.1685(5)  | 0.0870                  |
| C(23)  | 0.5187(5)  | 0.4492(2)  | 0.3431(6)  | 0.0478                  |
| O(23)  | 0.4979(4)  | 0.4607(2)  | 0.4002(4)  | 0.0692                  |
| C(31)  | 0.5081(5)  | 0.3342(3)  | 0.2110(5)  | 0.0549                  |
| O(31)  | 0.4683(4)  | 0.3172(2)  | 0.1723(4)  | 0.0805                  |
| C(32)  | 0.5188(5)  | 0.3599(3)  | 0.3548(5)  | 0.0533                  |
| O(32)  | 0.4836(4)  | 0.3600(2)  | 0.4092(4)  | 0.0746                  |
| C(33)  | 0.6253(5)  | 0.3161(3)  | 0.3000(5)  | 0.0561                  |
| O(33)  | 0.6559(4)  | 0.2888(2)  | 0.3214(4)  | 0.0760                  |
| C(41)  | 0.7246(6)  | 0.4500(3)  | 0.2851(5)  | 0.0643                  |
| O(41)  | 0.7524(5)  | 0.4801(2)  | 0.2814(5)  | 0.0896                  |
| C(42)  | 0.7533(6)  | 0.3728(3)  | 0.3132(6)  | 0.0712                  |
| O(42)  | 0.8033(5)  | 0.3539(3)  | 0.3295(5)  | 0.0981                  |
| C(43)  | 0.6543(5)  | 0.4105(3)  | 0.3927(6)  | 0.0636                  |
| O(43)  | 0.6411(5)  | 0.4139(3)  | 0.4568(4)  | 0.0876                  |
| N(2)   | 0.2732(3)  | 0.1584(2)  | 0.2477(4)  | 0.045(2)                |
| P(2)   | 0.3477(1)  | 0.16750(6) | 0.2058(1)  | 0.0369                  |
| C(211) | 0.4165(4)  | 0.1902(2)  | 0.2637(4)  | 0.044(2)                |
| C(212) | 0.4088(5)  | 0.2299(3)  | 0.2813(5)  | 0.064(3)                |
| C(213) | 0.4579(6)  | 0.2479(3)  | 0.3309(6)  | 0.078(3)                |
| C(214) | 0.5129(6)  | 0.2269(3)  | 0.3622(6)  | 0.081(3)                |
| C(215) | 0.5215(6)  | 0.1878(3)  | 0.3472(6)  | 0.080(3)                |
| C(216) | 0.4727(5)  | 0.1679(3)  | 0.2965(5)  | 0.059(2)                |
| C(221) | 0.3881(4)  | 0.1244(2)  | 0.1645(4)  | 0.041(2)                |
| C(222) | 0.3520(5)  | 0.0890(3)  | 0.1684(5)  | 0.053(2)                |
| C(223) | 0.3810(6)  | 0.0555(3)  | 0.1318(6)  | 0.067(3)                |
| C(224) | 0.4448(6)  | 0.0590(3)  | 0.0914(6)  | 0.069(3)                |
| C(225) | 0.4805(6)  | 0.0937(3)  | 0.0857(6)  | 0.076(3)                |
| C(226) | 0.4530(5)  | 0.1274(3)  | 0.1223(5)  | 0.061(3)                |
| C(231) | 0.3257(4)  | 0.2006(2)  | 0.1301(4)  | 0.042(2)                |
| C(232) | 0.3799(6)  | 0.2186(3)  | 0.0891(6)  | 0.071(3)                |
| C(233) | 0.3614(7)  | 0.2400(4)  | 0.0236(7)  | 0.096(4)                |

Table 2c (continued)

| Atom   | x         | y          | z         | $U_{iso}$ |
|--------|-----------|------------|-----------|-----------|
| C(234) | 0.2877(6) | 0.2434(3)  | 0.0037(7) | 0.083(3)  |
| C(235) | 0.2356(6) | 0.2278(3)  | 0.0453(6) | 0.074(3)  |
| C(236) | 0.2534(5) | 0.2051(3)  | 0.1089(5) | 0.060(2)  |
| P(3)   | 0.2425(1) | 0.14112(6) | 0.3244(1) | 0.0382    |
| C(311) | 0.1819(4) | 0.1771(2)  | 0.3651(4) | 0.041(2)  |
| C(312) | 0.1455(5) | 0.1692(3)  | 0.4338(5) | 0.057(2)  |
| C(313) | 0.0970(5) | 0.1970(3)  | 0.4629(5) | 0.063(3)  |
| C(314) | 0.0838(5) | 0.2310(3)  | 0.4246(5) | 0.061(3)  |
| C(315) | 0.1188(5) | 0.2388(3)  | 0.3582(6) | 0.065(3)  |
| C(316) | 0.1680(5) | 0.2116(2)  | 0.3278(5) | 0.050(2)  |
| C(321) | 0.1872(5) | 0.0984(2)  | 0.3048(5) | 0.047(2)  |
| C(322) | 0.1776(5) | 0.0690(3)  | 0.3572(5) | 0.058(2)  |
| C(323) | 0.1311(6) | 0.0370(3)  | 0.3396(6) | 0.080(3)  |
| C(324) | 0.0988(6) | 0.0359(3)  | 0.2723(6) | 0.080(3)  |
| C(325) | 0.1081(7) | 0.0629(4)  | 0.2194(7) | 0.098(4)  |
| C(326) | 0.1519(6) | 0.0969(3)  | 0.2351(6) | 0.084(3)  |
| C(331) | 0.3119(4) | 0.1278(2)  | 0.3925(4) | 0.039(2)  |
| C(332) | 0.3279(5) | 0.1520(3)  | 0.4534(5) | 0.064(3)  |
| C(333) | 0.3872(6) | 0.1423(3)  | 0.5006(6) | 0.077(3)  |
| C(334) | 0.4304(6) | 0.1105(3)  | 0.4850(6) | 0.077(3)  |
| C(335) | 0.4144(6) | 0.0871(3)  | 0.4252(6) | 0.067(3)  |
| C(336) | 0.3537(5) | 0.0954(3)  | 0.3778(5) | 0.054(2)  |

For **3**, the methyl H atom positions were identified from difference maps. Their positional parameters were refined using slack constraints. Computations were performed on a DEC VAX 11/725 with the Oxford CRYSTALS package [16]. Unit weights were used throughout. For each structure, refinement was continued until the sums of the shift/e.s.d. ratios were less than 0.05. Final *R*-values are given in Table 1. Fractional atomic coordinates of non-hydrogen atoms are in Tables 2a–c. Important bond lengths and angles are given in Table 3a–c. Full data are available as the supplementary material from the authors.

Table 3a

Distances (Å) and angles (deg) in **1**

|             |          |             |          |
|-------------|----------|-------------|----------|
| Fe(1)–Fe(3) | 2.567(1) | Fe(5)–Fe(8) | 2.572(1) |
| Fe(1)–Fe(4) | 2.606(1) | Fe(5)–N(2)  | 1.802(5) |
| Fe(1)–N(1)  | 1.789(5) | Fe(5)–P(3)  | 2.232(2) |
| Fe(1)–P(1)  | 2.248(2) | Fe(6)–Fe(7) | 2.574(1) |
| Fe(2)–Fe(3) | 2.595(2) | Fe(6)–Fe(8) | 2.589(1) |
| Fe(2)–Fe(4) | 2.581(1) | Fe(6)–N(2)  | 1.794(5) |
| Fe(2)–N(1)  | 1.794(5) | Fe(6)–P(4)  | 2.246(2) |
| Fe(2)–P(2)  | 2.233(2) | Fe(7)–Fe(8) | 2.534(1) |
| Fe(3)–Fe(4) | 2.535(2) | Fe(7)–N(2)  | 1.903(5) |
| Fe(3)–N(1)  | 1.920(5) | Fe(8)–N(2)  | 1.914(5) |
| Fe(4)–N(1)  | 1.907(5) |             |          |
| Fe(5)–Fe(7) | 2.584(1) |             |          |

Table 3a (continued)

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Fe(4)–Fe(1)–Fe(3) | 58.69(4) | N(2)–Fe(5)–Fe(8)  | 48.0(1)  |
| N(1)–Fe(1)–Fe(3)  | 48.3(2)  | Fe(8)–Fe(6)–Fe(7) | 58.78(4) |
| N(1)–Fe(1)–Fe(4)  | 47.0(2)  | N(2)–Fe(6)–Fe(7)  | 47.6(2)  |
| Fe(4)–Fe(2)–Fe(3) | 58.66(4) | N(2)–Fe(6)–Fe(8)  | 47.6(1)  |
| N(1)–Fe(2)–Fe(3)  | 47.7(2)  | Fe(6)–Fe(7)–Fe(5) | 88.29(4) |
| N(1)–Fe(2)–Fe(4)  | 47.6(2)  | Fe(8)–Fe(7)–Fe(5) | 60.32(4) |
| Fe(2)–Fe(3)–Fe(1) | 87.82(4) | Fe(8)–Fe(7)–Fe(6) | 60.91(4) |
| Fe(4)–Fe(3)–Fe(1) | 61.43(4) | N(2)–Fe(7)–Fe(5)  | 44.2(1)  |
| Fe(4)–Fe(3)–Fe(2) | 60.39(4) | N(2)–Fe(7)–Fe(6)  | 44.2(1)  |
| Fe(2)–Fe(4)–Fe(1) | 87.30(4) | N(2)–Fe(7)–Fe(8)  | 48.6(1)  |
| Fe(3)–Fe(4)–Fe(1) | 59.89(4) | Fe(6)–Fe(8)–Fe(5) | 88.22(4) |
| Fe(3)–Fe(4)–Fe(2) | 60.95(4) | Fe(7)–Fe(8)–Fe(5) | 60.80(4) |
| N(1)–Fe(4)–Fe(1)  | 43.3(2)  | Fe(7)–Fe(8)–Fe(6) | 60.30(4) |
| N(1)–Fe(4)–Fe(2)  | 44.0(2)  | N(2)–Fe(8)–Fe(5)  | 44.4(1)  |
| N(1)–Fe(4)–Fe(3)  | 48.7(2)  | N(2)–Fe(8)–Fe(6)  | 43.8(1)  |
| Fe(2)–N(1)–Fe(1)  | 175.8(3) | N(2)–Fe(8)–Fe(7)  | 48.2(1)  |
| Fe(3)–N(1)–Fe(1)  | 87.5(2)  | Fe(6)–N(2)–Fe(5)  | 175.1(3) |
| Fe(3)–N(1)–Fe(2)  | 88.6(2)  | Fe(7)–N(2)–Fe(5)  | 88.4(2)  |
| Fe(4)–N(1)–Fe(1)  | 89.6(2)  | Fe(7)–N(2)–Fe(6)  | 88.2(2)  |
| Fe(4)–N(1)–Fe(2)  | 88.4(2)  | Fe(8)–N(2)–Fe(5)  | 87.5(2)  |
| Fe(4)–N(1)–Fe(3)  | 83.0(2)  | Fe(8)–N(2)–Fe(6)  | 88.5(2)  |
| N(2)–Fe(5)–Fe(7)  | 47.4(2)  | Fe(8)–N(2)–Fe(7)  | 83.2(2)  |

Table 3b

Distances (Å) and angles (deg) in 2

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Fe(1)–Fe(3)       | 2.593(1) | Fe(2)–Fe(4)       | 2.572(1) |
| Fe(1)–Fe(4)       | 2.638(1) | Fe(2)–N(1)        | 1.790(4) |
| Fe(1)–N(1)        | 1.774(4) | Fe(3)–Fe(4)       | 2.552(1) |
| Fe(1)–P(1)        | 2.238(2) | Fe(3)–N(1)        | 1.929(4) |
| Fe(2)–Fe(3)       | 2.559(1) | Fe(4)–N(1)        | 1.878(4) |
| Fe(4)–Fe(1)–Fe(3) | 58.39(3) | Fe(2)–Fe(4)–Fe(1) | 86.23(3) |
| N(1)–Fe(1)–Fe(3)  | 48.1(1)  | Fe(3)–Fe(4)–Fe(1) | 59.92(3) |
| N(1)–Fe(1)–Fe(4)  | 45.3(1)  | Fe(3)–Fe(4)–Fe(2) | 59.93(3) |
| Fe(4)–Fe(2)–Fe(3) | 59.65(4) | N(1)–Fe(4)–Fe(1)  | 42.2(1)  |
| N(1)–Fe(2)–Fe(3)  | 48.8(1)  | N(1)–Fe(4)–Fe(2)  | 44.1(1)  |
| N(1)–Fe(2)–Fe(4)  | 46.9(1)  | N(1)–Fe(4)–Fe(3)  | 48.8(1)  |
| Fe(2)–Fe(3)–Fe(1) | 87.45(3) | Fe(2)–N(1)–Fe(1)  | 175.2(3) |
| Fe(4)–Fe(3)–Fe(1) | 61.69(3) | Fe(3)–N(1)–Fe(1)  | 88.8(2)  |
| Fe(4)–Fe(3)–Fe(2) | 60.42(3) | Fe(3)–N(1)–Fe(2)  | 86.9(2)  |
| N(1)–Fe(3)–Fe(1)  | 43.2(1)  | Fe(4)–N(1)–Fe(1)  | 92.5(2)  |
| N(1)–Fe(3)–Fe(2)  | 44.3(1)  | Fe(4)–N(1)–Fe(2)  | 89.0(2)  |
| N(1)–Fe(3)–Fe(4)  | 47.1(1)  | Fe(4)–N(1)–Fe(3)  | 84.2(2)  |

Table 3c

Distances (Å) and angles (deg) in 3

|             |          |             |          |
|-------------|----------|-------------|----------|
| Fe(1)–Fe(3) | 2.608(2) | Fe(2)–Fe(4) | 2.577(2) |
| Fe(1)–Fe(4) | 2.634(2) | Fe(2)–N(1)  | 1.786(6) |
| Fe(1)–N(1)  | 1.762(6) | Fe(3)–Fe(4) | 2.504(2) |
| Fe(1)–P(1)  | 2.194(2) | Fe(3)–N(1)  | 1.912(6) |
| Fe(2)–Fe(3) | 2.593(2) | Fe(4)–N(1)  | 1.907(6) |

Table 3c (continued)

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| Fe(4)–Fe(1)–Fe(3) | 57.05(4) | Fe(2)–Fe(4)–Fe(1) | 85.82(5) |
| N(1)–Fe(1)–Fe(3)  | 47.1(2)  | Fe(3)–Fe(4)–Fe(1) | 60.96(4) |
| N(1)–Fe(1)–Fe(4)  | 46.3(2)  | Fe(3)–Fe(4)–Fe(2) | 61.36(4) |
| Fe(4)–Fe(2)–Fe(3) | 57.92(4) | N(1)–Fe(4)–Fe(1)  | 42.0(2)  |
| N(1)–Fe(2)–Fe(3)  | 47.5(2)  | N(1)–Fe(4)–Fe(2)  | 43.9(2)  |
| N(1)–Fe(2)–Fe(4)  | 47.7(2)  | N(1)–Fe(4)–Fe(3)  | 49.1(2)  |
| Fe(2)–Fe(3)–Fe(1) | 86.03(5) | Fe(2)–N(1)–Fe(1)  | 179.3(4) |
| Fe(4)–Fe(3)–Fe(1) | 61.99(4) | Fe(3)–N(1)–Fe(1)  | 90.4(3)  |
| Fe(4)–Fe(4)–Fe(2) | 60.72(5) | Fe(3)–N(1)–Fe(2)  | 89.0(3)  |
| N(1)–Fe(3)–Fe(1)  | 42.5(2)  | Fe(4)–N(1)–Fe(1)  | 91.7(3)  |
| N(1)–Fe(3)–Fe(2)  | 43.5(2)  | Fe(4)–N(1)–Fe(2)  | 88.5(3)  |
| N(1)–Fe(3)–Fe(4)  | 48.9(2)  | Fe(4)–N(1)–Fe(3)  | 81.9(2)  |

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