*Inorganica Chimica Acta*, *165* (1989) 215–220

# Structure–Activity Correlation in Iron Nitrosyl Complexes: Crystal Structures of $[Fe(NO)_2(Cl)]_2(\mu\text{-dppe})$ and $Fe(NO)_2(dppe)$

H. LI KAM WAH, M. POSTEL*

*Laboratoire de Chimie Moléculaire, Unité Associée au C.N.R.S. no. 426, Université de Nice, 06034 Nice (France)*

and M. PIERROT

*Laboratoire de Cristallochimie, Université d'Aix-Marseille III, Marseille (France)*

(Received June 17, 1989)

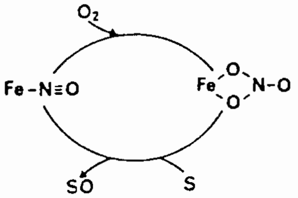
## Abstract

The nitrosyl dimer $[Fe(NO)_2(Cl)]_2$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) yields complex 2, $[Fe(NO)_2(Cl)]_2(\mu\text{-dppe})$; 2 is the first structurally characterized binuclear complex where dppe stands as the single bridge between two metallic centers without a metal–metal bond. Crystal data (at −10 °C): triclinic, space group $P\bar{1}$, $a = 9.047(3)$, $b = 11.310(4)$, $c = 8.663(3)$ Å, $\alpha = 92.3(1)$, $\beta = 116.1(1)$, $\gamma = 74.8(1)°$, $Z = 2$, $V = 765(1)$ Å$^3$, and $R_w = 0.064$ for 1393 reflections with $I > 3.0\sigma(I)$. When allowed to react with dppe, 2 gives $Fe(NO)_2(dppe)$ (4). Crystal data (at room temperature): monoclinic, space group $P2_1/C$, $a = 12.551(4)$, $b = 15.770(5)$, $c = 15.158(5)$ Å, $\beta = 123.9(1)°$, $Z = 4$, $V = 2488$ Å$^3$ and $R_w = 0.035$ for 1934 reflections with $I > 3.0\sigma(I)$. Comparisons between the structures of 2 and 4 indicate a greater amount of $NO^-$ character in the chloro dinitrosyl complex, consistent with its easy oxygenation into a nitrate via electrophilic attack of dioxygen on coordinated NO.

## Introduction

We have demonstrated that the iron–nitrato/iron nitrosyl couple constitutes a new alternative for the $O_2$ oxidation of alkenes [1, 2]. In this system, the nitrosyl ligand, N-bonded to iron, is oxidized by $O_2$ into a nitrato group, bidentate, O-bonded to iron, which, in turn, transfers oxygen to alkenes or phosphines and is thus reduced to the initial N-bonded nitrosyl group (Scheme 1).

The formation of nitrates from $Fe(NO)_2Cl(PPh_3)$ [1] or $[Fe(NO)_2(Cl)]_2(\mu\text{-dppe})$ [3], where dppe = 1,2-bis(diphenylphosphino)ethane, is clean and easy while a slow intricate reaction occurs when $Fe(NO)_2(PPh_3)_2$ or $Fe(NO)_2(dppe)$ are submitted to dioxygen [3].



Scheme 1.

This led us to search for a possible correlation between structure and activity. For comparison with the structures of $Fe(NO)_2Cl(PPh_3)$ [4] and $Fe(NO)_2(PPh_3)_2$ [5], the structures of $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ and $Fe(NO)_2(dppe)$ were of interest and are reported here.

## Experimental

The chlorobisnitrosyliron dimer $[Fe(NO)_2(Cl)]_2$ was obtained by the method described in the literature [6]. 1,2-Bis(diphenylphosphino)ethane was purchased from Fluka AG and was used without further purification. All the reactions were carried out under oxygen-free argon, and the solvents were freshly distilled from appropriate drying agents. Elemental analyses were performed by the Service Central de Microanalyses of the CNRS. Infrared spectra were recorded as KBr pellets on a Bruker FT-IFS 45 spectrometer. ESR spectra were measured on a Bruker 200 SRC spectrometer equipped with a variable-temperature accessory, both in the solid state and in solution. $^{31}P$ NMR spectra were recorded on a Bruker WH 90 spectrometer. $^{31}P$ chemical shifts are given in parts per million downfield from external $H_3PO_4$.

### *Synthesis of $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (2)*

The chlorobisnitrosyliron dimer $[Fe(NO)_2(Cl)]_2$ (0.090 g, 0.297 mmol) was dissolved in toluene (50 ml) and dppe (0.119 g, 0.298 mmol) was added in

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

small portions with stirring. A change of colour from reddish-yellow to violet was observed after complete addition of dppe. After one hour, no precipitate was observed and the reaction mixture was evaporated to yield a violet powder (0.200 g, 95%).

The violet powder was redissolved in 20 ml of toluene and addition of an equal volume of pentane produced violet parallepiped shaped crystals after one day at 0 °C.

IR (KBr pellet, cm$^{-1}$): $\nu$NO = 1786(s), 1724(s); $\nu$Fe–Cl = 334(m). *Anal.* Calc. for $Fe_2Cl_2C_{26}H_{24}N_4O_4P_2$: C, 44.55; H, 3.45; N, 7.99; P, 8.84; Fe, 15.93. Found: C, 44.56; H, 3.46; N, 7.33; P, 8.76; Fe, 16.24%. ESR (crystalline solid, room temperature): $g_\parallel = 2.017$, $g_\perp = 2.045$, $g_{iso} = 1/3(g_\parallel + 2g_\perp) = 2.036$. ESR (toluene, 193 K): $g = 2.036$.

### *Synthesis of Fe(NO)$_2$(dppe) (4) from 2*

Complex 2 (0.24 g, 0.342 mmol) was dissolved in toluene (50 ml) and dppe (0.136 g, 0.341 mmol) was added. A green precipitate formed immediately and a change of colour of the solution from violet to red was observed. The reaction mixture was stirred for 1 h and then filtered. To the filtrate was added an equal volume of pentane. After one night at 0 °C, red crystals were obtained (0.28 g, 0.54 mmol, 78%). Spectral characteristics for the red crystals: IR (KBr pellet, cm$^{-1}$): $\nu$NO = 1707(s), 1657(s). $^{31}$P NMR (toluene, ppm): $\delta = +80.1$(s). $^1$H NMR ($CD_2Cl_2$, ppm): $\delta = 2.5$ (d, $^2J$(P–H) = 15 Hz, 4H); $\delta = 7.5$ (m, 20 H). *Anal.* Calc. for $FeC_{26}H_{24}N_2O_2P_2$: C, 60.72; H, 4.70; N, 5.45. Found: C, 59.85; H, 4.78; N, 5.47%.

The green precipitate was washed with pentane (20 ml). Yield = 0.072 g. IR (KBr pellet): $\nu$NO = 1796(s) cm$^{-1}$. EPR ($CH_2Cl_2$, room temperature): $g = 2.033$, $a\langle ^{31}P\rangle = 50$ G.

### *Crystal Preparation*

Air-sensitive crystallographic quality crystals of $Fe_2Cl_2P_2N_4O_4C_{26}H_{24}$ (2) ($M = 701.06$) were isolated as transparent violet parallepipeds. They were grown by allowing a layer of pentane to diffuse slowly into a solution of 2 in toluene at 0 °C; they were washed with pentane, then dried under a stream of argon.

Single red longitudinal crystals of $FeN_2O_2C_{26}H_{24}P_2$ (4) ($M = 514.29$) were obtained similarly by slow diffusion of pentane into a solution of 4 in toluene at 0 °C. They were washed with pentane and dried under a stream of argon.

The crystals were sealed in Lindemann glass capillaries under a stream of dry nitrogen.

### *Crystallographic Data*

A summary of crystal data and intensity collections for 2 and 4 is given in Table 1. The unit cell constants were refined by least-squares from angular data for 25 reflections. The space group of 4 was obtained from systematic extinctions and confirmed by subsequent solution and refinement. No systematic absences were found for 2, consistent only with space groups $P1$ or $P\bar{1}$. $P\bar{1}$ was assumed and successful refinement of the structure in this space group confirmed this choice. A variation of 2.6% and 1.1% in the intensities of 600 reflections recorded periodically (3600 s for 2 and 7200 s for 4) were observed during the data collection of 2 and 4 respectively. The data were corrected for Lorentz and polarization factors but not for absorption.

Complex 2 was found to have a crystallographic centre of symmetry. The structures were solved on a PDP 11/44 computer by using the Enraf-Nonius SDP [7] programs. The atomic positions were obtained with program Multan [8] and subsequent Fourier difference series.

TABLE 1. Crystallographic data for **2** and **4**

| | $Fe_2Cl_2P_2N_4O_4C_{26}H_{24}$ (**2**) | $FeP_2O_2N_2C_{26}H_{24}$ (**4**) |
|---|---|---|
| $a$ (Å) | 9.047(3) | 12.551(4) |
| $b$ (Å) | 11.310(4) | 15.770(5) |
| $c$ (Å) | 8.663(3) | 15.158(5) |
| $\alpha$ (°) | 92.3(1) | |
| $\beta$ (°) | 116.1(1) | 123.9(1) |
| $\gamma$ (°) | 74.8(1) | |
| $V$ (Å$^3$) | 765(1) | 2488 |
| $Z$ | 2 | 4 |
| Formula weight | 701.06 | 514.3 |
| Space group | $P\bar{1}$ | $P2_1/C$ |
| $T$ (°C) | −10 | 25 |
| $\lambda$ (Å) | 0.71069 | 0.71069 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.52 | 1.37 |
| $\mu$ (cm$^{-1}$) | 12.63 | 7.55 |
| $R$ | 0.053 | 0.032 |
| $R_w$ | 0.064 | 0.035 |

The structures were refined by least-squares refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of all non-hydrogen atoms. The hydrogen atoms were then placed in calculated positions with isotropic temperature factors fixed at 6 Å$^2$ and were not refined. Their introduction into the refinement led to final $R$ and $R_w$ values of 0.053 and 0.064 for 2 and 0.032 and 0.035 for 4 respectively. The function minimized was $\Sigma w[F_o - F_c]^2$, where $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1968).

## Results and Discussion

### *Synthesis*

When dppe is allowed to react with $[Fe(NO)_2(Cl)]_2$ (1), with a Fe/P ratio of 1/1, the binuclear singly bridged complex 2 is formed.

The analytical and spectroscopic data confirm the binuclear formulation for 2. Characteristic infrared data are two $\nu$NO absorptions at 1786 and 1724 cm$^{-1}$ and a $\nu$Fe–Cl vibration at 334 cm$^{-1}$. Complex 2 is paramagnetic: the $g$ values of the ESR spectrum of 2 of axial symmetry measured in the solid state are $g_\parallel = 2.017$ and $g_\perp = 2.045$. In a toluene solution of 2 at 193 K, the signal is measured at $g = 2.036$ (1/3-$[g_\parallel + 2g_\perp]$). An X-ray structural investigation unambiguously established 2 as the symmetrical bridge-complex $[Fe(NO)_2(Cl)]_2(\mu$-dppe) in which the dppe ligand acts as a single bridge between two iron atoms (*vide infra*).

When compound 2 is allowed to react further with one equivalent of dppe in toluene at room temperature, two iron species form together: a green compound, 3, insoluble in toluene, and a red complex, 4, readily soluble in toluene. Adduct 3 which is currently under study in our laboratory, is extremely sensitive to even traces of air and, up to now, could not be unambiguously characterized in our hands.

Addition of an equal volume of pentane to the toluene solution of 4 produces red crystals of the known $Fe(NO)_2$(dppe) [9, 10] characterized by IR ($\nu$NO = 1707 and 1657 cm$^{-1}$), $^{31}$P NMR ($\delta$ = 80.1 ppm) and X-ray crystallography (*vide infra*).

### *Molecular Structure of $[Fe(NO)_2Cl]_2(\mu$-dppe) (2)*

The molecular structure of 2 is shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2.

The important feature in structure 2 is the presence of a single dppe bridge between the two iron atoms. The Fe...Fe distance of 6.82 Å excludes a metal–metal bond. Compound 2, a $\{Fe(NO)_2\}^9$ compound [11], is, to our knowledge, the first example of a crystal structure where dppe stands as the single bridge between two metallic centers without a metal–metal bond.

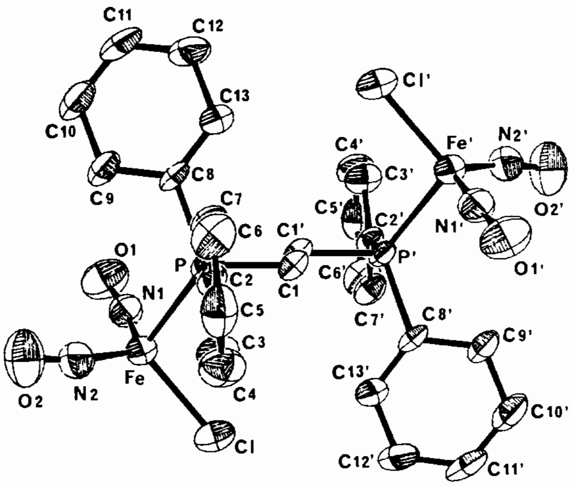


Fig. 1. Molecular structure of $[Fe(NO)_2Cl]_2(\mu$-dppe) (2). Hydrogen atoms are omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

TABLE 2. Principal bond lengths (Å) and angles (°) with e.s.d.s for compound 2

| | | | |
|---|---|---|---|
| Fe–N1 | 1.654(8) | Fe–N1–O1 | 169.5(7) |
| Fe–N2 | 1.707(8) | Fe–N2–O2 | 165.7(6) |
| Fe–Cl | 2.228(2) | N1–Fe–N2 | 117.1(3) |
| Fe–P | 2.356(2) | Cl–Fe–P | 101.75(9) |
| N1–O1 | 1.161(9) | Cl–Fe–N1 | 115.96(3) |
| N2–O2 | 1.156(8) | Cl–Fe–N2 | 116.4(2) |
| P–C1 | 1.833(7) | P–Fe–N1 | 99.3(4) |
| P–C2 | 1.817(7) | P–Fe–N2 | 101.8(3) |
| P–C8 | 1.829(6) | P–C1–C1' | 113.2(5) |
| C1–C1' | 1.54(1) | | |

Otherwise, 2 is best described as two distorted $Fe(NO)_2ClP$ tetrahedrons linked together by a single bridge in such a way that they are related to each other by a crystallographic inversion center found in the middle of $C_1C_1'$ bond, i.e. in the middle of the bridge. The two phosphorus atoms $P_1$ and $P_1'$ are *trans* oriented with respect to the $C_1C_1'$ bond.

The bond distances and angles for each $Fe(NO)_2ClP$ moiety compare all with those of $Fe(NO)_2Cl(PPh_3)$ [4] but for the P–Fe–Cl angle of 101.75(9)° in 2 as compared with 112.0(1)° in the monomeric adduct: this may be explained by steric effects, $Ph_2PCH_2–CH_2$ being less sterically demanding than $PPh_3$.

The two nitrosyl ligands are slightly bent (169.5(7)° and 165.7(6)°) and they adopt an 'attracto' conformation [12], the $O_1$–Fe–$O_2$ angle of 107.9 being less than the $N_1$–Fe–$N_2$ angle (117.1°).

### *Molecular Structure of $Fe(NO)_2$(dppe) (4)*

The molecular structure of 4 is illustrated in Fig. 2; selected bond angles and bond distances for 4 are gathered in Table 3.

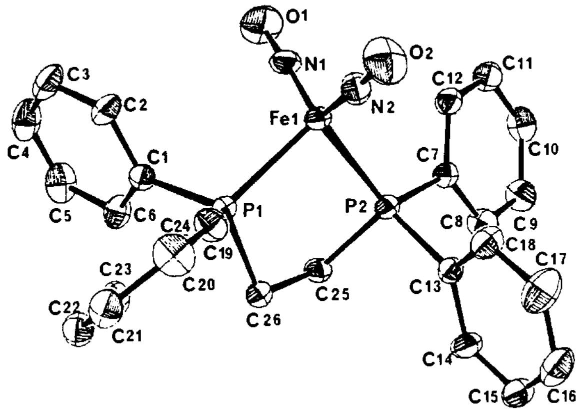


Fig. 2. Molecular structure of $Fe(NO)_2(dppe)$ (4). Hydrogen atoms are omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

TABLE 3. Principal bond lengths (Å) and angles (°) with e.s.d.s for compound **4**

| | | | |
|---|---|---|---|
| Fe1–N1 | 1.658(5) | Fe1–N1–O1 | 178.0(3) |
| Fe1–N2 | 1.651(4) | Fe1–N2–O2 | 176.0(6) |
| Fe1–P1 | 2.253(2) | N1–Fe1–N2 | 125.4(2) |
| Fe1–P2 | 2.253(2) | P2–Fe1–N2 | 114.0(2) |
| N1–O1 | 1.185(7) | P1–Fe1–N1 | 101.8(2) |
| N2–O2 | 1.200(5) | P1–Fe1–P2 | 85.92(5) |
| P1–C26 | 1.851(5) | P1–Fe1–N2 | 116.3(1) |
| P2–C25 | 1.852(3) | P2–Fe1–N1 | 106.2(2) |
| P1–C1 | 1.830(5) | P1–C26–C25 | 109.3(3) |
| P1–C19 | 1.829(5) | P2–C25–C26 | 107.4(3) |
| P2–C7 | 1.831(6) | | |
| P2–C13 | 1.836(5) | | |

The geometry of complex 4 is that of a distorted tetrahedron. Each iron atom is coordinated to two nearly linear nitrosyl ligands (Fe–N–O = 178.0(3) and 176.0(6)°) and to the two phosphorus donor sites of the ligand dppe. All the bond angles and distances are within expected ranges. The Fe–N and N–O bond lengths and N–Fe–N and Fe–N–O angles are in close agreement with those found in other iron dinitrosyl complexes containing linearly coordinated NO groups (Table 4). The Fe–P bond lengths of 2.253(2) Å compare favourably with similar distances in the corresponding isoelectronic complex [13] $Co(NO)_2(dppe)^+$ (Co–P = 2.249(3) and 2.244(3) Å). The P–Fe–P bite angle of 85.92(5)° is expected for this ligand (P–M–P = 87.8(9)° for $Co(NO)_2(dppe)^+$ [13], 86.3(1)° in $Ni(NO_2)_2(dppe)$ [14]).

The $Fe(NO)_2$ group is planar, the maximum deviation from this plane being 0.014 Å for atom N1. The N–Fe–N angle of 125.4° is larger than the O–Fe–O angle of 124.0°, indicating that the $Fe(NO)_2$ moiety adopts an 'attracto' conformation as usually observed for most iron dinitrosyl complexes except for $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)$-

TABLE 4. Distances (Å) and angles (°) in selected four-coordinate dinitrosyl metal complexes

| Compound | M–P | M–N | N–O | L–M–L | N–M–N | M–N–O | O–M–O | Reference |
|---|---|---|---|---|---|---|---|---|
| $Fe(NO)_2(dppe)$ | 2.253(2) | 1.658(5) | 1.185(7) | 85.92(5) | 125.4(2) | 178.0(3) | 124.0 | this work |
| | 2.253(2) | 1.651(4) | 1.200(5) | | | 176.0(6) | | |
| $[Fe(NO)_2Cl]_2(dppe)$ | 2.356(2) | 1.654(8) | 1.161(9) | 101.75(9) | 117.1(3) | 169.5(7) | 107.9 | this work |
| | | 1.707(8) | 1.156(8) | (L = P, Cl) | | 165.7(6) | | |
| $Fe(NO)_2L_2$<br>L = $[PhP(OCH_2CH_2)_2N(H)BPh_3]_2$ | 2.181(2) | 1.659(11) | 1.195(12) | 98.6(1) | 132.0(7) | 175.9(9) | 134.9(8) | 15 |
| $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ | 2.187(2) | 1.646(5) | 1.176(6) | 98.47(6) | 128.3(3) | 177.6(6) | 128.0(3) | 15 |
| | 2.193(2) | 1.638(5) | 1.194(6) | | | 177.9(5) | | |
| $Fe(NO)_2(PPh_3)_2$ | 2.267(2) | 1.650(7) | 1.190(10) | 111.9(1) | 123.8(4) | 178.2(7) | 122.4 | 5 |
| $Co(NO)_2(dppe)^+$ | 2.249(3) | 1.656(10) | 1.130(14) | 87.8(9) | 131.7(5) | 176.6(14) | 135.9(4) | 13 |
| | 2.244(3) | 1.671(11) | 1.142(13) | | | 172.3(15) | | |
| $Fe(NO)_2Cl(PPh_3)$ | 2.339(2) | 1.679(5) | 1.136(5) | 111.0(1) | 115.6(3) | 166.4(5) | not given | 4 |
| | | 1.681(5) | 1.163(7) | (L = P, Cl) | | 165.5(5) | | |

$BPh_3]_2$ [15] (Table 4). The angle between $Fe(NO)_2$ and $FeP_2$ planes is approximately 87°. The chelate ring is non-planar; the distances of atoms C25 and C26 from the $FeP_2$ plane are 0.740 and 0.033 Å respectively. The average $P{-}C(CH_2)$ distance of 1.851 Å is slightly longer than the $P{-}C(C_6H_5)$ distance of 1.831 Å as already observed in $Co(NO)_2(dppe)^+$ [13] and $Ni(NO_2)_2(dppe)$ [14].

### *Comparison of 2 and 4 in Relation to their Oxygenation*

Interesting and fruitful comparisons can be made between the structures of, on the one hand, $Fe(NO)_2(PPh_3)_2$ (**5**) [5] and $Fe(NO)_2(dppe)$ (**4**) and, on the other hand, $Fe(NO)_2Cl(PPh_3)$ (**6**) [4] and $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (**2**).

The coordination geometry adopted around iron is pseudotetrahedral with maximum deviation in **4** which, *a priori*, can be assigned to the small bite of dppe ($P{-}Fe{-}P = 85.92(5)°$). The larger N–Fe–N angle in **4** (125.4(2)°) as compared with **2** (117.1(3)°) would then be a consequence of this distortion. However, very similar changes are measured in the N–Fe–N angle on going from $Fe(NO)_2(PPh_3)_2$ (123.8(4)°) to $Fe(NO)_2Cl(PPh_3)$ (115.6(3)°) where no chelate effect occurs.

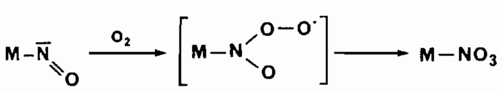
The nitrosyl groups are less linear in the chloro complexes ($M{-}N{-}O = 176.0(6)°$ and 178.0(3)° in **4**, 178.2(7)° in **5**, versus 169.5(7)° and 165.7(6)° in **2**, 166.4(5)° and 165.5(5)° in **6**). The Fe–N and Fe–P bonds are longer in the chloro complexes.

The greater bending of the nitrosyl groups and the longer M–N bonds in the chloro species indicate a greater amount of $NO^-$ character [13]. The larger N–M–N angle supports this picture.

Though the differences in structural parameters are in the order of a few standard deviations, we believe that they are real because of the chemical behavior of the complexes.

Hence, we have shown that oxidation by oxygen (1 atom) of the Fe–NO moiety in **2**, in the presence of dppe, results in the exclusive and rapid formation of the nitrato – and not the nitro – complex $Fe(NO_3)_2Cl(O_2dppe)$ [3] which parallels our obtention of $Fe(NO_3)_2Cl(OPPh_3)_2$ from $Fe(NO)_2Cl(PPh_3)$ in the presence of $PPh_3$ [1]. In marked contrast, a slow and intricate reaction occurs when **4** or **5** are submitted to dioxygen in the same conditions [3].

Two mechanisms have been proposed to be responsible for this formation of nitrate complexes from reaction of dioxygen with metal nitrosyls. The first one involves [16] an initial dissociation of nitric oxide from the complex and its capture by molecular oxygen. Thus, the production of $Co(NO_3)(dmgH)_2$ from $Co(NO)(dmgH)_2$ (dmgH = dimethylglyoximate $(1^-)$) and molecular oxygen [17] has been explained by nitric oxide dissociation. The second mechanism [18] postulates an electrophilic attack of oxygen on coordinated $NO^-$ ligand to produce a peroxynitrite intermediate followed by rearrangement (Scheme 2). It accounts well for the formation of nitrates from $Ir(NO)Cl(X)(CO)(PPh_3)_2$ [19] or $Pt(NO)(NO_3)(PPh_3)_2$ [18], which contain an $NO^-$ ligand.



Scheme 2.

The easier oxygenation of **2** and **6** together with their greater $NO^-$ character as compared to **4** and **5** is taken to indicate that the mechanism in Scheme 2 is likely to be responsible for the formation of nitrates in our Fe compounds.

## Supplementary Material

Tables containing crystallographic data for $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (**2**) and $Fe(NO)_2(dppe)$ (**4**), positional parameters, thermal parameters, bond angles and distances and least-square planes (7 pages for **2**; 8 pages for **4**); tables of observed and calculated structure factors (5 pages for **2**; 7 pages for **4**); figures illustrating the unit cell packing rearrangement for **2** (1 page) and for **4** (1 page) are available from the authors on request.

## Acknowledgement

We are grateful to the Centre National de la Recherche Scientifique for financial support of this work.

## References

1 F. Tomi, H. Li Kam Wah and M. Postel, *New J. Chem., 12* (1988) 289.
2 H. Li Kam Wah, M. Postel and F. Tomi, *Inorg. Chem., 28* (1988) 233.
3 H. Li Kam Wah and M. Postel, to be published.
4 J. Kopf and J. Schmidt, *Z. Naturforsch., Teil B, 30* (1975) 149.
5 V. G. Albano, A. Araneo, P. L. Bellon, G. Ciani and M. Manassero, *J. Organomet. Chem., 67* (1974) 413.
6 D. Ballivet-Tkatchenko, C. Billard and A. Revillon, *J. Polym Sci., 19* (1981) 1697.
7 B. A. Frenz, in H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld and G. C. Bassi (eds.), *Computing in Crystallography*, Delft University Press, The Netherlands, 1978, pp. 44–71.
8 P. Main, S. J. Fiske, S. E. Hall, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, *Multan 80*, a system

of computer programs for automatic solution of crystal structures from X-ray diffraction data, University of York, U.K. and University of Louvain, Belgium, 1980.

9 D. W. McBride, S. L. Stafford and F. G. Stone, *Inorg. Chem., 1* (1962) 386.

10 R. J. Mawby, D. Morris, E. M. Thorteinson and F. Basolo, *Inorg. Chem., 5* (1966) 27.

11 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev., 13* (1974) 339.

12 R. L. Martin and D. Taylor, *Inorg. Chem., 15* (1976) 2970.

13 J. A. Kaduk and J. A. Ibers, *Inorg. Chem., 16* (1977) 3283.

14 J. Kriege-Simondsen and R. D. Feltham, *Inorg. Chim. Acta, 71* (1983) 185.

15 G. Le Borgne, L. Mordenti, J. G. Riess and J. L. Roustan, *Nouv. J. Chim., 10* (1986) 97.

16 M. P. Doyle, R. Pickering, R. L. Dykstra and B. R. Cook, *J. Am. Chem. Soc., 104* (1982) 3392.

17 W. C. Trogler and L. G. Marzilli, *Inorg. Chem., 13* (1974) 1008.

18 S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal, R. Walters and C. Zuccaro, *J. Chem. Soc., Dalton Trans.,* (1981) 234.

19 M. Kubota and D. A. Phillips, *J. Am. Chem. Soc., 97* (1975) 5637.