

# Activation of molecular oxygen by iron nitrosyls in the presence of the bidentate phosphines 1,2-bis(diphenylphosphino)ethane and ethene

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## Abstract

Activation of molecular oxygen (1 atm, room temperature) by the nitrosyl dimer  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  in the presence of the bidentate phosphorus ligands PP (PP = 1,2-bis(diphenylphosphino)ethane, dppe, and 1,2-bis(diphenylphosphino)ethene, dppen) yields the nitrate molecular complexes  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{OPPO})$ , (2), while the ionic complexes  $[\text{FeCl}_4][\text{Fe}(\text{NO}_3)_2(\text{OPPO})_2]$ , (3) are obtained when  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-PP})$  is allowed to react with molecular oxygen. Complexes 2 and 3 transfer oxygen to phosphines. They catalyze the autoxidation of cyclohexene.

*Key words:* Activation; Molecular oxygen; Iron complexes; Nitrosyl complexes; Bidentate phosphine complexes

## Introduction

The selective incorporation of an oxygen atom into a substrate, particularly a hydrocarbon, is a key reaction both industrially and biologically. We have demonstrated that activation and transfer of molecular oxygen can be achieved on the Fe–NO and Fe–NO<sub>3</sub> couple through (i) splitting of dioxygen on a nitrosyl ligand coordinated to iron which results in the exclusive formation of nitrates and (ii) transfer of oxygen from these nitrates to olefins and phosphines [1, 2].

In our search for the best ligand environment for such a system, we became interested in the chelating or bridging diphosphines 1,2-bis(diphenylphosphino)ethane, dppe, *trans*- or *cis*-1,2-bis(diphenylphosphino)ethylene, tdppen or cdppen. We have already reported the reaction of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  (1) with these ligands to yield the binuclear complexes  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppe})$  (1a) and  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppen})$  (1c) [3]. The next step in our search, which is reported herein, was to determine whether the iron nitrosyl moiety, in the presence of such ligands, was still capable of both activating and transferring molecular oxygen.

## Results

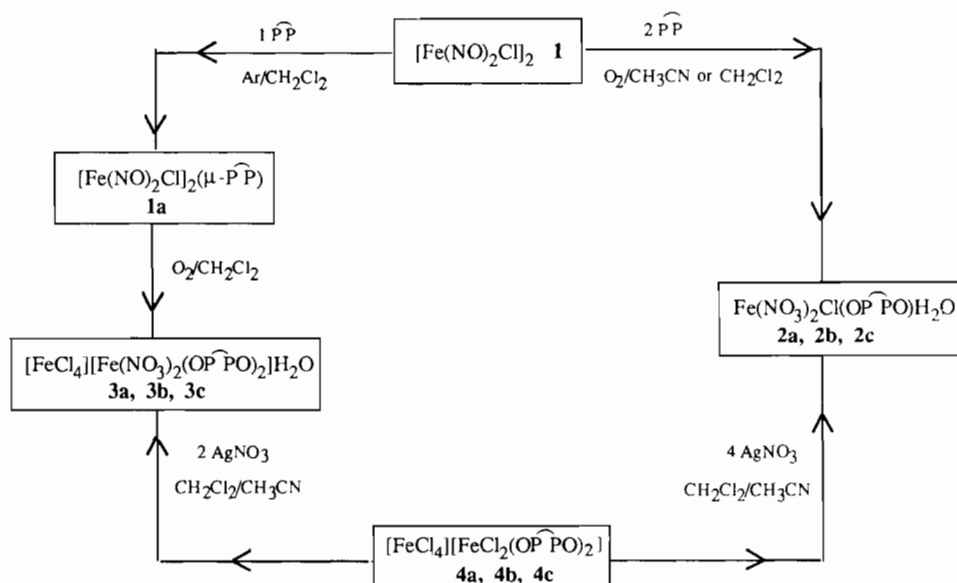
### *Preparation of nitrate iron complexes by O<sub>2</sub> oxidation of nitrosyl ligands*

The various nitrate complexes obtained in this study are illustrated in Scheme 1. Their analytical and spectral data are given in Table 1.

Bubbling oxygen through acetonitrile solutions of the chlorobisnitrosyl iron dimer  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  (1), at room temperature, in the presence of 2 equiv. of 1,2-bis(diphenylphosphino)ethane, dppe, caused a rapid change in colour from black to yellow in less than 5 min. After treatment of the reaction mixture, a yellow compound poorly soluble in the usual solvents, was isolated (76% yield); the analytical and spectral data for this compound indicate the formation of  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{dppe}) \cdot \text{H}_2\text{O}$  (2a). Conductivity measurements showed 2a to be non-ionic.

The oxidation of the nitrosyl ligand in 1 into coordinated nitrates in 2a is evidenced by IR spectroscopy (KBr pellets) which shows the complete disappearance of the nitrosyl vibrations while new absorptions, measured at 1514 and 1286 cm<sup>-1</sup>, are assignable to bound nitrates [4]. A vibration at 1385 cm<sup>-1</sup> detected only for KBr pellets is assigned to the NO<sub>3</sub><sup>-</sup> anion due to Br<sup>-</sup> anion exchange [5]. On the other hand, there is no IR spectral indication for the formation of nitro or

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Scheme 1.

nitrito groups and this is further supported by specific analysis of the  $\text{NO}_3$  and  $\text{NO}_2$  groups by the Griess reagent [6]. A vibration band at  $340 \text{ cm}^{-1}$  is assigned to the Fe-Cl moiety.

The simultaneous oxidation of the two phosphorus atoms of the ligand in **2a** is ascertained by a single  $\nu(\text{P}=\text{O})$  vibration at  $1165 \text{ cm}^{-1}$  ( $\nu(\text{P}=\text{O}) = 1180 \text{ cm}^{-1}$  in free  $\text{O}_2\text{dppe}$ ) together with the absence of the  $\nu(\text{P}-\text{C})$  characteristic for dppe ( $1097 \text{ cm}^{-1}$ ).

Compound **2a** is paramagnetic; the ESR signal, in a dichloromethane solution at room temperature, is measured at  $g = 2.021$  as a single line with no coupling of the electron with phosphorus, which is in agreement with the presence of a dioxygenated diphosphine [7].

The data for complex **2a** are all consistent with the structure illustrated in Scheme 2. An analogous structure with seven-coordinate iron and bidentate nitrate ligands was determined for  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{OPPh}_3)_2$  [1].

When the oxygenation of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  was conducted in the presence of 2 equiv. of *cis*- or *trans*-1,2-bis(diphenylphosphino)ethane, cdppen or tdppen, in dichloromethane or acetonitrile, the reaction yielded exclusively  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{cdppen})\cdot\text{H}_2\text{O}$  (**2b**) or  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{tdppen})\cdot\text{H}_2\text{O}$  (**2c**), which are analogues of **2a**. Contrary to compound **2b**, which is very soluble in dichloromethane and acetonitrile, **2c** is insoluble in all common organic solvents: this is consistent with a polymeric structure for **2c**, illustrated in Scheme 3, with the ligand, due to its *trans* configuration, forming a bridge between two iron atoms. The analytical and spectral data for **2b-2c** (Table 1) are consistent with the proposed formulations.

As expected from these results, the oxygenation of the binuclear complex  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppe})$ , in the

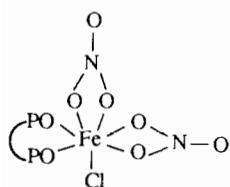
presence of 1 equiv. of dppe, yielded compound **2a** in high yields (92%).

On the other hand, the oxygenation of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppe})$  alone was found to be quite intricate: when oxygen was bubbled into solutions of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppe})$  in the absence of excess dppe, a rapid change in colour of the solution from purple to yellow-orange occurred together with the formation of a brown precipitate and brown fumes. From this latter brown precipitate, which represents *c.* 40% of the starting iron, no definite species could be identified in our hands: its IR print showed no vibration in the region assigned to the Fe-NO moiety, while vibrations measured at 3375, 875 and  $680 \text{ cm}^{-1}$  were taken to indicate the formation of hydrated  $\mu$ -oxo peroxy iron species [8, 9].

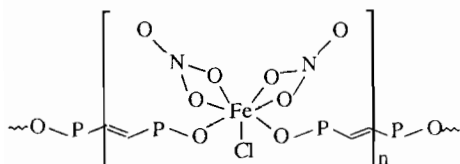
The IR spectrum (KBr pellets) of the yellow-orange complex **3a**, obtained from the solution and which accounted for 45% of the starting iron, showed vibrations characteristic for the coordinated diphosphine dioxide ligand  $\text{O}_2\text{dppe}$  and in particular a shifted  $\nu(\text{P}=\text{O})$  at  $1144 \text{ cm}^{-1}$ , and new bands at 1526, 1283 and  $804 \text{ cm}^{-1}$ , in the regions which are generally assigned to bidentate nitrates [4]. Further, a broad and intense vibration at  $380 \text{ cm}^{-1}$  was taken to indicate the presence of the  $[\text{FeCl}_4]^-$  anion in complex **3a** [10]. The ionic nature of **3a** was further confirmed by conductivity measurements in  $\text{CH}_3\text{CN}$  where it was found to behave as a 1:1 electrolyte. Compound **3a** is paramagnetic; the ESR spectrum of a  $\text{CH}_2\text{Cl}_2$  solution of **3a** at room temperature shows a singlet at  $g = 2.018$ , again consistent with a dioxygenated diphosphine ligand [7]. Both the spectral and analytical data for **3a** indicate the  $[\text{FeCl}_4][\text{Fe}(\text{NO}_3)_2(\text{O}_2\text{dppe})_2]$  formulation.

TABLE 1. Elemental analysis, IR and conductivity data for compounds 2–4

Complex	Anal.: found (calc.) (%)				IR (cm <sup>-1</sup> ) (KBr pellets)			Conductivity (CH <sub>3</sub> CN) $\Lambda$ ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> )			
	C	H	N	Cl	Fe	P	$\nu(\text{NO}_3)$		$\nu(\text{P}=\text{O})$	$\nu(\text{P}-\text{C})$	$\nu(\text{FeCl})$
Fe(NO <sub>3</sub> ) <sub>2</sub> Cl(O <sub>2</sub> dppe) · H <sub>2</sub> O ( <b>2a</b> )	46.6 (47.0)	3.9 (3.9)	4.2 (4.2)	5.5 (5.3)			1514; 1286	1165	1130	340	60
Fe(NO <sub>3</sub> ) <sub>2</sub> Cl( <i>r</i> -O <sub>2</sub> dppen) · H <sub>2</sub> O ( <b>2c</b> )	47.8 (47.2)	4.0 (3.6)		6.0 (5.3)			1516; 1286	1178; 1142	1123	326	
Fe(NO <sub>3</sub> ) <sub>2</sub> Cl( <i>cis</i> -O <sub>2</sub> dppen) · H <sub>2</sub> O ( <b>2b</b> )				5.2 (5.3)	7.5 (8.4)	8.2 (9.3)	1522; 1285	1138	1123	331	47.3
Fe(NO <sub>3</sub> )Cl <sub>2</sub> (O <sub>2</sub> dppe) · H <sub>2</sub> O ( <b>3a</b> )	49.1 (49.0)	4.0 (4.1)	2.3 (2.2)	11.3 (11.1)	7.8 (8.7)		1526; 1283; 804	1144	1128	380	103.1
Fe(NO <sub>3</sub> )Cl <sub>2</sub> ( <i>trans</i> -O <sub>2</sub> dppen) · H <sub>2</sub> O ( <b>3c</b> )		3.2 (2.2)	10.0 (11.1)	8.2 (8.8)	8.3 (9.7)		1516; 1277	1178	1136	356	
Fe(NO <sub>3</sub> )Cl <sub>2</sub> ( <i>cis</i> -O <sub>2</sub> dppen) · H <sub>2</sub> O ( <b>3b</b> )		2.6 (2.2)	11.4 (11.1)	8.6 (8.8)	8.9 (9.7)		1522; 1288	1138	1123	382	80
FeCl <sub>3</sub> O <sub>2</sub> dppe ( <b>4a</b> )				17.9 (17.9)	8.9 (9.4)	10.3 (10.4)		1169	1130	386	91.5
FeCl <sub>3</sub> O <sub>2</sub> tdppen ( <b>4c</b> )	52.9 (52.9)	3.8 (3.7)		17.3 (18.0)	9.7 (9.4)	10.4 (10.5)		1148	1123	380	
FeCl <sub>3</sub> <i>cis</i> -O <sub>2</sub> dppen ( <b>4b</b> )	53.1 (52.9)	3.7 (3.7)		17.8 (18.0)	8.7 (9.4)	10.3 (10.5)		1144	1121	380	75.5



Scheme 2.



Scheme 3.

Specific analysis of  $\text{NO}_3$  and  $\text{NO}_2$  groups by the Griess reagent [6] confirmed the presence of only nitrates (absence of even traces of nitrites) in complexes **2** and **3**. The formulations for compounds **2** and **3** were definitely confirmed through independent syntheses: **2** and **3** are easily obtained when the  $[\text{FeCl}_4][\text{FeCl}_2(\text{OPPO})_2]$  complexes are allowed to react with 2 or 4 equiv. of  $\text{AgNO}_3$ , respectively.

#### Oxygen transfer from the iron nitrate complexes **2** and **3**

The  $\text{O}_2\text{dppe}$  and  $\text{O}_2\text{cdppen}$  nitrate complexes **2** and **3** were found to be most reluctant to react stoichiometrically with olefins under anaerobic conditions. No reaction was observed between **2** or **3** and cyclohexene (olefin/Fe = 10/1) after 72 h at room temperature under argon; the unaltered nitrate complexes were quantitatively recovered.

On the other hand, **2** and **3** were found to react rapidly with phosphines in the absence of oxygen. Thus, when the nitrate complexes, in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  solutions, were allowed to react with  $\text{PPh}_3$  (tenfold excess) under argon at room temperature, a rapid change of colour from yellow to deep orange was observed. IR monitoring of the reaction showed the rapid disappearance of the  $\text{NO}_3$  vibrations together with the appearance of the band due to  $\text{OPPh}_3$  ( $\nu_{\text{P}=\text{O}} = 1188 \text{ cm}^{-1}$ ). The formation of  $\text{OPPh}_3$  is further confirmed through  $^{31}\text{P}$  NMR where the signal for free  $\text{OPPh}_3$  is easily detected at 23 ppm. Besides the formation of  $\text{OPPh}_3$ , the reaction gives a mixture of iron complexes which we could not isolate for further characterization.

The IR print of the iron residue of the reaction of complexes **2** or **3** with triphenylphosphine showed no vibration in the  $1650\text{--}1850 \text{ cm}^{-1}$  region attributable to the NO vibrator. On the other hand, new bands were measured at  $1385$ ,  $1330$  and  $850 \text{ cm}^{-1}$  (for **2a**) in the regions attributable to  $\nu(\text{NO}_2)_{\text{asym}}$ ,  $\nu(\text{NO}_2)_{\text{sym}}$  and  $\delta(\text{NO})_2$ , respectively, through comparison with the IR

data for various  $\text{Ni}(\text{NO}_2)_2\text{L}_2$  (L = phosphorous ligands) complexes [11]. However, specific analysis indicated the presence of only traces of  $\text{NO}_2$ .

#### Complexes **2** and **3** as catalysts in cyclohexene oxidation

The nitrate complexes **2** and **3** are nonetheless catalysts in the oxidation of cyclohexene by molecular oxygen. They catalyze the aerobic oxidation of cyclohexene to mainly 2-cyclohexene-1-one and 2-cyclohexene-1-ol; cyclohexeneoxide being formed only in trace amounts. It is noteworthy that  $[\text{FeCl}_4][\text{FeCl}_2(\text{O}_2\text{dppe})_2]$  (**4a**) was found to be inactive in this reaction indicating that the  $\text{NO}_3$  ligand does play a role in the catalysis.

The alkene conversion and the distribution of the reaction products were found to depend mainly on the solvent and, to a lesser extent, on the nature of the iron catalyst (Table 2): acetonitrile brought higher activities than dichloromethane and appears to favour formation of the ketone. Among all the systems studied in this work, the highest conversion is obtained in the presence of **2b** in acetonitrile together with the highest selectivity for the ketone: 2-cyclohexene-1-one (70%), 2-cyclohexene-1-ol (30%). For all our nitrate complexes, the main product is the  $\alpha,\beta$ -unsaturated ketone showing that allylic oxidation is the main process [12–14].

## Discussion

### Activation of oxygen

The reaction of molecular oxygen with the iron nitrosyl dimer **1**, in the presence of the bidentate PP ligands dppe or dppen, produces the molecular dinitrate complexes **2**  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{OPPO})$ , where (i) the nitrosyl ligand has been oxidized into a nitrate ligand and (ii) the diphosphine ligand has been oxidized to coordinated diphosphine dioxide. The same nitrate complexes **2** are selectively formed when the  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-PP})$  dimer is allowed to react with oxygen in the presence of excess PP ligand. Complexes **2** are analogous to  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{OPPh}_3)_2$  which we obtained in the presence of  $\text{PPh}_3$  [1].

On the other hand, the oxygenation of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-PP})$  produces the ionic nitrates  $[\text{FeCl}_4][\text{Fe}(\text{NO}_3)_2(\text{OPPO})_2]$  (**3**), which account for 45% of the starting iron. The formation of ionic complexes analogous to **3** was not observed in the presence of monophosphines [1].

Two mechanisms have been proposed to be responsible for the formation of nitrate complexes from the reaction of dioxygen with metal nitrosyls. The first one involves an initial dissociation of nitric oxide from the complex and its capture by molecular oxygen [15]. The second mechanism postulates an electrophilic attack of

TABLE 2. O<sub>2</sub> oxidation of cyclohexene catalyzed by iron nitrate complexes at room temperature after 72 h<sup>a</sup>

Complex	Solvent	Distribution of the oxygenated products <sup>b</sup> (%) <sup>c</sup>		Turnover <sup>d</sup>
		alcohol	ketone	
Fe(NO <sub>3</sub> ) <sub>2</sub> Cl(O <sub>2</sub> dppe)·H <sub>2</sub> O (2a)	CH <sub>2</sub> Cl <sub>2</sub>	39	61	19
	CH <sub>3</sub> CN	30	70	50
Fe(NO <sub>3</sub> ) <sub>2</sub> Cl( <i>cis</i> -O <sub>2</sub> dppen)·H <sub>2</sub> O (2b)	CH <sub>2</sub> Cl <sub>2</sub>	34	66	31
	CH <sub>3</sub> CN	30	70	78
[FeCl <sub>4</sub> ][Fe(NO <sub>3</sub> ) <sub>2</sub> (O <sub>2</sub> dppe) <sub>2</sub> ]·H <sub>2</sub> O (3a)	CH <sub>2</sub> Cl <sub>2</sub>	42	58	15
	CH <sub>3</sub> CN	28	72	48
[FeCl <sub>4</sub> ][Fe(NO <sub>3</sub> ) <sub>2</sub> ( <i>cis</i> -O <sub>2</sub> dppen) <sub>2</sub> ]·H <sub>2</sub> O (3b)	CH <sub>2</sub> Cl <sub>2</sub>	35	64	32
	CH <sub>3</sub> CN	30	68	36

<sup>a</sup>Reaction conditions: O<sub>2</sub> (1 atm); [complex] = 2 × 10<sup>-2</sup> M; [cyclohexene]/[complex] = 100. <sup>b</sup>Identified by GC-MS coupling. <sup>c</sup>GC determination using octane as internal standard. <sup>d</sup>Turnover = moles of products/moles of complex.

oxygen on the coordinated NO<sup>-</sup> ligand [16]. The nitrosonium character of the NO groups in [Fe(NO)<sub>2</sub>Cl]<sub>2</sub>(μ-dppe), as evidenced by the Fe–N–O angles of *c.* 169° [3a], is in contradiction with this second mechanism and we believe that, in our nitrosyl complexes, the first mechanism, i.e. dissociation of NO prior to oxygenation, is predominant.

NO dissociation from [Fe(NO)<sub>2</sub>Cl]<sub>2</sub>(μ-dppe) or [Fe(NO)<sub>2</sub>Cl]<sub>2</sub>, if it occurs, creates an unsaturation on iron and this is to favour a direct attack of oxygen on the metal centre: this could be responsible for the observed formation of superoxo-, peroxy- or oxo-iron species when [Fe(NO)<sub>2</sub>Cl]<sub>2</sub>(μ-dppe) alone is allowed to react with molecular oxygen. The influence of excess dppe ligand, in our oxygenation reactions, would then result from its coordination to iron with the consequences of (i) favouring NO dissociation, and (ii) hindering direct attack of oxygen on the metal. Both effects contribute to the selectivity of the reaction: thus, in the presence of excess diphosphine (P/Fe: 2/1), the oxygenation of the Fe–NO moiety selectively afforded high yields of the iron dinitrates 2.

#### Oxidation reactions

In our work, olefins are preferentially oxidized into the α,β-unsaturated ketone showing that allylic oxidation is the main process. The selectivity found for cyclohexene is characteristic of its autooxidation, a reaction that has long been known to be catalyzed by transition-metal complexes [12–14]. The main oxidation pathway by molecular oxygen involves a radical mechanism with formation of a hydroperoxide and its further decomposition induced by the metal centre.

The nitrate ligands in both the ionic [FeCl<sub>4</sub>][Fe(NO<sub>3</sub>)<sub>2</sub>(OPPO)<sub>2</sub>] (3) and molecular Fe(NO<sub>3</sub>)<sub>2</sub>-Cl(OPPO) (2) complexes are capable of transferring oxygen to phosphines. This oxygen transfer does not

regenerate the nitrosyl moiety. This is in marked contrast with what we have observed in the presence of monodentate phosphorus ligands: oxygen transfer from Fe(NO<sub>3</sub>)<sub>2</sub>Cl(HMPA)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>Cl(OPPh<sub>3</sub>)<sub>2</sub> or Fe(NO<sub>3</sub>)Cl<sub>2</sub>(HMPA) yields nitrosyls [1, 2]. Although further work is required to understand and improve the reactivity found for these nitrate complexes, our results seem to indicate that the nitrate groups in 2 or 3, through oxygen transfer to PPh<sub>3</sub>, could be transformed into nitro or nitrito groups. That only small amounts of Fe–NO<sub>2</sub> were found to be left after oxygen transfer from the Fe–NO<sub>3</sub> moiety in 2 or 3, is likely to be due to the known instability of iron nitrites; they could only be isolated in the case of iron picket-fence porphyrin complexes where the ligand-binding site is protected [17].

This tentative Fe–NO<sub>3</sub> to Fe–NO<sub>2</sub> transformation opens up a new alternative for the O<sub>2</sub> oxidation of organic substrates based on the M–NO<sub>3</sub>/M–NO<sub>2</sub> redox couples.

#### Experimental

##### General procedures

All experiments were carried out under argon or oxygen atmosphere using Schlenk tube techniques. Solvents were purified by published procedures and stored under argon. The ligands 1,2-bis(diphenylphosphino)ethane, dppe, *trans*-1,2-bis(diphenylphosphino)ethene, tdppen and *cis*-1,2-bis(diphenylphosphino)ethene, cdppen were purchased from Aldrich; their reaction with Me<sub>3</sub>NO afforded quantitative yields of the corresponding oxides O<sub>2</sub>dppe, O<sub>2</sub>tdppen and O<sub>2</sub>cdppen. AgNO<sub>3</sub> and PPh<sub>3</sub> were purchased from Aldrich and Fluka, respectively. [Fe(NO)<sub>2</sub>Cl]<sub>2</sub> [18] and the

$[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-PP})$  complexes [3] (**1a**) (PP = dppe) were prepared according to the literature.

IR spectra were recorded as KBr pellets or Nujol mulls 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.  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WH 90 spectrometer.  $^{31}\text{P}$  chemical shifts are given in ppm downfield from external  $\text{H}_3\text{PO}_4$ . Conductivity measurements were obtained with a Tacussel CDN6 conductometer. Elemental analyses were performed by the Service Central de Microanalyses of the CNRS. The analytical and spectral data are gathered in Table 1.

$\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{dppe})$  (**2a**),  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{cdppen})$  (**2b**) and  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{tdppen})$  (**2c**) from  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$

Dppe (1.342 g, 3.49 mmol) was added to a solution of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  (0.53 g, 1.75 mmol) in 50 ml of acetonitrile. Oxygen was bubbled through the solution at room temperature for 1 h, resulting in a colour change from black to orange–yellow. The reaction mixture was filtered and the solvent evaporated to dryness. The yellow powder was washed with pentane and dried under vacuum to yield 1.76 g of **2a** (76%). ESR ( $\text{CH}_2\text{Cl}_2$ , r.t.):  $g = 2.021$ .

The same procedure was applied to 0.64 g (1.61 mmol) of cdppen and 0.24 g (0.79 mmol) of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  in 50 ml of  $\text{CH}_2\text{Cl}_2$  to yield 0.60 g of  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{cdppen})$  (**2b**) (58%), and 0.495 g (1.25 mmol) of tdppen and 0.189 g (0.62 mmol) of  $[\text{Fe}(\text{NO})_2\text{Cl}]_2$  in 30 ml of  $\text{CH}_2\text{Cl}_2$  to yield 0.34 g of  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{tdppen})$  (**2c**) (42%). ESR ( $\text{CH}_2\text{Cl}_2$ , r.t.):  $g = 2.01$ .

$\text{Fe}(\text{NO}_3)\text{Cl}_2(\text{O}_2\text{dppe})$  (**3a**) from  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-PP})$  (**1a**) (PP = dppe)

Oxygen was bubbled through a dichloromethane solution (50 ml) of the purple  $[\text{Fe}(\text{NO})_2\text{Cl}]_2(\mu\text{-dppe})$  complex (0.2 g, 0.285 mmol) at room temperature for 15 min, resulting in a colour change to yellow. The reaction mixture was filtered and the solvent evaporated to dryness. The yellow powder thus obtained was washed with  $2 \times 20$  ml of pentane and dried under vacuum, to yield 0.82 g of **3a** (45%). ESR ( $\text{CH}_2\text{Cl}_2$ , r.t.):  $g = 2.018$ .

*Synthesis of  $\text{O}_2\text{dppe}$ ,  $\text{O}_2\text{cdppen}$  and  $\text{O}_2\text{tdppen}$*

The dppe and dppen dioxides were prepared through reaction of dppe or dppen with trimethylamine oxide following the published procedure [19].

$\text{O}_2\text{dppe}$ :  $^{31}\text{P}$  ( $\text{CDCl}_3$ , ppm):  $\delta = 32.8$ ; IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu(\text{P}=\text{O}) = 1188$ .

$\text{O}_2\text{-cis-dppen}$ :  $^{31}\text{P}$  ( $\text{CDCl}_3$ , ppm):  $\delta = 21$ ; IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu(\text{P}=\text{O}) = 1198$ .

$\text{O}_2\text{-trans-dppen}$ :  $^{31}\text{P}$  ( $\text{CDCl}_3$ , ppm):  $\delta = 22$ ; IR (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu(\text{P}=\text{O}) = 1186$ .

*Synthesis of  $\text{FeCl}_3\text{O}_2\text{dppe}$  (**4a**),  $\text{FeCl}_3\text{O}_2\text{cdppen}$  (**4b**) and  $\text{FeCl}_3\text{O}_2\text{tdppen}$  (**4c**)*

A solution of  $\text{O}_2\text{dppe}$  (1.24 g, 2.87 mmol) in dichloromethane (80 ml) was added dropwise with stirring to a solution of anhydrous iron(III) chloride (0.466 g, 2.87 mmol) in dichloromethane (70 ml). After 3 h, the orange solution was evaporated to dryness. The orange residue was washed with dichloromethane and pentane and dried under vacuum to yield 1.39 g of **4a** (82%). ESR ( $\text{CH}_2\text{Cl}_2$ , r.t.):  $g = 2.006$ .

The same experimental procedure was applied to the synthesis of **4b** and **4c**.

**4b**: 0.494 g of  $\text{FeCl}_3$  (3.05 mmol), 1.3 g of  $\text{O}_2\text{cdppen}$  (3.03 mmol) in 200 ml of  $\text{CH}_2\text{Cl}_2$ . Yield 1.5 g, 83%.

**4c**: 0.186 g of  $\text{FeCl}_3$  (1.15 mmol), 0.49 g of  $\text{O}_2\text{tdppen}$  (1.16 mmol) in 120 ml of  $\text{CH}_2\text{Cl}_2$ . Yield 0.57 g, 84%.

*Direct synthesis of  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{dppe})$  (**2a**),  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{cdppen})$  (**2b**),  $\text{Fe}(\text{NO}_3)_2\text{Cl}(\text{O}_2\text{tdppen})$  (**2c**),  $\text{Fe}(\text{NO}_3)\text{Cl}_2(\text{O}_2\text{dppe})$  (**3a**),  $\text{Fe}(\text{NO}_3)\text{Cl}_2(\text{O}_2\text{cdppen})$  (**3b**) and  $\text{Fe}(\text{NO}_3)\text{Cl}_2(\text{O}_2\text{tdppen})$  (**3c**)*

A solution of silver nitrate (0.298 g, 1.75 mmol) in acetonitrile (30 ml) was added dropwise to a solution of **4a** (0.531 g, 0.896 mmol) in acetonitrile (500 ml) to result in instantaneous precipitation of AgCl. The suspension was stirred for 1 h. The reaction mixture was filtered and the solvent evaporated to dryness. The yellow residue was washed with pentane and dried under vacuum to yield 0.45 g of **2a** (76%). The same experimental procedure was applied to prepare **2b–c** and **3a–c**.

**2b**: 0.41 g of  $\text{AgNO}_3$  (2.4 mmol), 0.7 g of **4b** (1.2 mmol). Yield 0.69 g, 88%.

**2c**: 0.323 g of  $\text{AgNO}_3$  (1.88 mmol) 0.576 g of **4c** (0.98 mmol). Yield 0.017 g, 3%.

**3a**: 0.076 g of  $\text{AgNO}_3$  (0.45 mmol), 0.27 g of **4a** (0.45 mmol). Yield 0.12 g, 41%.

**3b**: 0.07 g of  $\text{AgNO}_3$  (0.41 mmol), 0.25 g of **4b** (0.42 mmol). Yield 0.16 g, 59%.

**3c**: 0.078 g of  $\text{AgNO}_3$  (0.46 mmol), 0.295 g of **4c** (0.5 mmol). Yield 0.033 g, 10%.

*General procedure for the oxidation tests*

To a solution of the iron complex to be tested were added about 100 equiv. of cyclohexene together with n-octane as an internal standard for GC measurements. The resulting solution was stirred under an atmosphere of oxygen and the formation of the oxidation products monitored by GC analysis of aliquot samples. The oxygenated products were identified by GC-MS coupling

and comparison of the mass spectra with those of authentic samples.

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