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Reactivity of 2-(diphenylphosphino)pyridine and 2-(diphenylphosphine oxide)pyridine towards iron nitrosyl complexes and its relevance to oxygen activation

Patricia Guillaume, Michèle Postel *

Laboratoire de Chimie Moléculaire, Unité Associée au C.N.R.S. No. 426, Université de Nice, 06108 Nice Cedex 2, France

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Abstract

The nitrosyl dimer $[Fe(NO)_2Cl]_2$ (**1**) in the presence of 2-(diphenylphosphino)pyridine (PN) yields the $[Fe(NO)_2Cl(PPh_2py)]$ (**2**) complex in which the PN ligand is bound to iron monodentate through its phosphorus atom. **2** is unstable and rapidly evolves to $[Fe(NO)Cl(OPPh_2py)]$ (**3**): coordination of the nitrogen atom of the PN ligand results in NO substitution and oxygenation of the PN ligand to the bidentate 2-(diphenylphosphine oxide)pyridine (OPN). The same compound **3** is obtained when **1** is allowed to react with the OPN ligand. Oxidation by oxygen (1 atm) of the Fe–NO moiety in **2**, **3** or **1** in the presence of PN or OPN, results in the formation of the nitrato complex $Fe(NO_3)_2Cl(OPN)$ (**4**).

Keywords: Oxygen activation; Iron complexes; Nitrosyl complexes; Phosphino-pyridine complexes

1. Introduction

The oxidation of organic compounds by molecular oxygen catalyzed by transition-metal complexes is attracting considerable attention [1]. Recently, we have reported that the iron nitrate/iron nitrosyl couple could constitute a new alternative for the activation and transfer of molecular oxygen [2–5] through (i) splitting of dioxygen on a nitrosyl ligand coordinated to iron, which results in the exclusive formation of iron nitrates followed by (ii) oxygen transfer from these nitrates to olefins and phosphines.

Our results showed that the pentacoordinated $Fe(NO_3)_2Cl(OPPh_3)_2$ nitrato complex is capable of olefin epoxidation [2], while the tetracoordinated $Fe(NO_3)_2Cl(HMPA)$ [3] has lost all oxidizing property: we took this to indicate that a key factor for the oxygenation step is a high electron density on the $Fe(NO_3)_2$ moiety. On the other hand, the oxygen transfer from $Fe(NO_3)_2Cl(OPPh_3)_2$ to a substrate was shown to generate, as the reduced iron complex, the pentacoordinated 19-electron nitrosyl complex $Fe(NO_2)Cl(OPPh_3)_2$: this compound was found to be poorly stable and to encounter side-reactions leading to the termination of the Fe–NO/Fe–NO_3 catalytic cycle.

From these results, it appeared that an efficient oxidation catalytic cycle, based on the Fe–NO/Fe–NO_3 redox couple and oxygen as the oxidizing agent, does imply that these side-reactions can be prevented: this, in our opinion, could be made either by stabilizing the reduced 19-electron nitrosyl $Fe(NO)_2XL_2$ species, or by designing a new catalytic system implying assistance of the ancillary ligand L. We thus became interested in versatile bidentate ligands with two different coordination sites: we were searching for an AB ligand that would be (i) monodentate through A towards the formally (−I) iron atom of the $Fe(NO)_2Cl$ moiety and, therefore, generate a stable 17-electron nitrosyl $Fe(NO)_2Cl(A\text{-}B)$ complex, and (ii) bidentate through both A and B when coordinated to Fe(III) and, thus, afford an $Fe(NO_3)_2Cl(A\text{-}B)$ nitrate with sufficient electron density on iron to possess good oxygen transfer properties. With such an AB ligand, the catalytic cycle illustrated in Scheme 1 was expected to allow efficient O_2 epoxidation of alkenes.

We report here the reactivity of the iron nitrosyl dimer **1**, $[Fe(NO)_2Cl]_2$, in the presence of 2-(diphenylphosphino)pyridine (PN) and 2-(diphenylphosphine oxide)pyridine (OPN). These ligands appeared as promising candidates for our approach: a monodentate be-

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* Corresponding author.

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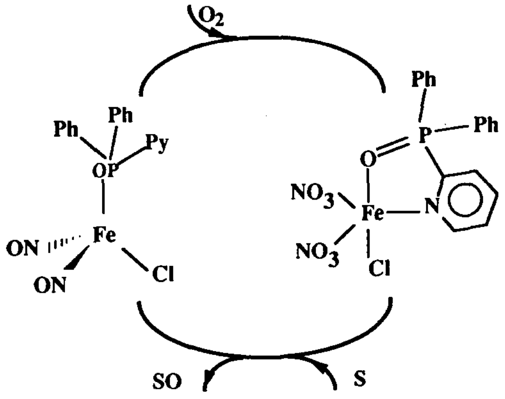


Scheme 1.

haviour has indeed been reported for the related cyclamphosphorane and cyclamphosphorane oxide ligands towards the $Fe(NO)_2Cl$ moiety [6].

2. Experimental

All experiments were carried out under nitrogen, argon or oxygen atmosphere using Schlenk tube techniques. Reagent grade solvents were purified by published procedures and stored under nitrogen. Trimethylamine oxide (Aldrich) was sublimed prior to use. The dimer $[Fe(NO)_2Cl]_2$ (**1**) [7] and the 2-(diphenylphosphino)pyridine ligand (PN) [8] were prepared according to the literature; reaction of the PN ligand with trimethyl amine oxide following a published procedure [6] afforded quantitative yields of 2-(diphenylphosphine oxide)pyridine (OPN).

Elemental analyses were performed by the Service Central de Microanalyses of the CNRS. IR spectra were recorded 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.

2.1. Synthesis of $[Fe(NO)_2Cl(PN)]$ (2)

0.30 g (1.14 mmol) of 2-(diphenylphosphino)pyridine was added to a solution of 0.18 g (0.59 mmol) of $[Fe(NO)_2Cl]_2$ (**1**) in toluene (50 ml) resulting in an immediate colour change of the brown reaction mixture to dark blue. After complete addition (15 min), the solution was evaporated to dryness to yield a dark blue powder which was washed thoroughly with pentane and dried under vacuum (0.45 g; 91%). *Anal.* Calc. for $FeClN_3O_2PC_{17}H_{14}$: Fe, 13.47; Cl, 8.55; N, 10.13; P, 7.48; C, 49.24; H, 3.40. Found: Fe, 13.7; Cl, 8.7; N, 9.2; P, 7.4; C, 48.0; H, 3.3%. IR (KBr pellets, cm^{-1}): ν(NO), 1792, 1726; ν(C=C, C=N), 1570, 1560; ν(P–C), 1097; ν(Fe–Cl), 326. ESR (CH_2Cl_2, r.t.): $g=2.008$; $a\langle ^{31}P\rangle = 62$ G. ^{31}P NMR (CH_2Cl_2, r.t., ppm): $\delta=65$.

2.2. Synthesis of $[Fe(NO)Cl(OPN)]$ (3)

To a solution of 0.097 g (0.32 mmol) of $[Fe(NO)_2Cl]_2$ (**1**) in toluene (30 ml), 0.18 g (0.64 mmol) of 2-(diphenylphosphine oxide)pyridine was added. The reaction mixture was stirred at r.t. for 2 h and filtered. The filtrate was evaporated to dryness and the brown residue was washed with pentane and dried under vacuum (0.20 g; 72%). *Anal.* Calc. for $FeClN_2O_2PC_{17}H_{14}$: Fe, 13.94; Cl, 8.85; N, 6.98; P, 7.74. Found: Fe, 13.9; Cl, 9.5; N, 6.7; P, 7.3%. IR (KBr pellets, cm^{-1}): ν(NO), 1771; ν(C=C, C=N), 1587 (broad); ν(P=O), 1146; ν(OP–C), 1121; ν(Fe–Cl), 322. ^{31}P NMR (CH_2Cl_2, r.t., ppm): $\delta=30$.

2.3. Synthesis of $[Fe(NO_3)_2Cl(OPN)]$ (4)

From the iron nitrosyl dimer $[Fe(NO)_2Cl]_2$ (1). To a solution of 0.48 g (1.58 mmol) of $[Fe(NO)_2Cl]_2$ (**1**) in toluene (60 ml), 0.85 g (3.2 mmol) of 2-diphenylphosphine)pyridine was added, and oxygen was bubbled through the resulting solution for 1 h. The reaction mixture was filtered. The filtrate was evaporated to dryness and the yellow residue was washed with pentane and dried under vacuum. (1.15 g; 70%). *Anal.* Calc. for $FeClN_3O_7PC_{17}H_{14}$: Fe, 10.90; Cl, 6.92; N, 8.20; P, 6.05. Found: Fe, 10.8; Cl, 6.9; N, 8.1; P, 6.4%. IR (KBr pellets, cm^{-1}): $\nu(NO_3)$, 1534, 1275, 828; ν(C=C, C=N), 1589 (broad); ν(P=O), 1167; ν(OP–C), 1124; ν(Fe–Cl), 326.

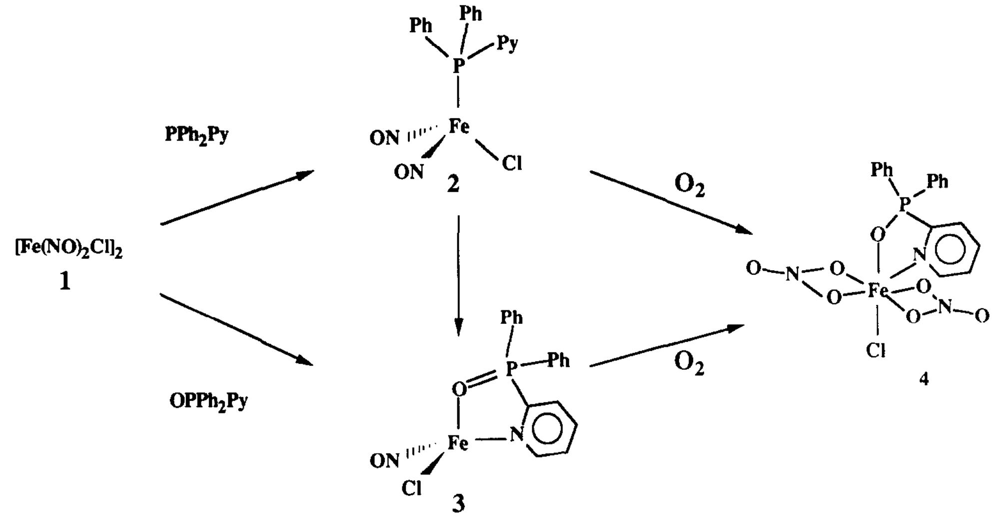
The same procedure was applied to 0.104 g (0.34 mmol) of $[Fe(NO)_2Cl]_2$ (**1**) and 0.19 g (0.68 mmol) of 2-(diphenylphosphine oxide)pyridine to yield 0.24 g of **4** (68%).

From the nitrosyl complexes 2 or 3. Oxygen (1 atm) was bubbled through a toluene (30 ml) solution of 0.12 g (0.29 mmol) $[Fe(NO)_2Cl(PN)]$ (**2**) for 1 h. The reaction mixture was filtrated, the yellow filtrate was evaporated to dryness and the resulting yellow powder thoroughly washed with pentane and dried under vacuum (0.11 g; 72%).

The same procedure when applied to 0.27 g (0.96 mmol) of **3** in 50 ml toluene, afforded 0.16 g of **4** (34%).

3. Results

The complexes used in this study are illustrated in Scheme 2.



Scheme 2.

3.1. Nitrosyl 2-(diphenylphosphino)pyridine and 2-(diphenylphosphine oxide)pyridine complexes

When 2-(diphenylphosphino)pyridine (PN) was allowed to react with **1**, $[Fe(NO)_2Cl]_2$, in a Fe/P ratio of 1/1, a dark blue complex **2** formed; the $Fe(NO)_2Cl(PN)$ formulation for **2** was supported by its analytical and spectroscopic data. The IR data showed two NO absorptions at 1792 and 1726 cm^{-1} and a single Fe–Cl vibration at 326 cm^{-1}; coordination of the PN ligand was characterized by ν(P–C) at 1097 cm^{-1} while the bands for the aromatic C=C and C=N vibrations were found to be unmodified with respect to the free ligand. These IR data indicate that the PN ligand in **2** is monodentate and bound to iron by its phosphorus atom only. Complex **2** is paramagnetic and its ESR spectrum, in CH_2Cl_2 at room temperature, shows a doublet at $g=2.008$: the hyperfine coupling constant of 62 G, which we attribute to one ^{31}P atom, is close to that found in $Fe(NO)_2Cl(PPh_3)$ [9]. The ^{31}P NMR spectrum for **2** could nevertheless be recorded to present one signal at 65 ppm.

Compound **2** is the only species that could be isolated (30%) in our hands when **1** was reacted with the PN ligand in a Fe/P = 2/1 ratio: no evidence could be found for a binuclear complex where the PN ligand would act as a disymmetrical bridge between two $Fe(NO)_2Cl$ moieties.

Adduct **2** is unstable in solution: toluene solutions of **2**, at room temperature under strictly controlled argon atmosphere, were found to gradually change colour from dark blue to brown. After 12 h, **2** had been totally converted into the brown complex **3**.

The presence in the IR spectrum of **3** of a strong vibration at 1146 cm^{-1} assignable to a coordinated phosphoryl group (ν(P=O) = 1202 cm^{-1} in free OPN) was taken to indicate that the PN ligand had been oxidized; this was further supported by the position of the ν(P–C) vibration at 1121 cm^{-1} in the region assignable to a coordinated OP–C moiety. Evidence for the presence of oxygenated OPN in **3** is also found in its ^{31}P NMR spectrum with one signal at 30 ppm. The oxidation of the PN ligand of **2** must be by the only source of oxygen in the medium, i.e. the NO group. Consistently, a single NO vibration appeared at 1771 cm^{-1} in the IR measured for **3**. It is noteworthy that, when the gas phase over toluene solutions of **2** was analyzed by GC, N_2 was detected while no evidence for O_2, NO or N_2O could be found: we take this result to indicate that the NO ligand, when it oxidizes the PN ligand of **2**, is transformed into N_2.

Finally, the displacement, in the IR spectrum of **3**, of the ν(aromatic C=C and C=N) vibrations to a broad band at 1587 cm^{-1} is strong evidence that the OPN ligand in **3** is also coordinated by nitrogen.

The analytical and spectroscopic data for the brown complex **3** are all consistent with a Fe(NO)Cl(OPN) formulation with the iron in a tetrahedral surrounding, a single NO group and a bidentate OPN ligand bound to iron by both its oxygen and nitrogen donor atoms.

The same compound **3** was obtained when $[Fe(NO)_2Cl]_2$ and 2-(diphenylphosphine oxide)pyridine were allowed to react in a Fe/P ratio of 1/1. The IR print taken for the reaction mixture immediately after mixing of the reagents showed only the print of **3**: no monodentate behaviour of the OPN ligand could be detected.

3.2. Reactivity towards oxygen

Bubbling oxygen into toluene solutions of the dinitrosyl dimer **1**, $[Fe(NO)_2Cl]_2$, in the presence of PN or OPN (2 equiv.) caused a rapid change in colour from black to yellow. Treatment of the reaction mixture afforded compound **4** which analyzed as $Fe(NO_3)_2(Cl)(OPN)$. The IR spectra measured on **4** (KBr pellets) showed the complete disappearance of the nitrosyl vibrations, while new absorptions were measured at 1534, 1275 and 828 cm^{-1} in the regions generally assigned to bound nitrates [10]; the presence of the bidentate coordinated 2-(diphenylphosphine oxide)-pyridine in **4** is indicated by a strong vibration at 1167 cm^{-1} assignable to a coordinated phosphoryl group and by a broad band at 1589 cm^{-1} attributable to the ν(aromatic C=C and C=N) of a coordinated pyridine.

It is noteworthy that the same dinitrato compound **4** was obtained when either the dinitrosyl **2** or the mononitrosyl **3** complex was allowed to react with molecular oxygen.

The formulation of **4** was further confirmed through independent preparation from anhydrous chloride, OPN and silver nitrate; its structure was unambiguously established by X-ray diffraction [11].

4. Discussion

Addition of 2-(diphenylphosphino)pyridine to $[Fe(NO)_2Cl]_2$ first yielded $Fe(NO)_2Cl(PN)$ (**2**) where, as expected, the PN ligand is coordinated to iron in a monodentate mode through its phosphorus atom. However, **2** is unstable in solution and evolves to $Fe(NO)Cl(OPN)$ (**3**) where the PN ligand has been oxidized, by the displaced NO group in **2**, to the bidentate OPN ligand in **3**.

The herein reported behaviour of the $Fe(NO)_2Cl$ moiety in the presence of the bidentate PN ligand is different from that observed in the presence of either monodentate or bidentate phosphines.

Paramagnetic complexes of the type $Fe(NO)_2XL$ (L = phosphine), when reacted with a monodentate phosphine L, are known to give the diamagnetic compounds $Fe(NO)_2L_2$ and only these [12]; the proposed mechanism postulates formation of an $Fe(NO)_2XL_2$ 19-electron intermediate which is partitioned between two pathways, one leading to the products through X displacement, and the other back to the reagents. Such a behaviour has been demonstrated with phosphines of various basicities, such as $L = PPh_3$, $P(n\text{-}C_4H_9)_3$ and $P(O\text{-}iPr)_3$.

On the other hand, we have recently shown that $[Fe(NO)X]_2(\mu\text{-}LL)$ complexes, where LL is a diphosphine ligand such as 1,2-bis(diphenylphosphino)ethane (dppe), have different reactivities, although they can be regarded as 'double' $Fe(NO)_2XL$ compounds [13,14]: when the Fe/P molecular ratio is forced to 1/1, the $[Fe(NO)X]_2(\mu\text{-}LL)$ complexes undergo both NO displacement and Cl redistribution to form the diamagnetic 18-electron $Fe(NO)_2(LL)$ on the one hand but also the paramagnetic $Fe(NO)Cl_2(LLO)$ complex where the diphosphine LL ligand has been partially oxygenated by the displaced NO group.

The selective evolution of **2**, a tetracoordinated $Fe(NO)_2XL$ complex, towards **3** is most likely to imply concerted coordination of the N donor site of the PN ligand and loss of NO [4]; the subsequent oxidation of the P site of the ligand by free NO is then expected. Our results here again illustrate that differences in the σ/π bonding character of the ancillary ligands play a key role in the stabilization of Fe–NO bonds [4].

The formation of the mononitrosyl tetracoordinated complex **3** a priori rules out the use of the PN or OPN ligand to accomplish the catalytic cycle illustrated in Scheme 1. Both complexes **2** and **3** were nevertheless found to activate molecular oxygen. Oxidation of the Fe–NO moiety in the presence of PN or OPN affords a nitrato complex but no nitro complex. The resulting dinitrato complex **4** was found to be capable of oxygen transfer to phosphines and to be a catalyst in cyclohexene autoxidation [11].

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