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Coordinated NO as a Source of Oxygen: Reactivity of the $Fe(NO)_2$ Moiety in the Presence of the Bidentate Phosphane 1,2-Bis(diphenylphosphino)ethane (dppe) and 1,2-Bis(diphenylphosphino)ethene (dppen)

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The nitrosyl dimer $[Fe(NO)_2Cl]_2$ (**1**) in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) or *trans*-1,2-bis(diphenylphosphino)ethene (tdppen) yields the binuclear complex $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (**2**) or $[Fe(NO)_2Cl]_2(\mu\text{-tdppen})$ (**6**). In the presence of excess diphosphine dppe, tdppen, or *cis*-1,2-bis(diphenylphosphino)ethene (cdppen), the $Fe(NO)_2X$ moiety undergoes (i) halogen displacement to yield $Fe(NO)_2(PP)$ complexes of $\{Fe(NO)_2\}^{10}$ configuration and (ii) unexpectedly, NO substitution, which results in $Fe(NO)Cl_2(OPP)$ species of $\{Fe(NO)\}^9$ configuration, where the diphosphine has been monooxygenated by NO.

Introduction

We have found that the iron–nitrato/iron–nitrosyl couple could constitute a new alternative for the oxidation and transfer of molecular oxygen:[1,2] the nitrosyl ligands in the dinitrosyliron dimers $[Fe(NO)_2X]_2$ (X = Cl, I) are oxidized by molecular oxygen in the presence of PPh_3, $OPPh_3$, or hexamethylphosphorotriamide (HMPA), to nitrato—and not nitro—ligands, from which oxygen is then transferred to phosphines and olefins.

Our results indicated that a key factor for the oxygenation step is a high electron density on the nitrato group;[2] thus, while the pentacoordinated $Fe(NO_3)_2ClL_2$ (L = $OPPh_3$,[1] HMPA[2]) complexes transfer oxygen to olefins and phosphines, the tetracoordinated $Fe(NO_3)_2Cl(HMPA)$ has lost all oxygen-transer properties. However, the pentacoordinated 19-electron nitrosyl complexes $Fe(NO)_2ClL_2$, which are left after oxygen transfer from the active nitrates, are poorly stable when L = $OPPh_3$ or HMPA: they encounter side reactions leading to the termination of the $Fe–NO/Fe–NO_3$ catalytic cycle.

Therefore, stabilization of these pentacoordinated nitrosyl $Fe(NO)_2ClL_2$ complexes appeared as a prerequisite in our search for a long-life oxidation catalyst able to shuttle between Fe–NO and $Fe–NO_3$ complexes by using molecular oxygen. We thus became interested in the chelating or bridging diphosphines 1,2-bis(diphenylphosphino)ethane (dppe) and *trans*- or *cis*-1,2-bis(diphenylphosphino)ethene (tdppen or cdppen):[3] we report here the behavior of the $Fe(NO)_2Cl$ moiety in the presence of these bidentate phosphines, which result in the unexpected formation of the pentacoordinated $Fe(NO)Cl_2LLO$ species.

Experimental Section

Solvents were purified by published procedures and stored under argon. 1,2-Bis(diphenylphosphino)ethane, *trans*-1,2-bis(diphenylphosphino)ethene, and *cis*-1,2-bis(diphenylphosphino)ethene were purchased from Aldrich and used without further purification. The dimer $[Fe(NO)_2Cl]_2$ was prepared according to the literature.[4] The preparation of the nitrosyl complexes was performed under an atmosphere of argon by using Schlenk tube techniques.

Elemental analyses were performed by the Service Central de Microanalyses of the CNRS. Infrared 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. The analytical and infrared data are gathered in Table I.

Synthesis of $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (2) and $[Fe(NO)_2Cl]_2(\mu\text{-tdppen})$ (6). The chlorodinitrosyliron dimer $[Fe(NO)_2Cl]_2$ (0.090 g, 0.297 mmol) was dissolved in toluene (50 mL), and dppe (0.119 g, 0.298 mmol) was added in small portions with stirring. A change of color from reddish yellow to violet was observed after complete addition of dppe. After 1 h, no precipitate was observed and the reaction mixture was evaporated to yield a violet powder (0.200 g, 95%). This powder was redissolved in 20 mL of toluene, and addition of an equal volume of pentane produced violet parallepiped-shaped crystals after 1 day at 0 °C. ESR (toluene, 193 K): $g = 2.036$, $a\langle^{31}P\rangle = 25$ G. ^{31}P NMR ($CDCl_3$, room temperature, ppm): $\delta = 39$.

The same procedure applied to $[Fe(NO)_2Cl]_2$ (0.142 g, 0.47 mmol) and tdppen (0.186 g, 0.47 mmol) afforded 0.29 g of **6** (88%) as a dark blue powder. $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature, ppm): $\delta = 56.32$. ESR (CH_2Cl_2, room temperature): $g = 2.036$, $a\langle^{31}P\rangle = 25$ G.

Synthesis of $Fe(NO)Cl_2(Odppe)$ (3) and $Fe(NO)_2(dppe)$ (4) from 2. A 0.24-g (0.342-mmol) sample of **2** 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 color 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 of **4** were obtained (0.28 g, 0.54 mmol, 78%). ^{31}P NMR (toluene, ppm): $\delta = 80.1$ (s). ^1H NMR (CD_2Cl_2, ppm): $\delta = 2.5$ (d, $^2J_{P-H} = 15$ Hz, 4 H), 7.5 (m, 20 H). The green precipitate was washed with toluene and pentane to afford **3** as a green powder (0.072 g, 17%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature, ppm): $\delta(PO) = 44.8$, $\delta(P) = 51.26$. ESR (CH_2Cl_2, room temperature: $g = 2.033$, $a\langle^{31}P\rangle = 50$ G.

Synthesis of $[Fe(NO)_2(tdppen)]_n$ (7) and $[Fe(NO)Cl_2(Otdppen)]_n$ (8). The chlorodinitrosyliron dimer $[Fe(NO)_2Cl]_2$ (0.095 g, 0.3 mmol) was dissolved in toluene (30 mL), and tdppen (0.249 g, 0.63 mmol) was added gently with stirring. The solution became a deep khaki color after complete addition, and a rust red precipitate settled at the bottom of the vessel. The mixture was stirred overnight to ensure complete reaction. The rust red powder separated by filtration was washed with toluene and hexane and then dried under vacuum to yield **7** (0.179 g, 58%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature, ppm): $\delta = 56.5$. A khaki-colored powder was extracted from the khaki filtrate by evaporation to yield **8** (0.133 g, 39%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature, ppm): $\delta(PO) = 32.94$, $\delta(P) = 65.55$. ESR (CH_2Cl_2, room temperature): $g = 2.037$, $a\langle^{31}P\rangle = 50$ G.

Synthesis of $Fe(NO)_2(cdppen)$ (9) and $FeCl_2(NO)(Ocdppen)$ (10). The chlorodinitrosyliron dimer $[Fe(NO)_2Cl]_2$ (0.182 g, 0.6 mmol) was dissolved in toluene (50 mL), and cdppen (0.48 g, 1.2 mmol) was added gently with stirring. The solution became deep red after complete addition. The reaction mixture was stirred overnight to deposit a green powder, which was separated by filtration, washed with toluene and hexane, and dried under vacuum to yield **10** (0.114 g, 17%), which is most unstable in air. All our efforts at recrystallization of **10** have so far been unsuccessful. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature, ppm): $\delta(PO) = 25.80$, $\delta(P) = 64.62$. A red powder was extracted from the red filtrate by evaporation. Crystals of **9** could be obtained by recrystallization in a 1/1 CH_2Cl_2–hexane mixture at 0 °C under argon (0.49 g, 79%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature, ppm): $\delta = 90.25$.

Results

Reaction of $[Fe(NO)_2Cl]_2$ with dppe. When dppe is allowed to react with **1** ($[Fe(NO)_2Cl]_2$) in a Fe/P ratio of 1/1, a violet binuclear singly bridged complex **2** is formed.

The analytical and spectroscopic data (Table I) confirm the binuclear formulation for **2**. Characteristic infrared data are two NO absorptions at 1786 and 1724 cm^{-1} and a single Fe–Cl vi-

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Table I. Elemental Analysis and IR Data for Compounds **2–10**

complex	% found (calcd) C	H	N	Cl	Fe	P	IR, cm^{-1} (KBr pellets) ν(NO)	ν(Fe—Cl)	ν(P=O)	ν(PC)
$[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (**2**)	44.56	3.46	7.33		16.24	8.76	1786 (s)	334		1099
	(44.55)	(3.45)	(7.99)		(15.94)	(8.84)	1724 (s)			
$Fe(NO)Cl_2(Odppe)$ (**3**)			2.16	14.89	9.65	9.90	1796 (s)	351	1165	1107
			(2.45)	(12.42)	(9.78)	(10.85)				
$Fe(NO)_2(dppe)$ (**4**)	59.85	4.78	5.47				1707 (s)			1097
	(60.70)	(4.71)	(5.45)				1657 (s)			
$[FeCl_4][FeCl_2(O_2dppe)_2]$ (**5**)				17.86	8.90	10.34		384	1169	1108
				(17.95)	(9.42)	(10.45)				
$[Fe(NO)_2Cl]_2(\mu\text{-tdppen})$ (**6**)			7.16	10.68	15.81	8.86	1786 (s)	335		1099
			(8.02)	(10.14)	(15.98)	(8.86)	1717 (s)			
$[Fe(NO)_2(tdppen)]_n$ (**7**)	60.40		4.70		8.99	11.75	1713			1094
	(60.94)		(5.47)		(10.91)	(12.10)	1084			
$[Fe(NO)Cl_2(Otdppen)]_m$ (**8**)			2.93		10.64	11.41	1789	351	1166	1112
			(2.46)		(9.82)	(10.89)				1084
$Fe(NO)_2(cdppen)$ (**9**)			5.39		10.84	12.43	1718 (s)			1097
			(5.47)		(10.90)	(12.06)	1666 (s)			
$Fe(NO)Cl_2(Ocdppen)$ (**10**)			2.93	12.24	10.38	11.12	1792	351	1188	1121
			(2.46)	(12.46)	(9.81)	(10.88)	1701			

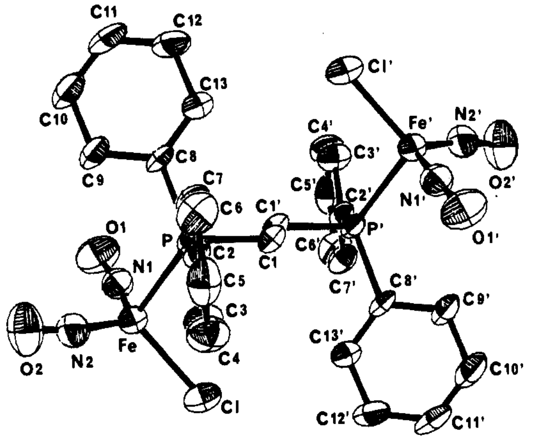


Figure 1. Molecular structure of $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$ (**2**).[3]

bration at 334 cm^{-1}. Complex **2** is paramagnetic ($g = 2.036$ in toluene at 193 K). Its ^{31}P NMR spectrum could nevertheless be recorded to present one signal at 38.70 ppm (−12.8 ppm in free dppe). An X-ray structural investigation[3] unambiguously established **2** as the symmetrical bridge complex $[Fe(NO)_2Cl]_2(\mu\text{-dppe})$, illustrated in Figure 1, in which the dppe ligand acts as a single bridge between two $Fe(NO)_2Cl$ moieties.

When complex **2** is allowed to react with a further 1 equiv of dppe, or when **1** reacts with 2 equiv of dppe, two iron species form together: a green compound **3**, insoluble in toluene, and a red complex **4**, readily soluble in toluene.

Addition of an equal volume of pentane to the toluene solution of **4** produces red crystals of the long-known $Fe(NO)_2(dppe)$,[5,6] which we characterized by IR spectroscopy (ν(NO) = 1707, 1657 cm^{-1}), ^{31}P NMR spectroscopy (δ = 80.1 ppm), and X-ray diffraction measurements.[3]

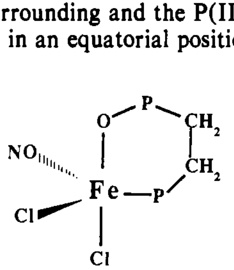
Adduct **3** is extremely sensitive to mere traces of air, and we have so far been unable to obtain crystals suitable for X-ray measurements.

The ESR spectrum of a CH_2Cl_2 solution of **3** at room temperature shows a doublet (50 G) at $g = 2.033$. Through comparison with the ESR spectrum reported[7] for $[Fe(NO)_2(dppe)]^+$, we tentatively attribute the 50-G hyperfine coupling constant to one ^{31}P nucleus located at an equatorial site of a distorted trigonal bipyramid around the iron atom. The detection of a doublet can be interpreted to mean that a dppe ligand in **3** spans the equatorial (expected $a\langle ^{31}P\rangle$ value ca. 55 G)[7] and axial positions in the TBP around the iron atom: coupling with the axial phosphorus nucleus is expected to be lower than 3 G,[7] i.e. too small to be detected under our conditions. The ESR data for **3** can also be taken to indicate that the dppe ligand has been partially oxygenated into $Ph_2PCH_2CH_2P(O)Ph_2$ so that coupling with the P(O) phosphorus atom is no longer detected.

The presence, in the IR spectrum of **3**, of a strong vibration at 1165 cm^{-1} assignable to a coordinated phosphoryl group (ν(P=O) = 1180 cm^{-1} in free O_2 dppe) is in favor of this second hypothesis: it shows that the diphosphine ligand has been oxidized, and this must be by the only source of oxygen in the medium, i.e. the NO group. Consistently, a single NO vibration appears at 1796 cm^{-1}.

Definite evidence for the presence of monooxygenated dppe, Odppe, in **3** is to be found in its ^{31}P NMR spectrum (CH_2Cl_2 solutions at room temperature) where two signals are detected at 44 and 51 ppm: these can be respectively assigned to the PO and P phosphorus atoms of a coordinated diphosphine monooxide Odppe (32.6 and −12.2 ppm, respectively, in free Odppe[8]).

The analytical and spectroscopic data for the green complex **3** are all consistent with a $Fe(NO)Cl_2(Odppe)$ formulation, with the iron in a TBP surrounding and the P(III) atom of the monooxygenated ligand in an equatorial position, as illustrated in structure **3**.



3

It is noteworthy that compound **3**, in the presence of mere traces of air, evolves toward $[FeCl_4][FeCl_2(O_2dppe)_2]$ (**5**), which we identified through comparison with an authentic sample prepared from anhydrous $FeCl_3$ and O_2dppe.[9] This evolution is taken to be responsible for the mediocre results in the elemental analysis of **3**.

Reaction of 1 with tdppen. The behavior of the $Fe(NO)_2Cl$ moiety in the presence of *trans*-1,2-bis(diphenylphosphino)ethene parallels that observed with dppe.

The binuclear violet compound $[Fe(NO)_2Cl]_2(\mu\text{-tdppen})$ (**6**) is easily obtained through quantitative reaction between **1** and tdppen in a 1/1 Fe/P ratio.

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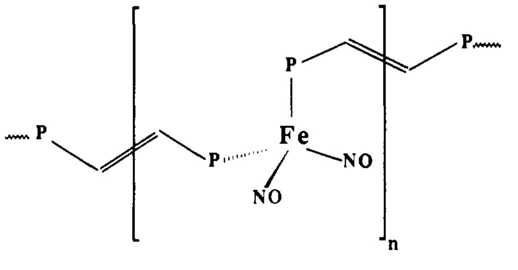
That **6** is analogous to **2** is evidenced by its analytical and spectroscopic data. The infrared spectra (KBr pellets) for **6** show two NO vibrations at 1786 and 1717 cm^{-1} (1786 and 1724 cm^{-1} for **2**) and one ν(Fe–Cl) at 335 cm^{-1} (334 cm^{-1} for **2**); **6** is paramagnetic, and its ESR signal in toluene solutions at 193 K) is measured at $g = 2.036$ ($g = 2.036$ for **2**).

Further reaction of **6** with **1** equiv of tdppen in toluene affords two compounds **7** and **8**, which are both very poorly soluble in the usual solvents; however, **8** is slightly in toluene and could thus be separated from **7**. The mediocre results in the iron analysis for **7** and **8** (Table I) are imputable to the tedious separation of these insoluble and sensitive complexes.

The data for the red complex **7** indicate the [Fe(NO)$_2$(tdppen)]$_n$ formulation (Table I); the two ν(NO) vibrations in the infrared spectrum for **7** (KBr pellets) at 1713 and 1666 cm^{-1} are close to those for **4**, Fe(NO)$_2$(dppe) (1707 and 1657 cm^{-1}). Like **4**, **7** is diamagnetic; its ^{31}P NMR spectrum recorded in CH$_2$Cl$_2$ solutions at room temperature shows a single, sharp line at 56.5 ppm. However, **7** differs from **4** in its very poor solubility.

A chelating bonding mode is not possible for tdppen, and we take our results to indicate that the discrete monobridge binuclear complex **6**, in the presence of excess tdppen, evolves toward **7**, the bridged polymeric analogue of **4**, illustrated in structure **7**.



7

The green compound **8** is formed together with **7** through reaction of **6** with tdppen. The analytical, IR, and NMR data for **8** are in agreement with the Fe(NO)Cl$_2$(Otppen) formulation analogous to that of **3**. Its infrared spectrum shows one ν(NO) at 1789 cm^{-1} (1796 cm^{-1} in **3**), one ν(coordinated P═O) at 1166 cm^{-1} (ν(P═O) = 1186 cm^{-1} in free Otdppen), and two ν(P—C), respectively characteristic of a coordinated phosphine fragment (ν(P—C) = 1084 cm^{-1}) and for a coordinated phosphine oxide fragment (ν(P—C) = 1112 cm^{-1}). Consistently, two signals are detected in the ^{31}P NMR spectra for toluene solutions of **8** at 64 and 33 ppm, which we assign to the P$^{\text{III}}$ and P$^{\text{V}}$═O phosphorus atoms in coordinated Otdppen (21.5 and −5.2 ppm in the free Otdppen ligand).

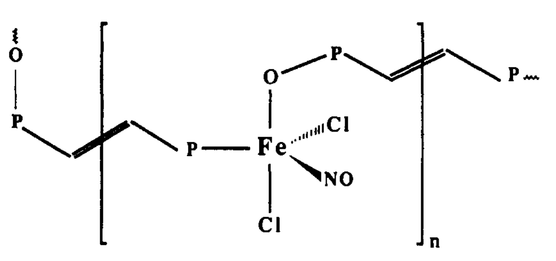
From these data, we propose for **8** the polymeric structure illustrated in structure **8a**, where the Otdppen ligand spreads the axial (PO) and equatorial (P) positions in the TBP surrounding of iron; structure **8b**, where the iron atoms are alternatively bridged by tdppen or the dioxygenated ligand O$_2$tdppen, cannot be excluded.

Reaction of 1 with cdppen. No clean reaction occurred with **1** and *cis*-1,2-bis(diphenylphosphino)ethene were mixed in a 1/1 Fe/P ratio: only very poor yields of Fe(NO)$_2$(cdppen) (**9**) could be isolated in our hands.

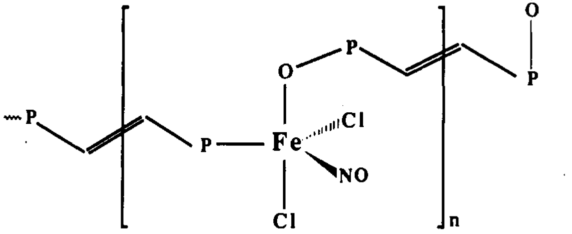
On the other hand, addition of 2 equiv of cdppen to the iron dimer **1** in toluene at room temperature immediately resulted in a red solution from which, after a few hours stirring, a green precipitate, **10**, deposited.

Adding hexane (1/1) to the red toluene solution afforded red crystals of Fe(NO)$_2$(cdppen) (**9**) analogous to **4**; **9** was characterized by IR (ν(NO) = 1718, 1666 cm^{-1}), ^{31}P NMR (δ = 90.2 ppm), and elemental analysis.

Adduct **10**, as was also the case for **3** (dppe) and **8** (tdppen), is extremely sensitive to air. The IR (ν(P═O) = 1177 cm^{-1}, ν(NO) = 1792 cm^{-1}, ν(Fe—Cl) = 250 cm^{-1}), NMR (^{31}P two signals in a 1/1 ratio at δ = 25.8 and 64.6 ppm), and analytical data for **10** are, here again, in agreement with the Fe(NO)Cl$_2$(Ocdppen) formulation.



8a



8b

Discussion

Addition of dppe or tdppen to [Fe(NO)$_2$Cl]$_2$ yielded [Fe(NO)$_2$Cl](μ-dppe) (**2**) or [Fe(NO)$_2$Cl](μ-tdppen) (**6**). The X-ray determination[3] of **2** showed that, from a structural point of view, [Fe(NO)$_2$Cl]$_2$(μ-dppe) is simply two Fe(NO)$_2$Cl(PR$_3$) units linked together: the structure of **2** is very similar to that of Fe(NO)$_2$Cl(PPh$_3$).[10]

Paramagnetic complexes of the type Fe(NO)$_2$XL (X = Cl, L = PR$_3$), when reacted with excess L, are known[11] to give the diamagnetic complexes Fe(NO)$_2$L$_2$, and only these; the proposed mechanism (reaction 1) postulates formation of a Fe(NO)$_2$XL$_2$

$$\mathrm{Fe(NO)_2XL + L \rightleftarrows \{Fe(NO)_2XL_2\} \rightarrow Fe(NO)_2L_2 + X} \quad (1)$$

intermediate, a 19-electron $\{\mathrm{Fe(NO)_2}\}^{11}$ compound,[12] which is partitioned between two pathways, one leading to the products and the other back to the reagents. Such a behavior has been observed with phosphines of various basicities, such as L = PPh$_3$, P(n-C$_4$H$_9$)$_3$, and P(O-i-C$_3$H$_7$)$_3$.

The reactivities of compounds **2** and **6**, which are double Fe(NO)$_2$XL complexes, in the presence of an excess of ligand, dppe or tdppen, are different. They undergo not only the expected halogen displacement, which results in the formation of the red complexes Fe(NO)$_2$(dppe) (**4**) and [Fe(NO)$_2$(tdppen)]$_n$ (**8**), but also NO substitution, this latter reaction resulting in the partial oxygenation of the phosphorus ligand, in green Fe(NO)Cl$_2$(Odppe) (**3**) and in Fe(NO)Cl$_2$(Otdppen) (**7**).

This reactivity is further confirmed in the presence of cdppen, where the analogous red Fe(NO)$_2$(cdppen) (**9**) and green Fe(NO)Cl$_2$(Ocdppen) (**10**) form when [Fe(NO)$_2$Cl]$_2$ is allowed to react with cdppen.

The easy formation of the green complexes **3**, **8**, and **10** is rather surprising.

Oxygenation of triphenylphosphane by coordinated NO has been observed only under drastic conditions:[13] thus, reaction of the bromodinitrosyliron dimer with PPh$_3$ in the molten state (140 °C) led to disproportionation of iron and oxidation of PPh$_3$ according to

$$\mathrm{[Fe(NO)_2Br]_2 + 5PPh_3 \rightarrow}$$
$$\mathrm{Fe(NO)Br_2(PPh_3)_2 + Fe(NO)_2(PPh_3)_2 + OPPh_3 + \tfrac{1}{2}N_2} \quad (2)$$

On the other hand, it has recently been shown that the diphosphines dppe, cdppen, and tdppen undergo autoxidation in air

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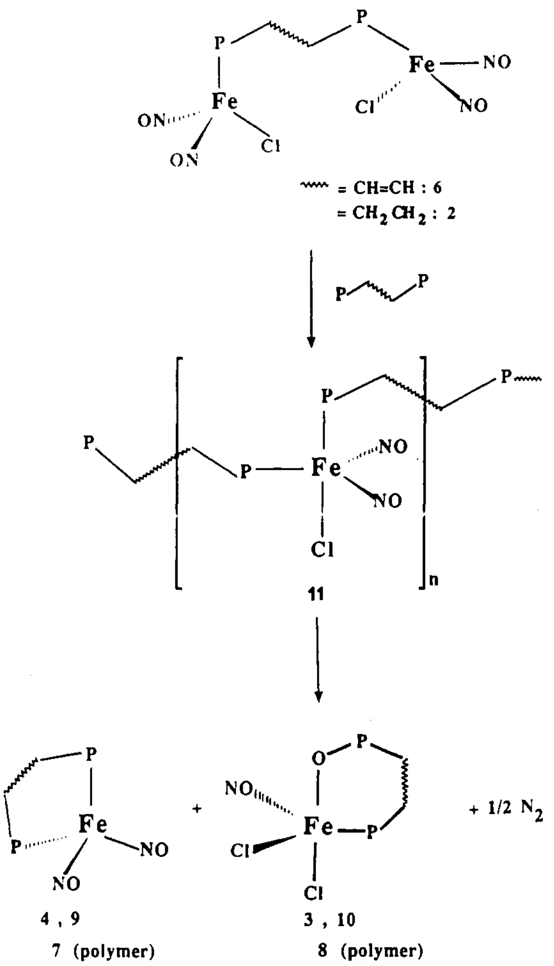
Scheme I



to produce first the diphosphine monooxide and then the dioxide;[8] however, this reaction is very slow and yields only 65% of oxidized dppe after 5 days at room temperature. Oxygenation of the diphosphine in our reactions could nevertheless arise from iron-catalyzed autoxidation: thus there are, to our knoweldge, only two structurally characterized complexes of a diphosphine monooxide, namely $MoCl_3O[Et_2PCH_2CH_2P(O)Et_2]$[14] and $\{RuCl_2[OC_6H_4(PMePh)_2][OC_6H_4(PMePh)(OPMePh)]\}$,[15] both resulting from oxidation of the diphosphine by "adventitious" oxygen. However, under our experimental conditions, where the usual procedures to exclude oxygen were strictly observed (so that the most oxygen-sensitive green complexes do not decompose), such a serendipitous reaction is most unlikely. Furthermore, when the gas phase analysis by chromatography (GC) was monitored as the reaction of **2** with dppe proceeded, N_2 was detected, while no evidence for O_2, NO, or N_2O could be found.

The mechanisms by which **3** and **4** (or the analogous **7**, **8** and **9**, **10**) are formed is not known, but the bidentate character of the phosphine appears obviously to be the driving force in these reactions: basicity is by no way to be inferred, as the behavior in reaction 1 accounts for monophosphines of such different basicities as PPh_3, $P(OiPr)_3$, and $P(nBu)_3$.[11]

We found that the red $Fe(NO)_2(PP)$ complexes **4** and **7** are recovered unchanged after several hours' contact with chlorine radicals generated in situ, further supporting simultaneous formation of the red $Fe(NO)_2$ and green $Fe(NO)Cl_2$ complexes from the same intermediate.

We take our results to indicate that the green $\{Fe(NO)\}^9$ species **3**, **8**, **10** are probably formed through an intramolecular redox reaction and rearrangement in a dimeric (or polymeric) pentacoordinated intermediate **11** according to eq 3. Excess electron density release in this 19-electron intermediate is responsible for the observed products (Scheme I) and results in NO reduction and phosphine oxidation. Reduction of NO to dinitrogen is supported by the GC analysis of the gas phase during the reaction. Further, we verified that the mass balance of the overall reaction fulfills eq 3.

$$[Fe(NO)_2Cl]_2(\mu\text{-}PP)_2]_n \rightarrow Fe(NO)_2(PP) + Fe(NO)Cl_2(PPO) + \tfrac{1}{2}N_2 \quad (3)$$

$$\{Fe(NO)_2\}^{11} \rightarrow \{Fe(NO)_2\}^{10} + \{Fe(NO)\}^{9}$$

$$\mathbf{11} \rightarrow \mathbf{4}, \mathbf{7}, \mathbf{9} + \mathbf{3}, \mathbf{8}, \mathbf{10}$$

The bidentate behavior of the chosen diphosphine does not allow for stabilization of pentacoordinated 19-electron $Fe(NO)_2Cl(PP)$ complexes but results in formation of pentacoordinated 17-electron $Fe(NO)Cl_2(PPO)$ species.

The nitrosyl complexes **2**–**10** do activate molecular oxygen to yield nitrates whose reactivities are currently under study in our laboratory.

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