Redox Reactions Involving $D^{7+2}_{\mathrm{NO(Fe)}}$ Dinitrosyl Iron Complexes. Oxidation of 2-Pyridyldiphenylphosphine into the Corresponding Phosphine Oxide Chelating a D^{6+0}_{NO} Iron

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The triphenylphosphine dinitrosyl iron and cobalt complexes $M(NO)_2(PPh_3)X$ (X = halogen) display an interesting difference in their reactions with an excess of PPh_3. Whereas the $D^{8+2}_{\mathrm{NO(Co)}}$ cobalt complexes* undergo a simple redox inactive substitution of PPh_3 for X^- to yield the stable $D^{8+2}_{\mathrm{NO(Co)}}$ cation $Co(NO)_2(PPh_3)_2^+$ [2, 3], the $D^{7+2}_{\mathrm{NO(Fe)}}$ iron halides are involved in a non-temporary one-electron reduction of the metallic center affording the $D^{8+2}_{\mathrm{NO(Fe)}}$ complex $Fe(NO)_2(PPh_3)_2$ [4, 5]. The formation of the latter was tentatively rationalized in terms of a homolysis of the Fe–X bond [4]. However, other pathways must be operative in the formation of the same $Fe(NO)_2(PPh_3)_2$ complex in the room temperature reaction of PPh_3 with $Fe(NO)_2(THF)_n^+$ [6]. To delineate their nature, we have found that the use of 2-pyridyldiphenylphosphine [PPh_2(2-Py)] instead of triphenylphosphine is beneficial.

Reaction under argon at 20 °C of 2.00 g (7.6 mmol) of PPh_2(2-Py) [7] with $Fe(NO)_2(THF)_n^+/BF_4^-$ [from 0.58 g (1.9 mmol) of $(Fe(NO)_2Cl)_2$ [8, 9] and 0.75 g (3.8 mmol) of $AgBF_4$ in 30 ml of dry tetrahydrofuran (THF), followed by separation of solid AgCl] resulted in the precipitation of a yellow powder over a 30-min period and the formation of the reduction product $Fe(NO)_2(PPh_2\text{-}(2\text{-}Py))_2$ (ν(NO) = 1720, 1680 cm^{-1}, prepared independently from $Fe(CO)_2(NO)_2$ and an excess of the ligand [10]) which remained in solution. The yellow THF-insoluble product (1) (0.55 g) was separated by filtration and crystals suitable for a structure determination by X-ray diffraction were grown under argon at 0 °C by slow diffusion of toluene into a concentrated solution of the compound in methylene chloride.

The structure of complex 1, which will be analyzed in more detail later in a comparative study with other chelate complexes of iron, is that of a dipositive octahedral $D^{6+0}_{\mathrm{NO(Fe)}}$ [*i.e.*, d^6 Fe(II)] iron complex with three chelating 2-pyridyldiphenylphosphine oxide ligands and two BF_4^- anions, as shown by the perspective view of Fig. 1.

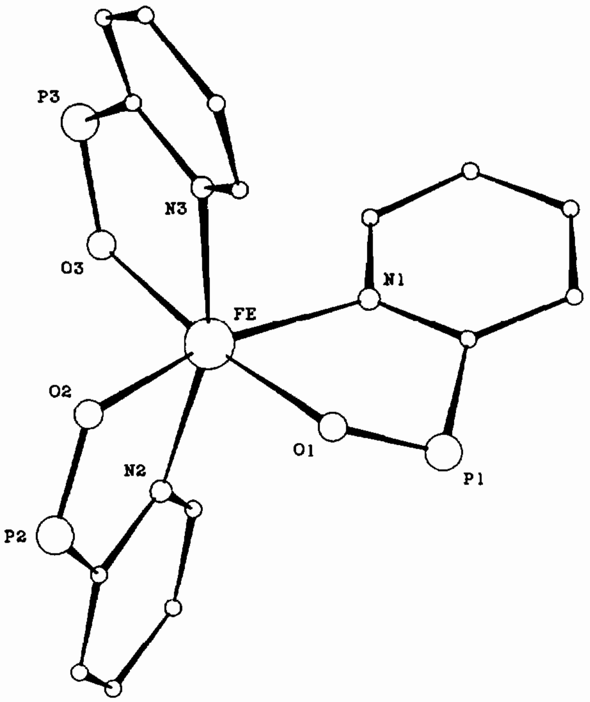

Fig. 1. Perspective view of the dipositive octahedral $D^{6+0}_{\mathrm{NO(Fe)}}$ complex 1. The two BF_4^- anions and the P-phenyl substituents have been omitted for clarity. Monoclinic, $P2_1/a$; $a = 18.714(1)$ Å, $b = 13.732(2)$ Å, $c = 21.653(2)$ Å; $\beta = 109.77(1)°$; $R = 0.097$. Mean values: Fe–O = 2.100[50] Å; P–O = 1.508[17] Å, Fe–N = 2.248[45] Å, Fe–O–P = 118.4[3.6]°; σ on mean values was calculated as $\sigma = [\Sigma_{i=1}^{n}(x_i - \bar{x})^2/(n-1)]^{1/2}$.

The formation of this NO-free $D^{6+0}_{\mathrm{NO(Fe)}}$ product together with a $D^{8+2}_{\mathrm{NO(Fe)}}$ dinitrosyl strongly points to the occurrence of a dismutation reaction (Rcl; eqn. (1)) of the D^{7+2}_{NO} iron center present in $Fe(NO)_2(THF)_n^+$ and in any of its derivatives from the substitution of PPh_2(2-Py) for THF (see ref. 1 for an analysis of non-temporary dismutation reactions in terms of the D^{a+n}_{NO} notation).

$$\begin{aligned} &\underset{(D^{7+2}_{\mathrm{NO}})}{2Fe(NO)_2(L)(L')_x^+} \longrightarrow \\ &\underset{(D^{8+2}_{\mathrm{NO}})}{Fe(NO)_2(L)(L')_x} + \underset{(D^{6+2}_{\mathrm{NO}})}{Fe(NO)_2(L)(L')_x^{2+}} \end{aligned} \qquad (1)$$

where L = PPh_2(2-Py); L′ = L and/or THF; $x \geq 1$.

Subsequent complete denitrosylation of the $D^{6+2}_{\mathrm{NO(Fe)}}$ intermediate of Rcl might then proceed

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*For the D^{a+n}_{NO} notation used in this paper, see ref. 1.

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according to, for example, Scheme II of ref. 11, with the phosphine ligand officiating as the ultimate O-acceptor. Once formed, the original role of the aminophosphine oxide is to complex the $D^{6+0}_{NO(Fe)}$ cation produced concomittantly, which allows the latter to remain in a readily detectable form.

In conclusion, this study has shown that the formation under mild conditions of a $D^{8+2}_{NO(Fe)}$ complex from the reaction of a $D^{7+2}_{NO(Fe)}$ iron reactant with a phosphine is accompanied by the formation of two oxidation products, a phosphine oxide and an Fe(II) metallic center, which, for the specific reaction studied, combine into a single product providing the first case of chelation of a first row transition metal by 2-pyridyldiphenylphosphine oxide [12]*.

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*A $PtBr_2$ complex containing the same chelating ligand has been described in ref. 12.