Nitrosyl–nitro Redox Couples with Metal Phthalocyanines: Synthesis and Characterization of Nitro Derivatives of Cobalt and Iron Phthalocyanine, Dioxygen Activation, Oxygen-atom Transfer and Stoichiometric and Catalytic Oxidation of Terminal Olefins†

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The complexes [Co(pc)(NO_2)(py)]·dce, [Co(pc)(NO_2)(py)]·thf, and [Fe(pc)(NO_2)(py)] (pc = phthalocyaninate, py = pyridine, dce = 1,2-dichloroethane and thf = tetrahydrofuran) have been isolated as stable crystalline materials. Their molecular and electronic structures have been investigated by IR and UV/VIS spectra, X-ray powder patterns, thermogravimetric and magnetic susceptibility measurements and Mössbauer spectra. The complexes should be regarded as six-co-ordinate low-spin cobalt(III) and iron(III) species. Reference is also made to their corresponding five-co-ordinate nitrosyl derivatives, [Co(pc)(NO)] and [Fe(pc)(NO)]. The Co(pc)- and Fe(pc)–NO/NO_2 systems have been studied with regard to their dioxygen activation and oxygen-atom-transfer reactions, in the oxidation of terminal olefins to the corresponding methyl ketones. Whereas oxidation with the Co(pc)–NO/NO_2 redox couple is nearly stoichiometric, catalytic and selective oxidation occurs with the parallel Fe(pc) system.

Dioxygen activation and oxygen transfer by metal complexes is widely investigated in the context of the catalytic oxidation of organic substrates.[1] The direct participation of the central metal ion of the complex in the uptake and transfer of oxygen is often expected either to prevent or limit the development of uncontrolled radical pathways and improve the selectivity. Of relevance is a peculiar and potentially promising route[2] in which the metal ion (M) is the site for the ligation of the NO/NO_2 redox couple, responsible for dioxygen activation and oxygen-atom donation to an external substrate. In a hypothesis for a bimetallic pathway,[2] a palladium(II) complex, for instance [$PdCl_2(NCPh)_2$], plays the role of the olefin activator. Alternatively, a monometallic approach was proposed,[3] in which the palladium(II) complex is the exclusive site for the oxygen-atom donation from the NO_2 group to the external substrate, a step requiring a preliminary transfer of the NO_2 group from the M–NO_2 complex to the palladium complex and subsequent reverse transfer of the NO group after donation.

Little attention has been paid in the recent literature to the examination of similar metal complexes with ligated NO/NO_2 redox couples, eventually to be employed for the oxidation by O_2 of organic substrates. We therefore describe here the synthesis of the nitro derivatives, [Co(pc)(NO_2)(py)]·dce **1a**, [Co(pc)(NO_2)(py)]·thf **1b** and [Fe(pc)(NO_2)(py)] **2** (pc = phthalocyaninate, py = pyridine, dce = 1,2-dichloroethane, and thf = tetrahydrofuran), and the characterization of their molecular and electronic structures by chemical and physical investigations. Since the parent nitrosyl derivatives, [Co(pc)(NO)] and [Fe(pc)(NO)], had been previously described,[4] the potential of these metal phthalocyanine NO/NO_2 redox couples as catalysts for the oxidation by O_2 of terminal olefins has also been examined. A short account of the synthesis of complex **1a** and oxygen-atom transfer from **1** to PPh_3 was given previously.[5]

Experimental

The complexes [Co(pc)] and [Fe(pc)] were Eastman-Kodak products. If necessary, they were purified by sublimation under vacuum [400–450 °C, 10^{-2} mmHg (*ca.* 1.33 Pa)]. Purity was checked by elemental analyses, IR spectra[6a] and magnetic susceptibility measurements.[6b] The complex [Fe(pc)Cl] was obtained by the method described by Barrett *et al.*[7] from [Fe(pc)] and concentrated HCl. The compounds $PdCl_2$, $AgNO_2$, PPh_3, and $OPPh_3$ were obtained commercially and used without further purification. The complex [$PdCl_2(NCPh)_2$] was obtained from $PdCl_2$ in boiling PhCN.[8] Pyridine was distilled over BaO. Oct-1-ene (Fluka) was previously purified by distillation and then passed through a Al_2O_3 column. A similar procedure was applied to hex-1-ene and dec-1-ene. Authentic samples of Octan-2-, -3- and -4-one, used for comparison in catalytic experiments, were used as provided by Fluka. Tetrahydrofuran, preliminarily kept in contact with sodium wires, was refluxed in the presence of sodium–benzophenone and distilled immediately before use. Acetonitrile was distilled over CaH_2. 1,2-Dichloroethane and toluene were freshly distilled before use. Gaseous NO was a Matheson product; N_2 and O_2 were UPP gases.

[Co(pc)(NO)] *and* [Fe(pc)(NO)].—As indicated elsewhere,[9] [Co(pc)(NO)] was prepared by the following procedure. A suspension of [Co(pc)] (0.500 g) in toluene or benzene (15 cm^3) was kept, in a closed vessel, in contact with gaseous NO at room temperature for 48–72 h, with stirring. After bubbling of N_2 into the suspension, solid [Co(pc)(NO)] was separated by filtration,

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† *Non-SI units employed:* BM ≈ 9.27×10^{-24} J T^{-1}, atm = 101 325 Pa.

washed with diethyl ether and dried under vacuum (0.48 g) (Found: C, 63.50; H, 2.75; N, 18.55. Calc. for $C_{32}H_{16}CoN_9O$: C, 63.90; H, 2.70; N, 18.65%). An identical procedure was used for the preparation of [Fe(pc)(NO)] (Found: C, 63.80; H, 2.75; N, 18.50 Calc. for $C_{32}H_{16}FeN_9O$: C, 64.20; H, 2.70; N, 18.75%).

Synthesis of [Co(pc)(NO_2)(py)]·dce **1a** *and* [Co(pc)(NO_2)(py)]·thf **1b**.—The complex [Co(pc)(NO)] (0.300 g, 0.50 mmol) was suspended in dce (or thf) (5 cm^3) in the presence of pyridine (45 µl, 0.56 mmol) in a reaction vessel contained in a Berghof autoclave. A pressure of 50–60 atm of O_2 was maintained at room temperature for 24 h while stirring the suspension. **CAUTION**: Explosions may be caused by long exposure of thf to a high oxygen pressure when the temperature exceeds 20–25 °C. At a reduced pressure the suspension was filtered and the solid obtained was washed with dce (or thf) and dried under vacuum (0.280 g) (Found: C, 58.80; H, 3.00; Cl, 8.75; N, 17.40. Calc. for $C_{39}H_{25}Cl_2CoN_{10}O_2$ **1a**: C, 58.90; H, 3.15; Cl, 8.90; N, 17.60. Found: C, 62.70; H, 3.85; N, 17.85%. Calc. for $C_{41}H_{29}CoN_{10}O_3$ **1b**: C, 64.05; H, 3.80; N, 18.20%).

The same reaction also takes place at room pressure; however, this implies longer reaction times (3–4 d) and use of more limited amounts of material (20–30 mg). No reaction is observed under the above experimental conditions when the solvent used is CH_2Cl_2 or benzene. In the absence of pyridine, under otherwise identical experimental conditions, no reaction is observed in most cases. In rare cases, oxidation of NO to NO_2 was observed. The oxidation product, however, gave analyses and IR spectra which did not lead to an unequivocal identification of the material obtained.

Complex **1** is also formed by refluxing a suspension of [Co(pc)] and $AgNO_2$ (1:1 molar ratio) in MeCN for 4–5 h in the presence of a stoichiometric amount of pyridine. The IR spectrum of the isolated solid shows that [Co(pc)] is totally converted into **1**. However, difficulties encountered with the purification of the material obtained, essentially because of the presence of Ag in the solid, makes this method less convenient than that starting from [Co(pc)(NO)] under oxygen pressure.

Synthesis of [Fe(pc)(NO_2)(py)] **2**.—The complex [Fe(pc)Cl] (0.300 g, 0.50 mmol) and $AgNO_2$ (0.080 g, 0.52 mmol) were suspended in MeCN (10 cm^3) in the presence of pyridine (45 µl, 0.56 mmol). The suspension, after stirring at room temperature for about 10 min, was filtered and the solid, which contains AgCl as impurity, separated by filtration. Elimination of AgCl was carried out by stirring the solid material in aqueous NH_3 (diluted 1:1) for 5 min. The solid obtained was washed abundantly with water, then with acetone, and dried under vacuum (0.290 g) (Found: C, 63.35; H, 3.30; Cl, 0.00; N, 20.15. Calc. for $C_{37}H_{21}FeN_{10}O_2$ **2**: C, 64.10; H, 3.05; Cl, 0.00, N, 20.20%). Complex **2**, like **1**, is a microcrystalline bluish material, insoluble in water and non-donor solvents, and very sparingly soluble in pyridine.

Attempts to prepare **2** from [Fe(pc)(NO)] in thf (or dce or CH_2Cl_2) under oxygen pressure, did not selectively lead to the corresponding nitro derivative, as was observed for complex **1**. The IR spectrum of the product formed is quite similar to that obtained by exposing **2** to an oxygen pressure under identical experimental conditions. This indicates that the product is very likely the result of further oxidation of **2** (its corresponding nitrate ?). However, its elemental analyses, IR spectrum and other data did not allow unequivocal identification.

Stoichiometric and Catalytic Oxygen-atom Transfer from Complexes **1** *and* **2** *to* PPh_3.—It has been demonstrated experimentally that the nitro derivatives **1** and **2** can be used for the oxidation, either stoichiometric or catalytic, of PPh_3. The stoichiometric process can be developed quantitatively under N_2 at 60–70 °C in dce, with stirring, for 1 h. The process can easily be followed by solution IR spectroscopy, semiquantitatively evaluating the ratio $OPPh_3/PPh_3$ by estimation of the relative intensity of the bands at 720 ($OPPh_3$) and 690 cm^{-1} (PPh_3) and comparison with reference spectra.[10] The solid residual phthalocyanine materials consist of the starting nitrosyl derivatives, as indicated by their IR spectra. For both complexes **1** and **2** in an oxygen atmosphere a catalytic evolution of the process is observed.

Stoichiometric and Catalytic Oxidation by O_2 *of Terminal Alkenes*.—Stoichiometric oxygen-atom transfer from complex **1** (or **2**) to oct-1-ene was easily determined in dce in a nitrogen atmosphere in the presence of [$PdCl_2(NCPh)_2$] as cocatalyst, by stirring the suspension at 60 °C for 3 h.

In a typical experiment, complex **1** (or **2**) (10 mg, 0.014 mmol), finely ground, was suspended in a solution of oct-1-ene (100 µl, 0.625 mmol) and the palladium cocatalyst (15 mg, 0.039 mmol) in thf (cm^3). The suspension, maintained in a small open vial at room temperature and under controlled stirring, was contained in a closed reaction vessel, and kept at 1 atm of O_2 for 22 h. Slow evaporation of thf from the vial normally occurred. At the end of the reaction the solid was separated by centrifugation and the solution brought to the initial volume by addition of thf (0.3–0.5 cm^3). The solid residue normally consists preponderantly of the phthalocyanine material and was examined separately. Gas chromatographic–mass spectrometric (GC–MS) analysis of the solution identified octan-2-, -3- and -4-one as the oxidation products formed from oct-1-ene. Quantitative GC analysis was performed by using the internal standard (tetradecane) method or by use of reference curves obtained by using authentic samples of the octanones systematically checked during the catalytic experiments. A Carlo Erba Fractovap 4200 instrument provided with a flame ionization detector was employed and a column, 2 m long and 4 mm in diameter, filled with CW 20 M supported on Supelcoport (80–100 mesh). The amount of sample injected was of 0.5 µl. The temperature of the column was maintained constant for 10 min and then varied in the range 60–220 °C at a speed of 3° min^{-1}. In some cases quantitative IR spectra were also evaluated in the region 1800–1600 cm^{-1} where the carbonyl groups of the octanones absorb. When this was done, always good correspondence of the total amount of octanones formed with the GC response was found.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 983 instrument in the range 4000–200 cm^{-1} by using Nujol mulls and CsI windows or KBr pellets. Room-temperature magnetic susceptibility measurements were carried out on a Gouy apparatus using a permanent magnet (7000 G, 0.7 T) and an aqueous $NiCl_2$ solution as calibrant. Thermogravimetric analyses were made on a DuPont 950 instrument in an inert atmosphere (N_2, 0.5 l min^{-1}). Elemental analyses (C, H, N and Cl) were obtained from the Laboratorio di microanalisi, Area della Ricerca di Roma (CNR). Mössbauer spectra were obtained at the University of Padova at 77 K as indicated elsewhere.[11]

Results and Discussion

Properties of the Complexes **1** *and* **2**.—The cobalt complexes **1a** and **1b** are air-stable crystalline materials. Thermogravimetric analysis indicates that they both lose the solvent molecules, *i.e.* dce and thf, respectively, at about 100 °C, forming [Co(pc)(NO_2)(py)] **1**. X-Ray powder spectra, different for **1a** and **1b**, become identical after elimination of the solvent. The pyridine molecule and the nitro group are simultaneously eliminated from **1** in the range 150–200 °C. The solid residue of the thermogravimetric analysis is [Co(pc)] in its β crystalline modification.[6] The iron complex **2**, devoid of solvent molecules and not isomorphous with **1**, is also air stable and loses pyridine and the NO_2 group in the range 150–200 °C, resulting in the formation of β-[Fe(pc)].[6]

Complexes **1** and **2** are slowly attacked by pyridine. Both species can be dissolved in pyridine and reobtained unchanged

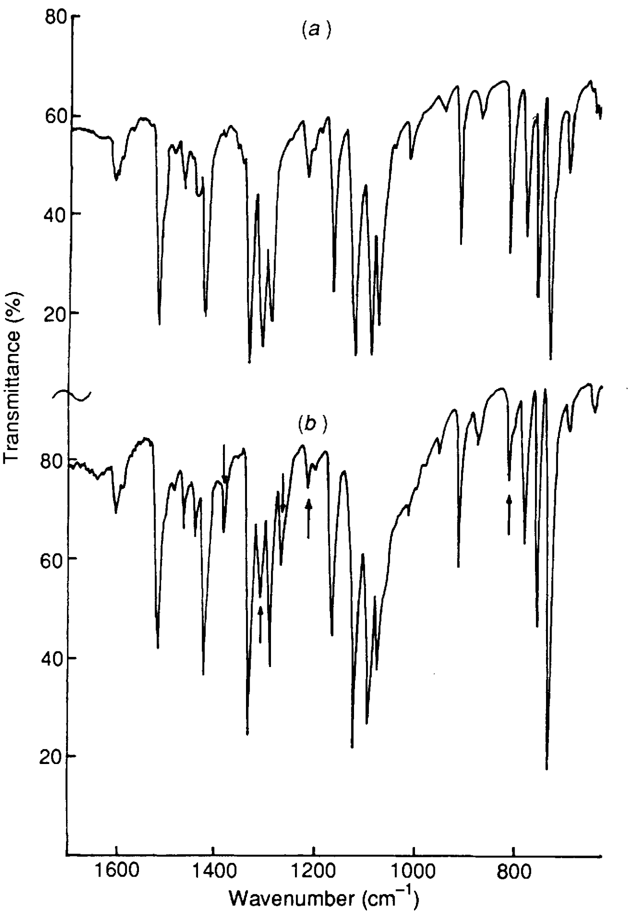

Fig. 1 Infrared spectrum (KBr) of complex **1**, forms A (*a*) and A + B (*b*)

after evaporation of the solvent; however, long standing of the solutions leads to loss of the NO_2 group and to the formation of the bis adducts [M(pc)(py)$_2$]. The corresponding nitrosyl derivatives, *i.e.* [Co(pc)(NO)] and [Fe(pc)(NO)], are immediately destabilized in liquid pyridine and appear to be also readily attacked by pyridine vapours,[4a] with the probable formation of six-co-ordinate intermediates of formula [M(pc)(NO)(py)] (M = Co or Fe), ultimately also forming the adducts [M(pc)(py)$_2$]. The instability of nitro and nitrosyl derivatives in the presence of excess of pyridine explains why only stoichiometric (1:1) amounts of pyridine were used for the preparation of **1** and **2**.

Characterization of Complexes **1** *and* **2**.—Infrared spectra, magnetic susceptibility measurements, and Mössbauer data provide some information as to the mode of binding of the ligated groups and of the oxidation and spin state of the cobalt and iron centres in the species under discussion.

Complex **1**. The IR spectra of the cobalt complexes **1a** and **1b**, virtually identical in all the regions explored, show complete absence of the very strong ν(NO) absorption (1705 cm^{-1}) observed for [Co(pc)(NO)][4b] and the presence of new characteristic absorptions at 1308vs, 1215w–m and 814vs cm^{-1}, plus a number of weak absorptions clearly ascribable to the presence of pyridine [Fig. 1(*a*)]. As already indicated,[5] the new bands can be unequivocally assigned to the presence of the NO_2 group co-ordinated to the cobalt atom through the nitrogen atom, *i.e.* as a nitro group (A), in keeping with assignments (ν_{asym}, ν_{sym} and δ, respectively) made for analogous macrocyclic Co–NO_2 systems.[2a,b,12] For both **1a** and **1b**, in some preparations, the solid samples obtained exhibit a spectrum with a lower relative intensity for the above-mentioned NO_2 absorptions, associated with the appearance of new absorptions at 1380 and 1270 cm^{-1} [Fig. 1(*b*)]. The intensity of these latter bands is found to be in general complementary to that of the former bands. They might be assigned to a different NO_2 group (B), also ligated as a nitro group, but likely to be differently affected in the solid state by the changed contacts with the immediately adjacent environment. Not in contrast with this hypothesis are the following observations: (*a*) elemental analyses do not distinguish between samples of type A or A + B; (*b*) such samples show in all cases identical X-ray powder patterns; (*c*) visible solution spectra in pyridine are identical both qualitatively and quantitatively [$\varepsilon_{668} = 1.41 \times 10^5$ (A), 1.40×10^5 dm^3 mol^{-1} cm^{-1} (A + B)]; (*d*) when samples containing B are suspended in MeCN and the mixture refluxed for 3–4 h significant conversion of B into A is observed, as easily verified by IR spectra; (*e*) both A and B react with PPh_3, and, whilst $OPPh_3$ is formed, the original nitrosyl derivative is totally regenerated, as also easily verified by IR spectra. In principle, of course, we might admit the B group to be bound as a nitrite (Co–O–NO). In keeping with this hypothesis would be observation (*d*), since nitrito $\longrightarrow$ nitro isomerism is not unusual and has been observed under similar experimental conditions.[13,14] Definitely less compatible with the same hypothesis are the IR spectral features, since the nitrito group should show, with respect to the nitro group, an increase in ν_{asym} and a decrease in ν_{sym},[13,15] and not an increase in both as observed. Secondly, the nitrito group can be regarded as having a scarce tendency to behave as an O-donor;[2d] if this is the case, its conversion into the corresponding nitrosyl group, which is in fact observed, might not be expected.

Complex **1** has a room-temperature magnetic moment of 0.9 B.M. Its parent nitrosyl derivative shows a value of 0.8 B.M. at room temperature, which is practically invariable in the range 300–80 °K. In both compounds the low paramagnetism observed can be assigned to the presence of small amounts of paramagnetic contaminants. Definitely, then, the present cobalt nitro and the nitrosyl complexes are spin paired and diamagnetic.

With the above IR and magnetic data at hand, a local charge distribution for the metal site in complex **1** of the type Co^+–$(NO_2)^-$ can easily be postulated, especially if account is taken of the many closely related examples reported in the literature and dealt with similarly.[2a,b,12,16] In the case of [Co(pc)(NO)], a bent Co–N–O fragment, implying a charge separation of the type Co^+–$(NO)^-$, explains the observed diamagnetism of the metal centre (d^6, low spin) and the facilitated attack of dioxygen on the N atom of the Co–N–O bond system in the formation of the corresponding nitro derivative.[12] Furthermore, the observed ν(NO) (1705 cm^{-1})[4b] for [Co(pc)(NO)] is in the range of values found for [Co(tpp)(NO)] (tpp = 5,10,15,20-tetraphenylporphyrinate) [ν(NO) 1689 cm^{-1}][17] and a number of similar cobalt complexes with bi- or tetra-dentate ligands [ν(NO) 1660–1600 cm^{-1}], for which identical geometry and charge separation have been established.[2a]

Complex **2**. The IR spectrum of the iron complex **2** is very similar to that of **1**, as far as the presence of bands due to pyridine and to the NO_2 group is concerned. Absorptions due to the NO_2 group are located at 1304, 1213 and 811 cm^{-1}, almost coincident in relative intensity and position with those found for **1** and, hence, undoubtedly indicative of the presence of the NO_2 ligated as a nitro group.

Complex **2** has a room-temperature magnetic moment of 2.2 B.M. For [Fe(pc)(NO)] a value of 2.3 B.M. has been found, nearly constant within the range 300–80 K; a slightly lower value (1.9 B.M.) was reported by Taube,[9] whereas the higher value (2.6–2.8 B.M.), previously reported by one of us,[18] was certainly affected by the presence of ferromagnetic impurities. In summary, the magnetic data concur to indicate for both the iron complexes the presence of one unpaired electron in low-spin centres.

The low-temperature (80 K) Mössbauer spectrum of complex **2** is shown in Fig. 2. It shows a main doublet with δ = 0.18 mm s^{-1} (referred to iron metal) and ΔE_Q = 2.43 mm s^{-1}.

Table 1 Oxidation of oct-1-ene by O_2 in the presence of complex **1** or **2** as catalysts in thf[a]

Experiment	Catalyst	Pd/M molar ratio	Turnover number[b]	Amount (%) of product		
				Octa-2-one	Octa-3-one	Octa-4-one
1	**1**	2.8	1.2	82.5	13.1	4.4
2	**1**	2.8	0.5	86.1	8.4	5.5
3	**1**	2.8	1.4	84.9	8.5	6.6
4	**1**	9.3	0.9	62.2	25.7	12.1
5	**1**	0	0			
6	[Co(pc)(NO)]	2.8	0			
7	**2**	2.8	8	98	2	0
8	**2**	2.8	9.5	98.8	1.2	0
9	**2**	2.8	8.1	98.5	1.5	0
10	**2**	9.3	11.7	83.9	12.1	4
11	**2**	0	0			
12	[Fe(pc)(NO)]	2.8	0			

[a] Similar results were obtained with hex-1-ene and dec-1-ene. Blank experiments were always conducted in parallel and, if necessary, appropriate corrections introduced. 2,6-Di(*tert*-butyl)-*p*-cresol was used as a radical inhibitor; in all cases no inhibiting effect was observed, which excludes a radical pathway for the oxidation process. In some cases p_{O_2} = 50 atm was used without significant change in the yield of products. [b] Turnover number = mmol of product/mmol of complex.

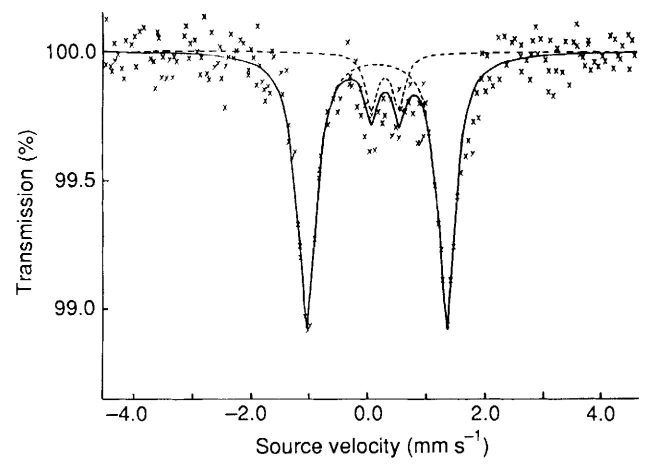

Fig. 2 Mössbauer spectrum at liquid-nitrogen temperature of complex **2**. The central small doublet, δ = 0.32 mm s^{-1} and ΔE_Q = 0.48 mm s^{-1}, reveals the presence in this particular sample of a low percentage (*ca.* 10%) of an iron(III) high-spin impurity, probably the μ-oxo dimer [{Fe(pc)}$_2$O]

These data compare well with those found for several six-coordinate low-spin iron(III) phthalocyanine derivatives recently reported[19] and a series of low-spin iron(III) porphyrin complexes.[20,21] Thus, the presence of low-spin (d^5) Fe^{III} in **2**, implying the Fe^+–$(NO_2)^-$ fragment, can be reasonably accepted. Two plausible formulations can be written for [Fe(pc)(NO)], requiring different oxidation states for the iron centre, *i.e.* Fe^{III}–$(NO)^-$ and Fe^{II}–$NO)^{\bullet}$, both of which might be compatible with a bent Fe–N–O fragment, a geometry found by X-ray diffraction in the low-spin porphyrin complexes [Fe(tpp)(NO)] (Fe–N–O 149.2°)[22,23] and also in [Fe(tpp)(NO)(mim)] (mim = 1-methylimidazole, Fe–N–O = 140°).[24] The observed ν(NO) (1695 cm^{-1}) for [Fe(pc)(NO)],[4b] close to that found for [Co(pc)(NO)] (1705 cm^{-1}),[4b] might suggest the formulation Fe^{III}–$(NO)^-$, also supported by X-ray photoelectron studies.[25] Care should be taken, however, in rigidly relating the ν(NO) position with charge location and geometry in the M–N–O bond systems, particularly intriguing when ν(NO) is at *ca.* 1700–1650 cm^{-1}, on the border for differentation between the opposite notations M^-–$(NO)^+$ (linear) and M^+–$(NO)^-$ (bent). The Mössbauer parameters reported by Taube[9] for [Fe(pc)(NO)] (δ = 0.43 mm s^{-1}, referred to iron metal, and ΔE_Q = 1.69 mm s^{-1}) led this author to suggest the alternative formulation Fe^{II}–$(NO)^{\bullet}$. This sounds reasonable if it is considered that these Mössbauer parameters are close to those of a number of monomeric iron(II) low-spin (d^6, diamagnetic) phthalocyanine[26,27] and porphyrin derivatives,[20,21] and far from those of iron(III) low-spin complexes of the same macrocycles, either monomeric,[19–21], or μ-oxo-bridged dimeric.[28] In the absence of more incisive information concerning the very likely bent Fe–(NO) moiety, no definite assignment can be made about the oxidation state of Fe and electron distribution within the Fe–N–O fragment.

Oxidative Catalysis by Complexes **1** *and* **2**.—The oxidative catalytic properties of complexes **1** and **2** and their respective nitrosyl compounds were examined by using dioxygen as the oxidant, terminal olefins as substrates and $[PdCl_2(NCPh)_2]$ as the olefin activator. The experiments were carried out at room temperature in different media (CH_2Cl_2, dce, benzene, thf, $MeNO_2$). Tetrahydrofuran is the only solvent in which significant results could be obtained. The reaction system for such oxidation reactions is heterogeneous since, whereas both the olefins and the palladium complex are soluble in thf, the catalysts employed, **1** and **2** and the nitrosyl complexes, are practically insoluble under the experimental conditions used. As summarized in Table 1, in all cases oxidation, when observed, transforms the olefins into the corresponding ketones.

The data, concerning the cobalt–nitro complex (experiments 1–3) show that the turnover numbers are within the range 0.5–1.5. They also show that the turnover number does not change significantly by increasing the Pd/Co ratio (experimental 4); this, instead, determines a lower selectivity towards the formation of octan-2-one. The residual solid phthalocyanine material is recovered preponderantly as [Co(pc)(NO)], which is inactive towards oxidation (see below). Clearly, therefore, after O-atom donation by the NO_2 group to the olefin, reoxidation of NO to NO_2 is disfavoured with respect to the more rapid dissociation of [Co(pc)(NO)(py)] into [Co(pc)(NO)] and pyridine. No attempts to lower the rate of dissociation by adding pyridine to the reacting system were made, since we found that substitution of pyridine for PhCN takes place at the palladium cocatalyst. In presence of an excess of pyridine $[PdCl_2(py)_2]$ is easily formed, as directly verified by us. As already anticipated, on the other hand, excess of pyridine causes the elimination of NO from [M(pc)(NO)(py)] and formation of the bis(pyridine) adduct. Absence of the palladium complex, *i.e.* lack of olefin activation, inhibits oxidation (experiment 5). As shown by experiment 6, [Co(pc)(NO)] does not oxidize the olefin, as expected, due to the anticipated difficulty found in its conversion by O_2 into the nitro derivative in the absence of pyridine.

For complex **2** (experiments, 7–10) the conversion of oct-1-

ene into octanones is catalytic with turnover numbers in the range 8–12. This is relevant, **2** being the first Fe–(NO/NO$_2$) redox couple tested and found to be catalytically active in oxidative processes by O$_2$. Similar iron-porphyrin NO/NO$_2$ redox couples appear not to have been examined so far, probably because of the lability of the nitro derivatives.[29] As can be seen from Table 1, in the case of complex **2**, selectivity towards the formation of octan-2-one is very high, being in all the experiments higher than 98%, with minimum amounts of octan-3-one formed and complete absence of octan-4-one. Such catalytic activity and good selectivity are comparable with those observed by Mares and co-workers for the oxidation by O$_2$ of monoolefins in the presence of the same palladium cocatalyst by using [Co(salphen)(NO$_2$)(py)][2a] [salphen = *o*-phenylenebis(salicylideneiminate)] and [Co(tpp)(NO$_2$)(py)],[2b] or rhodium complexes,[2d] as catalysts. As for **1**, the increase in the Pd/Fe ratio neither improves the yield of octanones formed nor the selectivity. The residual solid phthalocyanine material at the end of the experiments is here again the nitrosyl derivative, *i.e.* [Fe(pc)(NO)]. Experiments 11 and 12 lead to the same observations as in 5 and 6.

The oxidative behaviour observed for complexes **1** and **2** is interesting since, for the first time, it concerns two NO/NO$_2$ redox systems having identical molecular composition and differing only in the metal centres. It should also be observed that complex **2** is the first iron containing NO/NO$_2$ redox system observed to be catalytically active in the oxidation of olefins by O$_2$. The heterogeneity of the reaction medium in the above experiments (Table 1) and lack of kinetic data make it difficult to define whether the oxidation process develops through a bi-[2] or a mono-metallic[3] pathway. Thus, a discussion on this point would presently be essentially speculative and must wait for more incisive information.

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