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Nitrosyl and Nitro Derivatives of Phthalocyaninatocobalt(II): Reactivity with Dioxygen and Oxygen Atom Transfer

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Dioxygen activation and oxygen transfer processes operated by a transition metal complex are of biological [1] and practical importance [2] and have been part of our recent investigation by using transition metal phthalocyanines [3], PcM (Pc = phthalocyaninato anion, $C_{32}H_{16}N_8^{=}$, M = bivalent metal ion). Normally M is directly involved in both activation and transfer processes [1, 2]. Recently, however, there have been some examples reported in the literature [4] of redox reactions of the type:

$$L\cdot M\cdot NO \xrightarrow{O_2} L\cdot M\cdot NO_2$$

$$L\cdot M\cdot NO_2 + S \longrightarrow L\cdot M\cdot NO + SO$$

(L = ligand/s) where interaction with O_2 and oxygen transfer to the substrate (S) occur on the ligand (NO/NO_2) coordinated to the metal atom, with only an indirect participation of the latter. Attempts have been described to use these redox reactions for the selective oxidation of organic substrates [4].

We report here on a new system derived from phthalocyaninatocobalt(II), PcCo, involving the NO/NO_2 redox couple and show that this system can be used for the oxidation of substrates such as triphenylphosphine and terminal olefines (*i.e.* 1-octene).

PcCoNO, prepared for the first time in our laboratory by reaction of solid PcCo with gaseous NO [5], can also be easily obtained by suspending PcCo in THF in a NO atmosphere [6]. PcCoNO is stable indefinitely in air. In the presence of pyridine vapours, or when dissolved in pyridine, it transforms into the bispyridine derivative, $PcCo(py)_2$ [5a]; however, when suspended with stirring in dichloroethane containing a stoichiometric amount of pyridine (molar ratio 1:1) in an O_2 atmosphere (50–60 Atm) at room temperature for 24–48 h, PcCoNO is quantitatively converted into a new complex of formula $pyPcCoNO_2\cdot C_2N_4Cl_2$ (**P**). Such formulation is established on the basis of analytical data, thermogravimetric analysis, IR spectra and chemical behaviour.

P is an air-stable compound. Thermograms show that dichloroethane is lost at 90–100 °C and pyridine and NO_2 at *ca.* 200 °C, PcCo being recovered almost unchanged. The IR spectrum of **P** exhibits the various absorptions in the range below 1650 cm^{-1}, typical of the pyridine molecule, plus intense absorptions at 1308, 1215 and 814 cm^{-1}, which unequivocally establish the presence in **P** of the NO_2 group bound through the N atom, *i.e.* as a nitro ligand [7]. We assume that the pyridine molecule is also coordinated in the axial position *trans* to the NO_2 ligand. Thus **P** appears to be a six-coordinate monomeric complex resulting from the $NO \rightarrow NO_2$ transformation, due to interaction with O_2, and the associated ligation of the pyridine molecule. The suggested formulation makes this species formally very similar to the nitro derivatives previously described with TPPCo and Saloph Co [4]. As observed for PcCoNO, **P** is also converted, with a slow process, into $PcCo(py)_2$ by dissolving the NO_2 derivative in pyridine.

P can be used as oxidant for the stoichiometric and catalytic oxydation of triphenylphosphine. When **P** is treated with PPh_3 (molar ratio 1:1) in a N_2 atmosphere at 60–70 °C in dichloroethane for 2 h, a quantitative formation of $OPPh_3$ is observed. Correspondingly, **P** is reconverted into the nitrosyl derivative, as established by the appearance in the IR spectrum of the ν_{NO} absorption at 1705 cm^{-1} and the complete disappearance of all the bands typical of the nitro ligand. The oxygen atom transfer to PPh_3 can be operated catalytically at room temperature under an O_2 atmosphere (oxidation of PPh_3 was followed by IR spectra as described elsewhere [3c]; experiments were devoid of the $OPPh_3$ formed in parallel blanks).

Stoichiometric oxygen atom transfer occurs when **P** is suspended in dichloroethane, under N_2 at 60 °C for 3 h, in presence of 1-octene, and $(C_6H_5CN)_2\cdot PdCl_2$ is used as the olefin activator. In these experiments the NO_2 moiety is reproducibly reconverted into the NO group. IR and mass spectra and G.C. analysis indicate that 1-octene is mainly converted (85%) into 2-octanone.

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