Isolation and characterization of an oxidative degradation product of a polypyridine ligand

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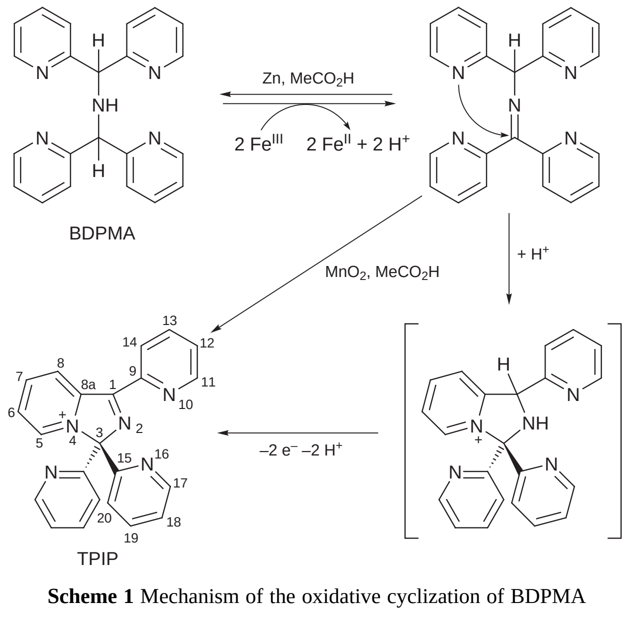
The origin of the fragility of a polypyridine ligand under oxidizing conditions is discussed.

The catalytic activity of non-heme complexes has been recently investigated in relation to non-heme containing enzymes having one or two iron centers.[1] Mononuclear iron complexes with polypyridine ligands have been studied as potential oxidation catalysts.[2] In order to compare the activity of a mononuclear polypyridine–iron complex with porphyrin or phthalocyanine iron catalysts in the oxidative degradation of chlorophenols,[3] we synthesized a new symmetric tetrapyridine ligand, bis[bis(2-pyridyl)methyl]amine (BDPMA, Scheme 1).[4] The iron(III) complex of this ligand, $\mathrm{Fe(BDPMA)(NO_3)_3}$, is able to catalyze the oxidative degradation of aromatic pollutants such as chlorinated phenols in the presence of $\mathrm{KHSO_5}$.[5] Unfortunately, the oxidation stopped at the quinone level (without formation of ring cleavage products which are observed with an iron–phthalocyanine catalyst)[3] and the catalyst seemed to be short-lived. In attempts to crystallize the iron(III) complex of this tetrapyridyl ligand, we found the reason for the low catalytic activity that we observed in chlorophenol oxidations. Instead of a metal complex, the cationic compound 1,3,3-tris(2-pyridyl)-3*H*-imidazo[1,5-*a*]pyridin-4-ium (TPIP) was surprisingly obtained.‡ This degradation product of the BDPMA ligand was completely characterized by ^{1}H NMR, FAB-MS spectrometry and X-ray analysis (Fig. 1).§ The key feature of this structure is the presence of a pyridinium entity with the three other pyridine substituents still intact. Formally, this modified ligand TPIP can be obtained from BDPMA by abstraction of four electrons and three protons. In the crystal structure, the bond lengths of the pyridinium moiety are as expected for such rings and the shortest bond length [N(1)–C(7)] of the imidazole moiety is in agreement with a double bond. The N(2)–C(1) bond of the five-membered ring is around 4 pm longer than the N(1)–C(1) bond, as expected for a C–N$^+$ bond of a pyridinium entity (Fig. 1). The angle between the two planes formed by the imidazopyridinium and the pyridine connected to the C(7) carbon atom (Fig. 1) is only 5°, strongly suggesting that the conjugation is extended to this pyridine.

The formation of TPIP can be explained by the oxidation of BDPMA in the presence of $\mathrm{Fe^{III}}$ species (in the absence of metal traces BDPMA is stable and has been completely characterized). The first step consists of a two-electron oxidation of BDPMA by 2 equiv. of iron(III). The resulting imine can be activated by protonation and then attacked by a pyridine nitrogen acting as internal nucleophile to generate a five-membered ring (Scheme 1). This reaction is already known for pyridyl substituted imines, which after cyclization, are further oxidized to imidazo[1,5-*a*]pyridines.[6] This is not possible in the present case because a quaternary carbon is created during the cyclization (C^3, Scheme 1). Consequently, only one C–N double bond can be obtained by dehydrogenation of the five-membered ring (step 3, Scheme 1), and the pyridinium nitrogen remains positively charged. The cationic TPIP was obtained with nitrate as counterion (Scheme 1).



Scheme 1 Mechanism of the oxidative cyclization of BDPMA

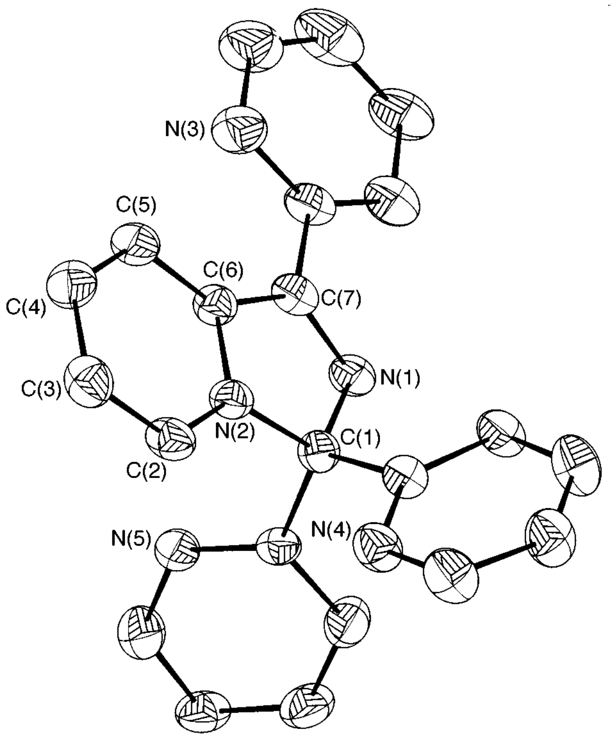


Fig. 1 Crystal structure of TPIP (atom numbering is differing from that presented in Scheme 1).§ Selected bond lengths (Å): N(1)–C(1) 1.457(4), N(1)–C(7) 1.293(5), N(2)–C(1) 1.498(4), N(2)–C(2) 1.336(4), N(2)–C(6) 1.364(4), C(2)–C(3) 1.374(5), C(3)–C(4) 1.383(6), C(4)–C(5) 1.388(5), C(5)–C(6) 1.377(5), C(6)–C(7) 1.471(5).

To prove this mechanism, we synthesized TPIP on a large scale *via* the imine. The latter is already known as precursor of BDPMA and has been reduced by Zn to obtain BDPMA.[4] For the oxidation, MnO_2 has been employed and TPIP was isolated in 73% yield.‡ A slow oxidation leading to the C–N double bond was observed in the presence of molecular oxygen, but we found that MnO_2 was the suitable oxidant to efficiently prepare TPIP.

The isolation and characterization of this degradation product is a significant illustration of the denaturation of a polypyridine ligand in oxidative conditions. The mechanism of the degradation was confirmed by the synthesis of the obtained product from the intermediary imine. The present work shows that ligands having easily oxidizable C–H bonds, *i.e.* activated in benzylic position or in α-position of a hetero atom, have to be avoided for stability reasons in the design of effective and long-lived oxidation catalysts.

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Notes and References

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‡ *Preparations*: TPIP [oxidation of BDPMA with $Fe(NO_3)_3$]: BDPMA (100 mg, 0.283 mmol) in methanol (2 ml) was added to a solution of $Fe(NO_3)_3{\cdot}9H_2O$ (105 mg, 0.260 mmol) in methanol (2 ml) and the mixture allowed to stand for 1 h. The solvent was evaporated and the residue dried under oil-pump vacuum for 3 h at 60 °C and *ca.* 10 mg of the obtained powder were dissolved in acetone. The solution was allowed to stand in an atmosphere of diethyl ether for two weeks. The solution became colorless, brown drops condensed and a large branched crystal was obtained, on which an X-ray analysis could be carried out. A yellow crystal was also obtained from an ethanolic solution in a methyl *tert*-butyl ether (MTBE) atmosphere. A part of this was cut and used for the presented X-ray structure. The remaining crystal was dissolved in dry $(CD_3)_2SO$ for ^{1}H NMR analysis and mass spectrometry. ^{1}H NMR [250 MHz, $(CD_3)_2SO$, 25 °C] δ 7.69 [dd, ^3J(HH) 7.7, ^3J(HH) 4.8 Hz, 2 H, 18-H], 7.91 [d, ^3J(HH) 7.9 Hz, 2 H, 20-H], 7.93 [ddd, ^3J(HH) 7.8, ^3J(HH) 4.8, ^4J(HH) 1.0 Hz, 1 H, 12-H], 8.14 [td, ^3J(HH) 7.7, ^4J(HH) 1.7 Hz, 2-H, 19-H], 8.32 [td, ^3J(HH) = 7.8 Hz, ^4J(HH) 1.7 Hz, 1 H, 13-H], 8.51 [ddd, ^3J(HH) 7.7, ^3J(HH) 6.2, ^4J(HH) 1.1 Hz, 1 H, 6-H], 8.75 [d, ^3J(HH) 4.8 Hz, 2 H, 17-H), 8.76 [d, ^3J(HH) 7.8 Hz, 1 H, 14-H], 9.08 [d, ^3J(HH) = 4.8 Hz, 1 H, 11-H], 9.13 [td, ^3J(HH) 7.7, ^4J(HH) 1.0 Hz, 1 H, 7-H], 9.60 [d, ^3J(HH) 8.0 Hz, 1 H, 8-H], 10.18 [d, ^3J(HH) 6.2 Hz, 1 H, 5-H]; FAB-MS (*meta*-nitrobenzyl alcohol): *m*/*z* (%): 350 (100).

TPIP (preparative synthesis): 300 mg (1.63 mmol) of bis(2-pyridyl)-ketone and 300 mg (1.63 mmol) of bis(2-pyridyl)methylamine[4] were dissolved in 10 ml of absolute isopropanol and dried over molecular sieves 3 Å for 1 h at room temperature. 350 μl (5.5 mmol) of glacial acetic acid was added under N_2 atmosphere and the reaction mixture refluxed for 5 h. 1.42 g (16.3 mmol) of MnO_2 was added (the oil bath was removed for the addition). After 1 h heating was switched off and the reaction mixture allowed to cool slowly. After 16 h, solids were removed by filtration. The solvent was evaporated (50 °C, 30 Torr) and the residue dissolved in 10 ml CH_2Cl_2 and washed with brine (2 × 5 ml). The crude reaction mixture was dissolved in MeOH and exposed to a MTBE atmosphere. 498 mg (1.19 mmol, 73%) of yellow crystals were obtained.

§ *Crystal data* for $C_{22}H_{16}N_6O_3$ (TPIP): M = 412.41, yellow pale crystal (0.20 × 0.20 × 0.10 mm), monoclinic, space group $I2/a$, a = 22.665(3), b = 8.4832(8), c = 23.415(3) Å, β = 117.83(2)°, U = 3982 Å^3, Z = 8, D_c = 1.37 g cm^{-3}, λ = 0.71073 Å, T = 160(2) K, μ(Mo-Kα) = 0.89 cm^{-1}, 25822 reflections (3166 independent) were collected on a STOE-IPDS diffractometer, 281 parameters were refined using the least-squares method on F[7], R = 0.051 and R_w = 0.055. CCDC: 182/925.

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