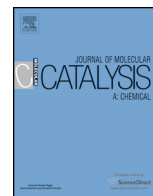




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Catalytic oxidation of alkene by cobalt corroles

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ABSTRACT

Four cobalt (III) corroles bearing different number of pentafluorophenyl and phenyl groups were synthesized and characterized by elemental analysis, HR-MS, UV–vis, NMR, XPS as well as cyclic voltammetry. The first investigation of cobalt corrole catalyzed oxidation of alkene was conducted by using styrene as substrate. The best yield was obtained in acetonitrile solvent in the air with TBHP oxidant (96% yield based on oxidant, up to 96 TON). Benzaldehyde was detected as the main product by using $\text{PhI}(\text{OAc})_2$, TBHP, KHSO_5 , PhIO as oxidants. In contrast, styrene oxide was found to be the major product when using *m*-CPBA oxidant. Nearly no products could be found by using H_2O_2 oxidant. Possible catalytic oxidation pathway was also discussed based on the observations of UV–vis changes of the catalytic system in the absence of substrate and in-situ HR-MS.

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1. Introduction

Metal corrole has been proved one type of efficient catalysts for oxidation [1]. In fact, lots of metal corroles such as chromium corroles [1], manganese corroles [2–5], and iron corroles [6–9] have been used in the catalytic oxidation of organic substrates. It was found that catalytic oxidation reactions by metal corroles are significantly affected by oxidants, solvents and the electronic structure of the catalysts. Cobalt corrole is a very important class of metal corroles. It is a kind of very promising non-precious-metal catalyst in fuel cell technology and a large number of investigations have been devoted to the catalytic reduction of oxygen by cobalt corroles [10–16].

Cobalt corrole has also been proved as efficient catalysts for cyclopropanation [17], water oxidation [18–21], hydrogen evolution [22–25], CO_2 reduction [26], and photocatalytic water splitting reaction [27]. Cobalt corroles are also potential detection sensor for CO [28–30]. It is well-known that $\text{Co}(\text{II})$ porphyrins are an efficient catalysts for the oxidation of alkene [31–34]. To the best of our knowledge, no studies about cobalt corrole catalyzed oxidation of organic substrates has been reported so far. Herein, we wish to report the catalytic oxidation of styrene by cobalt corroles bearing different electronic features (Scheme 1). The effect of solvents and oxidants on the catalytic reactions were also explored.

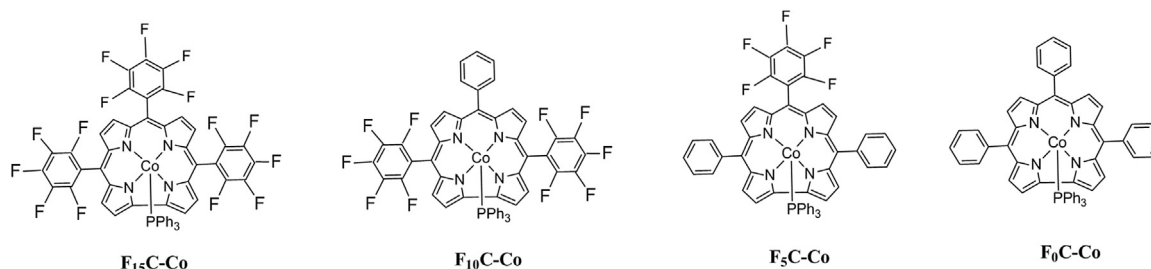
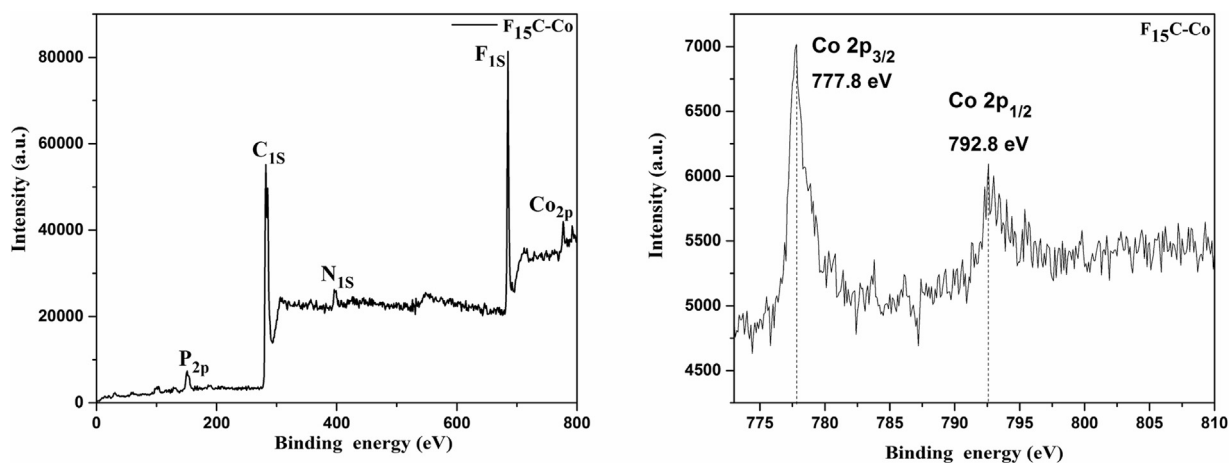
2. Experimental

2.1. Materials and methods

All chemicals and solvents were purchased from Sinopharm Chemical Reagents Co. Ltd. and used without further purification unless otherwise mentioned. Pyrrole was redistilled prior to use. Commercial analytical grade styrene (Aladdin) was passed through short column of basic alumina prior to use. Iodosylbenzene (PhIO) was synthesized by a reported method [35]. The supporting electrolyte in CV experiments, tetrabutylammonium perchlorate, was purchased from Fluka and recrystallized from ethanol at least three times. The ^1H NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker Avance III 400 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra DLD spectrometer. Mass spectras were taken on Bruker Esquire HCT plus mass spectrometer (ESI/MS) and Bruker maxis impact mass spectrometer with an ESI source (HR-MS). All cyclic voltammograms (CV) were performed in acetonitrile solutions containing 0.1 M TBAP (tetrabutylammonium perchlorate) using an Ingens Model 1030 and cobalt corroles (1×10^{-3} M) under nitrogen atmosphere at ambient temperature. A three-electrode system consisting of a glassy carbon working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode were employed. The scan rate was 100 mV/s. Half-wave potentials ($E_{1/2}$) for reversible or quasi-reversible redox processes were calculated as $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$, where E_{pa} and E_{pc} represent the anodic and cathodic peak potentials, respectively. The $E_{1/2}$ value for the ferrocenium/ferrocene couple under these conditions was 0.47 V. The freshly synthesized cobalt corrole solution ($\sim 3 \times 10^{-3}$ M) was taken in the cuvette and

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**Scheme 1.** Structures of cobalt (III) corrole complexes.**Fig. 1.** a (left) X-ray photoelectron spectroscopy of the chemical composition of **F₁₅C-Co 1b**. (right) Co 2p regions in **F₁₅C-Co**.

placed immediately in a thermostat cell holder in a UV–vis spectrophotometer. All experiments, unless specified otherwise, were carried out at room temperature. Electronic absorption measurements were performed on a Blue Star B UV–vis spectrophotometer connected with a thermostat. The absorbance data was collected over the range of 300–800 nm at 5 min interval. Each measurement was repeated three times at 25.0 ± 0.1 °C. The X-band CW EPR test was measured on a Bruker, A300-10-12 Bruker EPR spectrometer (microwave (mw) frequency 9.43 GHz). An mw power of 2.19 mW, a modulation amplitude of 0.4 mT, and a modulation frequency of 100 kHz were used. Measurement was done at a temperature of 103 K.

2.2. Synthesis of freebase corrole

All other A₃- and trans-A₂B free base corroles were prepared smoothly according to the reported procedures [6,36–38].

2.3. Synthesis of cobalt (III) corroles

Cobalt corrole **F₀C-Co** was synthesized which follows a method reported in the literature [15]; (5,10,15-tris(pentafluorophenyl) cobalt corrole **F₁₅C-Co** was synthesized according to the literature [39]; New cobalt corroles **F₁₀C-Co**, **F₅C-Co** were prepared by 20 mg corresponding free base corrole which was dissolved in 30 mL of ethanol containing 141 mg CoCl₂·4H₂O, triphenylphosphine (5.0 equivalents vs. the free base corrole) and 30 mg anhydrous NaOAc in 50 mL in a round bottom flask. The mixture was stirred for about for 1.5 h under room temperature and the progress of the reaction monitored by thin-layer chromatography until the starting corrole was consumed. After the completion of reaction, the sample was washed with dichloromethane and water for 2–3 times and was collected. The red fraction was evaporated to dryness and was puri-

fied by column chromatography on silica gel (200–300 mesh) using hexene/CH₂Cl₂ as eluent, respectively. The yields of cobalt corroles in all cases were about 75%. All reported ¹H NMR and ¹⁹F NMR as well as HRMS-ESI-MS spectra of cobalt corroles were given (see Figs. S1–S11 in the Supporting information).

2.4. 5,10,15-tris (phenyl) cobalt (III) corrole, F₀C-Co (III)

UV–vis. (CH₂Cl₂): λ_{max}, nm. ($\times 10^{-3}$ ε, L mol⁻¹ cm⁻¹). 385 (42.89), 562 (8.14). HR-MS (ESI): *m/z* found: 846.2273, calcd for C₅₅H₃₈CoN₄P: 846.2271; ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.3 Hz, 2H), 8.34 (d, *J* = 4.7 Hz, 2H), 8.16–7.97 (m, 7H), 7.68–7.49 (m, 11H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 3H), 6.71 (t, *J* = 7.4 Hz, 6H), 4.84–4.66 (m, 6H). Elemental analysis: found (%): C 78.58, H 4.78, N 6.16. calcd for (C₅₅H₃₈CoN₄P): C 78.19, H 4.53, N 6.63.

2.5. 5,15-bis (phenyl)-10-(pentafluorophenyl) cobalt (III) corrole, F₅C-Co (III)

UV–vis. (CH₂Cl₂): λ_{max}, nm. ($\times 10^{-3}$ ε, L mol⁻¹ cm⁻¹). 386 (43.72), 556 (6.66), 557 (6.66). HR-MS (ESI): *m/z* found: 935.1768, calcd for C₅₅H₃₃CoF₅N₄P: 935.1768; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 4.3 Hz, 2H), 8.34 (d, *J* = 4.6 Hz, 2H), 8.05 (d, *J* = 4.5 Hz, 2H), 8.00 (d, *J* = 4.8 Hz, 2H), 7.79 (s, 2H), 7.59 (t, *J* = 6.2 Hz, 8H), 7.49–7.37 (m, 15H); ¹⁹F NMR (376 MHz, CDCl₃) δ -137.95 (dd, *J* = 395.4, 24.2 Hz), -154.58 (t, *J* = 20.9 Hz), -162.19 to -162.74 (m). Elemental analysis: found (%): C 71.04, H 3.76, N 5.54. calcd for (C₅₅H₃₃CoF₅N₄P): C 70.67, H 3.56, N 5.99.

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