Supplementary Material (ESI) for Dalton Transactions

Supplementary Informations

Selective Extradiol Cleavage of Catechol Achieved in Organized Assemblies Using $[Fe(BPA)Cl_3]$ (BPA = bis(pyridylmethyl)amine)

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Complex Characterisation

The UV-Vis spectral data of **1** [380 nm (5200 M^{-1} cm^{-1}) and 285 nm (7120 M^{-1} cm^{-1})] in methanol agree well with the published data.[1]

Experimental Conditions

Electronic spectra were recorded on a Diode Array Spectrophotometer Agilent 8453. ^1H NMR spectra were recorded on a Bruker 200 MHz NMR spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed at 25 ± 0.2 °C using a three-electrode cell configuration. A platinum sphere, a platinum plate and Ag(s)/$AgNO_3$ were used as working, auxiliary and reference electrodes respectively. Platinum sphere electrode was sonicated for two minutes in dilute nitric acid, dilute hydrazine hydrate and in double distilled water to remove the impurities. The reference electrode for non-aqueous solution was Ag(s)/Ag^+ which consists of a Ag wire immersed in a solution of $AgNO_3$ (0.01 M) and *tetra-N*-butylammonium perchlorate (0.1 M) in acetonitrile placed in a tube fitted with a vycor plug. The instruments utilized included an EG & G PAR 273 Potentiostat/Galvanostat and P-IV computer along with EG & G M270 software to carry out the experiments and to acquire the data. The temperature of the electrochemical cell was maintained by a cryo-circulator (HAAKE D8-G). The $E_{1/2}$ observed under identical conditions for Fc/Fc^+ couple in acetonitrile was 0.100 V with respect to Ag/Ag^+ reference electrode. The experimental solutions were deoxygenated by bubbling research grade nitrogen and an atmosphere of nitrogen was maintained over the solution during measurement. **Electrochemistry of the complexes and adducts** were carried out in non-aqueous, aqueous and aqueous micellar solutions. The micellar solutions (0.1 M SDS, CTAB and TX 100) were prepared afresh each time using deoxygenated double distilled water (25 mL) and then deoxygenated using nitrogen. A stock solution (0.1 mL) of the complex and their corresponding catecholate adducts (1.0×10^{-2} M) were delivered into the micellar solutions and stirred well using a magnetic stirrer.

The reactions in micellar media were optimized by changing the ratio of concentrations of both the reactants [Fe(L)Cl_3] and H_2DBC, and by changing the concentration of micelles and volume of the whole bulk. No cleavage product was observed when [Fe(L)Cl_3] or micelle/solvent or H_2DBC was omitted in the reaction. The ratio of the concentrations of the reactants, [Fe(L1)(DBC)Cl] : micelle (SDS), which was found to give optimum activity is 8:1.

The reaction was found to proceed in water and in aqueous CTAB (8:1) and Triton X-100 (14:1) micellar solutions but at rates lower than in SDS medium.

Kinetic analyses of the catechol cleavage reactions were carried out by time-dependent measurement of the disappearance of the lower energy catecholate-to-iron(III) LMCT band at ambient temperature (25 °C) by exposing the catecholate adducts prepared in situ to molecular oxygen. The water and micellar solutions were equilibrated at the atmospheric pressure of O_2 at 25 °C and the solubility of O_2 at 25 °C in water is 8.1×10^{-4} M. Stock solutions of the adduct [Fe(L)(DBC)Cl] was generated in situ in methanol by treating the complex (1.0×10^{-2} M) with an equivalent amount of H_2DBC pretreated with two equivalents of Et_3N. Oxygenation was started by rapid delivery of a stock solution (0.1 mL) of the catecholate adduct (1.0×10^{-2} M) by syringe to O_2-saturated solvent (2.9 mL) or micellar solution (2.9 mL). Kinetic analyses of the catechol cleavage reactions were carried out by time dependent measurement of the disappearance of the lower energy DBC^{2-}-to-iron(III) LMCT band in presence and absence of chloride ions. Solution of the complex [Fe(L)Cl_3] in methanol was treated with three equivalents of $AgClO_4 \cdot H_2O$ dissolved in acetonitrile and the solution containing **Error! Not a valid link.**centrifuged to remove AgCl. Stock solution (6.0×10^{-3} M) of the adduct $[Fe(L)(DBC)(Sol)]^+$ was prepared in situ in methanol by treating the solution of $[Fe(L)(Sol)_3]^{3+}$ with an equivalent amount of H_2DBC pretreated with two equivalents of Et_3N.

The product analysis was carried out by stirring the complex $[Fe(L)(Sol)_3]^{3+}$ (0.1 mmol), H_2DBC (0.1 mmol) and triethylamine (0.2 mmol) in dichloromethane (20 mL) solvent under molecular oxygen over 12 h at room temperature. After the reaction was complete, the reaction mixture was concentrated under reduced pressure and extracted with diethylether (3×15 mL). The remaining residue was acidified with drops of con. HCl to decompose the metal complexes and extracted with diethylether (3×5 mL). The combined extracts were dried over Na_2SO_4 and then concentrated. The product analyses for reactions in aqueous and micellar solutions were carried out by stirring the complex [Fe(L)Cl_3] (0.1 mmol), H_2DBC (0.1 mmol) and triethylamine (0.2 mmol) in water (5 mL), SDS (0.1 M), CTAB (0.1 M) and TX-100 (0.1 M) micellar solutions (5 mL) under molecular oxygen over 12 h at room temperature. The reaction solutions were acidified with drops of con. HCl to pH 3 to decompose the metal complex and then extracted

with diethyl ether (3 × 15 mL). The diethyl ether solutions were passed through a lengthy silica column in order to remove the surfactant coming along with the ether layer and the extracts collected from the column were dried over Na_2SO_4 and then concentrated. The products were analyzed by using Hewlett Packard (HP) 6890 GC series Gas Chromatograph equipped with a FID detector and a HP-5 capillary column (30 m x 0.32 mm x 2.5 μm) GC-MS analysis was performed on a Perkin-Elmer Clarus 500 GC-MS instrument using a PE-5 (HP-5 equivalent) capillary column under conditions that are identical to that used for GC analysis.

The three major cleavage products a, **c** and **d** were isolated by column chromatography over silica gel (60-120 mess) using 5-10% ethylacetate in *n*-hexane and identified using retention times of GC-MS (EI) and 1H NMR spectroscopy. The other two minor products **e** and **f** were analyzed as a mixture and identified by GC-MS (EI) analysis. The regioisomers **e**/**f** and **c**/**d** were distinguished by comparison of their retention times of GC (FID) and GC-MS (EI) and the intensity of the fragmentation pattern in the mass spectrum. All of the products were quantified using GC (FID) with the following temperature program: injector temperature 130 °C; initial temperature 60 °C, heating rate 10 °C min^{-1} to 130 °C, then increasing at a rate of 2 °C min^{-1} to 160 °C, and then increasing at a rate of 5 °C min^{-1} to 260 °C; FID temperature 280 °C. GC-MS analysis was performed under conditions identical to those used for GC analysis; retention times in GC-MS (EI): 14.6 min for **d**, 15.9 min for **e**, 16.4 min for **c**, 18.1 min for **f** and 21.2 min for **a**.

References:

1 M. Y. M. Pau, J. D. Lipscomb and E. I. Solomon, *Proc. Natl. Acad. Sci.*, U. S. A., 2007, **104**, 18355.