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Synthesis and characterization of dendritic salicylaldimine complexes of copper and cobalt and their use as catalyst precursors in the aerobic hydroxylation of phenol

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ABSTRACT

A series of generation 1 (G1) and generation 2 (G2) salicylaldimine functionalized polypropylene imine dendrimers were used to prepare a range of new copper and cobalt metallodendrimers. These were found to be efficient catalysts in the aerobic hydroxylation of phenol using H_2O_2 and molecular oxygen as oxidants. The major products obtained were catechol and hydroquinone. The selectivity to these two products was greatly influenced by the nature of the metallodendrimer as well as by the pH of the reaction medium.

1. Introduction

Oxidative transformation of simple organic feedstocks to value-added chemicals is widely employed in industry and often plays a pivotal role in producing valuable starting materials for the fine chemical and pharmaceutical industries. The dihydroxy-benzenes, catechol and hydroquinone are two examples of such compounds produced via an oxidation process. Wet-air hydroxylation of phenol is a well-known synthetic route commonly employed to produce these dihydroxybenzenes. Some examples of the homogeneously catalysed hydroxylation of phenol are the Rhône-Poulenc process [1] which employs strong mineral acids as catalysts or the Hamilton process which employs Fenton's reagent as catalyst [2]. There are also several other examples where Fenton type systems have been employed using relatively mild reaction conditions [3–5].

The use of aqueous H_2O_2 and molecular oxygen are viewed as relatively benign oxidants. H_2O_2 is a fairly strong oxidant and a significant advantage is the production of water as a major by-product of the process. There is however still a need for suitable catalyst systems for the aforementioned oxidants to be employed successfully industrially. This has led to an increased interest in transition metal complexes as oxidation catalysts. Metal complexes based on porphyrins [6,7], phthalocyanines [7] and Schiff bases [8–11] are amongst the examples which have been employed as catalysts in the phenol hydroxylation reaction. These types of compounds have also been invoked as model systems to obtain mechanistic insight into the behaviour of enzymes such as cytochrome P-450 and peroxidases [12]. Due to the inherent problems of homogeneous catalysts, several attempts have been made to support these catalysts on different types of carriers e.g. polymeric supports [13] and inorganic supports such as mesoporous silica, zeolites and clays [13–17]. There is however only one example where phenol hydroxylation catalysts have been supported on dendrimers as carriers [18]. Dendrimers differ from other polymeric carriers in that they are monodispersed with well-defined molecular architectures.

In this paper we report on the preparation and characterization of new metallodendrimers of copper and cobalt and their evaluation as multinuclear catalysts in the hydroxylation of phenol. The catalytic behaviour of the dendritic complexes was compared with two mononuclear analogues. The behaviour of these catalysts in the hydroxylation process at different pH values is also discussed.

2. Experimental

2.1. Materials and instrumentation

Ligands and metal complexes were synthesized using standard Schlenk techniques under nitrogen using a dual vacuum/nitrogen

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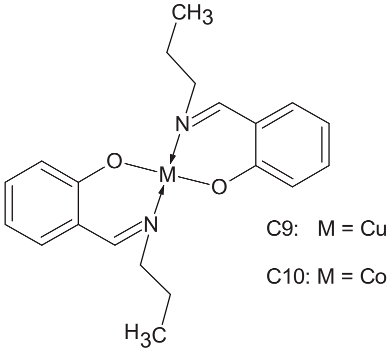

Fig. 1. Mononuclear N propylsalicylideneimine complexes of Cu and Co.

Schlenk line. The NMR spectra were recorded on a Varian Gemini 2000 spectrometer (^{1}H at 200 MHz, ^{13}C at 50.3 MHz) at room temperature using tetramethylsilane as an internal standard. The chemical shifts are reported in δ (ppm) and referenced relative to residual proton signals for the NMR solvent. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 PC FT-IR spectrophotometer as KBr pellets for solids or between NaCl plates for oils. GC-MS analysis was performed using a Finnigan-Matt GCQ-Gas chromatograph equipped with an electron impact ionisation source at 70 eV and a 30 m HP-MS capillary column with a stationary phase based on 5% phenylmethylpolysiloxane. ESI-MS spectra were obtained on a Waters API Q-TOF Ultima spectrometer calibrated with NaF. UV–Vis spectra were recorded on a GBC UV–VIS 920 spectrophotometer as dichloromethane solutions. Microanalyses were performed at the University of Cape Town's micro analytical laboratory.

Mononuclear copper [19] and cobalt [20] *N*-propylsalicylideneimine analogues of the dendritic complexes were prepared as described in the literature (Fig. 1).

2.2. General procedure for the synthesis of first and second generation peripherally functionalized salicylaldimine dendrimers, *L1*–*L4*

The dendritic salicyaldimine ligands, **L1**–**L4** were prepared as previously reported by us [21].

2.3. Synthesis of copper metallodendrimers, *C1*–*C4*

The synthesis of first and second generation copper metallodendrimers is described using the synthesis of metallodendrimer **Cl** as an example.

$Cu(OAc)_2{\cdot}H_2O$ (1 mmol) and dendritic ligand **L1** (0.5 mmol) were mixed in methanol (20 mL). The mixture was refluxed for 4 h. During this time a dark green solid precipitates from solution. The reaction mixture was allowed to cool to °0 C and the solid filtered off under vacuum and then dried. A similar procedure was used to synthesize the G2 Cu metallodendrimers using ligands **L3** and **L4**; the only difference being that in this case the ratio of $Cu(OAc)_2{\cdot}H_2O$ to ligand was 1:0.25. All the products were recrystallized from a 1:2 dichloromethane/ethanol mixture. The complexes were isolated as green solids in yields ranging from 60–75%.

2.4. Synthesis of cobalt metallodendrimers (*C5*–*C8*)

The synthetic protocol for the synthesis of the G1 and G2 cobalt metallodendrimers is illustrated using the synthesis of **C5** as an example.

$Co(OAc)_2{\cdot}4H_2O$ (1 mmol), NaOH (0.5 mmol) and the dendritic ligand **L1** (0.5 mmol) were added to methanol (20 mL). The resulting mixture was refluxed for 4 h. During this time, a brown solid settles out of solution. The solid material was filtered off using a Buchner funnel. The product was dissolved in CH_2Cl_2 and the mixture filtered under gravity. The solvent was removed from the filtrate yielding a brown solid residue. The product was recrystallized by dissolving in a minimum volume of CH_2Cl_2 and then layering the solution with ethanol. This yielded the cobalt metallodendrimers as brown powders with yields ranging from 60–70%. It should be noted that in the case of the generation 2 (G2) dendrimers, the ligand was reacted with 4 mol equivalents of $Co(OAc)_2{\cdot}4H_2O$.

2.5. General procedure for the hydroxylation of phenol

A 12-place RADLEYS Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system was employed to perform the hydroxylation reactions. In a typical reaction, phenol (1 mmol) and the appropriate catalyst (0.1 mmol) was placed in a 50 mL glass reaction vessel followed by the appropriately buffered solution (10 mL) which was saturated with oxygen for approximately 15 min prior to use. The temperature of the reactor was brought to 110 °C under an oxygen atmosphere and the mixture stirred at this temperature for 15 min. A 30% H_2O_2 (w/w) solution (1 mmol) was added and the reaction mixture stirred at 110 °C under an oxygen atmosphere for a further 6 h. The reaction mixture was cooled to room temperature and a 1 mL sample withdrawn, filtered through a syringe filter and diluted 20 times. The consumption of phenol and the oxidation products obtained were analysed by HPLC. Detection of the products was performed with a dual wavelength UV detector (254 and 275 nm). The mobile phased used was a mixture of 0.1% formic acid solution and acetonitrile.

3. Results and discussion

3.1. Synthesis and characterization of the dendritic ligands, *L1*–*L4*

The dendritic ligands were prepared as previously reported [21]. The authenticity of the ligands was confirmed by comparing its spectroscopic data with that reported by us previously.

3.2. Synthesis and characterization of complexes

3.2.1. Dendritic copper complexes (*C1*–*C4*)

The 1st generation dendritic copper complexes (**C1** and **C2**) and their 2nd generation analogues (**C3** and **C4**) were synthesized by reacting the appropriate ligand with 2 mol equivalents of copper acetate in refluxing methanol (Scheme 1). The complexes were isolated as green solids with yields varying between 60–75%. The copper complexes were found to be stable in solution as well as in the solid state.

3.2.2. Dendritic cobalt complexes (*C5*–*C8*), Scheme 2

The cobalt analogues of the abovementioned copper complexes were prepared using a slightly modified approach. The desired metallodendrimers were obtained by reacting the dendritic ligands with cobalt acetate in the presence of sodium hydroxide. No reaction is observed in the absence of a strong base which is required to deprotonate the phenoxy OH as the cobalt acetate is not basic enough to do so. All four cobalt metallodendrimers were isolated as brown solids in yields ranging from 60–70%. These dendritic cobalt complexes although stable in the solid state were prone to slow oxidation in solution, a phenomenon previously also observed for mononuclear *N*-(aryl)-salicylaldimine complexes of cobalt [22]. The complexes show good solubility in dichloromethane and THF.