Inorganica Chimica Acta 394 (2013) 649–655

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

S.F. Mapolie [a],*, J.L. van Wyk [b]

[a] Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa
[b] University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

ARTICLE INFO

Article history:
Received 7 April 2012
Received in revised form 27 June 2012
Accepted 11 September 2012
Available online 29 September 2012

Keywords:
Hydroxylation
Phenol
Salicylaldimine complexes
Phenol oxidation
Dendritic complexes
Metallodendrimers

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

---

* Corresponding author.
E-mail address: smapolie@sun.ac.za (S.F. Mapolie).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2012.09.006

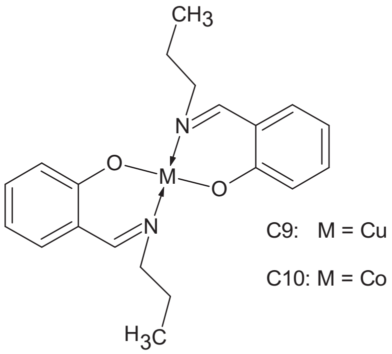


Fig. 1. Mononuclear N propylsalicylideneimine complexes of Cu and Co.

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.

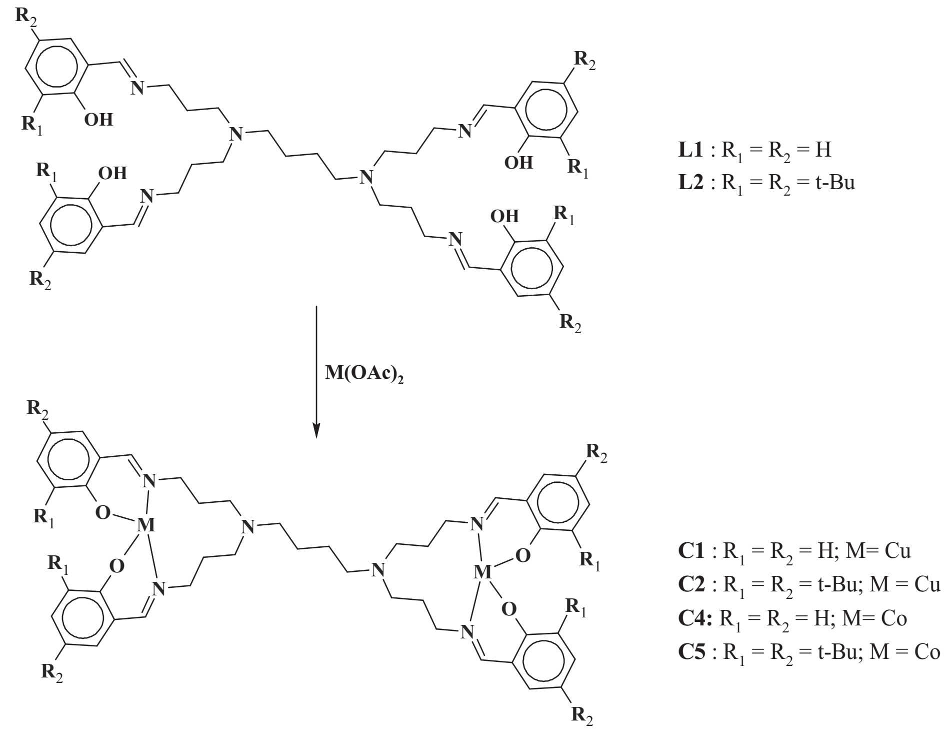
3.2. Synthesis and characterization of complexes

*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.



Scheme 1. Preparation of G1 metallodendrimers.

3.2.3. FT-IR spectra of the complexes

The dendritic copper and cobalt complexes were examined using FT-IR spectroscopy in the solid state (ATR). The IR spectra of the complexes show distinctive shifts of the ν(C═N) and the ν(C–O) bands. The shift of the ν(C═N) band for these complexes was relatively small compared to that for other salicylaldimine complexes. The IR spectra do however show a fairly significant shift of the ν(C–O) band to higher values of around 45 cm^{-1}. These ligands thus act as N, O chelating ligands. A summary of the IR data is given in Table 1.

3.2.4. UV–Vis spectra

The UV–Vis spectra of the dendritic complexes were recorded in dichloromethane. A summary of the UV data is shown in Table 1. In the case of the copper metallodendrimer four bands are observed in the spectra of complexes **C1**–**C4**. The first two bands observed in the region 233–241 nm and 269–280 nm can be assigned to intra ligand π–π* transitions associated with the aromatic rings of the ligands. A third band in the range 304–317 nm is assigned to the n → π* transitions of the azomethine chromophore. These first three bands are also present in the corresponding ligand on which the complex is based. A fourth band not present in the spectrum of the ligand is observed in the region 369–377 nm. This is assigned to a metal to ligand charge transfer (MLCT) transitions.

The spectra obtained for the copper metallodendrimers are similar to what is normally observed for square planar complexes of copper [23]. The UV–Vis spectra of the cobalt metallodendrimers show only two broad bands, one in the region 237–239 nm and the other in the region 348–360 nm. The latter is associated with metal–ligand charge transfer (MLCT) transitions [24].

Table 1
Infrared and UV–Vis spectroscopic data for copper (II) and cobalt (II) metallodendrimers.

Complex	UV–Vis λ_{max} (cm^{-1})	IR spectra (cm^{-1})[a]	
		ν(C═N)	ν(C–O)
C1	241, 272[b], 304[b], 369	1634	1325
C2	233, 280[b], 310[b], 377	1632	1326
C3	237, 269[b], 304[b], 370	1634	1325
C4	234, 277[b], 317[b], 377	1632	1325
C5	239, 348	1630	1306
C5	239, 359	1630	1319
C6	239, 360	1634	1308
C7	237, 358	1631	1321

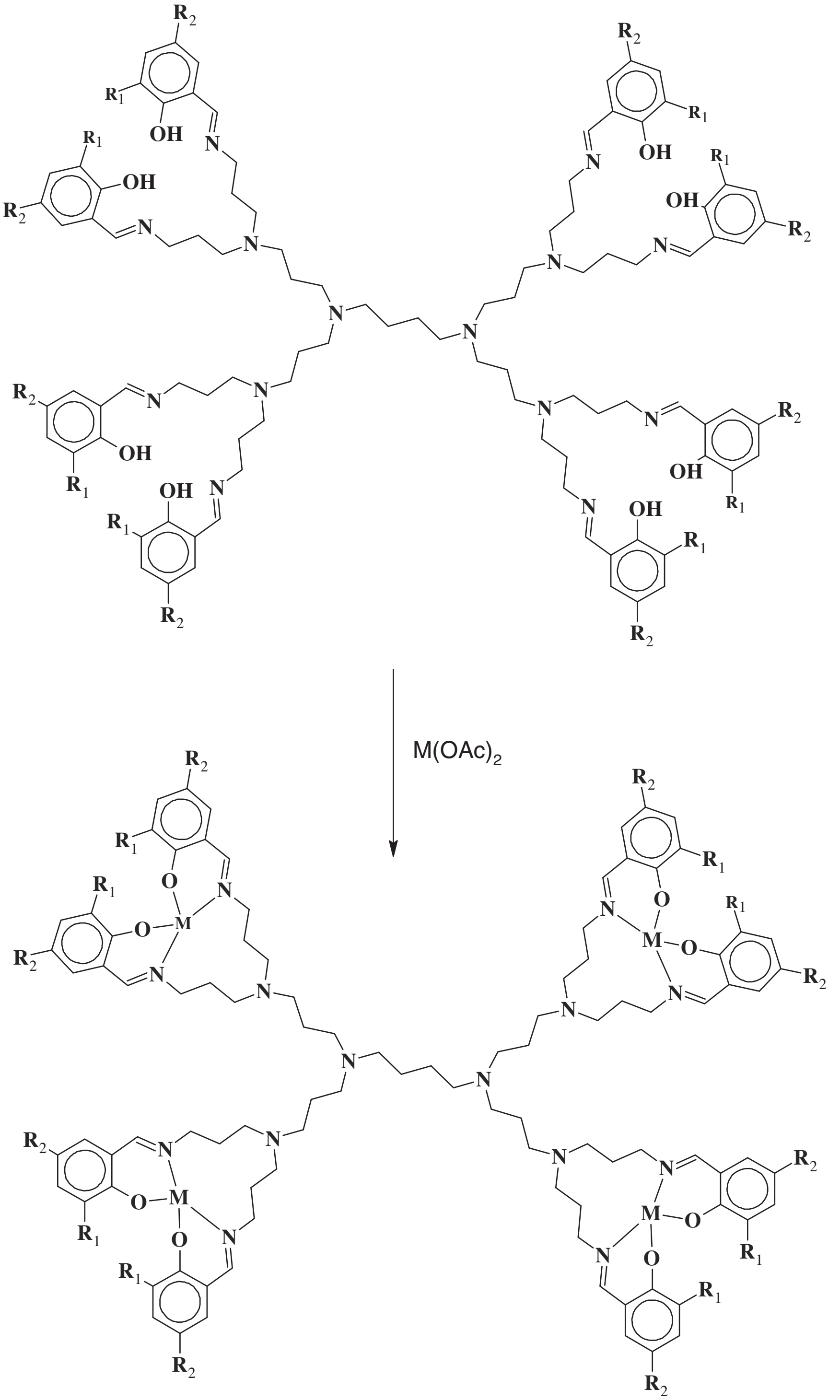
[a] Recorded as CH_2Cl_2 solutions with solution cell containing NaCl windows.
[b] Shoulder.

3.2.5. Electrospray ionisation mass spectrometry of complexes

All the metallodendrimers synthesized were analysed with electrospray ionisation (ESI) mass spectrometry. This confirmed the expected molecular weights of the obtained products. The ESI-MS data are summarized in Table 2.

All of the copper complexes typically show high mass ions due to the species $[M+H]^+$ whereas for the cobalt complexes the normal parent ions of the type M^+ were observed. The fragmentation pattern of the G1 copper metallodendrimer, **C1**, was found to be more complex compared to the fragmentation of the other G1 metallodendrimers. The most abundant peak in the spectrum of **C1** is a fragment produced by loss of a single phenolic ring of one of the salicylaldimine units. This was followed by loss of the oxygen group of one of the remaining phenolic groups in the form of H_2O. The sequential loss of the aromatic ring followed by loss of oxygen on the remaining phenolic groups is observed for the other salicylaldimine units in the complex.

The fragmentation pattern for the other first generation metallodendrimers was comparatively simpler. The most abundant ion in the mass spectra of the dendritic complexes, **C2**, **C5** and **C6** was the molecular ion. Hardly any fragmentation is observed in the mass spectra of these complexes, indicating that they are relatively stable under the conditions employed to record the mass spectra. The second generation dendritic complexes, **C3**, **C4**, **C7** and **C8** had more complicated ESI mass spectra. The metallodendrimer, **C7** was the only one of the second generation species to show a very



L3 : $R_1 = R_2 = H$
L4 : $R_1 = R_2 =$ t-Bu

C3 : $R_1 = R_2 = H$; M = Cu
C4 : $R_1 = R_2 =$ t-Bu; M = Cu
C7 : $R_1 = R_2 = H$; M = Co
C8 $R_1 = R_2 =$ t-Bu; M = Co

Scheme 2. Preparation of G2 metallodendrimers.

abundant molecular ion in its mass spectrum. In the case of all the others only weak molecular ions were observed due to a fair amount of fragmentation of the parent ion.

3.3. Phenol hydroxylation

The dendritic complexes of copper and cobalt prepared were evaluated as catalysts in the liquid phase hydroxylation of phenol. The catalytic reactions were carried out in deionized water over the pH range 3–6 using appropriately buffered solutions. The metal concentration was kept constant at 8.9×10^{-3} mol L^{-1} in all catalytic runs irrespective of the catalyst precursor employed. Thus using either first or second generation metallodendrimers, the metal concentration was kept constant by adjusting the amount of metallodendrimer employed. For all reactions a substrate (phenol) to metal ratio of 100:1 and phenol to H_2O_2 ratio of 1:1 were employed. The results for the catalytic activity as well as the selectivity are outlined in Tables 3 and 4. It should be noted that no hydroxylation is observed in the absence of catalyst. It thus appears that the metal complex is required to initiate the

Table 2
Elemental analysis and ESI mass spectrometry data for copper and cobalt metallodendrimers.

Complex	Formula	$[M+H]^+$ (calcd.) m/z	Anal found (calc.)		
			C	H	N
C1	$C_{44}H_{52}Cu_2N_6O_4 \cdot 1/2H_2O$	857.2 (857.01)	60.88(60.51)	5.98(6.12)	9.53(9.63)
C2	$C_{76}H_{116}Cu_2N_6O_4 \cdot 2EtOH$	1305.6 (1305.86)	68.71(68.78)	9.94(9.24)	6.28(6.02)
C3	$C_{96}H_{120}Cu_4N_{14}O_8 \cdot 3CH_2Cl_2$	1853.7 (1853.25)	54.36 (54.79)	6.62(7.09)	9.94 (9.32)
C4	$C_{160}H_{258}Cu_4N_{14}O_8 \cdot 4CH_2Cl_2$	2750.8 (2750.96)	63.07 (63.26)	8.72 (8.56)	5.49 (6.07)
C5	$C_{44}H_{52}Co_2N_6O_4 \cdot H_2O$	846.1 (846.79)[a]	61.30(61.11)	6.90(6.29)	10.00(9.72)
C6	$C_{76}H_{116}Co_2N_6O_4 \cdot 1/2CH_2Cl_2$	1295.6 (1295.64)[a]	68.71(68.66)	8.87(8.81)	6.05(6.28)
C7	$C_{96}H_{120}Co_4N_{14}O_8 \cdot 3CH_2Cl_2$	1833.7 (1833.80)[a]	56.46(56.93)	6.41(6.08)	9.09(9.39)
C8	$C_{160}H_{258}Co_4N_{14}O_8 \cdot H_2O$	2731.8 (2731.50)[a]	69.76(69.89)	9.47(9.16)	6.69(7.13)

[a] Represents $[M]^+$.

decomposition of H_2O_2 to the hydroxyl radical. Under our reaction conditions no consumption of H_2O_2 takes place in the absence of the metal complex.

3.3.1. The effect of pH on phenol conversion

It was observed that all the dendritic salicylaldimine complexes were active as catalysts in the hydroxylation of phenol. Reactions were carried out over a pH range of 3–6 to establish the optimum acidity of the reaction medium. It was established that the reaction works optimally at moderately acidic pH values. Attempts to use an alkaline pH resulted in no activity being observed for all the catalysts tested. For these dendritic catalysts optimum activity for both the G1 and G2 metallodendrimers were observed at pH 6. In the case of the copper complexes conversions at pH 6 ranges from 71–78% while under the same conditions the conversion for the cobalt complexes are in the range 49–62%. It is thus clear that the cobalt catalysts are slightly less active than the copper catalysts. It is thought that this is related to the relative stability of the two systems. As previously mentioned the cobalt catalysts tend to be less stable in solution than the copper catalysts. This has an impact on the catalyst life time and hence on the overall activity over time.

For the copper complexes the effect of pH on the activity is not so pronounced with conversion at pH 3 being only slightly lower than that at pH 6 (see Chart 1). It would thus appear that the active species derived from the copper precatalyst is relatively stable over the pH range evaluated. The activity of the cobalt complexes on the other hand shows a greater dependence on pH (Chart 2). In all cases the conversion at pH 6 far exceeds that obtained at pH 3. This observation is in agreement with what has been observed for other Schiff base complexes where the optimum catalyst activity was also observed to be pH dependent [23–26]. There appears to be some influence of the nature of the ligand on the overall catalyst activity with the catalysts having ^{t}butyl substituents on the salicylaldimine units having slightly better activity than those without. This is especially true for the copper systems at the optimum pH of 6. It is assumed that the bulky ^{t}butyl groups exert some stabilizing effect by hindering μ-oxo dimer formation. It is known that the interaction of two metal centres in such complexes leads to catalyst deactivation [28]. Such stabilization by bulky ligands mimics what occurs in the case of the natural enzymes [29]. The substituent effect is not so obvious in the case of the cobalt complexes.

Table 3
Effect of pH on activity and selectivity of Cu(II) metallodendrimers.[a]

Catalyst	pH	%W Dihydroxybenzenes[b]		% PhOH conversion	TOF[c]
		HQ	CT		
C1	3	42.1	57.9	62	10.3
	4	40.3	59.7	65	10.8
	5	40.8	59.2	70	11.6
	6	35.7	64.3	71	11.9
C2	3	41.7	58.3	70	11.6
	4	39.4	60.6	70	11.7
	5	41.5	58.5	72	12.0
	6	32.9	67.1	73	12.2
C3	3	42.3	57.7	74	12.3
	4	36.7	63.3	73	12.2
	5	41.2	58.8	72	12.2
	6	36.1	63.9	75	12.6
C4	3	42.6	57.4	60	10.0
	4	40.9	59.1	68	11.3
	5	42.1	57.9	70	11.7
	6	32.9	67.1	78	13.0
C9	3	38.6	61.4	54	9.0
	4	37.2	62.8	56	9.3
	5	41.2	58.8	59	9.8
	6	37.1	62.9	64	10.3

[a] Reaction performed in 10 mL H_2O, Phenol:Cu = 100:1; 110 °C at 1 atm O_2 for 6 h; 30% H_2O_2 as co-oxidant; Phenol:H_2O_2 = 1:1.
[b] HQ = hydroquinone; CT = Catechol.
[c] TOF = (mol phenol consumed/mol Cu)/h.

Table 4
The effect of pH on the activity and selectivity of Co(II) metallodendrimers.[a]

Catalyst	pH	% W Dihydroxybenzenes[b]		% Phenol conversion	TOF[c]
		HQ	CT		
C5	3	38.7	61.3	31	5.1
	6	14.45	85.55	62	10.3
C6	3	37.1	62.9	28	4.7
	6[d]	–	–	56	9.3
C7	3	37.0	63.0	31	5.2
	6	18.06	81.94	59	9.9
C8	3	35.2	64.8	28	4.6
	6[d]	–	--	49	8.2
C10	3	36.7	63.3	26	4.3
	6	18.16	81.84	51	7.7

[a] Reaction performed in 10 mL H_2O, Phenol:Co = 100:1; 10 °C at 1 atm O_2; 30% H_2O_2 as co-oxidant; Phenol:H_2O_2 = 1:1.
[b] HQ = hydroquinone; CT = catechol; product distribution given on a tar free basis.
[c] TOF = (mol phenol consumed/mol Co)/h.
[d] Neither CT nor HQ observed only a intractable tar-like material isolated.

3.3.2. The effect of pH on product selectivity

The major products observed under the reaction conditions employed were hydroquinone (HQ) and catechol (CT). In general catechol is the major product irrespective of the pH employed (Charts 3–5). However, for all systems higher amounts of catechol is produced at higher pH. The effect is more dramatic for the Co systems where the catechol amount is greater than 80% at pH 6 (Chart 6). Such high selectivity for catechol has also previously been observed by us in a study of mononuclear salicylaldimine complexes of cobalt [22]. The high selectivity for catechol is not unusual for transition metal-mediated hydroxylation proceeding via a reaction

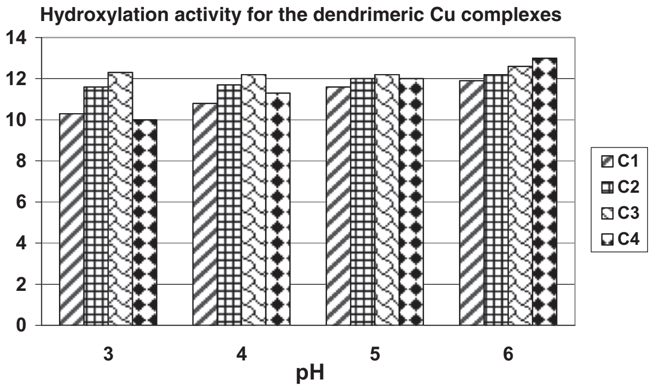


Chart 1.

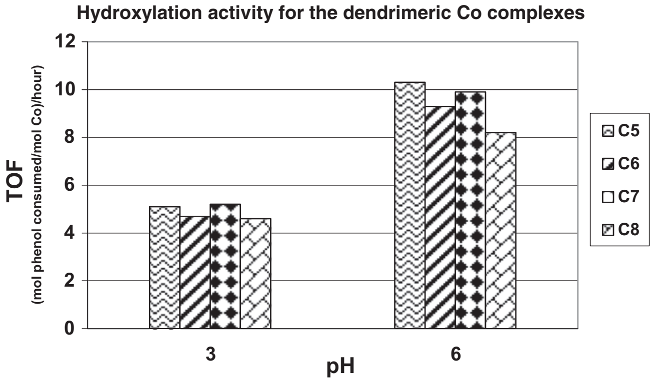


Chart 2.

pathway involving weak coordination of phenol and the oxidant (H_2O_2) to the metal centre. The binding of the two reacting partners in close proximity to each other results in a cis-arrangement. This in turn leads to ortho substitution of the phenol [27]. This is illustrated in Scheme 3. Reactions using **C6** and **C8** as catalyst precursors show no sign of the formation of dihydroxy benzenes. This is despite the fact that a substantial amount of phenol is consumed during the process. In these two cases a tar-like intractable material is observed as product. The isolated material is completely insoluble in all common organic solvents and could thus not be characterised.

3.3.3. The effect of the nature of the metal on the activity and product selectivity

In general a dependence of the activity and selectivity on the nature of the metal centre was observed for the reactions studied.

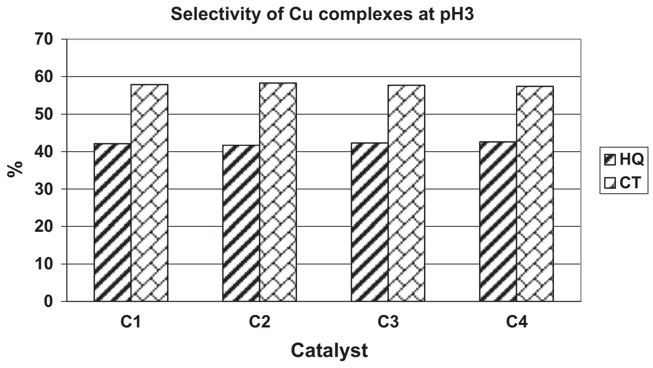


Chart 3.

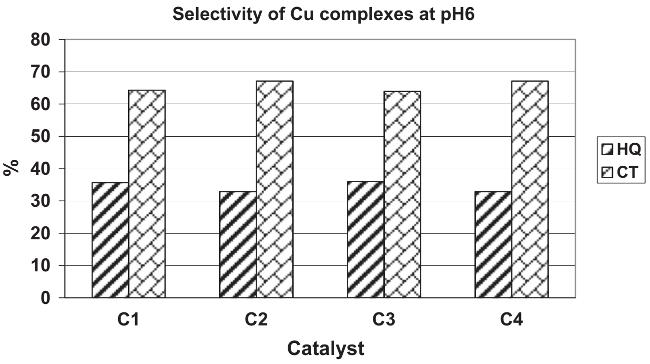


Chart 4.

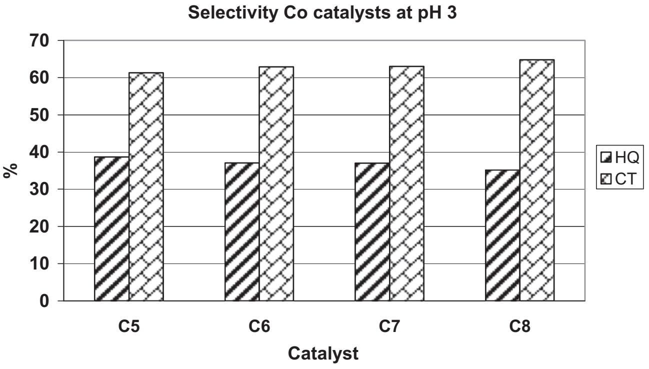


Chart 5.

On the whole copper dendritic catalysts were observed to be more active than the cobalt analogues when evaluated under similar conditions. This dependence of the activity on the nature of the metal centre was previously observed by our group when investigating the use of silica-supported bis(salicylaldimine) complexes of copper, cobalt and nickel in phenol oxidation reactions. It was observed that activity decreased in the order Cu > Co > Ni [17]. This is in clear agreement with what is observed for the dendritic catalysts in the current study. In the case of the copper catalysts the effect of pH is not as dramatic as was the case for the cobalt catalysts. The latter shows a dramatic increase in activity when the pH is increased to pH 6.

The selectivity of the reaction is also greatly impacted by the nature of the metal and to some extent the pH of the reaction medium. It was noted that the copper catalysts produced the dihydroxybenzenes in a 1:2 (HQ:CT) ratio over the pH range investigated with only slight deviation from this ratio with change

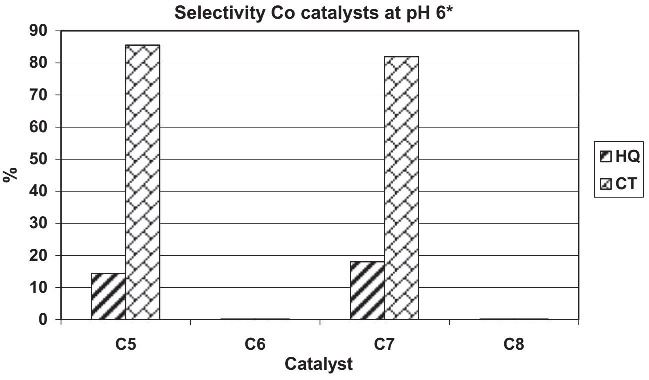
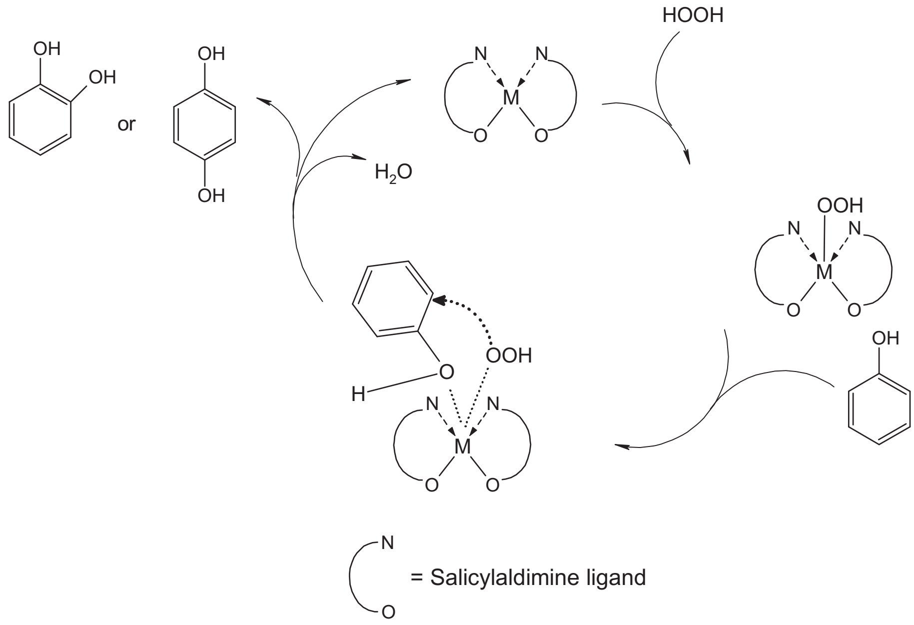


Chart 6.



Scheme 3. Mechanistic pathway for phenol hydroxylation.

in pH. Although similar ratios are obtained for the cobalt catalyst at pH 3, under more basic conditions a substantial increase in the formation of catechol is observed with the catechol levels being over 80% at pH 6 for all the cobalt catalysts.

3.3.4. Comparison of dendritic catalysts with mononuclear analogues

The catalytic behaviour of the dendritic complexes was compared against that of two model compounds, **C9** (copper) and **C10** (cobalt), Fig. 1. These model complexes were based on the *N*-propylsalicylideneimine ligand.

Compared to the mononuclear complex, **C9**, the dendritic complexes, **C1**–**C4** had slightly higher conversions. This is presumed to be largely due to the increased catalyst stability of the dendritic complexes compared to the mononuclear analogue. It was observed that in solution the mononuclear complexes are substantially less stable than their dendritic analogues. In addition it is known that catalyst deactivation can possibly occur via μ-oxo dimer formation [28]. This presumably is more facile for the mononuclear complexes than the sterically more encumbered dendritic complexes.

A similar trend is observed for the mononuclear cobalt complex, **C10** when compared with its dendritic analogues. It should be noted that there is no clear trend in selectivity for the mononuclear complexes versus the dendritic species.

4. Conclusions

The catalytic activity of copper (II) and cobalt(II) complexes of dendritic salicylaldimine ligands were evaluated in the hydroxylation of phenol in aqueous media under controlled pH conditions. All catalysts investigated were observed to be active in the phenol oxidation process with the major products detected being hydroquinone and catechol. All the catalysts seem to be more selective for catechol. In the case of the copper catalysts a CT:HQ ratio of roughly 2:1 was observed. The cobalt catalysts however showed a much more significant pH dependence of activity since the activity of the catalyst roughly doubled at pH 6. Also the cobalt catalysts show a remarkably high selectivity for catechol with about 80% of the product being this isomer.

Acknowledgements

Acknowledgements go to National Research Foundation (South Africa) and the Water Research Commission, South Africa. This work was also supported by Research Committees of Stellenbosch University and the University of the Western Cape.

References

[1] P. Maggioni, US Patent 3,914,322 (1975).
[2] G.A. Hamilton, J.P. Friedman, P.M. Campbell, J. Am. Chem. Soc. 88 (1966) 5266.
[3] F. Luck, Catal. Today 27 (1996) 195.
[4] W. Zhao, Y. Luo, P. Deng, Q. Li, Catal. Lett. 73 (2001) 199.
[5] J.G. Mei, S.M. Yu, J. Cheng, Catal. Commun. 5 (2004) 437.
[6] M.T. Hassenein, S.S. Gerges, M.A. Abdo, S.H. El-Khalafy, J. Porphyrins Phthalocyanines 9 (2005) 621.
[7] D.C. Sherrington, Pure Appl. Chem. 60 (1988) 401.
[8] H.-Q. Zeng, Q. Jiang, Y.-F. Zhu, X.-H. Yan, X.-B. Lang, H.-Y. Hu, Q. Liu, W.-Y. Lin, C.-C. Guo, J. Porphyrins Phthalocyanines 10 (2006) 96.
[9] A. Zombeck, R.S. Drago, B.B. Corden, J.H. Gaul, J. Am. Chem. Soc. 103 (1981) 7580.
[10] A. Haikarainen, J. Siplilä, P. Pietikainen, A. Pajunen, I. Mutikainen, Bioorg. Med. Chem. 9 (2001) 1633.
[11] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.
[12] W. Zeng, Z. Mao, X. Wei, J. Li, Z. Hong, S. Qin, J. Supramol. Chem. 2 (2002) 501.
[13] M.R. Maurya, S. Sikarwar, J. Mol. Catal. A: Chem. 263 (2007) 175.
[14] M.R. Maurya, I. Jain, S.J.J. Titinchi, Appl. Catal. A 249 (2003) 139.
[15] C.R. Jacobs, S.P. Varkey, P. Ratnasamy, Microporous Mesoporous Mater. 22 (1998) 465.
[16] M.R. Maurya, M. Kumar, S.J.J. Titinchi, H.S. Abbo, S. Chand, Catal. Lett. 86 (2003).
[17] S. Ray, S.F. Mapolie, J. Darkwa, J. Mol. Catal. A: Chem. 267 (2007) 143.
[18] J.N. Mugo, S.F. Mapolie, J.L. van Wyk Inorg, Chim. Acta 363 (2010) 2643.
[19] A.D. Garnovskii, A.S. Burlov, K.A. Lysenko, D.A. Garnovskii, I.G. Borodkina, A.G. Ponomarenko, G.G. Chigarenko, S.A. Nikolaevskii, V.I. Minkin, Russ. J. Coord. Chem. 35 (2009) 127.
[20] H. Nishikawa, S. Yamada, R. Tsuchida, Z. Anorg. Allg. Chem. 316 (1962) 278.
[21] R. Malgas-Enus, S.F. Mapolie, G.S. Smith, J. Organomet. Chem. 693 (2008) 2279.
[22] J.L. van Wyk, S.F. Mapolie, A. Lennartson, M. Håkansson, S. Jagner, Inorg. Chim. Acta 361 (2008) 2094.
[23] V.T. Kasumov, F. Koksal, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 58A (10) (2002) 2199.
[24] V.T. Kasumov, F. Köksal, Spectrochim. Acta A 60 (2004) 31.
[25] Q. Xie, J.-Z. Li, X.-G. Meng, C.-W. Hu, X.-C. Zeng, Transition Met. Chem. 29 (2004) 388.
[26] J. Zhang, Y. Tang, J. -Q Xie, J.-Z. Li, W. Zeng, C.-W. Hu, J. Serb. Chem. Soc. 70 (2005) 1137.
[27] K.C. Gupta, A.K. Sutar, J. Mol. Catal. A: Chem. 272 (2007) 64.
[28] Z.-W. Yang, Q.-X. Kang, H.-C. Ma, C.-L. Li, Z.-Q. Lei, J. Mol. Catal. A: Chem. 213 (2004) 69.
[29] E. Schön, D.A. Plattner, P. Chen, Inorg. Chem. 43 (2004) 3164.