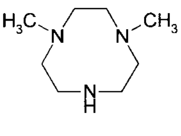
Selective Alkene Oxidation with H_2O_2 and a Heterogenized Mn Catalyst: Epoxidation and a New Entry to Vicinal *cis*-Diols**

Dirk E. De Vos, Stefaan de Wildeman, Bert F. Sels, Piet J. Grobet and Pierre A. Jacobs*

Selective oxidation of olefins produces valuable intermediates including epoxides and *cis*-dihydroxylated products.[1] Industrial epoxidations are frequently conducted with stoichiometric reagents (peracids, Payne's procedure).[2] *cis*-Dihydroxylation is currently not practiced on a large scale because of the price and toxicity of Os catalysts.[3] Aims in research on catalytic oxidation are: 1) using H_2O_2 instead of organic oxygen donors, 2) avoiding pollution with halides or toxic metals, for example by employing heterogenized reagents, and 3) generating stable products at, for example, nearly neutral pH to protect epoxides. In spite of impressive progress in this area, few systems, if any, meet all these requirements.[4] Catalysis with complexes of manganese and cyclic triamines such as 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) recently became a true alternative to the known conversions mediated by homogeneous manganese complexes.[5–8] For instance, the labile diepoxybutane is produced from H_2O_2 and butadiene monoxide in 80 % yield with a Mn-tmtacn-oxalate catalyst (> 90 % selectivity, 530 Mn turnovers).[7]

Here we describe the first satisfactory heterogenized equivalent of this new type of oxygen-transfer catalyst. A crucial element in the synthesis of the catalyst is the use of the asymmetrically substituted ligand 1,4-dimethyl-1,4,7-triazacyclononane (dmtacn, **1**). This molecule has not only the CH_3 substituents of the original tmtacn but also a secondary amino group for attaching a covalent tether. Even for α-olefins the new heterogenized Mn catalyst displays high activity and epoxide selectivity (up to 90 %, see Table 1). With disubstituted olefins the reaction yields (apart from the epoxide) a sizeable amount of the *cis*-diol (10–60 moles of *cis*-diol per mole of Mn). This is the first observation of a Mn-catalyzed *cis*-dihydroxylation.



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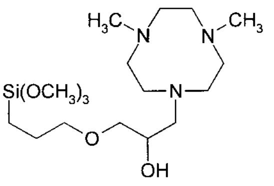

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Compound **1** was synthesized by selective detosylation of tritosylated 1,4,7-triazacyclononane (tacn), methylation of monotosylated tacn, and detosylation in H_2SO_4.[9] The free amine base was obtained as a light yellow oil, which was pure based on its ^1H NMR spectrum. To compare the dimethylated dmtacn with trimethylated tmtacn, homogeneous catalysis experiments were performed with complexes formed in situ from $MnSO_4 \cdot H_2O$ and dmtacn. The test reactions were the oxidation of styrene and 1-hexene in both acetone and acetonitrile (Table 1, entry 1). While the epoxidation of styrene with Mn-dmtacn in acetone was comparable to the reaction with the Mn-tmtacn catalyst,[6a] homogeneous Mn-dmtacn in acetonitrile as such was practically inactive for the epoxidation of 1-hexene. In this case epoxidation was marginal in comparison to peroxide decomposition, which is reportedly a binuclear reaction.[10]

Various approaches were followed to link dmtacn to a solid support: 1) reaction of dmtacn with commercial 3-chloropropylsilica and Et_3N (→Sil-p-dmtacn); 2) glycidylation of a mesoporous ordered silica (MCM-41)[11] or an amorphous precipitated silica with (3-glycidyloxypropyl)trimethoxysilane, followed by addition of dmtacn (→MCM-41-gp-dmtacn, Sil-gp-dmtacn); and 3) a "reversed" synthesis, in which dmtacn is first treated with (3-glycidyloxypropyl)trimethoxysilane, and the resulting silylating agent **2** is then immobilized on an amorphous SiO_2 surface (→dmtacn-gp-Sil). These procedures lead to surface loadings of the ligand between 0.2 and 0.8 $mmol\,g^{-1}$. The identity of the surface groups was checked for dmtacn-gp-Sil with solid-state ^{13}C NMR spectroscopy. Magic-angle spinning spectra were recorded in the cross-polarization mode for a glycidylated material and for a material with anchored dmtacn. In addition to the signals of the (ring-opened) glycidyloxypropyl chain ($\delta = 9$, 22, 65, 71, 73), other strong signals appear at $\delta = 52$ and 43 which are assigned to the CH_2 and the CH_3 groups of dmtacn. The metal-binding properties of this surface were examined by doping with Cu^{2+} ions. The EPR data indicate that each metal ion interacts with only a single heterogenized ligand.[12] This is a strong indication that in dmtacn-gp-Sil formation of dinuclear metal complexes is unlikely.

The heterogenized ligand was metalated by stirring in a solution of $MnSO_4 \cdot H_2O$ in methanol and thoroughly removing the excess metal sulfate. Epoxidations were started by consecutive addition of α-olefin, solvent, and H_2O_2. Table 1 first reveals that the best catalyst (dmtacn-gp-Sil) was prepared by "reversed" synthesis. While yields based on peroxide were around 50 %, an 82 % yield based on the substrate was obtained for styrene in acetone (93 % conversion, 280 Mn turnovers; entry 5). These activities are far higher than those of analogous systems in which the ligand has, for example, 2-hydroxyalkyl pendant arms instead of the two methyl substituents.[6c] Secondly, whereas the homogeneous Mn-dmtacn catalyst was inactive in the epoxidation of 1-hexene, the yields of 1,2-epoxyhexane achieved with the heterogenized catalysts were gratifying. Thus, even this weakly activated olefin successfully competes against peroxide disproportionation. This supports the idea that with the present catalyst binuclear pathways like that in H_2O_2 decomposition are unimportant.

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Explicit attention was devoted to the issue of catalyst heterogeneity by removing the catalyst from half of the reaction mixture (by centrifugation or filtration) and monitoring the progress of the reaction in suspension and in the clear solution. These tests were particularly satisfactory for the catalyst prepared by "reversed" synthesis (dmtacn-gp-Sil). When the reaction mixture was split at a styrene oxide yield of 30%, negligible further activity resided in solution (80 vs 32% yields).

Although conversions are satisfactory for the reactions of disubstituted olefins (Table 2), epoxide selectivities were more variable than for the reactions of α-olefins (see Table 1). For cyclohexene and *trans*-2-hexene limited allylic oxidation was observed (less than 8% of the products); the rest of the products were diols. Attempts to suppress diol formation by addition of base were unsuccessful. When the substrate in the reaction was replaced by 1,2-epoxyhexane or epoxycyclohexane, hardly any diols formed (<2 mol% after 24 h at 298 K). This proves that epoxide solvolysis is not the source of the observed diols.[13] Careful analysis of the products proves that *cis*-diols formed almost exclusively. Thus the reactions of Table 2 (entries 1–8) systematically produced the same diol that is formed in a stoichiometric oxidation with MnO_4^- and hardly gave the compounds obtained in strongly acidic medium from CH_3ReO_3 and H_2O_2.[4f]

The catalytic formation of *cis*-diols with H_2O_2 (up to 60 Mn turnovers) is a unique observation. Hitherto, such catalytic activity was known only for Os and Ru, in complexes containing two *cis* oxo ligands to form cyclic osmate or ruthenate esters.[14] With other d^0 catalysts such as CH_3ReO_3 proton acidity leads to the formation of *trans*-diols.[15] Note that permanganate cannot be formed for thermodynamic reasons from Mn^{2+} ions and H_2O_2. Moreover, dark brown precipitates (as with MnO_4^- under nonacidic conditions) were not observed with the heterogenized Mn catalyst. In the MnO_4^- oxidation, and in many catalytic Ru reactions, overoxidation is a major problem even at low conversion;[14] however, with the present Mn catalyst such side reactions are limited (e.g. for *cis*-2-hexene, the diol:dione ratio is 10:1). In both the epoxide and the diol fraction there is a limited loss of configuration. Stereoretention for the diol is always a little higher than for the epoxide (94 vs 91% for *cis*-2-hexene). A tentative explanation may be that epoxide and diol are formed from a single intermediate that is sufficiently long-lived to allow either some bond rotation or a *cis* insertion of a second, manganese-coordinated oxygen atom to form the *cis*-diol.

Scheme 1 shows models for a) homogeneous Mn-tmtacn in the absence of another ligand, b) Mn-tmtacn in the presence of an oxalato coligand, and c) Mn-dmtacn heterogenized by means of covalent linking. In solution binuclear structures

Table 1. Epoxidation of α-olefins with H_2O_2 and complexes of Mn and dmtacn (dmtacn was used in solution[a] or heterogenized in different ways on support materials).[b]

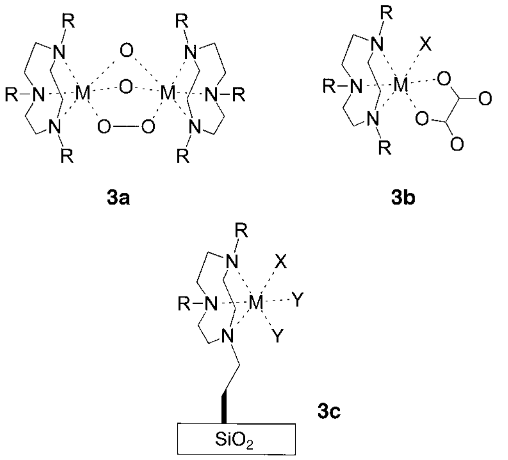
Entry	Catalyst	Loading [mmol g^{-1}]	Epoxide yield [%] (olefin conversion [%]; time [h])[c] olefin: styrene solvent: acetone	styrene CH_3CN	1-hexene CH_3CN
1	Mn-dmtacn, homogeneous[a]	–	59 (63; 2)	9 (11; 2)	0.1 (0.1; 2)
2	Sil-p-dmtacn	0.21	11 (12; 12)	4.5 (5.5; 12)	3 (4; 12)
3	Sil-gp-dmtacn	0.45	55 (69; 3)	50 (60; 1)	64 (75; 3)
4	MCM-41-gp-dmtacn	0.77	57 (67; 3)	23 (25; 3)	20 (29; 3)
5	dmtacn-gp-Sil "reversed"	0.57	82 (93; 3)	77 (85; 1)[d]	70 (92; 3)

[a] Conditions: H_2O_2:olefin:dmtacn:Mn = 1000:500:1.5:1; 1 mmol of substrate in 1 mL of solvent, 273 K. [b] Conditions: 10 mg of heterogenized catalyst, 1.72 mmol of olefin, 3.44 mmol of H_2O_2, 1 mL of solvent, 273 K. [c] Other products: 1,2-hexanediol from 1-hexene, and phenylethane-1,2-diol and phenylacetaldehyde from styrene. [d] First run: 255 turnovers. Second run: 150 turnovers. With an olefin:peroxide ratio of 1:1 the conversion is 52%.

Table 2. Epoxidation and vicinal dihydroxylation of disubstituted olefins with the heterogenized Mn-dmtacn catalyst and H_2O_2,[a] and homogeneous epoxidation with Mn-tmtacn, H_2O_2, and an oxalate cocatalyst.[b]

Entry	Substrate	*t* [h]	Conversion [%]	Selectivity [%] epoxide	(*c*:*t*)	diol	(*c*:*t*)	overox.[c]
	dmtacn-gp-Sil + Mn (heterogenized)							
1	*cis*-2-hexene	2	70	58	(91:9)	37	(94:6)	4
2	*cis*-2-hexene[d]	2	79	67	(86:14)	24	(88:12)	9
3	*trans*-2-hexene[e]	1	24	57	(11:89)	30	(6:94)	7
4	4-CH_3-*cis*-2-pentene	2	74	60	(86:14)	32	(87:13)	7
5	cyclohexene[f]	0.3	43	78		12	(99:1)	1
6	cyclohexene[f]	2	76	76		13	(97:3)	2
7	indene	3.5	43	57		35	(75:25)	4
8	norbornene	5	85	64		33	(99:1)	3
	Mn-tmtacn + Na-oxalate/oxalic acid (homogeneous)							
9	*cis*-2-hexene	1	72	99	(98:2)	<1		<1
10	*trans*-2-hexene	1	35	99	(2:98)	<1		<1
11	cyclohexene[g]	1	90	92		<1		<1

[a] Conditions: 10 mg of metalated catalyst (dmtacn-gp-Sil; estimated 5 μmol of dmtacn), 1 mmol of olefin, 2 mmol of H_2O_2, 1 mL of CH_3CN, 273 K. [b] Conditions: 1 μmol of $MnSO_4 \cdot H_2O$, 1.5 μmol of tmtacn, 0.67 mmol of olefin, 1.33 mmol of H_2O_2, 1 mL of CH_3CN; 3 μmol of cocatalyst (1.5 μmol of oxalic acid and 1.5 μmol of sodium oxalate in 0.1 mL of H_2O). [c] Overoxidation of the diols (mainly diones). [d] Solvent: acetone. [e, f, g] Fraction of allylic oxidation products in total products: 2% (e), 8% (f), 8% (g).



Scheme 1. Proposed structures for Mn-tmtacn oxidation catalysts (R = CH_3, M = Mn, X = activated "O" to be transferred; Y = nucleophile, e.g. H_2O). **3a**: In solution, dimers with catalase-type activity are formed. **3b**: In the presence of oxalate, catalase-type activity is suppressed and the transfer of X to an olefin is promoted. **3c**: With the heterogenized catalyst, both X and Y may be inserted into the olefin.

such as **3a** are readily formed; these are responsible for the catalase-type activity of the complexes.[10] Addition of oxalate to Mn-tmtacn may lead to a complex such as **3b**. This model is based on analogous structures known for Cu^{2+} and Cr^{3+} complexes.[16] Apparently, binding of the bidentate oxalato impedes formation of μ-peroxo-bridged dimers. Thus a pathway for peroxide disproportionation is blocked, and clean transfer of a single "O" (labeled X) is observed (Table 2, entries 9–11). Finally, in the heterogenized version **3c**, binuclear complexes are not formed due to the isolation of the ligands over the support. As a result, peroxide disproportionation is much less pronounced than with **3a**. Two labile coordination sites are available in positions adjacent to the transferred active oxygen (X); nucleophiles (e.g., Y = H_2O) on these sites might be inserted into the olefin, together with the "active" oxygen.[17] This model is the most plausible hypothesis for the coupled catalytic production of epoxides and *cis*-diols.

Experimental Section

The synthesis of dmtacn was based on literature procedures (^{1}H NMR: δ = 2.802 (m, 4H), 2.72 (m, 4H), 2.70 (s, 4H), 2.46 (s, 6H).[9] As an example of heterogenization, the synthesis of dmtacn-gp-Sil is described. A solution of dmtacn (0.118 g, 0.75 mmol) and 3-(glycidyloxy)propyltrimethoxysilane (0.236 g, 1 mmol) in toluene (30 mL) was stirred at 60 °C for 12 h. To this solution was added silica gel 60 (0.75 g, Fluka, 70–230 mesh; previously heated at 120 °C under vacuum). The mixture was stirred for 24 h at 90 °C. Then the powder was subjected to soxhlet extraction with CH_2Cl_2/EtOEt for 24 h, air-dried, and stored in a desiccator. Ligand loadings on the support were determined by thermogravimetric analysis (heating at 120 K h^{-1}; weight loss recorded between 473 and 873 K). Solid-state MAS ^{13}C NMR spectra were recorded with a Bruker AMX-300 instrument. EPR spectra were measured on a Bruker ESP 300 instrument.

A portion of the immobilized ligand (10 mg) was metalated by stirring it for 1 h in a solution of MeOH (1 mL), H_2O (250 µL), and $MnSO_4 \cdot H_2O$ (15 µmol). After centrifugation and removal of the excess metal sulfate, the olefin (1 or 1.72 mmol) and the solvent (1 mL) were added to the catalyst, and the reaction was started by addition over 10 min of a twofold excess of 35% aqueous H_2O_2 dissolved in 0.5 mL of the solvent. Analysis was performed by gas chromatography (GC-MS). The absence of hydroperoxides was systematically proved by injection with or without preliminary addition of PPh_3. The *cis*- and *trans*-diols were separated on GC columns with different polarities (CP-Sil 5 and CP-Sil 88). Comparison was made with authentic products (for the cyclohexane-1,2-diols, Akros), or with products synthesized with $KMnO_4$ (*cis*-diols) or CH_3ReO_3/H_2O_2 in aqueous $HClO_4$ (*trans*-diols).[4f]

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[17] As suggested by a referee, this hypothesis can be tested by addition of oxalate to the heterogenized Mn catalyst. This completely stops the dihydroxylation, while some epoxidation still goes on.

The *gem*-Diol Form of $(py)_2CO$ as a Ligand in Cobalt(II) Carboxylate Clusters: A Cubane Complex and a Novel Nonanuclear Species with a Vertex-Sharing Double Square Pyramidal Structure

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Evangelos G. Bakalbassis,* and Spyros P. Perlepes*

The study of polynuclear complexes of metals in moderate oxidation states has recently begun to lead not only to novel metal polyhedra but also to interesting physical properties. For example, nanosized polyiron and polymanganese complexes with high-spin ground states afford single-domain magnetic particles, which may display hysteresis effects of purely molecular origin.[1] To understand and exploit such phenomena, further examples of high-nuclearity clusters are required, and this is a challenge for the synthetic chemist. Several groups are pursuing routes to such complexes.[2]

We have developed the reaction of metal carboxylates with di-2-pyridyl ketone, $(py)_2CO$, which leads to incomplete replacement of the carboxylate ligands and the formation of large polynuclear arrays of copper[3] and manganese.[4] The structural diversity of these complexes stems from the ability of the singly and doubly deprotonated anions of the *gem*-diol form of $(py)_2CO$ and its derivatives to exhibit a variety of coordination modes, and sometimes two different modes occur in the same complex. We hoped that this strategy would prove to be generally applicable to the 3d metals, and this proved to be the case for cobalt(II). Here we report the cobalt(II) complexes **1** and **2**, which have unusual structures and interesting magnetic properties.

$[Co_9\{(py)_2CO_2\}_4(O_2CMe)_8(OH)_2]\cdot 14.6\,H_2O$ **1**

$[Co_4\{(py)_2C(OH)O\}_4(O_2CMe)_4]\cdot H_2O$ **2**

The course of the reaction between $Co(O_2CMe)_2\cdot 4\,H_2O$ and $(py)_2CO$ in MeCN under reflux depends on the molar ratio. Treatment of $Co(O_2CMe)_2\cdot 4\,H_2O$ with $(py)_2CO$ in a 2:1 molar ratio led to a pale purple solution and subsequent isolation of the nonanuclear complex **1** with doubly deprotonated ions of $(py)_2C(OH)_2$ as ligands; this is a consequence of the high $MeCO_2^-$ to $(py)_2C(OH)_2$ ratio (4:1) used in the reaction. Treatment of cobalt(II) acetate with one equivalent of $(py)_2CO$ led to crystals of the tetranuclear complex **2**, which contains singly deprotonated ions of $(py)_2C(OH)_2$ as ligands.

Complex **1** (Figure 1)[5] has a twofold axis passing through Co1 and is held together by two μ_4-OH^- ions, eight *syn,syn*-μ_2:η^1:η^1-$MeCO_2^-$ groups, and four $(py)_2CO_2^{2-}$ ligands, which adopt the unprecedented μ_5:η^1:η^3:η^3:η^1 coordination mode (**A**). The central Co site (Co1) is the shared apex of two square pyramids. An alternative description of **1** is as a square prism centered by an additional interstitial cobalt(II) ion (Co1). Each metal$\cdots$metal edge of

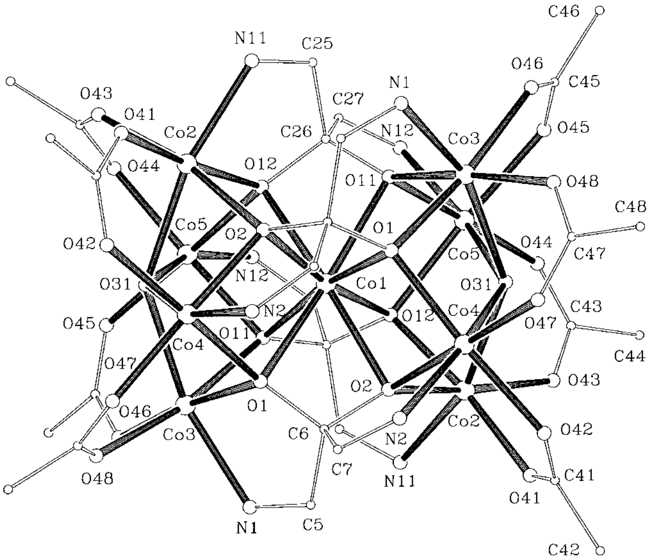
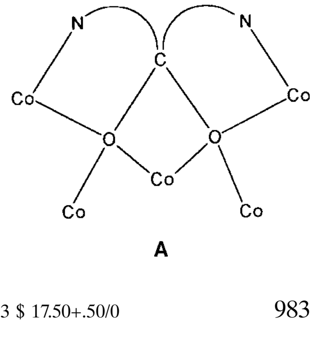


Figure 1. Crystal structure of **1**. Water molecules are omitted for clarity. Most carbon atoms of the pyridine rings have been omitted. Distances [Å]: Co–Co 3.10–6.52, Co1–O 2.24–2.27, Co2,3,4,5–O 2.02–2.31, Co–N 2.12–2.13.



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