

University of Groningen

Crystal and Molecular Structure and Reactivity of Jacobsen Epoxidation Catalyst N,N'-di(3-t-butyl-5-methyl salicylidene)cyclohexanediamine manganese(III)chloride·MeCN

Rispens, Minze T.; Meetsma, Auke; Feringa, Bernard

Published in:
Recueil des Travaux Chimiques des Pays-Bas

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1994

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Rispens, M. T., Meetsma, A., & Feringa, B. (1994). Crystal and Molecular Structure and Reactivity of Jacobsen Epoxidation Catalyst N,N'-di(3-t-butyl-5-methyl salicylidene)cyclohexanediamine manganese(III)chloride·MeCN. *Recueil des Travaux Chimiques des Pays-Bas*, 113(9), 413-415.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Crystal and Molecular Structure and Reactivity of Jacobsen Epoxidation Catalyst *N,N'*-di(3-*t*-butyl-5-methylsalicylidene)cyclohexanediamine manganese(III)chloride · MeCN

Minze T. Rispens, Auke Meetsma and Ben L. Feringa*

Department of Organic and Molecular Inorganic Chemistry, Groningen Center of Catalysis and Synthesis, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received July 22, 1994)

Abstract. The molecular structure of Jacobsen epoxidation catalyst *N,N'*-di(3-*t*-butyl-5-methylsalicylidene)cyclohexanediamine manganese(III)chloride · MeCN **1** is determined by single crystal X-ray and UV-Vis analysis. The epoxidation of dihydronaphthalene and dimethylchromene with amorphous and crystalline catalyst gave comparable enantiomeric excesses of 69 % and 92 % respectively.

Currently much effort is devoted to the development of new (enantio-)selective catalytic oxidations^{1,2,3} and functional mimics for monooxygenases.⁴ A major breakthrough in enantioselective epoxidation of unfunctionalized olefins was reported by Jacobsen and co-workers⁵ employing manganese(III) salen complexes as chiral catalysts. The highest enantioselectivities are generally observed with Mn(III) complexes based on C₂-symmetric *trans*-1,2-diaminocyclohexane salen ligands.

A mechanism to account for the often excellent π -face selectivity has been proposed, involving a side on approach of a *cis*-alkene opposite to the bulky *t*-butyl groups in **1** (figure 1).⁶ This mechanism has been extended to cinnamate esters and is substantiated with experiments to elucidate steric and electronic effects.⁷ The supposed steric effect of the doubly equatorial connected cyclohexane unit, responsible for the high enantioselectivity, is remarkable. Structural information to substantiate these stereodirecting effects and to gain insight into the subtle factors that govern enantioselectivity, is highly warranted.

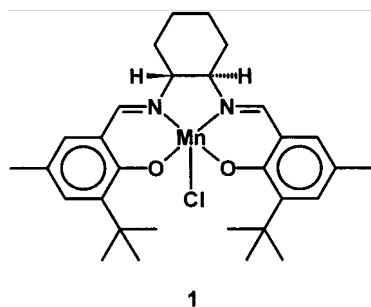


Fig. 1

We wish to report the crystal and molecular structure of *N,N'*-di(3-*t*-butyl-5-methylsalicylidene)cyclohexanediamine manganese(III)chloride · MeCN **1** (figure 1), which to the best of our knowledge is the first structural characterization of this type of epoxidation catalyst.

Compound **1** was synthesized analogously to literature procedure from (1*R*,2*R*)-cyclohexane diamine.⁸ Recrystallization of **1** from acetonitrile afforded black crystals,⁹ suitable for X-ray determination.¹⁰

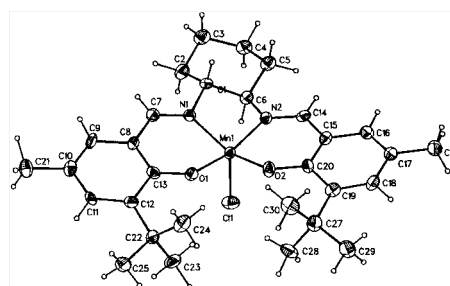
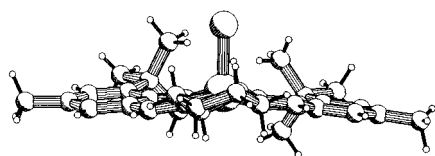


Fig. 2: ORTEP view of the molecular structure of *N,N'*-di(3-*t*-butyl-5-methylsalicylidene)cyclohexanediamine manganese(III)chloride · MeCN **1**. (Thermal ellipsoids are at the 50% probability level) Selected bond distances (Å) and bond angles (°) are as follows: Mn(1)-Cl(1) 2.390(2), Mn(1)-O(1) 1.871(5), Mn(1)-O(2) 1.853(5), Mn(1)-N(1) 2.017(5), Mn(1)-N(2) 1.959(6), Cl(1)-Mn(1)-O(1) 99.22(16), Cl(1)-Mn(1)-O(2) 103.07(16), Cl(1)-Mn(1)-N(1) 100.68(15), Cl(1)-Mn(1)-N(2) 94.58(15), O(1)-Mn(1)-O(2) 90.1(2), O(1)-Mn(1)-N(1) 90.1(2), O(1)-Mn(1)-N(2) 165.2(2), O(2)-Mn(1)-N(1) 155.9(2), O(2)-Mn(1)-N(2) 92.0(2), N(1)-Mn(1)-N(2) 82.0, Dihedral angle between both aromatic rings 169.0(3)°.

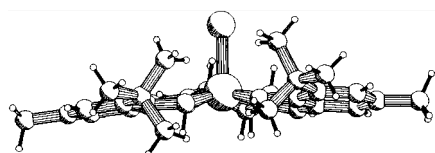
The unit cell contains two independent molecules of 5-coordinated Mn(III). The structure of **1** (figure 2) can be described as square pyramidal with manganese 0.315(1)Å¹¹ oriented out of plane

formed by O1, O2, N1 and N2 of the salen unit, towards the axially coordinating chloride ion. The Mn-O (1.871(5)Å and 1.853(5)Å) and Mn-N (2.017(5)Å and 1.959(6)Å) distances are normal for high spin manganese(III) complexes.¹² The distance between manganese and chlorine (2.390(2)) also is normal for chloride coordinated to manganese(III).^{12a} The two acetonitrile molecules which are incorporated in the unit cell are not coordinated to the manganese but fill lattice space not occupied by the two residues.

If the catalyst is examined in a side view (see figure 3), it is seen that the molecule is almost planar (the dihedral angle between both aromatic rings being 169.0(3)°), except for the axially coordinating chlorine and the *ortho*-positioned *t*-butyl groups. Although the steric hindrance for substrate approach from the di-*t*-butyl face (fig 3b) can be understood, the steric effect of the cyclohexane moiety (figure 3a) appears not to be very large. In fact, the main steric interaction of the cyclohexane ring seems to be the interference of an approaching alkene with the axial H₆ or H₁. However, complex **1** might upon formation of the salenMn(IV)=O complex, which is supposed to be the catalytically active species, undergo a change in geometry in which steric factors are more pronounced. Furthermore, it should be noted that the slight twist in the Mn-salen unit also could be of importance in the oxygen transfer step.



a.



b.

Fig. 3: Side view from the cyclohexane (a) and the di-*t*-butylsalen (b) sides of **1** (PLUTO).

To obtain further information about the nature of **1** in solution and the occurrence of an oxygen transfer mechanism an UV-Vis study was undertaken. UV measurements (figure 4) for catalyst **1** show no significant change if the catalyst is stirred in CH₂Cl₂ (figure 4a) or in a biphasic system (CH₂Cl₂/H₂O: pH= 12.5, figure 4b). In both cases the colour of the organic layer is orange, and maxima are found at λ = 323 and 440 nm. When the aqueous layer is changed to domestic bleach (Piek; ± 0.84 M NaOCl; for epoxidation conditions the domestic bleach is diluted to 0.60 M by 0.05 M Na₂HPO₄ and set to pH = 11.3), the colour is changed to a faded

yellow, and the spectrum shows a bathochromic shift (figure 4c). This indicates the formation of an oxygenated complex. Analogy with a proposed structure for the bisnaphthyl propylenediamine bridged manganese perchlorate complex suggests the formation of a Mn₂(O)OH-species.¹³ More appropriate is the formation of a manganese oxo complex, as is postulated by Jacobsen and co-workers as the catalytically active species.^{6,7} When Ph₃P is added to the CH₂Cl₂-layer of oxidized **1**, the color changes back to orange, and the UV-Vis spectrum of **1** (figure 4d) shows regeneration of catalyst **1**. This sequence has been extended to 4 cycles, indicating the reversibility of oxygenation (using NaOCl) and deoxygenation (using PPh₃).

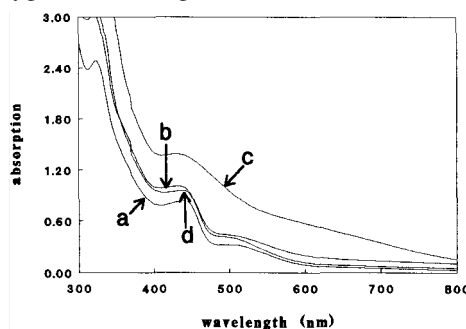


Fig. 4: a. catalyst **1** in CH₂Cl₂; b. catalyst **1** in H₂O (pH = 12.5)/CH₂Cl₂; c. after stirring with bleach; d. after addition of PPh₃ to c.

Epoxidation of dihydronaphthalene (1 mol % of **1**; aq. NaOCl) resulted in the formation of the corresponding epoxide in 36 % yield (e.e. 69 %).¹⁴ When dihydronaphthalene is used a range of side products is observed, including naphthalene, 1-naphthol and α-tetralone, due to allylic or benzylic oxidation. Using dimethylchromene, in which both activated positions are blocked, the corresponding epoxide was isolated in 87 % yield (e.e. 92 %).¹⁵ These results confirm that the structurally characterized complex **1** is indeed an enantioselective epoxidation catalyst.

In conclusion, we have determined the molecular structure of a (R,R)-cyclohexane-diamine based salen Mn(III) complex **1**, being a highly selective (69 - 92 % e.e.) Jacobsen epoxidation catalyst. The X-ray analysis shows an almost planar molecule, pointing to subtle steric (and electronic) effects, responsible for a remarkable high selectivity in these epoxidations. UV-Vis spectroscopy has demonstrated the reversible oxygenation-deoxygenation of **1**.

Acknowledgement

This work was supported by the Dutch Science Foundation (NWO/SON).

References and Notes

- ¹"Metal-Catalyzed Oxidations of Organic Compounds", R.A. Sheldon and J.K. Kochi, eds., Academic Press, N.Y., 1981; R.A. Johnson and K.B. Sharpless, "Catalytic Asymmetric Synthesis", Chapter 4.1, I. Ojima, ed., VCH, N.Y., 1993; E.N. Jacobsen, "Catalytic Asymmetric Synthesis", Chapter 4.2, I. Ojima, ed., VCH, New York, 1993.
- ²T.M. Meulemans, N.H. Kiers, B.L. Feringa and P.W.N.M. van Leeuwen, *Tetrahedron Lett.* **35**, 455 (1994).
- ³"Bioinorganic Catalysis", J. Reedijk, ed., Marcel Dekker, N.Y., 1993.
- ⁴M. Lubben, A. Meetsma, F. van Bolhuis, B.L. Feringa and R. Hage, *Inorg. Chim. Acta* **215**, 123 (1994); O.J. Gelling and B.L. Feringa, *J. Am. Chem. Soc.* **112**, 7599 (1990); O.J. Gelling, A. Meetsma and B.L. Feringa, *Inorg. Chem.* **29**, 2816 (1990); O.J. Gelling, F. van Bolhuis, A. Meetsma and B.L. Feringa, *J. Chem. Soc., Chem. Commun.* 552 (1988); B.L. Feringa, O.J. Gelling, M.T. Rispen and M. Lubben, *Proc. NATO Advanced Workshop on Metals in Supramol. Chem.*, in press.
- ⁵W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobsen, *J. Am. Chem. Soc.* **112**, 2801 (1990).
- ⁶E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.* **113**, 7063 (1991).
- ⁷E.N. Jacobsen, L. Deng, Y. Furukawa and L.E. Martínez, *Tetrahedron* **50**, 4323 (1994) and references cited therein.
- ⁸W. Zhang, E.N. Jacobsen, *J. Org. Chem.* **56**, 2296 (1991).
- ⁹Anal. calcd. for C₃₀H₄₀N₂O₂MnCl·CH₃CN (592.10): C 64.91, H 7.32, N 7.10, Mn 9.28, Cl 5.99; found: C 64.48, H 7.32, N 7.33, Mn 9.20, Cl 6.00%.
- ¹⁰Crystal data for **1**: C₃₀H₄₀N₂O₂MnCl·CH₃CN, *M* = 592.10, crystal size = 0.20 x 0.35 x 0.45 mm, triclinic, spacegroup *P1*, *a* = 11.909(1), *b* = 12.215(1), *c* = 13.458(1) Å, α = 63.551(5)°, β = 64.084(5)°, γ = 67.805(5)°, *V* = 1535.2(3) Å³, *Z* = 2, *D_x* = 1.281 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, $\mu(\text{Mo } K\alpha)$ = 5.31 cm⁻¹, *F*(000) = 628, *T* = 130 K, $\omega/2\sigma$ scan, $\Delta\omega$ = 0.90 + 0.34 tg θ , 1.79 < θ < 27.0, total unique data 6680 (*R*_{int} = 0.016), No. of observations [*I* ≥ 2.5 σ (*I*)] 5938, observations/variables 6.20, *R* = 0.032, *R_w* = 0.034, maximum peak in final Fourier difference synthesis 0.32 e/Å³. Data were collected on a Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX-2000 computer. Reduced cell calculations did not indicate any higher metric lattice symmetry, and examination of the final atomic coordinates of the structure did yield a pseudo center of inversion as extra metric symmetry element: coordinate equivalence with maximum deviation of 0.377 Å between C1 and C36 suggested a centrosymmetric space group. Lorentz and polarization correction were applied. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*. Enantiomorph selection was made by knowledge of the precursor compound stereochemistry. Final refinement on *F_o* by full matrix least-squares techniques (*Xtal*) with anisotropic thermal displacement parameters for the non-hydrogen atoms and one common thermal displacement parameter for the hydrogen atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- ¹¹In the second residue the manganese is 0.308(1) Å out of plane.
- ¹²a. V.L. Pecoraro and W.M. Butler, *Acta Cryst.* **C42**, 1151 (1986); b. X. Li and V.L. Pecoraro, *Inorg. Chem.* **28**, 3403 (1989); c. M. Mikuriya, Y. Yamato and T. Tokii, *Bull. Chem. Soc. Jpn.* **65**, 1466 (1992).
- ¹³C.A. McAuliffe, R.V. Parish, S.M. Abu-El-Wafa and R.M. Issa, *Inorg. Chim. Acta*, **115**, 91 (1986).
- ¹⁴When amorphous catalyst **1** was used the c.y. was 35% and the e.e. 69%.
- ¹⁵When amorphous catalyst **1** was used the c.y. was 87% and the e.e. 92%.