

Crystal structure of a chiral nitrido-manganese salen complex. The nitrogen analogue to the intermediate in the Jacobsen epoxidation reaction

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A chiral nitrido-manganese salen complex has been synthesised and characterised by X-ray diffraction; the geometrical and electronic structure of the complex are discussed in relation to the intermediate in asymmetric reactions.

The transfer of an oxygen atom(s) from high-valent oxo-metal complexes to alkenes in an enantioselective manner has been developed to be highly successful using asymmetric catalysis.¹ For the epoxidation of alkenes the use of chiral manganese salen complexes as the catalyst is among the most useful and widely applicable as it has proven effective for a variety of different alkenes.^{1a,2}

The intermediate in reactions using chiral manganese(III) salen complexes as the catalyst has been postulated to be an oxo-manganese(V) salen complex.^{1a,3} There are a number of indirect proofs for the oxo-manganese(V) salen intermediate, and recently direct proof by application of electrospray tandem MS appeared.⁴ A further aspect of reactions catalyzed by chiral manganese salen complexes, which also relates to the intermediate in the reaction, is the mechanism for the oxygen transfer process. The majority of the experimental results for the epoxidation reaction point to a mechanism starting with addition of the alkene to the oxygen atom in the oxo-manganese salen intermediate and the epoxide is formed by collapse involving a rotation of the carbon-carbon bond.^{1a,5} An alternative mechanism is based on the concept of metal-laoxetanes as intermediates in oxygen-transfer reactions⁶ and assumes that the alkene adds to the oxo-manganese bond in a [2 + 2] fashion followed by collapse giving the epoxide.⁷

Although much attention has been devoted to the intermediate in reactions catalyzed by chiral manganese(III) salen complexes no direct structural evidence for the intermediate is available. One way to obtain structural information about the intermediate could be to turn attention to the corresponding nitrogen analogue of the chiral oxo-manganese(V) salen complex as the structural difference between an O=Mn^V and a N≡Mn^V bond is small (*vide infra*). Here we present the preparation, characterisation and electronic structure analysis of the nitrogen analogue to the intermediate in the Jacobsen epoxidation reaction.

The dark brown chiral manganese(III) salen complex **1** reacts with NH₃ in CH₂Cl₂ at -50 °C using NBS as the oxidant to yield a deep green complex **2** isolated in 89% yield [reaction (1)].^{8†}

¹H NMR spectroscopic investigations of **2** give the following resonances in CDCl₃: δ_H 1.47 (s, 9H), 1.50 (s, 9H), 2.14 (s, 3H), 2.15 (s, 3H), 4.70 (d, *J* 11 Hz, 1H), 5.14 (d, *J* 11 Hz, 1H), 6.57 (s, 2H), 7.09–7.37 (m, 14 H), 7.55 (s, 1H), 7.62 (s, 1H). The ¹H NMR data show that the Bu^t, Me, CH=N and CH(Ph)CH(Ph)

hydrogen atoms are non-equivalent. The ¹³C NMR spectrum for **2** shows the following resonances: δ_C 20.4, 29.7, 35.6, 81.2, 81.4, 119.4, 120.5, 124.0, 128.8, 129.1, 129.4, 129.5, 131.3, 131.7, 134.7, 134.9, 135.6, 137.9, 141.1, 166.0, 166.2, 167.3, 167.5. These data for **2** show also the non-equivalence of several signals, most notably the signal for the chiral carbon and imine carbon atoms. The IR spectrum for **2** shows a N≡Mn stretch at 1049 cm⁻¹. Recrystallisation of the green complex gave crystals from MeOH (mp 206–208 °C) which were useable for X-ray analysis.

The structure of **2** is depicted in Fig. 1§ and shows the presence of the N≡Mn bond. The N≡Mn bond length is found to be 1.537 Å and similar to other N≡Mn bonds characterized.^{8,9} Other selected bond distances and angles are in the legend to Fig. 1. If one compares the N≡Mn bond length in **2** with, according to our knowledge, the only two other characterised O=Mn^V bonds (1.548 and 1.558 Å) in related types of complexes,¹⁰ the structural similarity between the N≡Mn^V and O=Mn^V fragments is obvious. It is also notable for the structure of **2** that the oxidation of the manganese atom causes a displacement of this atom by 0.49 Å out of the plane consisting of the four atoms coordinating to manganese. The displacement of the manganese atom when forming the N≡Mn^V complex probably causes the change in electronic environment at the chiral ligand which accounts for the non-equivalent resonances observed in the NMR spectra of **2**. The reactivity of **2** has also been briefly investigated under various reaction conditions, but compared with the corresponding chiral oxo-manganese(V) salen complex it is much less reactive.¹¹

In an attempt to obtain further insight into the structure and the chemical properties of the chiral nitrido-manganese(V) salen complex **2** the electronic structure has been investigated. A

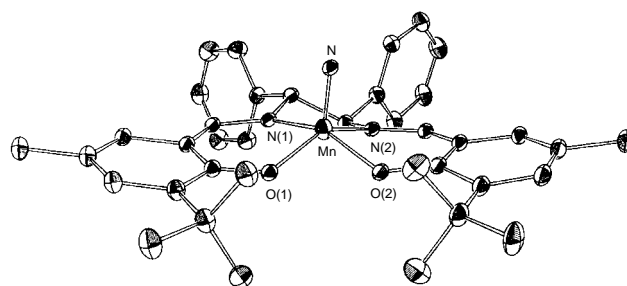
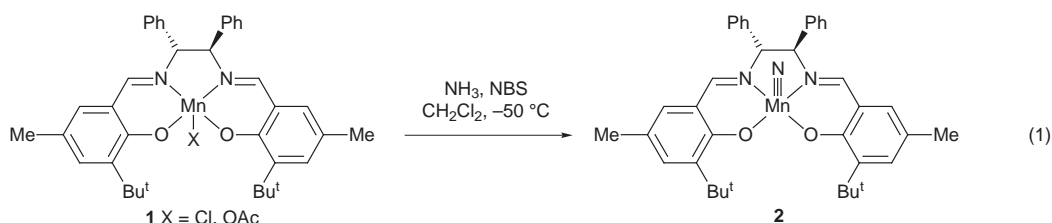
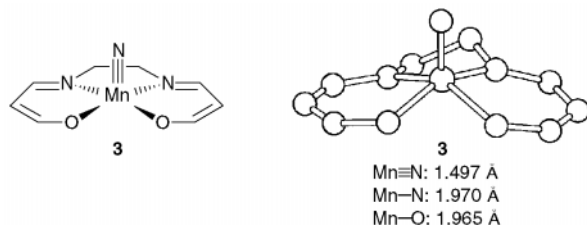


Fig. 1 Molecular structure of **2**. C-H hydrogen atoms are not shown (the other molecule is similar except that 12% have Mn and N on the other side of the salen plane). Selected distances (Å) and angles (°) for **2**: Mn–N 1.537(6), Mn–N(1) 1.949(6), Mn–N(2) 1.968(6), Mn–O(1) 1.903(6), Mn–O(2) 1.915(6), O(1)–Mn–N 109.8(3), O(2)–Mn–N 103.2(3), N(1)–Mn–N 101.6(3), N(2)–Mn–N 104.0(3).



model compound (**3**) for **2** was optimised using *ab initio* DFT calculations applying a B3LYP/6-31G* basis set and a TZV basis set for manganese.¹² For the singlet state of **3** the optimised structure is shown below with the calculated bond lengths at the manganese atom and it is notable that the N≡Mn, Mn–N and Mn–O bond lengths for **3** are similar to the same bonds in **2**. Furthermore, the displacement of the manganese atom (0.45 Å) out of the plane consisting of the four heteroatoms coordinating to manganese in **3** is also similar to the displacement in **2**. The simple model **3** seems thus to be a reliable model for **2**.



The calculations give a N≡Mn bond order of 2.8 indicating a bond with triple bond character. The charges on the nitrogen and manganese atoms are -0.15 and 0.87 , respectively. The frontier orbitals calculated for the N≡Mn bond in **3** give the HOMO at -5.71 eV and with only a minor contribution of the bonding combination of N p_x –Mn $d_{x^2-y^2}$, but this orbital is mainly located on the ligand. The second HOMO is at -6.00 eV and is mainly on the manganese atom as $d_{x^2-y^2}$; while the fourth HOMO at -7.62 eV is the bonding combination of N p_y –Mn d_{yz} . The LUMO and the third LUMO, at -1.60 eV and -0.95 eV, respectively, are the antibonding combination of N p_y –Mn d_{yz} and N p_x –Mn d_{xz} orbitals, respectively. The antibonding combination of N p_z –Mn d_{z^2} , the σ^*_{N-Mn} orbital, is at -0.20 eV.

It is interesting to compare the structure of the nitrido-manganese(v) salen complex **3** with the closely related oxo-manganese(v) salen complex. The structure of the latter is unknown, but the similarity in N≡Mn^V and O=Mn^V bond lengths (*vide supra*) is striking; however, the structural similarity does not account for the difference in reactivity. A comparison of the electronic structure for both the O=Mn^{V+} and O=Mn^V–Cl (optimised structures) obtained by *ab initio* DFT calculations¹² gives important information. The results for the two oxo-manganese complexes are alike, so only the former will be discussed here. The O=Mn bond length is optimised to be 1.546 Å which is similar to the two characterised O=Mn^V bonds (1.548 and 1.558 Å) in related types of complexes.¹⁰ The charges at oxygen and manganese are -0.20 and 1.18 , respectively. The bond length and charge considerations of the N≡Mn^V and O=Mn^V complexes are thus not that different. However, the O=Mn bond order is calculated to be 2.3, showing a much weaker bond than the N≡Mn bond, and, furthermore, the O=Mn^V complex also shows a different frontier orbital picture compared with the N≡Mn^V complex, as the related frontier orbitals of the former are found at lower energies, the HOMO at -10.65 eV, while the LUMO is at -7.92 eV. The lowering of the LUMO in O=Mn^V by 6.3 eV points to a significant difference in reactivity, when reacting with electron-rich alkenes. The more reactive chiral oxo-manganese(v) salen complex compared with the closely related chiral nitrido-manganese(v) salen complex is thus probably due to a much weaker O=Mn bond and lower lying unoccupied MOs in the former complex.

With the structural knowledge of the chiral nitrido-manganese(v) salen complex the remarkable enantioselectivity of the related oxo-manganese(v) salen complex might begin to be understood in detail as the present results allow one to analyse the approach of *e.g.* alkenes to the intermediate.

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Notes and References

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‡ Reaction conditions for the preparation of **2**. A solution of [(*R,R*)-diphenyl-*tert*-butylmethylsalen]Mn(Cl) (360 mg, 0.56 mmol) in 30 ml CH₂Cl₂ was cooled to -50 °C. NBS was added (470 mg, 2.8 mmol). Gaseous NH₃ was fed through the reaction mixture for 5–10 min and a colour change to green was observed. The reaction mixture was warmed and the contents transferred to a separator funnel with 25 ml H₂O added. The dark green organic phase was isolated and the aqueous layer extracted with 25 ml CH₂Cl₂. The combined organic phases were washed with 4 × 25 ml H₂O and the solvent removed. The solid material was re-dissolved in CH₂Cl₂ and purified by chromatography (Al₂O₃, 4 × 18 cm) with CH₂Cl₂ as the eluent. A dark green band was collected and recrystallized in MeOH.

§ Crystallographic data for **2**: C₃₈H₄₂N₃O₂Mn; *M_w*: 627.72; triclinic, space group *P1*, *a* = 10.2919(8), *b* = 12.0062(9), *c* = 14.139(1) Å, α = 88.543(1), β = 76.608(1), γ = 77.637(1)°, *V* = 1659.7(2) Å³, *Z* = 2. 6542 independent reflections measured at 120 K on a Siemens SMART CCD diffractometer. Mo-K α radiation. 4697 reflections with $I > 3\sigma(I)$ and 329 variables yield *R* = 0.052, *R_w* = 0.057. The two molecules are related by an approximate center of symmetry except for the chiral centers. This necessitated the use of severe constraints on the refinement.¹³ CCDC 182/904.

- For example, (a) asymmetric epoxidations: E. N. Jacobsen, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, ch. 4.2; (b) asymmetric dihydroxylation: H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483.
- See *e.g.*: E. N. Jacobsen, in *Comprehensive Organometallic Chemistry II*, ed. G. Wilkinson, F. G. A. Stone, E. W. Abel and L. S. Hegeudus, Pergamon, New York, 1995, vol. 12, ch. 11.1; T. Katsuki, *Coord. Chem. Rev.*, 1995, **140**, 189.
- See *e.g.*: E. N. Jacobsen, W. Zhang, A. R. Muci and M. L. Güler, *J. Am. Chem. Soc.*, 1991, **113**, 7063; P. J. Pospisil, D. H. Carstens and E. N. Jacobsen, *Chem. Eur. J.*, 1996, **2**, 974.
- D. Feringer and D. A. Plattner, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1718.
- See *e.g.*: M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Güler, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 948; N. S. Finney, P. J. Pospisil, S. Chang, M. Palucki, R. G. Konsler, K. B. Hansen and E. N. Jacobsen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1720.
- K. A. Jørgensen and B. Schiøtt, *Chem. Rev.*, 1990, **90**, 1483.
- P.-O. Norrby, C. Linde and B. Åkermark, *J. Am. Chem. Soc.*, 1995, **117**, 11035; T. Hamada, T. Fukuda, H. Imanishi and T. Katsuki, *Tetrahedron*, 1996, **52**, 515; C. Linde, M. Arnold, P.-O. Norrby and B. Åkermark, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1723.
- J. du Bois, J. Hong, E. M. Carreira and M. W. Day, *J. Am. Chem. Soc.*, 1996, **118**, 915; J. du Bois, C. S. Tomooka, J. Hong, E. M. Carreira and M. W. Day, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1645; J. du Bois, C. S. Tomooka, J. Hong and E. M. Carreira, *Acc. Chem. Res.*, 1997, **30**, 364.
- J. W. Bucjler, C. Dreher, K.-L. Lay, Y. J. A. Lee and W. R. Scheidt, *Inorg. Chem.*, 1983, **22**, 888.
- T. J. Collins and S. W. Gordon-Wylie, *J. Am. Chem. Soc.*, 1989, **111**, 4511; F. M. MacDonnell, N. L. P. Fackler, C. Stern and T. V. O'Halloran, *J. Am. Chem. Soc.*, 1994, **116**, 7431.
- A. S. Jepsen, A. Bøgevig and K. A. Jørgensen, unpublished results.
- Gaussian 94, Revision E. 2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
- X-Ray programs: SIR97, G. Casciaro, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Siliqi, M. C. Burla, G. Polidori and M. Camalli, *Acta Crystallogr., Sect. A*, 1996, **52**, C50; G. S. Pawley, *Adv. Struct. Res. Diffract. Methods*, 1972, **4**, 1; ORTEP III, M. N. Burnett and C. K. Johnson, Report ORNL-6895, Oak Ridge National Laboratory, Tennessee, 1996.

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