Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 1150–1153
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Note

A new square planar mononuclear Mn^{III} complex for catalytic epoxidation of stilbene

Lien-Hoa Tran [a], Lars Eriksson [b], Licheng Sun [c], Björn Åkermark [a,*]

[a] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden
[b] Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden
[c] Department of Chemistry, Organic Chemistry, Royal Institut Technology (KTH), Teknikringen 30, 100 44 Stockholm, Sweden

Received 11 October 2007; received in revised form 21 December 2007; accepted 6 January 2008
Available online 11 January 2008

Abstract

The manganese(III) complex (**2**) with a diamide ligand has been synthesized. This complex was found to catalyze both the epoxidation of (*Z*)- and (*E*)-stilbene with high conversion and the oxidation of benzyl alcohol to benzaldehyde.

Keywords: Manganese; Epoxidation; Oxidation of alcohols

1. Introduction

Manganese catalyzed epoxidation [1–5] and water oxidation [6–12] both probably proceed via Mn^{V} oxo complexes. These complexes have been found to be very elusive and attempts to detect such species in salen-Mn catalyzed epoxidations [5,13–15] suggest that they are unstable and are readily transformed into Mn^{IV} species. However, some time ago Collins and coworkers managed to isolate a few Mn^{V} oxo species [16,17], in which deprotonated amide functions have replaced the phenolic ligands in the salen complexes. Perhaps because of the over all negative charge, these complexes did not effect epoxidation unless positive ions such as Zn^{2+} were added [18].

2. Results and discussion

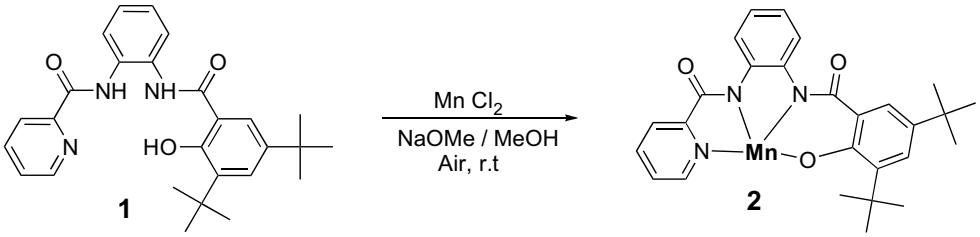
We would now like to report on the preparation of the Mn^{III} complex **2**, which is the potential precursor of a neutral oxo complex, related to the anionic ones presented earlier [16,17]. Although we have not yet succeeded in preparing a Mn^{V} oxo complex from **2**, we have been able to show that it catalyzes epoxidation of both (*Z*)- and (*E*)-stilbene, in contrast to some related complexes [16–18]. The reason could be that complex **2** is neutral and thus more electrophilic than these negatively charged complexes. It also catalyzes the oxidation of benzyl alcohol to benzaldehyde, all using iodosobenzene as oxidant (see Scheme 1).

Ligand **1** was prepared by reacting the acid chloride of 2-hydroxy-3,5-di-*tert*-butylbenzoic acid with the appropriate amine. This ligand **1** was then stirred with manganese(II) chloride and sodium methoxide in methanol solution under air, to give the crude complex **2** as a green powder. The green microcrystalline solid was dissolved in methanol and hexane was slowly diffused into this solution to give crystals, suitable for X-ray structure analysis (see Fig. 1).

Initial results of epoxidation of stilbene by using manganese(III) catalyst **2** (5 mol%) and PhIO (5 equiv.) as oxidant in either pure acetonitrile or a mixture of methylene chloride and acetonitrile (1:5) gave the epoxide in high conversion. By contrast, *tert*-butylhydroperoxide (TBHP) as an oxidant gave low conversion to the epoxide (<1%), and with hydrogen peroxide and sodium hypochlorite as oxidants, no epoxide formation could be detected. The

* Corresponding author. Tel.: +46 8 163223; fax: +46 8 154908.
E-mail address: bjorn.akermark@organ.su.se (B. Åkermark).

0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.01.009



Scheme 1. Synthesis of manganese(III) complex **2**.

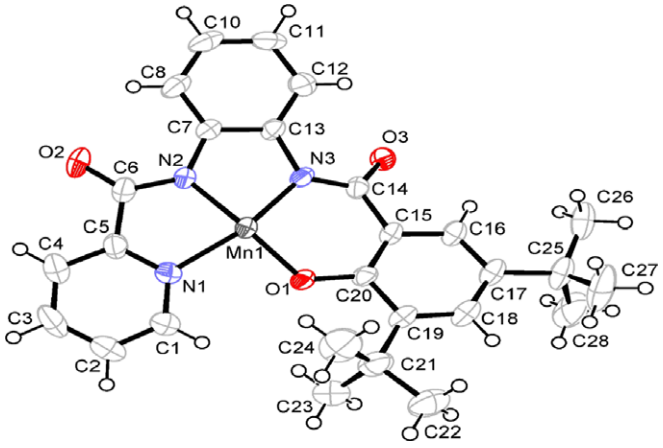
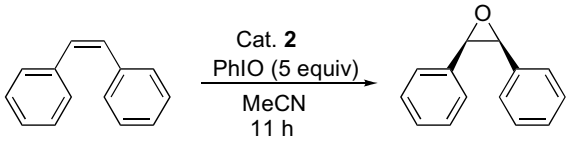


Fig. 1. ORTEP diagram of a square planar Mn^{III} amide complex **2**.

initial results also showed that substantial amounts of (*E*)-stilbene oxide were formed, in addition to the expected (*Z*)-stilbene oxide (Table 1). This cannot be explained by isomerization of (*Z*)-stilbene, which was less than 10% (Table 1). With a higher ratio of catalyst to substrate, the *cis*-specificity of the epoxidation increased (Table 1), perhaps because the epoxidation can compete with the conversion of the manganese intermediate to a diradical



In contrast, when salen-type catalysts are used, also (*E*)-stilbene could be epoxidized, using **2** as a catalyst (Table 2). The reaction was less facile than the epoxidation of (*Z*)-stilbene. Also in this case, the major product was the result of *cis*-addition of the oxygen to the alkene, but some of the

Table 1
Conversion and relative yield of isomers on the epoxidation of (*Z*)-stilbene

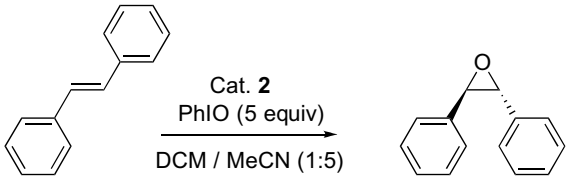
Entry	Mn (%)	Conversion (%)	Isomerization[a]	Ratio (*Z*/*E*)
1	5	100	4	2:1
2	10	100	9	5:1
3	15	100	9	5:1
4	20	100	10	5:1

[a] Isomerization of (*Z*)-stilbene (%).

Table 2
Conversion and relative yield of isomers on the epoxidation of (*E*)-stilbene

Entry	Mn (%)	Conversion (%)	Ratio (*Z*/*E*)
1	5	85	1:3
2	10	80	1:3
3	15	40	1:4
4	20	42	1:6

isomeric epoxide was formed. There are several possible reasons why the epoxidation is not stereospecific (for a discussion see Ref. [19] and references cited therein).



One reasonable explanation is that the Mn^{V} oxo complex which is probably formed initially, is partly converted to a Mn^{IV} oxo complex by the intramolecular oxidation of the coordinated phenolic part of the ligand. This should lead to the epoxidation via a diradical intermediate and the formation of a mixture of (*Z*)- and (*E*)- products from both (*Z*) and (*E*)-stilbene, as observed (cf. [19] and Tables 1 and 2).

In addition to the epoxidation, the high valent manganese oxo complex formed from the addition of iodosobenzene to the manganese(III) complex **2** was shown to oxidize benzyl alcohol to benzaldehyde and 1-methylbenzyl alcohol to acetophenone. The aliphatic alcohols 1-octanol and 2-octanol were also oxidized to the corresponding carbonyl compounds, albeit in a fairly low conversion. However, the attempts to oxidize a hydrocarbon, cyclohexane, failed.

Although the epoxidation is not completely stereospecific, our results open up a road to a new type of epoxidation catalyst, which is related to the salen-based catalysts but can be applied to both (*Z*)- and (*E*)-alkenes. The reason for the moderate stereo-specificity may be the ease of oxidation of the phenolic part of the ligand to give an intermediate with diradical character. The preparation of complexes with a less readily oxidized ligand is therefore in progress.

3. Experimental

3.1. General procedures

Solvents were dried by standard methods and the chemicals were purchased from Aldrich or Lancaster and used as received. Electrospray ionization mass spectra were determined, using a Bruker Daltonics BioApex-94c instrument and yields were determined by HPLC, using a Waters 2695 instrument, equipped with a Daicol–Chiralcol OD-H column, (0.46 mm × 25 cm), UV-detector, eluent isohexane/isopropanol 9/1. *N*-(2-amino-phenyl)pyridine-2-carboxamide was prepared according to a published procedure [20].

Single crystal X-ray diffraction data were recorded with a STOE IPDS, using Mo-radiation source ($\lambda = 0.71073$ Å). Data were processed by the diffractometer software [21]. The structure was solved by conventional direct methods using SHELXS97 [22] giving electron density maps where most of the non-hydrogen atoms could be resolved. The rest of the non-hydrogen atoms were located at different electron density maps and the structure model was refined with full matrix least square calculations on F^2 using the program SHELXL97-2 [23]. All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms, which were placed at geometrically calculated positions and let to ride on the atoms they were bonded to, were given isotropic displacement parameters calculated as $\xi \cdot U_{eq}$ for the non-hydrogen atoms with $\xi = 1.5$ for methyl hydrogen atoms (–CH_3) and $\xi = 1.2$ for methylenic (–CH_2–) and aromatic (–CH) hydrogen atoms. The picture is made with the program DIAMOND [24] with ellipsoids drawn at the 50% probability level. More details about the crystal structure can be found in the cif-file available as supplementary material.

3.2. Synthesis of ligand *1*

3,5-Di-*tert*-butylsalicylic acid hydrate (0.5 g, 2 mmol) was added in portions to a stirred solution of $SOCl_2$(2 ml). This reaction was heated at 60 °C for 15 h. Excess thionylchloride was removed in vacuo and then co-evaporated six times with dry chloroform to obtain a yellow-brown residue.

This yellow-brown residue was dissolved in dry CH_2Cl_2 and then triethylamine (1.4 ml) was added dropwise. To this stirred mixture, a solution of *N*-(2-amino-phenyl)pyridine-2-carboxamide (0.426 g, 2 mmol) in dichloromethane was added. This reaction mixture was stirred overnight at ambient temperature. After the addition of water (15 ml), it was extracted with dichloromethane (3 × 10 ml). The combined organic extracts were then washed with water (3 × 25 ml) and finally with brine (3 × 25 ml). After drying over night with Na_2SO_4, filtration and removal of the solvent by a rotavap, a yellow solid was obtained. This was crystallized from chloroform/pentane and the crystals were washed with ice-cold methanol to give white crystals (0.696 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9H), 1.43 (s, 9H), 7.26 (m, 1H), 7.33 (m, 1H), 7.39 (m, 1H), 7.47 (d, 1H), 7.52 (m, 1H), 7.67 (d, 1H), 7.91 (m, 1H), 7.95 (m, 1H), 8.31 (m, 1H), 8.63 (m, 1H), 10.10 (s, 1H), 10.25 (s, 1H), 12.80 (s, 1H).

^{13}C NMR (400 MHz, $CDCl_3$): δ 29.44, 29,45, 31.55, 31.56, 34.47, 35.24, 113.45, 120.72, 122.69, 124.47, 126.05, 126.78, 126.99, 127.05, 128.91, 129.40, 131.03, 137.73, 137.90, 139.95, 148.43, 148.56, 159.49, 163.53, 169.84.

HRMS-ESI (M+H) calcd for $C_{27}H_{31}N_3O_3Na^+$: 468.2258, found: 468.2251.

Elemental Anal. Calc. for $C_{27}H_{31}N_3O_3$: C, 72.78; H, 7.01; N, 9.43. Found: C, 72.88; H, 7.17; N, 9.27%.

3.3. Synthesis of complex *2*

To a solution of **1** (0.5 g, 1.12 mmol) in methanol (10 ml) was added NaOMe in one portion, followed by manganese(II) chloride (0.141 g, 1.12 mmol) and the color immediately turned dark brown. The mixture was then allowed to stir in aerobic atmosphere at ambient temperature for 1 h and a precipitate was formed. This was isolated by filtration through a glassfilter, washed with ice-cold chloroform, ice-cold pentane, and finally with ice-cold diethyl ether. After drying overnight under vacuum, **2**(0.486 g, 87% yield) was obtained as a light green microcrystalline solid.

Elemental Anal. Calc. for $C_{27}H_{28}$ MnN_3O_3–$MnCl_2$ 3:2: C, 55.8; H, 4.8; N, 7.2; Mn, 15.8. Found: C, 54.0; H, 5.0; N, 6.6; Mn, 13.7%.

The green microcrystalline solid was dissolved in methanol and hexane was slowly diffused into this solution to give a single crystal, suitable for an X-ray crystal structure determination.

3.4. General procedure for epoxidation

PhIO (0.110 g, 0.50 mmol) was added in one portion to a stirred suspension of stilbene (0.090 g, 0.50 mmol) and catalyst **2** (0.0124 g, 0.025 mmol) in CH_3CN (2 ml). This reaction mixture was then stirred at rt for 11 h. The reaction was quenched by filtering off catalyst **2** through a silica pad and the crude product was analyzed by HPLC. With (*Z*)-stilbene, the conversion to epoxide was 100% and with (*E*)-stilbene ca. 85%.

3.5. General procedure for the oxidation of alcohols

PhIO (0.220 g, 1 mmol) was added in one portion to a stirred suspension of benzyl alcohol (0.108 g, 1 mmol) and catalyst **2** (0.025 g, 0.050 mmol) in CH_3CN (2 ml). The reaction mixture was stirred at rt for 5 h. The reaction was then quenched by filtering off catalyst **2** through a silica pad and the crude product was analyzed by HPLC, showing essentially 100% conversion to benzaldehyde. The oxidation of 1-phenylethanol similarly gave acetophenone.

Acknowledgements

We thank the Swedish Foundation Strategic Research, The Swedish Energy Authority, and Knut and Alice Wallenberg Foundation for financial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.009.

References

[1] K. Srinivasan, P. Michaud, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
[2] E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993, p. 159.
[3] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[4] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2004) 1563.
[5] W.-Y. Hsieh, V. Pecoraro, Inorg. Chem. Acta 341 (2002) 113.
[6] J. Barber, Q. Rev. Biophys. 36 (2003) 71.
[7] P.E.M. Siegbahn, Curr. Opin. Chem. Biol. 6 (2002) 227.
[8] J.S. Vrettos, J. Limburg, G.W. Brudvig, Biochem. Biophys. Acta 1503 (2001) 229.
[9] L. Sun, L. Hammarström, B. Åkermark, S. Styring, Chem. Soc. Rev. 30 (2001) 36.
[10] B.A. Diner, F. Rappaport, Annu. Rev. Plant Biol. 53 (2002) 551.
[11] V.L. Pecoraro et al., Pure Appl. Chem. 70 (1998) 925.
[12] M. Lundberg, P.E.M. Siegbahn, Phys. Chem. Chem. Phys. 6 (2004) 4772.
[13] W. Adam, C. Mock-Knoblauch, C.R. Saha-Möller, M. Herderich, J. Am. Chem. Soc. 122 (2000) 9685.
[14] K.A. Campbell, M.R. Lashley, J.K. Wyatt, M.H. Nantz, R.D. Britt, J. Am. Chem. Soc. 123 (2001) 5710.
[15] D. Feichtinger, D.A. Plattner, Angew. Chem., Int. Ed. 36 (1997) 1718.
[16] T.J. Collins, S.W. Gordon-Wylie, J. Am. Chem. Soc. 111 (1989) 4511.
[17] J. Collins, R.D. Powell, C. Slebodick, E.S. Uffelman, J. Am. Chem. Soc. 112 (1990) 899.
[18] C.G. Miller, S.W. Gordon-Wylie, C.P. Horwitz, S.A. Strazisar, D.K. Peraino, G.C. Clark, S.T. Weintraub, T.J. Collins, J. Am. Chem. Soc. 120 (1998) 11540.
[19] C. Linde, M.F. Anderlund, B. Åkermark, Tetrahedron Lett. 46 (2005) 5597.
[20] G.R. Hanson, T.A. Kabanos, A.D. Keramidas, D. Mentzafos, A. Terzis, Inorg. Chem. 31 (1992) 2587.
[21] Stoe, IPDS diffractometer control software, version 2.87, Stoe & CIE GmbH, Hilpertstrasse 10, D-64295 Darmstadt, Germany, 1997.
[22] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467–473.
[23] G.M. Sheldrick, Computer Program for the Refinement of Crystal Structures, Göttingen, Germany, 1997.
[24] DIAMOND – Visual Crystal Structure Information System, Crystal Impact, Postfach 1251, D-53002 Bonn, Germany.