Tetrahedron Letters, Vol. 33, No. 8, pp. 1001-1004, 1992
Printed in Great Britain

0040-4039/92 $3.00 + .00
Pergamon Press plc

ALKENE AZIRIDINATION AND EPOXIDATION CATALYZED BY CHIRAL METAL SALEN COMPLEXES

Kenneth J. O'Connor, Shiow-Jyi Wey and Cynthia J. Burrows*

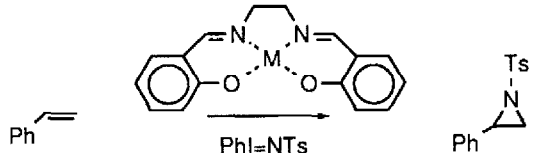
Department of Chemistry, State University of New York
Stony Brook, New York 11974-3400, USA

Summary. *New chiral metal salen complexes substituted in the 3 position with bulky silyl groups (TMS, TBDMS) have been synthesized. Although some of these complexes catalyzed the epoxidation of unfunctionalized olefins in moderate to high ee's, they catalyzed the aziridination of cis-β-methylstyrene without any asymmetric induction.*

The design of chiral Mn(salen) and Mn and Fe porphyrin complexes to catalytically transform unfunctionalized alkenes into optically active epoxides is one of the most challenging objectives in asymmetric synthesis today.[1] Interestingly, few researchers have investigated the aza analogue of this reaction, namely catalytic asymmetric aziridination.[2] Although there have been some investigations on the use of MnTPPX and FeTPPX for catalytic aziridination,[3] there have been no reports on the use of metal(salen) complexes as aziridination catalysts. This is surprising since chiral Mn (salen) complexes have enjoyed unprecedented success in asymmetric epoxidation.[1] As part of our on-going research efforts in metal-catalyzed asymmetric transformations,[4] we report studies of metal(salen) complexes as catalysts for aziridination of olefins with emphasis on whether this transformation could be accomplished with high enantiomeric excess (ee). The latter question was of particular interest to us since aziridines undergo facile ring opening and would then serve as valuable precursors for chiral diamines and amino alcohols.[5]

Initial efforts focused on screening a wide variety of metal(salen) complexes for catalytic activity, including complexes of Cr^{III}, Mn^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Rh^{III}, and Pd^{II}. The prototypical reaction involved the formation of *N*-tosyl-2-phenylaziridine by reacting styrene with PhI=NTs[6] in the presence of 5 mol% metal(salen) complex[7] (eqn 1). While almost all of the catalysts produced good yields of PhI and $TsNH_2$, only Mn(salen)Cl catalyzed the reaction to produce the aziridine (46% based on PhI=NTs added).[8] The catalytic oxidant in this reaction is presumably a L_nMn=NTs species (L_n=salen + Cl^-) which transfers its nitrogen group to the olefin.[9] To our knowledge, this is the first report of a metal(salen) complex effecting this type of nitrogen group transfer.

(1)



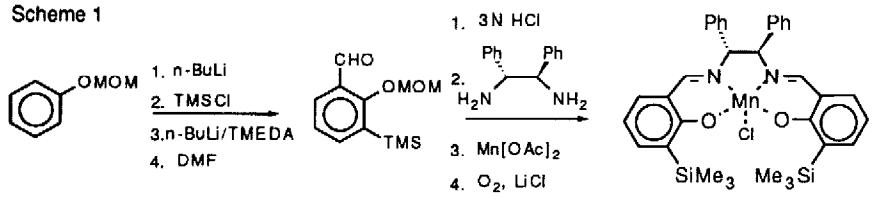
M = Fe^{III}, Co^{II}, Cr^{III}, Ni^{II}, Mn^{III}, Cu^{II}, Pd^{II}, Rh^{III}

Although catalytic aziridination is itself a useful transformation, the utility of the reaction would be heightened by

discovery of enantioselective catalysts. Consequently, chiral metal(salen) complexes substituted in the 3 position with silyl groups were synthesized. Since the placement of a t-butyl group at the 3 position of Mn(salen) complexes has been found to be crucial to the attainment of high ee's in asymmetric epoxidation,[1a,b] we hypothesized that substitution by silicon might be additionally advantageous for two reasons. First, a C-Si bond length is ≈20% longer than a C-C bond[10] and would presumably result in an increase in non-bonded interactions upon approach of the olefin to the metal center, as well as an increase in the face selectivity of the catalyst. In addition, the steric bulk at silicon can be easily varied so as to optimize the catalyst's activity in asymmetric transformations. Second, the formation of aryl-silyl bonds often proceeds in high yields[11] and would easily allow for multigram quantities of the catalyst to be synthesized.

Two approaches to silyl-substituted metal salen complexes were investigated. The first approach involved a series of ortholithiation reactions which served to install the TMS and formyl groups both ortho to the methoxymethyl directing group (78%, Scheme 1).[11,12] Deprotection of the MOM group, followed by condensation of the resulting salicylaldehyde with the chiral diamine provided the chiral ligand (80%). Formation of the Mn complex **(R,R)-1** was accomplished by refluxing the ligand with $Mn(OAc)_2.4H_2O$,[1a] followed by the addition of LiCl and air oxidation (78%).

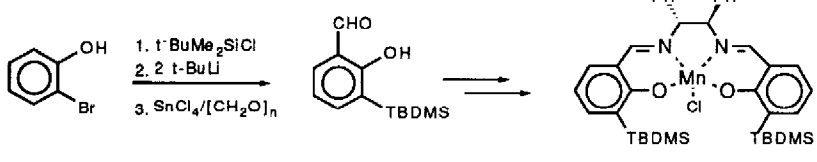
Scheme 1



(R,R)-1

The second approach utilized an intramolecular silyl rearrangement[13] to form the aryl-Si bond (Scheme 2). o-Bromophenol was first silylated with (t-Bu)$(CH_3)_2SiCl$, and the resulting o-bromosilyl ether was then metallated (2.1 equiv. t-BuLi) to afford 2-t-butyldimethylsilylphenol (82%). The phenol was allowed to react with $SnCl_4$ and $(CH_2O)_n$ as outlined by Casiraghi[14] to provide the salicylaldehyde (28%). The final steps of the synthesis of **(R,R)-2** were identical to those outlined in Scheme 1.

Scheme 2



(R,R)-2

The reaction of **(R,R)-1** (5 mol%) with a 5-fold excess of styrene in the presence of PhI=NTs provided the N-tosyl aziridine in a 20% yield and without any enantiomeric excess.[15] Similarly, *cis*-β-methylstyrene was converted to its corresponding N-tosylaziridine in somewhat lower yield, but also with complete lack of face selectivity. A similar result was obtained when using the more sterically hindered **(R,R)-2** catalyst. Surprised by the lack of asymmetric induction

displayed in the aziridination reactions, we decided to examine asymmetric epoxidation as another means of gauging the face selectivity of complexes **1** and **2**. Table 1 lists the ee's obtained from epoxidation reactions with styrene and cis-methylstyrene. Interestingly, these ee's were appreciable, despite the lack of enantioselectivity observed for the aziridination of styrene. This discrepancy strongly suggests that the transfer of the oxygen atom from a $L_nMn{=}O$ species is essentially concerted, whereas $L_nMn{=}NTs$ species transfer the nitrogen atom in a stepwise fashion, perhaps via a radical intermediate.

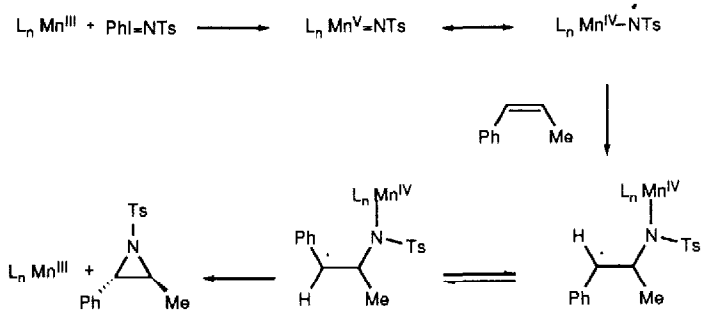
Table 1. Asymmetric Epoxidation of Unfunctionalized Olefins

Olefin	Catalyst	%ee[c,e]	Conversion(%)	Yield(%)[d]	Total Turnover
styrene[a]	(R,R)-1	18(R)	57	44	10
styrene[b]	(R,R)-2	33(R)	14	86	16
Z-methylstyrene[a]	(R,R)-1	23(1R,2S)	72	46	7
Z-methylstyrene[b]	(R,R)-2	53(1R,2S)	15	60	5

a) PhIO was used as the oxidant in CH_2Cl_2. b) Experimental conditions identical to those used in ref. 1a) were employed; NaOCl was the oxidant. c) %ee was determined by ^1H NMR analysis using $Eu(hfc)_3$. d) Determined by GC integration against an internal standard (PhCl) and corrected for the extent of olefin conversion. e) Assignment of absolute stereochemistry was made by a comparison of the shift reagent studies done with epoxides produced in these experiments with those done with enantiomerically enriched samples of known absolute configuration.[1a]

The intervention of radical intermediates in metal-catalyzed aziridination chemistry is well precedented for MnTPPX and FeTPPX systems.[3] Although Mn(V)=NTs species are believed to be formed initially, these species might also be formulated as Mn(IV)-N˙-Ts radicals[3] and might therefore add to olefins in a stepwise fashion (Scheme 3). Such a radical most likely has a sufficiently long lifetime to allow for C-C bond rotation to compete effectively with ring closure.[16] Nevertheless, this mechanism would predict initial face selectivity reflected in a diastereomeric excess at the methyl-substituted carbon of the substrate followed by thermodynamic control of ring closure at the benzylic carbon. The complete lack of ee observed calls into question the currently postulated mechanism of aziridination. In particular, it is possible that either an electron transfer pathway involving high valent manganese prevails, or that the reaction is catalyzed by a decomposition product of the Mn complex.

Scheme 3



One method of obtaining ee's comparable to those obtained in asymmetric epoxidation is to form a metal-imino species which transfers its nitrogen atom in a *concerted* fashion to the olefin. We are currently investigating the use of other nitrogen containing oxidants for this purpose and will report these results shortly.

Acknowledgement. Support of this work by a grant from the National Science Foundation (CHE-9006684) is gratefully acknowledged. We thank a referee for helpful comments.

References and Notes.

1. For Mn salen catalysis: (a) Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296-2298. (b) Zhang, W.; Loebach, J. L. ; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801-2803. (c) Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron Lett.* **1990**, *31*, 7345-7348. For MnTPPX and FeTPPX catalysis (TPP=tetraphenylporphyrin): (d) Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628-3634. (e) O'Malley, S.; Kodadek, T. *J. Am. Chem. Soc.* **1989**, *111*, 9116-9118.
2. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726-728.
3. (a) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. II* **1988**, 1517-1524. (b) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073-2074.
4. (a) Kinneary, J. F.; Wagler, T. R.; Burrows, C. J. *Tetrahedron Lett.* **1988**, *29*, 877-880. (b) Yoon, H.; Burrows, C. J. *J. Am. Chem. Soc.*, **1988**, *110*, 4087-4089. (c) Wagler, T. R.; Burrows, C. J. *Tetrahedron Lett.* **1988**, *29*, 5091-5094. (d) Wagler, T. R.; Fang, Y.; Burrows, C. J. *J. Org. Chem.* **1989**, *54*, 1584-1589. (e) Yoon, H.; Wagler, T. R.; O'Connor, K. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4568-4570.
5. Tseng, C. C.; Terashima, S.; Yamada, S. *Chem. Pharm. Bull.* **1977**, *25*, 166-170. (b) Swift, G.; Swern, D. *J. Org. Chem.* **1967**, *32*, 511-517.
6. Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361-362.
7. All metal salen complexes were prepared from published literature procedures.
8. A catalyst:PhI=NTs:styrene ratio of 1:20:200 was used (olefin was 1M in anhydrous CH_2Cl_2). If this reaction is not run under strictly anhydrous conditions, styrene oxide will also be produced in 10-15% yield.
9. Since Mn(V)=NTs species are readily hydrolyzed to form Mn(V)=O species[3], the formation of epoxides as by-products[7] serves as additional evidence for the existence of a metal-imino species under these reaction conditions.
10. Sieburth, S. M.; Manly, C. J.; Gammon, D. W. *Pestic. Sci.* **1990**, *28*, 289-307.
11. Townsend, C. A.; Bloom, L. M. *Tetrahedron Lett.* **1981**, *22*, 3923-3924.
12. Although the installation of a TMS group proceeded in high yield (>90%), introduction of bulkier silyl groups under the same reaction conditions proceeded in significantly lower yields (<10%).
13. Simchen, G.; Pfletschinger, J. *Angew. Chem. (Int. Ed. Engl.)* **1976**, *15*, 428-429.
14. Casiraghi, G.; Casnati, G.; Puglia, G., Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862-1865.
15. Enantiomeric excess was determined by ^{1}H NMR analysis (Bruker 600MHz) in the presence of 70 mol% $Eu(hfc)_3$.
16. Additional evidence to support the formation of radical intermediates was obtained by reacting other cis olefins under typical reaction conditions. Z-Stilbene afforded exclusively *E*-N-tosyl-2,3-diphenylaziridine and Z-methyl styrene afforded a 2:3 ratio of *Z*:*E*-N-tosylaziridines.

(Received in USA 15 July 1991; accepted 10 December 1991)