Antagonistic metal-directed inductions in catalytic asymmetric aziridination by manganese and iron tetramethylchiroporphyrins

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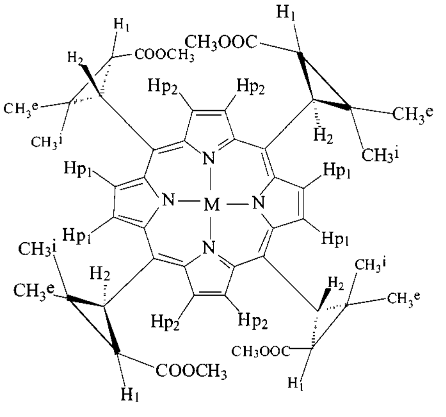
Catalytic asymmetric aziridination of styrene by [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane was achieved by manganese and iron tetramethylchiroporphyrins; opposite enantioselectivities were obtained with the two metal centers, and possible mechanisms are proposed to explain this unexpected result.

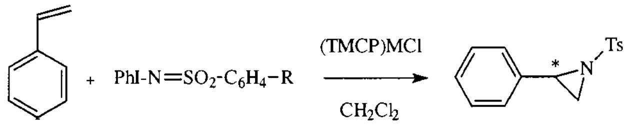
Amongst atom- and group-transfer processes, including epoxidation[1] and cyclopropanation,[2] aziridination is probably the least studied reaction. However, transition metal catalysed aziridination of olefins has been a topic of increasing interest in the past five years.[3] Several atom-transfer catalysts have been found to induce olefin aziridination by [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhINTS),[4] but generally they are only moderately efficient and the mechanisms of aziridination catalysis remain unclear. A number of chiral metalloporphyrins have been shown to catalyse the asymmetric epoxidation[1] and cyclopropanation[2] of olefins, but only one example of catalytic asymmetric aziridination of alkenes has been published up to now.[5] Metallochiroporphyrins are competent catalysts in the epoxidation of aromatic olefins,[6] thus it was tempting to assess their potential in catalytic nitrogen group transfer. Herein we report the catalytic activity of several metal complexes of tetramethylchiroporphyrin (TMCP) **1** in the asymmetric aziridination of styrene, and the opposite enantioselectivities induced by the iron(III) and manganese(III) centers.



M = $Mn^{III}Cl$, $Fe^{III}Cl$, $Co^{III}Cl$, Ni^{II}, Cu^{II}, $Ru^{II}(CO)$, $Rh^{III}I$.

Initial experiments were carried out in order to probe the efficiency of various transition metals. Ni^{II}, Cu^{II}, Co^{III} and Rh^{III} were found to be inefficient and Ru^{II} nearly so [Ru(CO)(TMCP) led to 4% yield, 20% ee]. As anticipated from earlier work,[7] Mn^{III} and Fe^{III} are potent catalysts,[8] although the aziridine yields are only moderate (Table 1).[9] Unexpectedly, the iron(III) catalyst favours the synthesis of (+)-*N*-tosyl-2-phenylaziridine whereas the manganese(III) complex of the same TMCP chiral ligand preferentially leads to the (−) enantiomer. This result is reminiscent of the well documented opposite enantioface selection exhibited by (*R*)-BINAP–Rh^{I} and (*R*)-BINAP–Ru^{II} complexes in the asymmetric hydrogenation of *N*-acylaminoacrylic acids,[10] but to our knowledge this is the first demonstrated case of antagonistic metal-directed asymmetric inductions in a catalytic group-transfer process.

Table 1 Catalytic asymmetric aziridination of styrene with (TMCP) complexes[a]



Entry	Substrate	M	R	Yield[b] (%)	% ee[c]
1	Styrene	Fe	Me	27	28 (+)
2	Styrene	Mn	Me	34	57 (−)
3	Styrene	Fe	OMe	27	n.d.[d]
4	Styrene	Mn	OMe	17	33 (−)
5	Dihydronaphthalene	Mn	Me	0	—
6	*cis*-Stilbene	Mn	Me	0	—

[a] *Reaction conditions*: (catalyst : $PhINSO_2Ar$: styrene = 1 : 50 : 500). [b] Isolated yields were based on the amount of $PhINSO_2Ar$ used. [c] Values of ee were determined by HPLC analysis (Whelk-O1 column), the sign corresponds to that of $[\alpha]_D$. [d] Not determined.

The X-ray structure of the MnCl(TMCP) catalyst was solved, and an ORTEP diagram is shown in Fig. 1. The complex exhibits a strong equatorial contraction, due to a highly ruffled macrocycle: the out of plane displacements of the C_{meso} atoms with respect to the 24-atom mean plane are *ca.* 0.73(1) Å. The average [Mn–Np] bond distance is short [1.974(2) Å] when compared to other manganese(III) porphyrins,[11] and especially to the very non-planar chloro[5,10,15,20-tetrakis(pentafluorophenyl)-2,3,7,8,12,13,17,18-octaphenylporphyrinato]manga-

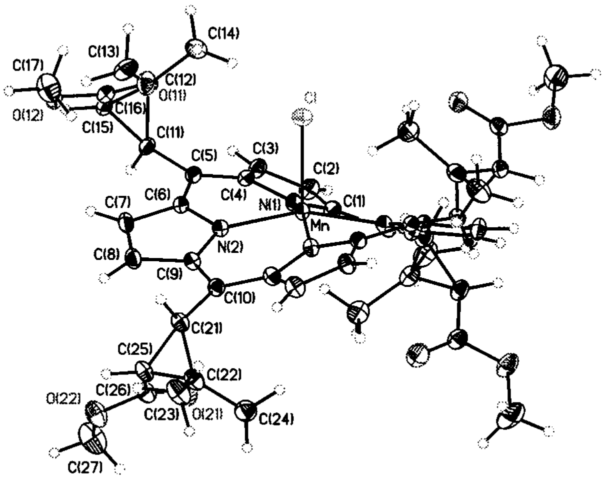
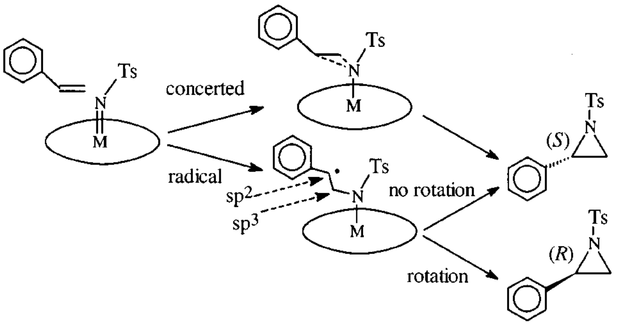


Fig. 1 ORTEP side view (30% probability) of **1** (M = MnCl). Selected bond lengths (Å): [Mn–Np] average 1.974(2), Mn–Cl 2.3475(9). Mn is displaced from the porphyrin mean plane towards Cl by 0.44(1) Å. The C_{meso} atoms are displaced alternatively up [+0.72(1) Å] and down [−0.74(1) Å] with respect to the 24-atom mean plane.



Scheme 1

nese(III) complex.[11d] The Mn–Cl bond distance [2.3475(9) Å] is similar to those observed for other chloromanganese(III) porphyrins.[11]

The MnCl(TMCP) complex is structurally very similar to FeCl(TMCP).[12] Hence, intermolecular steric interactions during the approach of the olefin towards the nitrenoid species are presumably similar for the two metal catalysts, implying that electronic effects are responsible for the observed opposite enantioselectivities. We speculate that each metal center favors one of two competing mechanisms (Scheme 1). The iron catalyst induces the preferential formation of the (+) enantiomer with the (*S*) absolute configuration[13] expected from steric exclusion during the side-on approach of the olefin in a concerted mechanism.[6b] In the case of the manganese catalyst, a radical intermediate which is sufficiently stable to allow an internal rearrangement can be invoked. Efforts towards a better understanding of these mechanisms and an extension of the scope of this catalytic system to other substrates are currently in progress.

Notes and references

† *Crystal data* for $C_{48}H_{52}N_4O_8MnCl\cdot CH_2Cl_2$: M = 988.25, tetragonal, a = b = 13.280(2), c = 26.529(5) Å, U = 4679.0(13) Å^3, T = 193(2) K, space group $P4_32_12$, Z = 4, μ(Mo-K) = 0.512 mm^{-1}, 22412 reflections measured, 4360 unique ($R_{\rm int}$ = 0.0494) which were used in all calculations. Final R indices [$I > 2\sigma(I)$], R = 0.0458, $R_{\rm w}$ = 0.1230, GOF = 1.034. CCDC 182/1224. See http://www.rsc.org/suppdata/cc/1999/989/ for crystallographic files in .cif format.

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2 M. P. Doyle, *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH, New York, 1993, p. 63.

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9 (*a*) We feel that formation of $TsNH_2$ is not entirely due to hydrolysis since experiments under highly anhydrous conditions did not lead to improved aziridine yields. We agree with P. Müller that the decomposition of the nitrene source must be competitive with the aziridination, and affords the sulfonamide after work-up;[4i] (*b*) In our case, addition of 4-phenylpyridine *N*-oxide resulted in lower yield and enantioselectivity with both catalysts.

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