DALTON COMMUNICATION

Activation of manganese nitrido complexes by Brønsted and Lewis acids. Crystal structure and asymmetric alkene aziridination of a chiral salen manganese nitrido complex

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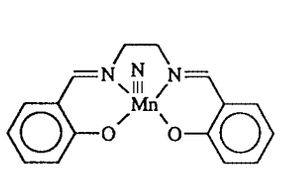
Styrene is readily converted to 2-phenylaziridine by salen manganese(V) nitrido complexes in the presence of Brønsted or Lewis acids such as F_3CCO_2H or BF_3, the crystal structure of a chiral manganese nitrido complex that can perform asymmetric alkene aziridination has been determined.

The conversion of alkenes to aziridines and amines by metal complexes has attracted much interest since Groves first reported that cyclooctene can be converted to a *N*-trifluoroacetylated aziridine product by a manganese(V) porphyrin nitrido complex in the presence of trifluoroacetic anhydride (TFAA).[1] Subsequently a number of metal catalysts, such as Fe and Mn porphyrin complexes,[2] and Cu(I,II) salts,[3] were found to effect the conversion of alkenes into *N*-tosylaziridines by PhI=NTs (Ts = tosyl). Recently Carreira and co-workers made use of $[Mn^V(N)(saltmen)]$[4] [saltmen = *N*,*N*′-1,1,2,2-tetramethylethylenebis(salicylideneaminato)] and $[Mn^V(N)(3\text{-R-sal-R}')_2]$[5] (H-3-R-sal-R′ = substituted salicylimine) to carry out the amination of silyl enol ethers and styrene, respectively. Very recently an asymmetric version of Carreira's methodology was reported by Komatsu and co-workers using a chiral manganese nitrido complex in the presence of *p*-toluenesulfonic anhydride, pyridine and pyridine *N*-oxide.[6] We previously reported that metal–oxo species can be activated toward the oxidation of hydrocarbons by Brønsted and Lewis acids such as trifluoroacetic acid (TFA), boron halides and simple metal salts.[7–9] We report here that this strategy also works for nitrido species; salen mangnese(V) nitrido species can be activated by acids such as TFA and BF_3 to convert alkenes into aziridines.

The manganese nitrido complexes shown below were investigated. Compounds **1**–**5** {[Mn(N)L]} were prepared using Carreira's method[4] by treatment of [Mn(L)Cl] with ammonia and bleach.† Initial experiments were carried out with compound **1**; upon adding 2 equivalents of TFA or BF_3 to a solution containing **1** and styrene, 2-phenylaziridine was produced (Table 1). This is the first report of direct generation of the parent aziridine from an alkene using metal complexes, all previous methods produced either the *N*-tosyl or *N*-trifluoroacetyl aziridine. Little (<2%) or no products arising from ring opening of the aziridine were detected. Lower yields of the aziridine were obtained when $Al(OTf)_3$ (40%) or $Fe(OTf)_3$ (35%) were employed, while weaker Lewis acids such as $ZnCl_2$ and $Cu(CF_3SO_3)_2$ were ineffective. For the more bulky complex **2**, similar yields were obtained with TFA (69%) or BF_3 (56%); however, $Al(OTf)_3$ and $Fe(OTf)_3$ were ineffective (yields <5%), suggesting that steric effects may play an important role in the aziridination reaction. Aziridination of other alkenes were also investigated using complex **1** and TFA or BF_3 (Table 1). Higher yields were obtained with α- and (*E*)-β-methylstyrene, however cyclooctene gave very low yields. For β-methylstyrene, 10–20% of the *E* isomer was produced in addition to the *Z* isomer of the phenylaziridine, while the *E*-substrate produced solely the *E* product.

Amination by manganese nitrido species in the presence of TFAA is believed to go through an acylimido intermediate.[1] In the present system we propose that active intermediates are Mn=NH for TFA and $Mn{=}NBF_3$ for BF_3. The imido group is transferred to the alkene to produce the parent aziridine (after hydrolysis in the case of BF_3).

Asymmetric aziridination was investigated using the chiral compounds **3**–**5**. In the presence of 3 equivalents of TFA, aziridination proceeded with high ee for compound **4** with the substrates styrene and (*E*)-β-methylstyrene, while a very low ee was observed for (*Z*)-β-methylstyrene. Compound **3** gave similar yields but lower ee (35%, 30% ee for styrene), while use of



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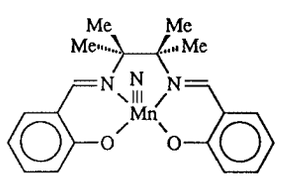

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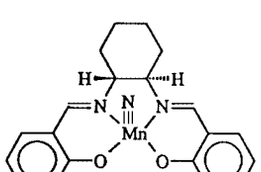

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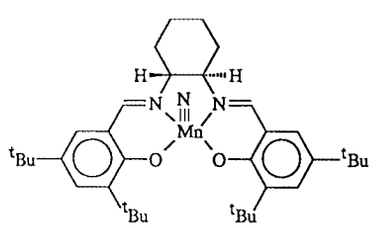

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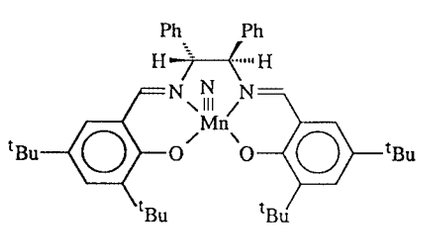

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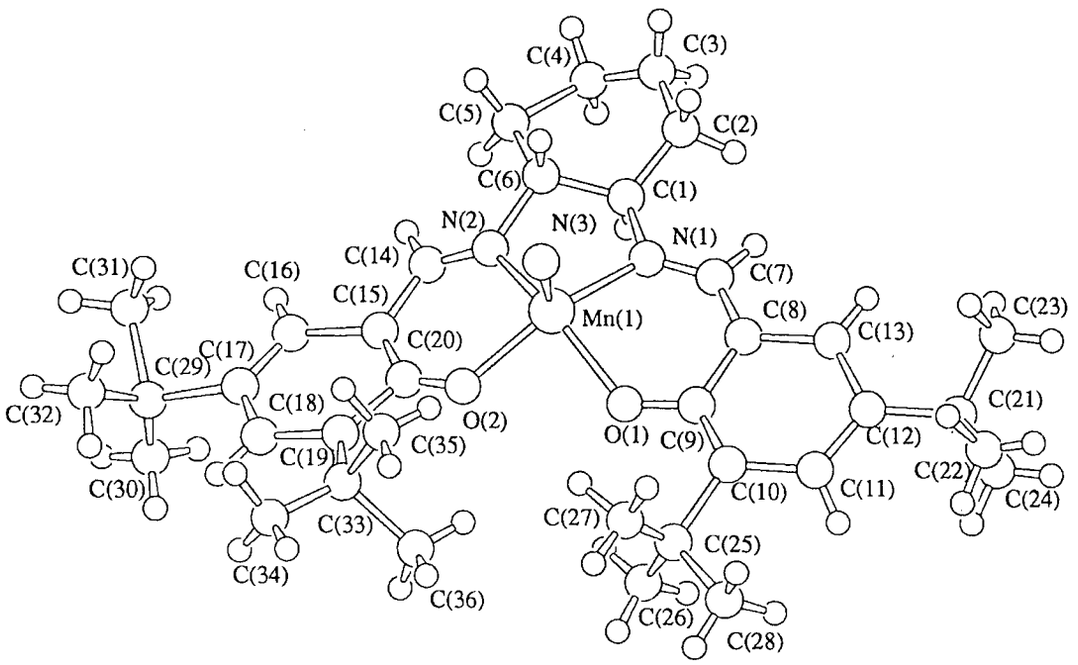
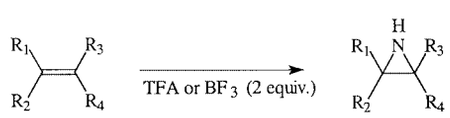


Fig. 1 Perspective view of **4(1)**. Selected bond lengths (Å) and angles (°) for both molecules: Mn(1)–O(1) 2.00(2), Mn(1)–O(2) 1.93(2), Mn(1)–N(1) 1.98(2), Mn(1)–N(2) 1.96(1), Mn(1)–N(3) 1.56(2), Mn(2)–N(6) 1.50(2), Mn(2)–O(3) 1.82(2), Mn(2)–O(4) 1.89(1), Mn(2)–N(4) 1.94(2), Mn(2)–N(5) 1.96(2); O(1)–Mn(1)–O(2) 87.0(7), O(1)–Mn(1)–N(1) 87.9(7), O(1)–Mn(1)–N(2) 150.2(6), O(1)–Mn(1)–N(3) 105.7(8), O(2)–Mn(1)–N(1) 153.9(6), O(2)–Mn(1)–N(2) 88.3(6), O(2)–Mn(1)–N(3) 103.3(9), N(1)–Mn(1)–N(2) 83.5(7), N(1)–Mn(1)–N(3) 102.7(9), N(2)–Mn(1)–N(3) 104.0(8), O(3)–Mn(2)–O(4) 80.3(6), O(3)–Mn(2)–N(4) 91.6(7), O(3)–Mn(2)–N(5) 138.9(6), O(3)–Mn(2)–N(6) 112.9(8), O(4)–Mn(2)–N(4) 155.0(6), O(4)–Mn(2)–N(5) 90.8(6), O(4)–Mn(2)–N(6) 105.0(8), N(4)–Mn(2)–N(5) 79.7(7), N(4)–Mn(2)–N(6) 99.9(8), N(5)–Mn(2)–N(6) 108.2(8).

Table 1 Aziridination of styrene derivatives with the nitrido complex **1**[a]



Substrate	2-Phenylaziridine (% yield)	
	$BF{\cdot}OEt_2$	TFA
Styrene	63	72
α-Methylstyrene	77	87
(*E*)-β-Methylstyrene	88 (*E*)	92 (*E*)
(*Z*)-β-Methylstyrene	51 (*Z*), 5 (*E*)	53 (*Z*), 12 (*E*)
Cyclooctene	8	8

[a] Conditions: complex **1**, 0.3 mmol; acid, 0.6 mmol; alkene, 4.0 mmol; temperature, −78 °C; solvent, MeCN (5 ml)–CH_2Cl_2 (10 ml).

compound **5** resulted in very low yields (*ca.* 7%). In Komatsu's method using Ts_2O and pyridine,[6] only compound **3** was found to be reactive; in the present system employing TFA to activate the nitrido complexes, however, the best result was obtained with compound **4**, which is more bulky than compound **3**. This finding is consistent with a Mn=N(Ts) intermediate in Komatsu's case, and a much less bulky M=NH intermediate in the present case.

The structure of **4**, a compound that can perform asymmetric aziridination of alkenes, has been determined by X-ray crystallography.‡ The asymmetric unit consists of two structurally similar molecules [**4(1)** and **4(2)**, both in *R*, *R* configuration] and the structure of **4(1)** is depicted in Fig. 1. Although the structure of another chiral salen manganese nitrido complex, [(*R*,*R*)-diphenyl-*tert*-butylmethylbis(salicylidene)ethane-1,2-diaminato]nitridomanganese, has recently been reported,[11] the ability of that complex to carry out asymmetric aziridination has yet to be demonstrated.

We are currently examining the effects of various other Lewis and Brønsted acids in order to improve the yields and ee. The mechanisms of aziridination in these systems are also under active investigation.

Table 2 Asymmetric aziridination of styrene derivatives with the nitrido complex **4**[a]

Substrate	Equiv. of TFA	*T*/°C	Yield (%)	ee (%)
Styrene	2	−40	29	55
Styrene	3	−40	36	81
(*E*)-β-Methylstyrene	2	−78	15	87
(*E*)-β-Methylstyrene	3	−78	20	91
(*Z*)-β-Methylstyrene	2	−78	7[b]	25

[a] See footnote to Table 1 for conditions. [b] A trace amount of the (*E*)-aziridine product was detected by ^1H NMR.

Acknowledgements

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Notes and references

† In a typical aziridination experiment, [Mn(N)L] (0.3 mmol) and alkene (4.0 mmol) in dry CH_2Cl_2 (10 ml) were cooled to −78 °C under argon. A solution of the acid (0.3–0.9 mmol) in MeCN (5 ml) was slowly added to the mixture over 15 min. The solution was allowed to warm to room temperature and then neutralised with saturated $NaHCO_3$ solution. The organic layer was analysed by GLC, GC-MS, and by NMR (after chromatography and isolation). The structure was confirmed by comparison with authentic samples prepared by a literature method.[10] In asymmetric reactions the aziridine product was first tosylated with TsCl and Et_3N, the ee was then determined by chiral HPLC analysis using a commercial Whelk-O column (Regis). Compound **3**: Found: C, 61.38; H, 5.27; N, 10.31. Calc. for $MnN_3C_{20}H_{20}O_2$: C, 61.70; H, 5.18; N, 10.79%. Compound **4**·$0.25C_6H_{14}$: Found: C, 71.59; H, 8.59; N, 6.47. Calc. for $MnN_3C_{37.5}H_{55.5}O_2$: C, 70.90; H, 8.81; N, 6.61%. Compound **5**: Found: C, 74.45; H, 8.01; N, 5.67. Calc. for $MnN_3C_{44}H_{54}O_2$: C, 74.24; H, 7.65; N, 5.90%.

‡ Crystal data: $MnC_{36}H_{52}N_3O_2{\cdot}0.25C_6H_{14}$ **4**, $M = 635.31$, triclinic, space group $P\bar{1}$ (no. 1), $a = 10.127(1)$, $b = 13.846(1)$, $c = 14.428(1)$ Å, $\alpha = 68.40(2)$, $\beta = 83.32(2)$, $\gamma = 87.45(2)°$, $U = 1868.2(4)$ Å^3, $Z = 2$, $\mu = 3.86$ cm^{-1}, $T = 298$ K. Of 8051 reflections, 4504 were unique with $R1 = 0.069$, $R = 0.086$, $R_w = 0.099$ with a goodness of fit of 2.19. Owing

to the poor quality of crystals (rapid solvent loss and weak diffraction nature), e.s.d.s on the bond lengths and angles are poor. Attempts to refine non-hydrogen atoms other than Mn were not successful. Refinement of partially occupied solvent molecules also led to an unreasonable model and hence a fixed contribution of the solvent was used instead. CCDC reference no. 186/1511. See http://www.rsc.org/suppdata/dt/1999/2411/ for crystallographic files in .cif format.

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