

Development of Mn(III)(Schiff Base) Complexes for the Catalyst of Olefin Oxygenation to Alcohols in the Presence of NaBH₄

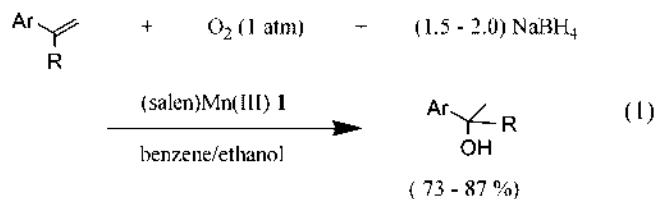
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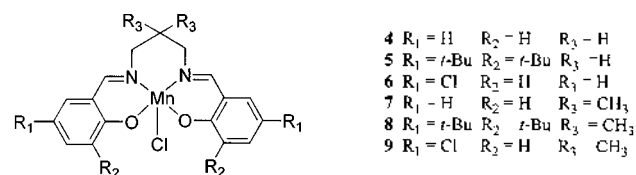
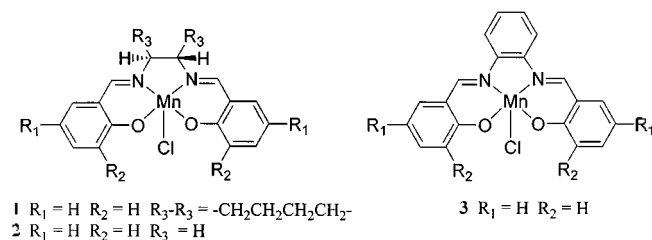
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Molecular oxygen would be the most desirable oxidant in organic synthesis in terms of costs and environmental considerations. Efforts have long been focused on the development of O₂-mediated oxidation methods.¹ We have reported previously the oxidative conversion of olefins to the alcohols, where molecular oxygen was used as the oxidant. In this process, we used a (salen)Mn(III)Cl complex **1** as the catalyst and sodium borohydride as the one-oxygen reducing agent.² Even though this process was performed under mild conditions, only conjugated vinyl arene substrates were oxidized with high efficiency (Eq. 1). Other olefin substrates, for example non-conjugated or non-vinyl olefins, showed very low reactivity. Therefore, we decided to develop better oxidation catalysts, which could be applicable to the variety of simple olefins.



For the screening of the catalytic activity, we have synthesized several Mn(III)-Schiff base ligand complexes. Tetradentate bis-salicylaldehyde type ligands were prepared by the coupling of salicylaldehydes and corresponding diamine compounds. The prepared Schiff base ligands were treated with manganese(II) acetate followed by air oxidation to provide Mn(III)(Schiff base) complexes.³ Eventually, three



types of manganese(III) complexes were prepared, *i.e.*, diaminoethane-derived Mn complexes (**1**, **2**), diaminobenzene-derived Mn complex (**3**), and diaminopropane-derived Mn complexes (**4-9**).

The catalytic activity of the complexes was examined using *trans*- β -methylstyrene (**10**) and allyl benzene (**11**) as the model substrate (Table 1). The reaction was carried out using 5 mol% Mn complexes and 1.5 equiv. of NaBH₄ under balloon pressure of O₂ at room temperature. Previously, employing the (salen)Mn(III) complex **1** as the catalyst, the compounds **10** and **11** were oxidized in only 39% and 10% conversion yield, respectively. When the Mn-salen complex **2** was tried as the catalyst, rather lower substrate conversion was observed (entry 2). Mn(III)(salen)phenyl type complex **3** also gave lower reactivity (entry 3). However, diamino-propane-derived Mn(III) complex **4** showed big improvement in the conversion yield. For example, using complex **4**, we converted olefins **10** and **11** in 86% and 38% yield, respectively (entry 4). Different types of related complexes were examined (entries 5-9), taking the complex **4** as the leading compound. From this screening, it was concluded that dimethyl-substituted complex analogue **7** has the best catalytic activity among the complexes in Table 1. We observed, interestingly, that introduction of the bulky and electron-rich *tert*-butyl group, as shown in **5** and **8**, resulted in activity decrease. Another interesting observation was that electron poor Cl-substituted complexes, such as **6** and **9**, showed comparable but no better catalytic activity over the simple complex **7**. From the results in Table 1, we concluded that complex **7** is the best choice for a catalyst for this oxidation system.⁴ The origin of the reactivity differences for these Mn(III)(Schiff Base) complexes is not clear at this point. It might be ascribed to their differences in electronic/steric properties around the Mn metal or in their physical properties, such as solubility in the reaction system.



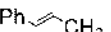

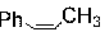

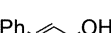
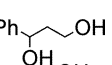












With the result in Table 1 at hand, we performed the oxidation with various type of olefin substrates.⁵ The results are summarized in Table 2. Non-conjugated vinyl compound, allyl benzene, gave the corresponding alcohol in 61% isolated yield (entry 1). This reaction was very regioselective, giving only Markovnikov type hydration product. Conjugated internal olefin, *trans*- β -methylstyrene was also well oxidized in 72% yield (entry 2). This conversion was also regioselective; only the compound oxidized at the benzylic position was observed. *Cis*- β -methylstyrene was also oxidized

Table 1. Screening of the Mn(III)(salen) type complexes for the oxidation catalyst using the substrates **10** and **11**

Entry	Mn(III) Complex	Conversion (%)	
		Ph-CH=CH ₂ 10	Ph-CH=CH-CH ₃ 11
1	1	39	10
2	2	5	1
3	3	18	0
4	4	86	38
5	5	30	21
6	6	95	58
7	7	96	70
8	8	13	12
9	9	85	66

^aReaction conditions: the substrate was treated with 1.5 equiv. NaBH₄ and 5 mol% Mn(III) complexes in the presence of O₂ (1 atm) at rt for 4 hrs. ^bConversion was obtained by GC analysis.

Table 2. Examples of olefin oxygenation reactions using the Mn(III) complex **7** as the catalyst

Entry	Olefins	+ O ₂ (1 atm) + 1.5 NaBH ₄		Alcohols	Isolated yield (%)
		5 mol% Mn(III) Complex 7 benzene/ethanol rt, 4 hrs			
1					61
2					72
3					71
4					65
5					82
6					65
7					81
8					70
9					38
10					20

in about the same yield as *trans* substrate (entry 3). Cinnamyl alcohol was converted to the corresponding alcohol in 65% yield, which shows that alcohol functionality rarely affects the reactivity (entry 4). Conjugated cyclic olefins, such as 1,2-dihydronaphthalene, indene, and dimethylchromene, were also good substrates for this oxidation procedure, providing the corresponding alcohols in 82%, 81% and 65% yield, respectively (entries 5-7). Tertiary alcohol was also obtained from the *tri*-substituted olefins. For example, phenyl dihydronaphthalene gave the alcohol in 70% yield (entry 8). But, 1-phenylcyclohexene showed poor conversion, leading to only 38% isolated yield. In this case, some starting material was left intact. Limonene was also subjected to the reaction condition (entry 10). The major compound, isolated in 20% yield, was identified to be tertiary alcohol resulting from the oxygenation on vinylic olefin over the electron-rich *tri*-substituted one.

By screening Mn(III)(Schiff Base) complexes, we have shown that one of the complexes, **7** is a very good catalyst for the olefin oxygenation process. Complex **7** was found to be easy to handle due to its stability in moisture and air. This process takes place under mild reaction conditions, *i.e.* balloon pressure of oxygen and room temperature. Further studies to expand the scope of this oxygenation process are in progress.

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References

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- Spectral data of the complex **7**: Elemental Analysis. Calcd for C₁₆H₂₀N₂O₂MnCl: C, 57.23; H, 5.06; N, 7.03. Found: C, 57.20; H, 4.78; N, 7.09. IR (KBr, cm⁻¹): 2959 (m), 2901 (m), 1628 (s), 1606 (s), 1544 (s), 1469 (s), 1444 (s), 1303 (s), 1277 (s); UV (MeOH): 374 nm.
- Typical reaction condition is as follows: In a 50 mL two-neck round bottomed flask were placed *trans*-β-methylstyrene (1.0 mmol, 118 mg), Mn(III) complex **7** (0.05 mmol, 118mg), and benzene as a solvent. After oxygen balloon was adapted to the reaction flask, flushing the vessel with O₂ was undertaken by evacuation/charging procedure three times. To this was added *via* syringe NaBH₄ (1.5 mmol, 54 mg) dissolved in 4 mL ethanol over 20 min with stirring. After the reaction mixture was stirred for 4 h at rt, it was poured into sat. NH₄Cl solution and extracted with diethyl ether. The organic layer was dried, concentrated and flash chromatographed to give 1-phenyl-1-propanol (99 mg, 72% yield) as the product.