

CITY UNIVERSITY OF HONG KONG

香港城市大學

Stoichiometric and Catalytic Oxidation of  
Organic Substrates by Manganese(V) and  
Osmium(VI) Nitrido Complexes

錳和鐵含氮配合物化學計量及催化氧化  
有機化合物之研究

Submitted to  
Department of Biology and Chemistry  
生物及化學系  
in Partial Fulfillment of the Requirements  
for the Degree of Doctor of Philosophy  
哲學博士學位

by

Kwong Hoi Ki  
鄺凱琦

December 2011  
二零一一年十二月

## **Abstract**

---

This thesis is divided into three parts. Part I reports the catalytic oxidation of alkenes and alcohols by a manganese nitrido complex  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$ . Part II describes the Lewis-acid activated catalytic oxidation of alkanes and aromatic hydrocarbons by an osmium nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$  ( $\text{Hquin}$  = quinaldic acid). Part III is concerned with C-H bond activation by some manganese(V) imido species, which are generated by reacting a (salen)manganese(V) nitrido complex  $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$  ( $\text{salen}$  =  $N,N'$ -ethylenebis(salicylideneaminato) dianion) with various Lewis acids.

In part I, it was found that the oxidation of alkenes and alcohols can be catalyzed by  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  effectively at room temperature using  $\text{H}_2\text{O}_2$  as the terminal oxidant. The reaction rate can be greatly increased by the presence of one equivalent of acetic acid. The nature of the active intermediate has been investigated using various mechanistic probes. When MPPH was used as a terminal oxidant in the oxidation of cyclooctene and cyclohexanol, high yields of MPPOH (>90%), cyclooctene oxide (90%) and cyclohexanol (75%) could be detected. In the oxidation of *cis*-stilbene using  $\text{H}_2\text{O}_2$ , high yield of *cis*-stilbene oxide (95%) could be obtained and only a small amount of *trans*-stilbene oxide (3%) could be detected. In the oxidation of cyclobutanol, 100% yield of cyclobutanone was generated while no ring-opening product was produced. These results indicate that ROOH undergoes heterolytic cleavage when it interacts with the manganese center. It is proposed that the manganese catalyst acts as a Lewis acid to facilitate the heterolytic O-O bond cleavage of ROOH. According to the results of computational study by using the DFT method, the accelerating effect of acetic acid is due to the stabilization of the Mn-(HOOH)

intermediate by hydrogen bonding.

In Part II, it was found that the oxidation of various alkanes and aromatic hydrocarbons with  $\text{H}_2\text{O}_2$  can be catalyzed by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$  effectively at room temperature in the presence of a Lewis acid. The KIE value for the competitive oxidation of cyclohexane and  $d_{12}$ -cyclohexane by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$  is 3.1. For the oxidation of aromatic hydrocarbons, the oxidation of aromatic ring occurs preferentially than the oxidation of side-chain. The major products are the corresponding phenols and benzoquinones. Products arising from the NIH shift of the aromatic ring substituents could also be detected. For  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$ , the KIE value for the competitive oxidation of benzene and  $d_6$ -benzene is 0.94. The use of MPPH as the terminal oxidant for the oxidation of *p*-xylene results in the formation of high yields of MPPOH and ring oxidized products. This result suggests that ROOH undergoes a heterolytic O-O bond cleavage when it interacts with the osmium center.

In Part III, it was found that some (salen)manganese(V) imido species generated from the reaction of the corresponding manganese(V) nitrido species with various Lewis acids are able to abstract H-atoms from hydrocarbons with weak C-H bonds. The products resulting from the C-H bond activation of various hydrocarbons have been analyzed, and mechanistic studies have been carried out.

## ***Table of Contents***

---

	<b>Page</b>
<b>Abstract</b>	<b>i</b>
<b>Acknowledgments</b>	<b>iii</b>
<b>Table of Contents</b>	<b>v</b>
<b>List of Schemes</b>	<b>xi</b>
<b>List of Tables</b>	<b>xvii</b>
<b>List of Figures</b>	<b>xix</b>
<b>Objectives</b>	<b>xxi</b>
<b>Chapter 1 Catalytic Oxidation of Alkenes and Alcohols by a Manganese(V) Nitrido Complex</b>	<b>1</b>
<b>1.1 Introduction</b>	<b>1</b>
1.1.1 Green Chemistry	1
1.1.1.1 Twelve Principles of Green Chemistry	2
1.1.1.2 Green metrics for chemical processes	3
1.1.2 Catalytic oxidation processes	5
1.1.2.1 Green solvents	7
1.1.2.2 Green oxidants	10
1.1.2.3 Renewable raw materials	13
1.1.2.4 Biomimetic oxidation catalysis	15
1.1.2.5 Biocatalysis	17
1.1.3 Manganese complexes as catalysts for epoxidation of alkenes	18
1.1.3.1 Manganese porphyrin complexes	19
1.1.3.2 Manganese salen complexes	23

## ***Table of Contents***

---

	<b>Page</b>
1.1.3.3 Manganese tacn complexes	<b>29</b>
1.1.3.4 Manganese complexes with aminopyridine ligand	<b>33</b>
1.1.3.5 Miscellaneous manganese catalysts	<b>36</b>
1.1.4 Catalytic oxidation of alcohols by manganese complexes	<b>40</b>
1.1.5 Catalytic oxidation of alkenes and alcohols by a manganese(V) nitrido complex	<b>46</b>
<b>1.2 Experimental</b>	<b>47</b>
1.2.1 Materials	<b>47</b>
1.2.2 Instrumentation	<b>47</b>
1.2.3 Catalytic oxidation	<b>48</b>
1.2.4 Computational study	<b>49</b>
<b>1.3 Results &amp; Discussion</b>	<b>50</b>
1.3.1 Catalytic epoxidation of alkenes by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>50</b>
1.3.1.1 Catalytic epoxidation of 2-methyl-2-pentene by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>50</b>
1.3.1.2 Stability of $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$ toward the catalytic epoxidation of 2-methyl-2-pentene by $\text{H}_2\text{O}_2$	<b>52</b>
1.3.1.3 Catalytic epoxidation of various alkenes by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>54</b>
1.3.2 Catalytic oxidation of alcohols by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$	<b>57</b>
1.3.3 Mechanistic studies	<b>60</b>
1.3.3.1 MPPH as a mechanistic probe	<b>60</b>
1.3.3.2 <i>cis</i> -stilbene as a mechanistic probe	<b>61</b>
1.3.3.3 Cyclobutanol as a mechanistic probe	<b>62</b>

## ***Table of Contents***

---

	<b>Page</b>
1.3.3.4 Kinetic isotope effects (KIE) of catalytic oxidation of benzyl alcohol by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>63</b>
1.3.4 Computational study	<b>63</b>
<b>1.4 Concluding remarks</b>	<b>67</b>
<b>Chapter 2 Lewis Acid Activated Catalytic Oxidation of Alkanes and Arenes by an Osmium(VI) Nitrido Complex</b>	<b>68</b>
<b>2.1 Introduction</b>	<b>68</b>
2.1.1 Osmium terminal nitrido complexes	68
2.1.2 Catalytic oxidation of alkanes and arenes by osmium complexes	83
2.1.3 Activation of transition metal complexes by Lewis acids	88
2.1.3.1 Lewis acids	88
2.1.3.2 Activation of metal oxo complexes by Lewis acids	89
2.1.3.3 Activation of metal nitrido complexes by Lewis acids	93
2.1.3.4 Lewis acid-activated catalytic oxidation of hydrocarbons by an osmium(VI) nitrido complex	95
<b>2.2 Experimental</b>	<b>96</b>
2.2.1 Materials	96
2.2.2 Instrumentation	97
2.2.3 Catalytic oxidation	97
<b>2.3 Results and Discussion</b>	<b>99</b>
2.3.1 Lewis acid activated catalytic oxidation of alkanes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$	99

## **Table of Contents**

---

	<b>Page</b>
2.3.1.1 Catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>99</b>
2.3.1.2 Effects of various Lewis acids on the catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{H}_2\text{O}_2$	<b>101</b>
2.3.1.3 Effects of various terminal oxidants on the catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3$	<b>101</b>
2.3.1.4 Stability of $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ toward the $\text{FeCl}_3$ -activated oxidation of cyclohexane by $\text{H}_2\text{O}_2$	<b>104</b>
2.3.1.5 Catalytic oxidation of various alkanes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>105</b>
2.3.2 Lewis acid activated catalytic oxidation of arenes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$	<b>110</b>
2.3.2.1 Catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>110</b>
2.3.2.2 Effects of various Lewis acids on the catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{H}_2\text{O}_2$	<b>113</b>
2.3.2.3 Effects of various terminal oxidants on the catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3$	<b>113</b>
2.3.2.4 Stability of $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ toward the $\text{FeCl}_3$ -activated oxidation of <i>p</i> -xylene by $\text{H}_2\text{O}_2$	<b>116</b>
2.3.2.5 Catalytic oxidation of various arenes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>117</b>
2.3.3 Mechanistic studies	<b>123</b>
2.3.3.1 Kinetic isotope effects	<b>123</b>

## ***Table of Contents***

---

	<b>Page</b>
2.3.3.2 MPPH as a mechanistic probe	<b>123</b>
2.3.3.3 Involvement of radicals	<b>124</b>
2.3.3.4 Proposed mechanism	<b>125</b>
<b>2.4 Concluding remarks</b>	<b>126</b>
<b>Chapter 3 Lewis-Acid Assisted C-H Bond Activation of Hydrocarbons</b>	<b>127</b>
<b>by a Manganese Nitrido Complex</b>	
<b>3.1 Introduction</b>	<b>127</b>
3.1.1 Manganese nitrido complexes	<b>127</b>
3.1.2 Manganese imido complexes	<b>132</b>
3.1.3 C-H bond activation by transition metal complexes	<b>135</b>
3.1.3.1 C-H bond activation by transition metal nitrido complexes	<b>135</b>
3.1.3.2 C-H bond activation by transition metal imido complexes	<b>140</b>
3.1.3.3 C-H bond activation by transition metal amido complexes	<b>142</b>
3.1.4 C-H bond activation by manganese complexes	<b>145</b>
3.1.4.1 C-H bond activation by manganese imido complexes	<b>145</b>
3.1.4.2 C-H bond activation by manganese oxo and hydroxo complexes	<b>146</b>
3.1.5 Lewis acid assisted C-H bond activation by a (salen)manganese(V) nitrido complex	<b>149</b>
<b>3.2 Experimental</b>	<b>150</b>
3.2.1 Materials	<b>150</b>
3.2.2 Instrumentation	<b>150</b>
3.2.3 Analysis of Organic Products	<b>150</b>

## ***Table of Contents***

---

	<b>Page</b>
<b>3.3 Results &amp; Discussion</b>	<b>152</b>
3.3.1 Formation of (salen)manganese(V) imido species	152
3.3.2 C-H bond activation of hydrocarbons by (salen)manganese(V) imido species	158
3.3.2.1 Reaction of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ with $\text{BF}_3$ in the presence of CHD	158
3.3.2.2 Reaction of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ with $\text{BF}_3$ in the presence of xanthene	160
3.3.2.3 Reaction of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ with $\text{BF}_3$ in the presence of DHA	163
3.3.2.4 Reaction of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ with $\text{BF}_3$ in the presence of various organic substrates	166
3.3.2.5 Reaction of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ with various Lewis acids in the presence of various organic substrates	167
3.3.3 Proposed mechanism for Lewis acid-assisted C-H bond activation of hydrocarbons by a (salen)manganese(V) nitrido complex	168
<b>3.4 Concluding Remarks</b>	<b>169</b>
<b>References</b>	<b>170</b>
<b>Appendix: List of Publications</b>	<b>201</b>

## List of Schemes

---

	Page
<b>Scheme 1.1</b> BHC synthesis of ibuprofen	7
<b>Scheme 1.2</b> Aerobic oxidation of alcohol catalyzed by PhenS*Ph(OAc) <sub>2</sub>	12
<b>Scheme 1.3</b> Direct oxidation of cyclohexene to adipic acid	13
<b>Scheme 1.4</b> Ring-opening of styrene oxide by <i>p</i> -anisidine	14
<b>Scheme 1.5</b> Chlorohydrin process	19
<b>Scheme 1.6</b> Manganese(III) porphyrin catalyzed epoxidation of styrene by NaOCl in the presence of pyridine as a co-catalyst	20
<b>Scheme 1.7</b> Asymmetric epoxidation of indene by NaOCl using Jacobsen's catalyst in the presence of P <sub>3</sub> NO	25
<b>Scheme 1.8</b> Epoxidation of 2,2-dimethylchromene by H <sub>2</sub> O <sub>2</sub> catalyzed by a manganese complex containing a pentadentate chiral salen ligand	26
<b>Scheme 1.9</b> Epoxidation of 6-nitro-2,2-dimethylchromene by PhIO using a manganese salen-based ion-pair catalyst	27
<b>Scheme 1.10</b> Epoxidation of 6-nitro-2,2-dimethylchromene by urea-H <sub>2</sub> O <sub>2</sub> using a dimeric homochiral manganese(III) salen catalyst	28
<b>Scheme 1.11</b> Chemoselective oxidation of cyclooctene by H <sub>2</sub> O <sub>2</sub> catalyzed by [Mn(tmtacn)] <sup>2+</sup> using various carboxylic acids as co-catalyst	32
<b>Scheme 1.12</b> Epoxidation of alkenes with CH <sub>3</sub> CO <sub>3</sub> H catalyzed by a manganese complex with a tetradentate tacn-derived ligand	33
<b>Scheme 1.13</b> Oxidation of benzyl alcohol with NaIO <sub>4</sub> catalyzed by Mn(TEPyP)	43
<b>Scheme 1.14</b> MPPH as a mechanistic probe	60

## List of Schemes

---

	Page
<b>Scheme 1.15</b> <i>cis</i> -stilbene as a mechanistic probe	<b>61</b>
<b>Scheme 1.16</b> Cyclobutanol as a mechanistic probe	<b>62</b>
<b>Scheme 1.17</b> Potential energy surface for the $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ catalyzed epoxidation of ethene with $\text{H}_2\text{O}_2$ in the presence of $\text{CH}_3\text{COOH}$ at B3LYP level using LanL2DZ basis set for Mn and 6-311+G(d,p) basis set for nonmetal atoms.	<b>65</b>
<b>Scheme 2.1</b> Substitution of chloride ligands of $[\text{Os}^{\text{VI}}(\text{N})(\text{Tp})\text{Cl}_2]$ with various anions	<b>69</b>
<b>Scheme 2.2</b> Oxidation of <i>trans</i> -stilbene with <i>m</i> -CPBA catalyzed by $[\text{Os}^{\text{VI}}(\text{N})(\text{Tp})(\text{OH})_2]$	<b>69</b>
<b>Scheme 2.3</b> Synthesis of osmium(VI) nitrido complexes containing arsine and stibine ligands	<b>70</b>
<b>Scheme 2.4</b> Synthesis of osmium(VI) nitrido complexes containing neutral N-donor ligands	<b>71</b>
<b>Scheme 2.5</b> Synthesis of dinuclear osmium nitrido complexes with neutral bridging ligands	<b>71</b>
<b>Scheme 2.6</b> Synthesis of osmium(VI) nitrido complexes containing a terpyridine ligand	<b>71</b>
<b>Scheme 2.7</b> Synthesis of $["\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{OSiMe}_3)_4]$ and its reaction with $\text{AlMe}_3$ and 3-mercaptopropionamide	<b>72</b>
<b>Scheme 2.8</b> Synthesis of osmium(VI) nitrido complexes containing thiolate and alkoxide ligands	<b>72</b>
<b>Scheme 2.9</b> Synthesis of osmium(VI) nitrido complexes containing thiophenoxy and phenoxide ligands	<b>73</b>

## List of Schemes

---

	Page
<b>Scheme 2.10</b> Synthesis of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_4]$ and its reaction with $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ , $(\text{HPy})(\text{BF}_4)$ and $\text{NaOH}$	<b>73</b>
<b>Scheme 2.11</b> Synthesis of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ and its reaction with various sulfur-containing ligands	<b>74</b>
<b>Scheme 2.12</b> Reaction of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ with cyclopentadienyl ligands	<b>74</b>
<b>Scheme 2.13</b> Reaction of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ with phosphines	<b>75</b>
<b>Scheme 2.14</b> Alkylation of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ with $\text{MgPhBr}$	<b>75</b>
<b>Scheme 2.15</b> Synthesis of $[^n\text{Bu}_4\text{N}][\text{trans-}\{\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{OH})_2\}]$ and its reaction with <i>p</i> -toluenesulfonic acid	<b>75</b>
<b>Scheme 2.16</b> Synthesis of $[\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ and its reactions with phosphines	<b>76</b>
<b>Scheme 2.17</b> Reaction of $[\text{Os}^{\text{VI}}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}]_2$ with various thiolate ligands	<b>76</b>
<b>Scheme 2.18</b> Synthesis of $[\text{Os}^{\text{VI}}(\text{N})(\text{Me})_3(\text{THF})_2]$ and its reaction with TMEDA	<b>76</b>
<b>Scheme 2.19</b> Synthesis of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{Ph})_4]$ and its reaction with $\text{KTp}$	<b>77</b>
<b>Scheme 2.20</b> Synthesis of $[^n\text{Bu}_4\text{N}][\text{Os}^{\text{VI}}(\text{N})(\text{Ph})_2\text{Cl}_2]$ and substitution of its chloride ligands with various ligands	<b>77</b>
<b>Scheme 2.21</b> Synthesis of nitridoosmium(VI) acetylide complexes	<b>78</b>
<b>Scheme 2.22</b> Synthesis of osmium(VI) nitrido complexes containing various anionic bidentate ligands	<b>79</b>
<b>Scheme 2.23</b> Synthesis of $[\text{Os}^{\text{VI}}(\text{N})(\text{tpm})\text{Cl}_2](\text{PF}_6)$	<b>80</b>

## List of Schemes

---

	Page
<b>Scheme 2.24</b> Synthesis of an osmium(VI) nitrido complex containing an oxygen tripodal ligand	<b>80</b>
<b>Scheme 2.25</b> Synthesis of osmium(VI) nitrido complexes containing di-, tri- and tetra-anionic tetradentate ligands	<b>81</b>
<b>Scheme 2.26</b> Reaction of $[\text{Os}^{\text{VI}}(\text{N})(\text{salophen})\text{Cl}]$ with $\text{CN}^-$ and $(\text{CF}_3\text{CO})_2\text{CH}^-$	<b>82</b>
<b>Scheme 2.27</b> Competitive reactions during oxidation of aromatic hydrocarbons	<b>84</b>
<b>Scheme 2.28</b> Friedel-Crafts alkylation and acylation	<b>88</b>
<b>Scheme 2.29</b> Mukaiyama aldol condensation	<b>89</b>
<b>Scheme 2.30</b> Hetero-Diels-Alder cycloaddition	<b>89</b>
<b>Scheme 2.31</b> Alkene alkylation	<b>89</b>
<b>Scheme 2.32</b> Proposed mechanism for alkane oxidation by barium ruthenate	<b>92</b>
<b>Scheme 2.33</b> Proposed mechanism for alkane oxidation by $\text{LiCl}$ -ferrate	<b>93</b>
<b>Scheme 2.34</b> Proposed mechanism for catalytic and stoichiometric oxidation of alkane by $[\text{Os}^{\text{VIII}}(\text{N})(\text{O})_3]^-/\text{FeCl}_3$	<b>94</b>
<b>Scheme 2.35</b> Proposed mechanism for catalytic oxidation of hydrocarbons by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$	<b>125</b>
<b>Scheme 3.1</b> Synthesis of $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$ and $[\text{Mn}^{\text{V}}(\text{N})(\text{saltmen})]$	<b>129</b>
<b>Scheme 3.2</b> Synthesis of Mn(V) nitridocyanometalates	<b>130</b>
<b>Scheme 3.3</b> Synthesis of manganese(V) nitrido complexes containing pyrazolone ligands	<b>131</b>
<b>Scheme 3.4</b> Principle reactions of $[\text{Mn}(\text{NBu}^t)_3\text{Cl}]$	<b>133</b>
<b>Scheme 3.5</b> Synthesis of various dimeric alkyl compounds from $[\text{Mn}(\text{NBu}^t)_3\text{Cl}]$	<b>133</b>

## List of Schemes

---

	Page	
<b>Scheme 3.6</b>	Synthesis of manganese(V) imido complexes containing a corrole ligand	<b>134</b>
<b>Scheme 3.7</b>	Synthesis of a manganese(V) imido complex containing a corrolazine ligand	<b>134</b>
<b>Scheme 3.8</b>	Photolysis of diazido(phosphane)nickel(II) complexes in the presence of cyclohexane and cyclohexene	<b>136</b>
<b>Scheme 3.9</b>	Fragmentation of $[(\text{NN}_4)\text{FeN}]^{2+}$ through C-C bond insertion of the nitrido-nitrogen atom in this complex	<b>137</b>
<b>Scheme 3.10</b>	Proposed mechanism for the photolysis of $(\text{C}_5\text{Me}_5)_2\text{U}[\text{N}(\text{SiMe}_3)_2](\text{N}_3)$	<b>137</b>
<b>Scheme 3.11</b>	Proposed mechanism for the solid-state thermolysis of $(^{\text{Mes}}\text{BPDI})\text{CoN}_3$	<b>139</b>
<b>Scheme 3.12</b>	Proposed mechanism for the formation of the double tuck-in rhodium compound	<b>140</b>
<b>Scheme 3.13</b>	Proposed mechanism for amidation of saturated C-H bond by $[\text{Ru}^{\text{VI}}(\text{Por})(\text{NTs})_2]$	<b>141</b>
<b>Scheme 3.14</b>	Proposed mechanism for activation of saturated C-H bond by $[\text{Zr}(\text{NHCMe}_3)(\text{CH}_3)(\text{ebthi})]$	<b>142</b>
<b>Scheme 3.15</b>	C-H bond activation by <i>trans</i> -(DMPE) <sub>2</sub> Ru(H)(NH <sub>2</sub> )	<b>143</b>
<b>Scheme 3.16</b>	Activation of C-H bond of cyclobutanone by <i>trans</i> -(DMPE) <sub>2</sub> Ru(H)(NH <sub>2</sub> )	<b>143</b>
<b>Scheme 3.17</b>	Proposed mechanism for C-H bond activation by $[\text{Mn}^{\text{V}}(\text{NTs})(\text{tpfc})]$	<b>145</b>

## *List of Schemes*

---

	Page
<b>Scheme 3.18</b> Proposed mechanism for the formation of the dimeric Mn(II) amido/aryl compound	<b>146</b>
<b>Scheme 3.19</b> C-H bond activation by $[\text{Mn}^{\text{III}}\text{H}_3\text{buea(O)}]^{2-}$	<b>147</b>
<b>Scheme 3.20</b> Proposed mechanism for the reaction of $[\text{Mn}^{\text{III}}\text{H}_3\text{buea(O)}]^{2-}$ with DHA	<b>147</b>
<b>Scheme 3.21</b> Proposed mechanism for the reaction of $[\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})]$ with DHA	<b>148</b>
<b>Scheme 3.22</b> C-H bond activation by $[\text{Mn}^{\text{III}}(\text{PY5})(\text{OH})](\text{CF}_3\text{SO}_3)_2$	<b>148</b>
<b>Scheme 3.23</b> Proposed mechanism for $\text{BF}_3$ assisted C-H bond activation of 1,4-cyclohexadiene by $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$	<b>168</b>

## List of Tables

---

	Page	
<b>Table 1.1</b>	E-factors of various segments of chemical industry	<b>4</b>
<b>Table 1.2</b>	Oxygen availability in various oxidants	<b>10</b>
<b>Table 1.3</b>	Selected examples of enzymes involved in oxidation reactions	<b>17</b>
<b>Table 1.4</b>	Mononuclear manganese epoxidation catalysts	<b>38</b>
<b>Table 1.5</b>	Dinuclear and trinuclear manganese epoxidation catalysts	<b>39</b>
<b>Table 1.6</b>	Catalytic epoxidation of 2-methyl-2-pentene by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>51</b>
<b>Table 1.7</b>	Successive runs of catalytic epoxidation of 2-methyl-2-pentene by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$	<b>53</b>
<b>Table 1.8</b>	Catalytic epoxidation of various alkenes by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>55</b>
<b>Table 1.9</b>	Catalytic oxidation of various alcohols by $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]/\text{H}_2\text{O}_2$	<b>58</b>
<b>Table 1.10</b>	Relative energetic (in kcal/mol) of epoxidation of ethene by $[\text{Mn}(\text{N})(\text{CN})_4]^{2-}$ with $\text{H}_2\text{O}_2$ and $\text{CH}_3\text{COOH}$ at gas phase and in acetonitrile	<b>66</b>
<b>Table 2.1</b>	Effects of $\text{FeCl}_3$ on the catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>100</b>
<b>Table 2.2</b>	Effects of various Lewis acids on the catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>102</b>
<b>Table 2.3</b>	Effects of various terminal oxidants on the catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3$	<b>103</b>
<b>Table 2.4</b>	Successive runs of catalytic oxidation of cyclohexane by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]/\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>104</b>

## List of Tables

---

	Page
<b>Table 2.5</b> Catalytic oxidation of various alkanes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>106</b>
<b>Table 2.6</b> Effects of $\text{FeCl}_3$ on the catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>112</b>
<b>Table 2.7</b> Effects of various Lewis acids on the catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>114</b>
<b>Table 2.8</b> Effects of various terminal oxidants on the catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3$	<b>115</b>
<b>Table 2.9</b> Successive runs of catalytic oxidation of <i>p</i> -xylene by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>116</b>
<b>Table 2.10</b> Catalytic oxidation of various monosubstituted arenes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>118</b>
<b>Table 2.11</b> Catalytic oxidation of various methyl-substituted arenes by $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ / $\text{FeCl}_3/\text{H}_2\text{O}_2$	<b>120</b>
<b>Table 3.1</b> Effects of the amount of $\text{BF}_3$ on the oxidation of CHD by $\text{Mn}^{\text{V}}(\text{N})(\text{salen})$	<b>158</b>
<b>Table 3.2</b> Effects of the amount of $\text{BF}_3$ on the oxidation of xanthene by $\text{Mn}^{\text{V}}(\text{N})(\text{salen})$	<b>162</b>
<b>Table 3.3</b> Effects of the amount of $\text{BF}_3$ on the oxidation of DHA by $\text{Mn}^{\text{V}}(\text{N})(\text{salen})$	<b>163</b>
<b>Table 3.4</b> $\text{BF}_3$ activated oxidation of various organic substrates by $\text{Mn}^{\text{V}}(\text{N})(\text{salen})$	<b>166</b>
<b>Table 3.5</b> $\text{Sc}(\text{OTf})_3$ activated oxidation of various alkanes by $\text{Mn}^{\text{V}}(\text{N})(\text{salen})$	<b>167</b>

## List of Figures

---

	Page	
<b>Figure 1.1</b>	The ideal synthesis	<b>3</b>
<b>Figure 1.2</b>	Examples of ionic liquids	<b>9</b>
<b>Figure 1.3</b>	Multi-component ionic liquid system: An ionic manganese complex embedded in [BPy][BF <sub>4</sub> ]	<b>22</b>
<b>Figure 1.4</b>	Structure of salen ligand	<b>23</b>
<b>Figure 1.5</b>	Structure of Jacobsen's catalyst	<b>24</b>
<b>Figure 1.6</b>	Structure of [Mn <sup>IV</sup> <sub>2</sub> (tmtacn) <sub>2</sub> ( $\mu$ -O) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	<b>29</b>
<b>Figure 1.7</b>	Structure of [Mn <sup>IV</sup> (tmtacn)(OMe) <sub>3</sub> ]PF <sub>6</sub>	<b>29</b>
<b>Figure 1.8</b>	Structure of glyoxylic acid methylester methyl hemiacetal	<b>32</b>
<b>Figure 1.9</b>	Proposed structure of the carboxylate-bridged dimanganese tmtacn intermediate	<b>32</b>
<b>Figure 1.10</b>	Structure of [Mn <sub>2</sub> O(OAc) <sub>2</sub> (TPTN)](ClO <sub>4</sub> ) <sub>2</sub>	<b>34</b>
<b>Figure 1.11</b>	Various aminopyridine N <sub>4</sub> ligands	<b>35</b>
<b>Figure 1.12</b>	Structure of the TEMPO-linked manganese porphyrin complex	<b>42</b>
<b>Figure 1.13</b>	Structure of the water-soluble Mn(III) salen complex	<b>44</b>
<b>Figure 1.14</b>	Structure of [Mn(3,3',5,5'- <i>t</i> -Bu <sub>4</sub> -salphen)Cl]	<b>44</b>
<b>Figure 1.15</b>	Plot of accumulated mmol of epoxide vs. number of consecutive runs of epoxidation of 2-methyl-2-pentene by (Ph <sub>4</sub> P) <sub>2</sub> [Mn <sup>V</sup> (N)(CN) <sub>4</sub> ]/H <sub>2</sub> O <sub>2</sub>	<b>52</b>
<b>Figure 2.1</b>	Structure of Os <sub>3</sub> (CO) <sub>11</sub> (L) (L = 2,3- $\eta$ -1,4-diphenylbut-2-en-1,4-dione)	<b>86</b>
<b>Figure 2.2</b>	Structure of Os <sub>3</sub> (CO) <sub>10</sub> ( $\mu$ -H) <sub>2</sub>	<b>87</b>
<b>Figure 2.3</b>	Structure of decamethylosmocene	<b>87</b>
<b>Figure 2.4</b>	Structure of [(TMC)Fe <sup>IV</sup> (O)-Sc(OTf) <sub>4</sub> (OH)]	<b>90</b>

## *List of Figures*

---

	Page	
<b>Figure 3.1</b>	ESI/MS (+ve mode) of a reaction mixture of [Mn(N)(salen)] (1.1 mM) and BF <sub>3</sub> (3.3 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) after 5 min.	<b>153</b>
<b>Figure 3.2</b>	UV-vis spectra for the reaction between [Mn(N)(salen)] (1 x 10 <sup>-4</sup> M) and Sc(OTf) <sub>3</sub> (1.0 equiv.) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v).	<b>154</b>
<b>Figure 3.3</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (2 mM) with Sc(OTf) <sub>3</sub> (4 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) after 20 min.	<b>156</b>
<b>Figure 3.4</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (2 mM) with Ca(OTf) <sub>2</sub> (4 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) after 20 min.	<b>157</b>
<b>Figure 3.5</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (0.3 mM) with BF <sub>3</sub> (0.9 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) in the presence of CHD (0.12 M) after 1 h.	<b>159</b>
<b>Figure 3.6</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (0.3 mM) with BF <sub>3</sub> (0.9 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) in the presence of xanthene (0.12 M) after 1 d.	<b>161</b>
<b>Figure 3.7</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (0.3 mM) with BF <sub>3</sub> (0.9 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) in the presence of DHA (0.12 M) after 50 min.	<b>164</b>
<b>Figure 3.8</b>	ESI/MS of a reaction mixture of [Mn(N)(salen)] (0.3 mM) with BF <sub>3</sub> (0.9 mM) in CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> CN (1:1 v/v) in the presence of DHA (0.12 M) after 1 d.	<b>165</b>

## ***Objectives***

---

This research work is divided into three parts. In part I, the catalytic oxidation of alkenes and alcohols by a manganese(V) nitrido complex  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  has been studied. In part II, the effects of Lewis acids on the activation of an osmium(VI) nitrido complex  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ , towards the catalytic oxidation of alkanes and aromatic hydrocarbons will be discussed. Part III describes the C-H bond activation of hydrocarbons by some manganese(V) imido species, which are generated by the reaction of a (salen)manganese nitrido complex  $[\text{Mn}^{\text{V}}(\text{N})(\text{salen})]$  with Lewis acids.

The objectives of the study in part I are as follows:

- (1) to study the epoxidation of alkenes and the oxidation of alcohols by using  $(\text{Ph}_4\text{P})_2[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_4]$  as a catalyst.
- (2) to study the mechanisms of catalytic alkene and alcohol oxidations by this system.

The objectives of the study in part II are as follows:

- (1) to investigate the effects of Lewis acids on the catalytic oxidation of alkanes and aromatic hydrocarbons by  $[\text{Os}^{\text{VI}}(\text{N})(\text{quin})_2\text{Cl}]$ .
- (2) to study the mechanisms of the catalytic oxidation of alkanes and aromatic hydrocarbons by this system.

The objectives of the study in part III are as follows:

- (1) to analyze the products generated by the C-H bond activation of hydrocarbons by some (salen)manganese(V) imido species.
- (2) to study the mechanism of the C-H bond activation of hydrocarbons by these manganese imido species.