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# Introduction and Aim

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## 1.1. Introduction

Research into the application of transition metal complexes in chemical processes has attracted much interest over the last century. Reasons are the novelty of the chemistry involved, its great potential and, as proven in numerous examples, the practical applications. All kinds of inorganic and organometallic compounds are used as catalysts or as reactants in a vast number of chemical reactions. Some of the important processes include hydrogenation of alkenes (Wilkinson catalyst), hydroformylation (cobalt and rhodium catalyst, oxo process), alkene oxidation (Wacker process), polymerization (Ziegler-Natta catalyst) and alkene isomerization (nickel catalyst).

The oxidation of alkenes to epoxides, aldehydes, ketones and glycols is a large and growing part of homogeneous catalysis with direct industrial applications.<sup>1,2</sup> The oxidation of organic substrates by direct oxygen atom transfer from transition metal complexes is of fundamental importance and has been investigated extensively. Reasons for this interest are the necessity for functionalization of lower alkenes, interest in understanding reactions of biological importance, the need for partial selective oxidation and the preparation of compounds with a specific spatial structure. The transition metal complexes seem to fulfil some of these requirements and many different systems are available that can utilize a variety of oxygen sources for these oxidation reactions. A number of complexes of interest will be discussed in further detail.

The active catalytic oxidant has been described as a mono- or bidentate coordinated alkyl hydroperoxide (hydrogen peroxide) or a bidentate coordinated peroxy group for the transition metal catalysed epoxidations using group 4 and 5 metals. The type of

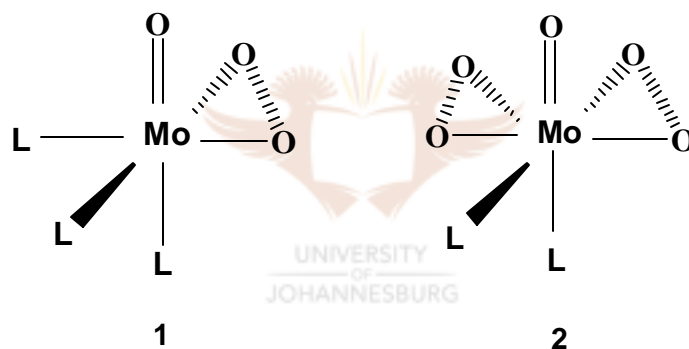
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<sup>1</sup> Parshall, G.W.; Ittel, S. D., *Homogenous catalysis: The applications and chemistry of catalysis by soluble transition metal complexes*, Wiley Interscience Publications, 2<sup>nd</sup> Ed., **1992**, 137.

<sup>2</sup> Sheldon, R.A., *Aspects of homogeneous catalysis*, Ugo, R., Ed., D. Reidel Publishing Company, **1981**, 4, 3.

active catalytic oxidant for group 6 and 7 transition metal epoxidations is an oxo metal complex. Hydroperoxides, hydrogen peroxide and molecular oxygen are used to generate the active oxidant for group 4 and 5 transition metal complexes, while for the group 6 and 7 transition metal complexes, iodosyl compounds, N-oxides, hypochlorite as well as various other synthetic methods are available to generate the active catalytic oxidant.<sup>3</sup>

Oxochromium(V) complexes formed from chromium(III)-salen [salen = N,N-ethylenebis(salicydeneaminato) ligand] or -TPP (-TPP = meso-tetraphenylporphyrinato) complexes can achieve the conversion of an alkene to its epoxide.<sup>3</sup> Monoperoxo-molybdenum complexes,  $[\text{MoO}(\text{O}_2)\text{L}_n]$  (1), and diperoxo-molybdenum complexes,  $[\text{MoO}(\text{O}_2)_2\text{L}_1\text{L}_2]$  (2), were also found to epoxidize many different types of alkenes.<sup>3,4</sup>



$[\text{MoO}(\text{O}_2)(2,6\text{-dipic})]\cdot\text{H}_2\text{O}$ ,  $[\text{MoO}(\text{O}_2)(\text{PhCON}(\text{Ph})\text{O})_2]$  and  $[\text{MoO}(\text{O}_2)\text{Cl}(\text{pic})]$  are some of the monoperoxo-molybdenum complexes that have been synthesized and  $[\text{MoO}(\text{O}_2)_2\cdot\text{HMPA}]\cdot\text{H}_2\text{O}$  is one example of a large variety of diperoxo-molybdenum complexes. The tungsten-peroxo complexes show similar behaviour to the molybdenum complexes and both mono- and diperoxo species are known. However, because of the low solubility of these tungsten complexes, their reactivity has not been studied to any large extent.

The manganese complexes that are commonly used as catalysts for alkene

<sup>3</sup> Jørgensen, K.A., *Chem. Rev.*, **1989**, 89, 431.

<sup>4</sup> Jacobsen, E.N., *Comprehensive Organometallic Chemistry II*, Abel, E.W.; Stone, F.G.A.; Wilkinson, G., Eds., Pergamon, **1995**, 12, 1097.

epoxidation are porphyrin type complexes.<sup>3,4</sup> The main reason is the relationship of these manganese porphyrin complexes to the biological oxidation systems. Oxomanganese(V)-salen complexes, formed from manganese(III)-salen complexes, show catalytic epoxidation activity as well.<sup>5</sup> Several complexes of the long-lived <sup>99</sup>Tc isotope have been prepared and tested for catalytic activity, but were found to be poor epoxidants with *tert*-butyl hydroperoxide (TBHP).<sup>3</sup> The catalytic activities of the rhenium complexes, which have also been tested, seem to be comparable to that of technetium and thus, have low activity.<sup>3</sup>

In contrast, significantly fewer methods are available for the analogous metal-mediated nitrogen atom transfer process, despite the enormous potential for the utilization of such a methodology in synthesis.<sup>6</sup> The aziridines, formed after the nitrogen atom transfer reaction between a metal complex and an alkene, are used as electrophiles and synthetic intermediates in the preparation of pharmaceuticals and agrochemicals.<sup>7</sup> As in the case of the oxygen atom transfer reagents of chromium and manganese in particular, most of the nitrogen atom transfer catalysts containing chromium and manganese have porphyrin or salen ligands or derivatives of these two ligands. Metallophthalocyanine complexes, structurally similar to porphyrins, have also been used as aziridination catalysts. The phthalocyanine complexes are more easily accessible and more stable to degradation compared to the porphyrin complexes. An optically active [Mn<sup>V</sup>N(salen)] complex was recently found to affect the stoichiometric and highly enantioselective aziridination of organic substrates.<sup>8</sup> However, the reaction of the optically active [Mn<sup>V</sup>N(salen)] complex will only proceed in the presence of triflic anhydride or trifluoroacetic anhydride.

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<sup>5</sup> Katsuki, T., *Coord. Chem. Rev.*, **1995**, *140*, 189.

<sup>6</sup> Du Bois, J.; Tomooka, C.S.; Hong, J.; Carreira, E.M., *Acc. Chem. Res.*, **1997**, *30*, 364.

<sup>7</sup> Jain, S.L.; Sain, B., *Journal of Molecular Catalysis A: Chemical*, **2003**, *195*, 283.

<sup>8</sup> Minakata, S.; Ando, T.; Nishimura, M.; Ryu, I.; Komatsu, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3392.

Over the last three decades, olefin metathesis has attracted much attention.<sup>9,10,11,12,13</sup> This is not surprising if the extensive possibilities that are offered by this methodology are taken into consideration, as well as the possibility of synthesizing new organic compounds by combining metathesis with epoxidation and aziridination.

The metathesis of alkenes is one of the most remarkable reactions catalyzed by transition metal complexes. This reaction can be catalysed by heterogeneous and homogeneous catalysts and the catalyst precursors used in both systems are strikingly similar. A wide variety of transition metal compounds will catalyse the metathesis reaction. The most important compounds contain the transition metals, tungsten, molybdenum and ruthenium, as well as osmium, rhenium, iridium, tantalum and titanium to a lesser extent. These compounds include catalyst precursors containing the transition metal center in high as well as low oxidation states.<sup>13</sup> The heterogeneous catalyst precursors generally consist of the transition metal oxide of an organometallic complex deposited on a high-surface-area support, whereas the homogeneous catalyst precursors mainly consist of a combination of a transition metal compound (usually a metal chloride or oxychloride) and an organometallic compound as co-catalyst and sometimes a third compound (called a promoter) or a well-defined carbene or alkylidene transition metal complex. The photolysis of  $[\text{Mo}(\text{CO})_6]$  or  $[\text{W}(\text{CO})_6]$  in a halogenated solvent, usually carbon tetrachloride, can also generate active metathesis catalysts.<sup>13</sup>

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<sup>9</sup> Ivin, K.J.; Mol, J.C., *Olefin Metathesis and Metathesis Polymerization*, Academic Press, **1997**.

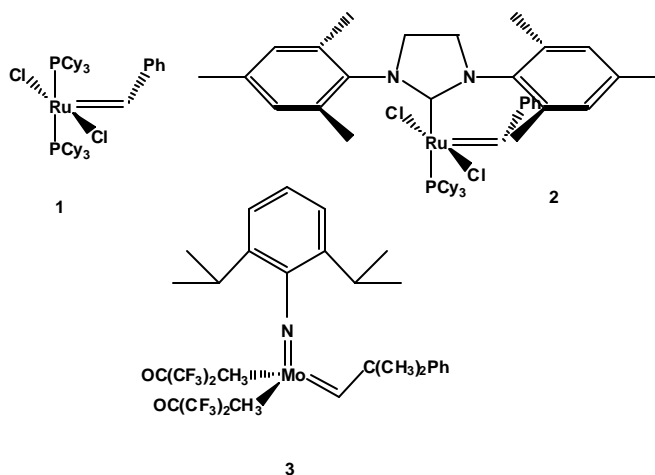
<sup>10</sup> Grubbs, R.H.; Miller, S.J.; Fu, G.C., *Acc. Chem. Res.*, **1995**, *28*, 446.

<sup>11</sup> Ivin, K.J., *Olefin Metathesis*, Academic Press, **1983**, 1.

<sup>12</sup> Mol, J.C., *Metathesis, Applied homogeneous catalysis with organometallic compounds*, Cornils, B.; Herrmann, W. A., Eds., VCH, **1996**, *1*, 318.

<sup>13</sup> Parshall, G.W.; Ittel, S. D., *Homogenous catalysis: The applications and chemistry of catalysis by soluble transition metal complexes*, Wiley Interscience Publications, 2<sup>nd</sup> Ed., **1992**, 217.

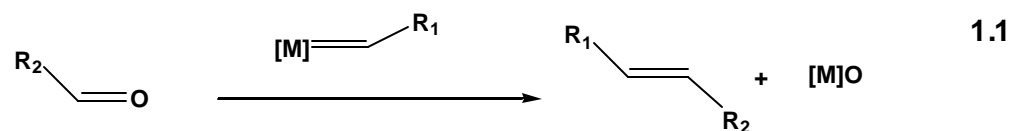
The following three catalyst precursors are commercially available today.<sup>14</sup>



While the ruthenium-based complex **1** has greater functional group compatibility than the molybdenum-based complex **3**, the molybdenum complex exhibits greater reactivity, particularly with sterically demanding and electron-deficient alkenes.<sup>14</sup> The development of *N*-heterocyclic carbenes (NHC) as ligands for ruthenium-based complexes closed the gap between the ruthenium and molybdenum-based systems. The *N*-heterocyclic carbene ruthenium complexes (**2**) have similar reactivity to the molybdenum complexes (**3**) where sterically demanding and electron-deficient alkenes are concerned, while maintaining the high functional group tolerance and air and moisture stability of complex **1**.<sup>14</sup>

The related transition metal alkylidene carbonyl olefination (eq. 1.1) has not been as extensively studied mechanistically or for the application in synthesis as the metal-mediated alkylidene metathesis reaction.<sup>10</sup> One of the reasons for this is the incompatibility of the traditional catalysts with the polar groups typically encountered in organic synthesis. It is now accepted that these two metal-mediated alkylidene reactions are mechanistically related and that metallacyclic and oxometallacyclic intermediates are involved in these reactions.

<sup>14</sup> Love, J.A.; Sanford, M.S.; Day, M.W; Grubbs, R.H., *J. Am. Chem. Soc.*, **2003**, 125, 10103.



A detailed understanding of the intrinsic mechanism of the abovementioned processes is essential in their application in industry and everyday life, especially when considering the impact of these industrial processes on the environment. Among impacts to consider would be substitution processes, such as the binding of substrates to homogeneous catalysts, active sites of metalloproteins and anticancer drugs, which take place during the course of these chemical reactions. Therefore, the importance of basic mechanistic studies to understand the different effects and variables that form part of the intrinsic mechanism of a chemical reaction cannot be over-emphasized.

The coordinated ligands in metal complexes to a large extent govern the reactions of these complexes in all chemical processes. It is thus crucial that the effects of the various ligands on factors such as solubility and reactivity of these complexes are clearly understood and quantified in order to enable intelligent manipulations to be made for inducing the desired effects. Basic chemical reactions like substitution, addition, oxidative addition and reductive elimination are of importance in most catalytic cycles. One of the ways of evaluating the effects of various ligands on the reactivity of a complex is by investigating octahedral substitution reactions. These reactions are very sensitive to variables such as steric and electronic effects and can give valuable information on the mechanism of the reaction being investigated.

The characterization of reactants and products by means of X-ray crystallography is also of utmost importance, since vital information concerning the geometry of the metal complex and the bonding characteristics of the ligands to the metal center can be determined. Information with regard to the crystallization modes of the different molecules that crystallize in the system can also be obtained. The data provides crucial information for the determination of a specific mechanism for a given reaction between an entering ligand and the metal complex.

## 1.2. Aim

It was discovered during a study of the monodentate substitution reactions of the  $[\text{MoO}(\text{OH}_2)(\text{CN})_4]^{2-}$  anion with cyanide, that the  $[\text{MoO}(\text{CN})_5]^{3-}$  product can react with molecular oxygen to form the peroxo complex,  $[\text{MoO}(\text{O}_2)(\text{CN})_4]^{2-}$ .<sup>15,16</sup> It is also known that the  $[\text{MO}(\text{OH}_2)(\text{CN})_4]^{n-}$  anions, with M = molybdenum(IV), tungsten(IV), technetium(V) and rhenium(V), behave very similarly with respect to protonation, substitution, etc.<sup>17,18,19</sup> No evidence of the epoxidation of alkenes catalyzed by these  $[\text{MO}(\text{O}_2)(\text{CN})_4]^{2-}$  anions [M = molybdenum(IV) and tungsten(IV)] was detected. However, the mentioned complexes oxidizes  $\text{PPh}_3$  (millimolar concentrations at room temperature) to  $\text{OPPh}_3$  with half lives of ca. 20 minutes.

The nitridotetracyano complexes of rhenium(V) and osmium(VI) were also studied in our laboratory.<sup>17,18</sup> Although these complexes were not tested for the aziridination reactions of alkenes, vital information could still be obtained from the studies of these complexes. Thus, to further our knowledge and understanding of the intrinsic characteristics and reaction mechanisms of these systems, it was decided to extend our research to the nitridotetracyano complexes of the first row metals of group 6, 7 and 8 and in this study, in particular, to the nitridotetracyano complexes of manganese(V).

An understanding of the mechanism of the reactions of the 1<sup>st</sup> generation Grubbs' catalyst,  $[(\text{Cy}_3\text{P})\text{C}_2\text{Ru}=\text{CHPh}]$ , is very important, since this can lead to a better understanding of metathesis reactions in general. It can also lead to a better controlled metathesis reaction with smaller catalyst loadings and the prevention of undesirable side reactions. The degradation of the catalyst can also be prevented if the effects of different external factors that can impact on these reactions are taken into account.

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<sup>15</sup> Arzoumanian, H.; Pettrignani, J.F.; Pierrot, M.; Ridouane, F.; Sanchez, J., *Inorg. Chem.*, **1988**, 27, 3377.

<sup>16</sup> Lorber, C., *Ph.D. thesis*, Louis Pasteur University, Strasbourg, France, **1995**.

<sup>17</sup> Leipoldt, J.G.; Basson, S.S.; Roodt A.; Purcell, W., *Polyhedron*, **1992**, 11, 2277.

<sup>18</sup> Leipoldt, J.G.; Basson, S.S.; Roodt A., *Advances in Inorganic Chemistry*, Sykes, A.G.; Ed., Academic Press; San Diego, **1993**, 40, 241.

<sup>19</sup> Roodt, A.; Abou-Hamdan, A.; Engelbrecht, H.P.; Merbach, A.E., *Advances in Inorganic Chemistry*, Sykes, A.G.; Ed., Academic Press; San Diego, **2000**, 49, 59.

With the abovementioned in mind, the following main objectives were set for this study:

- The preparation of manganese(V) complexes containing the  $[\text{MnN}(\text{CN})_5]^{3-}$  /  $[\text{MnN}(\text{CN})_4]^{2-}$  anions as starting materials.
- The synthesis and characterisation of the reaction products of the substitution reactions of the  $[\text{MnN}(\text{CN})_5]^{3-}$  /  $[\text{MnN}(\text{CN})_4]^{2-}$  complexes with mono- and bidentate ligands, including the X-ray structure determinations of these substitution products.
- Determination of the acid-base behaviour [acid dissociation constants, ( $\text{pK}_a$ )] of these complexes in order to investigate the steric and electronic impact of the different ligands.
- A detailed kinetic study on the substitution reactions of the  $[\text{MnN}(\text{CN})_5]^{3-}$  /  $[\text{MnN}(\text{CN})_4]^{2-}$  complexes with different mono- and bidentate ligands.
- A kinetic study of the auto-decomposition reaction 1<sup>st</sup> generation Grubbs catalyst and the reaction with oxygen to determine the rates of the reactions and possible intermediates.
- A kinetic study of the metathesis reaction of Grubbs 1<sup>st</sup> generation catalyst with 1-octene and ethene gas in solution to determine the rate of initiation of the catalyst precursor.
- The integration of the data from the above-mentioned reactions of 1<sup>st</sup> generation Grubbs catalyst to understand the mechanism of these reactions.