SYNTHESIS OF MOLYBDENUM AND TUNGSTEN COMPLEXES AND THEIR APPLICATION IN OLEFIN EPOXIDATION

LI SHENYU

NATIONAL UNIVERSITY OF SINGAPORE

2010
SYNTHESIS OF MOLYBDENUM AND TUNGSTEN COMPLEXES AND THEIR APPLICATION IN OLEFIN EPOXIDATION

LI SHENYU
(B.Sc., Soochow Univ.)

A THESIS SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

NATIONAL UNIVERSITY OF SINGAPORE

2010
Acknowledgements

I would like to express my wholehearted gratitude to my supervisors, Prof. Hor Tzi Sum, Andy and Dr. Zhao Jin for their profound knowledge, invaluable guidance, constant support, inspiration and encouragement throughout my graduate study. They are not only extraordinary supervisors, complete mentors, but truly friends. The knowledge, both scientific and otherwise, that I accumulated under their supervision, will aid me greatly throughout my life.

I am deeply grateful to our collaborators, Dr. Huang Kuo-Wei from the KAUST Catalysis Center and Division of Chemical and Life Sciences and Engineering, King Abdullah University of Science and Technology, for his contribution of the DFT calculations of our experimental findings. I wish to thank Mr Kee Choon Wee from Department of Chemistry, NUS, for his assistance in the ESI-MS tests of our compounds. I also wish to thank Ms. Geok Kheng Tan and Dr. Lip Lin Koh for determining the X-ray crystal structures.

I also give my sincere thanks to my colleagues: Dr. Bai Shiqiang; Chen Hsiao Wei; Chien Sheau Wei; Ding Nini; Gan Ching Ruey, Raymond; Hu Jian Jin; Jiang Lu; Qian Yao; Song Xiaolu; Wang Jing; Wang Pei; Wang Zhe; Wong Hui Lin, Valerie; Wu Xialu; Xue Fei; Dr. Zhang Wenhua and other labmates for their cordiality and friendship.

I wish to express my deepest appreciation to my family for their love and support. Without their help, I can not complete this work.

I want to express my appreciation to the members of instruments test in NMR, IR, GC-FID and Mass Lab. They gave me too much help for my research work.

Last but not least, my acknowledgement goes to National University of Singapore for the research scholarship and the financial support.
Table of Contents

Acknowledgements i
Table of Contents ii
Summary vii
List of Tables viii
List of Schemes viii
List of Figures ix
List of Abbreviations xi
List of Publications xiii

Chapter One: Introduction 1
1.1 General Introduction 1
1.2 Molybdenum Complexes of the Formula MoO₂R₂L (R = allyl, L = Lewis base ligand) 1
1.3 Molybdenum Complexes with Cyclopentadienyl Ligand and Their Behavior under Oxidation Conditions 2
1.4 Molybdenum(0) Complexes with Neutral Ligand and Their Behavior under the Oxidation Conditions 4
1.4.1 Mo Phosphine Complexes 5
1.4.2 Mo N-Hetercyclic Carbene Complexes 7
1.5 Asymmetric Epoxidation Reaction 9
1.6 Objectives 10
1.7 Reference 11

Chapter Two: Synthesis of Mo(0) and W(0) PNP Complexes and Their Application in Olefin Epoxidation 17
2.1 Introduction

2.2 Result and Discussion

2.2.1 Ligand Synthesis

2.2.2 Synthesis and Characterization of Compounds M(CO)₄[PN(R)P] (2-1 - 2-4).

2.2.3 Molecular Structure of Compounds 2-1b, 2-2, 2-3b, 2-4 Determined by Single-Crystal X-ray Diffraction.

2.3 Application of Compounds 2-1 - 2-3 in Epoxidation Catalysis.

2.4 Behavior of 2-1a, 2-1b and 2-3b under Oxidative Conditions.

2.5 Conclusions

2.6 Experimental Section

2.6.1 Synthesis of Compound 2-1 - 2-4

2.6.2 X-ray Crystallography

2.6.3 Catalytic reactions.

2.7 Reference

Chapter Three: Synthesis and Characterization of Molybdenum(0) and Tungsten(0) carbonyl N-Heterocyclic Carbene Complexes and Their Application in Olefin Epoxidation

3.1 Introduction

3.2 Result and Discussion

3.2.1 Synthesis and Characterization of Compounds M(CO)₄(NHC)₂ (3-1 - 3-2)

3.2.2 Synthesis and Characterization of Compounds 3-3 - 3-5.

3.2.3 Molecular Structure of Compounds 3-1b and 3-4 Determined by Single-Crystal X-ray Diffraction.
3.3 Application of Compounds 3-1 - 3-5 in Epoxidation Catalysis. 46

3.4 Examination of the Stability of Metal-NHC Ligand Bond under Oxidative Conditions. 49

3.4.1 Stability of Mo-C(NHC) Bonds in 3-1a and 3-1b under Oxidative Conditions. 49

3.4.2 Stability of Mo-C(NHC) Bonds in 3-3a and 3-3b under Oxidative Conditions. 50

3.4.3 Stability of Mo-C(NHC) Bonds in 3-5 under Oxidative Conditions. 51

3.5 Conclusions 52

3.6 Experimental Section 53

3.6.1 Preparation of Compounds 3-1 - 3-2 53

3.6.2 Preparation of 3-3a, 3-3b by Silver Mediated Transfer Route 55

3.6.3 Preparation of 3-4, 3-5 by Silver Mediated Transfer Route 56

3.6.4 X-ray Crystallography 57

3.6.5 Catalytic reactions 58

3.7 Reference 58

Chapter Four: Cyclopentadienyl Molybdenum(II/VI) N-Heterocyclic Carbene Complexes: Synthesis, Structure, and Reactivity under Oxidative Conditions 62

4.1 Introduction 62

4.2 Result and Discussion 64

4.2.1 Synthesis and Characterization of Compounds CpMo(CO)₂(NHC)Br (4-1 - 4-7). 64

4.2.2 Synthesis and Characterization of Compounds

[CpMo(CO)₂(NHC)(CH₃CN)][BF₄] (4-8 - 4-11). 67
4.2.3 Molecular Structure of Compounds 4-1, 4-2, 4-3, 4-4b, 4-5, 4-8, 4-9 and 4-10
Determined by Single-Crystal X-ray Diffraction.

4.3 Application of compounds 4-1 - 4-6, 4-8 - 4-11 and CpMo(CO)3Br in epoxidation catalysis.

4.4 Examination of the Stability of Metal-NHC ligand bond under oxidative conditions.

4.4.1 Stability of Mo-C(NHC) Bonds in 4-3, 4-4a and 4-6 under Oxidative Conditions.

4.4.2 Examination of the stability of Mo-C(carbene) bond in 4-8 - 4-11 under oxidative conditions and the formation of [CpMoO2(NHC)]BF4.

4.5 DFT Studies.

4.6 Conclusion

4.7 Experimental Section

4.7.1 Synthesis of 1,3-bis(2,4,6-trimethylphenyl)imidazolium bromide (IMesHBr).

4.7.2 Synthesis of Compounds 4-1, 4-2, 4-4a, 4-5 and 4-6.

4.7.3 Synthesis of Compounds 4-3 and 4-6.

4.7.4 Synthesis of (η5-C5H5)Mo(CO)2(IBz)Br (4-4a) and (η5-C5H5)Mo(CO)2(IBz)Cl (4-4b) from CpMo(CO)2PPh3Cl.

4.7.5 Synthesis of [(η5-C5H5)Mo(CO)2(NHC)(CH3CN)]BF4 (NHC = IMes, 4-8; NHC = IBz, 4-9; NHC = SIMes, 4-10; NHC = I*PhEt, 4-11).

4.7.6 Isolation and characterization of [IMesH]2[Mo6O19] from the oxidation of compound 4-3 by TBHP.

4.7.7 Synthesis of [CpMoO2(NHC)]BF4 (NHC = IMes, 4-14; NHC = IBz, 4-15; NHC = SIMes, 4-16; NHC = I*PhEt, 4-17).

4.7.8 X-ray Crystallography
4.7.9 Catalytic Reactions. 102

4.7.10 Computational Details. 102

4.8 Reference 103

Appendix X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters
Summary

This thesis comprises the synthesis of serious of molybdenum and tungsten complexes and their application in the olefin epoxidation reactions.

Chapter 1 provides a brief historic overview of the development of molybdenum and tungsten organometallic complexes. The development of asymmetric olefin epoxidation catalyzed by chiral Mo complexes in the last ten years has also been described.

Chapter 2 describe the synthesis of a serious of Mo and W based bis(diphenylphosphanyl)amine (PNP) complexes. The stability of metal-phosphine ligand bonds in these compounds under oxidative conditions has been investigated. The Mo complexes can be applied as active and selective olefin epoxidation catalysts.

Chapter 3 describe the synthesis of a series of Mo(0) and W(0) N-heterocyclic carbene (NHC) complexes. The reactivity of the monodentate and polydentate NHC complexes under oxidative condition has been investigated. The study of stability of metal-NHC bonds under the oxidative condition has been involved.

Chapter 4 describe the synthesis of a series of N-heterocyclic carbene (NHC) complexes with the formula CpMo(CO)$_2$(NHC)X (X=Br, Cl or BF$_4$). The stability of metal-NHC ligand bonds in these compounds under oxidative conditions has been investigated. The thermally stable Mo(VI) dioxo NHC complex [CpMoO$_2$(NHC)]$[BF_4]$ has been isolated by the oxidation of the ionic complexes. The ionic complexes can be applied as very active and selective olefin epoxidation catalysts. DFT calculations suggest that the presence of Br$^-$ destabilizes the Mo-NHC ligand bond in the CpMo(VI) oxo NHC carbene species.
List of Tables

Table 2.1 $^{31}P$($^1$H) NMR (121.44MHz, CDCl$_3$) data for the PNP ligands and complexes. 20

Table 4.1 Calculated bond lengths and angles vs. experimental data for CpMo(CO)$_2$(IMe)Br (4-1). 92

Table 4.2 Calculated structural parameters of CpMo complexes. 92

List of Schemes

Scheme 1.1 Synthesis of compound 1-3b 3
Scheme 1.2 Synthesis of compounds 1-3a – 1-3c 3
Scheme 1.3 Reaction of Mo(CO)$_4$(dppe) with Br$_2$ 6
Scheme 1.4 Reaction of W(CO)$_4$(dppe) with Br$_2$ 6
Scheme 2.1 Synthesis of ligands L1-L4 19
Scheme 2.2 Synthesis of compounds 2-1 – 2-4 20
Scheme 3.1 Synthesis of compounds 3-1 – 3-2 40
Scheme 3.2 Synthesis of compounds 3-3 – 3-5 42
Scheme 4-1 Structure of compounds 4-1 – 4-7 65
Scheme 4-2 Synthesis of compounds 4-8 – 4-11 68
Scheme 4.3 Synthesis of compounds 4-14 – 4-17 86
List of Figures

Figure 2.1 ORTEP diagram of compound 2-1b 22
Figure 2.2 ORTEP diagram of compound 2-2a 23
Figure 2.3 ORTEP diagram of compound 2-2b 24
Figure 2.4 ORTEP diagram of compound 2-3b 25
Figure 2.5 ORTEP diagram of compound 2-4a 25
Figure 2.6 ORTEP diagram of compound 2-4b 26
Figure 2.7 Time dependent yield of cyclooctene epoxide in the presence of compounds 2-1 to 2-3 as catalysts at 55 °C (Mo-based catalysts) or 90 °C (W-based catalysts) using TBHP as oxidant 27
Figure 2.8. Yield of the cyclooctene epoxide after 4 h (hatched bars), 8 h (grey and hatched bars) and 24 h (grey bars) of reaction time using the compounds 2-1 to 2-3 as catalysts in the presence of TBHP. 27
Figure 3.1 ORTEP diagram of compound 3-1b 45
Figure 3.2 ORTEP diagram of compound 3-5 46
Figure 3.3 Time dependent yield of cyclooctene epoxide up to 6h in the presence of compounds 3-1 to 3-5 as catalysts at 55 °C (Mo-based catalysts) or 90 °C (W-based catalysts) using TBHP as oxidant 47
Figure 3.4. Yield of the cyclooctene epoxide after 4 h (hatched bars), 8 h (grey and hatched bars) and 24 h (grey bars) of reaction time using the compounds 3-1 to 3-5 as catalysts in the presence of TBHP. 47
Figure 3.5. Kinetic $^1$H-NMR experiments on the reaction of compound 3-1a and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CDCl$_3$. 51
Figure 3.6. Kinetic $^1$H-NMR experiments on the reaction of compound 3-5 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CDCl$_3$. 54
Figure 4.1 ORTEP diagram of compound 4-1 69
Figure 4.2 ORTEP diagram of compound 4-2 70
Figure 4.3 ORTEP diagram of compound 4-3 71
Figure 4.4 ORTEP diagram of compound 4-4b 72
Figure 4.5 ORTEP diagram of compound 4-5 73
Figure 4.6 ORTEP diagram of the cation of \([\text{CpMo(CO)}_2(\text{IMes})(\text{CH}_3\text{CN})]^+\) in compound 4-8

Figure 4.7 ORTEP diagram of the cation of \([\text{CpMo(CO)}_2(\text{IBz})(\text{CH}_3\text{CN})]^+\) in compound 4-9

Figure 4.8 ORTEP diagram of the cation of \([\text{CpMo(CO)}_2(\text{SIMes})(\text{CH}_3\text{CN})]^+\) in compound 4-10

Figure 4.9 Time dependent yield of cyclooctene epoxide in the presence of compounds 4-1 - 4-6, 4-8 - 4-11 and CpMo(CO)_3Br as catalysts at 55 °C using TBHP as oxidant.

Figure 4.10 Yield of the cyclooctene epoxide after 4 h (hatched bars), 8 h (grey and hatched bars) and 24 h (grey bars) of reaction time using the compounds 4-1 – 4-6, 4-8 - 4-11 as catalysts in the presence of TBHP

Figure 4.11 ORTEP diagram of \([\text{IMesH}][\text{Mo}_6\text{O}_{19}]^-\)

Figure 4.12 The negative mode ESI-spectrum of the imidazolium salt \([\text{Mo}_6\text{O}_{19}][\text{IMesH}]_2\) obtained from the oxidation reaction between compound 4-3 and TBHP.

Figure 4.13 ESI monitoring of reaction between 10 equivalent of TBHP and compound 4-4a at 0min (a) and 25 min (b)

Figure 4.14 Kinetic $^1$H-NMR experiments on the reaction of compound 4-8 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CD$_3$CN.

Figure 4.15 Kinetic $^1$H-NMR experiments on the reaction of compound 4-10 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CD$_3$CN.

Figure 4.16 ORTEP diagram of \([\text{CpMoO}_2(\text{IBz})(\text{CH}_3\text{CN})][\text{Mo}_6\text{O}_{19}]^-\) in compound 4-15
List of Abbreviations

Bpy 2,2’-bipyridine
Cp cyclopentadienyl
Cp* pentamethyl cyclopentadienyl
Cp\(^{bz}\) pentabenzyl cyclopentadienyl
DFT density functional theory
dppe 1,2-bis(diphenylphosphanyl)ethane
dppe\(^{O2}\) bis(diphenylphosphineoxide)ethane
dppm bis(diphenylphosphanyl)methane
dppm\(^{O2}\) bis(diphenylphosphineoxide)methane
FAB-MS fast atom bombardment-mass spectrometry
GC-FID gas Chromatography - Flame Ionization Detector
I*PhEt bis ((S)-1’-phenylethyl)imidazolin-2-ylidene
IBz 1,3-dibenzylimidazol-2-ylidene
IME 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IMes 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IMesHBr 1,3-bis(2,4,6-trimethylphenyl)imidazolium bromide
I\(^{a}\)Pr 1,3-dipropylimidazol-2-ylidene
Mes 2,4,6- trimethylbenzyl
Mo\(^{6}\)O\(^{19}\) hexamolybdate
nbd norbornadiene
NHC N-heterocyclic carbene
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNP</td>
<td>bis(diphenylphosphanyl)amine</td>
</tr>
<tr>
<td>Py</td>
<td>pyridyl</td>
</tr>
<tr>
<td>Py$_2$NHC</td>
<td>1,3-dipicolylimidazol-2-ylidene</td>
</tr>
<tr>
<td>PyNHC</td>
<td>3-methyl-1-picolylimidazol-2-ylidene</td>
</tr>
<tr>
<td>SIMes</td>
<td>1,3-bis-(2,4,6-trimethylphenyl) imidazolin-2-ylidene</td>
</tr>
<tr>
<td>TBHP</td>
<td>tert-butylhydroperoxide</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
</tbody>
</table>
List of Publications

Journal Articles:


Conferences and Posters:


Chapter One: Introduction

1.1 General introduction

Lower olefin oxides are the raw materials and semi-finished products for the synthesis of many important products such as polyurethanes, polyesters, alkanolamines, and surface-active agents and others. In the past few decades, epoxidation reaction catalyzed by transition metal complexes has become an important way to accomplish the olefin epoxide. The transition metals that can be applied in this reaction range widely from Group 4 to 11. Molybdenum complexes are known as one of the best homogeneous catalysts for epoxidation with alkyl or aryl hydroperoxides as well as with other oxygen donors like H₂O₂, NaClO, PhilO, or KHSO₅. Many of the molybdenum compounds catalyzed the epoxidation of alkene in high yields. The yields of by-products are also lower compared to those from other metal complexes. Besides the high activity and selectivity, the relatively low price of molybdenum was found to be a big advantage and attract more and more attention. This kind of complexes include monomeric molybdenum compounds such as Mo(CO)₆ and MoO₂(acac)₂, molybdenum clusters such as [Mo₅O₂CR₂(H₂O)₆]²⁺, [C₅H₅N+(CH₂)₁₅CH₃][PMo₁₂O₄₀], ammonium molybdate [(NH₄)₆Mo₇O₂₄] and metallic molybdenum. Among them, low valent Mo carbonyl compounds such as Mo(CO)₆ and Mo(VI) oxo compounds such as MoO₂X₂(L) or MoO₂(acac)₂ catalyzing olefin epoxidation have been intensively studied particularly in the aspect of catalytic mechanism.

1.2 Molybdenum complexes with the formula MoO₂R₂L (R = allyl, L = Lewis base ligand)
Since the first metal oxo compound MoO₂Cl₂ was prepared by J. J. Berzelius in 1826, the study of Mo dioxo compounds have been continued in the 19th and 20th centuries. Introducing organic ligand to the metal center to generate an organometallic oxide was found to be a pathway to stabilize the metal oxo core. The first example of a dioxomolybdenum(VI) complex with a Mo-C σ bond is MoO₂(Mes)₂ (1-1) (Mes = 2,4,6-trimethylbenzyl), which is relatively stable to air and humidity as solid state. Compound 1-1 can be applied as catalyst in the ketone hydrosilylation or CO activation reaction. There was however no application reported in the catalytic olefin epoxidation. Compared with Mo oxo compounds MoO₂X₂(L)₂ (X = Br or alkyl, L = 2,2'-bipyridyl and its derivatives), compound 1-1 cannot form Lewis base adducts due to the steric bulk of the mesityl group.

Recently, the catalytic properties of MoO₂Me₂L₂ [L = substituted 1,4-diazobutadiene] (1-2) have been studied in detail. The compounds were found to be active for the epoxidation of olefins using tert-butylhydroperoxide (TBHP) as oxidant and at 55 °C. However, no epoxidation products could be obtained if H₂O₂ was employed as the oxidant.

1.3 Molybdenum complexes with Cyclopentadienyl Ligand and Their Behavior under Oxidation Conditions

Cp’MoO₂X (Cp’ = η⁵-C₅R₅ (R = H, CH₃, CH₂Ph); X = Cl, Br, alkyl) is another kind of important Mo(VI) dioxo complexes. In 1963, the first example of CpMoO₂Cl (1-3) was synthesized by air oxidation of CpMo(CO)₂(η³-C₃H₅) in the presence of HCl, but with very low yield. Since then, several pathways to compound 1-3 were developed. For instance, it can be prepared from the reaction of sodium cyclopentadienide with molybdenum dioxide dichloride (yield up to 20%) or by the irradiation of the binuclear compound (CpMoO₂)₂O with ultraviolet light (yield ca. 20%). Its bromo derivative CpMoO₂Br was also prepared.
with moderate yield. \( \text{Cp}^*\text{MoO}_2\text{Cl} \) (\( \text{Cp}^* = \text{pentamethyl cyclopentadienyl} \)) has been prepared by oxidation of the carbonyl complex [\( \text{Cp}^*\text{Mo(CO)}_2 \)]\(_2\) with oxygen to a \( \mu \)-oxo bridged dimer and following by the treatment with \( \text{PCl}_5 \). (Scheme 1.1)

![Scheme 1.1 Synthesis of compound 1-3b](image)

**Scheme 1.1 Synthesis of compound 1-3b**

![Scheme 1.2 Synthesis of compound 1-3a – 1-3c](image)

**Scheme 1.2 Synthesis of compound 1-3a – 1-3c**

A simple method was developed by Kühn *et al.* recently. \( \text{Cp'}\text{MoO}_2\text{Cl} \) (\( \text{Cp'} = \eta^5\text{-C}_5\text{R}_5 \), \( \text{R} = \text{H} \) 1-3a, \( \text{R} = \text{CH}_3 \) 1-3b, \( \text{R} = \text{CH}_2\text{Ph} \) 1-3c) can be synthesized in one step from the oxidation
of corresponding precursor Cp’Mo(CO)₃Cl. (Scheme 1.2) These three compounds are moisture sensitive and among them, compound 1-3c is significantly more stable than its Cp and Cp* counterparts, probably due to the steric bulk of the Cp’ ligand. Compound 1-3c also show highest catalytic activity in olefin epoxidation reaction. Cp’Mo(CO)₃Cl is a simple and convenient catalyst precursor of Cp’MoO₂Cl. It is also stable toward moisture.

1.4 Molybdenum(0) complexes with neutral ligand and their behavior under the oxidation conditions

Although many efficient epoxidation catalysts are organometallic oxides containing a metal in high oxidation state, many of them can be conveniently synthesized from low valent molybdenum precursors. The molybdenum(0) complex is usually easily-synthesized by thermal or photochemical methods. Comparing to the Mo dioxo complex, it is more stable under air condition. It can convert to Mo(VI) easily under proper oxidative conditions.

Compared with other neutral ligands, the carbonyl is easier to be oxidized and removed. Mo(CO)₆ was studied as a model and was applied as an efficient catalyst in the olefin epoxidation. Its oxidation product by tert-butyl hydrogen peroxide (TBHP) has been claimed to be Mo(VI)-1,2-diol complexes (1-4). However, in a review published in 2003, it was described that Mo(CO)₆ could be converted to cis-dioxo Mo(VI) complex (1-5) in the presence of TBHP.
If other neutral ligands are introduced to the Mo(0) carbonyl core, such as bpy (bpy = 2,2’-bipyridine), the oxidative product becomes more intricate. It was found recently that Mo\((\text{CO})_4\)(bpy) (1-6a) can be oxidized by TBHP, generating one dimensional organic-inorganic hybrid material \([\text{MoO}_3\text{(bpy)}]\).\(^{25}\) If bpy is substituted by \(t\)-butyl function group, the oxidation of complex 1-6b by TBHP generates polynuclear \([\text{Mo}_{8}\text{O}_{24}\text{(di-}^{3}\text{Bubipy)}_4]\) with a structure containing \(\text{Mo}_4(\mu_3\text{-O})_4\) cubane core.\(^{25a}\) This oxidation product shows moderate activity towards olefin epoxidation.

1.4.1 Mo phosphine complexes

Transition metal phosphine complexes have received more and more attention in recently years and are widely applied in the catalytic reaction such as C-C/C-N coupling reaction\(^{26a}\), hydrogenation\(^{26b}\) and hydrosilylation\(^{26c}\) etc. Diphosphines containing a single atom as spacer between the donor atoms, such as dpmm [dpmm = bis(diphenylphosphanyl)methane] and PNP [PNP = bis(diphenylphosphanyl)amine] (1-7) belong to the category of short-bite ligands and their coordination chemistry has attracted much interest.\(^{27}\) The PNP type of the ligand is capable of forming four-membered chelate rings with metal center and widely used as ligand in the complexation. For instance, Cr PNP complexes such as \([\text{Ph}_2\text{PN(}CH_2(\text{o-Et})C_6H_4)\text{PPh}_2\text{CrCl}_2(\mu_2\text{-Cl})]_2\)\(^{28}\) and \([\text{Cr(}\text{CO})_6(\text{Ph}_2\text{PN(}^{3}\text{Pr})\text{PPh}_2)]^+\)\(^{29}\) were found to have good selectivity and activity in catalytic reaction such as ethylene oligomerization. The first report on the synthesis and the molecular structure of Mo(0) PNP carbonyl compound, Mo\((\text{CO})_4\)PPh\(_2\)N(C\(_3\)H\(_3\))PPh\(_2\) was published 40 years ago.\(^{30}\) Since then, several Mo(0) and W(0) PNP complexes have been synthesized\(^{31}\). However, to the best of our knowledge, their catalytic activities towards to oxidation catalysis are still unknown.
Mo(0) and W(0) phosphine complexes such as M(CO)$_4$(dppe) (dppe = 1,2-bis(diphenylphosphanyl)ethane) or M(CO)$_4$(PEt$_3$)$_2$ can be oxidized to M(II) (M = Mo, W) or even higher oxidation state by thionyl chloride or halide.$^{32,33}$ For instance, M(CO)$_4$(dppe) (M = Mo, W) can be oxidized to M(CO)$_3$(dppe)Br$_2$ with M-P bond remains intact. If excess amount of Br$_2$ is used, the phosphine ligand can be oxidized to phosphine oxide and the M-P bond cleaves followed by the formation of a new M-O bond$^{32b}$. (see Scheme 1.3 and 1.4). It shows us a good example of the direct oxidation of the phosphine complexes without decomposition of L-M bond. Hence it is possible to apply a molybdenum or tungsten phosphine complex as catalyst in the epoxidation reaction.

\[
\begin{align*}
\text{Scheme 1.3 Reaction of Mo(CO)$_4$(dppe) with Br$_2$} \\
\text{Scheme 1.4 Reaction of W(CO)$_4$(dppe) with Br$_2$}
\end{align*}
\]

Recently, the Mo(VI) and W(VI) dioxo phosphine oxide complexes (1-8 to 1-11) with
similar structure to the oxidation products shown in Scheme 1.3 and 1.4 were synthesized and applied as efficient epoxidation catalysts using TBHP as oxidant.\textsuperscript{34} They are stable in air in either the solid state or in solution with no sign of decomposition. The TOF for the best catalyst \textit{1-10}\textsuperscript{34b} measured after 5 min reaction time is 847 mol mol\textsuperscript{-1}cat h\textsuperscript{-1}). Although it is lower than the TOF of Cp’MoO\textsubscript{2}Cl type of compounds,\textsuperscript{21} it is still higher than the reported dioxomolybdenum(VI) complexes containing nitrogen donor ligands.\textsuperscript{36}

![Chemical structures](image)

**1.4.2 Mo N-hetercyclic carbene complexes**

N-Heterocyclic carbenes (NHCs) have been widely used as phosphine alternatives as spectator ligands in the application of transition metal complex catalyzed reactions, such as C-C/ C-N coupling, olefin metathesis, and hydrogenation.\textsuperscript{35} One of the advantages of NHC ligands over phosphines is its better oxidation resistance.\textsuperscript{38} Because of the strong metal-carbon bond, some NHC complexes show extraordinary stability towards strong oxidizing agents like peroxodisulfate which makes it possible to be used in oxidation catalysis.\textsuperscript{39} A variety of catalytic oxidation reactions have been studied using NHC complexes, such as O\textsubscript{2}/CO fixation, the oxidation of alcohols, alkyne oxidation as well as the oxidation of terminal olefins to ketone. Most of the work in this area was conducted with Pd catalysts.\textsuperscript{40}

As a strong σ donor, NHC carbene has the property to stabilize the metal center of high oxidation state.\textsuperscript{41d} However, the study on the stability of M-NHC bond in high-valent metal complexes under oxidative conditions is still rare. Recently, a Mn(III) complex with a tetradentate NHC ligand was reported and applied as a catalyst for the epoxidation of styrene
using PhIO as oxidant to give styrene oxide, suggesting the formation of Mn$^{IV}$=O and Mn$^{V}$=O NHC intermediates during the oxygen transfer reactions. However, there was no spectroscopic evidence of such species reported. The first reported dioxo molybdenum(VI) N-heterocyclic carbene complex was provided by Herrmann (1-12). Later Royo reported a similar structure (1-13), by the direct reaction of MoO$_2$Cl$_2$(THF)$_2$ with free carbene. However, due to the extreme sensitivity, these compounds have not been fully characterized and it is impossible to use these compounds as catalyst.

Most of the carbene complexes with low-valent metal like Mo(0) and Mo(II) are stable to air and moisture and can be easily synthesized. Mo(0) carbonyl carbene with the structure of Mo(CO)$_6$(NHC)$_2$ or Mo(CO)$_6$(bis-NHC) have been synthesized many years ago. Their crystal structures and low temperature dynamic behavior have been studied. However, to the best of our knowledge, no catalytic application was have been investigated. For Mo(II), compounds CpM(CO)$_2$(IMes)H and [CpM(CO)$_2$(IMes)]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ (M = Mo, W; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been synthesized and employed in catalytic ketone hydrogenation reactions.

Some Mo(II) complexes containing ansa-bridged cyclopentadienyl-functionalized NHC complexes, (Cp$^x$-NHC)Mo(CO)$_2$I (Cp$^x$ = Cp, Cp* and Cp$^{B_3}$) have been reported. These
complexes, however, show much poorer activities towards olefin epoxidation comparing with CpMo(CO)$_3$X. Most recently, $M(\eta^3$-C$_3$H$_5$)(CO)$_2$(bis-carbene) (M = Mo and W) (1-14a), (1-14b) were prepared and applied in the olefin epoxidation using H$_2$O$_2$ as oxidant.$^{41d}$ They showed moderate activity and are even less active than the precursor of 1-14b (W(\eta^3$-C$_3$H$_5$)(CO)$_2$(MeCN)$_2$). IR and $^1$H NMR show the decomposition of compounds 1-14a and 1-14b in the presence of H$_2$O$_2$, both by the cleavage of M-C(NHC) bond and M-$\eta^3$-C$_5$H$_5$ bond.

1.5 Asymmetric epoxidation reaction

Transition metal catalytic asymmetric epoxidation is a useful technique for the synthesis of chiral compounds.$^{47}$ The first asymmetric epoxidation reaction catalyzed by chiral Ti complexes was developed by Sharpless et.al.in 1980s.$^{48}$ It converts allylic alcohols into epoxides with $ee\%$ (enantiomer excess value) more than 90%. The Jacobsen–Katsuki method uses Mn(salen) complexes and provides an efficient method for unfunctionalized and particularly cis olefins.$^{49}$

In the case of Mo catalyzed asymmetric epoxidation, the chiral porphyrins with Mo=O,$^{50}$ catalyzed the epoxidation of cis-$\beta$-methylstyrene up to 29% ee. Other chiral ligands such as bisoxazoline,$^{51}$ bidentate alcohol$^{52}$ and sugar derived Schiff-base ligands$^{53}$ with Mo oxo have been developed. This type of cis-MoO$_2$ moiety with chiral Lewis base ligands only give low or moderate $ee$ for the epoxidation of trans or cis-$\beta$-methylstyrene, because the ligand-metal interaction is not strong enough. Same problem is also observed in the case of Re(VII), MTO with chiral Lewis base ligand.$^{54}$

On the other hand, the development of the ansa-bridged structure of the Cp complex$^{52a-c}$ provided a possibility to introducing a chiral center into the catalyst, which may achieve the asymmetric epoxidation. It was found that the ansa-bridged Mo tricarbonyl complex like 1-15
possesses a comparable catalytic activity to its alkyl- and chloro-analogues of composition 
Cp’Mo(CO)3X (X = alkyl or Cl). However, the modified compounds 1-16 and 1-17 give 
only up to 20% ee in the asymmetric epoxidation of β-methylstyrene in the presence of 
TBHP. The 1H NMR shows that under the reaction conditions, the Cp-Mo-allyl ring break 
down due to the high ring strain.

Four carbon ansa-bridged complexes of the type [(η^5-C5H4(CH2)3-η^1-CH2)-Mo(CO)3] (1-18) and ansa-compounds with cycloalkyl moieties as bridging units (1-19) display greater 
stability under oxidative conditions. They were successfully applied as catalysts in olefin 
epoxidation reactions without noticeable catalyst decomposition or cleavage of the M-C 
bridge during the reaction. However, no chiral analogues of compounds 1-18 and 1-19 
have been reported.

1.6 Objectives

As discussed above, the behavior of the phosphine complexes under oxidant like Br2 suggests that it is possible to achieve a high valent metal phosphine oxide complex by direct 
oxidation method. Also, Mo and W with phosphine oxide give good activity in olefin 
epoxidation. We are interested to synthesize a series of M(CO)4(PNP) (M = Mo and W) and 
to study their reactivities with TBHP and their catalytic activity towards olefin epoxidation. 
Although some metal carbene complexes have been applied for the catalytic oxidation 
reactions as discussed above, the questions whether NHC metal complexes can be widely 
used as catalysts for the oxidation reactions and whether a metal-NHC ligand bond is stable
under strong oxidative conditions have not been addressed clearly enough. In order to search for metal NHC complexes with high catalytic activities toward olefin epoxidations and to understand the stability of the metal-NHC ligand bonds under oxidative conditions, we aim to synthesize some Mo(0) and cyclopentadienyl based Mo(II) carbene complexes and investigate their stability under oxidation conditions and applications in olefin epoxidations.

Obtaining Mo(0) or Mo(II) carbonyl complexes containing phosphine ligand or NHC carbene ligand with stable metal-ligand bond(s) would provide an avenue to introduce chiral phosphine ligand or NHC ligands to Mo(0) or Mo(II) carbonyl core as a possible route to develop active chiral selective catalysts for asymmetric epoxidation in which many systems such as Mo(II), Mo(VI) and Re(VII) have failed.55c-55f,54

1.7 Reference


[28] Elowe, P.R.; McCann, C; Pringle, P.G.; Spitzmesser, S.K.; Bercaw, J.E., Organometallics, 2006, 25, 5255


[33] (a) Moss, J. R.; Shaw, B. L. J. Chem. Soc. (A) 1970, 595. (b) Backhouse, J. R.; Lowe, H.


Chapter Two: Synthesis of Mo(0) and W(0) PNP complexes and their application in olefin epoxidation

Abstract

In this chapter, a series of M(CO)$_4$[Ph$_2$PN(R)PPh$_2$] complexes (R = CH$_2$Ph, M = Mo, $\textbf{2-1a}$; M = W, $\textbf{2-1b}$; R = Ph, M = Mo $\textbf{2-2a}$, M = W, $\textbf{2-2b}$; R = CH$_2$CH$_2$CH$_2$SMe, M = Mo, $\textbf{2-3a}$, M = W, $\textbf{2-3b}$; R = CH$_2$CH$_2$CH$_2$OMe, M = Mo, $\textbf{2-4a}$, M = W, $\textbf{2-4b}$) have been synthesized and characterized. The stability of metal-phosphine ligand bonds in these compounds under oxidative conditions has been investigated. The Mo complexes $\textbf{2-1}$-$\textbf{2-3}$ can be applied as a very active and selective olefin epoxidation catalyst. Under oxidative conditions (in the presence of tert-butyl hydrogen peroxide (TBHP)), compounds $\textbf{2-1}$ – $\textbf{2-4}$ decompose into phosphine oxide and other unidentified species.

2.1 Introduction

Diphosphines containing a single atom as spacer between the donor atoms, such as bis(diphenylphosphanyl)methane (dppm) and bis(diphenylphosphanyl)amine (PNP) belong to the category of short-bite ligands and their coordination chemistry has attracted much interest.\textsuperscript{1} PNP ligands, which have been widely used in complexation reactions, are capable of forming-four-membered chelate rings with the metal center. Another advantage of such ligands is that the preparative routes enable access to various structural modifications.\textsuperscript{2} One popular modification is to introduce a weak donor such as an ether group.\textsuperscript{3} For instance, in Cr-PNP complexes,\textsuperscript{4} the phosphine is firmly anchored to the metal, while the weak M-O interaction can readily be cleaved by substrates. This hemilabile coordination fashion has been widely applied in the design of homogeneous catalysts for different reactions such as
Heck and Suzuki cross coupling reaction\textsuperscript{5}, ethylene oligomerization\textsuperscript{6},\textit{et.al}. Since the first report of X-ray structure of Mo(CO)\textsubscript{4}(Ph\textsubscript{2}PN(Et)PPh\textsubscript{2}) in 1965\textsuperscript{7}, several molybdenum diphosphino amine (PNP) complexes containing different substituents adjacent to the N atom, such as \textsuperscript{1}Pr, allyl, Me, have been synthesized\textsuperscript{8-10}. Although Mo(CO)\textsubscript{6} and W(CO)\textsubscript{6} have been used as efficient catalysts for the olefin epoxidation since 1970\textsuperscript{11}, no M(0) phosphine complexes (including M(0)-PNP complexes) have been used in oxidation catalysis. However, it has been reported that some phosphine oxide complexes of Mo(VI) and W(VI) such as MO\textsubscript{2}Cl\textsubscript{2}(dppmO\textsubscript{2}) (dppmO\textsubscript{2} = bis(diphenylphosphineoxide)methane) give good catalytic activity in olefin epoxidation using TBHP as oxidant.\textsuperscript{12} It has been found that the M(0) complexes, such as M(CO)\textsubscript{4}(dppe) or M(CO)\textsubscript{4}(PEt\textsubscript{3})\textsubscript{2} (M = Mo and W, dppe = 1,2-bis(diphenylphosphanyl)ethane) can be oxidized to M(IV) or higher oxidation state complexes with phosphine oxide as ligand in the presence of oxidants, like thionylhalides\textsuperscript{13} or Cl\textsubscript{2}.\textsuperscript{14} During the oxidation reaction, both the original soft central metal and the soft phosphine ligand(s) are oxidized into hard metal (with higher oxidation state) and hard ligand (phosphine oxide). New coordination between the metal and the oxidized ligand may take place. Therefore, it could be possible to obtain high valent metal phosphine oxide complexes from low valent metal PNP complexes by the direct oxidation reaction. In this context, we are interested in the oxidation of M(0) PNP complexes in the presence of the oxidant TBHP in order to obtain M(VI) complexes containing PNP oxide as ligand. To our best knowledge, reactivities of these PNP complexes under oxidative conditions have not been reported.

In this section, the synthesis of a series of functionalized diphosphino amine Mo and W complexes with or without hemilabile donors and their activity in the olefin epoxidation are described. The structures of these new compounds have been characterized by NMR spectroscopy, IR spectroscopy, ESI or FAB-MS and, in several instances, X-ray crystallography.
2.2 Result and Discussion

2.2.1 Ligand Synthesis

A series of symmetric diphosphino ligands $L_1$- $L_4$ were synthesized according to the reported method.$^4, 15-17$ (see Scheme 2.1). Their resonances in $^{31}P\{^1H\}$NMR spectra appear at ca. 60-70 ppm.($Table$ 2.1)

$$
\begin{align*}
2\text{ PPh}_2\text{Cl} + \text{R-NH}_2 & \xrightarrow{\text{Et}_3\text{N}} \text{CH}_2\text{Cl}_2, \ 0^\circ\text{C} \\
\text{Ph} & \text{N} \\
\text{P} & \text{Ph} \\
\text{R} & \text{Ph} \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\
\text{Ph} & \\}$$

Scheme 2.1 Synthesis of ligands $L_1$-$L_4$

2.2.2 Synthesis and Characterization of Compounds $M(CO)_4Ph_2PN(R)PPh_2$ (2-1 – 2-4).

The tetracarbonyl Mo and W PNP complexes can be conveniently synthesized from the reaction of $M(CO)_3(MeCN)_3$ (M = Mo or W) with PNP ligands in THF based on our unpublished work.$^{10b}$ (see Scheme 2.2) The obtained yellow or white solid was purified by column chromatography and characterized by $^1H$ NMR and $^{31}P\{^1H\}$NMR, IR, FAB-MS or ESI-MS. The FAB for 2-1a, 2-1b, 2-2a, 2-2b and ESI-MS for 2-3a, 2-3b, 2-4a, 2-4b show four CO ligands coordinate to the metal center, in agreement with the X-ray single crystal structure (see below). The fragment of $[M^+]$, $[M^{+}-2CO]$ and $[M^{+}-4CO]$ were observed as strong peak in the MS spectra of 2-1a, 2-1b, 2-2a, 2-2b. In the compounds 2-3a, 2-4a, 2-4b, $[M^+]$ and $[M^{+}- CO]$ were observed. In compound 2-3b, $[M^+ - PPh_2]$ was observed.
Some Mo(CO)$_4$(Ph$_2$PN(R)PPh$_2$) complexes have been prepared from the reaction of the corresponding PNP ligand with the tetracarbonyl precursor Mo(CO)$_4$(μ$_4$-nbd)$_2$\textsuperscript{,2,18} However, in our work, the tricarbonyl precursor M(CO)$_3$(MeCN)$_3$ still yields similar tetracarbonyl products 2-1 – 2-4. This phenomenon has been reported as “CO scrambling”\textsuperscript{19} and it is usually promoted by CH$_2$Cl$_2$. As reported, the reaction can be divided into two steps. The first step involves the reaction between the bidentate ligand (L-L) and Mo(CO)$_3$(MeCN)$_3$ in acetonitrile to yield Mo(CO)$_3$(L-L)(MeCN). In the second step, Mo(CO)$_4$(L-L) is generated by dissolving Mo(CO)$_3$(L-L)(MeCN) in CH$_2$Cl$_2$. If the reaction between Mo(CO)$_3$(MeCN)$_3$ and L-L is carried out in CH$_2$Cl$_2$, the tetracarbonyl product will be generated directly. In our case, THF was used, which is a more substitutionally labile ligand compared to acetonitrile. This provides the possibility for ligand exchange with carbon monoxide, so that the tetracarbonyl products will be formed.
Compounds 2-1 – 2-4 are isolated as yellow or pale yellow solids and purified by column chromatography. They show good stability at room temperature both in solid state and in solution. They can be handled in a laboratory atmosphere and kept under air without decomposition.

The $^{31}$P{$^1$H} NMR spectra of 2-1 – 2-4 showed the expected signals downfield shifted with respect to free ligands (Table 2.1). Similar to the reported compounds Mo(CO)$_4$(Ph$_2$PN(o-C$_6$H$_4$OMe)PPh$_2$)$_2$ (δ 92.4 ppm) and W(CO)$_4$(Ph$_2$PN(iPr)PPh$_2$)$_2$ (δ 63.1 ppm), 2-1a – 2-4a give a singlet signal in the range δ 94.89-90.91 ppm, while a singlet ranging from δ 67.37-71.74 ppm was found for the tungsten analogues, 2-1b – 2-4b. For compounds 2-1a and 2-1b, the $^1$H NMR spectra of the methylene protons adjacent to N atom show a triplet centered at δ 4.12 and 4.07 ppm, respectively, due to the coupling with two equivalent phosphorus atoms. The infrared spectra of most compounds except 2-2a and 2-1b showed four intense v(CO) bands, typically in the region 2023-1870 cm$^{-1}$, consistent with a cis-tetracarbonyl molybdenum fragment$^{20}$. 2-2a gives a sharp peak at 2019 cm$^{-1}$ and a slightly broad peak at 1900 cm$^{-1}$. 2-1b gives a sharp peak at 1890 and two peaks at 1890 and 1879 cm$^{-1}$.

2.2.3 Molecular Structure of Compounds 2-1b, 2-2a, 2-2b, 2-3b, 2-4a, 2-4b Determined by Single Crystal X-ray Diffraction.

The single crystals of compounds 2-1b, 2-2a, 2-2b, 2-3b, 2-4a and 2-4b were obtained from the solution of MeCN at 0 °C. Their solid-state structures are shown in Figures 2.1-2.6 with selected bond lengths and angles. (The single crystal structures of 2-1b, 2-2a and 2-2b are obtained by Ms. Wong Huilin, Valerie. They are shown here for the comparison purpose.) In agreement with the FAB-MS and ESI-MS, in these complexes the metal centre is
coordinated by four CO ligands and the bidentate ligands L1 to L4, which have bite angles of ca. 65°, showing the distorted octahedral geometry. The metal-P-N-P metallacycles is essentially planar.

The Mo-P bonds in 2-4a (2.5213(5), 2.4851(5) Å) and 2-2a (2.5175(4), 2.5082(4) Å) are slightly longer than the reported Mo(CO)4(Ph2PN(o-C₆H₄OMe)PPh2)18 (2.5102(5) 2.4880(5)Å) and Mo(CO)4(OPh)2PN(Ph)P(OPh)28 (2.440(2) 2.427(2)Å) indicating L4 and L2 is a poorer π-acceptor ligand. The bite angle 2-2a (65.380(12)°) and 2-4a (65.083(17)°) are smaller than Mo(CO)4(Ph2PN(o-C₆H₄OMe)PPh2)18 (65.78(2)°) but larger than Mo(CO)4(OPh)2PN(Ph)P(OPh)28 (64.9(1)°). In the W complexes, all of the bite angles are larger than the reported W(CO)4(Ph2PN(iPr)PPh2)8 (64.7(1)°). The bite angle of 2-2b (65.372(18) °) is larger than other three compounds. The bond length of W-P (2.5078(6) and 2.4998(5) Å) in 2-2b is slightly longer than W(CO)4(Ph2PN(iPr)PPh2) (2.481(2) 2.500(3) Å)8. The M-CO bonds trans to ligand PNP are marginally shorter than the other two M-CO bonds. For instance, in 2-2a, Mo-C(10) (1.9910(17) Å ) and Mo-C(8)(1.9951(16) Å) are shorter than Mo-C(7) (2.0407(17) Å) and Mo-C(9) (2.0263(16)Å), although not as significant as in the Mo(CO)4(dppm)21, indicating the larger trans effect of CO than phosphine.
**Figure 2.1** ORTEP diagram of compound 2-1b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): W(1)-P(1) 2.5025(10), W(1)-P(2) 2.4694(11), W(1)-C(8) 1.986(4), W(1)-C(9) 2.033(5), W(1)-C(10) 2.013(5), P(1)-N(1), 1.719(3), P(2)-N(1) 1.709(3), W(1)-C(11) 2.008(5), P(1)-W(1)-P(2) 65.34(4), P(1)-N(1)-P(2) 103.05(17)

![ORTEP diagram of compound 2-1b](image)

**Figure 2.2** ORTEP diagram of compound 2-2a (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-P(1) 2.5175(4), Mo(1)-P(2) 2.5082(4), Mo(1)-C(7) 2.0407(17), Mo(1)-C(8) 1.9951(16), Mo(1)-C(9) 2.0263(16), Mo(1)-C(10) 1.9910(17), P(1)-N(1) 1.7142(12), P(2)-N(1) 1.7116(12), P(1)-Mo(1)-P(2) 65.380(12), P(1)-N(1)-P(2) 104.80(6)

![ORTEP diagram of compound 2-2a](image)
Figure 2.3 ORTEP diagram of compound 2-2b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): W(1)-P(1) 2.5078(6) W(1)-P(2) 2.4998(5), W(1)-C(7) 1.990(2), W(1)-C(8) 2.016(2), W(1)-C(9) 1.991(2), W(1)-C(10) 2.034(3), P(1)-N(1), 1.7116(18), P(2)-N(1) 1.7115(17), P(1)-W(1)-P(2) 65.372(18), P(1)-N(1)-P(2) 104.37(9)
Figure 2.4 ORTEP diagram of compound 2-3b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): W(1)-P(1) 2.4804(10), W(1)-P(2) 2.5043(9), W(1)-C(5) 2.009(4), W(1)-C(6) 1.980(4), W(1)-C(7) 2.033(4), W(1)-C(8) 1.984(4), P(1)-N(1) 1.704(3), P(2)-N(1) 1.702(3), P(1)-W(1)-P(2) 64.92(3), P(1)-N(1)-P(2) 103.55(16)

Figure 2.5 ORTEP diagram of compound 2-4a (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-P(1) 2.5213(5), Mo(1)-P(2) 2.4851(5), Mo(1)-C(5) 2.021(2), Mo(1)-C(6) 1.987(2), Mo(1)-C(7) 2.041(2), Mo(1)-C(8) 1.997(2), P(1)-N(1) 1.7103(17), P(2)-N(1) 1.7018(16), P(1)-Mo(1)-P(2) 65.083(17), P(1)-N(1)-P(2) 104.24(9)
Figure 2.6 ORTEP diagram of compound 2-4b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): W(1)-P(1) 2.4757(7), W(1)-P(2) 2.5088(7), W(1)-C(5) 1.993(3), W(1)-C(6) 2.035(3), W(1)-C(7) 1.990(3), W(1)-C(8) 2.015(3), P(1)-N(1), 1.703(2), P(2)-N(1) 1.706(2), P(1)-W(1)-P(2) 65.00(2), P(1)-N(1)-P(2) 103.58(11)

2.3 Application of Compounds 2-1 - 2-3 in Epoxidation Catalysis.

Complexes 2-1 - 2-3 have been examined as catalysts for the epoxidation of cyclooctene with TBHP. Compounds 2-4a and 2-4b were not involved due to their similar analogues to 2-3. The time-dependent curves for all catalytic reactions are shown in Figure 2.7. The epoxide yields after 4 h, 8 h and 24 h of reaction time using 2-1 - 2-3 as catalysts are shown in Figure 2.8. There was no significant formation of by-products (e.g. diol). Controlled reactions without catalysts showed no significant formation of the epoxide product. In order to test the catalytic activity of the free PNP ligand, L3 was also involved in the catalytic reaction, resulting epoxide only 4% at 24 h, 55 °C.
Figure 2.7. Time dependent yield of cyclooctene epoxide in the presence of compounds 2-1 to 2-3 as catalysts at 55 °C (Mo-based catalysts) or 90 °C (W-based catalysts) using TBHP as oxidant (catalyst : substrate : oxidant = 1:100:200).
The molybdenum complex \textbf{2-3a} is the best catalyst as shown in Figure 2.7. 100% yield was achieved after 4h reaction time. \textbf{2-3a} shows similarly high activities towards olefin epoxidation to the classic catalyst \textit{CpMo(CO)}_3\textit{Cl}^{22} and \textit{CpMo(CO)}_3(\textit{CH}_3)^{23}. The catalytic activities of compounds \textbf{2-1a} and \textbf{2-2a} are comparable to those of the \textit{MoCl}_2(\textit{O})_2(\textit{dppmO})^{12}, yielding 63% (6h) and 100% (24h) of epoxide in at 55°C, respectively. Compared to the Mo(0) complexes, compound \textbf{2-1a} - \textbf{2-3a} are more active than the reported tetracarbonyl Mo(bpy) complexes, which can be oxidized to oxo Mo(bpy) polymer and can catalyze the transformation of olefin to epoxide with 20% conversion at 55 °C after 6 h reaction time.\textsuperscript{24}

The W-PNP analogues, \textbf{2-1b} - \textbf{2-3b} catalyze cyclooctene to epoxide up to 60% at 90 °C after 24 h reaction time. The catalytic activity is lower than the polymer-supported tungsten carbonyl catalysts\textsuperscript{25} with \textit{H}_2\textit{O}_2, although no epoxide was generated by using TBHP as oxidant in that example. Compared to the W(VI) dioxo complexes with phosphine oxide, \textit{WCl}_2\textit{O}_2(\textit{dppmO})^{12}, \textbf{2-1b} - \textbf{2-3b} also show lower activity. Other reported W(VI) dioxo complexes, such as \textit{WCl}_2(\textit{O})_2(\textit{DME})^{26} catalyzes the epoxidation of \textit{cis}-cyclooctene resulting 75% of conversion at 90 °C after 6 h reaction time. The catalytic reactivity of WX_2(\textit{O})_2(\textit{L})_2 compounds (X = Cl or alkyl and L = bidentate nitrogen donors) have also been reported with low epoxide yields, i.e., about 30-40% at 90 °C after 6 h reaction time.\textsuperscript{26} These dioxo compounds have comparable catalytic activity to \textbf{2-1b} - \textbf{2-3b}.

The activities observed are almost independent of the substituent on the PNP ligands, although among them, compounds \textbf{2-3a} are slightly more active among the Mo complexes. \textbf{2-3b} did not show significantly higher activities compared to other two W-based catalysts.
During the course of catalytic reactions, the yellow color of 2-1 - 2-3 paled. This suggests that complexes 2-1 - 2-3 are oxidized during the oxidation reaction and the oxidative products are fairly active toward epoxidation.

2.4 The Behavior of 2-1a, 2-1b and 2-3b under Oxidative Conditions.

Kinetic $^1$H NMR and $^{31}$P NMR experiments on the oxidation reactions of 2-1a and 2-1b were carried out by treatment with 5-fold excess of TBHP (5.0-6.0 M in decane) at room temperature in CDCl$_3$. During the reaction, a yellow precipitate was formed. In the case of 2-1a, the singlet signal of the complex at $\delta$ 94.30 ppm in $^{31}$P NMR completely disappeared after 30 min. A new single signal at $\delta$ 31.29 ppm was observed after 5 min of the addition of TBHP. In $^1$H NMR spectrum, after 5 min of oxidation reaction, beside the signal of NC$_{6}H_{5}$ at 4.12 ppm, a new triplet signal appeared at $\delta$ 4.40 ppm with some weak multiplets. After 30 min, only the peak at $\delta$ 4.40 ppm and the weak multiplets can be observed in the spectrum. The IR study of the residue shows a sharp signal at 1211 cm$^{-1}$, which was assigned to P=O stretching frequency. And also, two bands appearing at 973 and 905 cm$^{-1}$ indicate the Mo=O vibrations.

Similar observations were noted in the oxidation reaction of 2-1b with TBHP. After 15 min, the signal at $\delta$ 30.88 ppm appeared at $^{31}$P NMR as singlet and $\delta$ 4.40 ppm at $^1$H NMR spectrum as triplet. Different from 2-1a, the resonance of 2-1b at $\delta$ 70.82 ppm at $^{31}$P NMR decreased slowly, and remained in the spectrum after 60 min. The phosphorus signal at c.a. $\delta$ 31 ppm can be assigned to the oxide of L1, [(Ph)$_2$P(O)N(CH$_2$Ph)P(O)(Ph)$_2$] as reported recently.$^{16}$

As for Compound 2-3b containing a S donor in the PNP ligand, in the $^{31}$P NMR spectrum, a new peak at $\delta$ 31.23 ppm is formed after 10 mins reaction time with TBHP. The singlet
signal at $\delta$ 67.44 ppm disappeared completely after 6 hours. In the $^1$H NMR, the resonance of NCH$_2$(CH$_2$)$_2$SMe at $\delta$ 3.03-2.98, shifted to 3.46-3.35 ppm after 6h. In order to identify the newly appeared NMR signals, the oxidation reaction of L3 with TBHP has been monitored by NMR. The $^{31}$P NMR signal at $\delta$ 63.46 ppm of ligand L3 disappears after 10 min of the reaction. A new singlet signal was observed at $\delta$ 31.46 ppm. In $^1$H NMR, the resonance of NCH$_2$(CH$_2$)$_2$SMe at $\delta$ 3.37-3.31 shifted to $\delta$ 3.45-3.30 ppm. Therefore, the new peaks can be identified to the phosphine oxide. Like 2-1a and 2-1b, M-P bond of 2-3b cleaved and phosphine oxide formed during the oxidation reaction.

As mentioned above, phosphine oxide can be used as ligand. Some examples show that the coordination of the phosphine oxide to high valent metals such as Mo(VI) and W(VI) leads to the chemical shift of $^{31}$P NMR to lower field. For instance, the chemical shift of MO$_2$Cl$_2$(dppmO$_2$) in CH$_2$Cl$_2$ appear at $\delta$ 38.4 (M = Mo) and 39.6 ppm (M = W), while the free ligand dppmO$_2$ resonances at $\delta$ 23.0 ppm. For MO$_2$Cl$_2$(L)$_2$ (L = P(O)MePh$_2$ $\delta$ = 30.0 ppm), the resonance of phosphorus appears at $\delta$ 44.4 (Mo) and 46.4 (W) ppm, respectively. However, no new $^{31}$P NMR signal located at lower field than that of the free ligand (phosphine oxide) has been observed after the oxidation of compounds 2-1a, 2-1b and 2-3b by TBHP. This indicates that after oxidation, compounds 2-1a, 2-1b and 2-3b are decomposed giving ligand oxide. No high valent metal phosphine oxide complex was formed during the oxidation reaction. The definite structure of the oxidized metal moiety is still unknown. However, this moiety could be the active catalyst for the olefin oxidation. W complexes show better oxidation resistance than the Mo analogues.

To compare with the four-membered metallacycle ring of diphosphino amine complexes, the oxidation resistance of M(CO)$_4$(dppe) (M = Mo or W) were tested under the same reaction conditions. Similar to the cases of 2-1 and 2-3b, the oxidation reaction of Mo(CO)$_4$(dppe) completes after 3 hours and the resonance of $^{31}$P signal shifts from $\delta$ 55.9 to
35.9 ppm. In the case of W(CO)₄(dppe), after 20min, a new signal appears at δ 36.6 ppm. Compared with the Mo-based complex, the reaction is fairly slow. After 3h reaction time, the signal at δ 41.2 ppm is still obvious. It has been reported that the ³¹P NMR signal in dppeO₂ complexes MoCl₄(dppeO₂) (dppeO₂ = bis(diphenylphosphineoxide)ethane) is at δ 31.6 ppm and in WOCl₃(dppeO₂) is at δ 30.9 ppm in DMSO.¹³ Comparing with the oxidation result of the free ligand dppe, the signal at c.a. δ 36 ppm can be assigned to free dppeO₂. Therefore, the five-membered metallacycle ring does not promote the formation of new M(VI) phosphine oxide compound after oxidation by TBHP either.

2.5 Conclusions

In this work, a series of diphosphino amine complexes with formula M(CO)₄(Ph₂PN(R)PPh₂) (M = Mo and W) have been synthesized and characterized. Complexes 2-1a - 2-4a show high activity that is comparable to phosphine oxide compound MoCl₂(O)₂(dppeO₂). W-based catalysts showed a lower reactivity than Mo-based catalysts even at higher temperature (90°C). The reactivities of 2-1a, 2-1b and 2-3b in the presence of TBHP were tested. The M-P bond cleaved under this condition, and the formation of ligand oxide were detected by ³¹P NMR, suggesting that the high oxidations state metal phosphine oxide complexes cannot be generated by directly oxidation of M(0) phophine complexes by TBHP.

2.6 Experimental Section

General Considerations. All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures.
and distilled under nitrogen and used immediately. TBHP (tert-butyl hydrogen peroxide, 5-6 M in decane) was purchased from Sigma-Aldrich. Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. $^1$H and $^{31}$P NMR were measured in CDCl$_3$ with AMX500 500 MHz FT NMR or AMX300 300 MHz FT NMR spectrometers. ($^1$H at 500 MHz, $^{31}$P at 202.40MHz or $^1$H at 300 MHz, $^{31}$P at 121.44MHz ). IR spectra were recorded on a Shimadzu IR-470 spectrometer using KBr pellets as IR matrix. ESI-MS was performed on a Finnigan LCQ quadrupole ion trap mass spectrometer. Sample was introduced into the ESI-source using a syringe pump. The following ESI-MS parameters were kept constant for all measurement: Spray voltage = +/- 3.5kV; Capillary Temperature = 100°C; Flow rate = 5 µL min$^{-1}$; Tube lens offset = 0V and capillary voltage = 0V. The spectra were obtained as an average of at least 20 scans. FAB-Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Catalytic runs were monitored by GC methods on the Agilent 6890 Series GC instrument with a J&W DB-1 column. The preparation of M(CO)$_3$(MeCN)$_3$ (M = Mo or W, 1.2 mmol) and M(CO)$_4$(dppe) (M = Mo and W) were based on the literature procedure.

2.6.1 Synthesis of Compound 2-1 to 2-4

L1-L4 (1 mmol) were added separately to a solution of M(CO)$_3$(MeCN)$_3$ (M = Mo or W, 1.2 mmol) in THF (20 mL). After stirring at 40 °C for 24 h, the reaction mixture was dried under vacuum and the resulted yellow solid was purified by column chromatography eluted by a mixture of hexane and ethyl acetate (10:1 to 5:1) to give the product as a yellow or white solid.

**Mo(CO)$_4$(bzPNP) (2-1a)** (460mg, yields 67 %) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) = 7.50-7.39 (m, 21H, Ph), 6.87(m, 2H, Ph), 6.32 (d, 2H, Ph), 4.12 (t, 2H, NCH$_2$Ph, $^2$J$_{H,P}$ =
10Hz). $^{31}$P{\textsuperscript{1}H}NMR(202.40 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 94.30(s). IR (KBr)/cm$^{-1}$: v(CO) 2018 (vs), v(CO) 1926(vs), v(CO) 1886(vs), v(CO)1877(vs). FAB-MS(+) m/z(%): 685.0 (86) [M$^+$], 629.1 (64) [M$^+$-2CO], 573.1(100) [M$^+$-4CO] Anal. Calcd for C$\textsubscript{35}$H$\textsubscript{27}$NO$\textsubscript{4}$P$\textsubscript{2}$Mo: C, 61.50; H, 3.98; N, 2.05. Found: C, 61.68; H, 4.27; N, 1.85.

W(CO)$_\textsubscript{4}$(bzPNP) (2-1b) (540mg, yields 70%) $^1$H NMR (500 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 7.49-6.88(m, 25H, Ph), 4.07(t, 2H, CH$_\textsubscript{2}$Ph, $^2$J$_{H-P}$ = 10.5Hz). $^{31}$P{\textsuperscript{1}H}NMR(202.40 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) =70.86 (s) IR (KBr)/cm$^{-1}$: v(CO) 2013 (vs), v(CO) 1890(vs), v(CO)1879(vs). FAB-MS(+) m/z(%): 771.2 (100) [M$^+$], 715.1(40) [M+-2CO], 659.2(16) [M+-4CO] Anal. Calcd for C$\textsubscript{35}$H$\textsubscript{27}$NO$\textsubscript{4}$P$\textsubscript{2}$W: C, 54.50; H, 3.53; N, 1.82. Found: C, 54.61; H, 3.73; N, 1.78.

Mo(CO)$_\textsubscript{4}$(PhPNP) (2-2a) (450mg, yields 67%) $^1$H NMR (300 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 7.47-7.37(m, 20H, Ph), 7.05-6.91(m, 3H, Ph), 6.51-6.89(d, 2H, Ph). $^{31}$P{\textsuperscript{1}H}NMR(121.44 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 94.89 (s) IR (KBr)/cm$^{-1}$: v(CO) 2014 (vs), v(CO) 1900(vs). FAB-MS(+) m/z(%): 671.1(80)[M$^+$], 615.0 (48) [M+-2CO], 559.1(100)[M$^+$-4CO]. Anal. Calcd for C$\textsubscript{34}$H$\textsubscript{25}$NO$\textsubscript{4}$P$\textsubscript{2}$Mo: C, 53.92; H, 3.33; N, 1.85. Found: C, 53.95; H, 3.67; N, 1.84.

W(CO)$_\textsubscript{4}$(PhPNP) (2-2b) (400mg, yields 54%) $^1$H NMR (500 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 7.46-7.40(m, Ph) $^{31}$P{\textsuperscript{1}H}NMR(202.40 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 71.74 (s) IR (KBr)/cm$^{-1}$: v(CO) 2014 (vs), v(CO) 1916(vs), v(CO) 1894(vs), v(CO) 1876(vs). FAB-MS(+) m/z(%): 757.0(76) [M$^+$], 701.0(36)[M$^+$-2CO], 645.1 (36) [M$^+$-4CO]. Anal. Calcd for C$\textsubscript{34}$H$\textsubscript{25}$NO$\textsubscript{4}$P$\textsubscript{2}$W: C, 53.92; H, 3.33; N, 1.85. Found: C, 53.95; H, 3.67; N, 1.84.

Mo(CO)$_\textsubscript{4}$(PNPS) (2-3a) (460mg, yield 68%) $^1$H NMR (500 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 7.48 (m, 20H, Ph), 3.05 (m, 2H, CH$_2$CH$_2$CH$_2$SC$_3$), 2.00 (m, 2H, CH$_2$CH$_2$CH$_2$SC$_3$), 1.78(s, 3H, CH$_2$CH$_2$CH$_2$SC$_3$), 1.26(m, 2H, CH$_2$CH$_2$CH$_2$SC$_3$). $^{31}$P{\textsuperscript{1}H}-NMR(202.40 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) = 91.02(s). IR (KBr)/cm$^{-1}$: v(CO) 2020 (vs), v(CO) 1920(vs), v(CO) 1902(vs), v(CO)1870(vs). ESI-MS(+) m/z(%): 530.1(100) [M$^+$-CH$_3$-Ph-2CO], 544.1 (35) [M$^+$-Ph-MeSCH$_2$], 665.9 (10)[M$^+$- CO]
W(CO)₄(PNPS) (2-3b) (550mg, yield 71%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.49-7.41 (m, 20H, Ph), 3.01 (m, 2H, N CH₂CH₂CH₂SCH₃), 2.00 (m, 2H, N CH₂CH₂CH₂SCH₃), 1.79(s, 3H, CH₂CH₂CH₂SCH₃), 1.30(m, 2H, CH₂CH₂CH₂SCH₃). ³¹P {¹H}- NMR (202.40 MHz, CDCl₃): δ (ppm) = 67.52(s) IR (KBr)/cm⁻¹: ν(CO) 2019 (vs), ν(CO) 1935(vs), ν(CO) 1893(vs), ν(CO)1870(vs). ESI-MS(+) m/z(%): 580.1 (100) [M⁺–PPh₂]

Mo(CO)₄(PNPO) (2-4a) (460mg, yield 70%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.52-7.47 (m, 20H, Ph), 3.06-2.90 (m, 2H, NCH₂CH₂CH₂OCH₃), 1.37-1.35 (m, 2H, NCH₂CH₂CH₂OCH₃), 1.25(s, 3H, NCH₂CH₂CH₂OCH₃), 0.89(m, br, 2H, NCH₂CH₂CH₂OCH₃). ³¹P {¹H}-NMR(202.40 MHz, CDCl₃): δ (ppm) = 90.91(s). IR (KBr)/cm⁻¹: ν(CO) 2023 (vs), ν(CO) 1908(vs), ν(CO)1867(vs), ν(CO) 1851(vs). ESI-MS(+) m/z(%): 687.7(100) [M⁺+H₂O], 633.9 (30) [M⁺-CO], 585.4 (30) [M⁺-3CO], 555.15 (60) [M⁺-4CO]

W(CO)₄(PNPO) (2-4b) (560mg, yield 74%) ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.52-7.47 (m, 20H, Ph), 3.06-2.90 (m, 2H, NCH₂CH₂CH₂OCH₃), 2.91 (t, 2H, NCH₂CH₂CH₂OCH₃), 2.17(s, 3H, NCH₂CH₂CH₂OCH₃), 0.8(m, br, 2H, NCH₂CH₂CH₂OCH₃). ³¹P {¹H}-NMR(121.44 MHz, CDCl₃): δ (ppm) = 67.37(s). ESI-MS(+) m/z(%): 775.8 (15) [M⁺+H₂O], 755.8 (10) [M⁺]

2.6.2 X-ray Crystallography

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS. Structure solutions and refinements were performed by using the programs SHELXS-97 and SHELXL-97. The structures were solved by direct
methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically.

2.6.3 Catalytic reactions.

_Cis-_Cyclooctene (0.4 g, 3.6 mmol), mesitylene (1 g, internal standard) and compounds 2-1 - 2-4 as catalysts (1 mol%, 0.036 mol) were added to the reaction vessel under an air atmosphere at 55 °C (Mo-based complexes) or 90 °C (W-based complexes). The reaction was started by the addition of TBHP (7.3mmol, 1.36mL, 5.0-6.0 M in _n_-decane). The course of the reactions was monitored by quantitative GC analysis (Agilent 6890 Series GC instrument with a J&W DB-1 column). Samples were taken in regular time intervals, diluted with CH₂Cl₂, and treated with a catalytic amount of MgSO₄ and MnO₂ to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into the GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (_r² = 0.999_) recorded prior to the reaction course.

2.7 Reference


[31] (a) Sheldrick, G. M. SHELXS-97 Program for crystal structure solution, University of
Göttingen, Göttingen, Germany, 1997; (b) Sheldrick, G. M. SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.
Chapter Three: Synthesis and Characterization of Molybdenum (0) and Tungsten (0) carbonyl N-Heterocyclic Carbene Complexes and Their Application in Olefin Epoxidation

Abstract:

A series of Mo(0) and W(0) N-heterocyclic carbene (NHC) complexes have been synthesized and fully characterized, including tetracarbonyl complexes M(CO)_4(NHC)_2 (NHC = IBz = 1,3-dibenzylimidazol-2-ylidene, M = Mo, 3-1a, M = W, 3-1b; NHC = InPr = 1,3-dipropylimidazol-2-ylidene, M = Mo, 3-2a, M = W, 3-2b); heptacarbonyl complexes M(CO)_5(IMes) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, M = Mo, 3-3a; M = W, 3-3b); bidentate NHC complex Mo(CO)_4(PyNHC) (PyNHC = 3-methyl-1-picolylimidazol-2-ylidene, 3-4) and tridentate NHC complex Mo(CO)_3(Py_2NHC) (Py_2NHC = 1,3-dipicolylimidazol-2-ylidene, 3-5). The reactivity of the monodentate and polydentate NHC complexes under oxidative condition has been investigated. Compound 3-1 to 3-5 can be applied as catalysts in the olefin epoxidation with moderate activities and good selectivity towards epoxide.

3.1 Introduction

Since the discovery of the first free stable N- hetercyclic carbene (NHC) ligand in 1991\textsuperscript{1}, NHCs have been widely used as spectator ligands in the application of transition metal complexes catalyzed reactions, such as C-C/C-N coupling, olefin metathesis, hydrogenation, etc.\textsuperscript{2} Recently, significant progress has also been achieved in the field of oxidation catalysis. A variety of oxidation reactions have been studied using NHC catalysts, such as O\textsubscript{2}/CO fixation, the oxidation of alcohols, alkyne, and terminal olefins, and most of the work in this
area was conducted with late transition metal catalysts. Because of the strong metal carbon bond, NHC complexes show extraordinary stability towards strong oxidizing agents like peroxodisulfate which makes it possible to achieve good activity in the oxidation reaction. As a strong sigma donor, NHC carbene has the property to stabilize the metal center of high oxidation state. However, the study of the coordination of high valent metal complexes with NHC ligand still remains in the early stages of development. The only two examples of dioxo Mo(VI) and W(VI) N-heterocyclic carbene complexes were provided by Herrmann and Royo in 1996 and later on.

Recently, the capability of Mo(II) and W(II) based carbene complexes to catalyze the olefin epoxidation with tert-butyl hydroperoxo (TBHP) or H₂O₂ has been studied by Royo et al. The catalysts show moderate to good activity. However, decomposition of these compounds was also found under the reaction condition. Compared with the study of Mo(II), Mo(0) based NHC complexes have been synthesized many years ago. Their crystal structures and low temperature dynamic behavior have been studied, but their oxidative decarbonylation reaction has never been investigated.

On the basis of study of the catalytic properties of Mo(0) and W(0) based NHC complexes toward the olefin epoxidation, and also the stability of their metal-NHC ligand bonds under strong oxidative conditions, we decided to expand our studies to the preparation of monodentate NHC based complexes with the formula M(CO)ₓ(NHC)₆₋ₓ (M = Mo and W, x = 4 or 5), and their catalytic applications. Their reactivities toward TBHP were studied by NMR and IR. The polydentate ligand was capable to stabilize the Mo or W oxo species. To compare with the monodentate ligand based complexes, two chelating Mo complexes were also prepared and their activity and reactivity was tested under the same condition.

### 3.2 Result and Discussion
3.2.1 Synthesis and Characterization of Compounds M(CO)₄(NHC)₂ (3-1 to 3-2).

The tetracarbonyl Mo and W NHC complexes were conveniently synthesized from the reaction between M(CO)₃(MeCN)₃ (M = Mo or W) and free carbene (prepared in situ) in THF (see Scheme 3.1). Compounds 3-1 and 3-2 were isolated as yellow solid and purified by column chromatography. No further attempt was made to improve the yield. They are stable at room temperature both in solid state and in solution. They can be handled in laboratory atmosphere and kept under air without decomposition.

![Scheme 3.1 Synthesis of compounds 3-1 – 3-2](image)

The composition and structure of compounds 3-1 and 3-2 were determined by elemental analysis, IR and NMR-spectroscopy (¹H, ¹³C), and FAB-MS.

From the mass spectra, four CO ligands were indicated to coordinate to the metal center. In the ¹³C NMR spectra, signals of the carbene carbon appear at δ 196.6 and 194.6 ppm for the two Mo complexes, and δ 190.0 and 188.1 ppm for the W analogues. The inequivalent of the two set of four carbonyls e.g. 3-1a at δ 218.5 and 210.4 ppm or 3-1b at δ 213.9 and 210.0 ppm suggests that the two carbene ligands are cis oriented in agreement with their IR spectra. In contrast, the similar structure W(CO)₄(bis-carbene)⁸a shows the chemical shift of the carbene carbon at δ 188.9 ppm, and two peaks of CO at δ 204.6 and 214.3 ppm. The chemical
shift of $^{13}$C(NHC) in the reported Mo(CO)$_4$(IMe)$_2$ (IMe=1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) appear at $\delta$ 201.3 ppm$^{8a}$. And the CO in Mo(CO)$_5$(L)$_{11}$ (L = 1,3,4,5-tetramethylimidazol-2-ylidene) appear at $\delta$ 212.60, 207.50 ppm. In $^1$H NMR spectra, the substituted groups on two NHC ligands show chemically equivalent, suggesting the symmetric coordination environment. Four protons in N-CH$_2$-Ph of 3-1a show only one singlet at 5.37 ppm, while the methylene groups in the same ligand display an AB type quartet in CpMo(CO)$_2$(IBz)Br (see Chapter 4), indicating the two protons are diastereotopic which may be due to restricted ligand rotation$^{12}$ at room temperature.

The Mo based complexes 3-1a and 3-2a give three strong absorptions of CO range from 1993-1810 cm$^{-1}$ and 1987-1832 cm$^{-1}$ indicate the cis-configuration, which are comparable to the reported Mo(CO)$_4$(IMe)$_2$$^{8a}$ with four CO absorptions at 1991-1835 cm$^{-1}$. The W-based 3-1b and 3-2b at 1982-1812 cm$^{-1}$ 2013-1879 cm$^{-1}$ are also comparable to analogue W(CO)$_4$(IMe)$_2$ at 1990-1837 cm$^{-1}$

Comparing with the reagent M(CO)$_3$(MeCN)$_3$, the product is a complex with four CO’s. This phenomenon was described as “CO scrambling” by Heinze et al.$^{10}$ as ligand exchange between MeCN and CO. (see chapter 2) The additional ligand CO in the final product was assumed to come from the M(CO)$_3$ moiety which may somewhat decrease the yield of the product. However, compared to the synthetic route of the tetracarbonyl metal precursor like Mo(CO)$_4$(nbd) (nbd = norbornadiene) $^{13}$, the preparation of M(CO)$_3$(MeCN)$_3$ is believed to be more convenient and efficient.

Increasing the amount of the imidazolium salt or increasing the reaction temperature did not yield the tricarbene product.

3.2.2 Synthesis and Characterization of Compounds 3-3 to 3-5.
Compounds 3-3 to 3-5 are prepared using the silver mediated transmetallation route\textsuperscript{14}. M(CO)\textsubscript{3}(MeCN)\textsubscript{3} (M = Mo or W) react with silver carbene which was formed \textit{in situ} generating 3-3 to 3-5 as products. (see Scheme 3.2). The compounds 3-3\textsuperscript{a}, 3-3\textsuperscript{b} can be also obtained directly by using free carbene, however, with lower yield and some unidentified by-product. Compounds 3-3\textsuperscript{a}, 3-3\textsuperscript{b} are isolated as pale yellow solid while 3-4, 3-5 are yellow. All of the compounds can be purified by column chromatography. No further attempt was given to improve the yield. They show good stability at room temperature, can be handled in laboratory atmosphere and kept under air without decomposition.

\begin{align*}
\text{Scheme 3.2 Synthesis of compounds 3-3 – 3-5}
\end{align*}

The composition and structure of compounds 3-3 to 3-5 were determined by elemental analysis, IR and NMR-spectroscopy ($^1$H, $^{13}$C) and FAB-MS. In the case of 3-3\textsuperscript{a} and 3-3\textsuperscript{b}, five carbonyl complexes was indicated from the spectra of FAB-MS(+). In the $^1$H NMR spectra of 3-3\textsuperscript{a} and 3-3\textsuperscript{b}, four $o$-methyl on the NHC ligands appear as a singlet (12H), indicating the equivalent environment of the two mesityl group. In the $^{13}$C NMR spectra, the
chemical shifts of the carbene carbon appear at $\delta$ 193.6 (3-3a) and 185.6 ppm (3-3b), similar as that in 3-1 and 3-2. CpM(CO)$_2$(IMes)H ($M = Mo$ and $W$, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)$^{15}$ containing same NHC ligand show chemical shift of the carbene carbon at $\delta$ 200.2 ppm (Mo-based analogue) and $\delta$ 184.1 ppm (W-based analogue) which is comparable to 3-3a and 3-3b respectively. The chemical shift of the five CO ligands in 3-3a ($\delta$ 211.4 and 205.3 ppm) are comparable to that of the reported Mo-based carbene complex Mo(CO)$_5$(L)$^{11}$ (L = 1,3,4,5-tetramethylimidazol-2-ylidene) at $\delta$ 212.60, 207.50 ppm. Similarly, the chemical shift of the five CO in 3-3b are indicated as normal ($\delta$ 200.4 and 197.0 ppm) compared to the reported analogue$^{11}$ ($\delta$ 201.75 and 199.02 ppm).

Compound 3-3a was firstly synthesized by the reaction with BEt$_3$(IMes) with Mo(CO)$_6$$^{8d}$. Like 3-1 and 3-2, increasing of the amount of NHC ligand cannot afford the dicarbene or tricarbene complexes. This may be partly due to the steric hindrance of the mesityl group on the ligand.

Compounds 3-4 and 3-5 containing NHC chelate ligands were thought to be more stable than 3-1a to 3-3a. FAB-MS spectrum of 3-4 suggests four carbonyls bind to Mo. For compound 3-5, FAB-MS show three COs. The $^{13}$C chemical shifts of the carbene carbon in compound 3-5 appear at 198 ppm, comparing with 3-4 (186 ppm), showing a slightly deshielding effect by the two pyridine groups. In compound 3-5, the three signals of the inequivalent carbonyls ($\delta$ ca. 224, 218 and 208 ppm) suggest that they are $fac$ oriented. In compound 3-4, three signals (225, 209, 201 ppm) were assigned to four CO. The chemical shift of carbene carbon in 3-4 and 3-5 shift to upfield compared to the monodentate NHC complexes mentioned previously$^{8a}$ ($\delta$ 220 to 230 ppm). The chemical shifts of CO in 3-4 and 3-5 are comparable to the other pyridine functionalized chelated Mo complexes$^{16}$ (ca. $\delta$ 220-210 ppm) In the $^1$H NMR spectrum of 3-5, the inequivalence of two NCH$_2$Py (singlet at ca. $\delta$ 5.61 and 5.14 ppm) suggests that the NHC ligand of 3-5 does not symmetrically coordinate to
the metal center. The splitting of these two methylene however, was not observed in the similar structure Pd(Me)(Py₂NHC)BF₄ which give only one singlet signal at δ 5.44 ppm at 60 °C or broad signal at room temperature.

3.2.3 Molecular Structure of Compounds 3-1b and 3-4 Determined by Single-Crystal X-ray Diffraction.

The single crystals of compounds 3-1b and 3-4 were obtained from the solution of MeCN at -19 °C. The solid-state structures are shown in Figures 3.1 and 3.2 with selected bond lengths and bond angles. In agreement with the NMR and IR data, in 3-1b, two carbene ligands are in cis configuration. The W-C(NHC) bond is 2.279(6) Å. The W-CO bond lengths are 1.966(7) (trans to L) and 2.021(4) Å (cis to L). In contrast, the bond lengths in the 16 electron W(II) carbene species [CpW(CO)₂IMes]⁺, W-C(NHC) (2.188(12) Å) and W-CO (1.928(15) and 1.934(19) Å) are shorter. The reported mono carbene complex W(CO)₅(NHC)₁¹ give a comparable bond length of W-C(NHC) (2.275(8) Å), and W-CO (cis to L as ca. 2.07-2.00 and trans to L as 1.973(11) Å). The decrease of bond length trans to carbene ligand indicates the NHC ligand as a strong donor ligand. CO-W-C(NHC) angles at ca. 90° or 180° indicate a slightly distorted octahedron configuration. N-C-W angles are almost equivalent (128.8(4) and 128.8(3) Å). In contrast, the two angles in [CpW(CO)₂IMes]⁺ are significantly different (113.9(8), 146.6(8) °) showing the distortion of NHC ligand.

In compound 3-4, the bite angle between the C(NHC) and N(Py) is 79.26(19)°, suggesting a considerable distorted octahedron configuration. The bite angle in 3-4 is smaller than the same ligand bound to Pd with the bite angle as 87°. The Mo-C(NHC) bond is 2.239(6) Å, shorter than the complex monodentate carbene Mo complexes (2.26(1)-
2.33(1)Å$^8a$. The pyridine coordinates to the Mo center with a Mo-N distance of 2.331(5)Å comparable to the Mo-N distance in Mo(CO)$_4$(PN)$_2$ (2.273 to 2.296 Å) (PN = 2-PyNHP(R)$_2$). Among the four carbonyl, the Mo–CO bond $trans$ to the pyridine N atom are shortest (1.946(6) Å), in agreement with the reported pyridine-Mo complexes$^{16}$.

![Figure 3.1. ORTEP diagram of compound 3-1b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): W(1)-C(1) 2.279(6), W(1)-C(18) 1.966(7), W(1)-C(19) 2.021(4), C(1)-W(1)-C(1A) 92.9(3), C(18)-W(1)-C(19) 86.5(2), C(18)-W(1)-C(1A) 175.5(3), C(18)-W(1)-C(1) 91.3(2), C(19)-W(1)-C(1A) 94.96(18), N(1)-C(1)-N(2) 102.2(4), N(1)-C(1)-W(1) 128.8(4), N(2)-C(1)-W(1) 128.8(3).]
Figure 3.2 ORTEP diagram of compound 3-4 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(7) 2.239(6), Mo(1)-N(1) 2.331(5), Mo(1)-C(11) 2.034(6), Mo(1)-C(12) 1.988(7), Mo(1)-C(13) 1.946(6), Mo(1)-C(14) 2.038(7), C(7)-Mo(1)-N(1) 79.26(19), C(11)-Mo(1)-C(14) 169.1(2), C(12)-Mo(1)-C(14) 88.6(3), N(2)-C(7)-N(3) 104.0(5), N(2)-C(7)-Mo(1) 121.7(4), N(3)-C(7)-Mo(1) 134.2(4)

3.3 Application of Compounds 3-1 to 3-5 in Epoxidation Catalysis.

Complexes 3-1 to 3-5 have been examined as catalysts for the epoxidation of cyclooctene with TBHP. The time-dependent curves for all catalytic reactions are shown in Figure 3.3. There was no significant formation of by-products (e.g. diol). Controlled reactions without catalyst showed no significant formation of the epoxide product. The epoxide yields after 4 h, 8 h and 24 h of reaction time using 3-1 to 3-5 as catalysts are shown in Figure 3.4.
Figure 3.3. Time dependent yield of cyclooctene epoxide up to 6h in the presence of compounds 3-1 to 3-5 as catalysts at 55 °C (Mo-based catalysts) or 90 °C (W-based catalysts) using TBHP as oxidant (catalyst : substrate : oxidant = 1:100:200).

Figure 3.4. Yield of the cyclooctene epoxide after 4 h (hatched bars), 8 h (grey and hatched bars) and 24 h (grey bars) of reaction time using the compounds 3-1 to 3-5 as catalysts in the presence of TBHP.
These Mo-based catalysts show low catalytic performance for the epoxidation of olefins comparing with the reported complexes Cp’MoO₂Cl₁⁹ (Cp’ = Cp, Cp*, CpBz). In the case of 3-1a, 3-2a, 3-4 and 3-5, after 24h, only up to 35% epoxide was yielded. This result is comparable with the similar tetracarbonyl complex cis-(CO)₄Mo(bpy) (17/46% conversion at 6/24 h)²⁰ and higher than those of the ansa-bridged cyclopentadienyl-functionalized NHC complexes, (Cp⁸-NHC)Mo(CO)₂I (Cp⁸ = Cp, Cp*) which give negligible epoxide yields after 5 h.⁷a Compounds 3-1a, 3-2a show a similar behaviour indicating that the replacement of substituent on the NHC ligand has little influence on the electronic situation at the metal centre and therefore also not on the catalytic performance. The performance of chelated complexes 3-4 and 3-5 are poor. The catalytic activity was not improved by the bidentate and polydentate ligands, although the similar tridentate donor-carbene-donor ligands have been shown to give rise to highly active, stable catalysts for Heck couplings.¹⁷, ²¹ Compound 3-3a shows higher activity among 3-1 to 3-5. However, compared with the moderate catalyst Mo(η³-C₃H₅)Cl(CO)₂(bis-NHC)⁷b (100%, 55 °C, 10h), the activity of 3-3a is still lower. Its behaviour under oxidation condition will be discussed later.

The activity of W-based catalysts 3-1b to 3-3b yielded epoxide up to 40%, 90 °C, 24h which is lower than the reported W oxo complexes like WCl₂(O)₂dppmO₂²² (70%, 90 °C, 6h) or W(allyl)₂(O)₂(Bubpy)²³ (ca. 30%, 90 °C, 24h) with TBHP. Their activity are still higher than the biscarbene complex W(η³-C₃H₅)Cl(CO)₂(bis-NHC)⁷b negligible epoxide yields after 10 h. In these examples the activity of W-based catalysts in H₂O₂ are also reported. Herein we tested the activity of 3-1b with H₂O₂ under 90 °C result with the yield of epoxide 18% (4h), 24% (8h), 32% (24h). The activity of 3-1b with H₂O₂ is slightly higher than with TBHP, although the difference is not as significant as reported example⁷b.

During the course of reactions using 3-1 to 3-5 as catalysts, formation of pale yellow or
white precipitates was observed. This suggests that an unidentified product formed during the oxidation reaction and which is poorly active towards epoxidation.

3.4 Examination of the Stability of Metal-NHC Ligand Bond under Oxidative Conditions.

The difference in the catalytic activity between 3-3a and other Mo-NHC compound prompted us to investigate the stability of 3-3a and 3-3b under the oxidative conditions (in the presence of TBHP) by using $^1$H NMR and IR. Similar studies were also carried out on 3-1a and 3-1b as comparison. Because of the chelated effect on the complex stabilization, compound 3-5 was also involved in the study.

3.4.1 Stability of Mo-C(NHC) Bonds in 3-1a and 3-1b under Oxidative Conditions.

Kinetic $^1$H NMR experiments on the oxidation reactions of 3-1a and 3-1b were carried out by treatment with 5-fold excess of TBHP (5-6M in decane) at room temperature in CDCl$_3$ upon stirring of the mixtures. In the case of 3-1a, the yellow color change to pale yellow with white precipitate formed. The characterization of this white precipitate will be carried out in future work. Beside the resonance of NCH$_2$Ph at $\delta$ 5.18 ppm in the $^1$H NMR spectrum, a new signal at $\delta$ 5.34 ppm(3.3H) appeared after 5 min of reaction. The signal at $\delta$ 9.59(0.6H) and $\delta$ 6.88 ppm(1.5H) were also observed. These new peaks were identified to be the characteristic signals of an imidazolium salt. After 30 min, the intensity of new peaks was increased significantly. After 1h, the resonances of 3-1a were mostly disappeared. The reaction can be completely finished in 2 hours. (see Figure 3.5) Similar observations were noted in 3-1b. After 30 min, the characteristic signals of the corresponding imidazolium salt appeared at $\delta$
9.54 (1H), 6.98 (2H), 5.43 (4H). The reaction of 3-1b with TBHP was much slower than 3-1a. After 1h, a large amount of 3-1b can be still observed in the spectrum. 3-1b decomposed completely within 12h under the reaction condition.

Similar to the recently reported Mo and W (η³-allyl) (bis-NHC) complexes⁷b, compound 3-1a and 3-1b show low stability on the reaction with TBHP, although 3-1b is more stable than 3-1a. The formation of imidazolium salt indicate the cleavage of the metal-C(NHC) bond.

![Figure 3.5. Kinetic ¹H-NMR experiments on the reaction of compound 3-1a and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CDCl₃.](image)

**Figure 3.5.** Kinetic ¹H-NMR experiments on the reaction of compound 3-1a and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CDCl₃.

**3.4.2 Stability of Mo-C(NHC) Bonds in 3-3a and 3-3b under Oxidative Conditions.**

Kinetic ¹H NMR experiments on the oxidation reactions of 3-3a and 3-3b were carried out firstly by treatment with 5-fold excess of TBHP (5-6M in decane) at room temperature in
CDCl$_3$ upon stirring of the mixtures. For both case of 3-3a and 3-3b, the colorless solution changes to slightly foggy slowly. For 3-3a, after the introduction of TBHP, a broad peak appearing at $ca.$ 8 ppm was assigned to the proton in TBHP. The singlet signals of $=CH$ (7.05 ppm) and the two set of $Me$ (2.34 ppm, 2.07 ppm) on the mesityl remained no significant change, even after 90mins. And the formation of the acidic proton of imidazolium salt (NCHN) which could appear at $ca.$ 9 ppm was not observed. 3-3a After 2h, the resulted mixture was filtered, dried under vacuum and washed with hexane. The resulted white solid was detected with IR. The strong absorption at 2059, 1921 and 1878 cm$^{-1}$ ($\nu$(CO)) remained, indicating that compared with 3-1a and CpMo(CO)$_2$(NHC)Br (see Chapter 4), 3-3a shows more persistence to oxidant like TBHP. The behavior of 3-3b is similar as that of 3-3a.

If the reaction of 3-3a were carried out in CD$_3$CN with 5 fold TBHP at 50 °C for 6h, however, beside the resonances of 3-3a (see experimental section), a set of new singlet signals appeared at $\delta$ 8.77(CNHC), 7.76($=CH$), 7.14 ($m$-H-Mes) ppm. By comparing the chemical shift with the corresponding imidazolium salt IMesHBr$^1c$ in CD$_3$CN, the $^1$H NMR spectrum of the reaction of 3-3a with TBHP showed the formation of imidazolium salt with yield of 60% (calculated from the integration on the NMR spectrum). After 24h, the signal of 3-3a almost disappeared. In the spectrum of IR, a strong peak appeared at 1927 cm$^{-1}$ which was assigned to be the stretching vibration of M-CO. And the sharp peaks at 901 and 846 cm$^{-1}$ were assigned to be the stretching vibration of cis-Mo=O.

The reaction of 3-3b was carried under 90 °C. After 6h, beside the resonances of 3-3b (see experimental section), new signal at $\delta$ 8.80 (CNHC), 7.71 ($=CH$), 7.41 ($m$-H-Mes) ppm appeared indicating the formation of imidazolium salt with the yield 55%. After 24 h, almost all of 3-3b has been oxidized. In the spectrum of IR, an absorption appearing at 1920 cm$^{-1}$ was assigned to be the residue of M-CO species. And the sharp peaks at 976 and 815 were assigned to be the stretching vibration of cis-W=O.
Compound 3-3a and 3-3b show more persistence toward oxidant. At room temperature, both of them can not react with TBHP. Under higher temperature similar to the catalytic condition, the carbene - metal bonds in 3-3a and 3-3b cleaved slowly, with the formation of the imidazolium salt and metal oxo bonds. Observed from IR spectra, the absorption at ca. 1920 cm\(^{-1}\), shows existence of mono M-CO bond in the complex or \textit{trans}-M-CO configuration. However, it was still unclear whether a mixture of metal oxide and metal carbonyls or metal oxide carbonyls such as MO\(_2\)(CO)\(_2\)\(^{24}\) were generated from this reaction.

3.4.3 Stability of Mo-C(NHC) Bonds in 3-5 under Oxidative Conditions.

Under the similar condition as 3-1a, compound 3-5 shows more unstable comparing with 3-3. A singlet signal appeared at \(\delta\) 9.8 ppm (characteristic signals of NCH\(_2\)N) after 20min. The intensity of two singlet of two CH\(_2\) (5.63, 5.17 ppm) in 3-5 decreased followed by the formation of a new singlet which almost overlapping the peak at \(\delta\) 5.63 ppm, was identified to be the two CH\(_2\) in the imidazolium salt. After 120 min, the peaks from imidazolium salt dominated the spectrum, showing the fully decomposition of 3-5. (See Figure 3.6)

Compared with 3-3a, compound 3-5 is significantly unstable to TBHP, although it gives slightly more persistence than 3-1a. The chelated ligand didn’t show enough capability on the complex stabilization as mentioned before\(^9\). And the Mo-C(NHC) cleaved after the introduction of TBHP. Similarly, complex [Pd(Py\(_2\)NHC)Me]BF\(_4\)\(^{17}\) was found to decompose at more than 100 °C, undergo reductive carbene alkyl coupling to give 2-alkyl imidazolium salt and Pd(0). However, it is still stable than the other Pd NHC complexes, which often decompose (via the same route) at room temperature or below.\(^{25}\) This would be due to the \textit{trans} configuration forced by the chelating donor ligand.\(^{17}\)

The behavior of 3-5 under oxidative condition may be an explanation on the low
catalytic activity similar to 3-1a.

Figure 3.6. Kinetic $^1$H-NMR experiments on the reaction of compound 3-5 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CDCl$_3$.

3.5 Conclusions

In this work, a series of NHC complexes with the formula, M(CO)$_4$(NHC)$_2$ (3-1 - 3-2), M(CO)$_5$(IMes) (3-3a, 3-3b), Mo(CO)$_4$(PyNHC) 3-4, and Mo(CO)$_3$(Py$_2$NHC) 3-5, have been synthesized and characterized. From kinetic study, the decomposition of the NHC-based catalysts was confirmed. The reaction between carbene complexes and TBHP produces the imidazolium salt, resulting from protonation of the NHC ligand, indicating the vulnerability of the M-C(NHC) bond under the oxidation conditions.

Complexes 3-1 to 3-5 show moderate catalytic activities towards the epoxidation of cyclooctene with TBHP, but still better than some other carbene complexes reported in the
literature. Changing the substituent on the NHC ligand may not improve the activity significantly. Among them, 3-3a gives a higher activity (ca. 60%, 24h). The kinetic studies of 3-3a and 3-3b show better persistence to the oxidant than other carbene complexes even under higher temperature. Chelate compounds 3-4 and 3-5 fail to show good activity. Kinetic study shows complete decomposition of 3-5 under the oxidation condition after 120mins.

3.6 Experimental Section

**General Considerations.** All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under nitrogen and used immediately. TBHP (tert-butyl hydrogen peroxide, 5~6 M in decane) was purchased from Sigma-Aldrich. Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. $^1$H and $^{13}$C NMR spectra were measured in CDCl$_3$ with AMX500 500 MHz FT NMR spectrometers. ($^1$H at 500 MHz, $^{13}$C at 75.43 MHz). FAB-Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. IR spectra were recorded on a Shimadzu IR-470 spectrometer using KBr pellets as IR matrix. Catalytic runs were monitored by GC methods on the Agilent 6890 Series GC instrument with a J&W DB-1 column. The preparation of imidazolium bromide, free carbene, and silver-IMes were based on the literature procedure. The synthesis of silver-PyNHC and silver-Py$_2$NHC are following same method. The acetonitrile complexes M(CO)$_3$MeCN$_3$ (M = Mo or W) are prepared from the reaction between M(CO)$_6$ and MeCN under reflux condition.

3.6.1 Preparation of Compounds 3-1 to 3-2

In 20ml of distilled THF, imidazolium bromide(1mmol) was treated with 1.5mmol of
KO\textsuperscript{t}Bu (1M in THF). The slurry was stirring under -70\(^\circ\)C for 2 hours. Then 1.2 mol of Mo(CO)\textsubscript{3}(MeCN)\textsubscript{3} (0.36 g) or W(CO)\textsubscript{3}(MeCN)\textsubscript{3} (0.47 g) which was dissolved in 10 ml distilled THF was introduced. The mixture was stirring under room temperature for 12 hours. The resulted yellow solution was dried under vacuum and the brown solid was purified by column chromatography (hexane: ethyl acetate = 5:1 to 2:1), yielding the yellow solid as final product.

\textbf{Mo(CO)\textsubscript{4}(IBz)\textsubscript{2} (3-1a).} (Yield: 0.31 g, 37\%) \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 7.27-7.10 (m, 10H, N-CH\textsubscript{2}-Ph), 6.65 (s, 2H, =CH), 5.37 (s, 4H, N-CH\textsubscript{2}-Ph). \textsuperscript{13}C NMR (125.77 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 218.5 (Mo-CO), 210.4 (Mo-CO), 196.6 (NCN), 136.4, 128.8, 128.2, 128.0 (Ph), 121.0 (=CH), 55.5 (N-CH\textsubscript{2}-Ph). IR (KBr/ cm\textsuperscript{-1}) \(v\) (CO) 1993 (vs), \(v\) (CO) 1860 (vs), \(v\) (CO) 1817 (vs). FAB-MS(+) : 706.2 (M +), 622.3 (M + -3CO), 594.3 (M + -4CO), 402.1 (M + -2CO-1L), 346.2 (M + -4CO-1L), 249.2 (L\textsuperscript{+}). EA Calcd for C\textsubscript{38}H\textsubscript{32}N\textsubscript{4}O\textsubscript{4}Mo: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.51; H, 4.61; N, 7.85.

\textbf{W(CO)\textsubscript{4}(IBz)\textsubscript{2} (3-1b).} (Yield: 0.22 g, 23\%) \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 7.28-7.11 (m, 10H, N-CH\textsubscript{2}-Ph), 6.63 (s, 2H, =CH), 5.34 (s, 4H, N-CH\textsubscript{2}-Ph). \textsuperscript{13}C NMR (125.77 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 210.0 (W-CO), 203.9 (W-CO), 190.0 (NCN), 136.2, 128.9, 128.4, 128.2 (Ph), 120.7 (=CH), 56.4 (N-CH\textsubscript{2}-Ph). IR (KBr/ cm\textsuperscript{-1}) \(v\) (CO) 1982 (vs), \(v\) (CO) 1856 (vs), \(v\) (CO) 1812 (vs). FAB-MS(+) : 794.2 (M\textsuperscript{+}), 708.3 (M\textsuperscript{+}-3CO), 594.3 (M\textsuperscript{+}-4CO), 488.1 (M\textsuperscript{+}-2CO-1L), 432.2 (M\textsuperscript{+}-4CO-1L), 249.3 (L\textsuperscript{+}). EA Calcd for C\textsubscript{38}H\textsubscript{32}N\textsubscript{4}O\textsubscript{4}W: C, 57.59; H, 4.07; N, 7.07. Found: C, 57.82; H, 4.30; N, 7.51

\textbf{Mo(CO)\textsubscript{4}(InPr)\textsubscript{2} (3-2a).} (Yield: 0.21 g, 34\%) \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 6.93 (s, 2H, =CH), 4.01-3.98 (m, 4H, N-CH\textsubscript{2}CH\textsubscript{2}Me), 1.70-1.65 (m, 4H, N-CH\textsubscript{2}CH\textsubscript{2}Me), 0.92-0.89 (t, 6H, N-CH\textsubscript{2}CH\textsubscript{2}Me), \(J\textsubscript{C-H} = 7.6\) Hz. \textsuperscript{13}C NMR (125.77 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 218.9 (Mo-CO), 210.8 (Mo-CO), 194.6 (NCN), 120.0 (=CH), 52.8 (N-CH\textsubscript{2}CH\textsubscript{2}Me), 24.3 (N-CH\textsubscript{2}CH\textsubscript{2}Me), 11.1 (N-CH\textsubscript{2}CH\textsubscript{2}Me). IR(KBr/ cm\textsuperscript{-1}) \(v\) (CO) 1987 (vs), \(v\) (CO) 1852 (vs),
\( \nu(\text{CO})_{1823} \) (vs). FAB-MS(+): 514.3 (M\(^+\)), 486.3 (M\(^+\)-CO), 458.3 (M\(^+\)-2CO), 153.2 (L\(^+\)). EA Calcd for C\(_{22}\)H\(_{32}\)N\(_4\)O\(_4\)Mo: C, 51.56; H, 6.29; N, 0.93 Found: C, 51.16; H, 5.78; N, 10.66

\( \text{W(CO)}_4(\text{I}^\text{Pr})_2 \) (3-2b). (Yield: 0.34g, 47%) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 6.93 (s, 2H, =CH), 3.98 (t, 4H, N-CH\(_2\)CH\(_2\)Me, \( ^1\)J\(_{C-H} \) = 8.2 Hz), 1.70-1.65 (m, 4H, N-CH\(_2\)CH\(_2\)Me), 0.91 (t, 6H, N-CH\(_2\)CH\(_2\)Me, \( ^1\)J\(_{C-H} \) = 7.55 Hz). \(^{13}\)C NMR (125.77 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 210.2 (W-CO), 204.20 (W-CO), 188.1 (NCN), 119.8 (=CH), 53.5 (N-CH\(_2\)CH\(_2\)Me), 24.2 (N-CH\(_2\)CH\(_2\)Me), 11.1 (N-CH\(_2\)CH\(_2\)Me). IR (KBr/ cm\(^{-1}\)) \( \nu(\text{CO})_{2013} \) (vs), \( \nu(\text{CO})_{1890} \) (vs), \( \nu(\text{CO})_{1879} \) (vs) FAB-MS(+): 600.3 (M\(^+\)), 572.3 (M\(^+\)-CO), 542.3 (M\(^+\)-2CO), 153.2 (L\(^+\)). EA Calcd for C\(_{22}\)H\(_{32}\)N\(_4\)O\(_4\)W: C, 44.01; H, 5.37; N, 8.74 Found: C, 42.60; H, 4.84; N, 8.74

### 3.6.2 Preparation of 3-3a, 3-3b by Silver Mediated Transfer Route

Ag\(_2\)O (232 mg, 1 mmol) was added to a solution of IMes HBr (340 mg, 1 mmol) in CH\(_2\)Cl\(_2\) (15 mL). After the mixture was refluxed for 7 h upon exclusion of light, the solution was filtered through Celite and the filtrate was dried under vacuum. The resulted solid was dissolved in distilled CH\(_2\)Cl\(_2\) (20 mL). Mo(CO)\(_3\)(MeCN)\(_3\) (0.30 g, 1 mmol) or W(CO)\(_3\)(MeCN)\(_3\) (0.39 g, 1 mmol) in distilled CH\(_2\)Cl\(_2\) (10ml) was added to this silver carbene solution. After the mixture was stirred for 12 hours at room temperature excluded light, the light yellow solution was dried under vacuum and the yellow solid was purified by column chromatography (hexane: ethyl acetate = 10:1) to give product as white solid.

\textbf{Mo(CO)}_5(\text{IMes}) (3-3a). (Yield: 0.23 g, 40%) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.06 (s, 2H, =CH), 7.03 (s, 4H, m-H-Mes), 2.36 (s, 6H, p-Me-Mes), 2.08 (s, 12H, o-Me-Mes). \(^1\)H NMR (500 MHz, CD\(_3\)CN): \( \delta \) (ppm) = 7.24 (s, 2H, =CH), 7.07 (s, 4H, m-H-Mes), 2.32 (s, 6H, p-Me-Mes), 2.05 (s, 12H, o-Me-Mes). \(^{13}\)C NMR (125.77 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 211.4 (Mo-CO), 205.3 (Mo-CO), 193.6 (NCN), 139.6 (i-Mes), 137.8 (p-Mes), 135.5 (o-Mes), 129.4
(m-Mes), 123.4 (=CH), 21.1 (p-Me-Mes), 17.7 (o-Me-Mes). IR (KBr/ cm⁻¹) ν(CO) 2059 (vs), ν(CO) 1924 (vs), ν(CO) 1879(vs). FAB-MS(+): 542.2(M⁺), 485.1(M⁺-2CO) 458.1(M⁺-3CO), 398.1 (M⁺-5CO), 305.2(L⁺). EA Calcd for C₂₆H₂₄N₂O₅Mo: C, 57.78; H, 4.48; N, 5.18

W(CO)₅(IMes) (3-3b). (Yield: 0.38g, 60%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.07(s, 2H, =CH), 7.04(s, 4H, m-H-Mes), 2.36 (s, 6H, p-Me-Mes), 2.09 (s, 12H, o-Me-Mes). ¹H NMR (500MHz, CD₃CN): δ (ppm) = 7.26(s, 2H, =CH), 7.07(s, 4H, m-H-Mes), 2.32 (s, 6H, p-Me-Mes), 2.06 (s, 12H, o-Me-Mes). ¹³C NMR(125.77 MHz, CDCl₃): δ (ppm) = 200.4 (W-CO), 197.0 (W-CO), 185.6 (NCN), 139.8 (i-Mes), 137.7 (p-Mes), 135.6 (o-Mes), 129.5 (m-Mes), 123.4 (=CH), 21.1(p-Me-Mes), 17.8(o-Me-Mes). IR (KBr/ cm⁻¹) ν(CO)2057(vs), ν(CO)1911 (vs), ν(CO)1876(vs). FAB-MS(+): 628.2(M⁺), 600.2 (M⁺-CO), 544.3(M⁺-3CO) 484.2 (M⁺-5CO), 305.3(L⁺). EA Calcd for C₂₆H₂₄N₂O₅W: C, 49.70; H, 3.85; N, 4.46 Found: C, 49.97; H, 3.85; N, 4.39

3.6.3 Preparation of 3-4, 3-5 by Silver Mediated Transfer Route

Ag₂O (232 mg, 1 mmol) was added to a solution of imidazolium salt (1 mmol) in CH₂Cl₂ (15 mL). After the mixture was stirring at room temperature for 12 h upon exclusion of light, the solution was filtered through Celite and the filtrate was dried under vacuum The resulted solid was dissolved in distilled CH₂Cl₂ (20 mL). Mo(CO)₃(MeCN)₃ (0.30g, 1 mmol) in distilled CH₂Cl₂ (10ml) was added to this silver carbene solution. After the mixture was stirred for 12 hours at room temperature excluded light, the brown solution was dried under vacuum and the brown solid was purified by column chromatography (hexane: ethyl acetate) to give product as yellow solid.

Mo(CO)₄(PyNHC) (3-4). (Yield: 0.07g 20%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 9.09-9.08 (d, 1H, Py), 7.73 (m, 1H, Py), 7.40-7.38 (d, 1H, Py), 7.16 (m, 1H, 1H, Py), 7.05 (s,1H, =CH), 6.91 (s,1H, =CH), 5.12 (s,2H, CH₂), 3.91(s,2H, CH₃) ¹³C NMR (125.77 MHz,
CDCl₃): δ (ppm) = 224.61 (Mo-CO), 208.72 (Mo-CO), 201.00 (Mo-CO), 186.26 (NCN), 157.09 (Py), 156.09 (Py), 156.04 (Py) 137.94 (Py), 123.02 (≡CH), 121.64 (≡CH), 56.61 (CH₂), 38.41 (CH₃). IR(KBr/ cm⁻¹) ν(CO)2002 (vs), ν(CO)1868 (vs), ν(CO)1812 (vs). FAB-MS(+): 383.0 (M⁺), 355.0 (M⁺-CO), 174.2 (L⁺). EA Calcd for C₁₄H₁₁N₃O₄Mo: C, 44.11; H, 2.91; N, 11.02 Found: C, 41.77; H, 3.26 N, 10.02

Mo(CO)₃(Py₂NHC) (3-5). (Yield: 0.12g 28%) ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 9.08-9.07 (d, 1H, Py), 8.58-8.57 (d, 1H, Py), 7.74-7.66 (m, 2H, Py), 7.40-7.39 (m, 2H, Py), 7.23-7.21 (m, 1H, Py), 7.16-7.15 (m, 2H, CH≡CH), 7.09-7.08 (m, 1H, Py), 5.61 (s, 2H, CH₂), 5.14 (s, 2H, CH₂). ¹³C NMR (125.77 MHz, CDCl₃): δ (ppm) = 224.26 (Mo-CO), 218.48 (Mo-CO), 208.52 (Mo-CO), 198.01 (NCN), 157.01 (Py), 156.13 (Py), 156.07 (Py), 149.39 (Py), 138.00 (Py), 137.19 (Py), 124.62 (≡CH), 123.14 (≡CH), 123.08 (Py), 122.99 (Py), 121.51 (CH₂), 121.13 (CH₂). IR(KBr/ cm⁻¹) ν(CO)1998 (vs), ν(CO)1868 (vs), ν(CO)1817 (vs). FAB-MS(+): 432.1 (M⁺), 376.1 (M⁺-2CO), 251.1 (L⁺). EA Calcd for C₁₈H₁₄N₄O₃Mo: C, 50.25; H, 3.28; N, 13.02. Found: C, 50.24; H, 3.69; N, 11.34.

3.6.4 X-ray Crystallography

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS. Structure solutions and refinements were performed by using the programs SHELXS-97 and SHELXL-97. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms
were placed geometrically and refined isotropically.

### 3.6.5 Catalytic reactions.

_Cis-_cyclooctene (0.4 g, 3.6 mmol), mesitylene (1 g, internal standard) and compounds 3-1 to 3-5 as catalysts (1 mol%, 0.036 mol) were added to the reaction vessel under an air atmosphere at 55 °C (Mo-based catalysts) or 90 °C (W-based catalysts). The reaction was started by the addition of TBHP (7.3 mmol, 1.36 mL, 5.5 M in _n_-decane). The course of the reactions was monitored by quantitative GC analysis (Agilent 6890 Series GC instrument with a J&W DB-1 column). Samples were taken in regular time intervals, diluted with CH₂Cl₂, and treated with a catalytic amount of MgSO₄ and MnO₂ to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate was injected into the GC column. The conversion of _cis-_cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (_r² = 0.999_) recorded prior to the reaction course.

### 3.7 Reference


(b) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Royo, B; *Catal Lett.* **2010**, 136, 222


P.; Williams, D. J.; White, A.H.; Skelton, B.W. *Organomet. Chem.* **2001**, *617–618*, 546


[34] (a) Sheldrick, G. M. SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; (b) Sheldrick, G. M. SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.
Chapter Four: Cyclopentadienyl Molybdenum(II/VI) N-Heterocyclic Carbene Complexes: Synthesis, Structure, and Reactivity under Oxidative Conditions

Abstract:
A series of N-heterocyclic carbene (NHC) complexes CpMo(CO)₂(NHC)X (NHC = IMe = 1,3-dimethylimidazol-2-ylidene, X = Br, 4-1; NHC = 1³Pr = 1,3-dipropylimidazol-2-ylidene, X = Br, 4-2; NHC = IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, X = Br, 4-3; NHC = IBz = 1,3-dibenzylimidazol-2-ylidene, X = Br, 4-4a and X = Cl, 4-4b; NHC = 1-methyl-3-propylimidazol-2-ylidene, X = Br, 4-5; NHC = SIMes = 1,3-bis-(2,4,6-trimethylphenyl) imidazolin-2-ylidene, X = Br, 4-6; NHC = I*PhEt = Bis ((S)-1‘-phenylethyl)imidazolin -2-ylidene, X = Br, 4-7) and [CpMo(CO)₂(NHC)(CH₃CN)][BF₄] (NHC = IMes, 4-8; NHC = SIMes, 4-9; NHC = IBz, 4-10, NHC = I*PhEt, 4-11) have been synthesized and characterized. The stability of metal-NHC ligand bonds in these compounds under oxidative conditions has been investigated. The thermally stable Mo(VI) dioxo NHC complex [CpMoO₂(NHC)][BF₄] (NHC = IMes, 4-14; NHC = IBz, 4-16) has been isolated by the oxidation of the ionic complex 4-8 and 4-10 by TBHP (tert-butyl hydrogen peroxide). Complex 4-8 - 4-11 can be applied as very active (TOFs up to 3400 h⁻¹) and selective olefin epoxidation catalysts. While under oxidative conditions (in the presence of TBHP), compounds 4-1 - 4-7 decompose into imidazolium bromide and imidazolium polyoxomolybdate. The formation of polyoxomolybdate as oxidation products had not been observed in a similar epoxidation catalyzed by Mo(II) and Mo(VI) complexes. DFT studies suggest that the presence of Br⁻ destabilizes the CpMo(VI) oxo NHC carbene species, consistent with the experimental observations.
4.1 Introduction

Recently, among the organic reactions catalyzed by N-heterocyclic carbenes (NHCs) complexes\(^1\), the study on the catalytic oxidation became attractive and significant progress has been achieved. A variety of catalytic oxidation reactions have been studied using NHC complexes, such as \( \text{O}_2/\text{CO} \) fixation, the oxidation of alcohol, alkyne oxidation, and the oxidation of terminal olefins to ketone, and most of the work in this area was conducted with palladium catalysts.\(^2\) Recently, a Mn(III) complex with a tetradeutate NHC ligand was reported and applied as a catalyst for the epoxidation of styrene using PhIO as oxidant to give styrene oxide, suggesting the formation of Mn\(^{IV}=\text{O} \) and Mn\(^{V}=\text{O} \) NHC intermediates during the oxygen transfer reactions. However, no spectroscopic evidence of the Mn\(^{IV/V}=\text{O} \) NHC species was given in this work.\(^3\) In view of the excellent catalytic activities shown in cyclopentadienyl Mo(II) carbonyl complexes, such as CpMo(CO)\(_3\)Cl and CpMo(CO)\(_3\)(CH\(_3\)), in the olefin epoxidation reaction with TBHP (\textit{tert}-butyl hydrogen peroxide) as oxidant,\(^4\)\(^-\)\(^7\) and potentially high oxidation resistance of NHC ligands, we are interested in the application of cyclopentadienyl molybdenum carbonyl N-heterocyclic carbene complexes in olefin epoxidations. This system could provide an avenue to introduce chiral NHC ligands to the \([\text{CpMo(CO)}\_n]\) core as a possible route to develop active chiral catalysts for asymmetric epoxidation in which many systems such as Mo(II), Mo(VI), and Re(VII) have failed.\(^7c\)\^-\(^e\)\(^8\) Compounds CpM(CO)\(_2\)(IMes)H and \([\text{CpM(CO)}\_2(\text{IMes})][\text{Br(C}_6\text{F}_5)_2]\) (M = Mo, W; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been synthesized and employed in catalytic ketone hydrogenation reactions.\(^9\) Recently, some Mo(II) complexes containing ansa-bridged cyclopentadienyl-functionalized NHC complexes, (Cp\(^{-}\)-NHC)Mo(CO)\(_2\)I (Cp\(^{-}\) = Cp, Cp*, and Cp\(^{\text{Bz}}\)), have been reported.\(^10\) These complexes, however, are much less active compared to CpMo(CO)\(_3\)X (X = Cl or CH\(_3\)) toward olefin epoxidation. It has been reported that some NHC complexes can undergo decomposition through different reaction routes, such
as reductive elimination, decomplexation or displacement by competing ligands. Although some metal NHC complexes have been applied for the catalytic oxidation reactions as discussed above, the study on questions whether NHC metal complexes can be widely used as catalysts for the oxidation reactions and whether metal-NHC ligand bonds are stable under strong oxidative conditions is still rare. In order to search for metal NHC complexes with high catalytic activities toward olefin epoxidations and to understand the stability of the metal-NHC ligand bonds with different electron donating NHC ligand or chiral NHC ligand under oxidative conditions, we herein report the synthesis and structure of a series of neutral NHC complexes CpMo(CO)₂(NHC)X (NHC = IMe = 1,3-dimethylimidazol-2-ylidene, X = Br, 4-1; NHC = 1,3-dipropylimidazol-2-ylidene, X = Br, 4-2; NHC = IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, X = Br, 4-3; NHC = IBz = 1,3-dibenzylimidazol-2-ylidene, X = Br, 4-4a, and X = Cl, 4-4b; NHC = 1-methyl-3-propylimidazol-2-ylidene, X = Br, 4-5, NHC = 1,3-bis-(2,4,6-trimethylphenyl) imidazolin-2-ylidene = SIMes, X = Br , 4-6; NHC = 1,3- bis((S)-1’-phenylethyl)imidazolin-2-ylidene = l*PhEt, X = Br, 4-7) and the ionic complex [CpMo(CO)₂(NHC)(CH₃CN)][BF₄] (NHC = IMes, 4-8; NHC = IBz, 4-9; NHC = SIMes, 4-10; NHC = l*PhEt, 4-11) and their applications in olefin epoxidations. Their reactivities toward TBHP were studied by NMR, ESI-MS, and DFT calculations. We also report the isolation and characterization of the thermally stable Mo(VI) dioxo complex, [CpMoO₂(NHC)][BF₄] ((NHC = IMes, 4-14; NHC = IBz, 4-15; NHC = SIMes, 4-16; NHC = l*PhEt, 4-17), obtained from the oxidation of 8-11 by TBHP.

4.2 Result and Discussion

4.2.1 Synthesis and Characterization of Compounds CpMo(CO)₂(NHC)Br (4-1 - 4-7).

Compounds, CpMo(CO)₂(NHC)X (X = Cl, Br) (4-1 - 4-7) (see Scheme 4.1) were
conveniently synthesized using a transmetallation route by refluxing CpMo(CO)\(_3\)Br with silver carbene formed *in situ* in toluene for 40 min. 4-1 - 4-7 could also be prepared, albeit in lower yields, using a similar method from CpMo(CO)\(_2\)PPh\(_3\)Br. A mixture of the chloride and bromide forms of 4-4 i.e., CpMo(CO)\(_2\)(NHC)X (X = Br (4-4a) and Cl (4-4b)) is obtained from CpMo(CO)\(_2\)LCl (L = CO, PPh\(_3\)) and imidazolium bromide. Compounds 4-1 - 4-7 are isolated as purple crystals and purified by column chromatography. No further attempt was made to improve the yield. They show good stability at room temperature both in solid state and in solution. They can be handled in laboratory atmosphere and kept under air without decomposition.

\[ \text{Scheme 4.1 Structure of compounds 4-1 – 4-7} \]

The composition and structure of compounds 4-1 - 4-7 were determined by IR and NMR-spectroscopy (\(^1\)H, \(^13\)C) and partly by elemental analysis. Among these compounds, 4-1 - 4-5 were determined by X-ray single crystal diffraction (see discussion below). For all compounds 4-1 - 4-7, in CD\(_3\)CN or CDCl\(_3\) the \(^13\)C-NMR signal of the Cp ring appears at \(\delta\) 95 - 97 ppm. And for 4-1 - 4-5 and 4-7 the \(^13\)C-NMR signals of carbene carbon appear at \(\delta\) 183-190 ppm which are comparable to the similar compounds (Cp’-NHC)Mo(CO)\(_2\)I (Cp’ = Cp, Cp*, and Cp\(_{\text{Bz}}\))\(^{10}\). In compound 4-6, \(^13\)C-NMR signals of the carbene carbon shift to lower field (\(\delta\) 218.5 ppm) due to the shielding effect from the electron rich NHC ligand. In
compounds 4-1 - 4-7 the inequivalence of the two carboxyls ($\delta$ ca. 254-256/247-255 ppm) at room temperature suggests that they are cis oriented and the metal center is chiral. Such inequivalence has been observed for CpW(CO)$_2$(IMes)H and [CpW(CO)$_2$(IMes)(H$_2$)][B(C$_6$F$_5$)$_4$] at -100 °C and for the adduct of [CpW(CO)$_2$(IMes)][B(C$_6$F$_5$)$_4$] with Et$_2$CHOH at -40 °C. For compounds 4-2, 4-4a, 4-4b and 4-5, the $^1$H-NMR spectra of the methylene protons adjacent to N atom show an AB-type quartet. In compounds 4-3 and 4-6, the methyl groups on the phenyl rings of the two sides of IMes ligand exhibit three discrete singlets in the $^1$H-NMR (6H each) spectra at room temperature owing to the inequivalence of methyl groups upon the coordination. Such inequivalence has not been observed for CpW(CO)$_2$(IMes)H under same condition. In the $^1$H NMR spectrum at 27 °C, the four ortho-methyl groups of the IMes ligand appear as a singlet (12 H), but at -100 °C two separate singlets (6H each) are observed; a similar situation is found in the $^{13}$C NMR spectrum(CDCl$_3$). For compound 4-6 in CDCl$_3$, the signals of phenyl rings and CH$_2$ on the imidazolium ring in $^{13}$C NHR spectra, show very broad peaks at 27 °C. When cooled to -50 °C, 12 significant signals were observed as the carbon on the phenyl rings and two signals as methylene. Also, in $^1$H NMR, the two singlet signals of m-Mes were split to 4 signals at -50 °C, with the integration of 1 proton each. Compound 4-7 gave two sets of Cp ring signals in $^1$H NMR spectra at room temperature. For the purification of compounds of type [CpMo(CO)$_2$Br(NHC)], cis-trans isomers or bromide and chloride analogues of the compound can usually be separated by column chromatography. As such, it is proposed that the presence of the two sets of Cp ring signals in $^1$NMR spectra is due to of the existence of optical isomers from the chiralities of both metal center and NHC ligand. Same phenomenon was also observed in the $^1$NMR spectra of the ionic analogue, 4-11. The IR spectra of compounds 4-1 - 4-7 in solid state exhibit $\nu_{\text{sym}}$(CO) at ca. 1950 cm$^{-1}$ and $\nu_{\text{asym}}$(CO) at ca. 1860 cm$^{-1}$. The experimentally measured value of $I_{\text{asym}}/I_{\text{sym}}$ also indicates that
the two CO ligands are *cis* to each other in these compounds. Compound 4-6 was also characterized by ESI-MS. The positive mode ESI spectrum shows one set of peak at m/z 519-529 corresponding to [CpMo(CO)₂(SIMes)]⁺, which gives isotopic distribution pattern that is in agreement with the simulation.

4.2.2 Synthesis and Characterization of Compounds [CpMo(CO)₂(NHC)(CH₃CN)][BF₄] (4-8 - 4-11).

The ionic complexes were synthesized by the reaction between CpMo(CO)₂(NHC)Br (compounds 4-3, 4-4, 4-6, 4-7) and AgBF₄ in CH₃CN at room temperature (see Scheme 4.2). Complexes 4-8 - 4-11 are less stable than compounds 4-1 - 4-7. They decompose under laboratory atmosphere after one day. The ¹H-NMR signal of Cp ring of 4-8 - 4-11 in CD₃CN shifts to lower field comparing with that of the neutral analogue 4-3, 4-4, 4-6, 4-7 which is comparable to the reported ionic compound [CpMo(CO)₂(IMes)(THF)] [B(C₆F₅)₄]⁹. Like compounds 4-1 - 4-7, the ¹³C NMR and the IR spectra of 4-8 - 4-10 indicate that two CO ligands are *cis* oriented. One acetonitrile molecule coordinates to the metal center according to NMR as well as X-ray single crystal diffraction (see discussion below). The positive mode ESI-MS spectrum of 4-8 shows one set of intense peaks at m/z 517-527 corresponding to [CpMo(CO)₂(IMes)]⁺ and two sets of weak peaks at 461-471 and 489-499 assigned to species [CpMo(IMes)]⁺ and [CpMo(CO)(IMes)]⁺, respectively, whose isotopic distribution patterns agree with the simulation. [BF₄]⁻ was observed in the negative mode ESI spectrum as two peaks at m/z 86 and 87 with characteristic isotopic pattern of the element B.
4.2.3 Molecular Structure of Compounds 4-1, 4-2, 4-3, 4-4b, 4-5, 4-8, 4-9 and 4-10

Determined by Single-Crystal X-ray Diffraction.

The single crystals of compounds 4-1, 4-2, 4-3, 4-4b and 4-5 were obtained from a mixture of hexane and ethyl acetate at -19 °C. The single crystals of compound 4-8 - 4-10 were obtained from a mixture of acetonitrile and ethyl ether at room temperature. Their solid state structures are shown in Figures 4.1-4.8 with selected bond lengths and angles. The molecular structures reveal the characteristic four-legged piano stool arrangement of half sandwich Mo(II) complexes. In agreement with the IR and NMR data, in all six compounds, two carbonyls are in cis configuration and the CO-Mo-CO bond angles are between 75° and 79°. In the ionic compounds 4-8 - 4-10, one acetonitrile coordinates to the Mo center with a Mo-N distance of ca. 2.17 Å. The Mo-C(carbene) bond lengths in 4-1 - 4-5 are longer than those reported with similar structure, such as CpMo(CO)₂(IMes)H (2.187(8) Å)⁹b and (Cp*-NHC)Mo(CO)₂I (Cp*-NHC = η⁵-C₄Me₄-CH₂-CHPh-NHCMe) (2.207(3) Å).₁⁰ The Mo-C(carbene) bonds are also slightly longer in 4-2, 4-3, and 4-8 (ca.2.24 Å ) than those in compounds 4-1, 4-4b, 4-5 and 4-9 (ca. 2.22 Å ). The Mo-C(carbene) bond in 4-10 (2.25 Å) is the longest in these structure due to the higher electron donation form the saturated imidazolium ring. The NHC ligand is coordinated symmetrically, as indicated by very similar
angles of N-C-Mo in compounds 4-1, 4-2, 4-3, 4-4b, 4-6 and 4-10. In 4-5, the angles are somewhat distorted perhaps attributed to the different R substituent in the NHC ligand. In 4-9, the angles are also slightly distorted perhaps due to the steric effect from the coordinated MeCN.

Figure 4.1. ORTEP diagram of compound 4-1 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(12) 1.941(3), Mo(1)-C(11) 1.977(3), Mo(1)-C(1) 2.224(3), C(12)-Mo(1)-C(11) 77.45(11), C(12)-Mo(1)-C(1) 109.61(10), C(11)-Mo(1)-C(1) 70.77(10), N(2)-C(1)-N(1) 103.5(2), N(2)-C(1)-Mo(1) 128.10(18), N(1)-C(1)-Mo(1) 128.26(18).
Figure 4.2. ORTEP diagram of compound 4-2 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): C(13)-Mo(1) 1.943(4), Mo(1)-C(14) 1.934(3), Mo(1)-C(1) 2.241(3), C(14)-Mo(1)-C(13) 78.21(13), C(14)-Mo(1)-C(1) 108.12(11), C(13)-Mo(1)-C(1) 75.02(12), N(1)-C(1)-N(2) 103.3(2), N(1)-C(1)-Mo(1) 129.45(19), N(2)-C(1)-Mo(1) 127.24(18).
Figure 4.3. ORTEP diagram of compound 4-3 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(6) 1.932(4), Mo(1)-C(7) 1.939(5), Mo(1)-C(8) 2.244(3), C(6)-Mo(1)-C(7) 76.6(2), C(7)-Mo(1)-C(8) 79.15(16), C(6)-Mo(1)-C(8) 107.24(14), N(1)-C(8)-N(2) 102.8(2), N(1)-C(8)-Mo(1) 129.55(19), N(2)-C(8)-Mo(1) 127.6(2).
Figure 4.4. ORTEP diagram of compound 4-4b (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(24) 1.924(3), Mo(1)-C(23) 1.984(5), Mo(1)-C(1) 2.221(3), C(24)-Mo(1)-C(23) 78.22(15), C(24)-Mo(1)-C(1) 109.47(13), C(23)-Mo(1)-C(1) 73.38(14), N(2)-C(1)-N(1) 103.3(3), N(2)-C(1)-Mo(1) 129.3(2), N(1)-C(1)-Mo(1) 127.4(2).
Figure 4.5. ORTEP diagram of compound 4-5 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(14) 1.948(2), Mo(1)-C(13) 1.973(2), Mo(1)-C(1) 2.224(2), C(14)-Mo(1)-C(13) 76.26(8), C(14)-Mo(1)-C(1) 105.13(7), C(13)-Mo(1)-C(1) 72.84(7), N(2)-C(1)-N(1) 103.38(15), N(2)-C(1)-Mo(1) 125.59(13), N(1)-C(1)-Mo(1) 131.02(13).
Figure 4.6. ORTEP diagram of the cation of [CpMo(CO)$_2$(IMes)(CH$_3$CN)]$^+$ in compound 4-8 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(6) 1.996(3), Mo(1)-C(7) 1.947(3), Mo(1)-C(10) 2.249(3), Mo(1)-N(3) 2.172(2), C(6)-Mo(1)-C(7) 75.97(13), C(6)-Mo(1)-C(10) 75.75(11), C(7)-Mo(1)-C(10) 110.34(12), N(1)-C(10)-N(2) 102.7(2), N(1)-C(10)-Mo(1) 128.0(2), N(2)-C(10)-Mo(1) 128.6(2).
Figure 4.7. ORTEP diagram of the cation of $[\text{CpMo(CO)}_2(\text{IBz})(\text{CH}_3\text{CN})]^+$ in compound 4-9 (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)-C(6) 2.2287(18), Mo(1)-C(23) 1.942(2), Mo(1)-C(24) 1.991(2), Mo(1)-N(3) 2.1763(16), C(23)-Mo(1)-C(24) 78.63(8), C(23)-Mo(1)-C(6) 105.24(7), C(24)-Mo(1)-C(6) 72.72(7), N(1)-C(6)-N(2) 103.22(15), N(1)-C(6)-Mo(1) 126.50(13), N(2)-C(6)-Mo(1) 130.05(13)
Figure 4.8. ORTEP diagram of the cation of \([\text{CpMo(CO)}_2(\text{SIMes})(\text{CH}_3\text{CN})]^+\) in compound 4-10 (30% probability ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Mo(1)-C(27) 1.948(3), Mo(1)-C(28) 1.992(3), Mo(1)-C(6) 2.250(3), Mo(1)-N(3) 2.171(2), C(6)-Mo(1)-C(27) 109.83(10), C(27)-Mo(1)-C(28) 75.31(11), C(28)-Mo(1)-C(6) 74.59(10), N(1)-C(6)-N(2) 107.0(2), N(1)-C(6)-Mo(1) 124.63(18), N(2)-C(6)-Mo(1) 127.13(19).

4.3 Application of compounds 4-1 - 4-6, 4-8 - 4-11 and \(\text{CpMo(CO)}_3\text{Br}\) in epoxidation catalysis.

Complexes 4-1 - 4-6 and 4-8 - 4-11 have been examined as catalysts for the epoxidation
of cyclooctene with TBHP in comparison with complexes, CpMo(CO)$_3$Cl$^4$ and CpMo(CO)$_3$(CH$_3$)$_7$.$^a$ Due to the lack of catalytic data of CpMo(CO)$_3$Br in the literature, the catalytic activity of CpMo(CO)$_3$Br has also been examined in this work. The time-dependent curves for all catalytic reactions are shown in Figure 4.9. There was no significant formation of by-products (e.g. diol). Controlled reactions without the Mo(II) catalysts showed no significant formation of the epoxide product. The epoxide yields after 4 h, 8 h and 24 h of reaction time using 4-1 - 4-6 and 4-8 - 4-11 as catalysts are shown in Figure 4.10.

![Figure 4.9](image_url)

**Figure 4.9.** Time dependent yield of cyclooctene epoxide in the presence of compounds 4-1 - 4-6, 4-8 - 4-11 and CpMo(CO)$_3$Br as catalysts at 55 °C using TBHP as oxidant (catalyst : substrate : oxidant = 1:100:200).
Complex CpMo(CO)₃Br and compounds 4-8, 4-9 show similarly high activities towards olefin epoxidation to those of complexes CpMo(CO)₃Cl and CpMo(CO)₃(CH₃). With a 0.1 mol% catalyst loading, the TOF (turnover frequency) of compound 4-8 reaches 3420 h⁻¹, which is higher than that of CpMo(CO)₃Br (2040 h⁻¹). Under similar conditions, CpMoO₂Cl catalyzed oxidations reach maximum TOFs of ca. 4000 h⁻¹. Compounds 4-10, 4-11 also show good activity, although slightly lower than 4-8 and 4-9. The saturated NHC (SIMes) as a rich electron ligand didn’t show significant improvement in the catalytic result. Compounds 4-1 - 4-6 show much lower catalytic activities, although they still appear to be higher the ansa-bridged cyclopentadienyl-functionalized NHC complexes, (Cp’-NHC)Mo(CO)₂I (Cp’ = Cp, Cp*) which give negligible epoxide yields after 5 h. In general, the activities observed are almost independent on the NHC ligands present in complexes 4-1 - 4-6, although among them, compounds 4-3, 4-4b and 4-6 are slightly more active (Figure 4.9). During the course

Figure 4.10. Yield of the cyclooctene epoxide after 4 h (hatched bars), 8 h (grey and hatched bars) and 24 h (grey bars) of reaction time using the compounds 4-1 – 4-6, 4-8 – 4-11 as catalysts in the presence of TBHP.
of reactions using 4-1 - 4-6 as catalysts, formation of pale yellow or white precipitates was observed (the characterization of precipitates is discussed below). This suggests that complexes 4-1 - 4-6 decompose during the oxidation reaction and the decomposition products are poorly active towards epoxidation.

4.4 Examination of the Stability of Metal-NHC ligand bond under oxidative conditions.

The significant difference in the catalytic activity between the neutral complexes 4-1 - 4-6 and the ionic complex 4-8 - 4-11 prompted us to investigate the stability of the metal-NHC ligand bond of these NHC complexes under the oxidative conditions (in the presence of TBHP) by using $^1$H NMR and ESI-MS.

4.4.1 Stability of Mo-C(NHC) Bonds in 4-3, 4-4a and 4-6 under Oxidative Conditions.

Kinetic $^1$H NMR experiments on the oxidation reactions of 4-3, 4-4a and 4-6 were carried out by treatment with 5-fold excess of TBHP (~5.5 M in decane over molecular sieves 4 Å) at room temperature in CD$_3$CN upon stirring of the mixtures. In the case of 4-4a, the purple color persisted for 15 min; then a fast change from purple to yellow occurred and a pale yellow precipitate was formed. The Cp resonance at $\delta$ 5.44 ppm in the $^1$H NMR spectrum disappeared completely after 15 min of reaction. A single signal at $\delta$ 6.56 ppm and a set of weak peaks at $\delta$ 6.43-6.26 ppm were observed. The characteristic signals of an imidazolium salt appeared at $\delta$ 7.41-7.43 (12H), 5.39 (4H), and 9.19 ppm (1H). After 20 min, besides the peaks from the imidazolium salt, only a set of very weak peaks at $\delta$ 6.54, 6.45, and 6.36 ppm could be observed. Similar observations were noted in 4-3 and 4-6. In the case of 4-3, after 15 min, the characteristic signals of the corresponding imidazolium salt appeared at $\delta$...
8.79 (1H), 7.76 (2H), 7.14 (4H), 2.36 (6H), and 2.12 ppm (12H). The peaks at δ 6.54-6.26 ppm are likely from the decomposition products of the Cp ligand. Similarly, in the case of 6, at 5 min, a weak peak at δ 4.66 ppm corresponding to the methylene protons of the imidazolium salt was observed beside the Cp ring signal (at δ 4.64 ppm). After 10 min, the purple color faded off totally to give a colourless solution and the 1H NMR signal of Cp ring at δ 4.64 ppm disappeared completely. Characteristic peaks corresponding to that of imidazolium salt appeared at δ 8.22(1H), 6.94 (4H) and 4.65 ppm (4H). The behavior of 4-3, 4-4a, 4-6 under the oxidative condition are similar to the (η^3-allyl)Mo(bis-NHC)Cl\textsuperscript{11d} which decomposed to form imidazolium salt in the present of TBHP.

By comparing the 1H NMR spectra of the corresponding imidazolium bromides in CD\textsubscript{3}CN, there is a shift of the signal of the proton of NCH\textsubscript{N} in the 1H NMR of the imidazolium salt formed from the reaction between 4-3, 4-4a or 4-6 and TBHP. This difference may be due to the presence of the excess amount of TBHP and 'BuOH formed during the oxidation reaction. It was confirmed by treating the NMR sample of IBzHBr in CD\textsubscript{3}CN with 0.05 mL of TBHP. It was observed that the signal of NCH\textsubscript{N} shifted from δ 9.29 to 9.15 ppm. Similarly, in the case of IMesHBr, the signal of NCH\textsubscript{N} shifted from δ 9.18 to 8.87 ppm after TBHP was added. As was observed in the kinetic reactions discussed above, a broad peak at ca. δ 9 ppm is due to the presence of TBHP. The imidazolium salt formed from the oxidation reactions is accordingly assigned as imidazolium bromide.

The pale yellow precipitate formed during the oxidation reactions using 4-3 as catalyst was found to be soluble in DMSO. It was characterized by IR, 1H NMR, ESI-MS, elemental analysis (see Experimental Section), and X-ray single crystal diffraction (see Figure 4.11). The IR spectrum shows strong absorptions at 955 and 800 cm\textsuperscript{-1} from the Mo=O bond stretching. The proton NMR spectrum shows that the obtained solid is a pure imidazolium salt with the most characteristic singlet peak at δ 9.63 ppm. In order to identify the anion,
ESI-MS analysis was performed. The imidazolium cation can be observed (m/z 305.3) in the positive mode spectrum. The negative mode spectrum reveals seven Mo-containing anionic species including \([\text{IMesH}[\text{Mo}_6\text{O}_{19}]]^-\) centered at m/z 1183, \([\text{HMo}_6\text{O}_{19}]^-\), \([\text{Mo}_6\text{O}_{19}]^{2-}\), \([\text{Mo}_5\text{O}_{16}]^{2-}\), \([\text{Mo}_4\text{O}_{13}]^{2-}\), \([\text{Mo}_3\text{O}_{10}]^{2-}\) and \([\text{HMoO}_4]^−\), which are assigned based on the m/z values, the difference in m/z between adjacent peaks and their isotopic distribution patterns (see Figure 4.12). Combining the spectroscopic results and the elemental analysis data, the pale-yellow precipitate is identified as \([\text{IMesH}]_2[\text{Mo}_6\text{O}_{19}]\) and was approved by the X-ray single crystal diffraction later. Single crystal of \([\text{IMesH}]_2[\text{Mo}_6\text{O}_{19}]\) was obtained from acetonitrile at room temperature. The bond lengths of Mo and terminal and bridged oxygen are comparable to the reported same anion.\(^{13}\)

The formation of polyoxomolydates as anion in metal complexes has been reported in the literature. For example, a reaction of \(\text{MoO}_2(\text{S}_2\text{CNMe}_2)\) with \(\text{RuCl}_3\cdot x\text{H}_2\text{O}\) in acetone at reflux afforded a Ru complex with \([\text{Mo}_6\text{O}_{19}]\) as anion.\(^{15a}\) Reactions of \(\text{MoO}_2(\text{acac})_2\) with corresponding ligands (L) in aqueous methanol have been reported to give complexes \([\text{Mo}_2\text{O}_2\text{L}_6][\text{Mo}_6\text{O}_{19}]\) (L = H\(_2\)O, dimethylformamide, etc.)\(^{15b}\) However, the polyoxomolydate species as oxidation products have not been characterized in the similar epoxidation reactions catalyzed by Mo(II) and Mo(VI) complexes in the presence of TBHP or H\(_2\)O\(_2\), although in some cases a white color precipitate could be observed in the epoxidation catalysis under similar conditions.\(^{4-6}\) In our system, the formation of polyoxomolydates may be due to the presence of trace amount of water in the oxidation system. The catalytic activity of \([\text{IMesH}]_2[\text{Mo}_6\text{O}_{19}]\) was examined in this work, and it was found that under the same catalytic conditions it shows similar activity as compound 4-3.
Figure 4.11. ORTEP diagram of \{[IMesH][Mo_8O_{19}]^\}\_ (30% probability ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) Mo(1)-O(1) 1.913(2), Mo(1)-O(2) 1.688(2), Mo(1)-O(3) 1.879(2), Mo(1)-O(10) 2.3084(3)
Figure 4.12. The negative mode ESI-spectrum of the imidazolium salt [Mo₆O₁₉][IMesH]₂ obtained from the oxidation reaction between compound 4-3 and TBHP.

ESI-MS analysis was carried out to follow the reaction between TBHP and 4-4a (ratio 10:1) in acetonitrile at room temperature. Initially, the positive mode ESI spectrum of 4-4a (Figure 4.13a) showed four sets of peaks centered at m/z 507.5, 467, 439, and 411, corresponding to \([\text{CpMo(CO)}₂\text{(IBz)}(\text{CH₃CN})]⁺\), \([\text{CpMo(CO)}₂\text{(IBz)}]⁺\), \([\text{CpMo(CO)}\text{(IBz)}]⁺\), and \([\text{CpMo(IBz)}]⁺\), respectively, and MS/MS analysis was performed to verify the presence of these species. After 25min of reaction time with TBHP, the ESI-MS spectrum indicated the decomposition of 4-4a (Figure 4.13b).

The peaks at m/z 249 and 577 are assigned to be \([\text{IBzH}]⁺\) and 4-12, respectively. The assignment of 4-13 to the peak at 293 m/z is strongly supported by the loss of 44 m/z in MS/MS coupled with CID (collision induced dissociation). Its detection suggests that free
carbene could be formed during the oxidation of CpMo(CO)$_2$(IBz)Br. This is supported by the well-documented reaction between carbene and CO$_2$.¹⁶ In our case, CO$_2$ is generated from the oxidation of CpMo(CO)$_2$(IBz)Br. Both set of peaks at $m/z$ 349 and 679 can be assigned to imidazolium derivatives on the basis of CID coupled with MS$^n$ and the isotopic distribution; however, their structures could not be interpreted satisfactorily with the current data. In the negative mode spectrum, the set of peaks from Br$^-$ was observed, which supports the presence of imidazolium bromide in the reaction solution. The peaks from [Mo$_6$O$_{19}$]$^{2-}$, [Mo$_5$O$_{16}$]$^{2-}$ and [Mo$_4$O$_{13}$]$^{2-}$ were identified from their characteristic isotopic distribution patterns and $m/z$ ratios.

[CpMoO$_2$(IBz)]$^+$ species was detected in the reaction mixture of 4-4a and TBHP only after 5min. However, its peaks overlap with those of [CpMo(CO)(IBz)]$^+$, but the isotopic distribution observed is in agreement with the theoretically predicted one based on the combination of both ions (see Figure 4.11). This is consistent with the observation of a singlet peak in the $^1$H NMR at 6.56 ppm which could be assigned to the protons of the Cp ring in the [CpMoO$_2$(IBz)]$^+$ species.
4.4.2 Examination of the stability of Mo-C(carbene) bond in 4-8 - 4-11 under oxidative condition and the formation of [CpMoO$_2$(NHC)][BF$_4$] 4-14 - 4-17.

Oxidation of compound 4-8 - 4-11 in CH$_3$CN by TBHP (~5.5 M in decane over molecular sieves 4 Å) gives the dioxo complex, [CpMoO$_2$(NHC)][BF$_4$], compound 4-14 - 4-17 (see Scheme 4.3).
**Scheme 4.3** Synthesis of compounds 4-14 – 4-17

Figure 4.14. Kinetic $^1$H-NMR experiments on the reaction of compound 4-8 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CD$_3$CN.

Compounds 4-14 and 4-16 demonstrate relatively higher stability compared to previously reported high oxidation state molybdenum NHC complexes obtained from the reactions between MoO$_2$Cl$_2$(THF)$_2$ and free NHC ligands. Its stability allowed us to fully characterize the dioxo complex 4-14. The formation of 4-14 and 4-16 were studied by the kinetic $^1$H-NMR experiments by the treatment of compound 4-8 and 4-10 with 5-fold excess...
of TBHP at room temperature in CD$_3$CN upon stirring of the mixture in a glovebox under argon (see Figure 4.14 and 4.15). In figure 4.14, after 5 min, 3 singles appeared at $\delta$ 6.26 ppm, 7.11 ppm and 7.85 ppm, respectively, in a ratio of 5:4:2 due to the formation of compound 4-14. The intensity of these three peaks increased with time, while the intensity of peaks from compound 4-8 decreased. After 80 min, the peaks from 4-14 dominated the spectrum. Comparing with $^1$H NMR spectrum of 4-8, the signal of Cp ring in 4-14, shifts to lower field significantly and the meta-CH groups in the two phenyl rings become equivalent with one single peak appearing at the average chemical shifts of the two nonequivalent meta-CH groups in the carbonyl precursor, 4-8. Similarly, four ortho-methyl groups at the phenyl rings are also equivalent with one single peak, implying a fast rotation of N-mesityl bond in the IMes ligand. The chemical shift of the CH=CH in the NHC ring also change significantly (ca. 0.4 ppm). The $^{13}$C NMR carbene carbon signal of 4-14 is shifted to higher field ($\delta$ 167 ppm) in comparison with that of low oxidation state complexes 4-3 and 4-6 ($\delta$ 189.7 and 183.9 ppm).

The formation of 4-14 has also been proved by ESI-MS analysis, IR and the elemental analysis. In ESI-MS, the characteristic peaks of [CpMoO$_2$(IMes)]$^+$ appear at m/z 494-504 and peaks of polyoxomolydates are not been observed. The IR spectrum shows the strong absorptions at 956 cm$^{-1}$ and 801 cm$^{-1}$ from the Mo=O stretching vibration. This work shows that thermally stable ionic Mo(VI) dioxo NHC complex can be formed through the oxidation of the carbonyl precursor. This is similar to the formation of Cp’MoO$_2$Cl (Cp’ = Cp, Cp*, Cp$^{Bz}$) from Cp’Mo(CO)$_3$Cl.$^4$ The high catalytic activity of compound 4-8 is attributed to the stability of the metal-NHC ligand bond in the [CpMoO$_2$(IMes)]$^+$ species, which is formed in situ in the catalytic epoxidation mixture containing precatalyst 4-8 and TBHP. Under the same condition, compounds 4-8 and 4-14 show very similar catalytic activities towards cis-cyclooctene epoxidation using TBHP as oxidant. These fact support that they are
mechanistically related.

\[ \text{Figure 4.15. Kinetic } ^1\text{H-NMR experiments on the reaction of compound 4-10 and TBHP (5.5 M in decane, 5-fold excess) at room temperature in CD}_3\text{CN.} \]

In figure 4.15, after 5 min, the appearance of two single peaks at \( \delta 4.30 \) and 6.31 ppm indicates the formation of compound 4-16 and the intensity of these peaks increases with time. On the other hand, the intensities of the singlet at \( \delta 4.88 \) (5H) and the multiplet at \( \delta 4.05 \) ppm (4H) from compound 4-10 decrease with time. By 10 h, the \(^1\text{H NMR spectrum was dominated by peaks from compound 4-16. There are some significant difference between the }\)

\(^1\text{H NMR spectra of compound 4-10 and that of 4-16. The signal of Cp ring shifted downfield significantly from } \delta 4.88 \text{ to 6.31 ppm. At 10 h, a singlet was observed for the phenyl protons at meta-position instead of two discrete singlets of compound 4-10. This suggests that the protons at meta-position of the phenyl ring are equivalent in compound 4-16. Additionally, a singlet at } \delta 2.34 \text{ ppm (12H) corresponding to the four methyl groups at ortho-positions on the} \]
phenyl rings was observed instead of two singlets with integration value of 6H each which also suggest that the methyl groups at ortho-position of the phenyl ring in compound 4-16 are equivalent. In addition, the methylene protons in compound 4-16 are also equivalent to each as a singlet was observed instead of a multiplet for that of compound 4-10. At the end of 10h, the signals of 4-16 dominate the spectrum indicating that the Mo-C(NHC) bond in 4-16 is stable under oxidative condition.

The formation of compounds 4-15 and 4-17 were also detected by $^1$H NMR. The signals of Cp appeared at δ 6.50 (4-15) and 6.42 ppm (4-17) (see experimental part). However, beside the signals of products, the characteristic signals of imidazolium salt were also observed in the spectra with the integration ratio 1:1 comparing with the dioxo complexes. The cleavage of Mo-C(NHC) bond was due to the less bulky NHC ligand involved. $^1$H NMR of compound 4-17 exhibits only one singlet corresponding to that of Cp ring at 6.42 ppm, unlike that of compound 7 and 11 which gives two neighbouring Cp ring signals in the $^1$H NMR spectra. This illustrates that compound 4-17 does not exist as a pair of optical isomer like compounds 4-7 and 4-11 as the metal centre in compound 4-17 is not chiral.

The single crystal of $\{[\text{CpMoO}_2(\text{IBz})(\text{CH}_3\text{CN})][\text{Mo}_6\text{O}_{19}]\}$ was obtained from acetonitrile solution of 4-15 at room temperature. The formation of polyoxomolydates may be due to the presence of trace amount of water in the oxidation system, as discussed above. As shown in figure 4.16, two Mo=O are cis configuration. The Mo=O bond lengths of 1.71 and 1.69 Å and the angle O-Mo-O at 109° are comparable to the similar CpMoO$_2$ species$^{14}$. The bond length of Mo-C(NHC) at 2.174 Å is shorter than the corresponding low valent compounds 4-4b (2.221 Å) and 4-9 (2.229 Å).
Figure 4.16. ORTEP diagram of \([\text{CpMoO}_2(\text{IBz})(\text{CH}_3\text{CN})][\text{Mo}_6\text{O}_{19}]^-\) (30% probability ellipsoids). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg) Mo(1)-O(1) 1.711(3), Mo(1)-O(2) 1.694(3), Mo(1)-C(1) 2.173(4), O(1)-Mo(1)-O(2) 109.23(18), O(1)-Mo(1)-C(1) 101.51(16), O(2)-Mo(1)-C(1) 98.59(17), N(1)-C(1)-Mo(1) 127.3(3), N(2)-C(1)-Mo(1) 126.9(3)

4.5. DFT Studies.

DFT calculations were performed at the B3LYP level of theory\(^{18-20}\) in order to gain more insight into the difference in the stability of Mo-NHC ligand bonds in the neutral compounds 4-1 - 4-7 and the ionic compounds 4-8 - 4-11 under the oxidative conditions. Compound 4-1 was chosen to maximize computational efficiency. Consistent with the X-ray molecular structure, the \textit{trans} isomer (4-1-\textit{trans}) is 8.9 kcal/mol less stable than 4-1. The geometrical parameters of the fully optimized structure are in general in good agreement of the experimental results, with slightly longer bond distances (Table 4.1). Gas phase geometry
optimization of CpMoO$_2$(IME)Br was performed using the same method. The trans isomer is 1.4 kcal/mol more stable than the cis isomer. For both cis and trans isomers, an increase of the Mo-ligand bond lengths was predicted (Table 4.2). This result promoted us to investigate the structure of [CpMoO$_2$(IME)]$^+$. Overall shortening of Mo=O, Mo-C(NHC), and Mo-Cp bonds was predicted upon removal of Br$^-$ from the coordination sphere (Table 4.2). This suggests that the coordination of Br$^-$ to Mo weakens the Mo-ligand bonds. The plausible destabilizing effect of Br$^-$ was further examined by calculating the IMe binding energies to [CpMoO$_2$]$^-$ and CpMoO$_2$Br fragments. It was found that in the gas phase, the dissociation of IMe from [CpMoO$_2$(IME)]$^+$ is highly thermodynamically disfavored ($\Delta G$ = 85.1 kcal/mol). In sharp contrast, the dissociation of IMe from trans-CpMoO$_2$(IME)Br is exergonic ($\Delta G$ = -7.9 kcal/mol). These results suggest that the presence of Br$^-$ may cause the dissociation of the carbene ligands in the oxidation products of compounds 4-1 - 4-7, i.e. CpMoO$_2$(NHC)Br, leading to the decomposition and deactivation of these Mo-oxo species. To examine this hypothesis, a CD$_3$CN solution of [CpMoO$_2$(IMes)]$^+$/[BF$_4$]$_2$ (4-14) was treated with one molar equivalent of $^8$Bu$_4$NBr. The $^1$H NMR spectrum indicated that the imidazolium salt was formed in the reaction mixtures and [CpMoO$_2$(IMes)]$^+$/[BF$_4$]$_2$ fully decomposed. It is similar to that of the reaction between CpMo(CO)$_2$(IMes)Br and TBHP. Furthermore, the formation of the corresponding imidazolium salt and the decomposition of CpMoO$_2$Br were also observed in the $^1$H NMR spectra of the reaction mixture when a CD$_3$CN solution of CpMoO$_2$Br, prepared from the oxidation of CpMo(CO)$_3$Br solution by TBHP,$^4$ was treated with one molar equivalent of free NHC, 1,3-bis(2,6-diisopropylpheny)imidazol-2-ylidene. While the decomposition route of CpMoO$_2$ species into polyoxomolybdates is not clear, these observations together with the calculation results confirm that the presence of Br$^-$ destabilizes the CpMo(VI) oxo NHC carbene species.
**Table 4.1** Calculated bond lengths and angles vs. experimental data for CpMo(CO)$_2$(IME)Br (4-1). (See Figure 4.1 for labeling)

<table>
<thead>
<tr>
<th>Bond Length (Å) or Angle (°)</th>
<th>Experimental (X-ray)</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-C1</td>
<td>2.224</td>
<td>2.242</td>
</tr>
<tr>
<td>Mo-Br</td>
<td>2.667</td>
<td>2.723</td>
</tr>
<tr>
<td>Mo-C11</td>
<td>1.977</td>
<td>1.981</td>
</tr>
<tr>
<td>Mo-C12</td>
<td>1.941</td>
<td>1.964</td>
</tr>
<tr>
<td>Mo-Cp</td>
<td>2.021</td>
<td>2.097</td>
</tr>
<tr>
<td>C1-Mo-Br</td>
<td>80.35</td>
<td>76.10</td>
</tr>
<tr>
<td>C11-Mo-C12</td>
<td>77.45</td>
<td>79.09</td>
</tr>
</tbody>
</table>

**Table 4.2** Calculated structural parameters of CpMo complexes.

<table>
<thead>
<tr>
<th>Geometrical parameters</th>
<th>CpMo(CO)$_2$(IME)Br</th>
<th>CpMoO$_2$(IME)Br</th>
<th>CpMoO$_2$(IME)$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Br</td>
<td>2.723</td>
<td>2.931</td>
<td>-</td>
</tr>
<tr>
<td>Mo-C(NHC)</td>
<td>2.242</td>
<td>2.254</td>
<td>2.182</td>
</tr>
<tr>
<td>Mo-Cp</td>
<td>2.097</td>
<td>2.233</td>
<td>2.177</td>
</tr>
<tr>
<td>Mo=O</td>
<td>-</td>
<td>1.745/1.717</td>
<td>1.715/1.715</td>
</tr>
</tbody>
</table>

**4.6 Conclusion**

In this work, a series of NHC complexes with the formula CpMo(CO)$_2$(NHC)X (4-1 - 4-7) and the ionic complexes [CpMo(CO)$_2$(IMes)(NHC)][BF$_4$] (4-8 - 4-11), as well as the oxidation products [CpMoO$_2$(NHC)] [BF$_4$] (4-14 - 4-17), have been synthesized and characterized. Chiral compound 4-7 is likely to exist as a pair of optical isomers due to chiralities of both the metal centre and the NHC ligand. Complexes 4-1 - 4-7 show low catalytic activities toward the epoxidation of cyclooctene with TBHP, while the ionic compounds 4-8 - 4-11 are a highly active catalyst comparable to compound CpMo(CO)$_3$Cl. Dioxo compound 4-14 - 4-17 can be formed *in situ* in the epoxidation reaction system (using TBHP as oxidant) catalyzed by 4-8 - 4-11. Compound 4-14 is tested to show similarly high catalytic activity to its precursor 4-8. This is similar to the olefin epoxidation catalyzed by CpMo(CO)$_3$Cl (using TBHP as oxidant), where CpMoO$_2$Cl is formed in situ in the reaction.
system. The latter 16e complex has been attributed to the actual catalyst species.\textsuperscript{4} For compounds 4-1 - 4-7, the proposed oxidation products are a class of Mo(VI) dioxo compounds with the formula CpMoO\textsubscript{2}(NHC)Br; however, these 18e complexes cannot be isolated. In our ESI-MS studies, only [CpMoO\textsubscript{2}(NHC)]\textsuperscript{+} species can be observed at the beginning of the reaction between TBHP and CpMo(CO)\textsubscript{2}(NHC)Br. CpMoO\textsubscript{2}(NHC)Br species decompose to imidazolium salts (bromide and polymolybdate) and some unidentified products, which leads to the poor catalytic activities of 4-1 - 4-7. Introducing the higher electron rich NHC ligand like SIMes didn’t seem to improve its stability. DFT calculations suggest that the presence of Br- destabilizes the Mo- NHC ligand bond in the CpMo(VI) oxo NHC carbene species. Combined with the experimental observations, the coexistence of Br- and NHC ligands in CpMoO\textsubscript{2}(NHC)Br is responsible for the decomposition of the species with a CpMoO\textsubscript{2} core in our system.

The high catalytic activity of the ionic compounds 4-8 - 4-11 shown in the olefin epoxidation reactions with TBHP as oxidant and the stability of their Mo-NHC ligand bond in the oxidation product are encouraging. This provides a possible route to introduce chiral and/or some functional groups to the [CpMo(CO)\textsubscript{2}(NHC)]\textsuperscript{+} core in order to develop active chiral selective catalysts or heterogenized catalysts for heterogeneous epoxidation reactions. The asymmetric epoxidation of the chiral compound 4-11 will be studied in the further work.

4.7 Experimental Section

**General Considerations.** All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under nitrogen and used immediately. TBHP (\textit{tert}-butyl hydrogen peroxide, 5.5 M in decane kept in 4Å molecular sieve) was purchased from Sigma-Aldrich. Elemental
analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. $^1$H and $^{13}$C NMR were measured in CD$_3$CN and CDCl$_3$ at room temperature unless stated otherwise with AMX500 500 MHz FT NMR spectrometer. ($^1$H at 500 MHz, $^{13}$C at 75.43 MHz). IR spectra were recorded on a Shimadzu IR-470 spectrometer using KBr pellets as IR matrix. ESI-MS was performed on a Finnigan LCQ quadrapole ion trap mass spectrometer. Sample was introduced into the ESI-source using a syringe pump. The following ESI-MS parameters were kept constant for all measurement: Spray voltage = +/- 3.5kV Capillary Temperature = 100 °C ; Flow rate = 5 µL min$^{-1}$; Tube lens offset = 0 V and capillary voltage = 0 V. The spectra were obtained as an average of at least 20 scans. Catalytic runs were monitored by GC methods on the Agilent 6890 Series GC instrument with a J&W DB-1 column. The preparation of imidazolium bromide, $^{19}$-24 and the corresponding silver NHC complexes$^{27}$-29 were based on the literature procedure. CpMo(CO)$_3$Br$_3$ and CpMo(CO)$_2$PPh$_3$Br$_3$ were prepared according to literature method.

4.7.1 Synthesis of 1,3-bis(2,4,6-trimethylphenyl)imidazolium bromide (IMesHBr).

To a solution of $N,N'$-Bis(2,4,6-trimethylphenyl)ethanediimine$^{32}$ (10 mmol) in toluene (20 mL) at 10 °C, paraformaldehyde (0.3g, 10 mmol) was added with vigorously stirring. After 30 min, the solution was cooled to 0 °C, and an aqueous solution of HBF$_4$ (50% w/v, 10 mmol, 2 g) was added dropwise. The resulted solution was stirred at room temperature for further 30 min and then heated to 40 °C for 12 h. After cooling to room temperature, Et$_2$O (10 mL) was added and the slurry was filtered and washed with ethyl acetate and THF, and vacuum dried, yielding IMesHBF$_4$ as a beige powder (Yield: 3.05 g, 78%). To the suspension of ethyl acetate solution (10 mL) of IMesHBF$_4$ (1.25mmol, 0.5g), saturated acetone solution of $^9$BuN$_4$Br (5 mmol, 1.6 g) was introduced dropwise. The mixture was stirring for 12 h at room temperature. The resultant suspension was filtered and washed with ethyl acetate, dried under vacuum, resulting in IMes HBr as a white powder. (Yield: 0.33 g, 69%).
4.7.2 Synthesis of Compounds 4-1, 4-2, 4-4a, 4-5 and 4-6.

Ag₂O (1 mmol) was added to a solution of the imidazolium bromide (1 mmol) in CH₂Cl₂ (15 mL). After stirring at room temperature for 24 h (exclusion of light), the reaction mixture was filtered through Celite. The filtrate was dried under vacuum and was dissolved in toluene (20 mL). CpMo(CO)₃Br (0.6 mmol) was then added to the toluene solution. After refluxing for 40 min under stirring, the obtained purple solution was dried under vacuum, and the purple solid was purified by column chromatography eluted by a mixture of hexane and ethyl acetate (2:1 to 5:1) to give the product as a purple solid.

(η⁵-C₅H₅)Mo(CO)₂(IMe)Br (4-1). (Yield: 70 mg, 30%) ¹H NMR (500 MHz, CD₃CN): δ (ppm) = 7.16 (s, 2H, =CH), 5.61 (s, 5H, Cp), 3.64 (s, 6H, NCH₃). ¹³C NMR (125.77 MHz, CD₃CN): δ (ppm) = 255.87 (s, Mo-CO), 251.80 (s, Mo-CO), 185.01 (s, NCN), 124.81 (s, =CH), 96.04 (s, Cp), 40.53 (s, NCH₃). IR (KBr)/cm⁻¹: νₛₗₜ(CO) 1955 (vs), νₐₛₗₜ (CO) 1832 (vs), Iₐₛₗₜ/Iₘₛₗₜ = 1.06 (predicted OC-Mo-CO angle 92°). Anal. Calcd for C₁₂H₁₃BrN₂O₂Mo: C, 36.67; H, 3.33; N, 7.13. Found: C, 36.96; H, 3.32; N, 6.89.

(η⁵-C₅H₅)Mo(CO)₂(InPr)Br (4-2). (Yield: 81 mg, 30%) ¹H NMR (500 MHz, CD₃CN): δ (ppm) = 7.26 (s, 2H, =CH), 5.56 (s, 5H, Cp), 4.05-4.00 (br m, 2H, NCH₂CH₂CH₃), 3.85-3.80 (br m, 2H, NCH₂CH₂CH₃), 1.81-1.74 (m, 4H, NCH₂CH₂CH₃), 0.94 (t, 6H, NCH₂CH₂CH₃, J = 7.55 Hz). ¹³C NMR (125.77 MHz, CD₃CN): δ (ppm) = 254.95 (s, Mo-CO), 251.19 (s, Mo-CO), 183.36 (s, NCN), 123.58 (s, =CH), 96.23 (s, Cp), 54.26 (s, NCH₂CH₂CH₃), 24.69 (s, NCH₂CH₂CH₃), 11.33 (s, NCH₂CH₂CH₃). IR (KBr)/cm⁻¹: νₛₗₜ(CO) 1946 (vs), νₐₛₗₜ (CO) 1841 (vs), Iₐₛₗₜ/Iₘₛₗₜ = 1.17 (predicted OC-Mo-CO angle 95°). Anal. Calcd for C₁₆H₂₁BrN₂O₂Mo: C, 42.78; H, 4.71; N, 6.24. Found: C, 42.70; H, 4.53; N, 6.21.

(η⁵-C₅H₅)Mo(CO)₂(IBz)Br (4-4a). (Yield: 160 mg, 50%) ¹H NMR (500 MHz, CD₃CN): δ
(ppm) = 7.40-7.26 (br m, 10H, CH₂Ph), 7.06 (s, 2H, =CH₂), 5.41 (s, 5H, Cp), 5.36-5.23 (q, 4H, NCH₂Ph, J = 15.75Hz). ¹³C NMR (125.77 MHz, CD₃CN): δ (ppm) = 254.04 (s, Mo-CO), 251.22 (s, Mo-CO) 186.95 (s, NCN), 138.00, 129.71, 128.81, 128.60 (phenyl), 124.38 (s, =CH), 96.16 (s, Cp), 56.36 (s, PhCH₂N). IR (KBr)/cm⁻¹: ν_sym(CO) 1952 (vs), ν_asym(CO) 1874 (vs), I_asym/I_sym =1.06 (predicted OC-Mo-CO angle 92°). Anal. Calcd for C₂₄H₂₁BrN₂O₂Mo: C, 52.86; H, 3.88; N, 5.14. Found: C, 53.19; H, 3.98; N, 5.09.

(η⁵-C₅H₅)Mo(CO)₂(IMe₅Pr)Br (4-5). (Yield: 115 mg, 45%) ¹H NMR (500 MHz, CD₃CN): δ (ppm) = 7.21 (s, 2H, =CH₂), 5.58 (s, 5H, Cp), 4.03-3.97 (m, 1H, NCH₂CH₂CH₃), 3.89-3.83 (m, 1H, NCH₂CH₂CH₃), 3.63 (s, 3H, NCH₃), 1.79-1.75 (m, 2H, NCH₂CH₂CH₃), 0.94 (t, 3H, NCH₂CH₂CH₃, J = 6.95Hz). ¹³C NMR (125.77 MHz, CD₃CN): δ (ppm) = 255.46 (s, Mo-CO), 251.47 (s, Mo-CO) 184.08 (s, NCN), 125.37 (s, =CH), 123.03 (s, =CH), 96.15 (s, Cp), 54.25 (s, NCH₂CH₂CH₃), 40.44 (s, NCH₃), 24.81 (s, NCH₂CH₂CH₃), 11.30 (s, NCH₂CH₂CH₃). IR (KBr)/cm⁻¹: ν_sym(CO) 1959 (vs), ν_asym(CO) 1858 (vs), I_asym/I_sym =1.09 (predicted OC-Mo-CO angle 93°). Anal. Calcd for C₁₄H₁₇BrN₂O₂Mo: C, 39.93; H, 4.07; N, 6.65. Found: C, 39.71; H, 4.23; N, 6.15.

(η⁵-C₅H₅)Mo(CO)₂(I*PhEt)Br (4-7). ¹H NMR (500 MHz, CD₃CN): 7.26–7.40 (m, 22H, Ph and =CH), 6.93 (s, 1H, NCHPh), 5.88-5.86 (m, 3H, NCHMePh), 5.55 (s, 3H, Cp), 5.44 (s, 5H, Cp), 1.78–1.80 (m, 11H, NCHMePh). ¹³C NMR (125.77 MHz, CD₃CN): δ (ppm) = 254.1 (s, Mo-CO), 251.6 (s, Mo-CO), 251.0 (s, Mo-CO), 187.5 (s, NCN), 186.40 (NCN), 142.3, 141.4, 129.9, 129.3, 129.2, 128.5, 128.3, 128.0, 127.2 (s, Ph), 121.7 (s, =CH₂), 121.5 (s, =CH₂), 96.7 (s, Cp), 96.5 (s, Cp), 59.9 (s, NCHMePh), 59.6 (s, NCHMePh), 21.7 (s, CH₃), 20.9 (s, CH₃). IR (KBr) / cm⁻¹ : ν_sym(CO) = 1954 (vs), ν_asym(CO) = 1854, I_asym/I_sym = 1.05 (predicted OC-Mo-CO angle 91°).

4.7.3 Synthesis of Compounds 4-3 and 4-6.
Ag₂O (232 mg, 1 mmol) was added to a solution of 1 mmol imidazolium salt (IMesHBr or SIMesHBr) in CH₂Cl₂ (15 mL). After the mixture was refluxed for 7 h upon exclusion of light, the solution was filtered through Celite and the filtrate was dried under vacuum and resulted solid was dissolved in distilled toluene (20 mL). CpMo(CO)₃Br (195 mg, 0.6 mmol) was added to the toluene solution of this silver carbene. After the mixture was stirred for 40 min under reflux, the purple solution was dried under vacuum and the purple solid was purified by column chromatography (hexane: ethyl acetate = 5: 1) to give product.

(η⁵-C₅H₅)Mo(CO)₂(IMes)Br (4-3). (Yield: 272 mg, 75%) as purple solid. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.14 (s, 2H, =CH), 7.05 (s, 2H, m-H-Mes), 7.00 (s, 2H, m-H-Mes), 4.71 (s, 5H, Cp), 2.38 (s, 6H, p-Me-Mes), 2.25 (s, 6H, o-Me-Mes), 2.17 (s, 6H, o-Me-Mes).

¹³C NMR (125.77 MHz, CDCl₃): δ (ppm) = 253.92 (s, Mo-CO), 246.60 (s, Mo-CO), 189.72 (s, NCN), 139.17 (s, i-Mes), 137.45 (s, p-Mes), 136.83 (s, o-Mes), 136.43 (s, o-Mes), 129.10 (s, m-Mes), 124.51(s, =CH), 94.75 (s, Cp), 21.06 (s, p-Me-Mes), 19.06 (s, o-Me-Mes). IR (KBr/cm⁻¹): νₚₛₘ(CO) 1956 (vs), νₚₘₚₚ(CO) 1860 (vs), Iₚₘₚₚ/Iₚₛₘ = 1 (predicted OC-Mo-CO angle 90°).

Anal. Calcd for C₂₈H₂₉BrN₂O₂Mo: C, 55.92; H, 4.86; N, 4.66. Found: C, 55.91; H, 4.72; N, 4.70.

(η⁵-C₅H₅)Mo(CO)₂(SIMes)Br (4-6). (0.04g, 8%). ¹H NMR (500MHz, CDCl₃, room temperature): δ (ppm) = 7.01 (s, 2H, m-H-Mes), 6.95 (s, 2H, m-H-Mes), 4.64 (s, 5H, Cp), 3.98-3.95 (m, 4H, NCH₂CH₂N), 2.50 (s, 6H, o-Me-Mes), 2.37 (s, 6H, o-Me-Mes), 2.33 (s, 6H, p-Me-Mes).

¹H NMR (500MHz, CDCl₃, -50 °C): δ (ppm) = 7.10 (s, 1H, m-H-Mes), 7.05(s, 1H, m-H-Mes), 7.00(s, 1H, m-H-Mes),6.94 (s, 1H, m-H-Mes), 4.62 (s, 5H, Cp), 4.07-3.96 (m, 4H, NCH₂CH₂N), 2.54 (s, 3H, o-Me-Mes), 2.44(s, 3H, o-Me-Mes), 2.40(s, 3H, o-Me-Mes) 2.38 (s, 3H, o-Me-Mes), 2.35 (s, 6H, o-Me-Mes). ²³C NMR (125.77MHz, CDCl₃, room temperature): δ (ppm) = 255.3 (s, Mo-CO), 247.1 (s, Mo-CO),
218.5 (s, NCN), 138.2 (s, br, p-Mes), 137.9 (s, br, o-Mes), 129.5 (s, br, m-Mes), 95.0 (s, Cp), 30.9 (s, p-Me-Mes), 21.0 (s, o-Me-Mes), 19.2 (s, o-Me-Mes). $^{13}$C NMR (125.77MHz, CDCl$_3$, -50 °C): $\delta$ (ppm) = 254.65 (s, Mo-CO), 248.50 (s, Mo-CO), 216.83 (s, NCN), 138.90, 138.52, 138.32, 138.07, 137.81, 136.53, 136.49, 136.05, 129.91,129.24, 129.01,128.42(s, Mes), 94.84 (s, Cp), 52.92, 50.70 (s, N-CH$_2$), 21.14, 21.06 (s, p-Me-Mes), 20.49, 19.12, 18.99, 18.93 (s, o-Me-Mes). ESI –MS (in CHCl$_3$, m/z (%)) = [M + – Br] = 525 (100), [M$^+$ – Br – 2CO] = 469 (23). IR (KBr) / cm$^{-1}$: $\nu$sym(CO) = 1959 (vs), $\nu$asym (CO) = 1863, $I_{asym}/I_{sym}$ = 1.11 (predicted OC-Mo-CO angle 93°) Anal. Calcd for C$_{28}$H$_{31}$BrN$_2$O$_2$Mo: C, 55.73; H, 5.18; N, 4.64. Found: C, 55.81; H, 5.18; N, 4.13.

4.7.4 Synthesis of ($\eta^5$-C$_5$H$_5$)Mo(CO)$_2$(IBz)Br (4-4a) and ($\eta^5$-C$_5$H$_5$)Mo(CO)$_2$(IBz)Cl (4-4b) from CpMo(CO)$_2$PPh$_3$Cl.

Ag$_2$O (232 mg, 1 mmol) was added to a solution of 1,3-dibenzylimidazolium bromide (329 mg, 1 mmol) in CH$_2$Cl$_2$ (15 mL). After the mixture was stirred for 24 h at room temperature upon exclusion of light, the solution was filtered through Celite and the filtrate was dried under vacuum and dissolved in distilled toluene (20 mL). CpMo(CO)$_2$PPh$_3$Cl (309 mg, 0.6 mmol) was added to the toluene solution of this silver carbene. After the mixture was stirred for 30 min under reflux, the purple solution was dried under vacuum and purified by column chromatography (hexane : ethyl acetate = 5: 1). The two purple bands were collected as 4-4a (Yield: 98 mg, 30%) and 4-4b (Yield: 30 mg, 10%). The spectroscopic data of 4-4b:

$^1$H NMR (500 MHz, CD$_3$CN): $\delta$ (ppm) = 7.40-7.23 (br m, 10H, CH$_2$Ph), 7.08 (s, 2H, =CH), 5.43 (s, 5H, Cp), 5.35-5.19 (q, 4H, NCH$_2$Ph, $J=15.75$Hz). $^{13}$C NMR (125.77 MHz, CD$_3$CN): $\delta$ (ppm) = 256.20 (s, Mo-CO), 252.40 (s, Mo-CO) 188.79 (s, NCN), 138.17, 129.72, 128.78, 128.47 (phenyl),124.36 (s, =CH), 96.60 (s, Cp), 55.95 (s, PhCH$_2$N). IR (KBr)/cm$^{-1}$: $\nu$sym(CO)
1953 (vs), \( \nu_{\text{asym}} \) (CO) 1872 (vs), \( I_{\text{asym}}/I_{\text{sym}} \) =1.23 (predicted OC-Mo-CO angle 96°). Anal. Calcd for C\(_{24}\)H\(_{21}\)ClN\(_2\)O\(_2\)Mo: C, 57.56; H, 4.23; N, 5.59. Found: C, 57.56; H, 4.31; N, 5.61.

### 4.7.5 Synthesis of [(\( \eta^5 \)-C\(_5\)H\(_5\))Mo(CO)\(_2\)(NHC)(CH\(_3\)CN)][BF\(_4\)] (NHC = IMes, 4-8; NHC = IBz, 4-9; NHC = SIMes, 4-10; NHC = I*PhEt, 4-11).

AgBF\(_4\) (0.19 g, 1 mmol) was added to a solution of compounds 4-3, 4-4a, 4-6, and 4-7 (1 mmol) in CH\(_3\)CN (20 mL). After stirring for 6 h at room temperature, the color of solution changed from purple to red. The reaction mixture was filtered through Celite, and the filtrate was dried under vacuum. The resulting dark red solid was recrystallized from acetonitrile and diethyl ether twice, yielding red crystals as the product

\[
[(\eta^5-C_5H_5)Mo(CO)_2(IMes)(CH_3CN)][BF_4] \quad (4-8) \quad \text{(yield: 0.5 g, 80%).}
\]

1H NMR (500 MHz, CD\(_3\)CN): \( \delta \) (ppm) = 7.49 (d, 2H, =CH), 7.14 (s, 2H, \text{m-H-Mes}), 7.09 (s, 2H, \text{m-H-Mes}), 4.94 (s, 5H, \text{Cp}), 2.36 (s, 6H, \text{p-Me-Mes}), 2.11 (s, 6H, \text{o-Me-Mes}), 2.02 (s, 6H, \text{o-Me-Mes}), 1.95 (s, 3H, CH\(_3\)CN). 13C NMR (125.77 MHz, CD\(_3\)CN): \( \delta \) (ppm) = 248.54 (s, Mo-CO), 248.18 (s, Mo-CO), 183.91 (s, NCN), 140.71 (s, i-Mes), 137.41 (s, \text{p-Mes}), 136.74 (s, \text{o-Mes}), 136.71 (s, \text{o-Mes}), 130.15 (s, \text{m-Mes}), 129.91 (s, \text{m-Mes}), 127.11 (s, =CH), 95.48 (s, \text{Cp}), 20.92 (s, \text{p-Me-Mes}), 18.39 (s, \text{o-Me-Mes}), 18.26 (s, \text{o-Me-Mes}). IR (KBr)/cm\(^{-1}\): \( \nu_{\text{sym}} \) (CO) 1953 (vs), \( \nu_{\text{asym}} \) (CO) 1870 (vs), \( I_{\text{asym}}/I_{\text{sym}} \) =1.12 (predicted OC-Mo-CO angle 93°), \( \nu \) (BF\(_4\)) 1038(vs). ESI-MS (in CH\(_3\)CN, \( m/z \)%): (M\(^+\) - CH\(_3\)CN) = [(CpMo(CO)\(_2\)(IMes))]\(^+\) = 523 (100). Anal. Calcd for C\(_{30}\)H\(_{32}\)BF\(_4\)MoN\(_3\)O\(_2\): C, 55.49; H, 4.97; N, 6.47. Found: C, 55.17; H, 5.05; N, 6.68.

\[
[(\eta^5-C_5H_5)Mo(CO)_2(IBz)(CH_3CN)][BF_4] \quad (4-9) \quad \text{1H NMR (500 MHz, CD\(_3\)CN): \( \delta \) (ppm) = 7.44-7.15 (m, 10H, CH\(_2\)Ph), 7.31 (s, 2H, =CH), 5.59 (s, 5H, \text{Cp}), 5.38-5.18 (q, 4H, NCH\(_2\)Ph, \( J=15.75\)Hz).}
\]

13C NMR (125.77 MHz, CD\(_3\)CN): \( \delta \) (ppm) = 248.29 (s, Mo-CO), 246.08 (s, Mo-CO) 182.04 (s, NCN), 137.44, 129.87, 128.90, 127.75, (phenyl), 125.78 (s, =CH), 95.96 (s, \text{Cp}), 55.89 (s, PhCH\(_2\)N). IR (KBr) / cm\(^{-1}\): \( \nu_{\text{sym}} \) (CO) = 1972 (vs), \( \nu_{\text{asym}} \) (CO) = 1879,
\[ I_{\text{asym}} / I_{\text{sym}} = 1.30 \text{ (predicted OC-Mo-CO angle 96°)}, \nu (\text{BF}_4) 1084. \]

\[ [(\eta^5-C_5H_5)Mo(CO)_2(\text{SIMes})(CH_3CN)][\text{BF}_4] \text{ (4-10)} \]

1H NMR (500MHz, CD$_3$CN): \( \delta \) (ppm) = 7.07 (s, 2H, \textit{m-H-Mes}), 7.01 (s, 2H, \textit{m-H-Mes}), 4.88 (s, 5H, \textit{Cp}), 4.11-4.00 (m, 4H, NCH$_2$CH$_2$N), 2.36 (s, 6H, \textit{p-Me-Mes}), 2.30 (s, 6H, \textit{o-Me-Mes}), 2.26 (s, 6H, \textit{o-Me-Mes}). 1.96 (s, 3H, CH$_3$CN)

13C NMR (125.77MHz, CD$_3$CN): \( \delta \) (ppm) = 250.5 (Mo-CO), 248.9 (Mo-CO), 213.4 (s, NCN), 139.7 (s, \textit{o-Mes}), 137.6 (s, \textit{p-Mes}), 130.5 (s, \textit{i-Mes}), 130.2 (s, \textit{m-Mes}), 95.7 (s, \textit{Cp}), 53.2 (s, NCH$_2$), 20.8 (s, \textit{o-Me-Mes}), 18.5 (s, \textit{p-Me-Mes}). IR (KBr) / cm$^{-1}$:

\( \nu_{\text{sym}}(\text{CO}) = 1974 \text{ (vs)}, \nu_{\text{asym}}(\text{CO}) = 1878, I_{\text{asym}} / I_{\text{sym}} = 0.80 \text{ (predicted OC-Mo-CO angle 84°)}, \nu (\text{BF}_4) 1084. \)

\[ [(\eta^5-C_5H_5)Mo(CO)_2(I^*\text{PhEt})(CH_3CN)][\text{BF}_4] \text{ (4-11)} \]

1H NMR (500MHz, CD$_3$CN): \( \delta \) (ppm) = 7.49-7.34 (m, 10H, \textit{Ph}), 7.19-7.17 (d, 2H, =CH), 5.78 (s, 5H, \textit{Cp}), 5.63-5.61 (m, 2H, NCHMePh), 1.86-1.83 (d, 6H, NCHMePh).

### 4.7.6 Isolation and Characterization of [IMesH]$_2$[Mo$_6$O$_{19}$] from the Oxidation of Compound 4-3 by TBHP.

Compound 4-3, CpMo(CO)$_3$(IMes)Br (0.6 g, 1mmol) was mixed with TBHP (5.5M in decane) (1 mL, 5.5 mmol) in CH$_3$CN (10 mL). After stirring for 12 h, the mixture was filtered and the filter cake was washed with CH$_2$Cl$_2$ and CH$_3$CN for three times and dried under vacuum giving a pale yellow solid (20 mg). 1H NMR (500MHz, DMSO): \( \delta \) (ppm) =9.63 (m, 1H, NCHN), 8.26(d, 2H, =CH), 7.20 (s, 4H, \textit{m-H-Mes}), 2.25 (s, 6H, \textit{p-Me-Mes}), 2.12 (s, 12H, \textit{o-Me-Mes}). 13C NMR (125.77 MHz, DMSO): \( \delta \) (ppm) =140.57 (s, NCHN), 138.44 (s, \textit{i-Mes}), 134.24 (s, \textit{p-Mes}), 130.93 (s, \textit{o-Mes}), 129.31 (s, \textit{m-Mes}), 124.76(s, =CH), 20.57 (s, \textit{p-Me-Mes}), 16.82 (s, \textit{o-Me-Mes}). IR (KBr)/cm$^{-1}$: \( \nu(\text{Mo=O}) 955.76 \text{ (vs)}, \nu(\text{Mo=O}) 800.05 \text{ (vs)}. \)

Anal. Calcd for C$_{42}$H$_{50}$N$_4$O$_{19}$Mo$_6$: C, 33.84; H, 3.38; N, 3.76. Found: C, 32.44; H, 3.31; N,
3.43.

4.7.7 Synthesis of [CpMoO$_2$(NHC)][BF$_4$] (NHC= IMes, 4-14; NHC= Ibz, 4-15; NHC=SIMes, 4-16; NHC=I*PhEt, 4-17).

Compound 4-3, 4-4a (0.5 mmol) and AgBF$_4$ (98 mg, 0.5 mmol) were dissolved in CH$_3$CN (15 mL). After stirring for 3 h at room temperature at the exclusion of light, the solution was filtered through Celite. TBHP (5.5M in decane, 2.5mmol) (0.45 mL) was introduced to the filtrate and stirring for 6 h. After removing the solvent, the resulted yellow oil was washed with Et$_2$O and THF, giving yellow solid as final product

[CpMoO$_2$(IMes)][BF$_4$] (4-14) (Yield: 0.12g, 40%). $^1$H NMR (500MHz, CD$_3$CN): $\delta$ (ppm) = 7.86 (s, 2H, =CH), 7.12 (4H, m-H-Mes), 6.26 (s, 6H, Cp), 2.35 (s, 6H, p-Me-Mes), 2.07 (s, 12H, o-Me-Mes). $^{13}$C NMR (125.77 MHz, CD$_3$CN): $\delta$ (ppm) = 167.60 (s, NCN), 142.22 (s, i-Mes), 135.75 (s, p-Mes & o-Mes), 130.36 (s, m-Mes), 129.66 (s, =CH), 95.48 (s, Cp), 21.02 (s, p-Me-Mes), 17.82 (s, o-Me-Mes). IR (KBr/cm$^{-1}$: $\nu$(Mo=O) 956 (s), $\nu$(Mo=O) 801 (s). ESI-MS (in CH$_3$CN, m/z (%)): M$^+$ = [(CpMoO$_2$(IMes)]$^+$ = 499 (100). Anal. Calcd for C$_{26}$H$_{29}$MoN$_2$O$_2$: C, 53.45; H, 5.00; N, 4.79. Found: C, 53.37; H, 5.44; N, 5.03.

[CpMoO$_2$(Ibz)][BF$_4$] (4-15). $^1$H NMR (500MHz, CD$_3$CN): $\delta$ (ppm) = 7.58 (s, 2H, =CH), 7.12-7.18 (m, 10H, Ph), 6.50 (s, 5H, Cp), 5.17 (s, 4H, NCH$_2$Ph)

[CpMoO$_2$(SIMes)][BF$_4$] (4-16) $^1$H NMR (500MHz, CD$_3$CN): $\delta$ (ppm) = 7.02 (4H, m-H-Mes), 6.31 (s, 5H, Cp), 4.29(s, NCH$_2$CH$_2$N) 2.35 (s, 12H, o-Me-Mes), 2.07 (s, 6H, p-Me-Mes).

[CpMoO$_2$(I*PhEt)][BF$_4$] (4-17)$^1$H NMR (500MHz, CD$_3$CN): $\delta$ 7.42-7.18 (m, 12H, Ph and =CH), 6.42 (s, 5H, Cp), 5.63-5.61 (m, 2H, NCHMePh), 1.90-1.89 (d, 6H, NCHMePh).
4.7.8 X-ray Crystallography

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.33 Structure solutions and refinements were performed by using the programs SHELXS-97 34a and SHELXL-97 34b. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically.

4.7.9 Catalytic reactions.

Cis-cyclooctene (0.4 g, 3.6 mmol), mesitylene (1 g, internal standard) and compounds 4-1 - 4-6, 4-8 - 4-11 as catalysts (1 mol%, 0.036 mol) were added to the reaction vessel under an air atmosphere at 55 °C. The reaction was started by the addition of TBHP (7.3mmol, 1.36mL, 5.5 M in n-decane). The course of the reactions was monitored by quantitative GC analysis (Agilent 6890 Series GC instrument with a J&W DB-1 column). Samples were taken in regular time intervals, diluted with CH2Cl2, and treated with a catalytic amount of MgSO4 and MnO2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into the GC column. The conversion of cyclooctene, and the formation of cyclooctene oxide were calculated from calibration curves (r² = 0.999) recorded prior to the reaction course.

4.7.10 Computational Details.
All quantum chemical calculations have been performed using Gaussian 03.\textsuperscript{18} The hybrid functional B3LYP\textsuperscript{19,20} was employed. Geometry optimizations were performed using the default convergence criteria without any geometric constraints. The LANL2DZ ECP basis set\textsuperscript{35} was applied for Mo, and the 6-31G+(d) basis set\textsuperscript{36} was employed for the rest of the C, H, N, and O atoms. Characterization of the stationary points as minima or transition-state structures, as well as the determination of zero-point energies (ZPEs), was performed with frequency calculations.

4.7 Reference


[34] a) Sheldrick, G. M. SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; b) Sheldrick, G. M. SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.


### Appendix

X-ray Crystal Data, Data Collection Parameters, and Refinement Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>2-1b</th>
<th>2-2a</th>
<th>2-2b</th>
<th>2-3b</th>
<th>2-4a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C\textsubscript{35}H\textsubscript{27}NO\textsubscript{4}P\textsubscript{2}W</td>
<td>C\textsubscript{34}H\textsubscript{25}NO\textsubscript{4}P\textsubscript{2}Mo</td>
<td>C\textsubscript{34}H\textsubscript{25}NO\textsubscript{4}P\textsubscript{2}W</td>
<td>C\textsubscript{32}H\textsubscript{29}NO\textsubscript{4}P\textsubscript{2}SW</td>
<td>C\textsubscript{32}H\textsubscript{29}NO\textsubscript{4}P\textsubscript{2}Mo</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>771.37</td>
<td>669.43</td>
<td>757.34</td>
<td>769.41</td>
<td>665.44</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>P\textsubscript{2}1/c</td>
<td>P\textsubscript{2}1/c</td>
<td>P\textsubscript{2}1/n</td>
<td>P\textsubscript{2}1/n</td>
</tr>
<tr>
<td><strong>Unit cell parameter</strong></td>
<td>a = 9.8862(6) Å, α = 67.9450(10)°, γ = 75.3790(10)°</td>
<td>a = 10.2222(5) Å, α = 90°, γ = 90°</td>
<td>a = 10.2084(6) Å, α = 90°, γ = 90°</td>
<td>a = 13.9985(6) Å, α = 90°, γ = 90°</td>
<td>a = 14.1260(7) Å, α = 90°, γ = 90°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>3159.4(4) Å\textsuperscript{3}</td>
<td>3070.1(2) Å\textsuperscript{3}</td>
<td>3060.9(3) Å\textsuperscript{3}</td>
<td>3150.5(2) Å\textsuperscript{3}</td>
<td>3088.8(3) Å\textsuperscript{3}</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4, Calculated density 4, 1.622 mg/m\textsuperscript{3}</td>
<td>4, 1.448 mg/m\textsuperscript{3}</td>
<td>4, 1.643 mg/m\textsuperscript{3}</td>
<td>4, 1.622 mg/m\textsuperscript{3}</td>
<td>4, 1.431 mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>3.797 mm\textsuperscript{-1}</td>
<td>0.570 mm\textsuperscript{-1}</td>
<td>3.917 mm\textsuperscript{-1}</td>
<td>3.871 mm\textsuperscript{-1}</td>
<td>0.568 mm\textsuperscript{-1}</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1520</td>
<td>1360</td>
<td>1488</td>
<td>1520</td>
<td>1360</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.24 × 0.08 × 0.06 mm\textsuperscript{3}</td>
<td>0.82 × 0.62 × 0.50 mm\textsuperscript{3}</td>
<td>0.30 × 0.20 × 0.14 mm\textsuperscript{3}</td>
<td>--</td>
<td>0.40 × 0.30 × 0.20 mm\textsuperscript{3}</td>
</tr>
<tr>
<td><strong>θ range of data collection</strong></td>
<td>1.12 to 27.50°</td>
<td>1.67 to 27.49°</td>
<td>1.67 to 27.48°</td>
<td>1.64 to 27.50°</td>
<td>1.66 to 27.50°</td>
</tr>
<tr>
<td><strong>Reflections collected/unique</strong></td>
<td>41748/14483 [R(int) = 0.0485]</td>
<td>39041/7036 [R(int) = 0.0251]</td>
<td>21257/6992 [R(int) = 0.0214]</td>
<td>22142/7221 [R(int) = 0.0352]</td>
<td>21573/7083 [R(int) = 0.0267]</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F\textsuperscript{2}</strong></td>
<td>0.990</td>
<td>1.061</td>
<td>1.046</td>
<td>1.033</td>
<td>1.047</td>
</tr>
<tr>
<td><strong>Final R indices[I&gt;2\sigma(I)]</strong></td>
<td>R\textsubscript{1} = 0.0384, wR\textsubscript{2} = 0.0767</td>
<td>R\textsubscript{1} = 0.0237, wR\textsubscript{2} = 0.0643</td>
<td>R\textsubscript{1} = 0.0201, wR\textsubscript{2} = 0.0481</td>
<td>R\textsubscript{1} = 0.0337, wR\textsubscript{2} = 0.0760</td>
<td>R\textsubscript{1} = 0.0343, wR\textsubscript{2} = 0.0876</td>
</tr>
<tr>
<td><strong>R indices(all data)</strong></td>
<td>R\textsubscript{1} = 0.0538, wR\textsubscript{2} = 0.0819</td>
<td>R\textsubscript{1} = 0.0254, wR\textsubscript{2} = 0.0653</td>
<td>R\textsubscript{1} = 0.0224, wR\textsubscript{2} = 0.0489</td>
<td>R\textsubscript{1} = 0.0434, wR\textsubscript{2} = 0.0801</td>
<td>R\textsubscript{1} = 0.0413, wR\textsubscript{2} = 0.0911</td>
</tr>
<tr>
<td>Compound</td>
<td>2-4b</td>
<td>3-1b</td>
<td>3-4</td>
<td>4-1</td>
<td>4-2</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>$C_{32}H_{29}NO_5P_2W$</td>
<td>$C_{84}H_{76}N_{12}O_8W_2$</td>
<td>$C_{14}H_{11}N_3O_4Mo$</td>
<td>$C_{12}H_{13}BrN_2O_2Mo$</td>
<td>$C_{16}H_{21}BrN_2O_2Mo$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>753.35</td>
<td>1749.27</td>
<td>381.20</td>
<td>393.09</td>
<td>449.2</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Triclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>Aba2</td>
<td>P-1</td>
<td>P2₁2₁2₁</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td>Unit cell parameter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ = 14.0515(19) Å</td>
<td>$a$ = 22.8892(13)Å</td>
<td>$a$ = 8.3796(10) Å</td>
<td>$a$ = 7.7917(4)Å</td>
<td>$a$ = 15.2517(6) Å</td>
<td></td>
</tr>
<tr>
<td>$b$ = 13.802(2) Å</td>
<td>$b$ = 19.9495(11)Å</td>
<td>$b$ = 8.9275(10)Å</td>
<td>$b$ = 11.5324(6)Å</td>
<td>$b$ = 7.8530(3) Å</td>
<td></td>
</tr>
<tr>
<td>$c$ = 16.618(2) Å</td>
<td>$c$ = 8.5384(5) Å</td>
<td>$c$ = 11.0747(13) Å</td>
<td>$c$ = 14.8374(8) Å</td>
<td>$c$ = 15.3594(6) Å</td>
<td></td>
</tr>
<tr>
<td>$\alpha$ = 90°</td>
<td>$\alpha$ = 90°</td>
<td>$\alpha$ = 78.487(2)°</td>
<td>$\alpha$ = 90°</td>
<td>$\alpha$ = 90°</td>
<td></td>
</tr>
<tr>
<td>$\beta$ = 107.559(3)°</td>
<td>$\beta$ = 90°</td>
<td>$\beta$ = 81.427(2)°</td>
<td>$\beta$ = 90°</td>
<td>$\beta$ = 106.7460(10)°</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ = 90°</td>
<td>$\gamma$ = 90°</td>
<td>$\gamma$ = 63.189(2)°</td>
<td>$\gamma$ = 90°</td>
<td>$\gamma$ = 90°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>3072.6(7) Å³</td>
<td>3898.9(4) Å³</td>
<td>722.89(15) Å³</td>
<td>1333.24(12) Å³</td>
<td>1761.60(12) Å³</td>
</tr>
<tr>
<td>Z Calculated density</td>
<td>4, 1.629 mg/m³</td>
<td>2, 1.490 mg/m³</td>
<td>2, 1.751 mg/m³</td>
<td>4, 1.958 mg/m³</td>
<td>4, 1.694 mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.904 mm⁻¹</td>
<td>3.012 mm⁻¹</td>
<td>0.929 mm⁻¹</td>
<td>3.975 mm⁻¹</td>
<td>3.020 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1488</td>
<td>1752</td>
<td>380</td>
<td>768</td>
<td>896</td>
</tr>
<tr>
<td>Crystal size</td>
<td>$0.80 \times 0.60 \times 0.30$ mm³</td>
<td>$0.48 \times 0.22 \times 0.20$ mm³</td>
<td>$0.20 \times 0.12 \times 0.10$ mm³</td>
<td>$1.10 \times 0.26 \times 0.24$ mm³</td>
<td>$0.50 \times 0.40 \times 0.34$ mm³</td>
</tr>
<tr>
<td>$\theta$ range of data collection</td>
<td>1.67 to 27.49°</td>
<td>1.78 to 27.49°</td>
<td>1.88 to 27.49°</td>
<td>2.24 to 27.49°</td>
<td>1.66 to 27.50°</td>
</tr>
<tr>
<td>Reflections collected /unique</td>
<td>21297/7024</td>
<td>13558/4338</td>
<td>5072/3278</td>
<td>9273 / 3013</td>
<td>11976 / 4046</td>
</tr>
<tr>
<td>[R(int) = 0.0303]</td>
<td>[R(int) = 0.0356]</td>
<td>[R(int) = 0.0255]</td>
<td>[R(int) = 0.0255]</td>
<td>[R(int) = 0.0227]</td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.023</td>
<td>1.056</td>
<td>1.179</td>
<td>1.015</td>
<td>1.055</td>
</tr>
<tr>
<td>Final R indices[I$&gt;2\sigma$(I)]</td>
<td>$R_1 = 0.0241$, $wR_2 = 0.0617$</td>
<td>$R_1 = 0.0341$, $wR_2 = 0.0770$</td>
<td>$R_1 = 0.0530$, $wR_2 = 0.1454$</td>
<td>$R_1 = 0.0202$, $wR_2 = 0.0476$</td>
<td>$R_1=0.0294$, $wR_2=0.0788$</td>
</tr>
<tr>
<td>R indices(all data)</td>
<td>$R_1 = 0.0274$, $wR_2 = 0.0631$</td>
<td>$R_1 = 0.0473$, $wR_2 = 0.0828$</td>
<td>$R_1 = 0.0616$, $wR_2 = 0.1584$</td>
<td>$R_1 = 0.0212$, $wR_2 = 0.0478$</td>
<td>$R_1=0.0318$, $wR_2=0.0800$</td>
</tr>
<tr>
<td>Compound</td>
<td>4-3</td>
<td>4-4b</td>
<td>4-5</td>
<td>4-8</td>
<td>4-9</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{28}H_{29}BrN_{2}O_{2}Mo</td>
<td>C_{24}H_{21}ClN_{2}O_{2}Mo</td>
<td>C_{14}H_{17}BrN_{2}O_{2}Mo</td>
<td>C_{30}H_{32}BF_{4}MoN_{3}O_{2}</td>
<td>C_{30}H_{34}BF_{4}N_{3}O_{2}Mo</td>
</tr>
<tr>
<td>Formula weight</td>
<td>601.38</td>
<td>500.82</td>
<td>421.15</td>
<td>649.34</td>
<td>651.35</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}/n</td>
<td>P-1</td>
<td>P2_{1}/c</td>
<td>P2_{1}/c</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>Unit cell parameter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 12.5547(10) Å</td>
<td>a = 8.3736(15) Å</td>
<td>a = 12.2315(8) Å</td>
<td>a = 10.0866(4) Å</td>
<td>a = 9.888(2) Å</td>
<td></td>
</tr>
<tr>
<td>b = 12.6940(11) Å</td>
<td>b = 11.306(2) Å</td>
<td>b = 15.0658(9) Å</td>
<td>b = 15.4291(6) Å</td>
<td>b = 15.360(3) Å</td>
<td></td>
</tr>
<tr>
<td>c = 17.0096(15) Å</td>
<td>c = 12.541(2) Å</td>
<td>c = 8.4076(5) Å</td>
<td>c = 19.6799(8) Å</td>
<td>c = 19.705(4) Å</td>
<td></td>
</tr>
<tr>
<td>α = 90°</td>
<td>α = 77.760(4)°</td>
<td>α = 90°</td>
<td>α = 90°</td>
<td>α = 90°</td>
<td></td>
</tr>
<tr>
<td>β = 105.730(2)°</td>
<td>β = 75.775(4)°</td>
<td>β = 100.5630(3)°</td>
<td>β = 103.5060(10)°</td>
<td>β = 103.288(5)°</td>
<td></td>
</tr>
<tr>
<td>γ = 90°</td>
<td>γ = 76.807(4)°</td>
<td>γ = 90°</td>
<td>γ = 90°</td>
<td>γ = 90°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>2609.3(4) Å³</td>
<td>1105.1(3) Å³</td>
<td>1523.07(16) Å³</td>
<td>2978.0(2) Å³</td>
<td>2912.5(11) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density</td>
<td>4.1531 mg/m³</td>
<td>2.1505 mg/m³</td>
<td>4.1837 mg/m³</td>
<td>2.1505 mg/m³</td>
<td>1.837 mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.061 mm⁻¹</td>
<td>0.737 mm⁻¹</td>
<td>3.487 mm⁻¹</td>
<td>0.497 mm⁻¹</td>
<td>0.509 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1216</td>
<td>508</td>
<td>832</td>
<td>1328</td>
<td>1336</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.32×0.28×0.12 mm³</td>
<td>0.44×0.08×0.06 mm³</td>
<td>0.80×0.26×0.18 mm³</td>
<td>0.64×0.42×0.18 mm³</td>
<td>0.60×0.14×0.10 mm³</td>
</tr>
<tr>
<td>θ range of data collection</td>
<td>1.80 to 27.50°</td>
<td>1.70 to 27.50°</td>
<td>1.69 to 27.49°</td>
<td>1.70 to 27.50°</td>
<td>1.70 to 27.50°</td>
</tr>
<tr>
<td>Reflections collected /unique</td>
<td>18142 / 5984</td>
<td>14227 / 5070</td>
<td>10673 / 3493</td>
<td>10673 / 3493</td>
<td>20565 / 6815</td>
</tr>
<tr>
<td>[R(int) = 0.0334]</td>
<td>[R(int) = 0.0519]</td>
<td>[R(int) = 0.0229]</td>
<td>[R(int) = 0.0282]</td>
<td>[R(int) = 0.0354]</td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.029</td>
<td>1.045</td>
<td>1.043</td>
<td>1.066</td>
<td>1.120</td>
</tr>
<tr>
<td>Final R indices[I&gt;2σ(I)]</td>
<td>R₁ = 0.0418, wR₂ = 0.1017</td>
<td>R₁ = 0.0476, wR₂ = 0.1142</td>
<td>R₁ = 0.0216, wR₂ = 0.0575</td>
<td>R₁ = 0.0406, wR₂ = 0.0575</td>
<td>R₁ = 0.0390, wR₂ = 0.0992</td>
</tr>
<tr>
<td>R indices(all data)</td>
<td>R₁ = 0.0591, wR₂ = 0.1086</td>
<td>R₁ = 0.0574, wR₂ = 0.1190</td>
<td>R₁ = 0.0230, wR₂ = 0.0581</td>
<td>R₁ = 0.0448, wR₂ = 0.0581</td>
<td>R₁ = 0.0462, wR₂ = 0.1115</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1098</td>
</tr>
<tr>
<td></td>
<td>4-10</td>
<td>4-16</td>
<td>[IMesH]₂[Mo₆O₁₉]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------------</td>
<td>---------------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂₆H₂₄BF₄N₃O₂Mo</td>
<td>C₄₄H₄₂Mo₆N₄O₂₃</td>
<td>C₄₄H₃₃Mo₆N₅O₁₉</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>593.23</td>
<td>1762.34</td>
<td>1531.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P-1</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>9.8246(12) Å</td>
<td>9.8862(5) Å</td>
<td>a = 10.7001(5) Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>11.9309(15) Å</td>
<td>8.4404(4) Å</td>
<td>b = 15.3922(7) Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>22.990(3) Å</td>
<td>31.7569(17) Å</td>
<td>c = 15.8533(7) Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>77.187(2)°</td>
<td>90°</td>
<td>α = 90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>83.435(2)°</td>
<td>94.4590(10)°</td>
<td>β = 96.2250(10)°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>76.056(2)°</td>
<td>90°</td>
<td>γ = 90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>2545.0(5) Å³</td>
<td>2641.9(2) Å³</td>
<td>2595.6(2) Å³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρ</td>
<td>1.548 mg/m³</td>
<td>2.215 mg/m³</td>
<td>2.190 g/cm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρm</td>
<td>0.574 mm⁻¹</td>
<td>1.920 mm⁻¹</td>
<td>1.484 mm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>1708</td>
<td>1512</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56 × 0.36 × 0.20 mm³</td>
<td>0.40 × 0.26 × 0.10 mm³</td>
<td>0.44 × 0.32 × 0.08 mm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.91 to 27.50</td>
<td>2.07 to 27.50°</td>
<td>1.85 to 27.50°</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>32965/11682</td>
<td>18240/6056</td>
<td>17932/5957</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[R(int) = 0.0247]</td>
<td>[R(int) = 0.0367]</td>
<td>[R(int) = 0.0291]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.060</td>
<td>1.105</td>
<td>1.129</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₁</td>
<td>0.0304, wR₂ =</td>
<td>R₁ = 0.0373, wR₂ =</td>
<td>R₁ = 0.0327, wR₂ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0810</td>
<td>0.0802</td>
<td>0.0770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₁</td>
<td>0.0349, wR₂ =</td>
<td>R₁ = 0.0442, wR₂ =</td>
<td>R₁ = 0.0385, wR₂ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0843</td>
<td>0.0829</td>
<td>0.0845</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>