

学校编码: 10384

分类号____密级

学 号: 20720080150004

UDC_____

厦 门 大 学

博 士 学 位 论 文

含有金属氢的锇碳多重键化合物及其衍生的锇杂环
的合成与反应性研究

Synthesis and Reactivity of Hydride Osmium–Carbon Multiple
Bonds and Their Derived Osmacycles

赵 茜 怡

指导教师姓名: 夏海平 教授

曹晓宇 副教授

专业名称: 有机化学

论文提交日期: 2012年06月

论文答辩时间: 2012年06月

学位授予日期: 2012年 月

答辩委员会主席: _____

评 阅 人: _____

2012年6月



**Synthesis and Reactivity of Hydride Osmium–Carbon Multiple Bonds
and Their Derived Osmacycles**

**A Dissertation Submitted to the Graduate School in Partial Fulfillment of
the Requirements for the Degree of Doctor Philosophy**

By

Qianyi Zhao

Supervised by

**Prof. Hai-Ping Xia
Asso. Prof. Xiao-Yu Cao**

Department of Chemistry

Xiamen University

June, 2012

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（ ） 1. 经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。

（ ） 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年 月 日

目 录

中文摘要.....	I
英文摘要.....	III
第一章 绪论	
1.1 烯基卡拜.....	2
1.1.1 烯基卡拜的合成方法.....	2
1.1.2 烯基卡拜的反应性.....	6
1.2 金属亚乙烯.....	10
1.2.1 金属亚乙烯的合成方法概述.....	10
1.2.2 金属亚乙烯的反应性.....	11
1.2.2.1 与金属卡拜、金属炔基化合物的相互转化.....	11
1.2.2.2 与亲电试剂的反应.....	12
1.2.2.3 与亲核试剂的反应.....	12
1.2.2.4 金属亚乙烯在复分解反应中的催化应用.....	16
1.3 金属杂环.....	17
1.3.1 金属苯.....	18
1.3.1.1 金属苯的合成方法.....	18
1.3.1.2 金属苯的反应性.....	20
1.3.1.3 异金属苯.....	24
1.3.2 金属苯炔.....	24
1.3.2.1 金属苯炔的合成.....	25
1.3.2.2 金属苯炔的反应性.....	27
1.3.3 金属吡啶.....	29
1.4 本论文的设想与目的.....	30
1.5 参考文献.....	31

第二章 钌烯基卡拜及其衍生物的反应性研究

2.1 前言.....	48
2.2 结果与讨论.....	49
2.2.1 [4+1]关环合成氧配位的钌烯基化合物及其反应性.....	49
2.2.2 碳-碳键断裂合成钌亚乙烯化合物及其反应性.....	56
2.2.3 [4+2]环加成合成钌、氮杂环己二烯.....	65
2.3 小结.....	71
2.4 实验部分.....	71
2.5 参考文献.....	78

第三章 钌亚乙烯的反应性研究

3.1 前言.....	81
3.2 结果与讨论.....	82
3.2.1 关环反应.....	82
3.2.1.1 [3+3]关环合成稳定的异金属苯.....	82
3.2.1.2 暂态异钌苯的合成.....	92
3.2.1.3 [5+1]关环合成钌苯.....	97
3.2.2 钌亚乙烯与炔酯、炔酮的反应.....	102
3.2.2.1 钌呋喃的合成与表征.....	102
3.2.2.2 钌烯基亚乙烯化合物与CO的反应.....	110
3.2.3 CO促进的碳-碳键的偶联反应.....	113
3.2.4 钌亚乙烯的其它反应.....	118
3.2.4.1 与腈、异腈的反应.....	118
3.2.4.2 与联烯的反应.....	121
3.3 小结.....	123
3.4 实验部分.....	124
3.5 参考文献.....	140

第四章 钷苯炔的合成及反应性

4.1 前言.....	147
4.2 结果与讨论.....	148
4.2.1 钷苯炔的合成.....	148
4.2.2 钷苯炔向异钷苯的转化.....	153
4.2.3 钷苯炔的亲核开环反应.....	156
4.2.4 钷苯炔的氧化反应.....	162
4.2.5 钷苯炔亲核开环产物的反应初探.....	166
4.3 小结.....	177
4.4 实验部分.....	178
4.5 参考文献.....	188

第五章 钷吡啶盐的反应性研究

5.1 前言.....	192
5.2 结果与讨论.....	193
5.2.1 钷吡啶盐与NaSCN的配体反应.....	193
5.2.2 钷吡啶盐与1, 10-菲啰啉的配体反应.....	203
5.2.3 钷吡啶盐与8-羟基喹啉的配体反应.....	208
5.2.4 钷吡啶盐的亲核加成反应.....	211
5.3 小结.....	214
5.4 实验部分.....	215
5.5 参考文献.....	221

第六章 论文的创新性和展望

6.1 论文的创新性.....	226
6.2 研究工作展望.....	227

附录 博士期间发表和交流的论文..... 229

致谢..... 230

厦门大学博硕士论文摘要库

CONTENTS

Abstract in Chinese	I
Abstract in English	III
Chapter 1 Introduction	
1.1 Alkenylcarbyne	2
1.1.1 Synthetic Methods of Alkenylcarbynes.....	2
1.1.2 Reactivity of Alkenylcarbynes.....	6
1.2 Metal Vinylidene	10
1.2.1 Brief Introduction for the Synthetic Methods of Metal Vinylidenes.....	10
1.2.2 Reactivity of Metal Vinylidenes.....	11
1.2.2.1 Interconversions with Carbyne and Alkynyl Complexes.....	11
1.2.2.2 Reactions with Electrophiles.....	12
1.2.2.3 Reactions with Nucleophiles.....	12
1.2.2.4 Catalytic Applications in Metathesis Reactions.....	16
1.3 Metallacycles	17
1.3.1 Metallabenzene.....	18
1.3.1.1 Synthetic Methods of Metallabenzenes.....	18
1.3.1.2 Reactivity of Metallabenzenes.....	20
1.3.2.3 Isometallabenzene.....	24
1.3.2 Metallabenzynes.....	24
1.3.2.1 Synthetic Methods of Metallabenzynes.....	25
1.3.2.2 Reactivity of Metallabenzynes.....	27
1.3.3 Metallapyridine.....	29
1.4 Scheme and Objective of the Dissertation	30
1.5 References	31

Chapter 2 Studies on the Reactivity of an Osmium–Hydride– Alkenylcarbyne and Its Derivatives

2.1 Introduction.	48
2.2 Results and Discussion	49
2.2.1 Synthesis and Reactivity of an Osmium Vinyl Compound.	49
2.2.2 Synthesis and Reactivity of Osmium Vinylidenes.	56
2.2.3 Synthesis of an Osma-aza-cyclohexadiene via [4+2] Cycloaddition.	65
2.3 Conclusions.	71
2.4 Experimental Section.	71
2.5 References.	78

Chapter 3 Studies on the Reactivity of an Osmium–Hydride– Vinylidene

3.1 Introduction.	81
3.2 Results and Discussion	82
3.2.1 Cyclization Reaction.	82
3.2.1.1 Stable Isometallabenzenes from a Formal [3+3] Cycloaddition.	82
3.2.1.2 Synthesis of Transient Isoosmabenzenes.	92
3.2.1.3 Synthesis of an Osmabenzene via [5+1] Cyclization.	97
3.2.2 Reactions with Ethyl Propiolate and an Alkynone.	102
3.2.2.1 Synthesis and Characterization of Osmafurans.	102
3.2.2.2 Reaction of an Osmium-Alkenyl-Vinylidene Compound with CO. . .	110
3.2.3 CO Induced Carbon–Carbon Coupling Reactions.	113
3.2.4 Other Reactions.	118
3.2.4.1 Reactions with Nitrile and Isocyanide.	118
3.2.4.2 Reactions with Allenes.	121
3.3 Conclusions.	123
3.4 Experimental Section.	124

3.5 References.	140
 Chapter 4 Studies on the Synthesis and Reactivity of an Osmabenzynes	
4.1 Introduction.	147
4.2 Results and Discussion	148
4.2.1 Synthesis of an Osmabenzynes.	148
4.2.2 Transformation from Osmabenzynes to Isoosmabenzene.	153
4.2.3 Nucleophilic Ring-opening Reaction.	156
4.2.4 Oxidation Reaction.	162
4.2.5 Preliminary Studies for the Reactivity of Ring-opening Products.	166
4.3 Conclusions.	177
4.4 Experimental Section.	178
4.5 References.	188
 Chapter 5 Studies on the Reactivity of an Osmapyridinium	
5.1 Introduction.	192
5.2 Results and Discussion	193
5.2.1 Ligand Substitution Reactions with NaSCN.	193
5.2.2 Ligand Substitution Reaction with 1,10-Phenanthroline.	203
5.2.3 Ligand Substitution Reaction with 8-Hydroxyquinoline.	208
5.2.4 Nucleophilic Addition Reaction.	211
5.3 Conclusions.	214
5.4 Experimental Section.	215
5.5 References.	221
 Chapter 6 Innovation and Future Work	
6.1 Innovations.	226

6.2 Future Work	227
Appendix: Publications from PhD Work	229
Acknowledgements	230

厦门大学博硕士学位论文摘要库

摘 要

含有金属-碳多重键的过渡金属配合物，如金属卡宾、金属卡拜等，具有独特的反应性和良好的催化活性，已经在许多重要的有机反应中得到了广泛应用，因此一直是金属有机化学研究的热点领域。本论文以含有金属氢的钨-碳多重键化合物钨烯基卡拜、钨亚乙烯为起点，通过对其反应性的研究，合成了多种结构新颖、形式各异的钨配合物，对它们进行了全面表征，并对部分反应机理进行了探讨以及部分产物的化学反应性进行了初步研究。全文共分为六章：

第一章为绪论，结合本论文的核心内容，分别总结了烯基卡拜、金属亚乙烯、金属杂环如金属苯、金属苯炔和金属吡啶的研究进展，并简述了本论文的主要设想和目的。

第二章主要拓展了烯基钨卡拜化合物 **2-1** 的反应性。考察了 **2-1** 与甲醇、水等亲核试剂的反应，实现了 **2-1** 与甲醇的[4+1]关环以及自身碳碳键的断裂这两种新型的反应类型。此外，还研究了在路易斯酸 AgClO_4 的协助下，**2-1** 与乙腈在室温下的[4+2]关环反应，合成了钨、氮杂环己二烯化合物。

第三章系统研究了含有金属氢的钨亚乙烯化合物 **2-4** 的反应性。考察了它与末端炔醇、端基炔、炔酮、炔酯、腈类以及联烯的反应，制备了一系列异钨苯、钨苯炔、钨苯、钨呋喃等钨杂环化合物以及钨环戊二烯基、钨乙烯基配合物。反应中涉及到了首例金属亚乙烯化合物的[3+3]关环反应，合成了第二例稳定的异金属苯。理论计算证实了季磷取代基和 $18e$ 结构其稳定存在的因素。一些反应中间态的捕捉，进一步明晰了反应的机理。总的来讲，这些反应有多种关环方式，产物结构形式各异，极大地丰富了金属亚乙烯的反应化学。钨亚乙烯化合物 **2-4** 也成为合成多种钨杂环化合物的有效前体。

第四章详细研究了异钨苯 **4-1** 向钨苯炔 **4-2** 的转化，并对 **4-2** 的反应性进行了探索。钨亚乙烯 **2-4** 与 $\text{HC}\equiv\text{CCH}(\text{OEt})_2$ 的反应经历了异钨苯 **4-1** 中间态，最终转化为钨苯炔 **4-2**，加酸能够促进该转化过程；**4-2** 与强亲核试剂能够在 C3 位置单一地发生亲核加成反应，逆向生成异钨苯或进一步开环，从而首次实现了异金属苯和金属苯炔的相互转化。理论计算解释了 **4-2** 亲核反应高效区域选择性的原因。钨苯炔 **4-2** 与浓 HNO_3 或 HIO_4 的反应实现了金属苯炔向金属苯的转化。此外，对亲核开环产物 **4-5** 和 **4-6** 在丙酮中的反应性进行了初探。

第五章主要研究了钷吡啶盐 **5-1** 的反应性。发现其与 NaSCN、1,10-菲罗啉、8-羟基喹啉均能发生配体取代反应。其中，与 NaSCN 的配体反应，可以通过调节不同的反应条件，从而定量地调控 SCN 取代配体的个数。进一步的研究还表明：乙腈能够有效的降低金属中心的电荷密度，从而提高环的亲电性。乙腈取代的钷吡啶盐化合物 **5-8** 能够与 CH₃ONa 发生类似于金属苯的亲核加成反应，得到钷、氮杂环己二烯化合物。该反应首次实现了金属吡啶的亲核加成。

第六章总结了本论文研究工作的创新性，并对后续的工作进行了展望。

关键词：烯基卡拜；金属亚乙烯；异钷苯；钷苯炔；钷吡啶盐

Abstract

Transition-metal complexes containing metal-carbon multiple bonds, such as carbene and carbyne, have been applied in many important organic reactions due to their special reactivity and excellent catalytic activities, thus a continuous hot topic of organometallic chemistry. The dissertation begins with the focus of two hydride osmium-carbon multiple bonds: a carbyne and a vinylidene. During the research of their chemical reactivity, a series of novel osmium complexes with different forms have been synthesized and fully characterized. In addition, some interesting mechanism and preliminary studies for the reactivity of some derivatives have also been carried out. This dissertation consists of the following six chapters:

In chapter 1, the synthetic methods, reactivity and applications of alkenylcarbyne and metal vinylidene are summarized. The research progress of metallacycles such as metallabenzene, metallabenzynes and metallapyridine are briefly reviewed. Furthermore, the research objectives of this dissertation are presented.

In chapter 2, extended exploration of the reactivity of an osmium-hydride-alkenylcarbyne complex **2-1** is described. Two new reaction modes, [4+1] Cyclization and Carbon-Carbon Cleavage, have been developed. With the help of AgClO_4 , a previous [4+2] cycloaddition of **2-1** with acetonitrile can take place at room temperature, giving an osma-aza-cyclohexadiene compound.

In chapter 3, reactions of an osmium-hydride-vinylidene complex **2-4** with alkynols, alkynes, ethyl propiolate, alkynones, nitriles, isocyanide and allenes have been studied in details. New iso-osmabenzenes, osmabenzynes, osmabenzene, metalated cyclopentadiene, η^5 -cyclopentadienyl and osmium vinyl complexes are the products. An unprecedented [3+3] cyclization reaction of metal vinylidene with alkynols has been found. This method provides a simple and efficient route to prepare the second examples of stable isometallabenzenes. DFT calculations suggest that both the phosphonium substituent and the $18e^-$ nature contribute to the high stability of iso-osmabenzenes. The capture of some intermediates clarifies the reaction mechanisms further. In general, the reactions of **2-4** are versatile and the products are

diverse, thus greatly enriching the chemistry of metal vinylidene. And compound **2-4** can be used as an efficient precursor for the construction of osmacycles.

In chapter 4, the interconversion of metallabenzynes and isometallabenzene has been achieved for the first time. Isoosmabenzene **4-1** can be transformed into osmabenzynes **4-2**. Osmabenzynes **4-2** undergo nucleophilic additions at C3 can “restore” isometallabenzenes, or go further to open the metallacycle. DFT calculations were carried out to rationalize the highly regioselective nucleophilic attack at C3. The oxidation reaction of **4-2** with HNO₃ or HIO₄ could generate osmabenzene **4-7**, which indicates a transformation from metallabenzynes to metallabenzene. The reactivity of ring-opening products has also been preliminarily studied.

In chapter 5, the reactivity of osmapyridinium **5-1** has been investigated. It can undergo ligand substitution reactions with NaSCN, 1,10-Phenanthroline and 8-Hydroxyquinoline to produce new osmapyridiniums. By changing reaction conditions, the number of SCN-substituted ligands can be controlled quantitatively. Further research demonstrates that replacement of a ligand by acetonitrile results in a decrease of electron density on the metallic center and an increase of electrophilicity around the metallacycle. The reaction of acetonitrile-substituted osmapyridinium **5-3** with CH₃ONa, through a nucleophilic attack similar to that of substituted metallabenzenes, led to a Jackson-Meisenheimer complex. This is the first nucleophilic addition reaction of metallapyridines.

In chapter 6, the innovation of the dissertation is concluded and the prospect of this research is presented.

Keywords: Alkenylcarbyne; Vinylidene; Isoosmabenzene; osmabenzynes; osmapyridinium

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士学位论文摘要库