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磷氰酸根负离子对构建新型含磷化合物的研究

The Phosphaetynolate Anion as the Building Block for
Construction of Novel Phosphorus Frameworks: An
Experimental and Theoretical Study

刘柳

指导教师姓名: 赵玉芬 教授

Guy Bertrand 教授

专业名称: 有机化学

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The Phosphaetynolate Anion as the Building Block for Construction of Novel Phosphorus Frameworks: An Experimental and Theoretical Study

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requirements for the degree of

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in

Chemistry

by

Mr. Liu Liu

Supervisors: Prof. Yufen Zhao

at

Department of Chemistry, Xiamen University

and Prof. Guy Bertrand

Department of Chemistry & Biochemistry, University of

California, San Diego

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DEDICATION

*Dedicated to my parents and sister
For their endless love and all aspects of support*

*Dedicated to my girlfriend Sunny
For her endless love and understanding*

致谢

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厦门大学博硕士论文摘要库

摘要

磷是一种非常重要的化学元素，并且涉及到化学科学的各个领域。磷化学的研究范围广泛，涉及从材料科学到生物化学。近年，对于磷氰酸根负离子（phosphaetynolate anion, PCO^- ）的研究表明，该离子可以作为“磷负离子”的供体，构建新型结构复杂的磷化合物。整篇博士学位论文以磷氰酸根负离子为出发点，以实验和理论相结合的研究方法，合成分离表征了一系列新型含磷化合物。论文共分为六章，在第一章绪论里，我们将介绍磷氰酸根负离子及其反应活性的背景。第二章，我们重点介绍以磷氰酸根负离子为原料，用紫外线照射的方法，制备第一例单线态的磷宾（phosphinidene）以及反应性研究。在第三章，我们将介绍第一例路易斯碱稳定的二配位磷正离子母体（parent phosphenium）的合成。第四章，我们将介绍磷氰酸根负离子过渡金属（Cu, Au, Co, Ir）化合物的合成及其反应活性研究。值得一提的是，利用 IrPCO 化合物特殊的反应性，合成制备了第一例双金属稳定的 $\text{P}=\text{P}$ （dimetalladiphosphene）结构。在第五章，我们将以现代量子化学的方法研究磷氰酸根负离子的环加成反应。解释阐明了电荷分布和轨道重叠对这类反应高选择性的调控作用。第六章是全文总结。

关键词： 磷氰酸根负离子，磷宾，二配位磷正离子，过渡金属，环加成，密度泛函理论

Abstract

Phosphorus is an essential element in all fields of chemical science, ranging from material science to biochemistry. Recently, phosphaynolate anion (PCO^-), formally featuring a phosphorus of oxidation state -1, has emerged to be an excellent building block for construction of structurally sophisticated compounds. The thesis will focus on synthesis and isolation of a series of phosphorus-containing compounds prepared from PCO^- . In Chapter 1, we will briefly introduce the background of PCO^- chemistry, including its synthesis and reactivity. In Chapter 2, we will prepare an extremely reactive monocoordinated phosphorus species from PCO^- under photolysis, namely a singlet phosphinophosphinidene. In Chapter 3, we successfully isolate the first base-stabilized parent phosphonium cation and related species. In Chapter 4, we prepare several transition metal phosphaynolate complexes MPCO ($\text{M} = \text{Cu}, \text{Au}, \text{Co}, \text{Ir}$) and study their reactivities. It is very important to note that IrPCO is unstable and rearranges into Ir-P=P-Ir , which is the first dimetalladiphosphene. Finally, in Chapter 5, a thorough theoretical study is carried out to understand the cycloaddition chemistry of PCO^- , showing that electronic properties of different unsaturated compounds play a crucial role in reactivity and regioselectivity.

Keywords: phosphaynolate anion, phosphinidene, phosphonium, transition metal, cycloaddition, DFT

目 录

DEDICATION	I
致谢.....	II
摘 要.....	IV
Abstract	V
目 录.....	VI
TABLE OF CONTENTS	VI
第一章 绪论	VIII
1.1 工业制备含磷化合物	1
1.2 低配位磷化合物的合成和反应性	2
1.2.1 磷氰酸类化合物的合成和反应	2
1.2.2 磷烯酮类化合物的合成和反应	4
1.3 论文研究的目的及主要内容	5
参考文献	6
第二章 单线态磷宾及其相关化合物的合成	8
2.1 引言	8
2.2 结果与讨论	10
2.2.1 磷宾中间体的捕获	10
2.2.2 单线态磷基磷宾的制备	13
2.2.3 磷基磷宾单体的反应活性研究	16
2.2.4 稳定的磷基磷烯酮的反应活性研究	17
2.3 小结	21
2.4 计算方法	22
2.5 实验部分	22
2.5.1 实验仪器及试剂	22
2.5.2 实验步骤及数据表征	22
参考文献	34
第三章 氮杂环卡宾稳定的二配位磷正离子母体 (PH₂⁺) 及其相关化合物的合成	39
3.1 引言	39
3.2 结果与讨论	40
3.2.1 氮杂环卡宾稳定的二配位磷正离子母体 (PHR ⁺ 和 PH ₂ ⁺) 的合成.....	40
3.2.2 氮杂环卡宾稳定的磷宾母体过渡金属配合物的合成.....	43
3.2.3 氮杂环卡宾稳定的磷宾母体路易斯酸配合物的合成.....	45
3.3 小结	45
3.4 计算方法	46
3.5 实验部分	46
3.5.1 实验仪器及试剂	46
3.5.2 实验步骤及数据表征	46
参考文献	51
第四章 磷氰酸根铜、金、钴、铀金属化合物的合成及反应活性研究	55
4.1 引言	55
4.2 结果与讨论	55
4.2.1 磷氰酸根钴和铀的金属化合物的合成及反应活性研究.....	55

4.2.2 磷氰酸根铜和金金属化合物的合成及反应活性研究.....	57
4.3 小结.....	61
4.4 计算方法.....	61
4.5 实验部分.....	62
4.5.1 实验仪器及试剂.....	62
4.5.2 实验步骤及数据表征.....	62
参考文献.....	70
第五章 磷氰酸根负离子环加成反应的理论研究.....	72
5.1 引言.....	72
5.2 结果与讨论.....	73
5.2.1 磷氰酸根负离子与缺电子炔烃的环加成反应理论研究.....	73
5.2.2 磷氰酸根负离子与烯酮和碳二亚胺环加成反应理论研究.....	77
5.2.3 磷氰酸根负离子与 2-羰基吡喃环加成反应理论研究.....	78
5.3 小结.....	79
5.4 计算方法.....	79
5.5 数据部分.....	80
参考文献.....	108
第六章 全文总结.....	110
个人简历.....	112

TABLE OF CONTENTS

DEDICATION	I
ACKNOWLEDGMENT	II
Abstract in Chinese.....	IV
Abstract	V
TABLE OF CONTENTS in Chinese	VI
TABLE OF CONTENTS	VIII
Chapter 1. Introduction	VIII
1.1 The industrial preparation of phosphorus compounds.....	1
1.2 Synthesis and reactivity of low-coordinated phosphorus compounds	2
1.2.1 Synthesis and reactivity of phosphoethynolate anion	2
1.2.2 Synthesis and reactivity of organic phosphaketene compounds.....	4
1.3 The goal of the thesis.....	5
Reference	6
Chapter 2. A room temperature stable singlet phosphinidene	8
2.1 Introduction	8
2.2 Results and discussion	10
2.2.1 Evidence for a transient phosphinidene	10
2.2.2 Preparation of a singlet phosphinophosphinidene	13
2.2.3 Reactivity of the singlet phosphinophosphinidene	16
2.2.4 Reactivity of a stable phosphanyl-phosphaketene	17
2.3 Conclusion.....	21
2.4 Computational details.....	22
2.5 Experimental section	22
2.5.1 General	22
2.5.2 Procedures and data.....	22
Reference.....	34
Chapter 3. Isolation of an NHC stabilized parent phosphonium (PH₂⁺) and related species	39
3.1 Introduction	39
3.2 Results and discussion.....	40
3.2.1 Isolation of an NHC stabilized parent phosphonium	40
3.2.2 Isolation of NHC parent phosphinidene transition metal complexes.....	43
3.2.3 Isolation of an NHC parent phosphinidene Lewis acid complex.....	45
3.3 Conclusion.....	45
3.4 Computational details.....	46
3.5 Experimental section	46
3.5.1 General	46
3.5.2 Procedures and data.....	46
Reference.....	51
Chapter 4. Phosphide delivery to transition metal complexes	55
4.1 Introduction	55
4.2 Results and discussion.....	55
4.2.1 Isolation and reactivity of Co- and Ir- η^1 PCO complexes	55

4.2.2 Isolation and reactivity of Cu- η^2 PCO and Au- η^1 PCO complexes	57
4.3 Conclusion	61
4.4 Computational details	61
4.5 Experimental section	62
4.5.1 General	62
4.5.2 Procedures and data	62
Reference	70
Chapter 5. Theoretical study of cycloaddition chemistry of PCO⁻	72
5.1 Introduction	72
5.2 Results and discussion	73
5.2.1 Cycloaddition chemistry of PCO ⁻ with electron-deficient alkynes	73
5.2.2 Cycloaddition chemistry of PCO ⁻ with Ph ₂ C=C=O and DIPPN=C=NDIPP	77
5.2.3 Cycloaddition chemistry of PCO ⁻ with 2H-pyran-2-one	78
5.3 Conclusion	79
5.4 Computational details	79
5.5 Data	80
Reference	108
Chapter 6. Conclusion of the thesis	110
Vita	112

第一章 绪论

1.1 工业制备含磷化合物

1669年，德国商人 Henning Brandt 将砂石、木炭、石灰、动物尿液放一起加热提炼出了白磷(图 1.1, P₄)^[1]。这是人类首次发现磷元素。

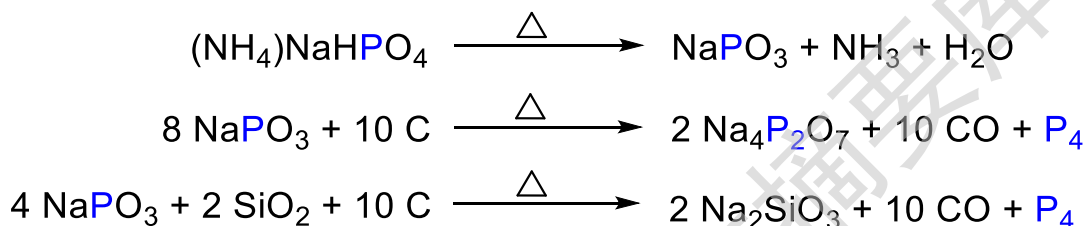


图 1.1 白磷 P₄ 的制备

事实上，近一个世纪以来，大多数含磷化学品的制备仍然采取白磷为原料^[2]。如图 1.2 所示，天然磷矿中(phosphate rock)的磷元素多以+5价的形式存在，经过湿法加工，可以直接转化为磷酸使用，但是此方法会产生大量的副产物石膏(CaSO₄)。另外一种方式是将磷矿用碳粉还原为白磷。在工业上，大多数白磷会被氧化为三氯化磷(PCl₃)，再转化为人类常用的有机磷化合物。

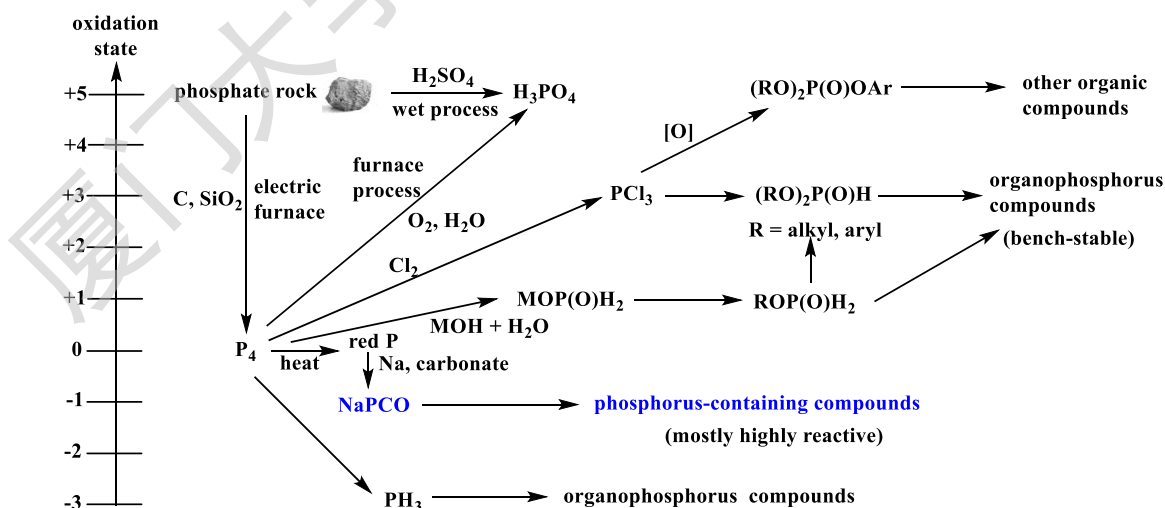


图 1.2 含磷化合物的制备

传统上, 氢亚磷酸酯(*H*-phosphonates)或氢次磷酸酯(*H*-phosphinates)是重要的磷工业中间体。自 1945 年, Todd^[3]发现了氢亚磷酸酯可以与亲核试剂的反应后, 以氢亚磷酸酯或二级磷氧(*H*-phosphine oxide)为磷源来制备含磷化合物的方法受到广泛重视并取得了许多进展^[4]。虽然磷烷(PH₃)是一种易自燃的剧毒气体, 但目前仍然有很多工业需要以其为原料^[2]。

1.2 低配位磷化合物的合成和反应性

1.2.1 磷氰酸类化合物的合成和反应

磷氰酸根负离子(phosphaethynolate anion, PCO⁻)是氰酸根负离子(cyanate anion, NCO⁻)的含磷类似物。在 1992 年, 磷氰酸根负离子的锂盐(LiPCO)^[5]首次被德国化学家 Becker 和 Westerhausen 成功合成。但是其合成方法苛刻, 并且 LiPCO 自身稳定性较差, 造成磷氰酸根负离子的研究并不多。在 2014 年, 瑞士化学家 Grützmaier 等人^[6]报道了一种高效简便合成磷氰酸钠(NaPCO)的新方法(图 1.3)。该方法以空气和水均稳定的红磷为起始原料, 用萘钠作为强还原剂, 并原位与叔丁醇、碳酸酯反应, 可以大量制备磷氰酸钠的二氧六环加合物。现代量子化学计算表明, 磷氰酸根负离子是以下两种主要共振式的杂合体(图 1.4)。有意思的是, 磷氰酸钠可以在水中存活数小时, 初步研究表明其对很多不饱和有机化合物有较高的活性^[7](图 1.5)。

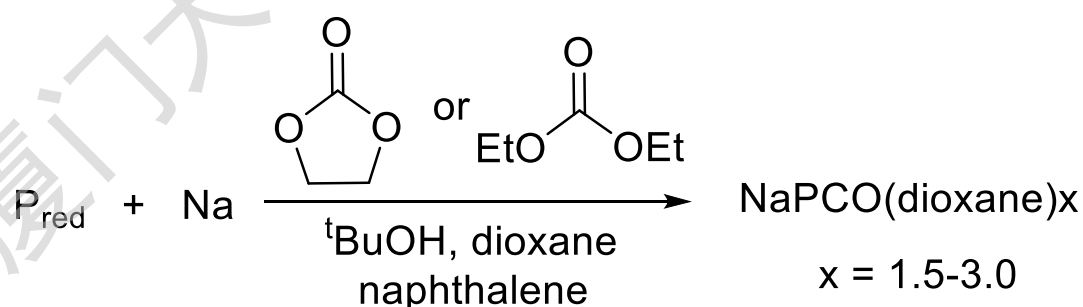


图 1.3 磷氰酸钠的合成

举例来说, 磷氰酸根负离子可以与烯酮(ketene)或者碳二亚胺化合物(carbodiimide)发生环加成反应, 生成四元环的阴离子产物^[7a](图 1.5A,C)。此外, 磷氰酸根负离子也可以与缺电子的炔烃发生环加成反应生成相应的磷杂苯^[7b](图

1.5B,E)。磷氰酸根负离子还可以与 2-羰基吡喃发生[2+4]环加成反应，脱去一分子的二氧化碳，形成磷杂苯酚产物^[7b](图 1.5D)。

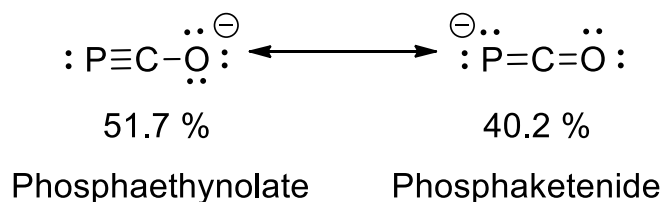


图 1.4 磷氰酸根负离子的自然共振分析

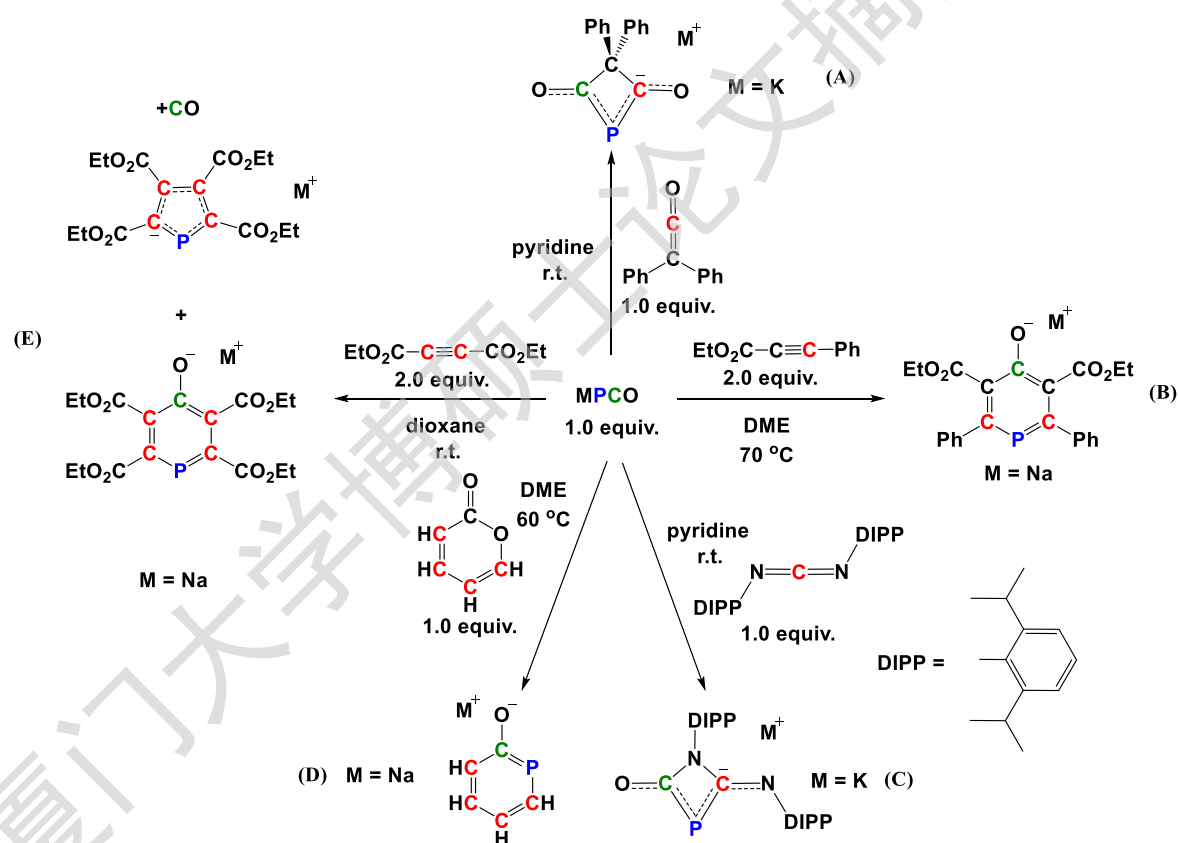


图 1.5 磷氰酸根负离子参与的环加成反应

由于磷氰酸根负离子有很强的还原性^[8]，所以可以被常用的氧化剂氧化(例如 I₂ 或者 SO₂)，生成四聚体双负离子^[9](图 1.6)。

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