

行政院國家科學委員會專題研究計畫 期中進度報告

有機金屬化合物在有機合成與材料的應用(2/3) 期中進度報告(精簡版)

計畫類別：個別型

計畫編號：NSC 95-2119-M-002-008-

執行期間：95年08月01日至96年11月30日

執行單位：國立臺灣大學化學系暨研究所

計畫主持人：林英智

報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫可公開查詢

中華民國 96 年 12 月 10 日

行政院國家科學委員會補助專題研究計畫 ☐ 成果報告
☒ 期中進度報告

(計畫名稱)

有機金屬化合物在有機合成與材料的應用(2/3)

計畫類別：☒ 個別型計畫 ☐ 整合型計畫

計畫編號：NSC 95-2119-M-002-008-

執行期間：95 年 8 月 1 日至 96 年 11 月 1 日

計畫主持人：林英智

共同主持人：

計畫參與人員：

成果報告類型(依經費核定清單規定繳交)：☒ 精簡報告 ☐ 完整報告

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執行單位：國立臺灣大學化學系暨研究所

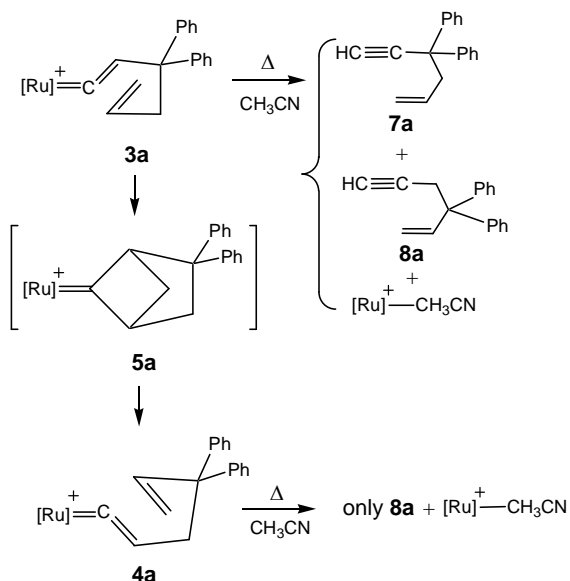
中 華 民 國 96 年 5 月 4 日

Abstract: This is a brief report including three parts: 1. Chemistry of ruthenium vinylidene complexes. 2. Photoluminescence of alkynyl complexes. 3. Chemistry of Iron vinylidene complexes. The new metathesis of the terminal vinyl group with the C=C of the vinylidene group is confirmed by ^{13}C labeling studies. A number of star-shaped molecules with silyl group and an aromatic core surrounded by extended π conjugative arms has been synthesized by using Sonogashira coupling methods and show excellent fluorescence intensity with high quantum yield. Finally Two iron complexes each containing 1-ferra-2,5-diphospha-[2.1.1] ring are prepared by deprotonation reaction of cationic vinylidene complexes $[\text{Fe}]=\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{R}^+$ ($[\text{Fe}] = (\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Fe}$, $\text{R} = \text{CH}=\text{CH}_2$, and Ph).

Keyword: ruthenium, vinylidene, photoluminescence, iron, alkynyl

I. Chemistry of ruthenium vinylidene complexes.

The cationic complex $\{[\text{Ru}]=\text{C}=\text{CHCPh}_2\text{CH}_2\text{CH}=\text{CH}_2\}\text{BF}_4$ (**3a**, $[\text{Ru}] = (\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}$) in solution transforms to $\{[\text{Ru}]=\text{C}=\text{CHCH}_2\text{CPh}_2\text{CH}=\text{CH}_2\}\text{BF}_4$ (**4a**) via a new metathesis process of the terminal vinyl group with the C=C of the vinylidene group which is confirmed by ^{13}C labeling studies. This transformation is irreversible as revealed by deuteration and decomplexation studies. The cationic complex $\{[\text{Ru}]=\text{C}=\text{CHCPh}_2\text{CH}_2\text{CMe}=\text{CH}_2\}\text{BF}_4$ (**3b**) undergoes a cyclization process yielding **6b** containing a η^2 -cyclic allene ligand which is fully characterized by single crystal X-ray diffraction analysis. Analogous complexes **4a'** and **6b'** ($[\text{Ru}] = (\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}$) containing dppe ligands were similarly obtained from protonation of the corresponding acetylide complexes via formation of vinylidene intermediate. Protonation of the acetylide complex containing a terminal alkynyl group $[\text{Ru}]^+-\text{C}\equiv\text{CCPh}_2\text{CH}_2\text{C}\equiv\text{CH}$ (**2c**) generates the vinylidene complex $\{[\text{Ru}]=\text{C}=\text{CH}-\text{CPh}_2\text{CH}_2\text{C}\equiv\text{CH}\}\text{BF}_4$ (**3c**) which again undergoes an irreversible transformation to give $\{[\text{Ru}]=\text{C}=\text{CHCH}_2\text{CPh}_2\text{C}\equiv\text{CH}\}\text{BF}_4$ (**4c**) possibly via a π -coordinated alkynyl complex followed by hydrogen and metal migration. No similar transformation is observed for the analogous dppe complex **3c'**. With an extra methylene group, complex $\{[\text{Ru}]=\text{C}=\text{CHCPh}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2\}\text{BF}_4$ (**3d**), as well as $\{[\text{Ru}]=\text{C}=\text{CHCPh}_2\text{CH}_2\text{Ph}\}\text{BF}_4$ (**3e**), are stable. Presence of a gem-diphenylmethylene moiety at the vinylidene ligand with appropriate terminal vinyl or alkynyl group along with correct steric environment implement such a novel reactivity in the ruthenium vinylidene complexes.

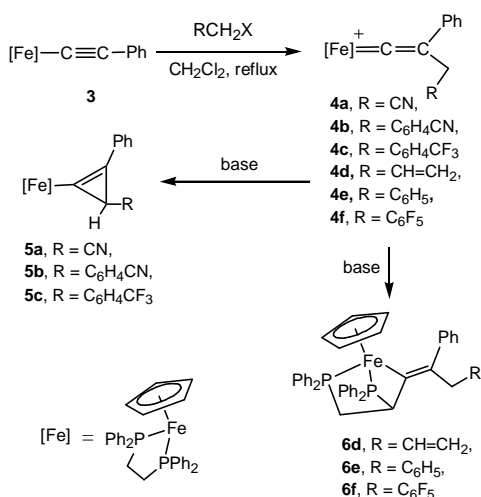


II. Photoluminescence of alkynyl complexes.

A series of star-shaped molecules with silyl group and an aromatic core surrounded by extended π conjugative arms has been synthesized by using Sonogashira coupling methods and show excellent fluorescence intensity with high quantum yield. These molecules undergo desilylation in the presence of $n\text{-Bu}_4\text{NF}$ to give terminal polyalkynyl compounds. By incorporating metal moieties such as palladium, platinum and gold into these compounds, star-shaped molecules can be obtained. Photophysical properties of these molecules are investigated spectroscopically in solution. These star-shaped molecules are characterized by IR, NMR (^1H , ^{31}P and ^{13}C) spectroscopy, as well as MALDI-TOF mass spectrometry.

III. Chemistry of Iron vinylidene complexes.

Two iron complexes each containing 1-ferra-2,5-diphospha-[2.1.1] ring are prepared by deprotonation reaction of cationic vinylidene complexes $[\text{Fe}]=\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{R}^+$ ($[\text{Fe}] = (\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Fe}$, $\text{R} = \text{CH}=\text{CH}_2$, and Ph). The deprotonation takes place at the methylene proton of the dppe ligand which is followed by an intramolecular addition giving the product. For similar vinylidene complexes with $\text{R} = \text{CN}$, $p\text{-C}_6\text{H}_4\text{CN}$ and $p\text{-C}_6\text{H}_4\text{CF}_3$, the deprotonation reaction gave the cyclopropenyl complexes. The deprotonation of the vinylidene complex with $\text{R} = \text{C}_6\text{F}_5$ gave both the cyclopropenyl complex and the product containing a 1-ferra-2,5-diphospha-[2.1.1] ring system. The electron- withdrawing ability of substituent near the C_γ -methylene group of the vinylidene ligand determines the selectivity of deprotonation. Characterizations of vinylidene, cyclopropenyl complexes and a complex containing a 1-ferra-2,5- diphospha-[2.1.1] ring are carried out using single crystal X-ray diffraction analysis.



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3. Chiung-Cheng Huang, Ying-Chih Lin,* Ping-Yu Lin, and Yu-Ju Chen (2006) Star-Shaped Molecules Containing Polyalkynyl Groups with Metal Moieties on Benzene and Triphenylene Cores. *Eur. J. Org. Chem.* **2006**, 4510–4518.
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Vinylidene Complexes Containing dppe Ligand *Organometallics* **2007**, 26, 1250 - 1255.

出國開會部分預備參加 2007 年 8 月 19-23 日之美國 234 屆化學年會。

出席國際學術會議心得報告

會議名稱:

The 17th International Symposium on Olefin Metathesis (ISOM 17)

地點:

Hilton Hotel Pasadena California U.S.A.

時間:

July 28-Aug 03 2007

林英智

台大化學系教授

The 17th International Symposium on Olefin Metathesis (ISOM 17) was held at Pasadena California on July 28-Aug 03 2007. The symposium was held in the Hilton Hotel Pasadena, a nice meeting place near the campus of Caltech. A small business company Materia was set up by a very successful research result of Prof. Grubbs. Materia is a small company with about 60 people focus mainly on applying the result of research activity in California Institute of Technology in business. The major product of the company is derived from the polymerization of DCPD (dicyclopentadienide) using Grubbs' catalyst. Because of easy fabrication of the process, the product could be easily molded into some specific shape. There are about 200 attendees including many chemists from Europe and Japan. The six days schedule is filled with oral presentations and two poster sessions. Many reports involve application of olefin metathesis in the organic synthesis particularly formation of macrocyclic ring in natural products and preparation of polymers. A few report even used the concept of metathesis to fix the conformation of biological molecules.

In the introduction session Professor Robert H Grubbs stressed that olefin metathesis is being recognized as a green chemistry. The reaction not only increases the efficiency in terms of synthetic steps and the lack of contaminating by-products but it also open new routes for the conversion of biomaterial into useful products. Products in which petroleum-based starting materials are being replaced by renewable sources are now starting to reach the market. A wide range of ruthenium-based alkylidene complexes is now commercially available and applications are now starting to become a commercial reality.

Professor Dixneuf, Pierre reported the transition-metal-catalyzed organic transformation of alkynes involving vinylidene intermediates. Vinylidene complexes, which can be mono-, di-, or polynuclear, are known for most transition metals and may be prepared by a variety of methods. The most pertinent route to mononuclear vinylidenes involves the reaction of an alkyne with a transition-metal substrate. The alkynes can be terminal or internal with alkyl/aryl/silyl substituents. Although the chemistry of (vinylidene)metal complexes has been extensively investigated, mononuclear bis(vinylidene) complexes remain unknown. A mononuclear bis(vinylidene) species was proposed as a reactive intermediate in the formation of tetrakis(trimethylsilyl)butatriene. They have isolated an unprecedented ruthenium bis(vinylidene) complex from the reaction of $[\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Ru-}$

(NCCH₃)₂ with silylalkyne.

The keynote speaker Hoveyda of the Boston College reported the synthesis, characterization, and reactivities of molybdenum bispyrrolyl complexes of the type Mo(NR)(CHR')(pyrrolyl)₂ where pyrrolyl is either the parent pyrrolyl or 2,5-dimethylpyrrolyl (Me₂Pyr) in the use of bispyrrolyl species as precursors to bisalkoxide catalysts of the type Mo(NR)(CHR')(OR)₂ or Mo(NR)(CHR')(diolate) through addition of an alcohol or a diol to Mo(NR)(CHR')(pyrrolyl)₂ complexes. Preliminary experiments suggest that bispyrrolyls are less reactive toward olefins than bisalkoxide species, but serve as effective precursors to Mo-based bisalkoxides or diolates. The high reactivities are observed for supported catalysts prepared through addition of bispyrrolyl species to silica where the predominant surface species is Mo(NR)(CHR')(pyrrolyl)(OSi_{surf}). High catalytic activities have been observed (and also rationalized through theoretical studies) for these and related pseudotetrahedral metal complexes that are asymmetric at the metal center. The synthesis of species of the type Mo(NR)(CHR')(OR')(pyrrolyl) and their use in catalytic enyne metathesis reactions are reported.

I submitted a poster with the title "Intramolecular Cyclization of Ruthenium Vinylidene Complexes with a Tethering Vinyl Group: Facile Cleavage and Reconstruction of C-C Double Bond". It was good to talk with top-notch scientist for research results at the poster session and obtained some valuable suggestions from them. I got the chance to chat with Professor Grubbs and Professor Dixneuf and had a nice exchange of research idea with them. The paper is just accepted by the Journal of the American Chemical Society.

