

行政院國家科學委員會專題研究計畫 期中進度報告

金屬有機化合物的應用(2/3)

計畫類別：個別型計畫

計畫編號：NSC92-2113-M-002-031-

執行期間：92 年 08 月 01 日至 93 年 07 月 31 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

報告類型：精簡報告

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 93 年 5 月 27 日

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計畫類別： ☒ 個別型計畫 ☐ 整合型計畫

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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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中 華 民 國 92 年 5 月 27 日

(二)中、英文摘要及關鍵詞(keywords)。

Abstract

This is the second mid term report for a three year project. We study the dimerization reactions of various acetylenes (Part I) and photoluminescence Zn (Part II) complexes. Using rhodium complex as a catalyst, the dimerization of various terminal arylalkynes in aprotic solvents (such as CH_2Cl_2 , THF and acetone) resulted in formation of (*E*)-1,4-disubstituted enyne **6** in high stereoselectivity. However, when CH_3OH is used as a solvent, dimerization of 1-arylalkynes with an electron-withdrawing group gave the other stereoisomeric product (*Z*)-1,4-disubstituted enyne **8** in the presence of 0.1 equiv. of CH_3I . With excess CH_3I , a competitive process, namely oxidative additions of CH_3I and alkyne to Rh metal center followed by reductive elimination, gave the alkylation product **4** of the terminal alkyne.

An efficient method was developed for the preparation of a series of zinc Schiff base complexes. Introduction of a pyridyl group as a bridging unit as well as incorporation of ethynyl and electron-donating groups into the salicylidene moiety of these complexes moderately enhance the photoluminescence intensity and quantum yield. Electron-rich palladium groups possibly influence the photophysical character through the bridging $\text{C}\equiv\text{C}$ bond. Crystal structure of the pyridine adduct of a salen Zn complex is determined by X-ray diffraction analysis.

摘要

本期中報告報導銦金屬催化乙炔化合物雙子化反應以及光致發光的鋅金屬化合物的兩個合成與反應的化學。乙炔化合物雙子化反應可以藉著溶劑來改變其雙子化反應的選擇性，用二氯甲烷作溶劑可以生成反式的共軛烯炔化合物。用甲醇作溶劑則可以生成順式的共軛烯炔化合物。在光致發光的鋅金屬化合物的化學合成，我們發現新的合成方法。且使用這合成方法，改變化合物其中的部分官能基，找出發光量子效率達 0.76 之鋅金屬配位化合物。這些反應的主要產物均使用單晶繞射的方法確定其固態結構。

Key words: Rhodium, acetylene dimerization, zinc, photoluminescence

鑰字：銦，炔類雙子化，鋅金屬配位化合物，光致發光

(三)報告內容：請包括前言、研究目的、文獻探討、研究方法、結果與討論（含結論與建議）等。若該計畫已有論文發表者，可以 A4 紙影印，作為成果報告內容或附錄，並請註明發表刊物名稱、卷期及出版日期。若有與執行本計畫相關之著作、專利、技術報告、或學生畢業論文等，請在參考文獻內註明之，俾可供進一步查考。

Part I.

Dimerization of terminal arylalkynes at ambient temperature catalyzed by $\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}$, (**2**) in the presence of CH_3I leads to formation of enyne with high conversion and high regio- and stereoselectivity. In aprotic solvent (such as acetone, CH_2Cl_2 or THF) dimerization of terminal alkynes $\text{HC}\equiv\text{C}(p\text{-C}_6\text{H}_4\text{X})$, (**1**, $\text{X} = \text{H}$, **a**; $= \text{NO}_2$, **b**; $= \text{C}(\text{O})\text{H}$, **c**; $= \text{CH}_3$, **d**; $= \text{CN}$, **e**; $= \text{NMe}_2$, **f**; $= \text{CF}_3$, **g**; $= \text{F}$, **h**; $= \text{Br}$, **i**; $= \text{I}$, **j**) leads to the (*E*)-1,4-disubstituted enynes **6** (**a~k**) in high selectivity. However, when MeOH is used as a solvent, the dimerization of 1-arylalkynes containing an electron withdrawing group affords the (*Z*)-1,4-disubstituted enyne **8**. Requirement of the presence of CH_3I for this conversion indicates that the process presumably involves initially a six-coordinated rhodium alkylacetylide intermediate by oxidative addition. The oxidative addition of ICH_2CN to **2** yielded the six-coordinated complex $\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})(\text{I})(\text{CH}_2\text{CN})$, (**5a**) which is catalytically inactive. The analogous complex **5b** with a *p*-nitro group on the phenyl acetylide ligand is characterized by X-ray diffraction analysis.

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Part II.

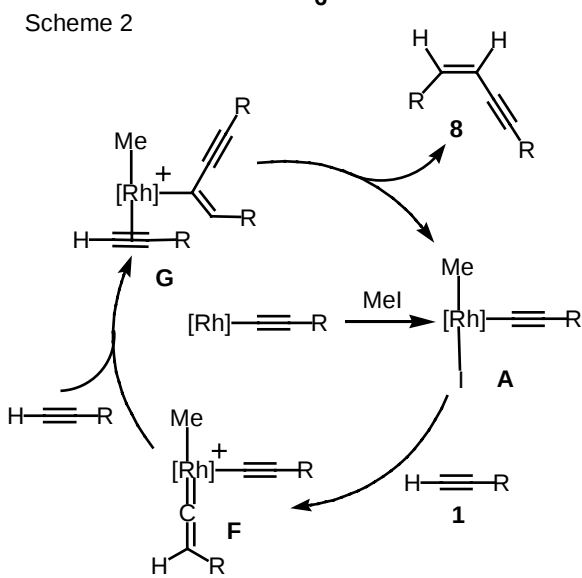
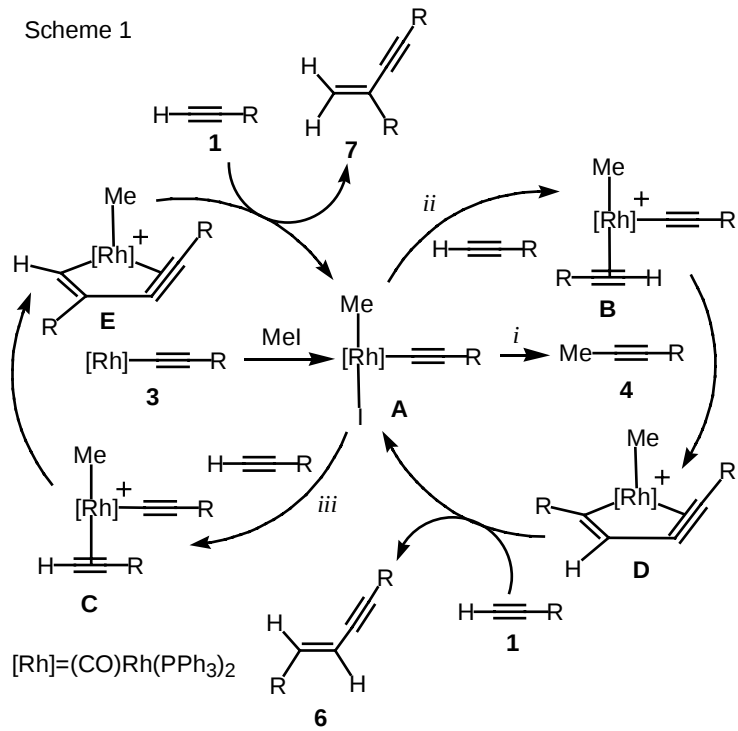
We have demonstrated that a series of novel luminescent Zn(II) Schiff base complexes could be readily synthesized. Preparation of zinc Schiff base complexes (see Scheme) were readily achieved by treatment of the corresponding salicylaldehyde with zinc acetate followed by addition of diamine in methanol. The desired solid state Zn (II) complexes formed from the reaction solution were readily collected via filtration. Terminal alkynyl groups in complex could be efficiently used for the preparation of hetero-trinuclear palladium derivatives. Preparation of the heterometallic trinuclear complex is achieved by the reaction of *trans*-Pd(PⁿBu₃)₂Cl₂ with zinc complex at the alkynyl terminus in the presence of CuI in Et₂NH. Replacement of two chlorides by cyanides at the Pd moiety could be achieved by the reaction with AgCN generating the bright orange complex.

The photoluminescence of the pyridyl-containing Schiff base complexes is very efficient relative to those with phenylene bridge. Addition of two ethynyl groups in the backbone enhances the fluorescence efficiency by a large margin. The *t*-butyl groups are not as advantageous as the ethynyl ones. The nitro and methoxy groups containing lone-pair electrons quench the photoluminescence. The heterometallic complexes appear color variation (wavelength alteration) of the fluorescence and give slightly higher quantum yield comparing with those of mononuclear complex.

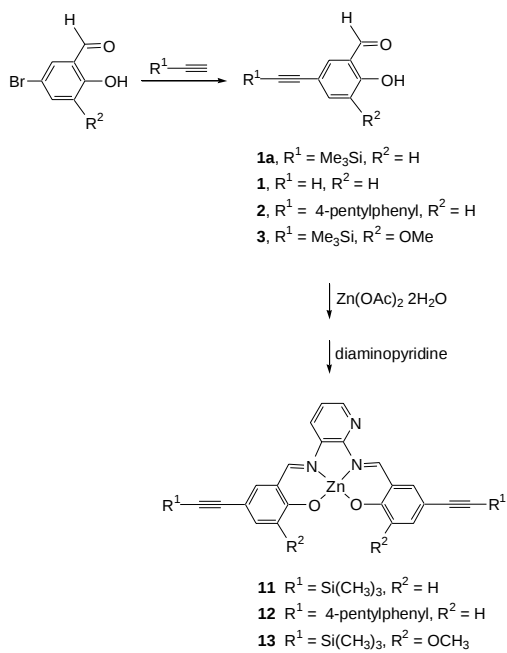
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(五)附表及附圖

Scheme 1 illustrates the mechanism on the reactions of part I of this report.



Scheme 2 illustrates the mechanism on the reactions of part II of this report.



(六)計畫成果自評部份，請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

On the basis of our findings we anticipate that new efficient methods for selective dimerization of acetylene should be developed from our findings in the reaction of acetylene catalyzed by rhodium complexes. In the preparation of zinc salophen complexes we find new synthetic method to prepare various new photoluminescence compounds. Some of these new products will be tested for fabrication. Novelty of these reactions deserves publication in scientific journal. This report is taken in part from two manuscripts. Manuscript describing results of Part I is currently submitted to *Organometallics* to be considered as a full paper. Manuscript describing results of Part II was published in *Dalton* early this year.