

行政院國家科學委員會專題研究計畫 成果報告

磷和氮官能化氮異環碳烯衍生物配位基金屬錯合物合成和 催化活性探討

計畫類別：個別型計畫

計畫編號：NSC93-2113-M-018-004-

執行期間：93年08月01日至94年07月31日

執行單位：國立彰化師範大學化學系暨研究所

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報告類型：精簡報告

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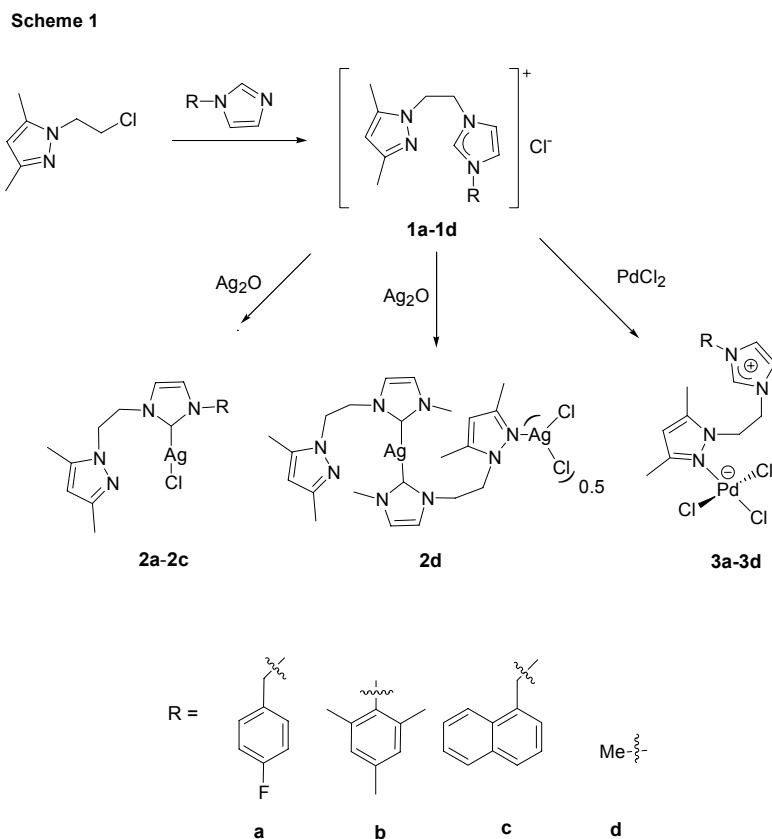
研究報告-精簡報告 (李漢文)

In this project, we continued on our interests in the functionalized *N*-heterocyclic carbene ligands and their transition metal complexes. We have successfully prepared several novel NHC ligands and applied them in several catalytic reactions. Three papers, financially supported by this grant, were successfully published. The details of them are listed below.

Publication 1: Lee, H. M.*; Chiu, P. L.; Hu, C-H.; Lai, C.-L.; Chou, Y.-C. “Synthesis and structural characterization of metal complexes based on pyrazole/imidazolium chlorides” *J. Organomet. Chem.* **2005**, *690(2)*, 403. (SCI)

In this work, a series of imidzoalium salt, L·HCl, for the potentially bidentate pyrazole/*N*-heterocyclic carbene was synthesized (Scheme 1). Reactions of a 2:1 mixture between L·HCl bearing bulky *N*-substitution and Ag₂O produced Ag(L)Cl, whereas a novel compound with unique stoichiometry AgL₂(AgCl)_{0.5}Cl was produced from L·HCl with *N*-methyl group under identical condition. Reactions of L·HCl with PdCl₂ produced zwitterionic Pd(II)Cl₃L·H. Selected structural determinations on L·HCl, Ag(L)Cl, AgL₂(AgCl)_{0.5}Cl, and Pd(II)Cl₃L·H revealed intriguing crystal chemistry in which the less-stable *gauche* rotamers were obtained exclusively. A preliminary application of the zwitterionic complexes PdLHCl in Heck coupling

reaction of aryl bromide with *n*-butyl acrylate shows effective activity.

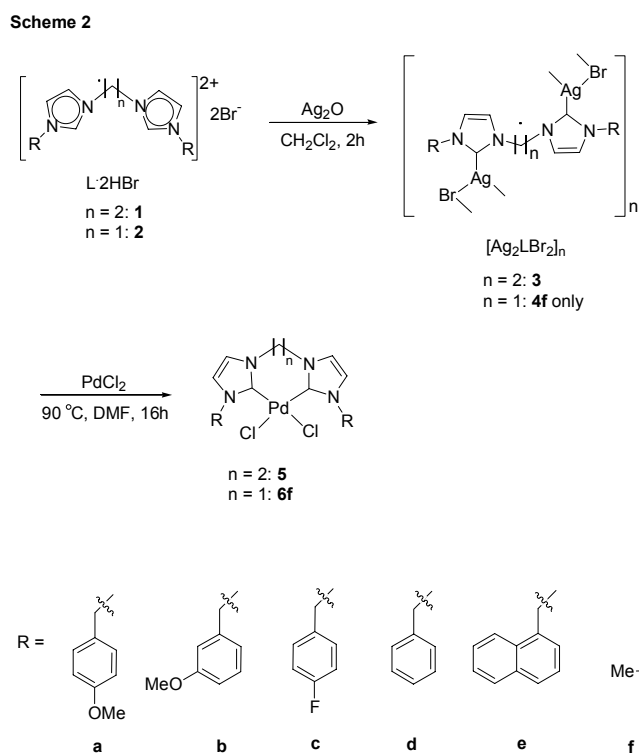


Publication 2: Chiu, P. L.; Chen, C. Y.; Zeng, J. Y.; Lu, C. Y.; Lee, H. M.*

“Coordination Polymers of Silver(I) with Bis(*N*-heterocyclic Carbene): Structural Characterization and Carbene Transfer” *J. Organomet. Chem.* **2005**, 690(6), 1682. (SCI)

In this paper, reactions of the ethylene- and methylene-bridged bis(imidazolium) salts with an equivalent amount of silver oxide in dichloromethane at room temperature produced readily the silver NHC compounds [Ag₂LBr₂] (Scheme 2).

These compounds are partially soluble in DMF. The X-ray structure determination on **3d** (L = 1,1'-dibenzyl-3,3'-ethylenediimidazolin-2,2'-diylidene) reveals the formation of bromide bibridged (Ag_2LBr_2)_n chains and a unique supramolecular motif with weak $\text{Ag}^{\cdots}\text{Ag}$ interactions of 3.429 Å. Similar to monomeric silver(I) NHC complexes, the silver coordination polymers can also act as carbene transfer reagents for the formation of chelating palladium NHC complexes in excellent yields.



Publication 3: Chiu, P. L.; Lee, H. M.* “The Chemistry of $\text{PC}^{\text{NHC}}\text{P}$ ligand: Silver and Ruthenium Complexes, Facial/Meridional Coordination, and Catalytic Transfer Hydrogenation” *Organometallics* **2005**, *24*, 1692. (SCI).

In this paper, *fac*-[Ru₂(μ-Cl)₃(PC^{NHC}P)₂]Cl (**3**) can be prepared by a novel silver carbene transfer reaction between [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂ and RuCl₂(PPh₃)₃ or a direct reaction between PC^{NHC}P·HCl and the ruthenium precursor (Scheme 3). The reactivity study shows that PC^{NHC}P ligand is capable of accommodating the extra steric requirement by switching readily from facial to meridional chelating mode, whereas a preliminary catalytic study indicates that complex **3** is an effective catalyst in transfer hydrogenation of ketones.

