

行政院國家科學委員會專題研究計畫 成果報告

多腓性碳烯螯合物的催化活性和超分子化學探討

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計畫主持人：李漢文

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研究報告-精簡報告 (李漢文)

In this grant proposal, we continued our interests in functionalized *N*-heterocyclic carbene ligands and successfully obtained new results, which have been successfully published in several SCI journals. Below are summaries of these works.

Publication 1: Zeng, J. Y.; Hsieh, M.-H.; Lee, H. M.* “Rhodium complexes of PC^{NHC}P ligand: oxidative addition of dichloromethane and catalytic hydrosilylation of alkynes affording (*E*)-allenylsilanes” *J. Organomet. Chem.* **2005**, *690*, 5662–5671. (*special issue for carbene chemistry*) (SCI) (2.025)

Summary: New rhodium complexes of PC^{NHC}P have been synthesized by using the silver transfer reagent, [Ag₃(PC^{NHC}P)₂Cl]Cl₂ (**2**). In the reaction between **2** and [Rh(COD)Cl]₂ in dichloromethane, the presumably formed nucleophilic Rh^I(PC^{NHC}P)Cl intermediate (**A**), undergoes a C—Cl bond activation of CH₂Cl₂ giving *cis,mer*-Rh^{III}(PC^{NHC}P)(CH₂Cl)Cl₂ (**3**) as the final product. Attempts to isolate **A** affords the oxidative degradation product of *mer*-Rh^{III}(PC^{NHC}P)Cl₃ complex (**4**). In contrast, the rhodium(I) center in Rh(PC^{NHC}P)(CO)Cl (**5**) is stabilized by the π-back bonding of C≡O ligand; a robust complex is, therefore, obtained. The solid-state structures of **2** and **3** were determined by X-ray diffraction. Complexes **3—5** are

catalyst precursors for efficient, chemoselective hydrosilylation of alkynes. For the reaction between phenylacetylene and dimethylphenylsilane, a rapid hydrosilylation occurs, producing isomers of alkenylsilanes; then a slow isomerization pathway converts (*Z*)-alkenylsilane to its (*E*)-isomer. For **3**, under catalytic condition, a facile reductive elimination of dichloromethane giving **A** is anticipated. The similarity in reactivity and selectivity between **3**—**5** suggests the involvement of **A** as the active species in a common catalytic cycle.

Publications 2: Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M.*

“Synthesis, Structural Characterization, Computational Study, and Catalytic Activity of Metal Complexes based on Tetradentate Pyridine/*N*-heterocyclic Carbene Ligand”

Organometallics **2005**, *24*, 6169–6178. (SCI) (3.473)

Summary: The ligand precursor, [LH₂]Br₂ (**1**), for the bis(NHC) ligand with *N*-picoly moieties is synthesized in 83% of yield. Complexation of **1** with palladium and nickel acetates produced the tetradentate complexes, [PdL]Br₂ (**2**) and [NiL]Br₂ (**3**), respectively, in quantitative yields. Complexes **2** and **3** were characterized by X-ray structural determination, which reveal a highly twisted helical coordination of L around the metal ions. In solution, however, the tetradentate chelate ring undergoes a rapid fluxional process of ring flapping. A theoretical study confirms that the

tetradentate coordination of L in **2** and **3** is energetically more favorable than the bidentate chelation mode with dangling picoly groups. A preliminary application of the tetradentate complex [NiL]Br₂ in Suzuki coupling of aryl halides with phenylboronic acid shows effective activity.

Publications 3: Chiu, P. L.; Chen, C. Y.; Lee, C.-C.; Hsieh, M.-H. Chuang, C.-H.; Lee, H. M.* “Structural Variations in Novel Silver(I) Complexes with Bitopic Pyrazole/*N*-heterocyclic Carbene Ligands” *Inorg. Chem.* **2006**, *45*, 2520. (3.851)

Summary: The synthesis and structural characterization of several new silver complexes of L (L = a bidentate ligand of pyrazole and *N*-heterocyclic carbene) are described. The result shows that the choice of counterions, *N*-substitutions of L, and reaction conditions are crucial which lead to a variety of structural motifs, including novel metallomacrocycles [Ag₂(μ-L)₂]²⁺ with or without Ag···Ag close contact, a mononuclear [AgL₂]⁺ complex, and a [LAg(NO₃)]_n coordination polymer. In particular, the nonbonding Ag···Ag distance and the overall geometry of the metallomacrocycles are controllable by the choices of different *N*-substitutions and counterions. All these complexes have been determined by X-ray diffraction. The solid-state aggregates are retained in solution as supported by the electrospray mass spectroscopic studies.

Publication 4: Chen, C. Y.; Zeng, J. Y.; Lee, H. M.* “Argentophilic interaction and anionic control of supramolecular structures in simple silver pyridine complexes” *Inorg. Chimi. Acta* **2006**, *in press (special issue for young investigators)* (SCI) (1.606)

Summary: The synthesis and characterization of three simple 1:2 silver(I) pyridine adducts of different counter-anions, $[\text{Ag}(\text{py})_2]^+ \cdot \text{X}^-$ ($\text{X} = \text{ClO}_4$, **1**; BF_4 , **2**; PF_6 , **3**), are reported. The structural studies for **1**—**3** reveal the presence of strong argentophilic interactions between $[\text{Ag}(\text{py})_2]^+$ ions, forming pairs of $[\text{Ag}(\text{py})_2]_2^{2+}$. The Ag...Ag contact distances are 2.96—3.00 Å. In **1** and **2**, pairs of $[\text{Ag}(\text{py})_2]_2^{2+}$ are further linked into 1-D infinite chains by a combined set of multiple Ag...Ag close contacts (3.34—3.37 Å), offset ‘head to head’ π — π stacking, and anion bridging interactions. Such combined set of interactions is anion-dependant with **1** and **2** containing anions of tetrahedral geometry (ClO_4^- and BF_4^-), affording essentially the same supramolecular architecture. Metal-anion interactions are crucial in organizing the 1-D chains into 3-D networks. The ES-MS studies of **1** and **2** provide positive evidence for the aggregation of silver(I) ions in solution. In contrast, for **3** with the counter-anion of octahedral PF_6^- , pairs of $[\text{Ag}(\text{py})_2]_2^{2+}$ are organized into a 3-D network via a combined set of Ag...F contacts, C(H)...F hydrogen bonds, and ‘head to tail’ π — π stacking interactions. No extended 1-D polymeric chains of silver ions are

present in 3.

Publication 5: Liao, C.-Y.; Lee, H. M.* “trans-dichlorobis(pyridine)palladium(II)”

Acta. Cryst. **2006**, *E62*, m680-m681. (SCI) (0.581)

Summary: The structure of the title compound, $C_{10}H_{10}N_2PdCl_2$ was determined at 150 K. It crystallizes in the triclinic space group $P\bar{1}$. The structure is a polymorph of a previously determined structure (Viossat *et al.*, 1993).