

# 行政院國家科學委員會專題研究計畫成果報告

計畫名稱：膦與烯胺雙芽配位基對催化聚合反應研究

計畫編號：NSC90-2113-M002-038

執行期限：88年8月1日至91年7月31日

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## 一、中文摘要

金屬鈀與膦-烯胺的合成與其聚合反應活性的性質探討，膦-烯胺配位體影響金屬能夠穩定聚合中間體作為塊共聚的方法。

**關鍵詞：**鈀，烯胺，配位體，聚合，共聚

### Abstract

Under mild conditions, palladium complexes containing phosphine-imine ligands underwent insertion with carbon monoxide and olefins. All inserted intermediates are isolated. Polymerization and copolymerization of olefin and CO with these palladium complexes are investigated.

**Keywords:** Palladium, imine, donor, polymerization, copolymerization.

## 二、緣由與目的

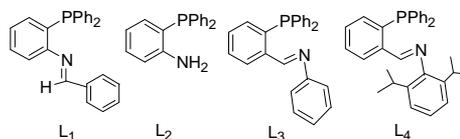
Late transition metal catalyzed polymerization and/or copolymerization of unsaturated substrates *via* migratory insertion manner is of great current interest. Many research groups are actively engaged in developing efficient catalysts with late transition metal ions coordinated by various donors. These investigation illustrate that both electronic and steric environment of the ligands are crucial in stabilizing the metal ion as well as in the selectivity/activity of the polymerization.

Due to the different donor/acceptor properties of the phosphorus and nitrogen donor centers, study of phosphine-imine (P~N) bidentates on either coordination or metal catalyzed organic transformation has received much attention.<sup>1-28</sup>

## 三、報告內容

### Preparation of ligands and complexes.

Preparations of  $L_1$  and its palladium complex  $[(L_1)PdMeCl]$  1 are reported in our earlier work, whereas  $L_2$  was prepared according to the previously published procedures. The ligands  $L_3$  and  $L_4$  were prepared by simple condensation of 2-diphenylphosphino-phenylbenzaldehyde with slight excess of aniline or 2,6-di-isopropylaniline respectively in methanol solution. By stirring at room temperature overnight, the corresponding imine product was isolated quantitatively, which was further characterized by spectroscopic methods. Some selected spectral data of  $L_1$ - $L_4$  are given in the Table 1.  $^{31}P$  NMR shows a single peak at -13.6 and -14.9 ppm for  $L_3$  and  $L_4$  respectively, being 2 - 3 ppm upfield than those of the starting 2-diphenylphosphino-benzaldehyde (-11.7 ppm in  $CDCl_3$ ). In the  $^1H$  NMR spectra the imine proton appears as a doublet at 9.06 and 8.94 ppm due to  $J_{P-H} = 5.1$  Hz for  $L_3$  and  $J_{P-H} = 5.7$  Hz for  $L_4$  respectively. Such long-range coupling is comparable with other known P~N ligands.



Reactions of equal molar amount of ligands ( $L_2 - L_3$ ) with  $Pd(COD)MeCl$  [ $COD = 1,5$ -cyclooctadiene] in THF solution afforded the complexes  $[Pd(P\sim N)MeCl]$  ( $P\sim N = L_2, 2; L_3, 3$ ) in quantitative yield. Cationic Pd(II) complexes with acetonitrile coordination were prepared by treating the related neutral  $[PdMeCl(P\sim N)]$  with one

equiv. of  $\text{AgBF}_4$  in a mixture of dichloromethane and acetonitrile solution.

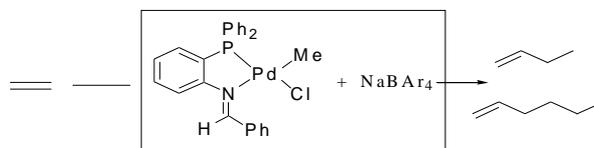
At 25 °C, consecutive bubbling of CO and ethylene into the dichloromethane solution of 1a uniquely resulted in the formation of 2, 3, 4 and 5 (Scheme 1).<sup>16</sup> Intermediates 3 and 5 isolated in solid state are stable. By contrast acyl complexes 2 and 4 decompose slowly in solution as well as in solid state. Appearance of single  $^{31}\text{P}$  signal for 2, 3, 4 and 5 at 18.4, 36.7, 19.9 and 36.8 ppm respectively suggests the quantitative formation of only one product in each step. Infrared spectrum of the compound 5 show two C=O stretching bands at 1712 and 1629  $\text{cm}^{-1}$  corresponding to free and coordinated carbonyl groups respectively. Coordination of the C=O moiety to the palladium is well documented *via* the formation of 5-membered chelation.<sup>10</sup> Possibility of six-membered chelation in compound 4 is ruled out based on  $^{13}\text{C}$  spectrum, which show two peaks at 223.1 and 206.6 ppm corresponding to metal bound acyl and free carbonyl group respectively. No shift in later peak is observed upon ethylene insertion leading to the formation of 5. Chelated carbonyl carbon in 5, however, is down field shifted and appeared at 231.3 ppm.

**Copolymerization of CO and olefins.** Using the new imine-phosphine complexes  $[\text{Pd}(\text{P-N})(\text{CH}_3)(\text{CH}_3\text{CN})](\text{BF}_4)$  ( $\text{P-N} = \text{L}_1$ ) as catalyst, copolymerization of E-CO can be carried out under mild conditions. In one of the typical reactions, 1a (22.0 mg, 0.03 mmol) with CO and ethylene (40 psi for each in a 200 mL autoclave) in 75ml of  $\text{CH}_2\text{Cl}_2$  at 75-80 °C produces 0.5 g of polyketone after 48 hrs.<sup>14</sup> Complex 1a also affords the copolymerization of norbornene /CO, but the fluorinated-benzaldimine-phosphine derivative 1b ( $\text{Ar} = p\text{-FC}_6\text{H}_4$ ) provides a better yield. The resulting material is a white solid and soluble in most of organic solvents. Molecular weight was determined by GPC analysis ( $M_n = 2500$ ,  $M_w/M_n = 1.26$ ).

**Heck reaction catalyzed by Pd(P~N) complexes.** Pd(II) complexes of the

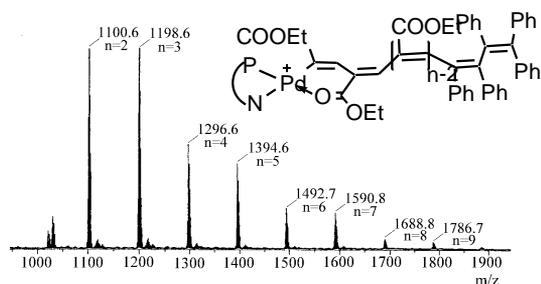
phosphine-nitrogen (P-N) bidentate donors act as efficient catalysts for the Heck reaction. In a typical example, reaction of phenyl iodide with methyl acrylate in *N*-methylpyrrolidinone (NMP) at ca 130 °C provides the Heck product with the turnover number up to 10<sup>6</sup>. In addition, the coupling reaction of 4-bromoacetophenone with olefin in a quantitative yield was achieved by using the same catalyst in the presence of sodium iodide.

**Dimerization and trimerization of ethylene.**  $[\text{Pd}(\text{P-N})(\text{CH}_3)(\text{CH}_3\text{CN})](\text{BF}_4)$  has been found to be a good catalyst for dimerization and trimerization of ethylene. In contrast to the diimine-palladium complexes which are known to catalyze the polymerization of various olefins, the imine-phosphine complex developed in this study is suitable for oligomerization of ethylene. It indicates that either the coordination of ethylene is probably overwhelming over other  $\alpha$ -olefins or insertion of high olefin is slow in such a system.

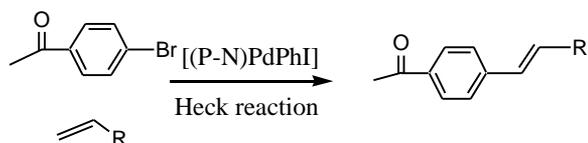


**Insertion of alkynes .** Neutral and Cationic Pd(II)-alkyl and Pd(II)-aryl complexes with phosphine-imine (P~N) ligand show unusual reactivity toward alkynes. No insertion of alkyne has been observed into the neutral palladium complexes or the cationic Pd-alkyl complex. On the other hand, smooth insertion of alkynes into the cationic complexes  $[(\text{P}\sim\text{N})\text{Pd}(\text{COMe})(\text{MeCN})]^+$  and  $[(\text{P}\sim\text{N})\text{Pd}(\text{Ph})(\text{MeCN})]^+$  was observed, resulting in the formation of singly and doubly insertion products respectively. All the inserted products were isolated and characterized by spectroscopic methods. Single crystal X-ray analysis for some alkyne insertion complexes indicate that the products are stabilized by intra-molecular coordination *via* either a carbonyl oxygen or a  $\pi$ -phenyl coordination with  $\eta^2$ -mode. Higher order insertions of ethylpropiolate in

complexes  $[(P\sim N)Pd(Ph)(MeCN)]^+$  (5) or  $[(P\sim N)Pd(C(Ph)=C(Ph)-C(Ph)=CPh_2)(MeCN)]^+$  (13), leading to the oligomeric species is found to proceed smoothly, but the di-substituted alkynes such as diphenylacetylene does not undergo such insertion. The insertion intermediates leading to oligomers is characterized by both spectral and Mass analyses. It is clear that the mixed-donor ligand as well as the reacting substrates affect the migratory insertion path of alkynes. The complexes with unsymmetrical ligand which can differentiate between the migratory insertion of alkynes over the intramolecular cyclization, may be a promising candidates for polymerization of alkynes.



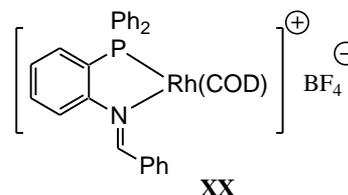
**Heck reaction.** Pd(II) complexes of the phosphine-nitrogen (P-N) bidentate donors act as efficient catalysts for the Heck reaction. In a typical example, reaction of phenyl iodide with methyl acrylate in *N*-methylpyrrolidinone (NMP) at ca 130 °C provides the Heck product with the turnover number up to  $10^6$ . In addition, the coupling reaction of 4-bromoacetophenone with olefin in a quantitative yield was achieved by using the same catalyst in the presence of sodium iodide.



**Polymerization of phenylacetylene.** The phosphine-imine(P~N)rhodium(I) complexes

(XX), containing a P~N and a COD ligands is an effective catalyst for polyphenylacetylene formation. Aqueous medium serves a good reaction environment and provides a convenient way of separation for the polymers from the reaction mixture.

In a typical experiment, a round-bottom flask (25 mL) charged with catalyst (0.01 mmol) was evacuated and flushed with nitrogen for several times, then phenylacetylene along with solvent was added. The reaction was carried out at 30 °C for 12 h and a polymer was isolated as an orange solid by filtration. The selectivity of *cis*-stereochemistry inclined to the polymers is observed in all instances. It seems that there is no obvious correlation of the stereo-regularity of polyphenylacetylene with the solvent systems. Molecular weight of the polymer can reach up to 30000 with PDI ~ 1.99.



**Conclusion.** In summary, the P~N bidentate ligands presented in this work allow us to study the influence of the chelation as well as the ancillary ligand on the insertion process with palladium center. Clearly, the phosphine-imine linked through *o*-phenylene backbone provides a unique ligand system to stabilize the metal-acyl species such as 14, which also reflects in the copolymerization of CO/ethylene. By examining the angle of N-Pd-P, the smaller bite angle appears in 14 might have effect on catalysis of copolymerization.

## Experimental Section

*General information.* All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen

from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over  $\text{CaH}_2$  and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. Complexes **1-4** were prepared from our earlier reported procedures.<sup>20,21</sup>

Nuclear magnetic resonance spectra were recorded in  $\text{CDCl}_3$  or acetone- $d_6$  on either a Bruker AC-E 200 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to  $\text{Me}_4\text{S}$  for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and relative 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR. Due to the complication of aromatic region, chemical shifts of non-aromatic carbons were reported. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted.

*Synthesis of **L**<sub>3</sub> and **L**<sub>4</sub>.* To a solution of 290 mg (1 mmol) of 2-diphenylphosfinobenzaldehyde in 10ml of anhydrous methanol under  $\text{N}_2$  was added 0.2 ml (2.1 mmol) freshly distilled aniline or 2,6-diisopropylaniline and the reaction mixture was stirred at room temperature overnight. Pure product for **L**<sub>3</sub> was obtained as yellow oil by evaporation of solvent and excess starting material under high vacuum for several hours, whereas ligand **L**<sub>4</sub> was isolated as a pale yellow precipitate, which was filtered and washed with methanol.

**L**<sub>3</sub>. (90%). IR (KBr) 1622  $\text{cm}^{-1}$  ( $\nu_{\text{C=N}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.65 - 7.45 (m, 18 H), 8.19 (m, 1 H), 9.06 (d, 1 H,  $J = 5.1\text{Hz}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -13.6. FABMS: 365.1 ( $\text{M}^+$ ).

**L**<sub>4</sub>. (80%). IR (KBr): 1632  $\text{cm}^{-1}$  ( $\nu_{\text{C=N}}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.99 (d,  $J = 7.0\text{ Hz}$ , 12 H) 2.74 (m, 2 H), 6.94 - 7.50 (m, 18 H), 8.34 (m, 1H), 8.94 (d, 1 H,  $J = 5.7\text{Hz}$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -14.9. FABMS: 450.2 ( $\text{M}^+$ ).

Other spectral and analytic data of complexes are appeared in the published articles. (see references)

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