

# 行政院國家科學委員會專題研究計畫 成果報告

## 立體阻障雙芽配基金屬化物之催化聚合應用(3/3)

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執行單位：國立臺灣大學化學系暨研究所

計畫主持人：劉緒宗

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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

立體阻障雙芽配基金屬化物之催化聚合應用

計畫類別： 個別型計畫          整合型計畫

計畫編號：NSC 94 - 2113 - M - 002 - 004

執行期間：      93 年   8 月      1 日至   94 年   10 月   31 日

計畫主持人：劉緒宗

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中 華 民 國      95      年      1      月      26      日

## 中英文摘要

### 中文摘要

配位體在聚合與催化反應的應用是計畫的主要內容，此計畫為三年期計畫，設計一系列具有立體阻障的雙芽供體，並合成其過渡金屬化合物作為催化劑應用於不飽和化物如烯類等的聚合反應與催化反應。此報告的研究主體中計合成多芽的配體，並由其與金屬的錯合反應，其中探討了結構的特性。利用了這些金屬化合物作了 C-C 鍵形成與氧化催化反應測試，而發現金屬錯合物中可以很有效率的將苯甲醇轉換成苯甲醛與衍生物，並且對 Heck, Suzuki coupling 反應有很好的效應；另外多芽配體合成與金屬化物的純化與鑑定。Part I. Palladium complexes in catalytic polymerization; Part II Copper complex in Oxidation; Part III Palladium nanoparticles in C-C bond formation.

**關鍵詞：**多芽配位體，催化，磷，亞胺，銅，鈀，氧化，C-C 鍵

### **Abstract:**

Ligand effect on catalysis and mediated polymerization was the major issue of this three-year research project. Design of a series of multiple dentates particularly with steric hindrance for transition metal complexes was the initial step for the study. Preparation and characterization of the metal complexes with the designed ligand were carried out via various approaches. Finally, the use of the prepared complexes for catalytic study was to search the best activity of catalyst for a certain reaction. This report includes three part. Part I. Palladium complexes in catalytic polymerization; Part II Copper complex in Oxidation; Part III Palladium nanoparticles in C-C bond formation.

**Keywords:** Multiple dentate, Catalysis, Phosphine, Imine, Copper, Palladium, Oxidation, C-C-bond.

## Part I. Palladium complexes in catalytic polymerization.

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>

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-benzaldehyde with slight excess of aniline or 2,6-di-isopropyl-aniline 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  $[Pd(P~N)MeCl]$  (**P~N** =  $L_2$ , 2;  $L_3$ , 3) in quantitative yield. Cationic Pd(II) complexes with acetonitrile coordination were prepared by treating the related neutral  $[PdMeCl(P~N)]$  with one equiv. of  $AgBF_4$  in a mixture of dichloromethane and acetonitrile solution.

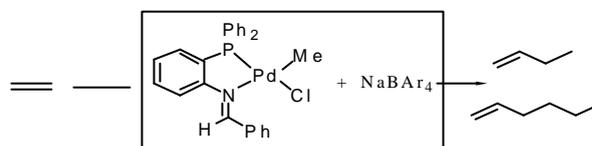
At 25 °C, consecutive bubbling of CO and ethylene into the dichloromethane solution of 1a uniquely resulted in the formation of 2, 3, 4 and 5 (Scheme 1).<sup>16</sup> Intermediates 3 and 5 isolated in solid state are stable. By contrast acyl complexes 2 and 4 decompose slowly in solution as well as in solid state. Appearance of single  $^{31}P$  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  $cm^{-1}$  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  $^{13}C$  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.

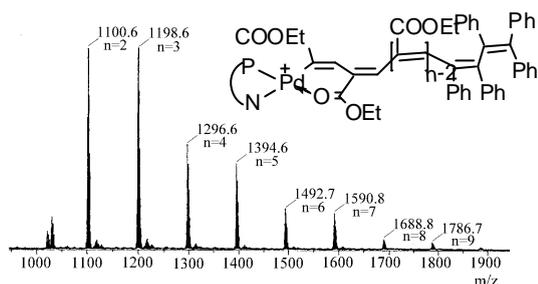
**Copolymerization of CO and olefins.** Using the new imine-phosphine complexes  $[\text{Pd}(\text{P-N})(\text{CH}_3)(\text{CH}_3\text{CN})](\text{BF}_4)$  ( $\text{P-N} = \text{L}_1$ ) as catalyst, copolymerization of E-CO can be carried out under mild conditions. In one of the typical reactions, 1a (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 ( $M_n = 2500$ ,  $M_w/M_n = 1.26$ ).

**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.

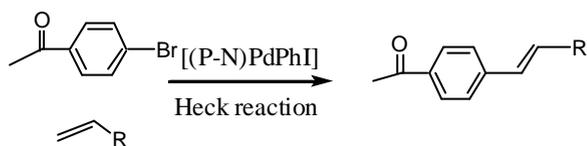
**Insertion of alkynes .** Neutral and Cationic Pd(II)-alkyl and Pd(II)-aryl complexes with phosphine-imine (P~N) ligand show unusual reactivity toward alkynes. No insertion of alkyne has been observed into the neutral palladium



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  $[(\text{P}\sim\text{N})\text{Pd}(\text{Ph})(\text{MeCN})]^+$  (5) or  $[(\text{P}\sim\text{N})\text{Pd}(\text{C}(\text{Ph})=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{CPh}_2)(\text{MeCN})]^+$  (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.

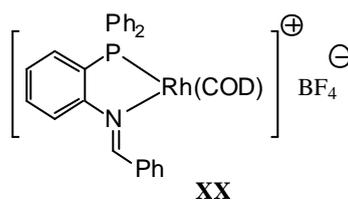


**Heck reaction.** Pd(II) complexes of the phosphine-nitrogen (P-N) bidentate donors act as efficient catalysts for the Heck reaction. In a typical example, reaction of phenyl iodide with methyl acrylate in *N*-methylpyrrolidinone (NMP) at ca 130 °C provides the Heck product with the turnover number up to 10<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.



**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.

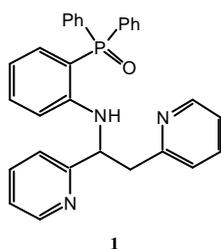


**Conclusion.** In summary, the P~N bidentate ligands presented in this work allow us to study the

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.

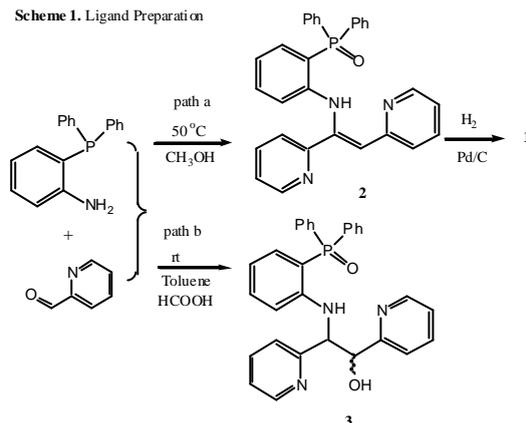
## Part II Copper complex in Oxidation

In order to understand and mimic functions of various families of copper proteins, there has been much research interests in developing model copper(II) complexes in both structure and reactivity aspects. Among various coordination mode for copper(II), complexes with five-coordinate adopting in a square pyramidal geometry were found in natural occurring metalloprotein such as hemocyanin, bleomycin and galactose oxidase. Thus a great number of copper(II) complexes containing chelating nitrogen donors including pyridinyl or imidazolyl ligands in model study were reported.<sup>1-8</sup> In such pursuit, we synthesized a designed tetradentate **1**, which includes two pyridine nitrogens, one secondary amine group and phosphine-oxide in its ligand set. The preparation and structural characterization of five-coordinate Cu(II) with this ligand are reported.

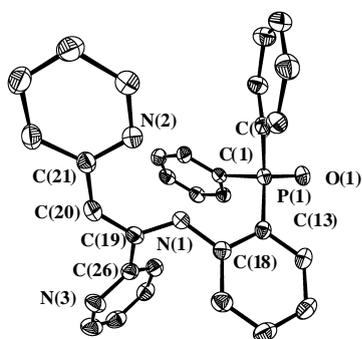


**Ligand preparation.** The desired ligand was prepared through the reaction of 2-diphenylphosphinoaniline with 2-pyridinecarbaldehyde followed by the hydrogenation (scheme 1, path a). Without any acid catalysis, the condensation reaction took place immediately in methanol at 50 °C and quantitatively provided the formation of enamine product **2**. Upon the recrystallization, this compound appears to be a clear, colorless single crystal. This reaction has also been investigated by Doherty (scheme 1, path b).<sup>9</sup> In the presence of formic acid, the adduct **3** from imine and aldehyde was obtained at ambient temperature in toluene. Presumably, the reaction at higher temperature in the polar solvent readily facilitates the dehydration to form **2**. Metal catalyzed hydrogenation of **2** in the presence of atmospheric hydrogen gave the desired ligand **1**.

Scheme 1. Ligand Preparation



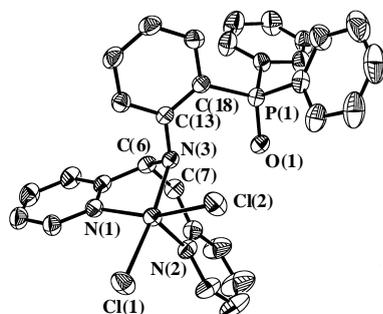
Compound **2** was characterized by both spectroscopic and x-ray crystallographic methods. A shift at 30.7 ppm in the <sup>31</sup>P NMR spectrum of **2** shows the existence of tertiary-phosphine oxide in the molecule. In addition to the aromatic protons, the appearance of one singlet absorption at 6.23 ppm in <sup>1</sup>H nmr, which is in the typical range for olefinic protons, suggests the formation of carbon-carbon double bond functionality. Although the spectral data of **2** are consistent with the proposed structure, the confirmation comes from the single crystal analysis. Figure 1 shows its ORTEP plot with 30% ellipsoid. All bond lengths and angles are in agreement with the reported values. The C(19)-C(20) bond length of 1.356(4) Å is typical distance for C=C, whereas the distance of 1.379(3) Å for C(19)-N(4) clearly illustrates the single bond nature between two atoms. These observations also confirm the enamine moiety in the presence of the molecule. As for the hydrogenated product **1** is easily characterized by both nmr spectroscopy and elemental analysis.



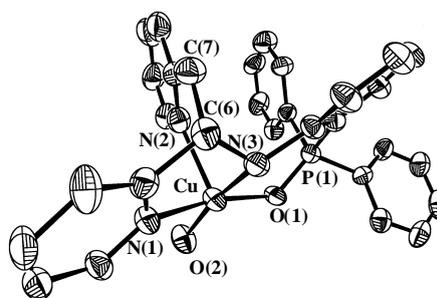
**Figure 1.** ORTEP Plot of **1**. Selected bond distances and angles: P(1)-C(1) 1.806(3) Å; P(1)-O(1) 1.483(2) Å; P(1)-C(13) 1.811(3) Å; C(18)-N(1) 1.412(3) Å; N(1)-C(19) 1.379(3) Å; C(19)-C(20) 1.356(4) Å; C(18)-N(1)-C(19) 125.3(2)°; N(1)-C(19)-C(20) 122.8(3)°; N(1)-C(19)-C(20) 118.2(2)°.

**Copper Complexes.** Under refluxing conditions, reaction of CuCl<sub>2</sub> with equimolar amount of **1** in absolute ethanol for 3 h provided the green complex [(**1**)CuCl<sub>2</sub>] **4**, whereas complexation of **1** with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O gave the ionic complex [(**1**)Cu(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> **5** in green solids. By the recrystallization, x-ray suitable crystals for both complexes can be accomplished. ORTEP plots of both complexes **4** and **5** are deposited in Figures 2-3, respectively. The copper(II) center in both complexes has the distorted square pyramidal geometry with one nitrogen donor [N(2)] from the ligand seated in the apical position. The basal plane in complex **4** was formed by two chloride

donors and two nitrogen atoms [N(1) and N(3)] from the ligand. The formation of a stable five-member chelate ring by the secondary amine N(3) and pyridine nitrogen N(1) is presumably an explanation for these two donors in the equatorial direction. The coordination mode of nitrogen donors in complex **5** is similar to those in **4**, but the oxygen atom [O(1)] of phosphine-oxide moiety of the ligand is bounded to metal center. Thus donor atoms of N(1), N(3), and O(1) as well as a water molecule formed the basal plane in **5**.



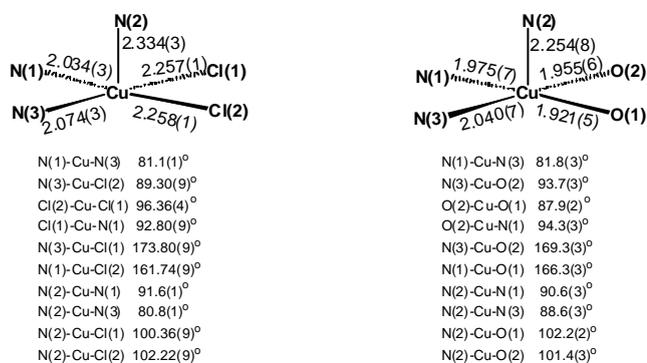
**Figure 2.** Molecular Structure of Copper Complex **4**.



**Figure 3.** ORTEP Drawing of the Cationic Part of **5**.

The bond distances and bond angles of basal plane of both complexes are summarized in the Figure 4. A significant difference in the structure of **4** compared to that of **5** is that all Cu-N lengths in **4** are longer those in **5** particularly the apical one. [Cu-N(2) = 2.334(3) Å in **4**; 2.254(8) Å in **5**] Also, bond lengths of Cu-N(1) are somewhat shorter than those of Cu-N(3), which is attributed to the different hybridization of nitrogen donors; the N(1) is a pyridinyl nitrogen, whereas N(3) is a secondary amine group. In both complexes, the distance of the apical nitrogen to copper center is longer by ca. 0.3 Å than those of equatorial ones, indicating a weak interaction in the apical orientation. All bond distance and bond angles in both complexes lie within normal ranges except N(2)-Cu-N(3) [80.8(1)°]. However, it is noticed that the angles Cl(1)-Cu-Cl(2) in **4** [96.36(4)°] much derived from the 90° as compared to the smaller derivation of O(1)-Cu-O(2) [87.9(2)°].

**Figure 4.** Comparison of bond distances and angles around the metal centers between **4** and **5**



In addition to crystallography, both EPR spectroscopic data and electronic absorption are in agreement with the structure. The X-band EPR spectra of **4** and **5** in methanol glass (80K) were determined and their data were collected in table 3. It appears that both complexes with the

parameters  $g_{\parallel} > g_{\perp}$  are typical monomeric square pyramidal copper(II) complexes with  $d_{x^2-y^2}$  ground state.<sup>10</sup> The spectra of **4** and **5** recorded as mulls show a broad band centered at 540 and 567 nm, respectively, which are in agreement of the d-d transitions for a square pyramidal copper(II) complex with pyridine donors.<sup>11</sup> Table 1 also includes the electronic absorptions in methanol of both complexes. The absorptions in UV region are assigned as the transition from the ligand itself, whereas the  $\lambda_{\max}$  around 370 nm is believed due to the LMCT band. In addition, complex **4** in methanol exhibits a d-d band around 740 nm with a shoulder to lower wave-numbers, a characteristic profile for the copper(II) species in square pyramidal geometry. This outcome also indicates that the complexes remain the same structural feature in solution.

**Table 1.** EPR spectroscopic data<sup>a</sup> and electronic absorptions of **1**, **4** and **5**.<sup>b</sup>

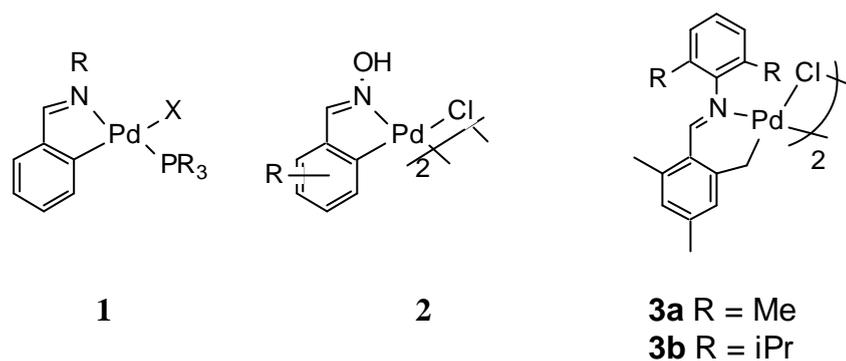
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (G)	$\lambda_{\max}$ <sup>b</sup>						
<b>1</b>				210(41.93)	260(13.06)	326(5.05)				
<b>4</b>	2.284	2.071	144	211(21.68)	261(15.01)	321(1.91)	371(0.85)	421(0.62)	743 (0.11)	
<b>5</b>	2.311	2.078	173	211(31.78)	261(10.79)	324(2.98)	369(2.13)	516(0.18)	700 (0.07)	

a. in methanol glass (80K). b. in methanol,  $\epsilon$  is given in the parenthesis. ( $\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ )

This new polydentate ligand gave the formation of square- pyramidal copper(II) complexes with all three nitrogen donors in facial arrangement, providing a possible model for the enzymatic reactions. The catalytic oxidation of alcohols and alkanes using these copper complexes are currently under investigation.

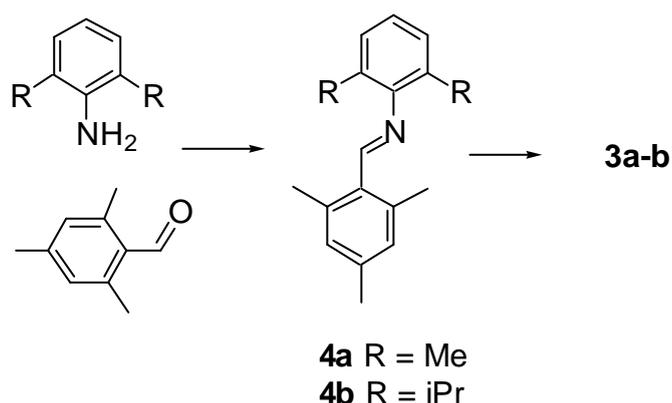
### Part III Palladium nanoparticles in C-C bond formation.

Suzuki-Miyaura coupling reaction provides a powerful method for preparation of unsymmetrical biaryls,<sup>1</sup> and the palladium complexes are known to be the most efficient catalyst among various metal systems. However, a high loading of catalyst and under inert atmosphere in most reactions are generally required for a better conversion, which does not meet the points of both economical and environmental senses.<sup>1-6</sup> Thus searching of new palladium complexes as catalysts has received much attention particularly for the use of aryl chloride as substrates,<sup>2- 8</sup> under aerobic conditions<sup>4</sup> or even in aqueous solution.<sup>5</sup> Accordingly, palladacycles were found to be the most promising catalysts in this regard.<sup>1d,6-8</sup> Recently, Bedford<sup>7</sup> and Nájera<sup>8</sup> have demonstrated that Suzuki coupling reaction of aryl chlorides with arylboronic acid in high conversion can be achieved by using the cyclopalladated imino-complexes **1** and **2**, respectively. In a previous communication, we have found that palladium complex **3b** could act as a catalyst for the coupling of aryl chloride with arylboronic acid in aqueous medium.<sup>9</sup> Here, we would like to report the detail studies of the preparation and characterization of a series of benzylic palladacycles as well as their catalytic activities toward Suzuki-Miyaura coupling reaction in ethanol under aerobic atmosphere.



**Preparation of Ligands and Complexes.** Substituted trimethylbenzylideneamines were prepared by the condensation of 2,4,6-trimethylbenzaldehyde with the substituted aniline (scheme1). Both infrared absorptions near  $1626\text{ cm}^{-1}$  and  $^{13}\text{C}$  nmr shifts around  $162 \sim 163\text{ ppm}$  of imines **4a-b** are characteristic for the functionality of C=N. Cyclopalladation reactions were carried out in a mixture of  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ , sodium acetate and the corresponding ligand in tetrahydrofuran at ambient temperature for 38 h. The desired palladium products **3a-b** were isolated as air stable solids upon crystallization. In both instances, the cyclopalladation readily occurs at benzylic to form an endo six-membered chelating ring and the product is in a chloro-bridged dipalladium structure, which is consistent with most of the related species.<sup>10</sup> The C-H activation at benzylic position is established by their  $^1\text{H}$  nmr and x-ray single-crystal determination. The appearance of signal 3.19 ppm for **3a** and 3.24 for **3b** with the integration of 2H in the  $^1\text{H}$  nmr spectra was assigned to the methylene protons of Pd-CH<sub>2</sub>- resulted from the C-H activation with the palladium complex.

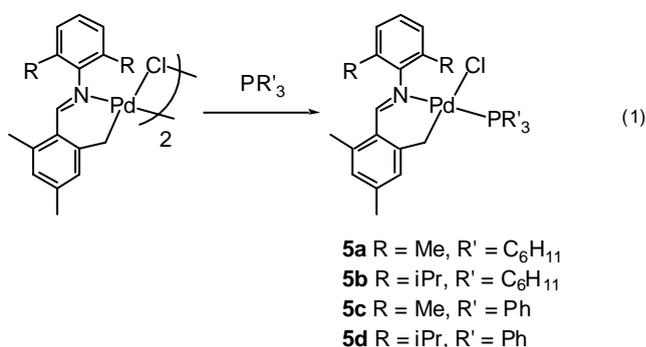
**Scheme 1.** Preparation of palladacycles.



The detail structure of palladacycles **3a** was proved by X-ray diffraction study on single crystals grown from a hexane/dichloromethane solution, whereas the structural characterization of **3b** has published previously.<sup>9</sup> Figure 1 displays the ORTEP plot of **3a** and table 1 summarizes the selected bond distances, bond angles and torsion angles. In both instances, the palladium metal

displays a slightly distorted square-planar geometry with nitrogen and carbon donors in *cis*-fashion. All bond distances and bond angles lie within normal ranges, which are essentially similar to those for **3b** except Pd(1)-N(1). The distance of Pd(1)-N(1) [2.024(3) Å] for **3a** is slightly shorter than that for **3b** [2.043(3) Å], which is attributed to steric difference between methyl and isopropyl groups. The length of C(7)-N(1) [1.298(4) Å] is characteristic for C=N double bond. The small bite angle N(1)-Pd(1)-C(1) [86.0(1)°] is similar to those benzylic type palladacycles reported by Sales and coworkers.<sup>10e</sup> It is noticed that the angle of Pd(1)-C(1)-C(2) [115.8(2)°] deviating from the angle for a tetrahedral geometry, similar to that for **3b**, is presumably due to the strain forced by the chelating rings. Those dihedral angles along the chelating ring of Pd(1)-N(1)-C(8)-C(7)-C(2)-C(1) in **3a** (table 1) indicates that this ring is adopted into a twist half-chair conformation, apparently resulting from the occurrence of two double bonds in the chelate ring.

**Phosphine-substituted Complexes.** Both palladacycles **3a** and **3b** readily underwent ligand substitution reaction with phosphines (Eq. 1) to give the corresponding complex. Both complexes were in air-stable crystalline forms. Appearance of only one signal around 40 ppm in <sup>31</sup>P NMR for both complexes **5a** and **5b** suggests the formation of single trialkylphosphine-substituted isomer out of the two possibilities. The benzylic methylene unit *cis*- to the phosphorus in **5a** and **5b** was established from the <sup>1</sup>H NMR spectra, where methylene group bound to the palladium appears as a doublet with a coupling constant  $J_{P-H} \approx 2 \sim 5$  Hz. This value is in the typical range reported for the *cis*-arrangement of the methylene group and phosphine in related species.<sup>10a,10e</sup> Even though both complexes could be easily characterized by means of spectral and elemental analysis, the crystal structure of **5b** was determined to confirm the details. Figure 2 displays the ORTEP drawing of **5b** and selected bond distances and bond angles are collected in Table 2. A method similar to that for the preparation of **5a-b** was employed to produce the triphenylphosphine adduct **5c-d**. Both spectroscopic and crystallographic analyses of **5c** verify the structure of **5c-d** (figure 3).

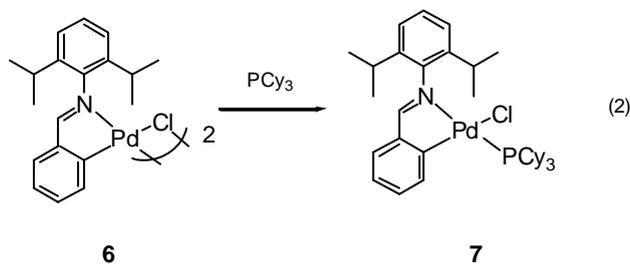


Both **5b** and **5c** show the square planar arrangement around the metal center with the phosphine and imine donor *trans* to each other, presumably due to the *trans* influence of these donors. All bond distances and bond angles are lie in the normal range of the close related complexes such as [Pd(TFA)(<sup>2</sup>N,C-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PCy<sub>3</sub>)] reported by Bedford and

coworkers.<sup>7a</sup> When two structures are compared, it is found that all bond distances and bond angles around the metal center are very close except the bond angle of P(1)-Pd(1)-C(1) and the bond length of Pd-P. The P(1)-Pd(1)-C(1) in **5b** [93.1(1)°] is considerably larger than that of the analogous angle in **5c** [88.57(9)°], reflecting a result of steric relief between the carbon donor and tricyclohexylphosphine. The Pd-P bond distance of **5b** [2.2683(7) Å] is slightly longer than that of **5c** [2.2388(7) Å], which is due to the contribution of palladium back-donation to the  $\pi$ -acidic nature of triphenylphosphine. For the conformation of chelating rings associated with metal center in **5b** and **5c** remains as a twist half-chair form as illustrated by the torsional angles along the ring consisted of Pd(1)-N(1)-C(8)-C(7)-C(2)-C(1). (table 2)

<<Insert Figures 2 and 3>> <<table 2>>

Another phosphine-substituted palladacycle **7** with five-member chelating was prepared via the substitution of **6** with tricyclohexylphosphine (Eq. 2). <sup>31</sup>P nmr chemical shift of **7** appeared at 43.1 ppm, which is in the typical range of the trialkylphosphine palladium complexes.<sup>7a,7c</sup> Crystal structure of **7** was determined (Figure 4). As expected, the molecular structure **7** shows a square planar geometry around the metal center. Out of four coordination sites, two are occupied by N~C ligand in *cis*-fashion and the other two by phosphine and chloride with nitrogen and phosphorus donors in *trans* arrangement. The bond lengths between the Pd and C, N, P and chloride donor atoms for **7** (table 2) are within the range and comparable with complexes **5b**. However, it is noticed that all bond angles around the metal center in **7** is much more derivated from the square-planar than in **5b**, due to the five-member chelate ring.



<<Figure 4>>

**Suzuki-Miyaura Coupling Reaction.** All palladacyclic complexes prepared in this work were subjected to evaluate their catalytic activities on the coupling reaction of phenylboronic acid with aryl halides. In a typical experiment for the reaction, aryl bromide, phenylboronic acid and K<sub>2</sub>CO<sub>3</sub> in a ratio of 1:1.5:2 were placed in the flask, followed by the addition of the solvent and the catalyst. In all instances the solvent was used as obtained commercially without further purification, while the deionized water was used for aqueous systems. The organic product was isolated by extraction and then analyzed by the <sup>1</sup>H nmr spectroscopy.

The initial screen on solvents were performed using **3b** as the catalyst precursor (table 3, entries 5 - 8). It appeared that the protic solvents including water gave much better results than any other organic solvents.<sup>9</sup> This coupling reaction running in DMF only provided moderate yield as compared with alcoholic solvents. This result is quite similar to that reported by Nolan and

coworkers for using palladacycle carbene complex in the coupling of aryl chloride with phenylboronic acid.<sup>3h</sup> It is noticed that the reactions can be carried out under atmosphere of air. Therefore, the activities of various palladium complexes were screened using ethanol as the solvent under aerobic conditions. Results are summarized in table 3.

As the molar ratio of [substrate]/[Pd] remains ~ 20000, all palladacyclic catalysts show good catalytic activities in Suzuki coupling. Among them, complexes **3a** and **3b** ought to be the best ones, even better than those phosphine-substituted complexes **5a-d**. For **3a** and **3b** appear that the steric hindrance of the ligand has less influence on the catalysis. However, the yield drops dramatically within a reasonable period of reaction time (~ 20 h) when the mol ratio of [substrate]/[Pd] increases up to  $10^6$  (entries 11,18), indicating a concentration limitation of these

**Table 3.** Results of coupling reactions catalyzed by palladacycles

entry	cat.(Pd mmol)	ArBr	[ArBr]/[Pd]	atm.	t (h)	Conv. <sup>b</sup> (%)
1	<b>3a</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	100
2	<b>3a</b> (2x10 <sup>-5</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	100000	air	10	91
3	<b>3a</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	18	62
4	<b>3a</b> (2x10 <sup>-3</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1000	air	20 <sup>c</sup>	100
5	<b>3b</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	100
6 <sup>d</sup>	<b>3b</b> (1x10 <sup>-4</sup> ) <sup>e</sup>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	75
7 <sup>e</sup>	<b>3b</b> (1x10 <sup>-4</sup> ) <sup>f</sup>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	28
8 <sup>f</sup>	<b>3b</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	100
9	<b>3b</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	64
10	<b>3b</b> (2x10 <sup>-5</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	100000	air	10	86
11	<b>3b</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	20	57
12	<b>3b</b> (2x10 <sup>-3</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1000	air	14 <sup>c</sup>	100
13	<b>5c</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	85
14	<b>5d</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	95
15	<b>5a</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	100
16	<b>5b</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	92
17	<b>6</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	86
18	<b>6</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	16	26
19	<b>7</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	83
20	<b>3b</b> (2x10 <sup>-5</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	100000	air	5	77
21	<b>3b</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	3	40
22	<b>3b</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	20	100
23	<b>3a</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	20	89
24	<b>5a</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	20	100
25	<b>5b</b> (2x10 <sup>-6</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	1000000	air	20	100
26 <sup>f</sup>	<b>3b</b> (1x10 <sup>-4</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Br	20000	air	3	100
27	<b>3a</b> (1x10 <sup>-3</sup> )	2,4,6-tri-MeC <sub>6</sub> H <sub>2</sub> Br	2000	air	3	76
28	<b>3b</b> (1x10 <sup>-3</sup> )	2,4,6-tri-MeC <sub>6</sub> H <sub>2</sub> Br	2000	air	3	69
29	<b>5b</b> (1x10 <sup>-3</sup> )	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> Cl	2000	air	17	72
30 <sup>f</sup>	<b>3a</b> (2x10 <sup>-4</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Cl	10000	air	1	96
31	<b>5b</b> (2x10 <sup>-5</sup> )	<i>p</i> -MeCOC <sub>6</sub> H <sub>4</sub> Cl	10000	air	3	80

<sup>a</sup>Reaction conditions: ArX (2 mmol), PhB(OH)<sub>2</sub> (3 mmol), catalysts, K<sub>2</sub>CO<sub>3</sub> (4 mmol), EtOH (5 mL), reflux. <sup>b</sup> Determined by <sup>1</sup>H-NMR spectroscopy based on ArX. <sup>c</sup> at 30 °C. <sup>d</sup> in DMF, <sup>e</sup> in CH<sub>3</sub>OH <sup>f</sup> in water and 0.5eq TBAB (tetrabutylammonium bromide) was added.

catalysts. Among these studies, we found that the palladacycle with six-member chelate ring **5a-d** were slightly better than those with five-member ones **6**. This observation is also applied for the phosphine-substituted palladacycles, i. e. the catalytic activities of **5a-d** are better than that of **7** (entries 13–16 versus 19). The catalytic activities of **3a-b** are generally as good as those for **5a-d**, indicating that phosphine ligands are not necessary in this reaction. It is worthy to mention that the coupling reaction can be carried out at room temperature (entry 4). A quantitative conversion was observed for the coupling of *p*-bromoanisole with phenylboronic acid catalyzed by **3b** in water with the presence of tetraalkylammonium salt (entries 8, 26).

As for the activated substrate (*p*-acetylphenyl bromide), the turnover number can reach up to  $10^6$  for **3b**, **5a** and **5b** (entries 22-25). In addition, complexes **3a** and **3b** catalyzed the coupling of the steric bulky substrate such as 2,4,6-(Me)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Br with phenylboronic acid in good conversions (entry 27-28).

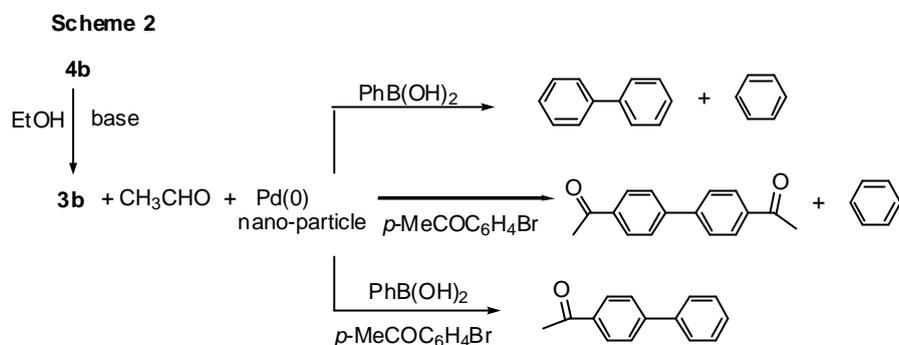
Under similar reaction conditions, the catalytic activities of these palladacycles toward aryl chloride appear to be lower than the bromo substrates (entry 29). However, the conversion can be improved by carrying the reaction in water medium and the presence of tetrabutylammonium salt (entries 30-31).<sup>9</sup> Overall, these palladium complexes prepared in this work behave highly catalytic activity on the Suzuki-Miyaura coupling reaction.

**Mechanistic Pathway of Catalysis.** In order to probe the reaction pathway, the course of the coupling reaction was monitored by taking samples and analyzed them by <sup>1</sup>H nmr and TEM. First, an aliquot from the reaction of **3b** with phenylboronic acid (2 eq.) in the presence of K<sub>2</sub>CO<sub>3</sub> and ethanol was examined by transmission electron microscopy, showing the formation of palladium particles with the diameter in the range of 50 ~ 60 nm (figure 5). Upon the addition of *p*-bromoanisole to the above solution, the coupling reaction underwent smoothly to yield *p*-methoxybiphenyl quantitatively, suggesting that the palladium nanoparticles might be the active catalyst for the reaction.

Further studies, we found that complex **3b** readily reacted with ethanol under basic conditions to generate acetaldehyde and the free ligand **4b** accompanied with palladium nanoparticles, but aggregate to produce the palladium black without the presence of other substrates. The formation of acetaldehyde is presumably due to the substitution of chloride ligands by ethoxide under basic conditions followed by the β-elimination.<sup>3h</sup> Addition of phenylboronic acid to the above solution yielded benzene and biphenyl immediately (table 4). On the other hand, *p*-acetophenyl bromide was converted into acetophenone and 4,4'-bisacetobiphenyl as evidenced by the <sup>1</sup>H nmr spectroscopy. However, the reaction of *p*-acetophenyl chloride was much slower than that of bromide (table 4, entry 2). The production of biphenyl derivatives and the reduced compounds is presumably *via* the addition of phenylboronic acid or *p*-acetophenyl bromide to the palladium nanoparticles followed by the reductive elimination (scheme 2). We also found that the decomposition rate of aryl bromide is much slower than that of arylboronic acid, revealing that the oxidative addition of aryl halide to

the metal is the rate limiting step in the cross coupling reaction. This also explain that the use of excess of arylboronic acid in the Suzuki-Miyaura reactions is generally required for better conversions. It should be mentioned that the reduction of aryl halides or arylboronic acid proceeded superiorly than that of the homo-coupling reaction.

<<Table 4>>



The decomposition rate of palladacycles in basic ethanol solution follows the order: **6** > **3b** > **5b** > **5d** (table 5). Complex **6** appeared to be slower than that of **3b**, but aggregated into larger nanoparticles (100 ~ 200 nm), which explained the activity difference between **6** and **3b** due to the size effect.<sup>11</sup> As for the phosphine substituted complex **5b** and **5d**, the decomposition was much slower than that of **3b** presumably due to the stabilization of the coordinating phosphine. Another finding is that the surfactant stabilized palladium nanoparticles appears to be less active than the ones generated *in situ*. In the presence of tetrabutylammonium bromide, palladium nanoparticles was obtained from the decomposition of complex **3b** in ethanol. The resulting palladium nanoparticles was used as the catalyst for the coupling reaction of PhB(OH)<sub>2</sub> and MeOC<sub>6</sub>H<sub>4</sub>Br to give the desired product but in a slower conversion rate by ca. 20 %.

It has been demonstrated that palladium nanoparticles can catalyze the C-C bond coupling reaction,<sup>12</sup> particularly under Jeffery condition for Heck reaction.<sup>13</sup> Unlike the palladium clusters stabilized by tetraalkylammonium salt, the nanoparticles generated from the reduction of palladacycles are presumably surrounded by the imine ligands, which tends to aggregate with the precipitation of palladium black. This reveals the weak stabilizing effect of these ligands toward nanoparticles. On the other hand, the loose protection gives these palladium particles in high activities toward the substrates.<sup>12</sup>

Furthermore, the low concentrations of palladium complexes may also avoid the rapid formation palladium black and the formation of larger nanoparticles, suggesting the extreme activity of metal clusters. However, the conversion decreases as the ratio [substrate]/[Pd] is higher than 10<sup>6</sup> (table 3 entries 3 and 11), showing a limitation of these nanoparticles in catalysis.

We have synthesized and characterized a new series of air-stable palladacycles. These palladium complexes were successfully applied in the Suzuki-Miyaura coupling reaction and behaved good catalytic activities, for example the turnover frequency up to 10<sup>7</sup> mol/mol(Pd)h for **3b** in the coupling of *p*-bromoanisole or *p*-bromoacetophenone with phenylboronic acid. Notable

were the reaction conditions employed, i. e. the moisture and air insensitive. Several observations confirm that the Suzuki-Miyaura coupling catalyzed by palladacyclic complex are *via* the palladium nanoparticles. Reactions of *p*-bromoacetophenone or arylboronic acid individually on the nanoparticles leading to the homo-coupled and reduced products was investigated, but the cross coupled ones were obtained when the aryl halide and arylboronic acid were presented. However, the pathway for the cross coupling and reduction process on these particles remains unclear. More work is necessary in order to work out the nature of these nanoparticles.

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