

# Carbonylative Coupling of 4,4'-Diiodobiphenyl Catalyzed by Pd(NHC) Complex

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## ABSTRACT

To develop a luminescent material with high color purity, luminous efficiency, and stability, we synthesized diketone by carbonylative Suzuki coupling in the presence of Pd(NHC) complex as the catalyst. Carbonylative coupling of 4,4'-diiodobiphenyl and phenylboronic acid was investigated to study in detail the catalytic ability of the Pd(NHC) complex. Reactions were carried out using both CO and metal carbonyls. Bis-(1,3-dihydro-1,3-dimethyl-2H-imidazol-2-ylidene) diiodo palladium was used as the catalytic complex. Reaction products biphenyl-4,4'-diylbis (phenyl-methanone) 3 and (4'-iodobiphenyl-4-yl)(phenyl) methanone 4 were obtained as a result of CO insertion into the palladium(II)-aryl bond. However, when pyridine-4-yl boronic acid was used in place of phenylboronic acid as the starting reagent, synthetic reaction yielding 3 and 4 were found not to occur.

**Keywords:** Carbonylative Coupling; Metal Carbonyl; Pd(NHC) Complex; 4,4'-Diiodobiphenyl; Phenylboronic Acid

## 1. Introduction

Aryl ketones and flavanoids are common scaffolds in many natural products and biologically active small molecules [1-7]. A carbonylative coupling method for the synthesis of aryl compounds with CO was pioneered by Heck [8-11]. This method is one of the most efficient and direct routes to synthesize aryl ketones as it forms two carbon-carbon bonds in a single step, in contrast to the conventional method of introducing ketone functional group in a stepwise fashion. Carbonylative coupling has since been further developed to synthesize a range of carbon nucleophiles [12], including those of tin [13-17], copper [18-22], boron [23-25], zinc [26], aluminum [27], magnesium [28], and silicon [29-31]. Our purpose is to synthesize a new distyryl biphenyl arylene (DBA) derivative as a blue-emitting material. To develop such a luminescent material with high color purity, luminous efficiency, and stability, first of all, we synthesized diketone with Pd(NHC) complex as a catalyst under a balloon of CO or metal carbonyl.

During the course of an on-going synthetic project for preparing aryl ketones, we decided to evaluate the applicability of *N*-heterocyclic carbene (NHC) ligands. NHC ligands have gained popularity in metal-catalyzed cross-coupling reactions for several reasons [32-35]: 1) the

steric bulk that they introduce around the metal center facilitates reductive elimination; 2) their strong  $\sigma$ -donating character enables facile oxidative addition; and 3) their greater stability at elevated temperatures relative to phosphine ligands enables their use under a broader range of reaction conditions. Carbonylative Suzuki coupling using the synthesized NHC-Pd complex was carried out under a balloon of CO or metal carbonyls. To study the scope of the process, the reaction conditions were optimized for the cross-coupling of 4,4'-diiodobiphenyl and phenylboronic acid with *N*-heterocyclic carbene (NHC) ligand under a balloon (1 atm) of CO or metal carbonyls. 4,4'-diiodobiphenyl 1) and phenylboronic acid 2) were reacted under CO (1 bar, a balloon) atmosphere in the presence of the Pd(NHC) complex catalyst formed in situ [36,37].

## 2. Experimental

### 2.1. Carbonylative Coupling Reaction under Carbon Monoxide

In a typical reaction, Pd(NHC) complex ( $2 \times 10^{-3}$  g,  $5 \times 10^{-2}$  mol) was dissolved in 15 mL anisole under  $N_2$  gas. After the formation of a pale brown homogeneous solution, phenylboronic acid (0.112 g,  $1 \times 10^{-3}$  mol), 4,4'-diiodobiphenyl (0.203 g,  $5 \times 10^{-4}$  mol), and potassium carbonate (0.425 g,  $1.5 \times 10^{-3}$  mol) were added. The at-

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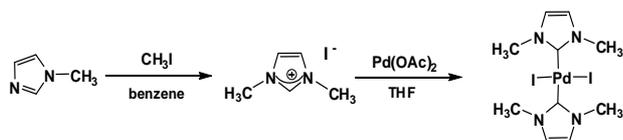
mosphere was changed to carbon monoxide and the reaction mixture was kept at 80 °C for 24 h. After elimination of Pd(NHC) complex by filtration, the reaction mixture was diluted with water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The neutralized solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. The reaction mixture was analyzed immediately by GC-MS. The residue was chromatographed on a silica gel (n-hexane:ethylacetate = 20:1, v/v) yield 3 (0.154 g, 42.6%) and 4 (4.9 × 10<sup>-2</sup> g, 12.7%).

## 2.2. Carbonylative Coupling Reaction under Metal Carbonyl

The mixture of 4,4'-diiodobiphenyl (0.203 g, 5 × 10<sup>-4</sup> mol), phenylboronic acid (0.112 g, 1 × 10<sup>-3</sup> mol), K<sub>2</sub>CO<sub>3</sub> (0.425 g, 1.5 × 10<sup>-3</sup> mol) and Di-(1,3-dihydro-1,3-dimethyl-2H-imidazol-2-ylidene)diiodopalladium (2 × 10<sup>-3</sup> g, 5 × 10<sup>-2</sup> mol) and Molybdenum hexacarbonyl (9.2 × 10<sup>-2</sup> mol, 0.7 eq) was stirred in 15 mL anisole under N<sub>2</sub>. The reaction mixture was kept at 80 °C for 24 h. After elimination of Pd(NHC) complex by filtration, the reaction mixture was diluted with water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The neutralized solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and concentrated. The reaction mixture was analyzed immediately by GC-MS. The residue was chromatographed on a silica gel (n-hexane:ethylacetate = 20:1, v/v) yield 3 (0.189 g, 52.3%) and 4 (5.2 × 10<sup>-2</sup> g, 13.5%).

## 2.3. Synthesis of Bis-(1,3-dihydro-1,3-dimethyl-2H-imidazol-2-ylidene) diiodopalladium

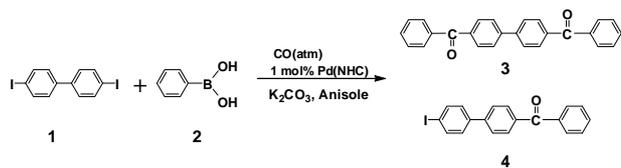
The synthetic scheme for producing bis-(1,3-dihydro-1,3-dimethyl-2H-imidazol-2-ylidene) diiodopalladium catalyst is as follows:



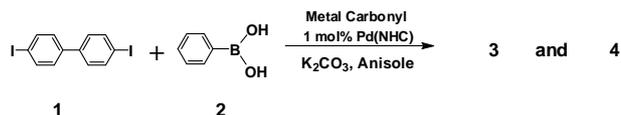
*N,N'*-dimethyl imidazolium iodide was obtained by the reaction of *N*-methylimidazole with methyl iodide. Following this, reaction of *N,N'*-dimethyl imidazolium iodide with palladium acetate resulted in NHC-Pd complex in good yield (72%).

## 3. Results and Discussion

The desired carbonylative products biphenyl-4,4'-diylbis(phenyl-methanone) 3 and (4'-iodobiphenyl-4-yl)(phenyl) methanone 4 were formed in all cases, irrespective of the reaction conditions.



When metal carbonyl [for Mo(CO)<sub>6</sub>: 3 = 42.6% and 4 = 12.7%; Mn<sub>2</sub>(CO)<sub>10</sub>: 3 = 6.6% and 4 = 33.1%; Co<sub>2</sub>(CO)<sub>8</sub>: 3 = 48.6% and 4 = 11.2%; Fe<sub>3</sub>(CO)<sub>12</sub>: 3 = 9.9% and 4 = 24.8%; Fe(CO)<sub>5</sub>: 3 = 62.5% and 4 = 10.6%] was used in place of CO, we achieved the same reaction products.

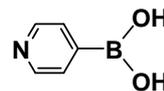


In reactions with Mn<sub>2</sub>(CO)<sub>10</sub> and Fe<sub>3</sub>(CO)<sub>12</sub> as metal carbonyls, yield of 4 was higher than that of 3. As seen in **Table 1**, various metal carbonyls were as effective as CO donors as CO itself. The plausible mechanism of diketone formation is assumed to be as shown in **Scheme 1**.

## 4. Conclusions

When metal carbonyl was used in place of CO, we achieved the same reaction products.

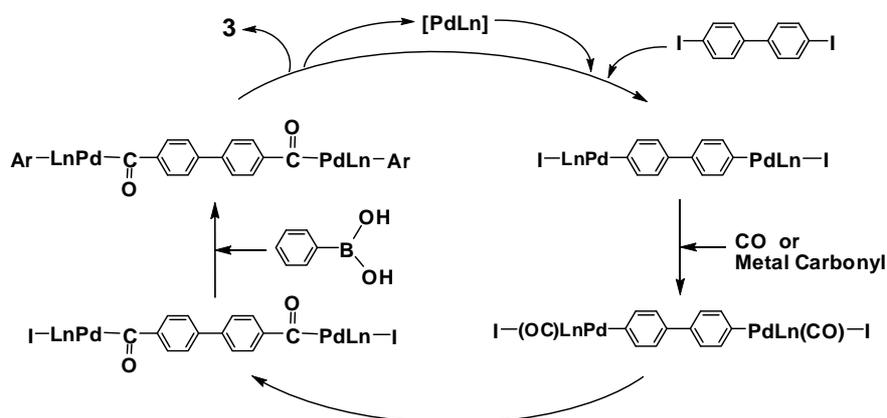
We assume that the two reactions needed to obtain 3 require a longer reaction time as 4 is formed as a reaction intermediate. When pyridine-4-ylboronic acid is used in place of phenylboronic acid,



carbonylative Suzuki coupling under CO or metal carbonyls [Mo(CO)<sub>6</sub>, Mn<sub>2</sub>(CO)<sub>10</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>, and Fe(CO)<sub>5</sub>] is found not to occur. In future, we intend to

**Table 1.** Carbonylative Suzuki coupling with phenylboronic acid and 4,4'-diiodobiphenyl.

Run	Iodide	Boronic acid	CO	Reaction time (h)	Yield (%)	
					3	4
1			CO (gas)	24 h	42.6	12.7
2			Mo(CO) <sub>6</sub>	24 h	52.3	13.5
3			Mn <sub>2</sub> (CO) <sub>10</sub>	24 h	6.6	33.1
4			Co <sub>2</sub> (CO) <sub>8</sub>	24 h	48.6	11.2
5			Fe <sub>3</sub> (CO) <sub>12</sub>	24 h	9.9	24.8
6			Fe(CO) <sub>5</sub>	24 h	62.5	10.6



Scheme 1. Simplified catalytic cycle showing the formation of 3.

synthesize various diketones by using heteroaromatic boronic acid to develop a luminescent material.

## 5. Acknowledgements

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