



## Synthesis of Biphenyl- 4,4'-Diyl *bis*(phenyl-methanone) via Carbonylative Coupling

DO-HUN LEE<sup>1,\*</sup>, JUNG-TAI HAHN<sup>2</sup> and DAI-IL JUNG<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Dong-A University, Busan 604 714, Republic of Korea

<sup>2</sup>Department of Beautycare, Youngdong University, Youngdong 370 701, Republic of Korea

\*Corresponding authors: Tel: +82 51 2007249; +82 51 2001053; E-mail: dohlee@dau.ac.kr; dijung@dau.ac.kr

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Luminescent materials have a major technological role for human kind in the form of application such as organic and inorganic light emitters for flat panel and flexible displays such as plasma displays, LCD displays and OLED displays. To develop a luminescent material with high colour purity, luminous efficiency and stability, we synthesized diketone by carbonylative Suzuki coupling in the presence of Pd(NHC) (NHC = N-heterocyclic carbene) 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-2*H*-imidazol-2-ylidene) diiodo palladium was used as the catalytic complex. Reaction products biphenyl-4,4'-diyl *bis*(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.

**Key Words:** Carbonylative coupling, Metal carbonyl, Pd(NHC) complex, 4,4'-Diiodobiphenyl, Phenylboronic acid.

### INTRODUCTION

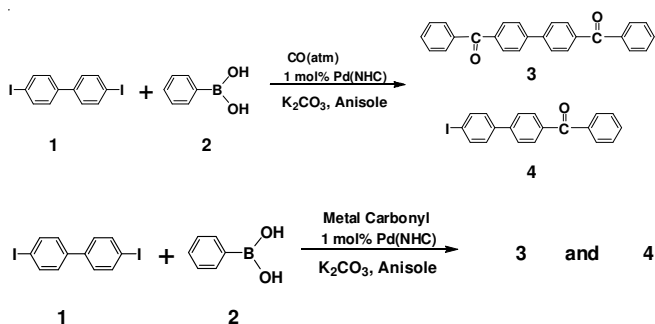
Aryl ketones are important structural motifs found in a number of natural and unnatural products of biological and medicinal interest<sup>1</sup>. A carbonylative coupling method for the synthesis of aryl compounds with CO was pioneered by Heck *et al.*<sup>2</sup>. This method is one of the most efficient 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<sup>3</sup>, including those of tin<sup>4</sup>, copper<sup>5</sup>, boron<sup>6</sup>, zinc<sup>7</sup>, aluminum<sup>8</sup>, magnesium<sup>9</sup> and silicon<sup>10</sup>. 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 colour 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. N-Heterocyclic carbene ligands have gained popularity in metal-catalyzed cross-coupling reactions for several reasons<sup>11</sup>: (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. The synthetic method for producing *bis*-(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodo palladium 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 (75 %). 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*<sup>12</sup>. The desired carbonylative products biphenyl-4,4'-diyl*bis*-(phenyl-methanone) **3** and (4'-iodobiphenyl-4-yl)(phenyl)methanone **4** were formed in all cases, irrespective of the reaction conditions.

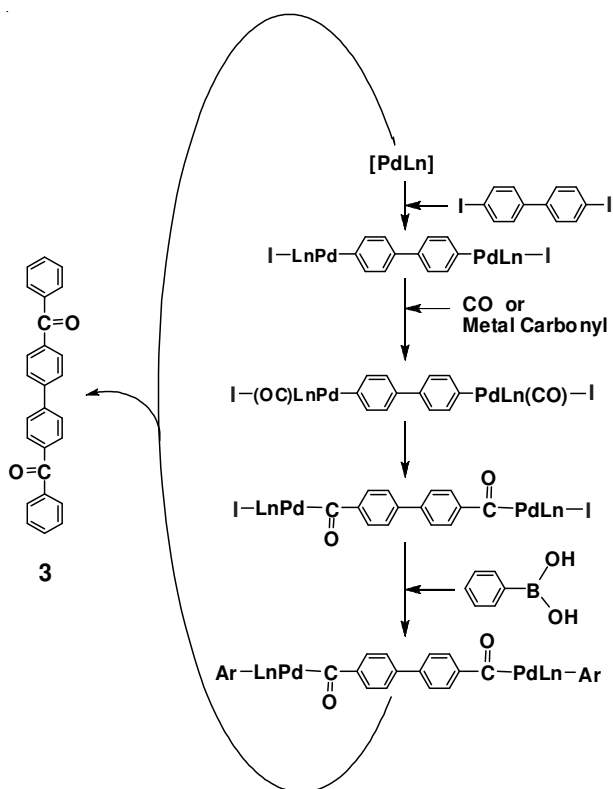
When metal carbonyl [for Mo(CO)<sub>6</sub>: **3** = 42.6 % and **4** = 12.7 %; Cr(CO)<sub>6</sub>: **3** = 47.3 % and **4** = 16.3 %; W(CO)<sub>6</sub>: **3** =

56.4 % and **4** = 12.7 %;  $\text{Mn}_2(\text{CO})_{10}$ : **3** = 6.6 % and **4** = 33.1 %;  $\text{Co}_2(\text{CO})_8$ : **3** = 48.6 % and **4** = 11.2 %;  $\text{Os}_3(\text{CO})_{12}$ : **3** = 42.1 % and **4** = 16.9 %;  $\text{Fe}_3(\text{CO})_{12}$ : **3** = 9.9 % and **4** = 24.8 %;  $\text{Fe}(\text{CO})_5$ : **3** = 62.5 % and **4** = 10.6 %] was used in place of CO, we achieved the same reaction products.



In reactions with  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Fe}_3(\text{CO})_{12}$  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-I**.



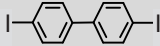

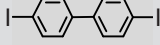

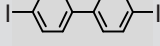

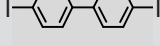

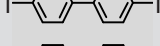









**Scheme-I:** Simplified catalytic cycle showing the formation of **3**

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 [ $\text{Mo}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Fe}(\text{CO})_5$ ] is found not to occur. In future, we intend to synthesize various diketones by using hetero-aromatic boronic acid to develop a luminescent material.

## EXPERIMENTAL

**1,3-Dimethylimidazolium iodide:** To a solution of 10.2 g, (0.12 mol) of 1-methylimidazole in 60 mL, of ethyl acetate was added 43.4 g, (0.306 mol) of methyl iodide. The mixture was refluxed overnight and a yellow oil separated during the course of the reaction. After cooling, the oil solidified giving 26.9 g, (98.8 % yield) of a hygroscopic solid. Two recrystallizations from ethyl acetate afforded colourless prisms, which after drying *in vacuo* at 75° had a melting point of 86.5–88 °C. Anal. calcd. for  $\text{C}_5\text{H}_9\text{N}_2\text{I}$ : C, 26.80; H, 4.05; I, 56.64; N, 12.50. Found: C, 26.94; H, 4.12; I, 56.89; N, 12.37. *Bis*-(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium: A solution of  $[\text{Pd}(\text{OAc})_2]$  (2.00 g, 8.9 mmol) and 1,3-dimethylimidazolium iodide (4.20 g, 18.7 mmol) in THF (150 mL) was heated for 0.5 h under reflux, during which time the initially brown solution bleached to yellow. After evaporation to dryness under vacuum, the residue was washed with diethyl ether ( $3 \times 50$  mL), taken up in  $\text{CH}_2\text{Cl}_2$  (100 mL) and the solution layered with *n*-pentane (200 mL). At 25 °C *bis*-(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium crystallized as a yellow solid that was highly soluble in  $\text{CHCl}_3$  and slightly soluble in THF and toluene. Yield: 3.70 g (75 %),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  = 7.24(s, 4H, NCH), 3.92 (s, 12H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100.1 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  = 168.2 (carbene-C), 122.3 (NCH), 8.2 ( $\text{CH}_3$ ); correct C, H, N analysis. 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  $\text{N}_2$  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 atmosphere 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  $\text{CH}_2\text{Cl}_2$  (20 mL). The neutralized solution was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated. The reaction mixture was analyzed immediately by GC-MS. The residue was chromatographed on a silica gel (*n*-hexane:ethyl acetate = 20:1, v/v) yield **3** (0.154 g, 42.6 %) and **4** ( $4.9 \times 10^{-2}$  g, 12.7 %) carbonylative coupling reaction under metal carbonyl. The mixture of 4,4'-diiodobiphenyl (0.203 g,  $5 \times 10^{-4}$  mol), phenylboronic acid (0.112 g,  $1 \times 10^{-3}$  mol),  $\text{K}_2\text{CO}_3$  (0.425 g,  $1.5 \times 10^{-3}$  mol) and di-(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium ( $2 \times 10^{-3}$  g,  $5 \times 10^{-2}$  mol) and molybdenum hexacarbonyl ( $9.2 \times 10^{-2}$  mol, 0.7 eq) was stirred in 15 mL anisole under  $\text{N}_2$ . 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  $\text{CH}_2\text{Cl}_2$  (20 mL). The neutralized solution was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated. The reaction mixture was analyzed immediately by GC-MS. The residue was chromatographed on a silica gel (*n*-hexane:ethyl acetate = 20:1, v/v) yield **3** (0.189 g, 52.3 %) and **4** ( $5.2 \times 10^{-2}$  g, 13.5 %).

TABLE-1  
CARBONYLATIVE SUZUKI COUPLING WITH PHENYLBORONIC ACID AND 4,4'-DIODOBIPHENYL

Run	Iodide	Boronic acid	CO	Reaction time (h)	Yield (%)	
					3	4
1			CO(gas)	24	42.6	12.7
2			Mo(CO) <sub>6</sub>	24	52.3	13.5
3			Cr(CO) <sub>6</sub>	24	47.3	16.3
4			W(CO) <sub>6</sub>	24	56.4	12.7
5			Mn <sub>2</sub> (CO) <sub>10</sub>	24	6.6	33.1
6			Co <sub>2</sub> (CO) <sub>8</sub>	24	48.6	11.2
7			Os <sub>3</sub> (CO) <sub>12</sub>	24	42.1	16.9
8			Fe <sub>3</sub> (CO) <sub>12</sub>	24	9.9	24.8
9			Fe(CO) <sub>5</sub>	24	62.5	10.6

#### ACKNOWLEDGEMENTS

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