



Synthesis of Biphenyl-4,4'-diylbis(naphthalene-1-ylmethanone) via Carbonylative Coupling

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More recently, an interest has been developed in three component carbonylation reactions, such as the carbonylative Suzuki, carbonylative Sonogashira and carbonylative Heck reactions, which allow for a significant increase in molecular complexity. 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 naphthalene-1-ylboronic acid was investigated to study the catalytic ability of 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)diiodopalladium was used as the catalytic complex. Reaction products biphenyl-4,4'-diylbis(naphthalene-1-ylmethanone) **3** and (4'-iodobiphenyl-4-yl)(naphthalene-1-yl)methanone **4** were obtained as a result of CO insertion into the palladium(II)-aryl bond. However, when pyridine-4-ylboronic acid was used in place of naphthalene-1-ylboronic acid as the starting reagent, synthetic reaction yielding **3** and **4** were found.

Keywords: Carbonylation reaction, Luminescent material, Pd(NHC) complex, 4,4'-Diiodobiphenyl, Naphthalen-1-yl boronic acid.

INTRODUCTION

Aryl ketones are common scaffolds in many natural products and biologically active small molecules¹. A carbonylative coupling method for the synthesis of aryl compounds with CO was pioneered by Heck *et al.*². 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 nucleophiles³, including those of tin⁴, copper⁵, boron⁶, zinc⁷, aluminum⁸, magnesium⁹ and silicon¹⁰. 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.

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 yellow oil separated during the course of the reaction. After cooling, the oil solidified giving 26.9 g (98.8 %) of a hygroscopic solid. Two recrystallizations

from ethyl acetate afforded colourless prisms, which after drying *in vacuo* at 75 °C had a melting point of 86.5-88 °C. Anal. calcd. for C₅H₉N₂I: 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 [Pd(OAc)₂] (2 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 × 50 mL), taken up in CH₂Cl₂ (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 CHCl₃ and slightly soluble in THF and toluene. Yield: 3.70 g (75 %), ¹H NMR (400 MHz, CDCl₃, 20 °C): δ 7.24 (s, 4H, NCH), 3.92 (s, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ 168.2 (carbene-C), 122.3 (NHC), 38.2 (CH₃); correct C, H, N analysis.

Carbonylative coupling reaction under carbon monoxide: In a typical reaction, Pd(NHC) complex (2 × 10⁻³ g, 5 × 10⁻² mol) was dissolved in 15 mL anisole under N₂ gas. After the formation of a pale brown homogeneous solution, naphthalen-1-ylboronic acid (**2**) (0.118 g, 1.0 × 10⁻³ mol), 4,4'-diiodobiphenyl (**1**) (0.203 g, 5 × 10⁻⁴ mol) and potassium carbonate (0.425 g, 1.5 × 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 CH₂Cl₂ (20 mL). The neutralized solution was extracted with CH₂Cl₂. The organic layer was dried (Na₂SO₄), 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** (0.141 g, 61.2 %) and **4** (3.9×10^{-2} g, 18 %).

Carbonylative coupling reaction under metal carbonyl:

The mixture of 4,4'-diiodobiphenyl (**1**) (0.203 g, 5×10^{-4} mol), naphthalene-1-ylboronic acid (**2**) (0.118 g, 1×10^{-3} mol), K₂CO₃ (0.425 g, 1.5×10^{-3} mol) and di-(1,3-dihydro-1,3-dimethyl-2*H*-imidazol-2-ylidene)diiodopalladium (2×10^{-3} g, 5×10^{-2} mol) and molybdenum hexacarbonyl (9.2×10^{-2} mol, 0.7 eq) was stirred in 15 mL anisole under N₂. 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 CH₂Cl₂ (20 mL). The neutralized solution was extracted with CH₂Cl₂. The organic layer was dried (Na₂SO₄), 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** (5.5×10^{-2} g, 23.8 %) and **4** (4.7×10^{-2} g, 21.6 %).

Biphenyl-4,4'-diylbis-(naphthalene-1-ylmethanone) (**3**):

Yield: 23.8 %; m.p.: 243–244 °C; ¹H NMR (200 MHz, CDCl₃): δ (ppm) 8.01 (m, 7H), 7.75 (m, 4H), 7.51 (m, 6H); ¹³C NMR (50 MHz, CDCl₃): δ (ppm) 197.5, 144.5, 137.3, 134.3, 132.1, 130.8, 129.8, 128.5, 127.5, 120.3; GC/MS *m/z* 462 (M⁺); Anal. Calcd. for C₃₄H₂₂O₂: C, 88.29; H, 4.79; O, 6.92; found: C, 88.22; H, 4.81; O, 6.96.

(4'-Iodobiphenyl-4-yl)(naphthalene-1-yl)methanone (**4**):

Yield: 21.6 %; m.p.: 215–216 °C; ¹H NMR (200 MHz, CDCl₃): δ (ppm) 7.93 (m, 5H), 7.55 (m, 4H); GC/MS *m/z* 434 (M⁺); Anal. Calcd. for C₂₃H₁₅IO: C, 63.61; H, 3.48; I, 29.22; O, 3.68; found: C, 63.57; H, 3.46; I, 29.22; O, 3.70.

RESULTS AND DISCUSSION

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 reasons¹¹: (1) the steric bulk that they introduce around the metal center facilitates reductive elimination; (2) their strong *s*-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 naphthalene-1-ylboronic acid with *N*-heterocyclic carbene (NHC) ligand under a balloon (1 atm) of CO or metal carbonyls. 4,4'-Diiodobiphenyl (**1**) and naphthalene-1-ylboronic acid (**2**) were reacted under CO (1 bar, a balloon) atmosphere in the presence of the Pd(NHC) complex catalyst formed *in situ*¹². The desired carbonylative products biphenyl-4,4'-diylbis(naphthalene-1-ylmethanone) (**3**) and (4'-iodobiphenyl-4-yl)(naphthalene-1-yl)methanone (**4**) were formed in all cases; irrespective of the reaction conditions.

When metal carbonyl [for Mo(CO)₆: **3** = 23.6 % and **4** = 21.5 %; Mn₂(CO)₁₀: **3** = 24.6 % and **4** = 11.1 %; Co₂(CO)₈: **3** = 5.7 % and **4** = 18.2 %; Fe(CO)₅: **3** = 28.6 % and **4** = 12.7 %; Fe₃(CO)₁₂: **3** = 3.2 % and **4** = 20.9 %] was used in place of CO (**3** = 30.6 % and **4** = 12.7 %), we achieved the same reaction products.

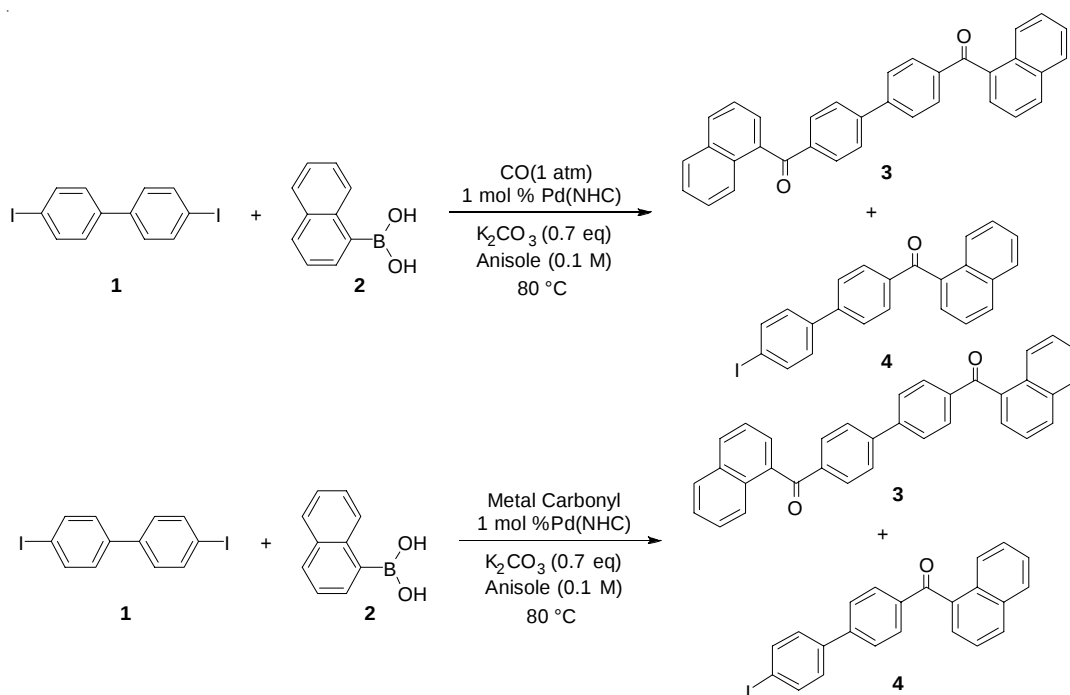
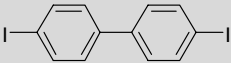
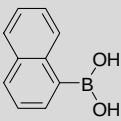
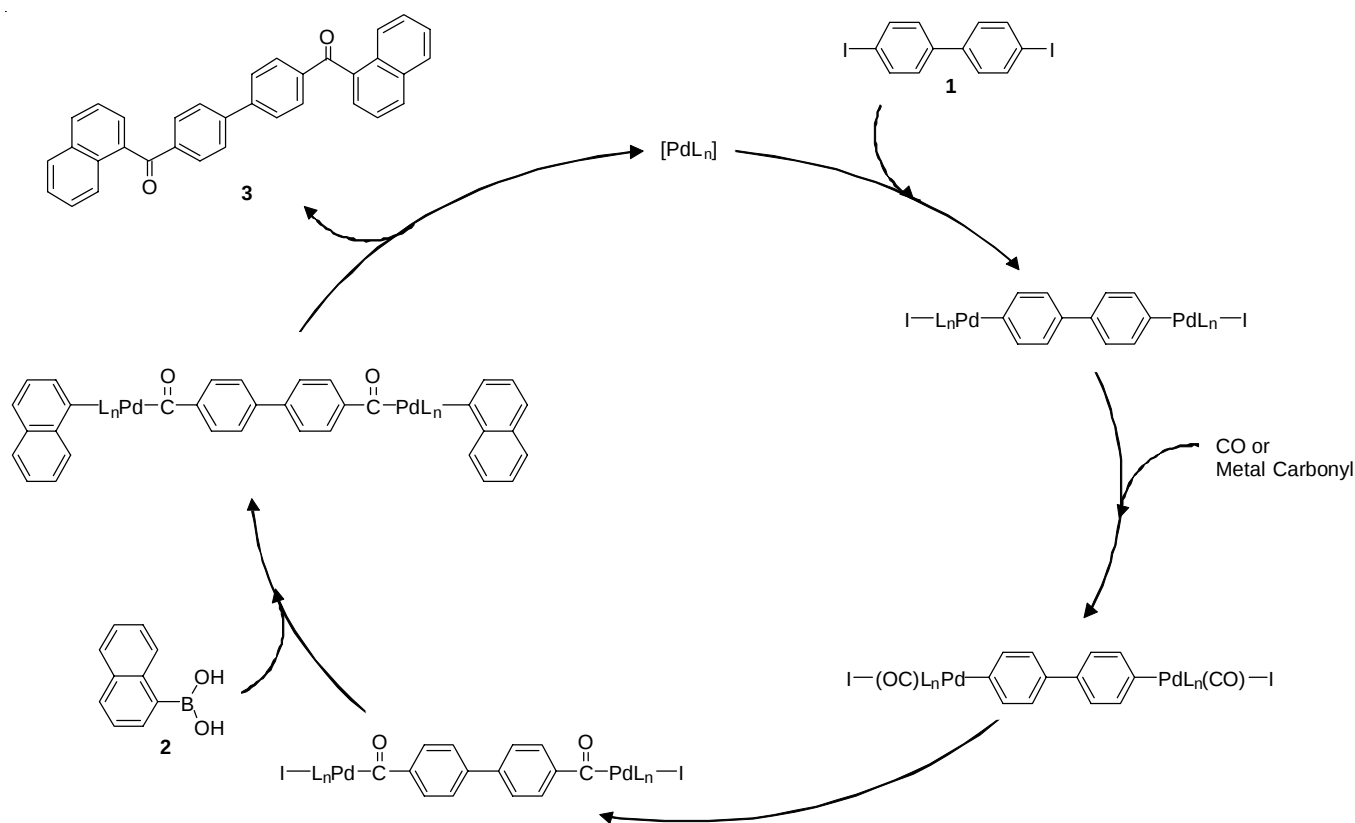


TABLE-1
 CARBONYLATIVE SUZUKI COUPLING WITH NAPHTHALENE-1-YLBORONIC ACID AND 4,4'-DIIODOBIPHENYL

Run	Iodide	Boronic acid	CO	Reaction time (h)	Yield (%)	
					3	4
1			CO	24	61.2	18.0
2			Mo(CO) ₆	24	23.8	21.6
3			Mn ₂ (CO) ₁₀	24	24.6	11.11
4			Co ₂ (CO) ₈	24	5.7	18.2
5			Fe(CO) ₅	24	28.6	12.7
6			Fe ₃ (CO) ₁₂	24	3.2	20.9

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

In reactions with Co₂(CO)₈ and Fe₃(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**.

It is assumed 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 naphthalene-1-ylboronic acid **2**, carbonylative Suzuki coupling under CO or metal carbonyls [Mo(CO)₆, Mn₂(CO)₁₀, Co₂(CO)₈, Fe(CO)₅ and Fe₃(CO)₁₂] is found not to occur. In future, we intend to synthesize various diketones by using hetero aromatic boronic acid to develop a luminescent material.

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