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

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Received September 22, 2012; revised November 3, 2012; accepted November 15, 2012

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], 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 σ-donating character enables facile oxidative addition; and 3) their greater stability at elevated temperatures relative to phosphineligands 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 × 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, phenylboronic acid (0.112 g, 1 × 10⁻³ mol), 4,4′-diiodobiphenyl (0.203 g, 5 × 10⁻⁴ mol), and potassium carbonate (0.425 g, 1.5 × 10⁻³ mol) were added. The at-
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 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:ethylacetate = 20:1, v/v) yield 3 (0.154 g, 42.6%) and 4 (4.9 × 10⁻² g, 12.7%).

2.2. Carbynylative Coupling Reaction under Metal Carbonyl

The mixture of 4,4'-diiodobiphenyl (0.203 g, 5 × 10⁻⁴ mol), phenylboronic acid (0.112 g, 1 × 10⁻⁳ mol), K₂CO₃ (0.425 g, 1.5 × 10⁻³ mol) and Di-(1,3-dihydro-1,3-dimethyl-2H-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 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:ethylacetate = 20:1, v/v) yield 3 (0.189 g, 52.3%) and 4 (5.2 × 10⁻² 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:

When metal carbonyl [for Mo(CO)₆: 3 = 42.6% and 4 = 12.7%; Mn₂(CO)₁₀: 3 = 6.6% and 4 = 33.1%; Co₂(CO)₈: 3 = 48.6% and 4 = 11.2%; Fe₃(CO)₁₂: 3 = 9.9% and 4 = 24.8%; Fe(CO)₅: 3 = 62.5% and 4 = 10.6%] was used in place of CO, we achieved the same reaction products.

In reactions with Mn₂(CO)₁₀ 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 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)₆, Mn₂(CO)₁₀, Co₂(CO)₈, Fe₃(CO)₁₂, and Fe(CO)₅] is found not to occur. In future, we intend to...

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

<table>
<thead>
<tr>
<th>Run</th>
<th>Iodide</th>
<th>Boronic acid</th>
<th>CO</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>Ph-B-OH</td>
<td>CO (gas)</td>
<td>24</td>
<td>42.6</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>Ph-B-OH</td>
<td>Mo(CO)₆</td>
<td>24</td>
<td>52.3</td>
<td>13.5</td>
</tr>
<tr>
<td>3</td>
<td>Ph-B-OH</td>
<td>Mn₂(CO)₁₀</td>
<td>24</td>
<td>6.6</td>
<td>33.1</td>
</tr>
<tr>
<td>4</td>
<td>Ph-B-OH</td>
<td>Co₂(CO)₈</td>
<td>24</td>
<td>48.6</td>
<td>11.2</td>
</tr>
<tr>
<td>5</td>
<td>Ph-B-OH</td>
<td>Fe₃(CO)₁₂</td>
<td>24</td>
<td>9.9</td>
<td>24.8</td>
</tr>
<tr>
<td>6</td>
<td>Ph-B-OH</td>
<td>Fe(CO)₅</td>
<td>24</td>
<td>62.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>
synthesize various diketones by using heteroaromatic boronic acid to develop a luminescent material.

5. Acknowledgements
The work was supported by a grant of Dong-A University (2012).

REFERENCES


