Abstract: Dimeric cyclometallated oxime palladium complex containing palladium-carbon covalent bond was found to efficiently catalyze the carbonylation reactions of aryl iodides with various alcohols to give esters in excellent yields with high selectivity. These complexes were also stable under a carbon monoxide atmosphere at high temperatures.

Key words: palladacycle, carbonylation, aryl iodides, turnover numbers, aromatic esters

Carbonylation of aromatic halides catalyzed by Pd(0) complexes is one of the versatile and convenient processes towards the synthesis of various aromatic carbonyl compounds, especially key intermediates in organic synthesis.1–3 The combination of aryl and vinyl halides with nucleophiles such as alcohols and amines leads to an interesting application in syntheses of natural products2,4 and polymers.5–8 Palladium-catalyzed carbonylation-polycondensation reactions are also well recognized by the polymer chemist in the synthesis of soluble organic polymers namely polyesters and polyamides.6–8 Even though many carbonylation catalysts have emerged in the past few decades, the search for new catalysts continues because of economical and environmental demands.9 In most of the above reactions, Pd(0) complexes with phosphine ligand were employed as catalysts. The major drawbacks of the use of phosphine ligands in such catalytic reactions are (i) the oxidation of phosphine to phosphine oxide causing degradation of the catalyst, (ii) reduction of the complex catalyst to metal, (iii) termination of the catalytic cycle, and (iv) separation of products from the complex reaction mixture containing phosphine and phosphine oxide. By considering the importance of palladium-catalyzed carbonylation reactions in various fields and to overcome the above-mentioned disadvantages, we focused our study on finding efficient palladium catalysts that are structurally important and stable under carbon monoxide atmosphere. Very few research groups have reported that Pd(II) complexes rather than traditional Pd(0) catalysts with PPh3 ligands were highly active in C–C bond forming reactions such as Heck reaction, Suzuki and Stille coupling and in which the high catalytic activity was explained by the oxidative addition mechanism.10 The study of the mechanism of oxidative addition involving Pd(II) to Pd(IV) is an interesting aspect of palladium catalyzed reactions and is attributed to higher activity of the catalyst.

In our present study, we investigated the synthesis of novel, covalently bonded, structurally stable cyclometallated dimeric oxime palladium(II) catalysts and their stability under carbon monoxide pressure. We also dealt with the mechanism of oxidative addition reactions of Pd(II) to aryl halides to give Pd(IV) complexes in carbonylation reactions. The Pd complex 1 has been synthesized from readily available benzophenone oxime and lithium tetrachloropalladate (Scheme 1).11 Such metal complexes with a covalently bonded palladium to the aromatic ring could be more stable and can perform as efficient catalysts under carbon monoxide atmosphere.

![Scheme 1](image-url)
ladium metal and no decomposition of the complexes were observed during the reaction. As shown in Table 1, most of the reactions gave the target esters in high yields. The reaction proceeded smoothly under carbon monoxide pressure of 0.1 to 1 MPa.

![Scheme 2](image)

**Table 1** Alkoxy and Phenoxycarbonylations of Aryl Iodides Catalyzed by Dimeric Oximepalladacycle 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>R¹–OH</th>
<th>Product</th>
<th>Yield (%) (isolated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>EtOH</td>
<td><img src="image" alt="EtOOC" /></td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>PhCH₂OH</td>
<td><img src="image" alt="COOCH₂Ph" /></td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>PhOH</td>
<td><img src="image" alt="COOPh" /></td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>I</td>
<td>EtOH</td>
<td><img src="image" alt="PhCOOEt" /></td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>I</td>
<td>PhCH₂OH</td>
<td><img src="image" alt="PhCOOC₂Ph" /></td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>I</td>
<td>PhOH</td>
<td><img src="image" alt="PhCOOPh" /></td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>H₃C</td>
<td>PhCH₂OH</td>
<td><img src="image" alt="H₃C-PhCOOC₂Ph" /></td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>H₃CO</td>
<td>EtOH</td>
<td><img src="image" alt="H₃CO-PhCOOE" /></td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>H₃CO</td>
<td>PhOH</td>
<td><img src="image" alt="H₃CO-PhCOOPh" /></td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td>Br</td>
<td>PhOH</td>
<td><img src="image" alt="Br-PhCOOPh" /></td>
<td>86</td>
</tr>
<tr>
<td>11</td>
<td>EtOOC</td>
<td>PhCH₂OH</td>
<td><img src="image" alt="EtOOC-PhCOOC₂Ph" /></td>
<td>83</td>
</tr>
<tr>
<td>12</td>
<td>I</td>
<td>EtOH</td>
<td><img src="image" alt="COOE" /></td>
<td>76</td>
</tr>
<tr>
<td>13</td>
<td>I</td>
<td>EtOH</td>
<td><img src="image" alt="EtOOC" /></td>
<td>80</td>
</tr>
<tr>
<td>14</td>
<td>I</td>
<td>PhOH</td>
<td><img src="image" alt="PhOOC" /></td>
<td>81</td>
</tr>
</tbody>
</table>

We emphasize that the complex 1 contains no phosphine ligand and has carbon–palladium covalent bonds. This is the first report of using 1 and such Pd(II) complexes as catalysts for carbonylation. It is noteworthy that oxidative addition [probably involving Pd(II) to Pd (IV)] with aryl halides takes place without affecting the Pd–C covalent bond.

The phenoxycarbonylation of 1-bromo-4-iodobenzene leads to 4-bromobenzoic acid phenyl ester in high yield. Reactivities for aryl bromides and chlorides were low under the conditions. These results prove that the complex 1 is highly selective to aryl iodides. We also examined the carbonylation reactions of various aryl iodides (5.0 mmol) with aliphatic alcohols as well as less reactive phenol using minimum amount of catalyst (0.0014 mmol, 1 mg) in order to investigate its catalytic activity. It leads to successful turnover number of 3915 and turnover frequency of 978. However, β-bromostyrene with phenol gave esters in lower yield.
bond. The large turnover number indicates that complex 1 is very stable even at high temperatures and has a longer lifetime.

In conclusion, the complex 1 proved to be an efficient catalyst for the carbonylation of various aryl iodides with different aliphatic alcohols as well as less reactive phenols to give corresponding esters in excellent yields with high selectivity. The complex 1 is decomposed to palladium salt and organic compounds after workup of the reaction. The detailed study on the mechanism of the catalytic cycle by isolating oxidative addition intermediate, which involves Pd(II) to Pd(IV) and characterization is under investigation by NMR and other techniques.

Furthermore, the activation of less reactive and less expensive aryl, vinyl bromides and chlorides for the carbonation reaction with alcohols and amines to achieve high turnover numbers and frequencies is in progress, which is of potential importance in industrial applications for the synthesis of organic soluble polyesters and polyamides.12

In a typical procedure, aryl iodide (2.5 mmol), alcohol (2.5–3.0 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 3.0 mmol) and catalyst (0.01 mmol) in benzene (5 mL) were taken in autoclave (50 mL), flushed with nitrogen 3 times and pressurized with carbon monoxide (0.5 MPa). The autoclave was placed in oil bath heated at 120 °C and the whole mixture was stirred for 3 h. After the reaction, the autoclave was cooled, excess carbon monoxide was purged, and benzene was evaporated in vacuo. The product was isolated by silica gel column chromatography (hexane–benzene). All the products were characterized by IR and 1H NMR.

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References


