Effect of transition metal complexes on aryl-aryl coupling

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The catalytic activity of NiCl₂(PPh₃)₂, CoCl₂(PPh₃)₂, CuCl₂(PPh₃)₂, FeCl₂(PPh₃)₂, [Ag (PPh₃)₂]Cl, Ni(dppe)Cl₂, Co(dppe)Cl₂, Cu(dppe)Cl₂ and [Ag(dppe)]Cl on aryl-aryl coupling has been investigated. NiCl₂(PPh₃)₂ shows highest activity.

Aryl-aryl coupling is a crucial step in the synthesis of natural biaryls. Ullmann and Bielecki in 1901 discovered the formation of biaryls by the condensation of two molecules of aryl halides in the presence of finely divided copper. In order to avoid the very high temperatures required, a number of new methods have been introduced by Semmelhack. In these Ni, Rh and Pd complexes such as Ni(COD)₂ and Ni(PPh₃)₄ used in stoichiometric amounts replace copper. Thus aryl halides could be coupled in high yields at temperatures as low as 45-50°C. Biaryls can also be prepared by coupling aryl Grignard reagents with aryl halides. The well established Nickel complex that can catalyze this coupling is the Tamao-Kumada catalyst NiCl₂(PR₃)₂ (R = alkyl or aryl). Apart from this, a wide range of other Nickel catalysts such as NiCl₂(dppe), [Ni(en)₂]Cl₂, Ni(acac)₂ can be used.

The coupling of Grignard reagents is known to be catalyzed by transition metal ions like Fe(II), Ca(II), Cu(I), Ni(II) and Ag(I). However, the effect of the complexes of these metals (except Ni complexes) on the coupling of ArMgX with ArX has not been investigated so far.

The present study aims at the examination of the effect of Fe(III), Co(II), Cu(II), Ni(II) and Ag(I) complexes on the coupling of Grignard reagent with aryl halides to create a Cₓaryl · Cᵧaryl linkage. The complexes studied are NiCl₂(PPh₃)₂, CoCl₂(PPh₃)₂, CuCl₂(PPh₃)₂, FeCl₂(PPh₃)₂, [Ag(PPh₃)₂]Cl, NiCl₂(dppe), CoCl₂(dppe), CuCl₂(dppe) and [Ag(dppe)]Cl.

The system chosen for this study is the coupling of phenyl magnesium bromide with bromobenzene to give biphenyl as the product under a standard set of conditions.

![Diagram](Note)

Bromobenzene was first converted to the corresponding Grignard reagent. Then bromobenzene followed by the complex chosen for the investigation in catalytic amount was added to the above reagent. The reaction was allowed to continue for 6 hr. Normal work up yielded biphenyl.

The activities of the complexes chosen, determined as the yield of biphenyl are given in the Tables I and II. The results suggest that the catalytic activity of NiCl₂(PPh₃)₂ is highest in the production of biphenyl.

The optimum quantity of the catalyst NiCl₂(PPh₃)₂ required for the coupling of PhMgBr with PhBr has also been investigated by performing a series of experiments using different mole ratios of PhMgBr and PhBr.

**Table I—Yields of biphenyl with triphenyl phosphine complexes as catalyst**

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Catalyst</th>
<th>Yield of biphenyl (in g)</th>
<th>% yield of biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl₂(PPh₃)₂</td>
<td>1.45</td>
<td>95.4</td>
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<tr>
<td>2</td>
<td>CoCl₂(PPh₃)₂</td>
<td>1.16</td>
<td>76.0</td>
</tr>
<tr>
<td>3</td>
<td>FeCl₂(PPh₃)₂</td>
<td>0.86</td>
<td>56.6</td>
</tr>
<tr>
<td>4</td>
<td>CuCl₂(PPh₃)₂</td>
<td>0.67</td>
<td>44.0</td>
</tr>
<tr>
<td>5</td>
<td>Ag(PPh₃)₂Cl</td>
<td>0.61</td>
<td>40.0</td>
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</tbody>
</table>

**Table II—Yields of biphenyl with dppe complexes as catalyst**

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Catalyst</th>
<th>Yield of biphenyl (in g)</th>
<th>% yield of biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl₂(dppe)</td>
<td>0.84</td>
<td>55.26</td>
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<tr>
<td>2</td>
<td>CoCl₂(dppe)</td>
<td>0.70</td>
<td>46.65</td>
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<tr>
<td>3</td>
<td>CuCl₂(dppe)</td>
<td>0.62</td>
<td>40.79</td>
</tr>
<tr>
<td>4</td>
<td>Ag(dppe)Cl</td>
<td>0.17</td>
<td>11.18</td>
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</tbody>
</table>

Coupling reaction time—6 hr
NiCl\(_2\)(PPh\(_3\))\(_2\). In this set of experiments PhMgBr was allowed to couple with PhBr for a period of 2 hr. The results are presented in Table III. This study revealed the optimum mole ratio of the Grignard reagent to Ni complex to be 100:1.

**Experimental Section**

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer using KBr wafer technique and UV spectra on a Hitachi U2001 spectrophotometer.

NiCl\(_2\)(PPh\(_3\))\(_2\): A solution of NiCl\(_2\).6H\(_2\)O (2.38 g, 0.01 mole) in water (2 mL) was diluted with glacial acetic acid (50 mL) and a solution of PPh\(_3\) (5.25 g, 0.02 mole) in glacial acetic acid was added. An olive green micro crystalline precipitate was formed, which was filtered, washed with glacial acetic acid and dried in vacuum desiccator (H\(_2\)SO\(_4\): KOH). The complex was further washed with pet. ether to remove traces of free PPh\(_3\) and was dried in vacuum desiccator (H\(_2\)SO\(_4\): KOH). The complex was further washed with glacial acetic acid and dried in vacuum desiccator (H\(_2\)SO\(_4\): KOH). The complex was further washed with glacial acetic acid and dried in vacuum desiccator (H\(_2\)SO\(_4\): KOH).

CoCl\(_2\)(PPh\(_3\))\(_2\): Prepared as above as sky blue microcrystals, yield 52.54%; IR (KBr): 3042 (s), 1185 (w), 1098 (s), 1040 (w), 1000 (m), 745 (s) and 695 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 265 and 663 nm.

FeCl\(_3\)(PPh\(_3\))\(_2\): Prepared as above by taking FeCl\(_3\) (0.005 mole) and PPh\(_3\) (0.015 mole). Pale green crystals were obtained, yield 11.58%; IR (KBr): 3042 (w), 1590 (m-w), 1485 (m), 1435 (s), 1150 (s), 1120 (s), 1090 (m), 1028 (w), 1000(m), 745 (m), 725 (s) and 680 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 267, 355 and 390 nm.

CuCl\(_2\)(PPh\(_3\))\(_2\): To a warm solution of CuCl\(_2\).2H\(_2\)O (0.8524g, 0.005 mole) a hot solution of PPh\(_3\) (2.623g, 0.01 mole) in minimum amount of ethanol was added slowly with constant stirring to give a white precipitate. The reaction mixture was boiled for 5 mins and kept at room temperature for 24 hrs. The precipitate was filtered, washed with dry acetone, dried in vacuum desiccator (H\(_2\)SO\(_4\): KOH). The complex was further washed with pet. ether to remove traces of PPh\(_3\), yield 1.5g (21.33%); IR (KBr): 3065 (w), 1475 (m), 1435 (s), 1100 (m), 1035 (w), 1005 (w), 750 (s) and 700 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 265 and 300 (sh) nm.

[Ag(PPh\(_3\))\(_2\)]Cl: To a solution of AgNO\(_3\) (0.05g, 0.0003 mole) in glacial acetic acid (10 mL), a solution of PPh\(_3\) (0.154g, 0.0006 mole) in glacial acetic acid was added slowly with continuous stirring under hot condition. To this reaction mixture, saturated solution of KCl was added to give white precipitate. The reaction mixture was boiled for 5 min and left at room temperature for 24 hr. The precipitate was filtered, washed with glacial acetic acid and dried in vacuum dessicator (H\(_2\)SO\(_4\): KOH). The complex was further washed with pet. ether and dried, yield 0.16g (27.32%); IR (KBr): 3050 (w), 1435 (s), 1100 (s), 1035 (w), 1005 (w), 750 (s) and 700 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 254 and 264 nm.

1,2-Bis(diphenylphosphino)ethane (dppe) was prepared according to literature\(^1\); m.p. 131-32\(^\circ\); IR (KBr): 3060 (w), 2930 (w), 1480 (m), 1435 (s), 1308 (w), 1180 (w), 1165 (w), 1100 (w), 1075 (w), 1032 (m), 1005 (w), 1030 (s) and 695 (s) cm\(^{-1}\); UV (1,4 dioxane): 277 and 325 (sh) nm.

NiCl\(_2\)(dppe): To a solution of dppe (0.251g, 0.63 m mole) in warm isopropanol (25 mL), NiCl\(_2\).6H\(_2\)O (0.1595g, 0.67 m mole) dissolved in 15 mL of 2:1 isopropanol and methanol was added slowly with continuous stirring when orange feathery crystalline needles precipitated out. The precipitate was centrifuged, washed with ether and dried, yield 0.19g (22.0%); IR (KBr): 3040 (m), 2900 (w), 1483 (m), 1435 (s), 1175 (w), 1100 (w), 1028 (w), 1000 (w), 875 (w), 750 (s), 720 (s) and 695 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 265, 270 (sh) and 658 nm.

CoCl\(_2\)(dppe): Prepared as above in the form of green feathery crystals, yield 42.34%; IR (KBr): 3040 (w), 1000 (w), 750 (m-s) and 700 (s) cm\(^{-1}\); UV (1,4 dioxane+MeOH): 260, 365 and 657 nm.

[Ag(dppe)]Cl: To a solution of dppe (0.078g, 0.195 mmoles) in warm isopropanol (12 mL), AgCl (0.03g, 0.209 mmoles) dissolved in minimum amount ofaq.ammonia was added slowly with continuous stirring. White feathery fine crystals precipitated out.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>PhMgBr mol</th>
<th>NiCl(_2)(PPh(_3))(_2) mol</th>
<th>% yield of biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.0005</td>
<td>11.1</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>0.00015</td>
<td>20.0</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>0.0001</td>
<td>30.5</td>
</tr>
<tr>
<td>4</td>
<td>0.005</td>
<td>0.000005</td>
<td>31.5</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
<td>0.0000125</td>
<td>22.0</td>
</tr>
</tbody>
</table>

**Coupling reaction time—2 hr**

Table III—Yields of biphenyl with different mole ratios of PhMgBr and Nickel complex
The precipitate centrifuged washed with ether and dried, yield 0.06g (55.56%); IR (KBr): 3070 (w), 1590 (w), 1540 (w), 1485 (m), 1435 (s), 1390 (m), 1178 (w), 1100 (s), 1030 (w), 1000 (w), 750 (m-s) and 700 (s) cm⁻¹; UV (1,4 dioxane+MeOH): 277 and 290 (sh) nm.

Coupling of phenylmagnesiumbromide with bromobenzene catalyzed by metal- phosphene-chloride complexes: Magnesium turnings (320 mg 0.013 mole) were taken in a two necked round bottomed flask fitted with a calcium chloride guard tube. A crystal of iodine was added to activate the magnesium. Bromobenzene (distilled over P₂O₅, 0.5 mL of total 1.275 mL; 0.012 mole) in 5 mL of anhyd. ether was added with stirring and started refluxing. Appearance of turbidity and bubbles indicated the initiation of the reaction. The remaining bromobenzene in 5 mL of ether was added (in 20 min) dropwise and further refluxed for 35 mins till all magnesium dissolved. To this reaction mixture 1.03 mL (0.01 mole) of bromobenzene in 5 mL of anhyd. diethyl ether and the metal phosphene halide complex (0.00012 mole) chosen for investigation were added and refluxed further for 6 hr. The reaction mixture was cooled and hydrolyzed with saturated solution of aq. Ammonium chloride. The ether extract on evaporation of the solvent gave the product which compared well with an authentic sample of biphenyl on TLC, m.p. 69-72°C.

References