TITLE:
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CITATION:
Uemura, Minoru ...[et al]. Cp*Li as a base: application to palladium-catalyzed cross-coupling reaction of aryl-X or alkenyl-X (X=I, Br, OTf, ONf) with terminal acetylenes. Tetrahedron 2008, 64(8): 1829-1833

ISSUE DATE:
2008-02-18

URL:
http://hdl.handle.net/2433/88969

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Cp*Li as a Base: Application to Palladium-Catalyzed Cross-Coupling Reaction of Aryl-X or Alkenyl-X (X = I, Br, OTf, ONf) with Terminal Acetylenes

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Abstract: The reaction of aryl-X or alkenyl-X (X = I, Br, OTf, ONf) with terminal acetylenes in the presence of a catalytic amount of Pd(OAc)2 provided the alkynylated products in good yields by using Cp*Li (Cp* = 1,2,3,4,5-pentamethyloclopentadienyl) as a base.

Keywords: pentamethyloclopentadiene, cross-coupling reaction, lithium acetylides, alkynylation

Introduction

Pentamethyloclopentadienide (Me₅C₅⁻, Cp*) has been used as a ligand of transition metal complexes for forty years.¹ Although Cp*⁻ has unique properties, such as six-electron donation and steric bulkiness by the five methyl groups on the five-membered ring, it has not been used for other purposes. Then we have been exploring applications of Cp*⁻ as a reagent in organic
Now, we have been interested in Cp* as a base. We expected that its strong basicity and steric bulkiness would exhibit interesting reactivities. We have found that the reaction of aryl-X or alkenyl-X (X = I, Br, OTf, ONf) with terminal acetylenes in the presence of a catalytic amount of palladium provided the alkynylated products in good yields by using Cp*Li as a base.

**Results and Discussions**

Treatment of a suspension of Cp*Li in THF with iodobenzene (1a), 1-octyne (2a), and a catalytic amount of Pd(OAc)$_2$ at reflux for 1 h gave 1-octynylbenzene (3aa) in 82% yield (Table 1, entry 7). Other lithium bases, such as $n$-BuLi, lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LHMDS), and lithium cyclopentadienide (CpLi) did not assist the coupling reaction efficiently (entries 1–4). However, lithium indenide resulted in formation of 3aa in 24% yield (entry 5). Interestingly, the reaction with lithium tetramethylcyclopentadienide, which lacks one methyl group compared with Cp*Li, gave 3aa in lower yield than that with Cp*Li yet in higher yield than that with CpLi (entry 6).

Although many kinds of alkynylmetal have been used for palladium-catalyzed cross-coupling reaction of aryl-X or alkenyl-X, there are no reports on the cross-coupling reaction with lithium acetylides. The coupling reaction with lithium acetylides is difficult because the reaction of a palladium catalyst with an excess amount of lithium acetylides provides lithium palladate 4, which does not exhibit any catalytic activity (eq 1). We thought that gradual formation of lithium acetylides by means of Cp*Li would avoid the formation of 4.
Table 1. Effect of lithium bases on palladium-catalyzed cross-coupling reaction of iodobenzene (1a) with 1-octyne (2a)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>lithium base</th>
<th>NMR yield /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-BuLi</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>lithium diisopropylamide (LDA)</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>lithium hexamethyldisilazide (LHMDS)</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>lithium cyclopentadienide (CpLi)</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>lithium indenide(^a)</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td>lithium tetramethylcyclopentadienide</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>Cp*Li</td>
<td>82(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Derived from indene and n-BuLi. \(^b\) Isolated yield.

\[ \text{Cl}_2\text{Pd}(\text{PPh}_3)_2 + \text{Li}-\text{C}≡\text{C}-\text{R} \rightarrow \text{Li}_2\text{Pd} + (\text{C}≡\text{C}-\text{R})_4 \] (1)

To confirm the gradual generation of lithium acetylides, we carried out the following experiments. Treatment of lithium acetylide 5 with Cp*H for 1 h at reflux followed by an addition of benzaldehyde at 0 °C gave a mixture of octynylated alcohol 6 and pentamethylcyclopentadienylated alcohol 7 (eq 2). On the other hand, 7 was obtained selectively by using the reaction mixture of 5 and Cp*H which was treated for 11 h at reflux. These facts indicate that the pKa value of Cp*H is smaller than that of 2a and that a high energy barrier exists.
between $2a + \text{Cp*Li}$ and $5 + \text{Cp*H}$. A similar reaction with cyclopentadiene (CpH), instead of CpH, only for 1 h followed by an addition of benzaldehyde did not give 6 but gave Cp adduct-derived compounds such as 6-phenylfulvene. This result means that the energy barrier between $2a + \text{CpLi}$ and $5 + \text{CpH}$ is lower than that between $2a + \text{Cp*Li}$ and $5 + \text{Cp*H}$. Not only the pKa values of lithium bases but also the high energy barrier is important to promote the cross-coupling reaction. The reaction of a mixture of $2a$ and $\text{Cp*Li}$ with benzaldehyde at reflux or at 0 ºC provided 6 or 7, respectively (eq 3). The results mean that 5 is generated only at reflux. The reason why 7 is not provided at reflux conditions is that nucleophilic addition reaction of $\text{Cp*Li}$ to benzaldehyde is thermally reversible and that of 5 to benzaldehyde is irreversible. We are sure that the equilibrium between $2a + \text{Cp*Li}$ and $5 + \text{Cp*H}$ is mostly biased toward $2a + \text{Cp*Li}$ and that a modest amount of $5 + \text{Cp*H}$ would be generated at reflux.

Table 2 summarizes the results obtained by the $\text{Cp*Li}$-mediated reaction of aryl iodides 1 with terminal acetylenes 2. Aromatic iodide 1 bearing an electron-donating group (Table 2, entry 7) or an electron-withdrawing group (entry 8) afforded 3 in high yields. Surprisingly, ester (entry 10) or cyano moiety (entry 11) on the aromatic ring did not undergo nucleophilic addition reaction of
Cp*Li or lithium acetylides during thermal conditions. Reaction of meta- or ortho-substituted 1 also proceeded smoothly (entries 12, 13). 1-Naphthyl iodide could be used in this reaction (entry 14). The reaction with phenylacetylene (2c) or trimethylsilylacetylene (2e) afforded 3 in good yields by using 15 mol% of triphenylphosphine (entries 3, 5).

**Table 2. Reactions of various aryl iodides 1 with terminal acetylenes 2**

<table>
<thead>
<tr>
<th>entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>isolated yield /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H (1a)</td>
<td>n-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt; (2a)</td>
<td>82 (3aa)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>c-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt; (2b)</td>
<td>85 (3ab)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>Ph (2c)</td>
<td>93 (3ac)&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>TES (2d)</td>
<td>69 (3ad)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>TMS (2e)</td>
<td>72 (3ae)&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>p-Me (1b)</td>
<td>2a</td>
<td>81 (3ba)</td>
</tr>
<tr>
<td>7</td>
<td>p-OMe (1c)</td>
<td>2a</td>
<td>82 (3ca)</td>
</tr>
<tr>
<td>8</td>
<td>p-CF&lt;sub&gt;3&lt;/sub&gt; (1d)</td>
<td>2a</td>
<td>70 (3da)</td>
</tr>
<tr>
<td>9</td>
<td>p-Cl (1e)</td>
<td>2a</td>
<td>71 (3ea)</td>
</tr>
<tr>
<td>10</td>
<td>p-COOEt (1f)</td>
<td>2a</td>
<td>83 (3fa)</td>
</tr>
<tr>
<td>11</td>
<td>p-CN (1g)</td>
<td>2a</td>
<td>74 (3ga)</td>
</tr>
<tr>
<td>12</td>
<td>m-Me (1h)</td>
<td>2a</td>
<td>83 (3ha)</td>
</tr>
<tr>
<td>13</td>
<td>o-Me (1i)</td>
<td>2a</td>
<td>83 (3ia)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>1-Naphthyl iodide (1j)</td>
<td>2a</td>
<td>67 (3ja)</td>
</tr>
</tbody>
</table>

<sup>a</sup> 15 mol% of PPh<sub>3</sub> was added. <sup>b</sup> The reaction was carried out at 50 °C for 2 h. <sup>c</sup> The reaction was carried out for 1.5 h.
Not only aryl iodides but also aryl bromides, triflate, or nonaflate could be also used as substrates in the \( \text{Cp}* \)-mediated reaction (Table 3). In these cases, triphenylphosphine was essential as a ligand.

**Table 3.** Reactions of various aryl bromides, triflates or nonaflates with 1-octyne (2a)

<table>
<thead>
<tr>
<th>entry</th>
<th>X</th>
<th>R</th>
<th>isolated yield /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>H</td>
<td>79 (3aa)</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>( p )-OMe</td>
<td>74 (3ca)(^c)</td>
</tr>
<tr>
<td>3</td>
<td>Br</td>
<td>( p )-CF(_3)</td>
<td>79 (3da)</td>
</tr>
<tr>
<td>4</td>
<td>OTf(^a)</td>
<td>H</td>
<td>58 (3aa)</td>
</tr>
<tr>
<td>5</td>
<td>ONf(^b)</td>
<td>H</td>
<td>88 (3aa)(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Tf = trifluoromethanesulfonyl \(^b\) Nf = 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonyl \(^c\) The reaction was carried out for 1.5 h.

By utilizing the advantages of \( \text{Cp}* \text{Li} \) as a base, we find two applications. The reaction of 2-iodobenzoic acid with 2 provided isocoumarin 8 and (Z)-3-alkylidenephthalide 9 in good yields (eq 4).\(^5\) We also found that \( \text{Cp}* \text{Li} \) can be used as a bulky base to prepare lithium enolates. With this reactivity, we accomplished one-pot synthesis of enynes 12 from ketone 10 \( \text{via} \) nonaflate 11 in good yields (eq 5).
Experimental

Instrumentation and Materials

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer unless otherwise noted. Chemical shifts ($\delta$) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and at 77.0 ppm for $^{13}$C. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 7.8 mL/min, UV and RI detectors). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene was purchased from Kanto Chemical Co. THF (dehydrated, stabilizer free) was purchased from Kanto Chemical Co., stored under nitrogen, and used without distillation. All reactions were carried out under argon atmosphere.

General Procedure for Palladium-Catalyzed Cross-Coupling Reaction of Aryl Iodides 1 with Terminal Acetylenes 2 Using Cp*Li: A solution of \( n \)-BuLi in hexane (1.60 M, 0.47 mL, 0.75 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.13 mL, 0.80 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 10 min at the same temperature. Pd(OAc)\(_2\) (8.4 mg, 0.038 mmol), \( 2a \) (82.7 mg, 0.75 mmol) in THF (0.5 mL), and \( 1a \) (102 mg, 0.50 mmol) in THF (0.5 mL) were added to the reaction mixture. The resulting mixture was stirred for 1 h at reflux. The reaction mixture was quenched with saturated aqueous NH\(_4\)Cl, and the mixture was extracted with hexane. The combined organic parts were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C-200, hexane) to afford \( 3aa \) (75.5 mg, 0.41 mmol, 82%).

General Procedure for Palladium-Catalyzed Cross-Coupling Reaction of Aryl Bromide, Aryl Triflate, Aryl Nonaflate with 1-Octyne (2a) Using Cp*Li: A solution of \( n \)-BuLi in hexane (1.60 M, 0.47 mL, 0.75 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.13 mL, 0.80 mmol) in THF (5 mL) at 0 °C. The white suspension was stirred for 10 min at the same temperature. Pd(OAc)\(_2\) (8.4 mg, 0.038 mmol), PPh\(_3\) (19.7 mg, 0.075 mmol), 1-octyne (82.7
mg, 0.75 mmol) in THF (0.5 mL), and bromobenzene (78.5 mg, 0.50 mmol) in THF (0.5 mL) were added to the reaction mixture, and the mixture was stirred for 1 h at reflux. The reaction was terminated with saturated aqueous NH₄Cl, and the mixture was extracted with hexane. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated \textit{in vacuo} to give a crude oil. Chromatographic purification on silica gel (Wakogel C-200, hexane) afforded 3aa (73.4 mg, 0.39 mmol, 79%).

General Procedure for Palladium-Catalyzed Annulation of 2-Iodobenzoic Acid with Terminal Acetylenes 2 Using Cp*Li: A solution of \textit{n}-BuLi in hexane (1.60 M, 0.78 mL, 1.25 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.20 mL, 1.3 mmol) in THF (5 mL) at 0 ºC. The mixture was stirred for 10 min at 0 ºC. Pd(OAc)₂ (8.4 mg, 0.038 mmol), 2a (82.7 mg, 0.75 mmol) in THF (0.5 mL), and 2-iodobenzoic acid (124 mg, 0.50 mmol) in THF (0.5 mL) were added to the reaction mixture, and the mixture was stirred for 1 h at reflux. After being quenched with water, the mixture was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated \textit{in vacuo} to give a crude oil. Purification on silica gel (Wakogel C-200, hexane – ethyl acetate = 20:1) afforded a mixture of 8a and 9a (8a:9a = 68:32, 80.8 mg, 0.35 mmol, 70%).

General Procedure for Palladium-Catalyzed One-Pot Synthesis of Enynes 12 from 10 via 11: A solution of \textit{n}-BuLi in hexane (1.60 M, 0.78 mL, 1.25 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.20 mL, 1.3 mmol) in THF (5 mL) at 0 ºC. The mixture was stirred for 20 min at the same temperature. Cyclohexanone (49.1 mg, 0.5 mmol) in THF (0.5 mL) was added to the resulting white suspension, and the mixture was stirred for 30 min
at 0 °C. 1,1,2,2,3,3,4,4,4-Nonafluoro-1-butanesulfonyl fluoride (181 mg, 0.60 mmol) in THF (0.5 mL) was added to the reaction mixture, and the mixture was stirred for 30 min at 0 °C. 1-Octyne (2a, 82.7 mg, 0.75 mmol) in THF (0.5 mL), PPh₃ (19.7 mg, 0.075 mmol), and Pd(OAc)₂ (8.4 mg, 0.038 mmol) were added to the reaction mixture, and the mixture was stirred for 1 h at reflux. Water was added to quench the reaction, and the mixture was extracted with hexane. The combined organic parts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C-200, hexane) to afford 12a (60.3 mg, 0.32 mmol, 64%).

**Preparation of Phenyl 1,1,2,2,3,3,4,4,4-nonfluoro-1-butanesulfonate:** A solution of n-BuLi in hexane (1.60 M, 3.44 mL, 5.5 mmol) was added to a solution of phenol (471 mg, 5.0 mmol) in THF (17 mL) at 0 °C. The mixture was stirred for 10 min at the same temperature. 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonyl fluoride (1.81 g, 6.0 mmol) in THF (1 mL) was added to the reaction mixture, and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C-200, hexane – ethyl acetate = 40:1) to afford phenyl 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonate (1.52 g, 4.0 mmol, 81%).

**Characterization Data**

The compounds 3aa, 3ac and 3ae are commercially available. The products 3ab, 3ad, 3ba,

10
3ca, 8 3da, 8 3ea, 9 3ga, 8 3ha, 8 3ia, 8 3ja, 10 12a, 11 12b, 12 and 12c 12 can be found in the literature.

**ethyl 4-[(1-octynyl)benzoate (3fa):** IR (neat) 2932, 2859, 1720, 1608, 1466, 1367, 1306, 1272, 1175, 1106, 1097, 1021, 857, 770, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 0.91 (t, J = 7.0 Hz, 3H), 1.28–1.64 (m, 8H), 1.39 (t, J = 7.0 Hz, 3H), 2.42 (t, J = 7.0 Hz, 2H), 4.36 (t, J = 7.0 Hz, 2H), 7.41–7.45 (m, 2H), 7.93–7.97 (m, 2H); ¹³C NMR (CDCl₃) δ 14.04, 14.30, 19.50, 22.53, 28.54, 28.60, 31.33, 61.01, 80.12, 93.90, 128.81, 129.13, 129.33 (×2), 131.39 (×2), 166.20. Found: C, 78.92; H, 8.78%. Calcd for C₁₇H₂₂O₂: C, 79.03; H, 8.58%.

**phenyl 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonate:** IR (neat) 1488, 1427, 1354, 1230, 1204, 1145, 1133, 1036, 891, 772, 686 cm⁻¹; ¹H NMR (CDCl₃) δ 7.28–7.31 (m, 2H), 7.37–7.42 (m, 1H), 7.44–7.48 (m, 2H); ¹³C NMR (CDCl₃) δ 107.44–118.48 (m, 4), 121.35 (×2), 128.35, 130.25 (×2), 149.89. Found: C, 31.87; H, 1.50%. Calcd for C₁₀H₃F₉O₃S: C, 31.93; H, 1.34%.

**3-hexylisocoumarin (8a) and (Z)-3-heptylideneephthalide (9a) (68:32):** IR (neat) 2929, 2857, 1782, 1733, 1658, 1484, 1161, 1024, 983, 759, 691 cm⁻¹; ¹H NMR (CDCl₃) δ 0.89 (t, J = 7.5 Hz, 3H), 1.24–1.74 (m, 8H), 2.47 (dt, J = 7.5, 7.5 Hz, 2×0.32H), 2.52 (t, J = 7.5 Hz, 2×0.68H), 5.64 (t, J = 7.5 Hz, 1×0.32H), 6.25 (s, 1×0.68H), 7.32–8.27 (m, 4H); ¹³C NMR (CDCl₃) δ 14.01, 14.05, 22.49, 22.56, 25.81, 26.85, 28.66, 28.96, 29.22, 31.48, 31.60, 33.51, 102.82, 109.76, 119.59, 120.10, 124.43, 124.98, 125.22, 127.49, 129.27, 129.48, 134.17, 134.67, 137.63, 139.58, 145.58, 158.33, 163.11, 167.21. Found: C, 78.13; H, 7.83%. Calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88%.

**3-cyclohexylisocoumarin (8b) and (Z)-3-cyclohexylmethylenephthalide (9b) (63:37):** IR (nujol) 1776, 1727, 1718, 1649 cm⁻¹; ¹H NMR (CDCl₃) δ 1.28–2.08 (m, 10H), 2.41–2.48 (m, 1×0.63H), 2.79–2.88 (m, 1×0.37H), 5.50 (d, J = 9.5 Hz, 1×0.37H), 6.23 (s, 1×0.63H), 7.34–8.27 (m, 4H);
$^{13}$C NMR (CDCl$_3$) $\delta$ 25.63, 25.86 ($\times 3$), 25.92 ($\times 2$), 30.56 ($\times 2$), 32.85 ($\times 2$), 35.28, 41.84, 100.85, 115.04, 119.64, 120.26, 124.37, 125.20, 125.22, 127.45, 129.27, 129.42, 134.15, 134.60, 137.74, 139.78, 144.16, 162.35, 163.12, 167.25. Found: C, 79.13; H, 7.20%. Calcd for C$_{15}$H$_{16}$O$_2$: C, 78.92; H, 7.06%. Mp 78.0–79.0 ºC.

Acknowledgment

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Government of Japan. M.U. acknowledges JSPS for financial support.

References and notes


5) The stereochemistry of 9 was determined by comparison with their closely related analogue.


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\[ \text{Cp}^*\text{Li} \text{ cat. } \text{Pd} \text{ THF, } \Delta \]

\[ \text{X} = \text{I, Br, OTf, ONf} \]