Cobalt-Catalysed [6+2] Cycloaddition of Internal Alkynes and Terminal Alkenes with Cycloheptatriene

Gerhard Hilt,* Anna Paul, Christoph Hengst
Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein Straße, 35043 Marburg, Germany
Fax +49(6421)2825677; E-mail: Hilt@chemie.uni-marburg.de
Received 12 May 2009

Abstract: The cobalt-catalysed [6+2] cycloaddition of cycloheptatriene with internal alkynes as well as with terminal alkenes is described. The cycloaddition process is most efficiently catalysed by cobalt dibromide[bis(triisopropylphosphite)] complexes in dichloromethane as the solvent of choice. In the cobalt-catalysed reaction of cycloheptatriene with norbornene an unexpected tricyclic [2+2] cycloaddition product was isolated in excellent yields.

Key words: alkyne, alkene, cobalt, cycloaddition, dienes

The application of cobalt complexes in cycloaddition reactions and other carbon–carbon bond formation processes is well documented.1 While the predominant application of cobalt catalysts lies in the formation of five-2 and six-membered-ring systems,3 recent reports describe the applications of cobalt catalysts for the formation of four-4 as well as eight-membered-ring systems.5 Only a few years ago Buono established a methodology for the first example of a cobalt-catalysed [6+2] cycloaddition process utilising cycloheptatriene6 (Scheme 1) as well as cyclooctatetraene or cyclooctatriene7 as starting materials in cobalt-catalysed cycloadditions applying mostly terminal alkynes such as phenylacetylene as starting materials.

Scheme 1 First cobalt-catalysed [6+2] cycloaddition reaction

Our own research led us primarily to an unprecedented cobalt-catalysed formation of an eight-membered ring system by a [4+2+2] cycloaddition process. Simultaneously we found a very reactive catalyst system, which performed the [6+2] cycloaddition as outlined in Scheme 1 when internal alkynes, such as hex-3-yne (Scheme 2), were used leading to the generation of bridged eight-membered cyclooctatriene derivatives of type 3.

As we have shown recently, cobalt phospine (or phosphite) based catalyst systems are of limited use for the [2+2+2] cyclotrimerisation of terminal as well as internal alkynes under reductive conditions.8 Accordingly, in the presence of a 1,3-diene or a cycloheptatriene as starting material a [4+2] or a [6+2] cycloaddition process becomes more favourable compared to the [2+2+2] cyclotrimerisation reaction pathway. In order to achieve further optimisation of the reaction and to minimise the amount of side products, a limited number of solvents and ligands were screened in the reaction of cycloheptatriene with hex-1-ene as test substrate to generate 5a (see Scheme 4; R = n-Bu). We chose this test system although in GCMS analysis three isomers (most likely: endo/exo-[6+2] cyclisation isomers of 5a and the hydrovinylation product) were detectable. Separation of these hydrocarbon molecules by column chromatography was very tedious with only limited success because of their highly unpolar nature.

In a brief survey of the solvents which had been most efficient over the course of our previous investigations concerning cobalt-catalysed reactions utilising trisopropyl phosphite as ligand, dichloromethane proved to be the solvent of choice resulting in a quantitative yield of 5a (>99%). Other solvents such as THF or acetonitrile gave inferior results. In the investigation concerning the applicable ligand in the reaction of cycloheptatriene with hex-1-ene for the formation of 5a, we focused mainly on ligand systems, which had been used successfully before in other investigations.3b,4a,5a Among these, diphosphine-type ligands such as bis-diphenylphosphinomethane (dppm) and 1,2-bis-diphenylphosphinoethane (dppe) were among the few successfully tested ligands yielding 5a in 51% and 76%, respectively, within 12 hours reaction time. Other bidentate diphenylphosphino-type ligands with a longer chain in between the two donor centres, such as dppp, dppb, dphp, and dppf were found to be unreactive under the present reaction conditions.8 Also, triphenylphosphine and triphenylarsine were unsuitable ligands in this transformation whereas 2-pyridylmethylidiphenylphosphine gave traces of the desired product 5a. Disulfide ligands such as ethylenediphenyl sulfide, a ligand

SYNTHESIS 2009, No. 19, pp 3305–3310
Advanced online publication: 10.07.2009
DOI: 10.1055/s-0029-1216900; Art ID: Z09709SS
© Georg Thieme Verlag Stuttgart · New York
type which proved to be very interesting in the [2+2+2] cyclotrimerisation reaction, or diimine-type ligands, such as bis-cyclohexylethlenedimine, or isopropyl-2-pyridin-2-ylmethylenamine gave no desired conversion to 5.

A selection of phosphite ligands were also tested in the conversion of cycloheptatriene with internal alkynes (according to Scheme 3). The results for the phosphite screening are summarised in Table 1.

Table 1 Cobalt-Catalysed [6+2] Cycloaddition of Internal Alkynes with Cycloheptatriene Utilising Phosphite Ligands

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>Ligand</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>P(OMe)_3</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>P(OEt)_3</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>P(Oi-Pr)_3</td>
<td>63</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>P(OMe)_3</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>P(OEt)_3</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>P(Oi-Pr)_3</td>
<td>63</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>P(OMe)_3</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>P(OEt)_3</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>P(Oi-Pr)_3</td>
<td>78</td>
</tr>
</tbody>
</table>

Table 2 Cobalt-Catalysed [6+2] Cycloaddition of Internal Alkynes with Cycloheptatriene

<table>
<thead>
<tr>
<th>Entry</th>
<th>R^1</th>
<th>R^2</th>
<th>Product 3</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Ph</td>
<td>3a</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>Et</td>
<td>3b</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>CH_3OMe</td>
<td>CH_3OMe</td>
<td>3c</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>CO_2Me</td>
<td>CO_2Me</td>
<td>3d</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>CH_3OTMS</td>
<td>3e</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>CH_3OTMS</td>
<td>3f</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>Me</td>
<td>CH_3OAc</td>
<td>3g</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>Et</td>
<td>Me</td>
<td>3h</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>Ph</td>
<td>Me</td>
<td>3i</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>Ph</td>
<td>Et</td>
<td>3j</td>
<td>36</td>
</tr>
<tr>
<td>11</td>
<td>Ph</td>
<td>CO_2Et</td>
<td>3k</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>Me</td>
<td>CO_2Et</td>
<td>3l</td>
<td>63</td>
</tr>
<tr>
<td>13</td>
<td>TMS</td>
<td>CO_2Et</td>
<td>3m</td>
<td>94</td>
</tr>
<tr>
<td>14</td>
<td>Ph</td>
<td>C=CPh</td>
<td>3n</td>
<td>10</td>
</tr>
</tbody>
</table>

Accordingly, transformations of internal alkynes 2 were performed with a catalyst system consisting of an in situ generated cobalt complex derived from CoBr_2 (5 mol%), the ligand P(Oi-Pr)_3 (10 mol%), zinc powder (10 mol%), and zinc iodide (10 mol%) in dichloromethane as solvent at ambient temperature for 12 hours (Scheme 3). The conversions of equimolar amounts of internal symmetrical as well as unsymmetrical alkynes 2 and cycloheptatriene (1.0 mmol scale) were conducted under these conditions for the formation of products of type 3 and the results are summarised in Table 2.

![Scheme 3](image)

Scheme 3 Cobalt-catalysed [6+2] cycloaddition of internal alkynes

The varying yields are mostly a reflection of the tendency of the alkyne to undergo a cobalt-catalysed cyclotrimerisation reaction. Generally, the cyclotrimerisation products can be purified by column chromatography on silica gel. Those substrates whose cyclotrimerisation tendency is small gave good to excellent yields. Sterically hindered alkynes such as 1,2-bis(trimethylsilyl)acetylene did not react under the present reaction conditions.

In an earlier study concerning cobalt-catalysed [4+2+2] cycloadditions, we found that the application of iron powder as additive gave the desired eight-membered products with increased chemoselectivity by reducing the amount of cyclotrimerisation by-products. In contrast to these reactions, the addition of iron powder in the present [6+2] cycloaddition reaction did not result in higher yields or increased chemoselectivity.

The application of terminal alkenes was also possible in the cobalt-catalysed [6+2] cycloaddition when isopropyl phosphite was used as ligand (Scheme 4). From the reaction of hex-1-ene, which was already mentioned above, besides the desired cycloadduct 5, also the side product 6 (R = Bu) of a cobalt-catalysed 1,4-hydrovinylation reaction could be isolated and characterised after tedious column chromatography in pure form.

![Scheme 4](image)

Scheme 4 Cobalt-catalysed [6+2] cycloaddition of terminal alkenes
Although many different alkenes were tested, only a few of them gave analytically pure compounds for a full characterisation. These results are summarised in Table 3.

Table 3 Cobalt-Catalysed [6+2] Cycloaddition of Terminal Alkenes with Cycloheptatriene

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Product 5</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bu</td>
<td>5a</td>
<td>99b</td>
</tr>
<tr>
<td>2</td>
<td>OBu</td>
<td>5b</td>
<td>83c</td>
</tr>
<tr>
<td>3</td>
<td>OAc</td>
<td>5c</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>CH₃N(Phth)</td>
<td>5d</td>
<td>99</td>
</tr>
</tbody>
</table>

a Alkene (1.0 mmol), cycloheptatriene (1.0 mmol), CoBr₂ (0.05 mmol), P(OiPr)₃ (0.10 mmol), Zn (0.10 mmol), ZnI₂ (0.10 mmol), CH₂Cl₂ (1 mL), 12 h, r.t.

b A mixture of four isomers was detected by GC/GCMS consisting of 57% 5a, 30% 5b, and two isomers in minor amounts.

c Mixture of four isomers. An analytically pure sample could not be isolated.

Besides the substrates shown in Table 3, silyl-protected allylic alcohols, allylbenzene derivatives, and allyl aryl ethers were also tested and in these cases mixtures of 3–5 isomers could be detected by GCMS analysis and isolated in 14–59% yields. The best results were obtained for vinyl ethers as well as for some terminal alkenes.

A rational for the other isomers detected by GCMS analysis, which were neither isolated nor characterised, was encountered when norbornene was used as starting material. Under these conditions out of many possible reaction pathways such as the herein described [6+2] cycloaddition, or a possible [4+2]/[2+2] cycloaddition, or a 1,4-hydroxylation reaction only a single product 8 was generated in excellent 96% yield. Two-dimensional NMR analysis and NOESY spectra revealed that product 8 was produced by a formal [2+2] cycloaddition as a single stereoisomer.

![Scheme 5 Cobalt-catalysed [2+2] cycloaddition of cycloheptatriene with norbornene](image)

In summary, we were able to demonstrate that internal alkenes are accepted substrates for the cobalt-catalysed [6+2] cycloaddition when phosphate ligands are used. On the other hand, the application of alkenes is limited to a few acceptable starting materials producing up to five isomers. Finally, the reaction of norbornene with cycloheptatriene gave a [2+2] cycloaddition tricyclic hydrocarbon product in excellent yields.

All reactions were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques in flame-dried glassware. CH₂Cl₂ was distilled over P₂O₅, MeCN over CaH₂, and THF over sodium/benzophenone. ZnI₂ was dried in vacuo at 150 °C prior to use. Commercially available materials were used without further purification. NMR spectra were recorded on Bruker Avance 300 or DRX 500 (¹H: 300 MHz or 500 MHz, ¹C: 75 MHz or 125 MHz) spectrometers using TMS as internal standard (δ = 0 ppm) unless otherwise noted. IR spectra were recorded on a Bruker IFS 200 Infraperomenter or a Nicolet Magna IR 750 spectrometer. MS and GC/MS spectra were measured on a Hewlett Packard 6890 GC system including a Hewlett Packard 5973 mass selective detector. For (high-resolution) mass spectra, a Finnigan MAT 95S and a Finnigan LTQ (ESI, HRMS) spectrometer were used. Analytical thin-layer chromatography was performed on Merck silica gel 60 F254. For column chromatography, Merck silica gel 60 (230–400 mesh ASTM) was used.

7.8-Diphenylbicyclo[4.2.1]nona-2,4,7-triene (3a): Typical Procedure

To a suspension of CoBr₂ (22 mg, 0.1 mmol, 5 mol%), P(OiPr)₃ (21 mg, 0.2 mmol, 10 mol%), Zn powder (13 mg, 0.2 mmol, 20 mol%), and ZnI₂ (64 mg, 0.2 mmol, 20 mol%) in CH₂Cl₂ (1.0 mL) were added cycloheptatriene (92 mg, 1.0 mmol, 1.0 equiv) and diphenylacetylene (178 mg, 1.0 mmol, 1.0 equiv) under argon. The reaction mixture was stirred at rt for 12 h. The reaction mixture was passed through a pad of silica using pentane–Et₂O (10:1) as eluent. The solvents were removed and the crude product was purified by flash chromatography using pentane–Et₂O as eluent.

1H NMR (300 MHz, CDCl₃) δ = 7.42–7.28 (m, 10 H), 6.50–6.40 (m, 2 H), 6.12–6.04 (m, 2 H), 3.85–3.77 (m, 2 H), 2.82–2.70 (m, 1 H), 2.04–1.96 (m, 1 H).

13C NMR (75 MHz, CDCl₃) δ = 139.3, 136.8, 136.1, 129.2, 128.1, 126.6, 124.8, 49.4, 30.6.

MS (EI): m/z (%) = 270 (100, M⁺), 255 (26), 239 (16), 192 (25), 178 (41), 165 (18), 115 (17), 91 (16).

7.8-Diethylbicyclo[4.2.1]nona-2,4,7-triene (3b)

1H NMR (300 MHz, CDCl₃) δ = 6.24–6.14 (m, 2 H), 5.77–5.69 (m, 2 H), 3.11 (t, J = 6.9 Hz, 2 H), 2.22–1.98 (m, 6 H), 1.02 (t, J = 7.6 Hz, 6 H).

13C NMR (75 MHz, CDCl₃) δ = 140.5, 136.2, 123.8, 46.2, 31.1, 19.3, 14.6.

MS (EI): m/z (%) = 174 (M⁺, 47), 145 (100), 129 (18), 117 (75), 115 (25), 105 (24), 91 (35).

7.8-Bis(methoxymethyl)bicyclo[4.2.1]nona-2,4,7-triene (3c)

IR (KBr): 3017, 2925, 2817, 1672, 1452, 1377, 1164, 1099, 958, 910, 798, 695 cm⁻¹.

1H NMR (300 MHz, CDCl₃) δ = 6.16 (dt, J = 3.3, 8.0 Hz, 2 H), 5.77 (qd, J = 3.6, 7.0 Hz, 2 H), 4.12 (d, J = 12.2 Hz, 2 H), 3.90 (d, J = 12.3 Hz, 2 H), 3.34–3.27 (m, 2 H), 3.25 (s, 6 H), 2.25–2.15 (m, 1 H), 1.38 (d, J = 11.4 Hz, 1 H).

13C NMR (75 MHz, CDCl₃) δ = 139.5, 135.3, 124.5, 66.1, 57.8, 45.3, 30.1.

MS (EI): m/z (%) = 206 (M⁺, 14), 174 (59), 159 (21), 142 (33), 129 (100), 115 (50), 91 (46).

HRMS: m/z calcd for C₂₅H₂₅O₂: 206.1297; found: 206.1296.

Dimethyl Bicyclo[4.2.1]nona-2,4,7-triene-7,8-dicarboxylate (3d)

1H NMR (300 MHz, CDCl₃) δ = 6.19–6.11 (m, 2 H), 6.00–5.92 (m, 2 H), 3.74 (s, 6 H), 3.54 (t, J = 6.9 Hz, 2 H), 2.36–2.26 (m, 1 H), 1.60 (d, J = 11.8 Hz, 1 H).

Synthesis 2009, No. 19, 3305–3310 © Thieme Stuttgart · New York
Trimethyl[8-phenylbicyclo[4.2.1]nona-2,4,7-trien-7-yl]methoxy)silane (3e)

1H NMR (300 MHz, CDCl3): δ = 7.33–7.19 (m, 5 H), 6.76–7.14 (m, 2 H), 5.88–5.77 (m, 2 H), 4.40 (d, J = 12.7 Hz, 1 H), 4.15 (d, J = 7.1 Hz, 1 H), 3.57 (t, J = 7.1 Hz, 1 H), 3.50 (t, J = 7.0 Hz, 1 H), 2.46–2.38 (m, 1 H), 1.69 (d, J = 11.4 Hz, 1 H), 0.07 (s, 9 H).

13C NMR (75 MHz, CDCl3): δ 139.6, 136.3, 136.0, 135.7, 129.1, 128.0, 126.8, 124.5, 124.4, 57.1, 48.6, 44.9, 30.3, −0.4.

MS (EI): m/z (%) = 296 (M+, 52), 281 (6), 268 (2), 255 (3), 242 (22), 229 (3), 218 (3), 205 (44), 191 (33), 178 (29), 165 (37), 155 (12), 142 (4), 129 (22), 115 (29), 103 (13), 91 (43), 73 (100), 65 (4).

HRMS (EI): m/z calcd for C18H28O3Si: 296.1596; found: 296.1581.

Trimethyl[8-methylbicyclo[4.2.1]nona-2,4,7-trien-7-yl]methoxy)silane (3f)

1H NMR (300 MHz, CDCl3): δ = 2.89–2.76 (m, 2 H), 2.59–2.48 (m, 2 H), 2.00–1.84 (m, 1 H), 1.70–1.58 (m, 1 H), 1.53–1.45 (m, 1 H), 0.85 (t, J = 7.2 Hz, 3 H), 0.02 (s, 9 H).

13C NMR (75 MHz, CDCl3): δ 139.2, 136.5, 135.7, 135.3, 129.4, 123.9, 122.6, 121.5, 120.4, 65.5, 49.1, 44.2, 30.1, 11.2, −0.4.

MS (EI): m/z (%) = 234 (M+, 11), 219 (6), 193 (2), 180 (4), 155 (4), 143 (21), 129 (80), 115 (17), 103 (9), 23 (100), 65 (5).

HRMS (EI): m/z calcd for C12H18O3Si: 234.1440; found: 234.1442.

1H NMR (300 MHz, CDCl3): δ = 7.31–7.15 (m, 5 H), 6.26–6.16 (m, 2 H), 5.84–5.75 (m, 2 H), 3.42 (t, J = 6.9 Hz, 1 H), 3.11 (t, J = 6.9 Hz, 1 H), 2.40–2.11 (m, 3 H), 1.68 (d, J = 11.2 Hz, 1 H), 1.07 (dt, J = 1.3, 7.5 Hz, 3 H).

13C NMR (75 MHz, CDCl3): δ = 140.2, 139.5, 139.4, 137.2, 134.4, 128.9, 127.9, 126.2, 124.3, 48.4, 46.7, 30.8, 20.1, 14.3.

HRMS (EI): m/z calcd for C17H16O3: 222.1409; found: 222.1408.

Ethyl 8-Phenylbicyclo[4.2.1]nona-2,4,7-triene-7-carboxylate (3k)

HRMS (EI): m/z calcd for C19H17O3: 221.1307; found: 221.1307.

7-Ethyl-8-bicyclo[4.2.1]nona-2,4,7-triene-7-carboxylate (3j)

HRMS (EI): m/z calcd for C19H17O3: 221.1307; found: 221.1307.

7-Methyl-8-bicyclo[4.2.1]nona-2,4,7-triene-7-carboxylate (3i)


7-Methyl-8-bicyclo[4.2.1]nona-2,4,7-triene (3i)

IR (film): 3053, 3017, 2925, 2854, 1948, 1717, 1681, 1598, 1492, 1442, 1376, 1319, 1217, 1175, 1031, 975, 913, 838, 761 cm−1.

1H NMR (300 MHz, CDCl3): δ = 7.31–7.10 (m, 4 H), 7.23–7.16 (m, 1 H), 6.31–6.22 (m, 2 H), 5.87–5.76 (m, 2 H), 3.46 (t, J = 6.9 Hz, 1 H), 3.19 (t, J = 7.0 Hz, 1 H), 2.44–2.35 (m, 1 H), 1.87 (s, 3 H), 1.69 (d, J = 11.2 Hz, 1 H).

13C NMR (75 MHz, CDCl3): δ = 140.7, 139.2, 137.0, 134.9, 133.0, 128.8, 127.9, 126.1, 124.6, 124.0, 49.9, 48.2, 30.5, 12.8.

MS (EI): m/z (%) = 208 (M+, 100), 193 (97), 178 (80), 165 (42), 152 (13), 139 (4), 129 (12), 115 (48), 103 (4), 91 (25), 82 (3), 77 (7), 65 (5).

HRMS (EI): m/z calcd for C16H16O3: 208.1252; found: 208.1267.
Trimethyl[8-(trimethylsilyl)bicyclo[4.2.1]nona-2,4,7-trien-7-yl]ethynylsilane (3m)

1H NMR (300 MHz, CDCl3): δ = 6.09–6.11 (m, 1 H), 5.49–5.50 (m, 3 H), 5.27 (d, J = 11.5, 0.8 Hz, 1 H), 5.64 (dd, J = 11.0, 7.1 Hz, 1 H), 5.05 (dd, J = 6.6, 2.4 Hz, 1 H), 2.79 (q, J = 8.5 Hz, 1 H), 2.65 (t, J = 6.9 Hz, 1 H), 2.29–2.13 (m, 2 H), 1.99 (s, 3 H, CH3), 2.00–1.90 (m, 1 H), 1.69 (d, J = 12.2 Hz, 1 H).

13C NMR (75 MHz, CDCl3): δ = 170.3, 139.5, 133.0, 125.7, 123.3, 84.3, 46.5, 45.2, 37.3, 29.9, 21.3.

MS (EI): m/z = 178 (M⁺, 19), 136 (3), 117 (60), 103 (6), 92 (100), 77 (13).

HRMS (EI): m/z calcd for C₁₇H₂₈O₃: 286.0949; found: 286.0949.

7-Phenyl-8-(phenylethynyl)bicyclo[4.2.1]nona-2,4,7-triene (3n)
IR (film): 3054, 2919, 2848, 2192, 1948, 1626, 1592, 1474, 1462, 1442, 1384, 1331, 1215, 1102, 1069, 1013, 912, 879, 845, 756 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 6.61–6.63 (m, 2 H), 7.38–7.29 (m, 6 H), 6.41–6.27 (m, 2 H), 5.95–5.88 (m, 2 H), 3.82 (t, J = 7.0 Hz, 1 H), 3.53 (t, J = 7.1 Hz, 1 H), 2.53–2.44 (m, 1 H), 1.81 (d, J = 11.5 Hz, 1 H).

13C NMR (75 MHz, CDCl3): δ = 143.1, 139.0, 138.4, 134.5, 131.4, 128.3, 128.2, 128.1, 128.0, 127.6, 124.3, 121.6, 115.6, 93.6, 87.1, 49.2, 46.4, 30.1.

MS (EI): m/z (%) = 294 (M⁺, 100), 278 (20), 265 (13), 252 (15), 239 (6), 226 (3), 215 (47), 202 (33), 189 (7), 178 (5), 165 (6), 152 (2), 139 (7), 126 (5), 115 (6), 91 (7), 77 (2).


Bicyclo[4.2.1]nona-2,4,7-trien-7-yl acetate (5b)
IR (KBr): 3021, 2938, 1736, 1436, 1374, 1242, 1025, 703, 608 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 6.06 (d, J = 10.6, 8.6 Hz, 1 H), 5.94 (dd, J = 11.4, 7.9 Hz, 1 H), 5.77 (d, J = 11.5, 0.8 Hz, 1 H), 5.64 (dd, J = 11.0, 7.1 Hz, 1 H), 5.05 (dd, J = 6.6, 2.4 Hz, 1 H), 2.79 (q, J = 8.5 Hz, 1 H), 2.65 (t, J = 6.9 Hz, 1 H), 2.29–2.13 (m, 2 H), 1.99 (s, 3 H, CH3), 2.00–1.90 (m, 1 H), 1.69 (d, J = 12.2 Hz, 1 H).

13C NMR (75 MHz, CDCl3): δ = 170.3, 139.5, 133.0, 125.7, 123.3, 84.3, 46.5, 45.2, 37.3, 29.9, 21.3.

MS (EI): m/z (%) = 178 (M⁺, 19), 136 (3), 117 (60), 103 (6), 92 (100), 77 (13).

HRMS (EI): m/z calcd for C₁₇H₂₈O₃: 286.0949; found: 286.0949.

References


(2) For recent reviews covering the Pauson–Khand reaction, see: (a) Omae, I. Appl. Organomet. Chem. 2009, 23, 91.


(d) Doszczak, L.; Fey, P.; Tacke, R. Synlett 2007, 753.


(8) dppp: 1,3-bis(diphenylphosphino)propane;
dppb: 1,4-bis(diphenylphosphino)butane;
dpph: 1,6-bis(diphenylphosphino)hexane;
dppf: 1,1’-bis(diphenylphosphino)ferrocene.