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Rhodium-Catalyzed 1,3-Acyl Migration Reaction of Acetylenic β-Keto Esters with Arylboronic Acids and Application to Two-Carbon Ring Expansion

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General. All reactions were carried out with standard Schlenk techniques under a nitrogen atmosphere. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300.07 MHz and ^{13}C at 75.46 MHz) spectrometer. All NMR data were obtained in $CDCl_3$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm. High-resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer.

Materials. Hydroxo(cycloocta-1,5-diene)rhodium(I) dimer[1] was prepared according to the literature procedure. 1,4-Dioxane was distilled over sodium–benzophenone ketyl. Water was degassed prior to use. All other commercially available resources were used without further purification. Acetylenic β-keto esters **1a–1d** and **5a–5g** were prepared from the corresponding β-keto esters and various propargyl bromides in the presence of NaH in THF. Ethyl 2-methyl-3-oxo-3-phenylpropanoate,[2] 2-ethoxycarbonyl-1-indanone,[3] 2-ethoxycarbonyl-1-tetralone,[4] and 2-methylindane-1,3-dione[5] were synthesized according to the corresponding literature methods. Ethyl 2-methylacetoacetate, ethyl 2-oxocyclohexanecarboxylate, ethyl 2-oxocyclooctanecarboxylate, 4-fluorophenylboronic acid, and 3-chlorophenylboronic acid were purchased from Aldrich Chemical Co. Ethyl 2-oxocyclopentanecarboxylate, 2-methylcyclohexane-1,3-dione, 1-bromo-2-butyne, 3-bromo-1-(trimethylsilyl)-1-propyne, 4-methylphenylboronic acid, and 3-methoxyphenylboronic acid were purchased from Tokyo Kasei Kogyo Co., Ltd. 1-Bromo-2-pentyne and phenylboronic acid were purchased from Wako Pure Chemical Industries, Ltd.

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General procedure for the rhodium-catalyzed 1,3-acyl migration reaction. To an oven-dried, N_2-purged flask were added a solution of substrate **1** or **5** (0.20 mmol, 1.0 equiv) in 1,4-dioxane/H_2O [2.0 mL/20 mL (100:1)], arylboronic acid **2** (2.0–5.0 equiv), and $[Rh(OH)(cod)]_2$ (2.3 mg, 0.005 mmol, 0.05 equiv of Rh). The reaction mixture was stirred at room temperature. After complete consumption of the substrate (3–12 h), the reaction was quenched with aq. NH_4Cl. Then, the resulting solution was stirred at room temperature overnight. The aqueous layer was extracted with ethyl acetate three times. The combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product **4** or **6**.

The ring-opening of **5c**, **5d** and **5f** required 3 weeks for completion.

Ethyl 2-hydroxy-1-methyl-2-phenyl-3-[(*Z*)-1-phenylethylidene]cyclobutane-1-carboxylate (**3**). This compound is unstable. Only ^{1}H NMR data are shown here: ^{1}H NMR: δ = 0.89 (t, *J* = 7.1 Hz, 3H), 1.48 (s, 3H), 2.09 (s, 3H), 2.19 (s, 1H), 2.42 (dq, *J* = 15.8, 1.1 Hz, 1H), 3.36 (dq, *J* = 15.6, 1.5 Hz, 1H), 3.49–3.70 (m, 2H), 7.12–7.63 (m, 10H).

Ethyl (*Z*)-4-benzoyl-2-methyl-5-phenylhex-4-enoate (**4aa**). IR (neat): 2980, 1732, 1651, 1449, 1246, 1183 cm^{-1}; ^{1}H NMR: δ = 1.21 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 2.26 (s, 3H), 2.59–2.77 (m, 2H), 2.92–3.05 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 6.91–7.06 (m, 5H), 7.10–7.18 (m, 2H), 7.22–7.29 (m, 1H), 7.57–7.63 (m, 2H); ^{13}C NMR: δ = 14.2, 17.7, 20.9, 35.6, 38.9, 60.4, 127.3, 127.7, 127.8, 128.2, 129.2, 132.1, 135.2, 137.5, 141.3, 142.6, 176.1, 200.6; HRMS (CI$^+$): Calcd for $C_{22}H_{25}O_3$, M+H$^+$ 337.1804. Found m/z 337.1804.

Ethyl (*Z*)-4-benzoyl-2-methyl-5-(4-fluorophenyl)hex-4-enoate (**4ab**). IR (neat): 2980, 1732, 1651, 1509, 1227, 1183 cm^{-1}; ^{1}H NMR: δ = 1.20 (t, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 6.6 Hz, 3H), 2.23 (s, 3H), 2.57–2.75 (m, 2H), 2.90–3.03 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 6.65–6,74 (m, 2H), 6.95–7.03 (m, 2H), 7.13–7.21 (m, 2H), 7.26–7.34 (m, 1H), 7.56–7.62 (m, 2H); ^{13}C NMR: δ = 14.1, 17.7, 20.9, 35.5, 38.8, 60.4, 114.7 (d, *J* = 20.9 Hz), 127.8, 129.1, 129.9 (d, *J* = 8.1 Hz), 132.3, 135.6, 137.2, 138.5 (d, *J* = 3.5 Hz), 140.0, 161.7 (d, *J* = 247.1 Hz), 176.0, 200.5; HRMS (CI$^+$): Calcd for $C_{22}H_{24}FO_3$, M+H$^+$ 355.1709. Found m/z 355.1708.

Ethyl (*Z*)-4-benzoyl-2-methyl-5-(4-methylphenyl)hex-4-enoate (4ac). IR (neat): 2980, 1732, 1653, 1449, 1248, 1183 cm^{-1}; ^{1}H NMR: δ = 1.20 (t, *J* = 7.1 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 3H), 2.12 (s, 3H), 2.23 (s, 3H), 2.57–2.75 (m, 2H), 2.91–3.03 (m, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 6.81 (d, *J* =

7.8 Hz, 2H), 6.88–6.96 (m, 2H), 7.12–7.20 (m, 2H) 7.23–7.32 (m, 1H), 7.58–7.64 (m, 2H); ^{13}C NMR: δ = 14.1, 17.6, 20.9, 21.0, 35.6, 38.8, 60.4, 127.6, 128.1, 128.5, 129.2, 132.0, 134.7, 137.0, 137.4, 139.6, 141.3, 176.1, 200.8; HRMS (CI$^+$): Calcd for $C_{23}H_{27}O_3$, M+H$^+$ 351.1960. Found m/z 351.1959.

Ethyl (*Z*)-4-benzoyl-2-methyl-5-(3-chlorophenyl)hex-4-enoate (**4ad**). IR (neat): 2980, 1732, 1653, 1449, 1242, 1183 cm^{-1}; ^{1}H NMR: δ = 1.21 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 7.2 Hz, 3H), 2.23 (s, 3H), 2.58–2.76 (m, 2H), 2.92–3.03 (m, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 6.86–6.94 (m, 3H), 6.99–7.03 (m, 1H), 7.14–7.22 (m, 2H) 7.25–7.34 (m, 1H), 7.54–7.62 (m, 2H); ^{13}C NMR: δ = 14.1, 17.7, 20.7, 35.5, 38.7, 60.5, 126.4, 127.3, 127.8, 128.2, 129.0, 129.1, 132.3, 133.6, 136.3, 137.2, 139.7, 144.2, 175.9, 200.2; HRMS (CI$^+$): Calcd for $C_{22}H_{24}ClO_3$, M+H$^+$ 371.1414. Found m/z 371.1412.

Ethyl (*Z*)-4-benzoyl-2-methyl-5-(3-methoxyphenyl)hex-4-enoate (**4ae**). IR (neat): 2980, 1730, 1656, 1578, 1221, 1179 cm^{-1}; ^{1}H NMR: δ = 1.21 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 2.24 (s, 3H), 2.58–2.71 (m, 2H), 2.92–3.03 (m, 1H), 3.63 (s, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 6.50 (ddd, *J* = 8.2, 2.8, 1.0 Hz, 1H), 6.54–6.58 (m, 1H), 6.63 (ddd, *J* = 7.8, 1.5, 0.9 Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 7.13–7.21 (m, 2H), 7.24–7.32 (m, 1H), 7.58–7.64 (m, 2H); ^{13}C NMR: δ = 14.1, 17.6, 20.7, 35.5, 38.8, 55.1, 60.4, 113.2, 113.6, 120.8, 127.6, 128.9, 129.0, 132.1, 135.2, 137.3, 141.0, 143.8, 158.8, 176.0, 200.6; HRMS (CI$^+$): Calcd for $C_{23}H_{27}O_4$, M+H$^+$ 367.1909. Found m/z 367.1910.

Ethyl (*Z*)-4-benzoyl-2-methyl-5-phenylhept-4-enoate (**4ba**). IR (neat): 2977, 1732, 1651, 1449, 1238, 1183 cm^{-1}; ^{1}H NMR: δ = 0.94 (t, *J* = 7.5 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 2.49–2.66 (m, 2H), 2.67–2.82 (m, 2H), 3.00 (dd, *J* = 14.1, 7.8 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 6.90–7.04 (m, 5H), 7.10–7.19 (m, 2H) 7.21–7.30 (m, 1H), 7.56–7.63 (m, 2H); ^{13}C NMR: δ = 12.7, 14.1, 17.7, 27.2, 34.7, 38.8, 60.4, 127.2, 127.6, 127.7, 128.9, 129.1, 132.0, 134.5, 137.6, 140.8, 147.3, 176.0, 200.6; HRMS (CI$^+$): Calcd for $C_{23}H_{27}O_3$, M+H$^+$ 351.1960. Found m/z 351.1959.

Ethyl (*Z*)-4-acetyl-2-methyl-5-phenylhept-4-enoate (**4ca**). IR (neat): 2979, 1732, 1676, 1352, 1177, 1121 cm^{-1}; ^{1}H NMR: δ = 0.87 (t, *J* = 7.7 Hz, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.58 (s, 3H), 2.36–2.69 (m, 4H), 2.78 (dd, *J* = 13.7, 8.6 Hz, 1H), 4.08–4.19 (m, 2H), 7.09–7.15 (m, 2H), 7.28–7.34 (m, 3H); ^{13}C NMR: δ = 12.5, 14.3, 17.2, 27.9, 31.3, 34.2, 38.8, 60.4, 128.0, 128.4, 128.5, 138.0, 141.4, 148.0, 176.0, 207.3; HRMS (EI$^+$): Calcd for $C_{18}H_{24}O_3$, M$^+$ 288.1725. Found m/z 288.1723.

Ethyl (*E*)-4-benzoyl-2-methyl-5-phenyl-5-trimethylsilylpent-4-enoate (**4da**). IR (neat): 2980, 1732, 1664, 1449, 1250, 1183 cm^{-1}; ^1H NMR: δ = 0.20 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 6.9 Hz, 3H), 2.49–2.63 (m, 1H), 2.68 (dd, *J* = 14.4, 6.9 Hz, 1H), 2.79 (dd, *J* = 14.1, 7.5 Hz, 1H), 3.97–4.08 (m, 2H), 6.72–6.79 (m, 2H), 6.84–7.00 (m, 3H), 7.19–7.28 (m, 2H), 7.32–7.39 (m, 1H), 7.61–7.67 (m, 2H); ^{13}C NMR: δ = 0.7, 14.1, 17.7, 37.4, 38.3, 60.4, 125.6, 127.4, 127.9, 128.2, 129.1, 132.5, 136.6, 142.1, 145.6, 149.6, 175.7, 200.0; HRMS (CI^+): Calcd for $C_{24}H_{31}O_3Si$, $M+H^+$ 395.2042. Found m/z 395.2044.

Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cycloheptane-1-carboxylate (**6a**). IR (nujol): 2924, 1725, 1684, 1161, 1102 cm^{-1}; ^1H NMR: δ = 1.29 (t, *J* = 7.1 Hz, 3H), 1.63–1.86 (m, 2H), 1.92–2.09 (m, 1H), 2.10 (s, 3H), 2.16–2.52 (m, 4H), 2.54–2.67 (m, 1H), 2.97 (d, *J* = 14.7 Hz, 1H), 4.18 (q, *J* = 6.9 Hz, 2H), 7.05–7.12 (m, 2H), 7.18–7.33 (m, 3H); ^{13}C NMR: δ = 14.2, 20.8, 22.5, 31.5, 32.6, 42.8, 45.3, 60.7, 126.95, 127.05, 128.1, 137.2, 140.1, 142.9, 174.8, 208.7; HRMS (EI^+): Calcd for $C_{18}H_{22}O_3$, M^+ 286.1569. Found m/z 286.1569.

Ethyl 9-oxo-8-[(*Z*)-1-phenylethylidene]-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate (**6b**). IR (nujol): 2924, 1732, 1663, 1595, 1186, 1159 cm^{-1}; ^1H NMR: δ = 1.30 (t, *J* = 7.2 Hz, 3H), 2.22 (s, 3H), 2.65 (dd, *J* = 14.7, 8.4 Hz, 1H), 2.95 (dd, *J* = 14.6, 7.4 Hz, 1H), 3.08–3.19 (m, 1H), 3.27–3.42 (m, 2H), 4.10–4.27 (m, 2H), 7.10–7.17 (m, 2H), 7.23–7.35 (m, 5H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H); ^{13}C NMR: δ = 14.3, 22.5, 28.6, 33.9, 41.9, 60.9, 127.1, 127.4, 128.2, 129.7, 130.7, 132.7, 134.5, 137.4, 137.8, 143.7, 147.2, 173.8, 195.7 (1 carbon overlapping); HRMS (EI^+): Calcd for $C_{22}H_{22}O_3$, M^+ 334.1569. Found m/z 334.1567.

Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cyclooctane-1-carboxylate (**6c**). IR (neat): 2938, 1732, 1684, 1443, 1179, 1028 cm^{-1}; ^1H NMR: δ = 1.27 (t, *J* = 7.2 Hz, 3H), 1.35–1.89 (m, 7H), 1.92–2.06 (m, 1H), 2.15 (s, 3H), 2.34–2.48 (m, 1H), 2.60 (dd, *J* = 13.8, 11.7 Hz, 1H), 2.93 (dd, *J* = 13.8, 3.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 7.11–7.19 (m, 2H), 7.21–7.33 (m, 3H); ^{13}C NMR: δ =14.3, 19.9, 24.4, 27.2, 29.7, 35.1, 43.1, 43.3, 60.6, 127.6, 127.7, 128.4, 135.8, 137.6, 142.5, 175.5, 215.4; HRMS (EI^+): Calcd for $C_{19}H_{24}O_3$, M^+ 300.1725. Found m/z 300.1723.

Ethyl 5,6,7,8,9,10-hexahydro-10-oxo-9-[(*Z*)-1-phenylethylidene]benzo[8]annulene-7-carboxylate (**6d**). IR (neat): 2936, 1732, 1653, 1597, 1445, 1240, 1184 cm^{-1}; ^1H NMR: δ = 1.22 (t, *J* = 7.2 Hz, 3H), 1.94–2.07 (m, 1H), 2.09–2.23 (m, 1H), 2.20 (d, *J* = 1.5 Hz, 3H), 2.66 (tdd, *J* = 12.0, 4.1, 2.9 Hz, 1H), 2.80 (dd, *J* = 14.9, 12.2 Hz, 1H), 2.89–2.98 (m, 1H), 3.02 (td, *J* = 14.7, 4.2 Hz,

1H), 3.65 (ddd, *J* = 14.3, 11.9, 4.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 6.96–7.05 (m, 2H), 7.08–7.23 (m, 5H), 7.40 (td, *J* = 7.4, 1.5 Hz, 1H), 7.69 (dd, *J* = 7.7, 1.4 Hz, 1H); ^{13}C NMR: δ = 14.2, 21.0, 31.8, 32.0, 32.1, 40.8, 60.7, 126.8, 126.9, 127.2, 128.0, 129.3, 131.3, 133.1, 136.2, 138.0, 138.9, 140.9, 142.7, 175.0, 199.8; HRMS (EI$^+$): Calcd for $C_{23}H_{24}O_3$, M^+ 348.1725. Found m/z 348.1725.

Ethyl 4-oxo-3-[(*Z*)-1-phenylethylidene]cyclodecane-1-carboxylate (**6e**). IR (neat): 2934, 1732, 1667, 1445, 1177, 1034 cm^{-1}; ^{1}H NMR: δ = 1.15–1.85 (m, 12H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.16 (s, 3H), 2.60–2.78 (m, 2H), 2.82–2.96 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.11–7.20 (m, 2H), 7.26–7.35 (m, 3H); ^{13}C NMR: δ = 14.3, 21.7, 22.6, 24.5, 26.6, 30.1, 31,9, 42.4, 43.4, 60.5, 128.1, 128.4, 140.8 142.2, 143.2, 176.1, 212.6 (2 carbon overlapping); HRMS (EI$^+$): Calcd for $C_{21}H_{28}O_3$, M^+ 328.2038. Found m/z 328.2039.

2-Methyl-4-[(*Z*)-1-phenylethylidene]cyclooctane-1,5-dione (**6f**). IR (nujol): 1700, 1671, 1367, 1306, 1125, 1073 cm^{-1}; ^{1}H NMR: δ = 1.12 (d, *J* = 6.3 Hz, 3H), 1.84–2.01 (m, 4H), 2.16 (s, 3H), 2.22–2.35 (m, 1H), 2.41–2.58 (m, 2H), 2.71 (dd, *J* = 13.4, 4.7 Hz, 1H), 2.93–3.07 (m, 1H), 7.12–7.19 (m, 2H), 7.25–7.33 (m, 3H); ^{13}C NMR: δ = 16.8, 19.8, 22.7, 38.4, 43.46, 43.51, 44.7, 127.7, 128.0, 128.5, 137.3, 138.1, 142.0, 213.0, 216.3; HRMS (EI$^+$): Calcd for $C_{17}H_{20}O_2$, M^+ 256.1463. Found m/z 256.1464.

5,9-Dioxo-6-methyl-8-[(*Z*)-1-phenylethylidene]-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (**6g**). IR (neat): 2975, 1682, 1592, 1443, 1375, 1240 cm^{-1}; ^{1}H NMR: δ = 1.31 (d, *J* = 6.6 Hz, 3H), 2.11 (s, 3H), 2.48 (dd, *J* = 14.9, 11.6 Hz, 1H), 2.88 (ddd, *J* = 15.3, 5.4, 0.9 Hz, 1H), 3.15–3.30 (m, 1H), 6.91–6.98 (m, 2H), 7.17–7.25 (m, 3H), 7.51–7.66 (m, 3H), 7.68–7.72 (m, 1H); ^{13}C NMR: δ = 17.2, 21.5, 32.1, 45.8, 127.2, 128.1, 128.3, 128.4, 131.9, 132.3, 136.0, 137.8, 138.2, 142.4, 143.4, 197.0, 205.3; HRMS (EI$^+$): Calcd for $C_{20}H_{18}O_2$, M^+ 290.1307. Found m/z 290.1306.