Stereoselective Bis-Functionalization of Arene Chromium Tricarbonyl Complexes Via Brook Rearrangements

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Supporting Information

General Procedures. The 300-MHz ^{1}H NMR and 75.5-MHz ^{13}C NMR sprecta were obtained on a GE/Bruker QE 300 FT-NMR spectrometer. Chemical shifts are reported in ppm relative to $(CH_3)_4Si$ (0 ppm, ^{1}H) or $CDCl_3$ (77.0 ppm, ^{13}C). IR spectra were obtained on a Nicolet 5DXB FT-IR spectrometer. High resolution mass spectral analyses were performed at the Mass Spectroscopy Center at Purdue University, West Lafayette, IN. The crude reaction mixtures were purified by flash column chromatography with silica gel obtained from Silicycle, Inc.

Materials. Allyl bromide, benzyl bromide, phenyl disulfide, 1,2-dibromo-tetrafluoroethane, benzaldehyde, and iodomethane were purchased from Aldrich Chemical Company and used as received. Benzophenone was purchased from Acros Chemicals and used as received. Tetrahydrofuran was purchased from Fisher Scientific, and distilled from the sodium benzophenone ketyl radical prior to use. Hexamethylphosphoric triamide (HMPA) was purchased from Aldrich Chemical Company and distilled from calcium hydride prior to use. Hexanes and ethyl acetate were purchased from Fisher Scientific and used as received. Arene complex **1** was prepared according to literature procedure.[1]

General Procedure for the Bis-alkylation of Arene Complexes: A degassed solution of arene complex **1** in THF was cooled to –78 °C under argon atmosphere. Methyllithium (1.2 equiv) was added dropwise via syringe, resulting in an immediate color change from red to pale yellow. After stirring at –78 °C for 45 min, the electrophile was added (liquids were added neat via syringe, solids were added via cannula as a solution in THF). The resultant solution was maintained at –78 °C for 1h, then warmed to room temperature over 3h. The reaction was then quenched by addition of H_2O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with aqueous brine solution, dried over $MgSO_4$, filtered, and the solvents were removed under reduced pressure. The products were purified by flash chromatography (silica gel, 19/1 hexane/EtOAc eluent system).

Arene Complex 4b. Arene complex **1** (60 mg, 0.19 mmol) and allyl bromide (0.17 mL, 1.9 mmol) were reacted according to the general procedure to afford arene complex **4b** as an orange oil (41 mg, 58% yield) and arene complex **4a** as an orange oil (23 mg, 36%

yield). Arene complex **4a**: IR (neat) ν 3087, 2959, 2899, 1965, 1884, 1253, 1119, 953, 845 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 5.58 (m, 1H), 5.33-5.21 (m, 4H), 4.55 (q, J = 6.6 Hz, 1H), 1.39 (d, J = 6.6 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR (CDCl$_3$) δ 233.0, 116.7, 92.9, 91.4, 91.3, 91.0, 68.3, 26.4, 0.2. Arene complex **4b**: IR (neat) ν 3084, 2959, 2901, 1962, 1894, 1640, 1446, 1253, 1097, 955, 845 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 5.95-5.80 (m, 1H), 5.77 (d, J = 6.6 Hz, 1H), 5.44 (app t, J = 6.2 Hz, 1H), 5.20-5.03 (m, 4H), 4.74 (q, J = 6.6 Hz, 1H), 3.38 (dd, J = 7.0, 15.8 Hz, 1H), 3.17 (dd, J = 5.9, 14.7 Hz, 1H), 1.48 (major) + 1.32 (minor) (d, J = 6.6 Hz, 3H), 0.20 (minor) + 0.10 (major) (s, 9H). ^{13}C NMR (CDCl$_3$) major isomer: δ 233.2, 134.8, 118.2, 114.6, 110.6, 95.2, 94.4, 90.8, 88.3, 66.4, 35.5, 25.9, 0.4; minor isomer: δ 233.4, 134.7, 118.6, 116.0, 108.4, 94.1, 91.3, 91.1, 89.8, 65.4, 35.2, 27.0, 0.1. HRMS calcd for C$_{14}$H$_{13}$CrO$_3$ (M$^+$+H – TMSOH) 281.0270, found 281.0256.

Arene Complex 4c. Arene complex **1** (394 mg, 1.25 mmol) and benzyl bromide (0.30 mL, 2.5 mmol) were reacted according to the general procedure to afford arene complex **4c** as an orange oil (273 mg, 52% yield) and arene complex **4a** as an orange oil (136 mg, 33% yield). Arene complex **4c**. IR (neat) ν 3064, 3030, 2957, 1963, 1883, 1452, 1252, 1093, 953, 843 cm^{-1}. ^{1}H NMR (CDCl$_3$) major isomer: δ 7.44-7.29 (m, 5H), 5.91 (d, J = 6.6 Hz, 1H), 5.51 (t, J = 6.6 Hz, 1H), 5.24 (t, J = 6.6 Hz, 1H), 4.95 (d, J = 6.6 Hz, 1H), 4.85 (q, J = 6.6 Hz, 1H), 3.98 (ABq, J = 16.1 Hz, Δ = 77 Hz, 2H), 1.59 (d, J = 6.6 Hz, 3H), 0.07 (s, 9H); minor isomer: δ 7.44-7.29 (m, 5H), 5.44 (t, J = 6.6 Hz, 1H), 5.30 (t, J = 6.6 Hz, 1H), 4.92 (d, J = 6.6 Hz, 1H), 4.90 (q, J = 6.6 Hz, 1H), 3.92 (ABq, J = 16.1 Hz, Δ = 25 Hz, 2H), 1.23 (d, J = 6.6 Hz, 3H), 0.30 (s, 9H). ^{13}C NMR (CDCl$_3$) major isomer: δ 233.2, 137.8, 129.03, 128.8, 127.02, 114.8, 111.6, 95.1, 94.4, 91.6, 88.4, 66.3, 37.3, 26.0, 0.1; minor isomer: δ 233.4, 137.6, 128.99, 128.8, 127.07, 116.3, 109.6, 94.0, 91.9, 91.4, 89.9, 65.4, 37.5, 26.9, 0.4. HRMS calcd for C$_{21}$H$_{24}$CrO$_4$Si (M$^+$) 420.0849, found 420.0846.

Arene Complex 4d. Arene complex **1** (101 mg, 0.321 mmol) and iodomethane (61 μL, 0.96 mmol) were reacted according to the general procedure to afford an inseparable mixture (88 mg) of arene complex **4d** (ca. 65% yield) and arene complex **4a** (ca. 15% yield) as an orange oil. Arene complex **4d**: IR (neat) ν 2959, 2900, 1962, 1883, 1253, 1121, 1094, 955, 844 cm^{-1}. ^{1}H NMR (CDCl$_3$) major isomer: δ 5.73 (d, J = 5.9 Hz, 1H), 5.43 (t, J = 5.9 Hz, 1H), 5.09 (t, J = 5.9 Hz, 1H), 5.02 (d, J = 6.6 Hz, 1H), 4.71 (q, J = 5.9 Hz, 1H), 2.23 (s, 3H), 1.48 (d, J = 5.9 Hz, 3H), 0.11 (s, 9H); minor isomer: δ 5.85 (d, J = 6.6 Hz, 1H), (remainder of aryl protons obscured by major isomer), 4.55 (q, J = 5.9 Hz, 1H), 2.15 (s, 3H), 1.33 (d, J = 5.9 Hz, 1H), 0.20 (s, 9H). ^{13}C NMR (CDCl$_3$) major isomer: δ 233.3, 113.9, 109.2, 95.2, 94.3, 92.0, 88.0, 66.7, 24.7, 18.6, 0.3; minor isomer: δ 233.5, 109.1, 106.6, 94.4, 92.1, 91.7, 89.1, 65.7, 26.3, 18.4, 0.1. HRMS calcd for C$_{15}$H$_{20}$CrO$_4$Si (M$^+$) 344.0536, found 344.0519.

Arene Complex 4e. Arene complex **1** (103 mg, 0.328 mmol) and benzaldehyde (0.17 mL, 1.6 mmol) were reacted according to the general procedure to afford arene complex **4e** as an orange oil, consisting of an inseparable mixture (ca. 6:1) of diastereoisomers (103 mg, 72% yield). IR (neat) ν 3577, 3436, 3087, 3066, 3033, 2959, 1964, 1887, 1600, 1495, 1451, 1373, 1254, 1097, 1024, 952, 847 cm^{-1}. ^{1}H NMR (CDCl$_3$) major isomer: δ

7.37-7.31 (m, 5H), 5.89 (d, *J* = 3.7 Hz, 1H), 5.71 (d, *J* = 7.3 Hz, 1H), 5.63 (d, *J* = 6.6 Hz, 1H), 5.51 (t, *J* = 6.6 Hz, 1H), 5.23 (t, *J* = 6.6 Hz, 1H), 4.57 (q, *J* = 6.6 Hz, 1H), 2.50 (d, *J* = 2.9 Hz, 1H), 1.40 (d, *J* = 6.6 Hz, 3H), -0.1 (s, 9H); minor isomer: δ 7.37-7.31 (m, 5H), 5.94 (d, *J* = 1.4 Hz, 1H), 5.43-5.29 (m, 3H), 5.16 (t, *J* = 6.6 Hz, 1H), 4.70 (q, *J* = 6.6 Hz, 1H), 2.35 (d, *J* = 2.9 Hz, 1H), 1.59 (d, *J* = 6.6 Hz, 3H), 0.1 (s, 9H). ^{13}C NMR ($CDCl_3$) major isomer: δ 233.0, 140.9, 128.8, 128.6, 127.8, 115.4, 114.8, 94.1, 93.9, 89.5, 88.0, 70.4, 67.0, 27.0, -0.2; minor isomer: δ 233.1, 129.9, 129.0, 128.3, 127.1, 116.3, 113.0, 93.5, 93.3, 89.2, 87.6, 68.1, 66.6, 26.6, -0.2. HRMS calcd for $C_{21}H_{24}CrO_5Si$ (M^+) 436.0798, found 436.0780.

Arene Complex 4f. Arene complex **1** (87 mg, 0.28 mmol), benzophenone (151 mg, 0.83 mmol) and HMPA (0.4 mL) were reacted according to the general procedure to afford arene complex **4f** as a yellow solid (94 mg, 77% yield) which was crystallized from hexanes to provide a single diastereomer. IR (neat) ν 3563, 3428, 3087, 3061, 2982, 2934, 1962, 1886, 1729, 1446, 1375, 1254, 1077, 1045 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.41-7.23 (m, 10H), 5.59 (d, *J* = 7.4 Hz, 1H), 5.51 (t, *J* = 6.2 Hz, 1H), 5.29 (q, *J* = 6.6 Hz, 1H), 5.12 (t, *J* = 7.4 Hz), 4.57 (d, *J* = 5.2 Hz, 1H), 3.68 (s, 1H), 1.41 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 232.7, 145.4, 144.0, 128.6, 128.5, 128.4, 128.2, 127.6, 127.3, 118.5, 116.8, 95.8, 93.6, 91.8, 90.1, 81.3, 65.1, 23.0. HRMS calcd for $C_{24}H_{19}CrO_4$ (M^++H - H_2O) 423.0688, found 423.0696.

Arene Complex 4g. Arene complex **1** (185 mg, 0.589 mmol) and phenyl disulfide (386 mg, 1.77 mmol) in THF (2.5 mL) were reacted according to the general procedure to afford an inseparable mixture (227 mg) of arene complex **4g** (ca. 83% yield) and arene complex **4a** (ca. 5% yield) as a yellow oil. Arene complex **4g**: IR (neat) ν 3078, 2958, 2899, 1964, 1886, 1441, 1252, 1099, 955, 845 cm^{-1}. ^{1}H NMR ($CDCl_3$) major isomer: δ 7.50-7.38 (m, 5H), 5.89 (d, *J* = 6.6 Hz, 1H), 5.34 (t, *J* = 6.0 Hz, 1H), 5.09-5.03 (m, 2H), 4.88 (d, *J* = 6.6 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H), 0.10 (s, 9H); minor isomer: δ 7.50-7.38 (m, 5H), 5.85 (d, *J* = 6.6 Hz, 1H), 5.26 (t, *J* = 6.0 Hz, 1H), 5.16 (t, *J* = 6.2 Hz, 1H), 5.09-5.03 (m, 2H), 4.88 (d, *J* = 6.6 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$) major isomer: δ 232.56, 133.2, 129.7, 128.8, 115.0, 112.2, 94.4, 93.3, 91.3, 91.0, 87.6, 66.6, 25.8, 0.2. minor isomer: δ 232.63, 132.7, 131.8, 128.7, 116.6, 108.5, 93.0, 92.9, 92.0, 90.0, 89.4, 66.4, 26.2, 0.2. HRMS calcd for $C_{17}H_{13}O_3CrS$ (M^++H – TMSOH) 348.9990, found 348.9990.

Arene Complex 4h. Arene complex **1** (250 mg, 0.795 mmol) and 1,2-dibromo-tetrafluoroethane (0.48 mL, 4.0 mmol) were reacted according to the general procedure to afford arene complex **4h** as a yellow oil (215 mg, 81% yield). IR (neat) ν 3091, 2959, 2900, 1964, 1906, 1445, 1403, 1373, 1253, 1181, 1099, 1037, 955, 847 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.91 (d, *J* = 6.6 Hz, 1H), 5.45-5.37 (m, 2H), 5.00 (t, *J* = 6.6 Hz, 1H), 4.88 (q, *J* = 5.9 Hz, 1H), 1.52 (d, *J* = 5.9 Hz, 3H), 0.10 (s, 9H); minor isomer: δ 5.85 (d, *J* = 6.6 Hz, 1H), 5.45-5.37 (m, 1H), 5.33 (t, *J* = 6.6 Hz, 1H), 5.06 (t, *J* = 6.6 Hz, 1H), 4.77 (q, *J* = 5.9 Hz, 1H), 1.40 (d, *J* = 5.9 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$) major isomer: δ 231.8, 114.5, 102.1, 94.9, 94.0, 92.1, 86.6, 68.3, 26.2, 0.2; minor isomer: δ 232.0, 114.8, 98.8, 93.7, 93.0, 90.6, 88.2, 68.3, 26.0, 0.1. HRMS calcd for $C_{14}H_{17}{}^{81}BrO_4Si$ (M) 409.9464, found 409.9466.

General Procedure for the Decomplexation of Arene Complexes: A solution of the arene complex in hexane (10 mL) was exposed to sunlight and air for 2-8 h. The resultant mixture was filtered through a celite pad, and the filtrate was concentrated under reduced pressure. Purification of the residue via flash chromatography (silica gel, 19/1 hexane/EtOAc) afforded the organic product.

Silyl Ether 5b. Arene complex **4b** (41 mg, 0.11 mmol) was treated according to the general procedure to afford **5b** as a clear, colorless oil (25 mg, 96% yield). IR (neat) ν 3076, 2958, 2926, 1638, 1449, 1251, 1092, 1028, 957 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.61 (dd, *J* = 1.5, 7.4 Hz, 1H), 7.32-7.16 (m, 3H), 6.03 (dddd, *J* = 6.6, 10.3, 12.5, 16.9 Hz, 1H), 5.19-5.04 (m, 3H), 3.50-3.48 (m, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 144.7, 137.3, 134.9, 129.5, 126.8, 126.6, 125.9, 115.8, 67.1, 36.6, 26.6, 0.2. HRMS calcd for $C_{14}H_{22}OSi$ (M^+) 234.1440, found 234.1429.

Silyl Ether 5c. Arene complex **4c** (93 mg, 0.22 mmol) was treated according to the general procedure to afford **5c** as a clear, colorless oil (59 mg, ca. 94% yield). IR (neat) ν 3062, 3027, 2957, 2925, 2857, 1495, 1452, 1251, 1092, 1028, 957, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) d 7.57 (d, *J* = 6.6 Hz, 1H), 7.26 (app t, *J* = 7.3 Hz, 3H), 7.21-7.16 (m, 2H), 7.10 (app t, *J* = 6.5 Hz, 3H), 5.01 (q, *J* = 5.9 Hz, 1H), 4.02 (s, 2H), 1.28 (d, *J* = 5.9 Hz, 3H), -0.08 (s, 9H). ^{13}C NMR ($CDCl_3$) d 145.0, 140.7, 135.6, 130.4, 128.8, 128.4, 126.8, 126.7, 126.1, 67.1, 38.7, 26.3, -0.1. HRMS calcd for $C_{17}H_{21}OSi$ (M^+ - CH_3) 269.1362, found 269.1353.

Silyl Ether 5d. A mixture of arene complexes **4d** and **4a** (88 mg, ca. 1.6/1) was treated according to the general procedure to afford **5d** as a clear, colorless oil (36 mg, ca. 82% yield). IR (neat) ν 3066, 3025, 2972, 2927, 2899, 1461, 1369, 1251, 1095, 1027, 957, 841, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.19 (dt, *J* = 1.5, 7.4 Hz, 1H), 7.12 (dt, *J* = 1.5, 7.4 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.04 (q, *J* = 5.9 Hz, 1H), 2.31 (s, 3H), 1.39 (d, *J* = 5.9 Hz, 3H), 0.05 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 144.7, 133.1, 130.0, 126.6, 126.1, 125.4, 67.5, 25.7, 18.9, 0.1. HRMS calcd for $C_{11}H_{17}OSi$ (M^+ - CH_3) 193.1049, found 193.1050.

Silyl Ether 5e. Arene complex **4e** (103 mg, 0.236 mmol) was treated according to the general procedure to afford **5e** as a clear, colorless oil, consisting of an approximately 4:1 mixture of diastereomers (62 mg, 87% yield). IR (neat) ν 3390, 3063, 3030, 2958, 2926, 2899, 1451, 1251, 1121, 1091, 1025, 956, 842, 761, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$) major isomer: δ 7.45 (d, J = 7.4 Hz, 1H), 7.34-7.21 (m, 8H), 6.15 (d, J = 4.4 Hz, 1H), 5.05 (q, *J* = 6.6 Hz, 1H), 2.88 (d, *J* = 4.4 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 3H), -0.07 (s, 9H); minor isomer: δ 7.51 (d, J = 7.4 Hz, 1H), 7.34-7.21 (m, 8H), 6.19 (d, *J* = 3.7 Hz, 1H), 5.16 (q, *J* = 6.6 Hz, 1H), 2.44 (d, *J* = 3.7 Hz, 1H), 1.22 (d, *J* = 5.9 Hz, 3H), 0.01 (s, 9H). ^{13}C NMR ($CDCl_3$) major isomer: δ 143.9, 143.1, 139.5, 128.4, 127.8, 127.5, 127.4, 127.2, 127.0, 126.6, 72.6, 68.8, 26.5, -0.1; minor isomer: δ 144.1, 143.5, 139.3, 127.9, 127.3, 126.9

(additional aryl peaks obscured by major isomer), 72.5, 67.4, 26.4, 0.1. HRMS calcd for $C_{18}H_{23}OSi$ (M^+ - OH) 283.1518, found 283.1511.

Diol 5f.[2] Arene complex **4f** (94 mg, 0.21 mmol) was treated according to the general procedure to afford **5f** as a clear, colorless oil (60 mg, 92% yield). IR (neat) ν 3058, 3026, 2972, 2926, 2860, 1598, 1490, 1446, 1073, 1028, 993 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.38-7.17 (m, 14H), 5.31 (q, *J* = 6.5 Hz, 1H), 1.62 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 145.9, 144.40, 144.37, 143.8, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 123.8, 120.9, 92.0, 77.8, 21.4. HRMS calcd for $C_{21}H_{21}O_2$ (M^++H) 305.1542, found 305.1528.

Silyl Ether 5g. Arene complex **4g** (175 mg, 0.40 mmol) was treated according to the general procedure to afford **5g** as a clear, colorless oil (113 mg, 94% yield). IR (neat) ν 3060, 2958, 2926, 1582, 1477, 1439, 1251, 1096, 1025, 957, 842 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.66 (d, *J* = 6.6 Hz, 1H), 7.37-7.16 (m, 8H), 5.37 (q, *J* = 5.9 Hz, 1H), 1.36 (d, *J* = 5.9 Hz, 3H), 0.02 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 148.6, 136.9, 133.7, 130.4, 129.6, 129.1, 128.4, 127.5, 126.6, 126.4, 67.6, 26.4, -0.02. HRMS calcd for $C_{17}H_{23}OSSi$ (M^++H) 303.1239, found 303.1238.

Silyl Ether 5h. Arene complex **4h** (263 mg, 0.643 mmol) was treated according to the general procedure to afford **5h** as a clear, colorless oil (150 mg, 95% yield). IR (neat) ν 3066, 2956, 2927, 2856, 1468, 1441, 1371, 1252, 1098, 1024, 956, 844. ^1H NMR ($CDCl_3$) δ 7.58 (dd, *J* = 1.5, 7.3 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.06 (dt, *J* = 1.5, 8.1 Hz, 1H), 5.15 (q, *J* = 6.6 Hz, 1H), 1.38 (d, *J* = 6.6 Hz, 3H), 0.06 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 145.7, 132.2, 128.3, 127.6, 127.5, 120.9, 69.6, 25.5, -0.04. HRMS calcd for $C_{11}H_{17}BrOSi$ (M^+-CH_3) 256.9997, found 256.9989.

References:

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