Supporting Information

Reactions of Novel Reactive Species Generated by Samarium(II)-mediated One-electron Reduction of Fischer-type Carbene Complexes

Kohei Fuchibe[†] **and Nobuharu Iwasawa***

General Information.

All the reactions were carried out under an argon atmosphere. All the materials were used after purification by distillation or recrystallization. NMR spectra were recorded on a Bruker DRX 500 (FT, 500 MHz, ^{1}H; 125 MHz, ^{13}C) or JEOL Lambda-300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C) instrument. Chemical shifts (δ) for ^{1}H (δ=7.24 ppm, $CHCl_3$) and ^{13}C (δ=77.0 ppm, $CDCl_3$) are referenced to internal solvent resonances. IR spectra were recorded on a JASCO FT/IR-200. High-resolution mass spectrometry (HRMS) was conducted with 70 eV electron impact ionization on a JEOL JMS-SX102A instrument using PFK as a standard. Flash column chromatography was conducted on silica gel (Merk Kieselgel 60 Art 7734) and preparative thin-layer chromatography was carried out on silica gel (Wako gel B-5F).

One-electron reduction of the tungsten phenyl carbene complex.

To a THF solution (1.5 ml) of the tungsten phenyl carbene complex **1a** (140 mg, 0.32 mmol) and methanol (50 μl) was added a THF solution (6.4 ml) of samarium diiodide (0.10 M, 0.64 mmol) at -78 °C. After the mixture was stirred for 2 h, the reaction was quenched with pH=7 phosphate buffer at this temperature. The product was extracted with ethyl acetate four times and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (hexane) to give *trans*-stilbene (18 mg, 60%). The spectral data of the product was in complete agreement with those of the authentic sample which is commercially available.

One-electron reduction of the tungsten aryl carbene complex in the presence of ethyl acrylate.

A typical procedure is described for the reaction of the tungsten phenyl carbene complex **1a**.

To a THF solution (3.8 ml) of the tungsten phenyl carbene complex **1a** (120 mg, 0.27 mmol), methanol (53 μl) and ethyl acrylate (162 mg, 1.6 mmol) was added a THF solution (6.8 ml) of samarium diiodide (0.10 M, 0.68 mmol) at -78 °C. After the mixture was stirred for 30 min, the reaction was quenched with pH=7 phosphate buffer at this temperature. The products were extracted with ethyl acetate four times and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by preparative TLC (hexane: ethyl acetate = 8: 1) to give ethyl 4-methoxy-4-phenylbutanoate **3a** (24 mg, 38%) and ethyl 4-phenyl-3-butenoate **4a** (17 mg, 33% as a *E*/*Z* mixture. *E*: *Z*=47: 53). The spectral data of the former product were in complete agreement with those in the literature.[1]

Ethyl 4-methoxy-4-phenylbutanoate: ^{1}H NMR δ 1.22 (3H, t, *J*= 7.2 Hz), 1.89- 2.11 (2H, m), 2.35 (2H, t, *J*= 7.4 Hz), 3.23 (3H, s), 4.09 (2H, q, *J*= 7.2 Hz), 4.13 (1H, dd, *J*= 5.6, 7.8 Hz), 4.13 (1H, dd, *J*= 5.7, 7.8 Hz), 7.24- 7.36 (5H, m); ^{13}C NMR δ 14.2, 30.6, 33.1, 56.7, 60.3, 82.8, 126.6, 127.7, 128.4, 141.5, 173.5; IR (neat) 2982, 1735, 1106, 702 cm^{-1}; HRMS Found: m/z 221.1179, Calcd for $C_{13}H_{17}O_3$ (M–H): 221.1178.

Ethyl 4-methoxy-4-(4-bromophenyl)butanoate: ^{1}H NMR δ 1.22 (3H, t, *J*= 7.1 Hz), 1.85- 2.12 (2H, m), 2.34 (2H, t, *J*= 7.7 Hz), 3.18 (3H, s), 4.05- 4.15 (1H, m), 4.09 (2H, q, *J*= 7.1 Hz), 7.14 (2H, d, *J*= 11 Hz), 7.46 (2H, d, *J*= 11 Hz); ^{13}C NMR δ 14.2, 30.4, 33.0, 56.8, 60.3, 82.1, 121.4, 128.3, 131.6, 140.7, 173.2; IR (neat) 2931, 1732, 1180, 823 cm^{-1}; Elemental analysis: Found: C 51.90%, H 5.91%, Calcd for $C_{13}H_{17}O_3Br$: C 51.84%, H 5.69%.

One-electron reduction of the chromium phenyl carbene complex

To a THF solution (8.0 ml) of the chromium phenyl carbene complex **11** (91 mg, 0.29 mmol) and methanol (55 μl) was added a THF solution (5.8 ml) of samarium diiodide (0.10 M, 0.58 mmol) at -78 °C. After the mixture was stirred overnight, a THF solution (1.0 ml) of ethyl acrylate (176 mg, 1.8mmol) was added at this temperature. The reaction mixture was warmed up to room temperature and further stirred for 1 h. The reaction was quenched with pH=7 phosphate buffer at this temperature. The products were extracted with ethyl acetate four times and the combined organic phase was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude products were purified by preparative TLC (hexane: ethyl acetate = 4: 1), ethyl 4-phenyl-3-butenoate (14 mg, 26% as a *E*/*Z* mixture. *E*: *Z*=16: 84), ethyl 4-methoxy-4-phenylbutanoate (3 mg, 5%) and ethyl 5-methoxy-4-oxo-5-phenylpentanoate (30 mg, 41%) were obtained. The spectral data of the last compound is shown below.

Ethyl 5-methoxy-4-oxo-5-phenylpentanoate: ^{1}H NMR δ 1.18 (3H, t, *J*= 7.2 Hz), 2.40- 2.57 (2H, m), 2.73 (1H, dt, *J*= 6.5, 18.6 Hz), 2.83 (1H, ddd, *J*= 6.5, 7.2, 18.6 Hz), 3.37 (3H, s), 4.06 (2H, q, *J*= 7.2 Hz), 4.70 (1H, s), 7.30- 7.45 (5H, m); ^{13}C NMR δ 14.1, 27.6, 32.4, 57.3, 60.6, 89.0, 127.0, 128.6, 128.8, 135.9, 172.6, 207.0; IR (neat) 2980, 1732, 1202, 702 cm^{-1}; HRMS Found: m/z 250.1215, Calcd for $C_{14}H_{18}O_4$: 250.1205.

1,4-Addition of the acyl chromate complexes to electron-deficient olefins.

A typical procedure is described for the reaction of the chromium butyl carbene complex with ethyl acrylate.

A THF solution of samarium diiodide-HMPA complex was prepared by adding HMPA (0.43 ml, 2.5 mmol) to a THF solution (8.5 ml) of samarium diiodide (0.10 M, 0.85 mmol) at room temperature. To a THF solution (2.7 ml) of the chromium butyl carbene complex (55 mg, 0.19 mmol) and methanol (38 µl, 1.7 mmol) was added the THF solution (8.9 ml) of samarium diiodide-HMPA complex at –78 °C. After the mixture was stirred for 20 min, a THF solution (1.5 ml) of ethyl acrylate (113 mg, 1.1 mmol) was added. The reaction mixture was warmed up to room temperature and was further stirred for 1 h. The reaction was quenched with pH=7 phosphate buffer and the products were extracted with ethyl acetate four times. The combined organic phase was dried over anhydrous magnesium sulfate. After purification by silica gel column chromatography, ethyl 5-methoxy-4-oxononanoate was obtained (36 mg, 85%). The spectral data of this product is shown below.

Ethyl 5-methoxy-4-oxononanoate: ^{1}H NMR δ 0.87 (3H, t, *J*= 6.8 Hz), 1.23 (3H, t, *J*= 7.1 Hz), 1.18- 1.40 (4H, m), 1.61 (2H, t, *J*= 6.8 Hz), 2.56 (2H, t, *J*= 6.6 Hz), 2.71- 2.89 (2H, m), 3.35 (3H, s), 3.59 (1H, t, *J*= 6.3 Hz), 4.10 (2H, q, *J*= 7.1 Hz); ^{13}C NMR δ 13.9, 14.2, 22.5, 27.2, 27.5, 31.8, 32.4, 58.2, 60.6, 87.2, 172.7, 211.5; IR (neat) 2958, 1733, 1716, 1205, 1099 cm^{-1}; HRMS Found: m/z 185.1179, Calcd for $C_{10}H_{17}O_3$ (M–EtO): 185.1177.

The spectral data of the compounds listed in Table 2 are shown below.

5-Methoxy-4-oxononanenitrile: ^{1}H NMR δ 0.86 (3H, t, *J*= 7.1 Hz), 1.20- 1.40 (4H, m), 1.52- 1.72 (2H, m), 2.56 (2H, t, *J*= 6.8 Hz), 2.81- 2.99 (2H, m), 3.34 (3H, s), 3.60 (1H, t, *J*= 6.2 Hz); ^{13}C NMR δ 11.1, 13.8, 22.4, 26.9, 31.4, 33.4, 58.3, 86.8, 119.0, 209.2; IR (neat) 2935, 2250, 1721, 1465, 1099 cm^{-1}; HRMS Found: m/z 183.1259, Calcd for $C_{10}H_{17}NO_2$: 183.1259.

Methyl 5-methoxy-3-methyl-4-oxononanoate: The spectral data of the mixture of two diastereomers (81: 19) are shown: ^{1}H NMR δ 0.88 (3H, t, *J*= 7.1 Hz), 1.10 (3×0.81H, d, *J*= 7.3 Hz), 1.11 (3×0.19H, d, *J*= 7.4 Hz), 1.23- 1.44 (4H, m), 1.52- 1.62 (1H, m), 1.67- 1.78 (1H, m), 2.30 (1×0.81H, dd, *J*= 5.7, 17.1 Hz), 2.31 (1×0.19H, dd, *J*= 5.4, 16.8 Hz), 2.76 (1×0.19H, dd, *J*= 9.0, 16.8 Hz), 2.79 (1×0.81H, dd, *J*= 9.3, 17.1 Hz), 3.17- 3.45 (1H, m), 3.36 (3×0.19H, s), 3.38 (3×0.81H, s), 3.63 (3H, s), 3.76 (1×0.89H, dd, *J*= 3.9, 8.1 Hz), 3.84 (1×0.19H, dd, *J*= 4.4, 7.6 Hz); ^{13}C NMR δ 13.9, 16.9, 22.5, 22.6, 27.4, 27.7, 29.7, 30.8, 31.8, 36.4, 37.6, 37.8, 38.0, 51.6, 51.7, 58.1, 58.4, 86.0, 86.4, 172.5, 172.7, 213.5, 214.1; IR (neat) 2957, 1738, 1715, 1200, 1100 cm^{-1}; Elemental analysis: found: C 62.58%, H 9.83%, calcd for $C_{12}H_{22}O_4$: 2.58%, H 9.63%.

3-(2-Methoxyhexanoyl)-1-cyclopentanone: The spectral data of the mixture of two diastereomers (50: 50) are shown: ^{1}H NMR δ 0.85- 0.90 (3H, m), 1.27- 1.39 (4H, m), 1.61- 1.69 (2H, m), 1.92- 2.04 (1H, m), 2.16- 2.25 (2H, m), 2.25- 2.41 (2.5H, m), 2.45 (1×0.5H, ddd, *J*= 1.5, 9.0, 18.5 Hz), 3.34 (3×0.5H, s), 3.37 (3×0.5H, s), 3.55- 3.63 (1H, m), 3.66- 3.70 (1H, m); ^{13}C NMR δ 13.8, 22.47, 22.48, 26.1, 26.5, 27.0, 27.3, 30.9, 31.3, 37.46, 37.48, 40.7, 41.2, 42.7, 42.8, 58.2, 58.3, 86.81, 86.83, 213.1, 213.3, 216.50, 216.51; IR (neat) 2956, 1746, 1713, 1103; Elemental analysis: found: C 67.69%, H 9.60%, calcd for $C_{12}H_{20}O_3$: C 67.89%, H 9.50%.

Dimethyl 4-methoxy-3-oxooctane-1,2-dicarboxylate: The spectral data of the mixture of two diastereomers (53: 47) are shown: ^{1}H NMR δ 0.86 (3H, m), 1.10- 1.40 (4H, m), 1.50-1.80 (2H, m), 2.70 (1×0.47H, dd, *J*= 6.0, 17.0 Hz), 2.79 (1×0.53H, dd, *J*= 6.0, 17.4 Hz), 2.90 (1×0.47H, dd, *J*= 8.4, 17.0 Hz), 2.92 (1×0.53H, dd, *J*= 8.1, 17.4 Hz), 3.33 (3×0.53H, s), 3.36 (3×0.47H, s), 3.64 (6×0.53H, s), 3.69 (6×0.47H, s), 3.74 (1×0.53H, t, *J*= 5.9 Hz), 3.83 (1×0.47H, dd, *J*= 6.0, 9.0 Hz), 4.21 (1×0.53H, dd, *J*= 6.0, 8.1 Hz), 4.24 (1×0.47H, dd, *J*= 6.0, 8.4 Hz); ^{13}C NMR δ 13.8, 22.4, 22.5, 26.8, 27.3, 30.7, 31.2, 31.9, 32.2, 49.7, 49.87, 49.91, 52.0, 52.49, 52.51, 52.56, 52.58, 58.4, 58.5, 84.4, 86.5, 168.7, 169.1, 171.3, 171.6, 205.4, 205.9; IR (neat) 2955, 1740, 1724, 1437, 1162; HRMS Found: m/z 243.1223, Calcd for $C_{12}H_{19}O_5$ (M-MeO): 243.1233.

Ethyl 5-methoxy-6-methyl-4-oxooctanoate: The spectral data of the mixture of two diastereomers (55: 45) are shown: ^{1}H NMR δ 0.82 (3×0.55H, d, *J*= 7.4 Hz), 0.848 (3×0.45H, d, *J*= 6.8 Hz), 0.849 (3×0.55H, t, *J*= 7.5 Hz), 0.88 (3×0.45H, t, *J*= 7.5 Hz), 1.19- 1.29 (1H, m), 1.22 (3H, t, *J*= 7.2 Hz), 1.37- 1.45 (1×0.45H, m), 1.49- 1.57 (1×0.55H, m), 1.69- 1.79 (1H, m), 2.54 (2×0.55H, t, *J*= 6.8 Hz), 2.55 (2×0.45H, t, *J*= 6.6 Hz), 2.69- 2.88 (2H, m), 3.29 (1×0.55H, d, *J*= 7.1 Hz), 3.33 (3×0.55H, s), 3.37 (3×0.45H, s), 3.47 (1×0.45H, d, *J*= 5.0 Hz), 4.10 (2H, q, *J*= 7.2 Hz); ^{13}C NMR δ 11.1, 11.6, 14.1, 14.7, 24.4, 24.8, 25.8, 27.4, 27.6, 33.0, 33.5, 33.9, 37.2, 37.8, 58.8, 59.1, 60.55, 60.57, 90.3, 91.7, 172.7, 173.3, 211.4, 211.5; IR (neat) 2965, 1737, 1517, 1205, 1097; HRMS Found: m/z 185.1180, Calcd for $C_{10}H_{17}O_3$(M–EtO): 185.1178.

5-Methoxy-6-methyl-4-oxooctanenitrile: The spectral data of the mixture of two diastereomers (56: 44) are shown: ^{1}H NMR δ 0.80- 0.93 (6H, m), 1.13- 1.27 (1H, m), 1.35- 1.45 (1×0.44H, m), 1.47- 1.56 (1×0.56H, m), 1.69- 1.78 (1H, m), 2.52- 2.59 (2H, m), 2.74- 2.97 (2H, m), 3.33 (1×0.56H, d, *J*= 6.8 Hz), 3.34 (3×0.56H, s), 3.36 (3×0.44H, s), 3.46 (1×0.44H, d, *J*= 5.1 Hz); ^{13}C NMR δ 11.08, 11.11, 11.5, 14.2, 14.7, 24.8, 25.6, 33.9, 34.5, 37.3, 38.0, 59.0, 59.4, 90.3, 91.3, 119.0, 128.4, 209.3, 209.7; IR (neat) 2966, 2250, 1720, 1462, 1096; Elemental analysis: Found: C 65.26%, H 9.35%, N 7.36%, Calcd for $C_{10}H_{17}NO_2$: C 65.56%, H 9.35%, N 7.65%.

2-Phenylethyl 5-methoxy-4-oxohexanoate: ^{1}H NMR δ 1.30 (3H, d, *J*= 7.2 Hz), 2.59 (2H, t, *J*= 6.8 Hz), 2.80- 2.85 (2H, m), 2.93 (2H, t, *J*= 7.1 Hz), 3.37 (3H, s), 3.76 (1H, q, *J*= 7.2 Hz), 4.29 (2H, t, *J*= 7.1 Hz), 7.16- 7.33 (5H, m); ^{13}C NMR δ 17.0, 27.4, 31.9, 35.0, 57.5, 65.0, 82.6, 126.5, 128.4, 128.8, 137.7, 172.6, 211.0; IR (neat) 2940, 1736, 1168, 702; Elemental analysis: found: C 67.86%, H 7.55%, calcd for $C_{15}H_{20}O_3$: C 68.16%, H 7.63%.

References

1) Gerkin, R. M.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 5850.