Supplementary Material

Addition of Olefins to Aromatic Ketones Catalyzed by Rh(I) Olefin Complexes.

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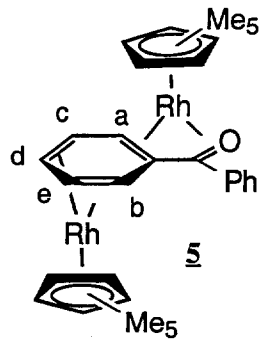
Preparation of $[C_5Me_5Rh(C_2H_3SiMe_3)_2]$, 1. The precursor $[C_5Me_5RhCl_2]_2$ (0.4g, 6.5×10^{-4}mol) was combined with an excess of zinc powder (~10x, 0.85g) in a Schlenk flask. To this was added 5-10 ml of tetrahydrofuran and vinyltrimethylsilane (10x, 1.3g). This reaction mixture was stirred at 20 °C for 12 hours. The reaction mixture turns homogeneous with only zinc powder as the remaining insolubles. After canula filtration, the solvent was removed *in vacuo* and the remaining solids were extracted with pentane until the solution remained colorless. The volatiles of the filtrate were removed and complex **1a** was obtained as a yellow-orange oil that solidified in the course of one hour in 72% (0.41g yield). The material was pure by NMR and elemental analysis at this stage. Recrystallization in acetone at -70 °C resulted in yellow material which showed one isomer by NMR spectroscopy. ^{1}H (400 MHz, 20°C, acetone-d_6) δ 2.11 (ddd, 10 Hz, 2.4 Hz, 1.6 Hz, 2H); 1.15 (m, 4H); 1.68 (s, 15H); 0.04 (s, 18H); ^{13}C (100.6 MHz, 20°C, acetone-d_6) δ 98.2 ($\underline{C}_5Me_5$); 47.8 (d, 15 Hz, $H_2\underline{C}$=); 45.5 (d, 15 Hz, =$\underline{C}$HSi); 9.8 ($C_5\underline{Me}_5$); 2.2 (-$SiMe_3$); Anal. Calcd. for $C_{20}H_{39}Si_2Rh$: H, 8.96; C, 54.77; Found: H, 8.99; C, 54.88.

Reaction of 1 with Excess Benzophenone: Formation of 6. A reaction of **1** (0.1g, 2.3×10^{-4} mol) in 1 ml cyclohexane-d_{12} with 10 equiv. benzophenone (0.41 g) was

followed by ^{1}H NMR spectroscopy at 50°C. Complex **6** was generated consuming all **1** after 8 hours while all vinyltrimethylsilane was converted to **3a**. Complex **6** was isolated from the brown reaction mixture as a brown powder after chromatography on alumina in a dry box eluting with pentane as the second fraction after separation from ketone **3a** (^{1}H NMR of **5** see Figure 1).



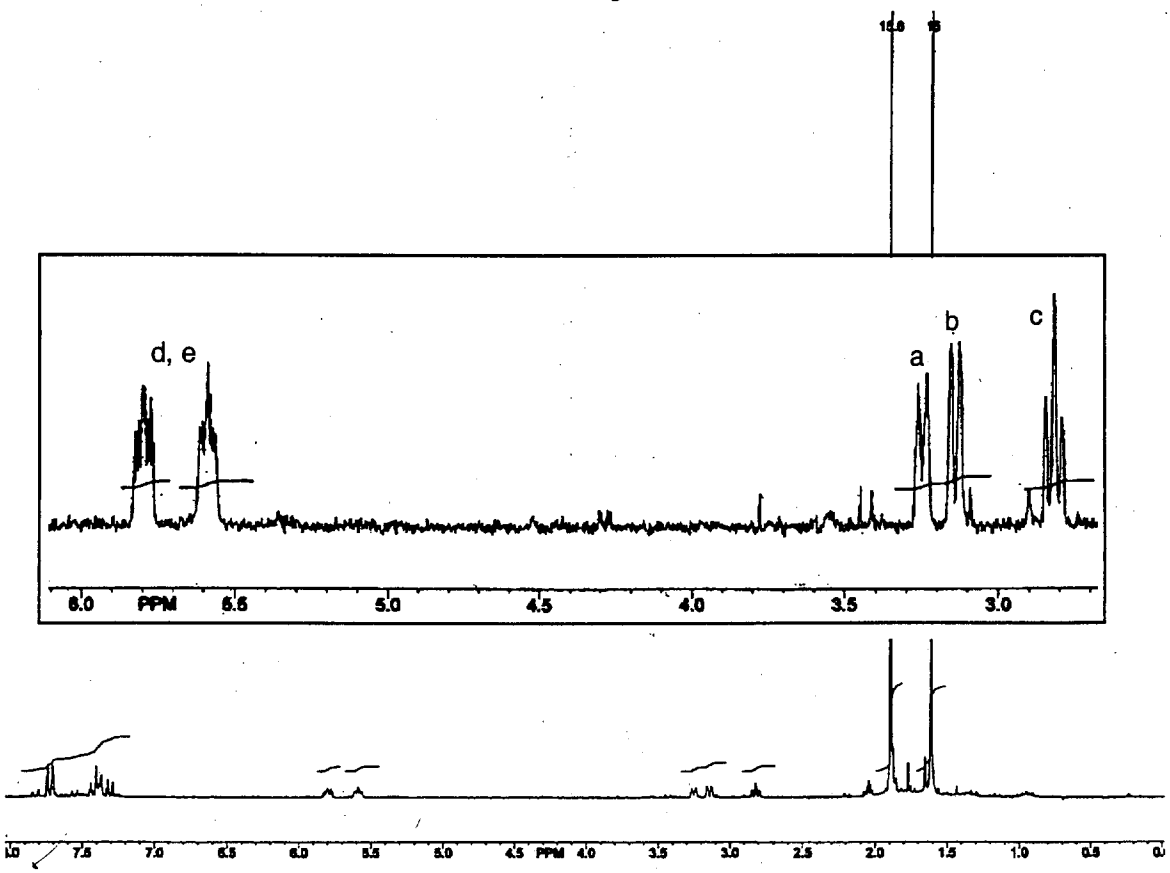


Figure 1. ^{1}H NMR of **6** in acetone-d_6. (a small amount of excess benzophenone is present).

6 [η^4,η^4-$(C_5Me_5Rh)_2C_6H_5C(O)C_6H_5$]. ^{1}H NMR (acetone-$d_6$, 300 MHz, 20 °C) 1.61 (s, 15H); 1.90 (s, 15H); 2.82 (dd, 6 Hz, 5 Hz, 1H); 3.12 (d, 5 Hz, 1H); 3.25 (d, 6 Hz, 1H); 5.58 (m, 1H); 5.82 (m, 1H); 7.38 (m, 3H); 7.72 (m, 2H).

Reaction of *p*-Chloroacetophenone with Vinyltrimethylsilane. To a solution of 0.01g 1 (2.3×10^{-5}mol) in cyclohexane-d_{12} were added 20 equiv. of *p*-chloroacetophenone and 20 equiv. of vinyltrimethylsilane. This reaction mixture was heated to 120 °C and the reaction progress followed by ^{1}H NMR spectroscopy. Figure 2 shows a ^{1}H NMR spectrum aquired during the reaction and details the product distribution.

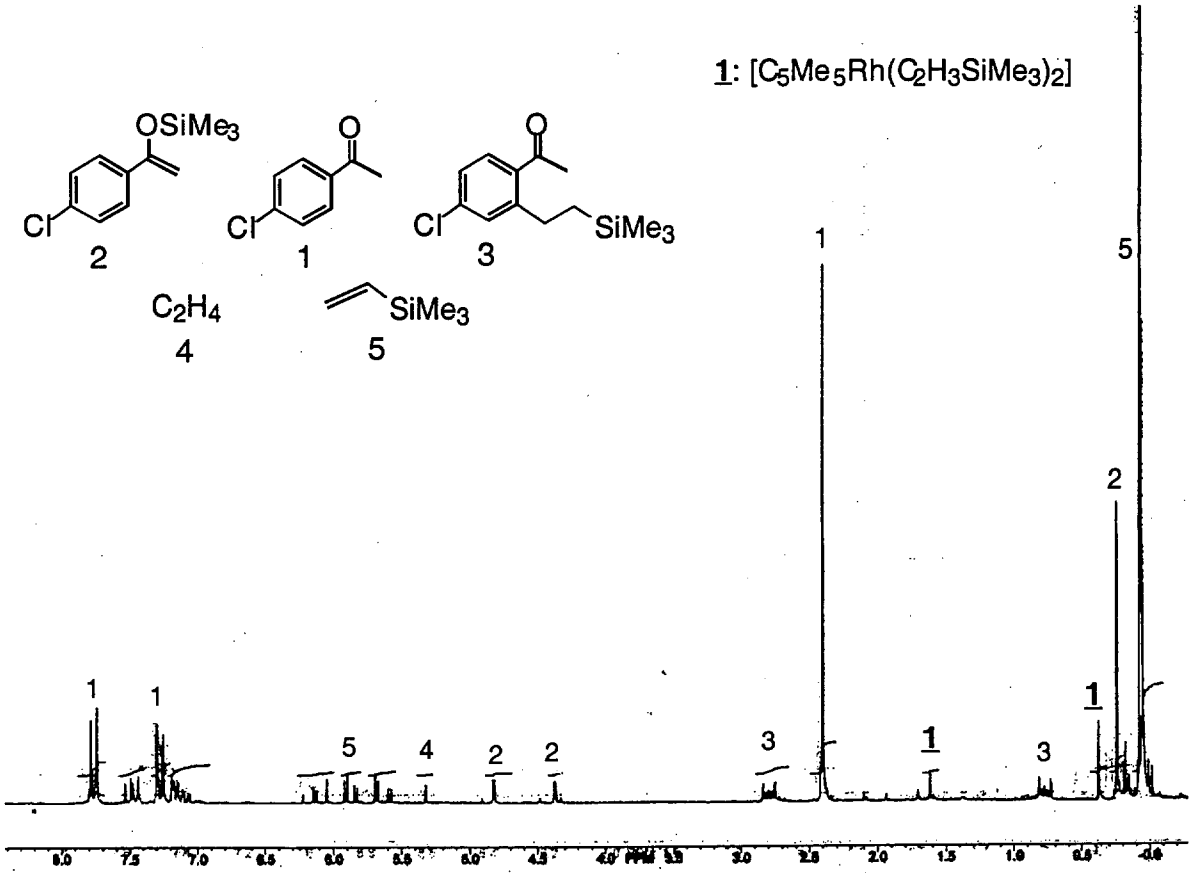


Figure 2. *In Situ* ^{1}H NMR Spectrum of the Reaction of *p*-Chloroacetophenone with Vinyltrimethylsilane in the Presence of 1 (0.01g, 2.3×10^{-5} mol, 120 °C, cyclohexane-d_{12}).

Additional resonances for substrates 1-5 coincide or are not assigned (aromatics) in this spectrum.

Catalytic Alkylation of Aromatic Ketones. Complex 1 (0.01g, 2.3×10^{-5} mol) was added to an NMR tube equipped with a Teflon screw cap or a thick-walled glass tube with a Teflon screw top and dissolved in cyclohexane (-d_{12} or h_{12}, if solubility required a different solvent (entry 8, Table 1) benzene was used). To this was added the required amounts of ketone and olefin (in general 4.6×10^{-4} mol each) by weight using a syringe. The sealed containers were removed from the drybox and kept at 120 °C in an oil bath. Samples prepared in NMR tubes were monitored during catalysis. The residual solvent resonance was used as an integration standard. After the reactions were terminated all volatiles were removed and the reaction mixture was analyzed by NMR spectroscopy to determine conversion. Column chromatography (flash-chromatography) on alumina gave in general pure material as judged by NMR spectroscopy. When vinyltrimethylsilane was not used as the olefin small impurities based on the initial conversion of vinyltrimethylsilane originating from complex 1 were present in some samples and proved difficult to separate by chromatography. A series of similar alkylated aromatic ketones are tabulated by Murai et al. (Bull. Chem. Soc. Jpn., **68**, 62-83, 1995) and compare well to the spectroscopic data summarized here.

Characterization of Hydroarylation Products.

3a. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.01 (s, 9H); 0.85 (m, 2H, -CH_2Si); 2.74 (m, 2H, -CH_2-Ar); 7.87 (m, 2H, -Ph); 7.02 - 7.27 (m, 7H, Ar). ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ - 1.83 (-$SiMe_3$); 19.8 (-CH_2-); 28.1 (-CH_2-); 197.7 (C=O); 125.3, 128.6, 128.9, 129.8, 130.2, 130.4, 132.9, 138.6, 138.6, 144.9 (-Ar). Anal. Calc.: H 7.85, C 76.54; Anal. Found: H 7.67, C 76.80.

3b. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.88 (s, 9H, ^{t}Bu); 1.51 (m, 2H, -CH_2-); 2.65 (m, 2H, -CH_2-); 7.81 (m, 2H, Ar); 7.06-7.24 (m, 7H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ 19.3 (-CH_2); 29.2 (-CMe_4); 32.6 (-CH_2-); 197.8 (C=O); 143.5, 138.5, 138.6, 133.0, 130.4, 130.1, 129.7, 129.0, 128.6, 124.9 (-Ar). MS/EI: 261.3

3c. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.83 (t, 3H, -CH_3), 1.21 (m, 4H, CH_2), 1.65 (m, 2H, -CH_2-); 2.82 (m, 2H, -CH_2-); 7.94 (m, 2H, Ar); 7.01-7.29 (m, 7H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ 197.8 (C=O); 14.1 (q, -CH_3); 22.7 (t, -CH_2-); 31.9, 32.0, 33.6 (t, -CH_2-); 142.2, 139.3, 132.9, 132.1, 130.4, 130.3, 130.0, 128.7, 125.3 (Ar). MS/EI: 252.3

3d. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.015 (s, 9H); 0.50 (m, 2H); 0.71 (m, 2H); 2.88 (m, 2H); 7.95 (m, 2H); 7.03 (m, 4H); 7.22 (m, 3H). ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ - 1.72 (-$SiMe_3$); 16.9 (-CH_2); 26.7 (-CH_2-); 37.6 (-CH_2-); 197.8 (C=O); 141.9, 139.4, 138.5, 133.0, 130.6, 130.4, 130.3, 130.0, 128.6, 125.4 (-Ar). MS/EI: 296.5

3f. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 3.21 (m, 1H, Ar-CH); 2.02 (m, 2H, CH_2); 1.65 (m, 4H, CH_2); 1.40 (m, 2H, CH_2); 7.98 (m, 2H, Ar); 7.01-7.19 (m, 7H, Ar). ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ 26.0, 35.5, 42.7 (-C_5H_9); 198.1 (C=O); 145.4, 139.9, 138.7, 133.1, 130.4, 128.6, 127.8, 126.9, 125.3 (Ar). MS/EI: 250.3

exo-**3g**. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 2.93 (m, 1H, CHAr); 2.15 (s, 1H, CH); 1.89 (s, 1H, CH); 1.35 (m, 2H, CH*H*); 1.13 (m, 2H, CH_2); 0.81 (m, 4H, CH_2CH_2); 6.92 (m, 7H, Ar); 7.51 (m, 2H, Ar). ^{13}C {^{1}H} NMR (acetone-d_6, 75.5 MHz, 20 °C) δ

199.0 (C=O); 151.6, 144.5, 143.7, 137.5, 135.2, 135.0, 134.6, 132.9, 130.0, 129.5 (Ar); 49.0, 47.9, 45.3, 42.5, 41.7, 35.7, 34.0 (norbornyl). MS/EI : 276.2

3h. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.01 (s, 9H, $SiMe_3$); 1.01 (m, 2H, CH_2); 3.02 (m, 2H, CH_2); 3.21 (s, 3H, OMe); 3.38 (s, 3H, OMe); 7,92 (d, 2H, Ar); 7.22 (d, 1H, Ar); 6.95 (s, 1H, Ar); 6.65 (d, 2H, Ar); 6.55 (d, 1H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -1.70 ($SiMe_3$); 19.8 (CH_2); 28.5 (CH_2); 54.8 (OMe); 198.1 (C=O); 163.5, 161.5, 149.3, 132.6, 132.4, 132.3, 131.3, 115.8, 110.1, 110.0 (Ar). Anal. Calc.: H 7.64, C 70.14.; Anal. Found: H 7.92, C 71.21.

4h. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ -0.01 (s, 18H, $SiMe_3$); 1.01 (m, 4H, CH_2); 2.99 (m, 4H, CH_2); 3.30 (s, 6H, OMe); 7.48 (d, 2H, Ar); 6.98 (s, 2H, Ar); 6.52 (d, 2H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ 195.7 (C=O); 162.0, 149.2, 133.5, 132.2, 116.8, 110.1 (Ar); 54.8 (OMe); 28.9 (CH_2); 19.7 (CH_2); -1.82 ($SiMe_3$); MS/EI: 442.7

3i. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ -0.02 (s, 9H, $SiMe_3$); 0.77 (m, 2H, CH_2); 2.62 (m, 2H, CH_2); 6.84 (t, 1H, Ar); 7.02 (d, 1H, Ar); 7.37 (d, 1H, Ar); 7.49 (d, 1H, Ar); 7.58 (d, 1H, Ar); 7.57 (s, 1H, Ar); 8.29 (s, 1H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -2.0 ($SiMe_3$); 19.4 (CH_2); 28.0 (CH_2); 194.7 (C=O); 149.2, 138.2, 133.0, 130.7, 129.5, 129.4, 128.2 (Ar); 129.1-130.0 (m, CF_3, Ar); 125.5-126.0 (m, CF_3, Ar); 126.2-126.8 (m, CF_3, Ar).

3j. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.01 (s, 9H, $SiMe_3$); 0.92 (m, 2H, CH_2); 2.83 (m, 2H, CH_2); 2.65 (m, 2H, CH_2); 2.72 (m, 2H, CH_2); 8.12 (m, 1H, Ar); 6.73 (m, 2H, Ar); 6.95-7.18 (m, 4H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -1.72 ($SiMe_3$); 19.9, 28.1, 32.0, 35.2 (CH_2); 200.3 (C=O); 144.1, 141.4, 139.9, 139.0, 131.8, 130.8,

130.2, 130.1, 128.2, 126.4, 125.2 (Ar); Anal. Calc.: H 7.84, C 77.87; Anal. Found: H 8.03, C 77.73.

7a ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ 0.08 (s, 9H, $SiMe_3$); 0.90 (m, 2H, CH_2); 2.97 (m, 2H, CH_2); 2.14 (s, 3H, Me); 7.23 (d, 1H, Ar); 7.08 (m, 2H, Ar); 6.89 (t, 1H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -1.7 ($SiMe_3$); 19.8 (CH_2); 28.9 (CH_2); 29.3 (CH_3); 200.3 (C=O); 146.4, 137.6, 131.4, 130.9, 129.6, 125.5 (Ar); see for comparison Murai et al. Bull. Chem. Soc. Jpn. **68**, 62-83 (1995).

7b ^{1}H NMR (C_6D_6, 400 MHz, 20 °C) δ 0.03 (s, 9H, $SiMe_3$); 0.73 (m, 2H, CH_2); 2.79 (m, 2H, CH_2); 1.92 (s, 3H, Me); 7.00-7.14 (m, 3H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -1.8 ($SiMe_3$); 19.5 (CH_2); 28.9 (CH_2); 26.1 (-Me); 199.2 (C=O); 148.9, 137.6, 131.4, 131.4, 131.0, 125.8 (Ar). Anal. Calc.: H 7.46, C 61.28; Anal. Found: H 7.63, C 60.62.

7c ^{1}H NMR (C_6D_6, 400 MHz, 20 °C) δ 0.04 (s, 9H, $SiMe_3$); 0.68 (m, 2H, CH_2); 2.74 (m, 2H, CH_2); 2.00 (s, 3H, Me); 7.44 (s, 1H, Ar); 7.14 (d, 1H, Ar) 6.92 (d, 1H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ -1.8 ($SiMe_3$); 19.4 (CH_2); 28.4 (CH_2); 27.6 (-Me); 199.9 (C=O); 146.7, 141.5, 129.3, 127.3, 123.2, 122.4 (Ar); 132.6 (q, CF_3). MS/EI: 288.4

8a ^{1}H NMR (acetone-d_6, 300 MHz, 20 °C) δ 0.91 (s, 9H, CMe_3); 1.33 (m, 2H, CH_2); 2.72 (m, 2H, CH_2); 2.01 (s, 3H, Me); 7.54 (s, 1H, Ar); 7.24 (d, 1H, Ar) 6.92 (d, 1H, Ar); ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz, 20 °C) δ 29.5 (CMe_3); 30.7 (CH_2); 29.6 (CH_2); 46.6 (-Me); 200.1 (C=O); 144.6, 141.5, 129.4, 127.3, 123.1, 122.6 (Ar). Anal. Calc.: H 8.01, C 70.44; Anal. Found: H 7.92, C 70.62.

9b ^{1}H NMR (C_6D_6, 300 MHz, 20 °C) δ -0.01 (s, 18H, $SiMe_3$); 0.73 (m, 4H, CH_2); 2.33 (m, 4H, CH_2); 2.07 (s, 3H, Me); 7.39 (s, 2H, Ar); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 75.5 MHz, 20 °C) δ -2.0 ($SiMe_3$); 19.1 (CH_2); 27.6 (CH_2); 32.3 (Me); 205.2 (C=O); 144.8, 128.5, 126.4, 122.8 (Ar); 131.0 (CF_3). MS/EI 388.2.