

Supplementary information
for
Formation of Acylruthenium Promoted by Coordination of AlMe₃
to (η^4 -Cyclopentadienone)Ru(CO)₃

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General. All manipulations were conducted under a nitrogen atmosphere using standard Schlenck or drybox techniques. ¹H and ¹³C nuclear magnetic resonance spectra (NMR) were recorded on JEOL JNM-GSX-270 (270 MHz) and JEOL JNM-400 (400 MHz) spectrometers. The chemical shifts in the ¹H nuclear magnetic resonance spectra were recorded relative to Me₄Si, C₆D₆ (δ 7.16) or CDCl₃ (δ 7.26). The chemical shifts in the ¹³C spectra were recorded relative to Me₄Si, C₆D₆ (δ 128.0) or CDCl₃ (δ 77.0). IR spectra were recorded on a JEOL JIR-AQS20M spectrometer. Elemental analyses were performed by the Instrumental Analysis Center, Faculty of Engineering, Osaka University. For the aluminum incorporated complexes, accurate elemental analyses were precluded by extreme air or thermal sensitivity and/or systematic problems with elemental analysis of organometallic compounds.⁹ For X-ray structure analysis of **3**, all measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-K α radiation at room temperature. For X-ray structure analysis of **5**, all measurements were made on a Rigaku RAXIS-II Imaging Plate diffractometer with graphite monochromated Mo-K α radiation at -50 °C.

Materials. All solvents used in this work were distilled prior to use. Toluene, benzene, n-hexane and C₆D₆ were purified by distillation from sodium benzophenone ketyl, CH₂Cl₂ and CDCl₃ from CaH₂. All commercially available reagents were distilled and degassed prior to use.

(η^4 -C₄Ph₄C(OAlMe₂Cl))Ru(CO)₃ (**2a**). To a solution of (η^4 -C₄Ph₄C=O)Ru(CO)₃ (200 mg, 0.352 mmol) in 10 mL of toluene was added 370 μ L (0.98 M) of a solution of AlMe₂Cl (0.363 mmol) in n-hexane and the reaction mixture was stirred for 1h at room temperature to give a pale yellow suspension. The suspension was concentrated in vacuo to give a yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a yellow solid (**2a**) (223 mg, 96%). ¹H NMR (C₆D₆, 400 MHz): δ -0.39 (s, 6H), 6.66 (t, *J* = 7.6 Hz, 4H), 6.74-6.78 (m, 6H), 7.01 (t, *J* = 7.6 Hz, 2H), 7.11

(t, $J = 7.6$ Hz, 4H), 7.56 (d, $J = 7.6$ Hz, 4H). ^1H NMR (CDCl_3 , 400 MHz): δ -1.15 (s, 6H), 6.95 (d, $J = 7.6$ Hz, 4H), 7.13 (t, $J = 7.8$ Hz, 4H), 7.25 (t, $J = 7.2$ Hz, 2H), 7.31-7.38 (m, 6H), 7.39-7.41 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ -7.2 ($\text{Al}(\text{CH}_3)_2$), 89.1 (C 3,4 of Cp), 107.4 (C 2,5 of Cp), 126.5-131.7 (aromatic), 158.1 (C1 of Cp), 190.2 (CO).

($\eta^4\text{-C}_4\text{Ph}_4\text{C}(\text{OAlMeCl}_2)\text{Ru}(\text{CO})_3$ (2b)). To a solution of ($\eta^4\text{-C}_4\text{Ph}_4\text{C}=\text{O})\text{Ru}(\text{CO})_3$ (200 mg, 0.351 mmol) in 10 mL of toluene was added AlMeCl_2 (43 mg, 0.381 mmol) and the reaction mixture was stirred for 1h at room temperature to give a pale yellow suspension. The suspension was concentrated in vacuo to give a yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a yellow solid (**2b**) (222 mg, 93%). ^1H NMR (C_6D_6 , 400 MHz): δ -0.38 (s, 3H), 6.66 (t, $J = 7.6$ Hz, 4H), 6.74-6.76 (m, 6H), 7.01 (t, $J = 7.4$ Hz, 2H), 7.12 (t, $J = 7.4$ Hz, 4H), 7.55 (d, $J = 7.2$ Hz, 4H). ^1H NMR (CDCl_3 , 400 MHz): δ -1.04 (s, 3H), 6.94 (d, $J = 8.0$ Hz, 4H), 7.14 (t, $J = 7.8$ Hz, 4H), 7.24-7.28 (m, 2H), 7.34-7.41 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 1.0 (AlCH_3Cl_2), 90.6 (C 3,4 of Cp), 107.7 (C 2,5 of Cp), 125.7-132.2 (aromatic), 155.1 (C1 of Cp), 190.7 (CO).

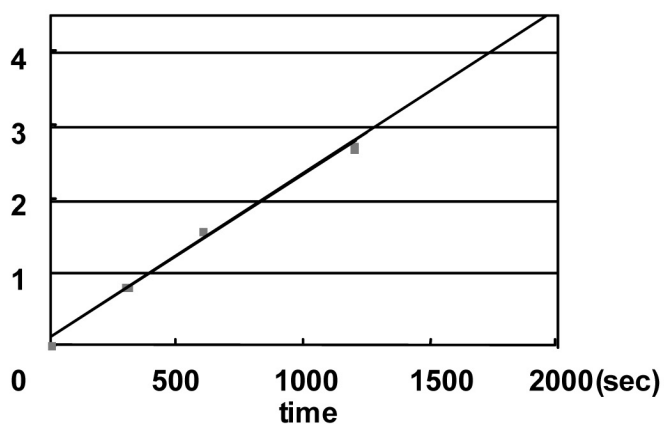
($\eta^4\text{-C}_4\text{Ph}_4\text{C}(\text{OAlCl}_3)\text{Ru}(\text{CO})_3$ (2c)). To a solution of ($\eta^4\text{-C}_4\text{Ph}_4\text{C}=\text{O})\text{Ru}(\text{CO})_3$ (201.7 mg, 0.354 mmol) in 10 mL of toluene was added AlCl_3 (50.2 mg, 0.377 mmol) and the reaction mixture was stirred for 1 h at room temperature to give a pale yellow suspension. The suspension was concentrated in vacuo to give a yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a yellow solid (**2c**) (233.3 mg, 94%). ^1H NMR (C_6D_6 , 400 MHz): δ 6.64 (t, $J = 7.8$ Hz, 4H), 6.70-6.77 (m, 6H), 7.03 (t, $J = 7.4$ Hz, 2H), 7.13 (t, $J = 7.6$ Hz, 4H), 7.50 (d, $J = 7.6$ Hz, 4H). ^1H NMR (CDCl_3 , 400 MHz): δ -1.04 (s, 3H), 6.83 (d, $J = 8.0$ Hz, 4H), 7.03 (t, $J = 7.8$ Hz, 4H), 7.16 (t, $J = 7.6$ Hz, 2H), 7.25-7.37 (m, 10H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 91.5 (C 3,4 of Cp), 107.4 (C 2,5 of Cp), 125.3-131.6 (aromatic), 150.8 (C1 of Cp), 189.2 (CO).

[($\eta^5\text{-C}_5\text{Ph}_4\text{OH})\text{Ru}(\text{CO})_3$][OTf] (3). To a solution of ($\eta^4\text{-C}_4\text{Ph}_4\text{C}=\text{O})\text{Ru}(\text{CO})_3$ (200 mg, 0.351 mmol) in 10 mL of toluene was added $\text{CF}_3\text{SO}_3\text{H}$ (59 mg, 0.396 mmol) and the reaction mixture was stirred for 1h at room temperature to give a pale yellow suspension. The suspension was concentrated in vacuo to give a pale yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a pale yellow solid (**3**) (223 mg, 88%). The complex was recrystallized from CH_2Cl_2 /benzene

solution to give a yellow crystal. ^1H NMR (CDCl_3 , 400 MHz): 6.98 (d, $J = 8.4$ Hz, 4H), 7.14 (t, $J = 7.8$ Hz, 4H), 7.26 (t, $J = 7.0$ Hz, 2H), 7.34-7.40 (m, 10H), 9.94 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): 90.4 (C 3,4 of Cp), 107.6 (C 2,5 of Cp), 125.1-131.7 (aromatic), 148.6 (C1 of Cp), 189.3 (CO).

($\eta^5\text{-C}_4\text{Ph}_4\text{C(OAlMe}_2\text{))Ru(CO)}_2\text{(COMe)}$ (4). To a solution of ($\eta^4\text{-C}_4\text{Ph}_4\text{C=O)Ru(CO)}_3$ (200 mg, 0.352 mmol) in 10 mL of toluene was added 360 μL (1.0 M) of a solution of AlMe_3 (0.360 mmol) in n-hexane at room temperature. After 1 h, solvent was evaporated, and dried in vacuo to give a yellow solid quantitatively (4) (217 mg, 96%). ^1H NMR (C_6D_6 , 400 MHz): -0.55 (s, 6H), 2.36 (s, 3H), 6.76 (m, 6H), 6.94-7.07 (m, 10H), 7.43 (d, $J = 7.6$ Hz, 4H). ^{13}C NMR (C_6D_6 , 100 MHz): -9.8 (AlCH_3), 53.1 (COCH_3), 93.8 (C 3,4 of Cp), 105.5 (C 2,5 of Cp), 130.3-142.9 (aromatic), 142.9 (C1 of Cp), 201.3 (CO), 289.8 (COMe). ^1H NMR (CDCl_3 , 400 MHz): -1.15 (s, 6H), 3.01 (s, 3H), 7.06 (d, $J = 7.2$ Hz, 4H), 7.13 (t, $J = 7.4$ Hz, 4H), 7.20 (t, $J = 7.2$ Hz, 2H), 7.24-7.28 (m, 10H). ^{13}C NMR (CDCl_3 , 100MHz): -10.1 (AlCH_3), 53.8 (COCH_3), 93.4 (C 3,4 of Cp), 104.6 (C 2,5 of Cp), 126.9-131.8 (aromatic), 141.3 (C1 of Cp), 199.5 (CO), 287.8 (COMe).

($\eta^5\text{-C}_5\text{Ph}_4\text{OH)Ru(CO)}_2\text{(COMe)}$ (5). To a solution of ($\eta^4\text{-C}_4\text{Ph}_4\text{C=O)Ru(CO)}_3$ (200 mg, 0.351 mmol) in 10 mL of toluene was added 370 μL (1.0 M) of a solution of AlMe_3 (0.370 mmol) in n-hexane at room temperature. After 1 h, aqueous HCl (5 mL, 1.0 N) was added to a solution and the mixture was stirred for 30 min at room temperature. The solution was dried (MgSO_4), filtered, and concentrated in vacuo to give a yellow solid quantitatively. The solid was washed with n-hexane and dried in vacuo to give a yellow solid (194 mg, 94%). An analytical sample was prepared by recrystallization from C_6H_6 /n-hexane solution. ^1H NMR (C_6D_6 , 400 MHz): δ 2.45 (s, 3H) 6.80-6.81 (m, 6H), 6.88-6.95 (m, 6H), 7.11 (dd, $J = 7.6, 8.0$ Hz, 4H), 7.45 (d, $J = 6.4$ Hz, 4H), 10.5 (s, 1H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 50.8 (COCH_3), 96.8 (C 3,4 of Cp), 107.0 (C 2,5 of Cp), 130.2-133.8 (aromatic), 202.2 (CO), 250.4 (COCH_3). ^1H NMR (CDCl_3 , 400 MHz): δ 2.76 (s, 3H), 7.00-7.02 (m, 4H), 7.09 (t, $J = 7.6$ Hz, 4H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.18-7.21 (m, 10H), 9.72 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 51.1 (COCH_3), 96.5 (C 3,4 of Cp), 106.4 (C 2,5 of Cp), 127.7-132.2 (aromatic), 130.5 (C1 of Cp), 201.3 (CO), 252.1 (COCH_3). Anal. Calcd for $\text{C}_{33}\text{H}_{24}\text{O}_4\text{Ru}$: C, 67.68; H, 4.13. Found: C, 67.41; H, 4.23.

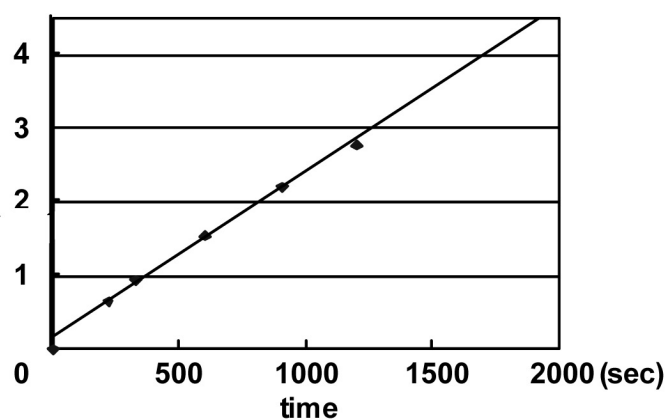


Plot of $\ln[C_0/C]$ vs time

$$\text{rate} = k_{\text{obs}} [\text{Adduct}(C)]$$

$$[C]_0 = 1.46 \times 10^{-2} \text{ M}$$

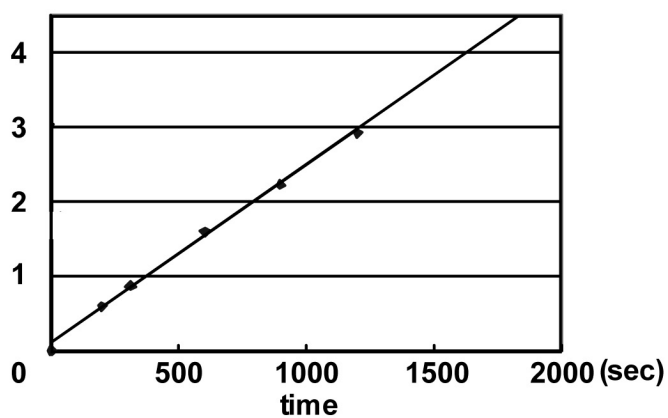
$$k_{\text{obs}} = 2.2 \times 10^{-3} \text{ s}^{-1}$$



Plot of $\ln[C_0/C]$ vs time

$$[C]_0 = 2.93 \times 10^{-2} \text{ M}$$

$$k_{\text{obs}} = 2.3 \times 10^{-3} \text{ s}^{-1}$$



Plot of $\ln[C_0/C]$ vs time

$$[C]_0 = 5.85 \times 10^{-2} \text{ M}$$

$$k_{\text{obs}} = 2.4 \times 10^{-3} \text{ s}^{-1}$$