

SUPPORTING INFORMATION

A New Coupling Reaction for the Synthesis of Ruthenium Halfsandwich Complexes with Sterically Demanding Cyclopentadienyl Ligands

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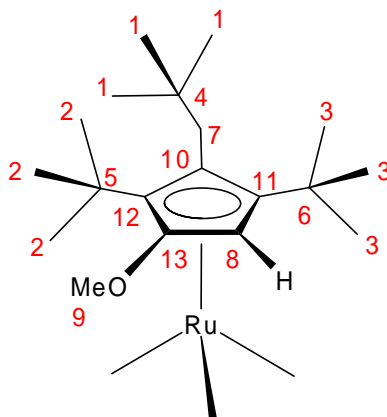
General: All experiments were performed inside a glovebox under an atmosphere of dinitrogen containing less than 1 ppm of oxygen and water. Thoroughly dried and deoxygenated solvents were used. Triphenylphosphine (PPh₃) and bicyclo[2.2.1]hepta-2,5-diene (NBD) were purchased from Fluka. Metallic Zn was a commercial product from Aldrich. *t*-Butylacetylene was purchased from Alfa Aesar. Tricyclohexylphosphine (PCy₃) was obtained from Strem Chemicals and RuCl₃(H₂O)_n from Precious Metals Online. All chemicals were used as received, unless otherwise stated. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker spectrometer at 400 MHz using deuterated solvents. CD₂Cl₂ and CDCl₃ (from Aldrich) for NMR experiments were degassed by three freeze-pump-thaw cycles and then purified by vacuum transfer at room temperature.

Synthesis of complex 3: [RuCl₃(H₂O)_n] (500 mg, 1.90 mmol) was dissolved in 25 mL THF with heating and then the solvent was distilled off at 72 °C, normal pressure using a rotavapor. Complete removal of the solvent at this temperature led to a green insoluble material. Hence, the last portion (~5 mL) of the solvent was removed under high vacuum. The procedure was repeated and then the resulting solid (reddish brown in color) was dissolved in 10 mL of dry MeOH under nitrogen followed by the addition of *t*-butylacetylene (1.0 mL, 8.0 mmol). The closed flask was heated at 55 °C for 24 h and

then kept at $-20\text{ }^{\circ}\text{C}$ for 24 h to ensure complete precipitation. The solid brown precipitate was isolated, washed with MeOH ($\sim 3.0\text{ mL}$) followed by hexane ($\sim 3.0\text{ mL}$) and dried under vacuum. Yield: 434 mg (51 %). Anal. Calcd for $\text{C}_{38}\text{H}_{66}\text{Cl}_4\text{O}_2\text{Ru}_2$: C, 50.78; H, 7.40. Found: C, 50.47; H, 7.36. Single crystals were obtained from cold methanol.

Synthesis of complex 4: The synthesis was performed analogously to that of complex 3 using ethanol (20 mL) instead of methanol. Yield: 365 mg (40 %). Anal. Calcd for $\text{C}_{40}\text{H}_{70}\text{Cl}_4\text{O}_2\text{Ru}_2$: C, 51.83; H, 7.61. Found: C, 51.30; H, 7.31.

^{13}C NMR peak assignment: The following numbering scheme was used for the assignment of the ^{13}C NMR data:



Synthesis of complex 5: Bicyclo[2.2.1]hepta-2,5-diene (NBD) (50 μL , 445 mmol) was added to a solution of complex 3 (100 mg, 111 μmol) in EtOH (5 mL) and stirred at $55\text{ }^{\circ}\text{C}$. The color of the solution changed from brown to light orange. After $\sim 3\text{ h}$, some faint white precipitate appeared. After 6 h, the solution was filtered to remove the precipitate. The EtOH solution was concentrated under reduced pressure to give the product in form of an orange microcrystalline material. The product was washed with ethanol and dried under vacuum. Yield: 67 mg (60 %). ^1H NMR (CD_2Cl_2 , $25\text{ }^{\circ}\text{C}$): δ (ppm) 5.19 (m, 1H, $\text{NBD}_{\text{CH}=\text{CH}}$), 4.83 (s, 1H, Cp-H), 4.67 (m, 1H, $\text{NBD}_{\text{CH}=\text{CH}}$), 4.47 (m, 1H, $\text{NBD}_{\text{CH}=\text{CH}}$), 3.72 (s, 3H, OCH_3), 3.55-3.70 (m, 3H, $\text{NBD}_{\text{CH}=\text{CH}}$, NBD_{CH} bridge), 2.56 (d, 1H, $-\text{CH}_2-$, $J = 16.36$), 2.36 (d, 1H, $-\text{CH}_2-$, $J = 16.40$), 1.36 (m, 2H, NBD_{CH_2}), 1.19 (s, 9H, t -Bu), 1.17 (s, 9H, t -Bu), 1.15 (s, 9H, t -Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , $25\text{ }^{\circ}\text{C}$): δ (ppm) 117.95, (C13),

87.67, 81.35, 80.76 (C10, C11, C12), 65.59, 62.53 (NBD_{CH=CH}), 59.23 (C9), 57.86 (NBD_{bridging C}), 53.09 (C8), 51.15 (NBD_{CH₂}), 40.59 (C7), 37.35, 36.29, 33.77 (C4, C5, C6), 35.55, 35.08, 33.61 (C1, C2, C3). Anal. Calcd for C₂₆H₄₁ClORu: C, 61.70; H, 8.17. Found: C, 61.58; H, 8.19.

Synthesis of complex 6: PCy₃ (62.3 mg, 222 μmol) and excess Zn dust (1.0 g) were added to a solution of complex **3** (100 mg, 111 μmol) in THF (5 mL) and stirred at ambient temperature for 12 h. The color of the solution changed from brown to deep purple. The solution was filtered followed by complete removal of the solvent under high vacuum. Hexane was added and removed in vacuum to ensure complete removal of the THF. The product was then extracted with hexane (5 mL) while the ZnCl₂ formed during reaction remained as a white solid. The product was obtained by removing the hexane in vacuum. Yield: 153 mg (99 %). ¹H NMR (CD₂Cl₂, 25 °C): δ (ppm) 4.15 (s, 1H, Cp-H), 3.55 (s, 3H, OCH₃), 3.23, (d, 1H, -CH₂-, ²J_{HH} = 16.6 Hz), 2.75 (d, 1H, -CH₂-, ²J_{HH} = 15.6 Hz), 1.47 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 1.16-2.20 (m, 30H, PCy₃). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C): δ (ppm) 35.39 (s, 1P, PCy₃). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C): δ (ppm) 121.25 (C13), 83.72, 81.92, 81.10 (C10, C11, C12), 61.10 (C9), 54.14 (C8), 39.31 (C7), 34.60, 34.52, 33.43 (C4, C5, C6), 35.14, 34.27, 33.92 (C1, C2, C3), 29.0-38.0 (PCy₃). Anal. Calcd for C₃₇H₆₆ClOPRu: C, 64.00; H, 9.58. Found: C, 63.97; H, 9.44. Single crystals were obtained by slow evaporation of a solution of complex **6** in CH₂Cl₂/hexane.

Synthesis of complex 7: Excess metallic Zn (1.5 g) was added to a solution of complex **3** (100 mg, 111 μmol) in THF (5 mL) and stirred for 5 min at ambient temperature followed by the addition of PPh₃ (58.3 mg, 222 μmol). Stirring was continued until the color of solution became violet and no excess PPh₃ was detected in the ³¹P NMR (after nearly 40 min). The Zn was filtered off and the solvent was removed in vacuum. Hexane (2 mL) was added and stirred for 5 min and the evaporated to ensure complete removal of the THF. The product was then extracted with hexane (4 mL) while the ZnCl₂ formed during reaction remained as a white solid. The product was obtained by removing the hexane in vacuum. Yield: 72 mg (48 %). The NMR spectra of the

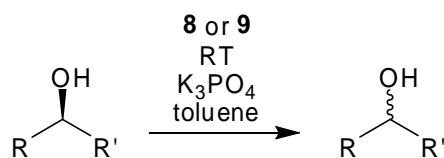
complex were recorded at -20 °C because broad peaks were observed at RT (25 °C), possibly due to hindered rotation of the π -ligand. ^1H NMR (CD_2Cl_2 , -20 °C): δ (ppm) 7.32-7.52 (m, 15H, PPh_3), 3.59 (s, 1H, Cp-H), 3.22 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.36$ Hz), 2.75 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.68$ Hz), 2.63 (s, 3H, OCH_3), 1.46 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), 1.10 (s, 9H, *t*-Bu). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -20 °C): δ (ppm) 35.08 (s, 1P, PPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -20 °C): δ (ppm) 129-136 (Ph), 120.04 (C13), 88.11, 83.43, 80.24 (C10, C11, C12), 57.73 (C9), 56.88 (C8), 37.02 (C7), 34.88, 32.97, 32.19 (C4, C5, C6), 33.30, 32.39, 31.98 (C1, C2, C3). Anal. Calcd for $\text{C}_{37}\text{H}_{48}\text{ClOPRu}$: C, 65.71; H, 7.15. Found: C, 65.88; H, 7.05. Single crystals were obtained from a solution of complex **7** in hexane.

Synthesis of complex 8: Excess zinc dust (50 mg) was added to a solution of complex **3** (200 mg, 222 μmol) in acetonitrile (10 mL). After stirring for 4 h at ambient temperature, the mixture was filtered to give a solution of a cationic tris(acetonitrile) complex. ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 4.03 (s, 1H, Cp-H), 3.54 (s, 3H, OCH_3), 2.70 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 2.35 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 1.40 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.12 (s, 9H, *t*-Bu). The solution of the cationic complex was stirred at ambient temperature under an atmosphere of CO. After 24 h, the solvent was removed in vacuum and the product was purified by column chromatography (silica gel, CH_2Cl_2). Yield: 190 mg (92 %). IR: ν (cm^{-1}) = 1968, 2025 (CO). ^1H NMR (CDCl_3 , 25 °C): δ (ppm) 4.82 (s, 1H, Cp-H), 3.76 (s, 3H, OCH_3), 2.92 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 2.36 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 1.48 (s, 9H, *t*-Bu), 1.37 (s, 9H, *t*-Bu), 1.13 (s, 9H, *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C): δ (ppm) 198.19, 198.60 (CO), 151.02 (C13), 111.14, 98.19, 95.69 (C10, C11, C12), 61.38 (C9), 58.15 (C8), 37.63 (C7), 33.19, 34.32 (C4, C5, C6), 32.05, 32.24 (C1, C2, C3). Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{ClO}_3\text{Ru}$: C, 53.66; H, 7.08. Found: C, 53.81; H, 7.16.

Synthesis of complex 9: The cationic tris(acetonitrile) complex intermediate was prepared as described for **8** using complex **4** as the starting material. ^1H NMR (CDCl_3 , 25 °C): δ (ppm) 3.98 (s, 1H, Cp-H), 3.70 (m, 2H, OCH_2CH_3), 2.70 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 2.34 (d, 1H, $-\text{CH}_2-$, $^2J_{\text{HH}} = 16.00$ Hz), 1.42 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu),

1.30 (t, 3H, OCH₂CH₃, ³J_{HH} = 7.00 Hz), 1.12 (s, 9H, *t*-Bu). Subsequent reaction with CO gave complex **9**. Yield: 192 mg (90 %). IR: ν (cm⁻¹) = 1967, 2024 (CO). ¹H NMR (CDCl₃, 25 °C): δ (ppm) 4.78 (s, 1H, Cp-H), 3.96 (m, 2H, OCH₂CH₃), 2.93 (d, 1H, -CH₂-, ²J_{HH} = 16.00 Hz), 2.36 (d, 1H, -CH₂-, ²J_{HH} = 16.00 Hz), 1.49 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 1.13 (s, 9H, *t*-Bu), 0.86 (t, 3H, OCH₂CH₃, ³J_{HH} = 7.00 Hz). ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ (ppm) 198.31, 198.72 (CO), 150.49 (C13), 111.12, 98.03, 95.48 (C10, C11, C12), 67.50 (OCH₂CH₃), 61.77 (C9), 37.61 (C7), 33.18, 34.35 (C4, C5, C6), 32.04, 32.06, 32.25 (C1, C2, C3), 14.49 (s, 1C, OCH₂CH₃). Anal. Calcd for C₂₂H₃₅ClO₃Ru: C, 54.59; H, 7.29. Found: C, 54.54; H, 7.39.

Racemization of secondary alcohols: the substrate (> 99 % ee, 0.25 mmol) dissolved in toluene (0.8 ml) was added to a flask containing the respective catalyst and K₃PO₄ (0.25 mmol). The reactions were stirred at RT under air. After the time given, the % ee values were determined by GC using a chiral column (Chrompack CP-Sil 8 CB).



entry	complex	substrate	[cat.] [mol %]	time [h]	ee [%]
1	8	(S)-1-phenylethanol	0.25	0.5	20
2	8	(S)-1-phenylethanol	0.25	1.0	0
3	9	(S)-1-phenylethanol	0.25	0.5	27
4	9	(S)-1-phenylethanol	0.25	1.0	3
5	8	(S)-4-phenyl-2-butanol	0.5	1.0	0
6	8	(S)-1-(3-naphthyl)ethanol	0.5	1.0	0
7	8	(s)-1-indanol	0.5	1.5	0