Electronic Supplementary Information for Dalton Transactions

Electronic Supporting Information

Reactions of $Tp(NH{=}CPh_2)(PPh_3)Ru{-}Cl$ with $HC{\equiv}CPh$ in the presence of H_2O: Insertion/Hydration Products

Chih-Jen Cheng,[a] Hung-Chun Tong,[a] Yih-Hsing Lo,*[b] Po-Yo Wang,[b]
Yih-Hsuan Fong[b] and Chia-Her Lin[c]

[a]*Department of Chemical Engineering, Tatung University, Taipei, Taiwan 106, Republic of China.*
[b]*Department of Science, Taipei Municipal University of Education, Taipei, Taiwan 100, Republic of China*. E-mail: *yhlo@mail.tmue.edu.tw;* Fax: (886)-2-2389-7641
[c]*Department of Chemistry, Chung Yuan Christian University, Chung Li, Taiwan 320, Republic of China.*

General Procedure. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagents grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in unit δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at National Taiwan University.

Preparation of Tp(PPh$_3$)(NH=CPh$_2$)Ru-Cl (1). To a solution of Tp(PPh$_3$)$_2$Ru-Cl (3.95 g, 4.50 mmol) in 100 mL toluene was added an excess of benzophenone imine (7.9 mL, 45.0 mmol) were added. The mixture was heated using a warm water bath for 30 min. A deep yellow color developed during this time. The reaction mixture was stirred for a further 2 h at room temperature. Then it was concentrated to approximately half of the volume and cooled to 0 °C. The yellow precipitate was filtered off, washed with ethanol and ether and dried was dried under vacuum to give the compound **1** (3.34 g, 95% yield). Spectroscopic data for **1** are as follows: ^{1}H NMR ($CDCl_3$): δ12.45 (s, 1H, HN), 8.13 (d, 1H, $J_{H\text{-}H}$ = 2.0 Hz, Tp), 6.73-7.70 (Ph, Tp), 6.45 (d, 1H, $J_{H\text{-}H}$ = 2.0 Hz, Tp), 6.11 (t, 1H, $J_{H\text{-}H}$ = 2.0 Hz, Tp), 5.95 (d, 1H, $J_{H\text{-}H}$ = 2.0 Hz, Tp), 5.78 (t, 1H, $J_{H\text{-}H}$= 2.0 Hz, Tp), 5.67 (t, $J_{H\text{-}H}$ = 2.0 Hz, 1H, Tp). ^{13}C NMR ($CDCl_3$): 179.9 (s, HN=*C*(Ph)$_2$), 105.2-148.4 (m, Ph, PPh$_3$, Tp). ^{31}P NMR ($CDCl_3$): δ 51.3. MS (*m*/*z*, Ru102): 793.2

(M^+), 758.1 (M^+ - Cl), 612.2 (M^+ - HN=C(Ph)$_2$). Anal. Calcd for $C_{40}H_{36}BClN_7PRu$: C, 60.58; H, 4.58; N, 12.36. Found: C, 60.43; H, 4.61; N, 12.42.

Reaction of complex 1 with HC≡CPh in the presence of H_2O.

Condition 1: To a distilled ethanol (20 mL) solution of **1** (0.1 g, 0.126 mmol) and H_2O (3 μL, 0.17 mmol) was added phenylacetylene (0.14 mL, 1.3 mmol) at -10 °C. The reaction mixture turned green in 2 h and staring material disappeared as indicated by ^{31}P NMR spectrum. Then the resulting green solution was dried *in vacuo*. The residue was extracted with hexane and the residual solid was further washed with diethyl ether to give the complex {Tp(PPh$_3$)(NH=CPh$_2$)Ru(=C=CHPh)}Cl (**2**) (0.88 g, 78% yield). The hexane extract was concentrated and was then eluted with CH_2Cl_2 on a silica gel packed column to give Tp(PPh$_3$)(NH=CPh$_2$)Ru(-C≡C-Ph)(=C=CHPh) (**3**) (0.006 g, 6% yield).

In a similar manner as above, solution of **1** (0.10 g, 0.126 mmol) and H_2O (3 μL, 0.17 mmol) was added trimethylsilylacetylene (0.18 mL, 1.3 mmol) at -10 °C, the reaction was performed to afford complex Tp(PPh$_3$)(NH=CPh$_2$)Ru(-C≡C-H)(=C=CH$_2$) (**3***) (0.013 g, 16% yield).

Condition 2: To a Schlenk flask charged with **1** (0.10 g, 0.126 mmol) were added H_2O (3 μL, 0.17 mmol), and distilled ethanol (20 mL). The mixture was stirred at room temperature for 5 h then the solvent was dried *in vacuo*. The residue was chromatographed on a silica gel column using CH_2Cl_2 as an eluent to give **3** (0.016 g, 16%) and Tp(PPh$_3$)(NH=CPh$_2$)Ru(-C(CH$_2$Ph)=CHC(O)Ph) (**4**) as a yellow solid (0.052 g, 52%).

Reaction of complex 2 with HC≡CPh in the presence of H_2O.

Acetone (20 mL) was added to a round-bottomed flask charged with complex **2** (0.10 g, 0.11 mmol) and H_2O (3 μL, 0.17 mmol). The reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure to 5 mL. To the solution was added 20 mL of *n*-hexane, whereupon a yellow compound was precipitated. The precipitate was filtered, washed with 10 mL of *n*-hexane and dried under vacuum to yield $Tp(PPh_3)(NH=CPh_2)Ru(-C(CH_2Ph)=CHC(O)Ph)$ (**4**) (0.006 g, 7 % yield) and $Tp(PPh_3)(NH=CPh_2)Ru(-C(Ph)=CHC(O)CH_2Ph)$ (**5**) (0.072 g, 82 % yield).

Spectroscopic data for **2**: ^{1}H NMR ($CDCl_3$): δ 11.58 (s, 1H, NH), 7.89 (br, 1H, Tp), 7.62 (br, 2H, Tp), 7.42-6.94 (m, PPh_3, Ph), 6.78 (br, 1H, Tp), 6.66 (br, 1H, Tp), 5.73 (br, 2H, Tp), 5.60 (br, 1H, Tp), 5.47 (br, 1H, Tp). 5.18 (d, J_{P-H} = 3.7 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 372.3 (t, J_{P-C} = 16.5 Hz, Cα), 176.4 (s, HN=*C*$(Ph)_2$), 146.2 - 106.8 (m, Ph, Tp, PPh_3, Cβ). ^{31}P NMR ($CDCl_3$): δ 37.5. MS (FAB) m/z: 860.2 (M^+ - Cl), 679.2 (M^+ -Cl, HN=C$(Ph)_2$), 577.1 (M^+ - Cl, HN=C$(Ph)_2$, C_2PhH). Anal. Calcd for $C_{48}H_{42}N_7BClN_7PRu$ (895.2): C, 64.40; H, 4.73; N, 10.95. Found: C, 64.37; H, 4.70; N, 10.89.

Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$): δ 7.85 (d, J_{H-H} = 2.2 Hz, 1H, Tp), 7.81 (d, J_{H-H} = 2.2 Hz, 1H, Tp), 7.69 (d, J_{H-H} = 2.2 Hz, 1H, Tp), 7.40 -7.07 (m, Ph), 6.86 (1H, Tp), 6.78 (1H, Tp), 6.76 (1H, Tp), 6.02 (t, J_{H-H} = 2.2 Hz, 1H, Tp), 5.98 (t, J_{H-H} =2.2 Hz, 1H, Tp), 5.85 (t, J_{H-H} =2.2 Hz, 1H, Tp), 4.85 (br, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 375.3 (d, J_{P-C} = 16.3 Hz, Ru=*C*), 136.3 (d, J_{P-C} = 12.3 Hz, Ru-*C*≡), 146.9 -105.6 (m, Ph, PPh_3, Tp).

^{31}P NMR (acetone): δ 49.1. MS (FAB) m/z: 780.2 (M^+ + 1), 678.1 (M^+ + 1 – C_2HPh), 577.1 (M^+ + 1 - C_2HPh, C_2Ph). Anal. Calcd for $C_{43}H_{36}N_6BPRu$ (780.2): C, 66.24; H, 4.65; N, 10.78. Found: C, 66.21; H, 4.59; N, 10.58.

Spectroscopic data for **3***: ^{1}H NMR ($CDCl_3$): δ 7.91 (1H, Tp), 7.84 (1H, Tp), 7.61 (1H, Tp), 7.51 -7.18 (m, Ph), 6.97 (1H, Tp), 6.88 (1H, Tp), 6.71 (1H, Tp), 6.01 (1H, Tp), 5.92 (1H, Tp), 5.76 (1H, Tp), 4.82 (br, 2H, CH), 1.54 (d, J_{H-H} = 3.2 Hz, 1H, ≡CH). ^{31}P NMR (acetone): δ 49.4. MS (FAB) m/z: 628.2 (M^+ + 1), 602.2 (M^+ + 1 – C_2H_2), 577.1 (M^+ + 1 - C_2H_2, C_2H). Anal. Calcd for $C_{31}H_{28}N_6BPRu$ (628.2): C, 59.34; H, 4.50; N, 13.39. Found: C, 59.23; H, 4.46; N, 13.29.

Spectroscopic data for **4**: ^{1}H NMR ($CDCl_3$): δ 7.68 (d, J_{H-H} = 2.1 Hz, 1H, Tp), 7.54 (s, 1H, =CH), 7.35 (d, *J*H-H = 2.1 Hz, 2H, Tp), 7.24-6.91 (m, PPh_3), 6.64 (d, J_{H-H} = 2.1 Hz, 2H, Tp), 5.71 (t, *J*H-H = 2.1 Hz, 2H, Tp), 5.36 (t, J_{H-H} = 2.1 Hz, 1H, Tp), 5.11 (d, J_{H-H} = 2.1 Hz, 1H, Tp), 4.64 (d, J_{H-H} = 17.3 Hz, C*H*HPh), 4.52 (d, J_{H-H} = 17.3 Hz, CH*H*Ph). ^{13}C NMR ($CDCl_3$): δ 198.4 (*C*=O), 171.3 (d, J_{P-C} = 14.1 Hz, Ru-*C*=), 148.3-122.7 (m, Ph, PPh_3, Tp, C_β), 54.9 (*C*H_2Ph). ^{31}P NMR ($CDCl_3$): δ 59.1. MS (FAB) m/z: 798.2 (M^+), 577.1 (M^+ -$CCH_2PhCHCPhCO$). Anal. Calcd for $C_{45}H_{40}BN_9P_2Ru$ (798.2): C, 64.75; H, 4.80; N, 10.54. Found: C, 64.57; H, 4.74; N, 10.45.

Spectroscopic data for **5**: ^{1}H NMR ($CDCl_3$): δ 8.03 (br, 1H, Tp), 7.96 (br, 1H, Tp), 7.83 (br, 1H, Tp), 7.65 (br, 1H, Tp), 7.43 - 7.10 (m, Ph), 7.04 (s, 1H, CH), 6.71 (s, 1H, CH), 6.53 (br, 1H, Tp), 6.24 (br, 1H, Tp), 6.03 (br, 1H, Tp), 5.83 (br, 1H, Tp), 5.40 (br, 1H,

Tp), 3.35 (d, $J_{H\text{-}H}$ = 16.8 Hz, 1H, C*H*HPh), 3.18 (d, $J_{H\text{-}H}$ = 16.8 Hz, 1H, CH*H*Ph). ^{13}C NMR ($CDCl^3$): δ 202.4 (*C*=O), 166.3 (d, $J_{P\text{-}C}$ = 14.0 Hz, Ru-*C*=), 148.3-122.7 (m, Ph, PPh_3, Tp, C_β), 51.3 (CH_2Ph). ^{31}P NMR ($CDCl_3$): d 51.4. Anal. Calcd for $C_{45}H_{40}BN_9P_2Ru$ (798.2): C, 64.75; H, 4.80; N, 10.54. Found: C, 64.57; H, 4.74; N, 10.45.