Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Experimental Supporting Information for

Activation of sp^3 Carbon-Hydrogen Bonds by a Ru(II) Complex and Subsequent Metal-Mediated C-C and C-N Bond Formation

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Experimental Section

General Methods. Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer {O_2 (g) < 15 ppm for all reactions}. Benzene, tetrahydrofuran, diethyl ether (stored over 4Å molecular sieves) were dried by distillation from sodium/benzophenone. Pentane was distilled over sodium. Acetonitrile and nitromethane were dried by distillation from CaH_2. Hexanes and methylene chloride (stored over 4Å molecular sieves) were purified by passage through a column of activated alumina. Organic impurities were removed from acetone by mixing with a $AgNO_3$ solution, followed by the addition of a NaOH solution, filtration and then drying over anhydrous $CaSO_4$.[1] The purified acetone was then distilled from $CaSO_4$, stored under a N_2 atmosphere, redistilled from $CaSO_4$ in a glovebox and stored over 4Å molecular sieves. A ^{1}H NMR spectrum of the purified acetone reveals clean material. Acetone-d_6 was distilled from $CaSO_4$ then degassed with three freeze-pump-thaw cycles and stored under a N_2 atmosphere over 4Å molecular sieves. Benzene-d_6, acetonitrile-d_3, and chloroform-d_1 were degassed with three freeze-pump-thaw cycles and stored under a N_2 atmosphere over 4Å molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer (operating frequency 75 and 100 MHz, respectively for ^{13}C NMR acquisitions). All ^{1}H and ^{13}C NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{19}F NMR spectra were obtained on a Varian 300 MHz or 400 MHz spectrometer (operating frequency 282 or 377 MHz) and referenced against an external standard of hexafluorobenzene (δ = -164.9). ^{31}P NMR spectra were obtained on a Varian 400 MHz spectrometer and referenced against an external standard of H_3PO_4 (δ = 0). Resonances due to the Tp ligand in ^{1}H NMR spectra are listed by chemical shift and multiplicity only (all coupling constants for the Tp ligand are ~ 2 Hz unless otherwise noted). GC-MS was performed using a HP GCD EI system with a 30 m x 0.25 mm HP-5 column with 0.25 mm film thickness. All other reagents were used as purchased from commercial sources. Pyridinium chloride was prepared from stoichiometric addition of 1M HCl in dioxane to a solution of pyridine in hexanes. The

resultant precipitate was collected via vacuum filtration, washed with hexanes, dried in vacuo and stored in a glovebox. The preparation, isolation, and characterization of Me_2Mg,[2] $TpRu(PMe_3)(NCMe)Me$ (**1**)[3] and $TpRu(PMe_3)(NCMe)Cl$[4] have been previously reported. Elemental analyses were performed by Atlantic Microlabs, Inc.

$TpRu(PMe_3)(NCMe)(CH_2CN)$ (2). $TpRu(PMe_3)(NCMe)Me$ (**1**) (0.091 g, 0.20 mmol) was dissolved in acetonitrile (15 mL) and heated to reflux for 20 hours. The volatiles were removed in vacuo, the resulting solid dissolved in minimal toluene, and an off-white solid was precipitated upon addition of approximately 25 mL of pentane. The precipitate was collected via vacuum filtration on a fine porosity frit and dried in vacuo (0.079 g, 0.17 mmol, 82%). ^{1}H NMR ($CDCl_3$, δ): 7.71, 7.69, 7.65, 7.64, 7.51, 7.29 (each 1H, each a d, Tp 3 or 5 positions), 6.22 (1H, m due to coupling with P, Tp 4 position), 6.18, 6.09 (each 1H, each a t, Tp 4 positions), 2.43 (3H, s, NCCH_3), 1.32 {9H, d, $^2J_{HP}$ = 8 Hz, P(CH_3)$_3$}, 0.97 (2H, 2 overlapping dd's, $^2J_{HH}$ = 15 Hz, $^3J_{HP}$ = 4 Hz, diastereotopic CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 142.5, 142.4, 140.4, 135.5, 135.0, 134.4 (each a d, J_{CP} = 2 Hz, Tp 3 and 5 positions), 120.2 (N*C*CH_3), 105.5, 105.3, 105.2 (Tp 4 positions), 94.7 (CH_2*C*N), 16.1 {d, $^1J_{CP}$ = 26 Hz, P(*C*H_3)$_3$}, 5.0 (NC*C*H_3), -15.9 (d, $^2J_{CP}$ = 9 Hz, *C*H_2CN). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 21.1 {*P*$(CH_3)_3$}. Anal. Calcd for $C_{15}H_{25}BN_7PRu$: C, 40.78; H, 5.13; N, 23.78. Found: C, 40.75; H, 5.20; N, 23.59.

$TpRu(PMe_3)[\kappa^2$-*N,N*-{$NHC(CH_3)\}_2C(CN)]$ (3). $TpRu(PMe_3)(NCMe)(CH_2CN)$ (**2**) (0.059 g, 0.125 mmol) was dissolved in acetonitrile (10 mL), placed in a pressure reactor, charged with 500 psi nitrogen pressure and heated to 180 °C for 20 hours. The volatiles were removed in vacuo, and the resulting solid was dried. The dried solid was dissolved in minimal C_6H_6 and applied to a plug of neutral silica. After washing the silica plug with 20 mL of C_6H_6, the product was collected using 5% THF (v/v) in C_6H_6. The yellow eluent was collected, and the volume was reduced in vacuo to approximately 1 mL. Upon addition of pentane, a yellow precipitate formed, which was collected via vacuum filtration through a fine porosity frit. The solid was washed with pentane and dried in vacuo (0.015g, 0.003 mol, 51%). ^{1}H NMR (C_6D_6, δ): 7.62, 7.03 (each 2H, each a d, Tp 3 or 5 positions), 7.48, 7.22 (each 1H, each a m due to coupling with phosphorus, Tp 3 or 5 position), 6.13 (2H, br s, N*H*) 6.01 (1H, m due to coupling with

phosphorus, Tp 4 position), 5.98 (2H, dt, $^{5}J_{CP}$ < 1 Hz, Tp 4 positions), 2.02 (6H, s, {*N*,*N*-N(H)C(C*H*$_3$)C(CN)C(C*H*$_3$)N(H)}), 0.74 {9H, d, $^{2}J_{HP}$ = 9 Hz, P(C*H*$_3$)$_3$}. ^{13}C{^{1}H} NMR (C_6D_6, δ): 163.3 {N*C*(Me)C}, 141.9 (2C, d, J_{PC} = 5 Hz, Tp 3 or 5 positions), 140.9 (d, J_{PC} = 5 Hz, Tp 3 or 5 position), 136.1 (2C, Tp 3 or 5 positions), 134.1 (Tp 3 or 5 position), 125.8 (*C*≡N), 106.3, 106.2, 106.1 (Tp 4 positions), 76.2 {NC(Me)*C*}, 28.5 {*N*,*N*-N(H)C(*C*H$_3$)C(CN)C(*C*H$_3$)N(H)}, 15.7 {d, $^{1}J_{CP}$ = 25 Hz, P(*C*H$_3$)$_3$}. ^{31}P{^{1}H} NMR (C_6D_6, δ): 25.2 {*P*(CH$_3$)$_3$}. Anal. Calcd for $C_{18}H_{28}BN_9PRu$: C, 42.20; H, 5.31; N, 24.61. Found: C, 42.94; H, 5.39; N, 23.88.

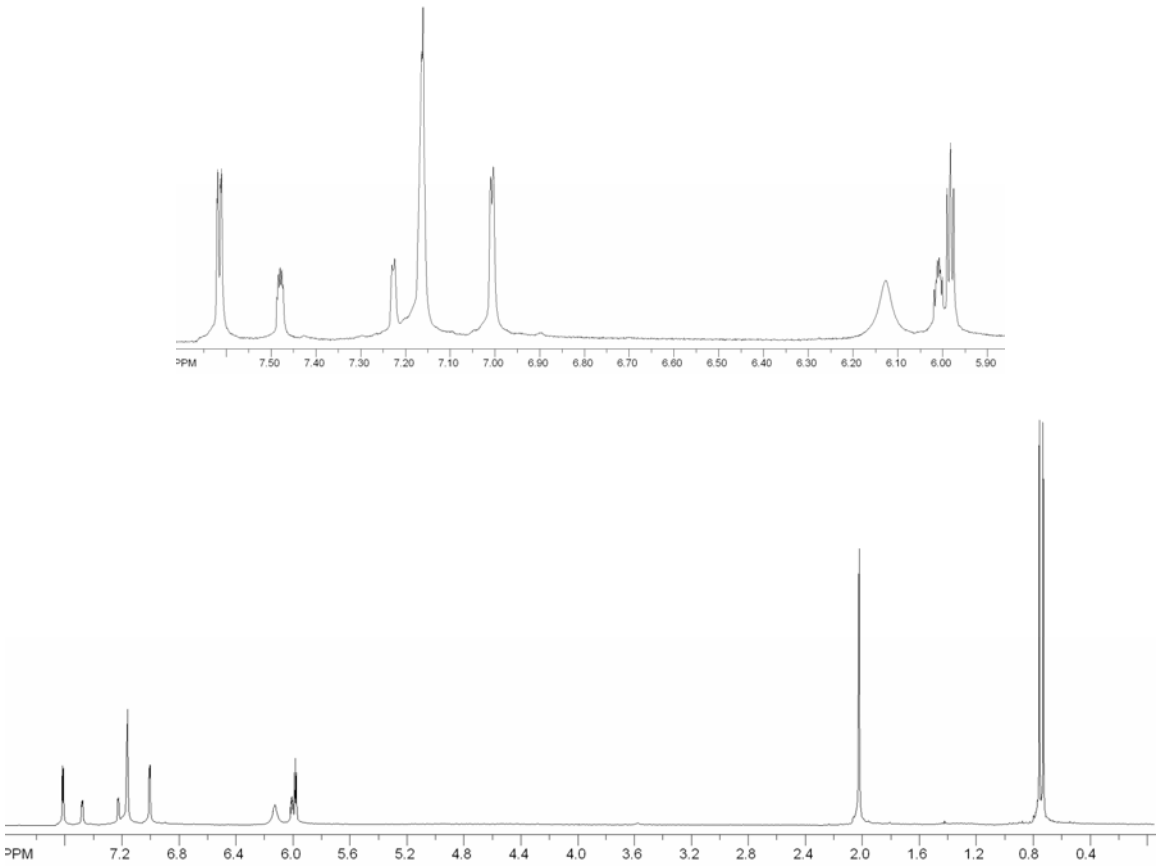

Figure S1. ^{1}H NMR spectrum of TpRu(PMe$_3$)[κ^2-*N*,*N*-{NHC(CH$_3$)}$_2$C(CN)] (**3**) in C_6D_6.

TpRu(PMe$_3$){κ^2-*O*,*N*-N(O)C(H)(NO$_2$)} (4). The complex TpRu(PMe$_3$)(NCMe)Me (**1**) (0.067 g, 0.150 mmol) was added to nitromethane (10 mL), and the solution was heated to reflux for 3 hours. The volatiles were removed in vacuo, and the dried solid was dissolved in minimal benzene. The solution was added to a silica plug, washed with approximately 20 mL of benzene, and the filtrate was discarded. The

product was collected by washing the silica plug with neat THF. The filtrate was dried in vacuo to a brown solid (0.046 g, 0.096 mmol, 64%). ^{1}H NMR ($CDCl_3$, δ): 8.75 (1H, N_2O_3CH), 7.96, 7.94, 7.76, 7.68, 6.91 (each 1H, each a d, Tp 3 or 5 positions), 7.56 (1H, m due to coupling with phosphorus, Tp 3 or 5 position), 6.36, 6.28 (each 1H, each a t, Tp 4 positions), 6.11 (1H, m due to coupling with phosphorus, Tp 4 position), 1.16 {9H, d, $^{2}J_{HP}$ = 9 Hz, $P(CH_3)_3$}. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 145.4, 144.9, 143.9, 136.3, 136.2, 135.1 (Tp 3 and 5 positions), 139.4 (N_2O_3CH), 106.8, 106.6 (Tp 4 positions), 105.9 (d, $^{4}J_{PC}$ = 2 Hz, Tp 4 position), 13.4 {d, $^{1}J_{CP}$ = 30 Hz, $P(CH_3)_3$}. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 13.6 {$P(CH_3)_3$}. EI MS: *m/z* (%)EI MS: *m/z* (%) $M_{theoretical}$: 480.0, M_{sample} = 480.1 (σ = 1.4 ppm), [M^+]; $M_{theoretical}$: 315.0, M_{sample} = 315.0, $[TpRu]^+$.

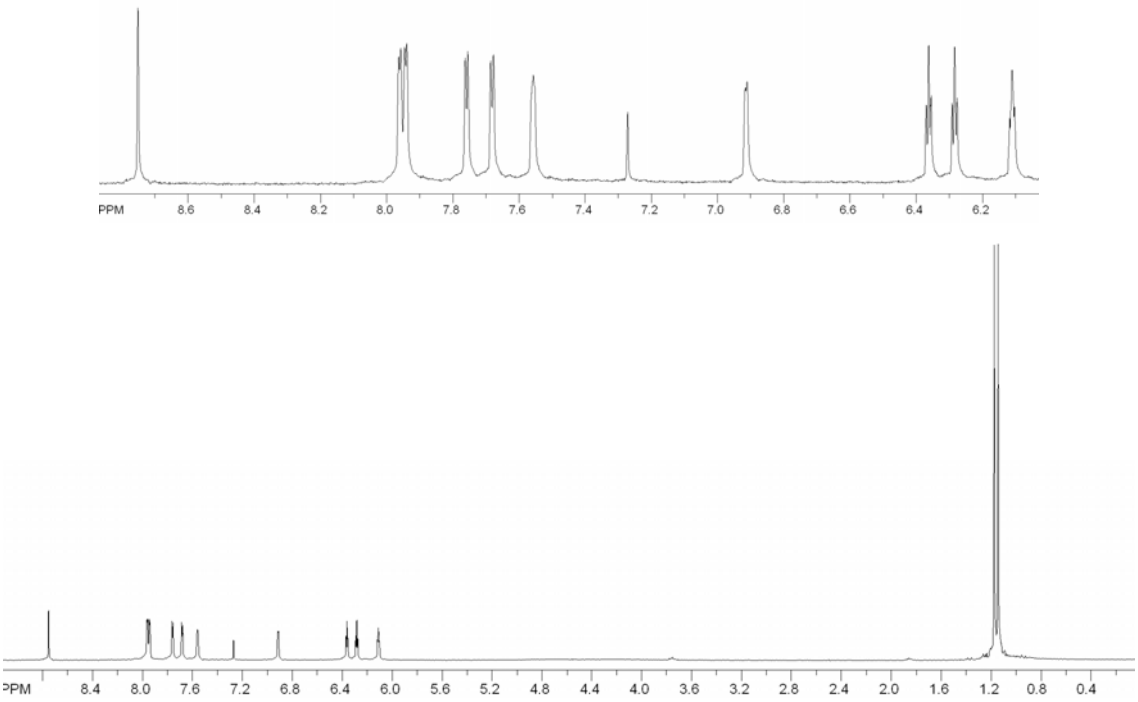

Figure S2. ^{1}H NMR spectrum of $TpRu(PMe_3)\{\kappa^2\text{-}O,N\text{-}N(O)C(H)(NO_2)\}$ (**4**) in $CDCl_3$.

$TpRu(PMe_3)\{\kappa^2$-*O*,*N*-OC(Me)C(H)C(Me)NH} (5). The complex $TpRu(PMe_3)(NCMe)Me$ (**1**) (0.205 g, 0.460 mmol) and acetonitrile (0.12 mL, 2.3 mmol) were combined with 10 mL of acetone in a pressure tube and heated to 80 °C for 24 hours. The volatiles were removed in vacuo. The resulting solid was dissolved in minimal Et_2O, applied to a plug of Grade 1 neutral alumina, and the product was collected by washing the plug with 30% Et_2O (v/v) in hexanes. The yellow filtrate was dried in vacuo to

a film (0.136 g, 0.279 mol, 61%). Note: This reaction also proceeds in acetone that has not been rigorously purified; however, the % yield of **5** is reduced. ^{1}H NMR (C_6D_6, δ): 7.67 (3H, overlapping resonances, Tp 3 or 5 positions), 7.60, 7.56, 7.02 (each 1H, each a d, Tp 3 or 5 positions), 6.44 (1H, br s, N*H*), 6.02 (2H, overlapping resonances, Tp 4 positions), 5.99 (1H, t, Tp 4 position), 4.92 {1H, d, $^{5}J_{HP}$ = 2 Hz, κ^2-*O*,*N*-OC(Me)C(*H*)C(Me)NH}, 2.00 {3H, κ^2-*O*,*N*-OC(C*H*$_3$)C(H)C(Me)NH}, 1.64 {3H, κ^2-*O*,*N*-OC(Me)C(H)C(C*H*$_3$)NH}, 1.01 {9H, d, $^{2}J_{HP}$ = 8 Hz, P(C*H*$_3$)$_3$}. ^{13}C{^{1}H} NMR (C_6D_6, δ): 177.1 {κ^2-*O*,*N*-O*C*(Me)C(H)C(Me)NH}, 163.3 {κ^2-*O*,*N*-OC(Me)C(H)*C*(Me)NH}, 143.1, 142.7, 141.3, 136.3, 135.5, 133.9 (Tp 3 and 5 positions), 106.2, 105.9 (each a d, J_{CP} = 5 Hz, Tp 4 position), 106.0 (Tp 4 position), 94.6 {d, $^{4}J_{CP}$ = 6 Hz, κ^2-*O*,*N*-OC(Me)*C*(H)C(Me)NH}, 27.9, 27.7 {κ^2-*O*,*N*-OC(*C*H$_3$)C(H)C(*C*H$_3$)NH} 15.4 {d, $^{1}J_{CP}$ = 24 Hz, P(*C*H$_3$)$_3$}. ^{31}P{^{1}H} NMR (C_6D_6, δ): 28.3 {*P*(CH$_3$)$_3$}. Anal. Calcd for $C_{17}H_{27}BN_7PRuO$: C, 41.82; H, 5.57; N, 20.08. Found: C, 42.64; H, 5.80; N, 20.09.

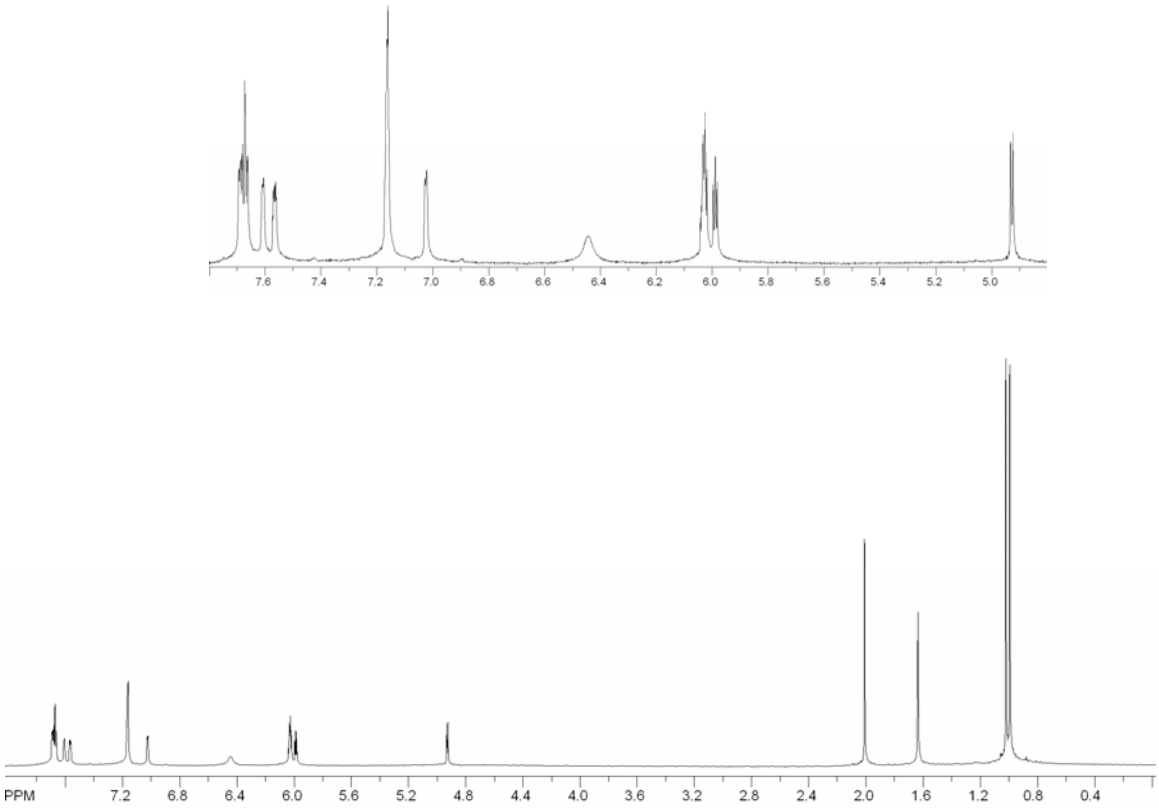

Figure S3. ^{1}H NMR spectrum of TpRu(PMe$_3$){κ^2-*O*,*N*-OC(Me)C(H)C(Me)NH} (**5**) in C_6D_6.

TpRu(PMe$_3$)(NCC$_6$F$_5$)Cl. The complex TpRu(PMe$_3$)(NCMe)Cl (0.077 g, 0.17 mmol) and pentafluorobenzonitrile (0.208 ml, 1.70 mmol) were added to benzene (20 mL), and the solution was heated to reflux for 9 hours. The volatiles were reduced in vacuo, and an orange solid was precipitated upon addition of approximately 25 mL of pentane. The precipitate was collected on a fine porosity frit and dried in vacuo (0.085 g, 0.14 mmol, 83%). ^{1}H NMR ($CDCl_3$, δ): 8.04, 7.80, 7.66, 7.39 (each 1H, each a d, Tp 3 or 5 positions), 7.71 (2H, overlapping Tp 3 or 5 position), 6.27 (1H, m due to coupling with phosphorus, Tp 4 position), 6.21, 6.17 (each 1H, each a t, Tp 4 positions), 1.46 {9H, d, $^2J_{HP}$ = 9 Hz, P(CH_3)$_3$}. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 148.8, (dm, $^1J_{CF}$ = 259, NCC_6F_5), 144.05 (dm, $^1J_{CF}$ = 264, NCC_6F_5), 143.8, 134.2 (each a d, J_{PC} = 2 Hz, Tp 3 and 5 positions), 143.1, 141.4, 135.9, 135.5 (Tp 3 and 5 positions), 137.9 (dm, $^1J_{CF}$ = 260, NCC_6F_5), 106.9 (m, NCC_6F_5), 106.0, 105.8, 105.7 (Tp 4 positions), 91.7 (m, ipso of NCC_6F_5), 15.3 {d, $^1J_{CP}$ = 28 Hz, P(CH_3)$_3$}. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 14.7 {P(CH$_3$)$_3$}. ^{19}F{^{1}H} NMR ($CDCl_3$, δ): -130.9 (2F, dm, $^3J_{FF}$ = 20 Hz, ortho NCC$_6F_5$), -142.6 (1F, tm, $^3J_{FF}$ = 20 Hz, para NCC$_6F_5$), -156.5 (2F, m, meta NCC$_6F_5$). Anal. Calcd for $C_{15}H_{25}BN_7PRu$ (NOTE: data include 0.2 equivalents of free THF, which was observed and integrated by ^{1}H NMR spectroscopy of the sample sent for analysis): C, 37.48; H, 3.26; N, 15.53. Found: C, 38.02; H, 3.45; N, 15.12.

TpRu(PMe$_3$)(NCC$_6$F$_5$)OTf. The complex TpRu(PMe$_3$)(NCC$_6$F$_5$)Cl (0.857 g, 1.38 mmol) and silver triflate (0.374 g, 1.46 mmol) were added to benzene (50 mL) and stirred for 5 hours at room temperature. The reaction mixture was passed through a plug of Celite over a coarse porosity frit. The filtrate was collected, and the solvent volume was reduced in vacuo. A yellow solid was precipitated upon addition of approximately 25 mL of hexanes. The precipitate was collected on a fine porosity frit via vacuum filtration and dried in vacuo (0.970 g, 1.32 mmol, 96%). ^{1}H NMR (C_6D_6, δ): 8.89, 7.64, 7.38, 7.12 (each 1H, each a d, Tp 3 or 5 positions), 7.45 (2H, overlapping resonances, Tp 3 or 5 positions), 6.10 5.88, 5.86 (each 1H, each a t, Tp 4 position), 1.26 {9H, d, $^2J_{HP}$ = 10 Hz, P(CH_3)$_3$}. ^{13}C{^{1}H} NMR (C_6D_6, δ): 149.3 (dm, $^1J_{CF}$ = 257, NCC_6F_5), 144.8, 144.2, 143.7, 137.2, 136.5, 135.0 (each a d, Tp 3 or 5 position), 144.6 (dm, $^1J_{CF}$ = 245, NCC_6F_5), 137.9 (dm, $^1J_{CF}$ = 257, NCC_6F_5), 119.8 (q, $^1J_{CF}$ = 318 Hz, Ru-O$_3$SCF_3), 111.1 (NCC_6F_5), 107.0 (2C, overlapping resonances, Tp 4 positions), 106.9 (Tp 4

position), 91.4 (m, ipso of NCC_6F_5), 14.8 {d, $^1J_{CP}$ = 28 Hz, $P(CH_3)_3$}. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 16.0 {$P(CH_3)_3$}. $^{19}F\{^1H\}$ NMR (C_6D_6, δ): -76.3 (CF_3), -131.2 (2F, dm, $^3J_{FF}$ = 22 Hz, ortho NCC_6F_5), -143.6 (1F, tt, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 5 Hz, para NCC_6F_5), -157.8 (2F, m, meta NCC_6F_5). $M_{theoretical}$: 733.0025, M_{sample} = 733.0015 (σ = 1.4 ppm), [M^+]; $M_{theoretical}$: 540.0, M_{sample} = 540.0, [$TpRu(PMe_3)(CO_3SF_3)^+$]; $M_{theoretical}$: 464.0, M_{sample} = 464.0, [$TpRu(CO_3SF_3)]^+$.

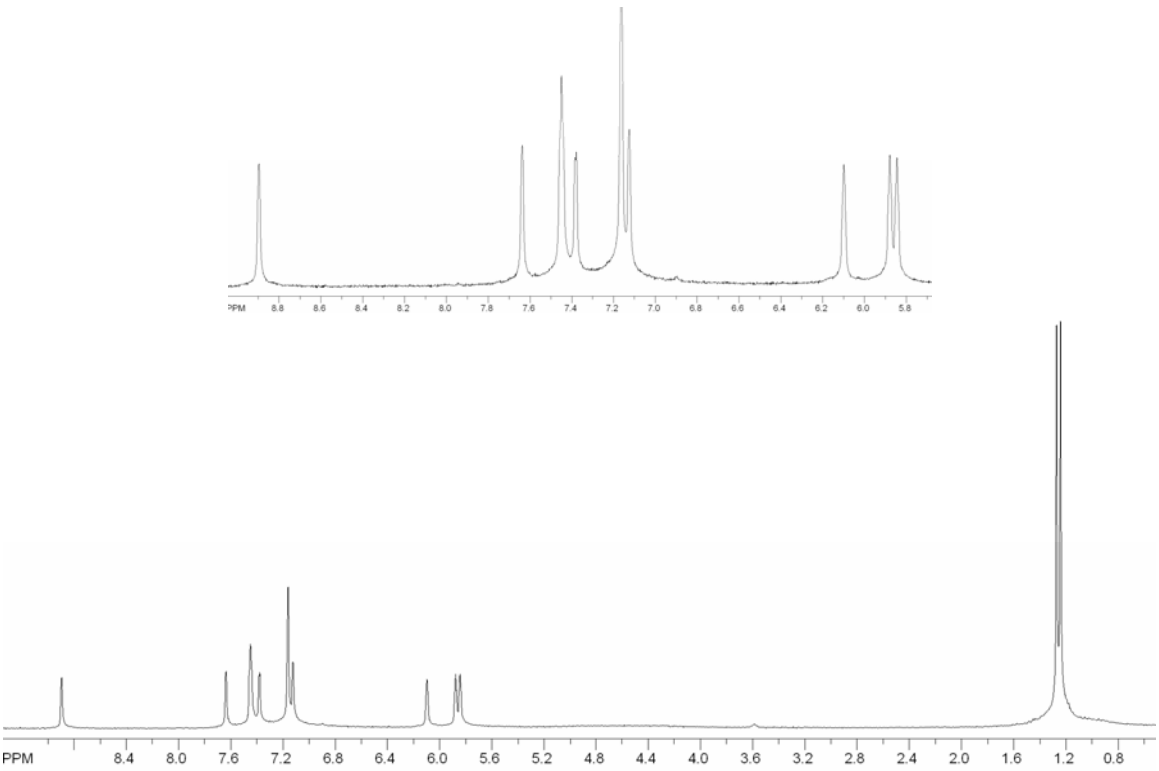

Figure S4. ^1H NMR spectrum of $TpRu(PMe_3)(NCC_6F_5)OTf$ in C_6D_6.

$TpRu(PMe_3)(NCC_6F_5)Me$ (7). To a homogenous solution of $TpRu(PMe_3)(NCC_6F_5)OTf$ (0.334 g, 0.457 mmol) in benzene (20 mL), a solution of Me_2Mg (0.013g, 0.228 mmol, in 10 mL of benzene with 10 drops of THF) was added dropwise. Upon addition of Me_2Mg solution, a color change to a deep red/violet was observed. After 1 hour of stirring at room temperature, the volatiles were reduced in vacuo to approximately 5 mL, and the solution was filtered through a plug of Celite over silica that was pre-treated with triethylamine. The substrates were washed with benzene (containing a few drops of triethylamine), and a deep red eluent was collected. The volatiles were removed in vacuo. The resultant film was reconstituted in pentane and then slowly dried in vacuo yielding a deep violet solid (0.168 g, 0.28 mmol, 61%). ^1H NMR (C_6D_6, δ): 7.99, 7.70, 7.63, 7.50 (each 1H, each a d, Tp 3 or 5 positions),

7.56 (2H, overlapping Tp 3 or 5 position), 6.15 (1H, m due to coupling with phosphorus, Tp 4 position), 6.13, 5.95 (each 1H, each a t, Tp 4 positions), 1.20 {9H, d, $^2J_{HP}$ = 8 Hz, P(CH_3)$_3$}, 0.81 (3H, d, $^2J_{HP}$ = 4 Hz, Ru-CH_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 148.5 (dm, $^1J_{CF}$ = 245, NCC_6F_5), 143.0, 141.8, 140.2, 135.8, 135.1, 134.5 (each a d, Tp 3 or 5 position), 141.9 (dm, $^1J_{CF}$ = 249, NCC_6F_5), 138.3 (dm, $^1J_{CF}$ = 257, NCC_6F_5), 105.9, 105.7, 105.6 (Tp 4 positions), 102.3 (NCC_6F_5), 93.5 (m, ipso of NCC_6F_5), 16.2 {d, $^1J_{CP}$ = 26 Hz, P(CH$_3$)$_3$}, -4.5 (d, $^2J_{CP}$ = 11 Hz, Ru-CH$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 16.9 {P(CH$_3$)$_3$}. ^{19}F{^{1}H} NMR (C_6D_6, δ): -135.5 (2F, dm, $^3J_{FF}$ = 20 Hz, ortho NCC$_6F_5$), -151.1 (1F, t, $^3J_{FF}$ = 22 Hz, para NCC$_6F_5$), -159.8 (2F, m, meta NCC$_6F_5$).

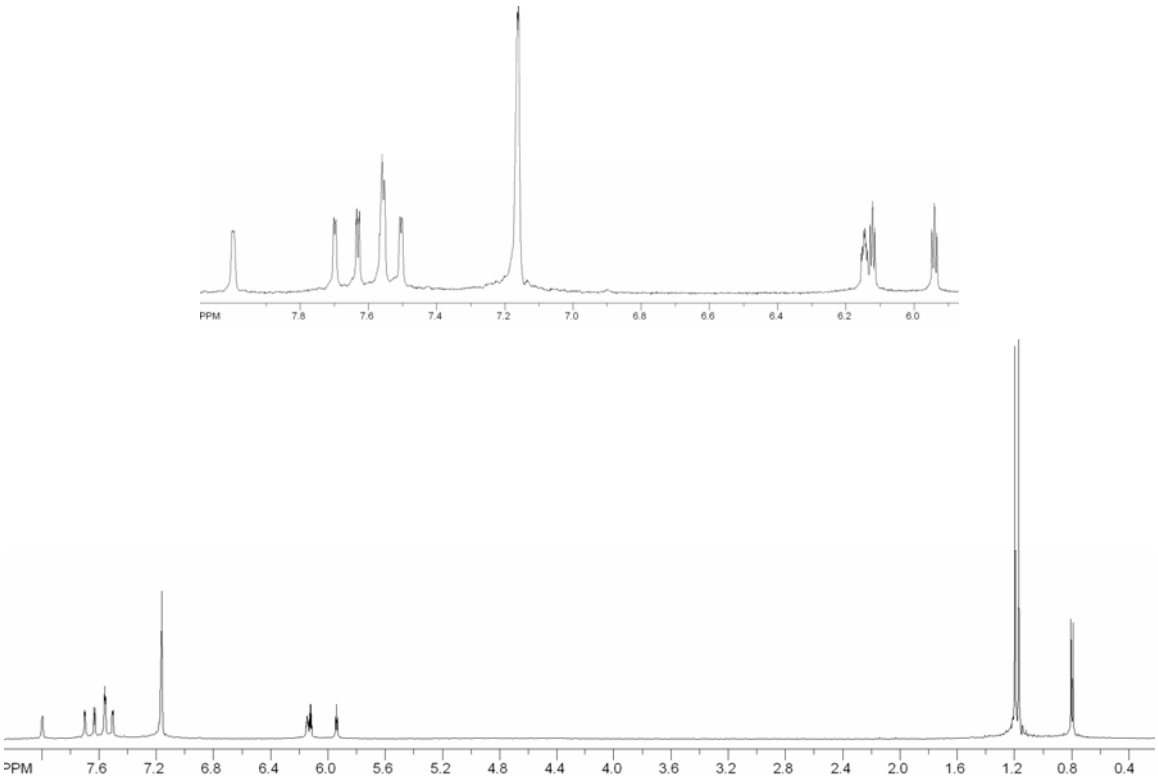

Figure S5. ^{1}H NMR spectrum of TpRu(PMe$_3$)(NCC$_6$F$_5$)Me (**7**) in C_6D_6.

TpRu(PMe$_3$){κ^2-*O*,*N*-OC(Me)C(H)C(C$_6$F$_5$)NH} (8). The complex TpRu(PMe$_3$)(NCMe)Me (**1**) (0.156 g, 0.261 mmol) was combined with 15 mL of acetone in a thick-walled glass pressure tube and heated to 100 °C for 20 hours. The volatiles were removed in vacuo, the resulting solid was dissolved in minimal dichloromethane, applied to a plug of Grade 1 neutral alumina, and the product was collected by washing the plug with 30% Et$_2$O in hexanes. The orange-yellow filtrate was dried in vacuo (0.129 g,

0.201 mol, 77%). ^{1}H NMR (C_6D_6, δ): 7.84, 7.66, 7.64, 7.61, 7.10 (each 1H, each a d, Tp 3 or 5 positions), 7.55 (1H, m due to coupling with phosphorus, Tp 3 or 5 position), 6.90 (1H, br s, N*H*) 6.11 (1H, m due to coupling with P, Tp 4 position), 6.02, 5.95 (each 1H, each a t, Tp 4 positions), 4.95 {1H, d, $^{5}J_{HP}$ = 2 Hz, κ^2-*O*,*N*-OC(Me)C(*H*)C(C_6F_5)NH}, 1.94 {3H, κ^2-*O*,*N*-OC(*Me*)C(H)C(C_6F_5)NH}, 1.09 {9H, d, $^{2}J_{HP}$ = 8 Hz, P(C*H*$_3$)$_3$}. ^{13}C{^{1}H} NMR (C_6D_6, δ): 178.3 {κ^2-*O*,*N*-O*C*(Me)C(H)C(C_6F_5)NH}, 150.8 {κ^2-*O*,*N*-OC(Me)C(H)*C*(C_6F_5)NH}, 144.0 (dm, $^{1}J_{CF}$ = 242 Hz, NC*C*$_6$F$_5$), 143.0, 142.8, 141.5, 136.6, 135.9, 134.2 (Tp 3 and 5 positions), 138.0 (dm, $^{1}J_{CF}$ = 249 Hz, NC*C*$_6$F$_5$), 118.0 (N*C*C$_6$F$_5$), 106.4, 106.0 (Tp 4 position), 106.2 (d, $^{4}J_{PC}$ = 2 Hz, Tp 4 position), 96.3 {κ^2-*O*,*N*-OC(Me)*C*(H)C(C_6F_5)NH}, 90.8 (m, ipso of NC*C*$_6$F$_5$), 28.0 {κ^2-*O*,*N*-OC(Me)C(*H*)C(C_6F_5)NH}, 15.4 {d, $^{1}J_{CP}$ = 25 Hz, P(*C*H$_3$)$_3$}. (NOTE: one set of NC*C*$_6$F$_5$ resonances could not be located in the ^{13}C NMR spectrum likely due to overlap with Tp resonances.) ^{31}P{^{1}H} NMR (C_6D_6, δ): 26.5 {*P*(CH$_3$)$_3$}. ^{19}F{^{1}H} NMR (C_6D_6, δ): -141.0 (2F, m, ortho NCC$_6$*F*$_5$), -155.4 (1F, t, $^{3}J_{FF}$ = 21 Hz, para NCC$_6$*F*$_5$), -161.1 (2F, m, meta NCC$_6$*F*$_5$). Anal. Calcd for $C_{22}H_{24}BN_7PRuF_5O$: C, 41.27; H, 3.78; N, 15.31. Found: C, 42.13; H, 3.96; N, 15.13.

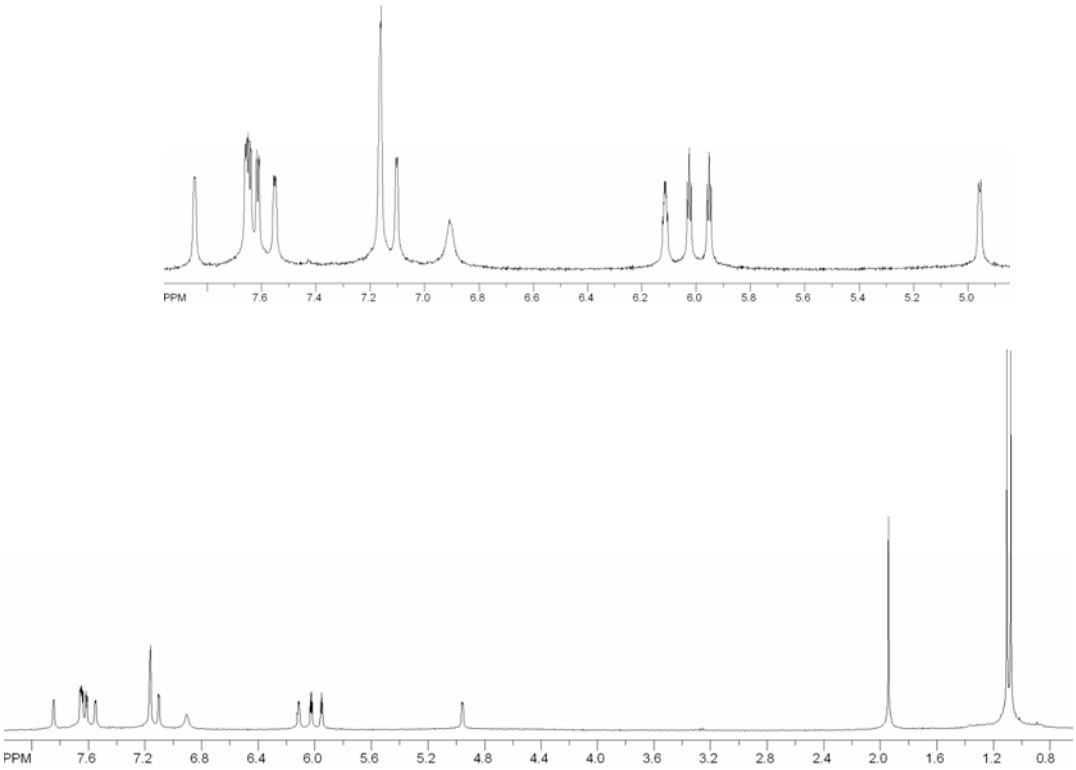

Figure S6. ^{1}H NMR spectrum of TpRu(PMe$_3$){κ^2-*O*,*N*-OC(Me)C(H)C(C_6F_5)NH} (**8**) in C_6D_6.

Kinetic Studies: Rate of C-D activation of $NCCD_3$ by $TpRu(PMe_3)(NCMe)Me$ (1). A solution of $TpRu(PMe_3)(NCMe)Me$ (**1**) (0.021 g, 0.047 mmol) in 1.5 mL of CD_3CN (28.7 mmol), with a small crystal of hexamethylbenzene as internal standard, was evenly divided into 3 screw-cap NMR tubes. The triplicate set was heated at 70 °C in a temperature regulated oil bath, and ^1H NMR spectra were periodically acquired through 3 half-lives (using a pulse delay of 5 seconds for data acquisition). The rate of C-D activation was followed by integration of the decreasing resonance due to the Ru-Me doublet at -0.19 ppm relative to the standard hexamethylbenzene. By ^1H NMR, $TpRu(PMe_3)(NCMe)Me$ (**1**) was observed to cleanly convert to $TpRu(PMe_3)(NCCD_3)(CH_2CN)$ (**2**) without observation of intermediates.

Kinetic Studies: KIE Determination for Acetonitrile Activation by $TpRu(PMe_3)(NCMe)Me$ (1). A solution of $TpRu(PMe_3)(NCMe)Me$ (**1**) (0.032 g, 0.071 mmol) in 2.0 mL of a 1:1 molar mixture of $NCMe/NCCD_3$ (1000 μL:999 μL) was equally divided into 3 screw-cap NMR tubes and heated (70 °C) for approximately 10 hours (~1 half-life). The samples were cooled to room temperature in a water bath, shaken and ^1H NMR spectra (300 MHz) were acquired (pulse delay of 5 seconds) to measure the ratio of CH_4 (δ = 0.18 ppm, s) to CH_3D (δ = 0.17 ppm, 1:1:1 t, $^1J_{HD}$ = 2 Hz).

Kinetic Studies: Rate of conversion to $TpRu(PMe_3)\{\kappa^2$-*O*,*N*-OC(Me)C(H)C(Me)NH} (4) from $TpRu(PMe_3)(NCMe)Me$ (1). A solution of $TpRu(PMe_3)(NCMe)Me$ (**1**) (0.033 g, 0.074 mmol) in 1.35 mL of $(CD_3)_2CO$ (18.3 mmol), with a small crystal of hexamethylbenzene as internal standard, was divided among 3 screw-cap NMR tubes. The triplicate set was heated at 60 °C in a temperature regulated oil bath, and ^1H NMR spectra were periodically acquired through 3 half-lives (using a pulse delay of 5 seconds). The concentration of $TpRu(PMe_3)(NCMe)Me$ (**1**), $TpRu(PMe_3)(NCMe)\{CH_2C(O)CH_3\}$ (**6**) and $TpRu(PMe_3)\{\kappa^2$-*O*,*N*-OC(Me)C(H)C(Me)NH} (**5**) were followed by integration of the decreasing resonances at -0.11, 8.16 and 7.25 ppm, respectively, relative to the standard hexamethylbenzene.

Reaction of $TpRu(PMe_3)\{\kappa^2$-*O*,*N*-OC(Me)C(H)C(Me)NH} (4) with pyridinium chloride. Pyridinium chloride (0.003g, 0.022mmol) was added to a solution of $TpRu(PMe_3)\{\kappa^2$-*O*,*N*-OC(Me)C(H)C(Me)NH} (**4**) (0.011g, 0.021 mmol), mesitylene (0.003 mL, 0.022 mmol) as standard and

$NCCD_3$ (~500 uL) in an NMR tube. An immediate ^1H NMR spectrum revealed broadening of all resonances associated with complex **4**. After heating the reaction at 60 °C for 10 hours, 86% yield of 4-amino-3-penten-2-one, $TpRu(PMe_3)(NCCD_3)Cl$ and free pyridine were observed by ^1H NMR spectroscopy. GC/MS further verified the presence of 4-amino-3-penten-2-one.

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Computational Supporting Information for

Activation of sp^3 Carbon-Hydrogen Bonds by a Ru(II) Complex and Subsequent Metal-Mediated C-C and C-N Bond Formation

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Computational Methods

As full experimental ligand models were studied the MOE program[i] and the MMFF94[ii] force field were initially used to identify the lowest energy conformations for subsequent refinement of geometries with DFT methods. All quantum calculations employed the Gaussian03 package.[iii]

The B3LYP functional (Becke's three-parameter hybrid functional[iv] using the LYP correlation functional containing both local and nonlocal terms of Lee, Yang, and Parr)[v] and VWN (Slater local exchange functional[vi] plus the local correlation functional of Vosko, Wilk, and Nusair)[vii] were employed in conjunction with the Stevens (SBK) valence basis sets and effective core potentials for all heavy atoms and the –31G basis set for hydrogen. The SBK valence basis sets are valence triplet-zeta for ruthenium, and double-zeta for main group elements. The basis sets of main group elements are augmented with a d-polarization function: $\xi_d = 0.8$ for boron, carbon, nitrogen and oxygen and $\xi_d = 0.55$ for phosphorus. The SBK scheme utilizes a semi-core (46-electron core) approximation for ruthenium and a full core approximation for main group elements.

All complexes modeled are closed-shell (diamagnetic) species and were modeled within the restricted Kohn-Sham formalism. All systems were fully optimized without symmetry constraint and analytic calculations of the energy Hessian were performed to confirm species as minima or transition states and to obtain free energies (using unscaled vibrational frequencies) in the gas phase at 1 atm and 298.15 K.

Table S1. Computed Enthalpic and Energetic Data[a]

Name	Stoichiometry	H	G	Comment	H_{rel}	G_{rel}
nitrile	$C_{15}H_{25}BN_7PRu$	-272.0724	-272.1603	$TpRu(PMe_3)(Me)(NCMe)$		
tppme	$C_{13}H_{22}BN_6Pru$	-249.0938	-249.1704	$TpRu(PMe_3)(Me)$		
	RH	**Substrate**				
ch4	CH_4	-8.0100	-8.0312	Methane		
mecn	C_2H_3N	-22.9353	-22.9640	Acetonitrile		
meno2	CH_3NO_2	-49.1579	-49.1911	Nitromethane		
acetone	C_3H_6O	-36.4444	-36.4793	Acetone		
cyh	C_6H_{12}	-40.9479	-40.9819	Cyclohexane		
thf	C_4H_8O	-43.2505	-43.2849	THF		
	M←X	**Adducts**	**of RH**			
meh_r	$C_{14}H_{26}BNPRu$	-257.1081	-257.191203	Agostic Methane Adduct	24.5	22.8
mecn_r2	$C_{15}H_{25}BN_7PRu$	-272.0724	-272.1603	κ^1-N Adduct	0.0	0.0
no2_r2	$C_{14}H_{25}BN_7O_2PRu$	-298.2806	-298.3705	κ^1-O Adduct	9.1	10.6
acetone_r2	$C_{16}H_{28}BN_6OPRu$	-285.5605	-285.6512	κ^1-O Adduct	13.1	15.3
cyh_r2	$C_{19}H_{34}BN_6PRu$	-290.0459	-290.1396	Agostic CyH Adduct	24.5	24.2
thf_r2	$C_{17}H_{30}BN_6OPRu$	-292.3647	-292.4544	κ^1-O Adduct	14.4	16.8
	Agostic	**RH**	**Adduct**			
meh_r	$C_{14}H_{26}BNPRu$	-257.1081	-257.191203	Agostic Methane Adduct	24.5	22.8
mecn_r	$C_{15}H_{25}BN_7PRu$	-272.0316	-272.1200	Agostic MeCN Adduct	25.6	25.3
no2_r	$C_{14}H_{25}BN_7O_2PRu$	-298.2563	-298.3460	Agostic $MeNO_2$ Adduct	24.3	26.0
acetone_r	$C_{16}H_{28}BN_6OPRu$	-285.5417	-285.6348	Agostic Acetone Adduct	24.9	25.6
cyh_r	$C_{19}H_{34}BN_6PRu$	-290.0459	-290.139594	Agostic CyH Adduct	24.5	24.2
thf_r	$C_{17}H_{30}BN_6OPRu$	-292.3477	-292.439548	Agostic THF Adduct	25.1	26.1
	TSs for	**Activation**	**of RH**	**ν_i**		
mets	$C_{14}H_{26}BNPRu$	-257.0812	-257.1623	393i	41.3	40.9
mecnts	$C_{15}H_{25}BN_7PRu$	-272.0158	-272.1003	704i	35.5	37.7
no2ts	$C_{14}H_{25}BN_7O_2PRu$	-298.2448	-298.3320	722i	31.5	34.7
acetonets	$C_{16}H_{28}BN_6OPRu$	-285.5180	-285.6064	575i	39.8	43.4
cyts	$C_{19}H_{34}BN_6PRu$	-290.0117	-290.1018	394i	45.9	47.9
thfts	$C_{17}H_{30}BN_6OPRu$	-292.3201	-292.4081	188i	42.4	45.9
	Ru-CH_2X Product	**Of**	**RH**	**C-H Bond Activation**		
ch2cn	$C_{14}H_{21}BN_7PRu$	-264.0557	-264.1349	η^3	4.2	9.7
ch2no2	$C_{13}H_{21}BN_7O_2PRu$	-290.2890	-290.3701	η^3	-2.5	4.5
ch2come-b	$C_{15}H_{24}BN_6OPRu$	-277.5638	-277.6452	η^3	4.8	12.8
cy	$C_{18}H_{30}BN_6PRu$	-282.0273	-282.1142	κ^1-C	29.9	33.9
ru-thf	$C_{16}H_{26}BN_6OPRu$	-284.3427	-284.4261	κ^1-C	21.9	28.3

Notes:

- H (298.15 K) and G (298.15 K) are given in atomic units and are calculated as described above in Computational Methods.
- H_{rel} and G_{rel} are the relative calculated enthalpies and free energies, respectively, and are quoted in kcal/mol. The values are calculated relative to $TpRu(PMe_3)(Me)(NCMe)$ + RH (*i.e.*, separated reactants).
- ν_i is the imaginary frequencies of the transition states and are given in cm^{-1}. The remaining species are all minima on their respective potential energy surfaces.

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