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Mechanism of Halide Exchange in Reactions of $CpRu(PPh_3)_2Cl$ with Alkyl Halides

Benjamin S. Rich, Noah B. Bissonnette, Alejandra Duran, Mulan Yang, Hope Meikle, Nithin Chintala, Sijia S. Dong* and Rein U. Kirss*

Department of Chemistry and Chemical Biology Northeastern University, Boston MA 02115.

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Experimental

All compounds described in this work were handled using Schlenk techniques or a M. I. Braun glove box under purified nitrogen atmospheres. $RuCl_3 \bullet xH_2O$ was purchased from Pressure Chemical, Inc. Tertiary phosphines, cyclopentadiene, 1-bromobutane,1-iodopropane, duraquinone, and dihydroanthracene (Fischer Acros Chemical, Inc.) were used as received. Solvents were purified by refluxing over Na/benzophenone (toluene, tetrahydrofuran, benzene, hexane, pentane), P_2O_5 (dichloromethane) or $MgSO_4$ (ethanol) and distilled prior to use. Chloroform-d^1, toluene-d^8, and benzene-d^6 (Cambridge Isotope Laboratories) were purified by distillation from CaH_2 ($CDCl_3$) or Na/benzophenone. Fluorobenzene (Fisher-Acros) was distilled from P_2O_5. For synthesis, ^{n}butyl bromide and ^{n}propyl iodide were used as received. Cyclopentadienylruthenium (II) phosphine compounds $CpRu(PPh_3)_2Cl$ (**1a**), [1] $CpRu(P\{p\text{-}CH_3C_6H_4\}_3)_2Cl$ (**1b**), [2a] $CpRu(P\{p\text{-}CH_3OC_6H_4\}_3)_2Cl$ (**1c**), [2b] $CpRu(P\{p\text{-}FC_6H_4\}_3)_2Cl$ (**1d**), [2c] and $CpRu[PPh_2(p\text{-}CH_3C_6H_4)]_2Cl$ (**1e**), [2c] were prepared by literature procedures. For comparison, samples of $CpRu(PPh_3)_2Br$ (**2a**) and $CpRu(PPh_3)_2I$ (**3a**) were also prepared by published methods. [3] Melting points were determined in capillary tubes using a Stanford Research Systems Digimelt apparatus. Elemental analyses (C, H) were performed by Columbia Analytical Services, Inc. Tucson, AZ.

NMR spectra were recorded at 400 MHz for ^{1}H, 162 MHz for $^{31}P\{^1H\}$ and 376 MHz for ^{19}F on a Mercury XL300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent ($CD_2\mathbf{H}Cl$ at δ 7.24 ppm or $C_6D_5\mathbf{H}$ at δ 7.15 ppm relative to TMS at 0.00 ppm). Phosphorus chemical shifts are reported relative to 85% $H_3\mathbf{P}O_4$ at 0.0 ppm. A HP6890 Series GC (Agilent HO-1 dimethylpolysiloxane column, 25 m x 0.200 nm x 0.4μm) coupled with a HP5973 mass selective detector was used for the gc/ms experiments.

*Synthesis of $CpRu(PPh_3)_2Br$ (**2a**)*

50.0 mg $CpRu(PPh_3)_2Cl$ (0.069 mmol) and 48 μL ^{n}BuBr (0.447 mmol) yielded 52.8 mg $CpRu(PPh_3)_2Br$ (100%) as an orange solid. ^{1}H and ^{31}P NMR spectra are consistent with those reported in the literature. ^{1}H ($CDCl_3$): δ 7.34 (br, 12H, aryl), 7.24 (dd, J= 6.8, 8.8 Hz, 6 H, aryl), 7.14 (d, J = 6.8 Hz, 12H, aryl), 4.12 s (5H, Cp). $^{31}P\{^1H\}$ ($CDCl_3$): δ 37.6 (s)

*Synthesis of $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2Br$(**2b**)*

65.0 mg $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2Cl$ (0.080 mmol) and 60 μL ^{n}BuBr (0.559 mmol) yielded 47.6 mg $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2Br$ (73%) as an orange solid. M.p. 137-139°C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.23 (m, 12H, aryl), 6.91 (d, J = 7.2 Hz, 12H, aryl), 4.08 (s, 5H, Cp), 2.30 (s, 18H, CH_3). $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): δ 36.8 (s)
Anal. Calcd for $C_{47}H_{47}P_2BrRu$: C, 66.04%; H, 5.54%. Found: C, 66.02%; H, 5.65%.

*Synthesis of $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2I$(**3b**)*

93.0 mg $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2Cl$ (0.113 mmol) and 115 μL ^{n}PrI (1.18 mmol) yielded 63.7 mg $CpRu[P(p\text{-}CH_3C_6H_4)_3]_2I$ (62%) as a red solid. Rec-crystallization from toluene leads to one equivalent of toluene in the

crystalline product. M.p. 132-134°C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.17 (br s, 12 Hz, 12H, aryl), 6.93 (d, J = 7.6 Hz, 12H, aryl), 4.15 (s, 5H, Cp), 2.36 (s, 3H, toluene), 2.32 (s, 18H, CH_3). The aryl resonances for the coordinated toluene are seen at 7.24 and 7.28 are assigned by comparison with the spectrum of toluene in $CDCl_3$ (7.31 d, 7.23 d, J= 7.6 Hz). Both of the coordinated toluene aryl resonances are obscured by the $CHCl_3$ resonance from the solvent. $^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$): δ 34.6 s

Anal. Calcd for $C_{47}H_{47}P_2IRu•C_7H_8$: C, 65.26%; H, 5.58%. Found: C, 64.96%; H, 5.63%.

*Synthesis of CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$Br (**2c**)*

118 mg CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$Cl (0.130 mmol) and 98 μL ^{n}BuBr (0.913 mmol) yielded 90.9 mg CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$Br (73%) as an orange solid M.p. 149-152°C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.28 (m, 12H, aryl), 6.66 (d, J = 8.8 Hz, 12H, aryl), 4.11 (s, 5H, Cp), 3.78 (s, 18H, CH_3O). $^{31}P\{^{1}H\}$(162 MHz, $CDCl_3$): δ 35.59 (s)

Anal. Calcd for $C_{47}H_{47}O_6P_2BrRu$: C, 59.37%; H, 4.98%. Found: C, 58.99%; H, 5.28%

*Synthesis of CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$I (**3c**)*

80.5 mg CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$Cl (0.089 mmol) and 61 μL ^{n}PrI (0.625 mmol) yielded 75.7 mg CpRu[P(p-$CH_3OC_6H_4)_3$]$_2$I (85%) as an orange solid M.p. 132-134°C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.28 (m, 12H, aryl), 6.67 (d, J = 8.8 Hz, 12H, aryl), 4.18 (s, 5H, Cp), 3.77 (s, 18H, CH_3O). $^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$): δ 34.5 (s)

Anal. Calcd for $C_{47}H_{47}O_6P_2IRu$: C, 56.53%; H, 4.75%. Found: C, 56.43%; H, 4.90%.

*Synthesis of CpRu[P(p-$FC_6H_4)_3$]$_2$Br (**2d**)*

110 mg CpRu[P(p-$FC_6H_4)_3$]$_2$Cl (0.132 mmol) and 100 μL ^{n}BuBr (0.934 mmol) yielded 114 mg CpRu[P(p-$FC_6H_4)_3$]$_2$Br (98%) as an orange solid. M.p. 154-156 °C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.30 (t, J = 8.8, 12 Hz, 12H, aryl), 6.88 (d, J = 8.8 Hz, 12H, aryl), 4.14 (s, 5H, Cp). $^{31}P\{^{1}H\}$(162 MHz, $CDCl_3$): δ 36.76 (s)

Anal. Calcd for $C_{41}H_{29}F_6P_2BrRu$: C, 56.05%; H, 3.33%. Found: C, 56.00%; H, 3.43%.

*Synthesis of CpRu[P(p-$FC_6H_4)_3$]$_2$I (**3d**)*

80.0 mg CpRu[P(p-$FC_6H_4)_3$]$_2$Cl (0.096 mmol) and 65.0 μL ^{n}PrI (0.666 mmol) yielded 86.5 mg CpRu[P(p-$FC_6H_4)_3$]$_2$I (97%) as an orange solid. M.p. 152-155°C d. ^{1}H (400 Mz, $CDCl_3$): δ 7.27 (br, 12H, aryl), 6.90 (d, J = 7.6 Hz, 12H, aryl), 4.21 (s, 5H, Cp). $^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$): δ 35.7 (s).

Anal. Calcd for $C_{41}H_{29}F_6P_2IRu$: C, 53.20%; H, 3.16%. Found: C, 52.79%; H, 3.19%.

*Synthesis of CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$Br (**2e**)*

65 mg CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$Cl (0.80 mmol and 60 μL ^{n}BuBr (0.56 mmol yielded 48 mg CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$Br (73%) as a red-orange solid after recrystallization from toluene/petroleum ether. M.p. 137-140° d. The aryl resonances for the phenyl and p-tolyl groups are not completely resolved from one another. In $CDCl_3$ ^{1}H (400 Mz, $CDCl_3$): δ 7.34 (br, J = 8H, aryl), 7.22 (d, J = 6.4 Hz, 8H, aryl), 7.13 (t, 8 H, aryl), 6.94 (d, J = 7.2 Hz, 4H,

aryl), 4.20 (s, 5H, Cp), 2.31 (s, 6 H, CH_3); (C_6D_6): 7.63 (br s, 8H), 7.54 (t, 4H), 6.91 (br s, 12 H), 6.72 (d, J=7.8 Hz, 4H, tolyl), 4.20 (s, 5H, Cp), 1.97 s (6H, tolyl CH_3) $^{31}P\{^1H\}$(162 MHz, $CDCl_3$): δ 36.9 (s); (C_6D_6): 37.8 (s).
Anal. Calcd for $C_{43}H_{39}P_2BrRu$: C, 64.65%; H, 4.92%. Found: C, 64.19%; H, 5.20%.

*Synthesis of CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$I (**3e**)*

65 mg CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$Cl (0.80 mmol and 54 µL ^{n}PrI (0.56 mmol) yielded 52 mg CpRu[PPh_2(p-$CH_3C_6H_4$)]$_2$I (72%) as a red solid after recrystallization from toluene/petroleum ether. M.p. 120-122 °C d ^1H (400 Mz, $CDCl_3$): δ 7.16-7.29 (m not completely resolved from br s, 12H, aryl), 7.16 (d, J = 7.6 Hz overlapping a likely m at 7.13, 12 H, aryl), 6.96 (d, J = 7.6 Hz, 4H, tolyl), 4.17 (s, 5H, Cp), 2.33 (s, 6 H, tolyl CH_3). $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): δ 36.0 (s).
Anal. Calcd for $C_{43}H_{39}P_2IRu$: C, 61.07%; H, 4.65%. Found: C, 60.57%; H, 4.76%.

Identification of volatile products

1-Bromobutane (20µL, 0.19 mmol) and 12 mg (0.016 mmol) **1a** were heated at 100°C in 20 µL fluorobenzene for 5 hours before adding $CDCl_3$. The ^1H NMR spectrum was compared with spectra of authentic compounds. ^1H (400 Mz, $CDCl_3$): δ 3.42 (t, $CH_3CH_2CH_2C\mathbf{H_2}Br$), 3.55 (t, $CH_3CH_2CH_2C\mathbf{H_2}Cl$).

A solution of 1-bromohexane (12 µL, 8.5 x 10^{-2} mmols) and **1a** (34 mg, 4.6 x 10^{-2} mmol) in 5 mL fluorobenzene was refluxed for 7 hours. Analysis of the filtered solution by gc/ms confirmed the presence of 1-chlorohexane.

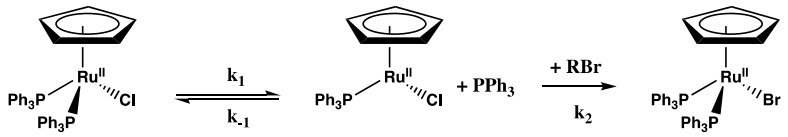
A 1:1 mixture of 1-chlorohexane and 1-iodobutane containing 5 mol% Cp*Ru(PPh_3)$_2$Cl in refluxing toluene led to a 1:1:1 mixture of 1-ClC_6H_{13}:1- IC_6H_{13}:1-IC_4H_9 by gc/ms analysis. Whether the more volatile 1-chlorobutane (b.p. 77°C) was lost during analysis or was not detected is not clear.

A solution of 1-bromobutane (20 µL, 0.18 mmols), styrene (21 µL, 0.18 mmol) and **1a** (11 mg, 1.5 x 10^{-2} mmol) in 5 mL fluorobenzene was refluxed for 7 hours. No evidence for products resulting from addition of 1-BrC_4H_9 to styrene was observed by gc/ms.

Computational Data

We report the Cartesian coordinates of all the structures optimized using Kohn-Sham density functional theory (M06/def2-SVP) in the xyz format in a separate zip file as part of the supplementary materials.

Derivation of the rate law



1a **2a**

$$\frac{d[2a]}{dt} = k_2\left[CpRu(PPh_3)Cl\right][BuBr] \qquad (1)$$

From the steady state approximation, $\frac{d[CpRu(PPh_3)Cl]}{dt} = 0$

$$\frac{d[CpRu(PPh_3)Cl]}{dt} = k_1[1a] - k_{-1}\left[CpRu(PPh_3)Cl\right][PPh_3] - k_2\left[CpRu(PPh_3)Cl\right][BuBr] = 0 \qquad (2)$$

Solving for $\left[CpRu(PPh_3)Cl\right]$:

$$\left[CpRu(PPh_3)Cl\right] = \frac{k_1[CpRu(PPh_3)_2Cl]}{k_{-1}[PPh_3] + k_2[BuBr]} \qquad (3)$$

Substituting the $\left[CpRu(PPh_3)Cl\right]$ into equation (1):

$$\frac{d[2a]}{dt} = \frac{k_1k_2[CpRu(PPh_3)_2Cl][BuBr]}{k_{-1}[PPh_3] + k_2[BuBr]} = -\frac{d[1a]}{dt} \qquad (4)$$

Where

$$k_{obs} = \frac{k_1k_2[BuBr]}{k_{-1}[PPh_3] + k_2[BuBr]} \qquad (5)$$

Table S1: Summary of Observed Rate Constants for the Reaction Between $CpRu(PPh_3)_2Cl$ (10.5 mM) and Organic Halides in C_6H_5F/10% C_6D_6

Organic halide	[RX] (mM)	T (°C)	k_{obs} x 10^6 s^{-1}
1-BrC_4H_9	105	50	1.62±0.05
2-Br-2-MeC_3H_6	110	50	0.56±0.02
1-IC_3H_7	72	40	1.0±0.1
CH_3I	69	40	7.2±0.6

Table S2: Summary of Rate Constants for the Reaction: $CpRu(PPh_3)_2Cl$ (**1a**)+ ^nBuBr in C_6H_5F/10% C_6D_6

[**1a**][a]	[^{n}BuBr]	[DHA]	[DQ]	[PPh_3]	T (°C)	$k_{obs,\ 1}$[b]	$k_{obs,\ 2}$	$k_{obs,\ 3}$	k_{ave}
10	103	0	0	0	34.7	0.58	0.53	[b]	0.55±.03
10	103	0	0	0	39.0	1.26	1.30	1.23	1.26±0.04
10	103	0	0	0	44.2	1.60	1.67	1.60	1.62±0.04
10	103	0	0	0	50.7	2.08	2.00	2.40	2.16±0.21
10	103	0	0	0	55.6	3.79	3.58	[b]	3.69±0.14
10	200	0	0	0	44.5	3.04	2.73	3.47	3.09±0.37
10	300	0	0	0	44.5	3.62	4.01	[b]	3.82±0.28
10	400	0	0	0	44.5	5.22	5.52	5.28	5.34±0.16
10	105	70	0	0	44.0	4.98	3.39	3.95	4.08±0.84
10	100	0	73	0	44.0	0.160	0.130	0.156	0.15±0.02
10.5	102	0	0	73	44.0	1.98	2.98	1.20	0.21±0.09

[a] all concentrations in mM. [b] pseudo first order rate constants x 10^6 s^{-1} [b] the third sample in these cases leaked leading to decomposition.

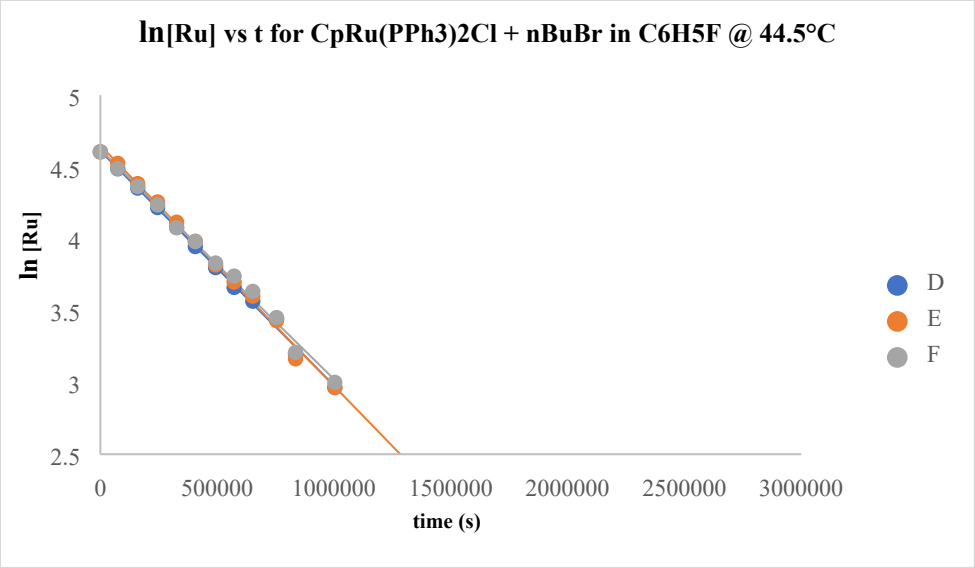


Figure S1: Representative plot of ln[**1a**] vs time (s) for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane at 44.5°C

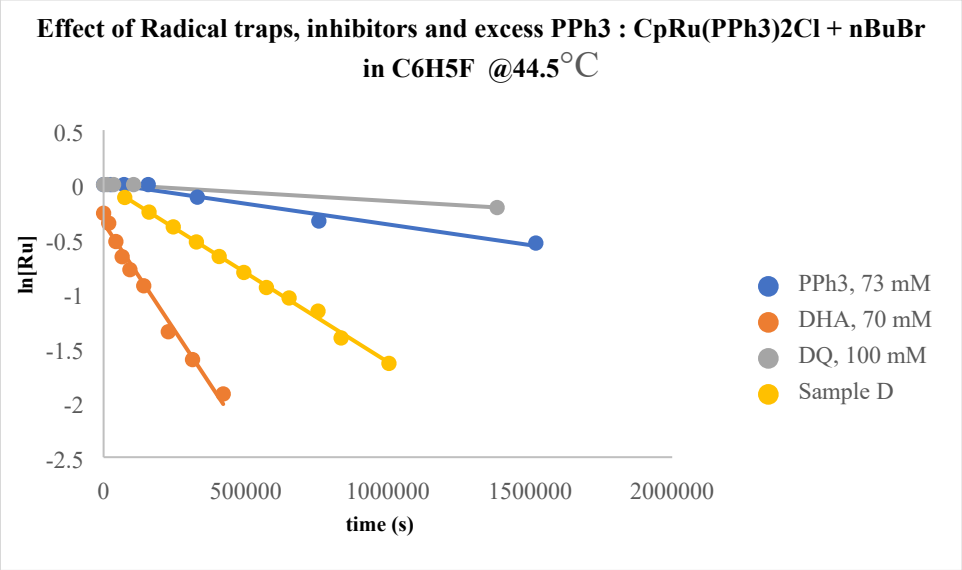


Figure S2: Effect of radical traps, initiators and excess PPh_3 on k_{obs} for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane at 44.5°C in fluorobenzene/10% benzene-d^6

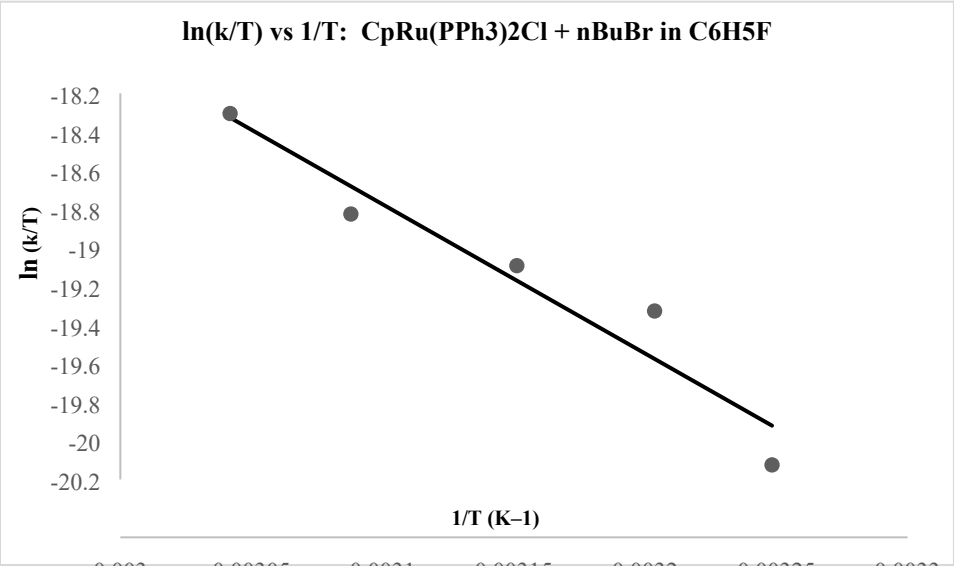


Figure S3: Eyring plot $\ln k_{obs}/T$ vs 1/T for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane in fluorobenzene/10% benzene-d^6

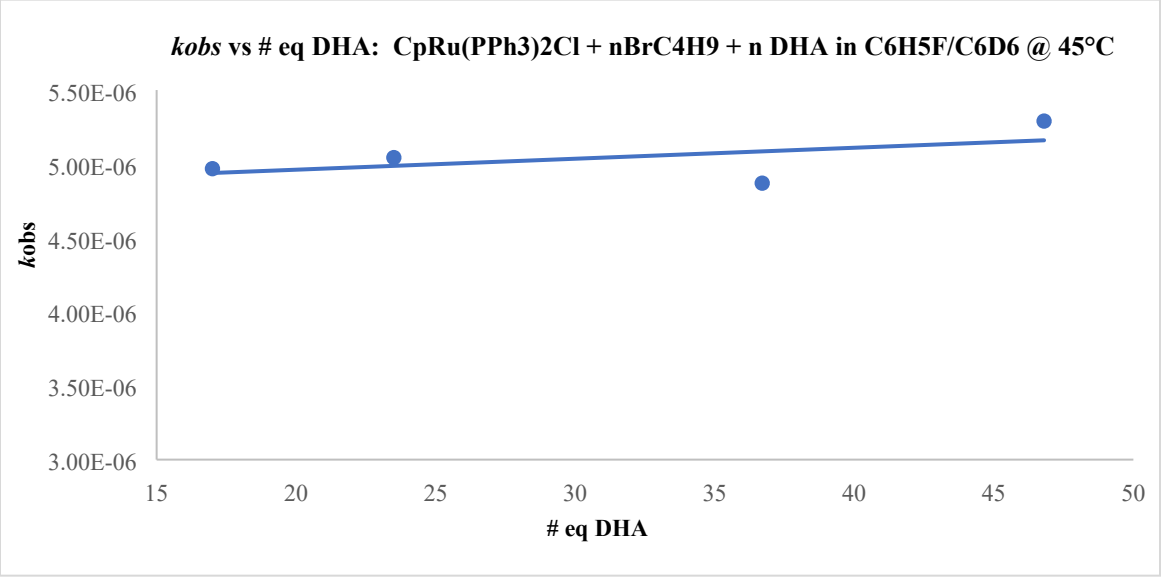


Figure S4: Plot of k_{obs} vs [DHA] for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane at 44.5°C in fluorobenzene/10% benzene-d^6. The values for k_{obs} in this plot reflect a single measurement at each concentration.

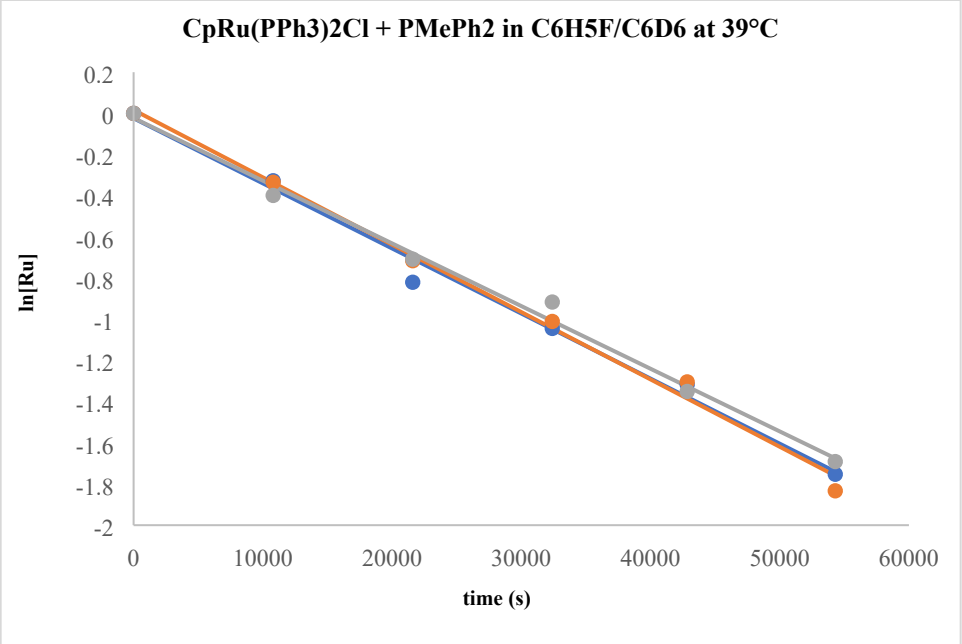


Figure S5: Plot of ln[**1a**] vs time (s) for the reaction between $CpRu(PPh_3)_2Cl$ and methyldiphenylphosphine at 40°C in fluorobenzene/10% benzene-d^6

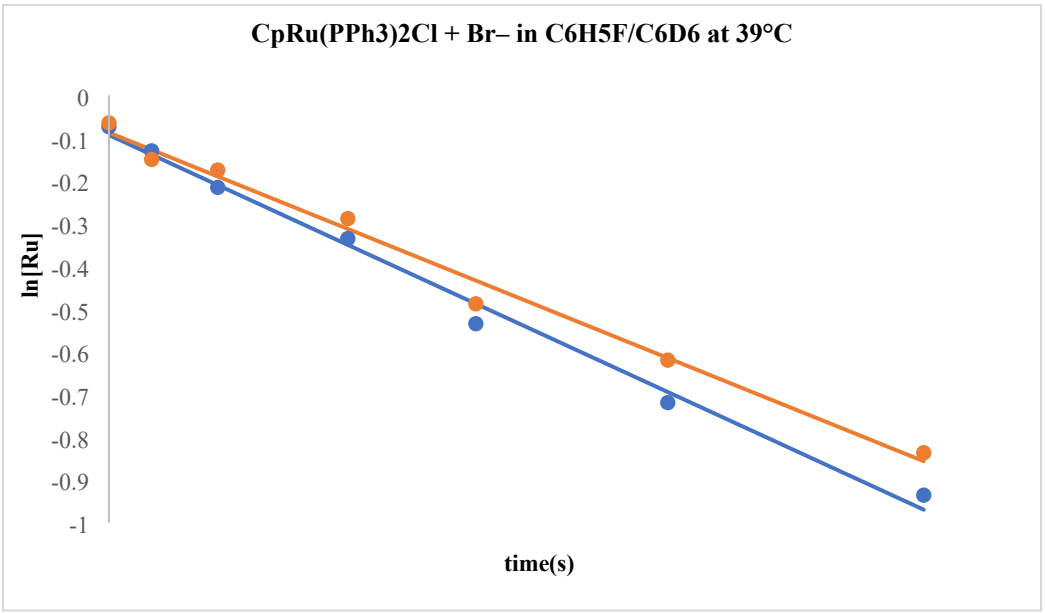


Figure S6: Plot of ln[**1a**] vs time (s) for the reaction between $CpRu(PPh_3)_2Cl$ and bromide ion at 44.5°C in fluorobenzene/10% benzene-d^6

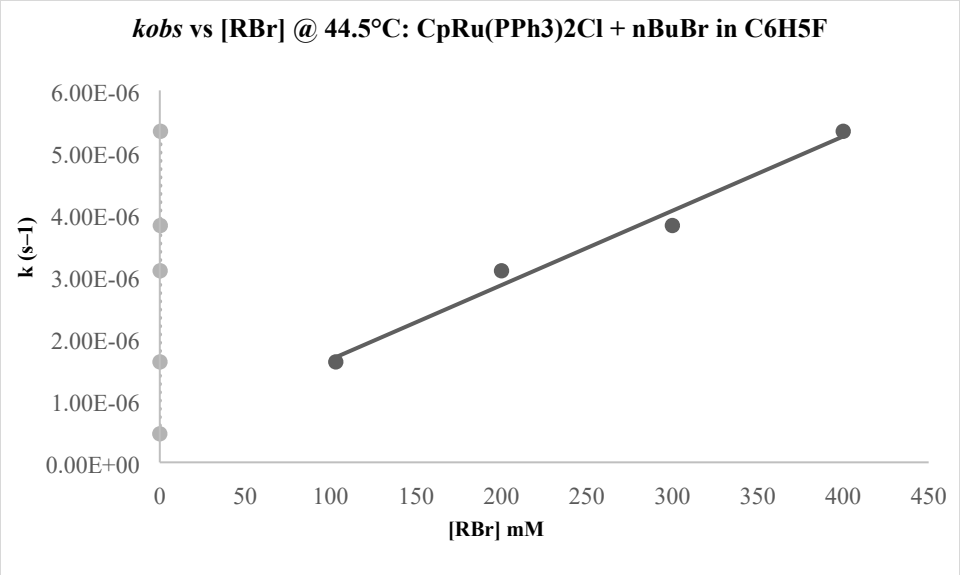


Figure S7: Plot of k_{obs} vs [^{n}butylbromide] for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane at 44.5°C in fluorobenzene/10% benzene-d^6

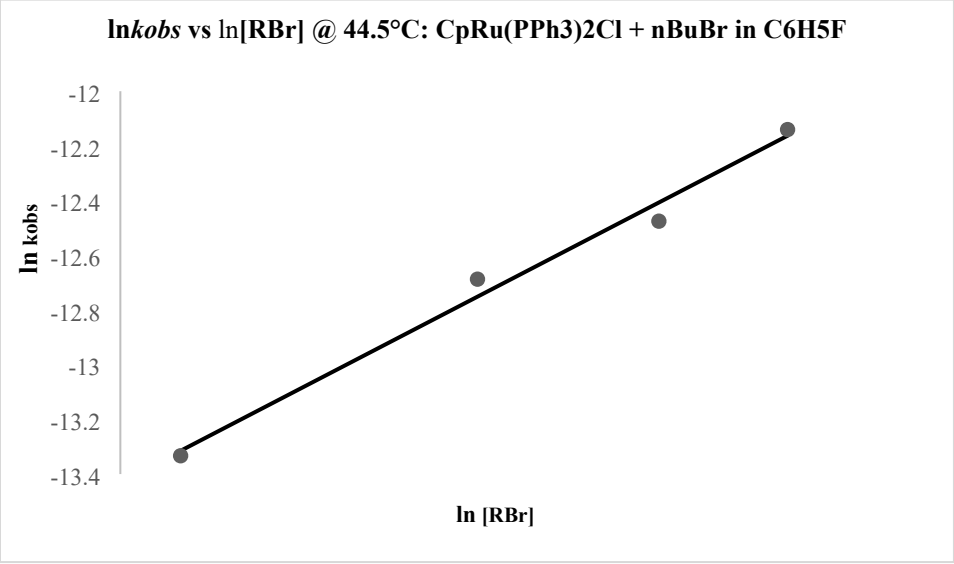


Figure S8: Plot of $\ln k_{obs}$ vs ln[^{n}butylbromide] for the reaction between $CpRu(PPh_3)_2Cl$ and bromobutane at 44.5°C in fluorobenzene/10% benzene-d^6

Table S3: Calculate Free Energies (ΔG, kJ/mol) for Intermediates in the Reaction:
$CpRu(PPh_3)_2Cl + EtBr \rightarrow CpRu(PPh_3)_2Br + EtCl$[a]

Reaction	Gas phase	C_6H_5F solvated[b]
$CpRu(PPh_3)_2Cl + EtBr \rightarrow CpRu(PPh_3)Cl(EtBr) + PPh_3$	102.40	99.02
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Cl(Br)\bullet\ \bullet Et$	145.74	138.35
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Cl(Br)(Et)$	33.83	28.79
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Br(EtCl)$	0.36	0.24
$CpRu(PPh_3)Br(EtCl) + PPh_3 \rightarrow CpRu(PPh_3)_2Br + EtCl$	-99.28	-95.61

[a] M06/def2-SVP [b] Gaussian PCM

Table S4: Calculated Energies (ΔG kJ/mol, ΔH kJ/mol) for Intermediates in the Reaction:
$CpRu(PPh_3)_2Cl + EtBr \rightarrow CpRu(PPh_3)_2Br + EtCl$[a]

	Gas Phase		C_6H_5F solvated[b]	
Reaction	ΔG	ΔH	ΔG	ΔH
$CpRu(PPh_3)_2Cl + EtBr \rightarrow CpRu(PPh_3)Cl(EtBr) + PPh_3$	76.98	99.38	72.06	94.81
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Cl(Br)\bullet\ \bullet Et$	67.56	126.24	63.65	120.77
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Cl(Br)(Et)$	48.18	39.39	43.32	35.10
$CpRu(PPh_3)Cl(EtBr) \rightarrow CpRu(PPh_3)Br(EtCl)$	-3.96	-0.94	-2.73	0.70
$CpRu(PPh_3)Br(EtCl) + PPh_3 \rightarrow CpRu(PPh_3)_2Br + EtCl$	-78.67	-103.50	-74.09	-100.35

[a] M06/def2-TZVP [b] Gaussian PCM

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