Supporting Information for

Troponate-/Aminotroponate Ruthenium-Arene complexes: Synthesis, Structure and Ligand Tuned Mechanistic Pathway for Direct C-H bond Arylation with Arylchlorides in water

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General Information, Materials and Instrumentation. All reactions were performed under open atmosphere except the catalytic reactions which were performed under Ar atmosphere using chemicals of high purity purchased from Sigma Aldrich and Alfa Aesar. Dichloro bridged arene-ruthenium(II) precursors $[\{(\eta^6-C_6H_6)RuCl_2\}_2]$ and $[\{(\eta^6-C_{10}H_{14})RuCl_2\}_2]$ were synthesized according to the literature procedures.^{S1}¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ³¹P NMR (161.97 MHz) spectra were recorded at 298 K using CDCl₃ or DMSO d_6 as the solvent on a Bruker Avance 400 spectrometer. Tetramethylsilane (TMS) was used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for CDCl₃ and 2.49 ppm for DMSO- d_6 in ¹H NMR, and to the centre of the triplet at 77.0 ppm for CDCl₃ and 39.50 ppm for DMSO- d_6 in ¹³C NMR. Suitable single crystals of complexes [Ru]-1 and [Ru]-3 along with the single crystal of ligand L3 were subjected to single-crystal X-ray structural studies using Agilent Technologies Supernova CCD system. ESI (positive and negative mode), and high-resolution mass spectra (HRMS) were recorded on a micro TF-Q II mass spectrometer. The voltammograms were recorded on a CHI620D electrochemical analyser in dichloromethane as the solvent and 0.1 M TBAF₆ as the supporting electrolyte. The electrodes used were glassy carbon as a working electrode, a Pt wire as a counter electrode and the Silver as a reference electrode. Infrared spectra (4000 to 500 cm⁻¹) were recorded with a BRUKER TENSOR 27 instrument in KBr pellets. CCDC deposition numbers of the ligand L3, and complexes [Ru]-1 and [Ru]-3 are 1431337, 1431336 and 1441581, respectively.



Table S1. Crystal data and structure refinement details for Ligand L3.

Crystal parameters	Ligand (L3)		
empirical formula	C ₁₃ H ₁₇ N O		
	202.20		
Fw	203.28		
<i>T</i> (K)	293(2)		
λ (Å)	1.54184		
Crust sustam	Monoclinic		
Cryst system	Wonoennie		
space group	P 21/n		
Cryst size, mm	0.14×0.12×0.11		
a. Å	12.1210(7)		
b, Å	8.5610(5)		
	12.4050(8)		
C, A	12.4050(8)		
α, deg	90.00		
β , deg	111.635(7)		
v. deg	90.00		
// 0			

$V, Å^3$	1196.56(12)
Ζ	4
$\rho_{\rm calcd}, {\rm g \ cm}^{-3}$	1.128
μ , mm ⁻¹	0.554
<i>F</i> (000)	440
θ range, deg	6.43-73.23
completeness to θ_{\max}	73.2
no. of data collected/unique data	4562 /1916
	[R(int) = 0.0254]
params/restraints	137/0
goodness of fit on F^2	1.042
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0607 wR2 = 0.1627
R indices (all data)	R1 = 0.0517 wR2 = 0.1499

 Table S2. Selected bond lengths and bond angles for Ligand L3.

Bond lengths (Å)			
O1-C13	1.2478(18)		
C13-C7	1.488(2)		
C13-C12	1.414(2)		
C7-C8	1.393(2)		
N1-C7	1.3317(19)		
N1-C1	1.4548(19)		

C1-C2	1.513(3)		
Bond angles (°)			
C1-N1-C7	128.62(13)		
N1-C7-C13	111.27(12)		
N1-C7-C8	122.60(14)		
N1-C1-C2	108.38(16)		
N1-C1-C6	110.53(15)		
O1-C13-C7	116.37(13)		
O1-C13-C12	120.07(14)		

 Table S3. Selected bond lengths and bond angles for complexes [Ru]-1 and [Ru]-3.

Bond lengths (Å)	[Ru]-1	[Ru]-3
Ru1-O1	2.0789(18)	2.0463(19)
Ru1-O2	2.079(2)	-
Ru1-N1	-	2.115(3)
Ru1-Ct	1.645	1.676
Ru1-C _{avg.}	2.167	2.188
Ru1-Cl1	2.4094(8)	2.4196(8)
01-C1	1.284(3)	1.277(4)
O2-C7	1.289(3)	-
N1-C7	-	1.319(4)
N1-C8	-	1.479(4)
C1-C7	1.454(4)	1.468(4)

C1-C2	1.403(4)	1.386(4)	
C2-C3	1.382(4)	1.384(5)	
Bond angles (°)			
O1-Ru1-O2	76.63(7)	-	
O1-Ru-N1	-	75.86(9)	
O1-Ru1-Cl1	84.48(6)	85.93(6)	
O2-Ru1-Cl1	84.47(6)	-	
N1-Ru-Cl1	-	84.68(7)	
C _t -Ru1-O1	131.17	126.70	
C _t -Ru1-O2	131.60	-	
C _t -Ru-N1	-	136.67	
C _t -Ru1-Cl1	129.63	128.18	
O1-Ru-C11	91.76(9)	-	
O1-Ru-C13	149.20(10)	86.99(10)	
O1-Ru-C15	-	129.76(10)	
O2-Ru-C11	144.18(11)	-	
N1-Ru-C13	-	140.67(11)	
O2-Ru-C13	133.18(9)	-	
N1-Ru-C15	-	96.90(11)	

S.No.	Complexes	Anodic pot. (E _{pa})	Cathodic pot. (E _{pc})	Oxidation half wave potential E _{1/2} (mV)	$\Delta E (mV)$
1	[Ru]-1	1.108	0.770	0.939	0.338
2	[Ru]-2	1.220	1.142	1.181	0.078
3	[Ru]-3	1.213	1.133	1.173	0.080
4	[Ru]-5	1.023	0.759	1.023	0.529
5	[R u]-6	1.237	1.168	1.202	0.069

 Table S4. Cyclic voltammetric data of ruthenium complexes.



Figure S1. Cyclic voltammogram of [Ru]-1 in dichloromethane.



Figure S2. Cyclic voltammogram of [Ru]-5 in dichloromethane.

Catalytic C-H bond arylation reactions

¹H NMR spectra of compounds C-H arylated products

2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine: Yield: 0.112 g (43%). ¹H NMR (400 MHz, **CDCl₃):** δ (ppm) = 8.64 (d, *J* = 4.0 Hz, 1H), 7.70-7.65 (m, 1H), 7.47-7.36 (m, 4H), 7.12-7.05 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 3.78 (s, 3H), ¹³C NMR (100 MHz, **CDCl₃):** δ (ppm) =159.48, 158.54, 149.42, 140.21, 139.37, 135.25, 133.73, 130.77, 130.44, 128.52, 127.29, 125.43, 121.29, 113.59, 55.19, **HRMS** (ESI) m/z: calculated 262.1226 [(C₁₈H₁₅NO + H)]⁺, Found: 262.1276 [(C₁₈H₁₅NO + H)]⁺.



2-(4,4'-dimethoxy-[1,1',3',1''-terphenyl]-2'-yl)pyridine: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.36 (d, *J* = 4.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.41-7.39 (m, 2H), 7.35-7.31 (m, 1H), 7.02 (m, 4H), 6.94-6.87 (m, 2H), 6.70-6.65 (m, 4H), 3.74 (s, 6H), ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 159.24, 158.08, 148.50, 141.43, 138.36, 135.09, 134.06, 130.68, 129.18, 128.15, 126.83, 120.86, 113.11, 55.12, HRMS (ESI) m/z: calculated: 368.1645 [(C₂₅H₂₁NO₂ + H)]⁺, Found: 368.1694 [(C₂₅H₂₁NO₂ + H)]⁺.

Mass spectral study of the reaction of [Ru]-1 with potassium acetate (KOAc).

To trap the carboxylate coordinated cyclometallated species, [**Ru**]-1 (0.025 mmol, 0.0098 g) was added with potassium acetate (0.05 mmol, 0.0049 g) and 5 mL water to the two necked round bottom flask. Reaction vessel was then provided with magnetic bar and was degassed with vacuum pump followed by the gassing with Argon. Reaction mixture was stirred for 3 h at 100 °C and after the completion of reaction time, mixture was cooled down. Crude reaction mixture was filtered through filter tip of 1000 μ L and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

Mass spectral study of the reaction of [Ru]-1 with potassium pivalate (KOPiv).

To trap the carboxylate coordinated cyclometallated species, [**Ru**]-1 (0.025 mmol, 0.0098 g) was added with potassium pivalate (0.05 mmol, 0.0070 g) and 5 mL water to the two necked round bottom flask. Reaction vessel was then provided with magnetic bar and was degassed with vacuum pump followed by the gassing with Argon. Reaction mixture was stirred for 3 h at 100 °C and after the completion of reaction time, mixture was cooled down. Crude reaction mixture was filtered through filter tip of 1000 μ L and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

Mass spectral study of the reaction of [Ru]-1 with 2-phenylpyridine in different catalyst to substrate ratio

[Ru]-1 was added with 2-phenylpyridine and 4-chloroanisole in C: S ratio 1:1, 1:2 and 1:5 in water (5 mL) followed by addition of potassium carbonate (3 equiv.). Reaction mixture was heated at 100 °C for 3 h under Ar atmosphere. After completion of reaction time, crude reaction mixture was filtered through filter tip of 1000 μ L and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further (Figure S3).



Figure S3. Relative abundance of Ru(II) cyclometallated species ([Ru]-A and [Ru]-B) with different catalyst to substrate ratio with [Ru]-1 catalyst under similar reaction conditions.

Time dependent mass spectral study of the reaction of [Ru]-1 with 2-phenylpyridine (S/C ratio 2:1).

To perform the time dependent study of two intermediates (**[Ru]-A** and **[Ru]-B**), a two necked round bottom flask was charged with **[Ru]-1** catalyst (0.05 mmol, 0.0196 g) and 2-phenylpyridine (0.1 mmol, 14.3 μ L). Reaction was carried out in water (5 mL) at 100 °C under Ar atmosphere for 3 h. 100 μ L of aliquot was withdrawn at 5 min, 10 min, 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min and 180 min. Crude reaction mixture was filtered through filter tip of 1000 μ L and further diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

Abundance of [Ru]-A and [Ru]-B species with different Ru(II) catalysts ([Ru]-1 to [Ru]-3)

To strengthen the presence of species **[Ru]-A** and **[Ru]-B** with different catalysts, 0.025 mmol Ru(II) catalyst (**[Ru]-1** to **[Ru]-3**) were taken separately in a two necked round bottom flask with 3 equiv. of K_2CO_3 and 0.05 mmol 2-phenylpyridine keeping S/C ratio 2:1 in 5 mL water under Ar atmosphere. Reaction was performed at 100 °C for 3 h and crude reaction mixture was filtered through filter tip of 1000 µL and further diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.



Figure S4. Relative abundance of Ru(II) cyclometallated intermediates **[Ru]-A** and **[Ru]-B** with different ruthenium(II) catalysts (**[Ru]-1** to **[Ru]-3**).

Mass spectral investigation for stability of complexes [Ru]-1 and [Ru]-2 in water

To check the stability of the complexes in water, a series of experiments were performed by stirring 0.010 g of ruthenium complexes (**[Ru]-1** or **[Ru]-2**) dissolved in water (5 mL) at room temperature or heating at 100 °C, with or without added K_2CO_3 (0.207 g) under Ar atmosphere. For mass spectral analysis, 100 µL of aliquots were withdrawn at different intervals of time as at 0 sec, 10 min, 1 h, 5 h, 10 h, 1 day, 3 days and 1 week from the crude reaction mixture, which were filtered and diluted with methanol before analysis by ESI-MS.



Figure S5. Mass spectral investigation for the stability of [Ru]-1 complex in water.



Figure S6. Mass spectral investigation for stability of [Ru]-2 complex in water.



Figure S7. Mass spectral investigation for stability of [Ru]-1 complex in water with K_2CO_3 .



Figure S8. Mass spectral investigation for stability of [Ru]-2 complex in water with K_2CO_3 .

Preparation of intermediate species $[(\eta^6-p-cymene)Ru(\kappa^2-C,N-2-phenylpyridine)CI]$

Reaction vessel was charged with the $[{(\eta^6-p-cymene)RuCl_2}_2]$ (0.5 mmol, 0.306 g) and potassium acetate (3.0 mmol, 0.294 g) in 25 mL of methanol under Ar atmosphere. Solution was stirred for 24 h at room temperature and the product was isolated by reducing volume under vacuum. Product was precipitated with ether and washed with *n*-hexane several times to remove excess/unreacted 2-phenylpyridine. Product was air dried and analyzed by ¹H NMR.



¹**H NMR (400 MHz, CDCl₃):** δ(ppm) = 9.24 (d, *J* = 4.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.19-7.17 (m, 1H), 7.06-7.01 (m, 2H), 5.59-5.55 (m, 2H), 5.17 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 8.0 Hz, 1H), 2.45-2.42 (m, 1H), 2.05 (s, 3H), 0.97 (d, *J* = 4.0 Hz, 3H), 0.85 (d, *J* = 8.0 Hz, 3H).

Reaction of the cycloruthenated species, [Ru]-A, with 4-chloroanisole.

Cyclometallated species **[Ru]-A** was taken (0.1 mmol, 0.039 g) in a two necked round bottom flask under Ar atmosphere followed by the addition of base (K_2CO_3 , 0.3 mmol, 0.0414 g) with 2.5 equivalent of 4-chloroanisole (0.25 mmol, 30 µL). 5 mL water was added and reaction mixture was stirred for 8 h at 100 °C. Resulting reaction mixture was cooled down to room temperature and extracted with ethyl acetate (3×10 mL) and solvent volume was reduced under pressure. Crude reaction mixture was analyzed with ¹H NMR.

Computational Study

Density functional theory (DFT) calculations were carried out using Gaussian 09 package^{S2} using Becke's three parameter exchange and the Lee-Yang-Parr's correlation functional (B3LYP).^{S3} 6-311G(d,p)^{S4-S5} basis functions are used for non-metals (C, H, O, N, P and Cl), whereas LANL2DZ-ECP (effective core potentials)^{S6-S7} is used for Ru. Water is used as an implicit solvent using the polarizable continuum model (PCM) as implemented in Gaussian 09.^{S8-S10} In all the calculations, D3 version of Grimme's dispersion corrections is included for long range interactions.^{S11} Harmonic vibrational frequencies are calculated to characterize the nature of the stationary points. Zero-point energy and entropy corrections (at 298.15 K) are included for the free energy calculations.



Optimized structures of [Ru]-1, [Ru]-2, and [Ru]-3. Here white, skyblue, blue, red, turquoise, green and teal colour balls denote the hydrogen, carbon, nitrogen, oxygen, phosphorous, chlorine, and ruthenium atoms, respectively.

The reaction free energies (ΔG_A for [**Ru**]-**A** and ΔG_B for [**Ru**]-**B**) are calculated for the formation of [**Ru**]-**A** and [**Ru**]-**B** are using the following equations:

$$\Delta G_{A} = (G_{A} + G_{H3O+} + G_{Cl-} + G_{troponate/aminotroponate}) - (G_{[Ru]-cat} + 2G_{H2O} + G_{phpy})$$
$$\Delta G_{B} = (G_{B} + G_{H3O+} + G_{Cl-} + G_{p-cvmene}) - (G_{[Ru]-cat} + 3G_{H2O} + G_{phpy})$$

where G_A , G_{H3O+} , G_{Cl-} , $G_{troponate/aminotroponate}$, $G_{[Ru]-cat}$, G_{H2O} , G_{phpy} , G_B and $G_{p-cymene}$ are the total free energies (with zero point and entropy corrections) of [**Ru**]-**A**, **H**₃**O**⁺, **Cl**⁻, **troponato/aminotroponato**, [**Ru**]-catalysts, **H**₂**O**, 2-phenylpyridine, [**Ru**]-**B** and *p*cymene, respectively.

We have calculated the binding energy (E_B) (Table 1) of the leaving groups (*p*-cymene and troponate/aminotroponate) to understand such trend. The binding energies are calculated using the following formula:

$$E_{B} = E_{[Ru]-cat} - (E_{([Ru]-cat) - (p-cymene)} + E_{(p-cymene)})$$

$$E_{B} = E_{[Ru]-Cat} - (E_{([Ru]-cat) - (troponate/aminotroponate)} + E_{(troponate/aminotroponate)})$$

where $E_{([Ru]-cat) - (p-cymene)}$ is the single point energy of the catalyst without *p*-cymene ligand, $E_{(p-cymene)}$ is the single point energy of the *p*-cymene within the geometry of catalyst, $E_{([Ru]-cat) - (troponato/aminotroponato)}$ is the single point energy of the catalyst without troponate/aminotroponate ligand, and $E_{(troponate/aminotroponate)}$ is the single point energy of the troponate/aminotroponate within the geometry of catalyst.

 Table S5.
 The binding energies (kcal/mol) calculated for *p*-cymene and troponate/aminotroponate ligands in ruthenium catalysts.

	[Ru]-1	[Ru]-2	[Ru]-3
<i>p</i> -cymene	-43.7	-37.6	-41.2
troponate/aminotroponate	-68.8	-85.8	-87.2

References:

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¹H NMR of 2-(isopropylamino)cyclohepta-2,4,6-trienone (L2).



¹H NMR of 2-(cyclohexylamino)cyclohepta-2,4,6-trienone (L3)



¹H NMR of [Ru]-1



¹³C NMR of **[Ru]-1**



Mass spectra of [Ru]-1



¹H NMR of [Ru]-2



Mass spectra of [Ru]-2



Mass spectra of [Ru]-3



Mass spectra of [Ru]-4



¹H NMR of [Ru]-5







Mass spectra of [Ru]-5



Mass spectra of [Ru]-6



Mass spectra of [Ru]-7



Mass spectra of [Ru]-8



¹H NMR of 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine



¹³C NMR of 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine



¹H NMR of 2-(4,4'-dimethoxy-[1,1',3',1''-terphenyl]-2'-yl)pyridine



¹³C NMR of 2-(4,4'-dimethoxy-[1,1',3',1"-terphenyl]-2'-yl)pyridine



¹H NMR of cyclometallated species [(η^6 -*p*-cymene)RuCl(κ^2 -*C*,*N*-phenylpyridine)]



IR data of [Ru]-1



IR data of [Ru]-5