# Catalytic $S_NAr$ of Unactivated Aryl Chlorides ESI

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## Procedure and Full Table of conditions

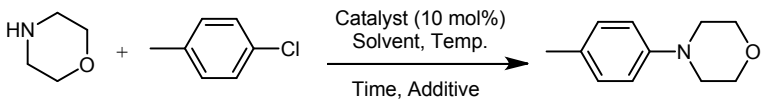
*Procedure S1:*

To a dried Schlenck tube under a $N_2$ atmosphere was added catalyst (67 μmol, 10 mol% relative to chlorotoluene), anhydrous, degassed chlorotoluene (80 μL, 0.67 mmol), anhydrous, degassed morpholine (167 μL, 2.0 mmol) and anhydrous, degassed solvent (1 mL). The reaction vessel was sealed and the mixture was stirred at the reaction temperature for the time indicated (e.g. 180 °C for 18 h). After the given reaction time, a sample of the crude reaction mixture (200 μL) was added to $CDCl_3$ (0.7 mL) and $^1$H-NMR was used to determine the reaction conversion.

*Initial solvent screen (no catalyst)*

*Procedure S1* was followed.

Table S1: Variation in solvent in the absence of catalyst. Conversions determined by $^1$H-NMR.



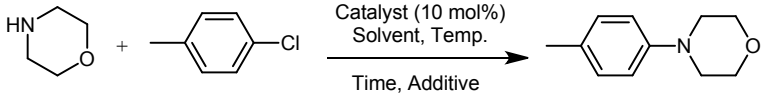

| Entry | Catalyst | Solvent | Temp. (°C) | Time | Additive | Conversion (%) |
|---|---|---|---|---|---|---|
| 1 | - | MeCN | 80 | 18 h | - | 0 |
| 2 | - | Toluene | 110 | 18 h | - | 0 |
| 3 | - | THF | 70 | 18 h | - | 0 |
| 4 | - | EtOH | 80 | 18 h | - | 0 |
| 5 | - | DMSO | 150 | 18 h | - | 0 |
| 6 | - | Cyclohexanone | 150 | 18 h | - | 0 |
| 7 | - | 1-Octanol | 180 | 18 h | - | 0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | - | 1-Octanol | 180 | 7 d | - | 0 |
| 9 | - | DMI | 180 | 18 h | - | 0 |
| 10 | - | NMP | 180 | 18 h | - | 0 |
| 11 | - | Cyclohexanol | 180 | 18 h | - | 0 |

*Solvent screen with [CpRu(p-cymene)$PF_6$] catalyst*

*Procedure S1* was followed.

Table S2: Variation in solvent using [CpRu(*p*-cymene)]$PF_6$ as the catalyst. Conversions determined by $^1$H-NMR.

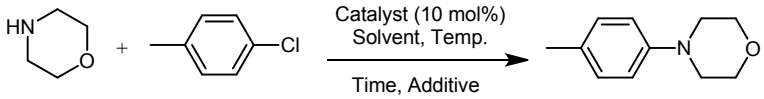



| Entry | Catalyst | Solvent | Temp. (°C) | Time | Additive | Conversion (%) |
|---|---|---|---|---|---|---|
| 1 | [CpRu(*p*-cymene)]$PF_6$ | *p*-Xylene | 180 | 18 h | - | 0 |
| | " | " | " | 4 d | | 0 |
| 2 | [CpRu(*p*-cymene)]$PF_6$ | Cyclohexanone | 180 | 18 h | - | 14 |
| | " | " | " | 4 d | | 27 |
| 3 | [CpRu(*p*-cymene)]$PF_6$ | Cyclohexanol | 180 | 18 h | - | 16 |
| | " | " | " | 4 d | | 26 |
| 4 | [CpRu(*p*-cymene)]$PF_6$ | DMSO | 180 | 18 h | - | 0 |
| | " | " | " | 4 d | | 0 |
| 5 | [CpRu(*p*-cymene)]$PF_6$ | DMI | 180 | 18 h | - | 17 |
| | " | " | " | 4 d | | 25 |
| 6 | [CpRu(*p*-cymene)]$PF_6$ | NMP | 180 | 18 h | - | 22 |
| | " | " | " | 4 d | | 50 |
| 7 | [CpRu(*p*-cymene)]$PF_6$ | Benzyl alcohol | 180 | 18 h | - | 0 |
| | " | " | " | 4 d | | 0 |
| 8 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | - | 25 |
| | " | " | " | 4 d | | 45 |

*Additive Screen*

*Procedure S1* was followed with the addition of the additive (1 eq. 0.67 mmol)

Table S3: Variation in additive. Conversions determined by $^1$H-NMR.



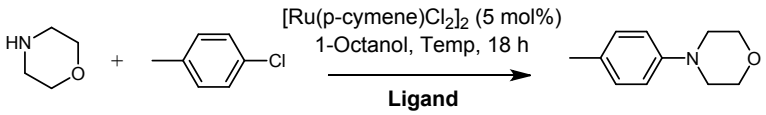

| Entry | Catalyst | Solvent | Temp. (°C) | Time | Additive | Conversion (%) |
|---|---|---|---|---|---|---|
| 1 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | - | 25 |
| 2 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $Na_2CO_3$ | 11 |
| 3 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $K_2CO_3$ | 0 |
| 4 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $Cs_2CO_3$ | 0 |
| 5 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $KO^tBu$ | 0 |
| 6 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $Et_3N$ | 21 |

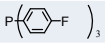
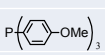
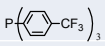
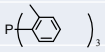
| | | | | | | |
|---|---|---|---|---|---|---|
| 7 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | $^{i}Pr_2NEt$ | 20 |
| 8 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | Mol. Seives | 25 |
| 9 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | Mol. Seives + $Et_3N$ | 22 |
| 10 | [CpRu(*p*-cymene)]$PF_6$ | 1-Octanol | 180 | 18 h | Mol. Seives + $^{i}Pr_2NEt$ | 25 |

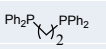
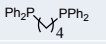
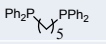
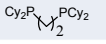
*Ligand Screen with [Ru(p-cymene)Cl$_2$]$_2$*

*Procedure S1* was followed with the following adjustments: in the place of catalyst (67 µmol, 10 mol% relative to chlorotoluene), [Ru(*p*-cymene)$Cl_2$]$_2$ (33 µmol, 5 mol% relative to chlorotoluene) was added; ligand (200 µmol, 3 equivalents relative to Ru) was added; each reaction was analysed after 18 h; 1- octanol (1 mL) was the solvent.

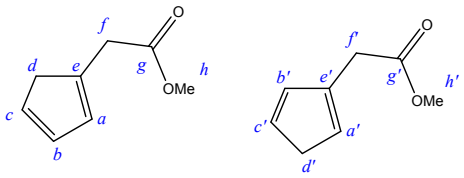
Table S4: Variation in ligand with [Ru(*p*-cymene)$Cl_2$]$_2$ catalyst. Conversions determined by $^{1}$H-NMR.




| Entry | Ligand | Product Conversion (%) | |
|---|---|---|---|
| | | T = 150 °C | T = 180 °C |
| 1 |  | 0 | 0 |
| 2 |  | 0 | 0 |
| 3 |  | 0 | 0 |
| 4 |  | 0 | 0 |
| 5 |  | 0 | 0 |
| 6 |  | 0 | 0 |
| 7 |  | 0 | 0 |
| 8 |  | 0 | 0 |

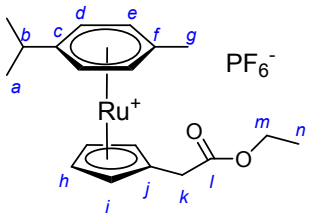
| Entry | Ligand | Product Conversion (%) | |
|---|---|---|---|
| | | T = 150 °C | T = 180 °C |
| 9 |  | 0 | 0 |
| 10 |  | 0 | 0 |
| 11 |  | 0 | 0 |
| 12 |  | 0 | 0 |
| 13 |  | 0 | 0 |
| 14 |  | 0 | 0 |
| 15 |  | 0 | 0 |
| 16 |  | 0 | 0 |

## Experimental Detail and Product Characterisation



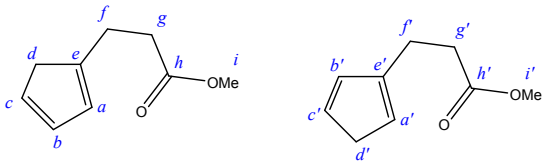

*Methyl (cyclopenta-1,3-dien-1-yl)acetate and Methyl (cyclopenta-1,4-dien-1-yl)acetate*

A solution of sodium cyclopentadienylide (2 M in THF, 6.45 mL) was diluted in THF (20 mL) and added dropwise to a stirred solution of methyl bromoacetate (1.22 mL, 12.9 mmol) in THF (10 mL) at -78 °C. The mixture was stirred for 3 h at -78 °C before $CH_2Cl_2$ (20 mL) was added to facilitate precipitation of NaBr, which was removed by filtration. The solvent was removed under reduced pressure from the filtrate to leave a 1 : 1 mixture of the *title products* as a yellow oil, which was used without further purification (1.78 g, quantitative); $\delta_H$ ($CDCl_3$) 6.36 – 6.06 (6H, m, $H^{a/a'/b/b'/c/c'}$), 3.50 (6H, s, $H^{h/h'}$), 3.29 (4H, m, $H^{f/f'}$), 2.85 (4H, m, $H^{d/d'}$); $\delta_C$ ($CDCl_3$) 174.0 ($C^{g/g'}$), 147.3 and 145.6 ($C^{e/e'}$), 135.6 – 130.5 ($C^{a/a'/b/b'/c/c'}$), 52.2 ($C^{h/h'}$), 44.5 and 42.3 ($C^{d/d'}$), 36.7 and 36.1 ($C^{f/f'}$); *m/z* (HRMS$^+$) 139.0766 $[M + H]^+$ ($C_8H_{11}O_2$ requires 139.0759).



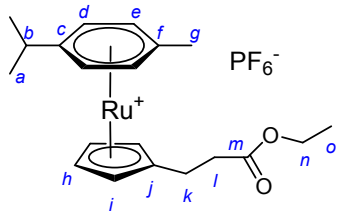

*Ethyl (cyclopentadienyl)acetate(p-cymene)ruthenium(II) hexafluorophosphate,* **2**

A 1 : 1 mixture of methyl (cyclopenta-1,3-dien-1-yl)acetate and methyl (cyclopenta-1,4-dien-1-yl)acetate (1.78 g, 12.9 mmol) was dissolved in dry, degassed (3 × free thaw cycle) EtOH (10.5 mL). $Na_2CO_3$ (312 mg, 2.94 mmol) and [Ru(*p*-cymene)$Cl_2$]$_2$ (300 mg, 0.49 mmol) were added and the mixture was stirred under argon at 75 °C for 16 h. The mixture was left to stand before the supernatant was decanted from residual salts and reduced in volume to 3.5 mL. An aqueous solution of $NH_4PF_6$ (0.3 M, 7.0 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a brown oil. Purification by column chromatography (silica, $CH_2Cl_2$ : EtOH 0 – 0.2% in 0.1% increments) gave the *title compound* as a yellow oil (228 mg, 45%); $\delta_H$ ($CDCl_3$) 6.28 (4H, m, $H^{d/e}$), 5.55 (2H, m, $H^i$), 5.46 (2H, m, $H^h$), 4.18 (2H, q, *J* 7.0 Hz, $H^m$), 3.52 (2H, s, $H^k$), 2.85 (1H, sept., *J* 7.0 Hz, $H^b$), 2.42 (3H, s, $H^g$), 1.32 (6H, d, *J* 7.0 Hz, $H^a$), 1.26 (3H, t, *J* 7.0 Hz, $H^n$); $\delta_C$ ($CDCl_3$) 169.3 ($C^l$), 112.6 ($C^c$), 101.8 ($C^f$), 95.1 ($C^j$), 87.2 ($C^e$), 84.8 ($C^d$), 81.7 ($C^i$), 80.1 ($C^h$), 60.8 ($C^m$), 32.6 ($C^k$), 31.8 ($C^b$), 22.7 ($C^a$), 18.8 ($C^g$), 13.6 ($C^n$); $\delta_P$ ($CDCl_3$) -144.3 (sept.); $\delta_F$ ($CDCl_3$) -72.5 (d); *m/z* (HRMS$^+$) 387.0938 $[M - PF_6]^+$ ($C_{19}H_{25}O_2{}^{102}Ru$ requires 387.0893); $R_f$ = 0.27 (silica, $CH_2Cl_2$ : 5% EtOH).



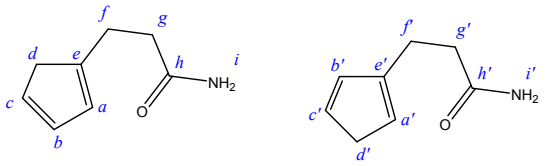

*Methyl 3-(cyclopenta-1,3-dien-1-yl)propanoate and methyl 3-(cyclopenta-1,4-dien-1-yl)propanoate*

A solution of sodium cyclopentadienylide (2 M in THF, 6.45 mL) was diluted in THF (20 mL) and added dropwise to a stirred solution of methyl 3-bromopropionate (1.41 mL, 12.9 mmol) in THF (10 mL) at -78 °C. The mixture was stirred for 3 h at -78 °C before $CH_2Cl_2$ (20 mL) was added to facilitate precipitation of NaBr, which was removed by filtration. The solvent was removed under reduced pressure from the filtrate to leave a 1 : 1 mixture of the *title products* as a yellow oil, which was used without further purification (1.96 g, quantitative); $\delta_H$ ($CDCl_3$) 6.36 – 6.06 (6H, m, $H^{a/a'/b/b'/c/c'}$), 3.63 (6H, s, $H^{i/i'}$), 2.92 (4H, m, $H^{d/d'}$), 2.63 – 2.75 (4H, m, $H^{f/f'}$), 2.57 (4H, t, $H^{g/g'}$); $\delta_C$ ($CDCl_3$) 174.0 ($C^{h/h'}$), 149.1 and 146.8 ($C^{e/e'}$), 135.5 – 127.3 ($C^{a/a'/b/b'/c/c'}$), 52.0 ($C^{i/i'}$), 47.3 and 44.2 ($C^{d/d'}$), 34.7 and 34.1 ($C^{g/g'}$), 26.9 and 26.1 ($C^{f/f'}$); *m/z* (HRMS$^+$) 152.0844 $[M + H]^+$ ($C_9H_{13}O_2$ requires 152.0837).



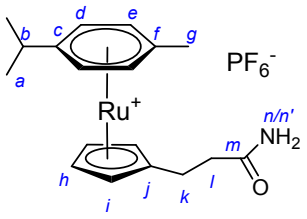

*Ethyl 3-(cyclopentadienyl)propanoate(p-cymene)ruthenium(II) hexafluorophosphate,* **3**

A 1 : 1 mixture of methyl 3-(cyclopenta-1,3-dien-1-yl)propanoate and methyl 3-(cyclopenta-1,4-dien-1-yl)propanoate (1.96 g, 12.9 mmol) was dissolved in dry, degassed (3 × free thaw cycle) EtOH (10.5 mL). $Na_2CO_3$ (312 mg, 2.94 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (300 mg, 0.49 mmol) were added and the mixture was stirred under argon at 75 °C for 16 h. The mixture was left to stand before the supernatant was decanted from residual salts and reduced in volume to 3.5 mL. An aqueous solution of $NH_4PF_6$ (0.3 M, 7.0 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 × 10 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a brown oil. Purification by column chromatography (silica, $CH_2Cl_2$ : EtOH 0 – 0.2% in 0.1% increments) gave the *title compound* as a yellow oil (230 mg, 43%); $\delta_H$ ($CDCl_3$) 6.29 (4H, m, $H^{d/e}$), 5.47 (2H, m, $H^i$), 5.39 (2H, m, $H^h$), 4.11 (2H, q, *J* 7.0 Hz, $H^n$), 2.83 (1H, sept., *J* 7.0 Hz, $H^b$), 2.66 (2H, t, *J* 7.5 Hz, $H^k$), 2.59 (2H, t, *J* 7.5 Hz, $H^l$), 2.40 (3H, s, $H^g$), 1.31 (6H, d, *J* 7.0 Hz, $H^a$), 1.22 (3H, t, *J* 7.0 Hz, $H^o$); $\delta_C$ ($CDCl_3$) 171.6 ($C^m$), 112.3 ($C^c$), 102.2 ($C^j$), 101.5 ($C^f$), 87.0 ($C^e$), 84.6 ($C^d$), 81.0 ($C^i$), 80.0 ($C^h$), 60.1 ($C^n$), 34.4 ($C^l$), 31.8 ($C^b$), 22.8 ($C^k$), 22.7 ($C^a$), 18.8 ($C^g$), 13.6 ($C^o$); $\delta_P$ ($CDCl_3$) -144.2 (sept.); $\delta_F$ ($CDCl_3$) -72.4 (d); *m/z* (HRMS$^+$) 401.1135 $[M - PF_6]^+$ ($C_{20}H_{27}O_2{}^{102}Ru$ requires 401.1049); $R_f$ = 0.27 (silica, $CH_2Cl_2$ : 5% EtOH).



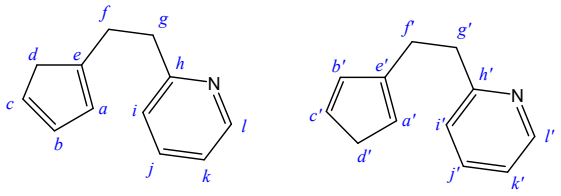

*3-(Cyclopenta-1,3-dien-1-yl)propanamide and 3-(cyclopenta-1,4-dien-1-yl)propanamide*

A solution of sodium cyclopentadienylide (2 M in THF, 2.56 mL) was diluted in THF (7 mL) and added dropwise to a stirred solution of 3-chloropropionamide (550 mg, 5.12 mmol) in THF (4 mL) at -78 °C. The mixture was stirred for 3 h at -78 °C before the reaction temperature was increased to 20 °C and the mixture was stirred for a further 14 h. The solvent was removed under reduced pressure to give yellow solid. Purification by column chromatography (silica, $CH_2Cl_2$ : $CH_3OH$ 0 – 1% in 0.1% increments, dry loaded) gave a 1 : 1 mixture of the *title compounds* as a white amorphous solid (246 mg, 35%); $\delta_H$ ($CDCl_3$) 6.38 – 6.00 (6H, m, $H^{a/a'/b/b'/c/c'}$), 5.40 (4H, br s, $H^{i/i'}$), 2.88 (4H, m, $H^{d/d'}$), 2.73 – 2.63 (4H, m, $H^{f/f'}$), 2.45 – 2.39 (4H, m, $H^{g/g'}$); $\delta_C$ ($CDCl_3$) 175.4 and 175.3 ($C^{h/h'}$), 147.7 and 145.5 ($C^{e/e'}$), 134.4 – 126.6 ($C^{a/a'/b/b'/c/c'}$), 43.4 and 41.4 ($C^{d/d'}$), 35.7 and 35.1 ($C^{g/g'}$), 26.3 and 25.6 ($C^{f/f'}$); *m/z* (HRMS$^+$) 160.0734 $[M + Na]^+$ ($C_8H_{11}NONa$ requires 160.0733); $R_f$ = 0.16 (silica, $CH_2Cl_2$ : 5% $CH_3OH$).



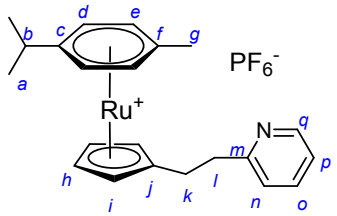

*3-(Cyclopentadienyl)propanamide(p-cymene)ruthenium(II) hexafluorophosphate,* **4**

A 1 : 1 mixture of 3-(cyclopenta-1,3-dien-1-yl)propanamide and 3-(cyclopenta-1,4-dien-1-yl)propanamide (210 mg, 1.53 mmol) was dissolved in dry, degassed (3 × free thaw cycle) EtOH (3.4 mL). $Na_2CO_3$ (97 mg, 0.92 mmol) and [Ru(*p*-cymene)$Cl_2$]$_2$ (94 mg, 0.15 mmol) were added and the mixture was stirred under argon at 75 °C for 16 h. The mixture was left to stand before the supernatant was decanted from residual salts and reduced in volume to 1.4 mL. An aqueous solution of $NH_4PF_6$ (0.15 M, 4.0 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 × 5 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a brown oil. Purification by column chromatography (silica, $CH_2Cl_2$ : EtOH 0 – 3% in 0.1% increments) gave the *title compound* as a yellow oil (85 mg, 55%); $\delta_H$ ($CDCl_3$) 6.82 (1H, br s, $H^n$), 6.33 (1H, br s, $H^{n'}$), 6.25 (4H, m, $H^{d/e}$), 5.42 (2H, m, $H^i$), 5.36 (2H, m, $H^h$), 2.82 (1H, sept., *J* 7.0 Hz, $H^b$), 2.62 (2H, t, *J* 7.2 Hz, $H^k$), 2.46 (2H, t, *J* 7.2 Hz, $H^l$), 2.38 (3H, s, $H^g$), 1.29 (6H, d, *J* 7.0 Hz, $H^a$); $\delta_C$ ($CDCl_3$) 172.8 ($C^m$), 112.2 ($C^c$), 103.1 ($C^j$), 101.4 ($C^f$), 86.9 ($C^e$), 84.6 ($C^d$), 80.9 ($C^i$), 79.8 ($C^h$), 35.3 ($C^l$), 31.7 ($C^b$), 22.9 ($C^k$), 22.7 ($C^a$), 18.8 ($C^g$); $\delta_P$ ($CDCl_3$) -144.2 (sept.); $\delta_F$ ($CDCl_3$) -72.5 (d); *m/z* (HRMS$^+$) 372.0948 $[M - PF_6]^+$ ($C_{18}H_{24}NO^{102}Ru$ requires 372.0896); $R_f$ = 0.05 (silica, $CH_2Cl_2$ : 5% EtOH).




*2-[2-(Cyclopenta-1,3-dien-1-yl)ethyl]pyridine and 2-[2-(cyclopenta-1,4-dien-1-yl)ethyl]pyridine*

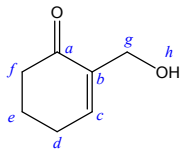
$PPh_3$ (6.98 g, 26.6 mmol) and $CBr_4$ (8.82 g, 26.6 mmol) were added to a solution of 2-Pyridineethanol (2.00 mL, 17.8 mmol) in anhydrous THF (40 mL). The mixture was stirred at 20 °C for 24 h before excess salts were removed by filtration. The crude 2-(2-bromoethyl)pyridine solution was cooled to -78 °C and a solution of sodium cyclopentadienylide (2M in THF, 8.90 mL) was added. The mixture was stirred for 16 h under an argon atmosphere, during which time the temperature increased to 20 °C. The solvent was removed under reduced pressure to give a black residue, which was triturated with hexane (15 mL) and then $Et_2O$ (50 mL). The organic fractions were passed through a plug of silica, which was washed with further fractions of $Et_2O$ (100 mL). All organic fractions were combined and the solvent removed under reduced pressure to give a 1 : 1 mixture of the *title compounds* as a brown oil, which was used without further purification (730 mg, 24%); $\delta_H$ ($CDCl_3$) 8.50 (2H, m, $H^{l/l'}$), 7.54 (2H, m, $H^{j/j'}$), 7.10 (4H, m, $H^{i/i'/k/k'}$) 6.43 – 6.00 (6H, m, $H^{a/a'/b/b'/c/c'}$), 3.00 (4H, m, $H^{g/g'}$), 2.87 (4H, m, $H^{d/d'}$), 2.80 (4H, m, $H^{f/f'}$); $\delta_C$ ($CDCl_3$) 161.7 ($C^{h/h'}$),149.6 ($C^{l/l'}$), 136.1 ($C^{j/j'}$), 149.3 and 146.2 ($C^{e/e'}$), 134.6 – 126.4 ($C^{a/a'/b/b'/c/c'}$), 122.8 ($C^{i/i'}$), 121.1 ($C^{k/k'}$), 43.4 and 41.2 ($C^{d/d'}$), 38.5 and 37.7 ($C^{g/g'}$), 30.7 and 29.7 ($C^{f/f'}$); *m/z* (HRMS$^+$) 194.0992 $[M + Na]^+$ ($C_{12}H_{13}NNa$ requires 194.0940).




*2-(2-Cyclopentadienylethyl)pyridine(p-cymene)ruthenium(II) hexafluorophosphate,* **5**

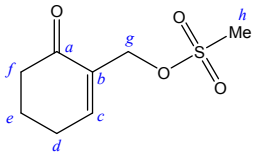
A 1 : 1 mixture of 2-[2-(cyclopenta-1,3-dien-1-yl)ethyl]pyridine and 2-[2-(cyclopenta-1,4-dien-1-yl)ethyl]pyridine (500 mg, 2.92 mmol) was dissolved in dry, degassed (3 × free thaw cycle) EtOH (6 mL). $Na_2CO_3$ (184 mg, 1.74 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (150 mg, 0.25 mmol) were added and the mixture was stirred under argon at 75 °C for 16 h. The mixture was left to stand before the supernatant was decanted from residual salts and reduced in volume to 2.5 mL. An aqueous solution of $NH_4PF_6$ (0.15 M, 11.5 mL) was added and the mixture was extracted with $CH_2Cl_2$ (3 × 15 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a brown oil. Purification by column chromatography (silica, $CH_2Cl_2$ : EtOH 0 – 1% in 0.1% increments) gave the *title compound* as a yellow oil (110 mg, 40%); $\delta_H$ ($CDCl_3$) 8.48, (1H, dd, *J* , 1.8 Hz, $H^q$), 7.60 (1H, td, *J* 7.5 Hz, 1.8 Hz, $H^o$), 7.18 – 7.10 (2H, m, $H^{n/p}$), 6.00 (4H, m, $H^{d/e}$), 5.13 (4H, m, $H^{h/i}$), 2.94 (2H, t, *J* 7.2 Hz, $H^l$), 2.68 (2H, t, *J* 7.2 Hz, $H^k$), 2.65 (1H, sept., *J* 7.0 Hz, $H^b$), 2.27 (3H, s, $H^g$), 1.21 (6H, d, *J* 7.0 Hz, $H^a$); $\delta_C$ ($CDCl_3$) 159.3 ($C^m$), 149.2 ($C^q$), 136.9 ($C^o$),

123.5 ($C^n$), 121.8 ($C^p$), 112.4 ($C^c$), 102.5 ($C^j$), 101.2 ($C^f$), 86.8 ($C^e$), 84.4 ($C^d$), 80.8 ($C^i$), 80.1 ($C^h$), 38.9 ($C^l$), 31.9 ($C^b$), 27.3 ($C^k$), 23.4 ($C^a$), 19.6 ($C^g$); $\delta_P$ ($CDCl_3$) -144.0 (sept.); $\delta_F$ ($CDCl_3$) -72.2 (d); *m*/*z* (HRMS$^+$) 406.1152 $[M - PF_6]^+$ ($C_{22}H_{26}N^{102}Ru$ requires 406.1103); $R_f$ = 0.10 (silica, $CH_2Cl_2$ : 5% EtOH).




*2-(Hydroxymethyl)cyclohex-2-en-1-one*[1]

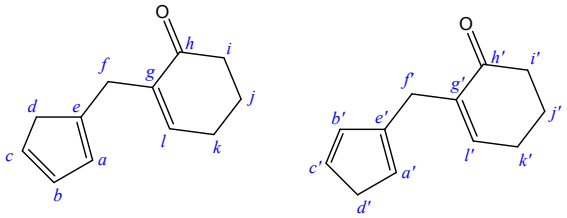
Following a literature procedure,[1] cyclohex-2-en-1-one (12.0 g, 0.125 mmol), formaldehyde (20.3 mL, 37% aqueous) and 4-(dimethylamino)pyridine (1.53 g, 2.50 mmol) were added to anhydrous THF (25 mL) and the mixture was stirred at 20 °C for 16 h. The mixture was acidified to pH 4 with the addition of dilute HCl and extracted with $CH_2Cl_2$ (3 × 30 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a yellow oil. Purification by column chromatography (silica, $Et_2O$ : 25 % $CH_2Cl_2$) gave the *title compound* as a yellow oil (7.38 g, 46%); $\delta_H$ ($CDCl_3$) 6.94 (1H, t, *J* 4.2 Hz, $H^c$), 4.22 (2H, d, *J* 6.0 Hz, $H^g$), 2.90 (1H, m, $H^h$), 2.40 (4H, m, $H^{d/f}$), 1.99 (2H, quin, *J* 6.3 Hz, $H^e$); $\delta_C$ ($CDCl_3$) 200.7 ($C^a$), 147.0 ($C^c$), 138.3 ($C^b$), 62.1 ($C^g$), 38.3 ($C^f$), 25.7 ($C^d$), 22.8 ($C^e$); *m*/*z* (HRMS$^+$) 149.0580 $[M + Na]^+$ ($C_7H_{10}O_2Na$ requires 149.0573); $R_f$ = 0.26 (silica, $CH_2Cl_2$ : 2.5% MeOH).




*(6-Oxocyclohex-1-en-1-yl)methyl methanesulfonate*

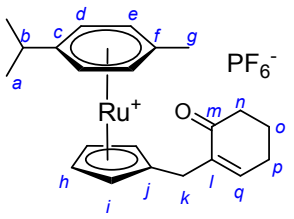
2-(Hydroxymethyl)cyclohex-2-en-1-one (310 mg, 2.46 mmol) was dissolved in anhydrous THF (15 mL). $Et_3N$ (1.03 mL, 7.39 mmol) and methanesulfonyl chloride (275 µL, 3.55 mmol) were added and the mixture was stirred at 0 °C for 1 h. The solvent was removed under reduced pressure and the yellow residue was dissolved in $CH_2Cl_2$ (25 mL) and washed with aqueous saturated NaCl solution (1 × 25 mL). The aqueous layer was re-extracted with $CH_2Cl_2$ (2 × 15 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the *title compound* as a yellow oil (260 mg, 52%); $\delta_H$ ($CDCl_3$) 7.12 (1H, t, *J* 4.2 Hz, $H^c$), 4.76 (2H, s, $H^g$), 3.01 (3H, s, $H^h$), 2.42 (4H, m, $H^{d/f}$), 1.99 (2H, quin, *J* 6.3 Hz, $H^e$); $\delta_C$ ($CDCl_3$) 197.5 ($C^a$), 151.6 ($C^c$), 132.9 ($C^b$), 67.1 ($C^g$), 37.9 ($C^f$), 37.4 ($C^h$), 26.0 ($C^d$), 22.5 ($C^e$); $R_f$ = 0.76 (silica, $CH_2Cl_2$ : 2.5% MeOH).

[1] Handy, S. T.; Omune, D., *Tetrahedron*, **2007**, *63* (6), 1366 - 1371




*2-(Cyclopenta-1,3-dien-1-ylmethyl)cyclohex-2-en-1-one and 2-(cyclopenta-1,4-dien-1-ylmethyl)cyclohex-2-en-1-one*

A solution of sodium cyclopentadienylide (2 M in THF, 0.67 mL) was diluted in THF (2 mL) and added dropwise to a stirred solution of (6-oxocyclohex-1-en-1-yl)methyl methanesulfonate (250 mg, 1.23 mmol) in THF (5 mL) at -78 °C. The mixture was stirred for 3 h at -78 °C before the reaction temperature was increased to 20 °C and the mixture was stirred for a further 14 h. The solvent was removed under reduced pressure to give yellow residue. Purification by column chromatography (silica, $CH_2Cl_2$) gave a 1 : 1 mixture of the *title compounds* as a yellow oil (54 mg, 25%); $\delta_H$ ($CDCl_3$) 6.60 (2H, m, $H^{l/l'}$), 6.34 – 5.96 (6H, m, $H^{a/a'/b/b'/c/c'}$), 3.22 (4H, m, $H^{f/f'}$), 2.85 (4H, m, $H^{d/d'}$), 2.39 (4H, m, $H^{k/k'}$), 2.29 (4H, m, $H^{i/i'}$), 1.92 (4H, quin., *J* 6.3 Hz, $H^{j/j'}$); $\delta_C$ ($CDCl_3$) 195.5 and 194.6 ($C^{h/h'}$), 149.5 and 146.7 ($C^{e/e'}$), 146.1 ($C^{l/l'}$), 134.8 – 128.1 ($C^{a/a'/b/b'/c/c'}$), 133.4 ($C^{g/g'}$), 43.4 and 41.4 ($C^{d/d'}$), 38.5 ($C^{i/i'}$), 30.3 and 29.4 ($C^{f/f'}$), 26.1 ($C^{k/k'}$), 23.1 ($C^{j/j'}$); *m*/*z* (HRMS$^+$)197.0940 $[M + Na]^+$ ($C_{12}H_{14}ONa$ requires 197.0937); $R_f$ = 0.68 (silica, $CH_2Cl_2$ : 2.5% $CH_3OH$).




*2-(Cyclopentadienylmethyl)cyclohex-2-en-1-one(p-cymene)ruthenium(II) hexafluorophosphate,* **6**

A 1 : 1 mixture of 2-(cyclopenta-1,3-dien-1-ylmethyl)cyclohex-2-en-1-one and 2-(cyclopenta-1,4-dien-1-ylmethyl)cyclohex-2-en-1-one (50 mg, 0.29 mmol) was dissolved in dry, degassed (3 × free thaw cycle) EtOH (5 mL). $Na_2CO_3$ (18.4 mg, 0.18 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (15.3 mg, 0.025 mmol) were added and the mixture was stirred under argon at 75 °C for 16 h. The reaction mixture was cooled and an aqueous solution of $NH_4PF_6$ (0.15 M, 1.2 mL) was added. Additional $H_2O$ was added (3 mL) before the mixture was extracted with $CH_2Cl_2$ (3 × 8 mL). The organic fractions were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a brown oil. Purification by column chromatography (silica, $CH_2Cl_2$ : EtOH 0 – 0.5% in 0.1% increments) gave the *title compound* as a yellow oil (5 mg, 3%); partial $\delta_H$ ($CDCl_3$) 6.88 (1H, t, *J* 4.2 Hz, $H^q$), 6.05 (4H, m, $H^{d/e}$), 5.25 (4H, m, $H^{h/i}$), 2.18 (3H, s, $H^g$), 2.00 – 1.52 (br m, $H^{n/o/p}$), 1.24 (6H, d, *J* 7.0 Hz, $H^a$); *m*/*z* (HRMS$^+$) 409.1166 $[M - PF_6]^+$ ($C_{22}H_{27}O^{102}Ru$ requires 409.1100); $R_f$ = 0.25 (silica, $CH_2Cl_2$ : 5% EtOH).

## Mass Spectrometry Calibration

Peaks in the mass spectrum are generally used for qualitative analysis. Quantitative analysis is difficult as the size of the peak in the mass spectrum is dependent upon not only the quantity of the compound but also the volatility and the propensity of the compound to ionise. To allow an approximate quantification of the amount of each complex during the exchange experiments, the following calibration was undertaken: to a solution of [CpRu(*p*-cymene)]$PF_6$ (5 mg) in $CDCl_3$ (0.7 mL), [CpRu($C_6Me_6$)]$PF_6$ was added in ~2 mg increments. After each addition, the ratio of [CpRu(*p*-cymene)]$PF_6$ : [CpRu($C_6Me_6$)]$PF_6$ was quantified using $^1$H-NMR spectroscopy. A mass spectrum was also recorded after each addition and the ratio of peaks in the mass spectrum was plotted as a function of the absolute ratio, determined by $^1$H-NMR. The resulting calibration curve (*Figure S1*) plotted as the percentage of [CpRu($C_6Me_6$)]$PF_6$ was used to approximate the extent of exchange in the arene exchange experiments described in the full text (*Scheme S1*).

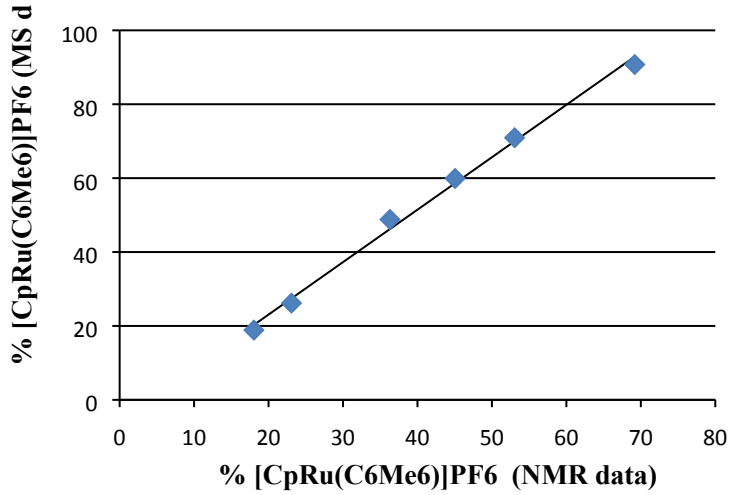
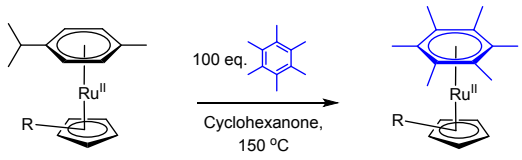



Figure S1. Calibration curve used to determine the percentage [CpRu($C_6Me_6$)]$PF_6$ from mass spectrometric data.

## Half Life Calculation

The half-life of each starting *p*-cymene complex under the exchange conditions shown (*Scheme S1*) was calculated for four complexes (**1**, **3**, **5** and **6**), according to *Procedure S2*. Data for complexes **1** and **5** are shown (*Figure S2*) and half-life values for each complex is given in *Table S5*.




**Scheme S1**

*Procedure S2*

[CpRu(*p*-cymene)]$PF_6$ (1.0 mg, 2.2 μmol), hexamethylbenzene (36.4 mg, 225 μmol) and dry, degassed cyclohexanone or 1-octanol (1.00 mL) were stirred at 150 °C in a sealed Schlenck tube. Aliquots were taken at ten selected time points and the extent of exchange was approximated using positive ion mode electrospray mass spectrometry and the calibration curve described above. The data were plotted as %starting *p*-cymene complex as a function of time (*Figure S2*). The half-life for each complex was calculated according to *Equation S1.1* and *Equation S1.2* using least squares fitting in Microsoft Excel.

$$[A]_t = [A]_0 e^{-kt} \qquad [S1.1]$$

$$t_{1/2} = \frac{ln2}{k} \qquad [S1.2]$$

[A] = concentration of starting *p*-cymene complex; $[A]_0$ = initial concentration of starting *p*-cymene complex; k = rate constant for exchange; t = time; and $t_{1/2}$ is the half-life of the starting complex.

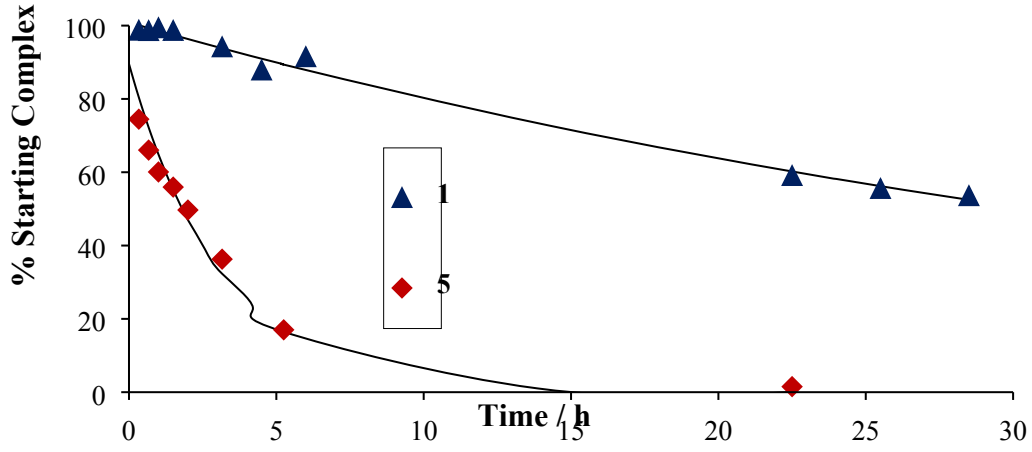



Figure S2: Percentage of arene exchange in the process shown in *Scheme S1* at ten time points for complexes **1** and **5**.

Table S5. Half-lives for complexes **1**, **3**, **5** and **6** calculated for the exchange process shown in *Scheme S1*, (conditions: cyclohexanone, 150 °C, 100 equivalents of incoming arene).

| Complex | Half Life |
|---|---|
| **1** | 34.0 ± 0.7 h |
| **3** | 22.8 ± 0.3 h |
| **5** | 2.2 ± 0.1 h |
| **6** | 27.8 ± 0.4 h |