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# Ruthenium(II) complexes possessing the $\eta^6$-*p*-cymene ligand ☆

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Dedicated to Robert J. Angelici

**Abstract**

Complexes possessing a soft donor $\eta^6$-arene and hard donor acetylacetonate ligand, $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac-}\mu\text{-CH})]_2[OTf]_2$ (**1**) (OTf = trifluoromethanesulfonate; acac = acetylacetonate) and $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**) {Ar′ = 3,5-$(CF_3)$–$C_6H_3$}, were prepared and fully characterized. The lability of the μ-CH linkage for complex **1** and the THF ligand of **2** allow access to the unsaturated cation $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})]^+$. The reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**) with KTp {Tp = hydridotris(pyrazolyl)borate} produces $[TpRu(\eta^6\text{-}p\text{-cymene})][BAr'_4]$ (**5**). The azide complex $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(N_3Ar)][BAr'_4]$ (**6**) forms upon reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**)with $N_3Ar$ (Ar = *p*-tolyl), and reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**) with $CHCl_3$ at 100 °C yields the chloride-bridged binuclear complex $[\{(\eta^6\text{-}p\text{-cymene})Ru\}_2(\mu\text{-Cl})_3][BAr'_4]$ (**7**). The details of solid-state structures of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac-}\mu\text{-CH})]_2[OTf]_2$ (**1**), $[TpRu(\eta^6\text{-}p\text{-cymene})][BAr'_4]$ (**5**) and $[\{(\eta^6\text{-}p\text{-cymene})Ru\}_2(\mu\text{-Cl})_3][BAr'_4]$ (**7**) are disclosed.


*Keywords:* *p*-Cymene; Ruthenium; Acetylacetonate; Half-sandwich complex

## 1. Introduction

The coordination chemistry of mono-metallic half-sandwich complexes has been of significant interest in inorganic and organometallic chemistry [1–5]. Formally charge-neutral $\eta^6$-arene ligands have played a prominent role in this field and can serve as ancillary ligands as well as intermediates for arene functionalization [6–13]. In terms of ancillary ligands, hexa-hapto aromatic Ru(II) complexes provide a flexible template upon which to build diverse coordination environments and to develop metal-mediated catalysis using the $\eta^6$-aromatic ligand to provide a site to potentially vary steric and electronic properties of the catalyst [14–28]. In addition, the use of Ru(II)–$\eta^6$-arene complexes in medicinal applications has been explored [29–36].

The combination of an $\eta^6$-arene ligand and a formally anionic oxygen-based ligand provides a coordination sphere with both "soft" (i.e., the arene) and "hard" (i.e., the oxygen-based ligand) donors. Along these lines, we report the preparation and preliminary reactivity of Ru(II) complexes that possess an $\eta^6$-*p*-cymene and $\kappa^2$-*O*,*O*-acac (acac = acetylacetonate) ligand.

## 2. Experimental

### 2.1. General procedures

Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ($O_2 < 15$ ppm for

☆ Congratulations to Bob Angelici on a career that has advanced the fields of inorganic and organometallic chemistry as well as inspired students and colleagues.

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all reactions in glovebox). Tetrahydrofuran was dried by distillation from sodium/benzophenone. Acetonitrile was dried by distillation from $CaH_2$. Hexanes (stored over 4 Å molecular sieves) and methylene chloride were purified by passage through a column of activated alumina. Benzene-$d_6$ and chloroform-$d_1$ were degassed using three freeze–pump–thaw cycles and stored under a nitrogen atmosphere over 4 Å molecular sieves. $^1$H NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer, and $^{13}$C NMR spectra (operating frequency 75 MHz) were recorded on a Varian Mercury 300 MHz spectrometer. 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 spectrometer (operating frequency 282 MHz) and referenced against an external standard of hexafluorobenzene ($\delta = -164.9$). Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in a standard three-electrode cell from −2.00 V to +2.00 V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate (TBAH) as electrolyte. Tetrabutylammonium hexafluorophosphate was dried under dynamic vacuum at 140 °C for 48 h prior to use. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate as an internal standard. The preparation, isolation and characterization of KTp, ($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)Cl and $NaBAr'_4$ {Ar′ = 3,5-$(CF_3)$-$C_6H_3$} have been previously reported [2,4,37,38]. All other reagents were used as received from commercial sources. Elemental analyses were performed by Atlantic Microlabs, Inc.

### 2.2. Preparation of complexes

#### 2.2.1. ($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)OTf (**1-OTf**)

($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)Cl (0.765 g, 2.07 mmol) was dissolved in 40 mL of THF. Upon addition of AgOTf (0.584 g, 2.27 mmol) a white precipitate (presumably AgCl) formed. The mixture was stirred for 30 min at room temperature, after which time it was filtered through a plug of Celite. The filtrate was concentrated to approximately 10 mL in vacuo, and hexanes (approximately 40 mL) were added to yield a precipitate. The product was collected via vacuum filtration through a fine porosity frit to give an orange solid (0.919 g, 92% yield). $^1$H NMR ($CDCl_3$, $\delta$): 5.64 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.42 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.17 (1H, s, acac-μ-CH), 2.97 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*$(CH_3)_2$), 2.31 (3H, s, *p*-cymene C–C*H*$_3$), 2.05 (6H, s, acac-$CH_3$), 1.39 (6H, d, $^3J_{HH} = 7$ Hz, CH(C*H*$_3)_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 187.5 (s, acac C–O), 119.4 (q, $^1J_{CF} = 319$ Hz, $SO_3CF_3$), 100.3 (s, acac C-H), 97.5 and 97.1 (each a s, *p*-cymene 1,4-positions), 80.5 and 78.3 (each a s, *p*-cymene 2,3-positions), 31.2 (s, *p*-cymene *C*H(Me)$_2$), 27.2 (s, *p*-cymene C-*C*H$_3$), 22.5 (s, acac $CH_3$), 17.9 (s, *p*-cymene CH(*C*H$_3)_2$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): −78.0 (s, $SO_3CF_3$). CV (THF, 100 mV/s, TBAH): $E_{p,a} = -1.13$ V, Ru(II/I). *Anal.* Calc. for $C_{32}H_{42}Ru_2F_6O_{10}S_2$: C, 39.67; H, 4.37; O, 16.52. Found: C, 39.10; H, 4.50; O, 16.58%.

#### 2.2.2. [($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*, *O*-acac)(*THF*)][$BAr'_4$] (**2**)

[($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac-μ-CH)]$_2$[OTf]$_2$ (**1**) (1.30 g, 2.7 mmol) was dissolved in 40 mL of THF. $NaBAr'_4$ (4.79 g, 5.4 mmol) was added to the solution, and the resulting mixture was stirred for 12 h. The volatiles were removed in vacuo, the residual material was dissolved in approximately 20 mL of $CH_2Cl_2$, and the solution was filtered through a plug of Celite. The filtrate volume was reduced to approximately 10 mL in vacuo, and hexanes (approximately 40 mL) were added to form a precipitate. The orange solid was collected via vacuum filtration through a fine porosity frit (2.26 g, 66% yield). $^1$H NMR ($CDCl_3$, $\delta$): 7.71 (8H, br s, *ortho* $BAr'_4$), 7.54 (4H, br s, *para*$BAr'_4$), 5.50 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.27 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.27 (1H, s, acac-CH), 3.49 (4H, m, α-THF), 2.79 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*$(CH_3)_2$), 2.15 (3H, s, *p*-cymene C–C*H*$_3$), 2.06 (6H, s, acac $CH_3$), 1.74 (4H, m, β-THF), 1.32 (6H, d, $^3J_{HH} = 7$ Hz, *p*-cymene CH(C*H*$_3)_2$).$^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 188.3 (s, acac C–O), 161.8 (1:1:1:1 quartet, $^1J_{CB} = 51$ Hz, *ipso*-C of $BAr'_4$), 134.9 (s, *para*-C of $BAr'_4$), 129.1 (q, $^2J_{CF} = 29$ Hz, *meta*-C of $BAr'_4$), 127.5 (q, $^1J_{CF} = 272$ Hz, $CF_3$ of $BAr'_4$), 117.6 (s, *ortho*-C of $BAr'_4$), 101.0, 98.9, 98.2 80.4, 78.7 (all s, *p*-cymene aromatic and acac C-H), 70.9 (s, α-C of THF), 31.3 (s, *C*H$(CH_3)_2$), 27.2 (s, acac methyl), 25.5 (s, β-C of THF), 22.2 (s, *p*-cymene C–C*H*$_3$), 17.7 (s, *p*-cymene CH(*C*H$_3)_2$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): −62.8 (s, $BAr'_4$). CV (THF, TBAH, 100 mV/s): $E_{1/2} = -0.78$ V, Ru(II/I). *Anal.* Calc. for $C_{51}H_{41}RuF_{24}BO_3$: C, 48.24; H, 3.25. Found: C, 47.87; H, 3.29%.

#### 2.2.3. [($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*, *O*-acac)(*NCMe*)][$BAr'_4$] (**3**)

[($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$] (**2**) (0.53 g, 0.42 mmol) was dissolved in 40 mL of NCMe, and the solution was stirred for approximately 10 min. The volatiles were removed in vacuo, and the residual material was dissolved in approximately 5 mL of $CH_2Cl_2$. The addition of hexanes (approximately 40 mL) afforded a precipitate. The orange solid was collected via vacuum filtration through a fine porosity frit (0.46 g, 88% yield).$^1$H NMR ($CDCl_3$, $\delta$): 7.71 (8H, br s, *ortho*$BAr'_4$), 7.54 (4H, br s, *para*$BAr'_4$), 5.52 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.21 (1H, s, acac-CH), 5.21 (2H, d, $^3J_{HH} = 5$ Hz, *p*-cymene Ar–CH), 2.75 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*$(CH_3)_2$), 2.18, 2.11 (each 3H, each a s, *p*-cymene C–C*H*$_3$ and NCC*H*$_3$), 1.98 (6H, s, acac $CH_3$), 1.28 (6H, d, $^3J_{HH} = 7$ Hz, *p*-cymene CH(C*H*$_3)_2$).$^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 188.1 (s, acac C–O), 161.9 (1:1:1:1 quartet, $^1J_{CB} = 50$ Hz, *ipso*-C of $BAr'_4$), 135.0 (s, *para*-C of $BAr'_4$), 129.1 (q, $^2J_{CF} = 34$ Hz, *meta*-C of $BAr'_4$), 124.8 (q, $^1J_{CF} = 273$ Hz, $CF_3$ of $BAr'_4$), 122.7 (s, N*C*CH$_3$), 117.7 (s, *ortho*-C of $BAr'_4$), 103.0, 100.7, 99.2, 84.4, 80.4 (all s, *p*-cymene aromatic and acac

C-H), 31.1 (s, *C*H($CH_3$)$_2$), 27.1 (s, acac methyl), 22.1 (s, *p*-cymene C-*C*$H_3$), 17.6 (s, *p*-cymene CH(*C*$H_3$)$_2$), 3.0 (s, NC*C*$H_3$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): −58.8 (s, $BAr'_4$). CV (NCMe, TBAH, 100 mV/s): $E_{p,a} = -1.24$ V, Ru(II/I). *Anal*. Calc. for $C_{49}H_{36}BF_{24}NO_3Ru$: C, 47.45; H, 2.93; N, 1.13. Found: C, 47.44; H, 2.92; N, 1.12%.

### 2.2.4. [($\eta^6$-*p*-*Cymene*)*Ru*($\kappa^2$-*O*, *O*-*acac*)(*PMe*$_3$)][*BAr*$'_4$] (**4**)

[($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$](**2**) (0.520 g, 0.41 mmol) was dissolved in 40 mL of dichloromethane. Trimethylphosphine (0.030 g, 0.45 mmol) was added to the solution, and the resulting mixture was stirred for 5 min. The solution volume was reduced to approximately 5 mL in vacuo, and hexanes (approximately 40 mL) were added to form a precipitate. The product was collected via vacuum filtration through a fine porosity frit to give a yellow solid (0.46 g, 88% yield). $^1$H NMR ($CDCl_3$, $\delta$): 7.71 (8H, br s, *ortho*$BAr'_4$), 7.54 (4H, br s, *para*$BAr'_4$), 5.50 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic C-H), 5.38 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic C-H), 5.38 (1H, s, acac-CH), 2.47 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*($CH_3$)$_2$), 1.93 (6H, s, acac $CH_3$), 1.84 (3H, s, *p*-cymene C–C$H_3$), 1.28 (9H, d, $^2J_{PH} = 12$ Hz, P(C$H_3$)$_3$), 1.18 (6H, d, $^3J_{HH} = 7$ Hz, *p*-cymene CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 189.8 (s, acac C–O), 161.9 (1:1:1:1 quartet, $^1J_{CB} = 50$ Hz, *ipso*-C of $BAr'_4$), 135.0 (s, *para*-C of $BAr'_4$), 129.1 (q, $^2J_{CF} = 31$ Hz, *meta*-C of $BAr'_4$), 124.8 (q, $^1J_{CF} = 273$ Hz, $CF_3$ of $BAr'_4$), 117.7 (s, *ortho*-C of $BAr'_4$), 105.0, 101.8, 96.6, 89.2, 87.8 (all s, *p*-cymene aromatic and acac C-H), 30.7 (s, *C*H($CH_3$)$_2$), 27.2 (s, acac methyl), 21.8 (s, *p*-cymene C-*C*$H_3$), 16.7 (s, *p*-cymene CH(*C*$H_3$)$_2$), 14.3 (d, $^1J_{CP} = 31$ Hz, P(*C*$H_3$)$_3$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): −58.8 (s, $BAr'_4$). CV (THF, TBAH, 100 mV/s): $E_{p,a} = -1.63$ V, Ru(II/I). *Anal*. Calc. for $C_{50}H_{42}BF_{24}O_2PRu$: C, 47.09; H, 3.32; O, 2.51. Found: C, 46.79; H, 3.29; O, 2.70%.

### 2.2.5. [*TpRu*($\eta^6$-*p*-*Cymene*)][*BAr*$'_4$] (**5**)

[($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$](**2**) (0.130 g, 0.102 mmol) was dissolved in 40 mL of dichloromethane, and KTp (0.037 g, 0.15 mmol) was added to the solution. The mixture was stirred for approximately 12 h. The solution was filtered through a plug of Celite, and the filtrate was concentrated to approximately 10 mL under reduced pressure. Upon addition of hexanes (approximately 40 mL), a red precipitate formed. The red solid was collected via vacuum filtration through a fine porosity frit (0.530 g, 45% yield). $^1$H NMR ($CDCl_3$, $\delta$): 7.99 (3H, d, $^3J_{HH} = 2$ Hz, Tp 3 or 5 positions), 7.70 (8H, br s, $BAr'_4$ *ortho*), 7.56 (3H, d, $^3J_{HH} = 2$ Hz, Tp 3 or 5 positions), 7.51 (4H, br s, $BAr'_4$ *para*), 6.29 (3H, t, $^3J_{HH} = 2$ Hz, Tp 4 positions), 5.68 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic C-H), 5.55 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic C-H), 2.92 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*($CH_3$)$_2$), 2.33 (3H, s, *p*-cymene C–C$H_3$), 1.17 (6H, d, $^3J_{HH} = 7$ Hz, *p*-cymene CH(C$H_3$)$_2$).$^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 161.8 (1:1:1:1 quartet, $^1J_{CB} = 50$ Hz, *ipso*-C of $BAr'_4$), 143.7 and 136.3 (each a s, Tp 3,5-positions), 135.0 (s, *para*-C of $BAr'_4$), 129.0 (q, $^2J_{CF} = 42$ Hz, *meta*-C of $BAr'_4$), 124.7 (q, $^1J_{CF} = 272$ Hz, $CF_3$ of $BAr'_4$), 117.7 (*ortho*-C of $BAr'_4$), 108.7, 107.5, 102.0, 85.7, 85.5 (all s, *p*-cymene aromatic and Tp 4 positions), 31.5 (s, *C*H($CH_3$)$_2$), 22.7 (s, *p*-cymene C-*C*$H_3$), 19.0 (s, *p*-cymene CH(*C*$H_3$)$_2$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): − 58.8 (s, $BAr'_4$). CV (THF, TBAH, 100 mV/s): $E_{p,a} = -1.45$ V, Ru(II/I). *Anal*. Calc. for $C_{51}H_{36}RuB_2F_{24}N_6$: C, 46.70; H, 2.77; N, 6.41. Found: C, 46.85; H, 2.94; N, 6.18%.

### 2.2.6. [($\eta^6$-*p*-*Cymene*)*Ru*($\kappa^2$-*O*, *O*-*acac*)(*N*$_3$(*p*-*tolyl*))[*BAr*$'_4$] (**6**)

[($\eta^6$-*p*-Cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$](**2**) (0.334 g, 0.263 mmol) was dissolved in 40 mL of dichloromethane, and *p*-tolylazide (0.052 g, 0.394 mmol) was added to the solution. The mixture was stirred for approximately 1 h. The solution was filtered through a plug of Celite, and the filtrate was concentrated to approximately 10 mL under reduced pressure. Upon addition of hexanes (approximately 40 mL), a black precipitate formed. The solid was collected via vacuum filtration through a fine porosity frit to give a red solid (0.170 g, 49% yield). $^1$H NMR ($CDCl_3$, $\delta$): 7.71 (8H, br s, *ortho*$BAr'_4$), 7.53 (4H, br s, *para*$BAr'_4$), 7.24 (2H, d, $^3J_{HH} = 9$ Hz, azide aromatic CH), 6.79 (2H, d, $^3J_{HH} = 9$ Hz, azide aromatic CH), 6.04 (1H, s, acac-CH), 5.82, 5.51, 5.13 (4H total, 1:2:1 integration, each a m, *p*-cymene aromatic CH), 2.79 (1H, sept, $^3J_{HH} = 7$ Hz, C*H*($CH_3$)$_2$), 2.20 (3H, s, *p*-cymene $CH_3$), 2.18 (3H, s, azide $CH_3$), 1.85 (6H, s, acac $CH_3$), 1.35 (6H, d, $^3J_{HH} = 7$ Hz, *p*-cymene CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 188.1 (s, acac C–O), 161.9 (1:1:1:1 quartet, $^1J_{CB} = 50$ Hz, *ipso*-C of $BAr'_4$), 137.1 (s, *ipso*-C of azide), 135.0 (s, *para*-C of $BAr'_4$), 131.5 (s, *para*-C of azide), 129.2 (q, $^2J_{CF} = 34$ Hz, *meta*-C of $BAr'_4$), 128.6 (s, *ortho*-C of azide), 125.0 (s, *meta*-C of azide), 124.8 (q, $^1J_{CF} = 273$ Hz, $CF_3$ of $BAr'_4$), 117.7 (s, *ortho*-C of $BAr'_4$), 86.5, 86.4, 86.2, 83.8, 83.6 (all s, *p*-cymene aromatic and acac C-H), 32.0 (s, *C*H($CH_3$)$_2$), 24.2 (s, azide $CH_3$), 23.2 (s, acac $CH_3$), 22.3 (s, *p*-cymene C–C$H_3$), 19.2 (s, *p*-cymene CH(*C*$H_3$)$_2$), 3.0 (s, NC*C*$H_3$). $^{19}$F{$^1$H} NMR ($CDCl_3$, $\delta$): −62.8 (s, $BAr'_4$). CV (THF, TBAH, 100 mV/s): $E_{p,a} = -0.50$ V, Ru(II/I). We were unable to obtain satisfactory elemental analysis of this complex.

### 2.2.7. {[($\eta^6$-*p*-*Cymene*)$_2$*Ru*]$_2$($\mu$-*Cl*)$_3$}[*BAr*$'_4$] (**7**)

A thick-walled glass tube was charged with [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$] (**2**) (0.200 g, 0.157 mmol) and 30 mL of $CHCl_3$. The solution was heated at 100 °C for three weeks. After filtration through a fine porosity frit, the solution was concentrated to approximately 10 mL. Hexanes (approximately 40 mL) were added to form a dark red precipitate. The dark red solid was collected via vacuum filtration through a fine porosity frit (0.090 g, 45% yield). $^1$H NMR ($CDCl_3$, $\delta$): 7.71 (8H, br s, *ortho*$BAr'_4$), 7.53 (4H, br s, *para*$BAr'_4$), 5.56 (2H, d, $^3J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 5.36 (2H, d,

$^{3}J_{HH} = 6$ Hz, *p*-cymene aromatic CH), 2.76 (1H, sept, $^{3}J_{HH} = 7$ Hz, C*H*$(CH_3)_2$), 2.18 (3H, s, *p*-cymene C–C*H*$_3$), 1.29 (6H, d, $^{3}J_{HH} = 7$ Hz, *p*-cymene CH$(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, $\delta$): 161.8 (1:1:1:1 quartet, $^{1}J_{CB} = 50$ Hz, *ipso*-C of $BAr'_4$), 135.0 (s, *para*-C of $BAr'_4$), 129.1 (q, $^{2}J_{CF} = 34$ Hz, *meta*-C of $BAr'_4$), 124.7 (q, $^{1}J_{CF} = 272$ Hz, $CF_3$ of $BAr'_4$), 117.7 (*ortho*-C of $BAr'_4$), 102.5, 97.3, 78.9 and 78.2 (all s, *p*-cymene aromatic), 31.7 (s, *C*H$(CH_3)_2$), 22.3 (s, *p*-cymene C–*C*H$_3$), 19.0 (s, *p*-cymene CH$(CH_3)_2$). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, $\delta$): −59.1 (s, $BAr'_4$). CV (THF, TBAH, 100 mV/s): $E_{p,a} = -0.92$ V, Ru(II/I). *Anal.* Calc. for $C_{52}H_{40}Ru_2BF_{24}Cl_3$: C, 43.37; H, 2.80. Found: C, 42.86; H, 2.89%.

### 2.2.8. Attempted catalytic aziridination

[(η$^6$-*p*-Cymene)Ru(κ$^2$-*O*,*O*-acac)(THF)][$BAr'_4$] (**2**) (0.010 g, 0.008 mmol), styrene (0.002 g, 0.156 mmol) and PhINTs (0.054 g, 0.156 mmol) were combined in a screw-cap NMR tube in $CDCl_3$ (0.5 mL). The reaction was monitored by $^{1}H$ NMR spectroscopy. After 48 h, complete decomposition of complex **2** was observed without production of aziridine [39].

### 2.2.9. Hydrogenation of styrene

[(η$^6$-*p*-Cymene)Ru(κ$^2$-*O*,*O*-acac)(THF)][$BAr'_4$] (**2**) (0.013 g, 0.010 mmol) and styrene (0.002 g, 0.2 mmol) were combined in a J-Young NMR tube in $CDCl_3$ (0.5 mL). The reaction was followed by $^{1}H$ NMR spectroscopy under 30 psi of dihydrogen pressure at 60 °C for 36 h. At this time, 31% yield of ethylbenzene was observed. No additional production of ethylbenzene occurred at longer reaction times, and $^{1}H$ NMR spectroscopy revealed decomposition of **2** to multiple products.

## 3. Results and discussion

The reaction of previously reported (η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac)Cl[2,4] with AgOTf results in chloride/triflate metathesis to produce (η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac)OTf (**1-OTf**) (Eq. (1)). Consistent with the exchange of chloride and triflate ligands, the $^{19}F$ NMR spectrum of **1-OTf** reveals a singlet at −78.0 ppm. We anticipated that this reaction would produce the monomeric product of simple chloride/triflate exchange, (η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac)OTf, however, a single crystal X-ray diffraction study has revealed that **1-OTf** does not have a Ru-OTf linkage, rather, the C-H moiety of the acac ligand serves to bridge two Ru centers to form the bimetallic complex [(η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac-μ-CH)]$_2$[OTf]$_2$ (**1**) (Fig. 1, Tables 1 and 2). Thus, in the solid-state, the acac π-system apparently forms a stronger bond with Ru than does the weakly coordinating triflate ligand. However, experimental evidence suggests that the dimeric μ-CH structure does not persist in solution (see below).

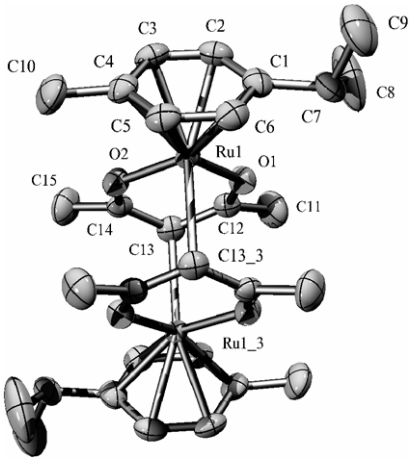
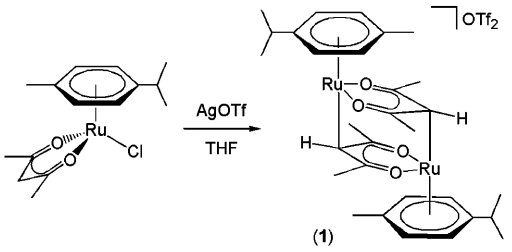



Fig. 1. ORTEP (scaled to enclose 30% probability) of [(η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac-μ-CH)]$_2$[OTf]$_2$ (**1**) (OTf anions are not depicted).

Table 1
Selected bond distances (Å) and angles (°) for [(η$^6$-*p*-cymene)Ru(κ$^2$-*O*,*O*-acac-μ-CH)]$_2$[OTf]$_2$ (**1**)

| | | | |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| Ru(1)–Cent[a] | 1.671 | Ru(1)–C(4) | 2.189(3) |
| Ru(1)–O(1) | 2.085(2) | Ru(1)–C(5) | 2.179(3) |
| Ru(1)–O(2) | 2.081(2) | Ru(1)–C(6) | 2.188(3) |
| Ru(1)–C(1) | 2.208(3) | Ru(1)–C(13)[b] | 2.315(3) |
| Ru(1)–C(2) | 2.190(3) | O(1)–C(12) | 1.242(3) |
| Ru(1)–C(3) | 2.179(3) | O(2)–C(14) | 1.246(3) |
| *Bond angles (°)* | | | |
| O(2)–Ru(1)–O(1) | 86.4(1) | O(1)–C(12)–C(11) | 115.9(3) |
| C(12)–O(1)–Ru(1) | 128.3(2) | C(13)–C(12)–C(11) | 118.1(3) |
| C(14)–O(2)–Ru(1) | 128.3(2) | C(12)–C(13)–C(14) | 120.0(2) |
| C(3)–C(4)–C(10) | 120.3(3) | O(2)–C(14)–C(13) | 125.6(2) |
| O(1)–C(12)–C(13) | 126.0(2) | O(2)–C(14)–C(15) | 116.1(3) |

[a] Cent corresponds to the centroid of the central six-membered ring of the *p*-cymene ligand.
[b] Symmetry transformations used to generate equivalent atoms: $-x+2$, $-y+2$, $-z+2$.




(1)

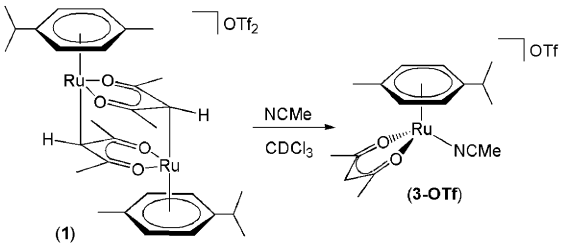
Examples of complexes with μ-CH bridging β-diketonate ligands are known [40]. The bond distance between Ru and the bridging acac carbon is 2.315(3) Å. This bond distance is longer than typical Ru$^{II}$–C bond distances of Ru–alkyl linkages [41–45], which are typically in the range of 2.16(2)–2.21(2) Å, as well as Ru–C bond distances of η$^2$-olefins and vinyl ligands. For example, the Ru–$C_{olefin}$ bond distances of *cis*-Ru(acac)$_2$(η$^2$- $C_2H_4$)(P$^i$Pr$_3$) are 2.172(5) Å and 2.181(5) Å,[46] and the Ru–$C_{vinyl}$ bond distance of Ru{C(C=CPh)=CHPh}(CO)(PPh$_3$)$_2$(κ$^2$-*N*,*S*-$C_4H_5N_3S$) is 2.111(4) Å [47]. The average bond distance for Ru–$C_{arene}$

Table 2
Selected crystallographic data for complexes **1**, **5** and **7**

| Complex | **1** | **5** | **7** |
|---|---|---|---|
| Empirical formula | $C_{16}H_{21}F_3O_5RuS$ | $C_{56}H_{46}B_2F_{24}N_6Ru$ | $C_{52}H_{40}BC_{13}F_{24}Ru_2$ |
| Formula weight | 483.46 | 1381.68 | 1440.14 |
| $T$ (K) | 223(2) | 293(2) | 110 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71070 |
| Crystal system | monoclinic | monoclinic | triclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 10.1067(8) | 12.9695(8) | 12.6470(3) |
| $b$ (Å) | 16.674(1) | 18.945(1) | 14.174(4) |
| $c$ (Å) | 11.752(1) | 24.865(2) | 16.992(5) |
| $\alpha$ (°) | 90 | 90 | 72.119(2) |
| $\beta$ (°) | 108.291(2) | 98.393(1) | 73.622(1) |
| $\gamma$ (°) | 90 | 90 | 86.217(1) |
| $V$ (Å$^3$) | 1880.4(3) | 6044.2(6) | 2780.5(1) |
| $Z$ | 4 | 4 | 2 |
| $\rho_{calc}$ (g/cm$^3$) | 1.708 | 1.518 | 1.720 |
| Crystal size (mm) | $0.26 \times 0.32 \times 0.34$ | $0.12 \times 0.28 \times 0.54$ | $0.20 \times 0.18 \times 0.16$ |
| Goodness-of-fit | 1.049 | 0.963 | 1.034 |
| $R_1$, $wR_2$ $\{I > 2\sigma(I)\}$ | 0.0332, 0.0912 | 0.0534, 0.1407 | 0.0331, 0.0775 |

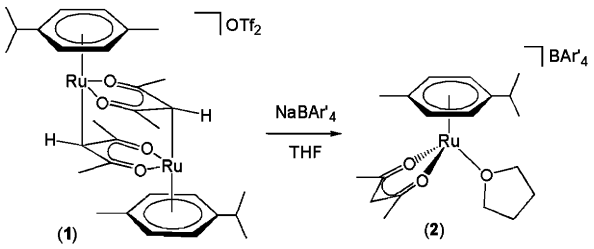
interactions is 2.189(3) Å. There are several examples of structurally characterized Ru(II) systems with $\eta^6$-*p*-cymene ligands. For instance, the [($\eta^6$-*p*-cymene)Ru(1,2,3,4-$Me_4$-1,3-butadiene)Cl][$ClO_4$] [48] system has an average Ru–$C_{arene}$ bond distance of 2.280(4) Å, the average Ru–$C_{arene}$ distance of [($\eta^6$-*p*-cymene)Ru($PPh_3$)$_2$Cl]$^+$[5] is 2.278(2) Å while those of [($\eta^6$-*p*-cymene)Ru(1,2-$S_2C_2B_{10}C_{10}$-S,S′)(arylamine)] [49] and [($\eta^6$-*p*-cymene)Ru[$S_2C_2(B_{10}H_{10})$](PPh$_3$)] [50] are 2.227(8) Å and 2.263(4) Å, respectively.

It is likely that the μ-CH bridging acac structure of [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac-μ-CH)]$_2$[OTf]$_2$ (**1**) does not persist in solution. For example, the chemical shift of the acac-CH moiety of **1** in $CDCl_3$ is 5.17 ppm. This value is quite similar to the analogous chemical shift of other acac complexes reported herein (the range is 6.04 ppm to 5.21 ppm), which is suggestive of a simple $\kappa^2$-*O*,*O* coordination mode. Other evidence suggests that ($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)OTf (**1-OTf**) is present in solution (see below). In addition, if the μ-CH bridging acac structure persists in solution, it is easily displaced. For example, placing **1** in $CDCl_3$ with acetonitrile produces [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)(NCMe)][OTf] (**3-OTf**) within 10 min at room temperature (Eq. (2)). The production of **3-OTf** has been observed by $^1$H NMR spectroscopy while [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*, *O*-acac)(NCMe)][BAr′$_4$] (**3**) has been isolated and characterized (see below).




(2)

In THF solution, **1** does not coordinate THF, which is consistent with the proposed ($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)OTf (**1-OTf**) formulation (Chart 1). In contrast, the reaction of **1** and NaBAr′$_4$ {Ar′=3,5-$(CF_3)_2C_6H_3$} in THF produces [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*, *O*-acac)(THF)][BAr′$_4$] (**2**) (Eq. (3)). Hence, THF does not compete with OTf for coordination to Ru but does displace the μ-CH linkage (Scheme 1). The $^1$H NMR spectrum of **2** reveals resonances at 3.49 and 1.74 ppm with resonances at 70.9 and 25.5 ppm in the $^{13}$C NMR spectrum due to the α- and β-positions, respectively, of the coordinated THF. In comparison, free THF peaks resonate at 3.76 and 1.85 ppm in $^1$H NMR spectrum and at 68.0 and 25.6 ppm in the $^{13}$C NMR spectrum. Thus, coordination of THF to the cationic Ru(II) results in a slight upfield shift of resonances ($^1$HMR spectrum) of the THF ligand.




(3)

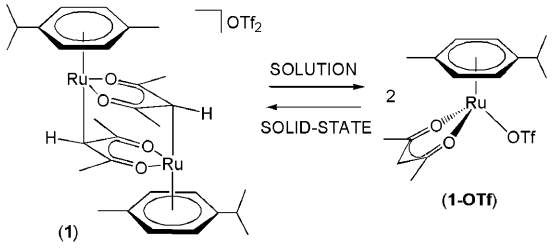
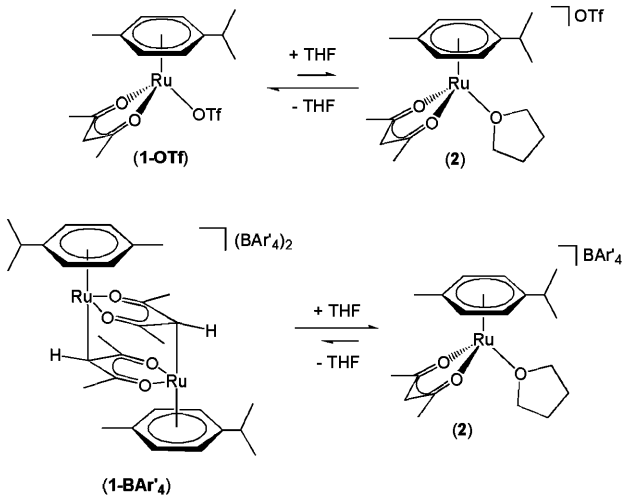
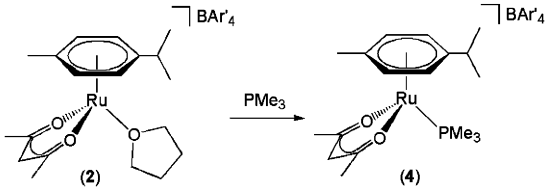



Chart 1. Competition between coordination of acac-CH and OTf.

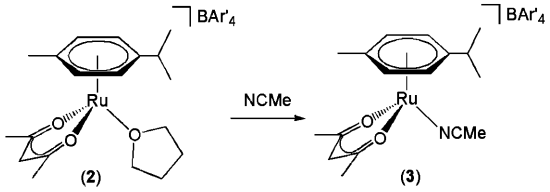



Scheme 1. Equilibria for coordination of THF as a function of counterion.

The THF ligand of **2** is quite labile. For example, the combination of **2** and $PMe_3$ in $CH_2Cl_2$ produces $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(PMe_3)][BAr'_4]$ (**4**) (Eq. 4). Performing this reaction in an NMR tube in $CDCl_3$ reveals the formation of free THF. Complex **2** also reacts with NCMe to produce $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(NCMe)][BAr'_4]$ (**3**) (Eq. (5)). Performing the reaction in $NCCD_3$ reveals complete conversion to **3** within 10 min with concomitant formation of free THF.




(4)




(5)

Thinking that the formally anionic and six-electron donating ligand Tp {Tp = hydridotris(pyrazolyl)borate} might displace the *p*-cymene ligand to form a charge neutral $TpRu(\kappa^2\text{-}O,O\text{-acac})L$ system, we reacted **2** with KTp. Instead of Tp/*p*-cymene exchange, the reaction of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**) and KTp results in the displacement of the anionic acac ligand and THF to produce $[TpRu(\eta^6\text{-}p\text{-cymene})][BAr'_4]$ (**5**) (Eq. (6)). In the downfield region of the $^1H$ NMR spectrum of **5**, there are three resonances due to the Tp ligand, which is consistent with the presence of a molecular $C_3$ axis of rotation. A single crystal X-ray diffraction study of **5** has confirmed its identity (Fig. 2). Bond distances and angles are presented in Table 3 with selected crystallographic data

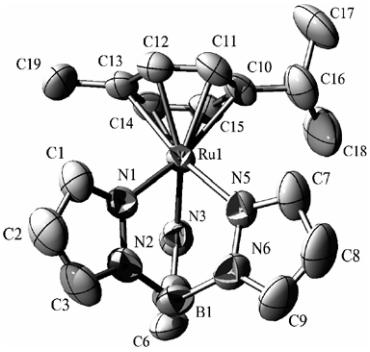


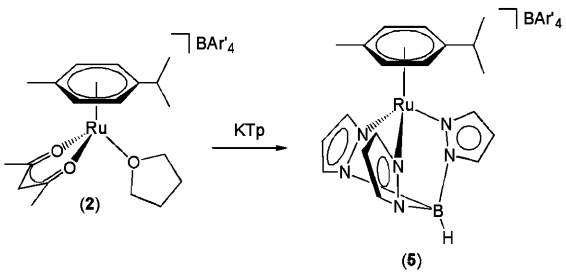

Fig. 2. ORTEP (30% probability) of $[TpRu(\eta^6\text{-}p\text{-cymene})][BAr'_4]$ (**5**) (the $BAr'_4$ counterion is not depicted).

Table 3
Selected bond distances (Å) and angles (°) for $[TpRu(\eta^6\text{-}p\text{-cymene})][BAr'_4]$ (**5**)

| | | | |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| Ru(1)–N(3) | 2.096(3) | Ru(1)–C(13) | 2.236(4) |
| Ru(1)–N(1) | 2.103(2) | C(10)–C(15) | 1.397(5) |
| Ru(1)–N(5) | 2.106(3) | C(10)–C(11) | 1.429(5) |
| Ru(1)–Cent[a] | 1.694 | C(10)–C(16) | 1.494(6) |
| Ru(1)–C(15) | 2.174(3) | C(11)–C(12) | 1.371(5) |
| Ru(1)–C(14) | 2.182(3) | C(12)–C(13) | 1.416(5) |
| Ru(1)–C(12) | 2.183(3) | C(13)–C(14) | 1.408(5) |
| Ru(1)–C(11) | 2.185(3) | C(13)–C(19) | 1.491(5) |
| Ru(1)–C(10) | 2.236(3) | C(14)–C(15) | 1.398(5) |
| *Bond angles (°)* | | | |
| N(1)–Ru(1)–Cent[a] | 129.0 | N(1)–Ru(1)–N(5) | 81.9(1) |
| N(3)–Ru(1)–Cent[a] | 127.1 | N(6)–B(1)–N(4) | 106.8(3) |
| N(5)–Ru(1)–Cent[a] | 131.5 | N(2)–B(1)–N(4) | 108.6(3) |
| N(3)–Ru(1)–N(1) | 86.7(1) | N(2)–B(1)–N(6) | 107.1(3) |
| N(3)–Ru(1)–N(5) | 84.3(1) | | |

[a] Cent corresponds to the centroid of the six-membered ring of the *p*-cymene molecule.

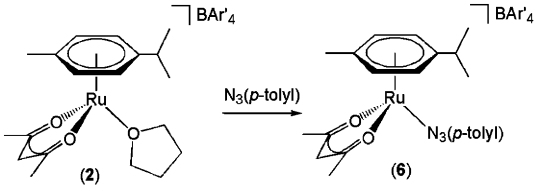
given in Table 2. The *p*-cymene ligand is asymmetrically coordinated to Ru with $Ru–C_{arene}$ bond lengths of the C-substituted aromatic positions {2.236(3) Å and 2.236(4) Å} longer than the $Ru–C_{arene}$ bond distances of unsubstituted positions {average $Ru–C_{arene}$ bond distance of unsubstituted positions = 2.181(3) Å}, which likely reflects a steric influence.




(6)

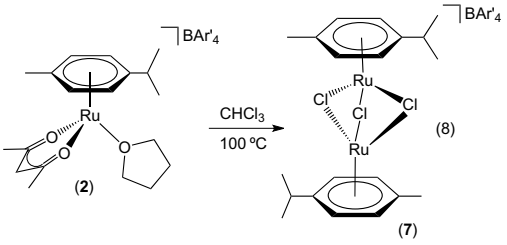
The reaction of complex **2** with $N_3(p\text{-tolyl})$ results in ligand exchange to produce $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-}acac)\{N_3(p\text{-tolyl})\}][BAr'_4]$ (**6**) (Eq. (7)). Evidence for the formation of **6** includes resonances in the $^1H$ NMR spectrum

in the aromatic region due to the *p*-tolyl group (7.24 and 6.29 ppm) as well as a singlet at 2.18 ppm assigned to the methyl of the *p*-tolyl fragment. Heating complex **6** does not result in clean transformation to a Ru imido complex but rather decomposition to multiple intractable systems.




(7)

Heating (100 °C) complex **2** in $CHCl_3$ or $CH_2Cl_2$ forms the binuclear complex $\{[(\eta^6\text{-}p\text{-cymene})_2Ru]_2(\mu\text{-}Cl)_3\}[BAr'_4]$ (**7**) (Eq. (8)). Qualitatively, the rate of the formation of **7** is faster in $CHCl_3$ than $CH_2Cl_2$. An X-ray diffraction study of a single crystal of complex **7** has confirmed its identity (Fig. 3). Bond distances and angles are presented in Table 4 with selected crystallographic data given in Table 2. The average bond distance from Ru to arene carbon is 2.167(2) Å, which is the closest $Ru–C_{arene}$ contact among the complexes **1**, **5** and **7**. The short $Ru–C_{arene}$ bond distances of **7** are likely due to the less sterically crowded coordination sphere versus complexes **1** and **5**. In addition, the $Ru–C_{arene}$ bond distance of the C-substituted positions {2.178(2) Å and 2.181(2) Å} are longer than the average distance of $Ru–C_{arene}$ of the unsubstituted positions {2.160(2) Å}.




(8)

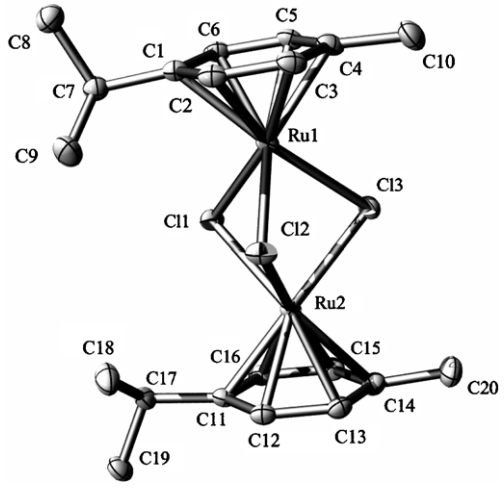


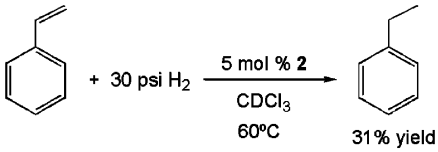

Fig. 3. ORTEP (50% probability) of $[\{(\eta^6\text{-}p\text{-cymene})_2Ru\}_2(\mu\text{-}Cl)_3][BAr'_4]$ (**7**) (the $BAr'_4$ counterion is not depicted).

Table 4
Selected bond distances (Å) and angles (°) for $[\{(\eta^6\text{-}p\text{-cymene})_2Ru\}_2(\mu\text{-}Cl)_3][BAr'_4]$ (**7**)

| | | | |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| Ru(1)–C(1) | 2.178(2) | Ru(2)–C(11) | 2.172(2) |
| Ru(1)–C(2) | 2.153(2) | Ru(2)–C(12) | 2.152(2) |
| Ru(1)–C(3) | 2.160(2) | Ru(2)–C(13) | 2.162(2) |
| Ru(1)–C(4) | 2.181(2) | Ru(2)–C(14) | 2.186(2) |
| Ru(1)–C(5) | 2.170(2) | Ru(2)–C(15) | 2.169(2) |
| Ru(1)–C(6) | 2.159(2) | Ru(2)–C(16) | 2.151(2) |
| Ru(1)–C(l1) | 2.4320(4) | Ru(1)–C(l1) | 2.4380(4) |
| Ru(1)–C(l2) | 2.4185(4) | Ru(1)–C(l2) | 2.4217(4) |
| Ru(1)–C(l3) | 2.4502(4) | Ru(1)–C(l3) | 2.4497(4) |
| *Bond angles (°)* | | | |
| C(1)–Ru(1)–Cl(1) | 96.94(4) | C(9)–C(7)–C(8) | 111.0(2) |
| C(1)–Ru(1)–Cl(2) | 112.64(4) | C(1)–C(7)–C(9) | 113.6(2) |
| C(1)–Ru(1)–Cl(3) | 166.70(4) | C(1)–C(7)–C(8) | 108.9(1) |
| C(4)–Ru(1)–Cl(3) | 93.71(5) | C(3)–C(4)–C(10) | 120.9(2) |
| C(4)–Ru(1)–Cl(2) | 126.60(5) | C(11)–Ru(2)–Cl(1) | 96.98(4) |
| C(4)–Ru(1)–Cl(1) | 150.20(5) | C(12)–Ru(2)–Cl(1) | 127.15(5) |
| C(7)–C(1)–Ru(1) | 128.5(1) | C(13)–Ru(2)–Cl(1) | 165.56(5) |
| C(10)–C(4)–Ru(1) | 128.1(1) | C(14)–Ru(2)–Cl(1) | 149.30(5) |
| Ru(1)–Cl(1)–Ru(2) | 84.12(1) | C(15)–Ru(2)–Cl(2) | 165.98(5) |
| Ru(1)–Cl(2)–Ru(2) | 84.76(1) | C(16)–Ru(2)–Cl(1) | 91.70(5) |
| Ru(2)–Cl(3)–Ru(1) | 83.49(1) | Cl(2)–Ru(2)–Cl(3) | 79.60(1) |

### 3.1. Catalysis

Since the THF ligand of $[(\eta^6\text{-}p\text{-cymene})Ru(\kappa^2\text{-}O,O\text{-acac})(THF)][BAr'_4]$ (**2**) is labile, we suspected that complex **2** might serve as a catalyst precursor. In order to test the ability of **2** to coordinate and activate substrates, we chose two reactions with substantial precedent: olefin aziridination and olefin hydrogenation. For the former, complex **2** shows no activity. For example, a $CDCl_3$ solution of PhINTs, styrene and 5 mol% of **2** results in no production of aziridine reaction after 48 h at room temperature. At this time, complex **2** is observed to decompose to multiple uncharacterized complexes. In contrast, a solution of styrene and 5 mol% **2** in $CDCl_3$ under 30 psi of dihydrogen results in the formation of ethylbenzene (Eq. (9)). Monitoring the reaction at 60 °C reveals 31% yield of ethylbenzene after 36 h. $^1H$ NMR spectroscopy reveals decomposition of **2** into multiple products, and prolonged reaction times do not result in additional production of ethylbenzene.




(9)

### 3.2. Cyclic voltammetry

The combination of the "soft" donor $\eta^6$-arene and "hard" oxygen-donor acac ligand sets up an interesting electronic mix. In order to probe the electron density of the new Ru systems, we performed cyclic voltammetry. Table 5 displays a list of complexes and observed potentials.

Table 5
The redox potentials for the various Ru(II) complexes

| Complex | Ru(II/I)[a,b] (V) |
|---|---|
| [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac){$N_3$(*p*-tolyl)}][$BAr'_4$] (**6**) | −0.50 |
| [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)(THF)][$BAr'_4$] (**2**) | −0.78 |
| {[($\eta^6$-*p*-cymene)$_2$Ru]$_2$($\mu$-Cl)$_3$}[$BAr'_4$] (**7**) | −0.92 |
| [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)OTf (**1-OTf**) | −1.13 |
| [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)(NCMe)][$BAr'_4$] (**3**) | −1.24 |
| [TpRu($\eta^6$-*p*-cymene)][$BAr'_4$] (**5**) | −1.45 |
| [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)($PMe_3$)][$BAr'_4$] (**4**) | −1.63 |

[a] Reported vs. NHE.
[b] All potentials are irreversible ($E_{p,a}$) except for complex **2**, which is reversible ($E_{1/2}$).

For all complexes, scans to positive potentials (2.0 V versus NHE) revealed no redox activity. Thus, the combination of the $\eta^6$-arene and acac or Tp ligands and overall cationic charge results in electron-deficient Ru(II) systems, which suggests that such complexes might be strongly Lewis acidic. In contrast, scans at negative potentials (versus NHE) result in reduction of the Ru complexes, which is consistent with Ru(II) to Ru(I) transformations. With the exception of complex **2**, the reductions are irreversible. The order of the absolute value of the reduction potentials for complexes of the general formula [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac)(L)][$BAr'_4$], $\mathbf{6} < \mathbf{2} < \mathbf{1} < \mathbf{3} < \mathbf{4}$, suggests that the relative donating ability of the ligands (from most donating to least donating) is: $PMe_3$ > NCMe > $\mu$-CH/OTf > THF > $N_3$(*p*-tolyl). The more negative reduction potential of complex **1** relative to **2** is consistent with the lack of coordination of THF upon dissolution of **1** in THF. The Ru(II/I) reduction potentials suggest that the $\mu$-$Cl_3$ moiety is more strongly donating than the combination of the $\kappa^2$-acac ligand and THF, but more weakly donating than the $\kappa^2$-acac ligand in combination with NCMe or $PMe_3$.

## 4. Conclusions

We have synthesized a series of complexes possessing the $\eta^6$-*p*-cymene and $\kappa^2$-acac ligands including structural characterization of three of these systems. The complexes [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*,*O*-acac-$\mu$-CH)]$_2$[OTf]$_2$ (**1**) and [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*, *O*-acac)(THF)][$BAr'_4$] (**2**) allow access to the cationic fragment [($\eta^6$-*p*-cymene)Ru($\kappa^2$-*O*, *O*-acac)]$^+$. Electrochemistry experiments suggest that the $\eta^6$-*p*-cymene/$\kappa^2$-*O*,*O*-acac fragment is overall poorly donating, which results in relatively electron-deficient complexes that might possess substantial Lewis acidity.

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## Appendix A. Supplementary material

Details of single crystal X-ray diffraction studies are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.10.012.

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