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Synthetic, structural, and spectroscopic studies of mixed sandwich Ru(II) complexes involving $\eta^6$-$p$-cymene with monodentate fluorine-containing phosphines or phosphites

John P. Lee, Michael J. Hankins, Ashley D. Riner and Titus V. Albu

Department of Chemistry, The University of Tennessee at Chattanooga, Chattanooga, TN, USA

ABSTRACT
Syntheses, structures, spectroscopy, and calculated structures for several Ru(II) complexes involving $p$-cymene and either fluorine-containing phosphines or phosphites are reported. The complexes are readily prepared by ligand substitution reactions from $[[\text{Ru}(p$-cymene)$\text{Cl}_2]_2$ to produce $[\text{Ru}(p$-cymene)$(L)$Cl$_2$] $[L = \text{P}(C_6H_4-p-F)_3$ (1), $\text{P}(C_6H_4-p$-CF$_3)_3$ (2), $\text{P}(C_6H_4(m$-CF$_3)_2)_3$ (3), $\text{PPh}_3$ (4), $\text{P}($OCH$_2$CF$_3)_3$ (5), $\text{P}($OCH(CF$_3)_2)_3$ (6), and $\text{POMe}_3$ (7)]. The structures for all seven complexes are supported by UV–vis and multi-nuclear NMR spectroscopy. Five complexes are characterized by single-crystal X-ray crystallography (1, 3, 5–7) and exhibit a distorted octahedral structure involving three donors from one phosphine or phosphite ligand, two chlorides, and the facially coordinating $\eta^6$-$p$-cymene ligand. Electronic structure theory computations have been performed on 1–7 along with the theoretical $[\text{Ru}(p$-cymene)$(\text{P}(C_6F_5)_3)\text{Cl}_2]$ (8). For all complexes, the HOMO is primarily Ru ($d_{xy}$ or $d_{x^2-y^2}$) in character. The LUMO shifts from primarily Ru ($d_{xz}$ or $d_{yz}$) to primarily phosphine ligand $\pi^*$ as the number of fluorines increases.

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$p$-Cymene; Ru complexes; fluorine; phosphine ligands; phosphite ligands; crystal structures

1. Introduction
The $\eta^6$-$p$-cymene ligand provides an important platform for the preparation of new organometallic Ru(II) complexes that in general are piano-stool pseudo-octahedral complexes [1–3]. The $p$-cymene stabilizes the complex preventing oxidation to Ru(III), is relatively inert to ligand substitution...
reactions, and can be functionalized to tune the properties of the arene-Ru complex [1]. Piano-stool complexes of the type [Ru(p-cymene)(L)Cl₂] are readily prepared by cleaving the bridging chlorides in ([Ru(p-cymene)Cl₂])₂ in the presence of a two-electron donor (L). Straightforward preparation has resulted in the preparation of a large number of complexes of the type [Ru(p-cymene)(L)Cl₂], where L = C- (e.g., N-heterocyclic carbene), N-, O-, or P-donor ligands, which show diverse reactivity [4–7]. However, in nearly all cases, complexes of the type [Ru(p-cymene)(L)Cl₂] lack fluorine on the donor ligand L, and systematic studies of the impact of fluorine or trifluoromethyl on Ru(II) are unknown [6, 8, 9]. The p-cymene-Ru(II) fragment serves as a stable electron-rich platform to explore the structural properties of fluorine-containing phosphine and phosphite ligands. It is well known that altering the steric and electronic properties of phosphines and phosphites can dramatically change the reactivity of organometallic compounds in both stoichiometric and catalytic reactions [10]. By combining the addition of fluorine or trifluoromethyl groups to trivalent phosphorus donor ligands, unique electronic properties imparted by the electron-withdrawing fluorine or trifluoromethyl group could result for the complex. These data, for example, could then be used in the rational design of a homogeneous catalyst for a particular reaction using a selected fluorine-containing phosphine or phosphite. The selected ligand would exhibit the desired electronic and steric properties, and the phosphorus donor would be deactivated toward ortho-metallation (phosphine) or cyclo-metallation (phosphite) all due to the electron-withdrawing fluorine substituents. Indeed, these fluorinated phosphine and phosphite ligands have been used in a variety of catalytic C–H functionalization reactions [11–13].

We report here the synthesis and full characterization, including electronic structure theory calculations, of a series of p-cymene supported Ru(II) complexes of the type [Ru(p-cymene)(L)Cl₂], where L includes {tris(4-fluorophenyl)phosphine (1), tris(4-trifluoromethylphenyl)phosphine (2), tris[3,5-bis(trifluoromethyl)phenyl]phosphine (3), triphenylphosphine (4), tris(2,2,2-trifluoroethyl)phosphite (5), tris[3,5-bis(trifluoromethyl)phenyl]phosphine (3), triphenylphosphine (4), tris(2,2,2-trifluoroethylphosphite (5), tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite (6), and trimethylphosphite (7)}. Compounds 3, 5, and 6 are new compounds, and full characterization including their X-ray crystal structures is presented. Complex 6 represents the first structurally characterized Ru compound involving tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite, and both 3 and 5 represent the first structurally characterized Ru(II) complexes with tris[3,5-bis(trifluoromethyl)phenyl]phosphine and tris(2,2,2-trifluoroethylphosphite, respectively [14]. Four compounds in the report (1, 2, 4, and 7) have been previously prepared, but not fully characterized [3, 6, 15, 16], and full spectroscopic analysis for all four as well as single-crystal X-ray structures for 1 and 7 are described. Compounds 4 and 7 do not contain fluorine, but were prepared to study the impact of the fluorine or trifluoromethyl group(s) in the respective phosphine and phosphite set of ligands. The structure of hypothetical [Ru(p-cymene){P(C₆F₅)₃}Cl₂] (8) was also calculated to examine the reasons for inability of its preparation.

2. Experimental

2.1. Materials

All reactions and procedures were performed under anaerobic conditions in a nitrogen-filled glove box or using standard Schlenk techniques. Glovebox purity was maintained over a catalyst bed and monitored by an oxygen analyzer (O₂(g) < 2 ppm for all reactions). Dichloromethane was purified by distillation from CaH₂. Hexanes were purified by distillation from sodium. Tetrahydrofuran was purified by distillation from sodium/benzophenone. C₆D₆ and CDCl₃ were degassed via three freeze–pump–thaw cycles and stored over 4 Å sieves. Synthetic and characterization details of [Ru(p-cymene){P(C₆H₄F)₃}Cl₂] (1) [6, 16], [Ru(p-cymene){P(C₆H₄CF₃)₃}Cl₂] (2) [16], [Ru(p-cymene)(PPh₃)Cl₂] (4) [3], and [Ru(p-cymene)(POMe₃)Cl₂] (7) [16] have been previously reported. All other reagents were used as purchased from commercial sources.
2.2. Measurements

$^1$H and $^{13}$C NMR spectra were obtained on a JEOL ECX 400 MHz spectrometer (operating frequency for $^{13}$C NMR was 100 MHz) and referenced against tetramethylsilane using residual proton signals ($^1$H NMR) or the $^{13}$C resonances of the deuterated solvent ($^{13}$C NMR). Resonances due to the p-cymene ligand are listed by chemical shift and multiplicity only (all coupling constants for the p-cymene ligand are 6 and 7 Hz for the aromatic and isopropyl-methyl/isopropyl-methine, respectively). $^{31}$P NMR spectra were obtained on a JEOL ECX 400 MHz (operating frequency = 376 MHz) spectrometer and referenced against external C$_6$H$_5$F (−113 ppm). UV–vis spectra were obtained on a Varian Cary UV–vis spectrophotometer in methylene chloride using 1 cm quartz cuvettes. Elemental analyses were performed by Atlantic Microlabs, Inc.

2.3. Syntheses of [Ru(p-cymene)(L)Cl$_2$] complexes

2.3.1. [Ru(p-cymene){P(C$_6$H$_4$F)$_3$}(Cl)$_2$] (1)

A 50-mL round-bottom flask was charged with [[Ru(p-cymene)Cl$_2$]]$_2$ (0.2029 g, 0.331 mmol) and CH$_2$Cl$_2$ (20 mL). To the orange solution was added P(C$_6$H$_4$(CF$_3$)$_3$) (0.2199 g, 0.695 mmol), and the mixture was left to stir for 3 h at room temperature. The volatiles were removed in vacuo to leave a dark red oil, and hexanes were added to precipitate a solid product. The resulting orange solid was collected by vacuum filtration and dried in vacuo (0.3529 g, 86% yield). $^1$H NMR (CDCl$_3$, $\delta$): 7.80–7.74 (6H, m, phosphine-ortho/meta), 91.0 (2C, m, phosphine-ortho/meta), 111.4 (1C, s, C$_p$-p-cymene CH), 90.6–90.4 (2C, m, phosphine-ortho/meta), 2.86 (1H, sept, $–$C$_p$CH(CH$_3$)$_2$), 1.83 (3H, s, C$_p$-p-cymene), 1.12 (6H, d, $–$CH(CH$_3$)$_2$). 13C{1H} NMR (CDCl$_3$, $\delta$): 30.6 (1C, s, C$_p$-p-cymene), 115.7–115.4 (6C, m, phosphine-C$_{ortho/meta}$), 111.4 (1C, s, C$_p$-p-cymene CH), 96.7 (1C, s, C$_p$-p-cymene CH), 88.8 (2C, d, C$_p$-p-cymene aromatic C, $^2$J$_{CP}$ = 2.9 Hz), 87.6 (2C, d, C$_p$-p-cymene aromatic C, $^2$J$_{PC}$ = 4.7 Hz), 30.7 (1C, s, CH$_3$/–CH(CH$_3$)$_2$), 22.0 (2C, s, $–$CH(CH$_3$)$_2$), 17.7 (1C, s, CH$_3$/–CH(CH$_3$)$_2$). $^{31}$P NMR (CDCl$_3$, $\delta$): 23.4 (s). $^{19}$F NMR (CDCl$_3$, $\delta$): −109.1 (s). UV–vis (CH$_2$Cl$_2$, nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$)): 377 (1.13 $\times$ 10$^3$).

2.3.2. [Ru(p-cymene){P(C$_6$H$_4$(CF)$_3$)}$_3$](Cl)$_2$ (2)

The procedure used was similar to that for 1 (with the exception that the stirring process was only for 2 h) using [[Ru(p-cymene)Cl$_2$]]$_2$ (0.102 g, 0.167 mmol), THF (20 mL), and P(C$_6$H$_4$(CF)$_3$)$_3$ (0.199 g, 0.399 mmol). Complex 2 was isolated as an orange-red solid in 72% yield (0.158 g). $^1$H NMR (CDCl$_3$, $\delta$): 7.97–7.93 (6H, m, phosphine-ortho/meta), 7.65–7.63 (6H, m, phosphine-ortho/meta), 5.21 (2H, d, p-cymene CH), 5.03 (2H, d, p-cymene CH), 2.79 (1H, sept, $–$CH(CH$_3$)$_2$), 1.83 (3H, s, C$_p$-p-cymene), 1.06 (6H, d, $–$CH(CH$_3$)$_2$). 13C{1H} NMR (CDCl$_3$, $\delta$): 135.5 (3C, d, phosphine-C$_{ipso}$, $^1$J$_{CF}$ = 10.5 Hz), 132.8 (3C, q, phosphine-C$_{para}$, $^2$J$_{CP}$ = 32.6 Hz), 125.4–125.3 (6C, m, phosphine-C$_{ortho/meta}$), 124.7 (3C, q, $–$CF$_3$, $^1$J$_{CF}$ = 273.2 Hz), 111.0 (1C, s, C$_p$-p-cymene CH), 95.7 (1C, s, C$_p$-p-cymene CH), 19.1 (2C, d, C$_p$-p-cymene aromatic C, $^2$J$_{PC}$ = 3.8 Hz), 86.9 (2C, d, C$_p$-p-cymene aromatic C, $^2$J$_{PC}$ = 6.7 Hz), 30.6 (1C, s, CH$_3$/–CH(CH$_3$)$_2$), 21.7 (2C, s, $–$CH(CH$_3$)$_2$), 17.6 (1C, s, CH$_3$/–CH(CH$_3$)$_2$). $^{31}$P NMR (CDCl$_3$, $\delta$): 25.3 (s). $^{19}$F NMR (CDCl$_3$, $\delta$): −63.1 (s). Anal. Calcd for C$_{119}$H$_{138}$F$_{27}$Cl$_2$PRu: C, 48.19; H, 3.37. Found: C, 48.22; H, 3.37. UV–vis (CH$_2$Cl$_2$, nm (($\varepsilon$/M$^{-1}$ cm$^{-1}$)): 382 (1.11 $\times$ 10$^3$).

2.3.3. [Ru(p-cymene){P(C$_6$H$_4$(CF)$_3$)}$_2$](Cl)$_2$ (3)

The procedure used was similar to that for 1 using [[Ru(p-cymene)Cl$_2$]]$_2$ (0.075 g, 0.122 mmol), THF (20 mL), and P(C$_6$H$_4$(CF)$_3$)$_3$ (0.213 g, 0.293 mmol). Complex 3 was isolated as an orange-red solid in 82% yield (0.196 g). $^1$H NMR (CDCl$_3$, $\delta$): 8.30–8.27 (6H, overlapping singlets, phosphine-ortho/meta), 8.02 (3H, s, phosphine-ortho/meta), 5.24–5.19 (4H, overlapping d’s, p-cymene CH), 2.53 (1H, sept, $–$CH(CH$_3$)$_2$), 1.89 (3H, s, C$_p$-p-cymene), 0.99 (6H, d, $–$CH(CH$_3$)$_2$). $^{13}$C{1H} NMR (CDCl$_3$, $\delta$): 135.4 (3C, d, phosphine-C$_{ipso}$, $^1$J$_{CF}$ = 44.1 Hz), 134.2 (6C, s, phosphine-C$_{ortho}$), 132.6 (6C, q, phosphine-C$_{meta}$, $^3$J$_{CF}$ = 9.6 Hz, $^2$J$_{CF}$ = 34.2 Hz), 125.6 (3C, s, phosphine-C$_{para}$), 122.8 (6C, q, $–$CF$_3$, $^1$J$_{CF}$ = 273.5 Hz), 112.5 (1C, s, C$_p$-p-cymene CH), 98.4 (1C, s, C$_p$-p-cymene CH), 90.6–90.4 (2C, m, C$_p$-p-cymene aromatic CH), 87.5–87.3 (2C, m, C$_p$-p-cymene aromatic CH), 30.6 (1C, s,
CH3/–CH(CH3)2, 21.8 (2C, s, –CH(CH3)2)). 17.7 (1C, s, CH3/–CH(CH3)2). 31P NMR (CDCl3, δ): 26.9 (s). 19F NMR (CDCl3, δ): −63.0 (s). Anal. Calcd for C34H28F18Cl2P2Ru: C, 41.82; H, 2.62. UV–vis (CH2Cl2, nm (ε/ M−1 cm−1)): 388 (1.04 × 103).

2.3.4. [Ru(p-cymene)](P[C6H4CH2]3)2(Cl)2 (4)
The procedure used was similar to that for 1 using [Ru(p-cymene)](Cl)2 (0.100 g, 0.163 mmol), THF (20 mL), and P(C6H5)3 (0.094 g, 0.358 mmol). Complex 4 was isolated as an orange solid in 76% yield (0.141 g). 1H NMR (CDCl3, δ): 7.81 (6H, td, phosphine-Η), 7.39–7.31 (9H, m, phosphine-Η), 5.17 (2H, d, p-cymene CH), 4.96 (2H, d, p-cymene CH), 2.83 (1H, sept, –CH(CH3)2), 1.85 (3H, s, CH3), 1.08 (6H, d, –CH(CH3)2). 31P NMR (CDCl3, δ): 24.7 (s). UV–vis (CH2Cl2, nm (ε/ M−1 cm−1)): 370 (2.17 × 103).

2.3.5. [Ru(p-cymene)](P[O(CH2CF3)3]2(Cl)2 (5)
A 50-mL round-bottom flask was charged with [Ru(p-cymene)](Cl)2 (0.200 g, 0.327 mmol) and THF (20 mL). To the orange solution was added P(OCH2CF3)3 (0.173 mL, 0.784 mmol), and the mixture was left to stir at room temperature for approximately 2 h. The volatiles were removed in vacuo to leave a dark red oil, and hexanes were used to precipitate a solid product. The red solid was collected by vacuum filtration and dried in vacuo (0.318 g, 77% yield). 1H NMR (CDCl3, δ): 2.35–2.28 (6H, m, –CH(CH3)2), 1.23 (6H, d). 13C{1H} NMR (CDCl3, δ): 35.5 (3C, q, 19F NMR (CDCl3, δ): −63.0 (s). Anal. Calcd for C34H23F18Cl2PRu: C, 41.82; H, 2.37. Found: C, 41.87; H, 2.62. UV–vis (CH2Cl2, nm (ε/ M−1 cm−1)): 348 (962), 482 (312).

2.3.6. [Ru(p-cymene)](P[O(CH2CF3)3]2(Cl)2 (6)
The procedure used was similar to that for 5 using [Ru(p-cymene)](Cl)2 (0.106 g, 0.173 mmol), THF (20 mL) and P(OCH2CF3)3 (1.6 mL, 0.521 mmol). Complex 6 was isolated in 51% yield (0.058 g). 1H NMR (CDCl3, δ): 5.79–5.76 (3H, m, overlap with p-cymene aromatic H, –CH(CH3)2), 5.74 (2H, d, p-cymene CH), 5.54 (2H, d, p-cymene aromatic C, 2JPC = 6.7 Hz), 89.9 (2C, d, p-cymene aromatic C, 2JPC = 7.6 Hz), 64.2 (3C, qd, –CH2CF3, 2JCP = 37.1 Hz and 1JCP = 5.5 Hz), 30.7 (s, –CH3/–CH(CH3)2), 21.8 (s, –CH(CH3)2), 18.2 (s, –CH3/–CH(CH3)2). 31P NMR (CDCl3, δ): 119.0 (s). 19F NMR (CDCl3, δ): −72.8. Anal. Calcd for C19H17Cl3F18O3PRu: C, 27.22; H, 2.03; Found: C, 27.21; H, 2.04. UV–vis (CH2Cl2, nm (ε/ M−1 cm−1)): 348 (962), 482 (312).

2.3.7. [Ru(p-cymene)](P[OME]3)2(Cl)2 (7)
The procedure used was similar to that for 5 using [Ru(p-cymene)](Cl)2 (0.148 g, 0.242 mmol), THF (20 mL), and trimethylphosphite (0.060 mL, 0.480 mmol). Complex 7 was isolated in 90% yield (0.187 g). 1H NMR (CDCl3, δ): 5.53 (2H, d, p-cymene CH), 5.38 (2H, d, p-cymene CH), 3.8 (9H, d, –CH3), 2.91 (1H, sept, –CH(CH3)2), 2.16 (3H, s, –CH3), 1.23 (6H, s, –CH(CH3)2). 13C{1H} NMR (CDCl3, δ): 110.0 (1C, s, p-cymene CH), 101.2 (1C, s, p-cymene CH), 89.2 (2C, d, p-cymene aromatic C, 2JPC = 5.75 Hz), 88.9 (2C, d, p-cymene aromatic C, 2JPC = 5.75 Hz), 54.4 (3C, d, 2JCP = 5.7 Hz, –P(OCH3)3), 30.5 (s, –CH3/–CH(CH3)2), 22.1 (s, –CH(CH3)2), 18.4 (s, –CH3/–CH(CH3)2). UV–vis (CH2Cl2, nm (ε/ M−1 cm−1)): 342 (1371), 477 (367).

2.4. X-ray crystallography data collection and processing

Table 1 contains crystal data, collection parameters, and refinement criteria for the crystal structures of 1, 3, 5, 6, and 7. Crystals were mounted on the tip of a Bruker SPINE-pin mount, and X-ray intensity data were measured at low temperature using an Oxford Cryosystems Desktop Cooler (200(2) K) for all structures with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART X2S.
Benchtop diffractometer [17]. Each structure was solved (XS) and refined (XL) using Olex2 [18, 19]. A direct-methods solution was calculated that provided the non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens in each structure were placed in ideal positions and refined as riding. All crystals were grown by layering a methylene chloride solution of the complex with hexane under an inert N2 atmosphere. Five of the six trifluoromethyl groups in 3 showed positional disorder. Each fluorine in the group was either modeled over three positions (33%/33%/33%) for F2, F6, F11, F12, and F15 or two positions (50%/50%) for F4, F10, F12, and F14, and refined isotropically separate from the remaining molecule. This refinement resulted in a single Alert Level B due to non-H atoms refined isotropically. The trifluoromethyl group of C14 in 5 showed positional disorder. Each fluorine in the group was modeled over three positions (33%/33%/33%) and refined isotropically separate from the remaining molecule. For 6, the solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of non-coordinated solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume/cell = 285.1 Å3 [4.8%], total electron count/cell = 10.3. Complex 7 shows two molecules in the asymmetric unit cell, data for both are shown in Table 2, and both molecules are presented in Figure S1 in the supporting information. One atom in 7, F4, was found to be prolate; however, this was not modeled as it was only in one of the two molecules in the asymmetric unit cell.

### 2.5. Details of electronic structure theory calculations

Electronic structure theory calculations were carried out for complexes presented in this study. For complexes where crystal structures were available (i.e., 1, 3–7), the crystal structures were used without modifications. Complexes 2 and 8 were constructed from 1 as described further. In 2, the fluorine attached to the benzene ring in 1 was replaced with a –CF3 group constructed to be similar to the –CF3...
groups in 3, specifically C\textsubscript{sp2}−C\textsubscript{sp3} bond distances of 1.4920 Å, C–F bond distances of 1.3100 Å, and C\textsubscript{sp2}−C\textsubscript{sp3}–F angles of 112.6°. Similarly, in hypothetical [Ru(p-cymene)\{P(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}\}Cl\textsubscript{2}], 8, the hydrogens attached to the benzene ring in 1 (four hydrogens for each benzene ring) were replaced with F with C\textsubscript{sp2}−F bond distances of 1.3667 Å, the average C\textsubscript{sp2}−F bond distance in 1. For comparison, 2 and 8 were also constructed based on complex 4 geometry by replacing hydrogens with either F or –CF\textsubscript{3} groups, and the results (not reported here) obtained for these geometries were essentially the same as the results presented here. The Cartesian coordinates for all complexes are given in the Supplementary data.

The electronic structure theory results reported here were obtained using the Hartree–Fock (HF, \textit{ab initio}) method [20] and the hybrid density functional theory (DFT) mPW1PW91 method [21] in conjunction with the 6-311+G(d,p) basis set for all atoms except Ru, for which the LANL2DZ effective-core potential basis set was used [22, 23]. Additional computations were carried out with smaller basis sets (i.e., 6-31 + G(d,p) and 6-31G(d,p) basis sets) suggesting that current results are basis set converged. The SCF procedure was carried out using quadratic convergency methodology. All systems were closed-shell systems, and we employed restricted wave function calculations. All electronic structure calculations were carried out using the Gaussian 03 program [24], and the molecular orbitals were visualized using Avogadro software [25].

3. Results and discussion
3.1. Syntheses and properties

The reaction of ([Ru(p-cymene)Cl\textsubscript{2}])\textsubscript{2} with two equivalents of phosphine or phosphite produces [Ru(p-cymene)(L)Cl\textsubscript{2}] as shown in Scheme 1. We report a more complete analysis of the four previously reported complexes (1, 2, 4, and 7) [3, 6, 15, 16] including their \textsuperscript{13}C NMR and UV–vis spectra as well as the single-crystal X-ray structures of 1 and 7. Complexes 4 (L = PPh\textsubscript{3}) and 7 (L = POMe\textsubscript{3}) do not involve fluorine and were prepared to make comparisons to the fluorine-containing phosphines and phosphites [3, 15, 16]. All complexes were isolated in good yield as analytically pure orange to red solids, and elemental analyses are consistent with the reported complex stoichiometries.

For phosphine complexes 1–4, their color was from orange for [Ru(p-cymene)(PPh\textsubscript{3})Cl\textsubscript{2}] (4) to brick red for [Ru(p-cymene)(P(C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})\textsubscript{3})Cl\textsubscript{2}] (3) as the number of fluorines increased. A less pronounced trend was found for the phosphite complexes, 5–7, where the color changed from light red for [Ru(p-cymene)(POMe\textsubscript{3})Cl\textsubscript{2}] (7) to dark brick red for [Ru(p-cymene)(POCH(CF\textsubscript{3})\textsubscript{3})Cl\textsubscript{2}] (6).

All complexes are air-stable in the solid-state. However, in solution, the complexes decompose to uncharacterized black products upon exposure to air. In particular, [Ru(p-cymene)(P(C\textsubscript{6}H\textsubscript{4}CF\textsubscript{3})\textsubscript{3})Cl\textsubscript{2}] (2), which was first isolated by Nolan \textit{et al}., decomposes readily in CDCl\textsubscript{3} solution. Indeed, Nolan reported this complex to be the least thermodynamically stable in a series of p-cymene-Ru(II) complexes that were prepared [16]. Neither the fluorine-containing phosphines (1–3) nor phosphites (5 and 6) showed

\[
\text{L} = \begin{array}{c}
\text{Phosphine} \\
\begin{array}{c}
\text{P} \\
\text{F} \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\end{array}
\end{array} \\
\begin{array}{c}
\text{Phosphite} \\
\begin{array}{c}
\text{P} \\
\text{O} \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CH}_3 \\
\end{array}
\end{array}
\]

\[
\begin{align*}
&\text{L} = \begin{array}{c}
\text{Phosphine} \\
\text{Phosphite}
\end{array} \\
&\begin{array}{c}
\begin{array}{c}
\text{P} \\
\text{F} \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\end{array} \\
\begin{array}{c}
\text{P} \\
\text{O} \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CF}_3 \\
\text{CH}_3 \\
\end{array}
\end{array} \\
\begin{array}{c}
(1) \\
(5)
\end{array} & \begin{array}{c}
(2) \\
(6)
\end{array} & \begin{array}{c}
(3) \\
(7)
\end{array} & \begin{array}{c}
(4) \\
(8)
\end{array}
\]

\begin{center}
\textbf{Scheme 1.} Preparation of [Ru(p-cymene)(L)Cl\textsubscript{2}] complexes.
\end{center}
significant water solubility even up to 100 °C, which is in contrast to the square planar Rh(I)- and Ir(I)fluorinated phosphine complexes that mediate biphasic hydrogenation of alkenes as reported by Gladysz et al. [26].

One ligand that is missing in the aromatic phosphine series (1–4) is tris(pentafluorophenyl)phosphine. The reaction of [(Ru(p-cymene)Cl2)]2 with tris(pentafluorophenyl)phosphine was attempted in either tetrahydrofuran or dichloromethane at room temperature or at reflux. All attempts resulted in no reaction, and the recovery of [(Ru(p-cymene)Cl2)]2 as observed by 1H NMR spectroscopy. A search for tris(pentafluorophenyl)phosphine in the Cambridge Structural Database (CSD) reveals only 26 hits involving d-block or lanthanide metal compounds [14]. Of those 26, only two ruthenium complexes involving at least one tris(pentafluorophenyl)phosphine ligand have been structurally characterized by single-crystal X-ray crystallography. Furthermore, both structurally characterized Ru complexes involve polymetallic Ru(I) [27, 28]. The lack of reactivity with the [(Ru(p-cymene)Cl2)]2 fragment is likely due to the significantly reduced basicity of the tris(pentafluorophenyl)phosphine, which requires a more electron-rich metal where the metal–ligand bonding is dominated by metal-to-ligand π-interactions. The theoretical structure of [Ru(p-cymene){P(C6F5)3}Cl2] (8) was calculated to explore the lack of reactivity between [(Ru(p-cymene)Cl2)]2 and tris(pentafluorophenyl)phosphine (see below).

3.2. Structural studies

The structures of 1, 3, 5, 6, and 7 were determined by single-crystal X-ray diffraction. We were unable to obtain a single crystal of 2 due to the instability of the complex in solution over time even under an inert nitrogen atmosphere, and the structure of 4 has been previously reported [15]. For 1 and 7 whose crystal structures were determined herein, only 1H NMR and combustion analysis of these two complexes had been previously reported [3, 16]. Selected bond distances and angles are given in Table 2, and structural perspectives are shown in Figures 1–5. All five structures feature facial coordination of the carbocyclic η6-p-cymene to give pseudo-octahedral geometry where the methyl/iso-propyl groups of the p-cymene show a staggered conformation with respect to the phosphine (or phosphite) ligand. The other face of the octahedron includes the two chlorides and one phosphine or phosphite to give a piano-stool complex with typical Ru–P and Ru–Cl bond lengths and angles.

A search of the CSD for structurally characterized Ru(II) complexes of either tris[3,5-bis(trifluoromethyl)phenyl]phosphine, tris(2,2,2-trifluoroethyl)phosphite, or tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite resulted in no examples [14]. However, tris(2,2,2-trifluoroethyl)phosphite has been coordinated to a Ru(0) complex and its X-ray structure determined [30], and other examples with d-block metals with this particular ligand include Ag(I) [31], Cu(I) [32], and Fe(II) [13]. In contrast, the bulkier phosphite, tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite, has been less widely structurally studied with only a single Rh(I) complex solved by single-crystal X-ray crystallography [11]. Finally, the CSD shows several examples of the tris[3,5-bis(trifluoromethyl)phenyl]phosphine ligand with a variety of d-block metals

| Table 2. Selected bond distances (Å) and angles (°) with esds in parentheses for 1, 3, 5, 6, 7, and related complexes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Ru–P            | Ru–C (average)  | C2–C3  | Cl1–Ru–Cl2 | Cl1–Ru–P | Cl2–Ru–P1 |
| 1               | 2.3483(16)      | 2.227(6)        | 1.399(9) | 89.54(5)   | 86.94(5) | 89.62(5) |
| 3               | 2.3344(9)       | 2.217(4)        | 1.389(6) | 90.74(3)   | 87.78(3) | 95.17(3) |
| 5               | 2.2553(9)       | 2.239(3)        | 1.395(5) | 88.88(3)   | 89.36(3) | 85.97(3) |
| 6b              | 2.2668(10)      | 2.240(4)        | 1.391(6) | 86.90(3)   | 83.57(3) | 95.46(3) |
|                 | [2.2584(9)]     | [2.253(3)]      | [1.385(5)] | [86.90(3)] | [83.57(3)] | [95.46(3)] |
| 7               | 2.2872(5)       | 2.2431(18)      | 1.394(3) | 87.81(19)  | 90.17(17) | 86.08(17) |
| [Ru(p-cymene)]{P(Ph)3}Cl2b,c | 2.3436(8)       | 2.218(2)        | 1.387(3) | 88.41(2)   | 87.09(2) | 90.27(2) |
|                 | [2.3442(6)]     | [2.215(2)]      | [1.389(3)] | [88.91(2)] | [89.78(2)] | [87.518(19)] |
| [Ru(p-cymene)]{P(OPh)3}Cl2d | 2.2624(8)       | 2.215(3)        | 1.374(5) | 87.45(3)   | 87.91(2) | 85.01(3) |

bC–C bond of p-cymene trans to phosphine or phosphite ligand.

cTwo molecules observed in the asymmetric unit.

dRef. [15].

eRef. [29].
**Figure 1.** Thermal ellipsoid perspective (50% probability) of 1. Note: Hydrogens omitted for clarity.

**Figure 2.** Thermal ellipsoid perspective (50% probability) of 3. Notes: Hydrogens and fluorines on C18 and C26 are omitted for clarity. A full figure of 3 showing all fluorines (and their modeled disorder) is available in the supporting information.
that include Pd(0) [33], Pd(II) [12], Rh(I) [34], Au(I) [35], Fe(0) [36], Pt(II) [37], and Ru(0) [38]. All complexes found in the CSD searches, regardless of ligand identity, involve an electron-rich metal, which suggests that the fluorine substituents impact the donor ability of the phosphine or phosphite by reducing the σ-donation (i.e., reduced Lewis basicity).

3.2.1. Structure of [Ru(p-cymene){P(C6H4F)3}Cl2]

The crystal structure of 1 is shown in Figure 1 and exhibits an average Ru–C bond length of 2.227(6) Å, an average C–C (p-cymene) bond length of 1.420(9) Å, and the Ru–P bond length was 2.348(2) Å. These data are in agreement with the related structure [Ru(p-cymene)(PPh3)Cl2] (4) where the Ru–P bond was 2.344(2) Å [15], which indicates the fluorine on each arene has little to no electronic influence on the complex. The C–C (p-cymene) range for 1 is from 1.399(9) to 1.435(9) Å where the shortest C–C bond length is for C2–C3 at 1.399(9) Å. The elongated Ru–C1 and Ru–C2 lengths at 2.259(6) and 2.258(5) Å, respectively, along with the shortened C2–C3 bond length, show an increased trans effect of the phosphine ligand to the p-cymene ligand. The sum of the Cl1–Ru–Cl2, P–Ru–Cl1, and P–Ru–Cl2 bond angles is 266.1(5)°, which is nearly identical to that reported for [Ru(p-cymene)(PPh3)Cl2] (4) (265.77°) [15], and indicates that the three fluorines have little to no steric influence on 1 where the sum of the three angles in a perfect octahedron would be 270°. The lack of steric influence is not surprising as the fluorines are in the para position of the phosphine. However, the close similarities in the Ru–P bond length between 1 and 4 is striking and suggests that the para-fluorine substituent has little to no electronic influence on the phosphine ligand. The absence of significant electronic influence was further confirmed in the similarities of the calculated structures for 1 and 4 (see below) where both show a similar HOMO–LUMO gap and the contributions to the HOMO and LUMO for both complexes are very similar.

Figure 3. Thermal ellipsoid perspective (50% probability) of 5.
Note: Hydrogens omitted for clarity.
3.2.2. Structure of \([\text{Ru}(p\text{-cymene})\text{P(C}_6\text{H}_3(\text{CF}_3)_2)_3\text{Cl}_2]\)

The crystal structure of 3 shown in Figure 2 exhibits an average Ru–C bond length of 2.217(4) Å, an average C–C (p-cymene) bond length of 1.414(6) Å, and the Ru–P bond length of 2.334(9) Å. The C–C (p-cymene) range for 3 is from 1.389(6) to 1.436(5) Å where the shortest C–C bond length is for C2–C3 at 1.389(6) Å, which is trans to the phosphine ligand. The elongated Ru–C1 and Ru–C2 lengths at 2.250(4) and 2.232(4) Å, respectively, along with the shortened C2–C3 bond length, show an increased trans effect of the phosphine ligand upon replacing the \(\text{para}\)-F substituents in 1 with the 3,5-bis(trifluoromethyl) groups of 3 regardless of the Ru–P bond length. The sum of the Cl1–Ru–Cl2, P–Ru–Cl1, and P–Ru–Cl2 bond angles is 263.1(3)° and indicates that replacing the \(\text{para}\)-F substituents in 1 with the 3,5-bis(trifluoromethyl) groups of 3 has some steric influence around the metal center. Observing only a slight change in steric influence may be surprising as the steric bulk has increased upon going from 1 to 3, and this is likely attributable, at least in part, to the more eclipsed conformation of the p-cymene ligand (Figure 2). For crystallographically characterized complexes reported herein and related \([\text{Ru}(p\text{-cymene})(\text{L})\text{Cl}_2]\) (L = P donor [29, 39], S donor [40], N donor [41], or C donor [42]), a staggered conformation of the p-cymene ligand is observed in relation to the \(\text{para}\)-methyl/isopropyl to L. The Ru–P bond length changes only minimally upon going from phenyl (4) to \(\text{para}\)-fluorophenyl (1) to 3,5-bis(trifluoromethyl) phenyl (3). However, inspection of the Ru–C\(_{\text{p-cym}}\) bond lengths and C\(_{\text{p-cym}}\)–C\(_{\text{p-cym}}\) bond lengths show that the 3,5-bis(trifluoromethyl) groups of 3 have a stronger trans influence with the bonds lengthening and contracting, respectively, when compared to 1, and the increased trans effect from 1 to 3 is likely due to increased steric interactions.

Figure 4. Thermal ellipsoid perspective (50% probability) of 6. Notes: Hydrogens and fluorines on C12 and C18 are omitted for clarity. A full figure of 6 showing all fluorines (and both molecules of the asymmetric unit cell) is available in the supporting information.
Figure 2 shows some –CF₃ groups with multiple fluorines due to positional disorder (other –CF₃ groups were disordered but omitted for clarity in Figure 2). For 3, the –CF₃ groups were refined isotropically where each fluorine either occupies a 1/3 or a 1/2 position as described in the Section 2. Due to the long distance from the Ru center to the disordered –CF₃ groups, which is from 5.4 to 8.4 Å depending on which fluorine the measurement is made, the impact of this model on the bond lengths and angles of interest is likely minimal.

3.2.3. Structure of [Ru(p-cymene){P(OCH₂CF₃)₃}Cl₂]

The crystal structure of 5 is shown in Figure 3 and exhibits an average Ru–C bond length of 2.239(3) Å, an average C–C (p-cymene) bond length of 1.424(5) Å, and Ru–P bond length of 2.255(9) Å. These data compare well to the previously reported structure of the phosphite complex [Ru(p-cymene){(P(OPh)₃)}Cl₂] [29] and of 7 reported herein (see below), where the Ru–P lengths were found to be 2.264(8) and 2.287(5) Å, respectively. The Ru–P bond length shortens in 5 compared to both complexes, which is likely attributable, at least in part, to the effect of the fluorines on the Ru-phosphite metal-to-ligand π-backbonding. The C–C (p-cymene) bond distances for 5 are 1.395(5)–1.438(5) Å where the shortest C–C bond length is for C2–C3 at 1.395(5) Å, which is trans to the phosphite ligand. The elongated Ru–C1 and Ru–C2 lengths at 2.270(3) and 2.284(3) Å, respectively, along with the shortened C2–C3 bond length, show an increased trans effect of the phosphite ligand. The sum of the Cl1–Ru–Cl2, P–Ru–Cl1, and P–Ru–Cl2 bond angles is 264.2(3)°, which indicates that the three trifluoroethyl groups have a slightly increased steric influence on 5 compared to complexes with phosphine ligands. This increased steric bulk is likely due to the change in hybridization from sp² for the aromatic phosphines to sp³ for the phosphites, and this is also shown in the previously reported [Ru(p-cymene){(P(OPh)₃)}Cl₂] given in Table 2 that contains the sp³ hybridized oxygens linking phosphorus to the aromatic sp² hybridized rings [29].
One of the trifluoromethyl groups on 5 (Figure 3) showed positional disorder. This was modeled by refining that –CF₃ group isotropically where each fluorine occupies a 1/3 position. Due to the long distance from the Ru center to the disordered –CF₃ group, between 5.5 and 6.1 Å depending on which fluorine, the impact of this model on the bond lengths and angles of interest is likely minimal.

3.2.4. Structures of [Ru(p-cymene){P(OCH(CF₃)₂)₃}Cl₂] and [Ru(p-cymene)(POMe₃)Cl₂]

The crystal structure of 6 is shown in Figure 4 and shows two independent molecules in the asymmetric unit cell (only one molecule shown in Figure 4), and data for both molecules are given in Table 2. The bond metrics do not change drastically going from 5 to 6 where the only slight change observed is the average Ru–C distance increases from 2.239(3) Å in 5 to 2.255(3) Å in 6, which is likely attributable solely to the increased steric bulk of the tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite ligand. Indeed, the Cl1–Ru–P angle in 6 decreased to 83.57(3)°, and comparing 5, 6, 7, and [Ru(p-cymene)(P(OPh)₃)Cl₂] from Table 2, the steric bulk of the phosphite R group increases: [Ru(p-cymene)(P(OPh)₃)Cl₂] (260.37°) < 5-CH₂CF₃ (264.2°) ≈ 7-CH₃ (264.1°) < 6-CH(CF₃)₂ (265.9°) where the angle given is equal to the sum of the Cl1–Ru–P, Cl2–Ru–P, and Cl1–Ru–Cl2 angles in each structure.

The crystal structure of 7 is shown in Figure 5 and does not show deviations from what was observed in the fluorinated complexes. The Ru–P length was 2.287(5) Å, only slightly longer than the triphe- nylphosphite complex. Trimethylphosphite, like the other ligands, does show a trans effect on the p-cymene ligand. The C–C (p-cymene) range for 7 is from 1.394(3) to 1.441(3) Å where the shortest C–C bond length is for C2–C3 at 1.394(3) Å, which, like the other complexes, is trans to the trimethylphosphite ligand.

3.3. NMR spectroscopy

The ¹H and ¹³C NMR spectra for all seven complexes show the correct number of peaks, splittings, and intensities associated with the p-cymene and phosphine/phosphite ligands. In all complexes, a mirror plane exists, which results in five proton resonances for the p-cymene ligand. Most diagnostic for the mirror plane are the set of two doublets for the aromatic hydrogens and one doublet for the iso-propyl methyl groups, and their chemical shifts do not vary significantly among the seven complexes. The newly prepared [Ru(p-cymene){P(C₆H₃(CF₃)₂)₃}Cl₂] (3) is characterized by ¹H NMR spectroscopy and shows the two p-cymene aromatic resonances to be overlapping doublets at room temperature. In contrast, 1, 2, and 4 show the p-cymene aromatic resonances to be doublets separated by 0.27, 0.18, and 0.21 ppm, respectively [3, 16]. This observation in 3 was explored by variable temperature ¹H NMR spectroscopy. Upon gentle warming to 30 °C, the overlapping doublets coalesce into a broad singlet with no further change upon increasing to 40 °C. The sample was then cooled to −20 °C where ¹H NMR spectra were collected at 10 °C intervals. At 10 °C, the overlapping doublets began to show decoalescence, and between 0 °C and −20 °C, the sample showed two clearly resolved doublets (0.20 ppm separation at −20 °C) with minimal change upon further cooling (Figure 6). At all temperatures, the p-cymene aromatic region was the only region observed to change, the dispersion between the two doublets at −20 °C at 0.20 ppm is within the range of that observed in 1, 2, and 4, the total integration for the peak(s) was four at all temperatures, and both the high- and low-temperature regimes are fully reversible (Figures S2–S4 in Supplementary data). The reversibility suggests a fluxional process on the NMR timescale; however, at this time, the mechanism that results in a broad singlet (fully coalesced doublets) for the p-cymene aromatic hydrogens at slightly elevated temperatures is unknown.

The ¹H NMR spectrum of 5 shows a complex multiplet centered at 4.57 ppm, which is assigned to the diastereotopic methylene protons of the phosphite ligand, and is best described as an AB₃,Y multiplet due to _3J_ coupling to both the –CF₃ group and the phosphorus (Figure 7). The methine protons of the phosphite ligand, tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphite, in 6 overlap with one of the downfield p-cymene aromatic doublets at 5.78 ppm, and the resonance is assigned based on chemical shift compared to free ligand and the total integration of the overlapping resonances.
The $^{13}$C NMR spectra show several noteworthy features. In all complexes, the $p$-cymene ligand shows three upfield resonances assigned to the iso-propyl methyl groups, the methine carbon, and the single methyl. Due to the mirror plane that bisects the six-membered aromatic ring through the alkyl substituents, the aromatic carbons of the $p$-cymene resonate as two singlets between 95 and 112 ppm and two doublets between 86 and 90 ppm. The doublets exhibit 4–7 Hz $^{2}J_{CP}$ coupling to the phosphorus of the phosphine or phosphite ligand. Interestingly, only two of the four resonances show coupling, which is likely attributable to only the faster relaxing methine carbons of the $p$-cymene aromatic ring experiencing weak coupling. Complex 1 shows a downfield doublet at 163.8 ppm ($^{1}J_{CF} = 254$ Hz) and a second doublet at 129.0 ppm ($^{1}J_{CP} = 48$ Hz), which are assigned based on coupling constants and chemical shifts, as carbons on the phosphine ligand that are one bond from fluorine and phosphorus, respectively. Although 2 has been previously reported, no $^{13}$C NMR data were presented. It was found that 2 decomposes (within hours) in CDCl$_3$ to uncharacterized products, but we were able to record the spectrum in C$_6$D$_6$. Unfortunately, the most downfield resonance of the –CF$_3$ quartet overlaps with solvent at 128 ppm. Complex 3 shows a downfield doublet at 135.5 ppm ($^{1}J_{CP} = 42$ Hz) and a quartet at 132.4 ppm ($^{3}J_{CF} = 28$ Hz), which are assigned as the P-C$_{ipso}$ and para-C on the phosphine ligand, respectively. The –CF$_3$ group resonates as a quartet at 124.3 ppm ($^{1}J_{CF} = 271$ Hz). The remaining ortho and meta carbons of the phosphine ligand resonate as broad multiplets at 134.0 and 125.4 ppm. Complex 3 shows a downfield doublet at 134.9 ppm ($^{1}J_{CP} = 34$ Hz) and a quartet of doublets at 132.3 ppm ($^{2}J_{CF} = 36$ Hz and $^{3}J_{CF} = 15$ Hz), which are assigned as the P-C$_{ipso}$ and meta-C on the phosphine ligand, respectively.
The –CF$_3$ group resonates as a quartet at 122.6 ppm ($^1J_{CF} = 272$ Hz). The remaining ortho and para carbons of the phosphine ligand resonate as broad singlets at 134.0 and 125.4 ppm, respectively. It is interesting to note the change in chemical shift of the P-C$_{ipso}$ resonance in 1–3. In 1, the fluorine is directly attached to the aromatic ring and causes that carbon (i.e., C$_{para}$-F) to be the most downfield shifted carbon. However, in 2 and 3, where there are more fluorines present, but not directly attached to the aromatic ring, the P-C$_{ipso}$ resonance is the most downfield resonance. Complex 5 shows two sets of quartets of doublets at 64.1 ppm ($^2J_{CF} = 37$ Hz and $^2J_{CP} = 6$ Hz) and 122.7 ppm ($^1J_{CF} = 277$ Hz and $^3J_{CP} = 11$ Hz), which are assigned to the –CH$_2$– and –CF$_3$ on the phosphite ligand, respectively. The methine carbon of the phosphite in 6 resonates as a multiplet at 73.4 ppm, which is 9 ppm downfield from the observed methylene resonance in 5. The downfield shift indicates the electron-deficient nature of the methine carbon; however, the –CF$_3$ groups in 6 show no significant chemical shift change from that observed in 5, and resonate as a quartet at 120.1 ppm.

All complexes show one singlet in their $^{19}$F and $^{31}$P NMR spectra. The $^{19}$F NMR chemical shift does not show any significant difference between free and coordinated ligand. However, the $^{31}$P NMR chemical shift does show significant change between free and coordinated ligand. The $^{31}$P spectra for the phosphine complexes, 1–4, show on average a 29 ppm shift downfield from free ligand, while the phosphite complexes, 5–7, exhibit a 25 ppm shift upfield from free ligand in their $^{31}$P spectra. It is challenging to make predictions on $^{31}$P chemical shifts. However, these data are consistent with the coordinated phosphites being more electron rich and the coordinated phosphines being more electron poor when compared to the free ligand.

### 3.4. Electronic spectroscopy

All seven complexes were vividly colored ranging from orange to brick red. The phosphite complexes, 5–7, are all red and show both a MLCT transition and a lower energy $d$–$d$ transition, which were assigned based on values of their extinction coefficients (Table 3). There is little difference in the electronic spectra.
between the three phosphite complexes. The higher energy transition is assigned as a metal-to-ligand-charge-transfer transition due to the electron-rich Ru(II) and the electron-accepting properties of the fluorinated phosphite ligand. For 5–7, in all cases, the \(d-d\) transition was well resolved and distinguishable. For a noncentrosymmetric low spin \(d^6\) complex, two spin-allowed \(d-d\) transitions are predicted (\(1A_1 \rightarrow 1T_1\) and \(1A_1 \rightarrow 1T_2\) based on pseudo-octahedral analysis; however, only one \(d-d\) transition is observed with the second likely obscured by the MLCT. Using the lower energy \(d-d\) transition, the value of the ligand field splitting parameter (\(\Delta_0\)) can be approximated and increases in the order of 6 (21,231 cm\(^{-1}\)) > 7 (20,964 cm\(^{-1}\)) > 5 (20,747 cm\(^{-1}\)) as shown in Table 2. This is what one would expect with 6-CH(CF\(_3\))\(_2\) with the most fluorinated phosphite being the largest. However, 5-CH\(_2\)CF\(_3\) and 7-CH\(_3\) are very similar only separated by 217 cm\(^{-1}\) and in reverse predicted order based on the number of fluorines. Furthermore, there is only a 752 cm\(^{-1}\) (9.0 kJ mol\(^{-1}\)) difference between the highest energy 6-CH(CF\(_3\))\(_2\) and lowest energy \(d-d\) transition 5-CH\(_2\)CF\(_3\). These data taken together suggest there is little electronic difference between the three phosphite ligands, in agreement with the solid-state structures where 5, 6, and 7 showed similar bond lengths with only 6 being slightly more sterically encumbering (see above).

In contrast to the phosphite complexes, the phosphine complexes 1–4 show both an incompletely resolved low energy shoulder, likely due to a \(d-d\) transition, and a direct correlation between the number of fluorines in the ligand and the MLCT energy. As the number of fluorines increases on the phosphines, the energy of the MLCT decreases for 1–4. Indeed, the plot shown in Figure 8 of the energy of the MLCT for 1–4 versus number of fluorines in the ligand reveals a decreasing trend, which becomes linear (\(R^2 = 0.995\)) if the triphenylphosphine complex is removed. It is interesting to note that the trend holds even though the fluorines are not bonded directly to the arene (i.e., –CF\(_3\)). The trend in MLCT energy appears to be an electron-withdrawing inductive effect that lowers the energy of the \(\pi^*\) orbitals. This was substantiated through the calculated structures where a trend was observed for 1–4 and hypothetical [Ru(p-cymene)[P(C\(_6\)F\(_5\))\(_3\)]Cl\(_2\)] (8) that as the number of fluorines increases, the LUMO moves from predominantly Ru \(d\) orbital to phosphate \(\pi^*\) in character (see below).

**Table 3.** Electronic transitions for 1–7.

<table>
<thead>
<tr>
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<th>Assignment</th>
<th>(\varepsilon) (L mol(^{-1}) cm(^{-1}))</th>
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<td>6</td>
<td>477</td>
<td>(d-d)</td>
</tr>
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</table>

**Figure 8.** Plot of energy of MLCT transition for 1–4 as a function of number of fluorines present on the phosphine ligand.
3.5. Calculated structures

Ab initio computations of molecular orbitals and HOMO–LUMO gap energies have been performed on 1–8, with the geometries either extracted from the crystal structure of 1, 3, 4, [15], and 5–7 or constructed (for 2 and 8) as explained in the Section 2. The HOMO and LUMO energies as well as the energy gaps are given in Table 4. As seen in Table 4, the trend in the energy gaps is $6 > 5 > 3 > 2 > 8 \cong 7 > 1 > 4$, which is in agreement with predictions based on both phosphite versus phosphine and the number of F atoms in the ligand. Complex 6-CHICF$_3$$_2$ having the most fluorinated phosphite (18 F’s), tris(1,1,1,3,3,3-hexafluoro-2-propyl)phosphate, coordinated and 4 being the least fluorinated phosphine (0 F’s), triphenylphosphine, coordinated representing the largest and smallest HOMO–LUMO gap, respectively. It is apparent that the number of fluorines plays a key role in the HOMO–LUMO gap energy. For example, 3 has a larger gap than the trimethylphosphite complex, 7, which suggests that the meta di-substituted phosphine, tris[3,5-bis(trifluoromethyl)phenyl]phosphine, in 3 results in a significant lowering of the arene $\pi^*$ orbitals of the phosphine. This likely results in the phosphine of 3 being a better $\pi$-acid and decreasing the energy of the HOMO as shown in Table 4. The similar HOMO–LUMO gap energy of 2 and 8 is interesting in that although there are three complexes that have a lower energy difference, 2 and 8 represent the least thermodynamically stable complexes. No reaction between [{Ru(p-cymene)Cl$_2$}]$_2$ and [Ru(p-cymene)Cl$_2$]$_{18}$ and 2 has been reported to be the least thermodynamically stable in a series of related complexes [16].

If the [Ru(PR$_3$)$_2$Cl$_2$] fragment is coordinated to a p-cymene ligand in an $\eta^6$ mode, the resulting frontier molecular orbital diagram is similar to that for an ML$_6$ octahedral complex. More specifically for [Ru(p-cymene)(PR$_3$)$_2$Cl$_2$], the lower lying set is comprised of a doubly degenerate set ($d_{xy}$ and $d_{x^2-y^2}$) and a singly degenerate ($d_{z^2}$) orbital, while the higher energy set is doubly degenerate ($d_{yz}$ or $d_{xz}$) [43]. In all complexes presented herein, only one of the doubly degenerate set ($d_{xy}$ and $d_{x^2-y^2}$) is shown for the HOMO, and only one of the doubly degenerate set ($d_{yz}$ or $d_{xz}$) is shown for the LUMO (Figure 9). All frontier orbitals are presented in the Supplementary data. The frontier molecular orbitals of 5, obtained at the mPW1PW91 level of theory, are shown in Figure 9(a) and (b). The HOMO is primarily Ru ($d_{xy}$ or $d_{x^2-y^2}$) along with a non-bonding $p$ orbital of the chlorines contributing. To a lesser extent, the HOMO contains p-cymene $\pi^*$ character and some phosphorus character. The LUMO consists of orbital contributions from the $d_{xz}$ or $d_{yz}$ orbital of Ru, p-cymene $\pi^*$ character, and Ru–Cl $\sigma^*$ character. These calculations are consistent with the single $d$–$d$ transition observed in the phosphite complexes (5–7). Interestingly, there is little variation between all seven complexes for their HOMO contributions (see Supplementary data). However, for the phosphine complexes (1–4 and 8), as the number of fluorines increases, the LUMO changes from primarily Ru $d_{xz}$ or $d_{yz}$ orbital in character to solely phosphine ligand $\pi^*$ in character (Figure 9(c) and (d)). These calculations are consistent with both the electronic spectrum for the phosphine complexes being dominated by a MLCT (i.e., the $d$–$d$ transition is obscured) and the experimental observation that as the number of fluorines increases on the phosphine, the energy of the MLCT decreased (Figure 8). Finally, the HOMO and LUMO were also calculated for the hypothetical complex [Ru(p-cymene)[P(C$_6$F$_5$)$_3$]Cl$_2$] (8). Like the other phosphine complexes, the pentafluorophenyl groups allowed for the LUMO to be predominantly phosphine ligand $\pi^*$ in character. However, the HOMO was found to have a reduced

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
<th>Gap (cm$^{-1}$)</th>
<th># F’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.32573</td>
<td>0.03242</td>
<td>7.86 × 10$^4$</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>−0.33457</td>
<td>0.02886</td>
<td>7.98 × 10$^4$</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>−0.34713</td>
<td>0.02790</td>
<td>8.23 × 10$^4$</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>−0.31246</td>
<td>0.03937</td>
<td>7.72 × 10$^4$</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>−0.34549</td>
<td>0.03600</td>
<td>8.37 × 10$^4$</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>−0.35568</td>
<td>0.03054</td>
<td>8.48 × 10$^4$</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>−0.32166</td>
<td>0.03883</td>
<td>7.91 × 10$^4$</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>−0.33184</td>
<td>0.02837</td>
<td>7.91 × 10$^4$</td>
<td>15</td>
</tr>
</tbody>
</table>
contribution from the phosphine (Figure 9(e) and (d)). The latter calculation supports the experimental observation that 8 cannot be prepared in the laboratory.

4. Conclusion

Several mixed sandwich piano-stool complexes containing η⁷-p-cymene, Ru(II), chloride, and either fluorine-containing phosphines or phosphites have been synthesized via direct ligand displacement from the dichloro-bridged \([\text{Ru}(\text{p-cymene})(\text{Cl})_2]_2\). All complexes are characterized in solution via \(^1\text{H}, ^{13}\text{C}\{^1\text{H}\}, ^{31}\text{P}\{^1\text{H}\}, \) and \(^{19}\text{F}\{^1\text{H}\}\) NMR spectroscopy, and five complexes were structurally characterized by single-crystal X-ray diffraction. All complexes show a distorted octahedral geometry formed by the facially coordinating carbocyclic η⁷-p-cymene ligand. The \(^{31}\text{P}\{^1\text{H}\}\) spectra consistently show a 25 ppm shift upfield from free ligand for the phosphite complexes 5–7 and a 29 ppm shift downfield from free ligand for the phosphine complexes 1–4. The electronic spectra are dominated by a single metal-to-ligand-charge-transfer transition that possesses either a lower energy unresolved shoulder or fully resolved peak for 1–3 and 5–7, respectively, which is assigned as a \(d-d\) transition. For phosphine complexes 1–4, the energy of the MLCT was found to correlate with the number of fluorine atoms present. Ab initio and DFT computations have been performed on 1–8 in order to determine their electronic structures. For the most part, the complexes show HOMOs and LUMOs that are primarily Ru \((d_{xy}, d_{x^2-y^2},\) or \(d_{z^2}\)) and Ru \((d_{xz}, d_{yz}\)) in character, respectively. The exception lies for the phosphine complexes where the LUMO becomes increasingly phosphine ligand \(\pi^*\) in character as the number of fluorines increases. A better understanding of the electronic properties of these fluorine-containing phosphine and phosphite ligands can lead to enhanced Ru organometallic complexes for homogeneous catalysis.
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Disclosure statement

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