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Site Selectivity of $[RuCp^*]^+$ Complexation in Cyclopenta[*def*]triphenylenes

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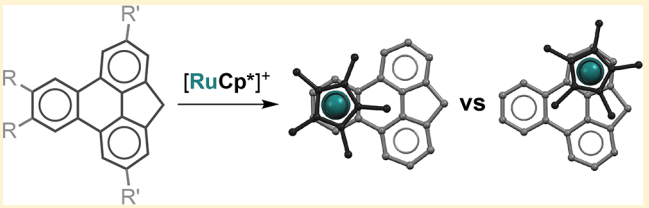
Supporting Information

ABSTRACT: A series of new cyclopenta-fused triphenylenes has been synthesized in high yield and reacted with $[Ru(\mu_3\text{-}Cl)Cp^*]_4$ to form $[RuCp^*(\eta^6\text{-arene})]PF_6$ complexes. Systematic variation of the cyclopenta[*def*]triphenylene allowed the site of complexation to be probed and the influence of the electronic and steric properties of the substituents in directing complexation to be assessed. As determined by NMR spectroscopy and X-ray crystallography, in all cases the $[RuCp^*]^+$ fragment complexes at a peripheral arene ring, rather than at the central arene ring or as a neutral η^5-cyclopentadienyl metallocene adduct. It was shown that electronic influences are minimal, while steric effects afford selective complexations. The electronic properties of the ligands and complexes were probed with electrochemistry, along with electronic absorption and emission spectroscopies.



INTRODUCTION

Cyclopentadienyl (Cp, $\eta^5\text{-}C_5H_5$) and pentamethylcyclopentadienyl (Cp*, $\eta^5\text{-}C_5Me_5$) ruthenium complexes with arene ligands have been extensively studied, forming η^6-sandwich complexes of the type $[RuCp(\eta^6\text{-arene})]^+$ and $[RuCp^*(\eta^6\text{-arene})]^+$ that are generally stable under atmospheric conditions.[1−7] The $[RuCp^*]^+$ fragment is known to strongly interact with aromatic hydrocarbons with a high tolerance to functional groups.[3] The resulting ruthenium sandwich complexes have been studied for their interesting electrochemical and spectroscopic properties, as well as their catalytic activity.[8,9] The most popular synthetic route toward simple $[RuCp^*(\eta^6\text{-arene})]^+$ complexes involves the formation of a $[RuCp^*(CH_3CN)_3]^+$ complex, which is reacted with the appropriate arene ligand with heating or UV irradiation.[2,5,10] These methods are generally useful and robust; however, the need for toxic or expensive Sn and Ag reagents leaves room for improvement. In 2007 Fairchild et al.[5] proposed a slightly altered route to these target $[RuCp^*(\eta^6\text{-arene})]^+$ complexes that involves the direct reaction of $[Ru(\mu_3\text{-}Cl)Cp^*]_4$, a precursor in previous pathways, with the arene and the aid of microwave irradiation. The water-soluble chloride salt of the resultant complex was obtained after short reaction times in high yields, and the reaction was shown to be reliable for a wide range of arene ligands. However, the arene ligands studied were mostly single ring benzene derivatives, naphthalene and quinoline being the exceptions, with the $[RuCp^*]^+$ forced to bind to the only arene ring present.

Site selectivity for complexation of $[RuCp^*]^+$ to substituted polyaromatic systems has been little studied. Previous work[1,6,11,12] gives some precious insight into the affinity of the $[RuCp^*]^+$ fragment for a range of mostly monosubstituted simple arene systems. Larger polycyclic aromatic hydrocarbon (PAH) ligands that complex $[RuCp^*]^+$ have all been unsubstituted.[13,14] To the best of our knowledge, no reports to date describe the site selectivity of $[RuCp^*]^+$ for PAHs with a range of substitution patterns and types. Furthermore, the presence of a peripheral cyclopenta-ring, capable of complexation upon deprotonation, allows the preference for benzenoid versus cyclopentadienyl donor site to be explored. This study introduces four new substituted cyclopentatriphenylene-based ligands (**1**−**4**) that contain multiple η^6-binding sites along with a single (potential) η^5-binding site. Unsubstituted cyclopenta[*def*]triphenylene (**1**) is a substructure of sumanene, which itself has a carbon framework found in buckminsterfullerene, C_{60}. Sumanene has a curved π-surface[15] and therefore offers a concave and convex surface for η^6-binding of metals. Amaya et al. formed a $[RuCp(\eta^6\text{-sumanene})]PF_6$ complex that was used to probe the facial selectivity of the $[RuCp]^+$ moiety.[16] The planar parent PAH triphenylene offers only two potential coordination sites; one of the three equivalent outer rings has been shown to bind $[RuCp^*]^+$.[13] The cyclopentatriphenylenes **1**−**4** synthesized herein offer a planar surface to investigate the relative effects of electron-donating and sterically bulky substituents on the preferred coordination site of the $[RuCp^*]^+$ moiety.

RESULTS AND DISCUSSION

Synthesis. 4*H*-Cyclopenta[*def*]triphenylene (**1**) is prepared in eight high-yielding steps, with an overall isolated yield of 64% starting from the commercially available precursor 9*H*-

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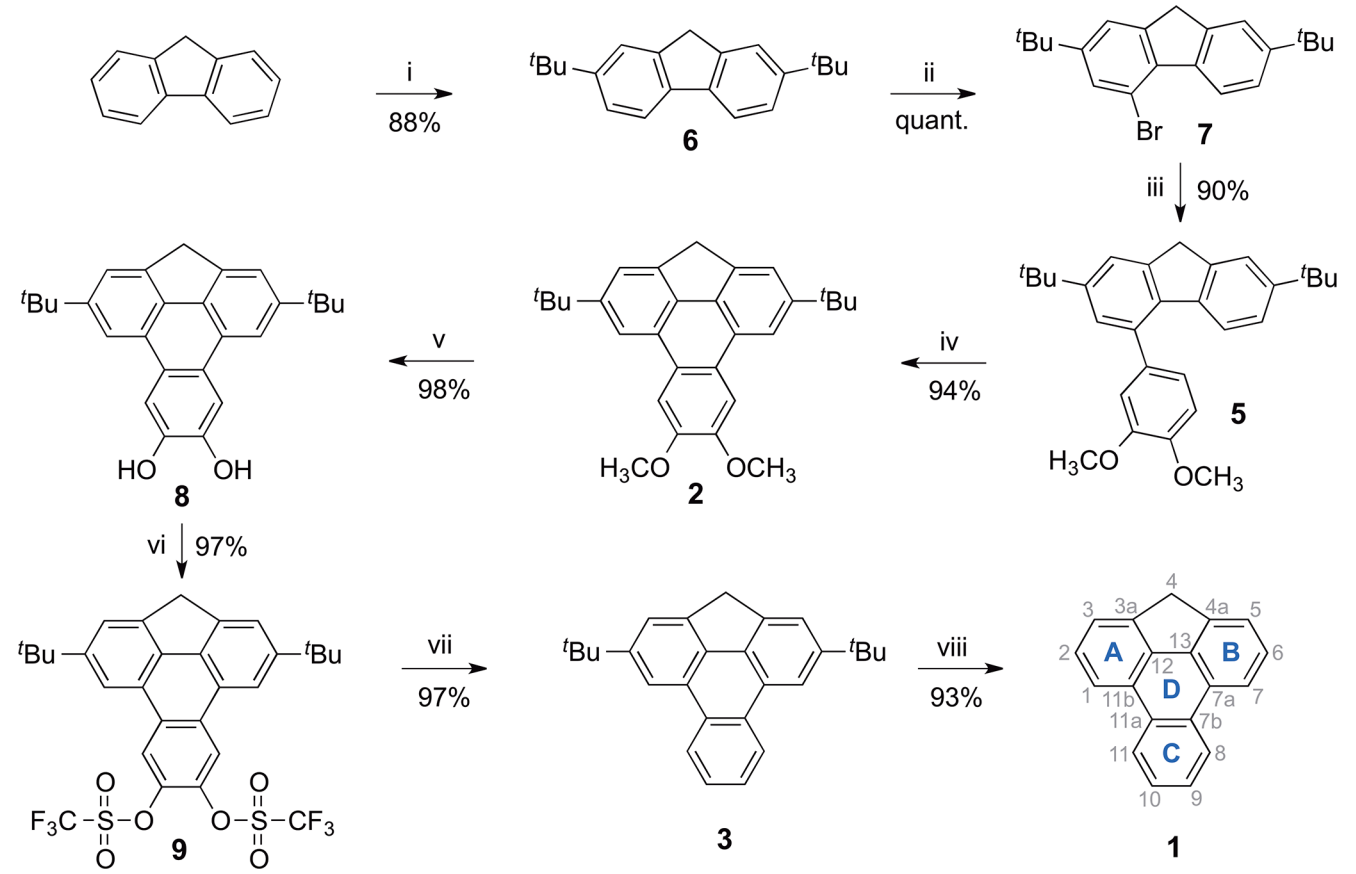
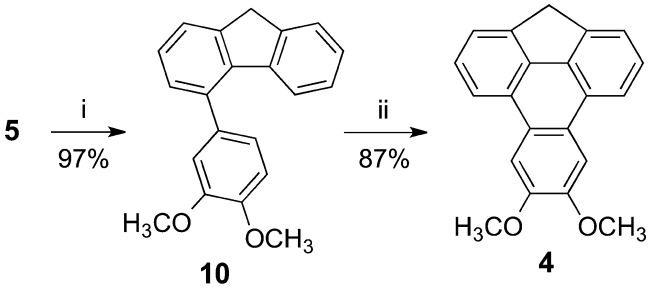
Scheme 1. Synthesis of 1, 2, and 3 from 9*H*-Fluorene with Numbering and Ring Labeling[a]



[a]Reaction conditions: (i) ^{t}BuCl, $FeCl_3$, CS_2, rt, 3 h; (ii) Br_2, I_2, CH_2Cl_2, 0 °C, 1 h; (iii) 3,4-dimethoxyphenylboronic acid, $PdCl_2$(dppf), K_2CO_3, toluene, H_2O, EtOH, 80 °C, 18 h; (iv) $FeCl_3$, CH_3NO_2, CH_2Cl_2, rt, 15 min; (v) BBr_3, CH_2Cl_2, rt, 3 h; (vi) Tf_2O, pyridine, CH_2Cl_2, 0 °C–rt, 40 min; (vii) Et_3SiH, $Pd(OAc)_2$, dppp, DMF, 60 °C, 18 h; (viii) $AlCl_3$, toluene, 60 °C, 3 h.

fluorene (Scheme 1). The compounds 2,6-di(*tert*-butyl)-9,10-dimethoxy-4*H*-cyclopenta[*def*]triphenylene (**2**) and 2,6-di(*tert*-butyl)-4*H*-cyclopenta[*def*]triphenylene (**3**) were formed as intermediates during the reaction sequence, and 10,11-dimethoxy-4*H*-cyclopenta[*def*]triphenylene (**4**) was synthesized in two high-yielding steps from 2,7-di-*tert*-butyl-4(3,4-dimethoxyphenyl)-9*H*-fluorene (**5**) (Scheme 2). Previously unreported compounds were fully characterized via ^{1}H and ^{13}C NMR spectroscopy (Supporting Information, Figure S1), IR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography for the cyclopentatriphenylene ligands **1**–**4** (Figures S3–S6).

Scheme 2. Synthesis of 4 from 5



Reaction conditions: (i) $AlCl_3$, toluene, rt, 2 h; (ii) $FeCl_3$, CH_3NO_2, CH_2Cl_2, rt, 15 min.

A series of new [RuCp*(η^6-arene)]PF_6 complexes have been synthesized using a minor variation to the method described by Fairchild and Holman[5] (Scheme 3). The reaction of cyclopentatriphenylenes **1**–**4** with [Ru(μ_3-Cl)Cp*]$_4$ (**11**), as a source of [RuCp*]$^+$, was performed in 50:50 THF/water, a larger proportion of THF than was used previously due to diminished water solubility of the cyclopentatriphenylene ligands when compared to single arene systems.[5] The reaction mixture in all cases was a dark brown-red color before heating and was nearly colorless after microwave irradiation. Moderate yields of the resultant complexes were isolated; however, some cyclopentatriphenylene starting material was also recovered in all cases. Increasing the reaction time did not increase the yield of the target complex, suggesting that **11** may slowly degrade to a colorless compound during heating or the complexes are not completely stable during the aqueous workup. The resulting complexes were isolated as light brown-white solids after workup, in which the Cl^- counterion was exchanged for the more organic-soluble PF_6^-. The product complexes were stored away from light (and water) but appeared to be quite stable, even while heating in organic solvents. Purification by chromatography or recrystallization from acetone/ether or CH_2Cl_2/ether afforded pure material that was characterized by ^{1}H, ^{13}C, and ^{31}P NMR, IR spectroscopy, mass spectrometry, elemental analysis, and, in most cases, X-ray crystallography.

The coordination site for all complexes was identified by ^{1}H NMR spectroscopy, where the aromatic proton signals

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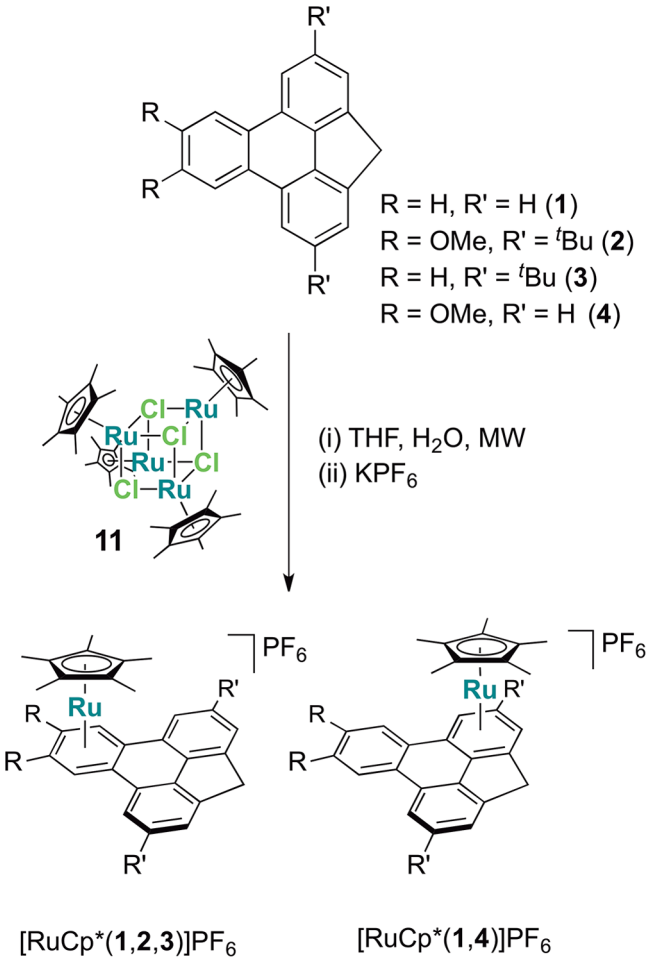
Scheme 3. Complexation of the Cyclopentatriphenylene Ligands with [RuCp*]$^+$



corresponding to the coordinated aryl ring were shifted upfield compared to the rest of the aromatic signals and the free ligand. Coordination to ring A/B reduces the symmetry of the triphenylene core, causing double the number of signals to be present when compared to the free ligand. In no case was there any sign of η^5-complexation to form a bis(cyclopentadienyl)-type sandwich complex nor η^6-complexation to the "empty" center ring D. Complexation at ring D would be unexpected, as the Clar model for PAHs[17] predicts rings A, B, and C to have stable discrete sextets of π-electrons, while complexation at ring D would disturb the aromatic stabilization of all three π-sextets. X-ray crystallography for most complexes was used to confirm the coordination site.

The coordination site for **2** was predicted to be ring C due to the electron-donating effect of the methoxy substituents combined with the blocking effect of the *tert*-butyl groups on rings A and B. The ^{1}H NMR spectrum for [RuCp*(η^6-**2**)]PF$_6$ contains three aromatic signals, all singlets, suggesting that the compound maintains the symmetry of the ligand upon complexation, and therefore the [RuCp*]$^+$ sits on the mirror plane that perpendicularly bisects the cyclopentatriphenylene core (Figure 1). One of the aromatic signals is seen particularly upfield from the rest (7.46 ppm compared to 8.04 and 8.42 ppm in $CD_3C(O)CD_3$), typical of arene protons coordinated to a [RuCp*]$^+$ moiety,[18,19] and were assigned as the ring C protons. The appearance of a large singlet (1.34 ppm) confirmed the presence of the methyl protons from the Cp* ring; however, it is worth noting that the chemical shift for this signal is ca. 0.6 ppm upfield compared with the related η^6-benzene complex.[3] This shift is presumably due to the shielding caused by the ring-current of adjacent rings A and B. Diffusion of diethyl ether vapor into a solution of [RuCp*(η^6-**2**)]PF$_6$ yielded single crystals suitable for X-ray diffraction; an ORTEP diagram of the cation structure is shown in Figure 2.

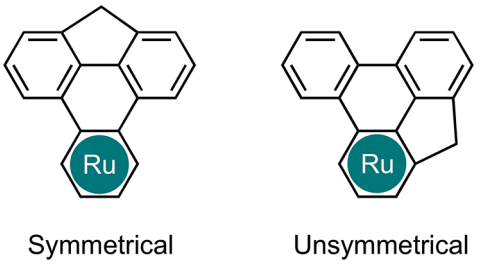


Figure 1. Comparison of the symmetrical and unsymmetrical complexation products of **1** with **Ru** representing the [RuCp*]$^+$ fragment.

In the absence of the methoxy substituents, as in **3**, the bulky *tert*-butyl groups provide enough steric hindrance to direct the complexation of [RuCp*]$^+$ to ring **C**, analogous to [RuCp*(η^6-**2**)]PF$_6$. The ^{1}H NMR spectrum of [RuCp*(η^6-**3**)]PF$_6$ contains only four aromatic signals, indicating that a symmetrical complex had been formed, with the two signals for ring C protons seen upfield when compared to the free ligand (7.50 and 6.41 ppm compared to 8.68 and 7.69 ppm).

Interestingly, if only the methoxy groups are present (ligand **4**), the complexation is seen exclusively at ring A/B. Coordination at ring A/B results in an unsymmetrical complex with two enantiomers that exhibit planar chirality (but with identical ^{1}H NMR spectra). The site of complexation suggests that the unfavorable steric effect due to the two methoxy substituents outweighs any gains due to the electron-donating effect of these substituents. The ^{1}H NMR spectrum of [RuCp*(η^6-**4**)]PF$_6$ is more complex than the two previous examples and a total of eight aromatic signals were identified, with three (7.25, 6.67, and 6.15 ppm) being upfield of the rest. These three signals are assigned as protons 1, 2, and 3 of ring A, where the [RuCp*]$^+$ moiety is bound. The close proximity of the [RuCp*]$^+$ center to the 4-methylene bridge causes the upward and downward facing methylene protons to be in significantly different chemical environments, each diastereotopic proton appearing as a doublet with a geminal coupling of 21.5 Hz. The 2D NOESY spectrum displays a cross-peak between one of the 4-methylene-bridge protons (4.16 ppm) and the Cp* methyl protons (1.35 ppm) (Figure S2). This NOESY signal was not observed for the previously described complexes (where the [RuCp*]$^+$ is further away) and allows the methylene bridge protons of [RuCp*(η^6-**4**)]PF$_6$ to be assigned with confidence. The HR-ESI mass spectrum of the crude product indicated the presence of a small amount of [RuCp*^{OH}(η^6-**4**)]PF$_6$, a side product due to oxidation of a Cp* methyl group; the hydroxylated product was separated from [RuCp*(η^6-**4**)]PF$_6$ using preparative chromatography. The formation of such a side product is analogous to the [RuCp*^{OH}]$^+$ impurity seen by Fairchild and Holman[5] and the [RuCp*^{OMe}]$^+$ impurity seen by Schmid and Lindel, for which a mechanism explaining its formation is proposed.[20] The

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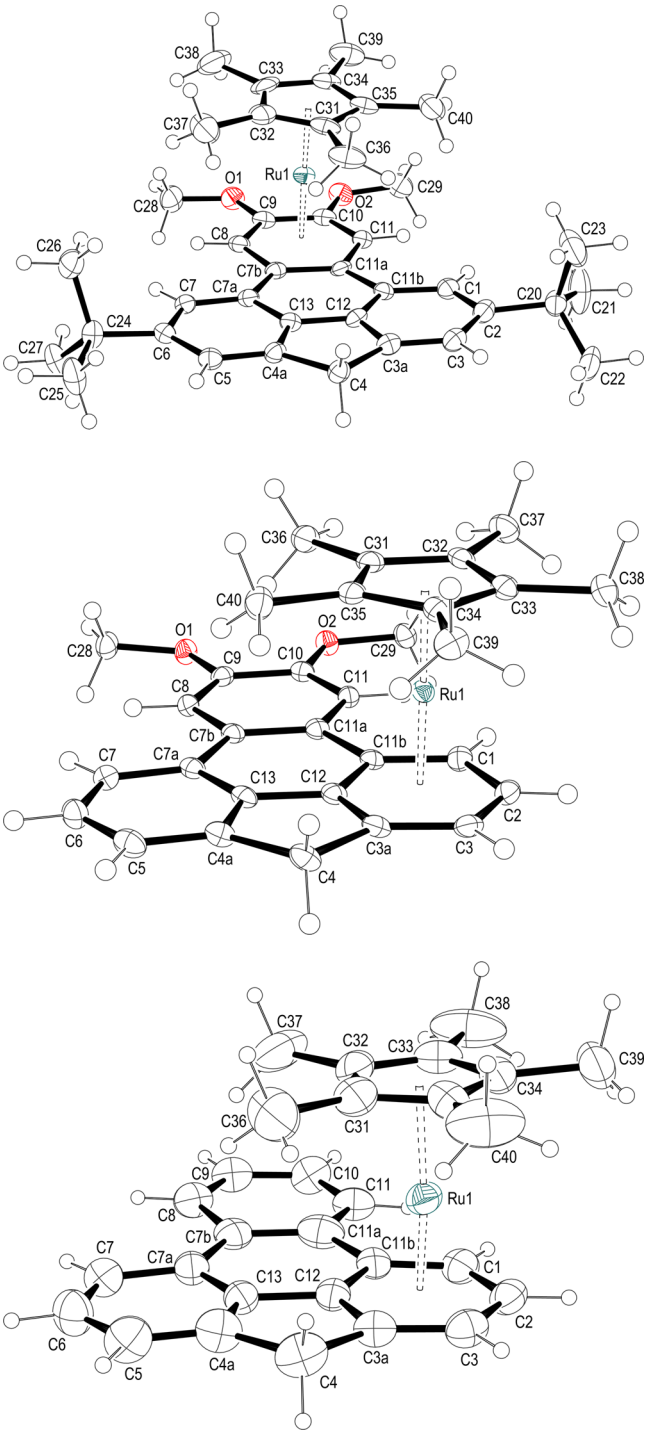

Figure 2. ORTEP diagrams of a crystal structure of [RuCp*(η^6-**2**)]PF_6·$(CH_2Cl_2)_2$ (top) and [RuCp*(η^6-**4**)]PF_6 (middle) shown with 50% displacement ellipsoids, and [RuCp*(η^6-**1**)]PF_6·$(CH_3C(O)CH_3)_{0.5}$ (bottom) shown with 30% displacement ellipsoids for the major disordered component; PF_6^- counterions and solvents omitted for clarity.

complex [RuCp*^{OH}(η^6-**4**)]PF_6 was fully characterized, and an ORTEP diagram of the crystal structure is shown in Figure 3.

The ^{1}H NMR spectrum of [RuCp*(η^6-**1**)]PF_6 is quite convoluted compared to the compounds above and previously reported [RuCp^R(η^6-triphenylene)]$^+$ complexes.[13,21] Fifteen aromatic signals are present, ranging from 8.76 to 6.19 ppm, suggesting that monocomplexation has occurred at ring A/B

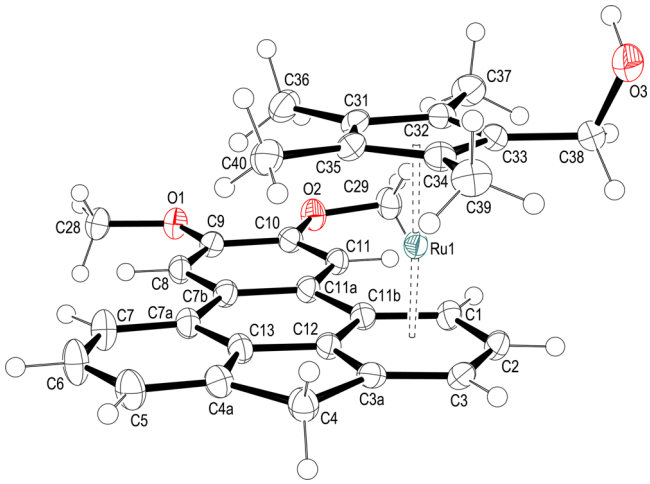

Figure 3. ORTEP of a crystal structure of [RuCp*^{OH}(η^6-**4**)]PF_6·$CH_3C(O)CH_3$ showing 50% displacement ellipsoids; PF_6^- counterion and solvent omitted for clarity.

and ring C, thereby giving a mixture of isomers. The only difference between the two isomers formed from complexation to ring A/B and ring C is where the 4-methylene bridge is located relative to the metal (Figure 1). Accordingly, the two isomers behave similarly in chromatography and could not be separated, so characterization was carried out on the mixture. Coordination to ring A/B results in an unsymmetrical complex (as a racemate), while coordination of ring C results in a symmetrical (achiral) complex (Figure 1).

The overall ratio of the unsymmetrical to symmetrical isomers by ^{1}H NMR integration was found to be 1:0.6, respectively. With the aid of 2D COSY, NOESY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR spectroscopic data the ^{1}H and ^{13}C NMR signals associated with each isomer were elucidated. The most upfield aromatic ^{1}H NMR signals were assigned to [RuCp*]$^+$-coordinated rings, and the diastereotopic methylene protons of the unsymmetrical isomer were easily distinguished by a NOESY cross-peak with the Cp* ring methyl protons.

X-ray Crystallography. Single crystals suitable for X-ray crystallography were grown for all four cyclopentatriphenylene ligands, and solid-state structures were determined (Figures S3−S6 show ORTEP and packing diagrams). For each cyclopentatriphenylene **1**−**4**, the carbon framework is close to planar, the methylene bridge insufficient to induce curvature as is seen for sumanene,[22] but nevertheless distorting the arrangement of the aromatic rings of the triphenylene moiety. Similar to triphenylene,[23] the crystal structure of **1** shows an offset face-to-face arrangement in "infinite" stacks for each of the two molecules in the asymmetric unit, with distances of 3.39 and 3.68 Å between aromatic cores. Cyclopentatriphenylene **2** forms a similar offset columnar stack, with a separation of 3.48 Å between aromatic cores, except in this case each molecule alternates its orientation so that the 4-methylene protons form bifurcated hydrogen bonds with the methoxy group oxygens of the neighboring molecules (Figure S4). In contrast, **3** and **4** both form discrete inversion-related offset dimers, with interplanar distances of 3.35 and 3.39 Å, respectively (Figures S5 and S6). Analogous to that in **2**, the packing of cyclopentatriphenylene **4** also utilizes bifurcated hydrogen bonds to strengthen the supramolecular assembly.

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Single crystals of the complexes were grown by vapor diffusion of ether into a concentrated solution of the complex in acetone or CH_2Cl_2, yielding colorless crystals in all cases. ORTEP diagrams of the $[RuCp^*]^+$ complexes of **1**, **2**, and **4** (Figure 2) and a hydroxylated byproduct formed during the reaction with **4** (Figure 3) are shown. Coordination of the $[RuCp^*]^+$ moiety causes structural changes in the cyclopentatriphenylene ligand, most notably in the elongation of the complexed aryl ring bonds of the arene ligand. The free cyclopentatriphenylene ligands **2** and **4** have average bond lengths of 1.404(6) [ring C] and 1.397(2) Å [ring A], which lengthen to 1.430(7) and 1.420(3) Å after complexation; this elongation upon metal binding is common in other $[RuCp^*(\eta^6\text{-arene})]^+$ sytems.[24−26] The C_6(centroid)−Ru−C_5(centroid) angles for $[RuCp^*(\eta^6\text{-}\mathbf{2})]PF_6$ and $[RuCp^*(\eta^6\text{-}\mathbf{4})]PF_6$ are 179.10° and 179.02°, respectively, indicating that the Cp* sits close to coplanar with the aryl ring directly above it.

The crystal structure of $[RuCp^*(\eta^6\text{-}\mathbf{1})]PF_6\cdot(CH_3C(O)CH_3)_{0.5}$ initially refined as the unsymmetrical isomer resulting from complexation to ring A/B, but residual electron density suggested a disordered structure with a partial occupancy methylene bridge opposite the ruthenium. It appears that the symmetrical complex (complexation at ring C) had cocrystallized at the same site as the major isomeric product and was refined accordingly with extensive use of restraints. The two components refined to 70:30, in agreement with the ^{1}H NMR integrations (although there is no requirement for the solid-state composition to match that of the bulk sample in solution). This observation indicates that the intermolecular interactions in the solid state for the two isomers are very similar, not surprising due to their very similar shape, differing only in the position of the methylene bridge (see Figure 1).

Figure 3 shows an ORTEP diagram of a crystal structure for $[RuCp^{*OH}(\eta^6\text{-}\mathbf{4})]PF_6\cdot CH_3C(O)CH_3$. The Cp* ring bears one methyl alcohol group formed by the oxidation of a methyl group during the reaction and for which the hydroxyl is H-bonded to the acetone oxygen (Figure S7). All the bond lengths and angles are comparable to $[RuCp^*(\eta^6\text{-}\mathbf{4})]PF_6$; however, the dihedral angle between the planes defined by the arene and cyclopentadienyl ring is only 1.6° compared to 5.8° in the analogous benzene compound $[RuCp^{*OH}(\eta^6\text{-benzene})]^+$ reported by Fairchild and Holman.[27]

The supramolecular structure of all the complexes exhibit dimers with the cyclopentatriphenylene cores π-stacking and the $[RuCp^*]^+$ coordinated to the outside faces (Figure 4). The 4-methylene protons of $[RuCp^*(\eta^6\text{-}\mathbf{2})]PF_6$ form bifurcated hydrogen bonds to the methoxy oxygens in a neighboring compound. The C−H···O bond lengths of 2.86 and 2.93 Å (C−H 0.99 Å) indicate weak intermolecular bonding.[28] The dimers formed by $[RuCp^*(\eta^6\text{-}\mathbf{4})]PF_6$ are more offset in nature than $[RuCp^*(\eta^6\text{-}\mathbf{2})]PF_6$ (with C−H···O distances of 4.36 and 3.78 Å), presumably because the *tert*-butyl groups are not present to lock the dimers into place.

Electrochemistry. Cyclopentatriphenylenes **1**−**4** and the corresponding $[RuCp^*(\eta^6\text{-arene})]PF_6$ complexes were investigated by cyclic voltammetry (acetone/^{n}Bu$_4$NPF$_6$, referenced against internal decamethylferrocene and converted to SCE). Of the four cyclopentatriphenylene ligands, only the two methoxy-substituted compounds (**2** and **4**) showed observable oxidations (Figure 5) in the working potential window, due to the electron-donating nature of the substituents increasing the HOMO energy. Cyclopentatriphenylene **2** was shifted to a slightly less positive value when compared to **4** ($E_{1/2}$ = 1.28 V compared to 1.34 V) due to the extra electron-donating ability of the *tert*-butyl substituents. No ligand showed any observable reductions in the range −2.1 to 1.5 V.

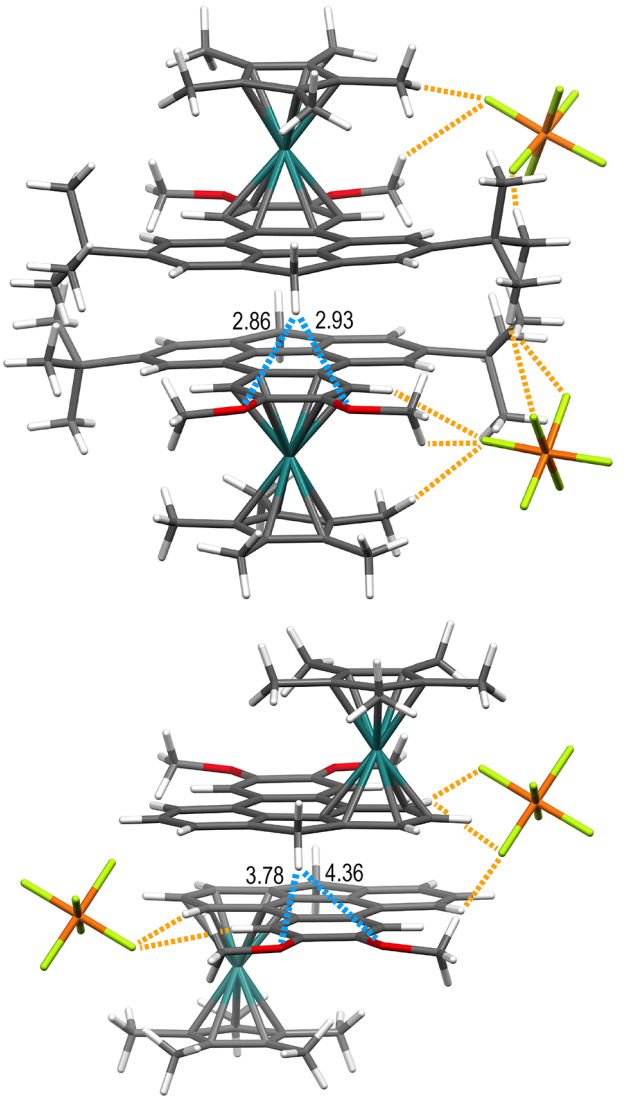

Figure 4. Molecular packing of $[RuCp^*(\eta^6\text{-}\mathbf{2})]PF_6\cdot(CH_2Cl_2)_2$ (top) and $[RuCp^*(\eta^6\text{-}\mathbf{4})]PF_6$ (bottom) showing C−H···O distances (Å, blue) and some C−H···F close contacts (2.36−2.64 Å, orange); solvent molecules omitted for clarity.

The complexes, however, display only nonreversible reductions, analogous to the behavior reported for $[RuCp^*(\text{arene})]^+$ derivatives and other 4d and 5d cationic 18-electron sandwich complexes and consistent with the reactivity of the resultant 19-electron neutral complex.[13,21,29−35] The complexes are all reduced at E_{pc} = −1.82 V, except $[RuCp^*(\eta^6\text{-}\mathbf{1})]PF_6$, which is reduced at −1.76 V. This anodic shift is thought to be due to the absence of the electron-donating *tert*-butyl and methoxy substituents, although the irreversibility of these process prevents a detailed analysis. $[RuCp^*(\eta^6\text{-}\mathbf{2})]PF_6$ and $[RuCp^*(\eta^6\text{-}\mathbf{3})]PF_6$ also display daughter peaks (reoxidations) that were probed using variable scan rates (50−2000 mV/s), becoming more pronounced as the scan rate increased, implying the daughter species is short-lived (Figures S8 and S9). It must be noted that when comparing the reduction potentials of the complexes, the coordination site is not consistent across all complexes and the CV data may not give

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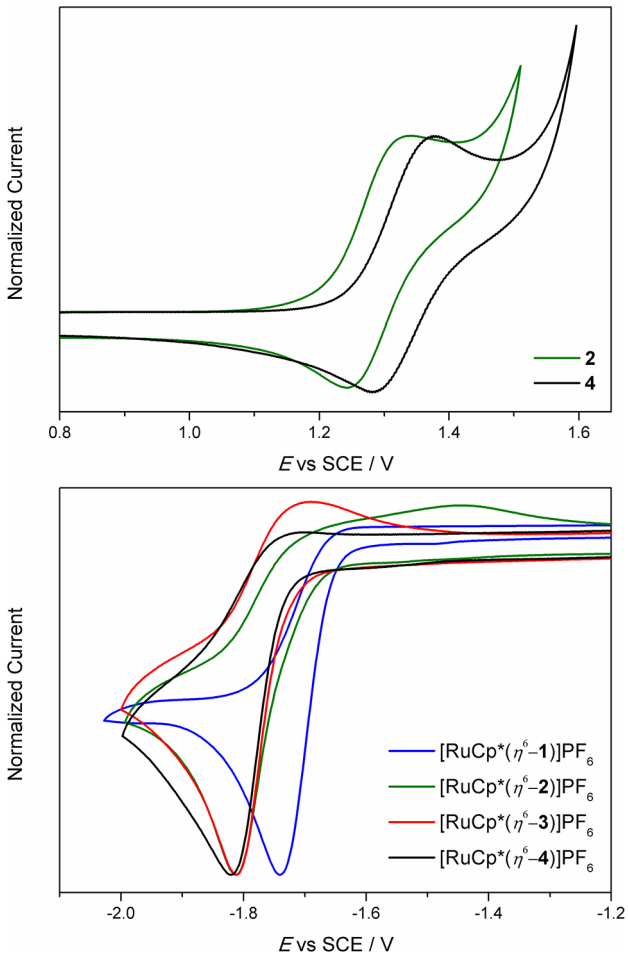

Figure 5. Cyclic voltammograms for **2** and **4** (top) and the complexes (bottom), measured in acetone with a scan rate of 100 mV/s.

an accurate representation of the effect of ligand substitution on redox behavior. The related [RuCp*(η^6-triphenylene)]PF_6 shows a one-electron irreversible reduction (E_{pc} = −1.87 V, propylene carbonate),[13] comparable to the behavior seen for [RuCp*(η^6-**1**)]PF_6.

Electronic Absorption/Emission. The absorption spectrum for cyclopentatriphenylene **1** (Figure 6) has a λ_{max} of 260 nm, which is slightly red-shifted when compared to triphenylene.[36] This is consistent with the electron-donating nature of the 4-methylene bridge decreasing the HOMO−LUMO gap and is supported by the further red-shift when the electron-donating methoxy and *tert*-butyl groups are introduced. The complexes, however, show no discernible trend, with [RuCp*(η^6-**4**)]PF_6 having λ_{max} at a much higher wavelength, compared to the other three complexes. The coordination site could also have a role to play, with [RuCp*(η^6-**4**)]PF_6 having full substitution on the ring C, while the other complexes either have full or some coordination to ring A/B. The ligands all show a similar higher energy shoulder peak, and the complexes show a similar lower energy shoulder peak, indicating the vibronic nature of the transitions. The complexes also display a weak low-energy band/tail at ~350 nm, characteristic of MLCT transitions.[37]

The emission spectra (Figure 7) also show a red-shift in moving from **1** (373 nm) to the most electron-rich ligand (**2**, 382 nm), analogous to the trend seen in the absorption spectrum. A broad low-energy shoulder can be observed and is

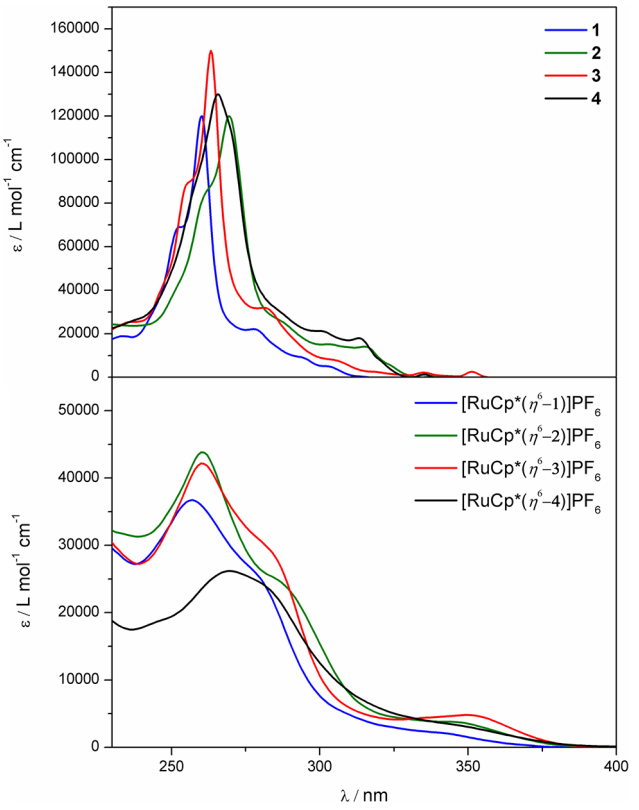

Figure 6. Absorption spectra of the ligands (top) and complexes (bottom), measured in CH_2Cl_2.

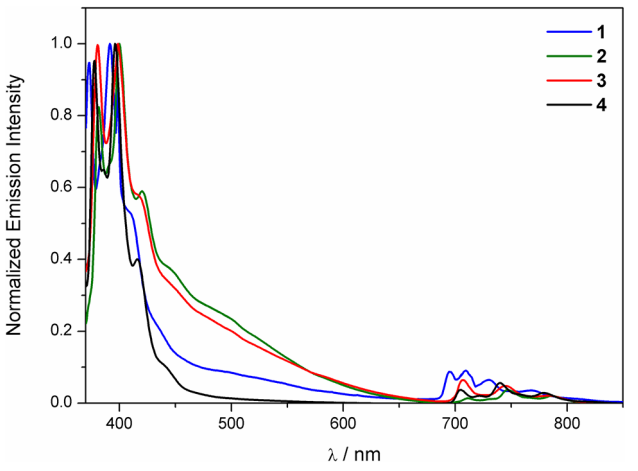

Figure 7. Emission spectra (351 nm excitation) of the ligands, measured in CH_2Cl_2.

characteristic of excimer formation.[38,39] An unusual low-energy emission (700−800 nm) is also observed across all ligands and is believed to originate from an uncharacterized second-order effect. In contrast, the complexes are nonemissive over the range 370−867 nm; this behavior is well known for group 8 sandwich complexes.[40−43]

CONCLUSION

A high-yielding route to 4*H*-cyclopenta[*def*]triphenylene **1** via substituted intermediates **2** and **3** has been described, providing access to potential ligands with a polycyclic core structure falling between the known triphenylene and sumanene PAHs. The complexation site of ligands **1**, **2**, **3**, and **4** with the

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$[RuCp^*]^+$ moiety was probed to elucidate the significance of both the electronic and steric properties of the substituents on each ligand. It was found that *tert*-butyl and even methoxy substituents provided enough steric hindrance to block coordination to aryl sites bearing these substituents when a less-hindered site was available. The low sensitivity of the $[RuCp^*]^+$ fragment to arene electronics and the importance of steric interactions agree with the conclusions of Nolan et al. resulting from a systematic thermochemical study.[1] In the absence of any substituents, the complexation of $[RuCp^*]^+$ was found to occur at both ring A/B and ring C, with the product distribution approximately following a statistical distribution. In no case did complexation occur on the "empty" ring **D**, attributed to an expected unfavorable perturbation of the π-sextet aromaticity of the other three benzenoid rings. Furthermore, the peripheral five-membered ring did not behave as a cyclopentadienyl analogue under the conditions of the complexation studies reported here. Reaction under basic conditions should facilitate the formation of η^5-complexes as analogues of the catalytically important fluorenyl metallocenes. The redox and electronic absorption/emission behavior of both the cyclopenta[*def*]triphenylene ligands and their $[RuCp^*]^+$ complexes was examined, with the results broadly in line with those reported for related smaller, unsubstituted PAHs.[13] While the ligands are blue emissive, introduction of a $[RuCp^*]^+$ fragment quenches this emission.

EXPERIMENTAL SECTION

General Experimental Procedures. Inert atmospheres were achieved under standard Schlenk techniques; if no conditions are stated, then the reaction was carried out open to the atmosphere. Microwave reactions were carried out in a sealed glass tube in a CEM Discover S Class microwave reactor at a fixed temperature by modulation of power (max 300 W). 2,7-Di(*tert*-butyl)-9*H*-fluorene (**6**)[44] and $[Ru(\mu_3\text{-Cl})Cp^*]_4$ (**11**)[3] were synthesized according to literature procedures or a variation thereof. All other chemicals were commercially purchased and used as received. Dry solvents were obtained from a Pure-Solv MD-6 solvent purification system; all other solvents were AR grade unless otherwise stated. Spectroscopic and electrochemical measurements used Aldrich spectroscopic or HPLC grade solvent. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Varian 500 AR spectrometer at 25 °C and are referenced to residual nonperdeuterated solvent: $CDCl_3$ (7.26 ppm) or $CD_3C(O)CD_3$ (2.05 ppm) and $CDCl_3$ (77.16 ppm) or $CD_3C(O)CD_3$ (29.84 ppm), respectively, as reported by Gottlieb et al.[45] ^{1}H and ^{13}C NMR spectra were assigned using 2D spectroscopies (COSY, NOESY, ^{1}H,^{13}C-HSQC, and ^{1}H,^{13}C-HMBC). ESI mass spectra were recorded on a Bruker MicrOTOF-Q mass spectrometer using a CH_2Cl_2 or acetone solution diluted into methanol. MALDI-TOF mass spectra were recorded on an Applied Biosystems 4800 Tandem TOF mass spectrometer with external calibration to within $m/z \pm 0.08$; solid analyte and TCNQ matrix were mixed using a mini mixer-mill, suspended in hexane and transferred to the sample plate. Microanalyses were performed at the Campbell Microanalytical Laboratory, University of Otago. IR spectra were recorded neat on a Bruker Alpha-P FTIR spectrometer with an attenuated total reflectance (ATR) module over the range 400−4000 cm^{-1}. The electrochemical cell for cyclic voltammetry was made up of a 1 mm diameter platinum rod working electrode embedded in a KeL-F cylinder with a platinum auxiliary electrode and a Ag/AgCl reference electrode. The potential of the cell was controlled by an ADI Powerlab 4SP potientiostat. Solutions were typically about 10^{-3} M in acetone with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte and were purged with argon for approximately 5 min prior to measurement. The default scanning rate was 100 mV s^{-1}, and the cyclic voltammograms were calibrated against the decamethylferrocenium/decamethylferrocene (Fc*) couple and are reported relative to the saturated calomel electrode (SCE).[46] Absorption spectra were recorded as DCM solutions on a PerkinElmer Lambda 950 UV−vis−NIR spectrometer. Emission spectra were recorded as 1×10^{-4} mol L^{-1} solutions, using a previously described instrument setup.[47]

*4-Bromo-2,7-di(tert-butyl)-9H-fluorene (**7**).* Fluorene **6** (3.00 g, 10.77 mmol) and I_2 (0.150 g, 0.59 mmol) were dissolved in DCM (21 mL) at 0 °C. A solution of Br_2 (0.6 mL, 11.65 mmol) in DCM (9 mL) was added dropwise, and the mixture stirred for 1 h at 0 °C. The product was extracted into Et_2O, washed with water and NaOH solution, then dried over $MgSO_4$. The solvent was removed *in vacuo* to afford **7** as a white solid (3.86 g, quant.). ^{1}H NMR (400 MHz, $CDCl_3$):[44] δ 8.45 (d, J = 8.0 Hz, 1H, H-5), 7.56 (s, 1H, Ar), 7.51 (s, 1H, Ar), 7.48 (s, 1H, Ar), 7.45 (dd, J = 8.0, 2.0 Hz, 1H, H-6), 3.90 (s, 2H, H-9), 1.38 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu).

*2,7-Di-tert-butyl-4-(3,4-dimethoxyphenyl)-9H-fluorene (**5**).* A mixture of **7** (2.50 g, 7.00 mmol), 3,4-dimethoxyphenylboronic acid (1.91 g, 10.5 mmol), K_2CO_3 (3.20 g, 23.1 mmol), toluene (40 mL), water (20 mL), and ethanol (10 mL) was deoxygenated. $PdCl_2$(dppf) (0.236 g, 0.29 mmol) was added, and the solution heated to 80 °C with stirring under argon for 18 h. The organic layer was extracted into DCM, washed with water, and dried over $MgSO_4$. The solvent was removed *in vacuo*, followed by purification via column chromatography (SiO_2, 20% DCM/PE), to afford **5** as a white solid (2.59 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 1.0 Hz, 1H, H-1), 7.53 (d, J = 1.0 Hz, 1H, H-8) 7.22 (d, J = 2.0 Hz, 1H, H-3), 7.11 (dd, J = 8.5, 1.5 Hz, 1H, H-6), 7.04−6.99 (m, 3H, H-2′,5′,6′), 6.94 (d, J = 8.0 Hz, 1H, H-5), 5.31 (s, 0.3H, CH_2Cl_2), 3.99 (s, 3H, OCH_3), 3.92 (s, 2H, H-9), 3.88 (s, 3H, OCH_3), 1.40 (s, 9H, ^{t}Bu-2), 1.32 (s, 9H, ^{t}Bu-7). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.3, 149.2, 148.8, 148.4, 144.1, 143.8, 139.1 (C-4a), 136.6, 136.5 (C-4b), 134.8, 125.9 (C-3), 123.5 (C-6), 122.1 (C-5), 121.8 (C-8), 121.4 (C-6′), 120.9 (C-1), 112.8 (C-2′/C-5′), 111.2 (C-2′/C-5′), 56.1 (2 × OCH_3), 37.3 (C-9), 34.9 (^{t}Bu-2, quat), 34.8 (^{t}Bu-7, quat), 31.8 (^{t}Bu-2, CH_3), 31.7 (^{t}Bu-7, CH_3). IR: $\tilde{\nu}$ (cm^{-1}) 2952(s), 1509(s), 1459(s), 1241(s), 1217(s), 1172(s), 1136(s), 1031(s), 833(s), 808(s). Anal. Calcd for $C_{29}H_{34}O_2 \cdot 0.1(CH_2Cl_2)$: C, 82.61; H, 8.15. Found: C, 82.31; H, 8.60. HR-ESI-MS: m/z 437.243 (100), 438.246 (32), 439.245 (5); calcd for $[M + Na]^+$ ($C_{29}H_{34}O_2Na$) 437.245 (100), 438.248 (32), 439.252 (5).

*2,6-Di(tert-butyl)-9,10-dimethoxy-4H-cyclopenta[def]-triphenylene (**2**).* A solution of **5** (1.05 g, 2.54 mmol) in HPLC grade DCM (170 mL) was purged with N_2 for 10 min and with the N_2 gently bubbling, $FeCl_3$ (1.65 g, 10.2 mmol) in nitromethane (10 mL) was added dropwise over 5 min. The dark solution was stirred and bubbled for a further 10 min, upon which the reaction was quenched with water (60 mL). The organic layer was washed with water until the aqueous layer was colorless and dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was purified using column chromatography (50% DCM/PE), yielding **2** (0.985 g, 94%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 2H, H-1,7), 8.03 (s, 2H, H-8,11), 7.78 (d, J = 1.0 Hz, 2H, H-3,5), 4.28 (s, 2H, H-4), 4.18 (s, 6H, OCH_3), 1.55 (s, 18H, ^{t}Bu). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.7, 149.0, 141.7, 134.9, 125.6, 125.3, 119.9 (C-5, 3), 114.9 (C-1, 7), 105.7 (C-8, 11), 56.3 (OCH_3), 37.8 (C-4), 36.0 (^{t}Bu, quat), 32.4 (^{t}Bu, CH_3). IR: $\tilde{\nu}$ (cm^{-1}) 2948(s), 2895(m), 1541(s), 1488(s), 1415(s), 1252(s), 1223(s), 1065(s), 835(s), 766(s). Anal. Calcd for $C_{29}H_{32}O_2$: C, 84.43; H, 7.82. Found: C, 83.94; H, 7.97. HR-ESI-MS: m/z 413.248 (100), 414.253 (25), 415.255 (4); calcd for $[M + H]^+$ ($C_{29}H_{33}O_2$) 413.248 (100), 414.251 (32), 415.254 (5). Crystals of **2** suitable for an X-ray diffraction structural determination were grown by slowly cooling a hot concentrated solution of **2** in MeOH.

*2,6-Di(tert-butyl)-9,10-dihydroxy-4H-cyclopenta[def]-triphenylene (**8**).* BBr_3 (0.58 mL, 6.06 mmol) was added dropwise to a solution of **2** (0.500 g, 1.21 mmol) in dry DCM (25 mL) at 0 °C. The solution was warmed to rt and left to stir for 3 h, upon which the excess BBr_3 was quenched with MeOH (20 mL) added dropwise. An additional 20 mL of DCM was added, the organic layer washed with water and brine and dried over $MgSO_4$, and the solvent removed *in vacuo* to give **8** (0.458 g, 98%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 2H, H-1,7), 8.11 (s, 2H, H-8,11), 7.76 (s, 2H, H-3,5), 5.47 (s, 2H, OH), 4.26 (s, 2H, H-4), 1.52 (s, 18H, ^{t}Bu). ^{13}C

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NMR (126 MHz, $CDCl_3$): δ 150.7, 143.4, 141.6, 134.9, 126.3, 125.2, 120.0 (C-2,5), 115.2 (C-1,7), 109.9 (C-8,11), 37.8 (C-4), 36.0 (^{t}Bu, quat), 32.4 (^{t}Bu, CH_3). IR: $\tilde{\nu}$ (cm^{-1}) 3495(m), 3299(m), 2960(s), 1569(m), 1474(m), 1417(m), 1264(s), 1199(m), 851(s). HR-ESI-MS: m/z 407.197 (100), 408.200 (31), 409.204 (10); calcd for $[M + Na]^+$ ($C_{27}H_{28}O_2Na$) 407.198 (100), 408.202 (30), 409.205 (5).

*2,6-Di(tert-butyl)-9,10-ditriflyloxy-4H-cyclopenta[def]triphenylene (**9**).* Triflic anhydride (2.84 mL, 16.88 mmol) was added dropwise to a solution of **8** (1.172 g, 3.05 mmol) and pyridine (1.5 mL, 18.6 mmol) in HPLC grade DCM (40 mL) at 0 °C. The solution was stirred for 30 min and a further 10 min at rt, upon which HCl (10%, 20 mL) was added. The yellow organic layer was washed with water and NH_4Cl (sat) and dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was purified using column chromatography (50% DCM/PE), yielding **9** (1.93 g, 97%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (s, 2H, H-8,11), 8.21 (s, 2H, H-1,7), 7.93 (d, J = 1.0 Hz, 2H, H-3,5), 4.32 (s, 2H, H-4), 1.55 (s, 18H, ^{t}Bu). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.0, 141.9, 138.4, 136.1, 132.2, 123.6, 122.8 (C-3,5), 119.0 (C-8,11), 118.9 (q, J_{CF} = 320.5 Hz, CF_3), 115.8 (C-1,7), 37.7 (C-4), 36.1 (^{t}Bu, quat), 32.2 (^{t}Bu, CH_3). IR: $\tilde{\nu}$ (cm^{-1}) 2963(m), 1412(s), 1212(s), 1132(s), 1104(s), 1019(m), 905(s), 848(s), 608(s). Anal. Calcd for $C_{29}H_{26}F_6O_6S_2$: C, 53.70; H, 4.04. Found: C, 53.58; H, 3.95. HR-ESI-MS: m/z 671.094 (100), 672.095 (36), 673.099 (17), 674.101 (4); calcd for $[M + Na]^+$ ($C_{29}H_{26}F_6O_6S_2$) 671.097 (100), 672.100 (33), 673.097 (16), 674.094 (4).

*2,6-Di(tert-butyl)-4H-cyclopenta[def]triphenylene (**3**).* Triethylsilane (1.05 mL, 6.57 mmol) was added to a mixture of **9** (0.813 g, 1.25 mmol), $Pd(OAc)_2$ (0.029 g, 0.13 mmol), and 1,3-bis-(diphenylphosphino)propane (0.052 g, 0.13 mmol) in DMF (30 mL) at 60 °C under argon. The reaction mixture was stirred for 18 h, then cooled to rt. The organic layer was extracted into ether, washed with water and $NaHCO_3$ (sat), and dried over $MgSO_4$. The solvent was removed *in vacuo* to give the crude product. Purification using column chromatography (SiO_2, 10% DCM/PE) yielded **3** (0.427 g, 97%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (dd, J = 6.0, 3.5 Hz, 2H, H-8,11), 8.35 (s, 2H, H-1,7), 7.83 (d, J = 1.0 Hz, 2H, H-3,5), 7.69 (dd, J = 6.0, 3.5 Hz, 2H, H-9,10), 4.29 (s, 2H, H-4), 1.55 (s, 18H, ^{t}Bu). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.8, 141.6, 135.5, 131.4, 126.6 (C-9,10), 125.6, 124.2 (C-8,11), 120.7 (C-3,5), 115.7 (C-1,7), 37.8 (C-4), 36.0 (^{t}Bu, quart), 32.4 (^{t}Bu, CH_3). IR: $\tilde{\nu}$ (cm^{-1}) 2944(s), 2899(s), 1596(m), 1415(s), 1361(m), 852(s), 762(s), 637(s). Anal. Calcd for $C_{27}H_{28}$: C, 91.99; H, 8.01. Found: C, 91.62; H, 7.66. HR-ESI-MS: m/z 352.218 (100), 353.223 (42), 354.225 (9); calcd for $[M]^+$ ($C_{27}H_{28}$) 352.219 (100), 353.222 (30), 354.225 (4). Crystals of **3** suitable for an X-ray diffraction structural determination were grown by slowly cooling a hot, concentrated solution of **3** in EtOH.

*4H-Cyclopenta[def]triphenylene (**1**).* $AlCl_3$ (0.158 g, 1.19 mmol) was added to a solution of **3** (0.417 g, 1.18 mmol) in dry toluene (80 mL) under argon. The suspension was heated to 60 °C and stirred for 3 h. Upon cooling the reaction mixture, HCl (100 mL, 0.2 M) was added. The organic layer was extracted into DCM, washed with water and NH_4Cl (sat), and dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was purified using column chromatography (SiO_2, 10% DCM/PE) to yield **1** (0.264 g, 93%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (dd, J = 7.0, 3.5 Hz, 2H, H-8,11), 8.33 (d, J = 8.0 Hz, 2H, H-1,7), 7.73 (dd, J = 7.0, 1.0 Hz, 2H, H-3,5), 7.72–7.67 (m, 4H, H-2,6,9,10) 4.31 (s, 2H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.8, 137.4, 131.0, 127.5, 127.1, 126.9, 124.3 (C-8,11), 122.6 (C-3,5), 119.5 (C-1,7), 37.6 (C-4). IR: $\tilde{\nu}$ (cm^{-1}): 1434(m), 1402(m), 1231(w), 747(s), 623(m), 549(m). Anal. Calcd for $C_{19}H_{12}$: C, 94.97; H, 5.03. Found: C, 94.74; H, 5.01. MALDI-TOF MS: m/z 240.05 (100), 241.05 (36), 242.05 (7); calcd for $[M]^+$ ($C_{18}H_{12}$) 240.09 (100), 241.10 (21), 242.10 (2). Crystals of **1** suitable for an X-ray diffraction structural determination were grown by slowly cooling a hot concentrated solution of **1** in MeOH.

*4-(3,4-Dimethoxyphenyl)-9H-fluorene (**10**).* $AlCl_3$ (0.401 g, 3.01 mmol) was added to a solution of **5** (0.500 g, 1.21 mmol) in dry toluene (100 mL) under argon. The orange suspension was stirred at rt for 2 h, upon which HCl (60 mL, 0.2 M) was added. The organic layer was extracted into DCM, washed with water and NH_4Cl (sat), and dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was purified using column chromatography (50% DCM/PE) to yield **10** (0.355 g, 97%) as a pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56–7.50 (m, 2H, H-1,8), 7.33 (t, J = 7.5 Hz, 1H, H-2), 7.24–7.21 (m, 2H, H-3,7), 7.09 (td, J = 8.0, 1.0 Hz, 1H, H-6), 7.06–7.00 (m, 4H, H-5,2′,5′,6′), 4.00 (s, 3H, OCH_3), 3.96 (s, 2H, H-9), 3.86 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.8, 148.5, 144.0, 143.8, 141.7, 139.0, 137.7, 134.1, 128.9 (C-3), 126.5 (C-7), 126.4 (C-6), 126.3 (C-2), 124.9 (C-8), 124.0 (C-1), 123.2 (C-5/C-6′), 121.3 (C-5/C-6′), 112.6 (C-2′/C-5′), 111.3 (C-2′/C-5′), 56.1 (2 × OCH_3), 37.1 (C-9). IR: $\tilde{\nu}$ (cm^{-1}) 3004(w), 2934(w), 1581(m), 1516(s), 1244(s), 1216(s), 1133(s), 810(m), 744(s), 598(m). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.47; H, 5.93. HR-ESI-MS: m/z 325.116 (100), 326.119 (24), 327.122 (3); calcd for $[M + Na]^+$ ($C_{21}H_{18}O_2Na$) 325.120 (100), 326.123 (23), 327.126 (3).

*10,11-Dimethoxy-4H-cyclopenta[def]triphenylene (**4**).* A solution of **10** (0.258 g, 0.85 mmol) in HPLC grade DCM (100 mL) was purged with N_2 for 10 min. With N_2 gently bubbling, $FeCl_3$ (0.553 g, 2.88 mmol) in nitromethane (3 mL) was added dropwise over 2 min. The dark solution was stirred and bubbled for a further 13 min, upon which the reaction was quenched with water (60 mL). The organic layer was washed with water until the aqueous layer was colorless and dried over $MgSO_4$, and the solvent removed *in vacuo* to give a solid. The crude solid was purified using column chromatography (40% DCM/PE), yielding **4** (0.223 g, 87%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (dd, J = 7.0, 1.5 Hz, 2H, H-1,7), 7.96 (s, 2H, H-8,11), 7.70–7.64 (m, 4H, H-2,3,5,6), 4.30 (s, 2H, H-4), 4.14 (s, 6H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.2 (C-9,10), 141.9, 136.8, 127.3 (C-2,3/C-6,5), 126.5, 125.1, 121.6 (C-2,3/C-6,5), 118.8 (C-1,7), 105.5 (C-8,11), 56.1 (OCH_3), 37.7 (C-4). IR: $\tilde{\nu}$ (cm^{-1}) 3016(w), 2960(w), 1615(m), 1540(m), 1433(s), 1257(m), 1163(m), 1062(m), 1041(m), 840(s), 757(s), 708(s). Anal. Calcd for $C_{21}H_{16}O_2 \cdot 0.2(CH_3CH_2OH)$: C, 83.03; H, 5.60. Found: C, 83.01; H, 5.52. HR-ESI-MS: m/z 323.104 (100), 324.107 (24), 325.114 (4); calcd for $[M + Na]^+$ ($C_{21}H_{16}O_2Na$): 323.104 (100), 324.108 (23), 325.111 (3). Crystals of **4** suitable for an X-ray diffraction structural determination were grown by slowly cooling a hot concentrated solution of **4** in EtOH.

General Procedure for Complexation. A mixture of $[Ru(\mu_3\text{-}Cl)Cp^*]_4$ (**11**) (0.060 g, 0.055 mmol), ligand (0.22 mmol), deoxygenated THF (6 mL), and water (6 mL) were sealed in a 30 mL microwave tube under argon. The dark brown mixture was heated in a microwave reactor at 130 °C for 15 min. Once cooled to rt, the pale brown mixture was left open to air for 30 min, then filtered through Celite, rinsing with water. Aqueous KPF_6 (20 mL, sat) was added to the solution, which was stirred for a further 30 min. The mixture was extracted with DCM and washed with water. The solvent was removed *in vacuo* to give the complex, which was purified via column chromatography (10% MeOH/DCM), if needed, yielding $[RuCp^*(\eta^6\text{-cyclopentatriphenylene})]PF_6$ as a white solid.

[RuCp(η⁶-**1**)]PF₆.* Yield: 0.035 g, 26%. ^{31}P NMR (162 MHz, $CD_3C(O)CD_3$): δ −144.3 (sept, J = 707 Hz). IR: $\tilde{\nu}$ (cm^{-1}) 2920(w), 2848(w), 1379(w), 1029(m), 836(s), 737(m), 557(s). Anal. Calcd for $C_{29}H_{27}F_6PRu$: C, 56.04; H, 4.38. Found: C, 56.26; H, 4.45. HR-ESI-MS: m/z 471.115 (15), 472.116 (5), 473.114 (6), 474.113 (36), 475.112 (44), 476.113 (58), 477.112 (100), 478.115 (29), 479.113 (54), 480.116 (16); calcd for $[M - PF_6]^+$ ($C_{29}H_{27}Ru$): 471.118 (15), 472.122 (5), 473.117 (6), 474.117 (36), 475.116 (44), 476.117 (58), 477.116 (100), 478.119 (29), 479.117 (54), 480.120 (16). Crystals of $[RuCp^*(\eta^6\text{-}\mathbf{1})]PF_6$ suitable for an X-ray diffraction structural determination were grown by vapor diffusion of ether into a concentrated sample of $[RuCp^*(\eta^6\text{-}\mathbf{1})]PF_6$ in acetone. *Symmetrical isomer.* ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.28 (d, J = 8.0 Hz, 2H, H-1,7), 7.95 (d, J = 7.5 Hz, 2H, H-3,5), 7.81 (t, J = 7.5 Hz, 2H, H-2,6), 7.30 (dd, J = 6.0, 3.5 Hz, 2H, H-8,11), 6.42 (dd, J = 4.5, 2.5 Hz, 2H, H-9,10), 4.38 (s, 2H, H-4), 1.40 (s, 15H, Cp*). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 143.2, 138.7, 129.7 (C-2,6), 126.9 (C-3,5), 123.8, 122.2 (C-1,7), 96.2 (Cp*-ring), 94.3, 88.9 (C-9,10), 83.4 (C-

dx.doi.org/10.1021/om5008852 | *Organometallics* XXXX, XXX, XXX–XXX

8,11), 38.2 (C-4), 9.3 (Cp*-CH_3). *Unsymmetrical isomer.* ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.76 (d, J = 7.5 Hz, 1H, H-7), 8.55 (d, J = 7.5 Hz, 1H, H-11), 8.47 (d, J = 7.5 Hz, 1H, H-8), 7.94−7.82 (m, 4H, H-5, 6, H-9, H-10), 7.16 (d, J = 6.0 Hz, 1H, H-1), 6.72 (d, J = 5.5 Hz, 1H, H-3), 6.20 (t, J = 5.5 Hz, 1H, H-2), 4.34 (d, J = 21.5 Hz, 1H, H-4b), 4.14 (d, J = 21.5 Hz, 1H, H-4a), 1.32 (s, 15H, Cp*). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 142.5, 133.4, 133.2, 131.7, 131.1, 129.6, 129.2, 127.7, 127.0 (C-11), 126.1 (C-7), 125.7, 121.8 (C-8), 104.1, 100.8, 95.1 (Cp*-ring), 92.7, 87.7 (C-2), 86.4 (C-3), 80.6 (C-1), 36.8 (C-4), 8.8 (Cp*-CH_3).

[RuCp(η^6-**2**)]PF_6.* Yield: 0.043 g, 27%. ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.42 (s, 2H, H-1,7), 8.04 (s, 2H, H-3,5), 7.46 (s, 2H, H-8,11), 4.40 (d, J = 21.5 Hz, 1H, H-4), 4.33 (d, J = 21.5 Hz, 1H, H-4), 4.18 (s, 6H, OCH_3), 1.53 (s, 18H, ^{t}Bu), 1.34 (s, 15H, Cp*). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 153.4, 142.9, 136.5, 124.8, 124.0 (C-3,5), 123.1, 119.1 (C-1,7), 94.5 (Cp*-ring), 91.1, 70.9 (C-8,11), 58.3 (OCH_3), 38.4 (C-4), 36.7 (^{t}Bu, quart), 32.3 (^{t}Bu, CH_3), 9.0 (Cp*-CH_3). ^{31}P NMR (162 MHz, $CD_3C(O)CD_3$): δ −144.3 (sept, J_{PF} = 707 Hz). IR: $\tilde{\nu}$ (cm^{-1}) 2958(m), 1415(m), 1266(m), 1200(m), 838(s), 765(m), 556(s). Anal. Calcd for $C_{39}H_{47}F_6O_2PRu$: C, 59.01; H, 5.97. Found: C, 58.77; H, 6.17. HR-ESI-MS: m/z 643.262 (13), 644.261 (6), 645.263 (6), 646.262 (33), 647.260 (45), 648.262 (60), 649.261 (100), 650.263 (38), 651.261 (54), 652.265 (20), 653.266 (4); calcd for $[M - PF_6]^+$ ($C_{39}H_{47}O_2Ru$): 643.265 (14), 644.268 (6), 645.264 (6), 646.263 (34), 647.263 (45), 648.263 (59), 649.262 (100), 650.265 (38), 651.263 (54), 652.266 (21), 653.269 (4). Crystals of [RuCp*(η^6-**2**)]PF_6 suitable for an X-ray diffraction structural determination were grown by vapor diffusion of ether into a concentrated sample of [RuCp*(η^6-**2**)]PF_6 in DCM.

[RuCp(η^6-**3**)]PF_6.* Yield: 0.090 g, 55%. ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.38 (s, 2H, H-1,7), 8.08 (s, 2H, H-3,5), 7.50 (dd, J = 4.5, 2.5 Hz, 2H, H-8,11), 6.41 (dd, J = 4.5, 2.5 Hz, 2H, H-9,10), 4.42 (d, J = 21.5 Hz, 1H, H-4), 4.35 (d, J = 21.5 Hz, 1H, H-4), 1.54 (s, 18H, ^{t}Bu), 1.40 (s, 15H, Cp*). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 153.5, 143.0, 136.8, 124.5 (C-3,5), 122.8, 119.0 (C-1,7), 96.0, 94.9 (Cp*-ring), 88.7 (C-9,10), 83.5 (C-8,11), 38.4 (C-4), 36.7 (^{t}Bu, quart), 32.3 (^{t}Bu, CH_3), 9.2 (Cp*-CH_3). ^{31}P NMR (162 MHz, $CD_3C(O)CD_3$): δ −144.3 (sept, J_{PF} = 707 Hz). IR: $\tilde{\nu}$ (cm^{-1}) 2923(s), 2853(m), 1735(m), 1255(m), 1029(m), 844(s), 557(s). Anal. Calcd for $C_{37}H_{43}F_6PRu$: C, 60.56; H, 5.91. Found: C, 60.57; H, 6.01. HR-ESI-MS: m/z 583.237 (14), 584.240 (6), 585.235 (6), 586.237 (34), 587.237 (45), 588.238 (59), 589.237 (100), 590.238 (38), 591.237 (54), 592.239 (20), 593.240 (4); calcd for $[M - PF_6]^+$ ($C_{37}H_{42}Ru$): 583.244 (14), 584.247 (6), 585.243 (6), 586.232 (34), 587.232 (45), 588.232 (59), 589.231 (100), 590.244 (36), 591.242 (54), 592.235 (20), 593.238 (4).

[RuCp(η^6-**4**)]PF_6.* Yield: 0.048 g, 32%. ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.47 (m, 1H, H-7), 8.25 (s, 1H, H-8), 8.04 (s, 1H, H-11), 7.84−7.79 (m, 2H, H-5,6), 7.25 (d, J = 6.0 Hz, 1H, H-1), 6.67 (d, J = 5.5 Hz, 1H, H-3), 6.15 (t, J = 6.0 Hz, 1H, H-2), 4.35 (d, J = 21.5 Hz, 1H, H-4b), 4.16 (d, J = 21.5 Hz, 1H, H-4a), 4.15 (s, 3H, OCH_3-9), 4.10 (s, 3H, OCH_3-10), 1.35 (s, 15H, Cp*). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 152.6 (C-9), 151.4 (C-10), 142.4 (C-4a), 131.4 (C-5/C-6), 129.5, 127.6, 124.5 (C-5/C-6), 121.5 (C-7), 120.7, 108.8 (C-11), 108.0 (C-8), 103.9 (C-3a), 100.4, 97.8, 94.8 (Cp*-ring), 93.8, 87.4 (C-2), 85.8 (C-3), 80.3 (C-1), 56.8 (OCH_3-10), 56.5 (OCH_3-9), 36.8 (C-4), 8.9 (Cp*-CH_3). ^{31}P NMR (162 MHz, $CD_3C(O)CD_3$): δ −144.3 (sept, J_{PF} = 708 Hz). IR: $\tilde{\nu}$ (cm^{-1}) 3096(w), 2918(w), 1610(m), 1390(m), 1211(m), 830(s), 555(s). Anal. Calcd for $C_{31}H_{31}F_6O_2PRu$: C, 54.63; H, 4.58. Found: C, 54.97; H, 4.61. HR-ESI-MS: m/z 531.139 (14), 532.143 (4), 533.139 (5), 534.138 (36), 535.137 (43), 536.138 (61), 537.136 (100), 538.140 (31), 539.137 (52), 540.141 (17), 541.144 (3); calcd for $[M - PF_6]^+$ ($C_{31}H_{31}O_2Ru$): 531.139 (15), 532.143 (5), 533.138 (6), 534.138 (35), 535.137 (45), 536.138 (58), 537.137 (100), 538.140 (31), 539.138 (54), 540.141 (17), 541.144 (3). Crystals of [RuCp*(η^6-**4**)]PF_6 suitable for an X-ray diffraction structural determination were grown by vapor diffusion of ether into a concentrated sample of [RuCp*(η^6-**4**)]PF_6 in acetone.

[RuCp^{OH}(η^6-**4**)]PF_6.* ^{1}H NMR (500 MHz, $CD_3C(O)CD_3$): δ 8.45 (m, 1H, H-6), 8.20 (s, 1H, H-8), 8.00 (s, 1H, H-11), 7.83−7.79 (m, 2H, H-5,6), 7.27 (d, J = 6.0 Hz, 1H, H-1), 6.71 (d, J = 5.5 Hz, 1H, H-3), 6.18 (t, J = 5.5 Hz, 1H, H-2), 4.34 (d, J = 21.0 Hz, 1H, H-4b), 4.18 (d, J = 21.0 Hz, 1H, H-4a), 4.14 (s, 3H, OCH_3-9), 4.09 (s, 3H, OCH_3-10), 3.87 (m, 2H, $CpCH_2$-1′), 1.47 (s, 3H, $CpCH_3$-2′/5′), 1.39 (s, 3H, $CpCH_3$-2′/5′), 1.23 (s, 3H, $CpCH_3$-3′/4′), 1.19 (s, 3H, $CpCH_3$-3′/4′). ^{13}C NMR (126 MHz, $CD_3C(O)CD_3$): δ 152.62 (C-9), 151.37 (C-10), 142.45 (C-4a), 132.85, 131.53 (C-5/6), 129.47, 127.53, 124.55 (C-5/6), 121.50 (C-7), 120.63, 108.73 (C-11), 107.90 (C-8), 104.33 (C-3a), 100.70, 95.64 (Cp-ring), 95.61 (Cp-ring), 95.50 (Cp-ring), 95.07 (Cp-ring), 94.95 (Cp-ring), 93.94, 87.08 (C-2), 85.57 (C-3), 80.06 (C-1), 56.75 (OCH_3-10), 56.54 (OCH_3-9), 55.05 ($CpCH_2OH$), 37.10 (C-4), 8.88 ($CpCH_3$-2′/5′), 8.87 ($CpCH_3$-2′/5′), 8.46 (2 × $CpCH_3$-3′,4′). ^{31}P NMR (162 MHz, $CD_3C(O)CD_3$): δ −144.3 (sept, J_{PF} = 707 Hz). IR: $\tilde{\nu}$ (cm^{-1}) 3582(m), 2948(w), 1611(m), 1538(m), 1268(m), 1212(m), 830(s), 762(s), 555(s). Anal. Calcd for $C_{31}H_{31}F_6O_3PRu$: C, 53.37; H, 4.48. Found: C, 53.78; H, 4.58. HR-ESI-MS: m/z 547.133 (14), 548.132 (5), 549.130 (7), 550.131 (36), 551.129 (45), 552.131 (60), 553.130 (100), 554.132 (31), 555.131 (55), 556.134 (16), 557.135 (3); calcd for $[M - PF_6]^+$ ($C_{31}H_{31}ORu$) 547.134 (14), 548.132 (5), 549.133 (6), 550.133 (35), 551.132 (45), 552.133 (58), 553.132 (100), 554.135 (31), 555.133 (54), 556.136 (17), 557.139 (3). Crystals of [RuCp*^{OH}(η^6-**4**)]PF_6 suitable for an X-ray diffraction structural determination were grown by vapor diffusion of ether into a concentrated sample of [RuCp*^{OH}(η^6-**4**)]PF_6 in acetone.

X-ray Crystallography. Crystallographic data collection and refinement details for **1**−**4**, [RuCp*(**1**,**2**,**4**)]PF_6, and [RuCp*^{OH}(**4**)]PF_6 are reported in Table S1 in the Supporting Information. Data were collected on an Agilent SuperNova with Atlas CCD using mirror monochromated microfocus Cu Kα radiation (λ = 1.541 84 Å) at 40 W. The data processing was undertaken within CrysAlisPro,[48] including a numerical absorption correction over a face-indexed model and/or a multiscan empirical correction. The structures were solved by direct methods with SHELXS-97[49,50] and extended and refined against all F^2 data with SHELXL-97[49,50] using the X-Seed interface.[51] The non-hydrogen atoms in the asymmetric unit were modeled with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C−H distances (sp^2-CH 0.95 Å, sp^3-CH_3 0.98 Å, sp^3-CH_2 0.99 Å) and isotropic displacement parameters estimated as $U_{iso}(H)$ = $1.2U_{eq}(C)$, except for CH_3, where $U_{iso}(H)$ = $1.5U_{eq}(C)$. Special conditions/variations to the general procedure are given below.

2: The fine needle crystals did not diffract strongly, some appearing to be twinned based on the diffraction pattern during screening and poor agreement with the best cell. Full collection was undertaken on a small specimen, resulting in weak data that refined with relatively high residuals (R_1 = 11.2%).

[RuCp(**1**)]PF_6:* The asymmetric unit contains the complex cation, a PF_6 anion, along with an acetone molecule on a mirror plane. The solution appeared to fit the unsymmetrical RuCp* complex; however, there was significant electron density in a bay position opposite the metal, suggesting a methylene bridge at this site. A disordered model with two complete cations was refined with rotation of the cyclopentatriphenylene by ca. 120°, and the Cp* by ca. 35°. This model is consistent with the cocrystallization of both isomeric products (refining to 70% unsymmetric, 30% symmetric), with the Ru atom approximately co-sited for both. Extensive use of restraints ensured the two components had similar and sensible geometric parameters; SAME restraints across the two cyclopentatriphenylenes and two Cp* orientations were used, along with FLAT restraints for the Cp* rings and some benzenoid rings. Most of the electron density was accounted for using this approach, although atomic precision is low.

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■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for **1**−**5**, **8**−**10**, and all complexes, 2D NOESY spectrum for [RuCp*(**4**)]PF_6, ORTEP diagrams for **1**−**4** and packing diagrams for **1**−**4**, and [RuCp*^{OH}(**4**)]PF_6, a table of X-ray crystallographic data and structure refinement parameters (along with CIFs), table of selected bond lengths for the ligands and complexes, and variable scan rate cyclic voltammograms for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determinations have also been deposited with the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk) as CCDC Nos. 1021293−1021300.

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Notes

The authors declare no competing financial interest.

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