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Synthesis and Structures of Ru(II)-*p*-Cymene Sandwich Complexes with Electron-Withdrawing Cyclopentadienyl Ligands

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Abstract

A modular synthetic route has been developed to prepare a new series of cationic ruthenium(II) complexes with electron-withdrawing 1,2-diacylcyclopentadienyl ligands. The 2-acyl-6-hydroxyfulvenes were synthesized from cyclopentadienide and acyl chlorides and converted to Tl(I) cyclopentadienyl salts using Tl_2SO_4/KOH. Transmetalation with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ followed by PF_6^- metathesis gives the complexes [Ru{η^5-1,2-C_5H_3(CO–R)$_2$}(η^6-*p*-cymene)][PF_6] (R = *t*-Bu, *p*-Tol, *p*-ClC_6H_4, *p*-IC_6H_4) in moderate to high yields. The new compounds were characterized by NMR and IR spectroscopy; mass spectrometry and elemental analysis were performed where applicable. X-ray analysis of one of the complexes confirms that electron-deficient Cp ligands retain η^5-coordination and structural planarity within Ru(II)–arene sandwich architectures, highlighting their potential utility in electronically tunable organometallic frameworks.

Keywords: ruthenium(II) sandwich complexes; *p*-cymene coordination; 1,2-diacylcyclopentadienyl ligand; X-ray crystallography; organometallic synthesis; thallium salts; cyclopentadienyl arene complexes

1. Introduction

Cationic ruthenium(II) complexes bearing η^6-coordinated arene ligand and ancillary neutral or anionic donor ligands have garnered widespread attention due to their robust structures and broad utility across diverse fields such as organic synthesis [1–3], medicinal chemistry [4,5], catalysis [6,7], transfer hydrogenation [8,9], and coordination-driven self-assembly [10]. Because their ligands can be readily exchanged or modified, these complexes offer a flexible platform for tuning reactivity and studying the influence of diverse ligand environments on metal-centered processes. While most examples involve neutral donor ligands paired with arenes [11,12], a less extensively explored subclass consists of mixed sandwich complexes with both η^5–cyclopentadienyl (Cp) and η^6–arene ligands, such as [Ru(η^5-Cp)(η^6–arene)]$^+$ [13,14]. Their well-defined structures make them valuable systems for probing ligand effects on metal reactivity [15]. These complexes typically incorporate electron-rich Cp ligands, such as pentamethylcyclopentadienyl (Cp*), which donate substantial electron density to stabilize the low-spin d^6 Ru(II) center [16]. In contrast, electron-poor Cp ligands, e.g., those bearing 1,2-diacyl groups, have received little attention in this context, despite their potential to modulate the electronic properties and reactivity of the cationic sandwich complexes.

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Our research group has long been focused on extending the π-conjugation of metal-bound cyclopentadienyl (Cp) ligands by building fused-ring systems through functional group transformations. The central approach involves the installation of a ketone or ester at the 1,2-positions of the Cp ring, often via 2-acyl-6-hydroxyfulvenes. Wallace and Selegue first demonstrated this strategy by synthesizing a pyridazine-fused pentamethylruthenocene through the condensation of a 1,2-diacyl Cp ligand with hydrazine [17]. Snyder and Tice extended this methodology to group VII metals, reporting the synthesis of analogous pyridazine-fused and thiophene-fused complexes from 1,2-diacyl Cp ligands coordinated to $Mn(CO)_3$ and $Re(CO)_3$ cores [18–20]. In a complementary direction, we utilized a ruthenocene diacyl chloride derivative, [Ru{1,2-$C_5H_3(COCl)_2$}(Cp*)], as a versatile synthon in Friedel–Crafts acylation reactions, generating ruthenocene-fused acenequinones [21]. These studies collectively established a robust modular platform for the synthesis of structurally complex metallocene-fused π-systems, particularly in neutral complexes.

In this work, we seek to extend this methodology into the domain of cationic ruthenium(II) sandwich complexes by combining diacylcyclopentadienyl ligands with η^6-coordinated *p*-cymene. To our knowledge, this represents one of the first examples of such systems and serves as a foundation for future derivatization.

2. Experimental Section

2.1. General Procedures

All reactions were carried out under dry nitrogen using standard Schlenk techniques unless otherwise stated. Organic solvents were purified by distillation under nitrogen after drying as follows: ethyl ether and tetrahydrofuran (THF) from sodium/benzophenone ketyl; dichloromethane and acetonitrile from CaH_2. Thallium(I) sulfate, α-phellandrene, dicyclopentadiene, and other reagents were obtained from commercial suppliers and used as received. $RuCl_3 \cdot 3H_2O$ was used to prepare [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ according to the literature method [22]. Dicyclopentadiene was thermally cracked to cyclopentadiene at 250 °C under nitrogen immediately before use. Fulvene **1a** [23] and thallium salts **2b** and **2c** [20] were prepared according to literature procedures. *p*-Iodobenzoyl chloride was prepared from *p*-iodobenzoic acid and oxalyl chloride [24]. Safety Note: Thallium(I) sulfate is highly toxic and should be handled with extreme care. All manipulations involving thallium compounds were performed using appropriate personal protective equipment and in a well-ventilated fume hood, following established institutional safety protocols. All thallium-containing waste was collected and disposed of according to hazardous waste regulations.

^1H and ^{13}C NMR spectra were recorded at 22 °C on a Varian Gemini-400 spectrometer (Varian, Inc., Palo Alto, CA, USA). Chemical shifts (δ) are reported in ppm relative to residual solvent resonances. Infrared spectra (Nujol mulls or KBr pellets) were recorded on an ATI-Mattson Galaxy Series 5000 FT-IR spectrometer (ATI Mattson Instruments, Inc., Madison, WI, USA); wavenumbers (ν) are given in cm^{-1}. Electron ionization mass spectra (EI, 70 eV) were obtained on a Thermo Finnigan PolarisQ quadrupole ion trap instrument (Thermo Finnigan, San Jose, CA, USA) at the University of Kentucky Mass Spectrometry Facility using a heatable direct insertion probe. Melting points were determined in open capillaries on a Thomas Hoover apparatus and are uncorrected. Elemental analyses were performed by the University of Illinois Microanalysis Laboratory (Urbana–Champaign, Urbana, IL, USA).

2.2. X-Ray Crystallography

Single-crystal X-ray diffraction data were collected at 90 K using a Nonius KappaCCD diffractometer (Nonius B.V., Delft, The Netherlands). Data collection and reduction employed Nonius COLLECT [25] and DENZO-SMN [26] with absorption correction by XABS2 [27]. Structure solution was by direct methods (SHELXS-97 [28]) and refined by full-matrix least squares on F^2 using SHELXL [29].

2.3. Experimental Procedures

2.3.1. Synthesis of 2-Acyl-6-Hydroxyfulvenes

1,2-C_5H_3(C(OH)C(CH_3)$_3$)(COC(CH_3)$_3$),1a. To a 500 mL three-necked round-bottom flask, cyclopentadiene (25.2 g, 381 mmol) was added dropwise to a stirred solution of n-butyllithium (160 mL, 2.5 M in hexane, 400 mmol) in anhydrous ethyl ether (150 mL) at 0 °C under nitrogen, a white precipitate of cyclopentadienyllithium that was stirred for 15 min. Pivaloyl chloride (30.6 g, 254 mmol) was added, and the resultant yellow suspension was stirred for an additional 2 h at room temperature. The reaction was quenched with 3% HCl (50 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl ether (3 × 50 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and volatiles were removed under reduced pressure to give an orange semi-solid. The crude product was purified by silica gel column chromatography using hexane/ether (60/40) as eluent. The first fraction was crystallized from methanol to give **1a** (7.65 g, 26%) as a yellow-orange powder. Mp: 88–89 °C (Lit. [17] 89–90 °C). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.47 (s, 18H, C(CH_3)$_3$), 6.38 (t, 1H, J = 3.5 Hz, CHCHCH), 7.20 (d, 2H, J = 3.5 Hz, CHCHCH), 19.32 (s, 1H, OH).

1,2-C_5H_3(C(OH)-4-IC_6H_4)(CO-4-IC_6H_4), 1d. Synthesis of **1d** was previously reported by Little and Koestler [30] without full characterization. Their procedure was followed with minor modifications. A 250 mL two-necked round-bottom flask was charged with sodium wire (0.94 g, 41 mmol) in ethyl ether (70 mL) at 0 °C under nitrogen. Cyclopentadiene (2.77 g, 42.0 mmol) was added dropwise, and the resultant suspension was stirred at room temperature for 2 h to generate cyclopentadienyl sodium. The mixture was cooled again to 0 °C, and a solution of *p*-iodobenzoyl chloride (6.24 g, 25.2 mmol) in ethyl ether (15 mL) was added. The mixture was allowed to warm to room temperature and stirred for an additional 1 h before quenching with 3 M HCl (100 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and volatiles were removed in vacuo to yield a yellow–brown semi-solid. Trituration with cold pentane and drying afforded **1d** (4.45 g, 67%) as a dark-yellow solid. The product was further purified by recrystallization from acetone. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 6.49 (t, 1H, J = 4 Hz, CHCHCH), 7.22 (d, 2H, J = 4 Hz, CHCHCH), 7.50 (dt, 4H, J = 8.4, 2.1 Hz, ArH), 7.84–7.85 (dt, 4H, J = 8.4, 2.1 Hz, ArH), 18.34 (s, 1H, OH). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, δ): 98.8, 123.8, 124.6 (Cp), 131.5, 137.2, 137.8, 141.9 (Ar), 184.6 (CO). IR (Nujol mull, ν/cm^{-1}): 1579 (C=O). Anal. Calcd for $C_{19}H_{12}O_2I_2$: C 43.38, H 2.30. Found: C 44.56, H 1.83.

2.3.2. Synthesis of Thallium(I) Salts

[Tl{1,2-C_5H_3(COC(CH_3)$_3$)$_2$}], 2a. Tl_2SO_4 (1.07 g, 2.12 mmol) was added in one portion to a stirred solution of **1a** (1.00 g, 4.27 mmol) in THF (50 mL) in a 200 mL Schlenk flask. Aqueous KOH (50 mL, 3.0 M) was then added, and the biphasic mixture was stirred at room temperature for 2 h. The resulting yellow suspension was filtered through a medium-porosity frit, and the solid was washed with deionized water until the filtrate was neutral, followed by ethyl ether (20 mL). The solid was dried under high vacuum overnight to afford **2a** as a bright yellow solid (941 mg, 50%). Mp: 175–185 °C (dec.). ^{1}H NMR (200 MHz,

$CDCl_3$, δ): 1.25 (s, 18H, $C(CH_3)_3$), 5.87 (t, 1H, J = 3.3 Hz, CHCHCH), 6.26 (d, 2H, J = 3.3 Hz, CHCHCH). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, δ): 29.5 ($C(CH_3)_3$), 42.7 ($C(CH_3)_3$), 108.4, 110.4 (CHCHCH), 126.5 (CC), 206.5 (CO).

[Tl{1,2-C_5H_3(CO-4-IC_6H_4)$_2$}], 2d. Compound **2d** was synthesized using the same procedure as described for **2a**, except that **1d** (3.12 g, 5.93 mmol) was used as the starting material and ethanol was employed as the solvent. The reaction afforded **2d** (2.75 g, 63.6%) as a dark-yellow solid. Mp: 200–230 °C (dec.). ^1H NMR (200 MHz, DMSO-d_6, δ): 5.68 (t, 1H, J = 3.6 Hz, CHCHCH), 6.23 (d, 2H, J = 3.6 Hz, CHCHCH), 7.37 (d, 4H, J = 8.0 Hz, ArH), 7.61 (d, 4H, J = 8.0 Hz, ArH). $^{13}C\{^1H\}$ NMR (50 MHz, DMSO-d_6, δ): 96.1 (CHCHCH), 110.5 (CC), 123.2 (CHCHCH), 124.7, 130.8, 135.8, 142.7 (Ar), 187.4 (CO). IR (KBr, ν/cm^{-1}): 1650 (C=O). MS (EI, 70 eV): *m*/*z* 729 (M^+), 525 ($[M - Tl]^+$). Anal. Calcd for $C_{19}H_{11}I_2O_2Tl$: C 31.28, H 1.52. Found: C 32.95, H 1.90.

2.3.3. Synthesis of Mixed-Sandwich [Ru{η^5-1,2-C_5H_3(CO–R)$_2$}(η^6-*p*-Cymene)][PF_6] Complexes

[Ru{η^5-1,2-C_5H_3(COC$(CH_3)_3$)$_2$}(η^6-*p*-cymene)][PF_6], 3a. In a 200 mL Schlenk flask, **1b** (689 mg, 1.57 mmol) was added to a stirred solution of [Ru(η^6-*p-cymene*)(μ-Cl)Cl]$_2$ (482 mg, 0.78 mmol) in acetonitrile (70 mL), and the reaction mixture was stirred at room temperature for 24 h. The resulting suspension was filtered through a thin pad of Celite, and methanol (7 mL) and NH_4PF_6 (747 mg, 4.58 mmol) were added to the filtrate, and the mixture was stirred at room temperature for an additional 2 h. Water (15 mL) was then added, and the product was extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, and the volatiles were removed in vacuo to give a gummy residue, which was triturated with cold pentane to afford **3a** (281 mg, 29%) as a yellow-reddish solid. Recrystallization by slow vapor diffusion of hexane into an ethyl ether solution of the complex using a cannula under nitrogen gave dark yellow crystals suitable for single-crystal X-ray analysis. Mp 125–127 °C. ^1H NMR (200 MHz, acetone-d_6, δ): 1.21 (s, 18H, $C(CH_3)_3$), 1.28 (d, 6H, ^3J = 6.9 Hz, *i*-Pr CH_3), 2.21 (s, 3H, $ArCH_3$), 2.82 (sept, 1H, ^3J = 6.9 Hz, *i*-Pr CH), 5.69 (t, 1H, ^3J = 2.6 Hz, CHCHCH), 6.05 (d, 2H, ^3J = 2.6 Hz, CHCHCH), 6.39–6.49 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6, δ): 18.7 ($ArCH_3$), 23.3 (*i*-Pr CH_3), 27.4 (CMe_3), 32.7 (*i*-Pr CH), 45.4 (CMe_3), 80.8, 83.0 (CHCHCH), 87.0, 90.6, 105.4, 114.8 (Ar), 99.5 (C=C), 205.2 (C=O). IR (Nujol mull, ν/cm^{-1}): 1710 (C=O), 833 (PF_6). MS (EI): *m*/*z* 468 ($M^+ - PF_6$). The complex was further characterized by single-crystal X-ray diffraction.

[Ru{η^5-1,2-C_5H_3(CO-4-tol)$_2$}(η^6-*p*-cymene)][PF_6], 3b. Complex **3b** was prepared as described for **3a**, using **2b** (762 mg, 1.51 mmol) as the starting material. Reaction with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (461 mg, 0.75 mmol) in MeCN (50 mL), followed by treatment with NH_6PF_6 (480 mg, 2.94 mmol), afforded **3b** (430 mg, 42%) as a light-brown solid. Analytically pure material was obtained by slow crystallization from hexane/CH_2Cl_2 (3:1); however, the resulting crystals were not suitable for single-crystal X-ray diffraction analysis. Mp 122–125 °C. ^1H NMR (200 MHz, CD_2Cl_2, δ): 1.20 (d, 6H, J = 6.8 Hz, i-Pr CH_3), 2.22 (s, 3H, *p*-cymene CH_3), 2.38 (s, 6H, *p*-tolyl CH_3), 2.71 (sept, 1H, J = 6.8 Hz, i-Pr CH), 5.70 (t, 1H, J = 2.5 Hz, CHCHCH), 5.74 (d, 2H, J = 2.5 Hz, CHCHCH), 6.11–6.19 (m, 4H, *p*-cymene ArH), 7.26 (dt, 4H, J = 8.4, 1.7 Hz, ArH), 7.66 (dt, 4H, J = 8.4, 1.8 Hz, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, δ): 19.2 (i-Pr CH), 22.0 (*p*-cymene CH_3), 23.4 (i-Pr CH_3), 32.2 (*p*-tolyl CH_3), 82.1, 83.0 (CHCHCH), 87.5, 90.2, 104.6, 114.0 (*p*-cymene Ar), 99.9 (ipso Cp), 129.5, 130.2, 133.8, 146.5 (p-tolyl Ar), 189.8 (CO). IR (Nujol mull, ν/cm^{-1}): 1698 (C=O), 832 (PF_6^-). Anal. Calcd for $C_{31}H_{31}F_6O_2PRu$: C 54.63, H 4.58. Found: C 53.23, H 4.17.

[Ru{η^5-1,2-C_5H_3(CO-4-ClC_6H_4)$_2$}(η^6-*p*-cymene)][PF_6], 3c. Complex **3c** was prepared as described for **3a**, except using **2c** (357 mg, 0.65 mmol) as starting material. Reaction with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (200 mg, 0.33 mmol) in MeCN (15 mL), followed by treatment

with NH_4PF_6 (200 mg, 1.22 mmol), afforded **3c** as a dark-brown solid (281 mg, 59%). Analytically pure material was obtained by slow crystallization from hexane/CH_2Cl_2 (3:1); however, the resulting crystals were not suitable for single-crystal X-ray diffraction analysis. Mp 110–114 °C. ^{1}H NMR (200 MHz, acetone-d_6, δ): 1.26 (d, 6H, J = 6.8 Hz, i-Pr CH_3), 2.29 (s, 3H, *p*-cymene CH_3), 2.79 (sept, 1H, J = 6.8 Hz, i-Pr CH), 5.94 (t, 1H, J = 2.8 Hz, CHCHCH), 6.21 (d, 2H, J = 2.8 Hz, CHCHCH), 6.38–6.51 (m, 4H, *p*-cymene ArH), 7.54 (dt, 4H, J = 8.8, 1.6 Hz, ArH), 7.95 (dt, 4H, J = 8.8, 1.6 Hz, ArH). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6, δ): 18.9 (i-Pr CH), 23.3 (i-Pr CH_3), 32.6 (*p*-cymene CH_3), 83.1, 84.1 (CHCHCH), 87.9, 90.9, 105.5, 114.8 (*p*-cymene Ar), 99.2 (ipso Cp), 130.1, 131.7, 135.9, 140.8 (*C*-Cl), 190.1 (CO). IR (Nujol mull, ν/cm^{-1}): 1693 (C=O), 832 (PF_6^-). Anal. Calcd for $C_{29}H_{25}F_6Cl_2O_2PRu$: C 48.21, H 3.49. Found: C 46.84, H 3.24.

[Ru{η^5-1,2-C_5H_3(CO-4-IC_6H_4)$_2$}(η^6-*p*-cymene)][PF_6], 3d. Complex **3d** was prepared as described for **3a**, using **2d** (405 mg, 0.56 mmol) as the starting material. Reaction with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (225 mg, 0.40 mmol) in MeCN (40 mL), followed by treatment with NH_4PF_6 (245 mg, 1.50 mmol), afforded **3d** (345 mg, 69%) as a dark-brown solid. Attempts to obtain single crystals suitable for X-ray diffraction by slow diffusion of hexane into a dichloromethane solution were unsuccessful. Mp 112–113 °C. ^{1}H NMR (200 MHz, acetone-d_6, δ): 1.26 (d, 6H, J = 6.9 Hz, i-Pr CH_3), 2.29 (s, 3H, *p*-cymene CH_3), 2.80 (sept, 1H, J = 6.9 Hz, i-Pr CH), 5.92 (t, 1H, J = 2.5 Hz, CHCHCH), 6.19 (d, 2H, J = 2.5 Hz, CHCHCH), 6.38–6.49 (m, 4H, *p*-cymene ArH), 7.68 (dt, 4H, J = 8.4, 1.8 Hz, ArH), 7.92 (dt, 4H, J = 8.4, 1.8 Hz, ArH). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, δ): 19.1 (i-Pr CH), 23.3 (i-Pr CH_3), 31.9 ($ArCH_3$), 79.0, 83.2 (CHCHCH), 87.4, 90.0, 104.6, 114.6 (*p*-cymene Ar), 98.6 (ipso Cp), 103.4, 130.3, 135.0, 138.8 (*C*-I), 189.7 (CO). IR (Nujol mull, ν/cm^{-1}): 1655 (C=O), 836 (PF_6^-). Anal. Calcd for $C_{29}H_{25}F_6I_2O_2PRu$: C 38.47, H 2.78. Found: C 38.23, H 2.34.

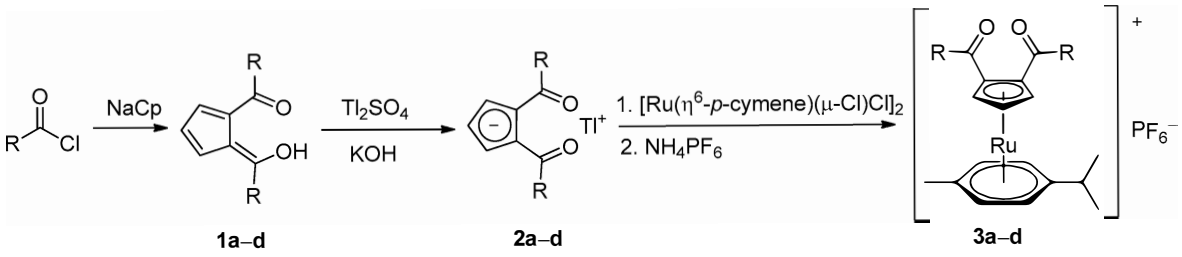
Attempted Synthesis of **[Ru{η^5-1,2-C_5H_3(C-4-tol)$_2$S}(η^6-*p*-cymene)][PF_6]**. In a 125 mL Schlenk flask, **3b** (100 mg, 0.146 mmol) was added to a stirred suspension of P_4S_{10} (500 mg, 1.03 mmol) and $NaHCO_3$ (100 mg, 1.18 mmol) in dichloromethane (40 mL). The reaction mixture was allowed to stir for 2 h at room temperature. The color changed from pale yellow to deep purple. The reaction mixture was then filtered through a thick pad of alumina, and the solvent was evaporated to about 10 mL. Ethyl ether was added dropwise to give a precipitate, which was separated by filtration and dried overnight to give purple powder (100 mg). The ^{1}H NMR spectrum of the product showed loss of the *p*-cymene ligand.

3. Results and Discussion

3.1. Synthesis and Spectroscopic Characterization

The syntheses of [Ru{η^5-1,2-C_5H_3(COR)$_2$}(η^6-*p*-cymene)][PF_6] (**3a**–**d**) are shown in Scheme 1. The 2-acyl-6-hydroxyfulvenes (**1a**–**d**) were conveniently synthesized by treating sodium or lithium cyclopentadiene with an acyl chloride in a 3:2 stoichiometric ratio [20,31]. The fulvenes exhibit intramolecular hydrogen bonding between the hydroxy group and the adjacent carbonyl oxygen as evidenced by the downfield signal (δ 16–20 ppm) of the enolic proton in their ^{1}H NMR spectra. Further, the cyclopentadienyl protons display a characteristic 2:1 doublet:triplet pattern, consistent with a plane of symmetry. Their IR spectra show strong ν(C=O) bands in the 1580–1650 cm^{-1} region, indicative of conjugated carbonyl groups engaged in intramolecular hydrogen bonding.

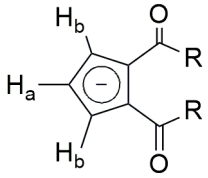
Thallium reagents **2a**–**d** were conveniently prepared in moderate yield by using Tl_2SO_4/KOH in THF/H_2O, rather than costly, thermally labile TlOEt [17,20,32]. The thallium salts are remarkably stable to air and moisture. Their formation is clearly evidenced by the complete disappearance of the enolic OH resonance in the ^{1}H NMR spectra and by slight upfield shifts in the Cp proton resonances relative to the parent fulvenes, consistent with increased electron density in the cyclopentadienyl anion (Table 1).



R = t-Bu (**a**), 4-Me-C_6H_4 (**b**), 4-Cl-C_6H_4 (**c**), 4-I-C_6H_4 (**d**)

Scheme 1. Synthesis of $[Ru\{\eta^5\text{-}1,2\text{-}C_5H_3(COR)_2\}(\eta^6\text{-}p\text{-cymene})][PF_6]$ (**3a**–**d**).

Table 1. Chemical shift values (δ in ppm) of Cp protons and IR stretching (cm^{-1}) of C=O in compounds **1d**, **2d**, and **3d**.



Compound	Cp-H (triplet)	Cp-H (doublet)	IR (C=O)
1d [i]	6.49	7.22	1579
2d [ii]	5.68	6.23	1650
3d [iii]	5.92	6.19	1655

[i] = $CDCl_3$, [ii] = DMSO-d_6, [iii] = acetone-d_6.

The thallium(I) salts **2a**–**d** undergo clean transmetalation with $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ [22] in a 2:1 stoichiometric ratio in acetonitrile at room temperature over 18–24 h. Subsequent anion metathesis with NH_4PF_6 in methanol affords the cationic ruthenium cyclopentadienyl–arene complexes **3a**–**d** in 30–70% yields. Reaction progress is conveniently monitored by the precipitation of thallium chloride, which is easily removed by filtration through Celite. Final purification is typically accomplished by trituration with cold pentane or ethyl ether or by slow crystallization from dichloromethane/hexane. The Cp proton chemical shifts range from 5.69 to 5.94 ppm for the outer protons and from 5.74 to 6.21 ppm for the inner protons (Table 1). The arene proton resonances appear in the range δ 5.81–6.51 ppm as AA′BB′ spin systems, clearly indicating η^6 coordination. The corresponding ^{13}C NMR resonances of the *p*-cymene ligand span the range 87–114 ppm. The IR spectra of **3a**–**d** show strong ν(C=O) absorptions in the 1655–1710 cm^{-1} range and medium-intensity ν(PF_6) absorptions at 832–836 cm^{-1}. Electron impact mass spectrometry of **3a** shows a peak at m/z 468 corresponding to $[M - PF_6]^+$. In contrast, EI-MS measurements of **3b**–**d** did not display intact cation peaks ($[M - PF_6]^+$) under the same conditions; only fragment ions of low diagnostic value were observed, consistent with the reduced volatility and increased thermal fragility of the heavier aryl-substituted complexes. Elemental analyses of complexes **3b**–**d** consistently appeared slightly lower C and H values than calculated (ΔC up to 1.4%; ΔH up to 0.44%) despite repeated purification and drying. The observed deviations may arise from incomplete combustion during microanalysis or trace inorganic residues associated with these heavy-metal PF_6^- salts.

3.2. Molecular Structure of **3a**

A thermal ellipsoid plot of the molecular structure of complex **3a** is shown in Figure 1. Crystallographic and refinement parameters are summarized in Table 2, and the crystal packing along three axes is shown in Figures S1–S3. The compound crystal-

lizes in an orthorhombic space group of type *Pna*2_1. The asymmetric unit contains one [Ru(η^5-Cp)(η^6-*p*-cymene)]$^+$ cation and one hexafluorophosphate (PF_6^-) counterion.

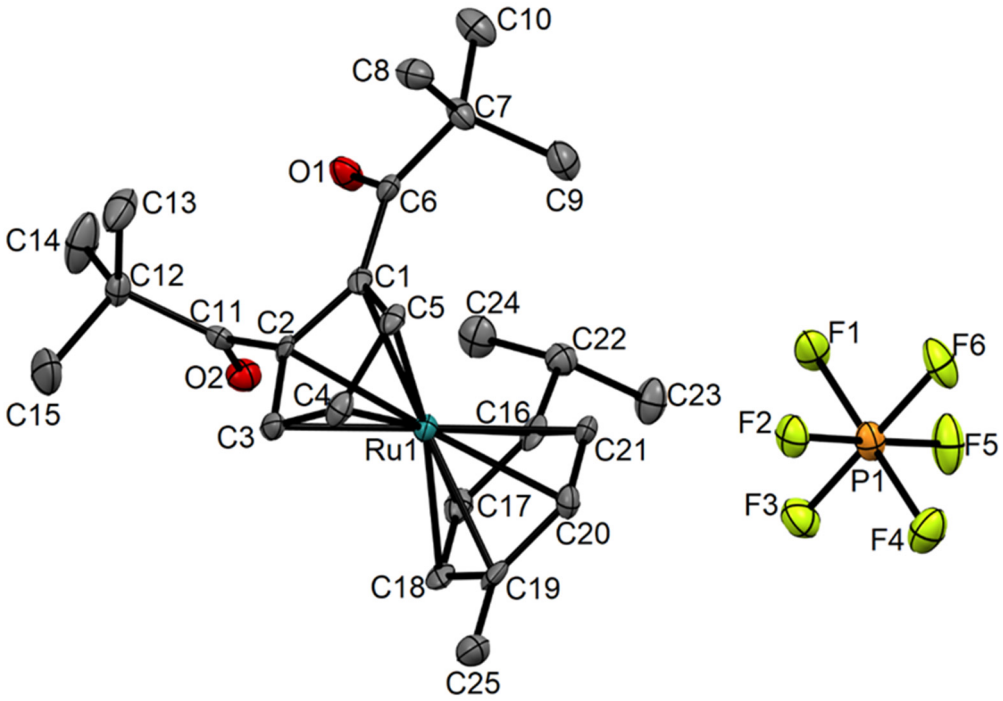


Figure 1. The molecular structure of **3a**, showing 50% probability displacement ellipsoids; H atoms omitted for clarity. Selected bond lengths (Å): Ru1–C1 2.187(3), Ru1–C2 2.186(4), Ru1–C3 2.184(4), Ru1–C4 2.164(4), Ru1–C5 2.178(3), Ru1–C16 2.262(4), Ru1–C17 2.211(4), Ru1–C18 2.196(3), Ru1–C19 2.210(3), Ru1–C20 2.211(4), Ru1–C21 2.218(4), C6-O1 1.225(5), C11-O2 1.215(5).

The cation of **3a** is an η^6–*p*-cymene–η^5–cyclopentadienyl ruthenium(II) sandwich complex, in which the Ru atom is positioned between two aromatic ligands. Ru1 is η^5-coordinated to a substituted cyclopentadienyl ring (C1–C5) and η^6-coordinated to the *p*-cymene ring (C16–C21). The η^5-Cp and η^6-*p*-cymene ligands are arranged in a near parallel fashion, with an interplanar angle of ca. 6.1° and a Ru-centered angle between their centroids of 175.1°, consistent with a well-aligned sandwich configuration. The Ru-centroid distances are 1.809 Å (Cp) and 1.710 Å (arene), in line with those observed in related Ru(II) sandwich complexes. Individual Ru–C bond distances reflect expected differences between η^5- and η^6-coordination. The Ru–C(Cp) distances span 2.164(4)–2.187(3) Å, whereas the Ru–C(*p*-cymene) distances are slightly longer, 2.196(3)–2.262(4) Å. The mean Ru–C(Cp) distance (ca. 2.180 Å) is therefore shorter than the mean Ru–C(arene) distance (ca. 2.218 Å). The results are consistent with trends observed in η^6–arene–η^5–cyclopentadienyl Ru(II) complexes and agree with the general expectation that the η^5-bound Cp ligand forms slightly stronger metal–carbon contacts compared to η^6–arene coordination [33].

The Ru–C distances to the two acyl-substituted cyclopentadienyl carbon atoms (C1 and C2) [2.186–2.187 Å] are slightly longer than those to the unsubstituted positions (C3–C5) [2.164–2.184 Å], reflecting the modest electron-withdrawing effect of the acyl groups. The carbonyl groups are well defined, with C=O distances of 1.225(4) and 1.215(5) Å, typical of localized ketone functionalities. Their orientations differ markedly: the C1–C6–O1 moiety is nearly coplanar with the Cp ring (interplanar angle ca. 2°), whereas the C2–C11–O2 fragment is nearly perpendicular (ca. 89°). The octahedral PF_6^- anion acts solely as a counterion. To the best of our knowledge, **3a** represents the first crystallographically characterized Ru(II) complex combining a 1,2-diacylcyclopentadienyl ligand with a η^6-*p*-cymene co-ligand.

Table 2. Crystal data and refinement parameters for compound **3a**.

Parameter	Value
Empirical formula	$C_{25}H_{35}F_6O_2PRu$
M_r	613.57
Deposition number	CCDC2517689
Temperature (K)	90.0(2)
Radiation type	Mo Kα
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
a (Å)	10.4848(2)
b (Å)	23.8423(5)
c (Å)	10.4241(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2605.83(9)
Z	4
Calculated density, D_x (Mg m^{-3})	1.564
μ (mm^{-1})	0.727
Crystal size (mm)	0.30 × 0.12 × 0.10
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan, empirical
θ range (°)	1.71–27.49
Reflections collected	24,539
Independent reflections	5947
R_{int}	0.0564
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5947/1/325
Goodness-of-fit on F^2	1.055
Final R indexes [I > 2σ(I)]	R_1 = 0.0337, wR_2 = 0.0584
Final R indexes (all data)	R_1 = 0.0590, wR_2 = 0.0655
Largest diff. peak/hole (e·Å^{-3})	1.434/−0.489

*3.3. Attempted Reactions of [Ru{η^5-1,2-C$_5$H$_3$(COR)$_2$}(η^6-p-Cymene)][PF$_6$] (**3a**–**d**)*

Attempts to convert the 1,2-diacylcyclopentadienyl ligands of **3a**–**d** to cyclopenta[*c*]thiophenes using established protocols [17,20,34] were unsuccessful. For example, a reaction of [Ru{η^5-1,2-C$_5$H$_3$(CO-4-tol)$_2$}(η^6-*p*-cymene)][PF$_6$] (**3b**) with P_4S_{10} and $NaHCO_3$ in CH_2Cl_2 gave a purple product, consistent with other cyclopenta[*c*]thiophene complexes. However, NMR analysis indicated loss of the *p*-cymene ligand and the presence of multiple unresolved signals, suggesting decomposition or formation of a mixture rather than a discrete cyclized product. No single, well-defined compound could be isolated for further characterization. Although the reactions were conducted under standard laboratory lighting, the possibility

that partial photochemical ligand dissociation contributes to the observed cymene loss in **3b** cannot be excluded.

4. Conclusions

We have developed a modular, three-step route to access a new family of cationic arene–ruthenium(II) complexes bearing electron-withdrawing 1,2-diacylcyclopentadienyl ligands. These results expand the range of electron-deficient Cp ligands compatible with Ru(II) half-sandwich frameworks, establishing a structural and synthetic foundation for future studies aimed at exploiting these electron-withdrawing Cp systems in organometallic reactivity and catalyst design. The successful synthesis and crystallographic characterization of representative complex **3a** confirms that electron-withdrawing Cp frameworks can be incorporated into cationic Ru(II)–arene systems. While heterocycle formation was not achieved under the studied conditions, the present work expands the scope of ruthenium sandwich complexes and lays the foundation for future reactivity studies involving electron-deficient π-ligands.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst16030201/s1. Figure S1: Packing diagram of **3a** along *a* axis; Figure S2: Packing diagram of **3a** along *b* axis; Figure S3: Packing diagram of **3a** along *c* axis. CIF file of compound **3a**.

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