

# Reactions of $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CHO})^+\text{OSO}_2\text{CF}_3^-$ ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) with substituted anilines forming ruthenium Schiff base complexes

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## Abstract

$\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CHO})^+\text{OSO}_2\text{CF}_3^-$  (**1**) ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) reacts with substituted anilines forming ruthenium Schiff base complexes containing an  $\eta^6$ -coordinated  $\text{Cp}^*\text{Ru}^+$  group. The 2:1 reaction of **1** with 1,4-phenylenediamine yielded only the monocondensation product, whereas the 2:1 reaction of **1** with 1,4-xylylenediamine yielded the dicondensation product.

**Keywords:** Ruthenium; Arene complexes; Schiff bases; Anilines; Benzaldehyde; Pentamethylcyclopentadienyl

## 1. Introduction

Primary amines react with aldehydes to form imines that are stable enough for isolation when at least one aryl group is bonded to the nitrogen or the carbon [1]. The reactivity of the  $\eta^5$ -formylcyclopentadienyl group in  $[(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{Cr}(\text{CO})_3]^-$  with acyl chlorides to form fulvene complexes [2] and the reactivity of ferrocenecarboxaldehyde with primary amines to form Schiff base side groups [3] is known. While studies involving the reactions of the formyl group in  $\eta^6$ -coordinated  $\text{Cr}(\text{CO})_3$  substituted benzaldehyde complexes with L-valinol [4], RLi [5], and N-methylhydroxylamine [6] have been published, there are no previous reports of the reactivity of the formyl group in an unsubstituted  $\eta^6$ -benzaldehyde complex.

This article reports the reactivity of the formyl group in  $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CHO})^+\text{OSO}_2\text{CF}_3^-$  with aryl primary amines. These compounds have the potential to exhibit properties essential for second-order non-linear optical (NLO) properties, important to optical device technology [7]. Described here are conjugated aromatic compounds having an electron-rich environment at one end and coordination of an organometallic moiety at the other end. They are polarizable dipolar molecules and are therefore candidates to display NLO properties.

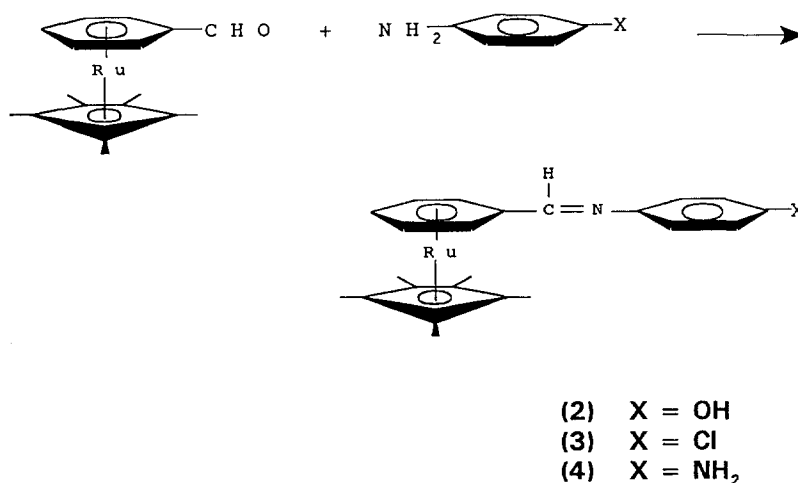
These products are also the first examples of the  $\text{Cp}^*\text{Ru}^+$  moiety selectively coordinated to a specific ring of a multiple aromatic ring system.

## 2. Results and discussion

The reactivity of the formyl group in benzaldehyde is enhanced upon coordination of the  $\text{Cp}^*\text{Ru}^+$  moiety forming  $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CHO})^+\text{OSO}_2\text{CF}_3^-$ . The cationic ruthenium withdraws electron density from the benzaldehyde ring which increases the electrophilic character of the formyl carbon. This allows the facile reaction with primary aryl amines to occur. The air-stable  $\text{Cp}^*\text{Ru}(\eta^6\text{-imines})^+$  produced via this reaction are highly colored salts owing to extensive conjugation throughout the complex.

$[\text{Cp}^*\text{Ru}(\text{NCCH}_3)_3]^+\text{O}_3\text{SCF}_3^-$  (**1**) was synthesized using the published procedure in Ref. [8]; purification of **1** was accomplished by using 2:3 diethyl ether:acetonitrile on a silica gel column under dry nitrogen.  $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CHO})^+\text{OSO}_2\text{CF}_3^-$  **1** reacts with aryl primary amines to form Schiff base condensation products. Reactions of **1** with 4-hydroxyaniline and 4-chloroaniline produce the predicted products **2** and **3**. The reaction of two equivalents of **1** with 1,4-phenylenediamine was predicted to form the dicondensation product. However, only the monocondensation product **4** was recovered; see Scheme 1.

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Scheme 1.

Since the p-amine group in **4** is unreactive towards **1**, we believe that the decrease in nucleophilic character of the nitrogen lone pair is due to increased participation of the lone pair with the extended conjugated system. To help substantiate this hypothesis, 1,4-xylenediamine was mixed with two equivalents of **1**. Since the methylene groups disrupt the extended conjugation throughout the complex, it was predicted and then confirmed that both amine groups would react with **1** producing **5**; see Scheme 2.

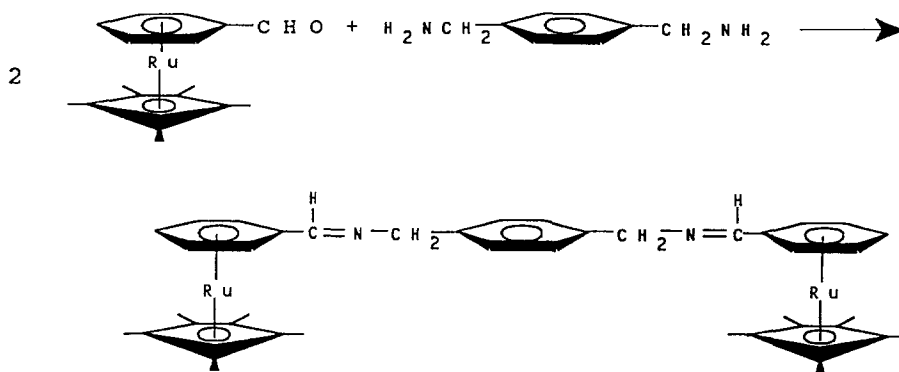
The reactivity of **1** with aryl primary amines containing an  $\eta^6$ -coordinated  $\text{Cp}^*\text{Ru}^+$  moiety was also investigated. To examine these reactions, several  $\text{Cp}^*\text{Ru}^+$  derivatives were synthesized, including  $\text{Cp}^*\text{Ru}(\eta^6\text{-aniline})^+$  (synthesis previously reported in Ref. [9]),  $\text{Cp}^*\text{Ru}(\eta^6\text{-4-chloroaniline})^+$  **6**,  $\text{Cp}^*\text{Ru}(\eta^6\text{-4-hydroxyaniline})^+$  **7**,  $\text{Cp}^*\text{Ru}(\eta^6\text{-1,4-phenylenediamine})^+$  (synthesis previously reported in Ref. [9]), and  $\text{Cp}^*\text{Ru}(\eta^6\text{-3,5-dimethoxyaniline})^+$  **8**.

All of the  $\text{Cp}^*\text{Ru}(\eta^6\text{-aniline})^+$  derivatives studied failed to react with **1** at ambient conditions in polar organic solvents. Starting materials were exclusively

present in the reaction mixture even after several days. The reactions of **1** with **8** and **1** with  $\text{Cp}^*\text{Ru}(\eta^6\text{-1,4-phenylenediamine})^+$  failed to occur even when heated to reflux overnight. These findings are attributed to the  $\text{Cp}^*\text{Ru}^+$  moiety effectively deactivating the amine group upon coordination. All attempted reactions of the  $\text{Cp}^*\text{Ru}(\eta^6\text{-aniline})^+$  derivatives with benzaldehyde also failed.

### 3. Experimental

All synthetic procedures were carried out under vacuum or a dry nitrogen atmosphere with glassware fitted with Teflon solvent seal connections using standard Schlenk techniques. Methanol was dried over  $\text{Mg}/\text{I}_2$ , diethyl ether was dried over lithium aluminum hydride, and methylene chloride was dried over  $\text{P}_2\text{O}_5$ . Acetonitrile was predried over  $\text{P}_2\text{O}_5$ , distilled, and dried over calcium hydride. Tetrahydrofuran (THF) was predried over potassium hydroxide, distilled, and dried over lithium aluminum hydride. Nitromethane was purified



Compound (5)

Scheme 2.

Table 1  
<sup>1</sup>H NMR data

	Imine proton	Non-coordinated aromatic ring protons	Coordinated aromatic ring protons	Cp* methyl protons	
(2)	8.37 (1H, s) 7.38 (OH)	7.27 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.7 Hz) 6.90 (2H, d, <sup>3</sup> J <sub>HH</sub> = 7.3 Hz)	6.36 (2H, d, <sup>3</sup> J <sub>HH</sub> = 7.8 Hz) 5.93–5.99 (3H, m)	1.91 (15H, s)	
(3)	8.36 (1H, s)	7.45 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.4 Hz) 7.30 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.0 Hz)	6.38 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.4 Hz) 5.97–6.07 (3H, m)	1.90 (15H, s)	
(4)	8.32 (1H, s) 4.45 (NH <sub>2</sub> )	7.20 (2H, d, <sup>3</sup> J <sub>HH</sub> = 7.7 Hz) 6.68 (2H, d, <sup>3</sup> J <sub>HH</sub> = 7.1 Hz)	6.31 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.1 Hz) 5.87–5.98 (3H, m)	1.86 (15H, s)	
	Imine proton	Non-coordinated protons	Coordinated ring protons	Methylene protons	Cp* methyl protons
(5)	8.31 (2H, s)	7.44 (4H, s)	6.33 (4H, d, <sup>3</sup> J <sub>HH</sub> = 6.3 Hz) 5.98–6.06 (6H, m)	3.31 (4H, s)	1.88 (30H, s)
	Aromatic ring	Amine protons	Cp* methyl	Other protons	
(6)	6.05 (2H, d, <sup>3</sup> J <sub>HH</sub> = 6.1 Hz)	3.88 (2H, broad)	1.92 (15H, s)	—	
(7)	5.41 (2H, d, <sup>3</sup> J <sub>HH</sub> = 5.8 Hz) 5.17 (2H, d, <sup>3</sup> J <sub>HH</sub> = 5.7 Hz)	4.26 (2H, broad)	1.86 (15H, s)	7.5 (1H, broad) (–OH)	
(8)	5.54 (1H, d, <sup>4</sup> J <sub>HH</sub> = 0.95 Hz) 5.28 (2H, d, <sup>4</sup> J <sub>HH</sub> = 0.95 Hz)	4.51 (2H, broad)	1.86 (15H, s)	3.68 (6H, s) (–OCH <sub>3</sub> )	

All spectra were taken in CD<sub>3</sub>CN with TMS as internal standard except **5**, which was taken in CD<sub>3</sub>OD.

by simple distillation. Spectroscopic grades of dimethylsulfoxide (DMSO) and chloroform were used without further purification. 4-Hydroxyaniline, 4-chloroaniline, 3,5-dimethoxyaniline, 1,4-phenylenediamine and 1,4-xylylenediamine were purchased from Aldrich Chemical Co. and used without further purification.

Solvent systems for the synthetic reactions were selected to increase the solubility of the starting materials. The solvent systems used in the synthetic procedures of **2** and **5** also allowed the products to precipitate from the reaction solution.

The <sup>1</sup>H NMR spectra (Table 1) were measured at 300 MHz and <sup>13</sup>C NMR spectra (Table 2) at 75.5 MHz with a Bruker AC-F 300 FTNMR spectrometer at Alma College, Alma, MI. Elemental analyses were performed by Desert Analytics of Tucson, AZ.

### 3.1. Cp\*Ru(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>CH=NC<sub>6</sub>H<sub>4</sub>OH-*p*)<sup>+</sup>OSO<sub>2</sub>CF<sub>3</sub><sup>–</sup> (**2**)

**1** (0.20 g, 0.39 mmol) was dissolved in 20 ml of 3:1 acetonitrile:diethyl ether. 4-Hydroxyaniline (0.042 g,

Table 2  
<sup>13</sup>C NMR data

	Imine carbon	Non-coordinated ring carbons	Cp* ring carbon	Coordinated ring carbon	Cp* methyl carbons	
(2)	157.5	153.3, 142.5, 123.3, 116.4	97.9	94.9, 88.4, 88.2, 86.4	10.3	
(3)	158.2	144.6, 132.9, 130.5, 123.3	98.2	93.9, 88.8, 88.5, 87.4	10.4	
(4)	149.9	149.0, 139.4, 123.3, 114.8	98.6	95.3, 88.0, 87.9, 86.0	10.1	
	Imine carbon	Non-coordinated carbons	Cp* ring carbons	Coordinated ring carbons	Methylene carbons	Cp* methyl carbons
(5)	160.0	139.3, 130.0	98.9	95.0, 89.1, 89.1, 87.4	65.6	10.7
	Aromatic ring carbons	Cp* ring carbons	Methoxy carbons	Cp* methyl carbons		
(6)	129.9, 115.1, 87.9, 73.5	96.6	—	9.8		
(7)	126.7, 120.2, 75.9, 72.5	94.9	—	10.4		
(8)	131.7, 121.1, 63.1, 62.6	93.4	57.5	10.4		

All spectra were taken in CD<sub>3</sub>CN with TMS as internal standard except **5**, which was taken in CD<sub>3</sub>OD.

0.39 mmol) was added and the solution was stirred for 4 h. The product was filtered, dried, and then reprecipitated from acetonitrile with diethyl ether producing a light pink air-stable powder; 0.16 g, 68% yield. Anal. Found: C, 49.12; H, 4.19.  $C_{24}H_{26}F_3NO_4RuS$  Calc.: C, 49.48; H, 4.50%.

3.2.  $Cp^*Ru(\eta^6-C_6H_5CH=NC_6H_4Cl-p)^+OSO_2CF_3^-$  (3)

**1** (0.20 g, 0.39 mmol) was dissolved in 20 ml of nitromethane. 4-Chloroaniline (0.05 g, 0.39 mmol) was added and the solution was stirred for 4 h. The solvent was removed by vacuum and the crude product was reprecipitated from nitromethane with diethyl ether producing a light purple air-stable powder; 0.14 g, 57% yield. Anal. Found: C, 47.68; H, 4.00.  $C_{24}H_{25}ClF_3NO_3RuS$  Calc.: C, 47.96; H, 4.19%.

3.3.  $Cp^*Ru(\eta^6-C_6H_5CH=NC_6H_4NH_2-p)^+OSO_2CF_3^-$  (4)

**1** (0.20 g, 0.39 mmol) was dissolved in 20 ml of acetonitrile. 1,4-Phenylenediamine (0.042 g, 0.39 mmol) was added and the solution was stirred for 4 h. (The reaction in 2:1 molar ratio also produced **4**.) The solvent was removed and the crude product was dried by vacuum. The crude product was dissolved in a minimum amount of acetonitrile and chromatographed through an alumina column under dry nitrogen with acetonitrile. A bright yellow band was collected, the solvent removed under vacuum, and the product triturated with diethyl ether. The resulting product was a bright green–yellow air-stable powder; 0.17 g, 72% yield. Anal. Found: C, 49.78; H, 4.81.  $C_{24}H_{27}F_3N_2O_3RuS$  Calc.: C, 49.56; H, 4.68%. See Scheme 1.

3.4.  $[Cp^*Ru(\eta^6-C_6H_5CH=NCH_2C_6H_4CH_2N=CH-\eta^6-C_6H_5)RuCp^*]^{2+}2[OSO_2CF_3]^-$  (5)

**1** (0.20 g, 0.39 mmol) was dissolved in 20 ml of 1:19 DMSO:chloroform. 1,4-Xylylenediamine (0.027 g, 0.20 mmol) was added and the solution was stirred for 2 h, after which time an off-white precipitate had formed. The crude product was filtered and dried under vacuum. The product was reprecipitated from acetonitrile with diethyl ether, filtered and dried under vacuum leaving a light tan powder; 0.18 g, 81% yield. Anal. Found: C, 48.38; H, 4.67.  $C_{44}H_{50}F_6N_2O_6Ru_2S_2$  Calc.: C, 48.79; H, 4.65%.

3.5.  $Cp^*Ru(\eta^6-4-H_2NC_6H_4Cl)^+OSO_2CF_3^-$  (6)

**1** (0.20 g, 0.39 mmol) was added to 20 ml of methanol followed by addition of 4-chloroaniline (0.046 g, 0.36 mmol). The solution was stirred for 1 h. The deep

red solution was filtered and the solvent removed, leaving a pink powder. The crude product was reprecipitated from methanol with diethyl ether twice, leaving an air-stable pink powder; 0.14 g, 76% yield. Anal. Found: C, 40.10; H, 4.00.  $C_{17}H_{21}ClF_3NO_3RuS$  Calc.: C, 39.81; H, 4.13%.

3.6.  $Cp^*Ru(\eta^6-4-H_2NC_6H_4OH)^+OSO_2CF_3^-$  (7)

**1** (0.20 g, 0.39 mmol) was added to 20 ml of 2:1 acetonitrile:diethyl ether followed by addition of 4-hydroxyaniline (0.039 g, 0.36 mmol). The solution was stirred overnight. The solvent was removed by vacuum and the crude product was reprecipitated from acetonitrile with diethyl ether twice, leaving an air-stable pink powder; 0.14 g, 79% yield. Anal. Found: C, 41.08; H, 4.18.  $C_{17}H_{22}F_3NO_4RuS$  Calc.: C, 41.29; H, 4.48%.

3.7.  $Cp^*Ru(\eta^6-3,5-H_2NC_6H_4(OCH_3)_2)^+OSO_2CF_3^-$  (8)

**1** (0.20 g, 0.39 mmol) was added to 20 ml of methanol followed by addition of 3,5-dimethoxyaniline (0.055 g, 0.36 mmol). The solution was stirred for 1 h. The deep red solution was filtered and the solvent removed, leaving a pink powder. The crude product was reprecipitated from methanol with diethyl ether twice, leaving an air-stable pink powder; 0.10 g, 52% yield. Anal. Found: C, 42.63; H, 4.52.  $C_{19}H_{26}F_3NO_5RuS$  Calc.: C, 42.38; H, 4.87%.

#### 4. Conclusion

The electrophilic character of the formyl group of benzaldehyde is enhanced upon  $\eta^6$ -coordination with the  $Cp^*Ru^+$  moiety. Reactions of  $Cp^*Ru(\eta^6-C_6H_5CHO)^+$  with aryl primary amines produce  $\eta^6$ -coordinated Schiff base complexes. The influence of the  $Cp^*Ru^+$  cation can extend through the conjugated amine complex and effectively deactivate the second amine group in 1,4-phenylenediamine. Coordination of  $Cp^*Ru^+$  with aryl amines deactivates the amine group to the extent that the  $\eta^6$ -coordinated anilines are unreactive even towards  $Cp^*Ru(\eta^6-C_6H_5CHO)^+$ .

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