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Synthesis, characterization, and X-ray structural analysis of some half-sandwich ruthenium(II) arene complexes with new N,S-donor Schiff base ligands

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Abstract

A series of cationic, half-sandwich ruthenium complexes with the general formula $[(\eta^6\text{-arene})RuCl(R^1S\text{-}C_6H_4\text{-}2\text{-}CH{=}NR^2)]^+$ (arene = *p*-cymene or hexamethylbenzene; $R^1 = CH_2Ph$, ^{i}Pr, or Et; R^2 = aryl) have been prepared from the reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with various N,S-donor Schiff base ligands derived from 2-(alkylthio)benzaldehyde and several primary amines. All of the ruthenium complexes were characterized by IR, ^{1}H NMR, electrochemistry, and UV/Vis spectroscopies. The *p*-cymene complexes undergo irreversible oxidations while the hexamethylbenzene complexes undergo quasi-reversible oxidations. The molecular structures of ligand **1a** and complexes **4a**, **4l**, and **5e** were determined by X-ray crystallography.

Keywords: Ruthenium complexes; Half-sandwich complexes; Schiff base; N,S ligands; Crystal structure; Cyclic voltammetry

1. Introduction

Schiff bases are popular ligands in coordination chemistry due to their ease of synthesis and their ability to be readily modified both electronically and sterically. Mixed-donor Schiff bases have been used extensively in catalysis [1]. Most of the mixed-donor Schiff base ligands developed to date have nitrogen with phosphorous [2] or oxygen [3] atoms as the other donor unit. Until recently, there have been relatively few reports of sulfur containing mixed-donor Schiff base ligands. Chakravarty and co-workers have utilized O,N,S-Schiff bases as ligands for models of copper-containing enzymes [4]. Also, we recently reported the synthesis of some arene ruthenium complexes with sulfur-containing Schiff base ligands derived from 2-(methylthio)aniline [5].

Ruthenium compounds are extremely versatile molecules. In particular, half-sandwich ruthenium complexes are excellent catalysts for a wide variety of organic reactions [6] and have shown promise as anticancer agents [7]. Interest in arene ruthenium chemistry began in 1957 with the discovery of complexes of the type $[Ru(\eta^6\text{-arene})_2]^{2+}$ [8]. However, complexes of this type are not useful precursors to mono-arene ruthenium complexes. The development of useful synthetic precursors with the general formula $[RuCl_2(\eta^6\text{-arene})]_n$ [9] led to a rapid growth in the field of arene ruthenium chemistry.

Since the early development of complexes of the type $[RuCl_{2-n}(\eta^6\text{-arene})(L)]^{n+}$ ($n = 0$, 1), where L is either a monodentate or bidentate ligand, there has been a flurry of research on the synthesis of related complexes containing other donor atoms. Recently, Lalrempuia and co-workers have used *para*-substituted *N*-(2-pyridylmethylene)phenylamines as bidentate *N*,*N*′-donor Schiff base ligands [10]. In the past 10 years the chemistry of bidentate phosphine ligands with ruthenium dimers has been well established [11]. Additionally, the chemistry of [N, O^-, (O^-)] donor ligands [12], [P, N, (O^-)] donor ligands [13], and to a much lesser extent sulfur donor ligands [5,14],

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along with the continued development of various [N, N′] donor ligands [15], continue to spur the growth of arene ruthenium chemistry.

Organometallic ruthenium(II) arene complexes of the type $[RuCl(\eta^6\text{-arene})(L_2)]^+$ (L_2 = two monodentate or one bidentate ligand) have also shown promising anticancer activity [7]. Since the clinical success of *cis*-platin in 1978, there has been much effort committed to develop less toxic drugs. Research in new drug design and delivery have reduced the toxic effects of the platinum-containing drugs, but complexes based on metals other than platinum have been investigated for their potential anticancer activity. Several ruthenium(II) and ruthenium(III) complexes have shown excellent antitumor activity. Recently, several reports detailing the anticancer activity of cationic half-sandwich ruthenium(II) arene complexes have appeared. Chen et al. have found that half-sandwich ruthenium(II) complexes containing a chelating diamine such as ethylenediamine (en) or its derivatives are effective anticancer agents [7c]. Even more promising is that these compounds show high activity for *cis*-platin resistant cancer cell lines.

The present work developed from our group's interest in the synthesis and utilization of new sulfur-containing, mixed-donor Schiff base ligands [5]. Herein, we report the synthesis and characterization of several new cationic half-sandwich ruthenium(II) complexes with chelating N,S-Schiff bases. Also included are the X-ray structures of the compounds $[RuCl(\eta^6\text{-}p\text{-cymene})(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\{p\text{-}C_6H_4OMe\})][PF_6]$, $[RuCl(\eta^6\text{-}p\text{-cymene})(PhCH_2\text{-}S\text{-}C_6H_4\text{-}2\text{-}CH{=}Nmesityl)][PF_6]$, $[RuCl(\eta^6\text{-}p\text{-cymene})(^i PrS\text{-}C_6H_4\text{-}2\text{-}CH{=}N\{p\text{-}C_6H_4Me\})][BPh_4]$, and $PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N(p\text{-}C_6H_4OMe)$.

2. Results and discussion

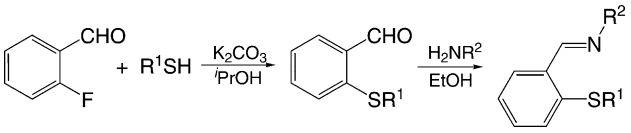
2.1. Ligand syntheses

The 2-(alkylthio)benzaldehydes were prepared by a modification of the literature procedure using 2-fluorobenzaldehyde and the corresponding alkanethiol (Scheme 1) [16]. The ligands were prepared by condensing anilines with the 2-(alkylthio)benzaldehydes in refluxing ethanol and were used without further purification. All of the ligands were characterized by ^{1}H NMR and IR spectroscopy. Additionally, the ligand **1a** was characterized by X-ray crystallography.

2.2. Synthesis and characterization of ruthenium complexes

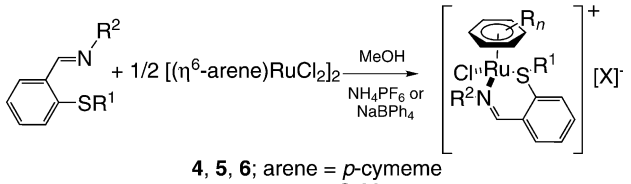
Treatment of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ or $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with the new N,S-donor Schiff base ligands in methanol followed by addition of a counter anion led to the formation of air-stable, cationic ruthenium(II) complexes with the general formula $[RuCl(\eta^6\text{-arene})(S\cap N)]^+$ (**4a–l**, **5a–e**, **6a–e**, **7a–b**). The complexes were synthesized in a manner similar to our previously reported half-sandwich ruthenium(II) complexes containing N,S-donor Schiff base ligands (Scheme 2) [5]. The complexes were easily isolated by suction filtration due to their low solubility in methanol. All of the ruthenium complexes are insoluble in water and only slightly soluble in alcoholic solvents. With the exception of **5b**, all of the complexes are soluble in chlorinated hydrocarbons and other polar solvents. Complex **5b** is only slightly soluble in chlorinated hydrocarbons, but soluble in highly polar solvents.

Unlike our previously reported N,S ligands [5], the Schiff base ligands reported here are stable with regards to hydrolysis when complexed to the ruthenium center as evidenced by the increased yields for the complexes. Analysis of the filtrate by ^{1}H NMR showed no evidence of aldehyde or aniline, indicating this new generation of



R^1	R^2	compound	R^1	R^2	compound
CH_2Ph	4-C_6H_4-OMe	**1a**	^{i}Pr	4-C_6H_4-OMe	**2a**
CH_2Ph	4-C_6H_4-Br	**1b**	^{i}Pr	4-C_6H_4-Br	**2b**
CH_2Ph	4-C_6H_4-OPh	**1c**	^{i}Pr	4-C_6H_4-OPh	**2c**
CH_2Ph	4-C_6H_4-^{i}Pr	**1d**	^{i}Pr	4-C_6H_4-^{i}Pr	**2d**
CH_2Ph	4-C_6H_4-Me	**1e**	^{i}Pr	4-C_6H_4-Me	**2e**
CH_2Ph	3-C_6H_4-CF_3	**1f**	Et	4-C_6H_4-OMe	**3a**
CH_2Ph	3-C_6H_4-I	**1g**	Et	4-C_6H_4-Br	**3b**
CH_2Ph	3-C_6H_4-OMe	**1h**	Et	4-C_6H_4-OPh	**3c**
CH_2Ph	C_6H_5	**1i**	Et	4-C_6H_4-^{i}Pr	**3d**
CH_2Ph	3,5-$C_6H_3Me_2$	**1j**	Et	4-C_6H_4-Me	**3e**
CH_2Ph	α-naphthyl	**1k**			
CH_2Ph	2,4,6-mesityl	**1l**			

Scheme 1.



4, **5**, **6**; arene = *p*-cymeme
7; arene = C_6Me_6

R^1	R^2	compound	R^1	R^2	compound
CH_2Ph	4-C_6H_4-OMe	**4a**	^{i}Pr	4-C_6H_4-OMe	**5a**
CH_2Ph	4-C_6H_4-Br	**4b**	^{i}Pr	4-C_6H_4-Br	**5b**
CH_2Ph	4-C_6H_4-OPh	**4c**	^{i}Pr	4-C_6H_4-OPh	**5c**
CH_2Ph	4-C_6H_4-^{i}Pr	**4d**	^{i}Pr	4-C_6H_4-^{i}Pr	**5d**
CH_2Ph	4-C_6H_4-Me	**4e**	^{i}Pr	4-C_6H_4-Me	**5e**
CH_2Ph	3-C_6H_4-CF_3	**4f**	Et	4-C_6H_4-OMe	**6a**
CH_2Ph	3-C_6H_4-I	**4g**	Et	4-C_6H_4-Br	**6b**
CH_2Ph	3-C_6H_4-OMe	**4h**	Et	4-C_6H_4-OPh	**6c**
CH_2Ph	C_6H_5	**4i**	Et	4-C_6H_4-^{i}Pr	**6d**
CH_2Ph	3,5-$C_6H_3Me_2$	**4j**	Et	4-C_6H_4-Me	**6e**
CH_2Ph	α-naphthyl	**4k**	CH_2Ph	4-C_6H_4-OMe	**7a**
CH_2Ph	2,4,6-mesityl	**4l**	CH_2Ph	4-C_6H_4-Br	**7b**

Scheme 2.

N,S-donor Schiff base ligands are more robust than our first generation ligands.

Coordination of the new N,S-donor Schiff base ligands to the cationic ruthenium(II) center is readily observed by changes in the IR and ^{1}H NMR. The C=N stretch for the ligand in the ruthenium complexes is typically 5–15 wavenumbers less than that of the corresponding free ligand. The imine N=C*H* peak shifts upfield for all of the ligands upon coordination. The amount the imine N=C*H* peak shifts upfield upon ligand coordination to the ruthenium center is variable and dependent on the ligand set. The imine protons of all of the ruthenium complexes appear between 8.46 and 8.56 ppm except complex **4l**. In complex **4l** (SCH_2Ph, N-mesityl), the imine N=C*H* shifts upfield by 0.85–7.91 ppm. This is significantly more than the shift for complexes **4a**–**k**. This is most likely due to increased steric interactions between the bulky mesityl group of the N,S ligand and the *p*-cymene ligand. The hexamethylbenzene complexes **7a**–**b** show smaller upfield shifts for the N=C*H* peak in the ^{1}H NMR spectra. The ^{1}H NMR spectra also show a loss of the twofold symmetry of the *p*-cymene ligand, similar to other reported *p*-cymene complexes [5,17]. The four aromatic hydrogens of the *p*-cymene ligand appear as four sets of doublets in the ^{1}H NMR spectra in the range of 5.3–5.6 ppm. The two isopropyl methyls of the *p*-cymene are also inequivalent, appearing as two doublets between 0.9 and 1.1 ppm. However, complex **4l** is again unique, with three very broad *p*-cymene aromatic hydrogen resonances at 5.82, 5.46, and 5.49 ppm. The two doublets for the isopropyl methyl groups appear farther downfield at 1.24 and 1.31 ppm, compared to the other complexes **4a**–**k**.

For all of the ruthenium compounds, the aromatic resonances for the ligand moieties appear in the range of 6.7–8.3 ppm. The complexes **4a**–**l** and **6a**–**e** also exhibit other interesting ^{1}H NMR characteristics. For complexes **4a**–**k**, the two benzyl CH_2 hydrogens are inequivalent. The two proton resonances are separated by approximately 1.2 ppm and appear as doublets near 4.6 and 3.4 ppm. The doublets are coupled to each other as confirmed by ^{1}H COSY experiments. Again, compound **4l** deviates from the rest of the other ruthenium complexes of this ligand set. While it also shows two doublets for the benzyl protons, they are much closer together, separated by only 0.33 ppm. Compounds **6a**–**e** show similar ^{1}H NMR properties to complexes **4a**–**l**. The CH_2 protons of the thioethyl group are also diastereotopic, resulting in an overlapping doublet of quartets near 3.3 ppm and a broad signal near 2.4 ppm for the two inequivalent hydrogens.

Complexes **5a**–**e** also show interesting ^{1}H NMR spectra. Similar to the isopropyl methyl groups on the *p*-cymene ligand, the two methyl groups of the $SCH(CH_3)_2$ moiety in complexes **5a**–**e** are also inequivalent. To assign the four isopropyl methyl doublets, ^{1}H COSY experiments were run. Complex **5d** has a third isopropyl group, and the large doublet which integrates as six protons is the result of the isopropyl methyl groups of the N-$C_6H_4{}^i$Pr fragment, which are equivalent on the NMR timescale.

The complexes **7a**–**b** show a large singlet near 1.7 ppm for the six methyl groups of the hexamethylbenzene ligand, similar to other related complexes [10,18]. As in complexes **4a**–**k**, the two benzyl protons of complexes **7a**–**b** appear as two doubles separated by 1.1 ppm.

2.3. Electrochemical behavior

The ruthenium complexes were analyzed by cyclic voltammetry. With the exception of complex **4l**, all of the *p*-cymene complexes undergo an irreversible oxidation in between 1180 and 1270 mV versus ferrocene/ferrocenium. Complex **4l** is the most difficult to oxidize, with an E_{pa} of 1339 mV. For the ligands prepared from monosubstituted anilines, a plot of E_{pa} versus Hammett constant, σ, reveals linear behavior for all three ligand classes (Fig. 1). As expected, stronger electron donating substituents on the N,S ligand lower the potential required to oxidize the metal center from ruthenium(II) to ruthenium(III). The substituent on the sulfur also plays a role in the oxidation potential. Comparing complexes with the same substituent on the nitrogen, the thioethyl complexes oxidize at the lowest potential, while the thioisopropyl complexes require greater potentials for oxidation. The hexamethylbenzene complexes **7a** and **7b** undergo quasi-reversible oxidations with $E_{1/2}$ values of 1037 and 1091 mV, respectively. There are few reports of electrochemical studies on cationic arene ruthenium complexes. The new N,S complexes reported here oxidize at a lower potential than the related 1,1′-bis(diphenylphosphino)ferrocene complexes, $[(\eta^6\text{-arene})RuCl(\eta^2\text{-dppf})]^+$ [19], but are more difficult to oxidize than the analogous iminophosphine complexes $[(\eta^6\text{-arene})RuCl(Ph_2PCH_2P(Ph_2){=}NC_5F_4N)]^+$ [13b] (Table 1). A related N,N-Schiff base complex, $[(\eta^6\text{-}C_6Me_6)RuCl(NC_5H_4\text{-}2\text{-}CH{=}N{-}N{=}CH\text{-}2\text{-}NC_5H_4)]^+$, [15b] also oxidizes at a higher potential than the N,S-Schiff base complexes reported here. The decrease in the oxidation potential upon changing from an η^6-*p*-cymene ligand to an η^6-hexamethylbenzene ligand is similar to related arene ruthenium complexes [13b,19].

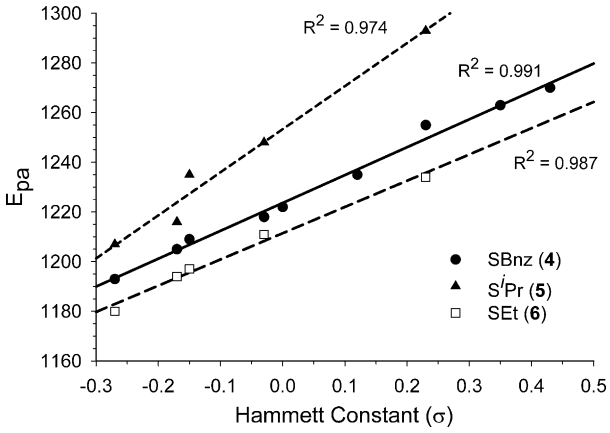


Fig. 1. A plot of E_{pa} vs. Hammett constant, σ, for complexes **4a**–**i** (solid circles), **5a**–**e** (solid triangles), and **6a**–**e** (open squares).

Table 1
Selected electrochemical data for cationic arene ruthenium complexes with the general formula $[(\eta^6\text{-arene})RuCl(L\cap L)]^+$

Complex	E_{pa} (mV)[a]	Ref.
$[(\eta^6\text{-}p\text{-cymene})RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}OMe)]^+$ (**4a**)	1193	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(Me_2CHS\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}OMe)]^+$ (**5a**)	1207	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(CH_3CH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}OMe)]^+$ (**6a**)	1180	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}Br)]^+$ (**4b**)	1255	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}Me)]^+$ (**4e**)	1205	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}3\text{-}CF_3)]^+$ (**4f**)	1270	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_2\text{-}2,4,6\text{-}Me_3)]^+$ (**4l**)	1331	This work
$[(\eta^6\text{-}p\text{-cymene})RuCl(dppf)]^+$[b]	1420	[19]
$[(\eta^6\text{-}p\text{-cymene})RuCl(Ph_2PCH_2P(Ph_2){=}NC_5F_4N)]^+$	980	[13b]
$[(\eta^6\text{-}C_6Me_6)RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}OMe)]^+$ (**7a**)	1037 (1082)[c]	This work
$[(\eta^6\text{-}C_6Me_6)RuCl(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}Br)]^+$ (**7b**)	1091 (1139)[c]	This work
$[(\eta^6\text{-}C_6Me_6)RuCl(dppf)]^+$[b]	1300	[19]
$[(\eta^6\text{-}C_6Me_6)RuCl(Ph_2PCH_2P(Ph_2){=}NC_5F_4N)]^+$	610	[13b]
$[(\eta^6\text{-}C_6Me_6)RuCl(NC_5H_4\text{-}2\text{-}CH{=}N{-}N{=}CH\text{-}2\text{-}NC_5H_4)]^+$	1700[d]	[15b]

[a] Reported vs. ferrocene/ferrocenium couple.
[b] dppf = 1,1′-bis(diphenylphosphino)ferrocene.
[c] $E_{1/2}$ for a quasi-reversible oxidation, E_{pa} value in parentheses.
[d] Reported vs. Ag/AgCl. To obtain values for complexes **7a** and **7b** vs. Ag/AgCl, add 445 mV to the potential reported vs. ferrocene/ferrocenium.

2.4. X-ray crystallographic studies

Single-crystal X-ray structure determinations were carried out for ligand **1a**, and compounds [**4a**][PF_6], [**4l**][PF_6], and [**5e**][BPh_4]. Crystallographic data are listed in Table 2. Selected bond lengths and angles are listed for each compound in Tables 3 and 4. The ArN=CHArS portion of the ligand **1a** is planar (Fig. 2). The imine double bond has a *trans*-geometry, indicating that rearrangement of the ligand must occur for η^2-NS coordination to occur. The C=N bond length is typical of other structurally characterized imines [20].

In the three ruthenium complexes analyzed by X-ray crystallography (Figs. 3–5), the N,S-donor Schiff base ligand is ligated to the cationic ruthenium atom in an η^2-fashion, resulting in a six-membered ring. The complexes are approximately octahedral with the η^6-*p*-cymene ring π-bonded to the ruthenium atom and occupying one face of the octahedron. The other three sites are occupied by the chloride and the N,S-donor Schiff base ligand. The ruthenium atom is situated 1.7069(5), 1.7158(5), and 1.7065(2) Å away from the center of the η^6-*p*-cymene ring for complexes **4a**, **4l**, and **5e**, respectively. The ruthenium–centroid distance for **4l** is longer than that of **4a**

Table 3
Selected bond lengths (Å) for **1a**, **4a**, **4l** · **DCE**, and **5e**

Bond	**1a**	**4a**	**4l** · **DCE**	**5e**
Ru–N		2.132(4)	2.120(2)	2.1194(15)
Ru–Cl1		2.4227(14)	2.3978(11)	2.4024(6)
Ru–S		2.3496(14)	2.3397(9)	2.3469(5)
Ru–Cent[a]		1.7069(5)	1.7158(5)	1.7065(2)
C7–S	1.8209(18)	1.849(6)	1.838(3)	1.847(2)
C10–S	1.7733(17)	1.785(6)	1.769(3)	1.7774(19)
C16–N	1.277(2)	1.280(7)	1.285(3)	1.287(2)
C20–N	1.421(2)	1.451(6)	1.457(3)	1.458(2)

[a] Cent = *p*-cymene ring centroid.

Table 2
Crystallographic data for **1a**, [**4a**][PF_6], [**4l**][PF_6] · **DCE**, and [**5e**][BPh_4]

Compound	**1a**	[**4a**][PF_6]	[**4l**][PF_6] · **DCE**	[**5e**][BPh_4]
Molecular formula	$C_{21}H_{19}NOS$	$C_{31}H_{33}ClF_6NOPRuS$	$C_{35}H_{41}Cl_3F_6NPRuS$	$C_{51}H_{53}BClNRuS$
Formula weight	333.43	749.13	860.14	859.33
Crystal size (mm)	$0.34\times0.32\times0.32$	$0.48\times0.08\times0.06$	$0.45\times0.36\times0.20$	$0.41\times0.36\times0.27$
T (K)	173	100	173	173
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	12.682(6)	14.915(3)	11.501(3)	9.781(2)
b (Å)	7.775(5)	8.3480(10)	14.465(6)	21.899(2)
c (Å)	17.883(11)	24.238(4)	22.605(8)	21.194(3)
β (°)	105.90(5)	96.464(3)	102.08(2)	108.690(10)
V (Å^3)	1695.8(17)	2998.7(9)	3677(2)	4300.2(11)
Z	4	4	4	4
ρ_{calc} (g/cm^3)	1.306	1.659	1.544	1.327
μ (mm^{-1})	0.198	0.800	0.802	0.511
R_1 (F)	0.0365	0.0766	0.0334	0.0275
wR_2 (F^2)	0.1028	0.1908	0.0840	0.0710
Goodness-of-fit	1.028	1.078	1.016	1.020

Table 4
Selected bond angles (°) for **1a**, **4a**, **4l · DCE**, and **5e**

Bond	1a	4a	4l · DCE	5e
N–Ru–Cl1		90.62(12)	87.13(6)	87.05(4)
S–Ru–Cl1		88.36(5)	82.43(3)	91.31(2)
N–Ru–S		86.82(12)	87.20(6)	89.22(4)
C10–S–Ru		106.39(19)	108.98(9)	109.63(6)
C10–S–C7	101.54(8)	98.8(3)	98.78(13)	102.55(9)
N–C16–C15	121.82(14)	128.5(5)	129.1(2)	128.45(17)
C16–N–C20	119.51(13)	114.8(5)	112.9(2)	115.45(15)

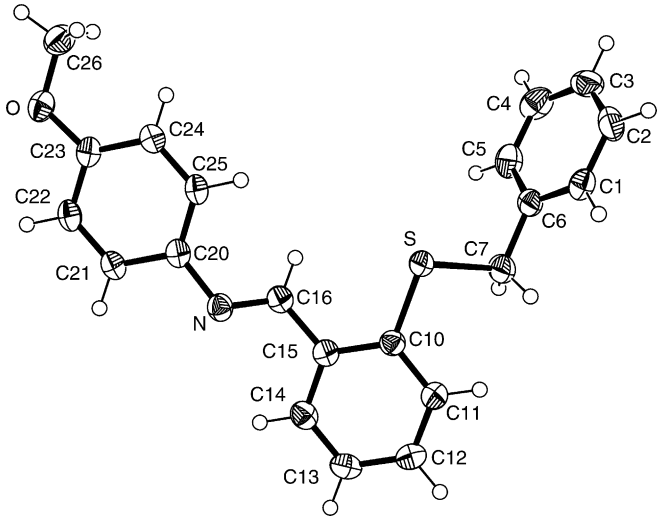


Fig. 2. Structural diagram of ligand **1a** showing the atom-numbering scheme (50% probability ellipsoids). The hydrogen atoms are shown as spheres of arbitrary size.

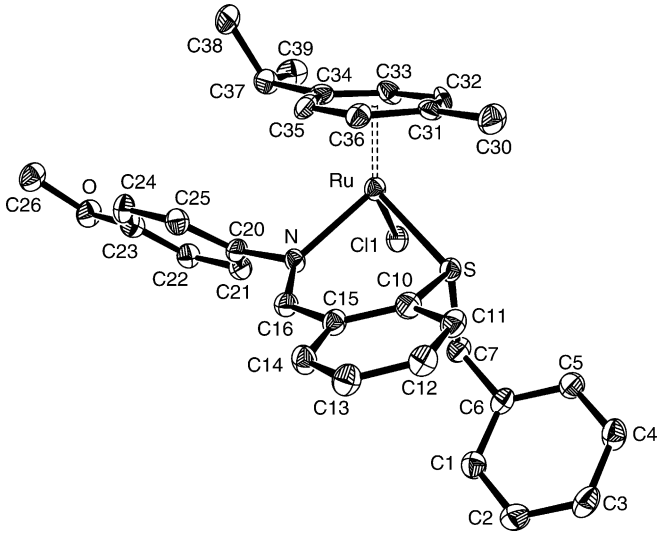


Fig. 3. Structural diagram of complex **4a** showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

and **5e** and is due to an increase in ligand size. The ruthenium–centroid distances are also in agreement with other structurally characterized cationic η^6-*p*-cymene complexes

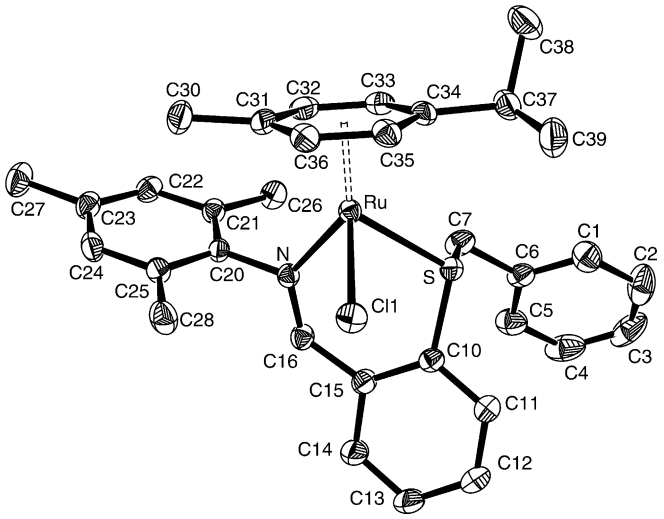


Fig. 4. Structural diagram of complex **4l** showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

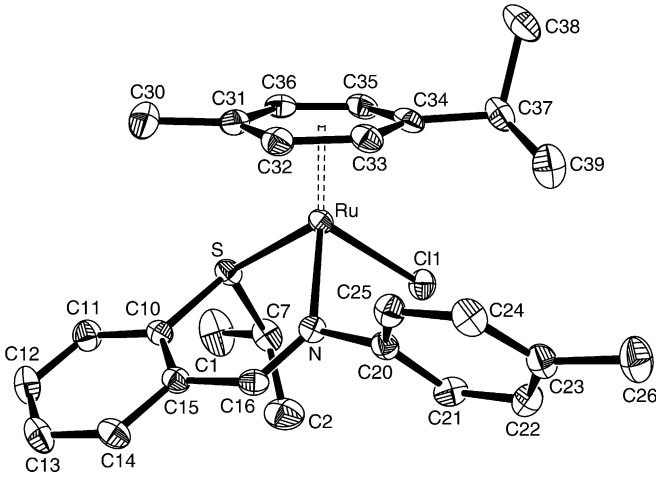


Fig. 5. Structural diagram of complex **5e** showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

of ruthenium [21]. The π-donor *p*-cymene ligand is planar in complexes **4a** and **5e**; however, in complex **4l**, the η^6-*p*-cymene ligand is distorted from planarity. The Ru–C31 bond length in **4l** is statistically longer than the other five Ru–C distances. This can be explained by the large steric bulk of the mesityl group of the Schiff base. It can also be seen from the ORTEP diagram in Fig. 5 that the methyl group of the *p*-cymene (C30) is being pushed up by the bulky mesityl group directly below it. Angle calculations using the software program MERCURY show that the C30–centroid–C37 angle is approximately 174° in **4l**, and about 177° in **4a** and **5e**. While these distortions are not significantly reflected in the coordination geometry of the complex, it does help explain some of the unusually broad ^{1}H NMR and IR characteristics of

complex **4l**. The Ru–S, Ru–Cl, and Ru–N distances are all in line with other structurally characterized η^6-arene ruthenium(II) imine and thioether complexes [21]. The bond angles through ruthenium range from 82° to 91° indicating a slight distortion from the idealized 90° angles of an octahedron. Comparison of the bond angles and lengths in the free ligand **1a** to the ruthenium complex **4a** show little change.

3. Conclusions

A series of new, sterically and electronically tunable sulfur-containing Schiff base ligands has been prepared from 2-(thioalkyl)benzaldehydes and amines. The reaction of $[RuCl_2(\eta^6\text{-arene})]_2$ with the new N,S-donor ligands yielded cationic, half-sandwich ruthenium complexes. The *p*-cymene complexes undergo irreversible oxidations while the oxidations of the hexamethylbenzene complexes are quasi-reversible. The molecular structure of ligand **1a** and complexes **4a**, **4l**, and **5e** were determined by single-crystal X-ray crystallography.

4. Experimental

4.1. General considerations

The complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ were synthesized using the literature procedures [22]. The 2-(thioalkyl)benzaldehydes were synthesized from 2-fluorobenzaldehyde and the corresponding alkanethiol by the literature procedure [16]. The spectroscopic properties of the aldehydes synthesized in this manner agreed the literature [16,23]. All other reagents were obtained from commercial sources and used without further purification. NMR spectra were collected on a Varian Gemini 400 MHz NMR spectrometer and recorded in ppm relative to residual $CHCl_3$ in $CDCl_3$ at 7.26 ppm or residual $CD_3C(O)CD_2H$ in $CD_3C(O)CD_3$ at 2.05 ppm. IR spectra were collected as Nujol mulls on a Nicolet 5sx infrared spectrometer. Melting points are uncorrected. Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois at Urbana-Champaign.

4.2. Cyclic voltammetry

The electrochemical studies were carried out in acetonitrile using a BAS CV-50W potentiostat. A conventional three-electrode cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode was used. The cyclic voltammograms were run in 0.1 M $[Bu_4N][PF_6]$ at a scan rate of 100 mV/s. The scanning limits were +0.5 to +1.9 V versus Ag/AgCl, and the ferrocene/ferrocenium couple appeared at +445 mV versus the Ag/AgCl reference. All potentials are reported versus the ferrocene/ferrocenium couple.

4.3. X-ray crystallography

Colorless crystals of **1a** suitable for crystallography were isolated by layering an ethanol solution of the ligand with water. Orange X-ray quality crystals of the ruthenium compounds [**4a**][PF_6], [**4l**][PF_6] · **DCE**, and [**5e**][BPh_4] were isolated by layering a solution of the ruthenium compound in 1,2-dichloroethane with *n*-heptane.

Data for **1a**, [**4l**][PF_6] · **DCE**, and [**5e**][BPh_4] were collected on a Bruker-Nonius CAD4/Mach3 diffractometer equipped with an Oxford Cryostreams Cobra cryostat using Mo Kα radiation at −100 °C. Data collection and cell refinement was performed using CAD4 express [24]. Data reduction was carried out using XCAD-4 [25]. Unit cell parameters were obtained from a least-squares refinement of 25 centered reflections. The data were corrected for absorption through use of empirical psi-scans [26].

Data for [**4a**][PF_6] were collected at Youngstown State University on a Bruker AXS SMART APEX CCD-equipped diffractometer at −173 °C. Cell refinement and data reduction were accomplished using SAINT+ [27]. Unit cell parameters were obtained from a least-squares refinement of 9644 centered reflections from the data collection. The data were corrected for absorption through use of the SADABS procedure. See Table 1 for a summary of crystal data and X-ray collection information.

Solution and data analysis were performed using the WinGX software package [28]. The structures of were solved by the Patterson method using the program DIRDIF-99 [29]. The refinements were completed using the program SHELX-97 [30]. Hydrogen atoms were assigned positions based on the geometries of their attached carbons. See Table 1 for final refinement parameters.

4.4. Synthesis of Schiff base ligands RS-C_6H_4-2-CH=N-Ar (*1–3*)

A similar procedure was used to synthesize all of the ligands. An example is provided below for ligand **1a**, $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-OMe. A 250 mL round bottom flask equipped with a reflux condenser was charged with 25 mL of absolute ethanol, 2-(benzylthio)benzaldehyde (2.507 g, 10.98 mmol) and *p*-anisidine (1.362 g, 11.05 mmol). The mixture was stirred under reflux for 24 h, cooled to room temperature, and placed in a freezer at −50°C for several hours. The yellow solid that formed was filtered, washed with cold ethanol, and dried in vacuo to yield 3.100 g of yellow precipitate in 85% yield. The other ligands **1**–**3** were prepared using the corresponding anilines and 2-(thioalkyl)benzaldehydes. Solid ligands were isolated by suction filtration and oils were isolated by removing the solvent on a rotary evaporator and used without further purification.

4.4.1. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-OMe (*1a*)

Yellow solid, 85% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.93 (s, 1H, C*H*=N), 8.12 (m, 1H, H_{ar}), 7.45 (m, 1H, H_{ar}), 7.34

(m, 2H, H_{ar}), 7.20 (m, 7H, H_{ar}), 6.92 (m, 2H, H_{ar}), 4.06 (s, 2H, SCH_2), 3.84 (s, 3H, OCH_3). IR (cm^{-1}, Nujol): 1613 (C=N). M.p. 92–93 °C.

4.4.2. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-Br (**1b**)

Beige solid, 72% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.84 (s, 1H, CH=N), 8.10 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.48 (m, 3H, H_{ar}), 7.38 (m, 2H, H_{ar}), 7.21 (m, 5H, H_{ar}), 7.01 (d, $J = 8.4$ Hz, 2H, H_{ar}), 4.05 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1615 (C=N). M.p. 69–71 °C.

4.4.3. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-OPh (**1c**)

Red-orange oil. ^1H NMR (δ, ppm, $CDCl_3$): 8.93 (s, 1H, CH=N), 8.14 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H, H_{ar}), 7.49 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H, H_{ar}), 7.37 (m, 4H, H_{ar}), 7.22 (m, 7H, H_{ar}), 7.13 (td, $J = 7.4$ Hz, 0.8 Hz, 1H, H_{ar}), 7.04 (m, 4H, H_{ar}), 4.07 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1616 (C=N).

4.4.4. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-^iPr (**1d**)

Red-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 8.99 (s, 1H, CH=N), 8.18 (m, 1H, H_{ar}), 7.48 (m, 1H, H_{ar}), 7.37 (m, 2H, H_{ar}), 7.25 (m, 7H, H_{ar}), 7.10 (dt, $J = 8.0$ Hz, 2.0 Hz, 2H, H_{ar}), 4.09 (s, 2H, SCH_2), 2.98 (sept, $J = 7.2$ Hz, 1H, $CH(CH_3)_2$), 1.32 (d, $J = 8.0$ Hz, 6H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1620 (C=N).

4.4.5. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-4-Me (**1e**)

Tan solid, 73% yield. ^1H NMR (δ, ppm, $CDCl_3$): 9.00 (s, 1H, CH=N), 8.20 (dd, $J = 6.8$ Hz, 2.0 Hz, 1H, H_{ar}), 7.49 (m, 1H, H_{ar}), 7.38 (m, 2H, H_{ar}), 7.25 (m, 7H, H_{ar}), 7.09 (d, $J = 8.4$ Hz, 2H, H_{ar}), 4.09 (s, 2H, SCH_2), 2.43 (s, 3H, CH_3). IR (cm^{-1}, Nujol): 1620 (C=N). M.p. 50–51 °C.

4.4.6. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-3-CF_3 (**1f**)

Brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 8.80 (s, 1H, CH=N), 8.12 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.55–7.13 (m, 12H, H_{ar}), 4.06 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1622 (C=N).

4.4.7. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-3-I (**1g**)

Brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 8.76 (s, 1H, CH=N), 8.09 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.55 (m, 1H, H_{ar}), 7.51 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.42–7.20 (m, 6H, H_{ar}), 7.15 (dd, $J = 7.6$ Hz, 1.6 Hz, 2H, H_{ar}), 7.10 (m, 2H, H_{ar}), 4.05 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1616 (C=N).

4.4.8. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_4-3-OMe (**1h**)

Yellow solid, 71% yield.^{1}NMR (δ, ppm, $CDCl_3$): 8.92 (s, 1H, CH=N), 8.12 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H, H_{ar}), 7.46 (m, 1H, H_{ar}), 7.40–7.17 (m, 8H, H_{ar}), 6.81 (ddd, $J = 8.4$ Hz, 2.8 Hz, 0.8 Hz, 1H, H_{ar}), 6.75 (m, 2H, H_{ar}), 4.06 (s, 2H, SCH_2), 3.85 (s, 3H, OCH_3). IR (cm^{-1}, Nujol): 1614 (C=N). M.p. 77–79 °C.

4.4.9. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_5 (**1i**)

Tan solid, 84% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.95 (s, 1H, CH=N), 8.17 (dd, $J = 7.6$ Hz, 2.0 Hz, 1H, H_{ar}), 7.48 (m, 1H, H_{ar}), 7.40 (m, 4H, H_{ar}), 7.28–7.18 (m, 8H, H_{ar}), 4.08 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1627 (C=N). M.p. 43–46 °C.

4.4.10. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_3-3,5-Me_2 (**1j**)

Yellow solid, 94% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.92 (s, 1H, CH=N), 8.14 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H, H_{ar}), 7.46 (m, 1H, H_{ar}), 7.37 (m, 3H, H_{ar}), 7.25 (m, 4H, H_{ar}), 6.90 (br s, 1H, H_{ar}), 6.80 (d, $J = 0.8$ Hz, 2H, H_{ar}), 4.08 (s, 2H, SCH_2), 2.38 (s, 6H, CH_3). IR (cm^{-1}, Nujol): 1616 (C=N). M.p. 58–60 °C.

4.4.11. $PhCH_2S$-C_6H_4-2-CH=N-α-$C_{10}H_7$ (**1k**)

Red-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 9.06 (s, 1H, CH=N), 8.43 (m, 1H, H_{ar}), 8.35 (m, 1H, H_{ar}), 8.90 (m, 1H, H_{ar}), 8.77 (d, $J = 8.0$ Hz, 1H, H_{ar}), 7.58–7.43 (m, 7H, H_{ar}), 7.36–7.21 (m, 5H, H_{ar}), 4.14 (s, 2H, SCH_2). IR (cm^{-1}, Nujol): 1615 (C=N).

4.4.12. $PhCH_2S$-C_6H_4-2-CH=N-C_6H_2-2,4,6-Me_3 (**1l**)

Yellow-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 8.76 (s, 1H, CH=N), 8.14 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H, H_{ar}), 7.16–7.41 (m, 8H, H_{ar}), 6.87 (s, 2H, H_{ar}), 4.08 (s, 2H, SCH_2), 2.31 (s, 3H, CH_3), 2.14 (s, 6H, CH_3). IR (cm^{-1}, Nujol): 1630 (C=N).

4.4.13. ^iPrS-C_6H_4-2-CH=N-C_6H_4-4-OMe (**2a**)

Yellow-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 9.19 (s, 1H, CH=N), 8.20 (m, 1H, H_{ar}), 7.53 (m, 1H, H_{ar}), 7.38 (m, 2H, H_{ar}), 7.27 (m, 2H, H_{ar}), 6.95 (m, 2H, H_{ar}), 3.84 (s, 3H, OCH_3), 3.30 (sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 1.29 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.14. ^iPrS-C_6H_4-2-CH=N-C_6H_4-4-Br (**2b**)

Red oil. ^1H NMR (δ, ppm, $CDCl_3$): 9.14 (s, 1H, CH=N), 8.20 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.54 (m, 3H, H_{ar}), 7.41 (m, 2H, H_{ar}), 7.12 (d, $J = 8.4$ Hz, 2H, H_{ar}), 3.31 (sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 1.29 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.15. ^iPrS-C_6H_4-2-CH=N-C_6H_4-4-OPh (**2c**)

Red-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 9.20 (s, 1H, CH=N), 8.22 (dd, $J = 7.2$ Hz, 2.0 Hz, 1H, H_{ar}), 7.54 (m, 1H, H_{ar}), 7.44–7.30 (m, 4H, H_{ar}), 7.28 (d, 2H, H_{ar}), 7.12 (td, $J = 7.2$ Hz, 0.8 Hz, 1H, H_{ar}), 7.05 (m, 4H, H_{ar}), 3.33 (sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 1.31 (d, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.16. ^iPrS-C_6H_4-2-CH=N-C_6H_4-4-^iPr (**2d**)

Red-brown oil. ^1H NMR (δ, ppm, $CDCl_3$): 9.19 (s, 1H, CH=N), 8.22 (m, 1H, H_{ar}), 7.55 (dd, $J = 6.8$ Hz, 1.6 Hz,

1H, H_{ar}), 7.39 (m, 2H, H_{ar}), 7.27 (d, $J = 8.0$ Hz, 2H, H_{ar}), 7.21 (d, $J = 8.0$ Hz, 2H, H_{ar}), 3.31 (sept, 1H, $J = 6.8$ Hz, SC*H*(Me)$_2$), 2.95 (sept, $J = 6.8$ Hz, 1H, C*H*(CH$_3$)$_2$), 1.28 (d, $J = 6.8$ Hz, 12H, SCH(C*H*$_3$)$_2$ + CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1620 (C=N).

4.4.17. ^{i}PrS-C_6H_4-2-CH=N-C_6H_4-4-Me (**2e**)

Red-brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.25 (s, 1H, C*H*=N), 8.24 (dd, $J = 7.2$ Hz, 2.0 Hz, 1H, H_{ar}), 7.55 (m, 1H, H_{ar}), 7.40 (m, 2H, H_{ar}), 7.22 (m, 4H, H_{ar}), 3.31 (sept, $J = 6.4$ Hz, 1H, C*H*(Me)$_2$), 2.40 (s, 3H, C*H*$_3$), 1.31 (d, $J = 6.4$ Hz, 6H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1620 (C=N).

4.4.18. EtS-C_6H_4-2-CH=N-C_6H_4-4-OMe (**3a**)

Yellow-brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.10 (s, 1H, C*H*=N), 8.15 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.46 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.38 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.30 (m, 3H, H_{ar}), 6.95 (m, 2H, H_{ar}), 3.84 (s, 3H, OC*H*$_3$), 2.93 (q, $J = 7.4$ Hz, 2H, SC*H*$_2$), 1.31 (t, $J = 7.4$ Hz, 3H, SCH$_2$C*H*$_3$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.19. EtS-C_6H_4-2-CH=N-C_6H_4-4-Br (**3b**)

Yellow-brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.04 (s, 1H, C*H*=N), 8.12 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.52–7.40 (m, 4H, H_{ar}), 7.32 (td, $J = 7.6$ Hz, 0.8 Hz, 1H, H_{ar}), 7.13 (m, 2H, H_{ar}), 2.94 (q, $J = 7.4$ Hz, 2H, SC*H*$_2$), 1.31 (t, $J = 7.4$ Hz, 3H, SCH$_2$C*H*$_3$). IR (cm^{-1}, Nujol): 1618 (C=N).

4.4.20. EtS-C_6H_4-2-CH=N-C_6H_4-4-OPh (**3c**)

Brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.10 (s, 1H, C*H*=N), 8.15 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.47 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.43–7.26 (m, 6H, H_{ar}), 7.11 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.06 (m, 4H, H_{ar}), 2.95 (q, $J =$ 7.4 Hz, 2H, SC*H*$_2$), 1.32 (t, $J = 7.4$ Hz, 3H, SCH$_2$C*H*$_3$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.21. EtS-C_6H_4-2-CH=N-C_6H_4-4-^{i}Pr (**3d**)

Yellow-brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.09 (s, 1H, C*H*=N), 8.15 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H, H_{ar}), 7.46 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.41 (td, $J = 7.2$ Hz, 1.6 Hz, 1H, H_{ar}), 7.43–7.21 (m, 5H, H_{ar}), 2.95 + 2.92 (sept, $J = 7.2$ Hz + q, $J = 7.4$ Hz, 3H total, (CH$_3$)$_2$C*H* + SC*H*$_2$), 1.31 + 1.29 (t, $J = 7.4$ Hz + d, $J = 7.2$ Hz, 9H total, SCH$_2$C*H*$_3$ + CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1617 (C=N).

4.4.22. EtS-C_6H_4-2-CH=N-C_6H_4-4-Me (**3e**)

Brown oil. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.08 (s, 1H, C*H*=N), 8.15 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H, H_{ar}), 7.47 (dd, $J = 8.0$ Hz, 1.2 Hz, 1H, H_{ar}), 7.40 (td, $J = 8.0$ Hz, 1.6 Hz, 1H, H_{ar}), 7.32 (m, 1H, H_{ar}), 7.19 (m, 4H, H_{ar}), 2.93 (q, $J = 7.4$ Hz, 2H, SC*H*$_2$), 2.39 (s, 3H, C*H*$_3$), 1.30 (t, $J = 7.4$ Hz, 3H, SCH$_2$C*H*$_3$). IR (cm^{-1}, Nujol): 1619 (C=N).

4.5. Synthesis of ruthenium η^6-p-cymene complexes [RuCl(η^6-p-cymene)(RS-C_6H_4-2-CH=N-Ar)]$^+$ (**4–6**)

A similar procedure was used to prepare all of the ruthenium cymene complexes. A detailed example is given for the preparation of [RuCl(η^6-*p*-cymene)(PhCH$_2$S-C_6H_4-2-CH=N-C_6H_4-4-OMe)][PF_6] ([**4a**][PF_6]). A 30 mL beaker was charged with 0.151 g (0.451 mmol) of **1a**, 0.134 g (0.219 mmol) of [$RuCl_2$(η^6-*p*-cymene)]$_2$ and 15 mL of methanol. The reaction mixture was rapidly stirred at room temperature for 3 h and gravity filtered to remove solid impurities. To the filtrate was added 0.0906 g (0.556 mmol) of NH_4PF_6. The mixture was cooled to −40 °C and a deep orange solid precipitated, which was collected by suction filtration, washed once with cold methanol, and dried in vacuo to yield 0.254 g of [**4a**][PF_6] in 77% yield. The other ruthenium complexes **4–6** were prepared using [$RuCl_2$(η^6-*p*-cymene)]$_2$ and the corresponding ligand. Complexes **5b** and **5e** were isolated as their tetraphenylborate salts using $NaBPh_4$ in place of NH_4PF_6. Complexes **7a** and **7b** were prepared by a similar procedure using [$RuCl_2$(η^6-C_6Me_6)]$_2$ and the corresponding ligand.

4.5.1. [RuCl(η^6-p-cymene)(PhCH$_2$S-C_6H_4-2-CH=N-C_6H_4-4-OMe)][PF_6] ([**4a**][PF_6])

Orange solid, 77% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.52 (s, 1H, C*H*=N), 7.93 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.82 (d, $J = 7.2$ Hz, 2H, H_{ar}), 7.69 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.35 (t, $J = 8.4$ Hz, 1H, H_{ar}), 7.21 (t, $J = 8.4$ Hz, 1H, H_{ar}), 7.14 (d, $J = 8.4$ Hz, 1H, H_{ar}), 7.10 (t, $J = 8.4$ Hz, 2H, H_{ar}), 7.00 (d, $J = 7.2$ Hz, 2H, H_{ar}), 6.75 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.48 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.44 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.38 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.34 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.58 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 3.43 (br d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 2.56 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 1.75 (s, 3H, C*H*$_{3\text{-cymene}}$), 1.03 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.92 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1606 (C=N). *Anal.* Calc. (found) for $C_{31}H_{33}ClF_6NOPRuS$: C, 49.70 (49.47); H, 4.44 (4.38); N, 1.87 (1.95)%. $E_{pa} = 1193$ mV.

4.5.2. [RuCl(η^6-p-cymene)(PhCH$_2$S-C_6H_4-2-CH=N-C_6H_4-4-Br)][PF_6] ([**4b**][PF_6])

Orange solid, 72% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.50 (s, 1H, C*H*=N), 7.95 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.71 (m, 3H, H_{ar}), 7.63 (d, $J = 8.4$ Hz, 2H, H_{ar}), 7.38 (td, $J = 7.6$ Hz, 0.8 Hz, 1H, H_{ar}), 7.22 (t, $J = 7.2$ Hz, 1H, H_{ar}), 7.14 (t, $J = 8.4$ Hz, 2H, H_{ar}), 7.09 (d, $J = 8.4$ Hz, 1H, H_{ar}), 6.75 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.54 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.46 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.39 (m, 2H, H_{cymene}), 4.57 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.41 (br d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 2.59 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 1.74 (s, 3H, C*H*$_{3\text{-cymene}}$), 1.03 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.90 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1597 (C=N). *Anal.* Calc.

(found) for $C_{30}H_{30}ClBrF_6NPRuS$: C, 45.15 (44.97); H, 3.79 (3.72); N, 1.76 (1.77)%. $E_{pa} = 1255$ mV.

4.5.3. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-4-OPh)][PF$_6$] ([**4c**][PF$_6$])

Tan solid, 48% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.56 (s, 1H, C*H*=N), 7.97 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.82 (d, $J = 8.8$ Hz, 2H, H_{ar}), 7.71 (td, $J = 8.4$ Hz, 0.8 Hz, 1H, H_{ar}), 7.38 (m, 3H, H_{ar}), 7.24–7.04 (m, 9H, H_{ar}), 6.76 (d, $J = 8.8$ Hz, 2H, H_{ar}), 5.56 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.47 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.42 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.39 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 4.59 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.40 (br d, $J = 13.2$ Hz, 1H, d, 1H, SC*H*$_2$), 2.61 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 1.75 (s, 3H, C*H*$_{3\text{-cymene}}$), 1.08 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.94 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1609 (C=N). *Anal.* Calc. (found) for $C_{36}H_{35}ClF_6NOPRuS$: C, 53.30 (53.60); H, 4.35 (4.28); N, 1.73 (1.82)%. $E_{pa} = 1218$ mV.

4.5.4. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-4-^{i}Pr)][PF$_6$] ([**4d**][PF$_6$])

Orange solid, 53% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.54 (s, 1H, C*H*=N), 7.95 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.74 (d, $J = 8.0$ Hz, 2H, H_{ar}), 7.70 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.35 (m, 3H, H_{ar}), 7.22 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.14 (t, $J = 7.6$ Hz, 2H, H_{ar}), 7.08 (d, $J = 7.2$ Hz, 1H, H_{ar}), 6.74 (d, $J = 7.6$ Hz, 2H, H_{ar}), 5.53 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.45 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.39 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.36 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.60 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.43 (br d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 2.98 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-SN}}$), 2.55 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-cymene}}$), 1.73 (s, 3H, C*H*$_{3\text{-cymene}}$), 1.29 + 1.28 (d, $J = 7.2$ Hz + d, $J = 6.8$ Hz, 6H total, CH(C*H*$_3$)$_{2\text{-SN}}$), 1.03 (d, $J = 6.8$ Hz, 3H, CH-(C*H*$_3$)$_{2\text{-cymene}}$), 0.79 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_{2\text{-cymene}}$). IR (cm^{-1}, Nujol): 1607 (C=N). *Anal.* Calc. (found) for $C_{33}H_{37}ClF_6NPRuS$: C, 52.07 (51.86); H, 4.90 (4.82); N, 1.84 (1.94)%. $E_{pa} = 1209$ mV.

4.5.5. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-4-Me)][PF$_6$] ([**4e**][PF$_6$])

Orange solid, 52% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.51 (s, 1H, C*H*=N), 7.94 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.70 (m, 3H, H_{ar}), 7.36 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.31 (d, $J = 8.0$ Hz, 2H, H_{ar}), 7.22 (t, $J = 7.2$ Hz, 1H, H_{ar}), 7.14 (t, $J = 7.2$ Hz, 2H, H_{ar}), 7.09 (d, $J = 7.2$ Hz, 1H, H_{ar}), 6.75 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.52 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.45 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.40 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.35 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 4.59 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.44 (br d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 2.56 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 2.42 (s, 3H, C*H*$_{3\text{-SN}}$), 1.75 (s, 3H, C*H*$_{3\text{-cymene}}$), 1.03 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.89 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1607 (C=N). *Anal.* Calc. (found) for $C_{31}H_{33}ClF_6NPRuS$: C, 50.78 (50.64); H, 4.54 (4.50); N, 1.91 (2.10)%. $E_{pa} = 1205$ mV.

4.5.6. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-3-CF$_3$)][PF$_6$] ([**4f**][PF$_6$])

Orange solid, 47% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.54 (s, 1H, C*H*=N), 8.21 (br s, 1H, H_{ar}), 8.00 (m, 2H, H_{ar}), 7.72 (m, 3H, H_{ar}), 7.38 (td, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.23 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.15 (t, $J = 7.6$ Hz, 2H, H_{ar}), 7.09 (d, $J = 7.6$ Hz, 1H, H_{ar}), 6.75 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.60 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.48 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.39 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.34 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.60 (d, $J = 12.8$ Hz, 1H, SC*H*$_2$), 3.44 (br d, $J = 12.8$ Hz, 1H, SC*H*$_2$), 2.56 (∼sept, $J = 7.2$ Hz, 1H, C*H*(Me)$_2$), 1.74 (s, 3H, CH$_{3\text{-cymene}}$), 1.02 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.81 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1609 (C=N). *Anal.* Calc. (found) for $C_{31}H_{30}ClF_9NPRuS$: C, 47.30 (47.09); H, 3.84 (3.84); N, 1.78 (1.81)%. $E_{pa} = 1270$ mV.

4.5.7. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-3-I)][PF$_6$] ([**4g**][PF$_6$])

Orange solid, 61% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.50 (s, 1H, C*H*=N), 8.26 (br s, 1H, H_{ar}), 7.90 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.75 (m, 3H, H_{ar}), 7.37 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.31 (t, $J = 8.0$ Hz, 1H, H_{ar}), 7.23 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.15 (t, $J = 7.6$ Hz, 2H, H_{ar}), 7.07 (d, $J = 7.6$ Hz, 1H, H_{ar}), 6.74 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.57 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.48 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.38 (appearent d, $J = 6.0$ Hz, 2H, H_{cymene}), 4.61 (d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 3.40 (br d, $J = 13.2$ Hz, 1H, SC*H*$_2$), 2.57 (∼sept, $J = 7.0$ Hz, 1H, C*H*(Me)$_2$), 1.77 (s, 3H, CH$_{3\text{-cymene}}$), 1.06 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.89 (d, $J = 6.8$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1603 (C=N). *Anal.* Calc. (found) for $C_{30}H_{30}ClF_6NPIRuS$: C, 42.64 (42.37); H, 3.58 (3.51); N, 1.66 (1.65)%. $E_{pa} = 1263$ mV.

4.5.8. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_4$-3-OMe)][PF$_6$] ([**4h**][PF$_6$])

Orange solid, 71% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.53 (s, 1H, C*H*=N), 7.93 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.69 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.45 (s, 1H, H_{ar}), 7.39 (m, 4H, H_{ar}), 7.22 (m, 1H, H_{ar}), 7.04 (m, 3H, H_{ar}), 6.95 (m, 1H, H_{ar}), 6.76 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.51 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.45 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.38 (m, 2H, H_{cymene}), 4.60 (d, $J = 12.8$ Hz, 1H, SC*H*$_2$), 3.92 (s, 3H, OC*H*$_3$), 3.44 (br d, $J = 12.8$ Hz, 1H, SC*H*$_2$), 2.57 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 1.75 (s, 3H, CH$_{3\text{-cymene}}$), 1.04 (d, $J = 7.2$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.87 (d, $J = 6.4$ Hz, 3H, CH(C*H*$_3$)$_2$). IR (cm^{-1}, Nujol): 1596 (C=N). *Anal.* Calc. (found) for $C_{31}H_{33}ClF_6NOPRuS$: C, 49.70 (50.06); H, 4.44 (4.42); N, 1.87 (1.93)%. $E_{pa} = 1235$ mV.

4.5.9. [RuCl(η^6-p-cymene)(PhCH$_2$S-C$_6$H$_4$-2-CH=N-C$_6$H$_5$)][PF$_6$] ([**4i**][PF$_6$])

Orange solid, 65% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.50 (s, 1H, C*H*=N), 7.90 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.76

(d, $J = 7.6$ Hz, 2H, H_{ar}), 7.67 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.50 (t, $J = 7.6$ Hz, 2H, H_{ar}), 7.39 (m, 2H, H_{ar}), 7.21 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.14 (m, 3H, H_{ar}), 6.78 (d, $J = 7.6$ Hz, 2H, H_{ar}), 5.49 (d, $J = 5.6$ Hz, 1H, H_{cymene}), 5.43 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.36 (m, 2H, H_{cymene}), 4.58 (d, $J = 12.8$ Hz, 1H, SCH_2), 3.47 (br d, $J = 12.8$ Hz, 1H, SCH_2), 2.57 (∼sept, 1H, $J = 6.8$ Hz, $CH(Me)_2$), 1.73 (s, 3H, $CH_{3\text{-cymene}}$), 1.01 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_2$), 0.83 (d, $J = 6.4$ Hz, 3H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1608 (C=N). *Anal.* Calc. (found) for $C_{30}H_{31}ClF_6NPRuS$: C, 50.11 (49.93); H, 4.35 (4.19); N, 1.95 (2.01)%. $E_{pa} = 1222$ mV.

4.5.10. [RuCl(η⁶-p-cymene)(PhCH₂S-C₆H₄-2-CH=N-C₆H₃-3,5-Me₂)][PF₆] ([4j][PF₆])

Orange solid, 70% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.51 (s, 1H, C*H*=N), 7.94 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.70 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.45 (br s, 2H, H_{ar}), 7.35 (td, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.22 (m, 1H, H_{ar}), 7.14 (t, $J = 7.6$ Hz, 2H, H_{ar}), 7.05 (m, 2H, H_{ar}), 6.75 (d, $J = 7.2$ Hz, 2H, H_{ar}), 5.51 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.44 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.36 (m, 2H, H_{cymene}), 4.61 (d, $J = 12.8$ Hz, 1H, SCH_2), 3.43 (br d, $J = 12.8$ Hz, 1H, SCH_2), 2.54 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 2.43 (s, 6H, $CH_{3\text{-SN}}$), 1.74 (s, 3H, $CH_{3\text{-cymene}}$), 1.04 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_2$), 0.87 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1610 (C=N). *Anal.* Calc. (found) for $C_{30}H_{30}ClF_6NPIRuS$: C, 51.44 (51.11); H, 4.72 (4.65); N, 1.87 (1.89)%. $E_{pa} = 1194$ mV.

4.5.11. [RuCl(η⁶-p-cymene)(PhCH₂S-C₆H₄-2-CH=N-α-C₁₀H₈)][PF₆] ([4k][PF₆])

Tan solid, 80% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.46 (s, 1H, C*H*=N), 8.01 (d, $J = 8.0$ Hz, 1H, H_{ar}), 7.91 (m, 4H, H_{ar}), 7.73 (m, 3H, H_{ar}), 7.54 (m, 2H, H_{ar}), 7.24 (m, 2H, H_{ar}), 7.04 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.00 (d, $J = 6.8$ Hz, 2H, H_{ar}), 5.53 (br d, $J = 5.2$ Hz, 1H, H_{cymene}), 5.35 (br d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.04 (br, 1H, H_{cymene}), 4.90 (br d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.76 (d, $J = 12.4$ Hz, 1H, SCH_2), 3.77 (br, 1H, SCH_2), 2.55 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 1.85 (s, 3H, $CH_{3\text{-cymene}}$), 1.12 (d, $J = 6.4$ Hz, 3H, $CH(CH_3)_2$), 0.98 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1597 (C=N). *Anal.* Calc. (found) for $C_{34}H_{33}ClF_6NPRuS$: C, 53.09 (53.05); H, 4.32 (4.30); N, 1.82 (1.90)%. $E_{pa} = 1249$ mV.

4.5.12. [RuCl(η⁶-p-cymene)(PhCH₂S-C₆H₄-2-CH=N-C₆H₂-2,4,6-Me₃)][PF₆] ([4l][PF₆])

Orange solid, 48% yield. ^1H NMR (δ, ppm, $CDCl_3$): 7.91 (s, 1H, C*H*=N), 7.45 (m, 2H, H_{ar}), 7.31–7.12 (m, 5H, H_{ar}), 7.06 (br s, 1H, H_{ar}), 7.00 (br, 2H, H_{ar}), 6.95 (br s, 1H, H_{ar}), 5.81 (br, 1H, H_{cymene}), 5.46 (br, 1H, H_{cymene}), 5.29 (br, 2H, H_{cymene}), 4.71 (d, $J = 12.4$ Hz, 1H, SCH_2), 4.38 (br d, $J = 12.4$ Hz, 1H, SCH_2), 2.66 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 2.37 (s, 6H, $CH_{3\text{-SN}}$), 2.33 (s, 3H, $CH_{3\text{-SN}}$), 1.72 (s, 3H, $CH_{3\text{-cymene}}$), 1.30 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.24 (d, $J = 6.4$ Hz, 3H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1608 (C=N). *Anal.* Calc. (found) for $C_{33}H_{37}ClF_6NPRuS$: C, 52.07 (51.90); H, 4.90 (4.90); N, 1.84 (1.91)%. $E_{pa} = 1331$ mV.

4.5.13. [RuCl(η⁶-p-cymene)(ⁱPrS-C₆H₄-2-CH=N-C₆H₄-4-OMe)][PF₆] ([5a][PF₆])

Orange solid, 62% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.44 (s, 1H, C*H*=N), 7.90 (m, 1H, H_{ar}), 7.84–7.70 (m, 5H, H_{ar}), 6.97 (dd, $J = 7.6$ Hz, 1.6 Hz, 2H, H_{ar}), 5.50 (br d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.42 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.34 (∼t, $J = 6.2$ Hz, 2H, H_{cymene}), 3.85 (s, 3H, OCH_3), 3.76 (∼sept, $J = 6.8$ Hz, 1H, $SCH(Me)_2$), 2.65 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_{2\text{-cymene}}$), 1.77 (s, 3H, $CH_{3\text{-cymene}}$), 1.36 (d, $J = 6.8$ Hz, 3H, $SCH(CH_3)_2$), 1.01 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$), 0.90 (d, $J = 6.8$ Hz, 3H, $SCH(CH_3)_2$), 0.83 (d, $J = 6.0$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$). IR ($cm^{-1}$, Nujol): 1611 (C=N). *Anal.* Calc. (found) for $C_{27}H_{53}ClF_6NOPRuS$: C, 46.25 (46.16); H, 4.74 (4.58); N, 2.00 (2.09)%. $E_{pa} = 1207$ mV.

4.5.14. [RuCl(η⁶-p-cymene)(ⁱPrS-C₆H₄-2-CH=N-C₆H₄-4-Br)][BPh₄] ([5b][BPh₄])

Tan solid, 78% yield. ^1H NMR (δ, ppm, $CD_3C(O)CD_3$): 8.81 (s, 1H, C*H*=N), 8.07 (m, 2H, H_{ar}), 7.92 (m, 2H, H_{ar}), 7.68 (br s, 4H, H_{ar}), 7.33 (m, 8H, $H_{o\text{-BPh4}}$), 6.92 (t, $J = 7.2$ Hz, 8H, $H_{m\text{-BPh4}}$), 6.77 (tt, $J = 7.6$ Hz, 1.2 Hz, 4H, $H_{p\text{-BPh4}}$), 5.81 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.74 (dd, $J = 6.0$ Hz, 1.2 Hz, 1H, H_{cymene}), 5.70 (dd, $J = 6.0$ Hz, 1.2 Hz, 1H, H_{cymene}), 5.61 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 3.71 (∼sept, $J = 6.8$ Hz, 1H, $SCH(Me)_2$), 2.76 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_{2\text{-cymene}}$), 1.82 (s, 3H, $CH_{3\text{-cymene}}$), 1.37 (d, $J = 6.8$ Hz, 3H, $SCH(CH_3)_2$), 1.06 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$), 0.99 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$), 0.88 (d, $J = 6.4$ Hz, 3H, $SCH(CH_3)_2$). IR (cm^{-1}, Nujol): 1612 (C=N). *Anal.* Calc. (found) for $C_{50}H_{50}BBrClNRuS$: C, 64.98 (64.79); H, 5.45 (5.33); N, 1.52 (1.71)%. $E_{pa} = 1293$ mV.

4.5.15. [RuCl(η⁶-p-cymene)(ⁱPrS-C₆H₄-2-CH=N-C₆H₄-4-OPh)][PF₆] ([5c][PF₆])

Orange solid, 77% yield. ^1H NMR (δ, ppm, $CDCl_3$): 8.46 (s, 1H, C*H*=N), 7.94 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.83 (m, 2H, H_{ar}), 7.77 (m, 2H, H_{ar}), 7.72 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.38 (m, 2H, H_{ar}), 7.17 (tt, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.05 (m, 4H, H_{ar}), 5.58 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.44 (dd, $J = 6.0$ Hz, 0.8 Hz 1H, H_{cymene}), 5.38 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.35 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 3.78 (∼sept, $J = 6.8$ Hz, 1H, $SCH(Me)_2$), 2.69 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_{2\text{-cymene}}$) 1.77 (s, 3H, $CH_{3cymene}$), 1.36 (d, $J = 7.2$ Hz, 3H, $SCH(CH_3)_2$), 1.05 (d, $J = 7.2$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$), 0.90 (d, $J = 6.8$ Hz, 3H, $SCH(CH_3)_2$), 0.84 (d, $J = 6.4$ Hz, 3H, $CH(CH_3)_{2\text{-cymene}}$). IR ($cm^{-1}$, Nujol): 1607 (C=N). *Anal.* Calc. (found) for $C_{32}H_{35}ClF_6NOPRuS$: C, 50.36 (49.97); H, 4.62 (4.53); N, 1.84 (1.93)%. $E_{pa} = 1248$ mV.

*4.5.16. [RuCl(η⁶-p-cymene)(ⁱPrS-C₆H₄-2-CH=N-C₆H₄-4-ⁱPr)][PF₆] ([**5d**][PF₆])*

Orange solid, 73% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.42 (s, 1H, C*H*=N), 7.86 (m, 2H, H_{ar}), 7.79 (td, $J = 7.2$ Hz, 1.2 Hz, 1H, H_{ar}), 7.73 (td, $J = 7.6$ Hz, 1.2 Hz 1H, H_{ar}), 7.66 (d, $J = 8.4$ Hz, 2H, H_{ar}), 7.32 (d, $J = 8.4$ Hz, 2H, H_{ar}), 5.53 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.41 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.37 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.31 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 3.78 (∼sept, $J = 6.8$ Hz, 1H, SC*H*(Me)$_2$), 2.95 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-SN}}$), 2.64 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-cymene}}$), 1.75 (s, 3H, C$H_{3\text{-cymene}}$), 1.36 (d, $J = 6.8$ Hz, 3H, SCH(CH_3)$_2$), 1.26 + 1.25 (d, $J = 7.2$ Hz + d, $J = 6.8$ Hz, 6H total, CH(CH_3)$_{2\text{-SN}}$), 1.01 (d, $J = 7.2$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$), 0.85 (d, $J = 6.8$ Hz, 3H, SCH(CH_3)$_2$), 0.75 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$). IR (cm^{-1}, Nujol): 1612 (C=N). *Anal.* Calc. (found) for $C_{29}H_{37}ClF_6NPRuS$: C, 48.84 (48.94); H, 5.23 (5.11); N, 1.96 (2.04)%. $E_{pa} = 1235$ mV.

*4.5.17. [RuCl(η⁶-p-cymene)(ⁱPrS-C₆H₄-2-CH=N-C₆H₄-4-Me)][BPh₄] ([**5e**][BPh₄])*

Orange solid, 78% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.90 (s, 1H, C*H*=N), 7.64–7.53 (m, 3H, H_{ar}), 7.37 (m, 8H, $H_{o\text{-BPh4}}$), 7.18 (m, 3H, H_{ar}), 7.11 (d, $J = 8.4$ Hz, 2H, H_{ar}), 6.94 (t, $J = 7.6$ Hz, 8H, $H_{m\text{-BPh4}}$), 6.83 (t, $J = 7.2$ Hz, 4H, $H_{p\text{-BPh4}}$), 4.98 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.92 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.79 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 4.71 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 3.64 (∼sept, $J = 6.6$ Hz, 1H, SC*H*(Me)$_2$), 2.57 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-cymene}}$), 2.42 (s, 3H, C$H_{3\text{-SN}}$), 1.40 (s, 3H, C$H_{3\text{-cymene}}$), 1.28 (d, $J = 6.8$ Hz, 3H, SCH(CH_3)$_2$), 0.96 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$), 0.81 (d, $J = 7.2$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$), 0.75 (d, $J = 6.4$ Hz, 3H, SCH(CH_3)$_2$). IR (cm^{-1}, Nujol): 1613 (C=N). *Anal.* Calc. (found) for $C_{53}H_{57}BClNRuS$: C, 71.28 (71.26); H, 6.22 (6.24); N, 1.63 (1.83)%. $E_{pa} = 1216$ mV.

*4.5.18. [RuCl(η⁶-p-cymene)(EtS-C₆H₄-2-CH=N-C₆H₄-4-OMe)][PF₆] ([**6a**][PF₆])*

Orange solid, 86% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.47 (s, 1H, C*H*=N), 7.94 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.89 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.78 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.71 (d, $J = 8.8$ Hz, 2H, H_{ar}), 6.97 (d, $J = 8.8$ Hz, 2H, H_{ar}), 5.47 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.41 (d, $J = 6.4$ Hz, 2H, H_{cymene}), 5.35 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 3.85 (s, 3H, OCH_3), 3.32 (m, 1H, SCH_2), 2.58 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 2.40 (br, 1H, SCH_2), 1.75 (s, 3H, C$H_{3\text{-cymene}}$), 1.10 (t, $J = 7.2$ Hz, 3H, SCH$_2$CH_3), 1.03 (d, $J = 6.4$ Hz, 3H, CH(CH_3)$_2$), 0.93 (d, $J = 7.2$ Hz, 3H, CH(CH_3)$_2$). IR (cm^{-1}, Nujol): 1608 (C=N). *Anal.* Calc. (found) for $C_{26}H_{31}ClF_6NOPRuS$: C, 45.45 (45.42); H, 4.55 (4.27); N, 2.04 (1.99)%. $E_{pa} = 1180$ mV.

*4.5.19. [RuCl(η⁶-p-cymene)(EtS-C₆H₄-2-CH=N-C₆H₄-4-Br)][PF₆] ([**6b**][PF₆])*

Orange solid, 87% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.45 (s, 1H, C*H*=N), 7.96 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.91 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.79 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.73 (td, $J = 7.6$ Hz, 1.2 Hz 1H, H_{ar}), 7.60 (br s, 4H, H_{ar}), 5.52 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.42 (m, 3H, H_{cymene}), 3.30 (m, 1H, SCH_2), 2.60 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_2$), 2.37 (br, 1H, SCH_2), 1.73 (s, 3H, C$H_{3\text{-cymene}}$), 1.11 (t, $J = 7.2$ Hz, 3H, SCH$_2$CH_3), 1.02 (d, $J = 7.2$ Hz, 3H, CH(CH_3)$_2$), 0.89 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_2$). IR (cm^{-1}, Nujol): 1601 (C=N). *Anal.* Calc. (found) for $C_{25}H_{28}BrClF_6NPRuS$: C, 40.80 (40.45), H, 3.83 (3.86); N, 1.90 (1.98)%. $E_{pa} = 1234$ mV.

*4.5.20. [RuCl(η⁶-p-cymene)(EtS-C₆H₄-2-CH=N-C₆H₄-4-OPh)][PF₆] ([**6c**][PF₆])*

Orange solid, 78% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.50 (s, 1H, C*H*=N), 7.98 (d, $J = 7.2$ Hz,1H, H_{ar}), 7.88 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.80 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.71 (m, 3H, H_{ar}), 7.39 (m, 2H, H_{ar}), 7.17 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.05 (m, 4H, H_{ar}), 5.53 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.41 (m, 3H, H_{cymene}), 3.32 (m, 1H, SCH_2), 2.63 (∼sept, $J = 6.8$ Hz, 1H C*H*(Me)$_2$), 2.40 (br, 1H, SCH_2), 1.76 (s, 3H, C$H_{3\text{-cymene}}$), 1.10 (t, $J = 7.2$ Hz, 3H, SCH$_2$CH_3), 1.07 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_2$), 0.93 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_2$). IR (cm^{-1}, Nujol): 1600 (C=N). *Anal.* Calc. (found) for $C_{31}H_{33}ClF_6NOPRuS$: C, 46.53 (46.79); H, 4.66 (4.62); N, 2.09 (2.13)%. $E_{pa} = 1211$ mV.

*4.5.21. [RuCl(η⁶-p-cymene)(EtS-C₆H₄-2-CH=N-C₆H₄-4-ⁱPr)][PF₆] ([**6d**][PF₆])*

Orange solid, 69% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.47 (s, 1H, C*H*=N), 7.95 (d, $J = 8.0$ Hz, 1H, H_{ar}), 7.88 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.79 (td, $J = 7.6$ Hz, 1.2 Hz, 1H, H_{ar}), 7.70 (td, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.64 (d, $J = 8.4$ Hz, 2H, H_{ar}), 7.33 (d, $J = 8.4$ Hz, 2H, H_{ar}), 5.51 (d, $J = 6.0$ Hz, 1H, H_{cymene}), 5.39 (m, 3H, H_{cymene}), 3.34 (m, 1H, SCH_2), 2.96 (∼sept, $J = 6.8$ Hz, 1H, C*H*(Me)$_{2\text{-SN}}$), 2.56 (∼sept, $J = 6.4$ Hz, 1H, C*H*(Me)$_{2\text{-cymene}}$), 2.42 (br, 1H, SCH_2), 1.75 (s, 3H, C$H_{3\text{-cymene}}$), 1.27 + 1.26 (d, $J = 6.4$ Hz, d, $J = 6.8$ Hz, 6H total, CH(CH_3)$_{2\text{-SN}}$), 1.11 (t, $J = 7.2$ Hz, 3H, SCH$_2$CH_3), 1.03 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$), 0.79 (d, $J = 6.8$ Hz, 3H, CH(CH_3)$_{2\text{-cymene}}$). IR (cm^{-1}, Nujol): 1608 (C=N). *Anal.* Calc. (found) for $C_{28}H_{35}ClF_6NPRuS$: C, 48.10 (47.79); H, 5.05 (4.96); N, 2.00 (2.04)%. $E_{pa} = 1197$ mV.

*4.5.22. [RuCl(η⁶-p-cymene)(EtS-C₆H₄-2-CH=N-C₆H₄-4-Me)][PF₆] ([**6e**][PF₆])*

Orange solid, 45% yield. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.45 (s, 1H, C*H*=N), 7.94 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.88 (d, $J = 7.6$ Hz, 1H, H_{ar}), 7.79 (t, $J = 7.2$ Hz, 1H, H_{ar}), 7.70 (td, $J = 7.6$ Hz, 1.6 Hz, 1H, H_{ar}), 7.60 (d, $J = 8.0$ Hz, 2H, H_{ar}), 7.27 (d, $J = 8.0$ Hz, 2H, H_{ar}), 5.51

(d, $J = 6.4$ Hz, 1H, H_{cymene}), 5.42 (d, $J = 6.4$ Hz, 2H, H_{cymene}), 5.38 (d, $J = 6.4$ Hz, 1H, H_{cymene}), 3.34 (m, 1H, SCH_2), 2.58 (∼sept, $J = 6.8$ Hz, 1H, $CH(Me)_2$), 2.40 (s, 3H, $CH_{3\text{-}SN}$), 1.76 (s, 3H, $CH_{3\text{-}cymene}$), 1.11 (t, $J = 7.2$ Hz, 3H, SCH_2CH_3), 1.03 (d, $J = 6.4$ Hz, 3H, $CH(CH_3)_2$), 0.89 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$). IR (cm^{-1}, Nujol): 1610 (C=N). *Anal.* Calc. (found) for $C_{26}H_{31}ClF_6NPRuS$: C, 46.53 (46.79); H, 4.66 (4.62); N, 2.09 (2.13)%. $E_{pa} = 1194$ mV.

4.6. Synthesis of ruthenium η^6-hexamethylbenzene complexes $[RuCl(\eta^6\text{-}C_6Me_6)(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}X)]^+$ (7)

4.6.1. $[RuCl(\eta^6\text{-}C_6Me_6)(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}OMe)][PF_6]$ ([**7a**][PF_6])

A 50 mL round bottom flask was charged with 0.0814 g (0.193 mmol) of ligand **1a**, 0.0805 g (0.120 mmol) $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$, and 20 mL of methanol. The reaction mixture was refluxed for 4 h, cooled to room temperature, and gravity filtered to remove solid impurities. The volume was reduced to 5 mL and 0.0565 g (0.347 mmol) NH_4PF_6 was added, and the reaction mixture cooled to −50 °C. The red-brown solid was isolated by suction filtration, washed with cold methanol, and dried in vacuo to give 0.1160 g (62%) of [**7a**][PF_6]. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.66 (s, 1H, C*H*=N), 8.24 (d, $J = 8.8$ Hz, 2H, H_{ar}), 8.08 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.69 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.34 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.15 (t, $J = 7.6$ Hz, 1H, H_{ar}), 7.05 (m, 5H, H_{ar}), 6.67 (d, $J = 6.8$ Hz, 2H, H_{ar}), 4.52 (d, $J = 13.2$ Hz, 1H, SCH_2), 3.88 (s, 3H, OCH_3), 3.41 (d, $J = 13.2$ Hz, 1H, SCH_2), 1.70 (s, 18H, $CH_{3\text{-}arene}$). IR (cm^{-1}, Nujol): 1607 (C=N). *Anal.* Calc. (found) for $C_{33}H_{37}ClF_6NOPRuS$: C, 51.00 (51.53); H, 4.80 (4.75); N, 1.80 (1.90)%. $E_{1/2} = 1037$ mV.

4.6.2. $[RuCl(\eta^6\text{-}C_6Me_6)(PhCH_2S\text{-}C_6H_4\text{-}2\text{-}CH{=}N\text{-}C_6H_4\text{-}4\text{-}Br)][PF_6]$ ([**7b**][PF_6])

A solution of 0.0637 g (0.0953 mmol) of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ and 0.0726 g (0.193 mmol) of ligand **1b** in 20 mL of methanol was refluxed for 4 h. The reaction mixture was cooled to room temperature, gravity filtered to remove solid impurities, and the volume reduced to 5 mL. An excess of NH_4PF_6 (0.0655 g; 0.402 mmol) was added, and the reaction mixture cooled to −50 °C. The red-brown solid was isolated by suction filtration, washed with cold methanol, and dried in vacuo to give 0.0819 g (52%) of [**7b**][PF_6]. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.67 (s, 1H, C*H*=N), 8.21 (d, $J = 8.8$ Hz, 2H, H_{ar}), 8.15 (d, $J = 7.2$ Hz, 1H, H_{ar}), 7.71 (td, $J = 7.6$ Hz, 0.8 Hz 1H, H_{ar}), 7.65 (d, $J = 8.8$ Hz, 2H, H_{ar}), 7.38 (td, $J = 8.0$ Hz, 1.2 Hz, 1H, H_{ar}), 7.14 (m, 2H, H_{ar}), 7.06 (t, $J = 7.6$ Hz, 2H, H_{ar}), 6.68 (d, $J = 6.8$ Hz, 2H, H_{ar}), 4.52 (d, $J = 13.2$ Hz, 1H, SCH_2), 3.42 (d, $J = 13.2$ Hz, 1H, SCH_2), 1.72 (s, 18H, $CH_{3\text{-}arene}$). IR (cm^{-1}, Nujol): 1591 (C=N). *Anal.* Calc. (found) for $C_{32}H_{34}BrClF_6NPRuS$: C, 46.53 (47.03); H, 4.15 (4.05); N, 1.70 (1.81)%. $E_{1/2} = 1091$ mV.

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Appendix A. Supplementary material

Crystallographic data for compounds [**1a**][PF_6], [**4a**][PF_6], [**4l**][PF_6] · **DCE**, and [**5e**][BPh_4] have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC Nos. 297726–297729. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.017.

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