Arene vs Thiophene Reduction in the System $(C_6R_6)Ru(C_4R_4S)^{2+}$ and the Protonation of η^4-Thiophene Ligands

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Abstract: Reaction of $[(C_6Me_6)RuCl_2]_2$ with 4 equiv of AgOTf (OTf is OSO_2CF_3) followed by the addition of various thiophenes gave the salts $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4R_4S)](OTf)_2$ (**1a-c**) where C_4R_4S is thiophene (**1a**), 2,5-dimethylthiophene (**1b**), and 2,3,4,5-tetramethylthiophene (**1c**). Cobaltocene reduction of **1b,c** produced yellow-orange $(C_6Me_6)Ru(C_4R_4S)$ (**2b,c**). ^1H and ^{13}C NMR spectroscopic studies (20 to -70 °C for **2b**) showed that these neutral complexes are described as $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$. Electrochemical reduction of **1c** occurs in two one-electron steps at -442 and -607 mV vs Ag/AgCl. These potentials are close to those for $[Ru(\eta^5\text{-}C_4Me_4S)_2]^{2+}$ but 400 mV more anodic than those for $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$, indicating that the thiophene ligand is a better electron acceptor than the arene. Treatment of **2c** with $Mo(CO)_5(THF)$ afforded $(\eta^6\text{-}C_6Me_6)Ru\{(\eta^4{:}\eta^1\text{-}C_4Me_4S)Mo(CO)_5\}$. Complexes **2b, c** were protonated with NH_4PF_6 affording $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4HR_4S)]PF_6$ (**3b,c**). While $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S)$ (**2a**) appears to be unstable at room temperature, in situ protonation at -78 °C afforded $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_5S)]PF_6$ (**3a**) which was isolable. ^1H NMR spectra of **3a-c**, assigned using homonuclear decoupling and 2-dimensional ^1H-^1H COSY NMR methods, indicate that protonation occurs at the carbon α to sulfur. Treatment of **3a** with ND_4PF_6 gave only one stereoisomer of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4DS)]PF_6$ (**3a-d_1**). The X-ray crystallographic study of **3b** confirms that the protonation has created an sp^3 carbon center with an equatorial hydrogen. The metal coordination sphere consists of an allyl, a thioether, and hexamethylbenzene. Thus protonation reengages the metal-sulfur bond in the conversion of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$ to $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S\text{-}2\text{-}H)]^+$. It is proposed that the hydrogen arrives at the 2-carbon position via the intermediacy of a metal hydride, followed by an agostic complex. $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)]PF_6$ (**3b**) crystallizes in the space group $P2_1/c$ with a = 14.111 (4) Å, b = 9.381 (2) Å, c = 15.820 (3) Å, β = 90.12 (2)°. Refinement of 3102 reflections converged to a final R of 0.039 (R_w = 0.049). The $C(sp^3)$-S bond in **3b** is 1.91 (2) Å, 0.1 Å longer than a normal $C(sp^3)$-S bond. Protonation of $(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ with NH_4PF_6 afforded $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)]PF_6$, which is spectroscopically analogous to **3a-c**.

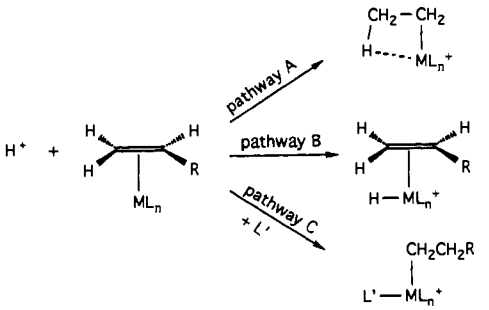
Introduction

The protonation of metal complexes is of both considerable practical and fundamental interest. Practical motivations arise from the fact that protonation of metal complexes is often intimately related to the pathways for metal-ion promoted hydrogen production, the addition of protic substrates to unsaturated organic ligands, and the heterolytic activation of hydrogen.[1] From the fundamental perspective protonation/deprotonation is one of the chief chemical methods for causing change without altering the electron count of the target molecule.

The protonation of 18e metal complexes containing olefinic ligands generally leads to one of three results (Scheme I). Illustrative is the protonation of (arene)Ru(diene) and (C_5Me_5)-Rh(diene) which affords products featuring agostic interactions[2] whereby a fragment of a saturated hydrocarbon serves as a ligand to the metal center (pathway A in Scheme I).[3] These agostic complexes appear to arise via initial protonation at the metal followed by migration of the proton to the coordinated olefin. Supporting this proposal and demonstrating the finely balanced energetics of such systems, protonation of the analogous osmium and iridium diene complexes affords the hydrido diene cations (pathway B in Scheme I). Furthermore it was shown that Lewis bases displace the agostic interaction leading to a classical alkyl complex (pathway C in Scheme I).

The present paper probes the protonation of a special type of metal diene complex, those containing η^4-thiophene ligands. The protonation of thiophene ligands is of interest as it represents a potential pathway by which hydrogen atoms can be transferred to the heterocycle in the course of the hydrodesulfurization (HDS)

Scheme I



process which involves the hydrogenolysis of C-S bonds in organosulfur impurities found in fossil fuels.[1] Since most metal thiophene complexes are cationic and show electrophilic character, protonation of the coordinated heterocycle is not feasible. The recent discovery of η^4-thiophene complexes,[4] however has added a whole new dimension to the question of thiophene reactivity as the reduction confers nucleophilic properties to the heterocycle.

Since HDS is practiced on a very large scale for the removal of organosulfur impurities from fossil fuels, HDS mechanisms are being studied heavily from the perspectives of organometallic[5] and surface chemistry.[6] On the basis of recent solution studies, two

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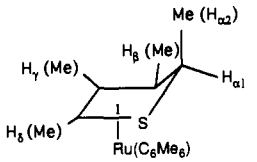
Table I. ^{1}H NMR Data of New Compounds[a]



	C_6Me_6 (C_5Me_5)	α	β	γ	δ
1a[b]	2.70 (s)	7.31 (t)[g]	7.24 (dd)[h]	7.24 (dd)[h]	7.31 (t)[g]
1b[b]	2.65 (s)	2.55 (s)	7.01 (s)	7.01 (s)	2.55 (s)
1c[b]	2.50 (s)	2.41 (s)	2.26 (s)	2.26 (s)	2.41 (s)
2b[c]	1.83 (s)	1.26 (s)	4.41 (s)	4.41 (s)	1.26 (s)
2b (−70 °C)[d]	1.80 (s)	1.30 (s)	4.48 (s)	4.48 (s)	1.30 (s)
2c[c]	1.74 (s)	1.27 (s)	1.75 (s)	1.75 (s)	1.27 (s)
3a[e]	2.04 (s)	3.93 (exo)[i] 3.83 (endo)	3.45 (m)[i]	5.13 (m)[i]	5.99 (m)[i]
3b[e]	2.28 (s)	0.82 (d)[j] 3.99 (q of d)	3.64 (t)[j]	4.89 (d)[j]	2.38 (s)
3c[f]	2.20 (s)	0.82 (d)[k] 3.48 (q)	1.48 (s)	1.84 (s)	2.33 (s)
4c[e]	1.85 (s)	0.92 (d)[l] 4.31 (q)	1.59 (s)	1.95 (d)[l]	2.44 (s)

[a] Spectra recorded at 20 °C unless noted otherwise, referenced to TMS. [b] CD_3COCD_3 solution. [c] C_6D_6 solution. [d] $C_6D_5CD_3$ solution. [e] CD_2Cl_2 solution. [f] $CDCl_3$ solution. [g] Apparent triplet, J(H,H) = 1.8, 2.1 Hz. [h] J(H,H) = 1.8, 2.4 Hz. [i] $J(H_{endo},H_{exo})$ = 10.0, $J(H_{endo},H_\beta)$ = 2.5, $J(H_{exo},H_\beta)$ = 1.0, $J(H_{exo},H_\gamma)$ = 0.5, $J(H_{endo},H_\delta)$ = 0.5, $J(H_\beta,H_\gamma)$ = 3.5, $J(H_\beta,H_\delta)$ = 1.0, $J(H_\gamma,H_\delta)$ = 2.5 Hz. [j] $J(H_\alpha,CH_3)$ = 6.3, $J(H_\alpha,H_\beta)$ = 2.7, $J(H_\beta H_\gamma)$ = 3.6 Hz. [k] $J(H_\alpha,CH_3)$ = 6.6 Hz. [l] $J(H_\alpha,CH_3)$ = 6.3, $J(H_\gamma,^{103}Rh)$ = 0.9 Hz.

general pathways can be envisioned whereby a metal catalyzes the desulfurization of thiophenes. The first emphasizes partial ring hydrogenation followed by cleavage of the C–S bonds. Models for this involve hydride reduction of cationic thiophene complexes.[7] The second means by which metals can desulfurize thiophenes entails cleavage of the heterocycle followed by hydrogenation of metallacyclic intermediates.[8] The stoichiometric HDS of benzothiophene using iron carbonyls giving ethylbenzene has been demonstrated to proceed via direct insertion of metal into a C–S bond.[9] In this report we present results which could interrelate these two pathways since we will show how reduction of the metal thiophene ensemble facilitates protonation of the heterocycle. The proposed involvement of protons shows how heterolytic hydrogen activation, often invoked in discussions of HDS mechanisms,[10] could play a direct role in thiophene activation.

Results

Synthesis of Ru–Thiophene Complexes. The divalent ruthenium thiophene complexes $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4R_4S)](OTf)_2$ (**1a–c**) (C_6Me_6 is hexamethylbenzene) were obtained from the reaction of $[(C_6Me_6)RuCl_2]_2$ with thiophene, 2,5-dimethylthiophene, and 2,3,4,5-tetramethylthiophene according to eq 1. This synthetic

$$[(C_6Me_6)RuCl_2]_2 + 2C_4R_4S + 4Ag^+ \rightarrow 2[(C_6Me_6)Ru(C_4R_4S)]^{2+} + 4AgCl \quad (1)$$

1a, $R_4 = H_4$
1b, $R_4 = 2,5\text{-}Me_2H_2$
1c, $R_4 = 2,3,4,5\text{-}Me_4$

method involves the in situ use of $[(C_6Me_6)Ru(OTf)_2]_n$; analogous reagents were previously shown by us to be highly arenophilic.[11] The lemon yellow salts **1a–c** are air stable and soluble in acetone. The ^{1}H NMR data support the expected sandwich structures with C_1 symmetry.

Reduction of Arene–Ru–Thiophene Dications. Cobaltocene reduction of complexes **1b,c** at −78 °C yielded bright yellow products **2b,c** via the same procedures developed for the preparation of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ (eq 2).[4a] Reduction of **1a** at

$$[(C_6Me_6)Ru(C_4R_4S)]^{2+} + 2Cp_2Co \rightarrow (C_6Me_6)Ru(C_4R_4S) + 2Cp_2Co^+ \quad (2)$$
2a–c

−78 °C yielded an orange yellow solution believed to contain $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S)$ (**2a**). However, such solutions quickly turn red upon warming to room temperature, and the ^{1}H NMR analysis of the solid isolated at room temperature, focusing only on the $C_6(CH_3)_6$ region, shows that a mixture of products is formed in this process. Complex **2b** is more stable than the thiophene derivative as it can be handled at room temperature. Although we were unable to obtain analytically pure samples of **2b**, the ^{1}H and ^{13}C NMR data are convincingly similar to that for the tetramethylthiophene derivative **2c**, which was obtained in analytically pure form. Both **2b** and **2c** exhibited mass spectra consistent with their formulas. We observed the molecular ions as well as strong peaks corresponding to the formulas $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4SO_n)$ (n = 1 and 2). Previous work had shown that $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ reacts with air to give $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)$.[12] Compounds **2b,c** appear less stable in toluene solution than in diethyl ether and alkanes with $t_{1/2}$ = 8.2 (40 °C) and 6.0 h (85 °C), respectively. A detailed study showed that the decomposition of **2b** is first order over 8 half-lives and that the organic decomposition products consist of 95% and 17% of the theoretical amount of C_6Me_6 and $2,5\text{-}Me_2C_4H_2S$, respectively. The fate of the unaccounted for $2,5\text{-}Me_2C_4H_2S$ is of continuing interest; we presume that it has reacted with the ruthenium center.

^{1}H and ^{13}C NMR spectroscopic studies showed that **2b,c** are properly described as $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$, again indicating C_1 symmetry. The formulation $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$ vs $(\eta^4\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4R_4S)$ was first indicated by the observation of only three resonances in the ^{1}H NMR spectra (Table I). In the case of complex **2b**, both ^{1}H and ^{13}C NMR spectra are invariant to −70 °C although ring-folding dynamics for η^4- to η^6-C_6Me_6 in $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_6Me_6)$ is slow on the ^{1}H NMR time scale at 60 MHz and 10 °C.[13] The ^{13}C NMR chemical shifts

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Table II. ^{13}C NMR Data of New Compounds (CH_3 Resonances in Parentheses)[a]

	C_6Me_6 (C_5Me_5)	α^b	β^b	γ^b	δ^b	other
1a[c]	109.21 (17.83)	98.46	94.47	94.47	98.46	*d*
1b[c]	107.96 (16.61)	110.89 (12.08)	97.17	97.17	110.89 (12.08)	122.07[e]
1c[c]	108.76 (17.37)	111.56 (13.47)	106.37 (10.51)	106.37 (10.51)	111.56 (13.47)	122.08[f]
2b[g]	94.69 (16.28)	40.87 (19.18)	75.02	75.02	40.87 (19.18)	
2b (−70 °C)[h]	94.58 (15.78)	40.55 (19.41)	74.56	74.56	40.55 (19.41)	
2c[g]	94.12 (15.78)	38.00 (16.97)	84.65 (12.36)	84.65 (12.36)	38.00 (16.97)	
3a	100.66 (17.50)	61.48	47.66	80.74	70.59	
3b[i]	100.27 (17.73)	73.89 (29.04)	56.44	79.23	85.16 (16.31)	
3c[j]	99.07 (16.15)	73.26 (25.73)	65.65 (12.64)	84.13 (16.72)	89.25 (15.16)	
4c[i]	100.32 (9.60)[h]	70.78 (26.57)[k]	77.01 (12.89)[k]	91.91 (14.75)[k]	97.37 (10.73)[k]	

[a] Spectrum recorded at 20 °C unless noted otherwise. Referenced to TMS. [b] For numbering scheme, see Table I. [c] CD_3COCD_3 solution. [d] The carbon resonance of the CF_3SO_3 was not observed due to limited solubility of **1a** in CD_3COCD_3. [e] $J(^{13}C,^{19}F)$ = 319.6 Hz. [f] $J(^{13}C,^{19}F)$ = 319 Hz. [g] C_6D_6 solution. [h] $C_6D_5CD_3$ solution. [i] CD_2Cl_2 solution. [j] $CDCl_3$ solution. [k] $J(^{13}C_5Me_5\text{-}^{103}Rh)$ = 6.75, $J(^{13}C_\alpha\text{-}^{103}Rh)$ = 2.55, $J(^{13}C_\beta\text{-}^{103}Rh)$ = 9.40, $J(^{13}C\gamma\text{-}^{103}Rh)$ = 9.10, $J(^{13}C_\delta\text{-}^{103}Rh)$ = 5.85, $J(^{13}CH_{3\alpha}\text{-}^{103}Rh)$ = 2.02 Hz.

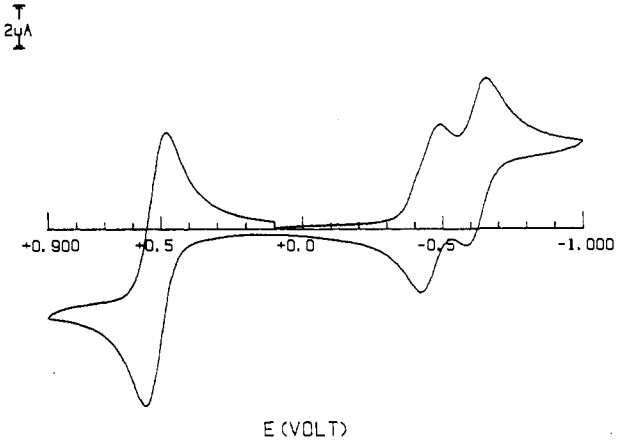

Figure 1. Cyclic voltammogram of an acetone solution (0.1 M Bu_4NPF_6) of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4Me_4S)](OTf)_2$ (10^{-3} M) and $(C_5H_5)_2Fe$ (10^{-3} M). Scan rate was 50 mV/s (vs Ag/AgCl).

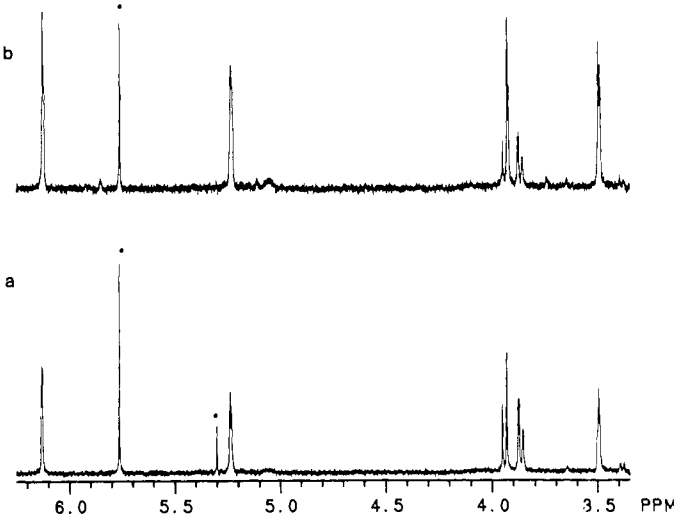

Figure 2. 500-MHz ^1H NMR spectra (20 °C) of $CDCl_3$ solutions of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)]PF_6$ (**3b**, spectrum a) and $[(\eta^6\text{-}C_6Me_6)\text{-}Ru(\eta^4\text{-}C_4H_4S\text{-}2\text{-}D)]PF_6$ (**3b**-d_1, spectrum b). The latter contains ~28% unlabeled **3b**. Only the regions for the C_4H_4S-2-H(D) signals are shown. Peaks labeled with an asterisk arise from Cp_2CoOTf (5.76 ppm) and CH_2Cl_2 (5.31 ppm).

for the α-carbon centers in the C_4R_4S ligands are shifted upfield by 70 ppm upon reduction (Table II). These values, 40.87 (**2b**) and 38.00 (**2c**) ppm, are similar to the 42.87 ppm value observed previously in $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$.[14] The ^{13}C NMR shifts for C_6Me_6 change by only 14 ppm upon conversion of **1b,c** to **2b,c**.

The reduction of **1c** was also examined by cyclic voltammetry (Figure 1). We observed two waves at −442 and −607 mV vs Ag/AgCl. The ratio of the anodic to cathodic currents indicates that the reductions are reversible. The plot of i_p vs (scan rate)$^{1/2}$ over the range 50–800 mV/s for the first reduction step was linear, indicating that the reduction is diffusion controlled. ΔE_p for both reduction waves changed from 100 to 60 mV as scan rates were slowed from 800 to 100 mV/s. The electrochemical results on **1b** were qualitatively similar both in wave form and potential to those for **1c**; however, faster scan rates were required to achieve quasireversibility.

The structural assignment for **2c** was also supported by its reactivity with $Mo(CO)_5(THF)$ to give $(C_6Me_6)Ru\{(\eta^4\text{:}\eta^1\text{-}C_4Me_4S)Mo(CO)_5\}$. This type of complexation reaction has been observed previously.[8b]

Protonation of $(C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$. THF solutions of **2b,c** were found to react readily with protic reagents. We initially examined the reaction of **2c** with trifluoromethanesulfonic acid but obtained a mixture of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4HMe_4S)]^+$ and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4Me_4S)]^{2+}$. The dication apparently arises via the reduction of protons to dihydrogen. Protonations of **2a–c** were effected by treating the THF solutions of the Ru(0) precursors with an excess of NH_4PF_6. Even the unstable $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S)]$ could be protonated with NH_4PF_6 at low temperatures. Once isolated, these monoprotonated complexes do not react further with HOTf. It is interesting to note that we observed initial formation of a red intermediate that dissappeared upon warming to room temperature. Boekelheide et al. also observed a transient red intermediate upon protonation of $[Ru(C_6Me_6)_2]$ and attributed it to the hydrido $[RuH(C_6Me_6)_2]^+$.[15] The yellow air stable salts of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4HR_4S)]PF_6$ (**3a–c**) were obtained after recrystallization from dichloromethane/diethyl ether (eq 3). Cobaltocene reduced solutions of **1a** were also found to react with ND_4PF_6 at low temperature to give $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4H_4S\text{-}2\text{-}D)]PF_6$ (**3a**-d_1).

$$(C_6Me_6)Ru(C_4R_4S) + NH_4PF_6 \xrightarrow{-NH_3} \underset{\textbf{3a–c}}{[(C_6Me_6)Ru(C_4R_4S\text{-}2\text{-}H)]PF_6} \quad (3)$$

The 300-MHz ^1H NMR analysis shows that **3a–c** were obtained as single stereoisomers of low symmetry. In the case of the 2,5-dimethylthiophene complex **3b**, one methyl group on the thiophene appears as a doublet, establishing that the added proton is located on a carbon α to the sulfur. The $^1H\text{–}^1H$ COSY spectrum of **3a** established the coupling pattern. It was also found that in **3a** decoupling of the hydrogen atom attached to carbon adjacent to the methylene group gave a spectrum consisting of AB and AM multiplets which showed some long-range (1,3- and 1,4-) couplings. The ^1H NMR spectrum of **3a**-d_1 indicates that the deuterium was stereospecifically incorporated into the α-position (Figure 2). The percent incorporation of deuterium was determined by ^1H NMR

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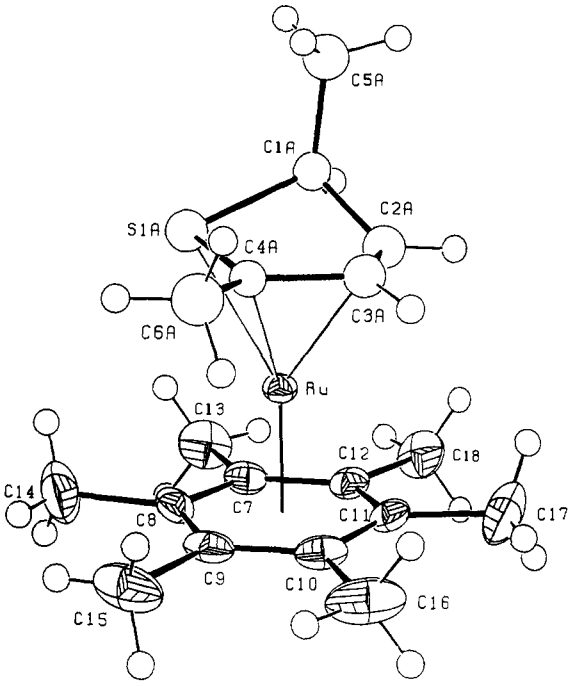

Figure 3. ORTEP plot of the cation in $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)]PF_6$ with thermal ellipsoids drawn at the 35% probability level.

analysis to be 72%. The $^2H\{^1H\}$ NMR spectrum of **3a**-d_1 showed one signal at 3.83 ppm.

It was also found that the previously reported $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ reacts with NH_4PF_6 to give $[(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)]PF_6$ (**4c**). The characterization data for **4c** are rather similar to those for **3c**. The ^{103}Rh couplings to the ^{13}C signals of the C_4Me_4S-2-H carbon atoms were observed. The ^1H NMR spectrum consists of signals from five types of methyls, one of which is a ^{103}Rh-coupled doublet, and one is a ^1H-coupled doublet. The unique equatorial proton appears as a quartet. The structure of **4c** has also been determined by single-crystal X-ray structure study.[16]

Crystallographic Characterization of $[(C_6Me_6)Ru(2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)]PF_6$. Crystals were first grown of the tetramethylthiophene derivative **3c**. The preliminary structure solution generally resembled that for the dimethylthiophene complex described below, but the structure was severely disordered. The crystallographic study of **3b** proved relatively less complicated (Figure 3). The protonated thiophene five-membered ring exhibits a 2-fold disorder resulting from the superposition of the two enantiomeric cations. The structures of the two components of the disorder model were quite similar (±0.01 Å in all distances, ±2° in all angles) and the ensuing discussion will focus only on molecule "A". The complex is best described as $[(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S\text{-}2\text{-}H)]PF_6$ wherein the Ru center is coordinated by an allyl, hexamethylbenzene, and a thioether. The Ru–S distance of 2.326 (3) Å is only slightly shorter than the averaged Ru–S distance 2.339 and 2.373 Å in the thiacrown ether complexes $[Ru(9\text{-}S\text{-}3)_2](OTf)_2$,[17] and $[Ru(12\text{-}S\text{-}3)_2](BF_4)_2$,[17] respectively, and 2.372 Å in $RuCl_2[(tol)_2P\text{-}8\text{-}dibenzothiophene]_2$.[18] The added proton is equatorial. This stereochemistry is opposite to the case of $Mn(CO)_3(\eta^4\text{-}C_4H_4S\text{-}2\text{-}CN)$[19,20] where the CN group is axial. Atoms C2A, C3A, C4A, and S1A are planar to within 0.040 Å. The dihedral angle between planes C2A–C3A–C4A–S1A and S1A–C1A–C2A is 38.9°. A particularly noteworthy structural result is the C(sp^3)–S distance C1A–S1A which is 1.91 (1) Å, 0.1 Å longer than C(sp^3)–S bonds typically seen in aliphatic thioethers and sulfonium salts. C–S distances in coordinated thioether ligands tend to be longer than in simple thioethers; some examples are as follows: $(C_4H_8S)_3RhCl_3$, 1.809–1.831 (5) Å,[21] $[Ru(9\text{-}S\text{-}3)_2](OTf)_2$, 1.814–1.840 (3) Å,[17] and $[Ru(12\text{-}S\text{-}3)_2](BF_4)_2$, 1.812–1.827 (2) Å.[17] A listing of ten C–S distances for sulfonium ions which contain at least one acylic C–S bond reveals a range from 1.79 to 1.82 Å.[22] The C(sp^3)–S distance in $Mn(CO)_3(\eta^4\text{-}C_4H_4S\text{-}2\text{-}CN)$[19] is 1.831 (6) Å.

Discussion

The chemistry of ruthenium(0) thiophene complexes has been successfully investigated for the first time. The project exploited the fact that the $(C_6Me_6)Ru^{2+}$ fragment forms particularly robust thiophene complexes. In contrast, we have been unable to prepare thiophene or dimethylthiophene adducts of $(C_5Me_5)Rh^{2+}$. The hexamethylbenzene also plays an important role in the stability of the reduced derivatives since $Ru(C_4Me_4S)_2$ decomposes readily under ambient conditions.[23] The order of the kinetic stability of the Ru(0) thiophene complexes correlates with the degree of ring methylation, following a trend seen previously.[24] It is intriguing that the decomposition of **2a–c** affords the majority of the available hexamethylbenzene but only ~15% of the thiophene. Thiophene is known to decompose on the clean Ru surfaces at 125 K.[25] It is also significant that the decomposition of **2b** proceeds via a first-order pathway. In contrast it was previously found that $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ decomposes via an associative pathway with loss of C_4Me_4S to give $\{(C_5Me_5)Rh\}_3(\eta^4\text{:}\eta^1\text{-}C_4Me_4S)_2$.

The three principal conclusions drawn from this work are described below.

(*a*) *Thiophene ligands are reduced in preference to arenes.* This was tested by comparing arene and thiophene ligands within the same complex. The spectroscopic data for compounds **2b,c** clearly support the formulation $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$. Furthermore, the ^1H and ^{13}C NMR spectra of **2b** remain unchanged over the range of 20 to −70 °C. In contrast ring folding (η^4- to η^6-) occurs with a barrier of 67.4 kJ/mol in $Ru(C_6Me_6)_2$.[13] The preferential reduction of the thiophene vs the arene ligand is consistent with the relatively milder reduction potentials for the homoleptic complexes $[Ru(C_4Me_4S)_2]^{2+}$ (−392, −568 mV vs Ag/AgCl)[21] vs $[Ru(C_6Me_6)_2]^{2+}$ (2e at −976 mV).[26] The average reduction potential for **1c**, at −525 mV, differs by only 45 mV from that of $[Ru(C_4Me_4S)_2]^{2+}$. The value, −525 mV, is far less than the average of the reduction potentials for the homoleptic C_6Me_6 and C_4Me_4S complexes which is −728 mV. This indicates that the reduction is localized on the thiophene ligand. The mild potentials with which thiophenes are reduced underscore the importance of the η^4-bonding mode in the coordination chemistry of thiophenes.

(*b*) *Complexes with η^4-thiophene ligands are highly basic.* The effective Brönsted basicity of the η^4-C_4R_4S complexes appears relatively high since the protonation requires only NH_4PF_6 (pK_a = 9.24). Previous studies on the protonation of $(C_5Me_5)Rh$(diene) and (arene)Ru(diene) employed strong acids like HBF_4, HPF_6, and HOTf (pK_a's ~ −20).[3] An earlier study showed that $(C_5Me_5)Rh$(diene) could be protonated with trifluoroacetic acid

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Table III. Microanalytical Data (Theoretical Values in Parentheses)

	C	H	S
$[(C_6Me_6)Ru(C_4H_4S)](OTf)_2$	33.52 (33.49)	3.41 (3.43)	14.91 (14.90)
$[(C_6Me_6)Ru(2,5\text{-}Me_2C_4H_2S)](OTf)_2$	35.45 (35.66)	3.89 (3.89)	14.56 (14.28)
$[(C_6Me_6)Ru(C_4Me_4S)](OTf)_2$	37.70 (37.66)	4.30 (4.31)	13.74 (13.71)
$(C_6Me_6)Ru(C_4Me_4S)$	60.14 (59.52)	7.66 (7.49)	7.48 (7.94)
$(C_6Me_6)Ru(C_4Me_4S)Mo(CO)_5$	47.17 (46.95)	4.82 (4.73)	4.03 (5.01)
$[(C_6Me_6)Ru(C_4H_4S\text{-}2\text{-}H)]PF_6$	39.11 (38.94)	4.80 (4.70)	6.71 (6.50)
$[(C_6Me_6)Ru(2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)]PF_6$	41.47 (41.46)	5.33 (5.22)	6.32 (6.15)
$[(C_6Me_6)Ru(C_4Me_4S\text{-}2\text{-}H)]PF_6$	43.37 (43.71)	5.74 (5.68)	5.39 (5.83)

(pK_a = 0.23).[27] Furthermore, Bennett et al. found that the resulting agostic complexes could be deprotonated by Na_2CO_3 (pK_a of HCO_3^- = 10.33).[3] We propose that the effective basicity of the M(η^4-C_4R_4S) subunit is enhanced because protonation at carbon is *coupled* to thioether ligation. Thus the equilibrium constant for the conversion of **2a–c** to **3a–c** (eq 3) is the product of two successive equilibria, K_a, for the formation of the agostic (or metal hydride) complex and the formation constant related to the binding of the thioether (eq 4).

$$K = \frac{[(C_6Me_6)Ru(\text{agostic-}C_4R_4HS)^+]}{[H^+][(C_6Me_6)Ru(C_4R_4S)]} \times \frac{[(C_6Me_6)Ru(\eta^4\text{-}C_4R_4S\text{-}2\text{-}H)^+]}{[(C_6Me_6)Ru(\text{agostic-}C_4R_4HS)^+]} \quad (4)$$

(c) *The protonation reaction is stereoselective, giving the endo addition adjacent to sulfur.* Only one isomer is observed by both ^1H and ^{13}C NMR spectroscopies for all three thiophene derivatives. The stereochemistry of the added hydrogen atom is equatorial (endo) based on the crystallographic determination. This stereochemical result suggests that the proton arrives at the carbon center via initial protonation at the metal (Scheme II). Recent work on the protonation of $(C_5Me_5)Rh$(diene) and (arene)Ru(diene) supports a mechanism that proceeds via agostic intermediates, although in our case such an intermediate would be expected to have only a transient existence as it would be susceptible to displacement (intramolecularly) by the thioether.[2] Thus the overall reaction sequence connecting compounds **2a–c** to **3a–c** involves each of the three pathways described in Scheme I.

Other examples of η^4-C_4R_4S-2-H complexes are of the type $Mn(CO)_3(\eta^4\text{-}C_4R_4S\text{-}2\text{-}H)$.[28] Angelici and co-workers synthesized these compounds by the reduction of $[Mn(CO)_3(\eta^5\text{-}C_4R_4S)]^+$ using BH_4^- and $HFe(CO)_4^-$. These analogous deuteride reductions gave both endo and exo $Mn(CO)_3(\eta^4\text{-}C_4R_4S\text{-}2\text{-}D)$ in a ~1:4 ratio. The protonation of $Ru(C_6Me_6)_2$ and other related low-valent complexes of cyclic π-hydrocarbons is known to proceed stereoselectively, resulting in endo addition of the proton.[29]

Concluding Remarks

Our results are possibly relevant to the hydrogenolysis of thiophenes by sulfided metal catalysts insofar as reduction followed by protonation is equivalent to and, we think, more realistic than hydride reduction. Metal sulfide catalysts are known to react with hydrogen to give surface SH groups.[10] The protic character of bridging SH ligands has been demonstrated.[30] Thus one can envision the following sequence of events for partial hydrogenation of thiophene by a sulfided catalyst: thiophene coordination, electron transfer to the heterocycle, proton transfer to the ring, and then C–S cleavage. This proposal, in conjunction with the finding that **3a** undergoes C–S bond cleavage,[31] lays the basis for further studies on the reactivity of partially hydrogenated thiophene ligands.

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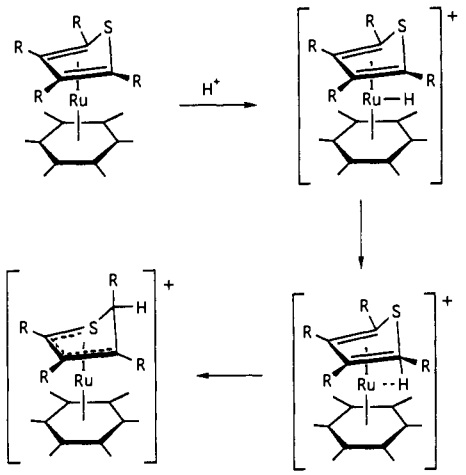
Scheme II



Experimental Section

General procedures were described recently.[14] The following starting materials were prepared using literature methods: $[(C_6Me_6)RuCl_2]_2$[32] and C_4Me_4S.[8b] The loading of samples for field desorption mass spectra results in air exposure. ND_4PF_6 was prepared by dissolving NH_4PF_6 in D_2O (99.9% D) followed by evaporation. Electrochemical measurements were recorded on 0.1 M Bu_4NPF_6 electrolyte acetone solutions which were 0.001 M in the analyte. The instrument was a BAS-100 employing platinum as working and auxilliary electrodes. Analytical and NMR data are presented in Tables I–III.

$[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4R_4S)](OTf)_2$ (1a–c). The following procedure for **1a** is representative. Under an atmosphere of Ar, 0.778 g of solid AgOTf (3.028 mmol) was added to an orange slurry of 0.505 g of $[(C_6Me_6)RuCl_2]_2$ (0.755 mmol) in 50 mL of CH_2Cl_2. A white solid precipitated immediately. After being stirred for *ca.* 2 h, the mixture was filtered. To the deep red filtrate was added ~3 mL of thiophene, resulting in the formation of a yellow precipitate. After 3 h, the cream-yellow solid was collected by filtration. This material was extracted into acetone, which was concentrated to ca. 5 mL, and diluted with ca. 50 mL of CH_2Cl_2 to give yellow microcrystals. Yield: 0.700 g (72%). $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4Me_2H_2S)](OTf)_2$ (**1b**) and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}C_4Me_4S)](OTf)_2$ (**1c**) were prepared via similar methods in 80–85% yield.

$(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$ (2b,c). The following procedure for **2b** is representative. To a yellow slurry of 0.484 g of $[(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}2,5\text{-}Me_2C_4H_2S)](OTf)_2$ (0.718 mmol) in 30 mL of freshly distilled THF at −78 °C was added 0.275 g of solid Cp_2Co (1.452 mmol). The light yellow slurry gradually assumed an orange color. After 3 h at −78 °C, the slurry was allowed to warm to room temperature and then filtered. The filtrate was evaporated and the resulting dark brown solid was extracted with hexane. The orange hexane extract was filtered and evaporated leaving bright yellow-orange microcrystals. Yield: 0.210 g (79%). $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (**2c**) was prepared via a similar method in 83% yield.

$(\eta^6\text{-}C_6Me_6)Ru\{(\eta^4{:}\eta^1\text{-}C_4Me_4S)Mo(CO)_5\}$ (2c·Mo(CO)$_5$). A solution of 0.132 g of $Mo(CO)_6$ (0.489 mmol) in 20 mL of THF was photolyzed for ca. 6 h, resulting in a yellow solution. This solution was transferred to a Schlenk flask containing 0.101 g of $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}C_4Me_4S)$ (0.250 mmol). After being stirred for 2 h, the reaction solution was filtered and evaporated. The residue was extracted with hexane yielding a bright yellow solution, evaporation of which gave $(\eta^6\text{-}C_6Me_6)Ru\{(\eta^4{:}\eta^1\text{-}C_4Me_4S)Mo(CO)_5\}$. Yield: 0.12 g (75%). ^1H NMR (d_6-benzene): 1.62 (s, 6 H), 1.52 (s, 18 H), 1.15 (s, 6 H). $^{13}C\{^1H\}$ NMR

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Table IV. Crystal and Experimental Data for **3b**

formula	$C_{18}H_{27}F_6PRuS$
crystal system	monoclinic
space group	$P2_1/c$
a, Å	14.111 (4)
b, Å	9.381 (2)
c, Å	15.820 (3)
β, deg	90.12 (2)
V, Å^3	2094 (2)
Z	4
density (calcd), g cm^{-3}	1.654
color	yellow
dimensions, mm	0.1 × 0.3 × 0.5
temp, K	198
diffractometer	Enraf-Nonius CAD4
μ, cm^{-1}	9.56
transm factor range	0.913–0.759 (numerical)
2θ limit, deg	2.0–11.0 ($\pm h \pm k \pm l$), 2.0–41.0 ($+h \pm k - l$), 41.0–52.0 ($+h \pm k - l$)
no. of intensities measd	5081
no. of unique intensities	4100
no. of intensities with $I > 2.58\sigma(I)$	3102
R	0.039
R_w	0.049
$\rho(r)$, e Å^{-3}	0.91

(d_6-benzene): 214.91 (*C*O), 207.49 (*C*O), 95.49 (C_6Me_6), 85.51 (C_4Me_4S), 44.76 (C_4Me_4S), 15.62 ($C_6(CH_3)_6$), 14.80 ($C_4(CH_3)_4S$), 11.48 ($C_4(CH_3)_4S$). IR (KBr, ν_{CO}, cm^{-1}): 2057, 1981, 1929, 1891, 1855. FDMS: 632–646 (M^+).

[(C_6Me_6)Ru(η^4-C_4R_4S-2-H)]PF_6 (3b,c) and [(C_5Me_5)Ru(η^4-C_4Me_4S-2-H)]PF_6 (4c). The following procedure for **3b** is representative. A mixture of 0.116 g of (C_6Me_6)Ru(η^4-$C_4Me_2H_2S$) (**2b**) (0.308 mmol) and 0.593 g of NH_4PF_6 (3.63 mmol) was dissolved in 40 mL of THF. After 5 h, the solvent was removed under vacuum and the residue was washed with 30 mL of toluene and then exposed to air. The residue was recrystallized by dissolution in CH_2Cl_2 followed by dilution with Et_2O. Yield: 0.126 g (79%). [(η^6-C_6Me_6)Ru(η^4-C_4Me_4S-2-H)]PF_6 (**3c**) and [(C_5Me_5)Rh(η^4-C_4Me_4S-2-H)]PF_6 (**4c**) were prepared via the same method in yields of 90 and 66%, respectively.

[(η^6-C_6Me_6)Ru(η^4-C_4H_4S-2-H)]PF_6 (3a). A 40-mL THF slurry of 0.507 g of [(η^6-C_6Me_6)Ru(C_4H_4S)]$(OTf)_2$ (**1a**) (0.785 mmol) was treated at −78 °C with 0.301 g of cobaltocene (1.592 mmol). The reaction solution gradually assumed an orange color. After 2 h at this temperature, the mixture was quickly filtered through a canula into a 500-mL flask containing 1.268 g of solid NH_4PF_6 (7.779 mmol) under Ar. The resulting red solution was stirred at −78 °C for 2 h. Upon warming to room temperature the color of the solution became yellow. Workup as described for **3b,c** produced a yellow solid. The 400-MHz ^{1}H NMR spectrum showed that the yellow solid consisted of a 1:0.29 mixture of **3a** and Cp_2CoOTf. A solution of this mixture in ca. 100 mL of CH_2Cl_2 was extracted with H_2O and dried over anhydrous Na_2SO_4. Removal of solvent gave analytically pure **3a**. Yield: 0.271 g (70%).

[(η^6-C_6Me_6)Ru(η^4-C_4H_4S-2-D)]PF_6 (3a-d_1). At −78 °C, a 40-mL THF solution of Cp_2Co was added to a 40-mL THF slurry of 0.409 g of [(η^6-C_6Me_6)Ru(η^5-C_4H_4S)]$(OTf)_2$ (**1a**) (0.634 mmol) via cannula. The resulting mixture gradually assumed an orange color. After 1.5 h, the solution was filtered through a medium filter into a 250-mL flask containing 1.70 g of ND_4PF_6 (10.2 mmol). This reaction flask had been pretreated by refluxing D_2O (99% D) followed by drying under vacuum. The mixture was stirred at −78 °C for 2 h. The workup, accomplished as described for **3b,c**, produced a yellow brown solid. The integrated 400-MHz ^{1}H NMR spectrum showed that the CH_2Cl_2 extract was a mixture of **3a**-d_1 and Cp_2CoOTf in a molar ratio of 1:0.14. Pure **3a**-d_1 was obtained via the same method described for **3a**. Yield: 0.26 g (83%). The integrated ^{1}H NMR spectrum showed that all of the deuterium was incorporated into the α-equatorial position. The degree of deuteration, based on the integrated intensities of equatorial-H_α peak, was 72%.

Table V. Selected Bond Distances (Å) and Angles (deg) for **3b**

Ru–S1A	2.326 (3)	C1A–C2A	1.43 (1)
Ru–C2A	2.23 (1)	C2A–C3A	1.45 (2)
Ru–C3A	2.170 (10)	C3A–C4A	1.47 (1)
Ru–C4A	2.10 (1)	C4A–S1A	1.71 (1)
S1A–C1A	1.91 (1)	C1A–C5A	1.51 (2)
S1A–Ru–C2A	67.4 (3)	S1A–C1A–C2A	97.3 (7)
S1A–Ru–C3A	69.4 (3)	S1A–C1A–C5A	112.4 (8)
S1A–Ru–C4A	45.0 (3)	C2A–C1A–C5A	120.2 (9)
C1A–S1A–C4A	94.1 (5)	C1A–C2A–C3A	111.7 (9)
S1A–C4A–C3A	107.4 (7)	C2A–C3A–C4A	111.5 (8)

Crystal Structure Analysis of [(η^6-C_6Me_6)Ru(η^4-2,5-$Me_2C_4H_2S$-2-H)]PF_6 (3b). The yellow, transparent, tabular crystal had well-developed faces. There were no crystallites or other contaminating substances attached to the surface of the sample. The crystal was mounted with epoxy to a thin glass fiber and then cooled to −75 °C with the (1 0 1) scattering planes roughly normal to the spindle axis. The data crystal was approximately bound by the {0 1 0}, {1 0 −1}, { 1 0 1} forms and (−1 1 0) face. Distances from the crystal center to these facial boundaries were 0.05, 0.16, 0.25, and 0.09 mm, respectively.

The structure was solved by Patterson methods (SHELXS-86). After the ruthenium position was determined, subsequent least-squares refinements and difference Fourier syntheses revealed positions for the disordered five-member ring and remaining non-hydrogen atoms. The methyl hydrogen atoms were included as fixed contributors in "idealized" positions. The disordered hydrogen atoms were independently refined; however, owing to high correlation coefficients, C–H bond lengths were constrained preceding each cycle. In the final cycle of least-squares refinement, isotropic thermal coefficients were refined for disordered non-hydrogen atoms, anisotropic thermal coefficients were refined for ordered non-hydrogen atoms, and common isotropic thermal parameters were varied for disordered and methyl hydrogen atoms. Successful convergence was indicated by maximum shift/error for the last cycle. The highest peaks in the final difference Fourier map were in the vicinity of the disorder ligand; the final map had no other significant features. The Fourier map had no significant features either. A final analysis of variance between observed and calculated structure factors showed no systematic errors. The crystallographic data are summarized in Table IV. Selective bond distances and angles are presented in Table V.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond angles and distances for [(C_6Me_6)Ru(η^4-2,5-$Me_2C_4H_2S$-2-H)]PF_6 (10 pages); listing of structure factors (21 pages). Ordering information is given on any current masthead page.