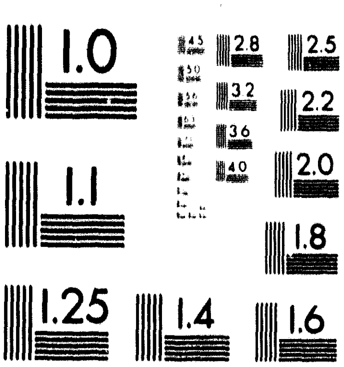
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Progress Report for DOE DEFG02-90ER14146

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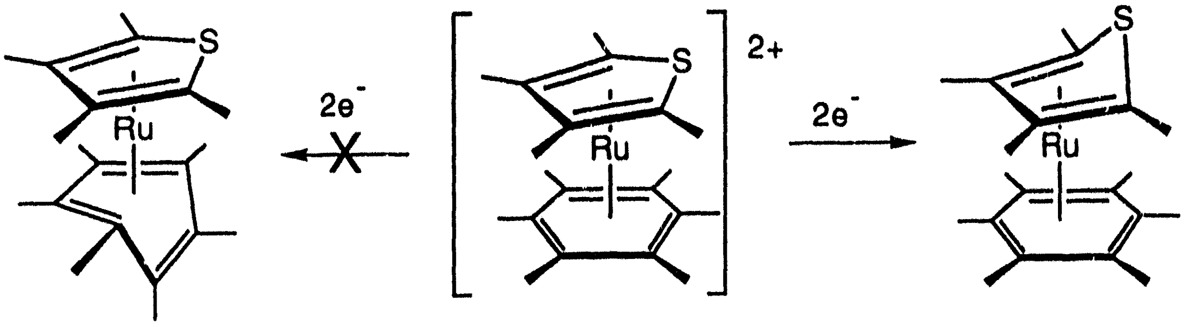
The principal findings of the project, which was initiated August 15, 1990, are summarized in the sections below.

Reduction of Coordinated Thiophenes

This study probed the relative acceptor abilities of arene and thiophene ligands through the study of complexes containing both thiophenes and arenes. It was found that thiophene ligands are reduced in preference to arenes (eq. 1). This is evident not only in the structures and spectroscopy but also by the reduction potentials. The E^{o}'s for $[Ru(C_4Me_4S)(C_6Me_6)]^{2+/+/0}$ (-442, -607 mV) are closer to those for $[Ru(C_4Me_4S)_2]^{2+/+/0}$ (-392, 568 mV) but far more cathodic than for $[Ru(C_6Me_6)_2]^{2+/0}$ (-976 mV). The ease of electrochemical reduction is one of the defining differences between arenes and thiophenes. Interestingly thiophenes are also better *donors* than arenes. This trend reflects their decreased homo/lumo gap compared to arenes.



(1)

Using methods developed for the mixed arene/thiophene complexes, we have isolated and characterized $Ru(C_4Me_4S)_2$. This complex is thermally unstable (>-20 °C), as one would expect for an active desulfurization agent (Ru^0) attached only to its own substrate (thiophene). It exhibits a simple two line ^1H NMR spectrum indicative of a dynamic averaging via rapid making and breaking of the Ru-S bonds. The ^{13}C NMR shifts aupport this proposal as they occur near the average seen for η^4- and η^5-C_4Me_4S. The stable adduct $Ru(C_4Me_4S)_2 \cdot Fe(CO)_4$ is shown in Figure 1.

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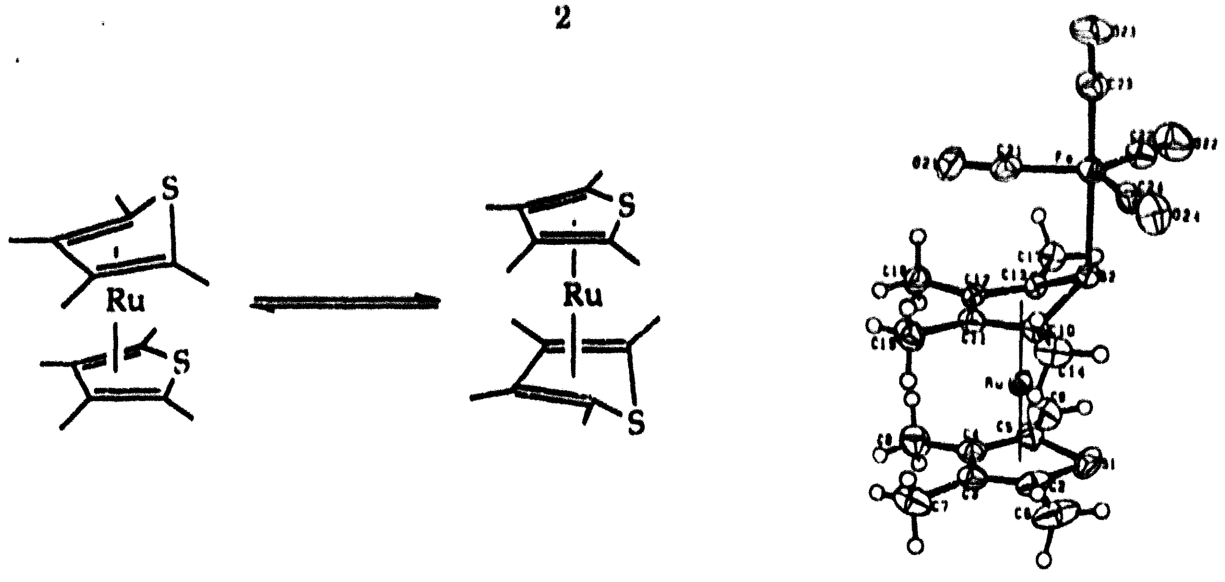
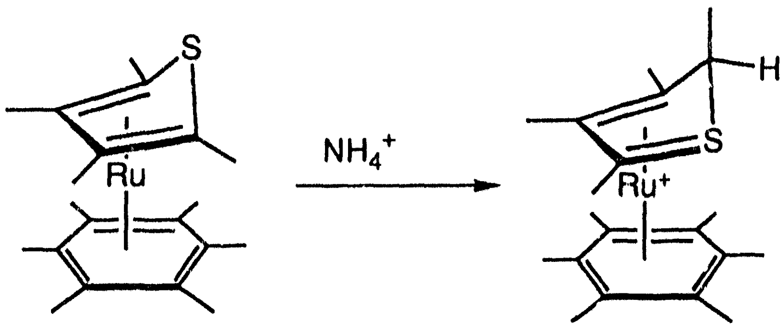


Figure 1.Dynamic ring thiophene ring folding in $Ru(C_4Me_4S)_2$ and structure of its $Fe(CO)_4$ adduct.

Protonation of Reduced Thiophene Complexes

This project examined a new pathway whereby hydrogen can be transfered to thiophene. This relates directly to the possibility that the hydrogenolysis of the heterocycle proceeds via proton transfer from surface SH groups. We found that $(C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$ ($R_4 = Me_4, Me_2H_2, H_4$) and $Cp^*Rh(\eta^4\text{-}C_4Me_4S)$ are easily protonated with NH_4^+. The basicity of the $\eta^4\text{-}C_4R_4S$ complexes is orders of magnitude greater than conventional dienes, possibly because protonation at carbon is coupled to formation of a Ru-S bond. The stereochemistry of the protonation, established by two crystallographic determinations (Figure 2), indicates that the proton attacks the metal then migrates to the heterocycle.



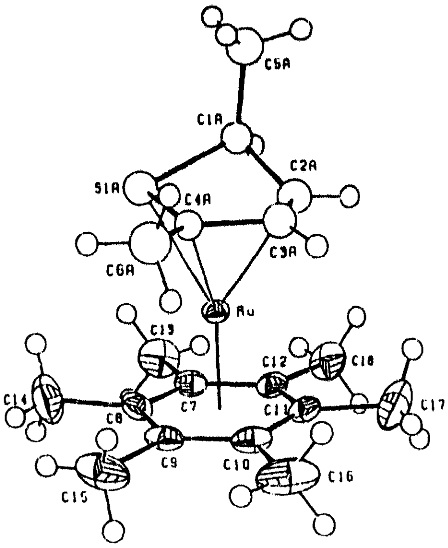


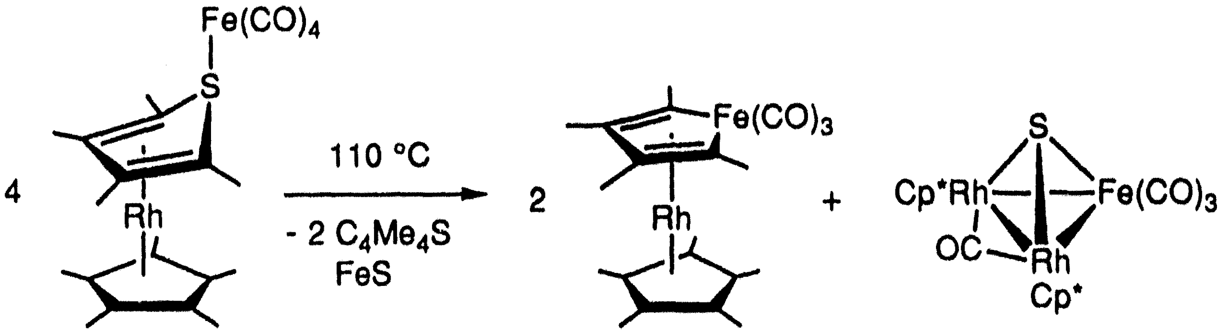
Figure 2. Formation and structure of $[(C_6Me_6)Ru(\eta^4\text{-}2\text{-}H\text{-}C_4Me_2H_2S)]^+$.

Protonation weakens one C-S bond. The C(sp^3)-S bond in the protonated complex is 0.13 Å longer than a conventional C(sp^3)-S bond and 0.2 Å longer than a C-S bond in a thiophene. In unpublished work we have shown that the protonated thiophene complex $(C_6Me_6)Ru(\eta^4\text{-}2\text{-}H\text{-}C_4HS)^+$ undergoes intramolecular C-S scission to give an equilibrium mixture containing the ring-opened isomer.

These results indicate that thiophene hydrogenation can readily proceed via electron transfer to the heterocycle followed by protonation of the reduced thiophene metal ensemble. This proposal suggests a role for the often discussed heterolytic activation of hydrogen by metal sulfides since it is well known that sulfided catalysts react with hydrogen to give surface SH groups which are protic.

Bimetallic Thiophene Desulfurization

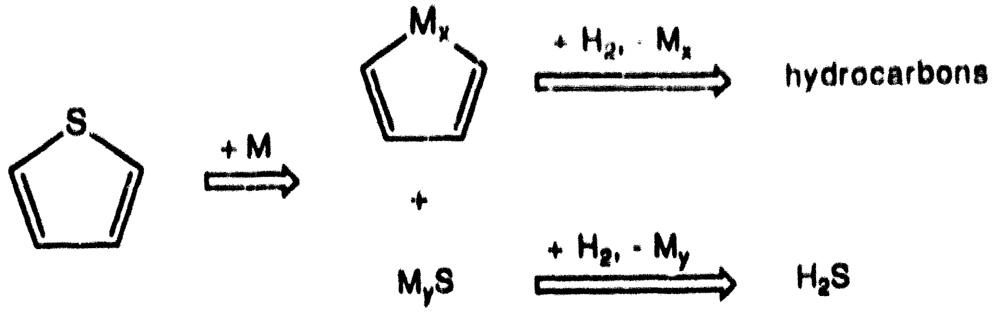
The first example of homogeneous desulfurization of thiophenes involved the reaction of C_4H_4S with iron carbonyls. We developed a project to elucidate the pathway for such metal carbonyl-promoted desulfurizations. It was found that $Cp^*Rh(\eta^4\text{-}C_4Me_4S)$ was desulfurized by $Fe_3(CO)_{12}$ via the thermal decomposition of $Cp^*Rh[(\eta^5{:}\eta^1\text{-}C_4Me_4S)Fe(CO)_4]$ (eq. 2).



(2)

Excellent mass balance was achieved and all three organometallic compounds were characterized by X-ray diffraction. Isotopic labelling showed that C_4Me_4S remains attached to the same rhodium center throughout the desulfurization.

This result illustrates the two distinct roles served by the metals in the desulfurization of the heterocycle (eq. 3). One set of metals combines to stabilize the hydrocarbon residue in the form of a metallacycle while a second group of metals binds the extruded sulfur atom to give a cluster. Thiophene desulfurization in essence involves replacement of a sulfur atom by metals. The metallacycle thus formed is activated towards hydrogenolysis.



(3)

It is striking that the desulfurization of one thiophene requires the action of *five* metals. This illustrates the advantages of multimetallic desulfurization agents such as clusters and surfaces. The finding that both the hydrocarbon and sulfur are stabilized in heterometallic environments is reminiscent of the synergism well known for heterometallic hydrodesulfurization catalysts (e.g. Co-Mo).

Thermal desulfurization of $(C_6Me_6)Ru(\eta^4\text{-}Me_2C_4H_2S)$ with $Fe_3(CO)_{12}$ gives $(C_6Me_6)Ru(\eta^5\text{-}Me_2C_4H_2Fe(CO)_3$, which was also structurally characterized.

Thermal Decomposition of η^4-Thiophene Complexes

The reduced η^4-thiophene complexes $(C_6Me_6)Ru(\eta^4$ $C_4Me_4S)$ and $Cp^*Rh(\eta^4\text{-}C_4Me_4S)$ undergo clean oligomerizations with evolution of one third equiv C_4Me_4S to give trimetallic derivatives of the type $[(ring)M]_3(\eta^4{:}\eta^1\text{-}C_4R_4S)_2$ (see Figure 3 for the unpublished Ru_3 compound). The kinetics are bimolecular and both M_3 products were characterized crystallographically. These observations indicate a pattern whereby reduction of the heterocycle leads sequentially to η^4-thiophene and then to $\eta^4{:}\eta^1$-thiophene. Our measurements represent a sort of temperature programmed desorption spectroscopy in solution, i.e. substrates are attached to the metal and their thermal behavior is tracked, in our case by NMR. Further thermolysis of $[Cp^*Rh]_3(\eta^4{:}\eta^1\text{-}C_4R_4S)_2$ results in C-S cleavage giving $Cp^*_2Rh_2C_4Me_4S$.

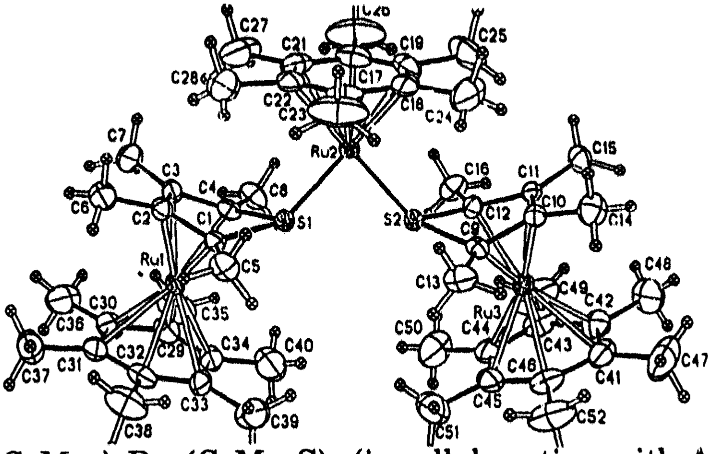


Figure 3. Structure of $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (in collaboration with A. L. Rheingold).

Metal Ion-Promoted Hydrolysis of Thiophenes

Studies on the metal ion promoted desulfurization of thiophenes with water is premised on the recurring role of metal catalysts in many hydration/ hydrolysis processes, e.g. in metalloenzymes. Initial breakthroughs were obtained with $[Cp^*Rh(C_4Me_4S)]^{2+}$ but the program has been broadened to include Ru, Os, and Ir with several different thiophenes. The key finding was that cleavage of the C-S bond occurs upon the deprotonation of 2-hydroxythiophenyl complexes $[(ring)M(C_4R_4S\text{-}2\text{-}OH)]^+$, one of which was characterized crystallographically (Figure 4).

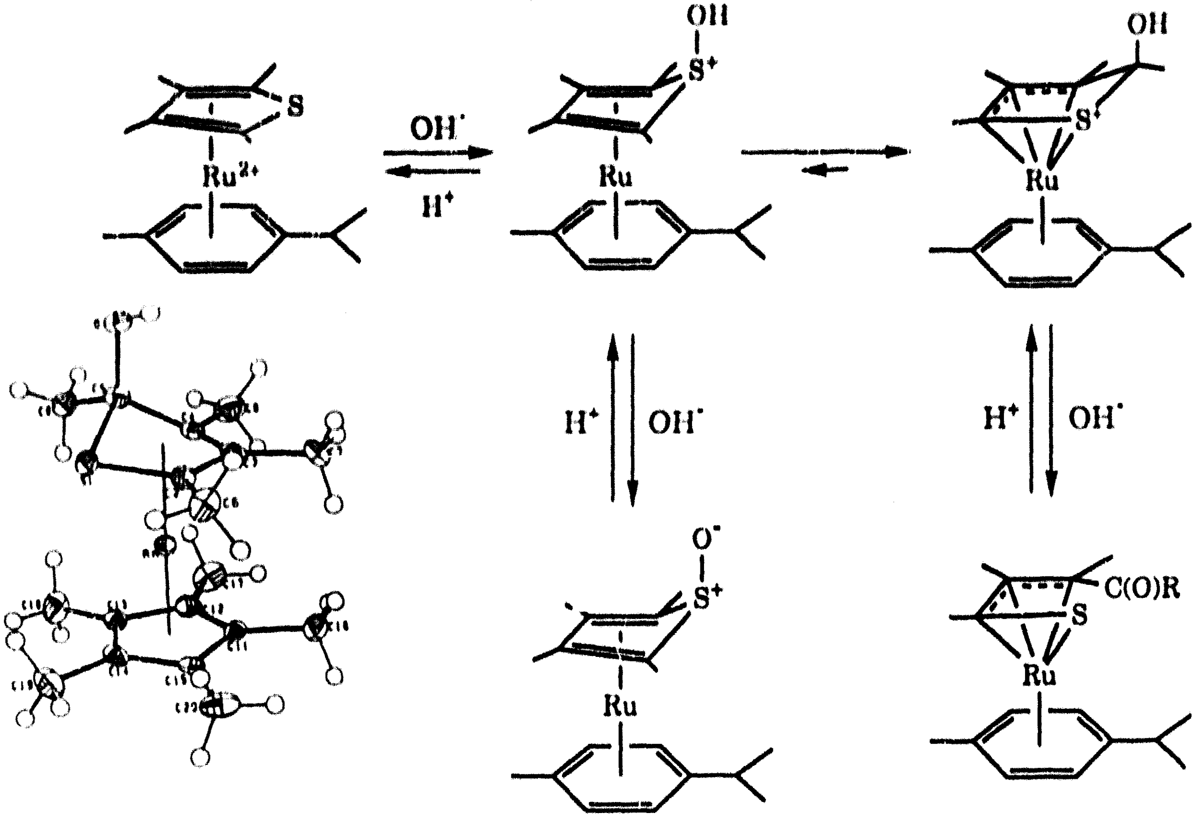
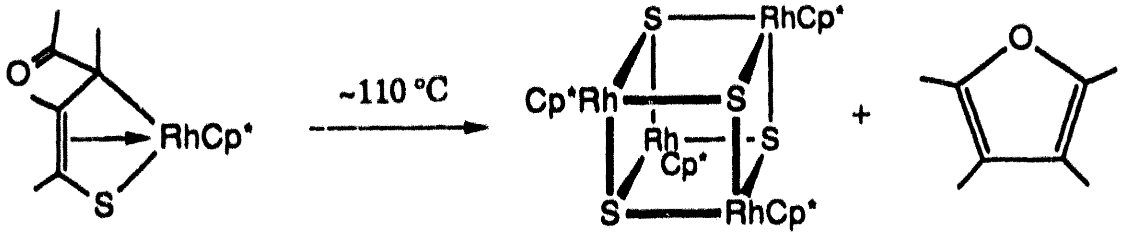


Figure 4. Chemical conversions highlighting the role of S-OH and C-OH intermediates. Inset, structure of $[Cp^*Rh(\eta^4\text{-}2\text{-}OH\text{-}C_4Me_4S)]^+$.

The remaining details of the base hydrolysis process centered on the very surprising discovery that the initial site of attack of OH^- is *sulfur*. High $[OH^-]$ leads to deprotonation of this S-OH species giving isolable sulfoxides while at lower $[OH^-]$ the hydroxy group relocates from sulfur to an α carbon resulting in the aforementioned 2-hydroxythiophenyl complexes. It is plausible that other apparent carbon-centered additions to thiophene ligands proceed via attack at sulfur followed by migration from sulfur to carbon. Protic acids reverse both the S- and C-centered base hydrolysis processes.

Thermal Fragmentation of Hydrolyzed Thiophene Ligands

The acylthiolato complexes that result from thiophene hydrolysis undergo well-behaved thermal fragmentation. In the case of $Cp^*Rh(SC_3Me_3COMe)$ the fragmentation process follows first order kinetics giving tetramethylfuran. The overall change is one of heteroatom metathesis (O for S in C_4Me_4S). The metal-containing product is the cubane cluster $Cp^*_4Rh_4S_4$ (eq. 2). The initial stages of this subproject were funded jointly with NSF.



(2)

This decomposition rate is unaffected by PPh_3 but proceeds via an intermediate which can be intercepted as $Cp^*_2Rh_2S_2(PPh_3)$ (also described by Bergman et al). The possibility of trapping other intermediates (e.g. Cp^*RhS) is still being examined. The corresponding decomposition of the acyl thiolate $(arene)Ru(SC_4Me_4O)$, derived from the base hydrolysis of $[(arene)Ru(C_4Me_4S)]^{2+}$, gives an inorganic ruthenium sulfide RuS_x where x ~ 1. Attempts to intercept intermediates in this thermal decomposition process using PPh_3 revealed a bimolecular pathway to $Ru(\eta^6\text{-}SC_4Me_4O)(PPh_3)_2$ and free arene (Figure 5). The analogous Ir and Os complexes is under study.

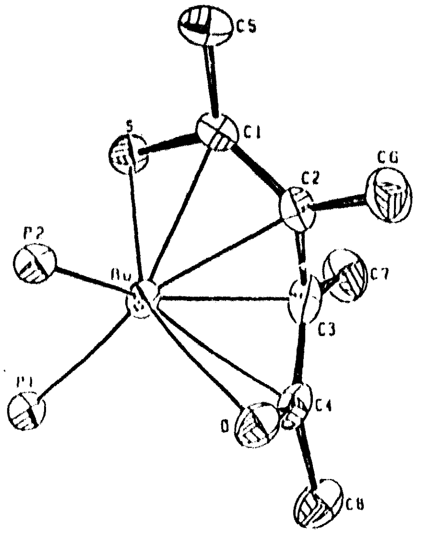


Figure 5. Structure of $Ru(PPh_3)_2(\eta^6\text{-}SC_4Me_4O)$, Ph groups omitted for clarity.

The Organic Chemistry of Hydrolyzed Thiophene Ligands

This project focused on a survey of the reactivity of the hydrolyzed thiophene complexes utilizing (arene)Ru derivatives of thiophene and its methylated derivatives. The findings are summarized in the reaction network below (arene ligands omitted for clarity). A key finding centered on the isomerism of the acyl thiolates and their differing reactivity towards protons. We were able to directly observe the S-OH species in the addition of first equivalent of OH^- to the dicationic thiophene complexes.

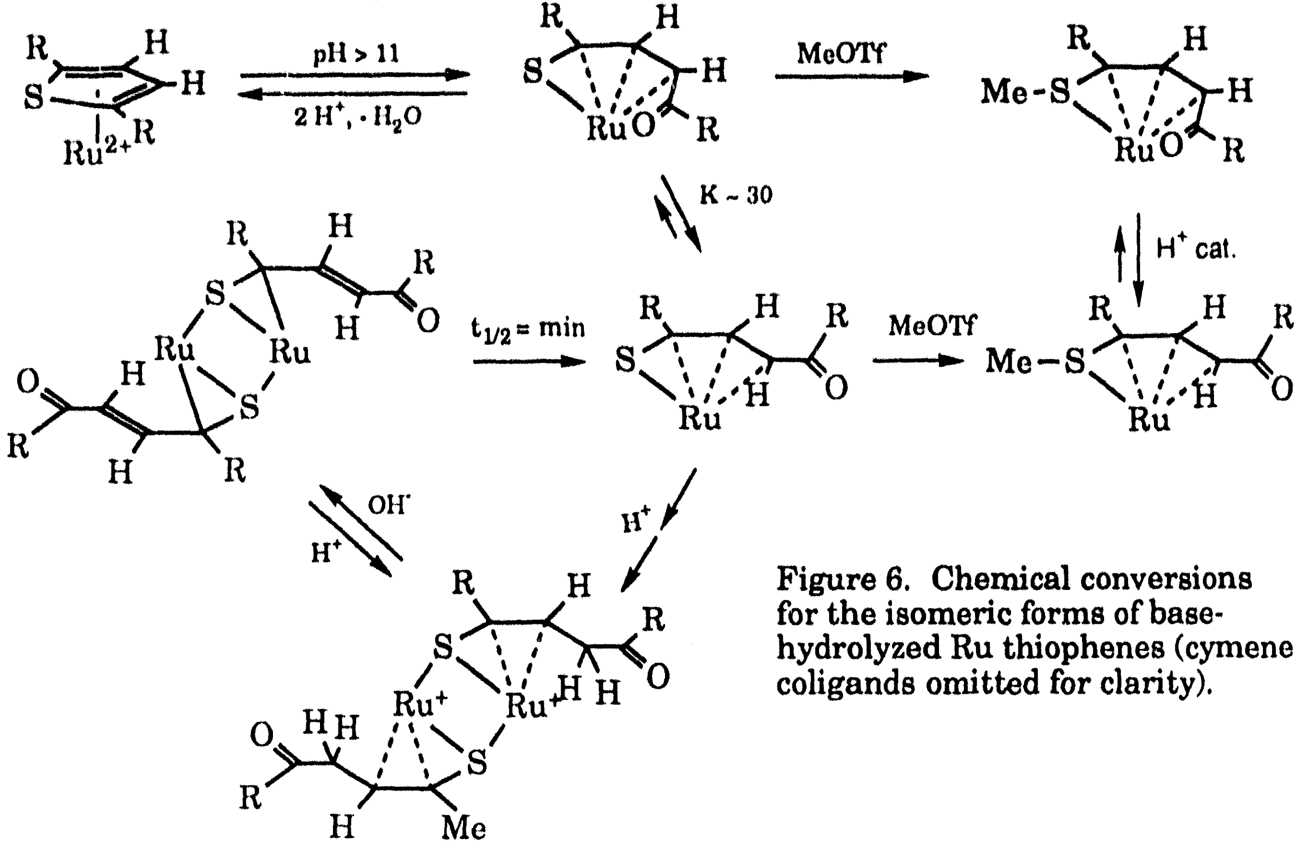


Figure 6. Chemical conversions for the isomeric forms of base-hydrolyzed Ru thiophenes (cymene coligands omitted for clarity).

DISCLAIMER

Publications from this work

1. "Thermolysis of $Cp^*Rh(\eta^4:\eta^1\text{-}C_4Me_4S)Fe(CO)_4)$: A Case Study in Thiophene Desulfurization"
   Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R.
   Organometallics **1991**, *10*, 1002.

2. "Redistribution of Reduced Thiophene Ligands in the Conversion of $(C_5R_5)Rh(\eta^4\text{-}C_4Me_4S)$ to $[(C_5R_5)Rh]_3(\eta^4\text{-}C_4Me_4S)_2$"
   Luo, S.; Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 1732.

3. "The Coordination Chemistry of Thiophenes"
   Rauchfuss, T. B. *Progress in Inorganic Chemistry* **1992**, *39*, 234.

4. "Arene vs Thiophene Reduction in the System $(C_6R_6)Ru(C_4R_4S)^{2+}$ and the Protonation of η^4-Thiophene Ligands"
   Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

5. "Base Hydrolysis of Coordinated Thiophene in $(C_5R_5)Rh(C_4Me_4S)^{2+}$: Nucleophilic Attack at Divalent Sulfur and the Reversible Cleavage of C-S Bonds"
   Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R.*J. Am. Chem.Soc.* **1992**, *114*, 8521.

6. "Bis(tetramethylthiophene)ruthenium (0) and Its $Fe(CO)_4$ Adduct"
   Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1992**, *11*, 3498.

7. "Base Hydrolysis of Ruthenium(II) Thiophene Complexes and Reactions of the Coordinated Ligands"
   Krautscheid, H.; Feng, Q.; Rauchfuss, T. B.submitted to *Organometallics*.

8. "A Thiophenylene Complex $[CpFe(CO)_2]_2C_4H_2S$"
   Rheingold, A. L.; Ogilvy, A. E.; Rauchfuss, T. B. submitted to *Acta Cryst.*

9. "Thiophene Hydrogenolysis by Ruthenium in Solution and in the Solid State"
   Luo, S.; Mainz, V. M.; Gan, Z.; Rauchfuss, T. B. in preparation (attached).

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