

The Addition of Oxygen to Coordinated Thiophene

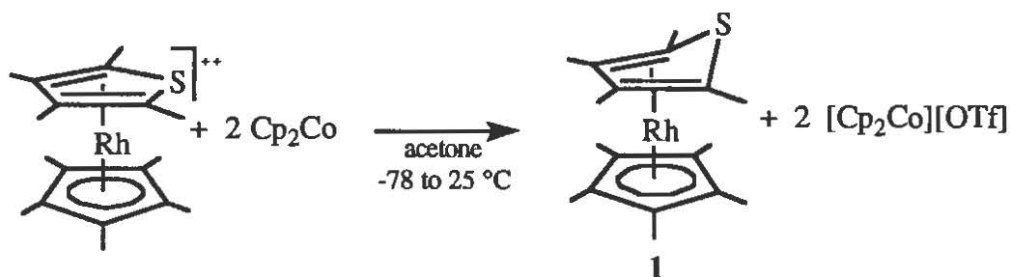
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Final Seminar

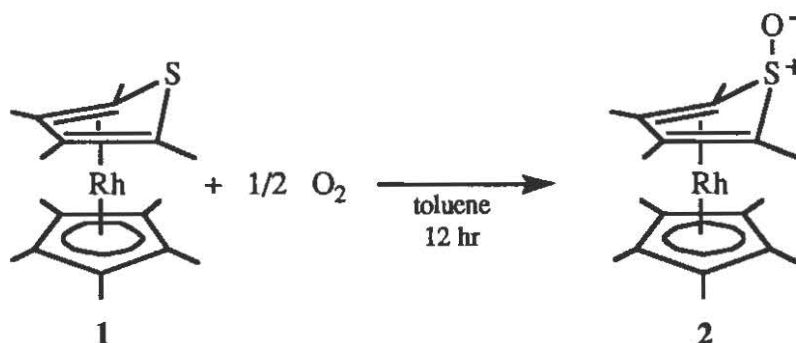
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The well explored hapticity change of 18 electron arene complexes upon 2 electron reduction (η^6 to η^4) [1] is a key concept in the stoichiometric and, possibly, the catalytic chemistry of arenes. We have investigated the stability of an analogous tetra-hapto bonding mode for thiophenes in transition metal complexes. To insure maximal stability for such complexes, we have employed the permethylated thiophene ligand 2,3,4,5-tetramethylthiophene (TMT) throughout most of this work.

The cyclic voltammogram for $[\text{Cp}^*\text{Rh}(\text{TMT})]^{2+}$ (TMT = tetramethylthiophene) showed two consecutive reversible one-electron reductions. We found that a two electron chemical reduction of $[\text{Cp}^*\text{Rh}(\text{TMT})]^{2+}$ with cobaltocene produced an η^4 -TMT complex (1), a previously unobserved bonding mode for thiophene [2].

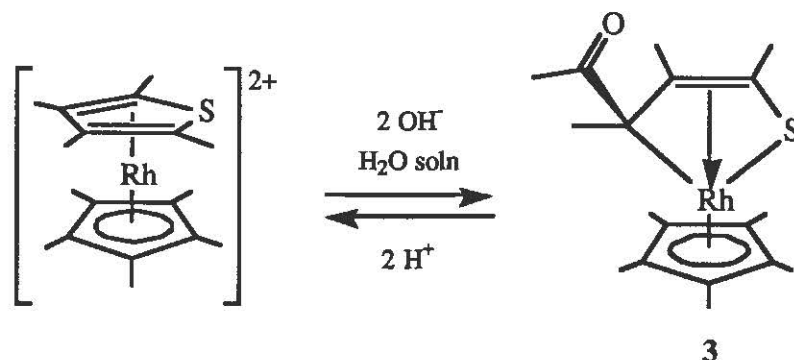


While attempting to grow single crystals of the very air-sensitive complex $\text{Cp}^*\text{Rh}(\text{TMT})$, a transparent orange single crystal was analyzed by x-ray diffraction. The crystal did not contain $\text{Cp}^*\text{Rh}(\text{TMT})$, but rather was unambiguously shown to be the thiophene-S-oxide complex, $\text{Cp}^*\text{Rh}(\text{TMT}-1-\text{O})$ (2). This observation led us to investigate the oxygenation of the η^4 -TMT complex. Free thiophene is not sensitive to oxidation by molecular oxygen, and when stronger oxidizing agents are used, the resulting thiophene sulfoxides and sulfones formed are unstable due to their susceptibility to Diels-Alder additions [3]. In contrast, the thiophene in 1 reacts with O_2 to form a sulfoxide complex [4].

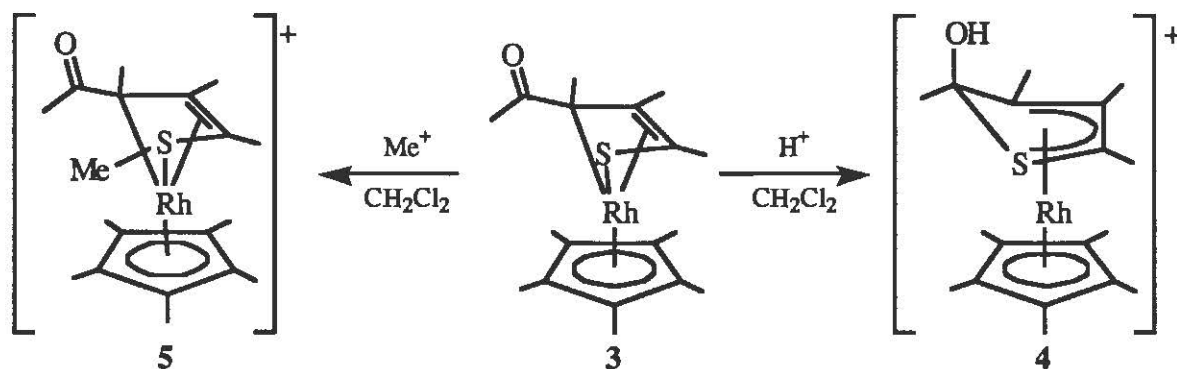


An alternative synthesis for 2 was found that employs the addition of two equivalents of KOSiMe_3 to the Rh(III) complex $[\text{Cp}^*\text{Rh}(\text{TMT})]^{2+}$, although the reaction was not efficient. This represents the first observation of nucleophilic attack at the sulfur atom of coordinated thiophene. Previous examples of nucleophilic addition to cationic thiophene complexes resulted in addition to the α -carbon, sometimes occurring with C-S bond cleavage [5].

When $[\text{Cp}^*\text{Rh}(\text{TMT})]^{2+}$ was treated with aqueous KOH in place of KOSiMe_3 , an entirely new compound was generated, isomeric with the thiophene-1-oxide. This species features a ring-opened thiophene derivative in the form of an acetylpropenethiolate ligand ($\text{Cp}^*\text{Rh}(\text{Me}_3\text{APT})$ (**3**), where APT = acetylpropenethiolate) [6]. The structure of the propenethiolate ligand is very similar to substituted thioacrolein complexes prepared by Dittmer via oxidative addition of substituted thietes (*cyclo*- $\text{C}_3\text{R}_4\text{S}$) to metal carbonyls [7]. The base hydrolysis of other transition metal-thiophene complexes revealed that the action of aqueous KOH could yield either the thiophene-1-oxide, the ring-opened acetyl complex, or both, depending upon the metal and the ancillary ligand utilized in the initial sandwich complex.



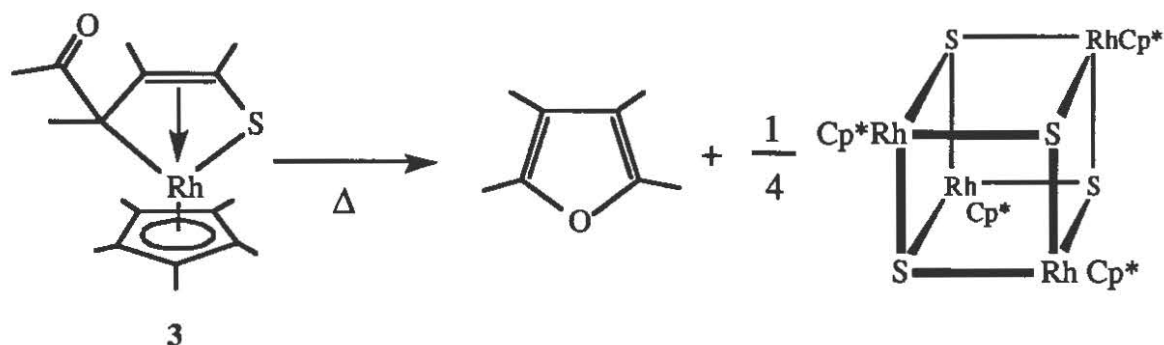
Monoprotonation of **3** resulted in reformation of the original C-S bond, in the form of a 2-hydroxythiophenyl complex, $[\text{Cp}^*\text{Rh}(\text{TMT}-2\text{-O})]^+$ (**4**). The mechanism for the protonation of **3** invokes a nucleophilic role for the terminal thiolate sulfur. This nucleophilic character was demonstrated by the reaction of MeOTf with **3**, which yielded the S-methylated product $[\text{Cp}^*\text{Rh}(\text{MeSC}_3\text{Me}_3\text{C}(\text{O})\text{Me})]^+$ (**5**).



Protonation of the tetramethylcyclopentadienyl analog of **2** also yielded the 2-hydroxythiophenyl complex, which in turn readily deprotonated to give the acetylpropenethiolate complex, $(\text{C}_5\text{Me}_4\text{H})\text{Rh}(\text{Me}_3\text{APT})$. This indicated that the thiophene-1-oxide complex is the *kinetic* product of the base hydrolysis, while the acetylpropenethiolate complex, e.g. **3**, is the thermodynamic product.

This information allowed us to postulate a mechanism for the addition of hydroxide to cationic thiophene complexes [8]. Initial attack of hydroxide occurs at the sulfur atom, yielding an S-hydroxy complex. This intermediate can either be deprotonated, to yield the TMT-1-O complex, or the hydroxide can migrate to the α -carbon followed by deprotonation, yielding the acetylpropenethiolate complex. The competition between deprotonation and migration is very sensitive to electronic effects.

Gentle thermolysis of **3** quantitatively converts the complex into tetramethylfuran and $[\text{Cp}^*\text{Rh}_4\text{S}_4]$, a rhodium sulfur cubane, via a unimolecular pathway [6].



The existence of a new bonding mode for thiophene, as in the case of **1**, might have implications for catalytic hydrodesulfurization, the industrial process used to remove sulfur from fossil fuels. In addition, the elucidation of new methods for oxydesulfurization could also lead to new synthetic approaches for organosulfur chemistry.

References

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