

Chemistry of Ruthenium η^4 -Thiophene Complexes

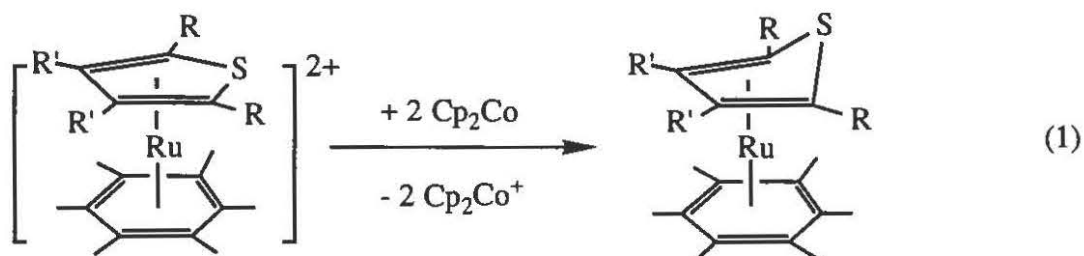
Shifang Luo

Final Seminar

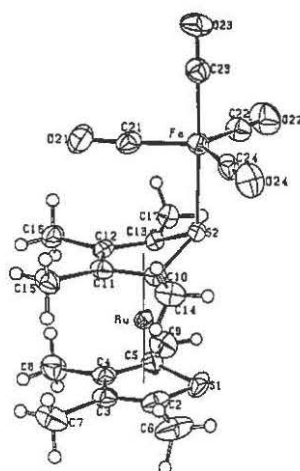
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The organometallic chemistry of transition metal thiophene complexes has been of increasing interest with recent emphasis on structural and reactivity principles [1]. These studies are relevant to the practical hydrodesulfurization (HDS) process, which is operated on enormous scale in the petroleum industry to remove S-containing impurities from the crude fossil oils by hydrotreating over a $\text{MoS}_2\text{-Co}_9\text{S}_8/\gamma\text{-Al}_2\text{O}_3$ catalyst [2]. Our interests in the chemistry of Rh and Ru η^4 -thiophene complexes stem from their high catalytic activity [3], and the unusual reactivity exhibited by η^4 -thiophene ligands [4]. This lecture will deal only with my research on the ruthenium complexes. Research on the rhodium complexes has already appeared [4f,4g].

The starting complexes $(\text{C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-thiophene})$ (thiophene = $\text{C}_4\text{H}_4\text{S}$, 2,5- $\text{Me}_2\text{C}_4\text{H}_2\text{S}$, 2,3,4,5- $\text{Me}_4\text{C}_4\text{S}$) were synthesized from the cobaltocene reduction of the corresponding $[(\text{C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-thiophene})]^{2+}$ salts (eq. 1), which in turn were prepared from the reaction of $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ with thiophenes in the presence of AgOTf (OTf is $\text{OSO}_2\text{CF}_3^-$).

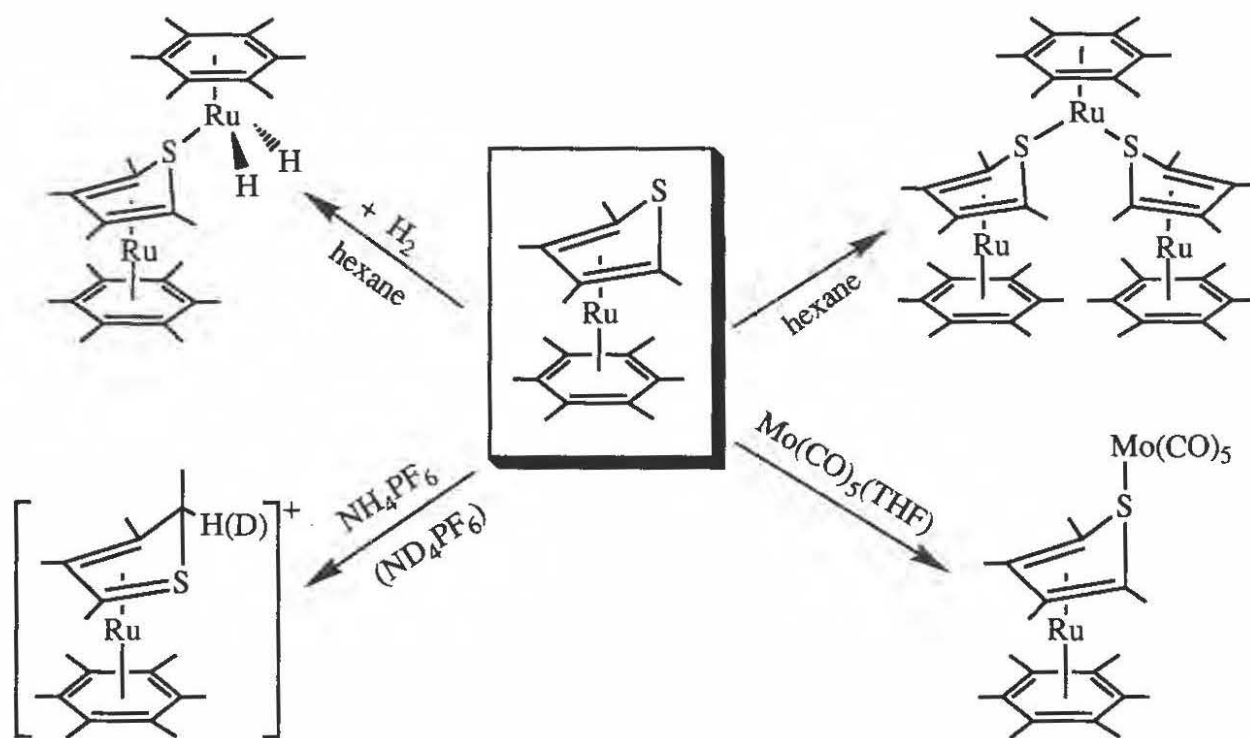


The thiophene ligand is reduced in preference to the arene. This is consistent with the relatively milder reduction potentials for the homoleptic complexes $[\text{Ru}(\text{C}_4\text{Me}_4\text{S})_2]^{2+}$ (-392, -568 mV vs. Ag/AgCl) [5] vs. $[\text{Ru}(\text{C}_6\text{Me}_6)_2]^{2+}$ (2e at -976 mV) [6]. The average reduction potential for $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{C}_4\text{Me}_4\text{S})]^{2+}$ (-525 mV) differs by only 45 mV from that of $[\text{Ru}(\text{C}_4\text{Me}_4\text{S})_2]^{2+}$ [7]. The redox-induced hapticity method also allowed the preparation of the thermally unstable complex $(\eta^5\text{-C}_4\text{Me}_4\text{S})\text{Ru}(\eta^4\text{-C}_4\text{Me}_4\text{S})$ whose structure has been confirmed by the single crystal X-ray diffraction study on its thermally stable adduct $(\eta^5\text{-C}_4\text{Me}_4\text{S})\text{Ru}(\eta^4\text{-}\eta^1\text{-C}_4\text{Me}_4\text{S})\text{Fe}(\text{CO})_4$ (a) [8].



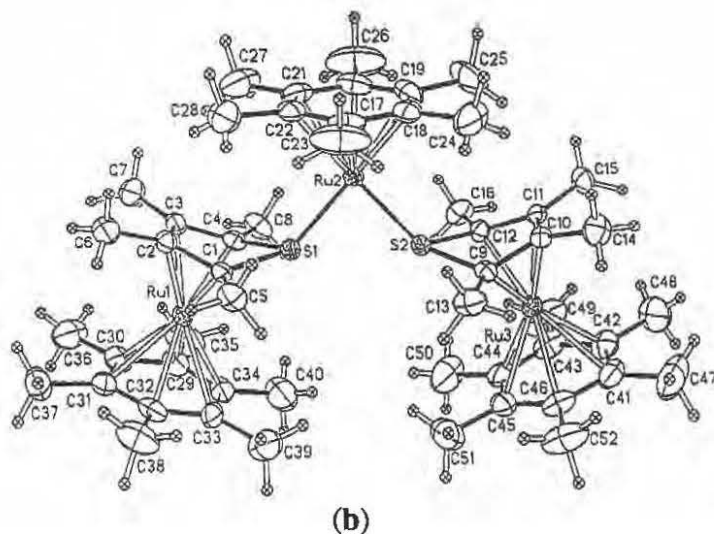
(a)

Having prepared a series of Ru(0) thiophene derivatives, our studies have focused on their reactivity. Scheme I lists the reactions for the thermally most stable $(C_6Me_6)Ru(\eta^4-C_4Me_4S)$.



Scheme I. Reactions of $(C_6Me_6)Ru(\eta^4-C_4Me_4S)$

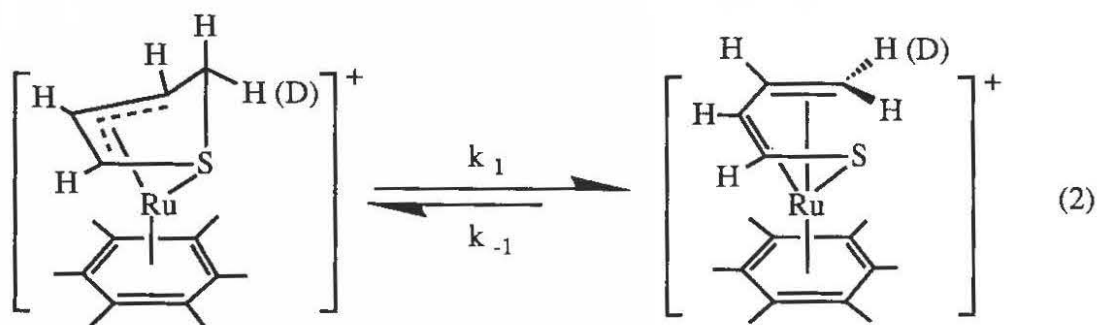
The thermal decomposition of Ru(0) thiophene ensembles^{4f,4g,9} closely resembles the Temperature Programmed Desorption (TPD) technique widely employed in surface science studies,¹⁰ with the advantage that structural assignments in later case are very secure. Thermolysis of $(C_6Me_6)Ru(\eta^4-C_4Me_4S)$ in non-aromatic solvents such as hexane produced the trinuclear product $(C_6Me_6)_3Ru_3(C_4Me_4S)_2$ (Scheme I), whose structure has been determined by single crystal X-ray diffraction study (b).



In an effort to hydrogenate the coordinated thiophene ligand, $(\text{C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_4\text{Me}_4\text{S})$ was thermolyzed in the presence of H_2 which produced the hydride $(\text{C}_6\text{Me}_6)\text{Ru}(\text{C}_6\text{Me}_6)\text{-Ru}(\eta^4\text{-}\eta^1\text{-C}_4\text{Me}_4\text{S})(\text{H})_2$ instead. When the thermolysis of $(\text{C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_4\text{Me}_4\text{S})$ was conducted in aromatic solvents, arene exchange reaction between $\eta^6\text{-C}_6\text{Me}_6$ and aromatic solvents occurs. In dilute solutions, only arene exchange products $(\eta^6\text{-solvent})(\text{C}_6\text{Me}_6)_2\text{-Ru}_3(\text{C}_4\text{Me}_4\text{S})_2$ (solvent = C_6D_6 , toluene) were obtained while in concentrated solutions both $(\text{C}_6\text{Me}_6)_3\text{Ru}_3(\text{C}_4\text{Me}_4\text{S})_2$ and $(\eta^6\text{-solvent})(\text{C}_6\text{Me}_6)_2\text{Ru}_3(\text{C}_4\text{Me}_4\text{S})_2$ were obtained [11].

$(\text{C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_4\text{R}_4\text{S})$ can be protonated with the weak acid NH_4PF_6 to give $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-2-H-C}_4\text{R}_4\text{S})]\text{PF}_6$ (Scheme I). Both NMR spectroscopy and the X-ray crystallographic study on $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-2-H-2,5-Me}_2\text{C}_4\text{H}_2\text{S})]\text{PF}_6$ reveal that the protonation reaction occurs stereo- and regioselectively such that the added proton in the products is in the endo position of the carbon α to sulfur [7]. It is proposed that the hydrogen arrives at the carbon position via the intermediacy of a metal hydride, possibly via an agostic complex [12,13].

"Temperature programmed decomposition" of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-2-H-C}_4\text{H}_4\text{S})]\text{PF}_6$ revealed C-S bond oxidative addition at the Ru center to afford the ring opened thiapentadienyl complexes $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{S})]\text{PF}_6$ both in solution and solid state (eq. 2).



The solution process is first order with $k_{\text{eq}} = 4.38$ at 45°C . The conversion occurs with the retention of the configuration at carbon as shown in eq 2. The solid state conversion has been successfully monitored by solid state CP/MAS ^{13}C NMR spectroscopy [14].

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