

Stereodynamics in Cyclopentadienyl Ruthenium Sulfur Clusters

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Dynamic ligand processes are frequently observed in transition metal cluster chemistry [1]. If the ligand dynamics effect changes in formal electron counts at the metal cluster atom sites then metal-metal bond movements may be expected. Examples of reversible metal-metal bond cleavage are known to be driven by ligand migration [2a], geometrical isomerization [2b], and other ligand-centered processes. Rare are examples of metal-metal bond mobility in the absence of ligand dynamic processes [2]. Ideal candidates for such studies are metal clusters which do not have fully bonded metal frameworks; in these cases bond/no bond equilibria might be anticipated. The electron rich clusters of the type $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{E}_4$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) are ideal candidates for studying this effect.

This situation is observed in $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4(\text{TCNQ})_2$ where the cluster dication is chiral by virtue of three localized Ru-Ru bonds [3]. In this mixed valence cluster, the Ru(III) sites have one Ru-Ru bond while the Ru(IV) sites have two Ru-Ru bonds (Figure 1).

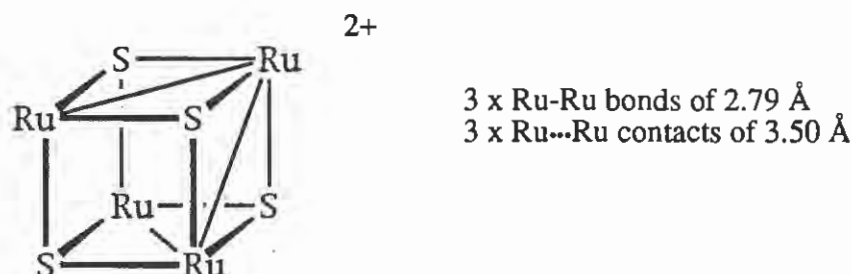


Figure 1. Idealized structure of the Ru_4S_4 core in $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4^{2+}$
(MeC_5H_4 ligands omitted for clarity)

In this work I examined diamagnetic salts of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4^{2+}$, obtained by chemical oxidation of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4$ as shown in equation 1.



The 500 MHz ^1H NMR spectrum of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4(\text{PF}_6)_2$ at temperatures above 20 °C shows a single broad resonance assigned to $\text{CH}_3\text{C}_5\text{H}_4$ and two broad resonances assigned to $\text{CH}_3\text{C}_5\text{H}_4$. These resonances sharpen at higher temperatures while one observes two $\text{CH}_3\text{C}_5\text{H}_4$ resonances and eight $\text{CH}_3\text{C}_5\text{H}_4$ resonances at -43 °C (Figure 2). The low temperature pattern is consistent with a chiral cluster as observed in the solid state structure of the TCNQ⁻ salt. Similar dynamic behavior is observed for $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{Se}_4(\text{PF}_6)_2$, while $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{Te}_4(\text{PF}_6)_2$ shows only slight line broadening at -40 °C. The dynamics were further tested through two sets of control experiments. First, the insensitivity of the coalescence temperature (T_c) to concentration showed the dynamics to be *intramolecular*. Second, the energetics of the dynamics were found to be similar for the MeC_5H_4 and $\text{Me}_3\text{SiC}_5\text{H}_4$ cases, indicating the dynamic behavior is not influenced by steric interactions between the RC_5H_4 ligands. The activation parameters were evaluated from the coalescence temperatures and lineshape analyses.

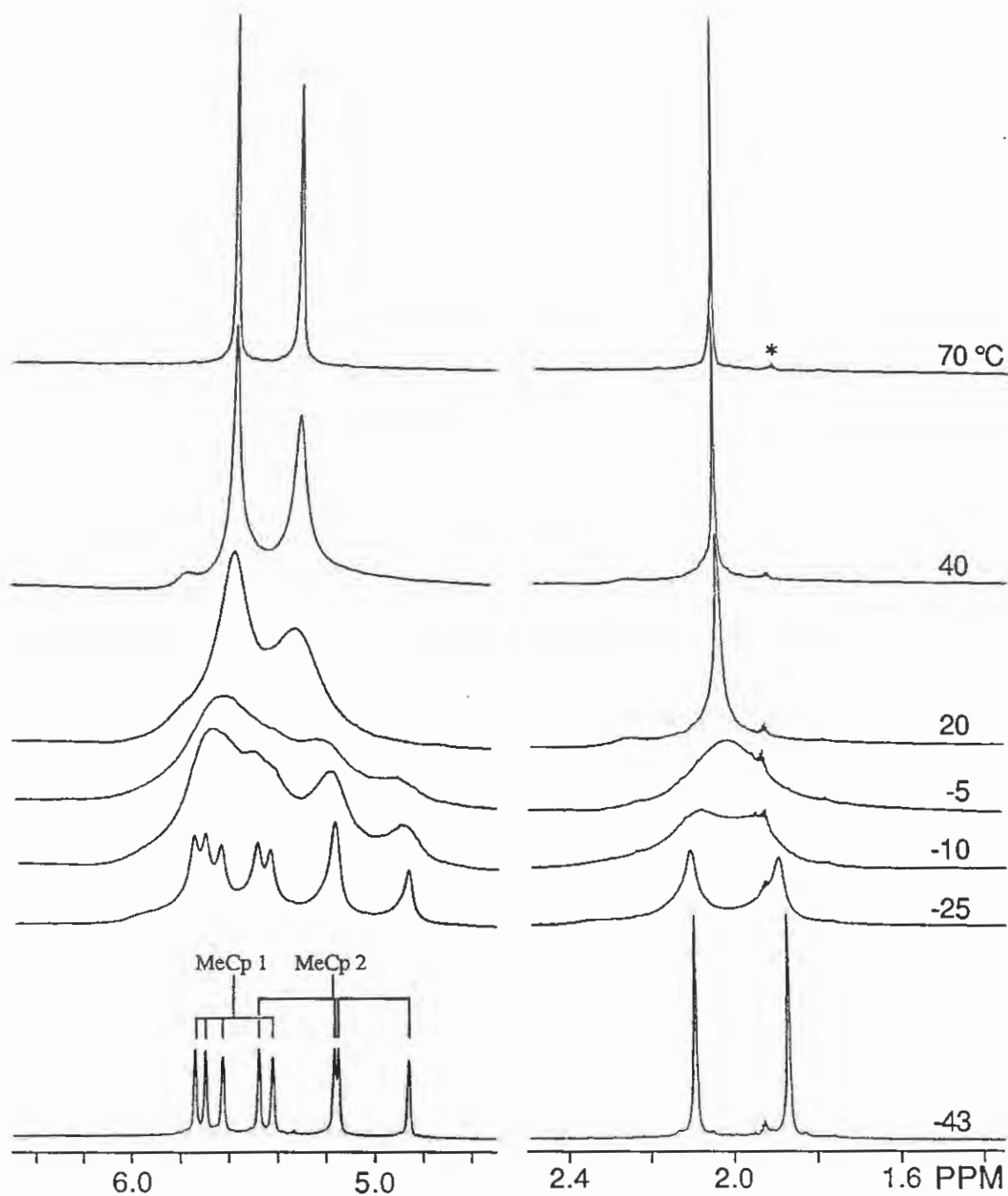
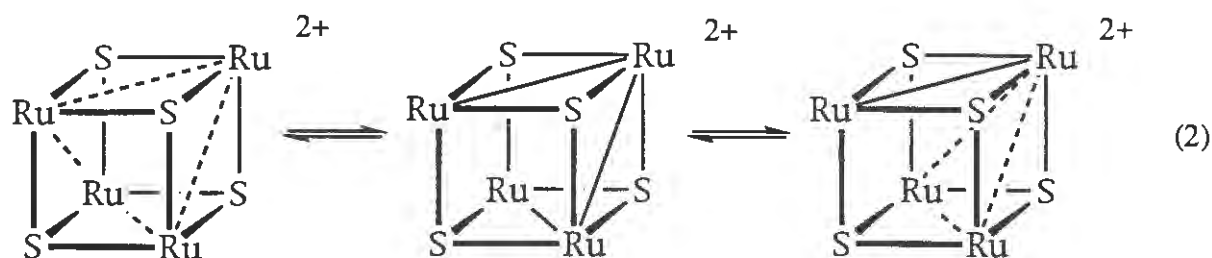


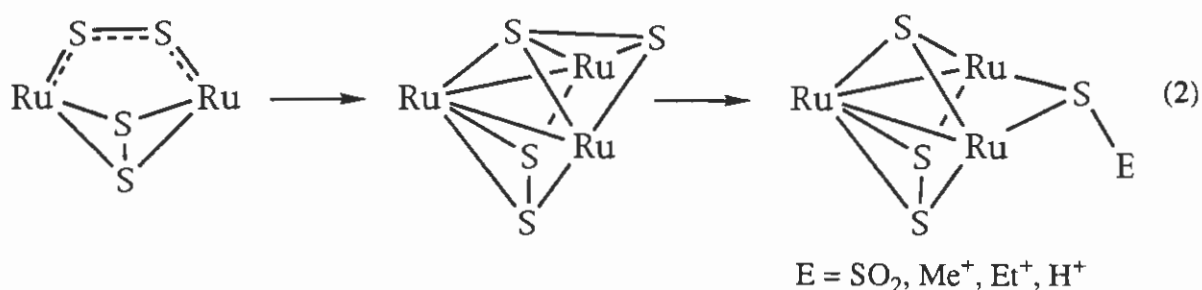
Figure 2. Variable Temperature ^1H NMR spectra (500 MHz) of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4(\text{PF}_6)_2$ in CD_3CN (* = CD_2HCN).

The fluxional behavior of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{E}_4(\text{PF}_6)_2$ ($\text{E} = \text{S}, \text{Se}$) can be attributed to a dynamic process involving rapid movement of one Ru-Ru bond within the cluster framework or the formation of an intermediate (or transition state) with various degrees of Ru-Ru bond delocalization (eq. 2).



The mechanism of these dynamics was further studied with the S-methylated clusters $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SCH}_3)]\text{CF}_3\text{SO}_3$ and $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SCH}_3)](\text{PF}_6)_2\text{CF}_3\text{SO}_3$. The ^1H NMR spectrum of $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SCH}_3)]\text{CF}_3\text{SO}_3$ at 20°C in the methyl region shows a 1:2:1 intensity pattern $\text{CH}_3\text{C}_5\text{H}_4$, consistent with its solid state structure. As the temperature is increased, two of these resonances (1:2 intensity ratio) broaden and begin to coalesce. This experiment shows (i) that the M-M bonds can be dynamic even when nonadjacent, (ii) in these situations the barrier is higher than when the M-M bonds are adjacent, and (iii) that metal-metal bond dynamics are not necessarily a consequence of mixed valency (all sites are Ru^{III}). In contrast, the limiting ^1H NMR spectrum (500 MHz) of the mixed valence cluster $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SCH}_3)](\text{PF}_6)_2\text{CF}_3\text{SO}_3$ shows *four* $\text{CH}_3\text{C}_5\text{H}_4$ signals and *sixteen* (two overlapping) $\text{CH}_3\text{C}_5\text{H}_4$ signals. As the temperature is increased, the $\text{CH}_3\text{C}_5\text{H}_4$ signals and three of the $\text{CH}_3\text{C}_5\text{H}_4$ signals broaden and merge to give four (two overlapping) $\text{CH}_3\text{C}_5\text{H}_4$ in a 1:1:3:3 and two $\text{CH}_3\text{C}_5\text{H}_4$ signals in a 3:1 intensity ratio. A lineshape fitting of the variable temperature ^1H NMR spectra for $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SCH}_3)]^{3+}$ required *three* rate constants to model the spectra. This experiment establishes that the dynamics do not involve a "simple" delocalized intermediate.

Parallel with the above work we examined dynamics in $(\text{C}_5\text{Me}_5)_4\text{Ru}_4\text{S}_4^{2+}$. This species exhibits a simple NMR spectra, even low temperatures. In related studies, salts of $(\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{S}_4^+$ were obtained from the reaction of $(\text{C}_5\text{Me}_5)\text{Ru}(\text{CH}_3\text{CN})_3^+$ with $(\text{C}_5\text{Me}_5)_2\text{Ru}_2\text{S}_4$ [5]. The 500 MHz ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra indicate equivalent C_5Me_5 rings although crystallographic studies revealed an unsymmetrical structure (eq. 2), so here it is again necessary to involve dynamic Ru-Ru bonds. This species exhibits a new bonding mode for a persulfide ligand and a new structural motif for M_3S_4 clusters. Furthermore, this cluster cation is reactive towards electrophiles (SO_2 , H^+ , Me^+ , Et^+), apparently via additions to the $\mu_3, \eta^5\text{-S}_2$ ligand. ^1H NMR spectra of $(\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{S}_3(\text{SR})^{2+}$ ($\text{R} = \text{Me}, \text{Et}$) show a 2:1 intensity pattern showing that additions to the S-centers inhibits the Ru-Ru bond motion. Structural studies on $(\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{S}_3(\text{SEt})^{2+}$ and $(\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{S}_3(\text{S}_2\text{O}_2)^+$ show that the core structure and orientation of the addend are similar.



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