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 \((\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{E}_4\) (E = S, Se, 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 Ru4S4 core in (MeC5H4)4Ru4S42+](image)

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

\[
2 \text{[Cp}_2\text{Fe]}\text{PF}_6 + (\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4 \rightarrow (\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4\text{(PF}_6\text{)}_2 + 2 \text{Cp}_2\text{Fe} \tag{1}
\]

The 500 MHz \(^1\text{H}\) NMR spectrum of \((\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4\text{(PF}_6\text{)}_2\) 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 \((\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{Se}_4\text{(PF}_6\text{)}_2\), while \((\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{Te}_4\text{(PF}_6\text{)}_2\) 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 \(\text{MeC}_5\text{H}_4\) and \(\text{Me}_3\text{SiC}_5\text{H}_4\) cases, indicating the dynamic behavior is not influenced by steric interactions between the \(\text{RC}_5\text{H}_4\) ligands. The activation parameters were evaluated from the coalescence temperatures and lineshape analyses.
Figure 2. Variable Temperature $^1$H NMR spectra (500 MHz) of (MeC$_5$H$_4$)$_4$Ru$_4$S$_4$(PF$_6$)$_2$ in CD$_3$CN (* = CD$_2$HCN).
The fluxional behavior of \((\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{E}_4(\text{PF}_6)_2\) (\(E = \text{S}, \text{Se}\)) 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).

\[
\begin{align*}
\text{Ru} & \quad \text{S} & \quad \text{Ru} & \quad \text{S} & \quad \text{Ru} & \quad \text{S} & \quad \text{Ru} & \quad \text{S}
\end{align*}
\]

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 \(^1\text{H}\) 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 \(^1\text{H}\) 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 \(^1\text{H}\) 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 \((\text{C}_5\text{Me}_5)\text{Ru(CH}_3\text{CN})_3^{+}\) with \((\text{C}_5\text{Me}_5)_2\text{Ru}_2\text{S}_4\) [5]. The 500 MHz \(^1\text{H}\) and \(^{13}\text{C}[^1\text{H}]\) NMR spectra indicate equivalent \(\text{C}_5\text{Me}_5\) 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 \(\text{M}_3\text{S}_4\) clusters. Furthermore, this cluster cation is reactive towards electrophiles (\(\text{SO}_2\), \(\text{H}^+\), \(\text{Me}^+\), \(\text{Et}^+\)), apparently via additions to the \(\mu_3, \eta^3\)-S2 ligand. \(^1\text{H}\) NMR spectra of \((\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{S}_3(\text{SR})^{2+}\) (\(R = \text{Me}, \text{Et}\)) 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.
References


