Geometric Isomerism Based on Metal−Metal Bonds

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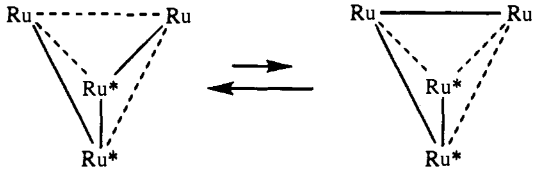
The stereodynamics of metal−metal bonds has remained virtually unexplored until very recently. It is now known that the barriers for the degenerate reorientation of metal−metal bonds can be substantial.[1,2] This opens the way for the preparation of clusters which differ on the basis of their metal−metal bonding networks. A test of this idea entails demonstration that clusters can exist as *geometric isomers* based exclusively on the relative positions of M−M bonds. This type of process assumes added significance to the extent that M−M bonding provides an electrochemically addressable means of controlling the structures of multimetallic frameworks.

The reaction of $(C_5Me_5)_2Ru_2S_4$[3] with 2 equiv of $(C_5H_5)Ru(MeCN)_3{}^+$[4] (MeCN solution, 25 °C) proceeds according to eq 1.[5] The red-brown salt $[(C_5H_5)_2(C_5Me_5)_2Ru_4S_4](PF_6)_2$ ($[\mathbf{1}](PF_6)_2$) was obtained in high yield and good purity.[6,7]

$$(C_5Me_5)_2Ru_2S_4 + 2(C_5H_5)Ru(MeCN)_3{}^+ \rightarrow (C_5H_5)_2(C_5Me_5)_2Ru_4S_4{}^{2+} + 6MeCN \quad (1)$$

The solid state structure of $[\mathbf{1}](PF_6)_2{\cdot}CH_2Cl_2$ was determined by single-crystal X-ray diffraction (Figure 1).[8] The dication has idealized C_2 symmetry and can be described as a distorted cubane with three bonding Ru−Ru contacts (2.812−2.822 Å) and three nonbonding Ru $\cdots$ Ru contacts (3.472−3.582 Å). To this extent, the results mirror those seen for $[(RC_5H_4)_4Ru_4S_4]^{2+}$ (R = Me, Me_3Si) wherein the cyclopentadienyl ligands are all of the same type.[1] It is of particular interest to note the positions of the $(C_5Me_5)Ru$ and $(C_5H_5)Ru$ sites relative to the three Ru−Ru bonds. The $(C_5Me_5)Ru$ centers each support two metal−metal bonds, suggesting that these metal centers are more highly oxidized, which we will describe as Ru^{IV}. The $(C_5H_5)Ru$ centers on the other hand support only one Ru−Ru bond and are assigned as Ru^{III}. In this way the cluster can be described as $\{[(C_5H_5)Ru^{III}]_2[(C_5Me_5)Ru^{IV}]_2S_4\}^{2+}$.

The room temperature ^1H NMR spectrum for $\mathbf{1}^{2+}$ showed broad singlets for C_5H_5 and C_5Me_5 in the expected ratio of 5:15, while at lower temperatures we observe decoalescence of both signals concomitant with the appearance of two subspectra (Figure 2). These subspectra are assigned to a pair of *geometric isomers* of $\mathbf{1}^{2+}$ *which differ on the basis of the arrangements of their Ru−Ru bonds*. The NMR patterns indicate that the major isomer is the same as that seen in the solid state. The minor species occurs to the extent of ~23% (−90 °C, Me_2CO solution). This minor species is unsymmetrical with integrated signal intensities of 5:5:15:15. The ^1H NMR chemical shift pattern of the unsymmetrical isomer is very revealing. One C_5H_5 resonance occurs very close to that of the major isomer; this is assigned to a $(C_5H_5)Ru^{III}$ site. The second C_5H_5 shift appears 0.5 ppm downfield, suggesting that it arises from a $(C_5H_5)Ru^{IV}$ site. Furthermore, one C_5Me_5 resonance for the minor isomer is within 0.03 ppm of that in the major isomer while the second peak appears 0.16 ppm upfield and is assigned to the $(C_5Me_5)Ru^{III}$ site. Comparable chemical shift trends are seen also in the ^{13}C NMR spectra. Thus the chemical shifts for the minor isomer support its description as $\{[(C_5H_5)Ru^{IV}][(C_5H_5)Ru^{III}][(C_5Me_5)Ru^{IV}][(C_5Me_5)Ru^{III}]S_4\}^{2+}$. As shown in eq 2, this isomerism can be viewed as a competition between oxidation of one $(C_5Me_5)Ru$ and $(C_5H_5)Ru$ site.[9]



(2)

(Ru = (C_5H_5)Ru; Ru* = (C_5Me_5)Ru)

The equilibrium constant of 0.30 corresponds to a potential difference of ~18 mV (183 K),[10] the direction of the equilibrium favoring oxidation of the $(C_5Me_5)Ru$ site, as expected on the basis of inductive effects. At first it is surprising that the equilibrium constant is not smaller since the inductive effect of five methyl groups on a cyclopentadienyl ligand is typically ~250 mV, at least in metallocenes.[11] The absence of conventional substituent effects suggests a fundamental difference between the redox of clusters, where metal−metal bonding is involved,[12] and mononuclear complexes.

Control experiments support the proposed equilibrium. The dynamic process is unimolecular since the ^1H NMR line broadening (of the C_5H_5 signal) is independent of concentration. The ^1H NMR spectrum of $\mathbf{1}^{2+}$ is unaffected by the presence of added $(C_5H_5)Ru(MeCN)_3{}^+$, showing that at least one form of metal exchange is not operative (in fact the clusters are very robust). The equilibrium constant for the isomerization (eq 2) was measured from −90 to −40 °C. The temperature dependence of ln K_{eq} allowed determination of $\Delta H \sim 1.86$ kJ mol^{-1} and $\Delta S \sim -0.43$ J mol^{-1} K^{-1}. The exchange-broadened ^1H NMR spectra were simulated using a model that assumed a single equilibrium.[13]

In order to obtain a more complete picture of the underlying structural patterns we prepared $\mathbf{1}^0$. Electrochemical studies

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(1) Houser, E. J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1993**, *32*, 4069. Houser, E. J.; Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7441.

(2) Venturelli, A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1994**, *116*, 4824.

(3) Houser, E. J.; Dev, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1993**, *12*, 4678.

(4) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(5) For previous examples of this strategy for the preparation of cubane clusters with mixed cyclopentadienyl ligands, see: Williams, P. D.; Curtis, M. D. *Inorg. Chem.* **1986**, *25*, 4562.

(6) $[(C_5H_5)_2(C_5Me_5)_2Ru_4S_4](PF_6)_2$: dark-brown crystals in 85% yield from acetone−hexanes. ^1H NMR $[(CD_3)_2CO]$, at 20 °C: 5.72 (brs, 10 H), 1.96 (brs, 30 H). At −90 °C, major isomer, 5.70 (s, 10 H), 1.96 (s, 30 H); minor isomer, 6.15 (s, 5 H), 5.69 (s, 5 H), 1.99 (s, 15 H), 1.80 (s, 15 H). $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO]$ at −90 °C: major isomer, 108.0, 89.3, 11.1; minor isomer, 108.3, 103.8, 91.2, 89.0, 10.9, 9.4. FAB-MS (*m/z*): 934. CV (mV, vs Ag/AgCl, MeCN): −217, −367. Anal. Calcd (found) for $C_{30}H_{40}F_{12}P_2Ru_4S_4{\cdot}(CH_3)_2CO$: C, 30.93 (31.16); H, 3.61 (3.69); Ru, 31.55 (29.32); S, 10.01 (10.05).

(7) The intermediate in this assembly process has been shown to be $(C_5H_5)(C_5Me_5)_2Ru_3S_4{}^+$, an analog of the recently described but still structurally undefined $(C_5Me_5)_3Ru_3S_4{}^+$: Houser, E. J.; Krautscheid, H.; Rauchfuss, T. B.; Wilson, S. R. *J. Chem. Soc., Chem. Commun.* **1994**, 1283. $(C_5Me_5)_2Ru_2S_4$ doses not appear to add *2* equiv of $(C_5Me_5)Ru(MeCN)_3{}^+$, perhaps for steric reasons.

(8) $C_{30}H_{40}F_{12}P_2Ru_4S_4{\cdot}CH_2Cl_2$: orthorhombic, $Pna2_1$; $a = 14.551(3)$ Å, $b = 22.871(5)$ Å, $c = 12.686(2)$ Å, $V = 4221.8(14)$ Å^3, $Z = 4$; 4171 reflections (198 K, Enraf-Nonius CAD4 diffractometer) were refined to a final $R = 0.0321$, $R_w = 0.0766$.

(9) Note that all of the clusters discussed in this paper are racemic.

(10) Using the Nernst equation: RT/F at 183 K = 15.06 mV for a 1e$^-$ process ($(C_5Me_5)SRu^{III/IV}$ vs $(C_5H_5)SRu^{III/IV}$) leading to $E = (15.06) \ln K_{eq}$.

(11) Geiger, W. E. In *Organometallic Radical Processes*; Trogler, W. T., Ed.; Elsevier: Amsterdam, 1990.

(12) Mueller-Westerhoff, U. T.; Rheingold, A. L.; Sweigers, G. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1352; *Angew. Chem.* **1992**, *104*, 1398. Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.

(13) A standard two-site model was employed, with two rate constants to reflect the fact that $K_{eq} \neq 1$. We thank Dr. Z. Gan for assistance with this calculation. The simulations (see supplementary material) were matched visually with the observed spectra.

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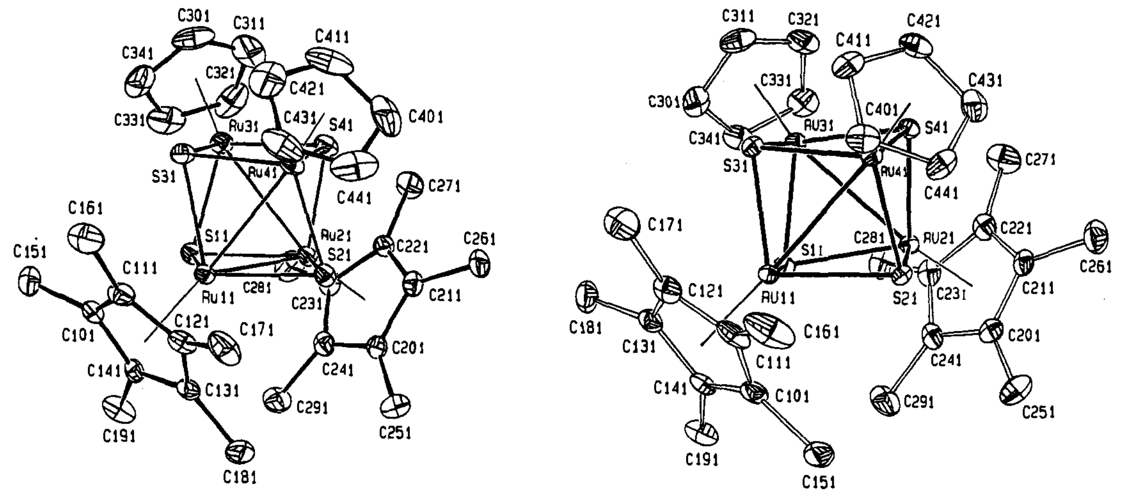


Figure 1. Structures for $[(C_5H_5)_2(C_5Me_5)_2Ru_4S_4](PF_6)_2$ (anion not shown, left) and $[(C_5H_5)_2(C_5Me_5)_2Ru_4S_4]^0$ ($\mathbf{1}^0$, right). The Ru–Ru bonding distances are all within 0.02 Å of 2.81 Å.

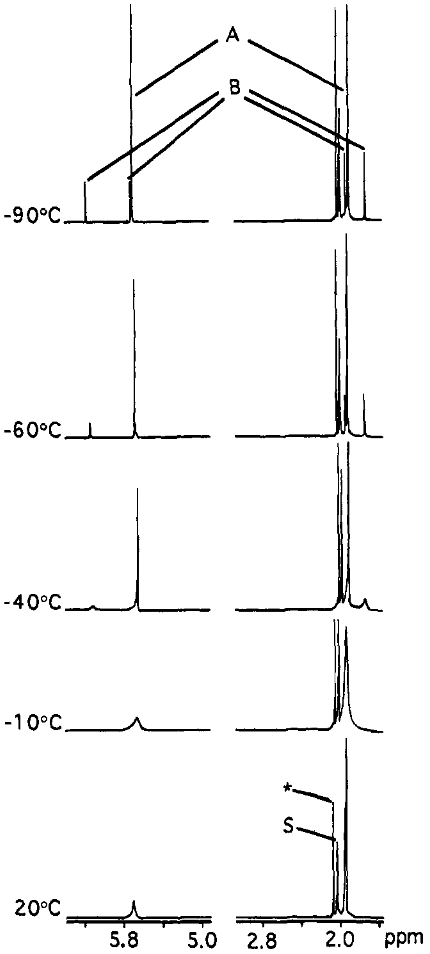
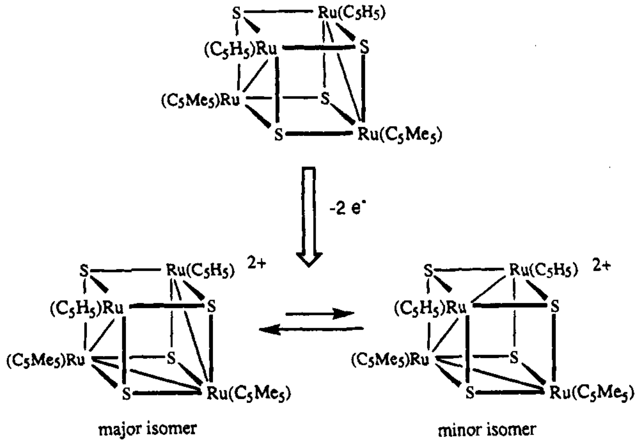


Figure 2. ^{1}H NMR spectra (500 MHz) for acetone-d_6 solutions of $[(C_5H_5)_2(C_5Me_5)_2Ru_4S_4](PF_6)_2$ at various temperatures (A, major isomer; B, minor isomer, (*), acetone; S, acetone-d_6).

Scheme 1



revealed that $\mathbf{1}^{2+}$ undergoes a pair of reversible 1e$^-$ reductions at $E_{1/2} = -214$ and -370 mV (vs Ag/AgCl, in CH_3CN). The neutral cluster was indeed prepared by reduction of $\mathbf{1}^{2+}$ with 2 equiv of $Co(C_5H_5)_2$. ^{1}H and ^{13}C NMR data indicate that $\mathbf{1}^0$ adopts a symmetric structure.[14] This was confirmed by single-crystal X-ray diffraction, which shows that the Ru_4S_4 core adopts a C_2 symmetric structure (Figure 1).[15] The pair of Ru–Ru bonds are equivalent and are situated between (C_5H_5)Ru and (C_5Me_5)Ru sites. The results are summarized in Scheme 1.

The findings reported in this paper provide the first example of geometric isomerism based on the relative orientation of metal–metal bonds. These studies also show that the regiochemistry of cluster redox can be manipulated through selection of the ancillary ligands.

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Supplementary Material Available: Tables of positional and thermal parameters and bond angles and distances for the structures of $\mathbf{1}^0$ and $\mathbf{1}^{2+}$, spectroscopic data including simulated NMR spectra, and calculations of ΔH and ΔS (13 pages); observed and calculated structure factors for neutral $Cp_2Cp^*{}_2Ru_4S_4$ and dication $Cp_2Cp^*{}_2Ru_4S_4(PF_6)_2{\cdot}CH_2Cl_2$ (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[14] $(C_5H_5)_2(C_5Me_5)_2Ru_4S_4$: dark-red crystals in 75% yield from THF–CH_3OH. ^{1}H NMR (C_6D_6): 4.66 (s, 10H), 1.60 (s, 30H). ^{13}C{^{1}H} NMR (C_6D_6): 95.1, 83.6, 9.84. FD-MS (*m/z*): 934. CV (mV, vs Ag/AgCl, CH_2Cl_2): -138, -413. Anal. Calcd (found) for $C_{30}H_{40}Ru_4S_4$: C, 38.61 (38.08); H, 4.32 (4.61); Ru, 43.30 (44.55); S, 13.74 (13.38).

[15] $C_{30}H_{40}Ru_4S_4$: triclinic, $P\bar{1}$, $a = 11.258(2)$ Å, $b = 11.681(3)$ Å, $c = 12.548(4)$ Å, $\alpha = 103.30(2)°$, $\beta = 90.22(2)°$, $\gamma = 99.37(2)°$; $V = 1583.0(7)$ Å^3, $Z = 2$; 4661 reflections (198 K, Enraf-Nonius CAD4 diffractometer) were refined to $R = 0.0259$, $R_w = 0.0660$.