

Mobile Metal-Metal Bonds in Platinum Metal Sulfide Clusters

Anne Venturelli

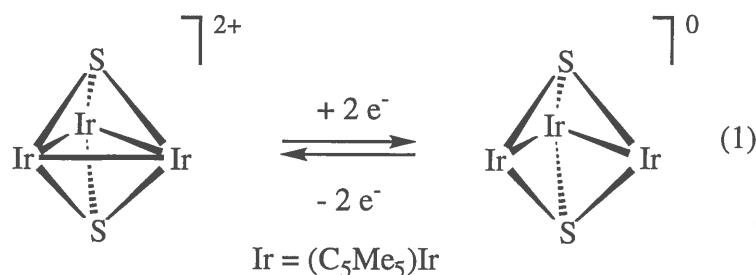
Final Seminar

January 18, 1996

Dynamic cluster rearrangements are common in transition metal chemistry. Such rearrangements are fluxional and definable on the NMR timescale ($\Delta G^\ddagger \sim 20\text{-}80$ kJ/mol) [1]. These dynamic processes generally involve migration of ligands about the cluster core; however, occasionally this fluxionality is also accompanied by changes in the metal-metal bonding [2].

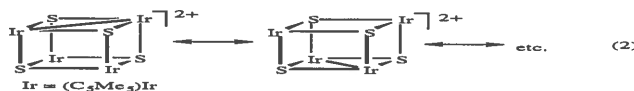
The goal of the first part of this thesis was to examine the dynamics of metal-metal bonds in the absence of other changes in ligation. This was accomplished through studies of mixed valence diamagnetic clusters of Ru, Os, Rh, and especially Ir. In this project we took advantage of the fact that metal-metal bonds can be formed or cleaved by redox processes.

The yellow dicationic complex $(C_5Me_5)_3Ir_3S_2^{2+}$ was obtained by treatment of $[(C_5Me_5)IrCl_2]_2$ with $(Me_3Si)_2S$, followed by purification via aqueous ion exchange chromatography. Crystallographic studies indicate that the dication consists of a trigonal bipyramidal Ir_3S_2 core with three Ir-Ir bonds of 2.88 Å. Due to the high symmetry of $(C_5Me_5)_3Ir_3S_2^{2+}$, the dication exhibits no structural dynamics. A low symmetry derivative can be synthesized by cobaltocene reduction of the dication yielding the neutral cluster $(C_5Me_5)_3Ir_3S_2^0$ (eq 1). This *nido* species contains two metal-metal bonds amongst the three edges.



The 1H NMR spectrum of $(C_5Me_5)_3Ir_3S_2^0$ consists of two broad signals in a 2:1 ratio at room temperature. These signals collapse and sharpen into one singlet at elevated temperatures. These variable temperature 1H NMR studies reveal the dynamic behavior attributable to the mobility of the metal-metal bonds in this 50e cluster.

Modifying the $[(C_5Me_5)IrCl_2]_2 / (Me_3Si)_2S$ reaction by the addition of elemental sulfur affords the green 70e cluster $(C_5Me_5)_4Ir_4S_4^{2+}$. This mixed valence species adopts a cubane structure consisting of interpenetrating Ir_4 and S_4 tetrahedra with one Ir-Ir bond of 2.76 Å. Variable temperature 1H NMR studies indicate that this Ir-Ir bond is fluxional in solution (eq 2).



Treatment of $[(C_5Me_5)RhCl_2]_2$ with $(Me_3Si)_2S$ yields the neutral rhodium sulfide cubane and the dicationic $(C_5Me_5)_3Rh_3S_2^{2+}$ salt. The 70e $(C_5Me_5)_4Rh_4S_4^{2+}$ species is prepared by oxidation of $(C_5Me_5)_4Rh_4S_4^0$ with silver salts. The dichotomy between the syntheses of the rhodium and iridium clusters will be discussed. Variable temperature 1H NMR studies on $(C_5Me_5)_4Rh_4S_4^{2+}$ reveal that the ΔH^\ddagger values for the barrier to single M-M bond migration in the Rh_4 and Ir_4 clusters are almost the same (~ 40 kJ/mol).

To determine if mixed valency is a prerequisite for M-M bond movement, we synthesized the homovalent cluster $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SMe})^+$, via the reaction of $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4$ with MeO_3SCF_3 . Dynamic NMR experiments on $(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_3(\text{SMe})^+$ also demonstrate the mobility of the metal-metal bonds. This 68e species contains two bonds which most likely move in a pairwise fashion, consistent with the larger ΔH^\ddagger value of 88 kJ/mol. This experiment established the fact that mixed valency is not a requirement for M-M bond migration.

In a separate study we examined the preparation of M_3S_4 clusters where M is a platinum metal. M_3S_4 clusters are common when one metal is molybdenum or tungsten, but they are otherwise rare [3]. Mixed metal M_3S_4 clusters were obtained by the reaction of $(\text{C}_5\text{Me}_5)\text{Rh}(\text{CH}_3\text{CN})_3^{2+}$ with $(\text{C}_5\text{Me}_5)_2\text{Ru}_2\text{S}_4$. In the solid state, $(\text{C}_5\text{Me}_5)_3\text{RhRu}_2\text{S}_4(\text{CH}_3\text{CN})^{2+}$ consists of an unsymmetrical RhRu_2S_4 core containing an isosceles triangle of metal atoms with one Ru-Ru bond of 2.88 Å (Figure 1).

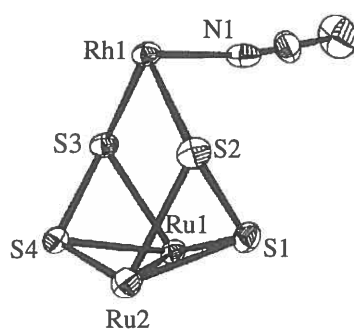


Figure 1. Structure of $(\text{C}_5\text{Me}_5)_3\text{RhRu}_2\text{S}_4(\text{CH}_3\text{CN})^{2+}$ (pentamethylcyclopentadienyl ligands omitted for clarity).

Variable temperature ^1H NMR spectra reveal that the cluster is fluxional, due to dynamics involving both the persulfide and acetonitrile ligands. $(\text{C}_5\text{Me}_5)_3\text{RhRu}_2\text{S}_4(\text{CH}_3\text{CN})^{2+}$ reacts with acetone to form the $(\text{C}_5\text{Me}_5)_3\text{RhRu}_2\text{S}_3(\text{SCH}_2\text{COCH}_3)^+$ species concomitant with cleavage of an S-S bond (Figure 2). This reaction is reversed by the addition of HO_3SCF_3 .

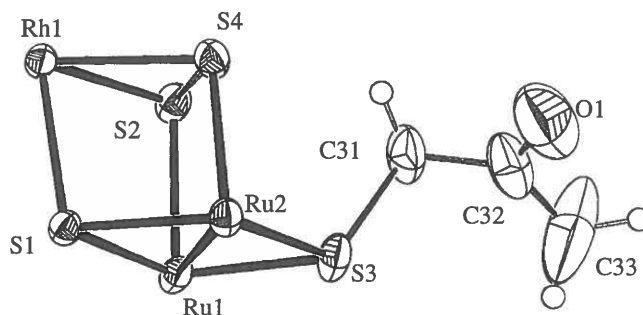


Figure 2. Structure of $(\text{C}_5\text{Me}_5)_3\text{RhRu}_2\text{S}_3(\text{SCH}_2\text{COCH}_3)^+$ (pentamethylcyclopentadienyl ligands omitted for clarity).

References

1. *The Chemistry of Metal Cluster Complexes*; Shriver, D. F.; Kaesz, H. D.; Adams, R. D., Ed.; VCH: New York, 1990.

2.
 - (a) Carmona, D.; Ferrer, J.; Mendoza, A.; Lahoz, F. J.; Reyes, J.; Oro, L. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1171-1173.
 - (b) Bailey, D. A.; Balch, A. L.; Olmstead, M. M.; Reedy, Jr., P. E. *Inorg. Chem.* **1987**, *26*, 2413-2418.
 - (c) Kubas, G. J.; Vergamini, P. J. *Inorg. Chem.* **1981**, *20*, 2667-2676.
3.
 - (a) Brunner, H.; Kauermann, H.; Wachter, J. J. *Organomet. Chem.* **1984**, *265*, 189-198.
 - (b) Cowans, B. A.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 995-1004.