

Studies of Metal-Metal Bonded Compounds in Catalysis; John F. Berry, PI

This project has funded a broad range of fundamental studies in the research labs of Prof. John Berry at the University of Wisconsin – Madison. The overall goals of this research are (1) to define the fundamental coordination chemistry underlying successful catalytic transformations promoted by metal-metal bonded compounds, and (2) to explore new chemical transformations that occur at metal-metal bonded sites that could lead to the discovery of new catalytic processes. Transformations of interest include metal-promoted reactions of carbene, nitrene, or nitrido species to yield products with new C–C and C–N bonds, respectively. The most promising suite of transition metal catalysts for these transformations is the set of metal-metal bonded coordination compounds of Ru and Rh of the general formula $M_2(\text{ligand})_4$, where M = Ru or Rh and ligand = a monoanionic, bridging ligand such as acetate. Development of new catalysts and improvement of catalytic conditions have been stymied by a general lack of knowledge about the nature of highly reactive intermediates in these reactions, the knowledge that is to be supplied by this work. Our three specific objectives for this year have been (A) to trap, isolate, and characterize new reactive intermediates of general relevance to catalysis, (B) to explore the electronic structure and reactivity of these unusual species, and how these two properties are interrelated, and (C) to use our obtained mechanistic knowledge to design new catalysts with a focus on Earth-abundant first-row transition metal compounds.

This grant has enabled several students to successfully complete PhD work: **Dr. Kasia Kornecki**, **Dr. Amanda Corcos**, and **Dr. Tristan Brown**. Other students who worked on these projects are **Ryan Pakula**, **Tzuhsiung Yang**, and **Sungho Park**. Outlined below are our major accomplishments from the period of 2013 – 2016.

Goal 1: To define the fundamental coordination chemistry underlying successful catalytic transformations promoted by metal-metal bonded compounds.

The focus in this grant period has been on the preparation and study of compounds containing two metals (M) and a reactive main group fragment (E) aligned in a M–M=E linear array. These structures contain multiple bonds that interconnect the M and E groups, and are structures that had been proposed, but never observed, before our work. In 2008, the Berry group discovered the first compound with hetero-cumulenic bonding within a highly oxidized $Ru\equiv Ru\equiv N$ core. No other example of a compound containing tandem metal-metal and metal-ligand multiple bonds had been previously reported. In 2013, we reported the first characterization of a $Rh-Rh=CR_2$ carbene complex (*Science*, **2013**, 342, 351-354). This was an extraordinarily impactful result because we have been able to characterize for the first time a highly reactive intermediate that had been proposed in the literature since the 1970's. The application of Rh²-carbene chemistry to synthetic organic chemistry is enormous: such species are invoked in

cyclopropanation and C–H functionalization reactions, *inter alia*, including some reactions that are exquisitely stereoselective (Figure 1).

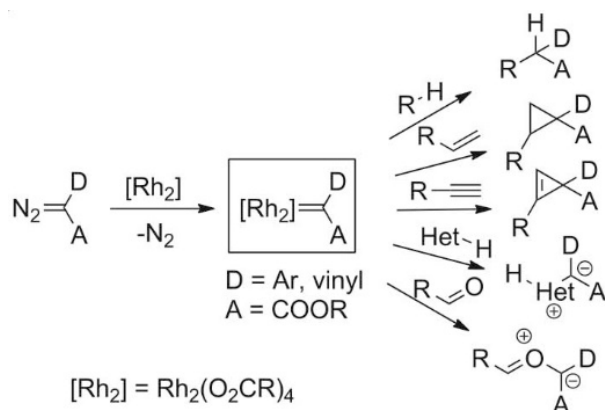


Figure 1. Catalytic reactions proposed to proceed via a Rh–Rh=CR₂ intermediate.

Starting in 2011, our group also made significant contributions to nitrene transfer catalysis via compounds proposed to have an Rh–Rh=NR structure. In this grant period we reported two studies of the most successful C–H amination catalyst, Rh₂(esp)₂. This catalyst is broadly accepted as the more generally successful catalyst for performing nitrene transfer reactions, especially insertions of nitrenes into C–H bonds to form new C–N bonds. This C–H amination reaction is an enabling method in synthetic organic chemistry. It is widely recognized that many small molecules can poison the catalyst, and we have reported a deliberate structural and spectroscopic study of a systematic series of such compounds ligated to the Rh₂(esp)₂ catalyst (*Inorg. Chem.* **2015**, 54, 8817–8824; Figure 2). Highlights of this study include direct observation of the Rh–Rh stretching frequencies that provide intimate detail about the strength of the Rh–Rh bond, and a correlation of the Rh–ligand bond distance to the HOMO–LUMO energy.

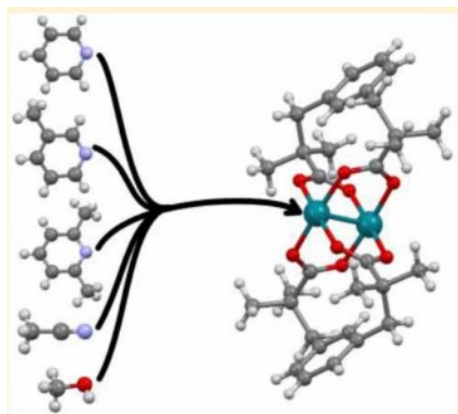


Figure 2. Structure of the Rh₂(esp)₂ catalyst.

In a further experimental & computational study, we examined oxidation of Rh₂(esp)₂ to the [Rh₂(esp)₂]⁺ cation as well as the potential catalytic competence of the [Rh₂(esp)₂(nitrene)]⁺ intermediate (*J. Am. Chem. Soc.* **2016**, 138, 2327–2341). Experimentally, we found that the [Rh₂(esp)₂]⁺ cation has a surprising electronic structure with an unpaired electron in an orbital of δ symmetry rather than the expected π-symmetry orbital. The computational results provided deep insights into the nature of C–H amination by the [Rh₂(esp)₂(nitrene)]⁺ species and how the electronic structure controls the mechanism

(concerted vs stepwise) of C–H amination. Concerted reaction pathways require a low-spin nitrene intermediate, whereas high-spin intermediates necessarily must react via a stepwise mechanism.

Goal 2: To explore new chemical transformations that occur at metal-metal bonded sites that could lead to the discovery of new catalytic processes.

In this grant period we have focused on discovering new chemistry of Ru–Ru≡N and Ru–Ru=O species. We have focused on developing ‘synthetic cycles’, sequences of reactions that can form the basis of a novel catalytic transformation. One such reaction sequence that we have discovered is shown in Figure 3 (*Eur. J. Inorg. Chem.* **2013**, 3808–3811). In this scheme, we are able to transfer an N atom to PPh₃ to form [H₂NPPh₃]Cl as an isolable salt. The Ru₂ material recovered from this reaction can be reformed in a straightforward manner to our starting complex.

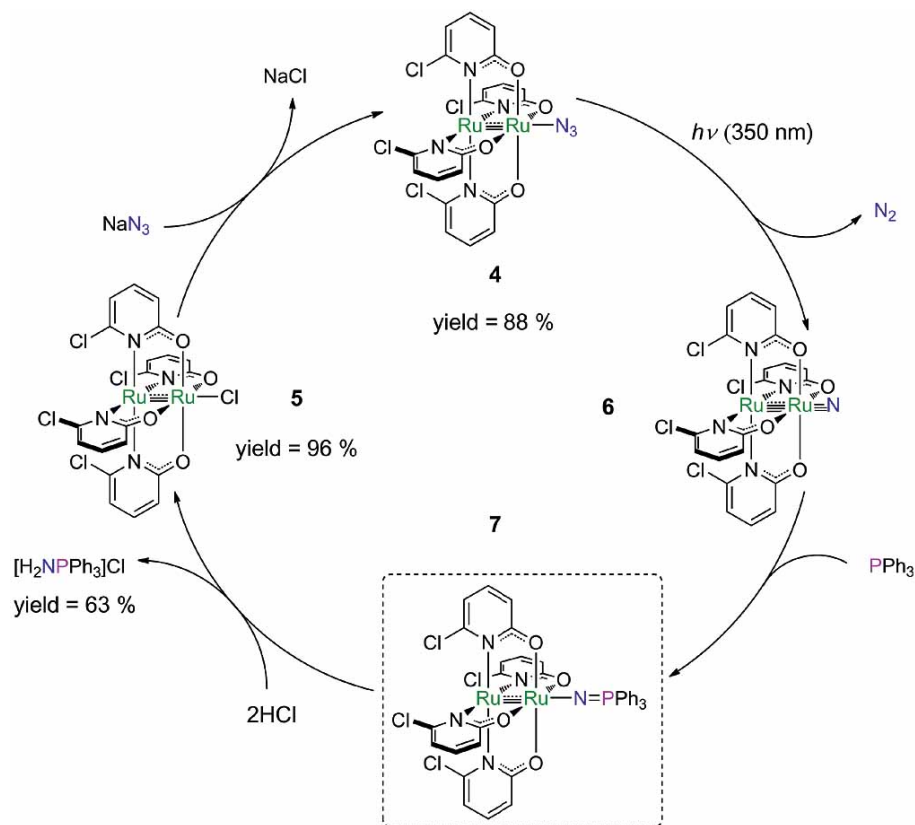


Figure 3. Synthetic cycle for N atom transfer.

A similar synthetic cycle was achieved using photolysis of Ru₂-oxanion compounds to form a transient Ru–Ru=O complex, a completely novel synthetic strategy (*J. Am. Chem. Soc.* **2016**, 138, 10032–10040; Figure 4). The novelty of incorporating oxanion photolysis into a synthetic cycle hinged on the ability to regenerate the starting material, which was achievable in this case because the reduced Ru₂ species is known to photochemically oxidize dichloromethane. In the course of this study, we discovered a number of related, new Ru₂ complexes, which, though of less relevance to the field of catalysis, have been reported on the basis of their own novelty (*Dalton Trans.* **2016**, 45, 2386–2389; *Dalton Trans.* **2017**, 46, 5532–5539). These results include the first example of a coordination complex containing the linear [AgF₂][–] anion as a ligand, and various new starting materials containing labile axial ligands.

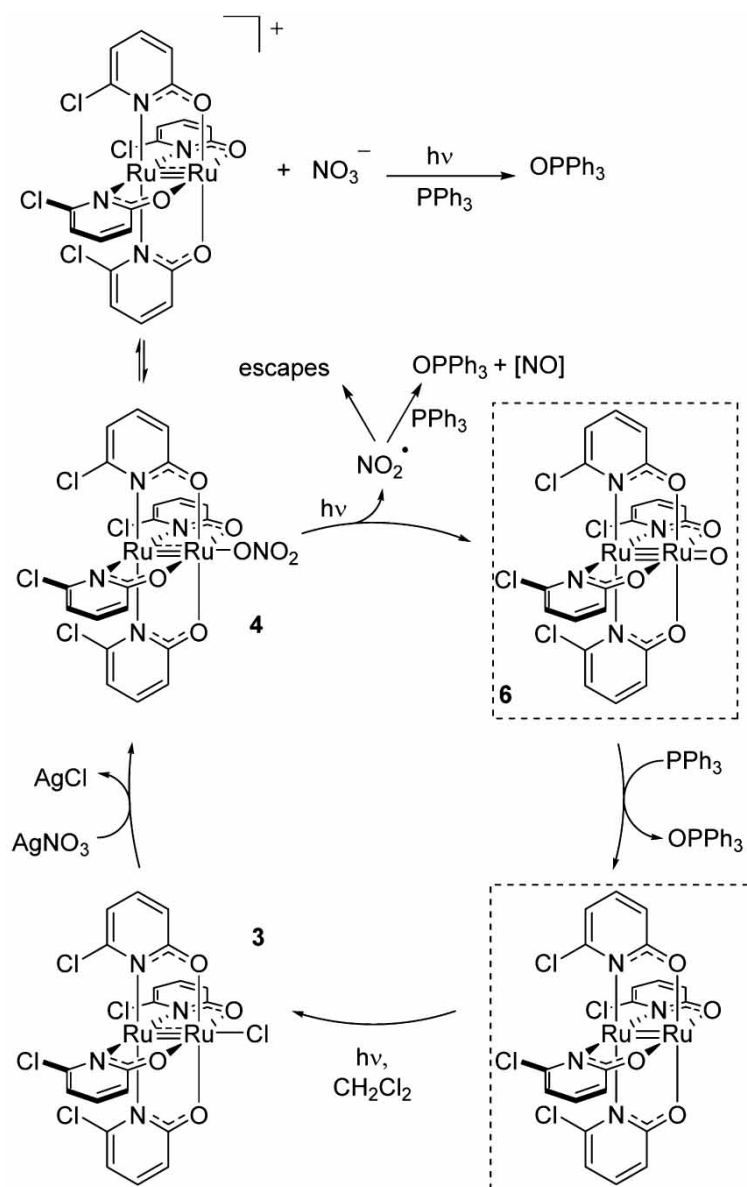


Figure 4. Synthetic cycle for oxygen atom transfer.

A further focus of this grant period was on exploring the fundamental coordination chemistry of reduced Ru_2 complexes to see whether they could serve as a platform for the activation of nitrogen or ammonia, with the overall goal of discovering novel catalytic methods to incorporate N atoms into organic substrates where the N-atom sources are the cheap and widely available N_2 or NH_3 . To this end, we performed a systematic exploration of the strength of metal-ligand bonds to reduced Ru_2 species (*Inorg. Chem.* **2015**, *54*, 8571-8589). The major conclusions of this work are that N_2 and NH_3 should both be able to coordinate to the reduced Ru_2 unit. The binding strength is correlated strongly to the σ -donating ability of the ligand; thus, NH_3 is proposed to bind more strongly. Additionally, the Ru_2 complexes are found to form a stable dimer that prevents N_2 binding.