

Exploiting the Reactivity of Metal-Metal Bonds in a Diruthenium Nitride Complex

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Metal-metal multiple bonds were first recognized in rhenium halide clusters in the 1960s, despite being alluded to in earlier years by crystallographically characterized short metal-metal distances.¹ In the decades that followed, a wide array of complexes featuring metal-metal bonds were synthesized. These encompassed virtually all transition metals, although metal-metal bonding has been observed more frequently in 4d and 5d metals.² In addition, these complexes have proved to be useful in a variety of catalytic transformations.

Perhaps the most prolific catalysts featuring metal-metal bonds are the dirhodium tetracarboxylates.^{2,3} This family of catalysts has shown competency in both carbene and nitrene insertion into unactivated C-H bonds. In particular, Du Bois and coworkers have been successful in utilizing dirhodium tetracarboxylates to catalyze C-H amination using iminoiodinanes as a nitrene source.²⁻⁴ A proposed catalytic cycle for this transformation is shown in Figure 1.

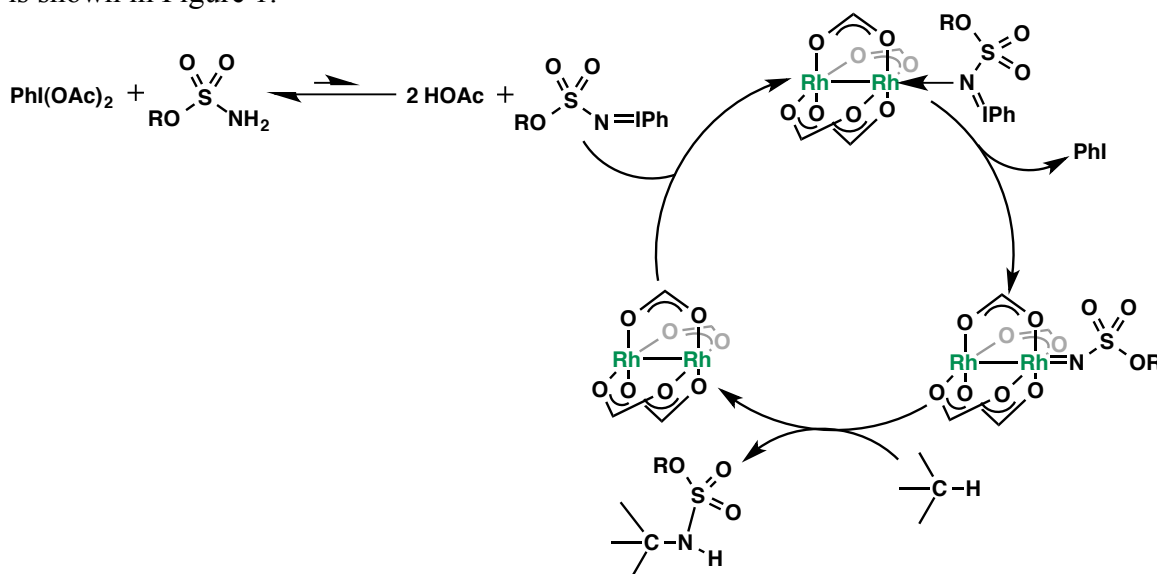


Figure 1. Proposed catalytic cycle of C-H amination by dirhodium tetracarboxylates

The iminoiodinane can be formed in situ by addition of a hypervalent iodine source, typically $\text{PhI}(\text{OAc})_2$, to a sulfamate ester. This species can then bind axially to one rhodium center and subsequent release of iodobenzene leads to the formation of a rhodium-nitrenoid intermediate.⁵ Insertion of the nitrene into an intermolecular or intramolecular aliphatic C-H bond reforms the starting complex. Although the nitrenoid intermediate has been implicated in this catalytic cycle and supported by a body of computational work, it has thus far been too transient for isolation and thorough characterization.^{2,5}

Intrigued by the unique structural and electronic properties of this nitrenoid intermediate, Berry and coworkers set out to independently synthesize and characterize a complex containing metal-metal and metal-ligand multiple bonds.⁶ This was

accomplished by photolysis at 77 K of the previously synthesized $\text{Ru}_2(\text{DPhF})_4\text{N}_3$ complex (DPhF = *N,N'*-diphenylformamidinate) to trap the terminal nitride species, as shown in Figure 2.

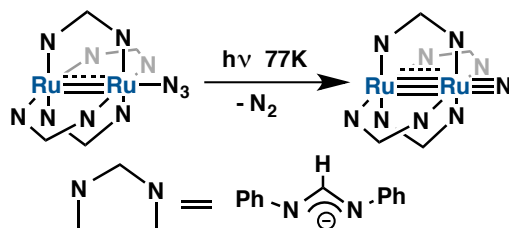


Figure 2. Synthesis of the diruthenium nitride

This nitrido species was then characterized by a multitude of spectroscopic techniques. Electron paramagnetic resonance spectroscopy revealed a sharp $S=1/2$ axial signal, consistent with the photooxidation of the $S=3/2$ azide starting material.^{6,7} Resonance Raman spectroscopy gave a Ru-nitride stretch of 822.6 cm^{-1} , which is significantly lower than the range of 1000 to 1100 cm^{-1} observed in mononuclear Ru^{VI} -nitrido complexes, indicating a weakening of the Ru-nitride bond with the addition of metal-metal bonding.⁶ Further corroborating this bond weakening, X-ray absorption spectroscopy showed lengthening of the Ru-nitride bond by 0.16 \AA compared to the average in mononuclear Ru^{VI} -nitride complexes. In addition, the Ru-Ru bond length was also elongated by approximately 0.09 \AA from the azide complex.⁷ Berry and coworkers attribute this spectroscopic data to the presence of 3-center/4-electron bonding, where electron density from the axial nitride is delocalized along the linear metal-metal-ligand unit.⁵

A similar terminal diruthenium nitrido was subsequently synthesized by the Berry group and shown to undergo aryl C-H amination as shown in Figure 3. When using thermolysis, the azide starting material is proposed to go through a nitrido intermediate, which readily undergoes C-H insertion to yield the aryl aminated product. This represents the first example of a nitride insertion into an aryl C-H bond and highlights the unique reactivity of 3-center/4-electron bonding manifolds. Because of the delocalization of electron density along the linear 3-center unit, the terminal nitride exhibits increased electrophilic behavior and is able to insert into aryl C-H bonds, even below room temperature.

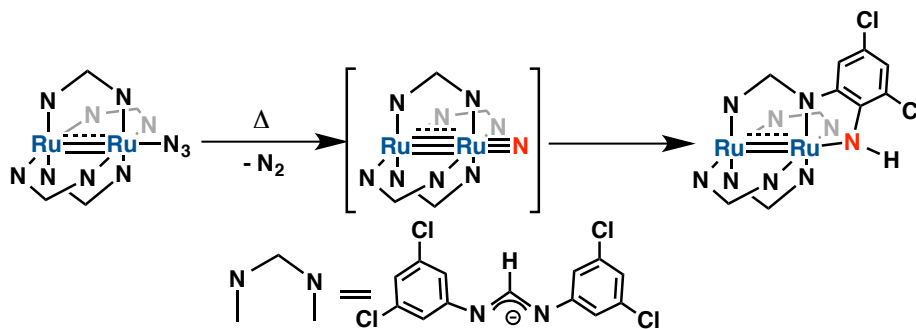


Figure 3. Aryl C-H amination by a diruthenium nitride complex

The reactivity of the diruthenium nitride complexes synthesized by Berry and coworkers mirrors what has been seen in dirhodium tetracarboxylate complexes for several decades.⁵ With the elucidation of the electronic nature of the 3-center/4-electron bonding present in both systems, further work can be done to improve the scope and selectivity of catalytic nitrene transfer.

References:

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