

Completing a Photocatalytic Cycle for Hydrogen Evolution: Photoinduced Halide Elimination from Bimetallic Complexes

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Dihydrogen, which can be generated from water splitting, is an appealing energy source because of its high energy density by mass.^{1,2} However, given the complexity of water splitting, photocatalytic HX splitting (X = halide) has been studied as a simpler two-electron, two-proton pathway to H₂.³ The difficulty of regenerating the active photocatalyst by photoreductive halide elimination limits the overall quantum efficiency of the process.⁴ Understanding photochemical multielectron transformations is crucial to solving this limitation in the design of HX splitting catalysts.

Photochemistry confers access to the excited states of molecules capable of undergoing ligand exchange, energy transfer, and charge transfer (redox) events.⁵ Bimetallic photocatalysis relies on the accessibility of the metal-metal $d\sigma \rightarrow d\sigma^*$ excited state, which usually involves significant ligand-to-metal charge transfer (LMCT) character.⁶⁻⁸ A series of dirhodium mixed-valence complexes can perform photoinduced hydrogen evolution, as shown in **Figure 1**. However, Rh₂(II,II)X₄ is a thermodynamic sink due to the high Rh-X bond strength, making the regeneration of the active catalyst challenging, owing to low quantum yields for this step (below 1%).⁹

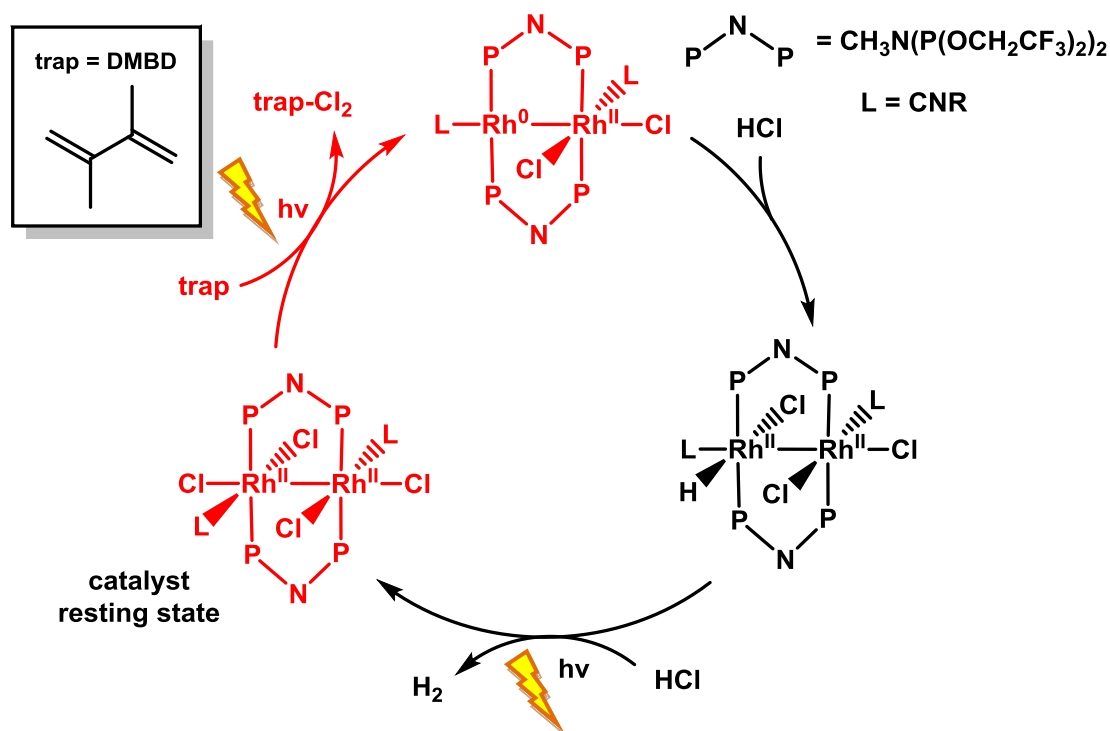


Figure 1. Photocatalytic cycle for HCl splitting. **In red:** regeneration of active catalyst by halide photoreductive elimination from bimetallic Rh₂(II,II)Cl₄.

Here, three bimetallic model systems (**Fig 2**) for halide photoreductive elimination are explored. The first system makes use of a platinum-rhodium bimetallic core. This approach combines the ability of dirhodium complexes to perform H₂ photoelimination and the ability of

diplatinum complexes to undergo photoelimination of halides with quantum yields as high as 40% in high trap concentrations.^{4,10} Accordingly, a heterobimetallic Pt-Rh complex was designed to incorporate both of these reactivities (**Fig 2a**). One of the Pt-Rh complexes showed a maximum quantum efficiency of 23.4%.

The second model also makes use of a heterobimetallic core composed of a late transition metal and a main group metal. In this system, the tellurium center functions as an electron reservoir to modulate electron density and reactivity at the platinum center. The tellurium center serves as a σ -donor to Pt upon oxidative addition of chlorine to form a Te-Pt complex (**Fig 2b**). The tellurium is also able to decrease σ -donation upon photoreduction, functioning as an electronic buffer for the system. This buffering effect of tellurium facilitates the two-electron redox chemistry of the Te-Pt complex.¹¹ The maximum quantum efficiency achieved for photoelimination of halide was 4.4%.

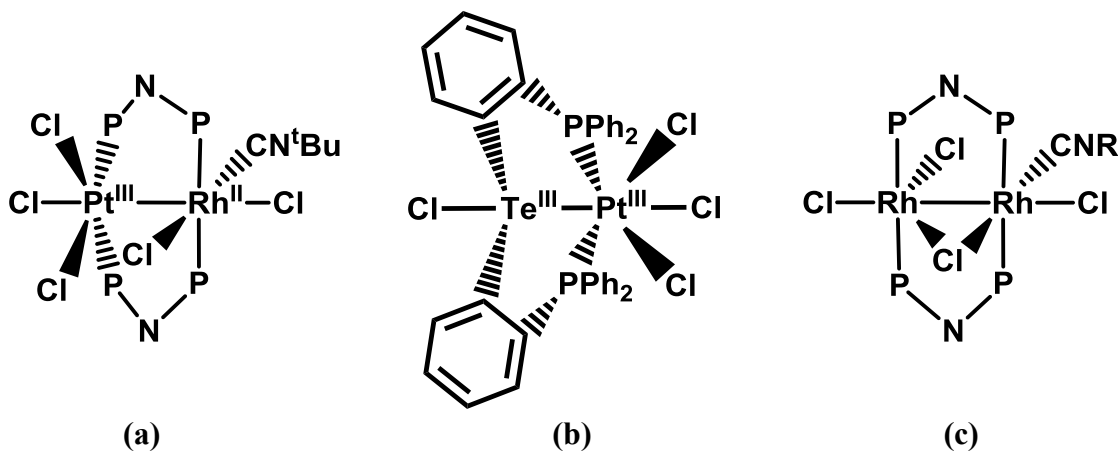


Figure 2. Relevant complexes in approaching photoinduced halide elimination.

The third model system (**Fig 2c**) is based on mechanistic studies of the photoelimination of halogens from mixed-valence $\text{Rh}_2(\text{III},\text{I})$ and homovalent $\text{Rh}_2(\text{II},\text{II})$ complexes to form the mixed valence $\text{Rh}_2(0,\text{II})$ core. The halide elimination is presumed to proceed by two sequential photochemical reactions, the first resulting in the generation of a bridging-chloride intermediate. It is proposed that bimetallic complexes with halide-bridged cores could reductively eliminate halides in higher quantum yields. For the chloride-bridge complex, the photoreduction quantum efficiency observed was 0.80%, which is more efficient than the non-bridged analogs $\text{Rh}_2(\text{III},\text{I})$ (0.29%) and $\text{Rh}_2(\text{II},\text{II})$ (0.47%).¹²

These model systems have demonstrated possible routes to regenerate the active catalyst through photoreductive elimination, despite the quantum yields are still modest. Although the reactivity of these systems towards hydrogen evolution has not been fully explored, these complexes point the way to more efficient halide photoreductive elimination systems. This photochemistry is also relevant to the regeneration of oxygen reduction catalysts and other systems that rely on excited state chemistry.^{13,14}

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