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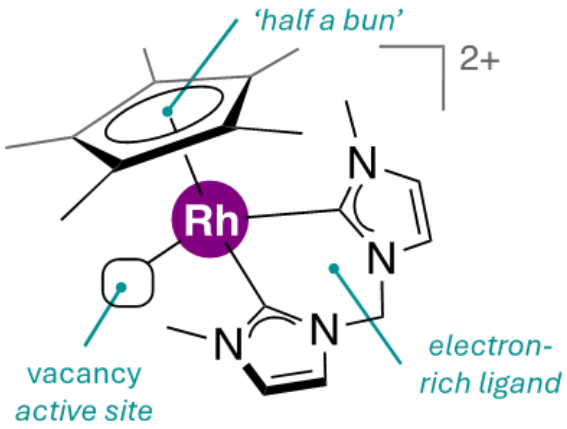
RESEARCH CONNECTION

Half-sandwich complexes for hydrogen storage

By Carson McDonald & Shrinwantu Pal, PhD



What you need to know

Since the 1960s, half-sandwich organometallic complexes have been proven as effective catalysts for hydrogenation and dehydrogenation reactions. These complexes feature a ligand such as 1,2,3,4,5-Pentamethylcyclopentadienyl (Cp*), which represents 'half a bun' in the sandwich, with the metal centre representing the 'meat. The metal centre is further supported by ancillary ligands. By selecting more electron-rich ancillary ligands, more efficient catalysts can be envisioned.

Why this research is important

With climate change and emission reductions being critical global concerns, alternative energy sources are needed to sustainably meet future energy demands. A primary candidate for fossil fuel replacement is hydrogen (H_2). As opposed to fossil fuels, combustion of H_2 does not emit CO_2. Widespread incorporation of compressed H_2 as a primary fuel source is plagued by storage limitations and safety concerns. The use of light organic hydrogen carriers (or LOHCs) as H_2 surrogates can bypass these restrictions. However, to leverage LOHCs, appropriate catalysts capable of reversible storage and delivery of H_2 at atmospheric pressures must be developed.

We are developing rhodium and iridium catalysts featuring 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) ligands—these popular complexes are called 'half-sandwich' complexes.

A class of ancillary ligands popularly used in half-sandwich complexes is bipyridine. By choosing more electron-donating ancillary ligands, enhancement in catalyst efficiency may be envisioned. With this rationalization, we considered bis-carbene as an alternative to bipyridine as the ancillary ligand, and successfully synthesized bis-imidazolyl methane. Before coordination, bis-imidazolium methane is deprotonated, resulting in the two inter-nitrogen carbon centres, each having a lone pair of electrons that can coordinate to the metal centre. Since bis-imidazolyl methane coordinates via carbon, it makes the metal centre more electron-rich than bipyridine ancillary ligands because carbon is less electronegative than nitrogen.

How the research was conducted

The *Pal Lab* uses a system of "computation-directed experiments" for the realization of potential catalysts.

First, Density Functional Theory (DFT) calculations are performed to assess the viability of a proposed complex in catalysis. If catalytic turnover is deemed feasible, small-scale syntheses are undertaken to realize the target complexes. In-house nuclear magnetic resonance (NMR) and mass spectrometric analysis are conducted on successfully synthesized complexes. Through collaborations with the University of Manitoba and the University of Winnipeg, X-ray crystallographic analysis is also available to our group. The final stage in assessing each candidate is catalysis. Dehydrogenation of liquid organic hydrogen carriers (LOHCs) is done under air-free conditions using an inert atmosphere glovebox. Catalysis cannot occur on the benchtop due to the sensitivity of the metal-hydride intermediates to oxygen. Finally, using the dehydrogenated LOHCs, the catalytic efficiency of each complex in hydrogenation (i.e., H_2 storage) is also assessed by using H_2 to reverse the reaction.

What the researchers found

Having recently optimized and scaled up the synthesis of bis-imidazolium methane as our ligand precursor, we have subsequently successfully synthesized Cp* bis-imidazolyl methane complexes of rhodium and iridium. Although preliminary results indicate that the Rh complex is catalytically active for dehydrogenation, further optimization of catalytic conditions is required for high throughput catalysis. Additionally, we are investigating the Ir complex for mechanistic analysis since the Ir intermediates are more stable and less catalytically active than the Rh analogues. The structural and mechanistic insights will furnish information that will allow us to modify the catalysts toward more efficient catalysis.

How this research can be used

Low pressure and mobile storage of H_2 is a hurdle that must be overcome for this fuel source to become mainstream. Current storage practices involve high-pressure tanks that compress H_2 into a usable form. This brings challenges in safety concerns of storing a flammable fuel at high pressures. The use of transition metal catalysts to store H_2 within surrogates can overcome these restrictions by storing H_2 at near-atmospheric pressures. With this, safe storage of H_2 can be achieved in mobile applications. The proposed system would employ LOHCs (methanol, isopropanol, etc.) as hydrogen surrogates. These surrogates would be filled into a vehicle and safely stored until H_2 needs to be released by the same catalyst, now operating in reverse. The released H_2 will serve to produce energy on demand.

About the researchers

Dr. Shrin Pal is an assistant professor at Brandon University specializing in inorganic and organometallic chemistry. PalS@BrandonU.CA

Carson McDonald is a graduate student in the Master of Science (Environment & Life Sciences) program and is investigating organometallic synthesis and catalysis under the supervision of Dr. Pal.

Keywords

Hydrogen energy, sustainable catalysis, hybrid fuel cells

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Editor: Christiane Ramsey Ramseyc@brandonu.ca
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