

Lanthanide-Supported Nickel and Cobalt Catalysts for CO₂ Hydrogenation

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Carbon dioxide, a byproduct of petroleum use, is a promising single-carbon feedstock for the petrochemical industry. Molecular catalysts that hydrogenate CO₂ rely predominantly on precious metals to achieve high activity. The goal of this project is to develop efficient base-metal catalysts for CO₂ hydrogenation. Specifically, we focus on the use of bifunctional catalysts, where a lanthanide ion (Ln³⁺) is used as a support to tune an active transition metal center. The Lewis acidic Ln metalloligand, which is a sigma acceptor or Z-type ligand, imparts electrophilic reactivity to the base metal (M) by withdrawing electron density via a direct M→Ln bonding interaction. In catalysis, Z-type ligands are emerging, and they are predominately use a main group ion. Hence, using *f*-block metal ions as Z-type metalloligands is a new research direction. Also, since bonding interactions between *d-f* metals are still in the early stage, this project is well poised to make significant advancements in the understanding of *d-f* bonded complexes, including fundamental knowledge about their bonding, redox/magnetic properties, reactivities, and potential catalytic applications.

The second project year began with the publication of a *Chemical Science* paper that detailed our discovery and development of Ni-Lu compounds using our self-designed ligands, [(ⁱPr₂PCH₂NAr)₃tacn]³⁻ and [ⁱPr₂PCH₂NPh]⁻, to tune the coordination number of the Lu ion, which directly impacts the Ni-Lu bonding interaction. In the paper, we illustrate that catalytic olefin hydrogenation is four-fold faster when we employ the more flexible ligand, [ⁱPr₂PCH₂NPh]⁻, because it allows for a shorter (and presumably stronger) Ni-Lu bond.

During the second project year, we were able to expand the family of Ni-Ln coordination complexes to include Ln = La, Ce, Sm, Dy, Er, and Yb. In addition, we have included other trivalent ions for comparative purposes, including Ga, Sc and Y. To date, we have synthesized and structurally characterized a total of 10 isostructural Ni-Z complexes. This is a big advancement for us, since we are now able to study systematically a larger series to define the extent to which the properties and reactivities among these Ni-Z complexes can be varied. The Z-type metalloligands differ widely in two intrinsic properties, the ionic radius (size) and the Lewis acidity. We will examine if these parameters will be useful descriptors for catalysis, including activity and selectivity.

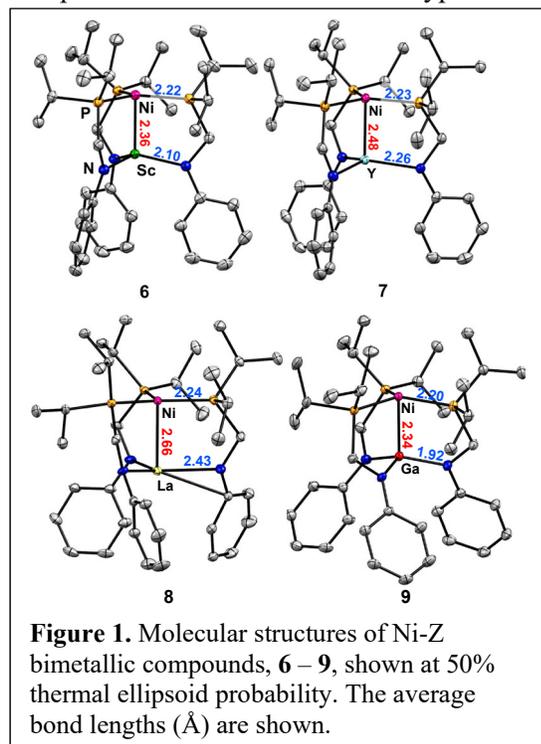


Figure 1. Molecular structures of Ni-Z bimetallic compounds, **6** – **9**, shown at 50% thermal ellipsoid probability. The average bond lengths (Å) are shown.

A NiZ(L)₃ series, where Z is Sc, Y, Ga, Lu, and La, has been investigated as catalysts for the semi-hydrogenation of alkynes (Figure 1, Table 1). The choice of the Z-type metalloligand has an impact on the catalytic activity and selectivity. For the model substrate, diphenylacetylene, a few catalysts, Ni-Y, Ni-Lu, and Ni-Ga, showed excellent conversion to *E*-stilbene in >90% yield. Ni-Sc was sluggish, and Ni-La decomposed during catalysis, and hence, significantly curtailed the conversion of Z-stilbene to *E*-stilbene. Of the top three performers, Ni-Y, was superior in exhibiting “perfect” chemo- and regioselectivity with no more than trace formation of other byproducts. We were able to show that the choice of the Z-type metalloligand determines the catalyst resting state. For the larger supporting ions (Y, Lu, La), the alkyne adduct was observed as the resting state (Figure 2), whereas for smaller ions (Sc, Ga) the catalyst resting state was the either a H₂ adduct or the Ni-Z precatalyst. The stability of this intermediate for the larger supporting ions

