

Project Title: High-Spin Cobalt Hydrides for Catalysis

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Principal Investigator: Patrick L. Holland, University of Rochester

Students: Thomas Dugan (graduate student)
Nicole Wedgwood (graduate student)
Chi Chen (graduate student)
Malik Al-Afyouni (graduate student)
Benjamin Dible (postdoctoral)
Aydin Kavara (postdoctoral)
Jonathan Goldberg (undergraduate student)
Maxwell Hecht (undergraduate student)

Collaborators: Daniel Weix, University of Rochester
Thomas Cundari, University of North Texas
Elena Rybak-Akimova, Tufts University

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Research Goals

Explore the catalytic ability of low-coordinate cobalt complexes in small-molecule catalysis. Determine the mechanisms of organometallic transformations at metals with high-spin electronic configurations. The low coordination number and unusual spin states are anticipated to give novel and useful reactivity patterns, leading to exciting transformations that make catalysts more efficient.

Significant Achievements and Results

- *Synthesis of a "Masked Two-Coordinate" Cobalt Complex:* We isolated the highly unsaturated species $L^{tBu}Co$, which "slips" one of its imine donors to form an η^6 interaction with an arene. The isomerization is reversible upon addition of donor ligands. We established the mechanism of the ligand coordination/decoordination, including intermediate slipping in a CO complex.
- *Bimetallic C-F Bond Cleavage:* $L^{tBu}Co$ reacts with aryl fluorides to give $L^{tBu}CoAr$ and $[L^{tBu}CoF]_2$. We established the mechanism of this rare example of multimetallic C-F bond activation using kinetic studies. Another Co-F compound exists as an unusual Co-Sn-Co assembly.
- *Catalytic Alkene Isomerization by Cobalt Complexes:* $L^{tBu}CoR$ complexes catalyze the isomerization of simple terminal alkenes specifically to *Z*-2-alkenes. This is an unprecedented case of selective alkene isomerization to give a single isomer that is not the thermodynamic product. The mechanism of this transformation, and the determinants of selectivity, were established using a combination of computational and mechanistic studies.
- *Carbon Dioxide is Reduced by the Cobalt Complexes.* The cobalt(I) complex reduces CO_2 to carbonate and to a dicobalt(II) oxo complex. The mechanism of this reaction has been established.

- *Spin-State Crossing in Beta-Hydride Elimination by Iron and Cobalt*: Based on usual organometallic principles, high-spin complexes are not expected to engage in "two-electron" organometallic reactions that require an empty *d* orbital. However, these reactions work! We showed using DFT that the ability of some complexes to do beta-hydride elimination comes from the pairing of electrons to empty a key *d* orbital during the reaction pathway.

Potential Impact

Organometallic chemists have traditionally used catalysts with strong-field ligands that give low-spin complexes. However, complexes with a weak ligand field have weaker bonds and lower barriers to geometric changes, suggesting that they may lead to more rapid catalytic reactions. Developing our understanding of high-spin complexes requires the use of a broader range of spectroscopic techniques, but has the promise of changing the mechanism and/or selectivity of known catalytic reactions. These changes may enable the more efficient utilization of chemical resources. A special advantage of cobalt and iron catalysts is that the metals are more abundant and cheaper than those currently used for major industrial processes that convert unsaturated organic molecules and biofeedstocks into useful chemicals. Most importantly, we have discovered that the cobalt catalysts described here give distinctive and useful selectivities that give advantages over known catalysts.

Recognitions

I received a Fulbright Award for supporting a sabbatical in Germany during the spring of 2012. During this time, I learned to do density-functional calculations, under the guidance of Frank Neese at the Max Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr. Our calculations already have been useful for explaining the selectivity of the isomerization reactions (see below).

I was appointed to the Executive Committee of the Division of Inorganic Chemistry of the ACS for 2010-2012, and to the Editorial Board of *Inorganic Chemistry* in 2013. I was also elected to be the chair of the Inorganic Reaction Mechanisms Gordon Conference in 2017.

Finally, I received a 2013 Blavatnik Award for Young Scientists. This prize is awarded by the New York Academy of Sciences to scientists in all fields. It is an honor for any chemist to be chosen, and I am acting as a representative of research in sustainable chemistry.

Background for Project

First-row metal complexes offer potential advantages in terms of mechanistic possibilities for organometallic chemistry. This opportunity arises from the availability of multiple spin states throughout the catalytic cycle when one uses complexes with weak-field ligands (those that give high-spin electronic configurations).¹ Recall that effective catalysis requires minimal energy variation throughout a catalytic cycle, with low barriers for all steps. In complexes with multiple spin-state possibilities, (a) ligand-field effects are lessened, making the energies of various intermediates and transition states more similar, (b) metals can often "jump" back and forth between potential-energy surfaces of different spin states, enabling the reaction to bypass high-energy transition states that would be lower reaction rates if "trapped" on a single potential-energy surface.

Most known first-row catalysts have low-spin electronic configurations at the metals.² The more rapid development of diamagnetic catalysis is probably because of the preconceptions that (a) paramagnetic complexes cannot be evaluated by NMR, and (b) high-spin organometallic complexes are unstable, decomposing readily through radical pathways. In my group's research, we have seen that neither of these assumptions is true, and that

the door is open to exploration of organometallic catalysis with high-spin complexes. We use bulky bidentate ligands L^{Me} and L^{tBu} (Figure 1) as spectator ligands that are strongly binding but give high-spin complexes because the π -donor β -diketiminates are weak-field ligands. The steric bulk and stability enable the isolation of key organometallic species, and we have isolated numerous alkyl, alkenyl, η^2 -alkene, η^2 -alkyne, and other complexes of iron(0), iron(I), iron(II), cobalt(0), cobalt(I), and cobalt(II).³ However, we have been hampered by (a) the lack of catalytic reactions from these complexes, and (b) a lack of mechanistic understanding, particularly about potential spin-state changes during the reactions. In the 3 years of this grant + 1 year no-cost extension, we overcame many of these challenges, and established a basis for future progress.

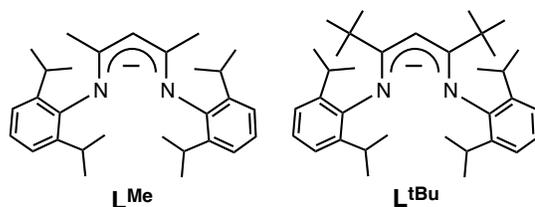


Figure 1. Bulky β -diketiminato ligands.

Results

Novel low-coordinate cobalt complexes, including a "masked two-coordinate" complex. In 2009, we reported dimeric cobalt(II) and cobalt(I) hydride complexes (Figure 2).⁴ The cobalt(I) hydride complex on the right was the first hydride complex of any transition metal that is three-coordinate at the metal. This is exciting because the complex has both open coordination sites and hydride ligands, both harbingers of exciting reactions. However, we put this complex "on hold" for an even more interesting compound.

This new compound started from the cobalt(I) dinitrogen complex $L^{tBu}CoN_2CoL^{tBu}$.⁵ The N_2 can be displaced by THF (tetrahydrofuran) to form $L^{tBu}Co(THF)$. THF can be removed to give the cobalt(I) complex $L^{tBu}Co$, in which one of the two nitrogen atoms of the ligand has dissociated from the metal, and one arene ring has coordinated to the cobalt ion (Figure 3, top center).⁶ Despite the great popularity of the β -diketiminato ligands (>300 papers, >1000 compounds), this is the first observation of this binding mode for a β -diketiminato. The isomerization to this binding mode in $L^{tBu}Co$ is *reversible*, because addition of donor ligands causes the return of the standard bidentate coordination in a three-coordinate complex. Because it can readily revert to the bidentate form, we view this compound as a "masked" two-coordinate complex. We have now characterized the products $L^{tBu}Co(\text{donor})$, where donor = THF, N_2 , PPh_3 , and pyridine. We also have used $L^{tBu}Co$ as a precursor to a cobalt(II) fluoride complex, which provides a cleaner route to the hydride complex $[L^{tBu}CoH]_2$ (Figure 3, bottom).

The isomerization of diketiminato upon ligand binding raises an interesting mechanistic question: does the ligand isomerize before or after ligand binding? Kinetic studies showed that the reaction rate has a first-order dependence on $[ligand]$, and a marked dependence on the identity of the added ligand.⁶ These data establish that ligand binding precedes diketiminato isomerization.

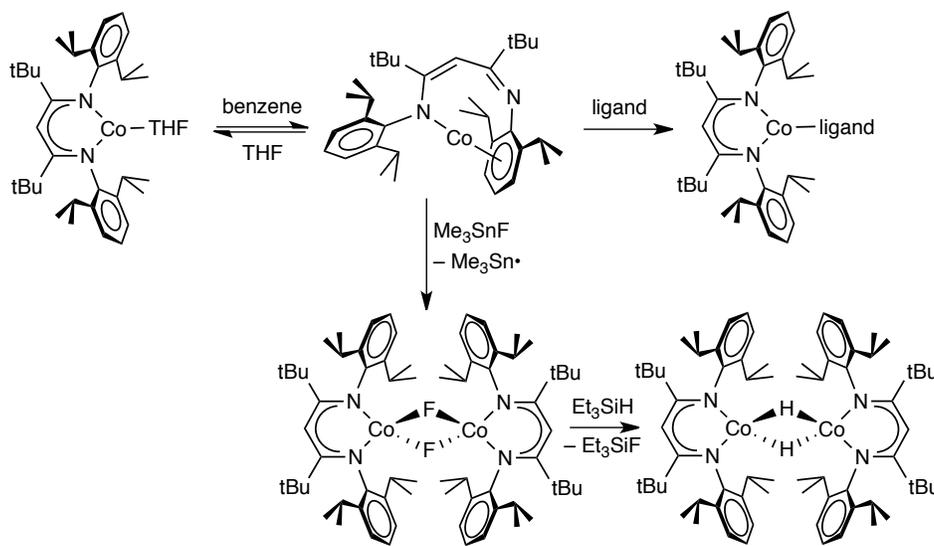


Figure 3. Formation and some reactions of $L^{tBu}Co$, in which the β -diketiminato ligand has isomerized.

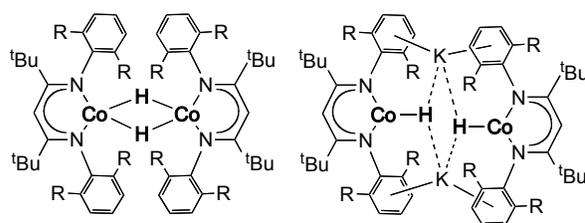


Figure 2. Cobalt(II) (left) and cobalt(I) (right) hydride complexes. R = isopropyl.

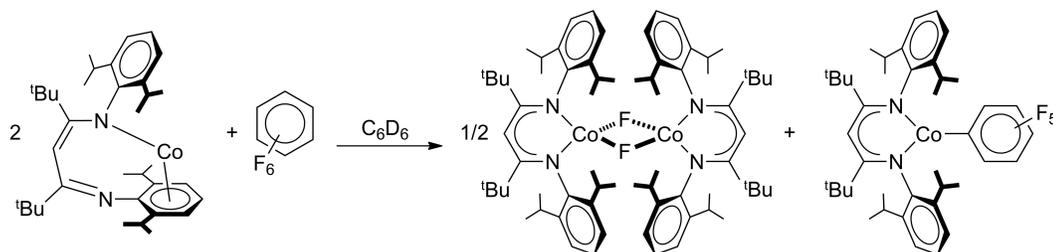


Figure 4. The C-F activation of hexafluorobenzene by $L^{tBu}Co$. This cobalt compound also activates fluorobenzene and other substituted fluoroarenes.

C-F Bond Activation through a New Mechanism. We have also observed that the cobalt(I) complex $L^{tBu}Co$ reacts cleanly with fluorinated aromatic compounds to cleave aryl C-F bonds (Figure 4). The products are the cobalt(II) fluoride complex $[L^{tBu}CoF]_2$ and the cobalt(II) aryl complex $L^{tBu}CoAr$ ($Ar =$ aryl fragment). To our knowledge is the first example of homolytic bimetallic cleavage of C-F bonds.⁷ In further work, we reported a detailed study of the mechanism of this process, using a combination of solvent effects, rate trends with different fluoroarenes, and consideration of the rate law for C-F bond activation.⁸ The rate-limiting step of the reaction is C-F oxidative addition to cobalt(I) to form an unobserved cobalt(III) hydride aryl complex, which then transfers H to another cobalt.

Alkene Isomerization Gives Unprecedented Selectivity. The isomerization of simple terminal alkenes to internal isomers with *Z* stereochemistry is rare, because the more-stable *E* isomers are typically formed. In recently submitted work, we showed (Figure 5) that cobalt(II) catalysts $L^{tBu}CoR$ catalyze the isomerization of simple 1-alkenes specifically to the 2-alkene as the less stable *Z* isomer. This selectivity for isomerization is different than catalysts of Ru and Rh, which typically give a mixture of the most stable isomers.⁹ The catalysis proceeds via an "alkyl" mechanism, with a three-coordinate cobalt(II) alkyl complex as the resting state. β -Hydride elimination and [1,2]-insertion steps are rapid ("chain walking"), as shown by isotopic labeling experiments. DFT calculations show the likely structures and energetics of intermediates, which in turn suggests that the *Z* selectivity arises from steric interactions in the transition state for β -hydride elimination. Specifically, the *Z*-alkene can "roll" in one direction in the transition state to avoid unfavorable interactions with the bulky substituents of the diketiminate ligand. These studies provide a mechanistic understanding for catalytic alkene isomerization by high-spin cobalt complexes, and demonstrate the effectiveness of steric bulk in controlling the stereoselectivity of alkene formation.

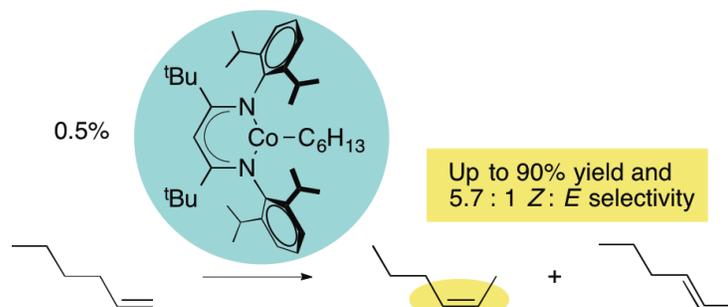


Figure 5. Catalytic alkene isomerization by $L^{tBu}Co(alkyl)$ complexes specifically gives the *Z* isomer.

Spin crossover in high spin organometallic complexes. Both of the alkene reactions described in the previous section depend on [1,2]-insertion and β -hydride elimination (β HE) steps. It is surprising that this reaction can take place in high spin iron(II)- and cobalt(II)-alkyl complexes, because the canonical description of these reactions requires empty d orbitals. Therefore, we undertook density functional theory investigations on the pathways for β HE in high-spin complexes. Specifically, we compared alkyl complexes of iron(II) and cobalt(II) supported by β -diketiminate (which undergo β HE) to tris(pyrazolyl)borate iron(II)-alkyl complexes (which are resistant to β HE). In both cases, we explored β HE transition states on the high-spin potential energy surface, and on a lower-spin surface arising from spin crossover that gives a vacant d orbital (Figure 6). Importantly, only the spin-crossover accelerated pathways matched experimental rates. The lower spin transition state has a square planar geometry that is ideal for depopulating one in-plane d orbital that can accept the electrons from the β -hydrogen. The energy of the square planar transition state is increased by steric bulk around the metal center and by increases in coordination number at iron, explaining the resistance to β HE in TpFeR.

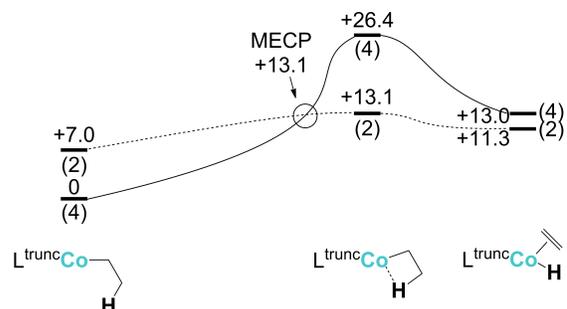


Figure 6. Spin-crossover during β HE by cobalt(II) alkyl complexes. The Minimum Energy Crossing Point (MECP) between spin state surfaces is shown. The numbers are relative energies in kcal/mol, and the numbers in parentheses are multiplicities ($2S + 1$).

Importance of mechanistic studies. It should be evident at this point that we strive to determine the details of each reaction through careful mechanistic studies. This strategy creates the fundamental knowledge necessary for future advances. All the reactions described above are excellent examples of applying the methods of detailed organometallic mechanistic studies to high-spin complexes, which is a specialty of our group. Continued studies in this area are urgently needed in order to pave the way for use of inexpensive metals for organometallic chemistry in the future.

Synthesis of novel ligand scaffolds. As part of our exploration of different β -diketimines, we have created β -diketimines in which the aryl substituents are "super-sized" by use of triarylmethyl groups in the para-positions. Unfortunately, these were not beneficial for iron and cobalt organometallic reactions. In an effort to find a use for the "super-sized" anilines, we used them to create the "super-sized" N -heterocyclic carbene ligands shown in Figure 7. Even though the substituents are far from the metal center, the palladium catalysts give a significant increase in the rate of Suzuki-Miyaura coupling relative to the smaller analogues.¹⁰ Thus, we are making additional discoveries about ligand steric effects that contribute to the organometallic community.

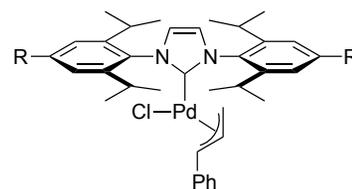


Figure 7. Super-sized NHC ligands, which give surprisingly high activity for Suzuki-Miyaura coupling.

Reversible carbon dioxide splitting. CO₂ is an abundant chemical feedstock, and fundamental research into its reduction and reactions is important. However, the very strong C=O bonds often prevent reactivity. We have found that L^{tBu}Co reacts with 1 equiv of CO₂ to split the strong C=O double bond with reduction to a carbonyl complex and a carbonate complex (Figure 8). Both products have been characterized in detail. The compound L^{tBu}Co(CO) is particularly notable, because it has an η² interaction with one aryl ring. This structure may be viewed as an intermediate stage in the "slipping" process described above, and with excess CO it goes to the previously characterized L^{tBu}Co(CO)₂, which has the usual diketiminate binding mode.

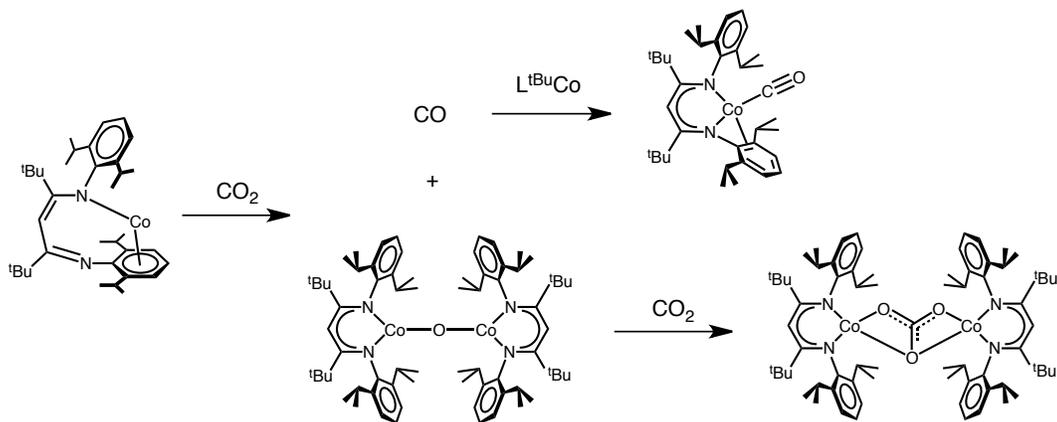


Figure 8. Carbon dioxide activation by L^{tBu}Co.

The mechanism of the transformation is likely to proceed through the unobserved dicobalt(II) oxo intermediate L^{tBu}CoOCOL^{tBu}, which can be independently synthesized. The oxo species reacts with CO₂ to give the carbonate as expected.

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Publications from this DOE grant:

- Malik A. Al-Afyouni, William W. Brennessel, Patrick L. Holland, "Stepwise CO Binding and CO₂ Activation with a Masked Two-Coordinate Cobalt(I) Complex," manuscript in preparation.
- Chi Chen, Thomas R. Dugan, William W. Brennessel, Daniel J. Weix, and Patrick L. Holland, "Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes," submitted.
- Sarina M. Bellows, Thomas R. Cundari, Patrick L. Holland, "Spin Crossover During β -Hydride Elimination in High Spin Iron(II) and Cobalt(II) Alkyl Complexes," *Organometallics* **2013**, *32*, in press.
- Thomas R. Dugan, Jonathan M. Goldberg, William W. Brennessel, Patrick L. Holland, "Low-Coordinate Cobalt Fluoride Complexes: Synthesis, Reactions, and Production from C-F Activation Reactions," *Organometallics* **2012**, *31*, 1349-1360.
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