

## Electronically Flexible Ligands for Realizing the Cluster-Surface Analogy

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Over the previous year of funding from the ACS-PRF, we have used a class of metal complexes described in the preliminary results of our original grant application to explore the coordination chemistry of dinuclear, bridging nitride complexes. We are interested in these species for their relation to adsorbed surface atoms (adatoms), which are known intermediates in multiple catalytic cycles that form the backbone of industrial chemistry. These include the Haber-Bosch synthesis of ammonia (surface nitrides), the Fischer-Tropsch synthesis of alkanes (surface carbides), and the Ostwald process for ammonia oxidation to nitric acid (surface nitrides and oxides). The importance of adatoms to these technologies has spawned decades of research on the molecular coordination chemistry of terminal oxide, nitride, and carbide ligands. Adatoms, however, commonly bridge multiple metal sites (Figure 1, top). These bridging interactions influence the hybridization and binding energy of adatoms, meaning the reactivity of surface atoms would be expected to differ from that of terminal ligands at mononuclear coordination complexes.

In order to model the chemistry occurring on the surfaces of metallic heterogeneous catalysts, molecular inorganic chemists have investigated the reactivity of low-valent, M–M bonded cluster complexes (~2-4 metal atoms) generally supported by strong-field ligands like carbonyls, hydrides, and phosphines. This “cluster-surface analogy” was rooted in an early desire to merge the control and selectivity of homogeneous catalysis with the reaction scope, robustness, and high rates of catalytically active metallic surfaces. Work in this area is limited, however, by two major hurdles, namely i) a limited conceptual link between the electronic structures of metal surfaces and those of molecular clusters, and ii) an inability to control the rearrangements of metal clusters when modelling surface restructuring. While an impressive array of catalysts have been generated using the cluster-surface analogy, new strategies are needed in order to generate molecular compounds that can both model and exploit the unique electronic and geometric changes that occur on metallic surfaces (Figure 1, bottom).

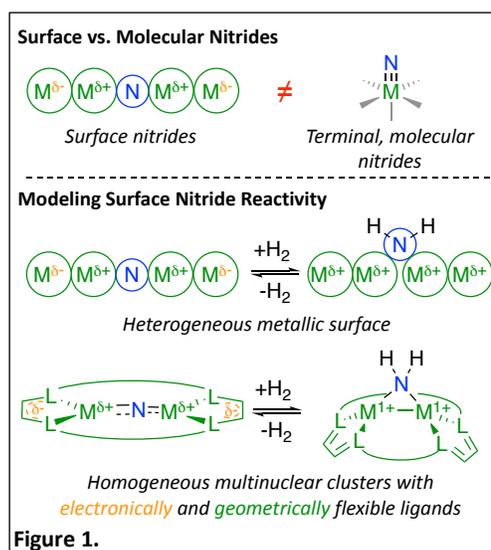


Figure 1.

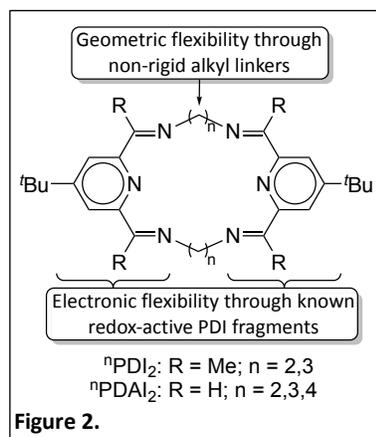


Figure 2.

To model the properties of a metallic surface, we have made use of the  ${}^n\text{PDI}_2$  and  ${}^n\text{PDAI}_2$  ligand sets (Figure 2). These dinucleating ligands exhibit electronic flexibility through their redox-active ligand fragments (pyridyldiimine, PDI), which are known to contribute significantly to the valence manifolds of 3d metal ions. By building these redox-active fragments into cluster complexes, we are generating highly delocalized valence electronic structures that approximate the characteristics of metal atom chains but include the steric and electronic control afforded by organic ligand frameworks. Importantly, the  ${}^n\text{PD(A)}_2$  series of ligands incorporate these redox-active ligand fragments within geometrically flexible macrocycles, in which the PDI units are linked with catenated methylene groups. Doing so provides not only kinetic stability to the cluster but also the controlled rearrangements needed to accommodate changes in both the hybridization of substrates (*e.g.*  $sp \rightarrow sp^3$ ) and the formation/cleavage of M–M bonds.

The  ${}^n\text{PDI}_2$  class of ligands was described in the preliminary results of our original grant proposal, but we have developed the  ${}^n\text{PDAI}_2$  ligand set with the aid of ACS-PRF funding. The  ${}^n\text{PDAI}_2$  ligand class is notable in that the use of aldehyde groups allow for the formation of the larger  ${}^4\text{PDAI}_2$ , a ring-size that is unavailable to the analogous  ${}^n\text{PDI}_2$  ligands. The  $[\text{}^n\text{PD(A)}_2]\text{MX}_2$  macrocyclic complexes [ $M = \text{Sr, Ba}$ ;  $X = \text{CF}_3\text{SO}_3$  (OTf)] serve as viable synthons for an array of dinuclear transition metal systems. The size of the macrocycle favors the formation of homodinuclear cluster complexes, as evidenced by the wide variety of complexes that we have isolated to date with this system (>100 crystal structures on V–Cu).

With the aid of ACS-PRF funding, we have found that  ${}^n\text{PDI}_2$  is able to support the first example of a putative dicobalt bridging nitride ( $[\text{Co}_2\text{N}]^{3+}$ , Figure 3). This conclusion was evidenced by the solution-phase thermolysis of a  $\text{Co}_2(\mu\text{-N}_3)$  complex in the presence of excess  $\text{PMe}_3$  to yield a  $\text{Co}_2(\mu\text{-NH}_2)$  product ( $[\text{Co}_2\text{NH}_2]^{3+}$ ). Isotopic labelling

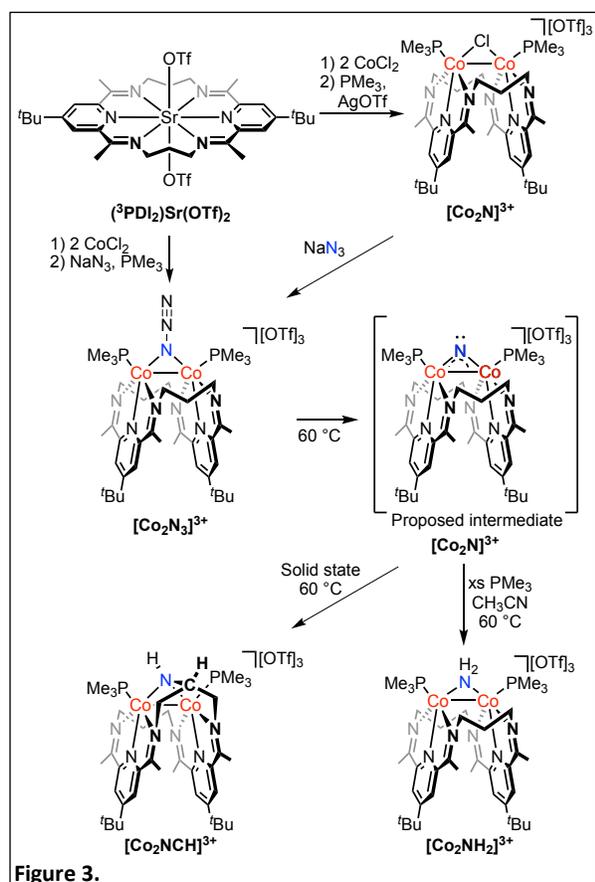


Figure 3.

Preliminary investigations into the reactivity of  $[\text{Fe}_2\text{N}]^+$  have revealed the ability of this nitride to perform intermolecular insertion chemistry with silanes. Treatment of  $[\text{Fe}_2\text{N}]^+$  with 1.0 eq. of either  $\text{PhSiH}_3$  or  $\text{Ph}_2\text{SiH}_2$  at elevated temperatures generates the  $\mu$ -silylamide complexes  $[\text{Fe}_2\text{N}(\text{H})\text{SiR}_3]^+$ , which exhibits a folded ligand geometry. Initial mechanistic studies indicate that either a rapid radical rebound following initial HAT or the direct insertion of the nitride into the E–H bond is occurring. Reactions of  $[\text{Fe}_2\text{N}]^+$  with tertiary silanes ( $\text{Ph}_3\text{SiH}$ ,  $\text{Et}_3\text{SiH}$ ) afford the parent  $\mu$ -amide complex  $[\text{Fe}_2\text{NH}_2]^+$ , with no indication of Si–H bond insertion. Further work is underway to elucidate the salient features of this reaction chemistry and apply it toward the activation of other strong E–H bonds, including those in dihydrogen, boranes, and alkanes.

Overall, funding from the ACS-PRF has impacted my career by providing support to what has turned into a central research project in my group. The results from our work over the previous year have provided a compelling view of how this chemistry will be impactful to the field over time. These examples are useful for attracting new, talented graduate students to the group and in making a compelling case for additional funding to support this research from other extramural funding agencies.

The students who have participated in this project have gained valuable skills in the synthesis and characterization of air-sensitive coordination complexes. The techniques they have used include Schlenk line and glovebox techniques for handling air-sensitive compounds as well as a wide range of physical methods for characterizing these compounds, including variable temperature NMR, IR, UV-vis and Moessbauer spectroscopies, SQUID magnetometry, and cyclic voltammetry. Students have also learned how to perform the advanced computational techniques needed for modelling the complex electronic structures of these highly correlated systems (DFT, TD-DFT, CASSCF, MRCI). Finally, the connection between our chemistry and the chemistry that is known to occur on metallic surfaces has induced the students on this project to attain a broader view of the field than what they would experience in researching a project with a focus solely on molecular systems.

experiments revealed that N–H bond formation occurs via HAT between a transient  $\mu$ -nitride and the ligand's alkyl linkers. This conclusion was further supported by solid-state thermolysis of  $\text{Co}_2(\mu\text{-N}_3)$ , which resulted in the quantitative formation of a C–H insertion product ( $[\text{Co}_2\text{NCH}]^{3+}$ ). The C–H insertion product is not observed during the solution-phase thermolysis, suggesting that the constrained movement of the ligand within the crystalline lattice alters the reactivity profile of the transient nitride/imide.

Related investigation into a series of diiron complexes allowed for the isolation of the diiron(III)  $\mu$ -nitride  $[(^3\text{PDI}_2)\text{Fe}(\mu\text{-N})(\text{PMe}_3)_2][\text{OTf}]$  ( $[\text{Fe}_2\text{N}]^+$ ; the  $(^3\text{PDI}_2)\text{Fe}_2(\mu\text{-N})$  core of this cation is shown in Figure 4), which exhibits an unfolded ligand framework and a linear  $\mu\text{-N}$  geometry ( $\angle\text{Fe-N-Fe} = 177.1(3)^\circ$ ). This diamagnetic species represents an extremely rare example of a low-valent  $\text{Fe}_2\text{-}\mu\text{-nitride}$  (formally  $\text{Fe}^{\text{II}}_2$ ) and notably includes the nitride in the basal plane of a pseudo-tetragonal geometry, similar to the surface species of the Mittasch catalyst. The crystallographically determined Fe–( $\mu\text{-N}$ ) bond lengths of ca. 1.68 Å are suggestive of a bond order between typical Fe–N single and double bonds. The PDI moieties in the macrocyclic ligands were each found to be mono-reduced according to the imine C=N and C–C bond lengths in X-ray structures, highlighting the redox-active nature of the ligand. Computational studies reveal a valence manifold that is densely packed in terms of energy separation and highly delocalized in orbital character.

