

Secondary Coordination Sphere Meets Secondary Bonding:

Novel Ligand Design & Catalysis

Introduction This project concerns the careful design and synthesis of ligands and metal complexes that possess appropriately located functionalities with strong dipoles (C=O, P=O, and S=O units) to create a secondary coordination sphere that can engage in secondary bonding with substrates (Figure 1, bottom). Previously reported ligands with secondary coordination sphere functionalities have used hydrogen bonding as a directing tool (Figure 1, upper).

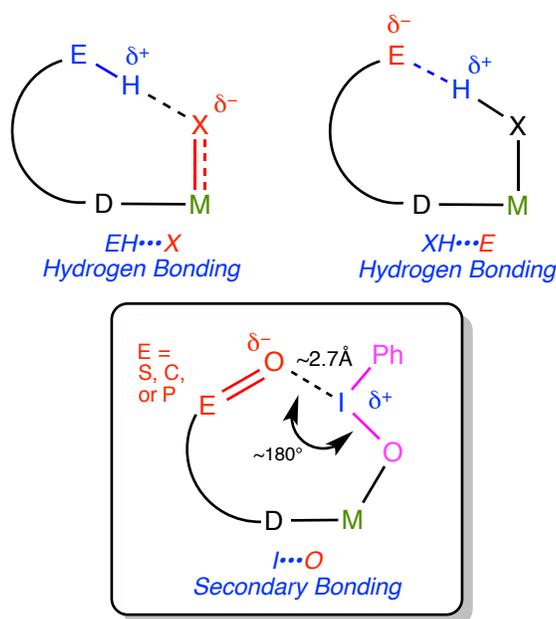


Figure 1.

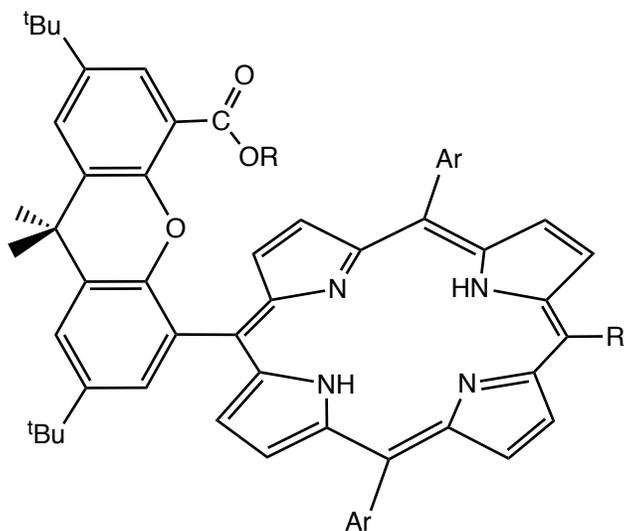
We set out to examine hypervalent iodine reagents such as iodosylbenzene that are insoluble in common organic media due to their solid state aggregation by secondary bonding ($\text{I} \cdots \text{O}$ interactions). The outcomes and impacts of the proposed research include the discovery of the fundamental design principles for introducing secondary bonding into the secondary coordination sphere that could lead to advances in the rational synthesis of new catalysts that utilize hypervalent main group species. There are three specific main aims for this proposal.

i. Prepare ligands for potential use for secondary bonding in the secondary coordination sphere

ii. Synthesize and characterize new complexes in secondary bonding in the secondary coordination sphere

iii. Bind hypervalent iodine reagents to complexes

Year 2 Progress We have made further progress on the first two aims above. In the previous reporting period we focused on Nocera-type "Hangman" porphyrin complexes that ligands that dangle acid-base functional groups in the secondary coordination sphere for hydrogen bonding (Scheme 1).

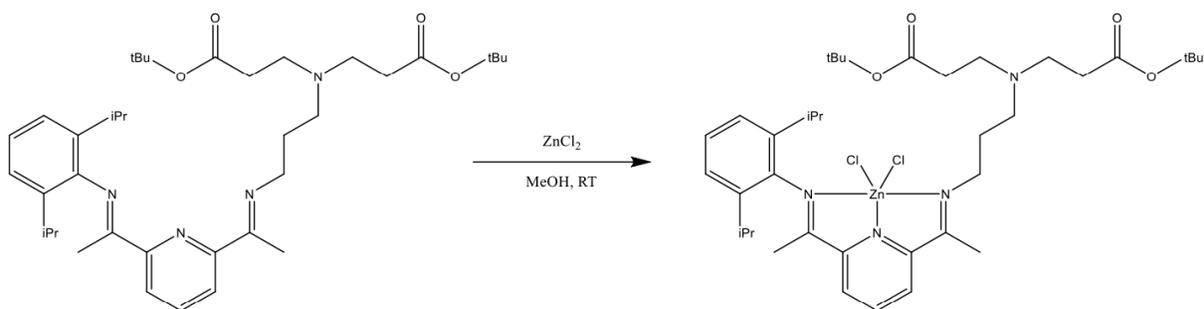


Scheme 1. Examples of hangman ligands.

We followed the protocols developed by the Nocera group for synthesis of these types of porphyrins (Scheme 2, Ar = mesityl) and prepared a zinc complexes. The reaction of these Zn-porphyrin complexes with iodosylbenzene (PhI=O) was systematically investigated in order to

isolate an iodosylbenzene-Zn-porphyrin complex. Unfortunately, after many attempts, we did not find conditions that allowed isolating such a species.

We thus changed our strategy to a new ligand platform. Di-imido-pyridine (DPI) type ligands bearing two sterically demanding aryl group have become a large and important class of ancillary ligands in organometallic chemistry and catalysis. This ligand platform is very versatile and many modification are possible to suit the users intended purpose. Using published routes to asymmetric PDI-type ligands we prepared the ligand (DPI') shown in Scheme 2 and used it to generate the corresponding ZnCl_2 complex. The design of this ligand was based on estimates provided from molecular modeling that showed the remote ester functionalities ($\text{C}=\text{O}$ bonds of ester groups in particular) should be able to reposition themselves for coordination to the iodine center of an *O*-bound iodosylbenzene.



Scheme 2.

The structure of the DPI'-ZnCl₂ complex was successfully determined from a single crystal X-ray analysis (Figure 1).

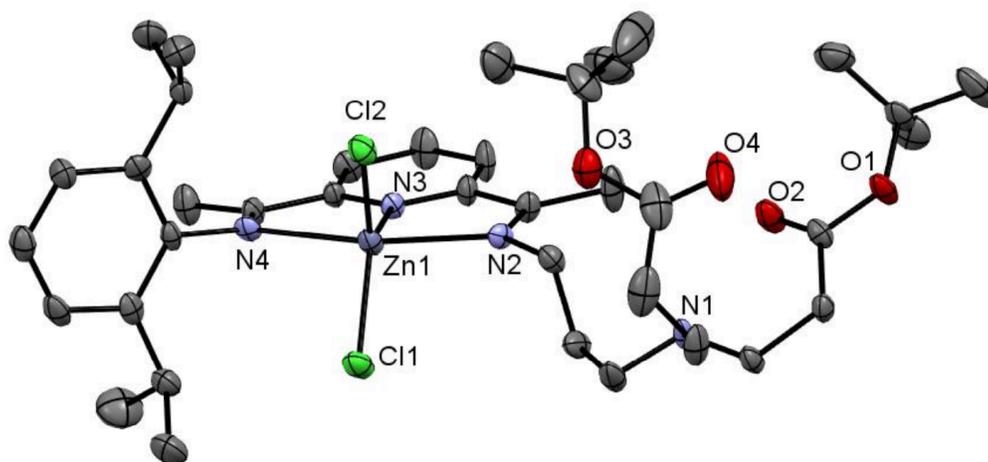


Figure 1. Structure of DPI'-ZnCl₂ complex.

We have also determined a structure of related [DPI'-CoCl₂][HCoCl₄] complex, Figure 2. In this case the reaction product is more complicated, and it is believed that HCl released during the reaction has led to protonation of one of the amine linkers and formation of the CoCl₄ anion.

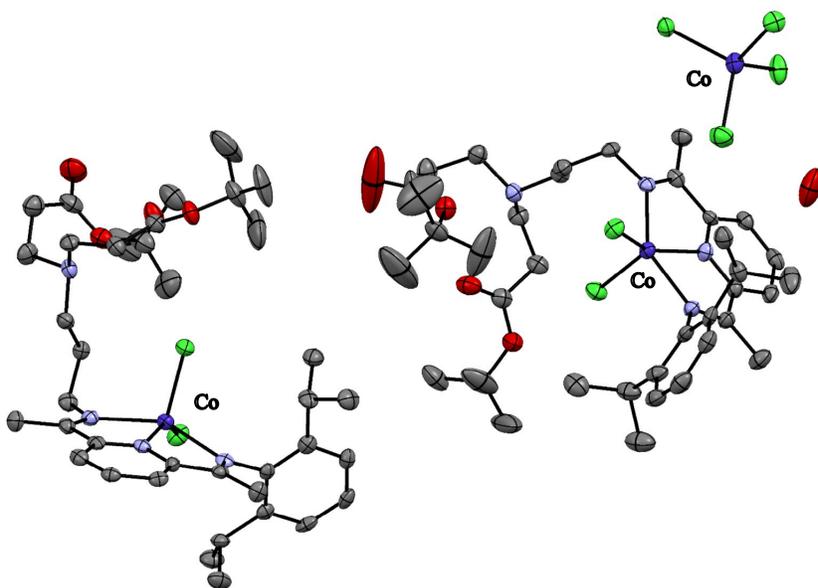


Figure 2. Structure of [DPI'-CoCl₂][HCoCl₄] complex (and water of crystallization).

During our studies we have also prepared a general precures to other potential DPI' type ligand Zn-complexes, as shown in Figure 3. The dangling hydroxyl group should allow us to attach other types of secondary coordination sphere elements.

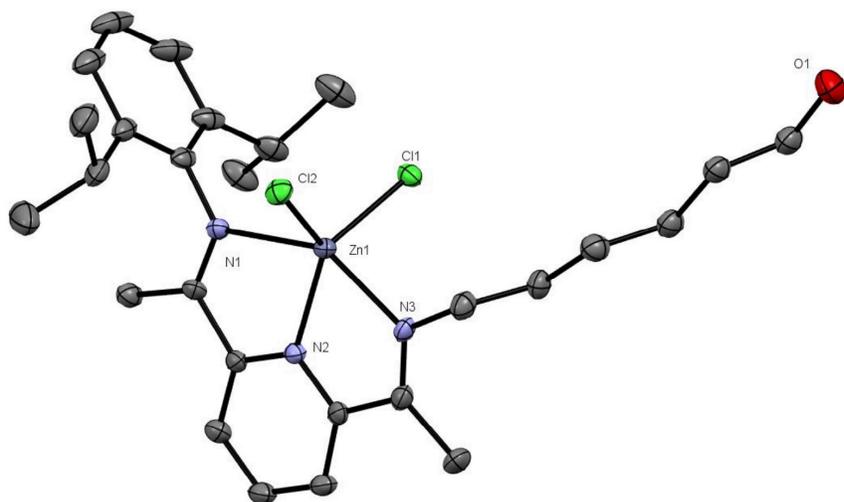


Figure 2. Structure of DPI''-ZnCl₂ complex.

The study of the reactions of these complexes with hypervalent iodine reagents such as iodosylbenzene and PhINTs are planned to continue on past the funding period.