



# Graduate Students Seminar

Department of Chemistry

**Thursday, June 29<sup>th</sup>, 2023**

**Time 14:00**

**Bldg. 43 Room 015**

## Alex Blahman

Under the supervision of Prof. Sebastian Kozuch

### **Inversed Bonding-Backbonding: Metal to Ligand $\sigma$ and Ligand to Metal $\pi$ Dative Interactions**

While many bonding patterns are known and studied, an inverse bonding-backbonding (IBBB) with a metal to ligand  $\sigma$  donation and a ligand to metal  $\pi$  backdonation (a " $\sigma$ Z- $\pi$ L" interaction) is unheard of.

This work consisted innumerable attempts of constructing in-silico potential candidates and testing them via quantum chemistry methods coupled with self-written Python – data analysis scripts. Due to the complexity of the required electronic behavior, most of those attempts did not show the desired IBBB pattern within stable transition-metal complexes. We believe that IBBB involving d orbitals in transition metals is impossible, but a  $\pi$  charge transfer to a post-transition metal empty p orbital can do the trick.

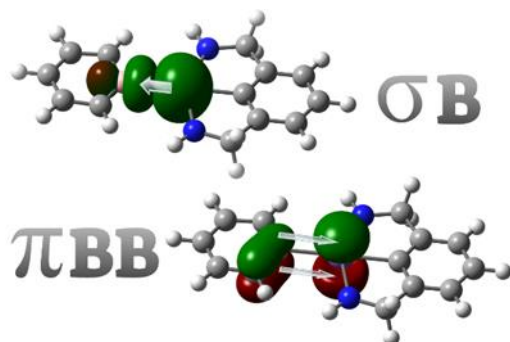
Herein, we show one such case consisting of:

- 1) A triel-benzene ligand (e.g. borabenzene), where the triel in the ring has an empty lone pair that can act as a  $\sigma$  acceptor, whereas the aromatic electronic system serves as a  $\pi$  donor.
- 2) A pnictogen-X3 pincer complex (e.g. Bi with an NCN or OCO pincer ligand), whose HOMO, a lone pair forced to be in the molecular plane, is a  $\sigma$  donor, and the LUMO is a p AO on the pnictogen, working as a  $\pi$  acceptor.



The findings are supported by calculating orbital interactions using NBO (Natural Bonding Orbitals) analysis, testing for charge-transfer via DDM (Density Difference Maps) and relaxed force constant computation of Bi-B (and other pnictogen-triell pairs).

This kind of interaction is, as far as we know, the first of its kind, and helps fill the table of all the possible combinations of ligand/complexes bond types.



A. Blahman, S. Kozuch, *Isr. J. Chem.* 2022, e202200072