



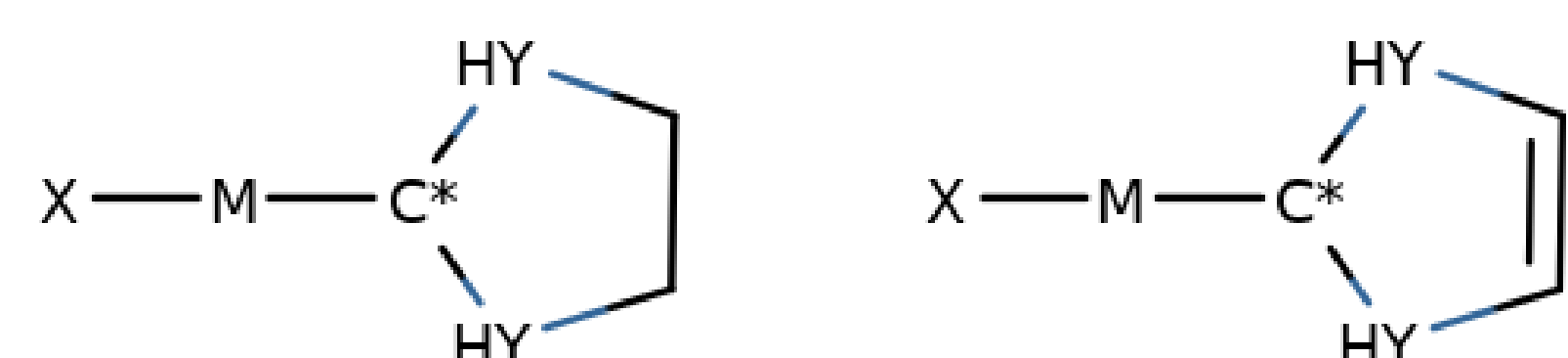
The Role of Electrical Interaction and Charge Transfer in Coinage Metal-Carbene Complexes

Bryan E. Walker and Eric D. Glendening

Department of Chemistry and Physics, Indiana State University, Terre Haute, IN 47809

Introduction

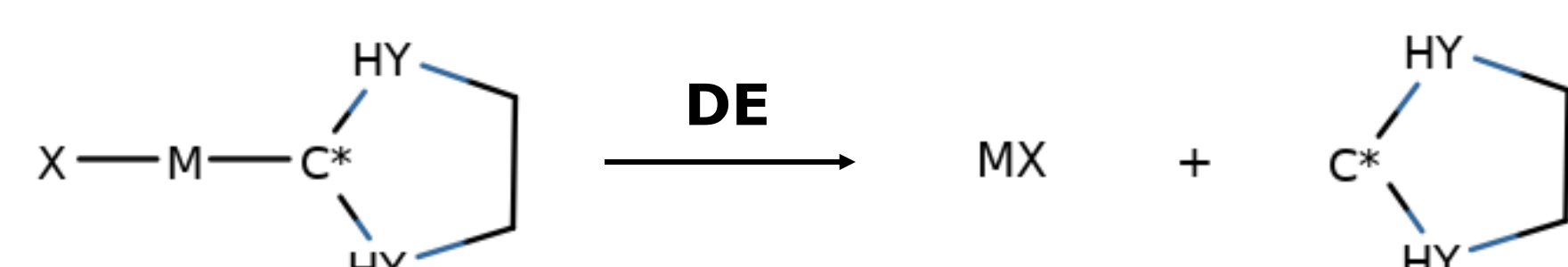
Carbenes are formally hypovalent organic compounds that are electron deficient at one carbon atom. Carbenes bind strongly, by 40-80 kcal/mol, to metal atoms to form organometallic complexes. We use computational chemistry methods with natural bond orbital (NBO) analysis to examine the influence of electrical (electrostatic and polarization) interactions and charge transfer on the stabilities of metal-carbene complexes. We focus attention on heterocyclic carbenes of the following **saturated** and **unsaturated** forms



where C* is the carbene center and

M (metal atom) = **Cu, Ag, Au**;
X (halide) = **Cl, Br**;
Y (heteroatom) = **N, P, As**.

Density functions theory calculations were performed using the B3LYP hybrid density functional and the cc-pVTZ triple-zeta basis sets, with effective core potentials for Ag and Au. Dissociation energies (**DE**) were evaluated for the fragmentation of the complexes into metal halide and free carbene, e.g.



All geometries were optimized using Gaussian-16 Rev C.01 and characterized by frequency calculations. No zero-point energy corrections were applied to the DEs.

Natural Energy Decomposition Analysis

The strength of the metal-carbene interaction was assessed using the natural energy decomposition analysis (NEDA) of the NBO program. NEDA partitions the interaction energy

$$\Delta E_{\text{int}} = \text{EL} + \text{CT} + \text{CORE}$$

into electrical (EL), charge transfer (CT), and core repulsion (CORE) components. The latter is principally associated with the Pauli repulsions that prevent atoms from penetrating each other. EL arises from the classical Coulombic interactions (both electrostatic and polarization) of the fragments, and CT arises from quantum mechanical electron sharing.

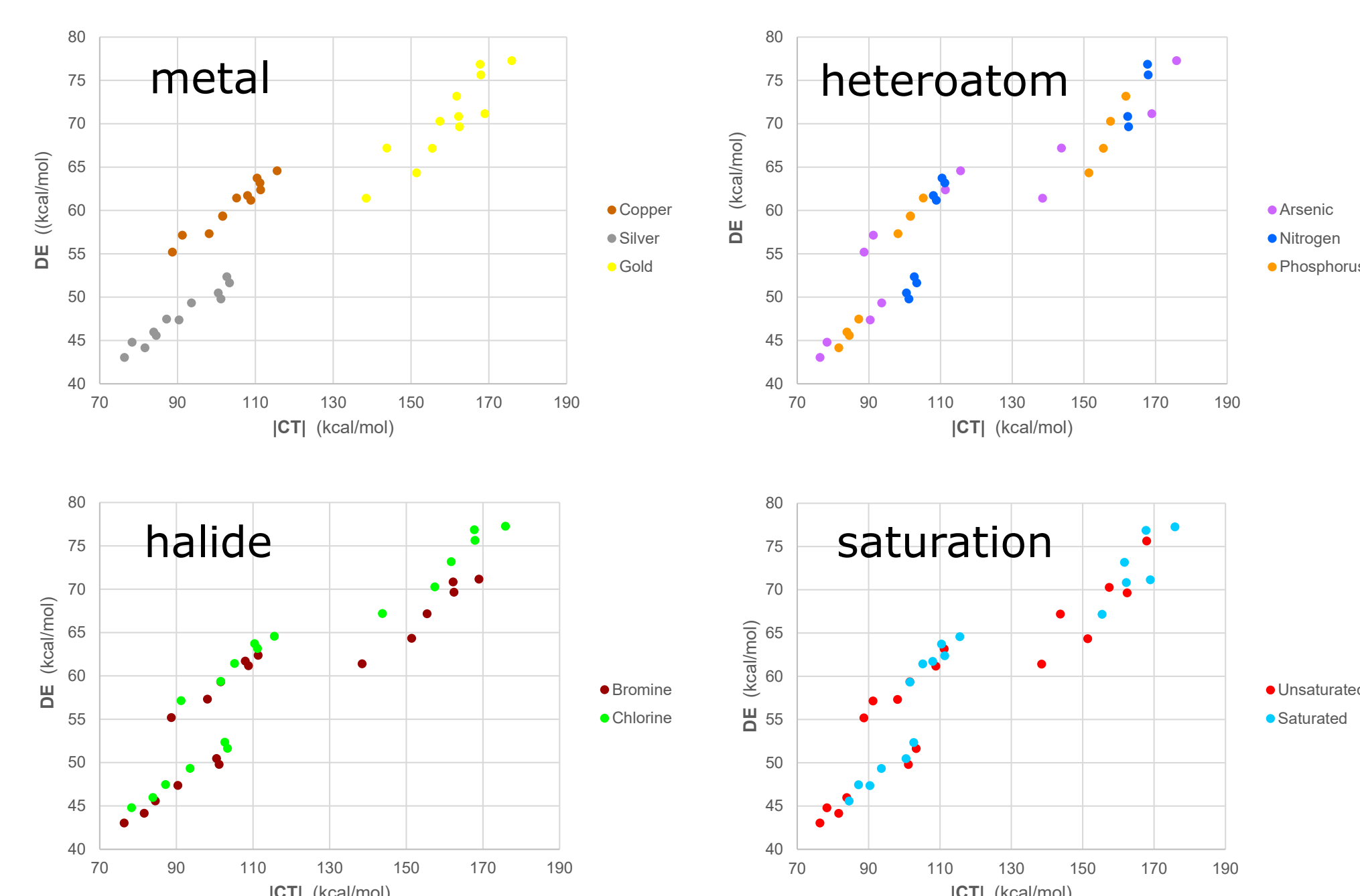


electrical interaction

charge transfer

Charge Transfer

The following plots show how DE depends on CT.

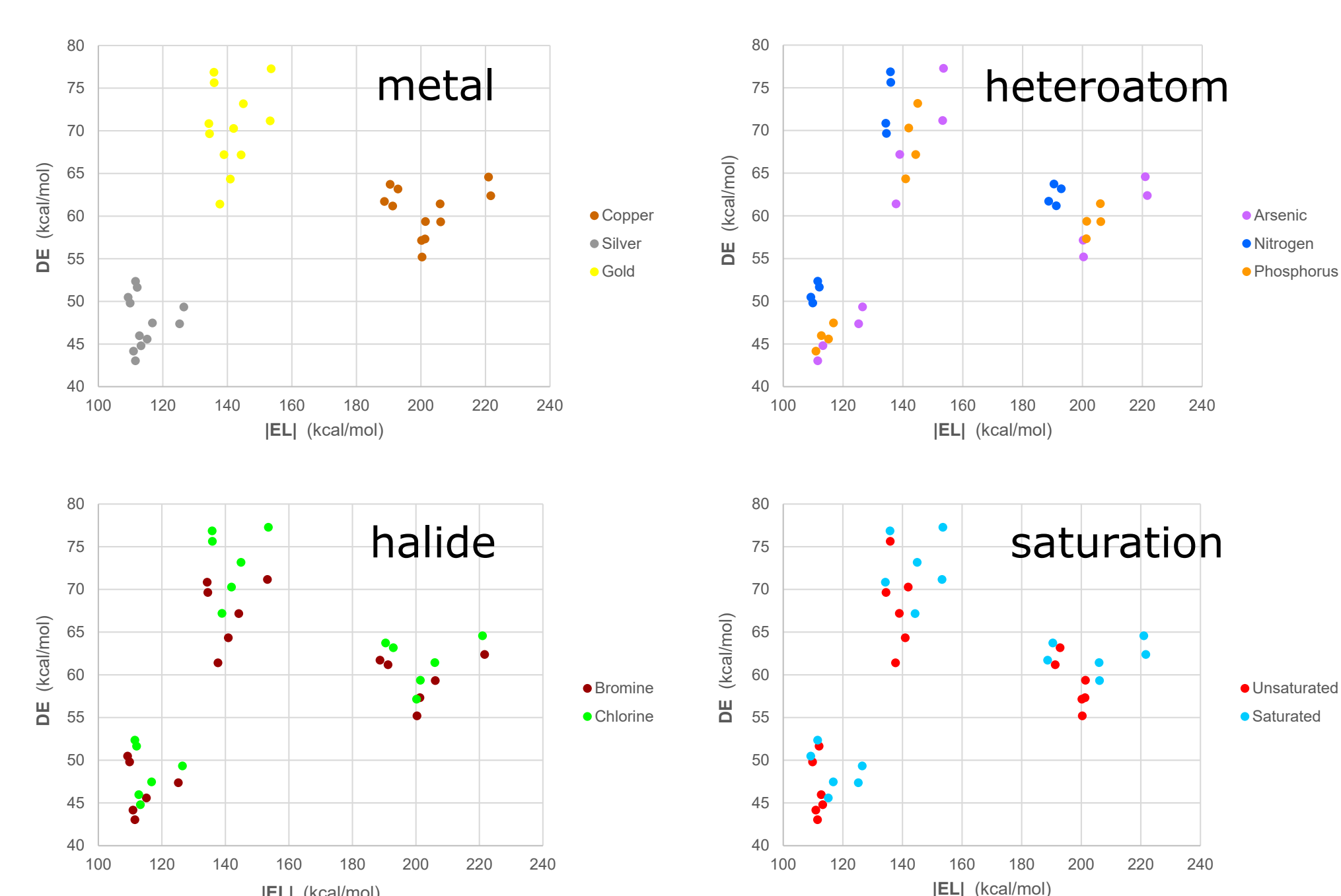


DEs are strongest for the Au complexes and weakest for the Ag complexes. We find that DE is fairly well correlated with CT, stronger CT resulting in stronger binding of the carbene to the metal center. The extra strong DEs for the Au complexes is likely a consequence of the relativistic contraction of this metal atom.

CT tends to be stronger for N heteroatoms than for P, and for the Cl halide than for Br. The dependence on the As heteroatom and on ring saturation is more challenging to characterize.

Electrical Interaction

The following plots show how DE depends on EL.

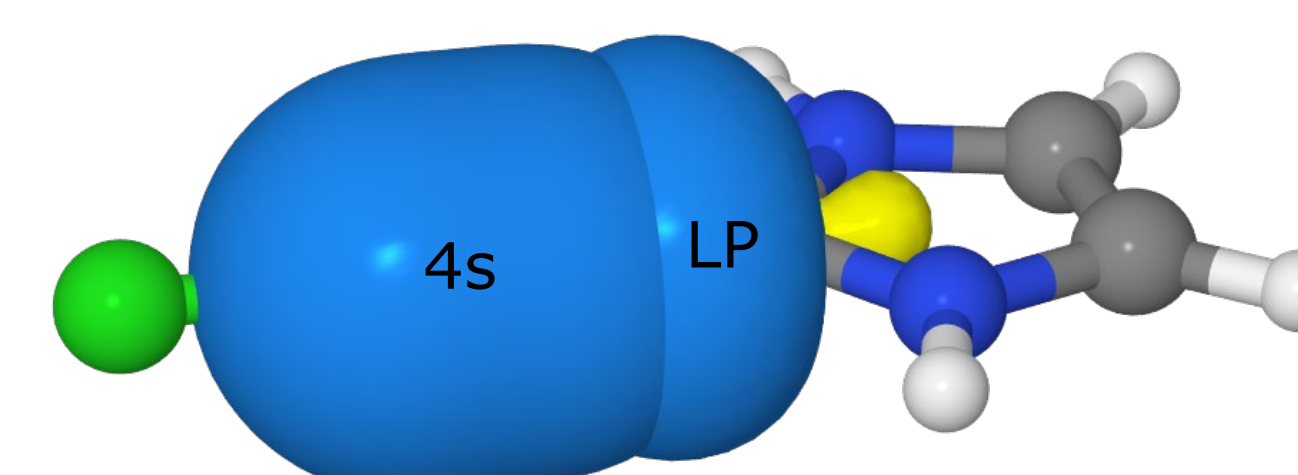


DEs are not particularly well correlated with EL.

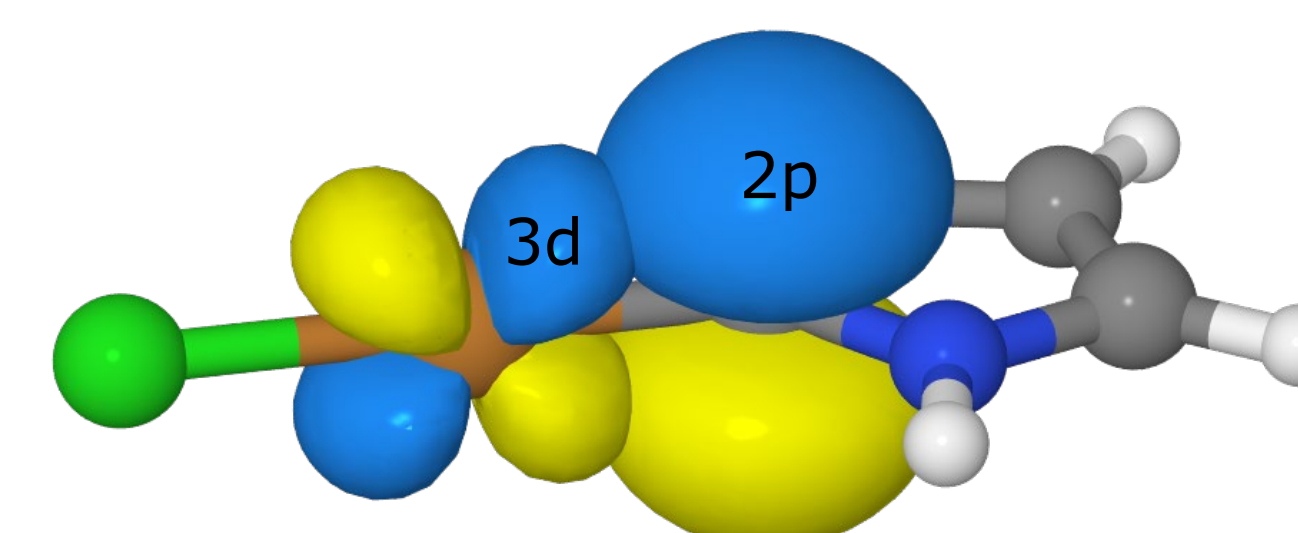
EL is considerably stronger than CT in the Cu complexes, whereas EL and CT are more nearly equal for Ag and Au. EL generally increases across the series $N < P < As$, likely due to the increasing polarizability of the heteroatom (and, hence, stronger induced dipole of the carbene ligand).

Electron Delocalization

CT arises from the donor-acceptor interactions that delocalize electrons between the carbene and metal center. The following are examples of the interactions that take place in the unsaturated Cu-carbene complex ($X=Cl$; $Y=N$). The leading sigma-type interaction transfers 0.50 electrons from a lone pair on the carbene center into the formally empty Cu 4s orbital. The interaction stabilized the complex by over 200 kcal/mol.



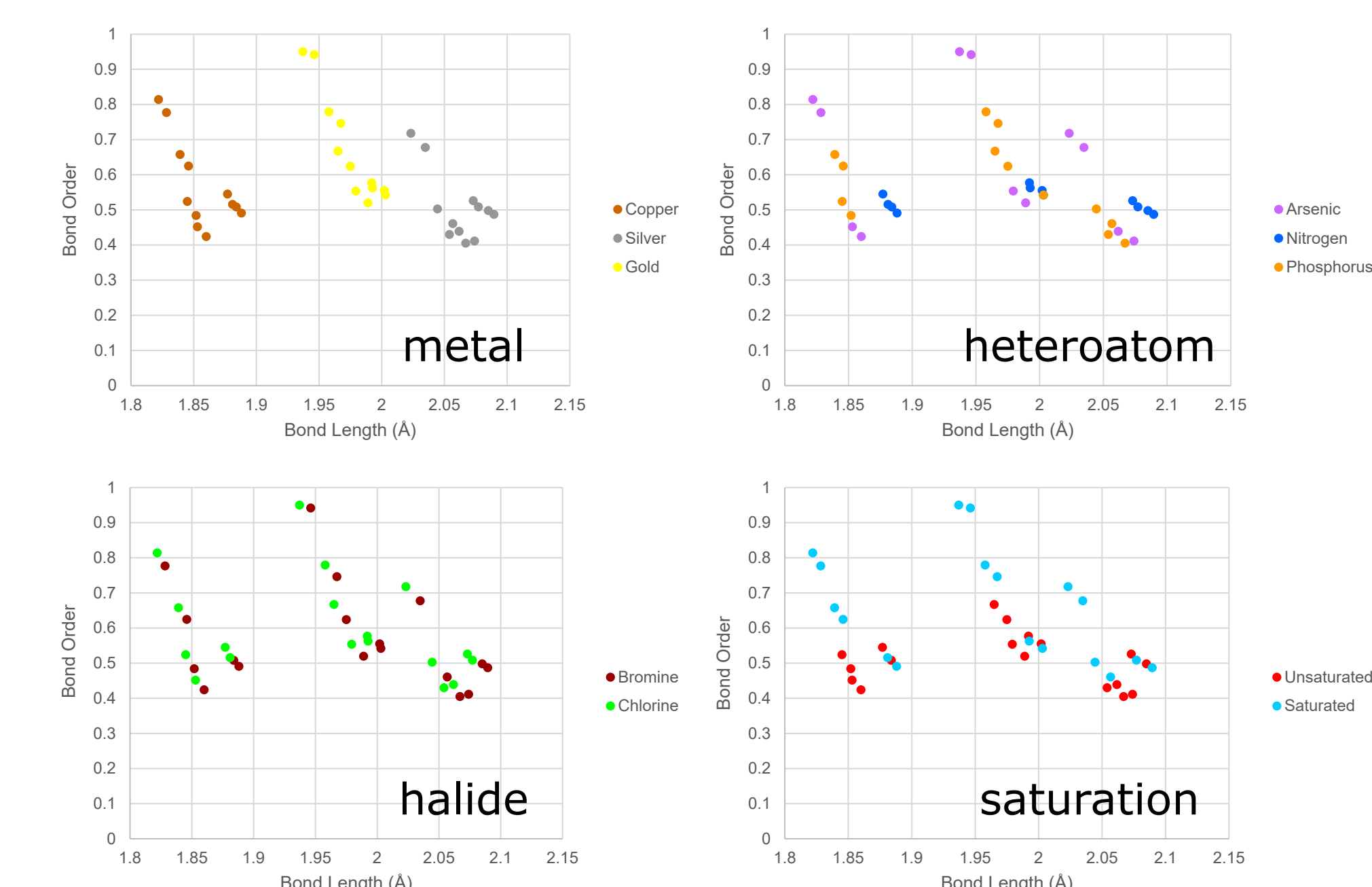
There is also a weaker pi-type interaction (only stabilizing by 23 kcal/mol) that transfers about 0.05 electrons from a Cu 3d orbital into a formally empty 2p orbital on the carbene center.



This interaction is weaker, in part, because the orbital overlap is smaller.

Bond Length/Bond Order Correlation

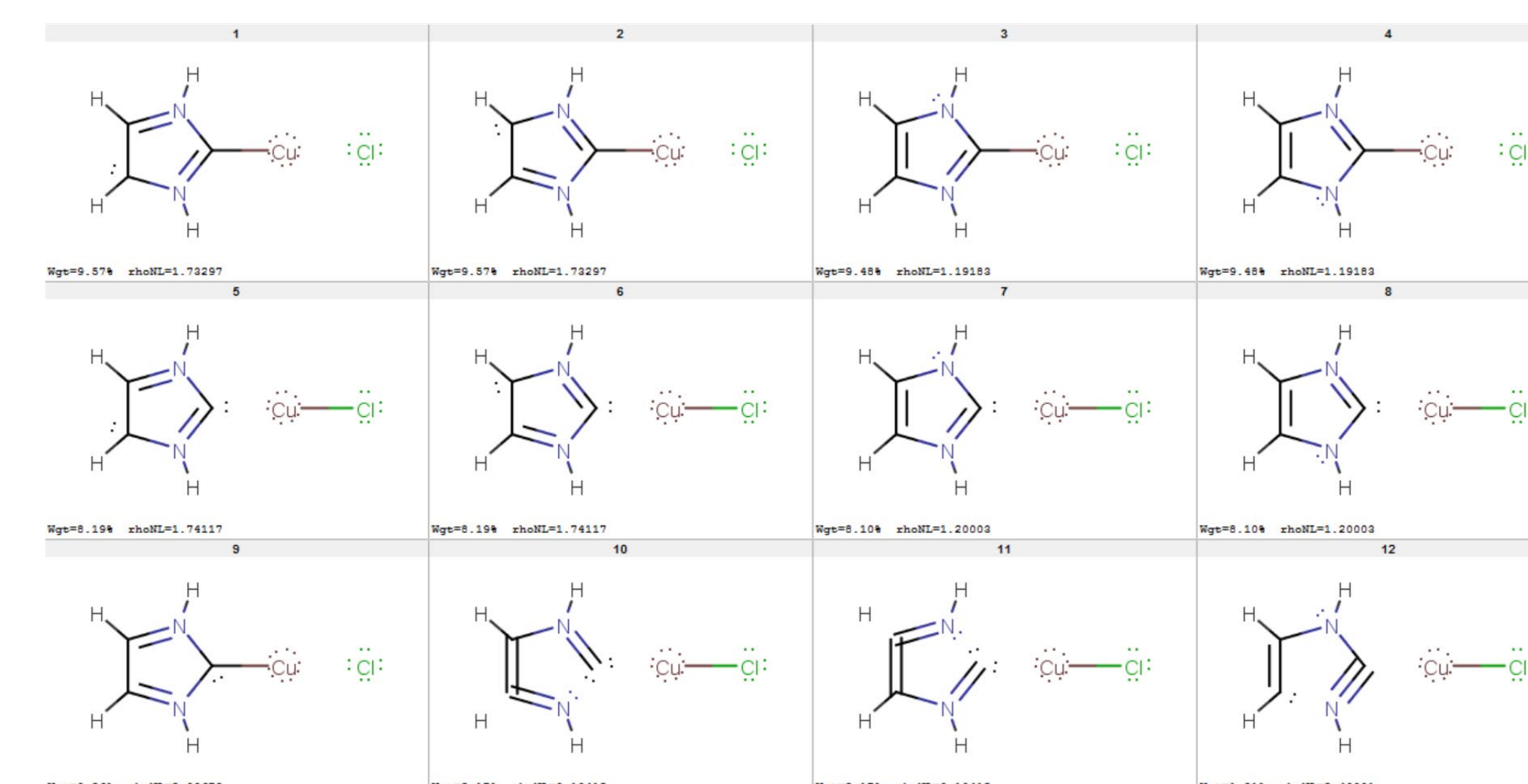
We used the natural resonance theory (NRT) method of the NBO program to examine the correlation between M-C bond lengths and bond order. Bond orders were determined from the optimized NRT expansions as shown on the right.



Bond lengths are fairly well correlated with bond order for each metal atom, with shorter bond lengths corresponding to higher bond order. The largest bond orders were observed in the Au-C bonds (particularly with As heteroatoms). Bond orders tend to be smaller for unsaturated heterocycles than for saturated.

Resonance and Bond Orders

The following is the optimized resonance hybrid for one of the Cu-carbene complexes. Analysis reveals a highly delocalized heterocycle and metal center, because many structures contribute to the hybrid, with no resonance structure contributing more than 10%.



The "natural" bond order for a pair of atoms is determined by resonance averaging the integer number of bonds between the atoms across the resonance structures of this hybrid. The bond orders for Cu-C and Cu-Cl in this case are 0.545 and 0.477, respectively, revealing that the Cu center participates in only about one bond on average. In other words, the Cu center is monovalent in this carbene complex.

Conclusions

1. Dissociation energies for the coinage metal-carbene complexes are more strongly correlated with charge transfer than with electrostatic and polarization effects.
2. Charge transfer in the carbene complexes principally arises from sigma-type donor-acceptor interactions in which a carbon lone pair donates electron density into an empty valence orbital of the metal center. Pi-type back-bonding interactions between a d-type orbital of the metal and the carbene 2p orbital are also important but are weaker than the sigma-type interactions.
3. Metal-carbene interactions are stronger for Au than for either Cu or Ag, probably due to the relativistic contraction of the Au atom. Interactions also tend to be stronger for Cl halides (rather than Br) and N heteroatoms (rather than P). As heteroatoms can give strong interactions, perhaps due to the high polarizability of the As atom. Ring saturation appears to have limited influence on the interactions.

Acknowledgements

The authors gratefully acknowledge the financial support of the ISU Department of Chemistry and Physics, the ISU Office of Academic Affairs, and College of Arts and Sciences, and the Center for Student Research and Creativity.