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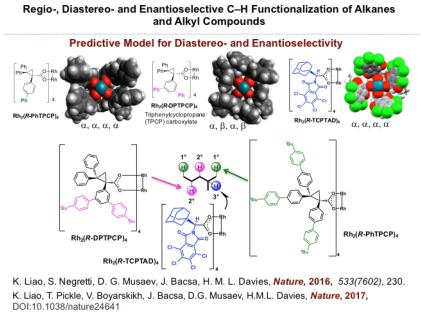
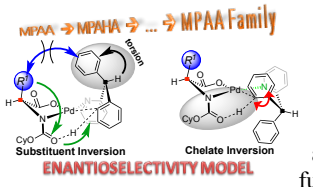
Atomistic/molecular level understanding of catalysis is essential for designing new and more efficient catalysts for particular tasks. This cannot be achieved by experimental techniques alone: the fast-emerging field of computational catalysis significantly complements experiments by providing intricate details. Musaev-group uses state-of-the-art computational techniques *in a truly collaborative way with our experimental colleagues,* as well as develops new theoretical/method approaches, to advance understanding of mechanisms, governing factors, intimate roles of each reaction components of vital processes: including, but not limited to: (**A**) Light-driven robust multi-electron transfer catalysts for water oxidation **(***with C. Hill and T. Lian*); (**B**) Stereoselective C-H functionalization (*with members of the CCI-NSF CCHF center*), (**C**) Advancement of theoretical methods for the treatment of interfacial electron transfer.

CCHF Research Engagement-general summary of the collaborative research. For example, the acquired atomistic-level knowledge on the Stereoselective C-H functionalization is vital for: (a) improvement of existing methodologies, (b) development of novel strategies, (c) design of general predictive tools, and (c) design of more stable (with a high TONs), faster and highly selective catalysts (including earth-abundant 1st-row transition metals), of stereoselective C-H bond functionalization. In such, we have initiated active collaborative research portfolio with dozens projects in the frontier of chemical sciences. Here are only a few of them:

I. Development new synthetic methodologies for catalyst controlled selective C–H functionalization (*with Huw M. L. Davies (Emory)***).** We, in collaboration with Davies-group, intend to develop catalyst controlled strategies for the selective functionalization of traditionally "unactivated" C-H bonds (see Scheme 1). The Davies group pioneered the development of more hydrocarbon soluble dirhodium tetracarboxylates catalysts, such as Rh-TBSP, Rh-DOSP, and others, which became the established catalyst for these types of reactions. Here we collaborate to elucidate factors impacting reactivity and selectivity of these classes of Dirhodium tetracarboxylates by utilizing computation and experimental approaches.



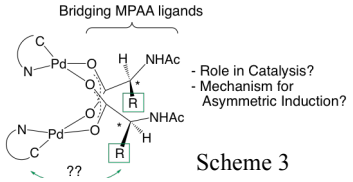
Scheme 1



Scheme 2.

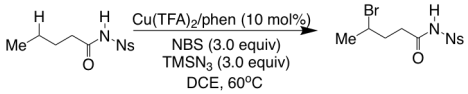
II. Predictive model development for asymmetric induction and ligand design. We, in collaboration *with J.Q. Yu (Scripps)*, have developed a novel predictive model for asymmetric induction from the viewpoint of rationalizing chiral, bidentate ligands for C-H activation via metal insertion. Currently, we are applying it to explain the observed trends in enantioselectivity of the Pd(II)-catalyzed asymmetric C-H activation, and to design novel, highly selective chiral ligands for C-H functionalization.

III. We are expanding our novel predictive model to bimetallic catalysts. Currently, we are collaborating with *Lewis-group (U. Chicago)* to determine the exact role of the Pd-dimer species on the enantioselectivity of the Pd-catalyzed C-H functionalization and asymmetric induction mechanism (Scheme 3).

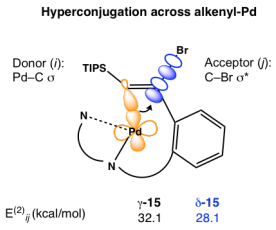


Scheme 3

IV. Mechanism of Copper catalyzed Bromination of distal C(sp^3)-H bond (*with J. Q. Yu (Scripps)***).** Efficient introduction of a halogen atom into a C(sp^3)-H bond has a profound influence in synthetic organic chemistry. We are working together with Yu-group to elucidate mechanism of the newly reported Cu^{II}/phenanthroline-catalyzed bromination of γ-C-H bonds of aliphatic amides and δ-C-H bonds of alkyl amines (Scheme 4). Our study is expected to provide insights into the nature of: (1) active species, (2) oxidants, as well as (3) origin of regioselectivity of the reaction.



Scheme 4.



Scheme 5

V. Understanding C-H Functionalization site-selectivity in a directed alkynylation (*with R. Sarpong (Berkeley)***)** We are expanding the well-established directing group strategy to the complex molecules with inherent *N,N*-bidentate chelating groups to perform selective C(sp^2)–H alkylynation. Currently, we found that C-H alkynylation by TIPS-alkyne-*bromide* proceeds via a redox neutral migratory insertion pathway. We uncovered novel β-Pd effect (see Scheme 5) that facilitates the alkyne product formation. Currently, we are expending this new phenomena to other transition metal catalyzed C-H alkynation on similar substrates.