

Abstract

The thesis entitled “**Palladium(II) and Ligand-bridged Palladium(II)/Tin(IV) Catalysts in Suzuki Coupling and Friedel-Crafts Alkylation & Nucleophilicity Parameter of Tin(IV) Reagents**” is primarily an effort to understand the stereo-electronic features in a metal-ligand core that dictate the reactivity and selectivity of a catalyst in electrophilic and nucleophilic reactions; examples being Friedel-Crafts alkylation (FC) and Suzuki coupling (SC). Since philicity of a reagent profoundly guides reactivity and selectivity, a computational study on nucleophilicity of organometallic reagents is carried out. The results are described in four chapters; important results are highlighted below.

Chapter A.2 describes synthetic studies on SC between ArB(OH)_2 and $\text{Ar}'\text{-X}$ using $[\text{Pd(II)}]$ pre-catalysts namely Pd(bipy)Cl_2 **1**, Pd(dppap)Cl_2 **2**, $\text{Pd(dppap)(Ph}_2\text{P}^{\text{III}}=\text{O)Cl}$ **3**, Pd(dppe)Cl_2 **4**, and Pd(COD)Cl_2 **5**. Mechanistic studies *via* CV, LSV, UV-Vis, ^{11}B , ^{31}P NMR, kinetics, intermediate trapping, crystallography, and DFT indicated the following: (a) there is a direct role of Ar-B(OH)_2 in the reduction of pre-catalyst $[\text{Pd(II)}]$ to active $[\text{Pd(0)}]$ catalyst; (b) the hemilabile ligand influences solution stability of active $[\text{Pd(0)}]$; (c) facile oxidative addition of aryl halide takes place across active $[\text{Pd(0)}]$ generated from **2**, **3**, and **4**; (d) the stereoelectronic features of a ligand dictates the turn-over frequency (TOF), regeneration cycle (γ) as well as the CDA-derived ratio ($\pi\text{-b}/\sigma\text{-d}$). Due to high TOF and γ -value, **3** was employed in aryl-aryl, heteroaryl-aryl, and aryl-benzyl coupling; TOF in the range of 50000-400000 h^{-1} is achieved with a loading of 0.001-0.00001 mol%.

Chapters A.3 and A.4 make inquiry on “how does donor-acceptor communication in a heterobimetallic compound promote Friedel-Crafts reactivity?”. Towards this ligand-capped heterobimetallic $\text{Pd}^{\text{II}}/\text{Sn}^{\text{IV}}$ complexes $[(\text{N}^{\text{P}})(\mu\text{-X})(\text{Ph}_2\text{P}^{\text{III}}\text{O})\text{Pd}^{\text{II}}(\text{SnX}_4)]$ **6-7** were synthesized ($\text{X} = \text{Cl, Br}$), characterized, and mechanism of formation was elucidated via structural, NMR, DFT studies. It is concluded that donor-acceptor interaction between palladium center and the electrophilic tin(IV) center makes the latter more electrophilic. As a proof-of-principle a catalytic combination of **6**/ AgPF_6 was used successfully in Friedel-Crafts alkylation between aldehyde and arenes/heteroarenes yielding triarylmethanes. The catalytic combination of **6**/ AgPF_6 also promoted Friedel-Crafts/Suzuki Coupling (FC/SC) sequence for tandem construction of three carbon-carbon bond from bromo-substituted aromatic aldehyde, an arene/heteroarene, and aryl/heteroaryl boronic acid.

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In Chapter B we have investigated the nucleophilicity of organometallic reagents including organotin. By using the inverse concept of electrophilicity and nucleophilicity and two different available equations from the literature for electrodonating power, the global nucleophilicity index (N) of 99 organotin and 10 allyl-metal reagents (metal = Li, Mg, Zn, B, In, Si, Sn) have been calculated at B3LYP/LANL2DZ, 6-31G(d) level of theory. In addition, a local nucleophilicity index (N_k^-) was used as a local descriptor. Both N and N_k^- values were employed to explain experimental reactivity and regioselectivity trends in organometallic reagents including aryltin and allyltin reagents.

Keywords: Organometallic; Pd^{II}, Pd^{II}/Sn^{IV} complex; Organotin; Heterobimetallic; Lewis acid; Ligand effect; Donor–acceptor interaction; Catalysis; Friedel–Crafts Reaction; Suzuki Coupling; Triarylmethane; DFT; CDA-analysis; Nucleophilicity.