

Table of Contents

1 Palladium Trimer Enabled Catalysis	16
1.1 Introduction.....	16
1.2 Results and Discussion.....	20
1.2.1 Formation of a Trinuclear Palladium Complex.....	20
1.2.2 Stoichiometric Reactivity of the Palladium Trimer with Aryl Halides	23
1.2.3 Computational Study on the Carbon-Halogen Bond Activation by the Palladium Trimer	25
1.2.4 Chemoselective C-P bond Formation Catalyzed by the Palladium Trimer.....	30
1.2.5 Chemoselective Cross-Coupling of Aryl Iodides Enabled by the Palladium Trimer	36
2 Computational Study on Ligand Effects in Catellani-type Transformations	46
2.1 Introduction.....	46
2.2 Results and Discussion.....	50
2.2.1 Influence of Ligand Choice on the Reaction Pathway	51
2.2.2 Influence of Base on the Reaction Pathway.....	54
2.2.3 Influence of the Substrate's Electronics on the Reaction Pathway	55
3 Design of Multidentate Ligands Stabilizing Monomeric Ni^I Species	62
3.1 Introduction.....	62
3.2 Results and Discussion.....	64
3.2.1 Synthesis of Monomeric Ni ^{II} Complexes	65
3.2.2 Reduction to Ni ^I Species.....	73
3.2.3 Stoichiometric Reactivity of the Ni ^I Species	80
4 Supporting Information	84
4.1 General Experimental Details.....	84
4.2 Supporting Information for Chapter 1	86
4.2.1 Formation of a Trinuclear Palladium Complex.....	86
4.2.2 Stoichiometric Reactivity of the Palladium Trimer with Aryl Halides	93
4.2.3 Chemoselective C-P-bond Formation.....	100
4.2.4 Chemoselective Cross-Coupling of Aryl Iodides.....	108
4.2.5 Computational Details for Chapter 1.....	125
4.3 Supporting Information for Chapter 2	136
4.4 Supporting Information for Chapter 3	178
4.4.1 Synthesis and Characterization of Ni ^{II} tmtaa	178
4.2 Optimized Synthesis and Characterization of [Ni ^{II} scc] ⁺ OTf	180
4.4.3 Reduction of Ni ^{II} Complexes to Ni ^I Species	187
4.4.4 Reductive Dehalogenation of Alkyl Bromides.....	191
5 Literature	194