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Mechanistic Studies of Catalytically Relevant On-Metal N-Heterocyclic Carbene Transformations

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N-Heterocyclic Carbenes (NHCs) have many advantages to their phosphine analogues and have been used for a variety of catalytic applications. Bis-NHCs in particular have been used where bidentate phosphine complexes have previously been used including polymerisation and cross coupling reactions. Our group has been interested in palladium bis-NHCs with a wide variety of different N-substituents and linker lengths for catalytic applications.

We recently discovered an unexpected ligand rearrangement for a bis-NHC palladium complex when reacting the ethylene linked N-mesityl imidazolium salt with Pd(OAc)2. Along with the expected chelate formation an unusual C-C coupling product was also formed. DFT calculations indicate the formation is through the decomposition of a normal - abnormal intermediate via an on-metal ligand rearrangement. Given the extensive usage of this ligand class in catalysis and the decomposition route leading to this product it is important to understand and thus prevent its formation.

DFT investigations established will be presented as well as synthetic studies probing the mechanism. Symmetrical analogues have been synthesised as well as unsymmetrical analogues blocking the C2 position.

An alternative mechanism has also been explored for the decomposition of the chelate product to the C-C coupled product via the formation of a 1:2 ligand: palladium species. The NHC bridged dipalladium product has been isolated and structurally confirmed by X-ray crystallography and shown to offer high yielding access to C-C coupled decomposition products.

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Summary

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