

Oxidative Addition of Aryl Electrophiles to a Prototypical Nickel(0) Complex: Mechanism and Structure/Reactivity Relationships

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Lay Summary

By controlling the chemical groups attached to single atoms of metals, we can prepare metal complexes that can perform a number of valuable chemical reactions. These metal complexes activate our starting materials in such a way that the overall energy that is required for the reaction to proceed is decreased. The field of metal-mediated catalysis is huge, with catalysts based on metals such as palladium, platinum, rhodium, and iridium being especially popular. The Nobel Prizes in 2001 (Sharpless, Noyori, Knowles; for chirally catalysed oxidation and reduction reactions), 2005 (Grubbs, Schrock, Chauvin; for the development of alkene metathesis), and 2010 (Suzuki, Negishi, Heck; palladium-catalysed cross-couplings) were awarded as a result of work in this field.

The citation for the 2010 Nobel Prize was “*for palladium-catalyzed cross couplings in organic synthesis*” in which two molecules with specific functional groups are coupled together using a (typically palladium) catalyst. These methods have revolutionised some areas of chemistry, and are particularly heavily-used in the synthesis of active pharmaceutical ingredients for drug products. However, palladium is expensive and supplies are somewhat limited. Attention is now turning to metals such as iron, cobalt, and nickel, which might replace palladium in some reactions or allow us to develop entirely new chemical reactions.

Our manuscript describes our studies of one specific step in nickel-catalysed cross-coupling reactions. During a process called oxidative addition, the nickel atom loses two electrons and forms bonds to one of the substrates. This activates this substrate for subsequent steps in which a bond is selectively formed between this substrate and another coupling partner. The problem is that this step must occur quickly for the reaction to be viable, and it must give the desired intermediate complex without decomposing. We have measured the rate at which the process occurs with a number of different possible substrates, so that we can understand which are easiest to perform with our catalyst, and which need further investigation and optimisation. We also showed that, for certain substrates, the nickel complex that is formed after oxidative addition decomposes rapidly to form new complexes that are not active catalysts.

The manuscript improves our knowledge of how nickel behaves in these important cross-coupling reactions, and how the structure of the substrates can affect this. It lays the groundwork for future studies to examine and understand how changes to the groups supporting the nickel atom affect the reactivity of the resulting metal complex.