Catalysis Using Highly Unsaturated Transition Metal Complexes

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The use of sterically demanding *m*-terphenyl ligands allows the isolation of highly unsaturated transition metal complexes which show unusual bonding modes and stoichiometric reactivity towards small molecules.[1,2] Our recent investigations show that these first-row transition metal complexes are also precatalysts for a number of chemical transformations, showing unusual reactivity due to their low coordination number and the unique steric pocket created by the bulky *m*-terphenyl ligands (Figure 1). They are efficient precatalysts for the cyclotrimerisation of isocyanates, exhibiting high selectivity and allowing the formation of mixed species through cross-coupling reactions.[3] Low-coordinate iron(II) complexes are active in the catalysis of hydrophosphination reactions that produce phosphinocarboxamide (**I**) or phosphinodicarboxamides (**II**) products selectively, through the effective mono- or diinsertion of isocyanates into the P–H bond.[4] The diinsertion products (*e.g.* **III**), asymmetric phosphorus analogues of biuret, are a new family of derivatised phosphinodicarboxamides.

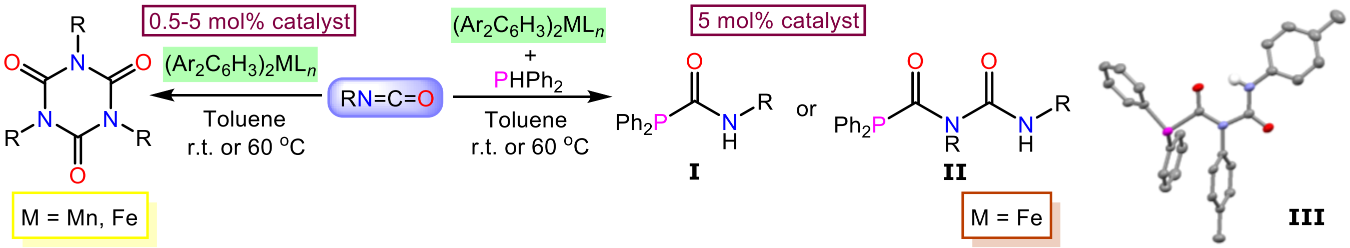

Figure 1. Cyclotrimerisation and hydrophosphination of isocyanates.

Low-coordinate manganese complexes are precatalysts for the dehydrogenation of dimethylamine-borane ($Me_2NH{\cdot}BH_3$), where small changes in the coordination environment impart significant differences in the reaction, occurring through a homogeneous or heterogeneous mechanism.[5] These reactions provide a tantalising snapshot of the potential range of catalysis available with low-coordinate *m*-terphenyl precatalysts, using earth abundant and environmentally benign first-row transition metals.

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