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A New and Novel Approach to the Formation of Metal-Metal Bonded Complexes using "Inorganic Grignard Reagents"

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The synthesis, structure, bonding and reactivity of molecular compounds containing unusual metal-metal bonds continues to be a topic of considerable interest. We have added to this field by utilising extremely bulky monodentate amido ligands for the stabilisation of a number of low oxidation state transition metal complexes, of which some have shown reactivity comparable to that of the classical Grignard Reagent.

These complexes were initially prepared from the reduction of amido metal halide precursors (LMX) (L = bulky amido ligand; M = transition metal, X = a halide) with the novel magnesium(I) reducing agent [{(MesNacnac)Mg}2]. Using bulky ligands, this reduction step often yields the formation of a low coordinate transition metal(I) dimer (LMML). However, by using extremely bulky ligands, the formation of the dimer is unfavourable and a number of novel LM-Mg(MesNacnac) heterobimetallic complexes can instead be isolated. These unprecedented complexes contain the first examples of a number of metal-metal bonds, such as manganese-magnesium and zinc-magnesium.

The metal-magnesium bonded compounds have shown to act as "inorganic Grignard Reagents" in reactions with a number of metal(I) and metal(II) halide complexes, in which their LM fragments are transferred onto other metal centres. This novel reactivity is still being investigated but has already allowed access to number of previously inaccessible hetero-bimetallic and even trimetallic complexes. All aforementioned complexes were structurally characterised by X-ray crystallography using the Australian Synchrotron MX beamlines.

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Summary

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