An Unusual Bimetallic C$_{sp}$-$^{3}$-C$_{sp}$-$^{3}$ Coupling Mechanism From a [Pd$^{II}$(P$^{AzA}$)(Me)]$_{2}$ Dimer

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Ligands bearing conformationally flexible moieties such as carboxylate and allyl groups can prevent decomposition pathways,$^{1}$ as well as promote fundamental reaction steps in a catalytic cycle.$^{2}$ Thus, these ligands are attractive candidates for the generation of potentially longer living and more efficient catalysts. Isoelectronic to the carboxylate and allyl groups, is the 1-azaallyl moiety. A key attribute of 1-azaallyl ligands are their ability to isomerize between different coordination modes, and a variety of distinct coordination modes have been identified.$^{3}$

The Blacquiere group has designed and synthesized the new phosphine 1-azaallyl (P$^{AzA}$) family of ligands. Coordination of a P$^{AzA}$ ligand to [Pd$^{II}$ClMe(COD)] generated a [Pd$^{II}$Me(P$^{AzA}$)]$_{2}$ dimer, with the nitrogen of the 1-azaallyl group bridging the two metal centres (Scheme 1a). Thermolysis of this dimer results in the formation of two new Pd products, along with the reductive elimination of ethane (Scheme 1b). C-C bond formation is achieved from a mono-methyl Pd$^{II}$ precursor; thus, the reaction represents an unusual example of bimetallic reductive elimination without the need of an external oxidant. Furthermore, a unique coordination mode of the 1-azaallyl unit is observed in each of the Pd products, suggesting the ability of this ligand to adopt different coordination modes is crucial to this reaction. Preliminary mechanistic data will be discussed, which suggests a reaction pathway that is distinct from other recognized C-C coupling mechanisms.

![Scheme 1](image)