

REDUCTIVE ELIMINATION

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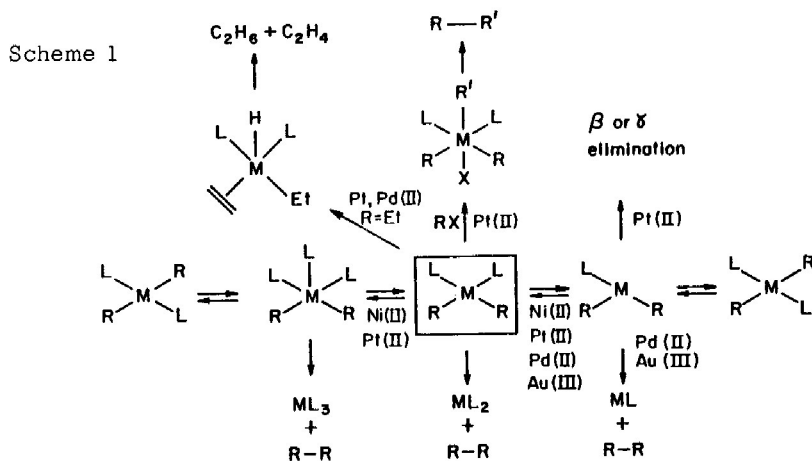
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Abstract - Reductive elimination of an alkane from a transition metal center is a common organometallic reaction, occurring for a wide range of metals, coordination numbers and geometries, and ligands. This contribution presents a theoretical analysis of the reaction, focusing on the options available as the metal and its coordination sphere change.

The coupling of two coordinated alkyl groups into an alkane, 1, is a common step in stoichiometric and catalytic organometallic reaction sequences.



This useful reaction proceeds for a great variety of metals, d electron counts and coordination numbers and is especially efficiently accomplished by d^8 transition metal centers such as Ni(II), Pt(II), Pd(II), Au(III). But the simple form of the summary equation 1 masks a multitude of mechanistic choices. Some of these are shown in Scheme 1.



The most common starting point for these reactions is a preformed square-planar 16 electron, d^8 cis dialkyl (or tri- or tetra-alkyl for Au(III)) complex which appears in the middle of the Scheme. The two other ligands, marked L, are typically phosphines. Depending on the size and electronic characteristics of the phosphine substituents one may observe associative or dissociative steps away from the four-coordinate complex. Both elementary processes have been clearly demonstrated in the Grubbs system, where $M=Ni(II)$ and R_2 is a tetramethylene bridge (1). Evidence is in fact in hand for the dissociative step in most such reactions.

The four-coordinate complex eliminates R-R cleanly and easily in the Ni(II) case only. For

