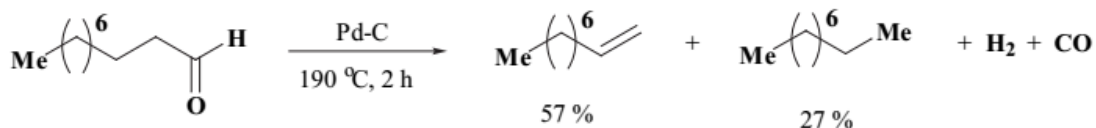


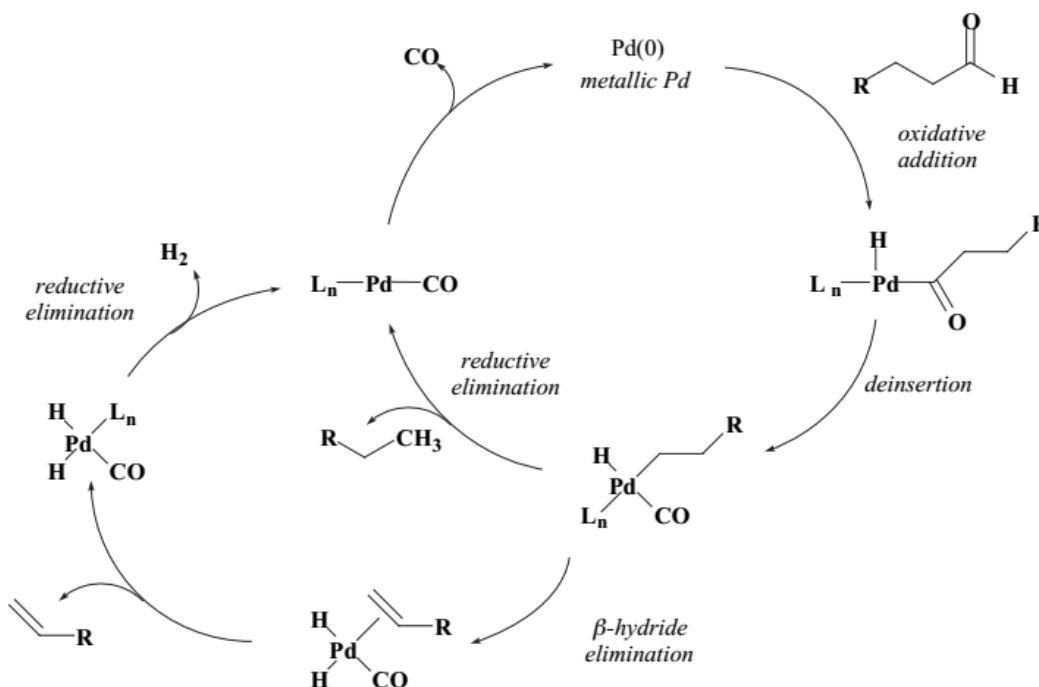
Palladium-mediated decarbonylation of aldehydes

An early study using carbon palladium metal (heterogeneous catalysis) to trigger decarbonylation of aldehydes yielding mixtures of alkene and alkane products ... "Much attention has recently been given to the usefulness of palladium in organic synthesis.



Proposed mechanism

CO is thought to dissociate quickly at 200 oC, rendering this cycle catalytic at certain temperatures in metallic palladium. There was no known reaction to the oxidizing addition of aldehydes to metallic palladium to form the acyl complex. Tsuji and coworkers proposed this mechanism based on analogous reactions formed with acyl halides. Part of the proof presented for this oxidative addition was that metallic palladium dissolves partly in acyl halides.



This method has clear limitations including high reaction temperatures, product mixture formation and heterogeneity which makes it difficult to change the reactivity of the catalyst. Thus a more useful, homogeneous catalytic system was sought. Based on this postulated mechanism for decarbonylation with palladium, it was reasoned that a complex that could effect this process efficiently should have the following properties: (1) low valent, coordinately unsaturated metal (e.g. 4-coordinate d8 complex) to make possible the oxidative addition of aldehydes or acid halides and (2) the complex should be able to coordinate carbon monoxide. Wilkinson's catalyst satisfies both of these requirements.

O'Connor and coworkers found that in contrast to other azides which were decomposed under the reaction conditions, the relatively stable azide diphenylphosphoryl azide (DPPA) was effective in removing the CO ligand from chlorocarbonylbis(triphenylphosphine)rhodium and was thus able to render the decarbonylation reaction catalytic with Wilkinson's catalyst. DPPA is a ready to use, non-explosive, high-boiling azide used as a peptide synthesis reagent.

