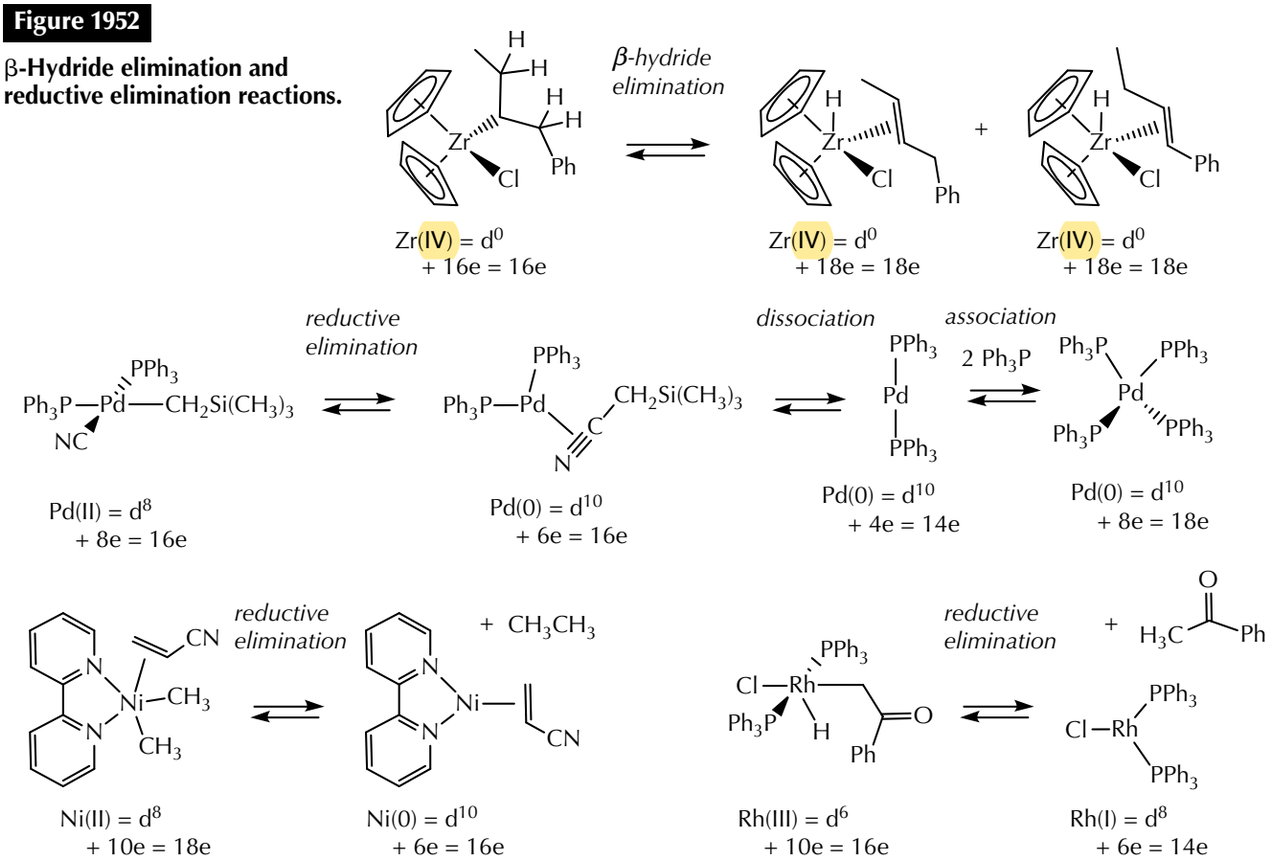
Figure 1952

β-Hydride elimination and reductive elimination reactions.



In Figure 1939, a part of the catalytic cycle for hydrogenation using the solid phase (heterogenous) Pd-C catalyst was illustrated. In the late 1950s and early 1960s, transition metal compounds were discovered that could catalyze hydrogenation reactions. Soluble in organic solvents, these compounds are called homogeneous catalysts. Homogeneous catalysts are often experimentally more convenient, selective, and/or efficient to use than their heterogeneous counterparts (e.g., Pd-C), and the detailed knowledge of their mechanisms allows chemists to make improvements more easily. One of these compounds is the Wilkinson catalyst (Figure 1953), first reported in 1965.

The Wilkinson catalyst is a soluble, d^8 Rh(I) 16-electron compound. It functions as a hydrogenation catalyst in the following 4-step mechanism. This example illustrates most of the reactions of transition metal compounds introduced so far.

Activate: Triphenylphosphine ligands are strong donors and stabilize structures. To get to the catalytic form of the compound, one of the phosphine ligands dissociates and a solvent molecule (ethanol) takes its place (d^8 Rh(I) 16e to d^8 Rh(I) 16e).

Step 1: Molecular hydrogen associates with the open shell rhodium, which then undergoes an oxidation addition of the hydrogen to form two new Rh-H bonds (d^8 Rh(I) 16e to d^6 Rh(III) 18e).

Step 2: The solvent molecule (ethanol) dissociates, and the alkene substrate associates (d^6 Rh(III) 18e to d^6 Rh(III) 18e).

Step 3: The alkene undergoes a hydrometallation addition of Rh-H, and the solvent molecule returns to occupy the vacant spot (d^6 Rh(III) 18e to d^6 Rh(III) 18e).

Step 4: The R-Rh-H undergoes a reductive elimination and the product dissociates, restoring the original form of the catalyst (d^6 Rh(III) 18e to d^8 Rh(I) 16e).