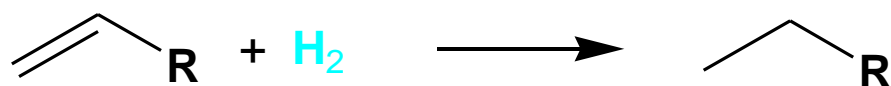
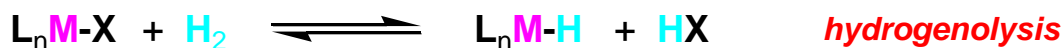
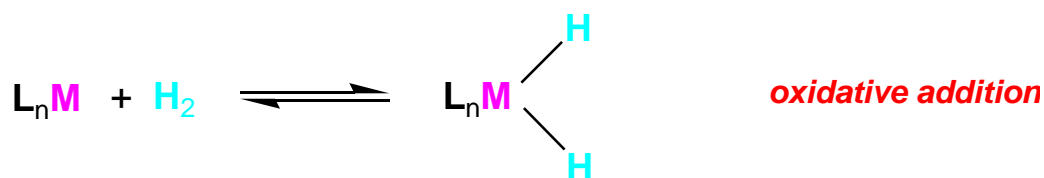


Hydrogenation Catalysis

Hydrogenation is the addition of H₂ to a multiple bond (C=C, C≡C, C=O, C=N, C≡N, N=O, N=N, N≡N, etc) to reduce it to a lower bond order. The most common and simple type of hydrogenation is the reduction of a C=C double bond to a saturated alkane:



There are three different ways that transition metal catalysts can activate H₂ for performing hydrogenation catalysis:



Oxidative addition: the most common method of activating H₂ on a metal with d electrons (d² or higher). Metal center typically needs to have an empty coordination site in order to bind the H₂ first, prior to the oxidative addition.

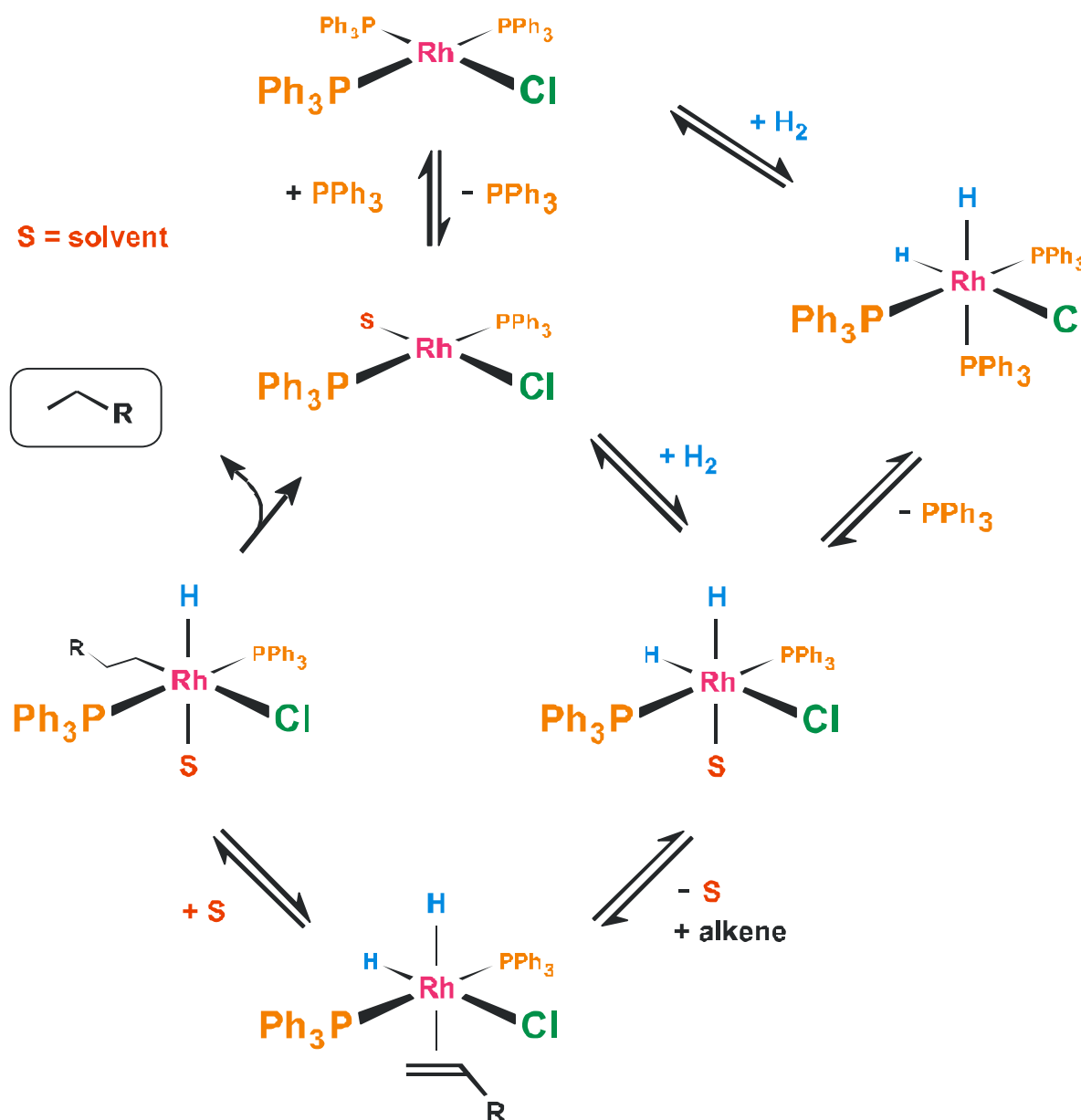
Hydrogenolysis: the only way that early transition metals with d⁰ counts can activate H₂. Lanthanides and actinides also typically use hydrogenolysis. As with oxidative addition, the metal center needs to have an empty orbital to bind the H₂ and an anionic ligand (e.g., alkyl, halide) that can be protonated off. No change in oxidation state of the metal.

Heterolytic cleavage: in many ways quite similar to hydrogenolysis except that the proton produced does not directly react with an anionic ligand coordinated to the metal, but rather with an external base that typically has to transfer it back to the metal center to complete the catalytic cycle. Ru(+2) is the most common metal that uses heterolytic cleavage as a mechanism. No change in oxidation state of the metal.

Wilkinson's Catalyst: $\text{RhCl}(\text{PPh}_3)_3$ was the first highly active homogeneous hydrogenation catalyst and was discovered by Geoffrey Wilkinson (Nobel prize winner for Ferrocene) in 1964. R. Coffey discovered it at about the same time while working for ICI (Imperial Chemical Industries). It was very simply prepared by reacting $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with excess PPh_3 in EtOH:



The two initially proposed mechanistic routes are as follows:



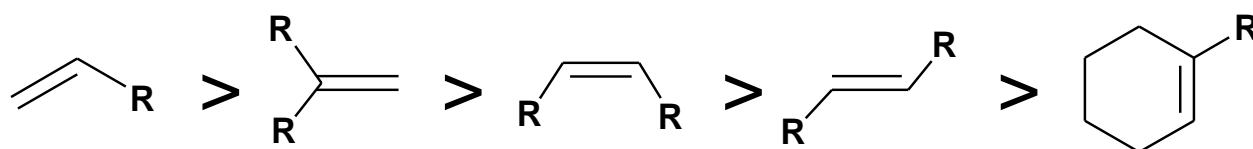
It has been clearly shown that PPh_3 is readily lost due to steric crowding and that the inner catalyst cycle with a weakly coordinated solvent molecule is about 1000 times faster than the outer cycle that has 3 PPh_3 ligands coordinated to the metal.

Osborn later discovered that cationic complexes like $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$ were considerably more active for hydrogenations relative to Wilkinson's catalyst. The reason for this is that the cationic metal center is more electrophilic and this favors alkene coordination, which is often the rate determining reaction step. Also by only having 2 PPh_3 ligands present one could keep the catalyst on the far more reactive catalytic cycle.

Crabtree discovered that the cationic Ir catalyst, $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]^+$ (py = pyridine), was even more reactive. The Ru catalyst, $\text{HRuCl}(\text{PPh}_3)_3$, is even more reactive for 1-alkenes. Rate data is shown in the following table:

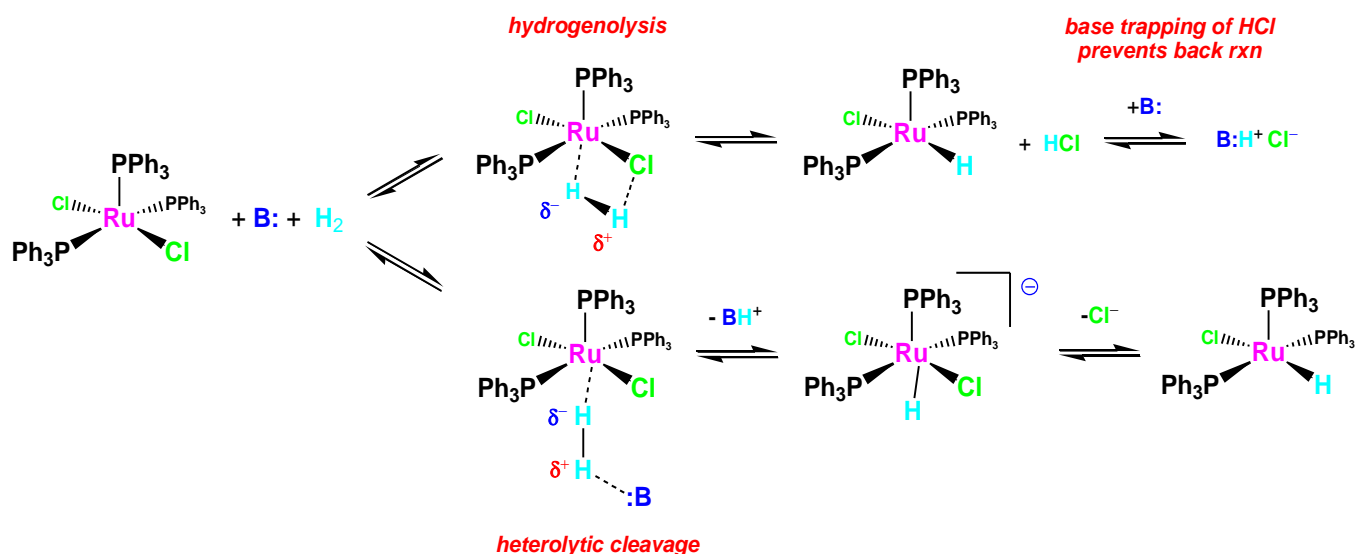
Catalyst	Temp °C	Solvent	TOF (hr^{-1})		
			1-hexene	cyclohexene	$\text{Me}_2\text{C}=\text{CMe}_2$
$[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]^+$	0	CH_2Cl_2	6,400	4,500	4,000
$[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]^+$	0	CH_2Cl_2	5,100	3,800	50
$[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]^+$	0	acetone	10	0	0
$[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+$	25	CH_2Cl_2	4,000	10	0
$\text{HRuCl}(\text{PPh}_3)_3$	25	C_6H_6	9,000	7	0
$\text{RhCl}(\text{PPh}_3)_3$	25	$\text{C}_6\text{H}_6/\text{EtOH}$	650	700	0
$\text{RhCl}(\text{PPh}_3)_3$	0	$\text{C}_6\text{H}_6/\text{EtOH}$	60	70	0

Alkene bulkyness also plays an important role with the following general trend in hydrogenation rates:

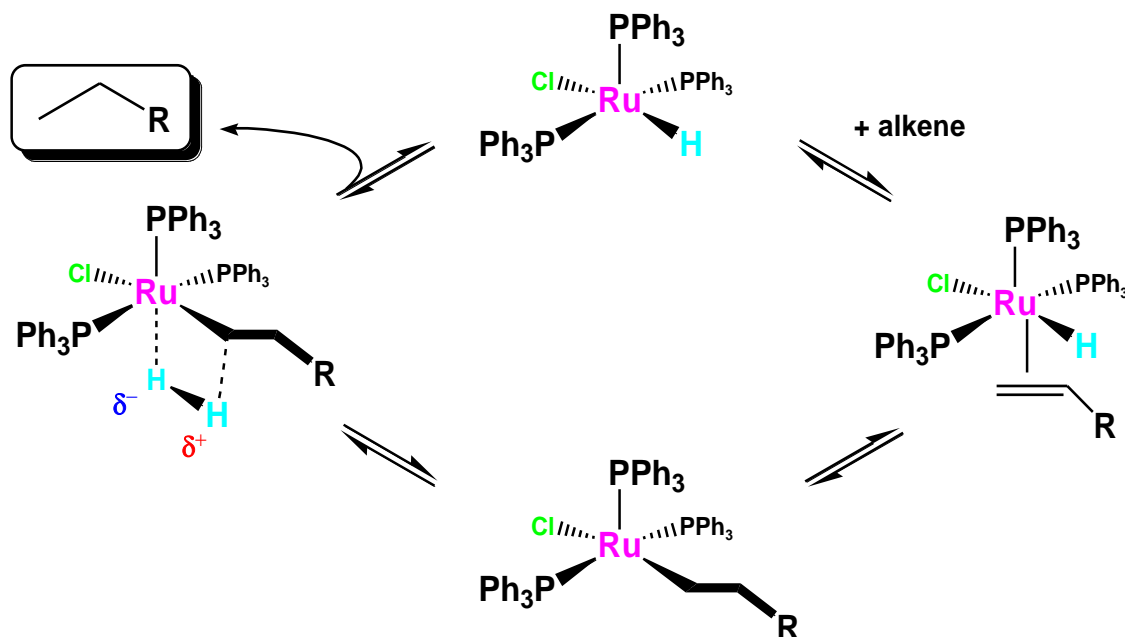


Ru Heterolytic H₂ Activation

Ru has a strong tendency to perform a heterolytic activation of H₂ instead of oxidative addition to make a metal dihydride. This can occur either via hydrogenolysis or heterolytic cleavage mechanisms, giving the same net result:



Shown below is a proposed catalytic cycle for Ru(+2) catalyzed hydrogenation:

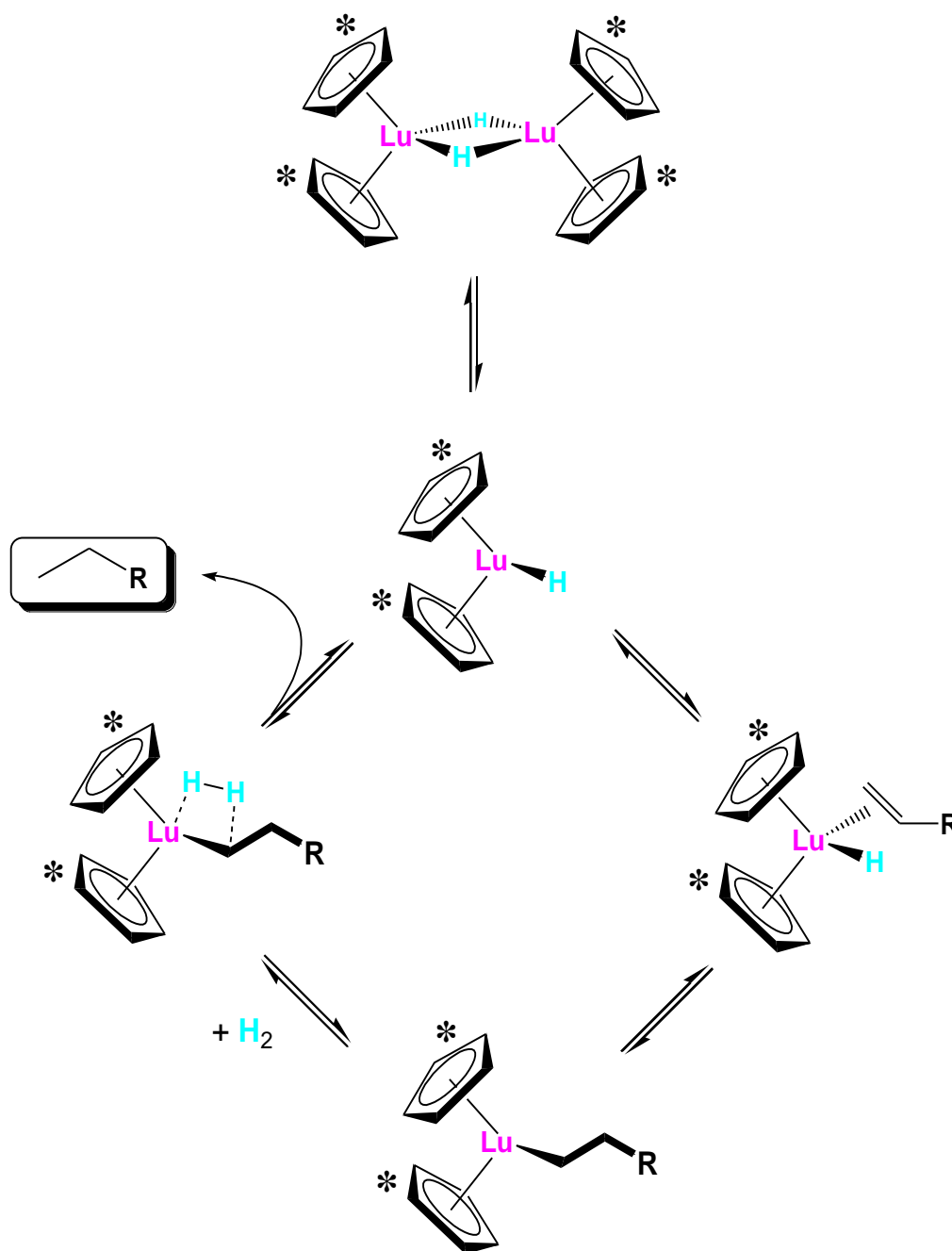


Note that there is no change in oxidation state of the Ru(+2)!

Lanthanide Hydrogenation Catalysts

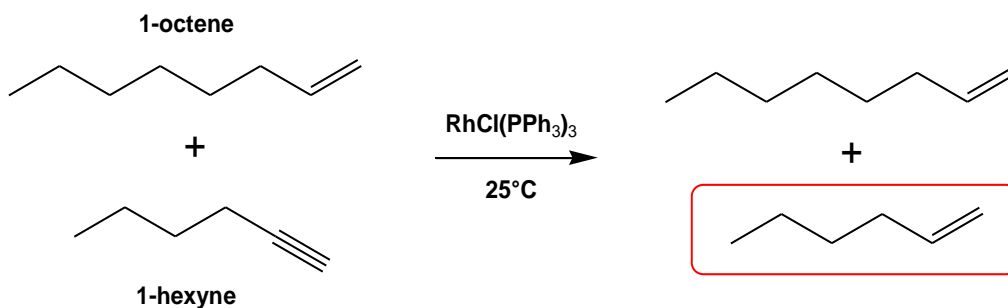
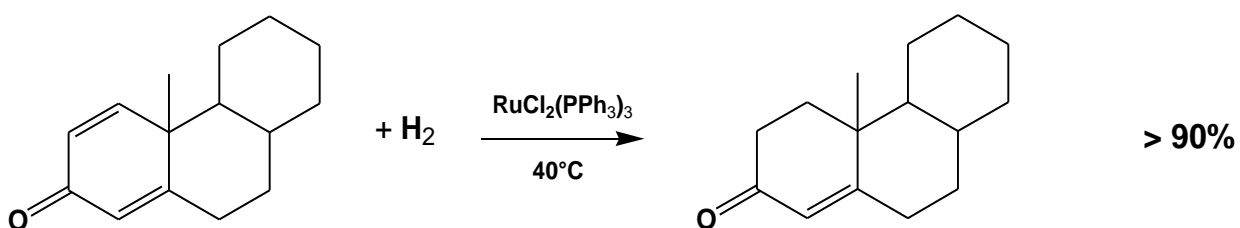
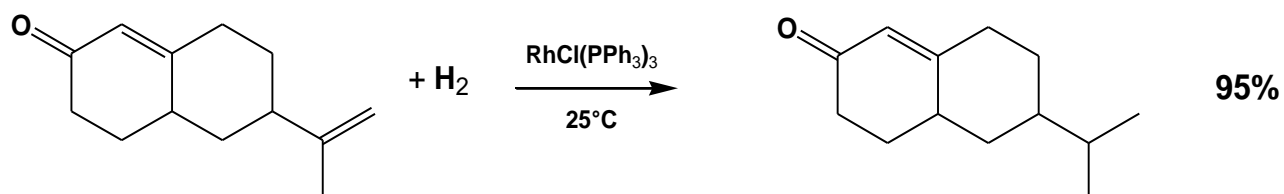
Tobin Marks reported the extraordinary activity of $(\text{Cp}^*_2\text{LuH})_2$ for the hydrogenation of alkenes and alkynes. The monometallic complex catalyzes the hydrogenation of 1-hexene with a TOF = 120,000 hr^{-1} at 1 atm H_2 , 25°C!! This is one of the most active hydrogenation catalysts known.

The proposed mechanism is shown below:

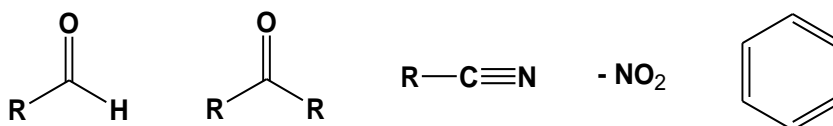


Selectivity:

Hydrogenation catalysts typically will selectively hydrogenate the most reactive multiple bonds first. Steric and electronic effects play an important role in this. Consider the following examples:

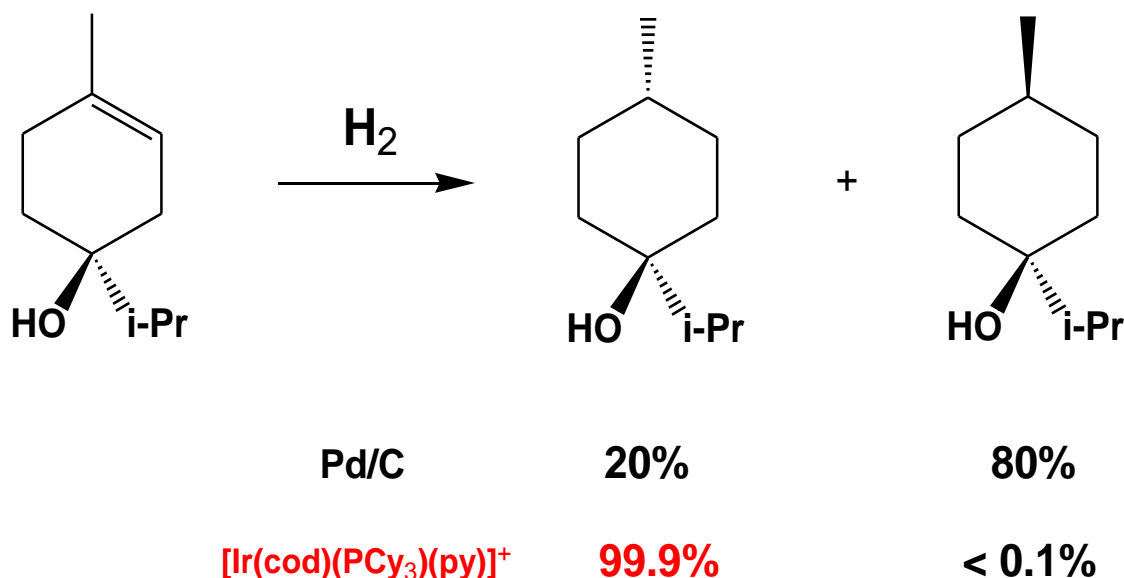


Typically NOT hydrogenated under mild conditions:

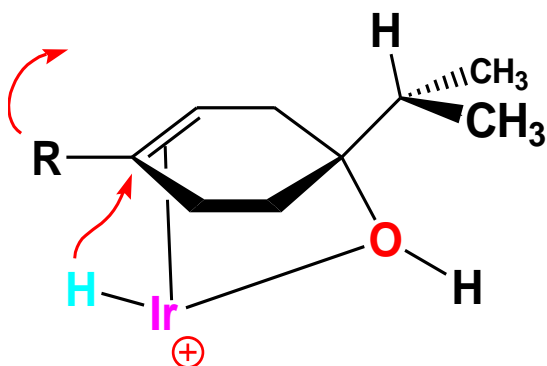


Directing Effects

Crabtree has demonstrated some very interesting substrate directing effects in hydrogenation:



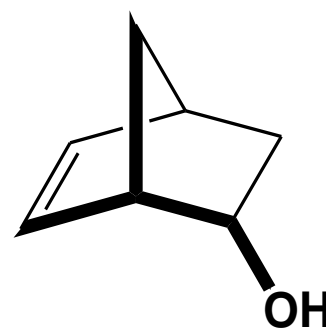
The weak ligand bonding of the OH group on the substrate directs one specific side of the alkene to coordinate to the metal center in order to form an alkene-OH chelate to the Ir.



positive charge on Ir is important to attract the partial negatively charged OH group. One also needs the presence of an empty orbital

Group binding affinities: amide > OH > OR > ester ~ ketone

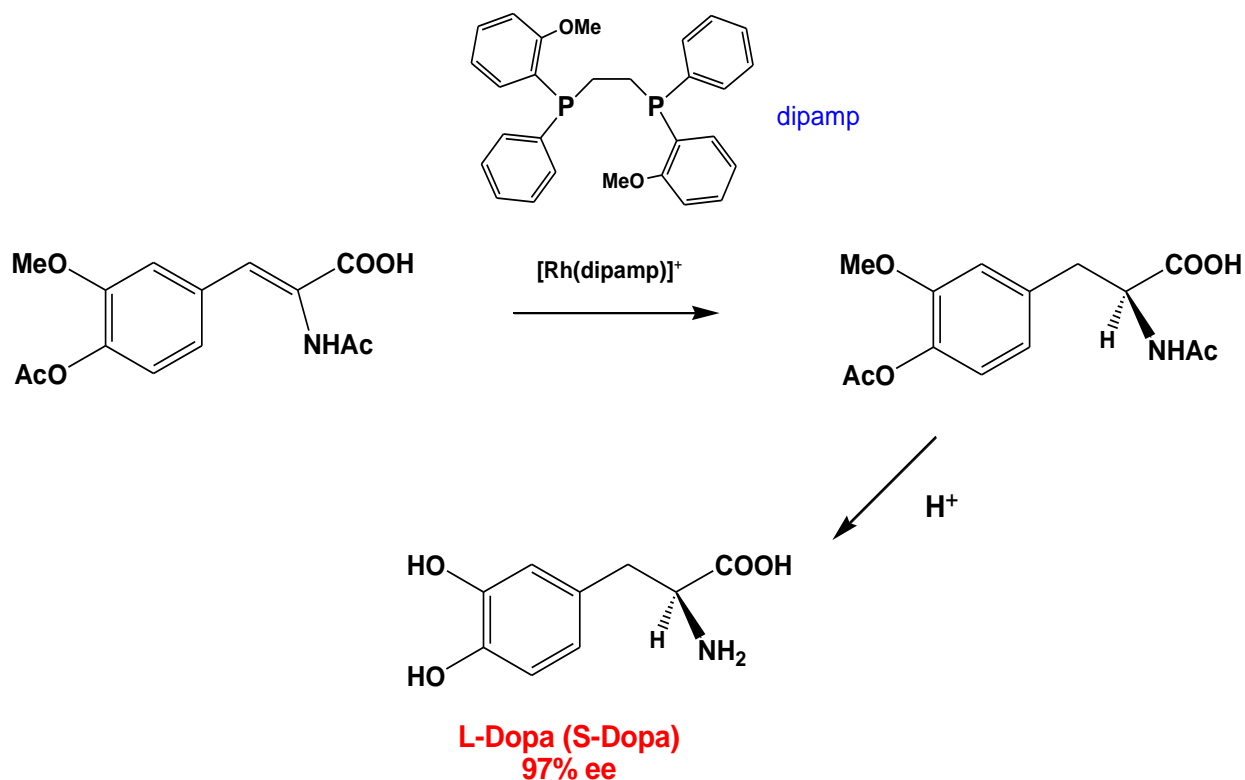
Amine groups bind too strongly and inhibit catalysis. Rigid structures with stronger chelates, like the norbornene ligand shown to the right, are also poor substrates.



Asymmetric Hydrogenation

95% of all hydrogenations use heterogeneous catalysts like Pd on carbon (Pd/C) or Raney Nickel (a highly porous form of Ni that is an excellent and highly active hydrogenation catalyst). One area where homogeneous catalysis rules is *asymmetric hydrogenation*. This involves the use of a chiral catalyst and an alkene substrate that generates a chiral carbon center on hydrogenation.

The first dramatic example of this was reported in 1968 by Bill Knowles and coworkers at Monsanto for the asymmetric hydrogenation of α -acetamidocinnamic acid to produce L-Dopa, an important pharmaceutical for the treatment of Parkinson's disease.



more to come !! (I'm still working on this section)