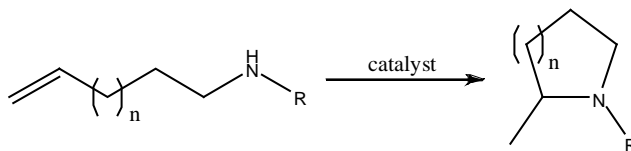


## Intramolecular Hydroamination of Unactivated Alkenes

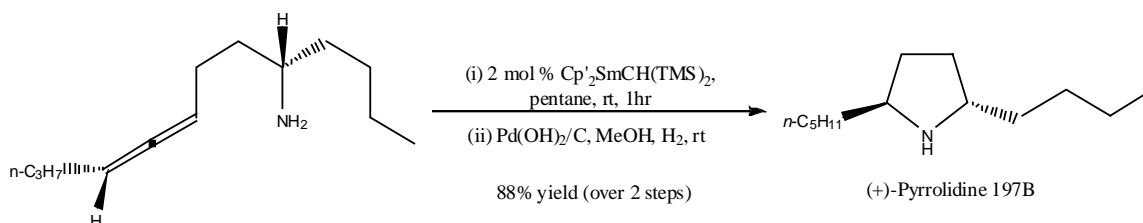
Nitrogen-containing heterocycles are to be found in a large number of natural products of interest. Coupled with the limitations of traditional C-N bond formation reactions, there is much interest in catalytic hydroamination as a route to nitrogen heterocycles.



**Generic Scheme:** Intramolecular hydroamination.

### 1. Lanthanide Catalysts

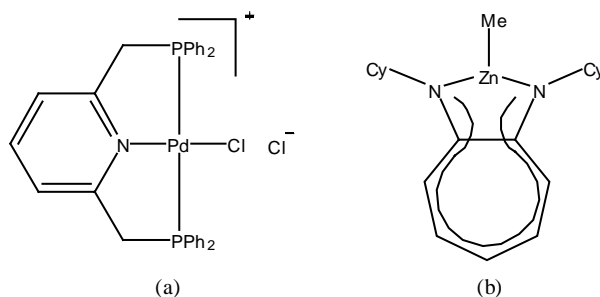
Well developed - but catalysts are hugely sensitive to functional groups, air and moisture. This restricts their use in organic synthesis (see example).



**Scheme 1:** Example of lanthanide catalysis in synthesis.

Ref: Acc. Chem. Res., 2004, 673. (*Full paper*)

Very recently a number of groups have begun to report a range of more tolerant catalysts based on late transition metals.



**Figure 1:** Examples of catalysts reported for intramolecular hydroamination.

## 2. Pd (II) Catalysts

Typical conditions: 5 mol % of catalyst (**Fig. 1(a)**) (but as low as 1 mol % without appreciable loss of yield), rt, 2-16 hr, yields of 70-100%.

N sources: amides and carbamates.

Ref: J. Am. Chem. Soc., 2006, 4247.

## 3. Pt (II) & Au (I) Catalysts

Typical conditions: 2.5-5 mol % of catalyst, from 120°C to rt, 12-24 hr, yields of most recent examples of 85-100%.

N sources: amines, carbamates, carboxamides, ureas.

Refs: J. Am. Chem. Soc., 2005, 1070.  
Angew. Chem. Int. Ed., 2006, 1747.  
Chem. Comm., 2006, 4143.  
Org. Lett., online.

## 4. Zn (II) Catalysts

Key advantage: Zn is inexpensive and non-toxic.

Typical conditions: 2.5 mol % of catalyst (**Fig. 1(b)**), 80°C, hours to days, yields of 80-100%.

N sources: amines.

Refs: Angew. Chem. Int. Ed., 2005, 7794.  
Chem. Comm., 2006, 3405.