

Electronegativity: V(1.63); Nb(1.6); Ta(1.5)

These elements are commonly found in +2, +3, +4, and +5 oxidation states (this lack of adherence to well defined oxidation states may impede their development as catalysts).

Most common oxidation states.

V: +3 > +4, > +5

Nb: +5 > +4 > +3

Ta: +5 >> +4 > +3

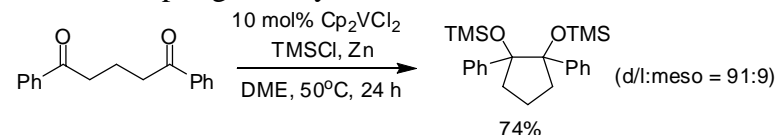
Vanadium

The most common use of vanadium catalysts is in the oxidation of olefins and sulfides; *the epoxidation of allylic alcohols and homoallylic alcohols is extremely useful.*

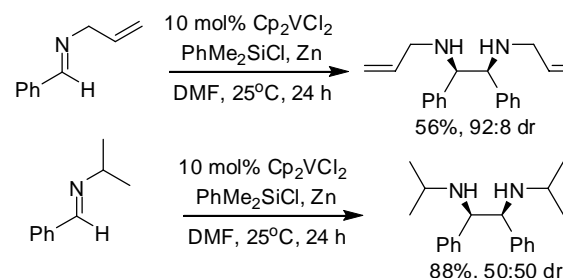
Note: There is little catalytic chemistry that involves the intermediacy of V—alkyl complexes.

Low-valent vanadium complexes often undergo efficient electron transfer reactions.

Pinacol coupling: aldehydes *JOC* **1998**, 2812;

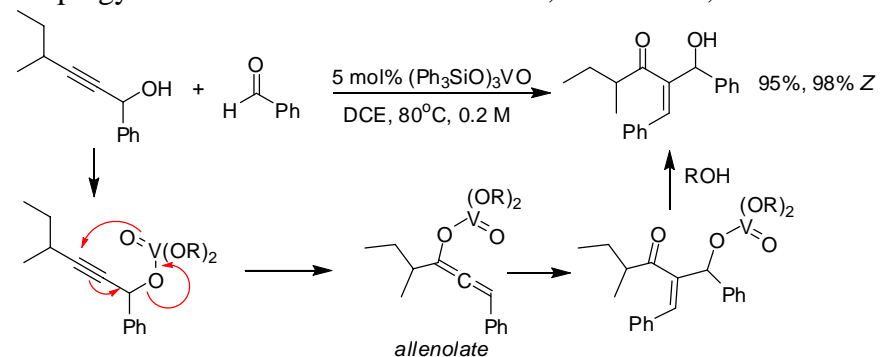


aldimines *JOC* **1998**, 9421.

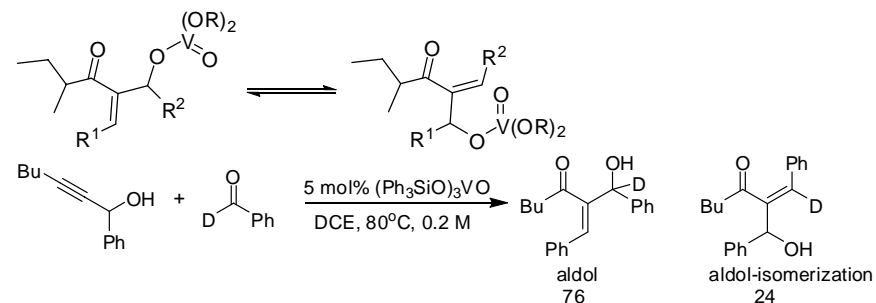


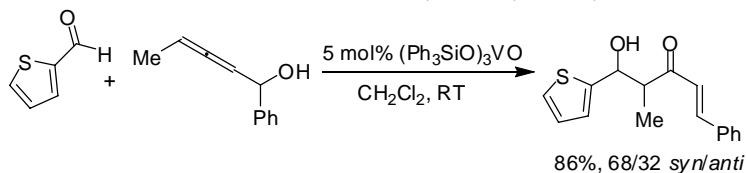
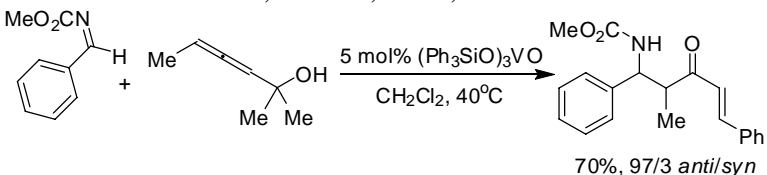
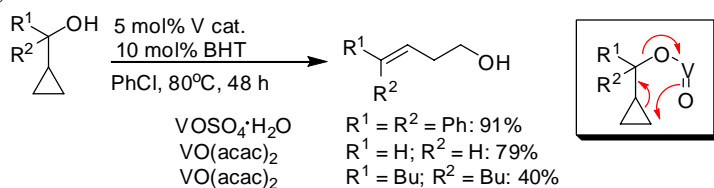
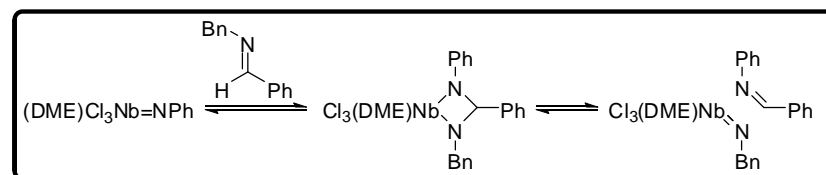
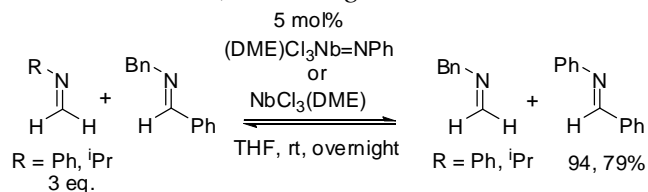
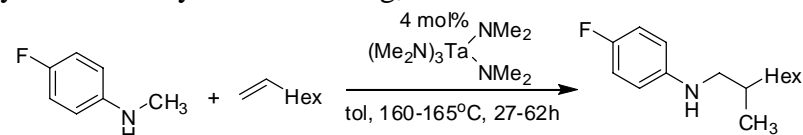
Sigmatropic rearrangement of vanadium esters is common.

Propargylic alcohols to allenolates: Trost, *JACS* **2001**, 1230.

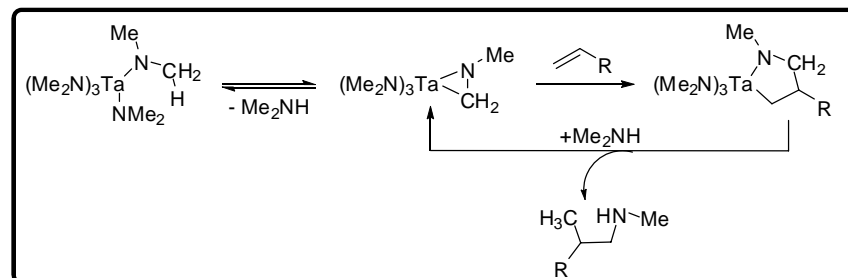
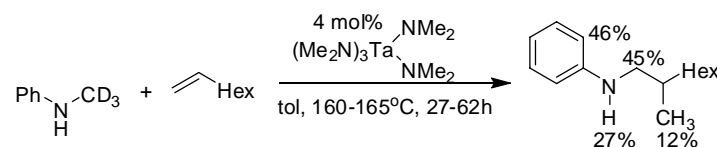
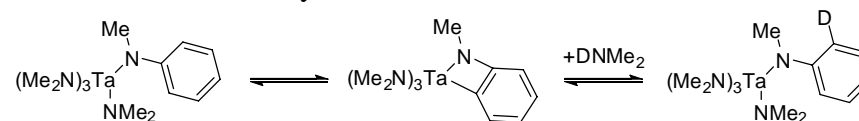


Note: Yields for aliphatic aldehydes are lower (ca. 50%).

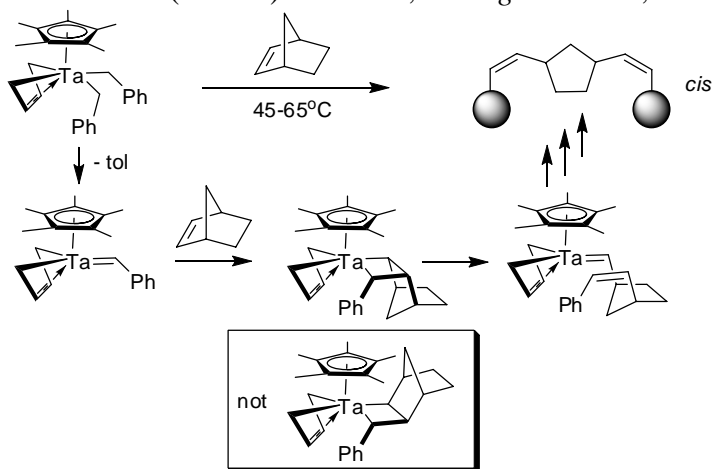


Enolates from allenic alcohols: Trost, *JACS*, **2001**, 12736.Imines favor anti: Trost, *ACIEE*, **2003**, 2063.Rearrangement of cyclopropyl carbinols: Uemura, *Chem. Lett.* **2005**, 380**Niobium**Imine metathesis: Bruno, J. W. *Orgmet* **2000** 4672.**Tantalum**Hydroaminoalkylation: Hartwig, J. F. *JACS* **2007** 6690.

Potential mechanism:

Mechanism predicts that the product CH₃ is derived from the olefin.*ortho*-deuteration likely results from reversible aromatic metalation

Olefin metathesis: (ROMP) Mashima, K. *Orgmet.* **1998**, 4183.



Note: The authors characterize the metallacyclobutane intermediate by NMR and X-ray crystallography when acenaphylene is used as the olefin.

