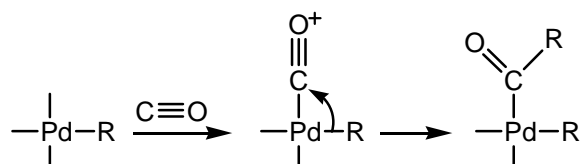
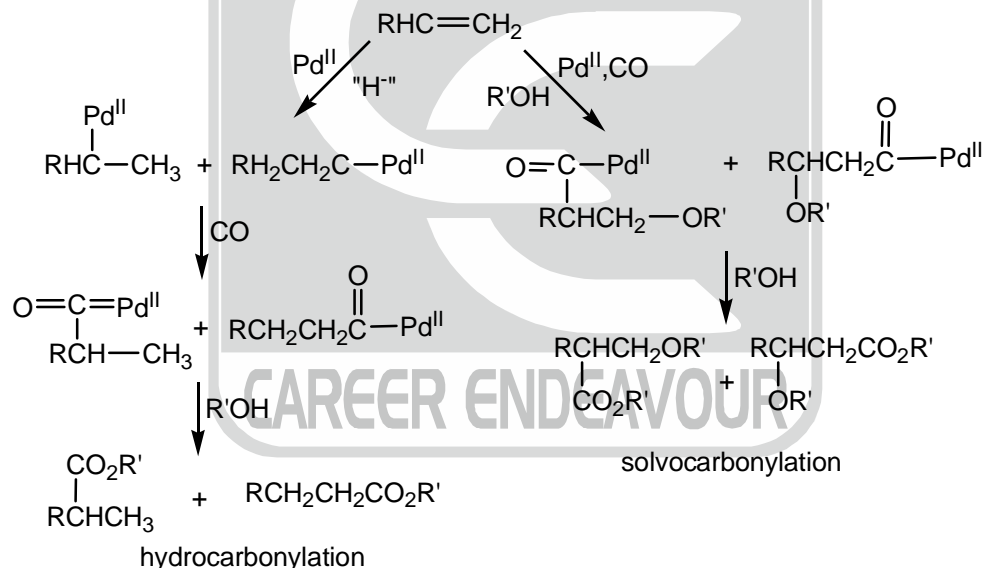


#### 4.6.7. Carbonylation Reactions:

Carbonylation reactions involve coordination of carbon monoxide to palladium and a transfer of an organic group from palladium to the coordinated carbon monoxide.

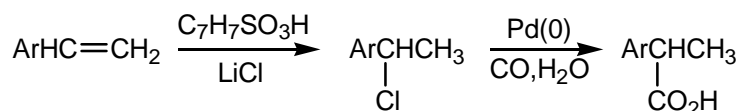


Carbonylation reactions have been observed using both Pd(II)-alkene complexes and  $\sigma$ -bonded Pd(II) species formed by oxidative addition. Under reductive conditions, the double bond can be hydrocarbonylated, resulting in the formation of a carboxylic acid or ester. In nucleophilic solvents, the intermediate formed by solvopalladation is intercepted by carbonylation and addition of nucleophilic solvent. In both types of reactions, regioisomeric products are possible.



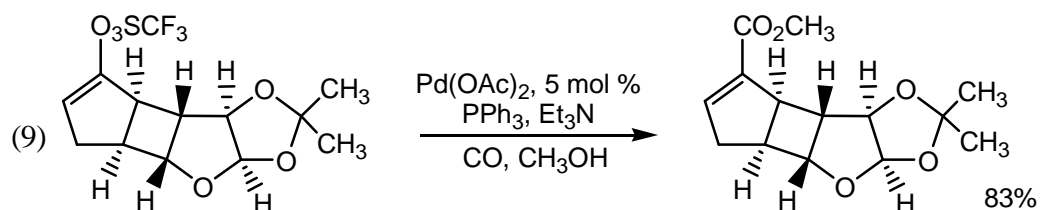
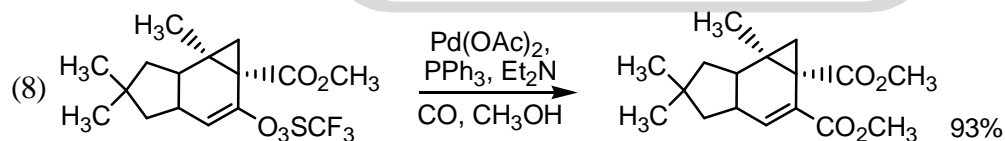
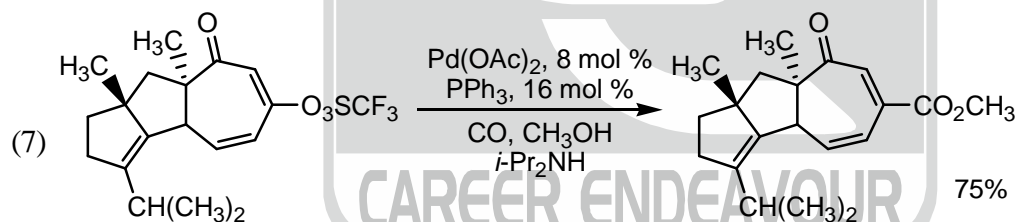
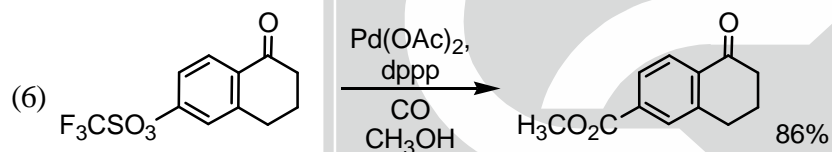
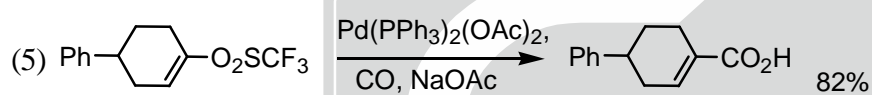
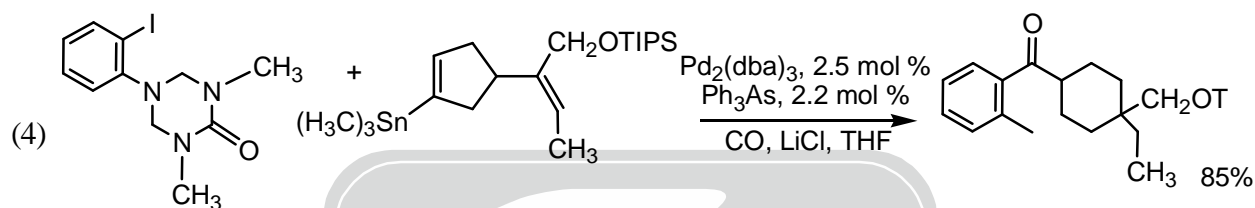
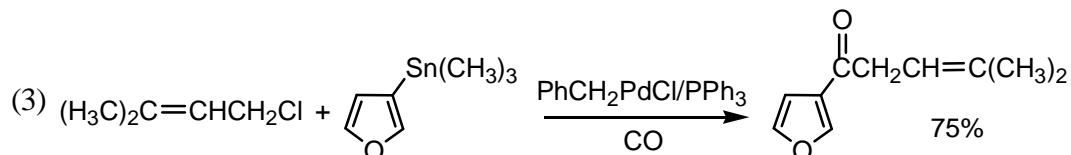
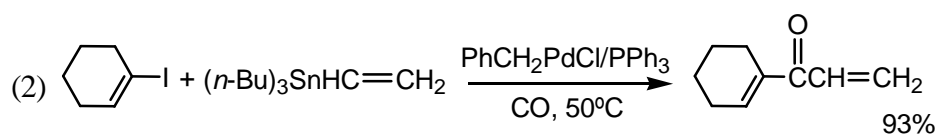
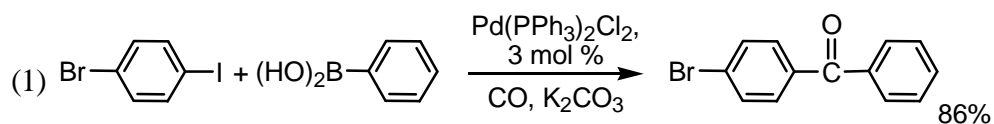
#### 4.6.8. Hydrocarbonylation :

The hydrocarbonylation reaction can be applied to the synthesis of  $\alpha$ -arylpropanoic acids of the NSAIDS type. For this synthesis to be effective, selective carbonylation of the more-substituted  $\text{sp}^2$  carbon is required. Although many carbonylation conditions are unselective,  $\text{PdCl}_2(\text{PPh}_3)_2$  with p-toluenesulfonic acid and LiCl achieves excellent selectivity. The selectivity is thought to involve the formation of a benzylic chloride intermediate.



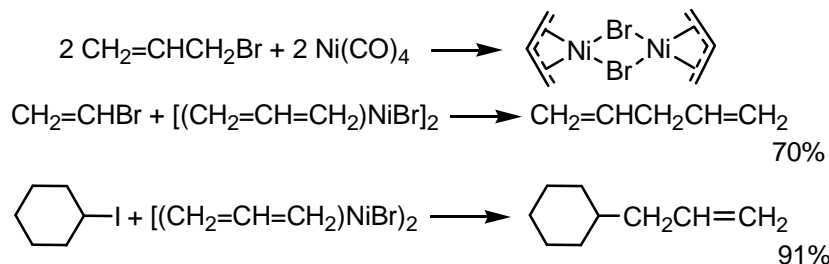


## EXAMPLES:

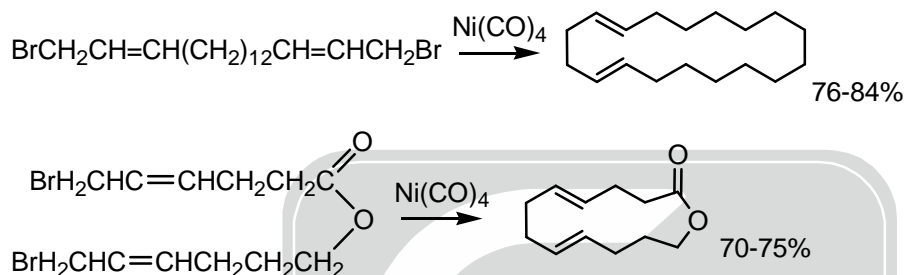


### 4.7. ORGANONICKEL COMPOUNDS:

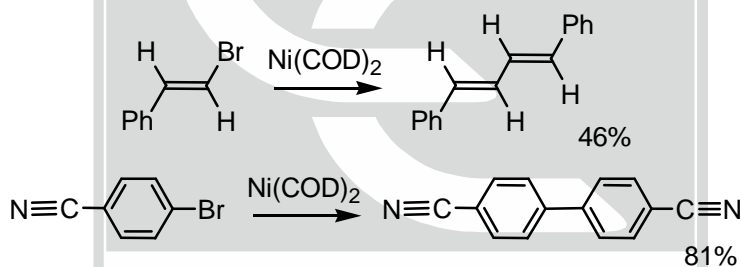
The early synthetic processes using organonickel compounds involved the coupling of allylic halides, which react with nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , to give  $\pi$ -allyl complexes. These complexes react with a variety of halides to give coupling products.



Nickel carbonyl effects coupling of allylic halides when the reaction is carried out in very polar solvents such as DMF or DMSO. This coupling reaction has been used intramolecularly to bring about cyclization of *bis*-allylic halides and was found useful in the preparation of large rings.

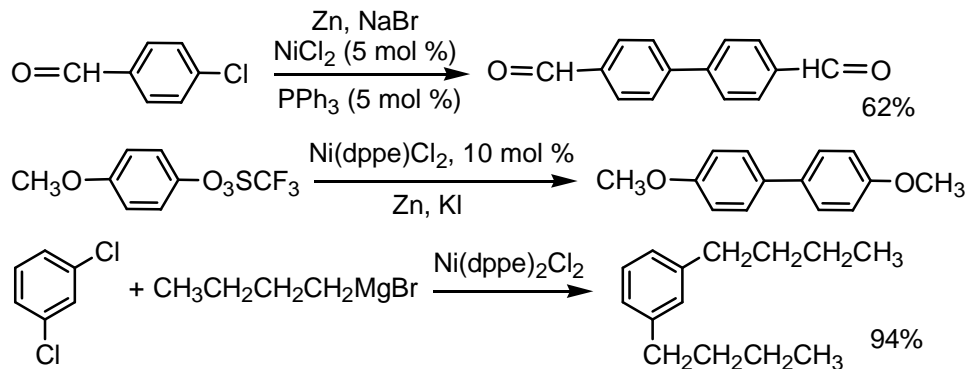


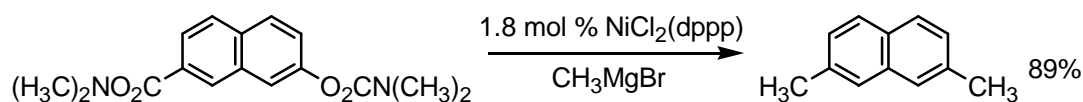
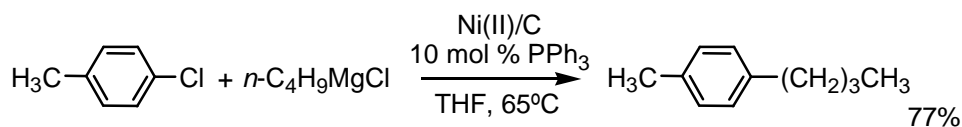
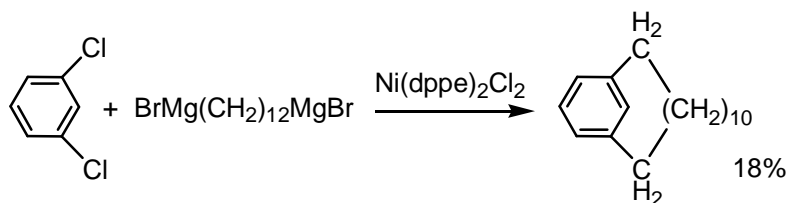
Nickel carbonyl is an extremely toxic substance, but a number of other nickel reagents with generally similar reactivity can be used in its place. The Ni(0) complex of 1,5-cyclooctadiene,  $\text{Ni}(\text{COD})_2$ , can effect coupling of allylic, alkenyl, and aryl halides.



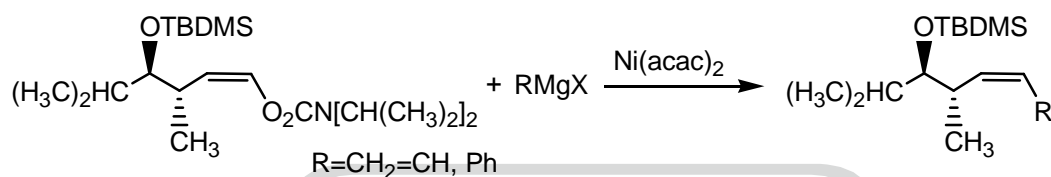
Tetrakis-(triphenylphosphine)nickel(0) is an effective reagent for coupling aryl halides, and medium rings can be formed in intramolecular reactions.

The homocoupling of aryl halides and triflates can be made catalytic in nickel by using zinc as a reductant for in situ regeneration of the active Ni(0) species.

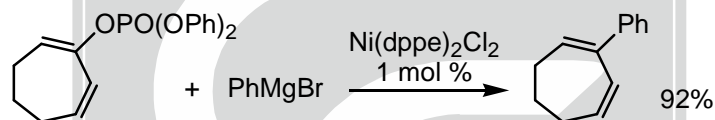




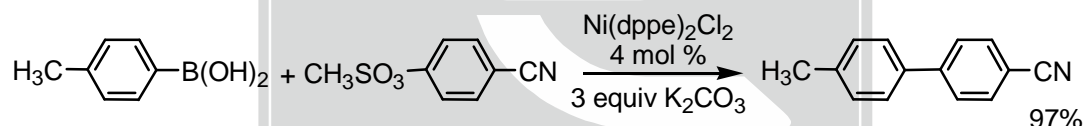
Vinyl carbamates are also reactive.



Similarly, nickel catalysis permits the extension of cross coupling to vinyl phosphates, which are in some cases more readily obtained and handled than vinyl triflates.

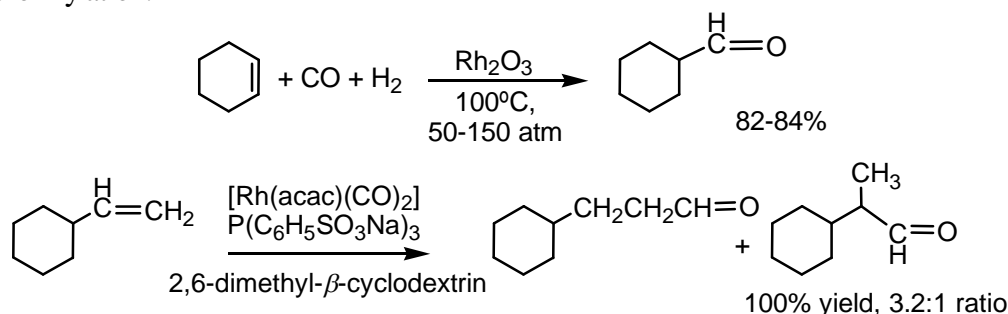


Nickel can also be used in place of Pd in Suzuki-type couplings of boronic acids. The main advantage of nickel in this application is that it reacts more readily with aryl chlorides and methanesulfonates than do the Pd system. These reactants may be more economical than iodides or triflates in large-scale syntheses.

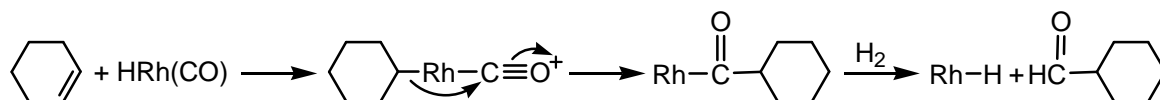


#### 4.8. ORGANORHODIUM & ORGANOCOBALT COMPLEX:

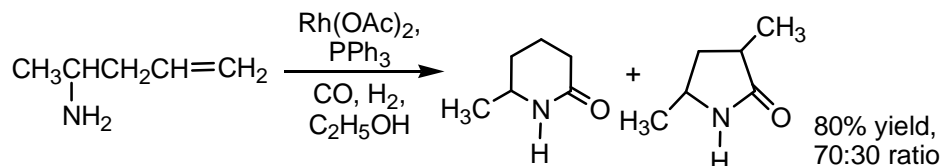
Rhodium and cobalt participate in several reactions that are of value in organic syntheses. Rhodium and cobalt are active catalysts for the reaction of alkenes with hydrogen and carbon monoxide to give aldehydes, known as hydroformylation.



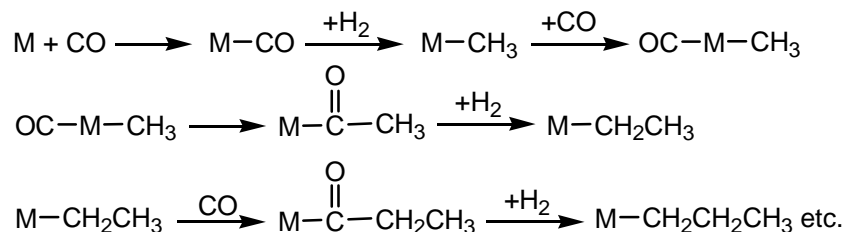
The key steps in the reaction are addition of hydridorhodium to the double bond of the alkene and migration of the alkyl group to the complexed carbon monoxide. Hydrogenolysis then leads to the aldehyde.



Carbonylation can also be carried out under conditions in which the acylrhodium intermediate is trapped by internal nucleophiles.



The steps in the hydroformylation reaction are closely related to those that occur in the Fischer-Tropsch process, which is the reductive conversion of carbon monoxide to alkanes and occurs by a repetitive series of carbonylation, migration, and reduction steps that can build up a hydrocarbon chain.

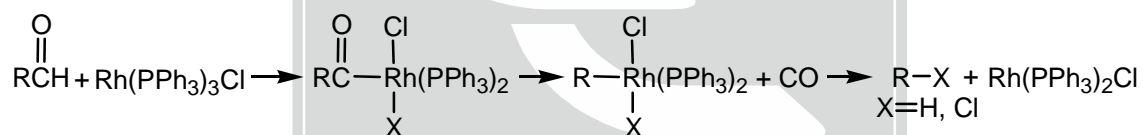


The Fischer-Tropsch process is of considerable economic interest because it is the basis of conversion of carbon monoxide to synthetic hydrocarbon fuels, and extensive work has been done on optimization of catalyst systems.

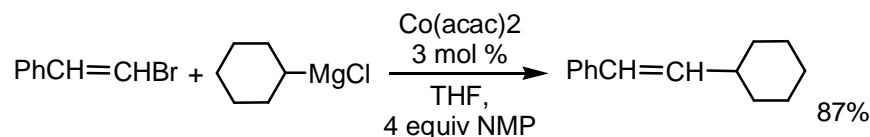
The carbonylation step that is involved in both hydroformylation and the Fischer-Tropsch reaction can be reversible. Under appropriate conditions, rhodium catalyst can be used for the decarbonylation of aldehydes and acyl chlorides.



An acylrhodium intermediate is involved in both cases. The elimination of the hydrocarbon or halide occurs by reductive elimination.



Although the very early studies of transition metal-catalyzed coupling of organometallic reagents included cobalt salts, the use of cobalt for synthetic purposes is quite limited. Vinyl bromide and iodides couple with Grignard reagents in good yield, but a good donor ligand such as NMP or DMPU is required as a cocatalyst.



Co(acac)<sub>2</sub> also catalyzes cross coupling of organozinc reagents under these conditions.

