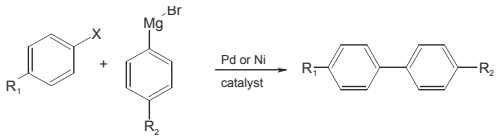
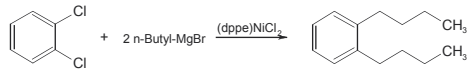
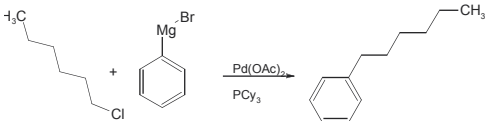
KUMADA-COUPLING [1,2,3]

Precious-Metal catalysts from Acros Organics for coupling reactions in organic synthesis (VI)





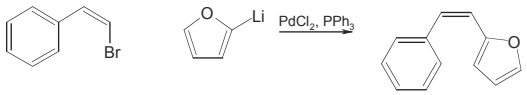


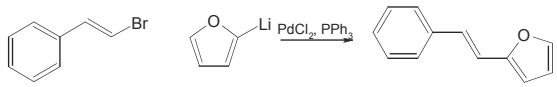
The Kumada-coupling is the nickel[4]- or palladium-catalysed reaction between aryl- and vinyl-halogenides or –triflates and aryl-, alkenyl- or alkyl- grignard-reagents[5,6]. Also heteroaryl-[7] and alkyl[8]-halides can be coupled with Grignard reagents.

The reactivity of the halogenides follows the order I > Br > Cl when Palladium is used as catalyst, whereas with certain nickel-catalysts the order is: Cl > I > Br[5].

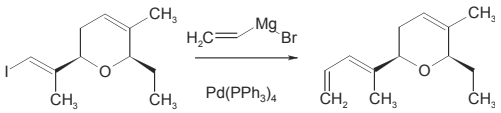
(Z)-Alkenyl-grignards couple non-stereospecific with nickel catalysts[2], but the reaction is stereospecific ("retention of configuration") with palladium-catalysts[9]. The phosphine-ligand has also a strong influence on the yield. Bidentate ligands generally bear a higher activity than monodentate phosphines. Bis(diphenylphosphino)propane (AO 31005) is optimal for most reactions[2].

The Kumada-coupling is somewhat limited because of the incompatibility of Grignard-reagents with certain functional groups[10].





Murahashi et al[11,12] have used numerous functionalized and non-functionalized organolithium compounds instead of Grignard-reagents for a Kumada-like coupling reaction.



In a recent example the Kumada coupling was used for an intermediate step in the total synthesis of (+)-Ambrucitin[13].

SOME CATALYSTS AND REAGENTS FROM ACROS ORGANICS FOR THE KUMADA COUPLING

Nickel & Palladium catalysts and Ligands

[1,3-Bis-Diphenylphosphino-propane] nickel(II)chloride, 99%	29159
Nickel acetylacetonate, 96%	12826
Bis(triphenylphosphine)nickel(II)chloride, 98%	21750
Tetrakis(triphenylphosphine)nickel(0), 95%	22398
[1,2-Bis-Diphenylphosphino-ethane] nickel (II) chloride	36323
Bis(triphenylphosphine)nickel(II)bromide, 99%	31632
Nickel(II) chloride hexahydrate, 99.9999%	19357
Nickel(II) chloride hexahydrate, p.a.	27051

1,2-Bis(dicyclohexylphosphino)ethane nickel(II) chloride	30116
1,1'-Bis-(diphenylphosphino)ferrocene	34801
1,2- Bis-(diphenylphosphino)ethane, 98+%	14791
1,3-Bis(diphenylphosphino)propane, 97%	31005
1,4-Bis-(diphenylphosphino)butane, 98%	29646
Bis(triphenylphosphine)palladium(II)chloride, 98%	29925
Tetrakis(triphenylphosphine)palladium(0), 99%	20238
1,1'-Bis(diphenylphosphino)ferrocene palladium(II)dichloride, complex with dichloromethane	34868

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