Transition Metal Catalysis – Catalytic Cycles

Topic	Cycle	Catalyst	Notes
Addition to Alkene	Hydrogenation $H_2C=CH_2 + H_2 \rightarrow H_3C-CH_3$	$RhCl(PPh_3)$ Wilkinson's Catalyst	• Phosphine ligands best • Fast turnover (bulky group – *dissociation*, good donor – *oxidative addition*)
	Hydrosilation $H_2C=CH_2 + HSiR_3 \rightarrow H_3C-CH_2SiR_3$	H_2PtCl_6	• Catalysed by whole range of catalysts • $HSiR_3$ – super proton • Forms linear products
	Hydrocyanation $H_2C=CH_2 + HCN \rightarrow H_3C-CH_2CN$	$Ni(P[O(o\text{-}tolyl)]_3$	• Strong donor phosphine's do not give turnover • Isomerise internal alkenes to give terminal products • Hydrocyanation of butadiene to give *adiponitrile*
	Hydroformylation $H_2C=CH_2 + CO + H_2 \rightarrow H_3C-CH_2CHO$	$HCo(CO)_4$ / $HRh(PPh_3)_2(CO)$	• Co: Harsh conditions, moderate selectivity, competitive hydrogenation • Rh: Mild conditions, excess phosphine needed for high selectivity
Carbonylation	Reppe / BASF	Cobalt-based	
	Monsanto $CH_3OH + CO \text{ –(HI)}\rightarrow CH_3COOH$	$[RhI_2CO_2]^-$ Rhodium-based	
	BP Cativa	Iridium-based	• Better than Rh at forming alkyl bond • Promoted by species such as $[Ru(CO)_3I_2]_2$
	Polyketone Formation	$[PdL_2(OR)]^+$	• Addition of alkene and CO to give polyketone

Coupling Reactions	Grignard RMgX	$Ni(acac)_2$ / $(dppe)NiCl_2$ / $FeCl_3$ / $CoCl_2$ / $CrCl_2$	
	Negishi RZnX	$(Ph_3P)_4Ni$ / $(Ph_3P)_2PdCl_2$	
	Stille $RSnR'_3$	$Pd(dba)_3$	• Make sure you have no beta-hydrogens • Me_3Sn best choice for control but $^tBu_3Sn$ much safer • Tin compounds toxic • Aided by bulky ligands and highly basic additives (CsF)
	Sonogashira Cu-C≡C-R	$(MeCN)_2PdCl_2$	• Base required to remove HX liberated
	Mizoroki-Heck H_2C=CHR	PdL_n Pd(0) or Pd(II)	• Coupling of an aryl halide with an alkene
Carbenes	Fisher	$M=CH_2X$ X = Heteroatom	• Metal in low oxidation state • Back-bonding present • Oxidation state (-2)
	Schrock	$M=CH_2R$ R = Hydrogen or Carbon *Alkylidene*	• Metal in high oxidation state • Back-bonding present • Oxidation state (-2)
	Nucleophillic	R_2C: Free carbene	• Introduced using lone pair (like phosphines) • Stabilised by heteroatom substituents ie Nitrogen • No Back-bonding present • Neutral so oxidation state (0)

Metathesis	Schrock's	$Mo(=CHCMe_2Ph)(=NAr)(-OR)_2$	• Highly active • React with hindered alkenes • Control reactivity by altering alkoxide groups • Poor functional group tolerance
	Grubb's	$RuCl_2(PCy_3)_2(=CHPh)$ $RuCl_2(PCy_3)(:C(NR_2)_2)(=CHPh)$ $RuCl_2(NR_2)_2(:C(NR_2)_2)(=CHPh)$	• Undergo the Chauvin mechanism
Alkene Polymerisation	Ziegler	$TiCl_4$	• Activated by $AlEt_3$ • Mild conditions • Controlled process – yields isotatic, high density • Undergoes Cossee-Arlman Mechanism
	Metallocene	$MCl_2(Cp)_2$ Co-catalyst: $AlClR_2$	• Weak co-catalyst to pull off Cl
		$MCl_2(Cp)_2$ Co-catalyst: MAO	• Strong co-catalyst to pull off Cl • Scavenges water
		$MR_2(Cp)_2$ Co-catalyst: $[CPh_3][B(C_6F_5)_4]$	• Triphenylcarbenum (Trityl) salts • $[Ph_3C]^+$ powerfull alkyl abstractor