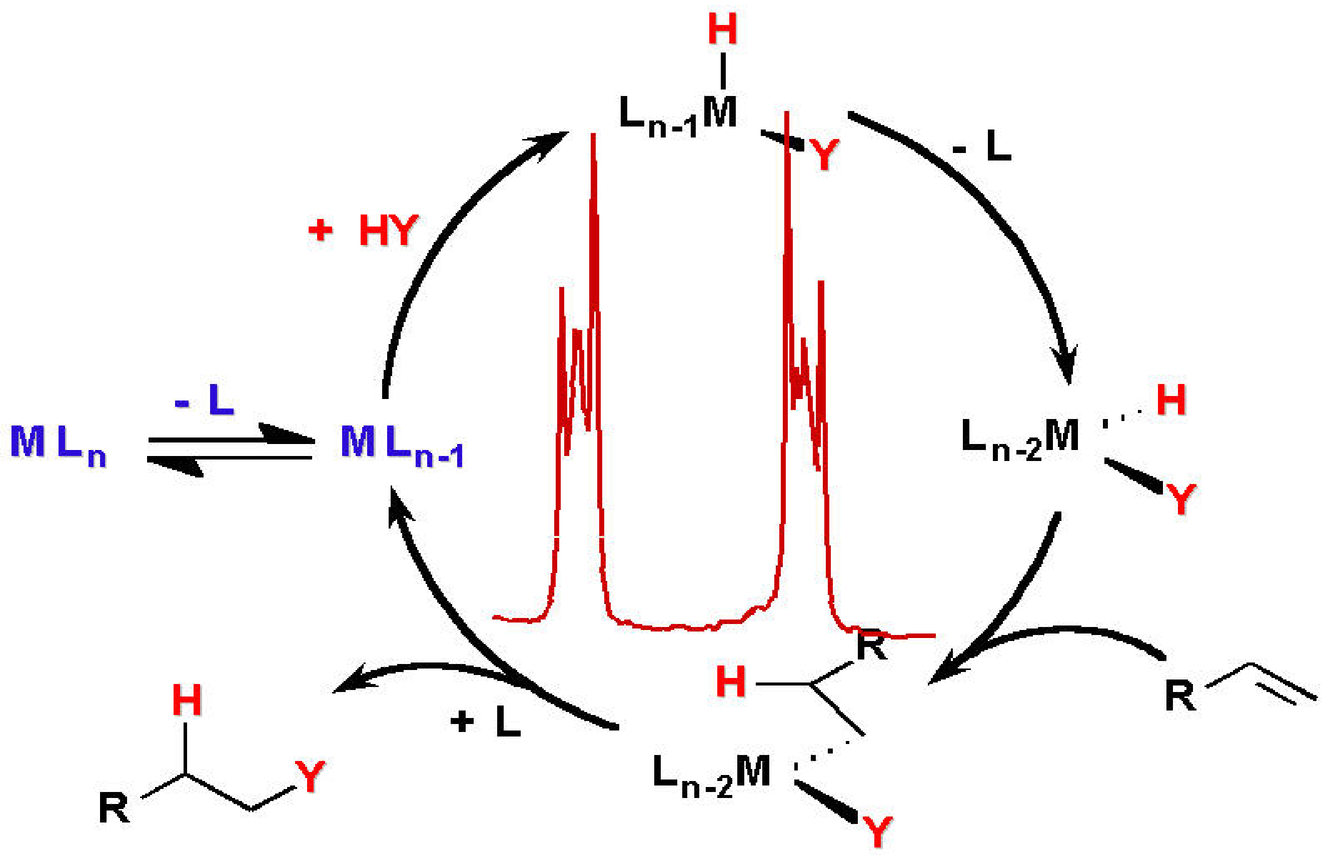
Inorganic Chemistry
6H290



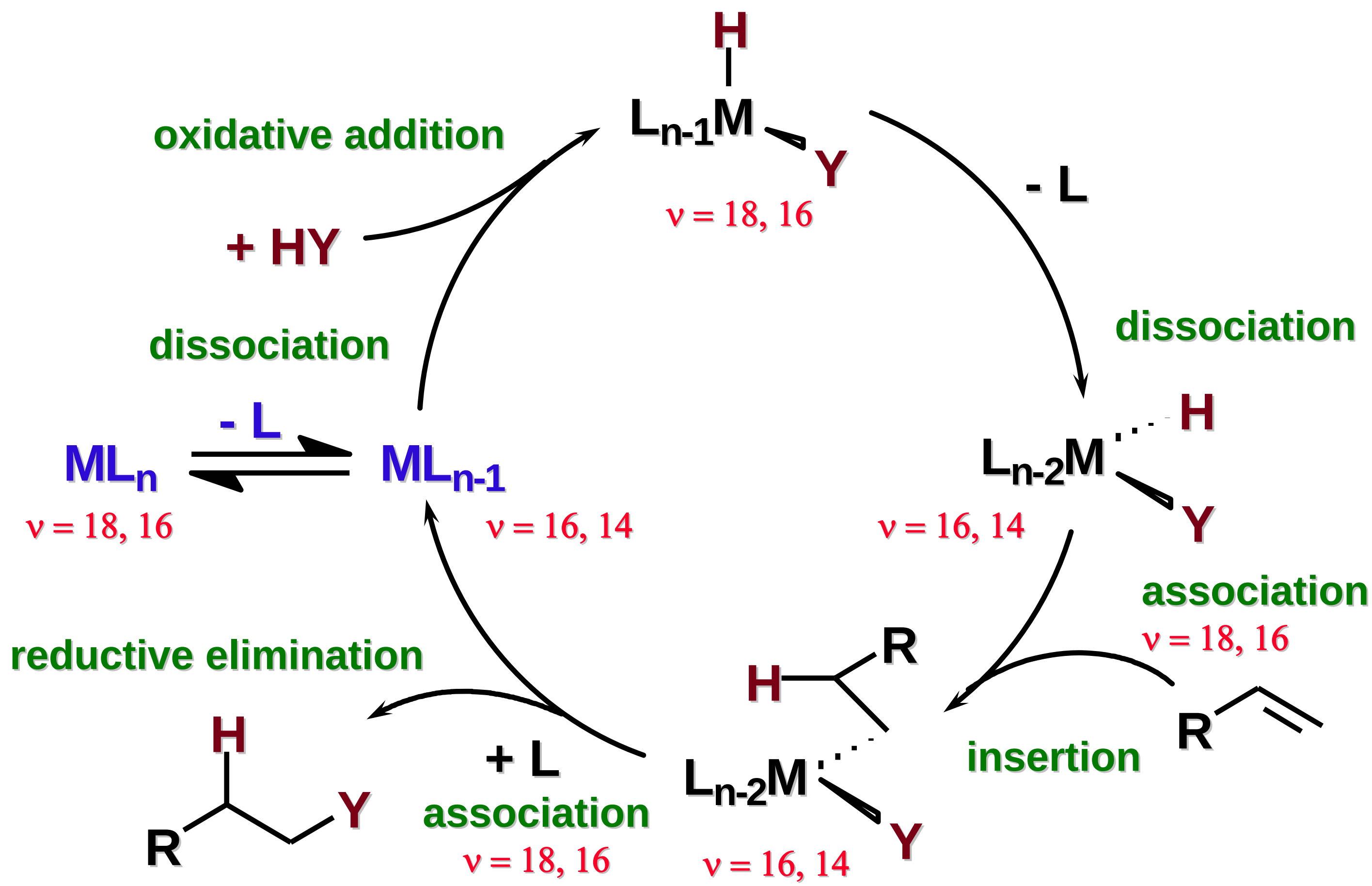
Catalysis
Woe, 05-11-2008, H27

Comparison of Catalytic Principles

Advantages and disadvantages of heterogeneous, homogeneous, and bio catalysis

	heterogeneous	homogeneous	biocatalysis
Conditions	generally harsh	mild	mild
Activity	changing	high	i.g. very high
Selectivity	changing	high	i.g. very high
Catalyst life-time	high	changing	i.g. low
Catalyst recycling	solved	expensive	expensive
Sensitivity agains poisons	high	low	high
Diffusion problems	possible	none	only whole cells
Mechanistic understanding	low	medium to good	medium

Catalytic Cycle and Elementary Steps



- Most elementary steps have been discussed in chapter 24 (reaction mechanisms)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.00794(7)																		helium 2 He 4.002602(2)
lithium 3 Li 6.941(2)	beryllium 4 Be 9.012182(3)												boron 5 B 10.811(7)	carbon 6 C 12.0107(8)	nitrogen 7 N 14.00674(7)	oxygen 8 O 15.9994(3)	fluorine 9 F 18.9984032(5)	neon 10 Ne 20.1797(6)
sodium 11 Na 22.989770(2)	magnesium 12 Mg 24.3050(6)												aluminium 13 Al 26.981538(2)	silicon 14 Si 28.0855(3)	phosphorus 15 P 30.973761(2)	sulfur 16 S 32.066(6)	chlorine 17 Cl 35.4527(9)	argon 18 Ar 39.948(1)
potassium 19 K 39.0983(1)	calcium 20 Ca 40.078(4)		scandium 21 Sc [illegible]	titanium 22 Ti [illegible]	vanadium 23 V [illegible]	chromium 24 Cr [illegible]	manganese 25 Mn [illegible]	iron 26 Fe [illegible]	cobalt 27 Co [illegible]	nickel 28 Ni [illegible]	copper 29 Cu [illegible]	zinc 30 Zn 65.39(2)	gallium 31 Ga 69.723(1)	germanium 32 Ge 72.61(2)	arsenic 33 As 74.92160(2)	selenium 34 Se 78.96(3)	bromine 35 Br 79.904(1)	krypton 36 Kr 83.80(1)
rubidium 37 Rb 85.4678(3)	strontium 38 Sr 87.62(1)		yttrium 39 Y [illegible]	zirconium 40 Zr [illegible]	niobium 41 Nb [illegible]	molybdenum 42 Mo [illegible]	technetium 43 Tc [illegible]	ruthenium 44 Ru [illegible]	rhodium 45 Rh [illegible]	palladium 46 Pd [illegible]	silver 47 Ag [illegible]	cadmium 48 Cd 112.411(8)	indium 49 In 114.818(3)	tin 50 Sn 118.710(7)	antimony 51 Sb 121.760(1)	tellurium 52 Te 127.60(3)	iodine 53 I 126.90447(3)	xenon 54 Xe 131.29(2)
caesium 55 Cs 132.90545(2)	barium 56 Ba 137.327(7)	57-70 *	lutetium 71 Lu [illegible]	hafnium 72 Hf [illegible]	tantalum 73 Ta [illegible]	tungsten 74 W [illegible]	rhenium 75 Re [illegible]	osmium 76 Os [illegible]	iridium 77 Ir [illegible]	platinum 78 Pt [illegible]	gold 79 Au [illegible]	mercury 80 Hg 200.59(2)	thallium 81 Tl 204.3833(2)	lead 82 Pb 207.2(1)	bismuth 83 Bi 208.98038(2)	polonium 84 Po [208.9824]	astatine 85 At [209.9871]	radon 86 Rn [222.0176]
francium 87 Fr [223.0197]	radium 88 Ra [226.0254]	89-102 **	lawrencium 103 Lr [illegible]	rutherfordium 104 Rf [illegible]	dubnium 105 Db [illegible]	seaborgium 106 Sg [illegible]	bohrium 107 Bh [illegible]	hassium 108 Hs [illegible]	meitnerium 109 Mt [illegible]	ununnilium 110 Uun [illegible]	unununium 111 Uuu [illegible]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]		ununhexium 116 Uuh [289]		ununoctium 118 Uuo [293]

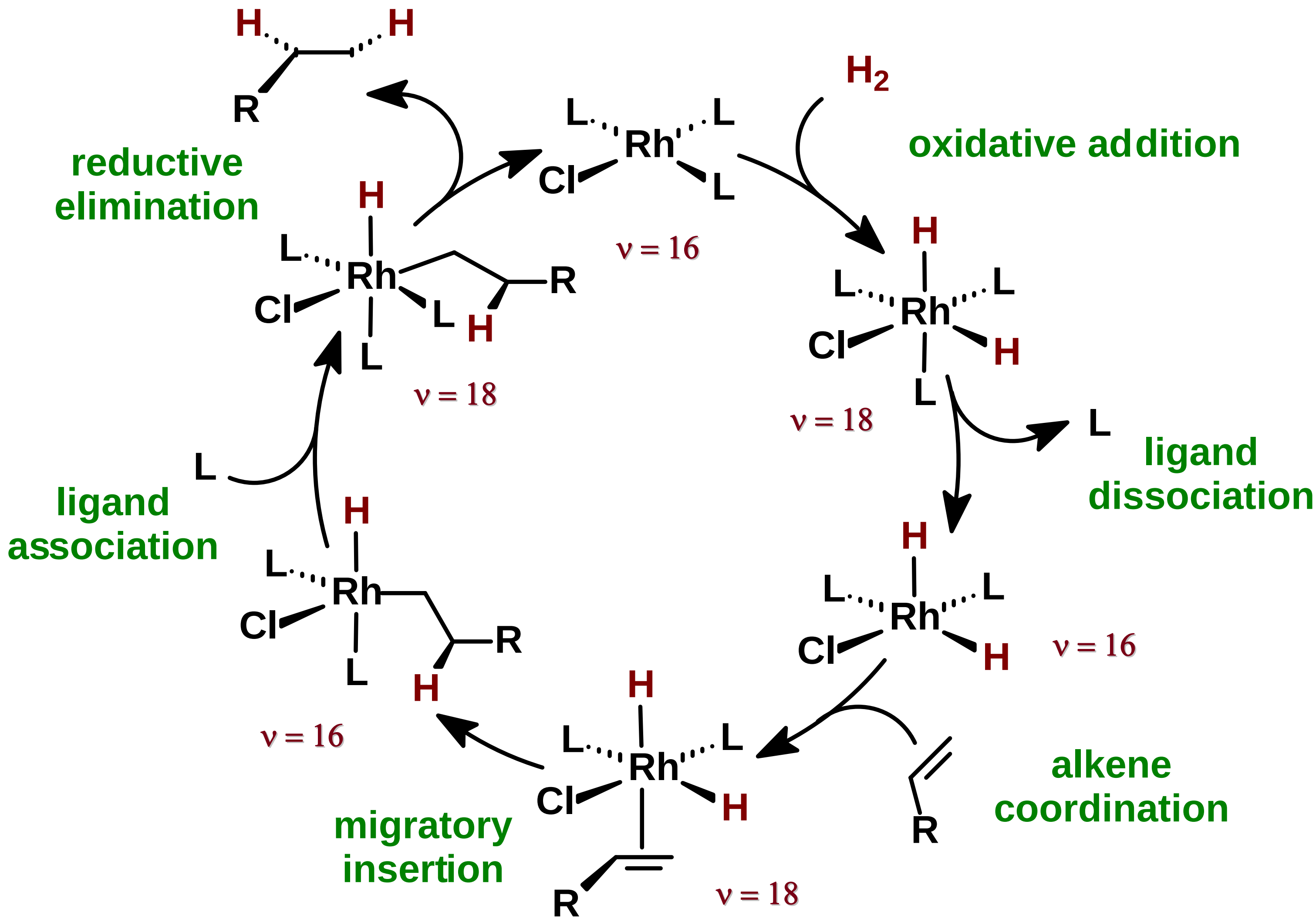
Key:

element name atomic number symbol 1997 atomic weight (mean relative mass)

*lanthanoids	lanthanum 57 La [illegible]	cerium 58 Ce [illegible]	praseodymium 59 Pr [illegible]	neodymium 60 Nd [illegible]	promethium 61 Pm [illegible]	samarium 62 Sm [illegible]	europium 63 Eu [illegible]	gadolinium 64 Gd [illegible]	terbium 65 Tb [illegible]	dysprosium 66 Dy [illegible]	holmium 67 Ho [illegible]	erbium 68 Er [illegible]	thulium 69 Tm [illegible]	ytterbium 70 Yb [illegible]
**actinoids	actinium 89 Ac [illegible]	thorium 90 Th [illegible]	protactinium 91 Pa [illegible]	uranium 92 U [illegible]	neptunium 93 Np [illegible]	plutonium 94 Pu [illegible]	americium 95 Am [illegible]	curium 96 Cm [illegible]	berkelium 97 Bk [illegible]	californium 98 Cf [illegible]	einsteinium 99 Es [illegible]	fermium 100 Fm [illegible]	mendelevium 101 Md [illegible]	nobelium 102 No [illegible]

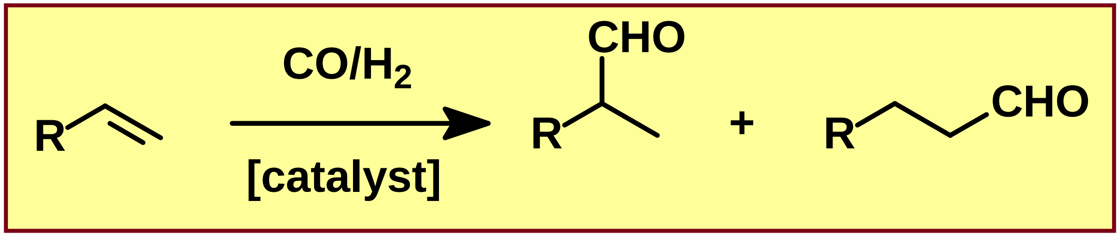
- **electron deficiency compounds**
- **ionic compounds**
- **d-metals, M-C σ-bonding and π-bonding**
- **covalent M-C σ-bonding**
- **metalloids**
- **non-metals**

Homogeneous Hydrogenation



- H_2 activation is the rate limiting step

Hydroformylation



- The hydroformylation reaction was found by O. Roelen in 1938 during his work on Fischer-Tropsch synthesis

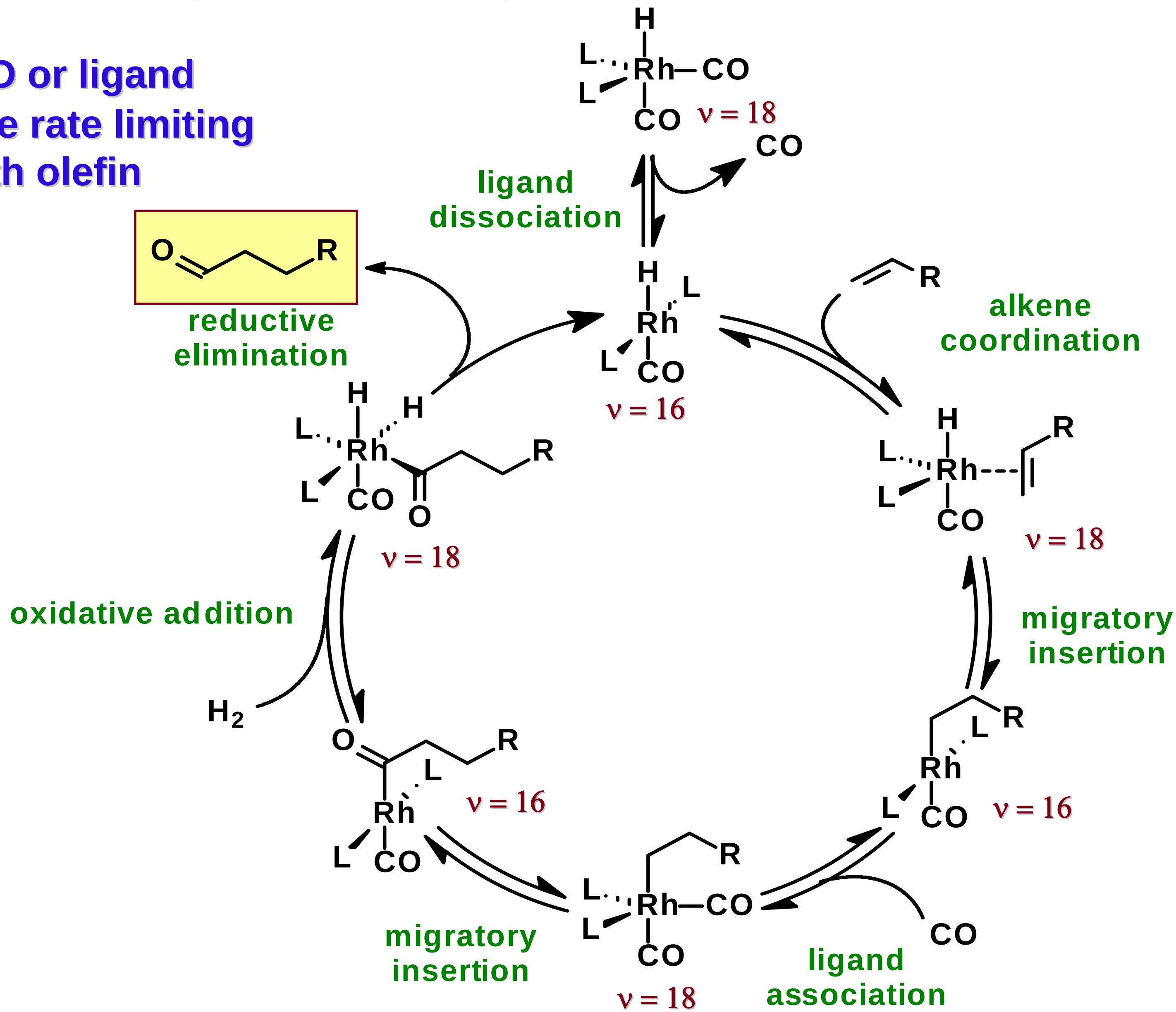
- Very important reaction for the production of softeners for plastics and detergent alcohols.

- Bulky substituents increase the linearity of the product.

- Acceptor ligands increase the rate of the reaction by accelerating ligand and CO dissociation and olefin coordination.

Hydroformylation

- In most cases CO or ligand dissociation is the rate limiting step, together with olefin coordination.



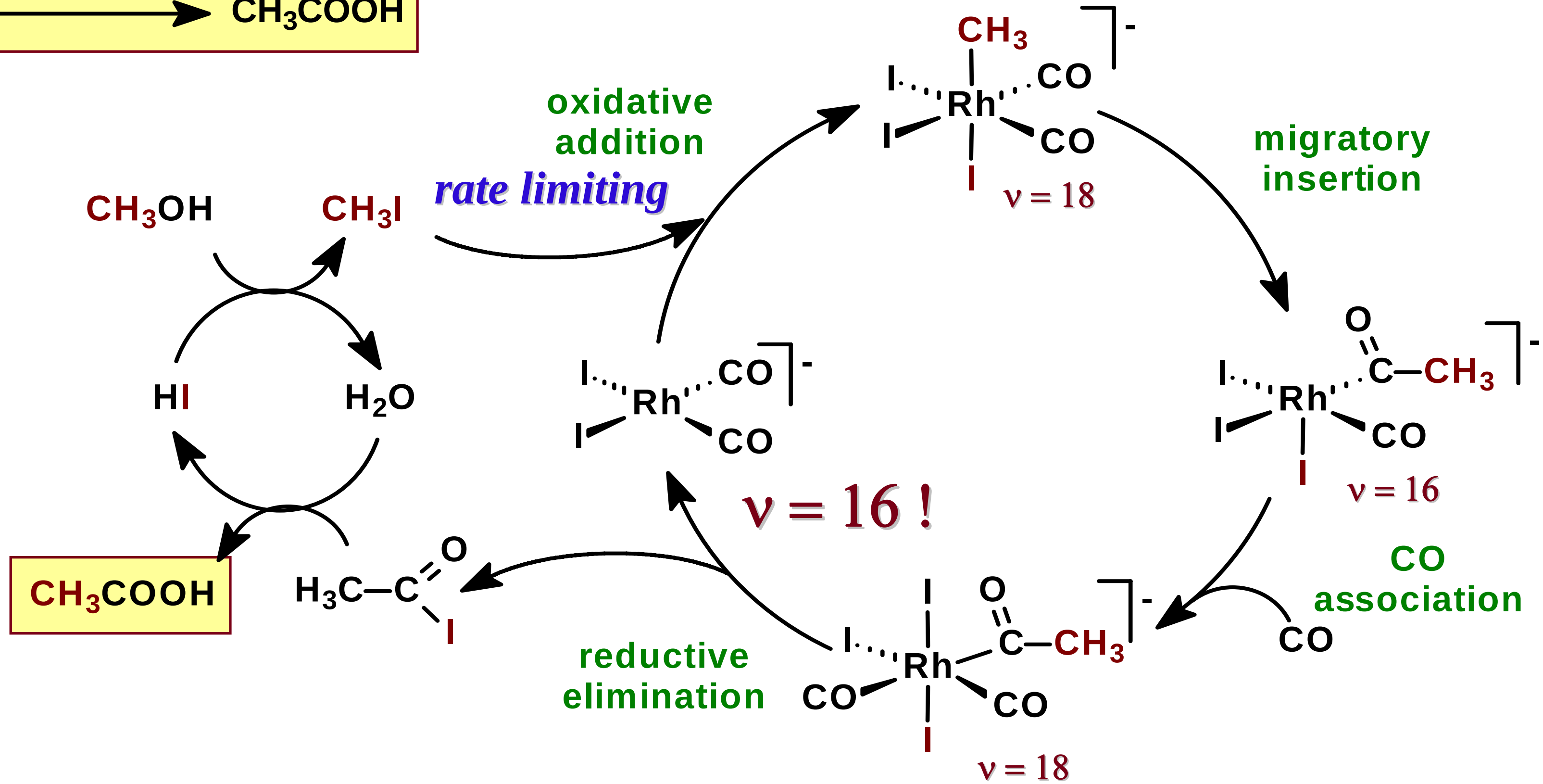
Type I rate law:

$$r = \frac{A[\text{alkene}][\text{Rh}]}{B + [L]}$$

Monsanto Acetic Acid Process

Carbonylation of Methanol

$$CH_3OH + CO \xrightarrow{[RhI_2(CO)_2]^-} CH_3COOH$$

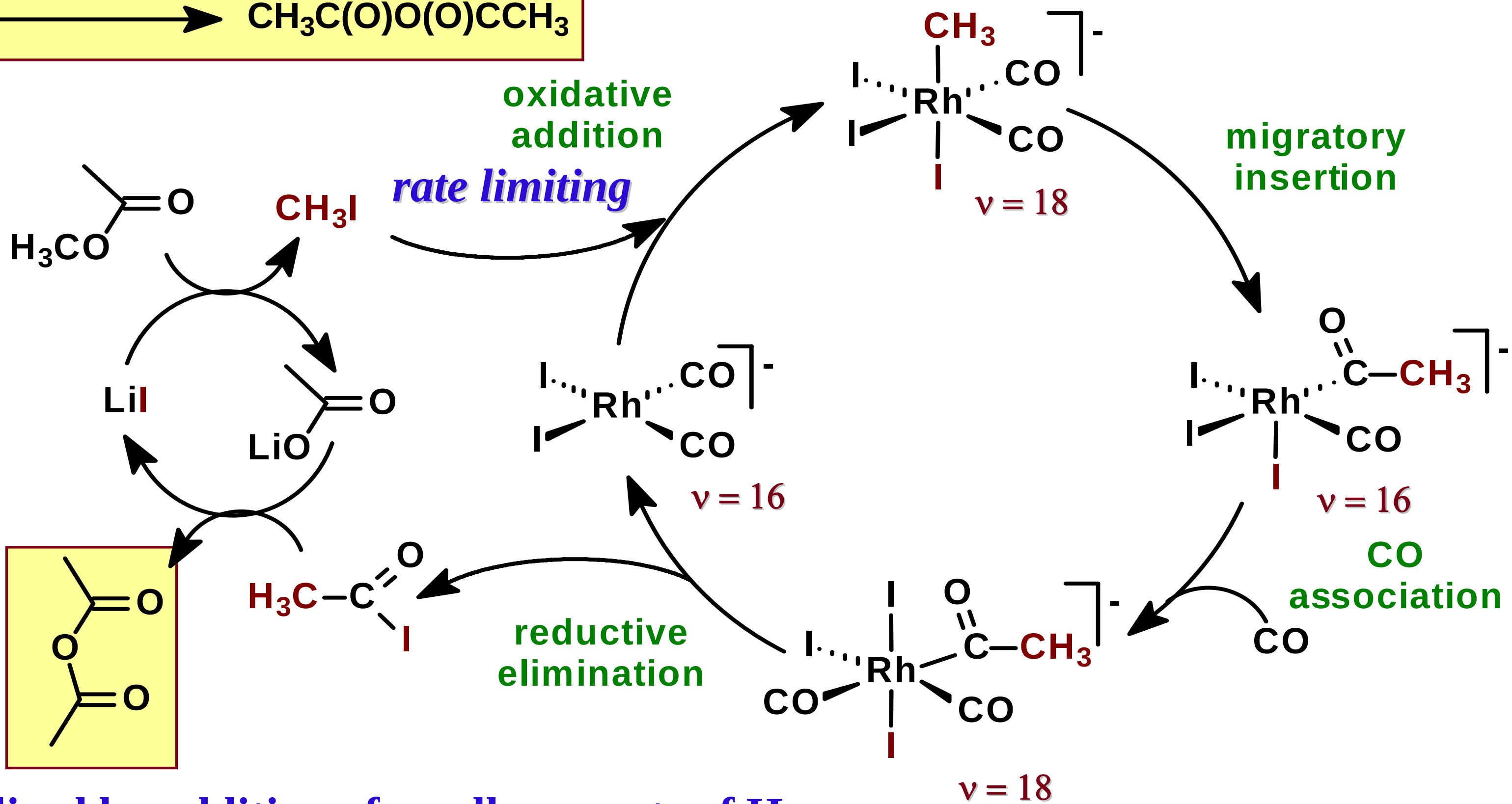


- **Currently ~ 3.5 Mt/a produced worldwide, 60% of all acetyl compounds based on this process.**
- **New BP process uses $[IrI_2(CO)_2]^-$ with $Ru_2(CO)_6I_2(\mu\text{-}I)_2$ as cocatalyst**

Tennessee-Eastman, Acetic Anhydride

Carbonylation of Methyl Acetate

$$H_3CC(O)OCH_3 + CO \xrightarrow{[RhI_2(CO)_2]^-} CH_3C(O)O(O)CCH_3$$



- Catalyst is stabilized by addition of small amounts of H_2.

$$[Rh(CO)_2I_2]^- + 2\,HI \longrightarrow [Rh(CO)_2I_4]^- + H_2$$

$$[Rh(CO)_2I_4]^- \longrightarrow RhI_3\,(sol) + 2\,CO + I^-$$

- Process conditions are highly corrosive! => Expensive Hastelloy must be used.

Direct Oxidation of Ethene

Wacker Process

$$C_2H_4 + 1/2\ O_2 \xrightarrow{[Pd^{(0)}/\ Cu^{(II)}]} CH_3CHO$$

- An important feature is that the oxygen atom in the product acetaldehyde stems from water by nucleophilic attack of the coordinated olefin.

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow H_3CCHO + Pd^{(0)} + 2\ HCl$$

- The whole process only becomes catalytic by the re-oxidation of $Pd^{(0)}$ with $Cu^{(II)}$.

$$Pd^{(0)} + 2\ [CuCl_4]^{2-} \longrightarrow [PdCl_4]^{2-} + 2\ [CuCl_2]^{-}$$

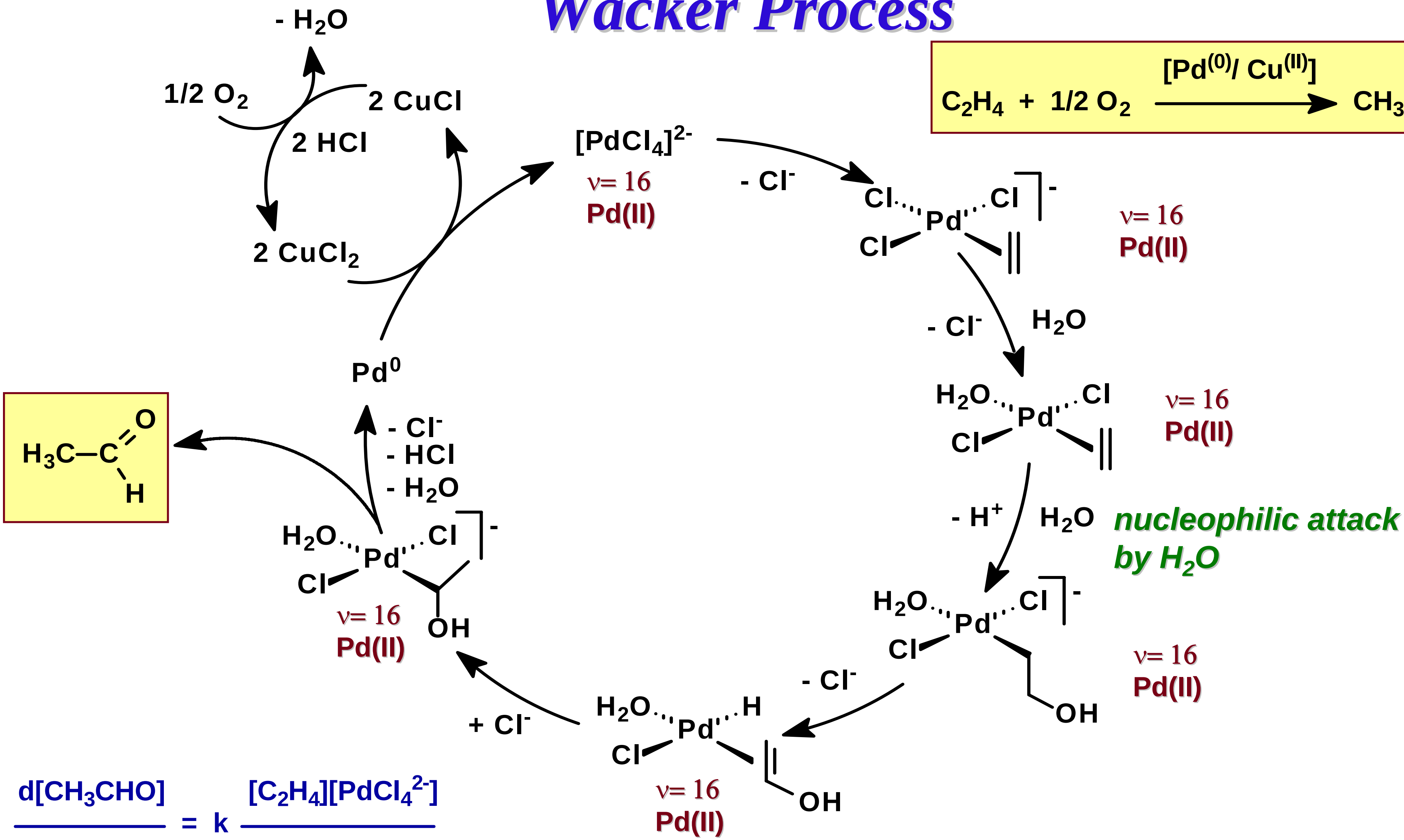
$$2\ [CuCl_2]^{-} + 1/2\ O_2 + 2\ HCl \longrightarrow 2\ CuCl_2 + 2\ Cl^{-} + H_2O$$

- Behalf of ethene, all other olefins give the corresponding ketone in the Wacker oxidation.
- Substitution of water is possible (e.g. by CH_3COOH), giving rise to other products.

Direct Oxidation of Ethene

Wacker Process

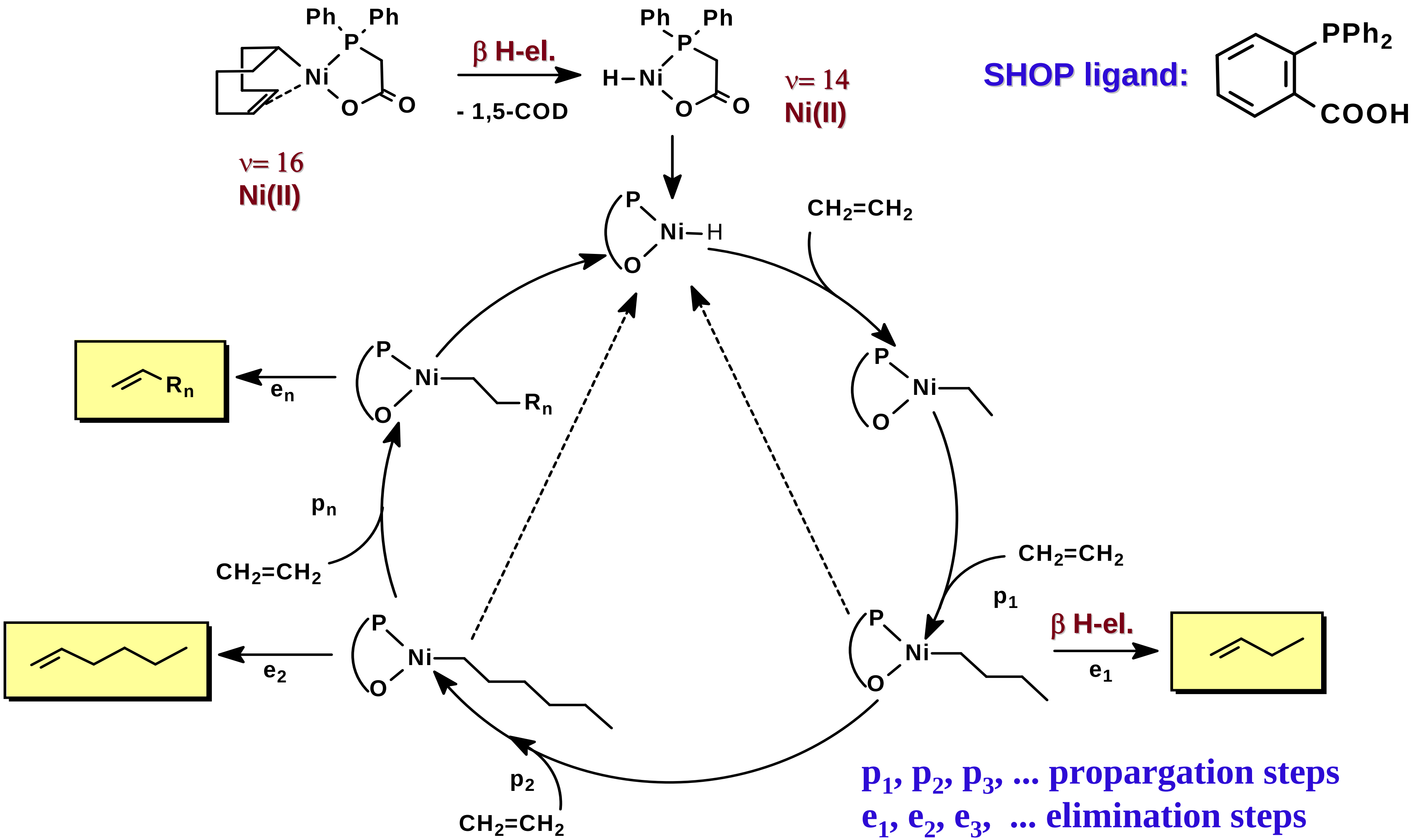
$$C_2H_4 + 1/2\ O_2 \xrightarrow{[Pd^{(0)}/\ Cu^{(II)}]} CH_3CHO$$



$$\frac{d[CH_3CHO]}{dt} = k\,\frac{[C_2H_4][PdCl_4^{2-}]}{[H^+][Cl^-]^2}$$

Ethene Oligomerization

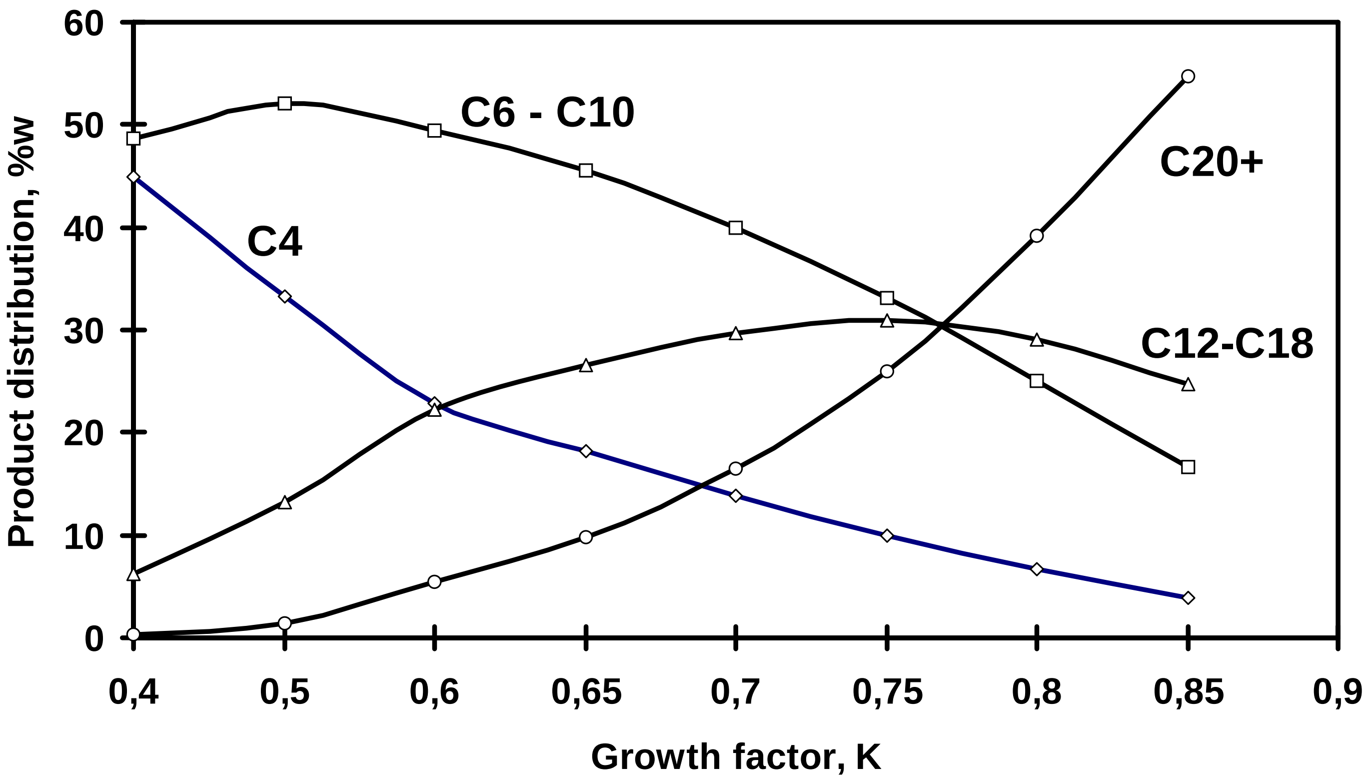
Shell Higher Olefin Process (SHOP)



p_1, p_2, p_3, ... propargation steps

e_1, e_2, e_3, ... elimination steps

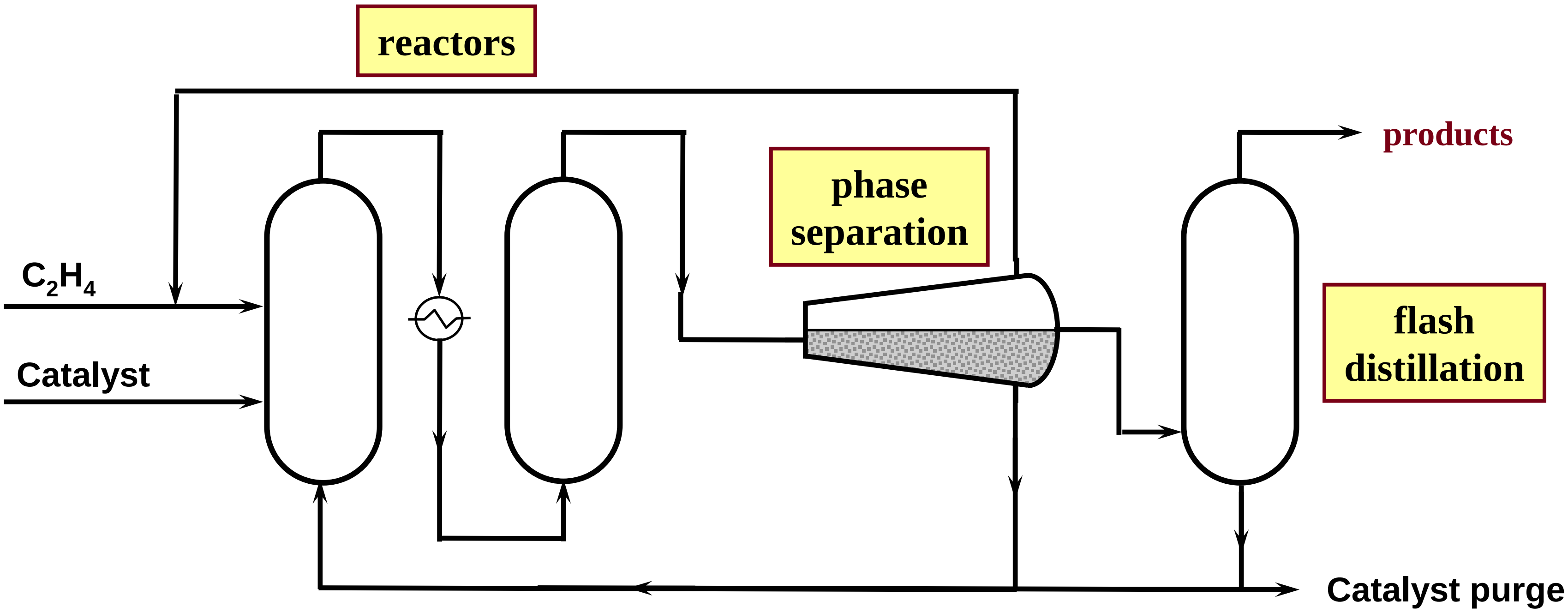
Shell Higher Olefin Process (SHOP) Product Distribution



- **The chain length of the α-olefins is determined by the geometric factor *K* of molar growth**

$$K = \frac{n\left(C_{n+2} - \text{olefins}\right)}{n\left(C_n - \text{olefins}\right)}$$

Shell Higher Olefin Process (SHOP)



- The catalyst complex is soluble in butanediol-1,3
- Shell's higher olefin process was the first example using a two-phase catalyst separation.
- 98% linear α-olefins are obtained as important intermediates for low density polyolefins and detergents.

Alkene Polymerization

- The metal catalyzed coordination polymerization of elkenes was developed by Ziegler and Natta

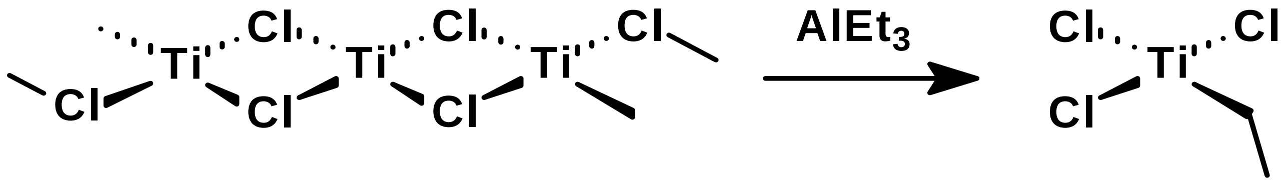
➢ Early catalysts derived from $TiCl_4$ and an alkylating agent, e.g. $AlEt_3$

$$TiCl_4 + AlEt_2Cl \longrightarrow TiCl_3 * 0.15\ AlCl_3 * 0.2\ AlEtCl_2$$

brown β-$TiCl_3$

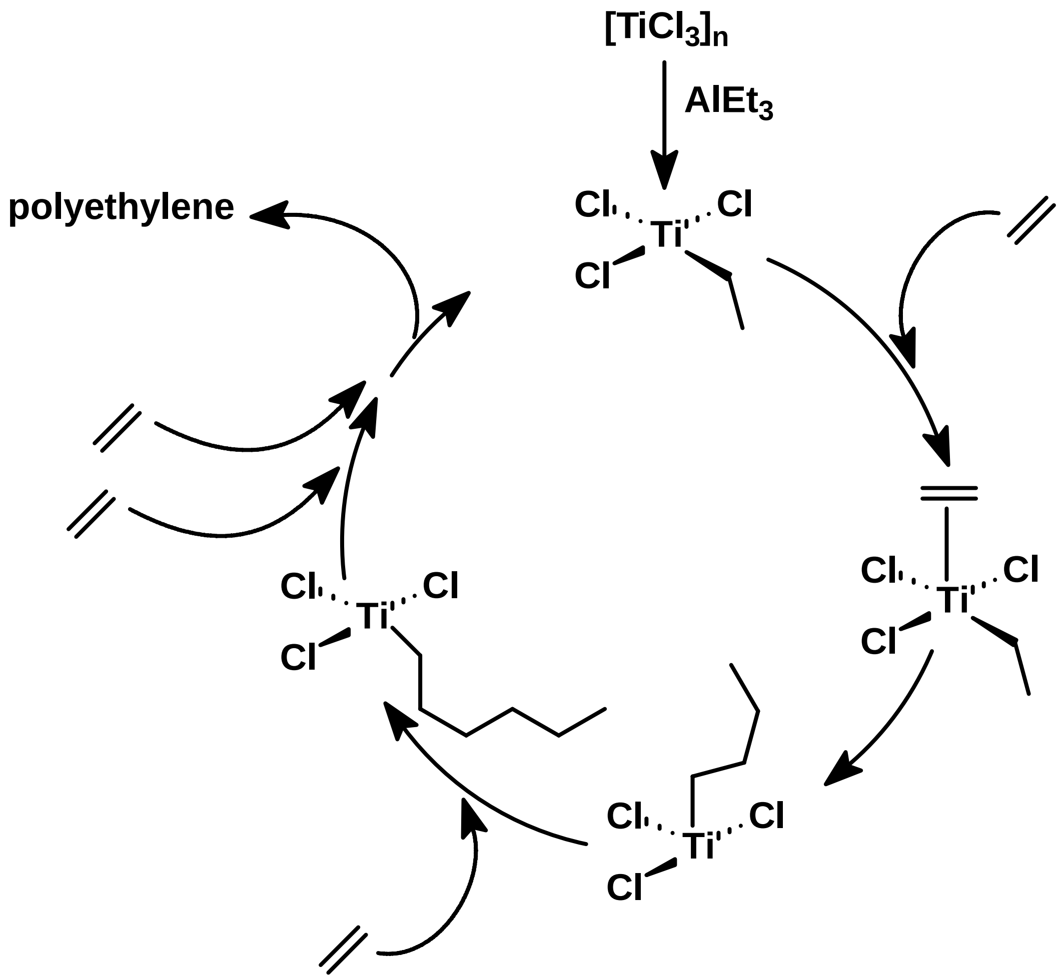
➢ Washing, followed by warming converts it to the active polymeric purple δ-$TiCl_3$

➢ Final activation by alkylation gives the active catalyst



Alkene Polymerization

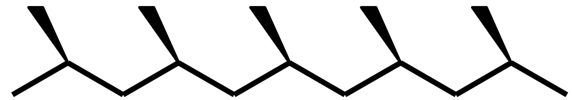
- Cossee - Arlman Mechanism



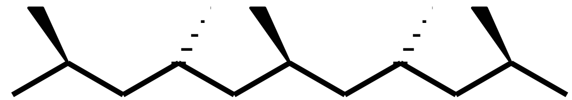
Configuration of Polymers

Tacticity

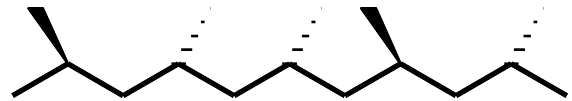
isotactic



syndiotactic



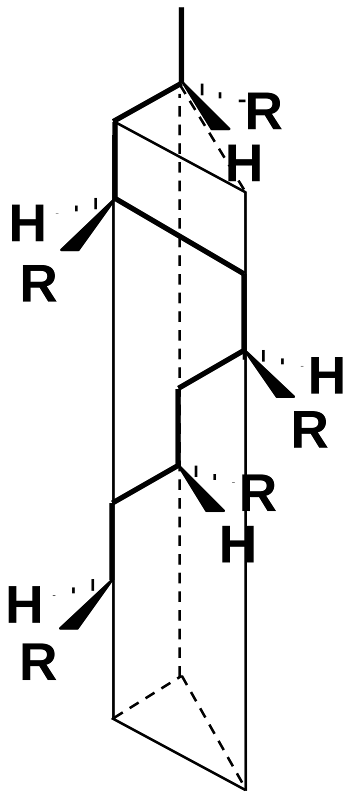
atactic



cis- and *trans*-tacticity

Conformation of Polymers

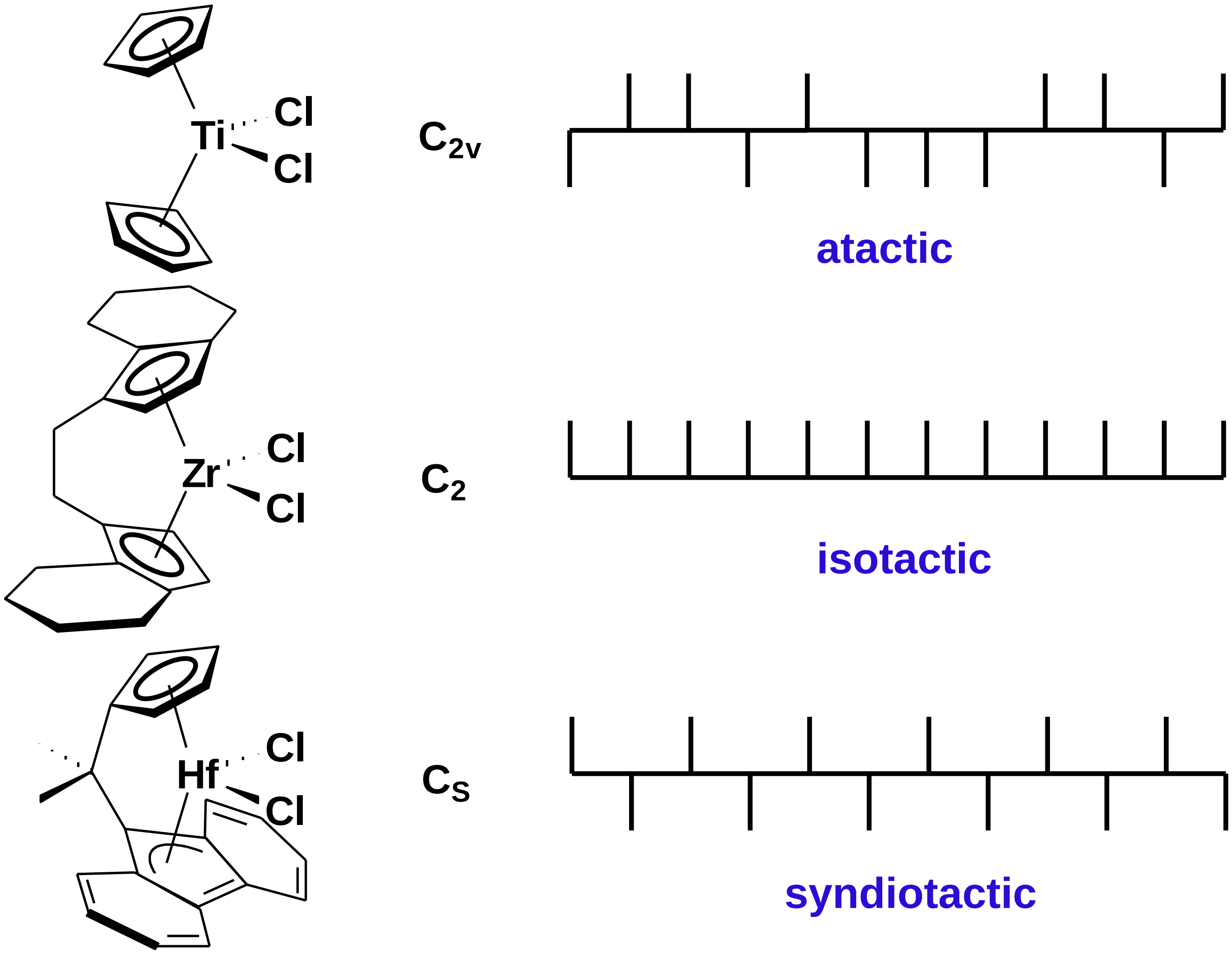
- Spacial arrangement of the polymer chain



e.g. for isotactic polypropylene

3/1-helix, 3 monomer units in 1 turn

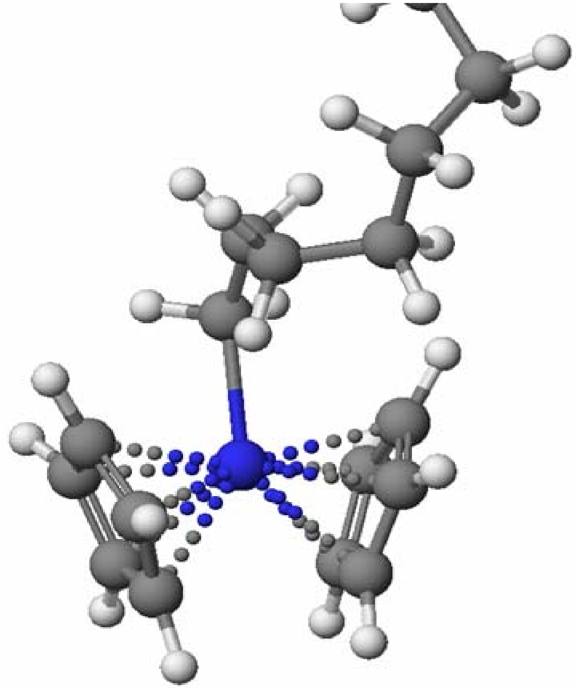
Selective Polymerization of Propene



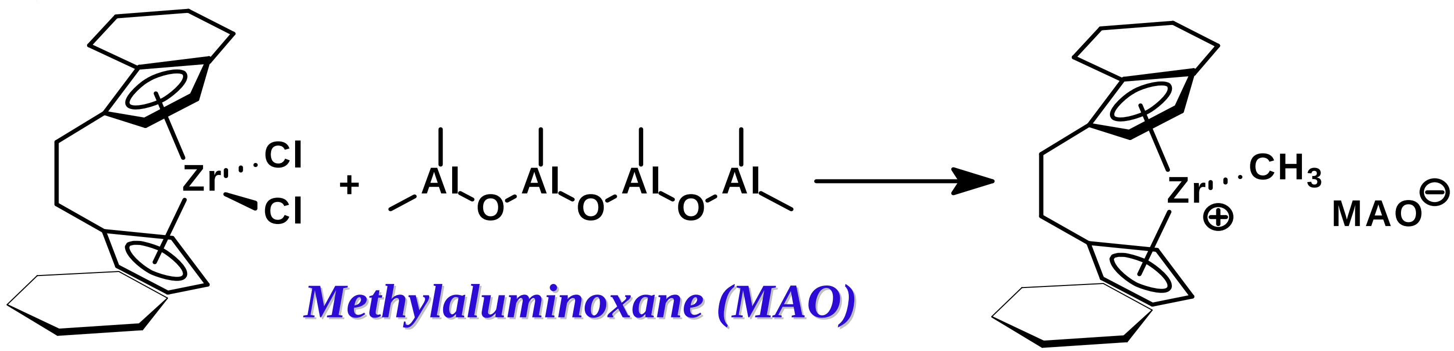
W. Kaminsky, M. Arndt in *Appl. Homog. Catal. with Organomet. Comp.* (Eds.: B. Cornils, W. A. Herrmann) Vol. 1, VCH **1996**, pp. 220-236.

Alkene Polymerization

Fliping Mechanism for Metallocenes

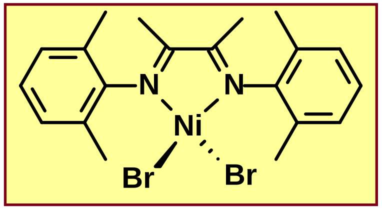


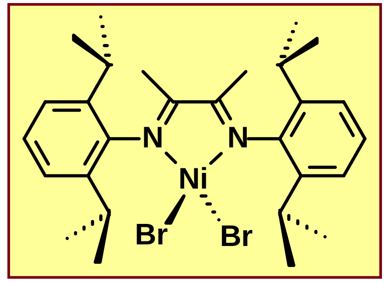
- **catalyst activation**

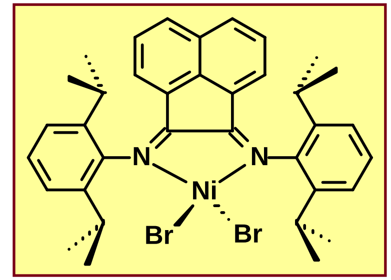


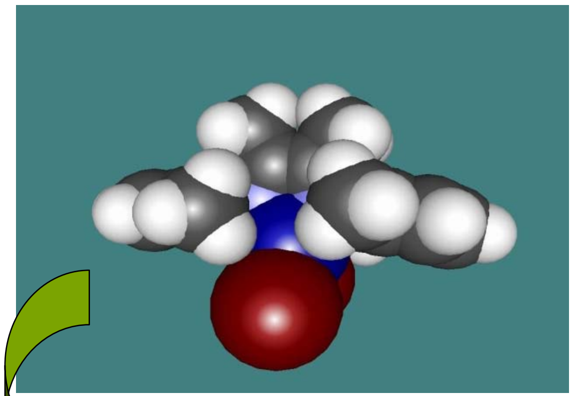
Methylaluminoxane (MAO)

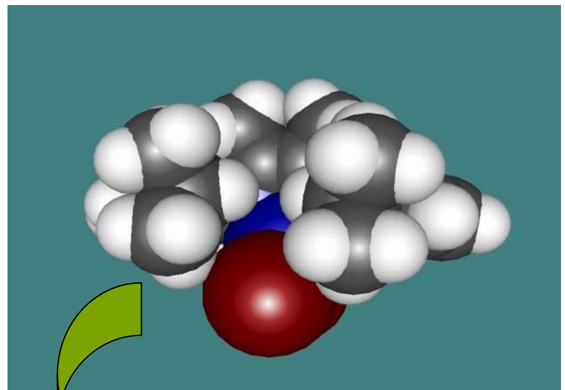
Polyethylene with Designer Catalysts

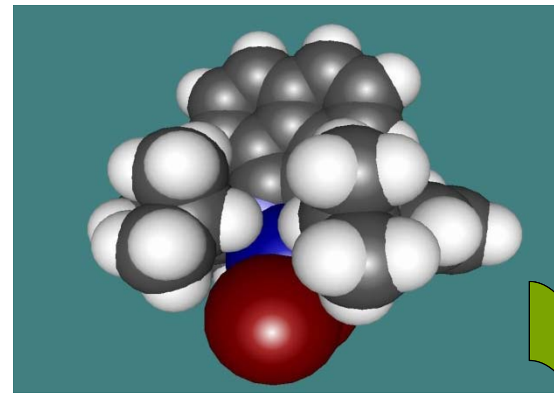


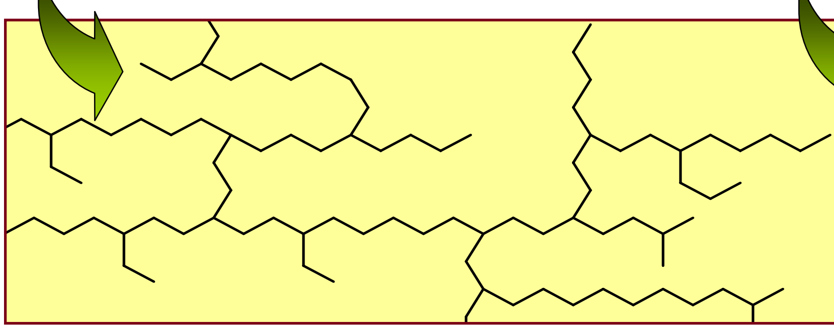






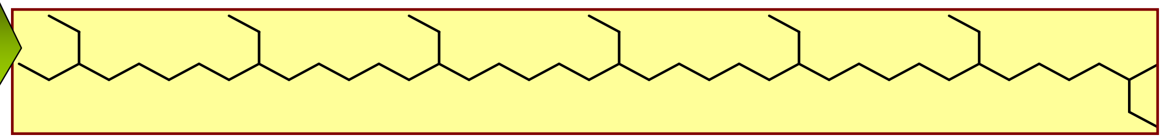






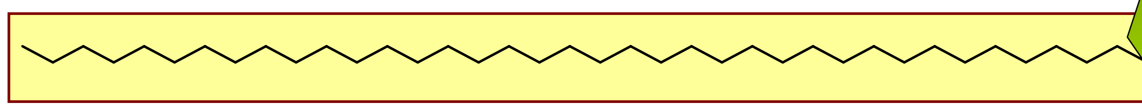
highly branched polymer

=> rubber



polymer with short chain branches

=> soft, films



highly linear polymer

=> hard, fibers

Inorganic Chemistry 6BA40
Slides available:
http://www.hybridcatalysis.com/teachingcorner.htm