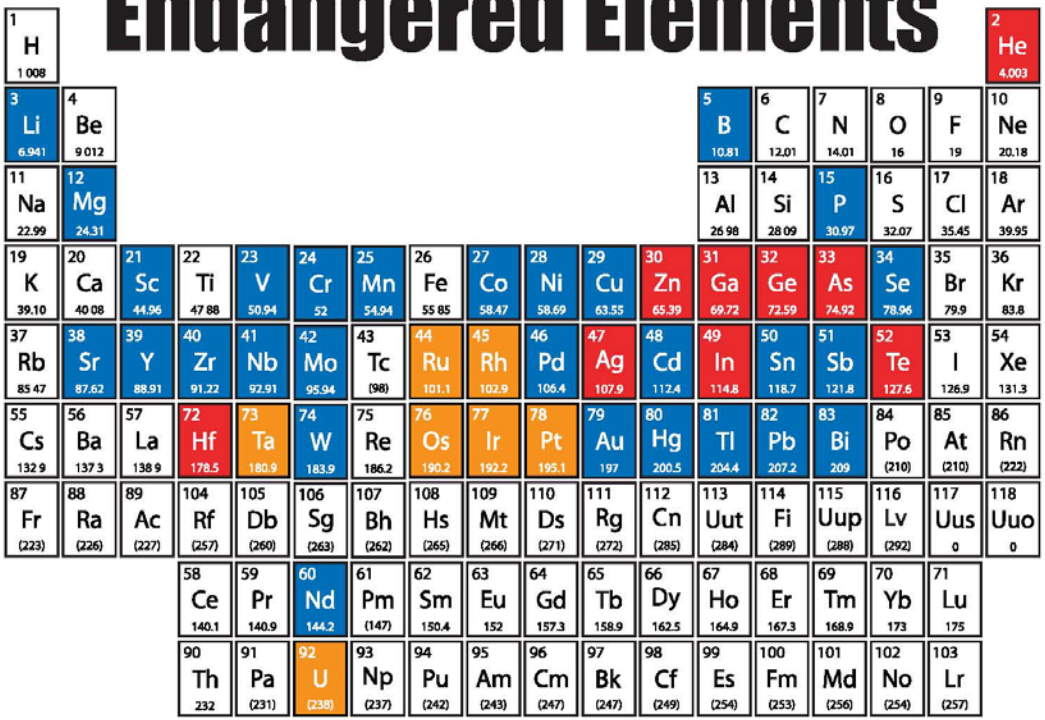
TEXAS A&M UNIVERSITY

Endangered Elements



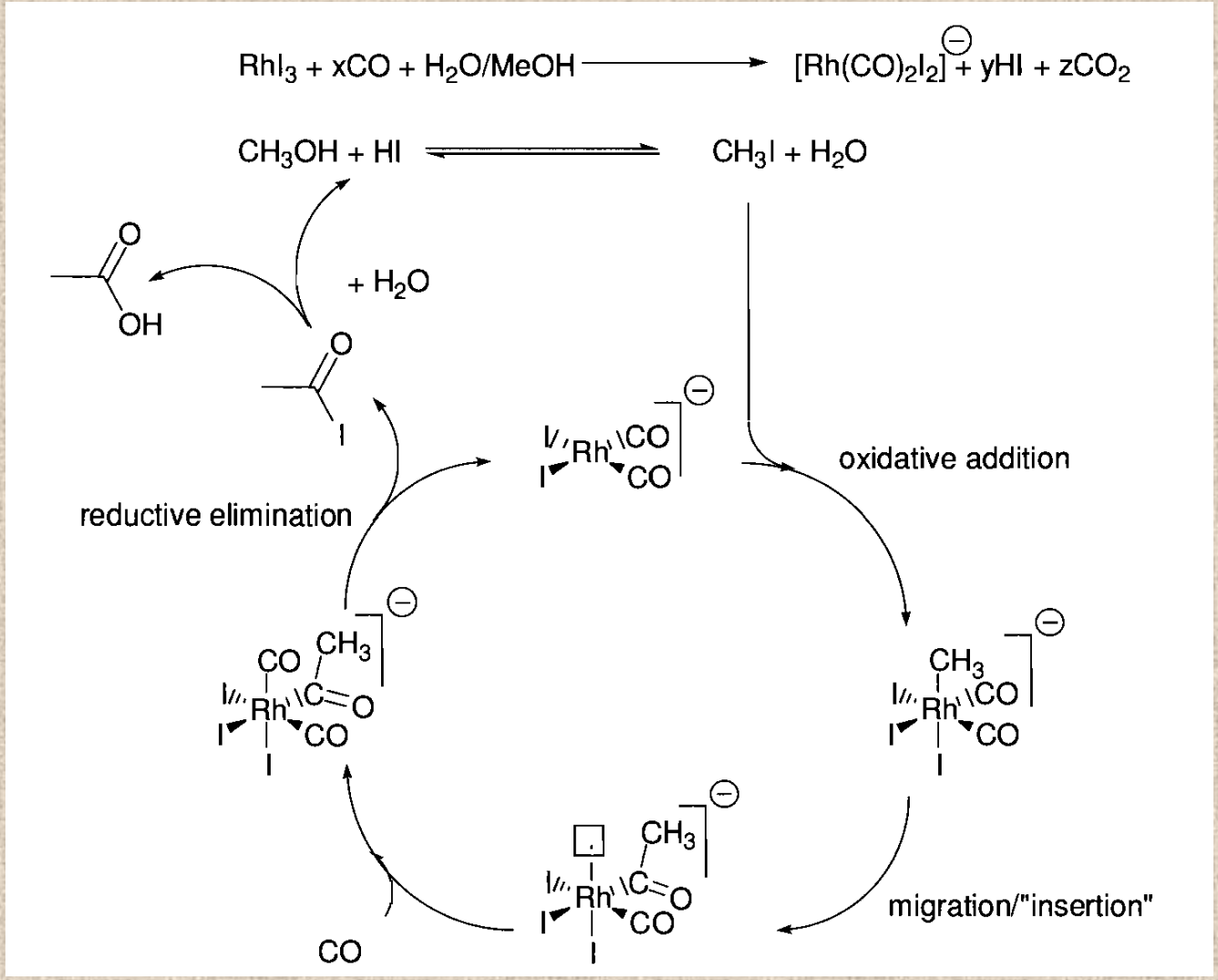
SOURCE: CHEMISTRY INNOVATION KNOWLEDGE TRANSFER NETWORK

ACS Chemistry for Life®

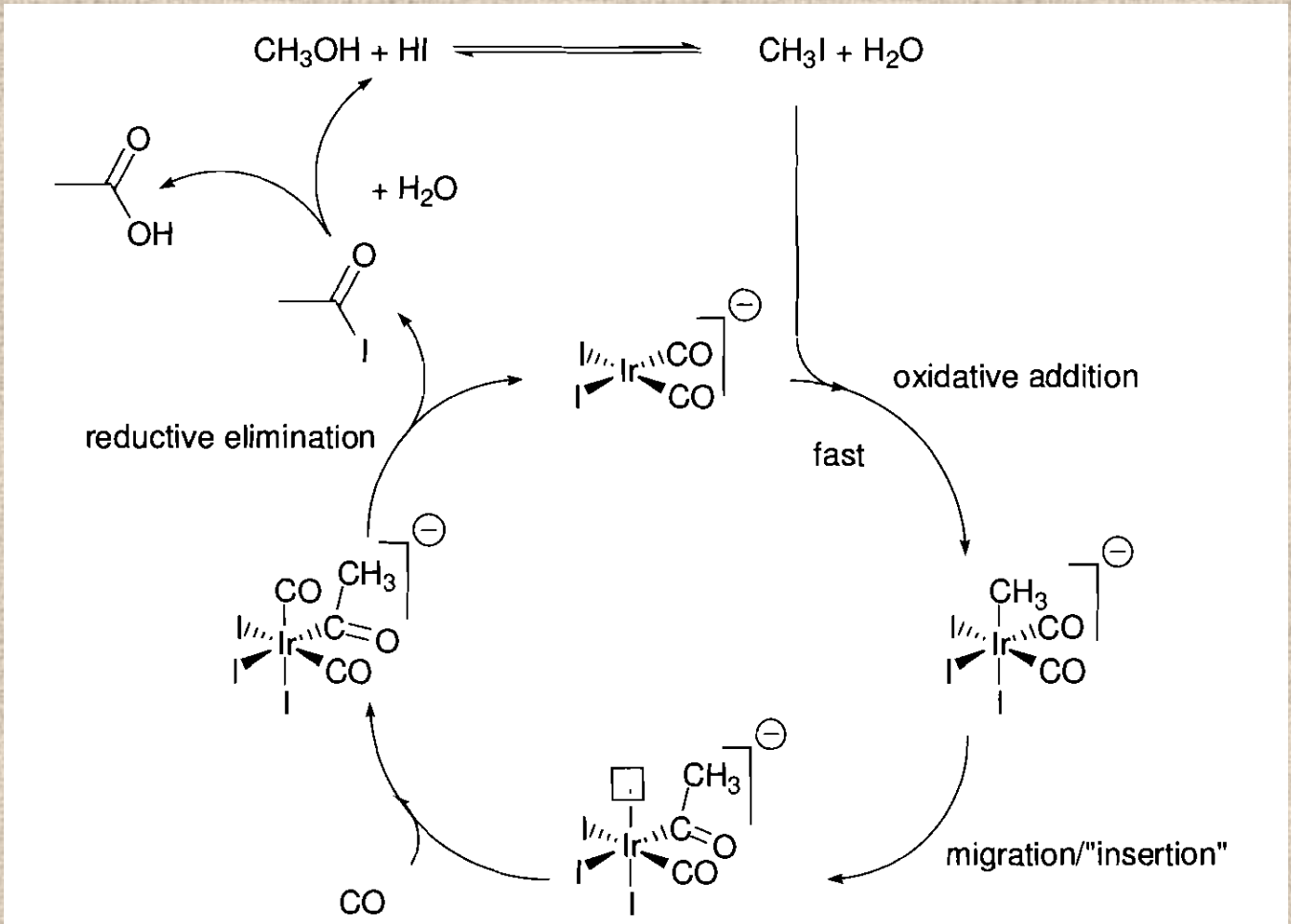
AMERICAN CHEMICAL SOCIETY

ACS Green Chemistry Institute®

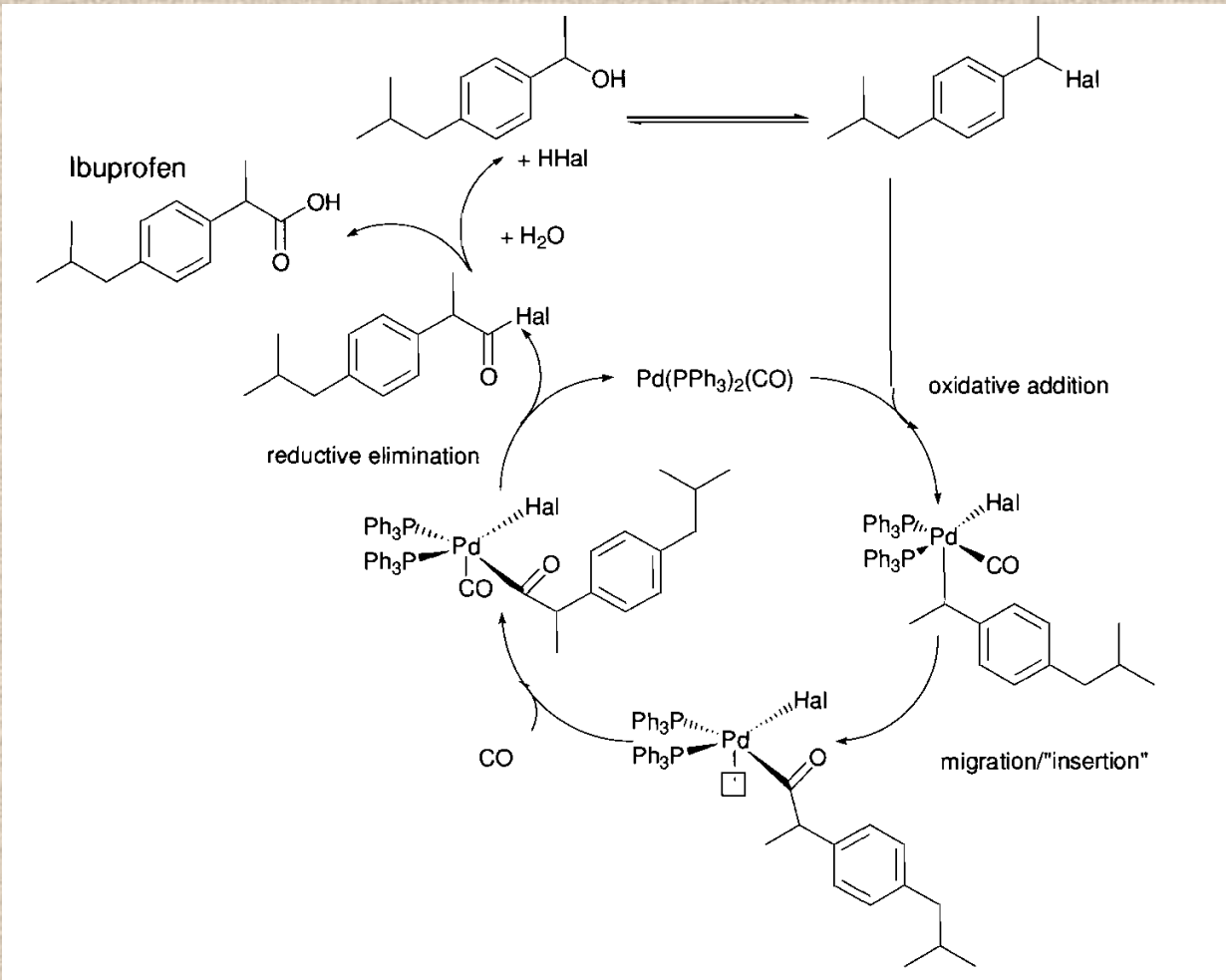
Monsanto's Acetic Acid Synthesis



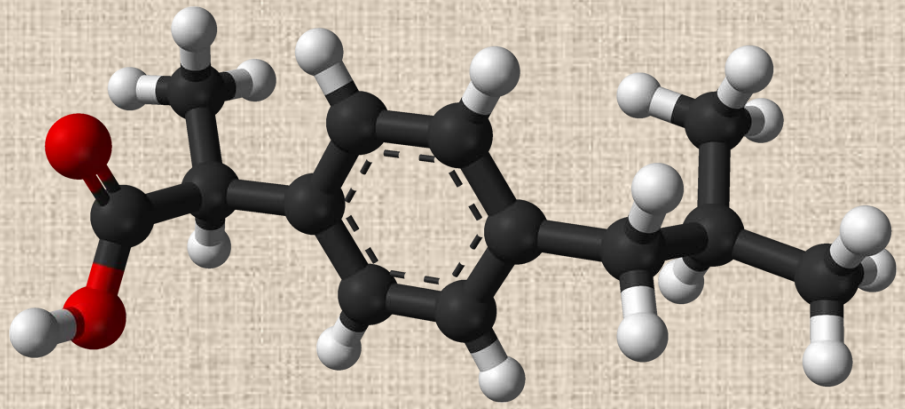
Cativa Process

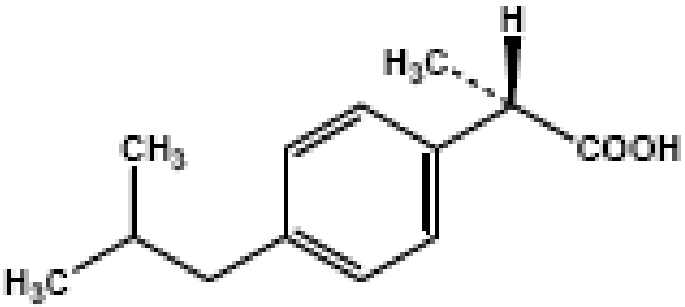


Industrial carbonylation in the Ibuprofen synthesis of Celanese

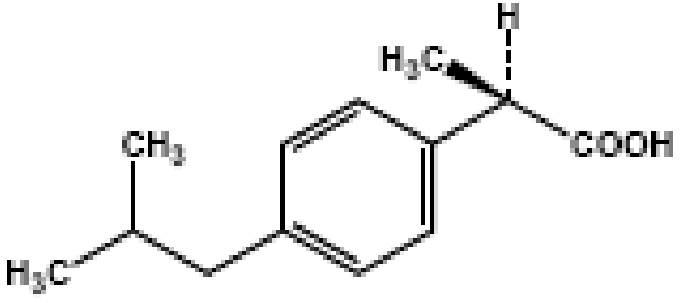


S-ibuprofen



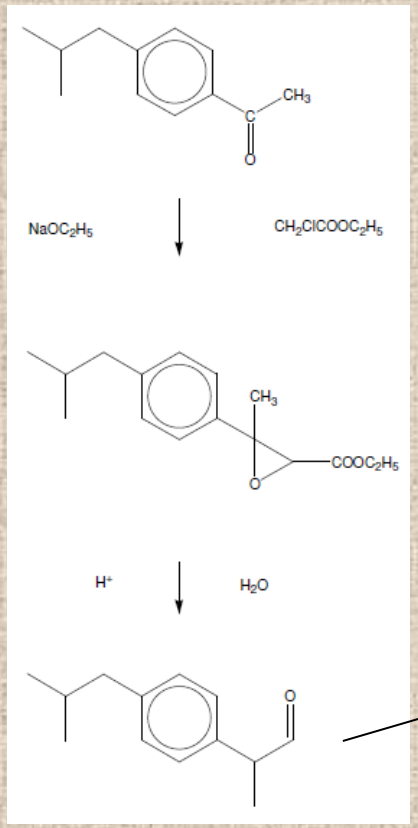


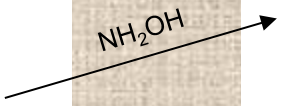
S-Ibuprofen

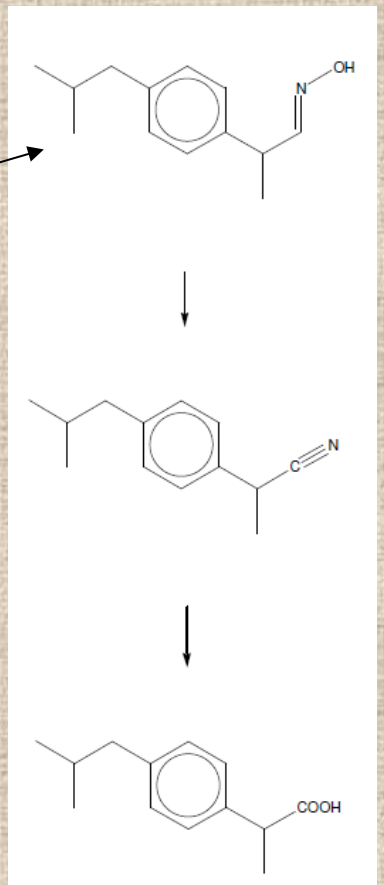


R-Ibuprofen

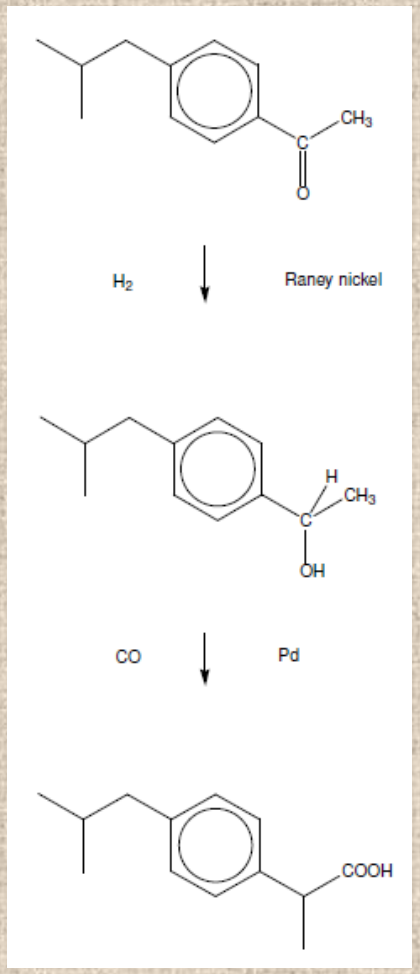
Original Multistep Synthesis of Ibuprofen





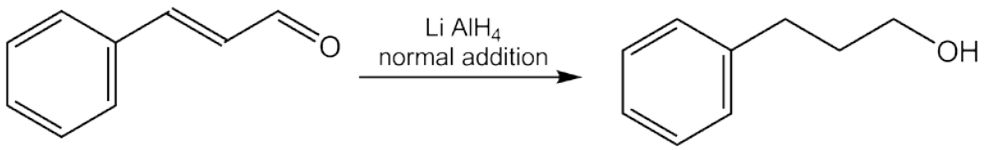


Greener Synthesis of Ibuprofen



In class assignment (01.26.2011)

A typical organic laboratory reaction is shown below, in which an aldehyde is reduced to an alcohol via a typical reducing agent, namely lithium aluminum hydride.



In this experiment, 5.8 g of $LiAlH_4$ was added into a flask, and to this was added 25 mL of THF (density 0.88 g/mL). By use of an addition funnel, a solution of 10 g of cinnamaldehyde (reactant shown above) in 75 mL of THF was dropped into the lithium aluminum hydride solution and gently heated to a reflux.

After mixture of these reactants, the solution was cooled and 12 mL of aqueous sodium sulfate (let's just use water density of 1 g/mL, as the solubility of sodium sulfate at cool temperatures is near 12 g/100 mL). 95 mL of dilute sulfuric acid was then added (use the density of water again), and the layers were separated and extracted by 120 mL of diethyl ether (density 0.7134 g/mL). Assume a 90% product yield.

(Source: http://www.ch.ic.ac.uk/local/organic/16.html)

Convert all mL to g and evaluate the following factors:

a) Total Atom Economy of the reaction as shown in the above scheme
b) E-factor of this synthetic route
c) Q-factor of this synthetic route

Electron-Counting Rules

Neutral	Negative	Ligand L
1	2	alkyl, aryl, hydride, halide (X)
2	-	ethylene, monoolefin, CO, phosphine
3	4	p-allyl, NO
4	-	diolefin
4	6	cyclobutadiene (C_4H_4 or $C_4H_4^{2-}$)
5	6	cyclopentadienyl
6	-	arene, triolefin
8	10	cyclooctatetraene (C_8H_8 or $C_8H_8^{2-}$)

Green Chemistry

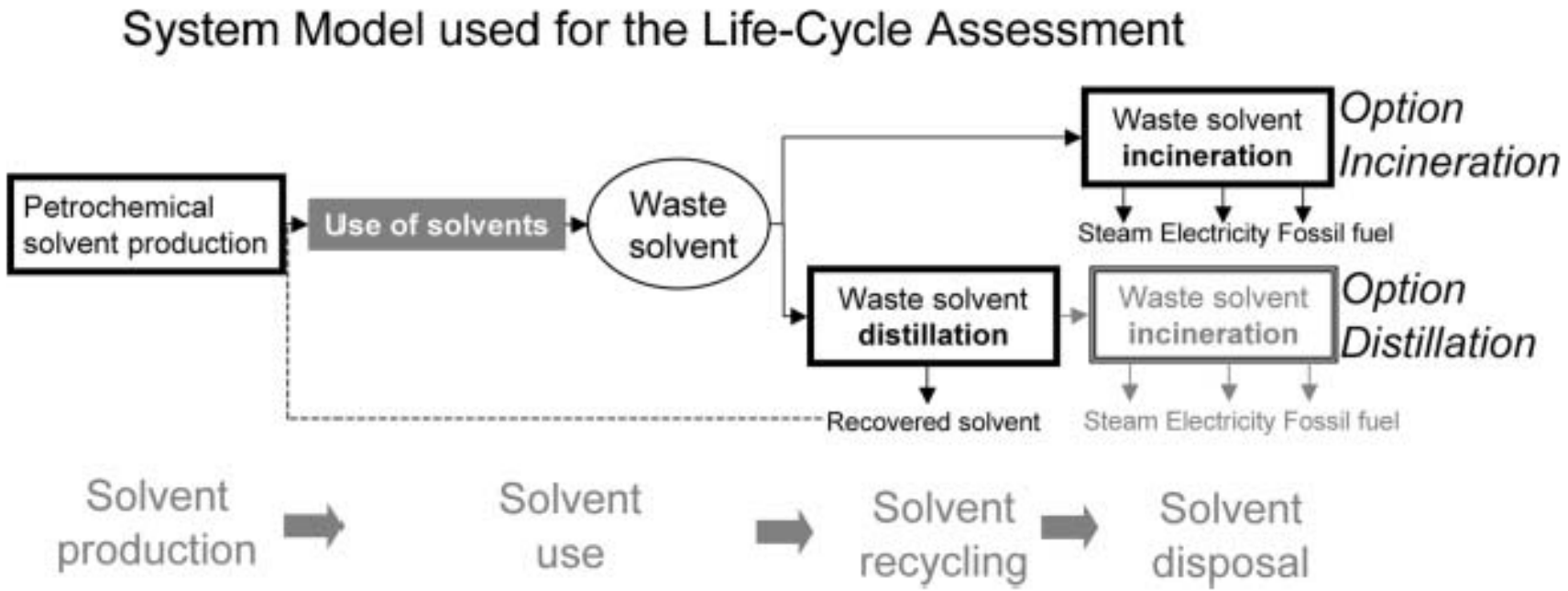


Fig. 1 System model of the solvent assessment using the life-cycle assessment method.

Table 1 Specification of solvent treatment processes used in this work. These assumptions reflect general conditions in the Swiss chemical industry according to the opinion of an expert panel[21]

Parameter	Assumptions	Comment
Incineration technology	Hazardous waste incinerator	Model description see ref. 19
Distillation technology	Batch distillation	Detailed description see ref. 20
Use of energy and ancillaries	Average use batch distillation	According to statistical analysis[20]
Production of energy and ancillaries	Average European production	Data were taken from ref. 16
Solvent recovery	Average solvent recovery of 90%	According to the opinion of an expert panel[21]
Residue treatment	Incineration	Most commonly used technology for organic solvents[22]

Table 2 Results of the life-cycle assessment of the 26 organic solvents. The total CED of a treatment option is calculated based on these results: CED (Option Distillation) = CED (Solvent Production) + CED (Solvent Distillation); CED (Option Incineration) = CED (Solvent Production) + CED (Solvent Incineration)

Solvent	CAS-No.	Solvent production CED per kg solvent/MJ-eq.	Solvent distillation CED per kg solvent/MJ-eq.	Solvent incineration CED per kg solvent/MJ-eq.
Acetic acid	64-19-7	55.9	−34.9	−15.5
Acetone	67-64-1	74.6	−53.6	−33.9
Acetonitrile	75-05-8	88.5	−79.6	−29.7
Butanol (1-)	71-36-3	97.3	−74.6	−39.9
Butyl acetate	123-86-4	121.6	−95.9	−34.1
Cyclohexane	110-82-7	83.2	−63.4	−53.5
Cyclohexanone	108-94-1	124.7	−99.7	−40.4
Diethyl ether	60-29-7	49.8	−31.9	−40.2
Dioxane	123-91-1	86.6	−63.8	−27.6
Dimethylformamide	68-12-2	91.1	−67.6	−25.9
Ethanol	64-17-5	50.1	−31.2	−31.7
Ethyl acetate	141-78-6	95.6	−72.0	−27.6
Ethyl benzene	100-41-4	85.1	−64.9	−49.8
Formaldehyde	50-00-0	49.3	−28.8	−15.9
Formic acid	64-18-6	73.9	−50.1	−4.7
Heptane	142-82-5	61.5	−43.7	−54.5
Hexane	110-54-3	64.4	−46.7	−55.2
Methyl ethyl ketone	108-10-1	64.2	−44.6	−37.6
Methanol	67-56-1	40.7	−21.7	−22.2
Methyl acetate	79-20-9	49.0	−29.2	−22.8
Pentane	109-66-0	73.2	−54.5	−55.3
Propyl alcohol (*n*-)	71-23-8	111.7	−87.3	−36.5
Propyl alcohol (iso-)	67-63-0	65.6	−46.1	−36.5
Tetrahydrofuran	109-99-9	270.8	−230.7	−37.5
Toluene	108-88-3	80.0	−60.0	−49.3
Xylene	1330-20-7	72.5	−53.1	−49.9

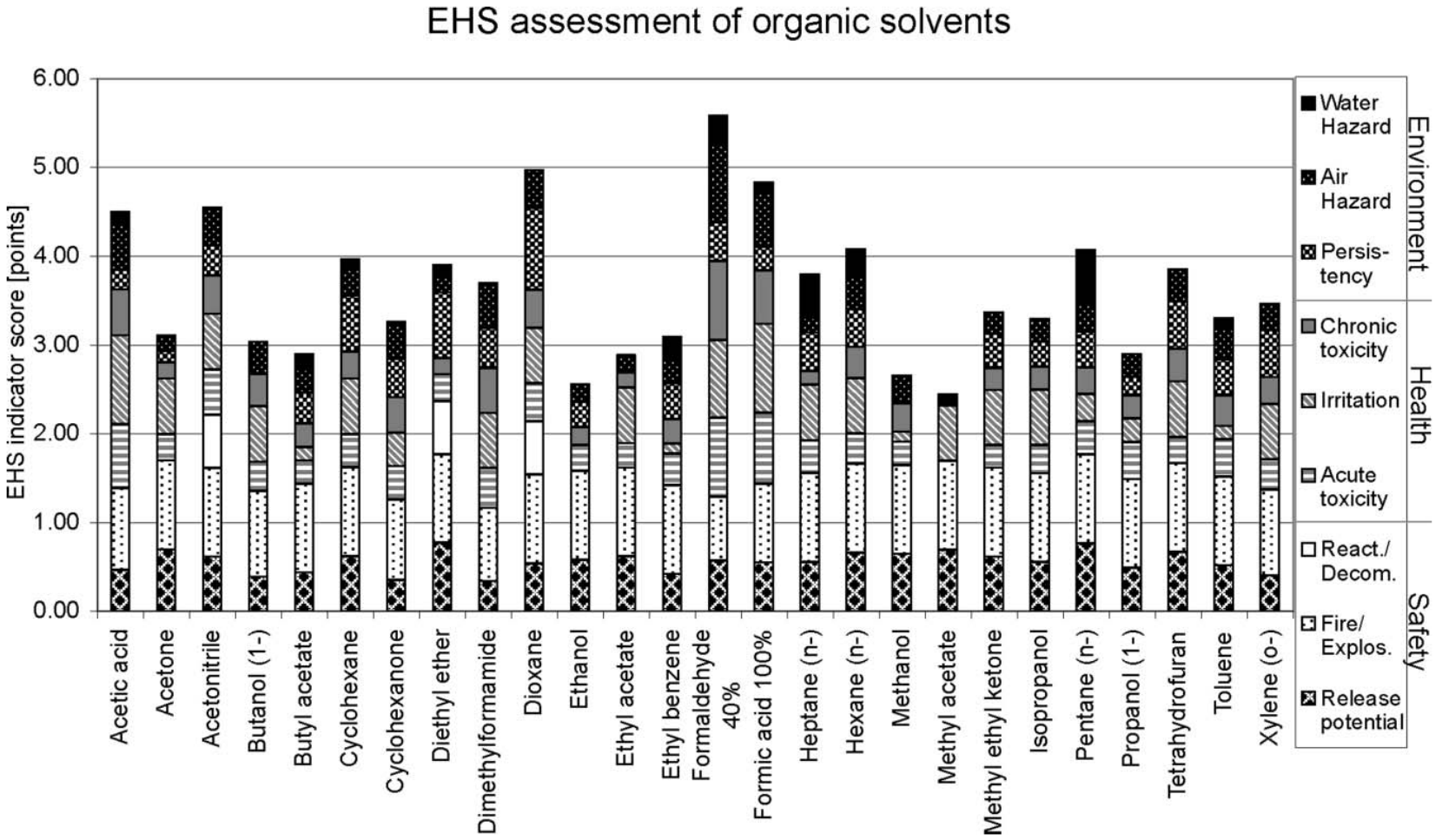


Fig. 2 Results of the EHS method for the 26 pure organic solvents (step (1) in the framework for the assessment of green solvents). The EHS result score is composed of environmental indicators (water and air hazard, persistency), as well as indicators for health (chronic and acute toxicity and irritation) and safety (reaction/decomposition, fire/explosion, release potential) hazards. The results were calculated using the EHS-Tool.[14]

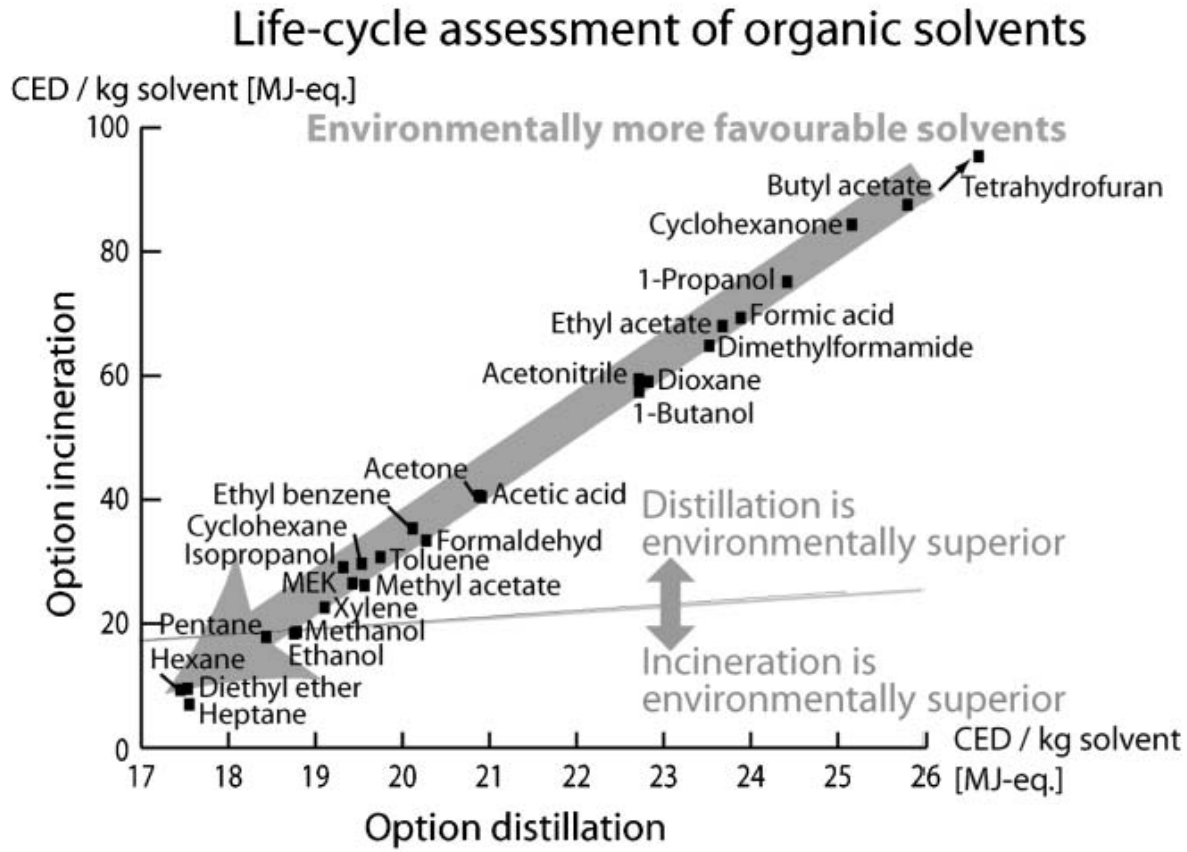


Fig. 3 Life-cycle assessment of the treatment options, incineration and distillation, for the 26 solvents (step (2) in the framework for the assessment of green solvents). Tetrahydrofuran is out of range (CED of 40.1 (distillation) and 233.4 (incineration) MJ-eq.). The results were calculated using the Ecosolvent-Tool.[15]

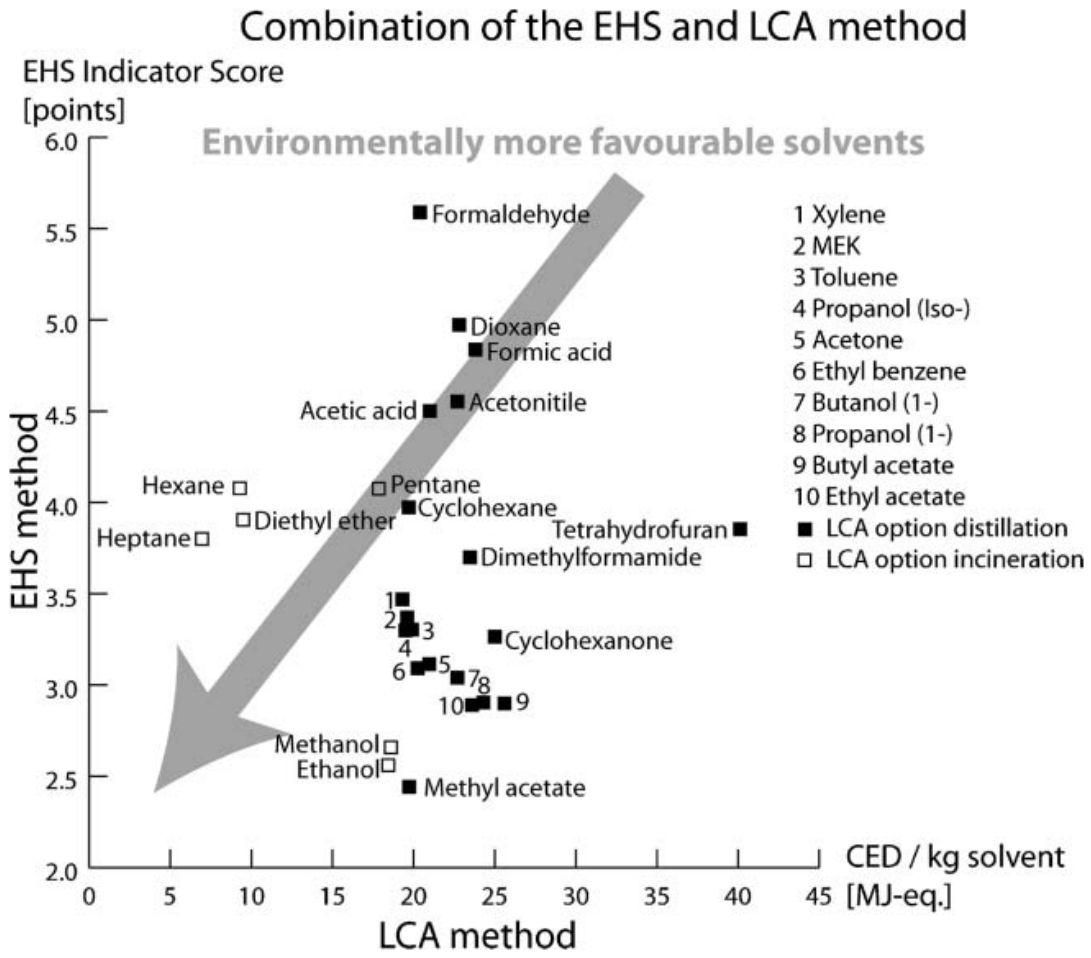


Fig. 4 Environmental assessment of the 26 organic solvents: combination of the EHS method with the LCA method (step (3) of the framework for the assessment of green solvents).

Table 3 The 5 binary solvent mixtures and their varying compositions investigated in the case study. Data were taken from Bentley *et al.*[13]

Mixture name (% v/v) main component/secondary component	Solvent composition/kg	Product selectivities at 25 °C (dominating product) as reported in Bentley *et al.*
Option 1: methanol–water		
MeOH H_2O (90%)	methanol (0.71), water (0.29)	1.36 1.39 (ester product)
MeOH H_2O (10%)	methanol (0.08), water (0.92)	1.28 1.40 (ester product)
Option 2: ethanol–water		
EtOH H_2O (90%)	ethanol (0.71), water (0.29)	0.55 0.71 (acid product)
EtOH H_2O (10%)	ethanol (0.08), water (0.92)	0.78 0.80 (acid product)
Option 3: methanol–ethanol		
MeOH EtOH (80%)	methanol (0.63), ethanol (0.37)	1.54 (ester product)
MeOH EtOH (20%)	methanol (0.16), ethanol (0.84)	1.51 (ester product)
Option 4: *n*-propyl alcohol–water		
n-PrOH H_2O (90%)	*n*-propyl alcohol (0.72), water (0.28)	0.32 0.61 (acid product)
n-PrOH H_2O (10%)	*n*-propyl alcohol (0.08), water (0.92)	0.78 0.82 (acid product)

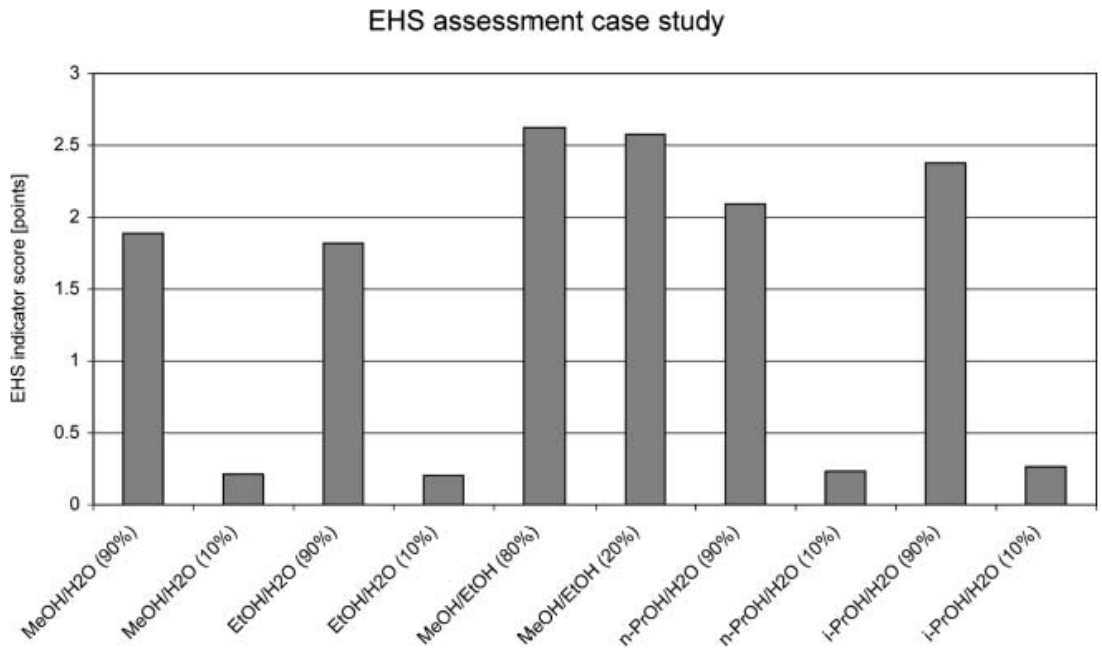


Fig. 5 EHS assessment of the 5 solvent mixtures of the case study at different shares of main and secondary component (step (1) in the framework for the assessment of green solvents). The results were calculated using the EHS-Tool.[14]

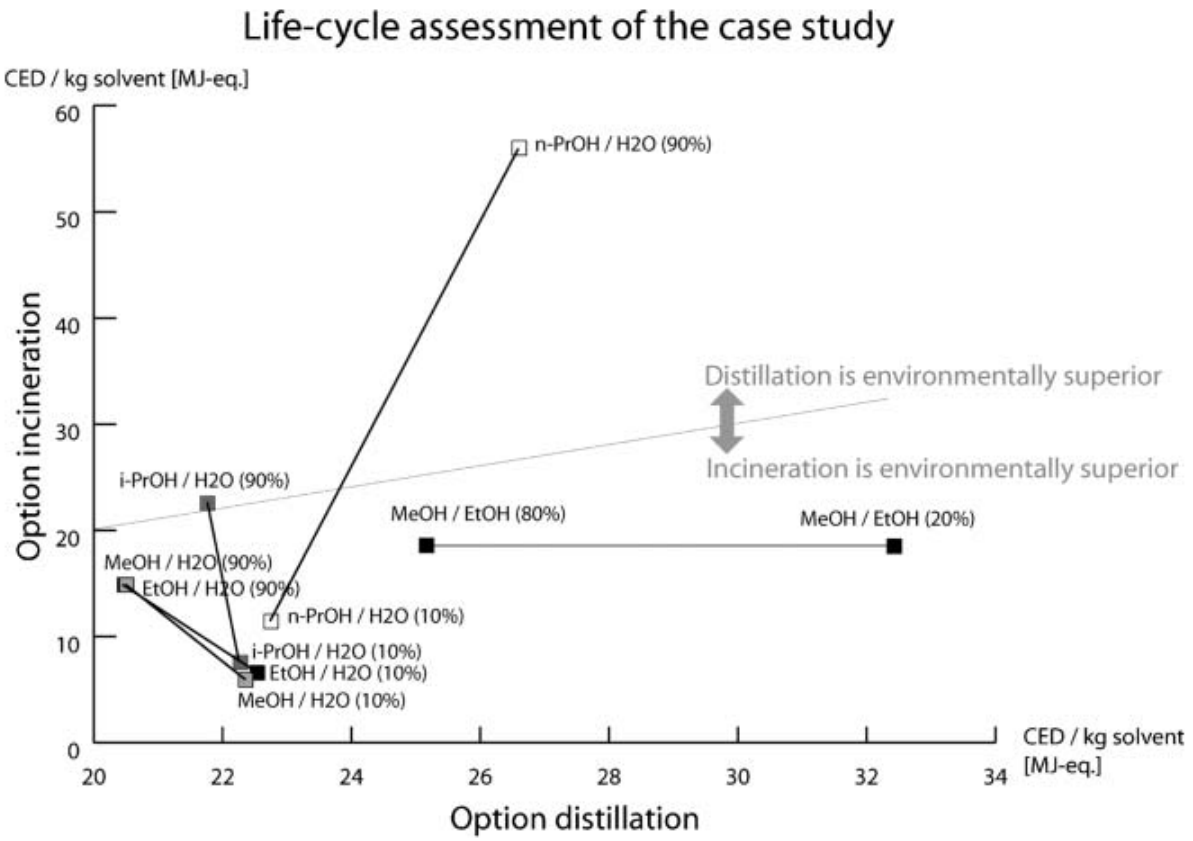


Fig. 6 Life-cycle assessment of the treatment options, incineration and distillation, for 5 solvent mixtures (step (2) in the framework for the assessment of green solvents). The values were calculated using the Ecosolvent-Tool.[15]

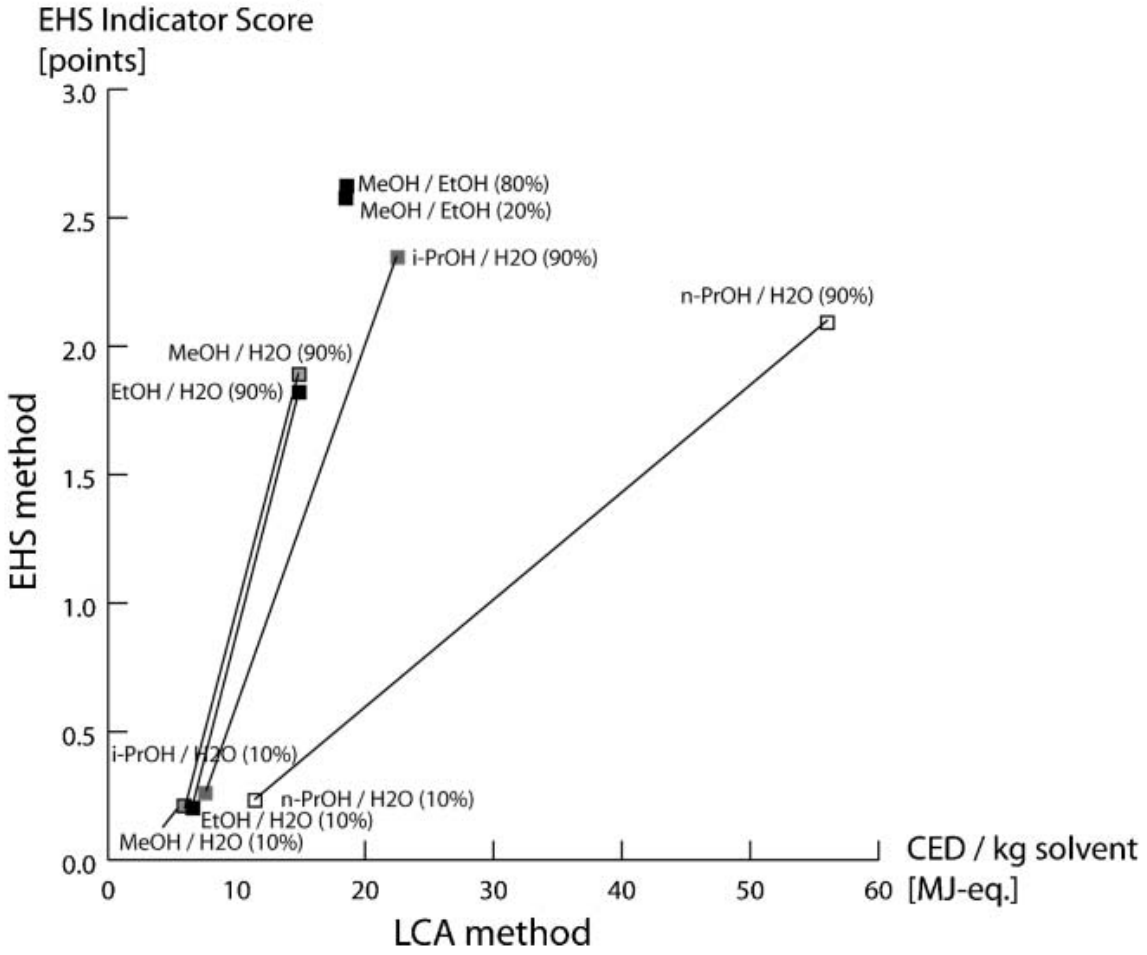


Fig. 7 Environmental assessment of the 5 binary solvent mixtures with various shares of the components.

In class assignment (02.02.2011)

1. The EHS indicator scores of methanol and dioxane are 2.7 and 5.00, respectively. What is the meaning of these indicators?

2. On the other hand, their life-cycle assessment scores based on cumulative energy demands (CED) can be calculated from their solvent production (CED) in kg/m_j-e_q. of 40.7 and 86.6, solvent distillation (CED) of -21.7 and -63.8, and solvent incineration (CED) of -22.2 and -27.6 values for methanol and dioxane, respectively. What are their life-cycle assessment values?

3. Which is the greener solvent? Why?

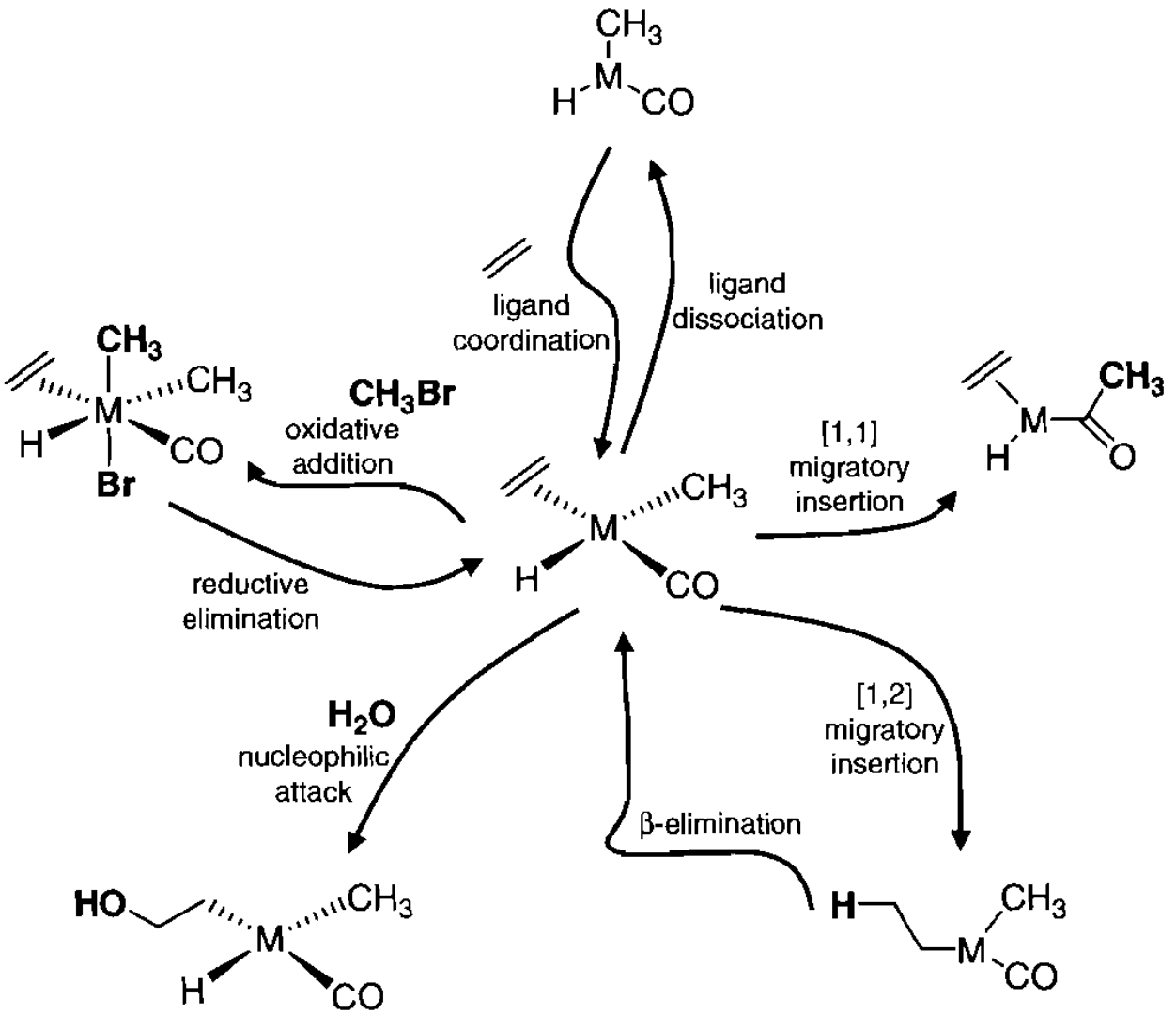


Figure 3.2 The main elementary steps in homogeneous catalysis.

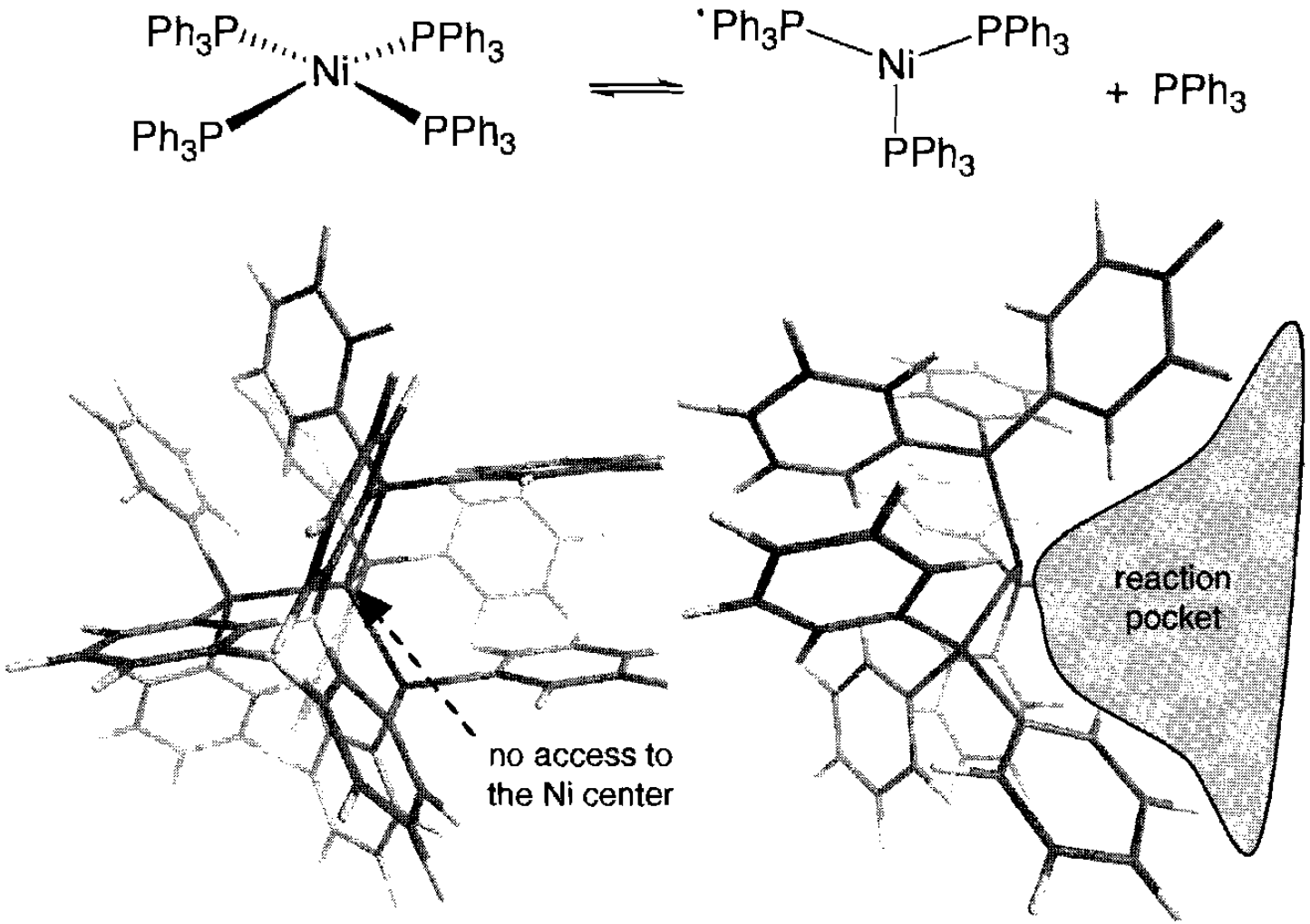


Figure 3.17 Schematic drawing and 3D structure of $Ni[P(Ph)_3]_4$, also showing the reaction pocket created by the dissociation of one of the triphenylphosphine ligands.

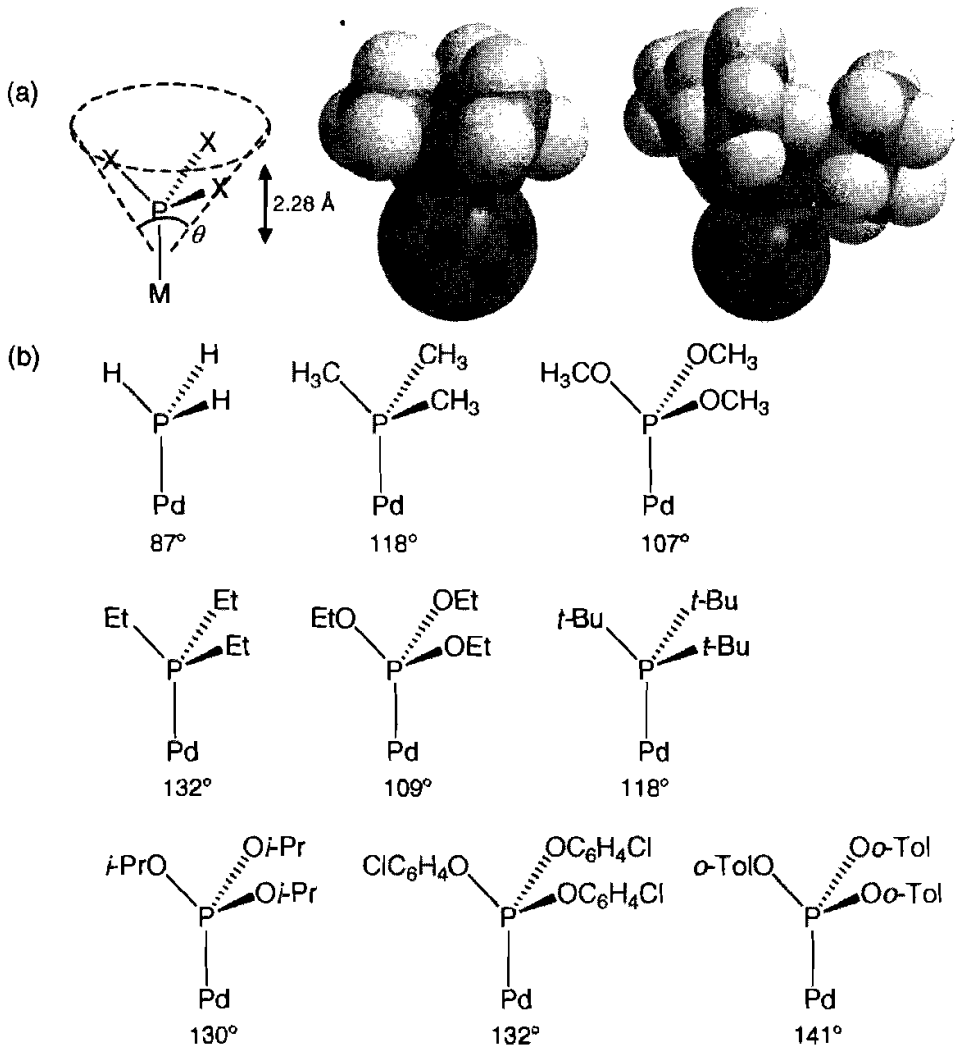


Figure 3.18 **a** Schematic drawing and space-filling model showing the calculation of the cone angle for symmetric and nonsymmetric ligands; **b** examples of some ligands with their respective cone angle values.

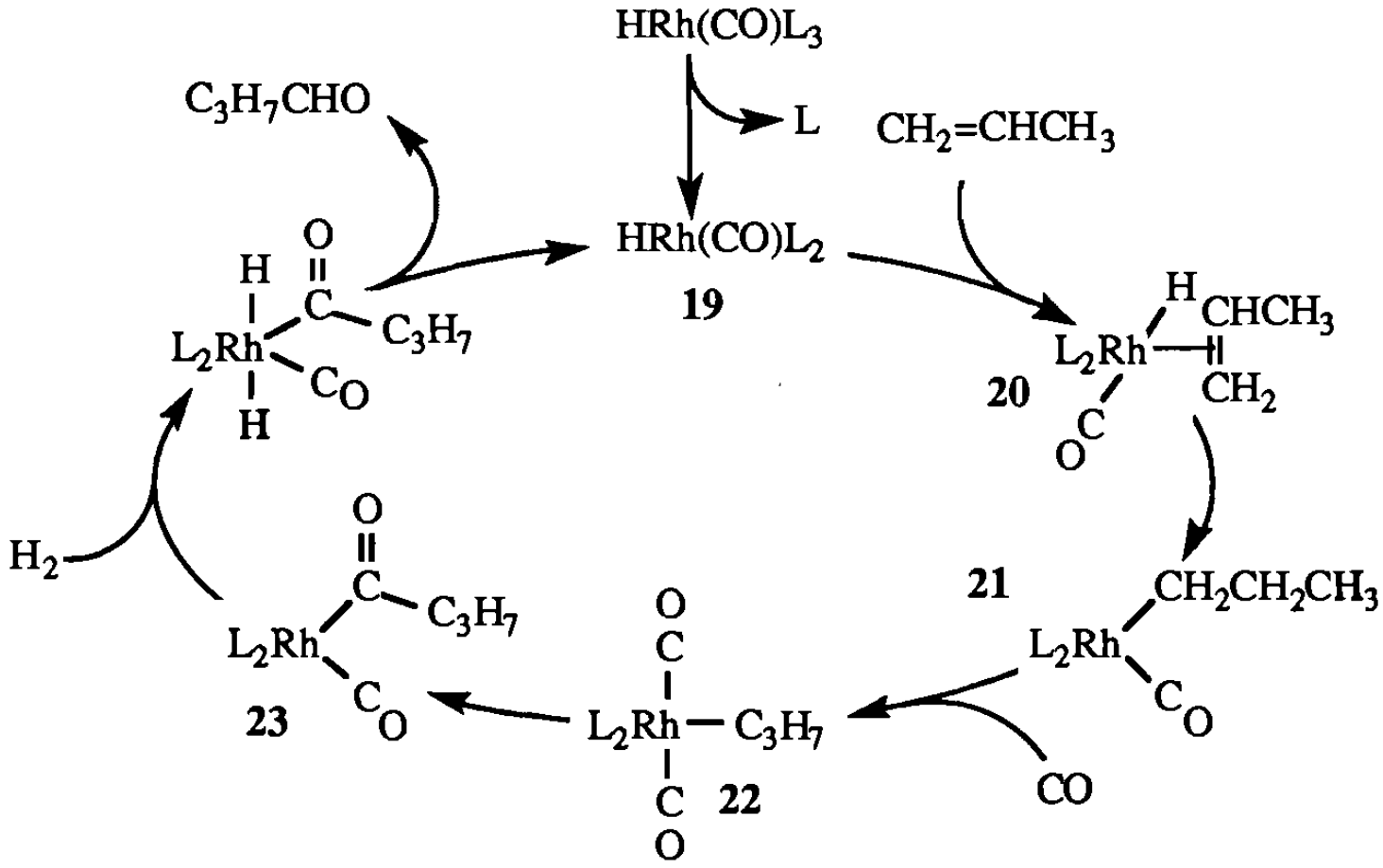


Figure 5.8 Rhodium-catalyzed hydroformylation of propene (L = PAr_3).

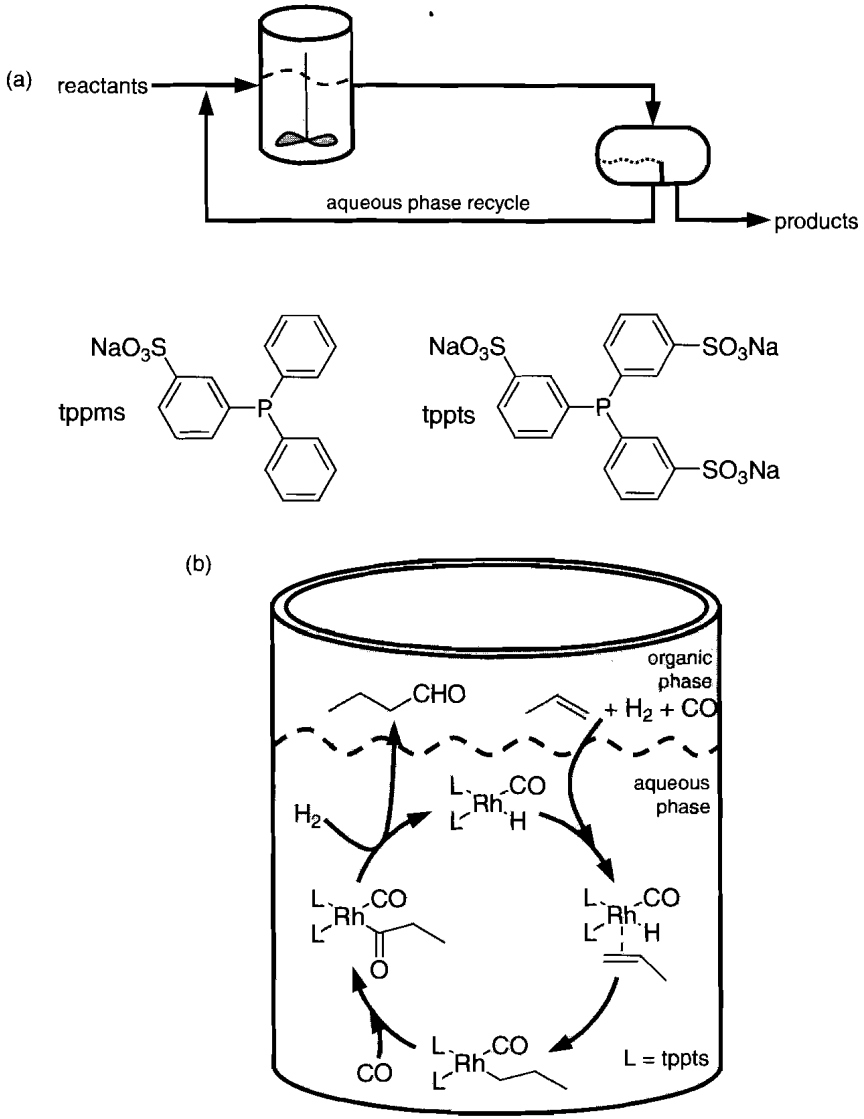


Figure 4.24 **a** A general process schematic for aqueous biphasic catalysis, and examples of water-soluble phosphine ligands; **b** the catalytic cycle for the Ruhrchemie/Rhône–Poulenc hydroformylation of propene.

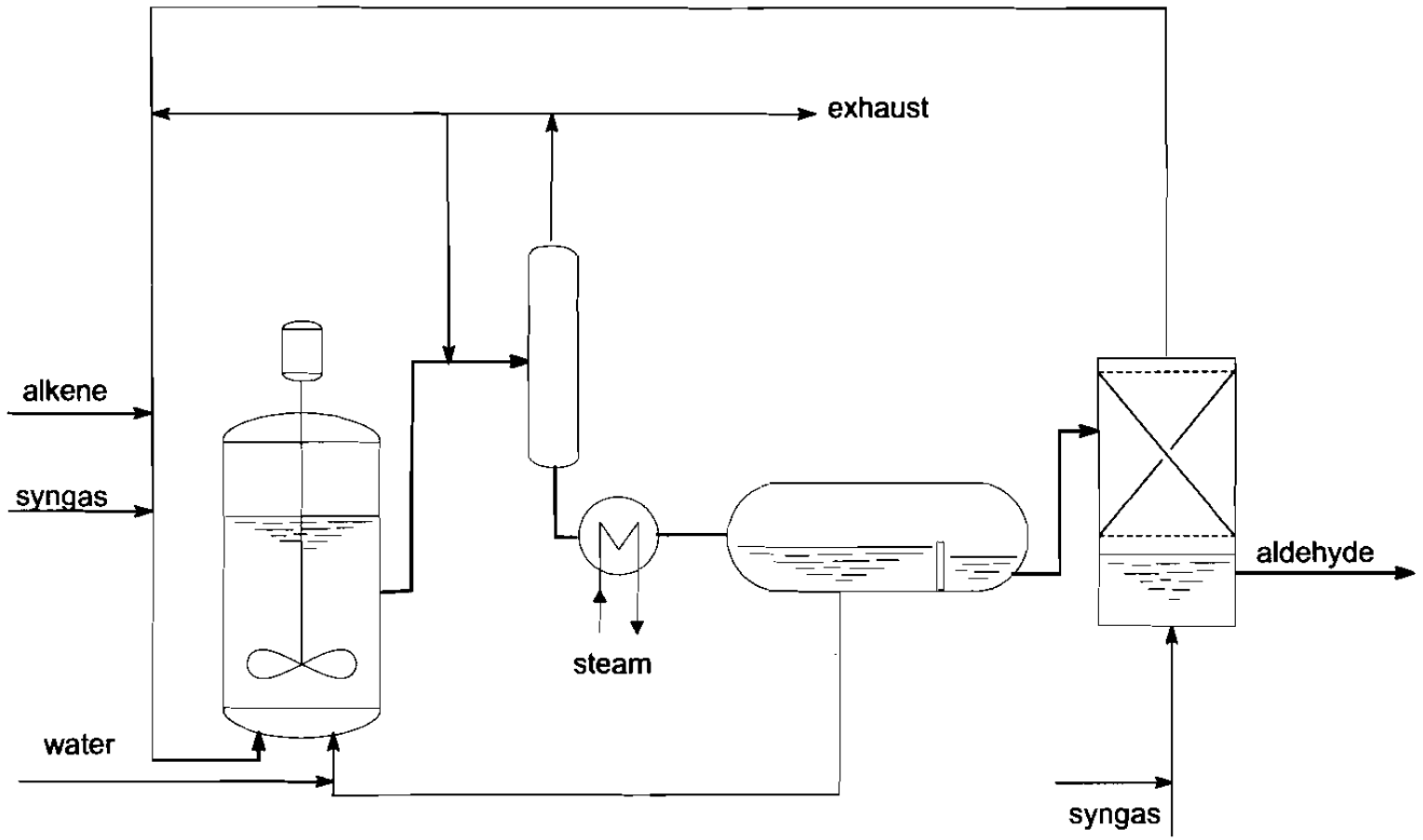


Figure 8.7. Ruhrchemie/Rhône-Poulenc process

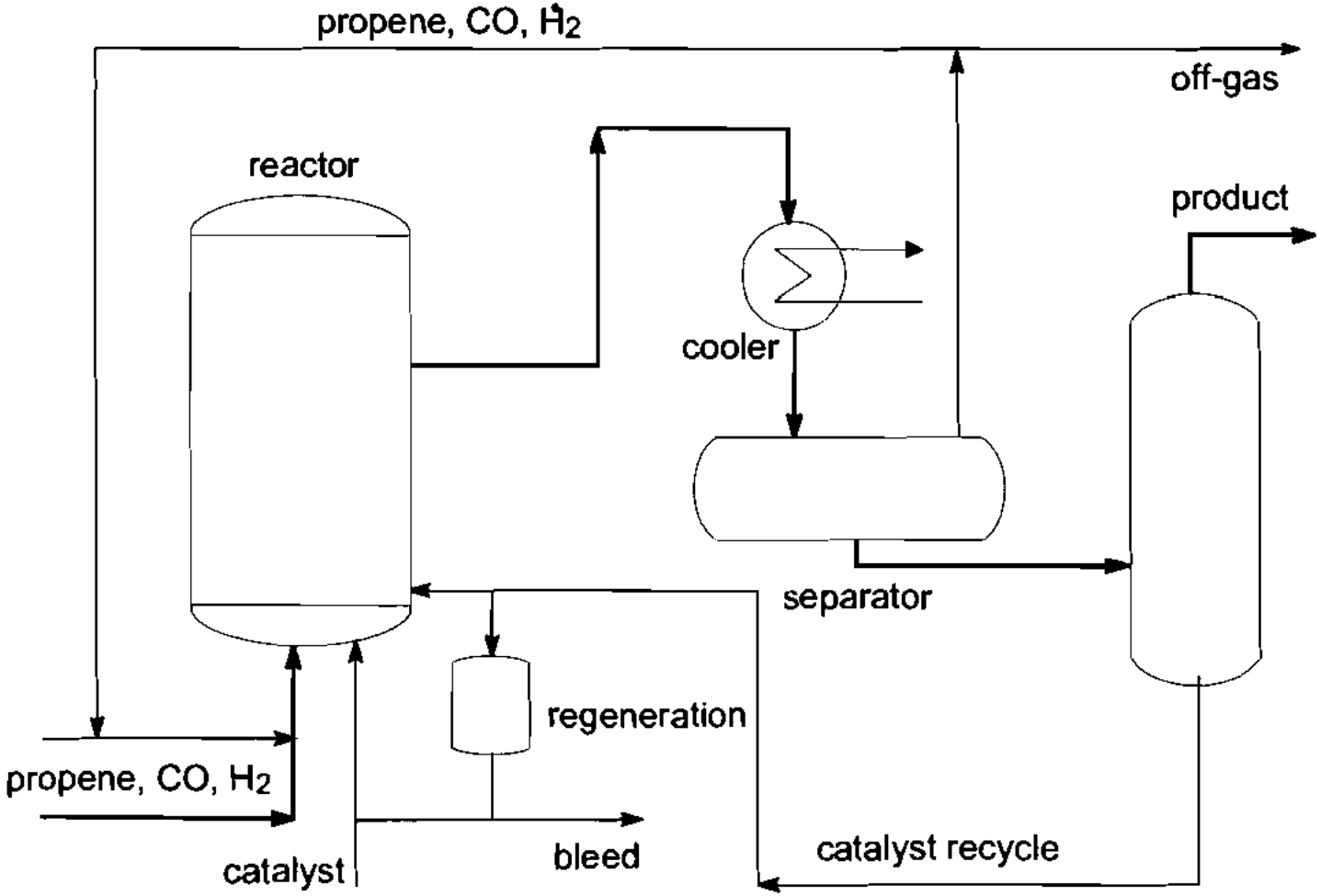


Figure 8.5. LPO process scheme with removal of product in liquid phase

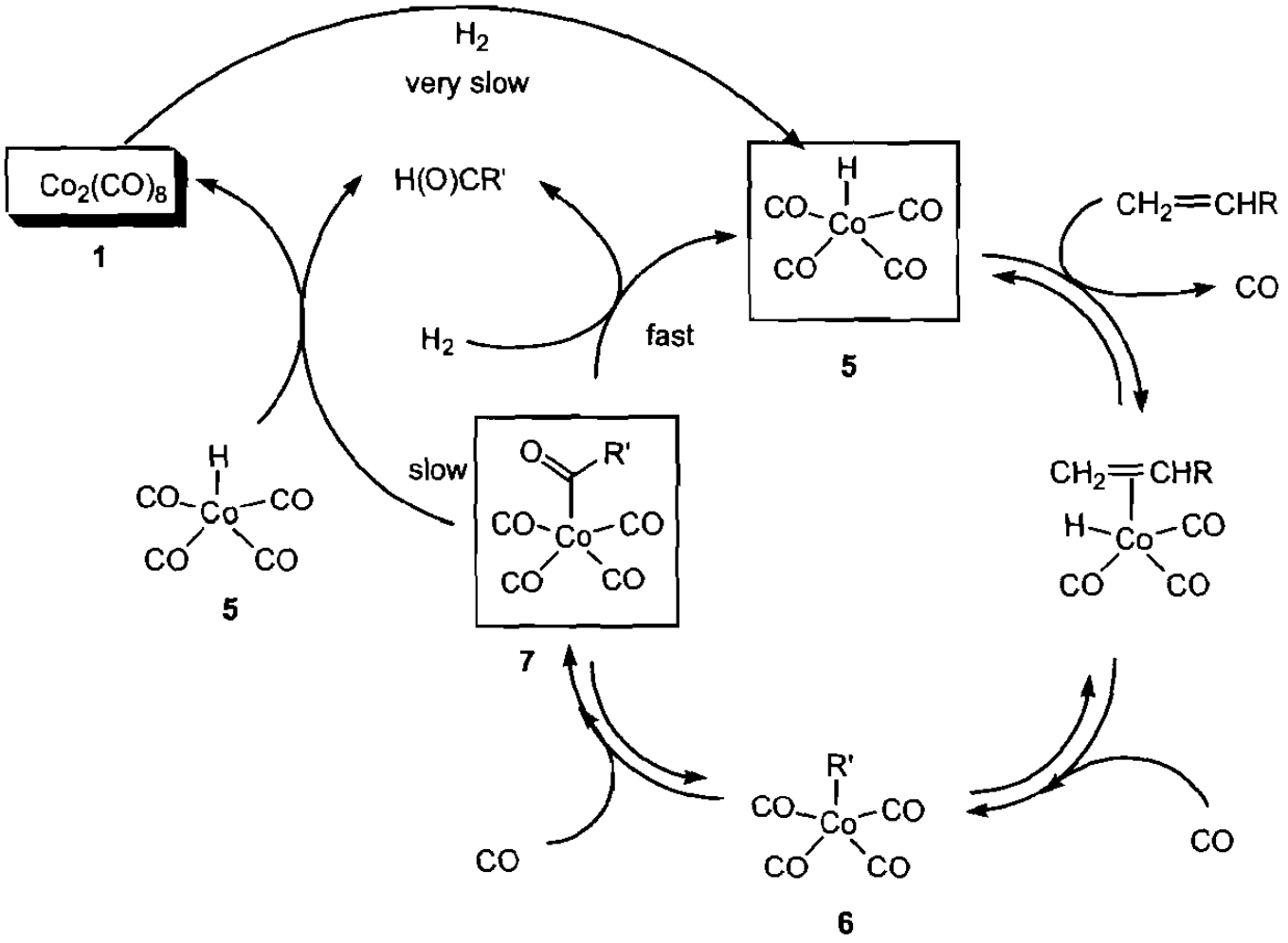


Figure 7.8. Cobalt carbonyl mechanism after Mirbach [1]

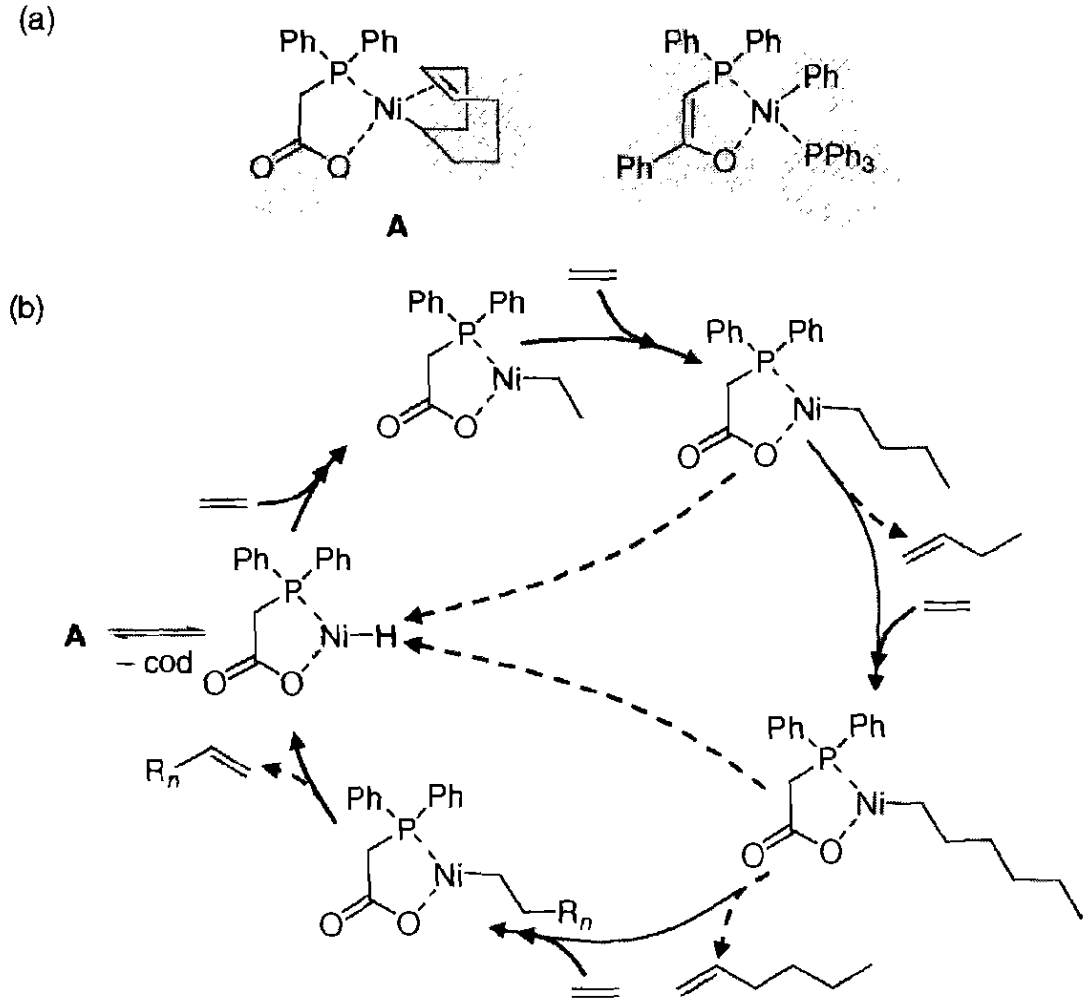


Figure 3.29 **a** Two examples of nickel catalyst precursors, highlighting the "chelate part" and the "organic part"; **b** a simplified catalytic cycle for the SHOP oligomerization step (the reverse reaction arrows are omitted, for clarity).

(a)

$$Pd^{2+} + H_2O + \mathbf{CH_2{=}CH_2} \longrightarrow Pd^0 + 2H^+ + \mathbf{CH_3CH{=}O}$$

$$Pd^0 + 2Cu^{2+} \longrightarrow Pd^{2+} + 2Cu^+$$

$$2Cu^+ + 2H^+ + \mathbf{1/2O_2} \longrightarrow 2Cu^{2+} + H_2O$$

} The three redox processes

(b)

$$CH_2{=}CH_2 + 1/2O_2 \longrightarrow CH_3CH{=}O$$

(c)

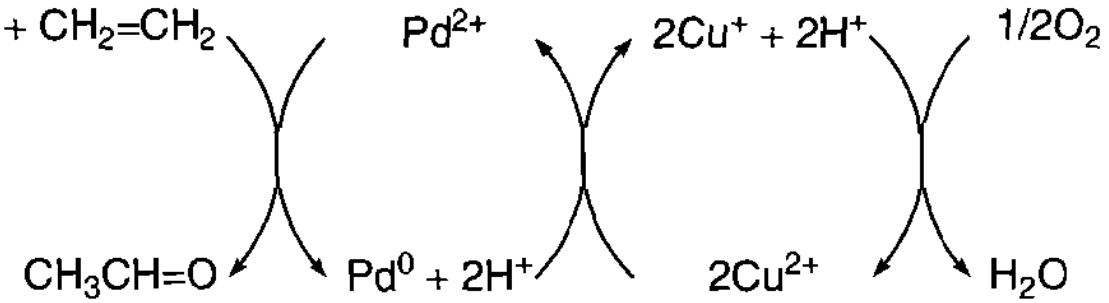


Figure 3.30 **a** The three stoichiometric redox reactions and **b** the net reaction of the Wacker oxidation system; **c** a simplified representation of the Pd and the Cu catalytic cycles (the "reverse reaction" arrows are omitted, for clarity).

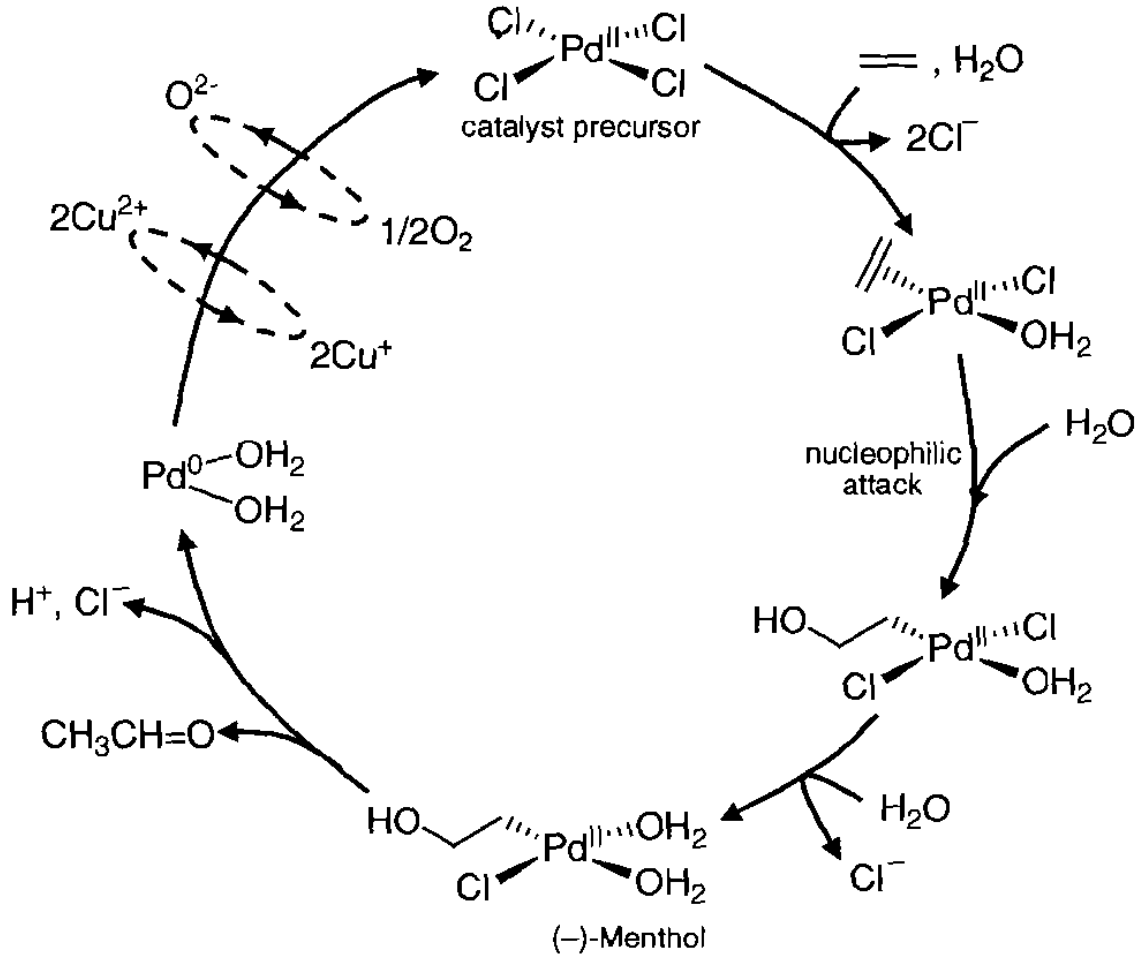


Figure 3.31 Simplified schematic of the palladium Wacker catalytic cycle for oxidizing ethene to acetaldehyde (the "reverse reaction" arrows are omitted, for clarity). The broken circles represent the copper and oxygen redox cycles.

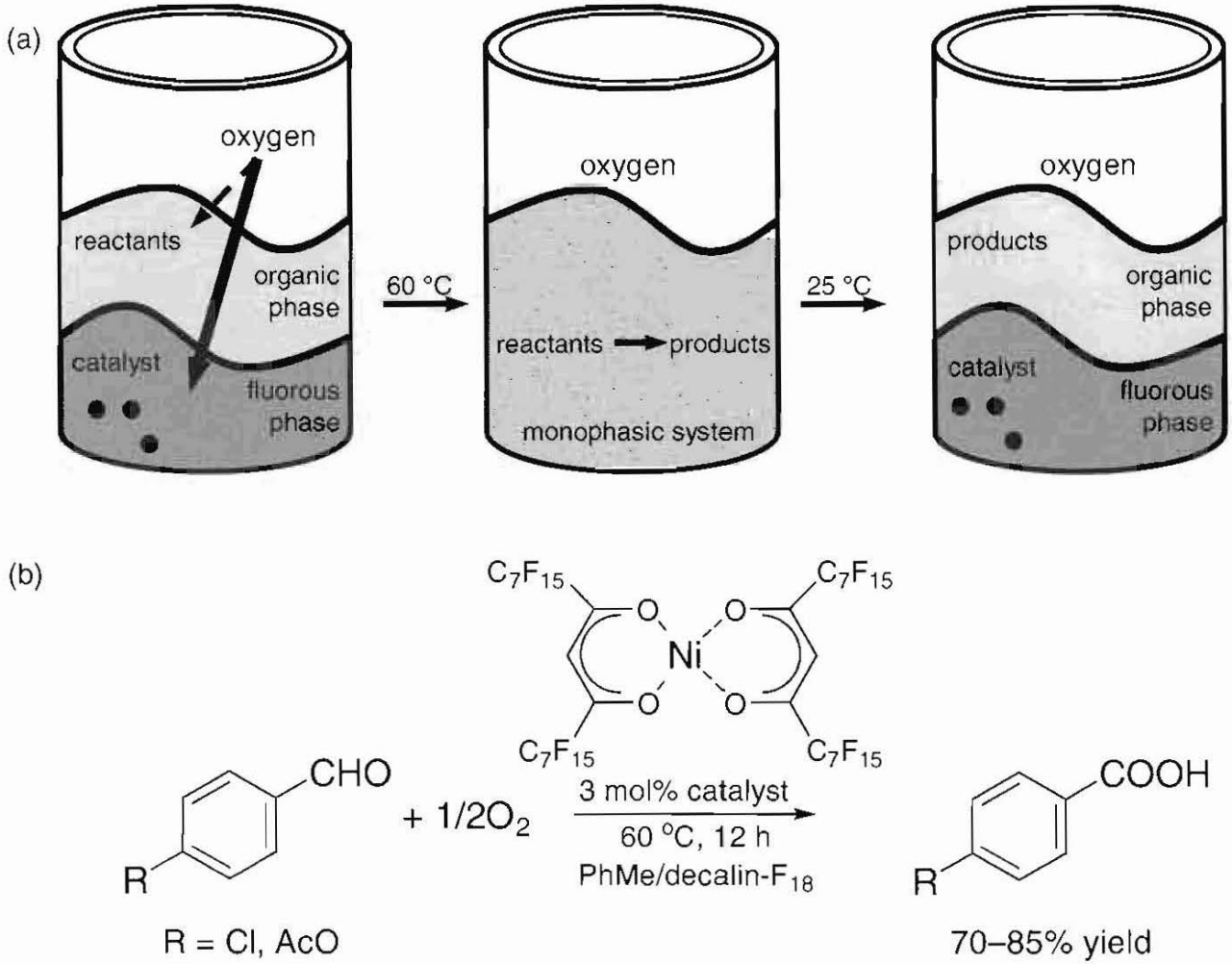


Figure 4.26 **a** Temperature-controlled mixing and separation of fluorous and organic phases; **b** its application in nickel-catalyzed oxidation of aldehydes by Klement *et al.*

Practice Problems for d-electron counting

Chem 484

a) $Re(CO)_5Br$

b) $[Fe(CO)_4]^{2-}$

c) $Mo(\eta^6\text{-}C_6H_6)_2$

d) $CpCo(CO)_2$

e) $[(C_6H_6)_2Ru]^{2+}$

f) $Re(CO)_5Me$

g) $W(PMe_3)_6$

h) $[Cp^*_2WH_3]^+$

i) $Fe(CO)_4Br_2$

j) $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$

k) $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Mn(CO)_5$

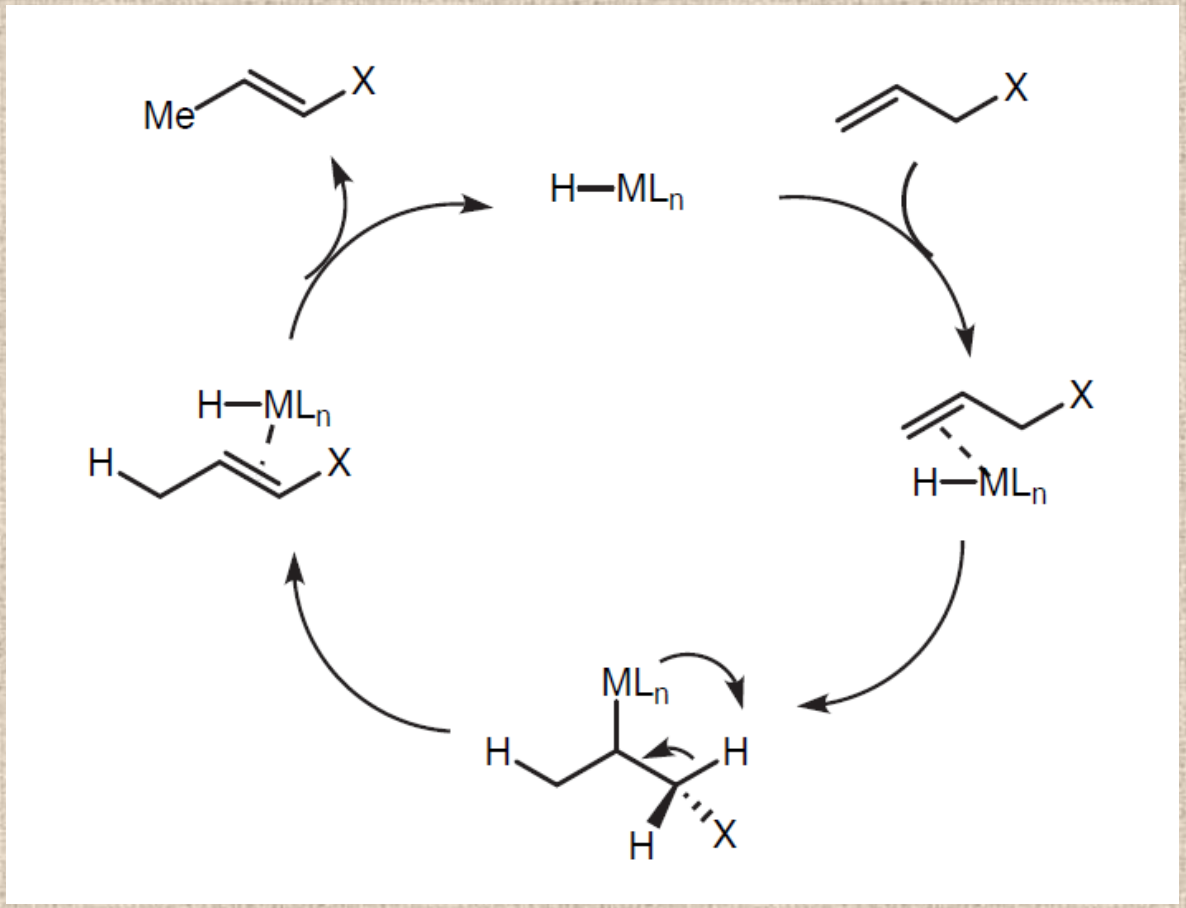
l) $[CpFe(CO)_2]_2$

NOTE: Go to the following website below for additional help

http://www.ilpi.com/organomet/electroncount.html

Olefin Isomerization Mechanism

Hydride Addition-Elimination



Common Catalysts:

$HCo(CO)_4$

$(Ph_3P)_3RhCl$

$HRuCl(PPh_3)_3$

Calculating Molecular Weights

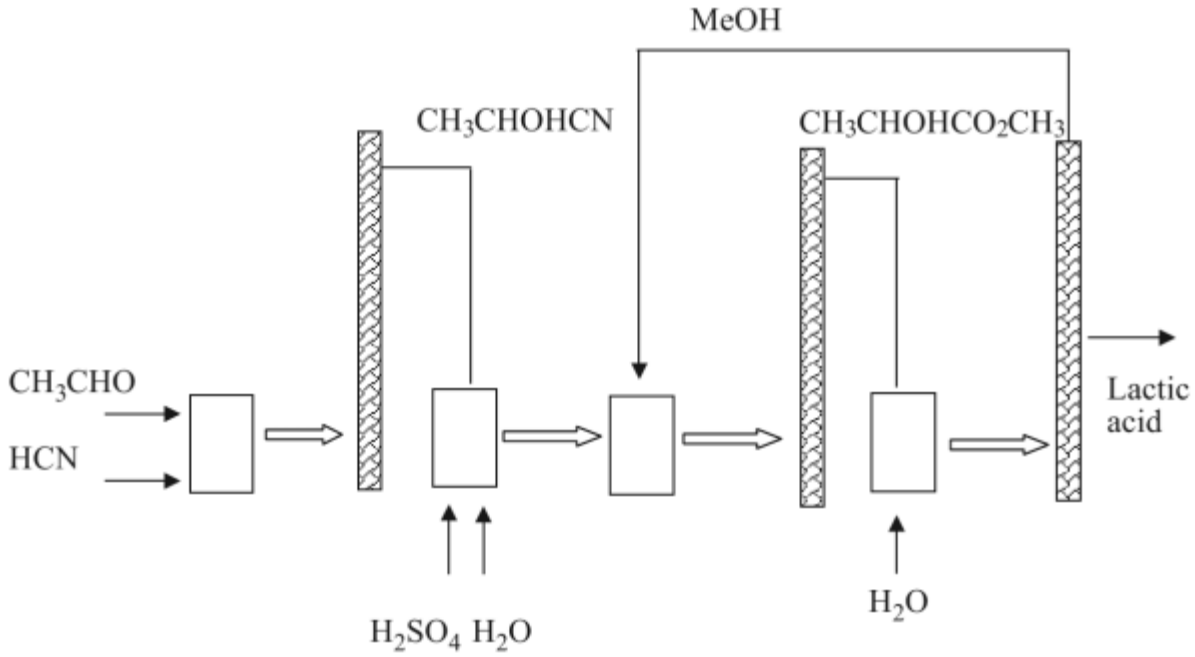
(number average molecular weight)

Number of Molecules, N_i	Mass of Each Molecule, M_i	Total Mass of Each Type of Molecule, N_iM_i
1	800,000	800,000
3	750,000	2,250,000
5	700,000	3,500,000
8	650,000	5,200,000
10	600,000	6,000,000
13	550,000	7,150,000
20	500,000	10,000,000
13	450,000	5,850,000
10	400,000	4,000,000
8	350,000	2,800,000
5	300,000	1,500,000
3	250,000	750,000
1	200,000	200,000
	Total Mass = NiMi = 50,000,000	

Calculating Molecular Weights (weight average molecular weight)

Number of Molecules	Mass of Each Molecule	Total Mass of Each Type of Molecule	Weight Fraction Type of Molecule	
(N_i)	(M_i)	(N_iM_i)	(N_iM_i/N_iM_i)	(W_iM_i)
1	800,000	800,000	0.016	12,800
3	750,000	2,250,000	0.045	33,750
5	700,000	3,500,000	0.070	49,000
8	650,000	5,200,000	0.104	67,600
10	600,000	6,000,000	0.120	72,000
13	550,000	7,150,000	0.143	78,650
20	500,000	10,000,000	0.200	100,000
13	450,000	5,850,000	0.117	52,650
10	400,000	4,000,000	0.080	32,000
8	350,000	2,800,000	0.056	19,600
5	300,000	1,500,000	0.030	9,000
3	250,000	750,000	0.015	3,750
1	200,000	200,000	0.004	800
	Weight Average Molecular Weight = W_iM_i = 531,600			

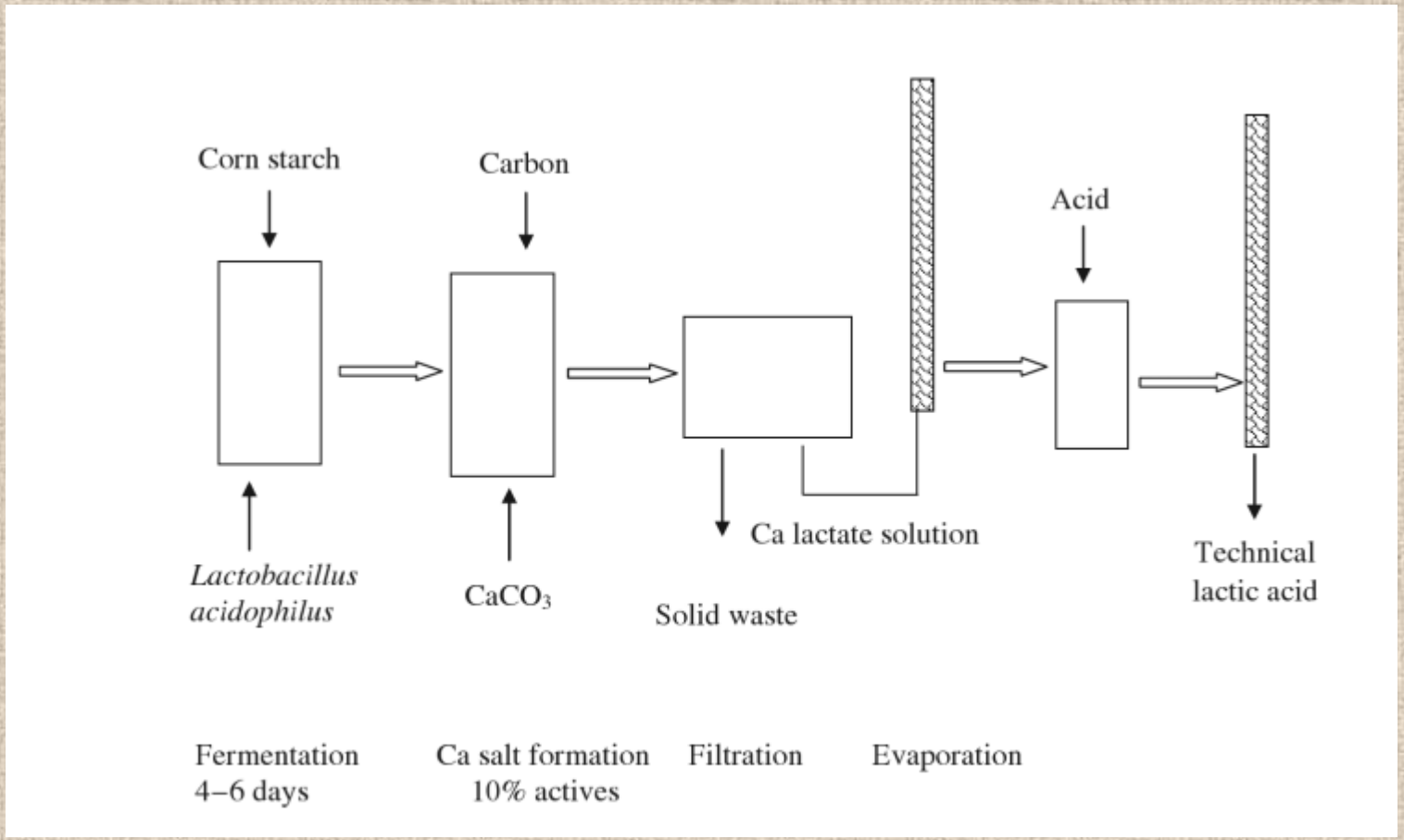
Chemical Route to Lactic Acid



Atom economies

Reaction	Hydrolysis	Esterification	Hydrolysis
100%	60%	100%	100%

Fermentation Route to Lactic Acid



Comparison of Renewable and Non-Renewable Routes to Lactic Acid

Parameter	*Renewable*	*Non-renewable*
Energy use	High	Lower
Hazard potential	Low	High
Waste generation	High	Low
Nature of waste	Benign	Non-benign contamination possible?
Feedstock	Renewable	Non-renewable
Plant size	Larger	Smaller