

Hydroformylation

Chem 462 Inorganic Chemistry
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11/6 (Thursday)

Contents

I. Introduction (concept and importance)

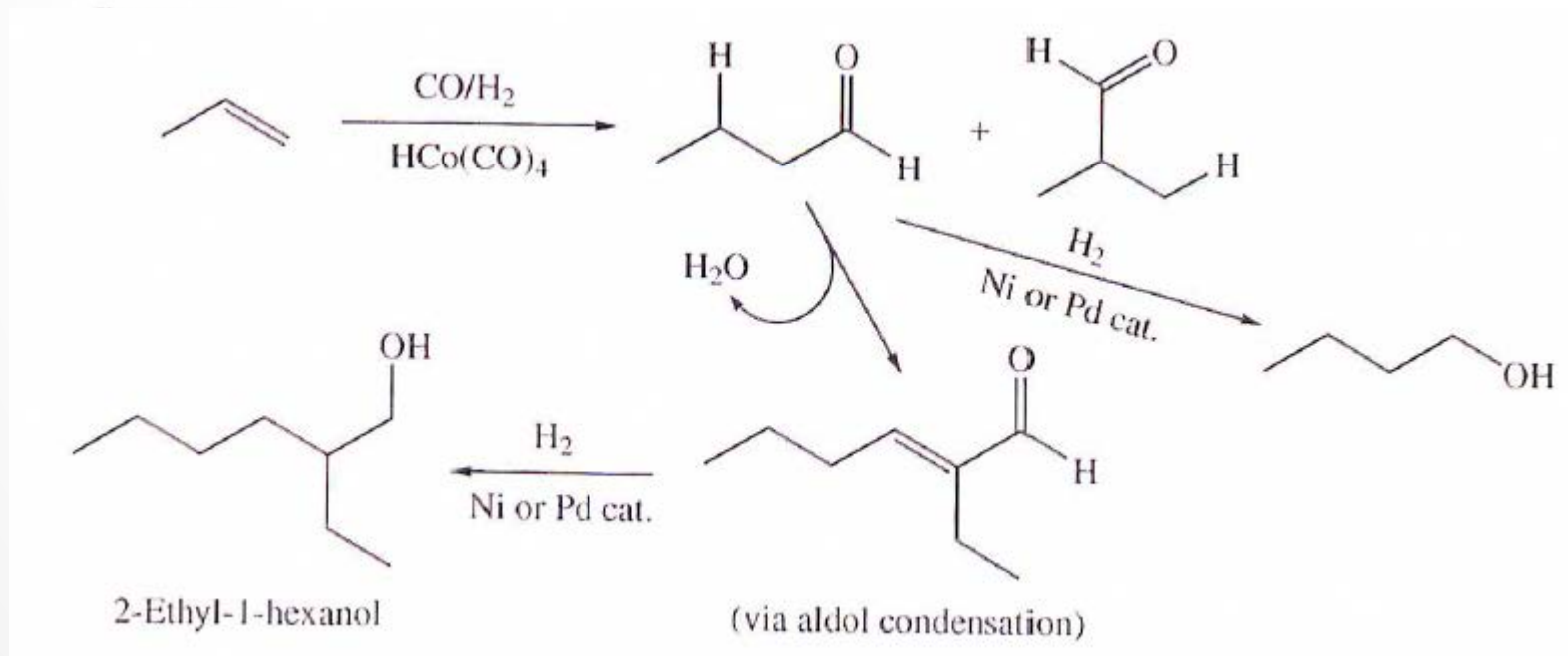
II. Hydroformylation Reaction

- Cyclic mechanism (monometallic and bimetallic)
- Different type of ligands and metals
- Currently developed rhodium catalysts

III. Conclusion

Introduction

- **What is hydroformylation?**
 - produces aldehyde from alkene via
 - addition of a CO and H₂ to an alkene

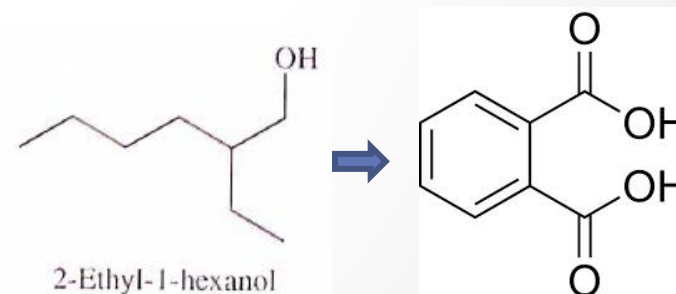
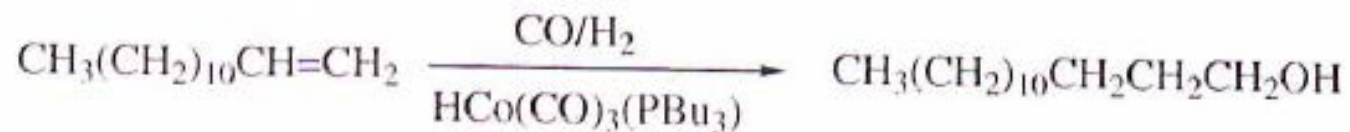


Introduction

- **Why hydroformylation is industrially important:**

- ready availability of 1-alkene from the petrochemical industry
- the large increase in production of plastics, which require plasticizing agents (diester of phthalic acid), derived from hydroformylation
- industrially useful compounds produced by hydroformylation (long carbon chain alcohols (detergents))

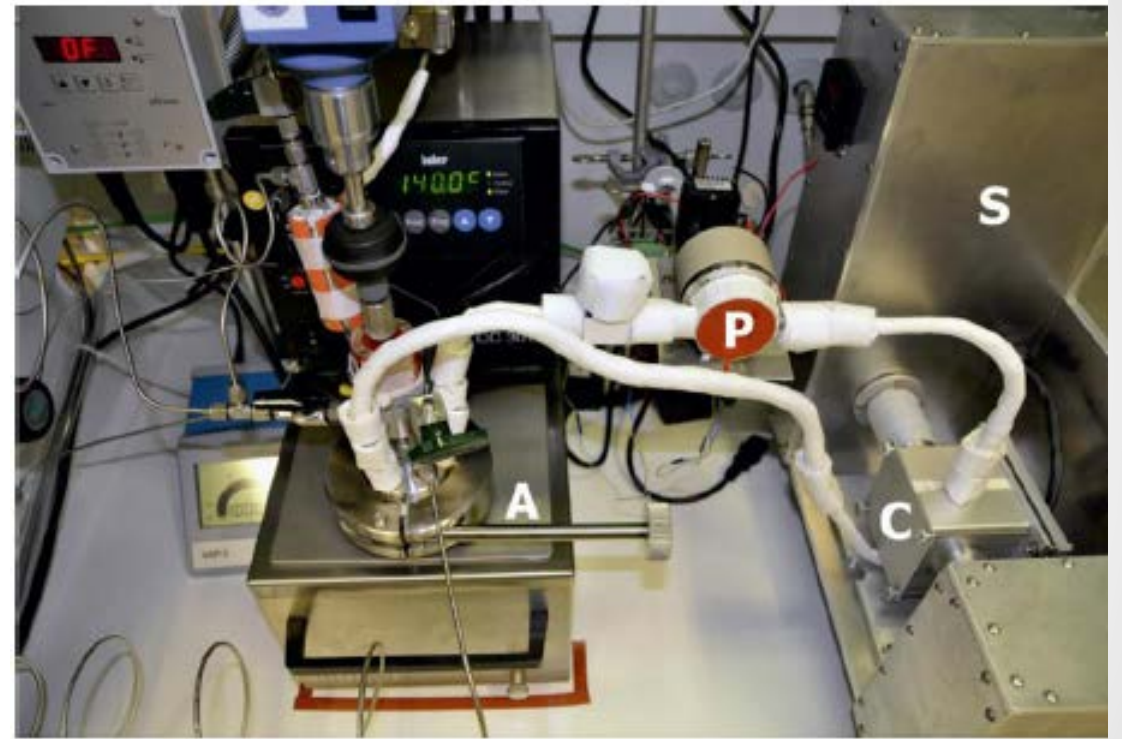
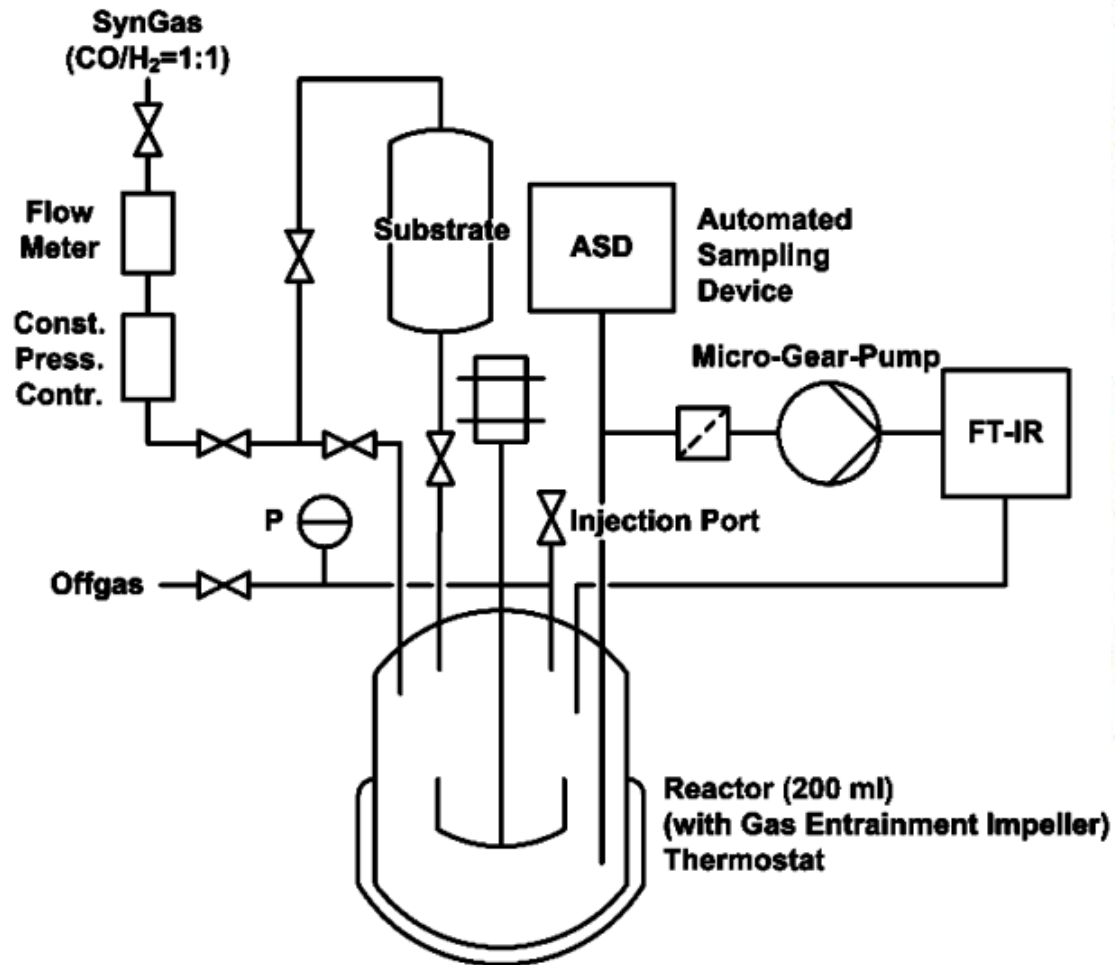
C₁₁-C₁₅ Alkenes:



Introduction

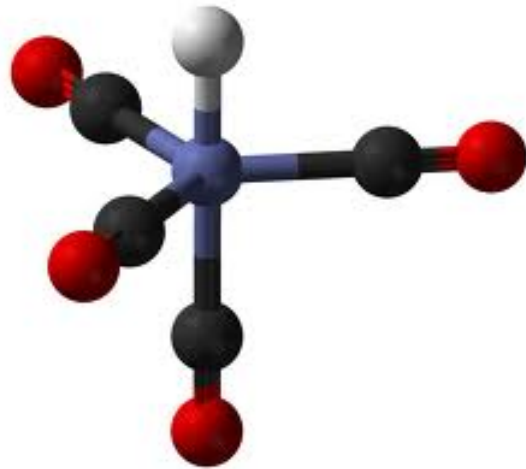
- **Various catalysts employed in hydroformylation reaction**
 - 1) Cobalt Catalyst: $\text{HCo}(\text{CO})_4$
 - 2) Cobalt Phosphine-Modified Catalyst: $\text{HCo}(\text{CO})_3(\text{PR}_3)$
 - 3) Rhodium Phosphine Catalyst: $\text{HRh}(\text{CO})(\text{PPh}_3)_3$
 - 4) Aqueous phase Rhodium Catalyst: TPPTS (Triphenylphosphinetrisulfonate)
 - 5) New generation of Rhodium Catalyst: bidentate phosphine ligands

Experimental setup with reactor system

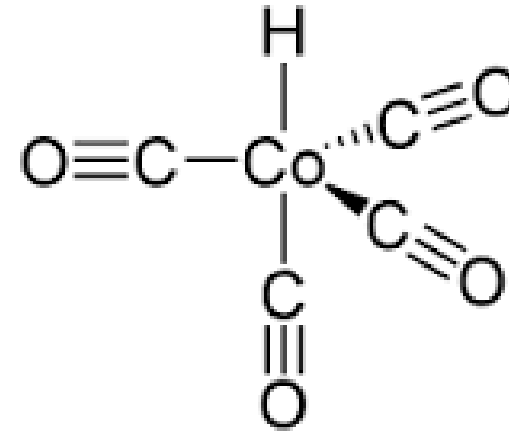


A: autoclave unit
C: IR transmission cell
P: micro-gear pump
S: FTIR spectrometer

Cobalt Catalyst: $\text{HCo}(\text{CO})_4$



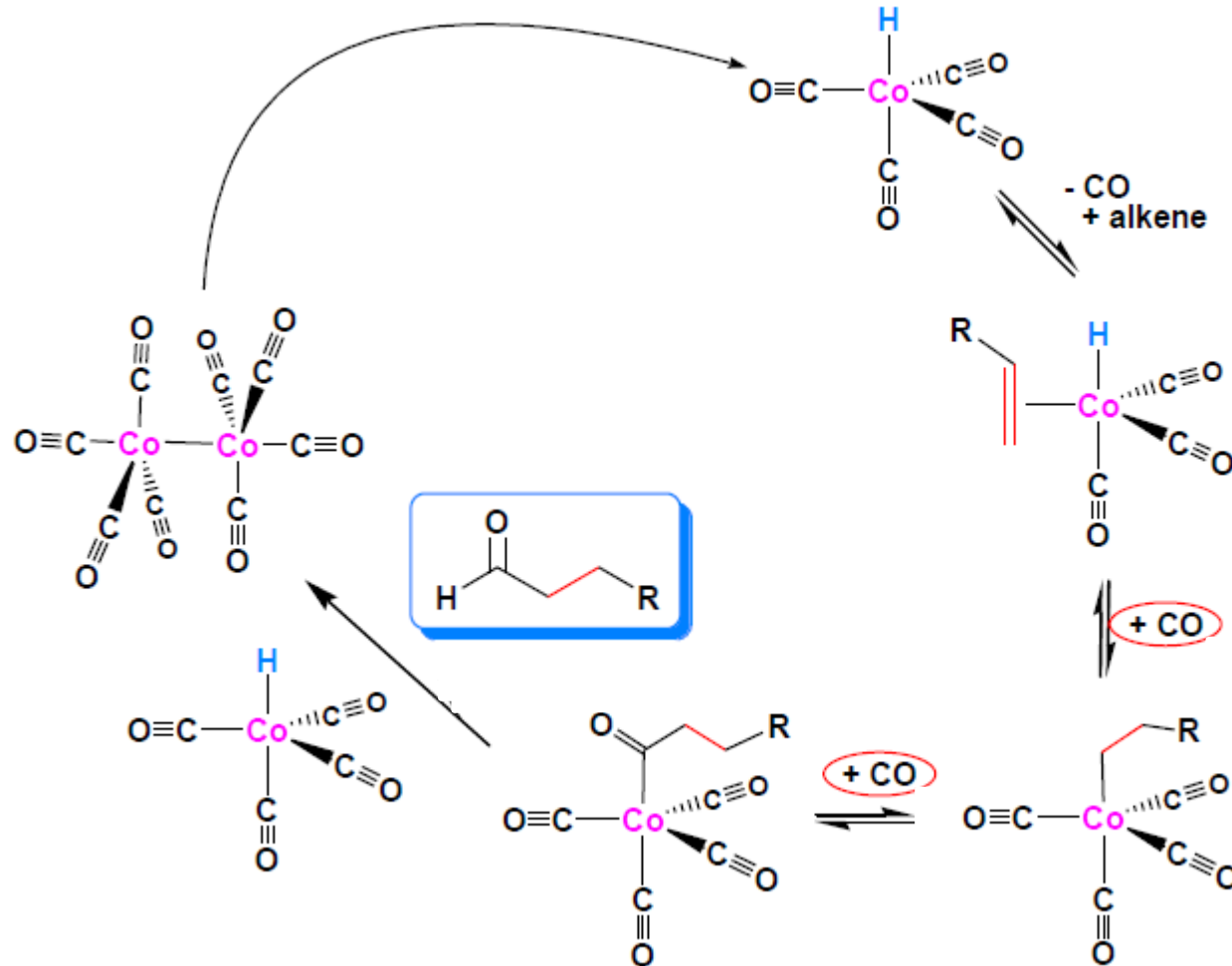
$\text{HCo}(\text{CO})_4$



- oldest homogeneous catalysis process still in use
- total H_2/CO (ratio= 1:1) pressures of 200- 300 bar and 110- 180 °C
- ratio of linear to branched aldehyde: ca. 4 to 1
- decomposed to metallic Co at high temperature and low CO pressure

Hydroformylation Mechanism

- Bimetallic



Cobalt Catalyst

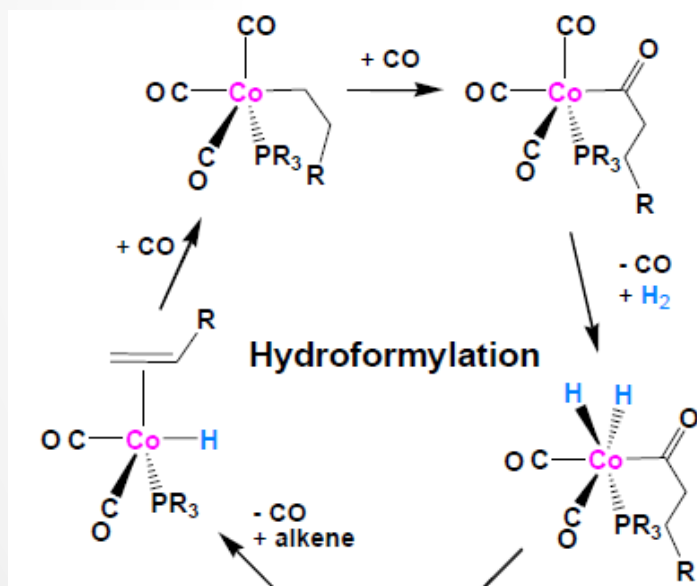
- **Kinetics**

$$\frac{d(\text{aldehyde})}{dt} = k[\text{alkene}][\text{Co}][\text{H}_2][\text{CO}]^{-1}$$

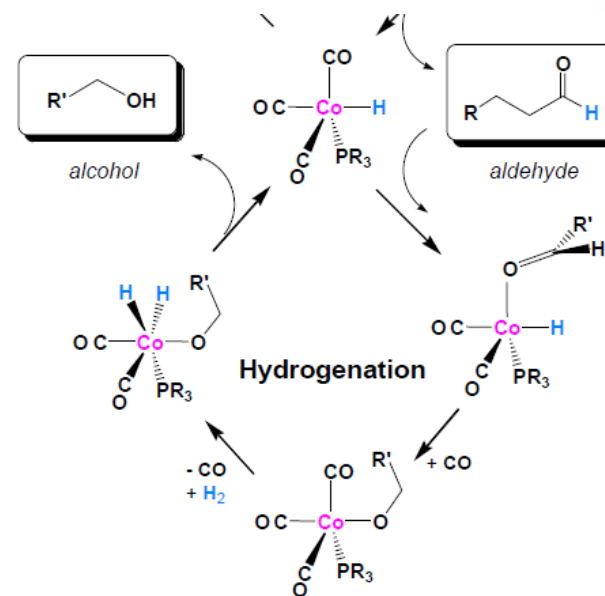
- inversely proportional to CO concentration because CO dissociation from the coordinatively saturated $18e^-$ species is required
- using a 1:1 ratio of H_2/CO , the reaction rate is independent of pressure
- $\text{HCo}(\text{CO})_4$ is only stable under certain minimum CO partial pressures at a given temperature
-
- CO pressure $\uparrow \rightarrow$ reaction rate \downarrow & high ratio of linear to branched product
- CO pressure $\downarrow \rightarrow$ reaction rate \uparrow & branched alkyl \uparrow (reverse β -elimination)

Cobalt Phosphine-Modified Catalyst

- The addition of PR_3 ligands cause a dramatic change in rate and regioselectivity due to electronic and steric effect of substitution of PR_3
 - Electronic effect of PR_3 :
 - stronger Co-CO bond (do not decompose) \rightarrow less CO pressure
 - stronger Co-CO bond \rightarrow less active than $\text{HCo}(\text{CO})_4 \rightarrow$ 5- 10 times slower
 - hydridic characteristic of hydride \rightarrow increase the hydrogenation capability



at 100- 180 °C
and 50- 100 bar
5- 10 slower



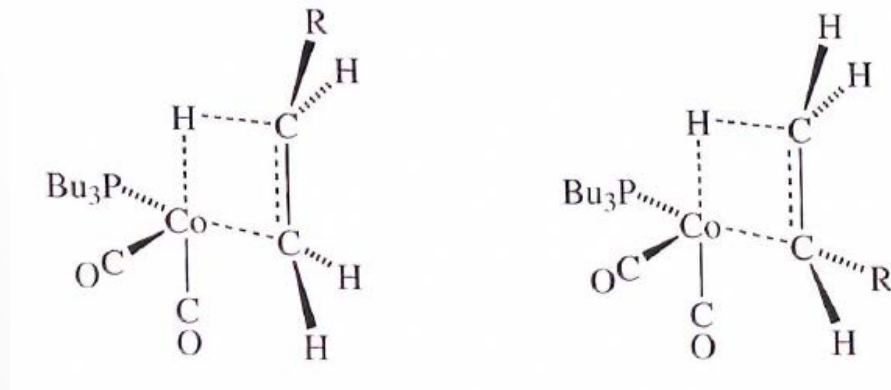
Two stage of
hydroformylation
and hydrogenation
combined into one
step

Cobalt Phosphine-Modified Catalyst

- The addition of PR_3 ligands causes a dramatic change in rate and regioselectivity due to electronic and steric effect of substitution of PR_3

➤ **Steric effect of PR_3 :**

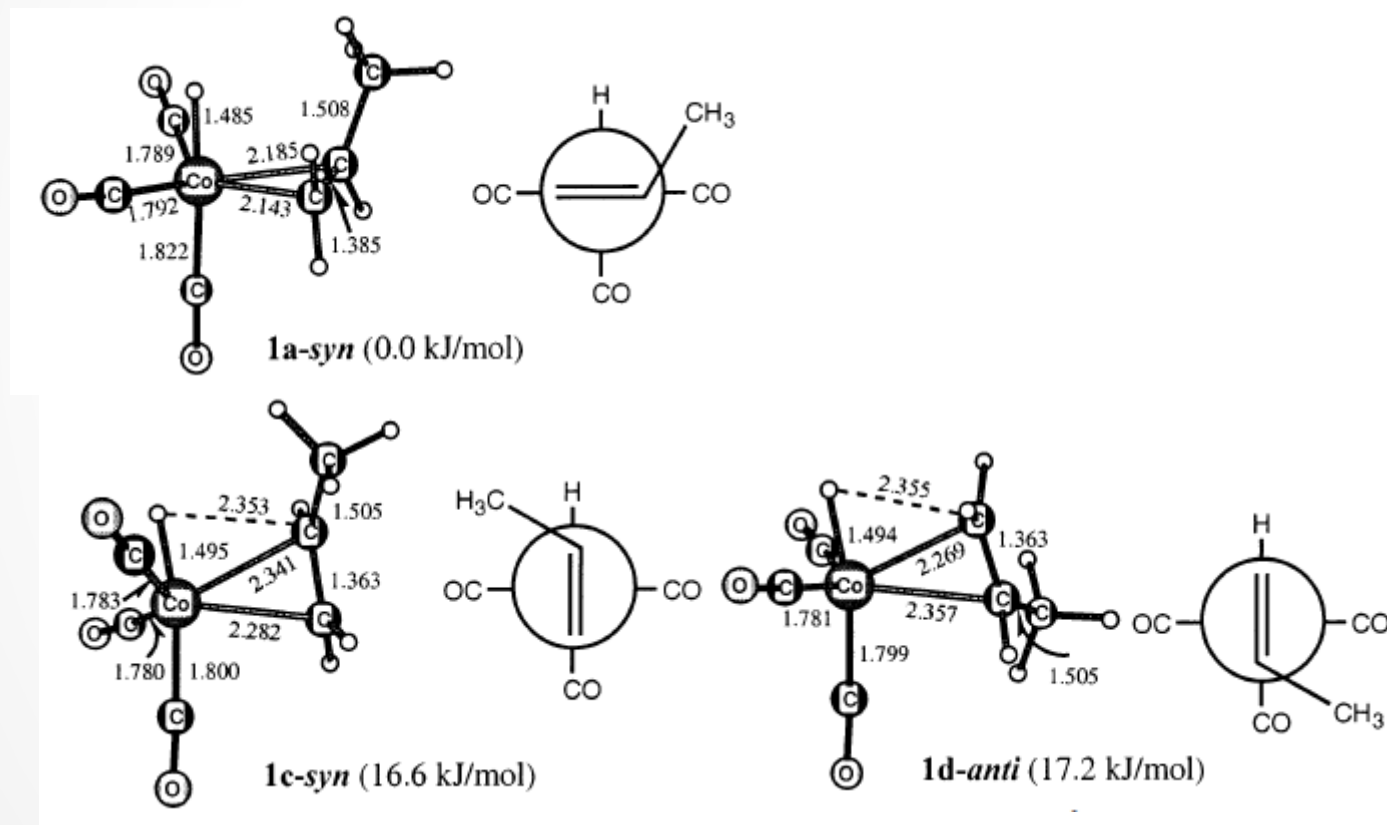
- Bulky PR_3 group influences the insertion direction of alkene to Co complex and geometry of intermediate (favors Anti-Markovnikov; Hydrogen transferred to carbon with bulkier R group)



Linear: Branched = 9: 1

Cobalt Phosphine-Modified Catalyst

- Geometry and relative energies of alkene adducts from $\text{HCo}(\text{CO})_4$ calculated by DFT



Cobalt Phosphine-Modified Catalyst

- Relationship between steric effect and regio-selectivity

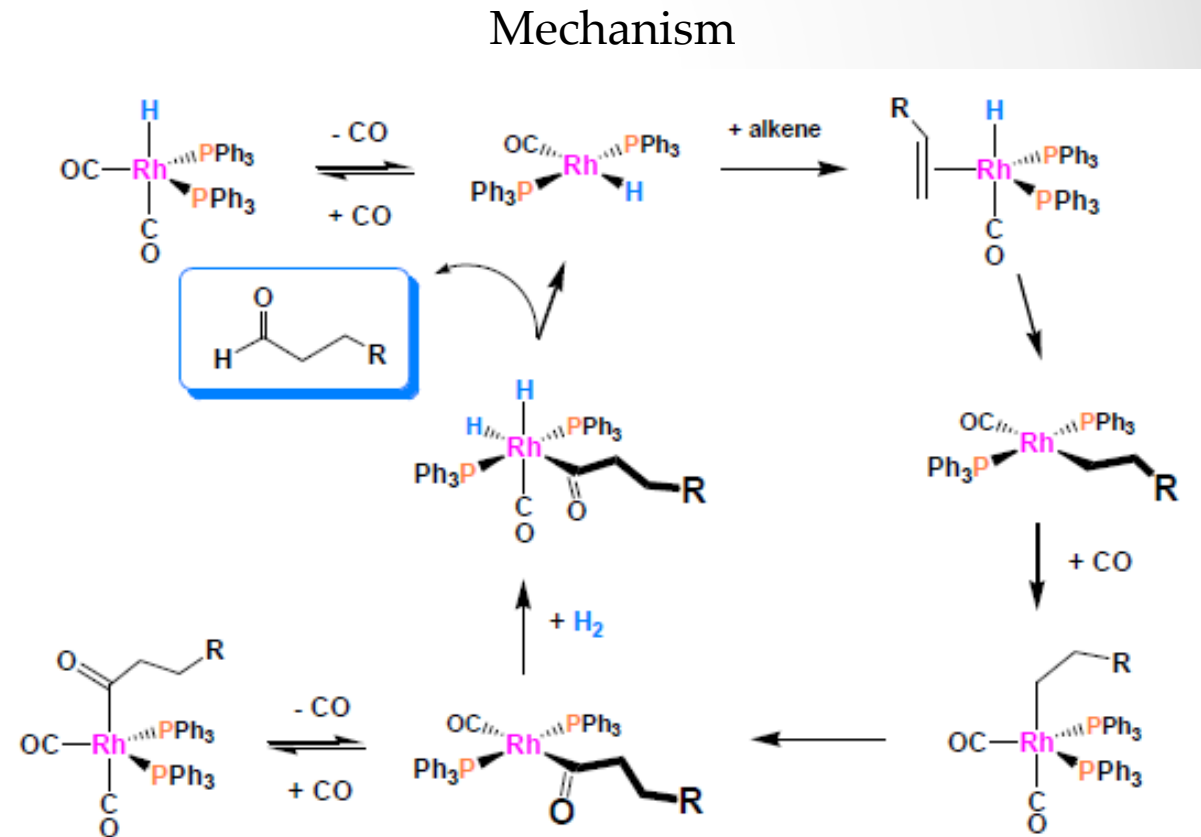
Table 1. Hydroformylation of 1-hexene using $\text{Co}_2(\text{CO})_8/2\text{P}$ as catalyst precursor. 160°C, 70 atm, 1.2:1 H_2/CO

PR_3	pK_a	Tolman ν (cm^{-1})	Cone Angle $^\circ$	$k_r \times 10^3$ (min^{-1})	% Linear Prod	Aldehyde to alcohol
$\text{P}(i\text{-Pr})_3$	9.4	2059.2	160	2.8	85.0	--
PEt_3	8.7	2061.7	132	2.7	89.6	0.9
PPr_3	8.6	2060.9	132	3.1	89.5	1.0
PBu_3	8.4	2060.3	136	3.3	89.6	1.1
PEt_2Ph	6.3	2063.7	136	5.5	84.6	2.2
PEtPh_2	4.9	2066.7	140	8.8	71.7	4.3
PPh_3	2.7	2068.9	145	14.1	62.4	11.7

➔ Steric and electronic effect of substitution of PR_3 affects the linear to branched ratio

Rhodium Catalyst

- *Advantage of Rh catalyst over Co catalyst:*
 - Rh complex 100-1000 more active than Co complex
 - at ambient condition (15-25 bar, 80-120 °C)
 - energy saving process
 - linear to branched ratios as high as 15 to 1



Rhodium Catalyst

- Selective catalyst with the substitution of PR_3 ligands
- Rate determining steps are not fully understood

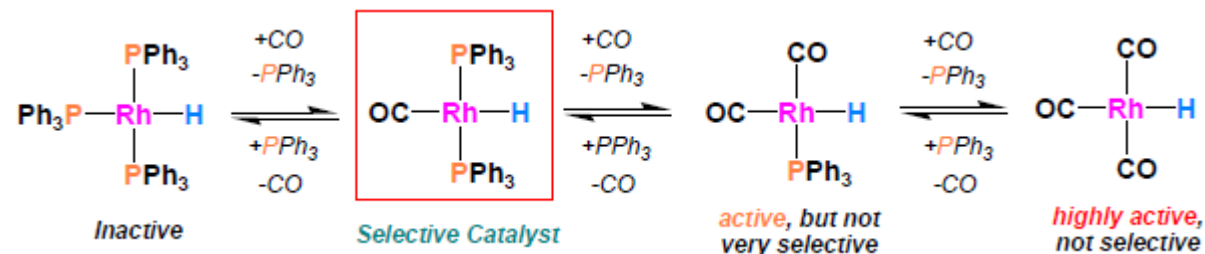
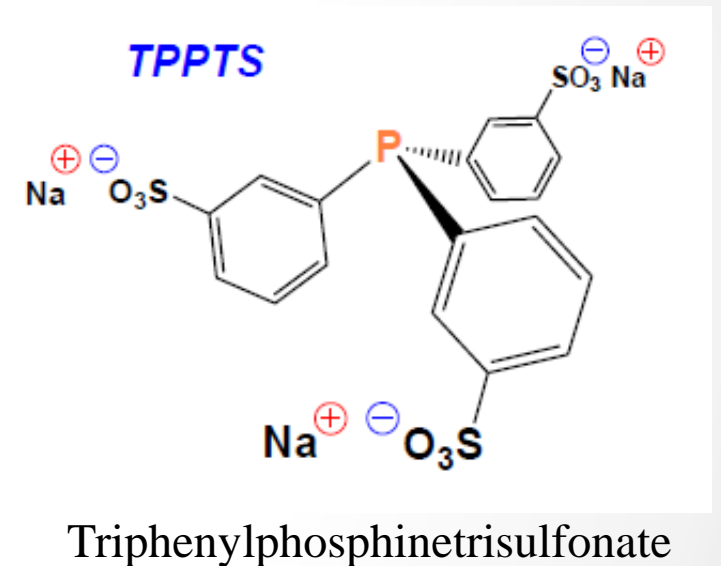


Table 2. Rate constants and Regioselectivities for the Hydroformylation of 1-Hexene using $\text{Rh}(\text{acac})(\text{CO})_2$ with Different PPh_3 Concentrations. Reaction Conditions: 90 psig (6.2 bar), 1:1 H_2/CO , 90° C.

[Rh] (mM)	[PPh ₃] (M)	PPh ₃ /Rh ratio	k_{obs} (min ⁻¹ mM Rh ⁻¹)	l:b ratio
0.5	0.41	820	0.032	11
1	0.82	820	0.016	17

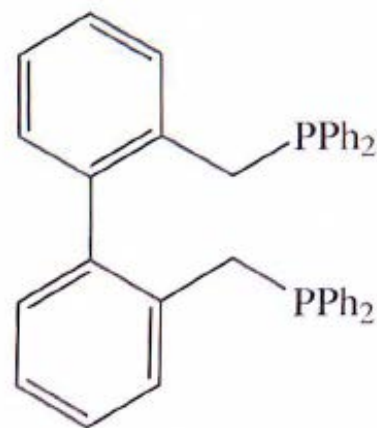
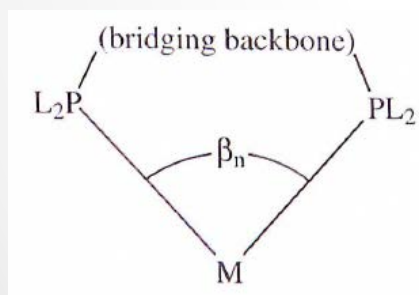
Water Soluble Rhodium Catalysts

- Water soluble catalyst are made using sulfonated PR_3 ligands
(3,3',3''-Phosphanetriyltris (benzenesulfonic acid) trisodium salt; TPPTS)
- Runs at mild conditions (at 18 bar and 85- 90 C°)
- Easily separated because water-soluble catalysts remain in aqueous phase and aldehyde is separated into organic phase with higher regioselective ratio between linear and branch.



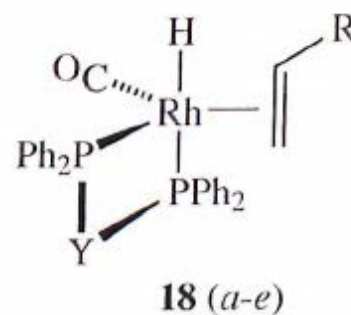
Bidentate Phosphine Rh Catalyst

- Over the past 20 years, research was focused on bidentate ligands because of remarkably increased regioselectivity between linear and branched aldehydes
- Bite angle: P-M-P angle
- High regioselectivity is related to the stereochemistry of complex combined with the electronic and steric factors of bidentate PR_3



BISPI

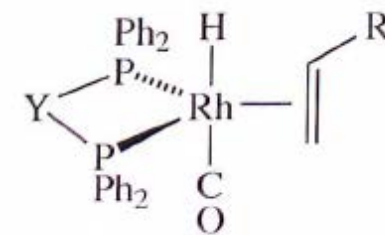
(2,2'-bis[diphenylphosphinomethyl]-1,1'-biphenyl)



18 (a-e)

(β : small)

Y = Bridging backbone

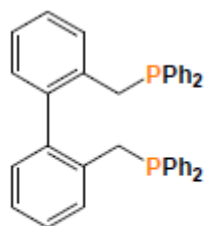


19 (e-e)

(β : large)

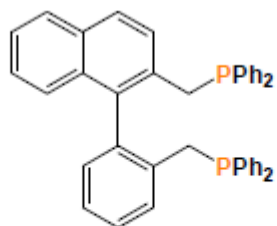
Bidentate Phosphine Rh Catalyst

- Various bidentate phosphine and phosphite ligands

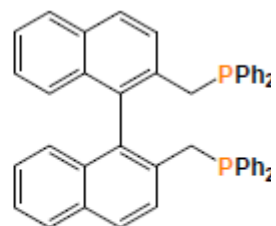


Bisbi

113-123°

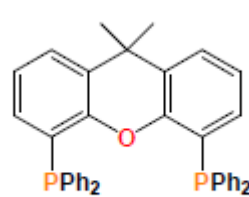


Bisbi*



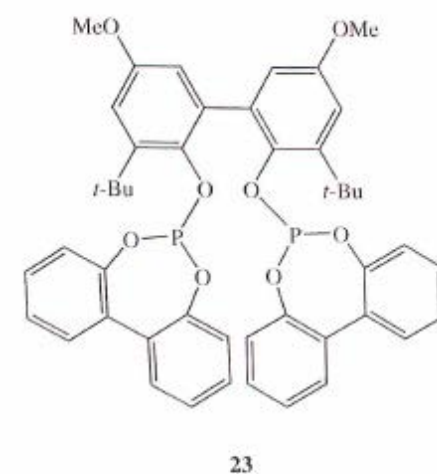
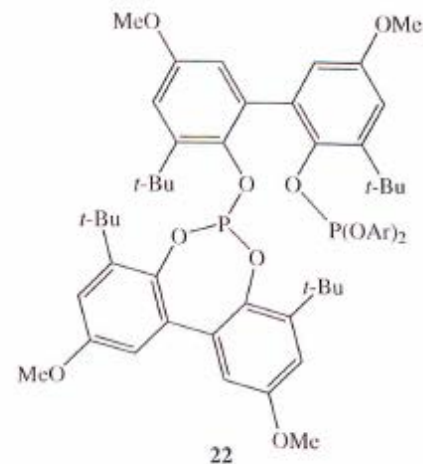
Naphos

120°



Xantphos

111°



Hydroformylation of 1-hexene (at 90 °C, 6.2 bar, 1:1 H₂/CO, acetone solvent)

Catalyst (1 mM)	Init TOF (min ⁻¹)	Aldehyde L:B	% iso
Rh/PPh ₃ (1:400)	13(1)	9:1	< 0.5
Rh/Bisbi (1:5)	25(2)	70:1	< 0.5
Rh/Naphos (1:5)	27(1)	120:1	1.5
Rh/Xantphos (1:5)	13(2)	80:1	5.0

→ L:B = 30:1, 98% conversion

- *Angew. Chem.* 2012, 124, 11195 –11200

Computational Mechanism

Other Aspects of Hydroformylation

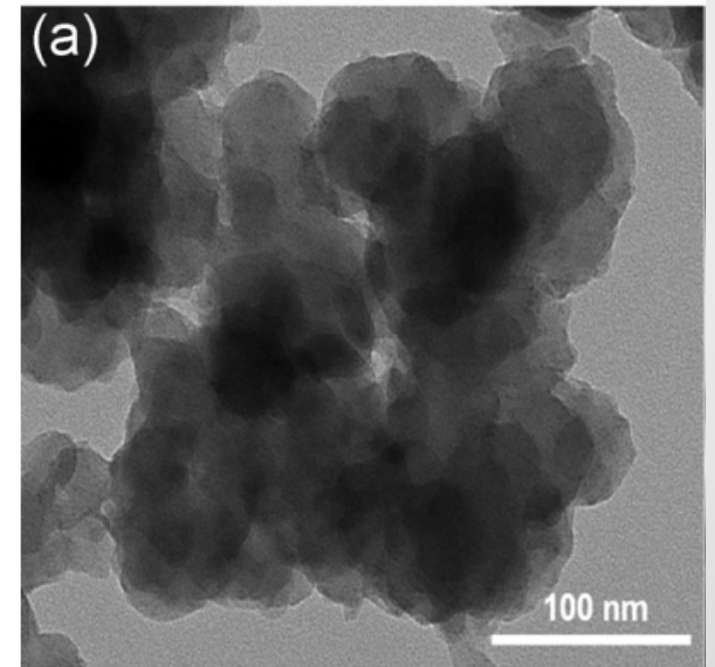
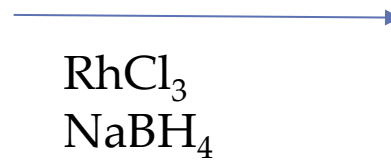
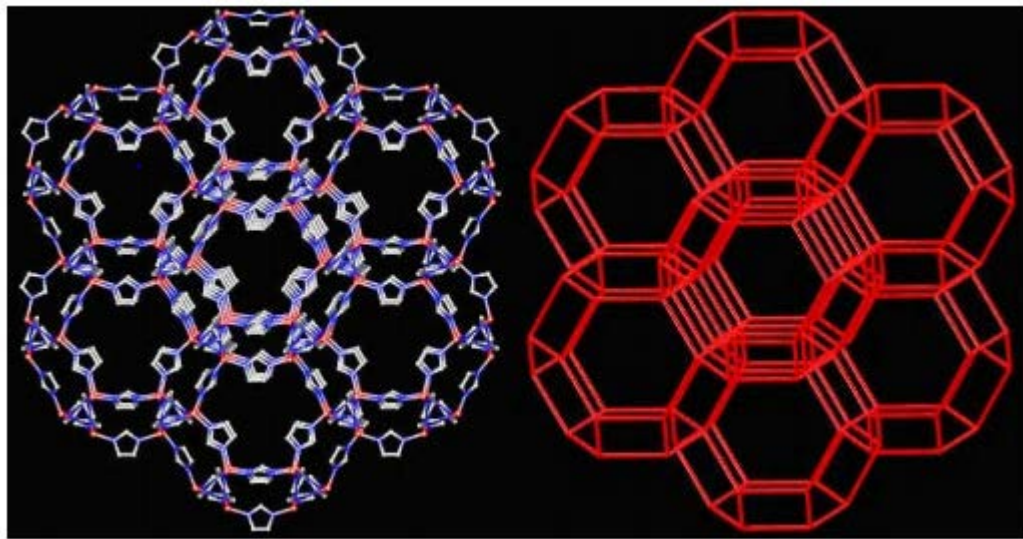
- The overall effectiveness of other metals are compared with Co and Rh.

Rh	>	Co	>	Ir	>	Ru	>	Os	>	Mn	>	Fe	>	Cr, Mo, W, Ni, Re		
Rel. Reactivity:		10^4-10^3		1		10^{-1}		10^{-2}		10^{-3}		10^{-4}		10^{-6}		$< 10^{-6}$

Improvements and Modifications: MOF Assisted Hydroformylation

- Rhodium nanoparticles in ZIF-8
- Facilitate separations in industrial processes
 - Homogeneous vs heterogeneous catalysis

ZIF-8

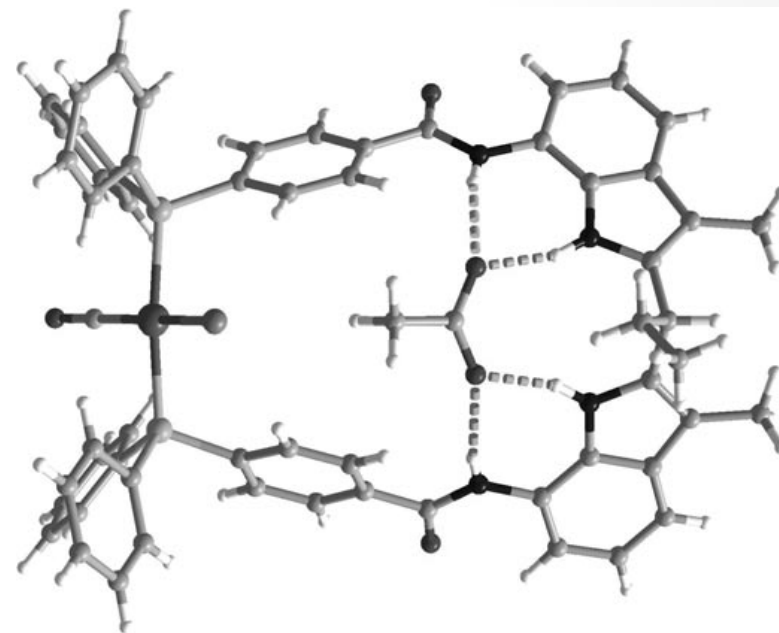
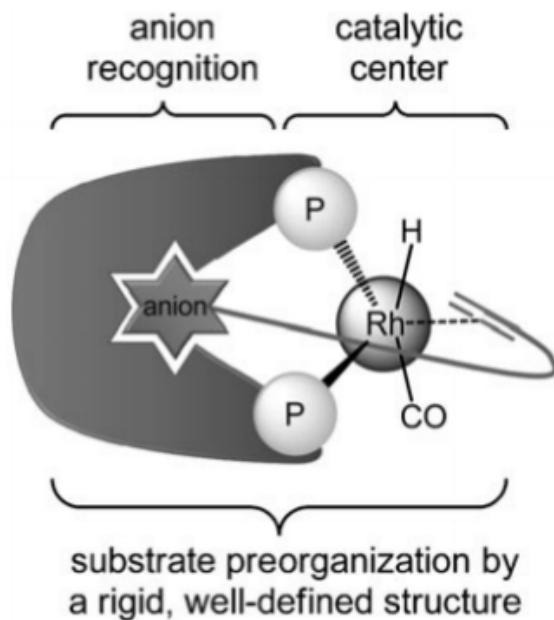
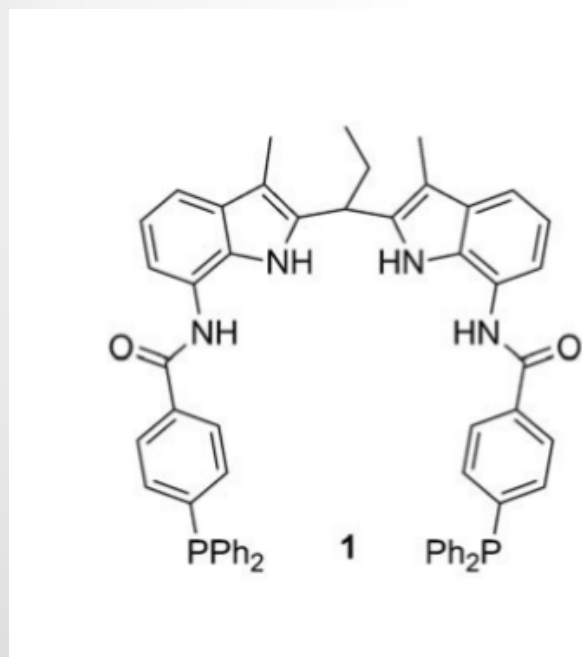
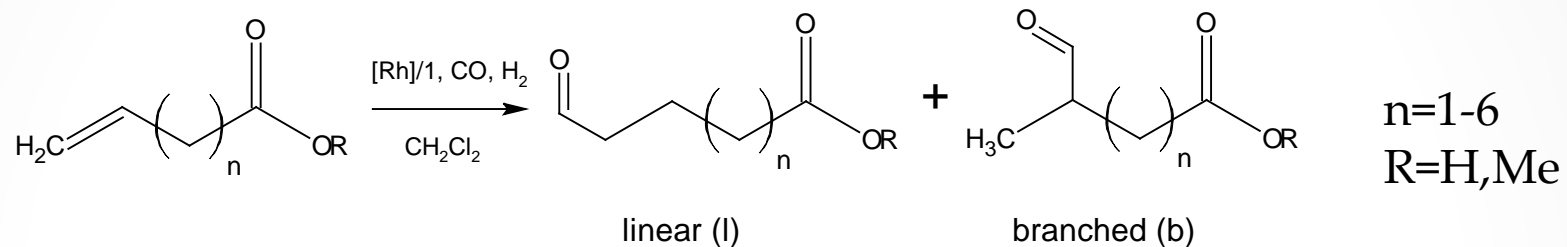


Hydroformylation of Alkenes by Rh NP in ZIF-8

Entry	Alkene	Yield of aldehydes (%)	Yield of iso ^a (%)	Yield of n ^b (%)	n/iso
1	1-Hexene	92	48	44	0.9
2	1-Heptene	87	58	29	0.5
3 ^c	1-Heptene	0	0	0	0
4	1-Octene	86	51	35	0.7
5	1-Dodecene	76	41	35	0.9
6	1-Tetradecene	79	53	26	0.5
7	Styrene	94	68	26	0.4

^aiso: Branched aldehydes; ^bn: Linear aldehydes; ^ccatalyzed by ZIF-8, reaction time 24 h.

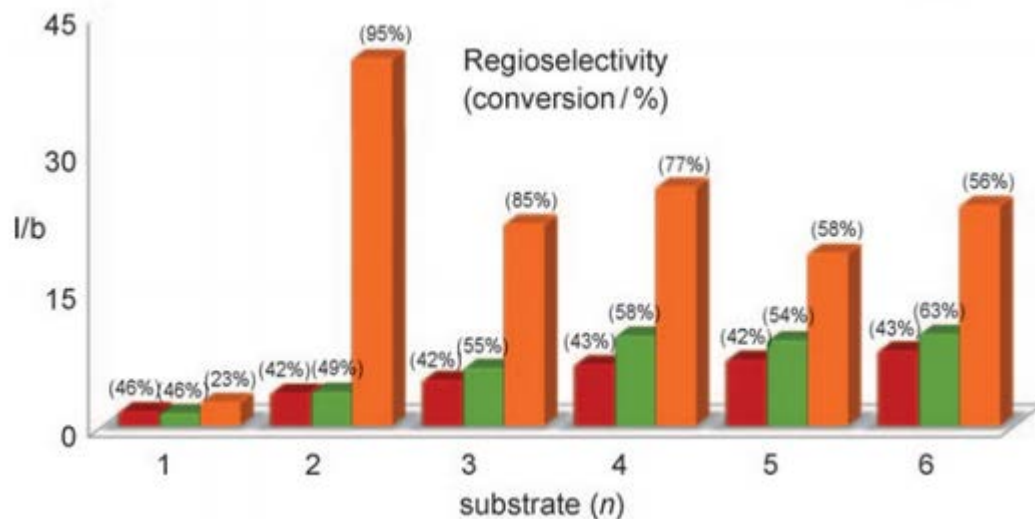
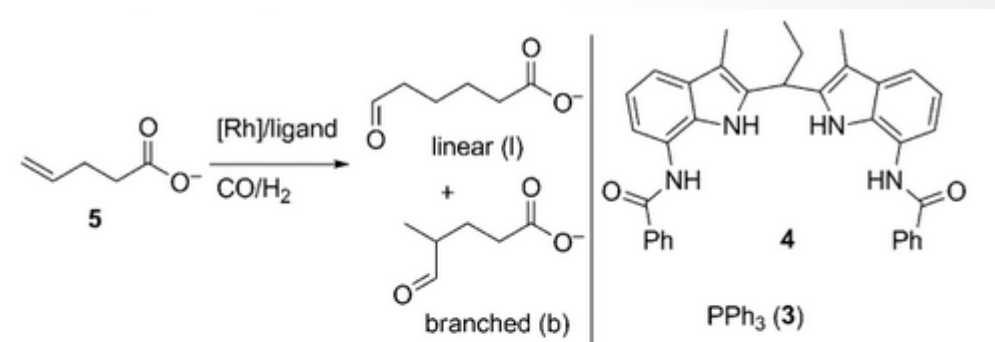
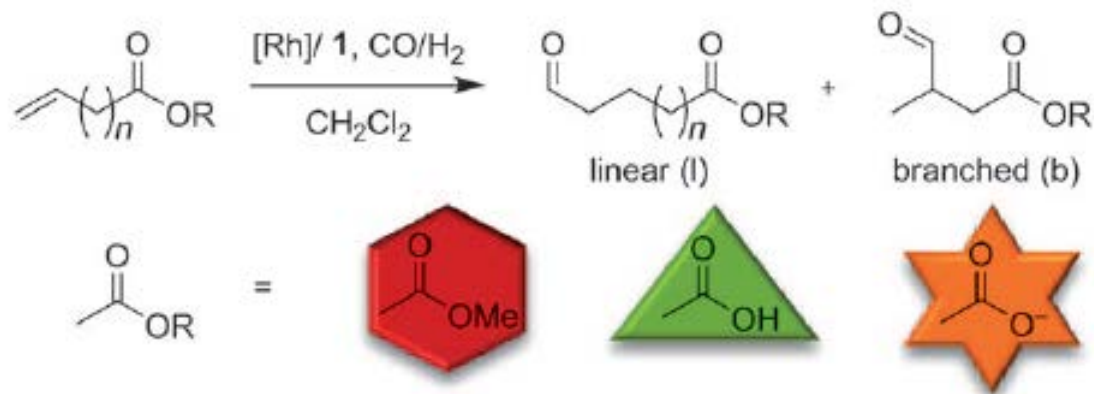
Regioselective Ligand DIMPhos



TBA[Rh(1·AcO)(CO)Cl]; TBA=tetrabutylammonium

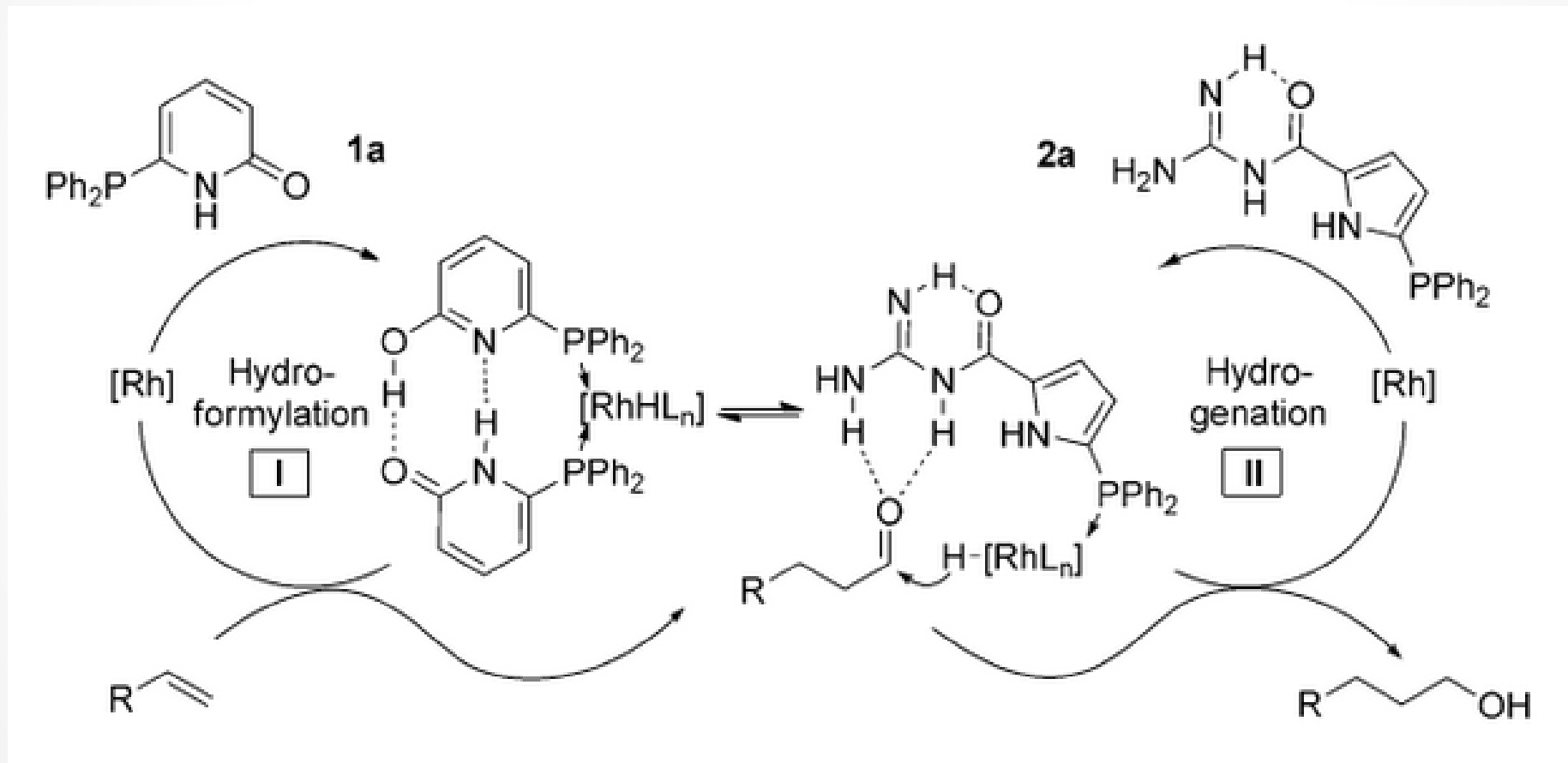
Angew. Chem. 2011, 123, 416–420

Conversion Results and Regioselectivity

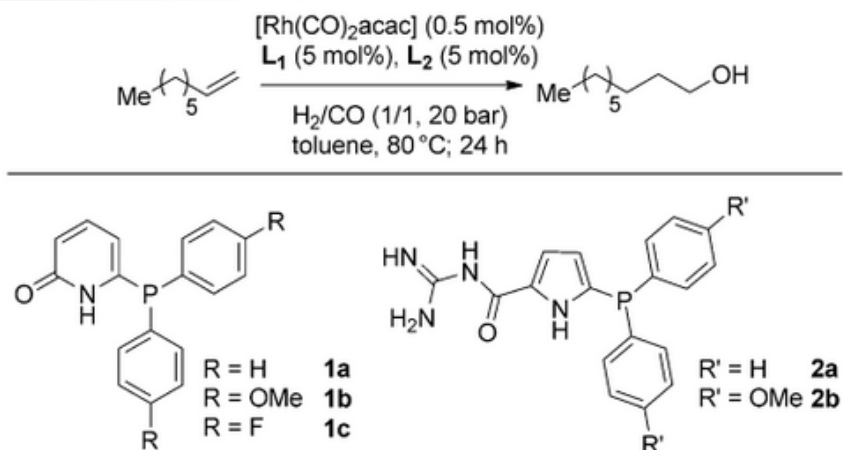


Entry	Ligand	Conversion [%]	Regioselectivity [l/b ratio]
1	1	95 (80) ^[b]	40 (> 50) ^[b]
2	4/3 (1:2)	100	2.9
3 ^[c]	3	100	3.1
4	–	13	1.8

Tandem Hydroformylation/Hydrogenation



Tandem Hydroformylation/Hydrogenation



Entry	L ₁	L ₂	RCHO [%] ^[a]	l:b ^[a]	ROH [%] ^[a]	l:b ^[a]
1	PPh ₃	–	99	82:18	0	–
2	1a	–	99	95:5	0	–
3	2a	–	2	–	98	81:19
4 ^[b]	1a	2a	5	–	95	97:3
5	1a	2b	1	–	99	93:7
6	1b	2b	5	33:67	95	91:9
7	1c	2b	5	37:63	95	96:4

[a] Determined by GC analysis. [b] Reaction time was increased to 72 hours. acac = acetylacetonate.

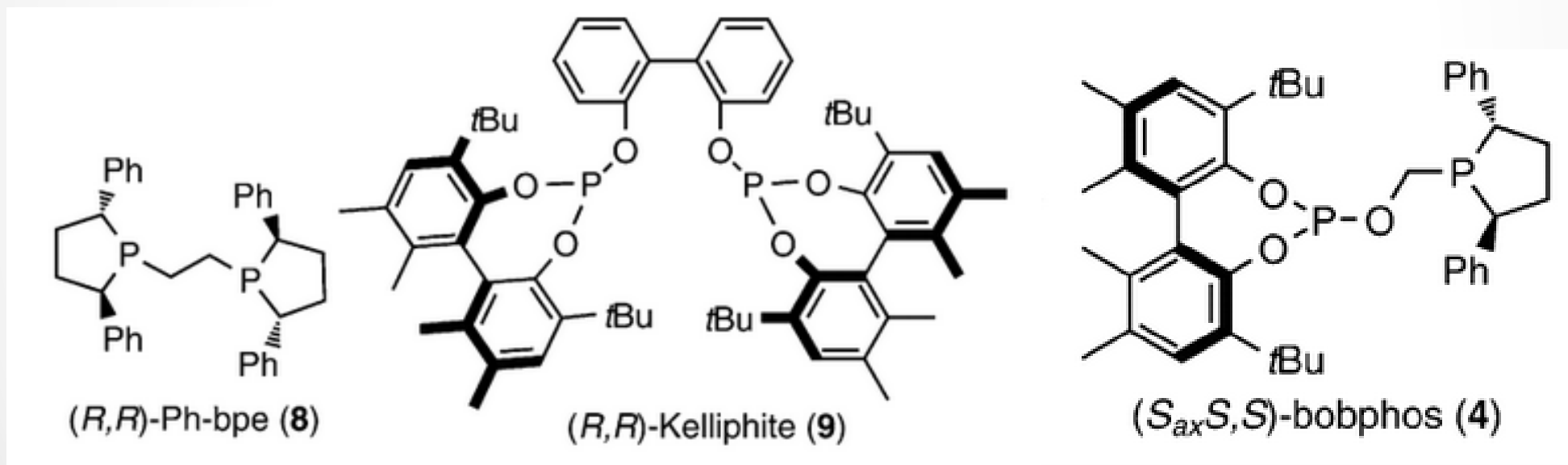
➔ High demand in industry for linear alcohols as well as linear aldehydes

➔

- 1) one-pot conversion of alkenes to linear alcohols through hydroformylation/hydrogenation by using a single metallic catalyst;
- 2) high linear/branched regioselectivity;
- 3) simultaneous chemoselective reduction of the intermediate aldehyde with molecular hydrogen gas (no alkene hydrogenation).

Shifting Focus: Branched Hydroformylation Products

- Production of enantio-enriched branched products.
- Applications in pharmaceuticals



Shifting Focus: Branched Hydroformylation Product

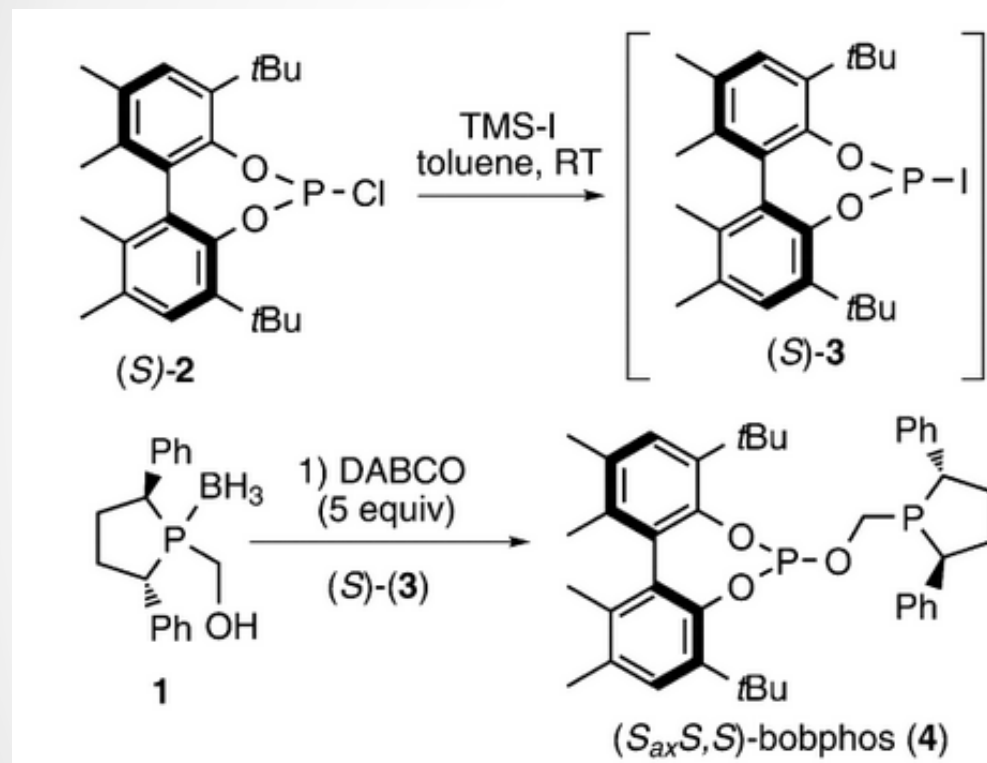
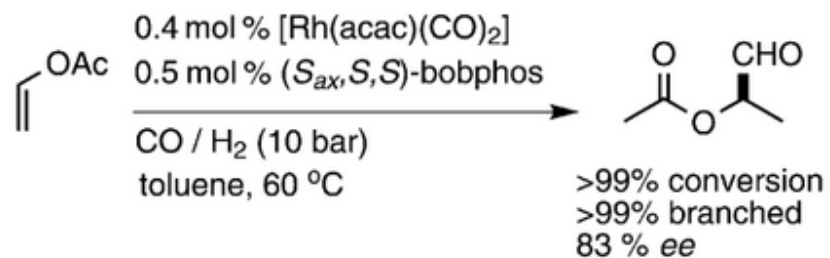


Table 1: Hydroformylation of allyl benzene (**10a**) using a range of hydroformylation catalysts at room temperature.

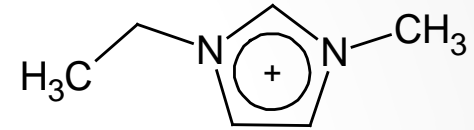
Entry ^[a]	Ligand	Product yield [%] ^[b]	<i>b:l</i> ^[b]	<i>ee</i> ^[c]
1	Ph ₃ P	46	1:1.1	n.d.
2	5	86	1:1.2	n.d.
3	6	91	1:1.1	n.d.
4	7	93	1:1.8	n.d.
5	dppe ^[d]	56	1:1.0	n.d.
6	dppf ^[d]	52	1:1.2	n.d.
7	8	66	1:1.1	0
8	9	87	1:1.0	5
9	4	64 ^[e]	4.0:1	90
10	4	39 ^[f]	3.6:1	88

[a] 0.4 mol% [Rh(acac)(CO)₂] and 0.5 mol% bidentate ligand or 1.2 mol% monodentate ligand were stirred at 5 bar syngas at 50 °C for

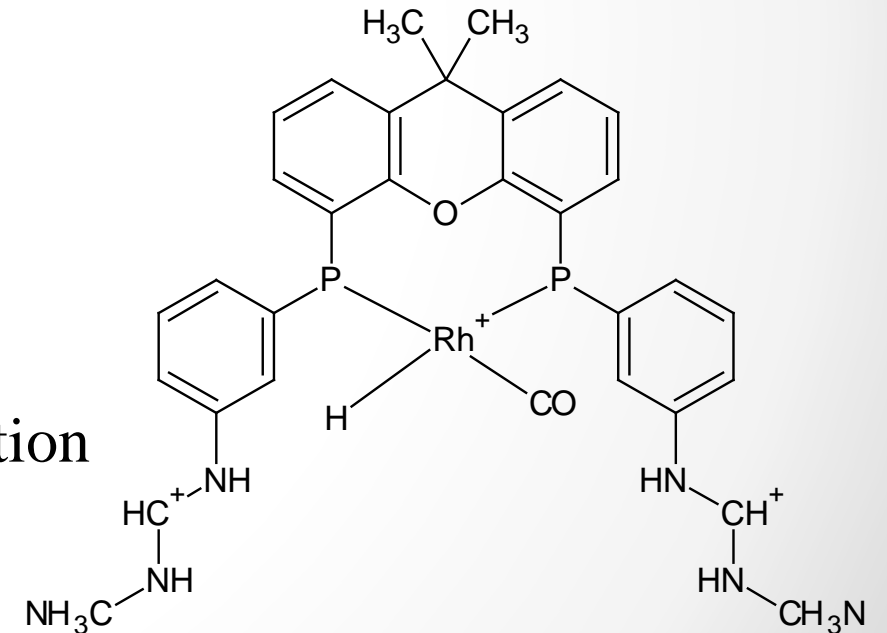


Making Expensive Catalysis More Efficient

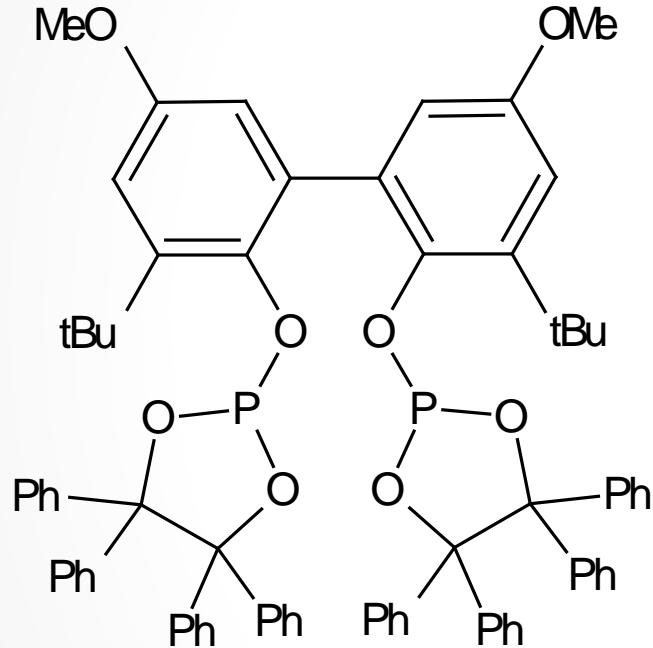
- Advantage of the utilizing Ionic Liquids (IL)
 - What is an ionic liquid?
 - Salts that exist as a liquid at room temperature
 - No vapor pressure
 - Large liquid ranges
- Disadvantage
 - Very very very expensive
 - Require complicated ligands to provide for solvation



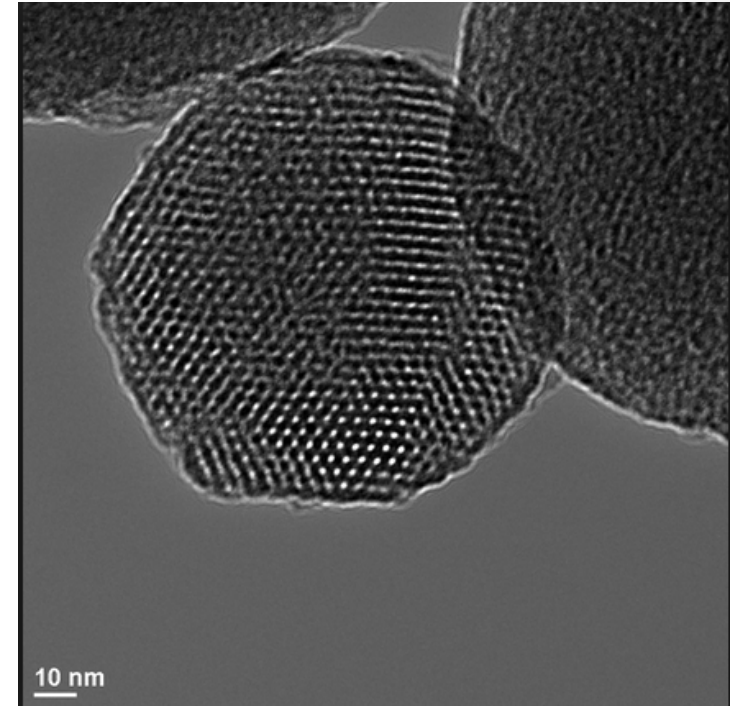
Ethyl methyl Imidazolium (EMIM)



Supported Ionic Liquid Phase (SILP)



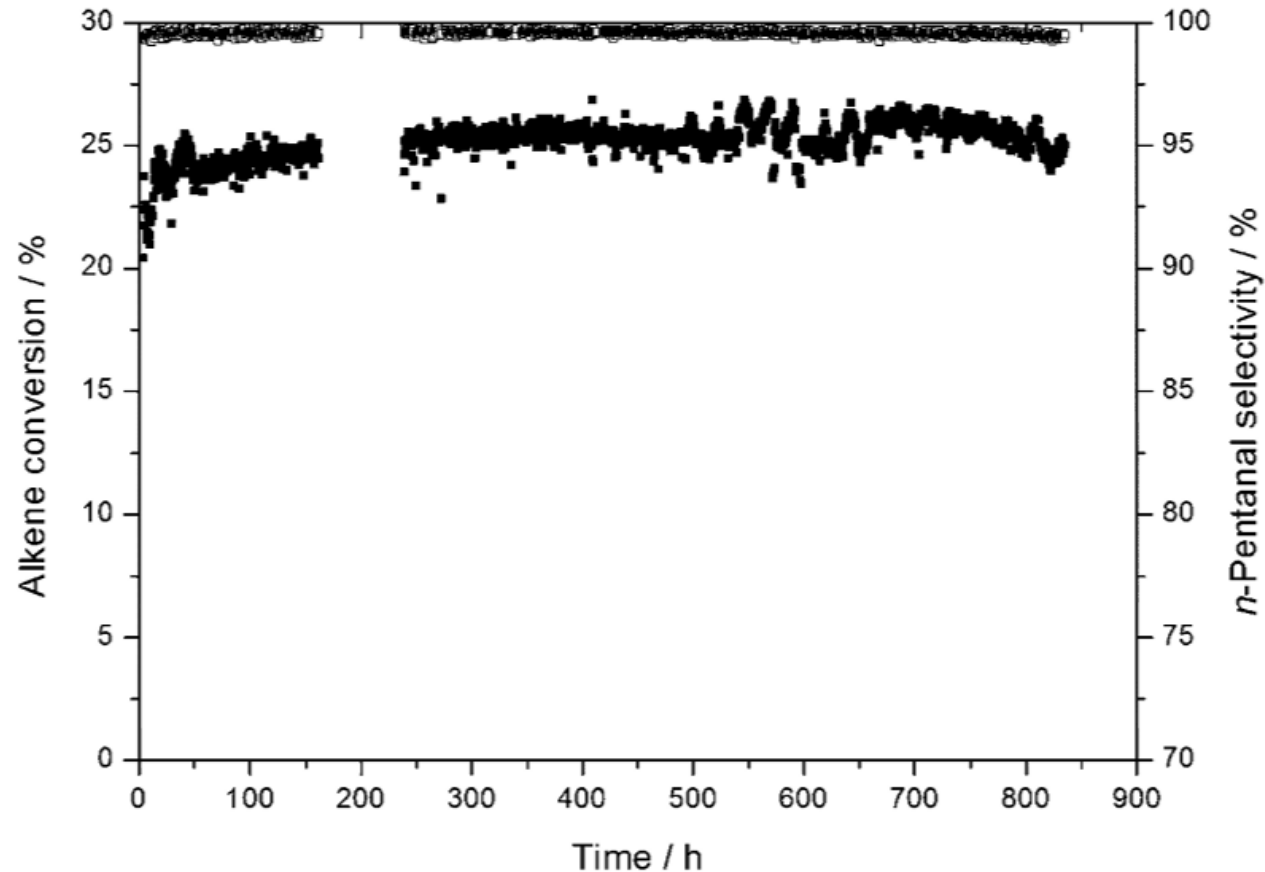
+ Rh[CO]₂(acac) + [EMIM][NTf₂]



What is this Particular SLIP Good For?

- Minimizes IL usage
 - Only a small film adsorbed in mesoporous silica as opposed to solvent usage
- Selective linear hydroformylation of 1-butane
 - Mixed C4 gas feedstock
 - Continuous flow hydroformylation
 - Minimal catalyst deactivation

Experiment: Mixed C4 feedstock



Feedstock composition:

- 1-butene: 25.6 %
- Trans-2-butene: 9.1%
- cis-2-butene: 7.0%
- Butane: 14.9%
- Isobutane: 43.1%
- 1,3-butadiene: 0.3%

Conclusion

- Through the catalyzed hydroformylation reaction, olefins are converted into aldehydes; mechanism and corresponding energy calculation were demonstrated.
- The different type of phosphine ligands and cobalt- and rhodium-based catalysts were introduced; bidentate phosphine Rh catalyst showed the highest ratios of linear to branched aldehyde even at ambient conditions.
- Enantio- and regio-selectivity can be increased if specifically designed ligands on Rh catalysts are used.