Chair of Inorganic and Metal-Organic Chemistry
Department of Chemistry
Technical University of Munich

Homogeneous Catalysis 1: Basics

Mirza Cokoja

South German Catalysis Institute Grad School Course

Obertauern, March 04th, 2020

Book recommendations

Organometallic chemistry

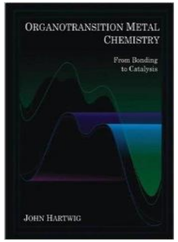
- J. F. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, 2010
- R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals,* 6th Ed., J. Wiley & Sons, 2014

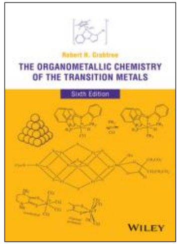
Homogeneous catalysis

- D. Steinborn, *Fundamentals of Organometallic Catalysis*, Wiley-VCH, 2012
- A. Behr, P. Neubert, *Applied Homogeneous Catalysis*, Wiley-VCH, 2012

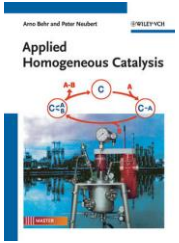
Industrial catalysis

- H.-J. Arpe, *Industrial Organic Chemistry*, 4th Ed., Wiley-VCH, 2003


ORGANOTRANSITION METAL CHEMISTRY
From Bonding to Catalysis
JOHN HARTWIG


Robert H. Crabtree
THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS
Sixth Edition
WILEY


Dirk Steinborn
Grundlagen der metallorganischen Komplexkatalyse
STUDIUM


Arno Behr and Peter Neubert
WILEY-VCH
Applied Homogeneous Catalysis
MASTER


H.-J. Arpe
WILEY-VCH
Industrielle Organische Chemie
Bedeutende Vor- und Zwischenprodukte
Sechste, vollständig überarbeitete Auflage

About me

CV

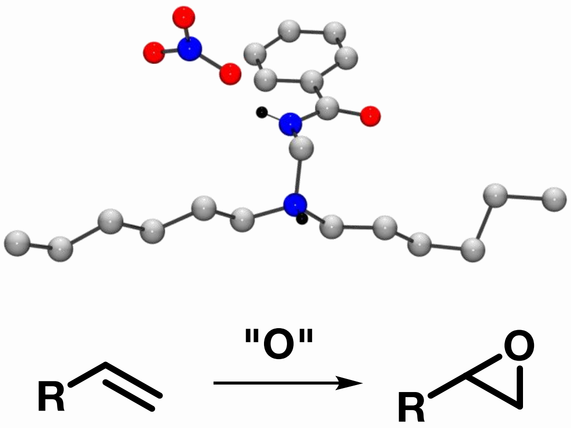
- 2007: PhD in Bochum (with R.A. Fischer)
- 2008: Postdoc in Toulouse (AvH, with B. Chaudret)
- Since 2009: Researcher@TUM

Teaching

- Inorganic and Metal-Organic Chemistry
- Homogeneous Catalysis

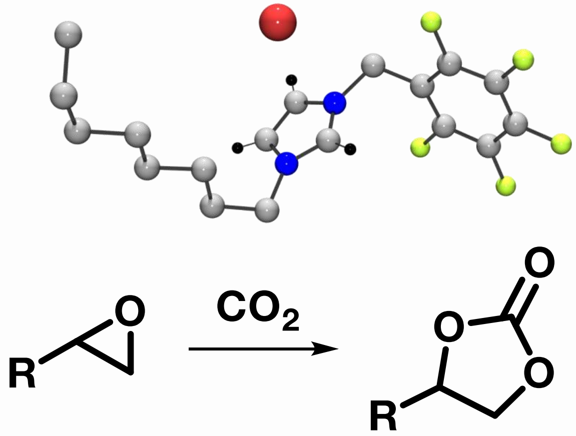
My research interests

ILs as micellar catalysts



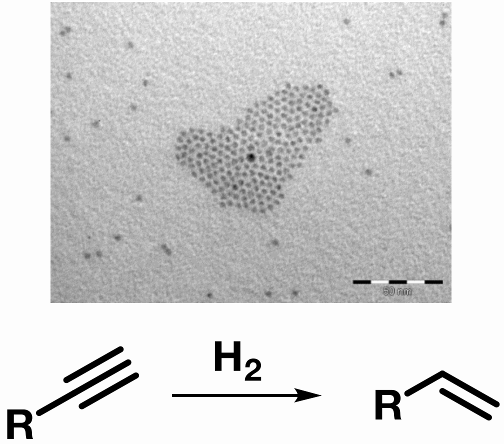
ChemSusChem **2016**, *9*, 1773
Chem. Commun. **2015**, *51*, 3399
Catal. Sci. Technol. **2014**, *4*, 3845
ChemSusChem **2014**, *7*, 429
Chem. Eur. J. **2013**, *19*, 5972

CO_2 upgrading



ChemCatChem **2015**, *7*, 94
Chem. Eur. J. **2014**, *20*, 11870
Catal. Sci. Technol. **2014**, *4*, 1534
Catal. Sci. Technol. **2014**, *4*, 1638
ChemSusChem **2014**, *7*, 1357

Selective hydrogenations



J. Colloid Interface Sci. **2016**, *478*, 72
Catal. Commun. **2017**, *100*, 85

What are your expectations?

Angewandte Essays

Homogenous Catalysis

DOI: 10.1002/anie.201305308

Oligomerization of Ethylene to α-Olefins: Discovery and Development of the Shell Higher Olefin Process (SHOP)

*Wilhelm Keim**

multiphase catalysis · olefins · oligomerizations · polymer chemistry · SHOP

Dedicated to Professor Karl Ziegler and Professor Günther Wilke

12492 **Wiley Online Library** © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim *Angew. Chem. Int. Ed.* **2013**, 52, 12492 – 12496

Wilhelm Keim studied chemistry at the Universities of Münster and Saarbrücken (diploma) and obtained his doctorate 1963 at the Max-Planck-Institut für Kohlenforschung in Mülheim. He completed a one-year postdoctorate at the Columbia University in New York (1964–1965) and worked from 1965 to 1973 as a chemist, group leader, head of department and manager for Shell Development, USA. From 1973 to 2000 he held the Lehrstuhl für Technische Chemie und Petrolchemie at RWTH Aachen. He has received numerous prestigious honors.

Luck, talent, and hard work: Currently, over a million tons of α-olefins are manufactured per annum using the Shell Higher Olefin Process (SHOP). The discovery of the process was the result of correct model conceptions and lucky coincidence. W. Keim, one of the main participants in the development of SHOP, gives a personal account of the events.

Angewandte Chemie International Edition

Essays

Homogenous Catalysis

The Shell Higher Olefin Process

Synthesis of middle, *internal* olefins from a mixture of long and short *terminal* olefins

→ Sequence of three processes (ca. 12 million tons per year):

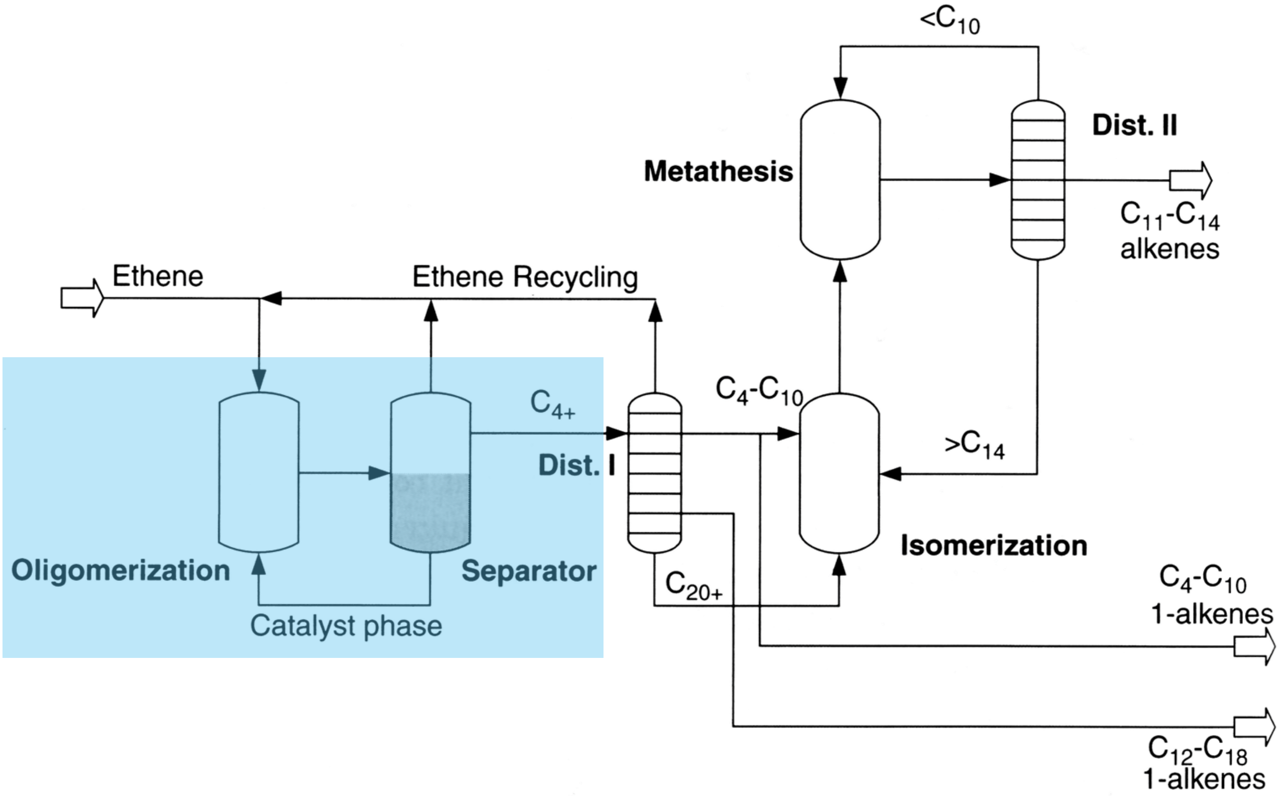
1) Olefin oligomerization (homogeneous Ni-cat.)

2) Olefin isomerization (Na/K or MgO)

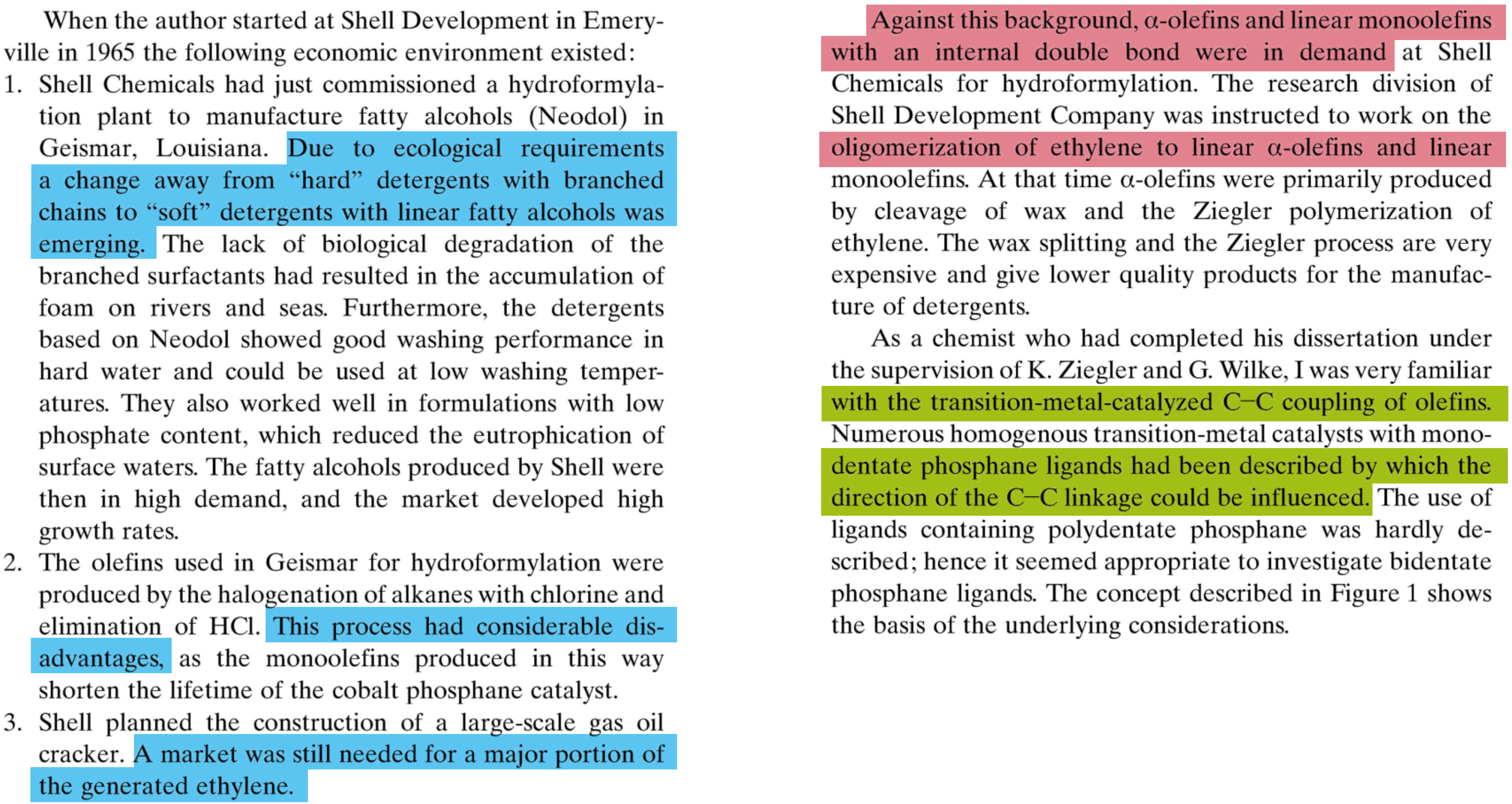
3) Olefin metathesis (Co/Mo oder Re)

The Shell Higher Olefin Process

Flow diagram of the process



The driving force



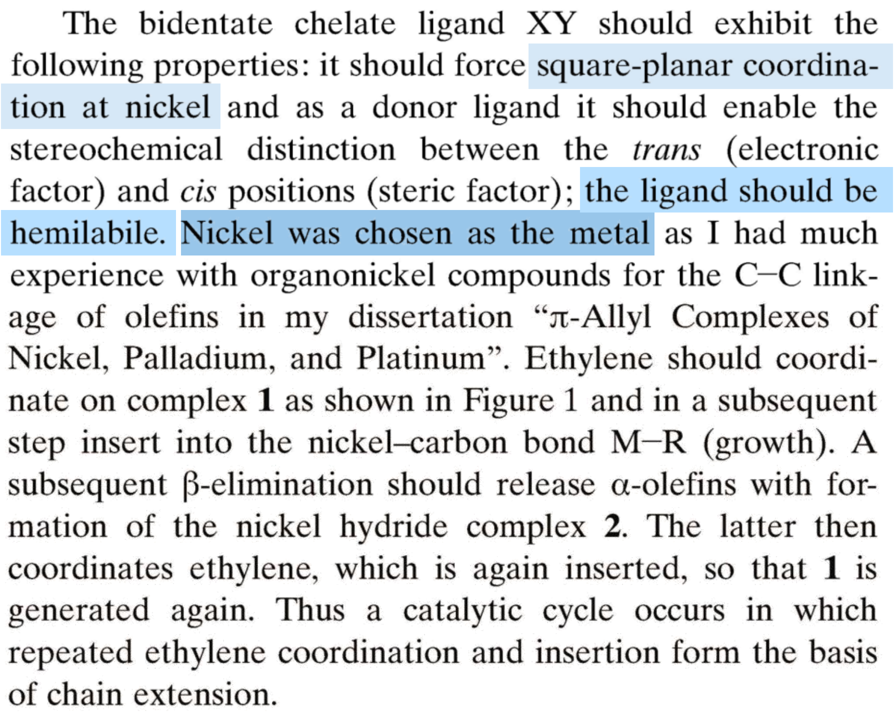
When the author started at Shell Development in Emeryville in 1965 the following economic environment existed:

1. Shell Chemicals had just commissioned a hydroformylation plant to manufacture fatty alcohols (Neodol) in Geismar, Louisiana. Due to ecological requirements a change away from "hard" detergents with branched chains to "soft" detergents with linear fatty alcohols was emerging. The lack of biological degradation of the branched surfactants had resulted in the accumulation of foam on rivers and seas. Furthermore, the detergents based on Neodol showed good washing performance in hard water and could be used at low washing temperatures. They also worked well in formulations with low phosphate content, which reduced the eutrophication of surface waters. The fatty alcohols produced by Shell were then in high demand, and the market developed high growth rates.
2. The olefins used in Geismar for hydroformylation were produced by the halogenation of alkanes with chlorine and elimination of HCl. This process had considerable disadvantages, as the monoolefins produced in this way shorten the lifetime of the cobalt phosphane catalyst.
3. Shell planned the construction of a large-scale gas oil cracker. A market was still needed for a major portion of the generated ethylene.

Against this background, α-olefins and linear monoolefins with an internal double bond were in demand at Shell Chemicals for hydroformylation. The research division of Shell Development Company was instructed to work on the oligomerization of ethylene to linear α-olefins and linear monoolefins. At that time α-olefins were primarily produced by cleavage of wax and the Ziegler polymerization of ethylene. The wax splitting and the Ziegler process are very expensive and give lower quality products for the manufacture of detergents.

As a chemist who had completed his dissertation under the supervision of K. Ziegler and G. Wilke, I was very familiar with the transition-metal-catalyzed C–C coupling of olefins. Numerous homogenous transition-metal catalysts with monodentate phosphane ligands had been described by which the direction of the C–C linkage could be influenced. The use of ligands containing polydentate phosphane was hardly described; hence it seemed appropriate to investigate bidentate phosphane ligands. The concept described in Figure 1 shows the basis of the underlying considerations.

Designing the catalyst



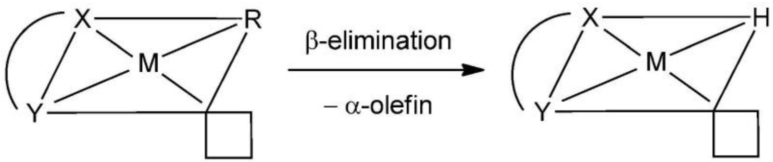
The bidentate chelate ligand XY should exhibit the following properties: it should force square-planar coordination at nickel and as a donor ligand it should enable the stereochemical distinction between the *trans* (electronic factor) and *cis* positions (steric factor); the ligand should be hemilabile. Nickel was chosen as the metal as I had much experience with organonickel compounds for the C–C linkage of olefins in my dissertation “π-Allyl Complexes of Nickel, Palladium, and Platinum”. Ethylene should coordinate on complex **1** as shown in Figure 1 and in a subsequent step insert into the nickel–carbon bond M–R (growth). A subsequent β-elimination should release α-olefins with formation of the nickel hydride complex **2**. The latter then coordinates ethylene, which is again inserted, so that **1** is generated again. Thus a catalytic cycle occurs in which repeated ethylene coordination and insertion form the basis of chain extension.

Why square-planar?

Why hemilabile?

Why nickel?

How & why does this catalysis work?



1 **2**

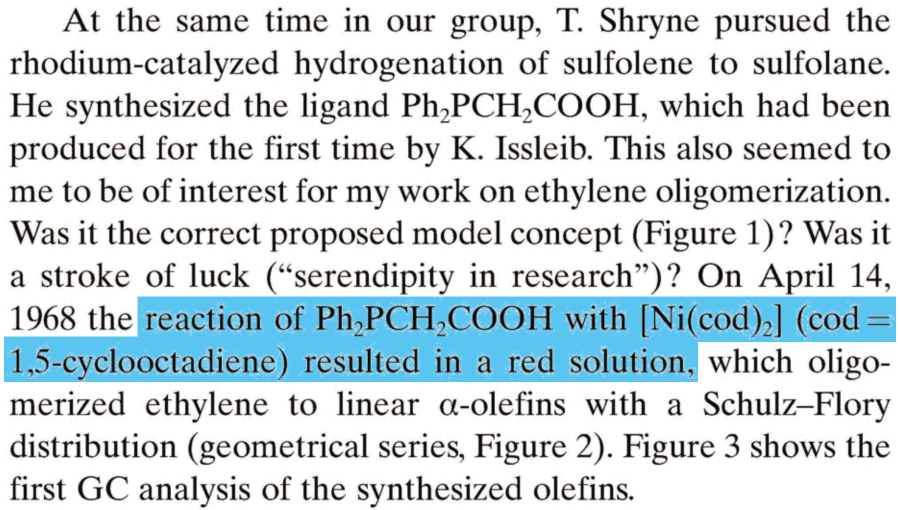
R = growing, linear, ethylene-derived carbon chain

M = nickel

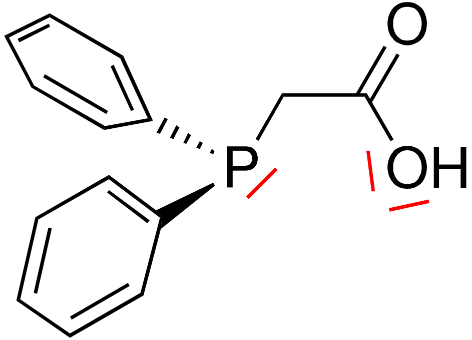
X⌒Y = bidentate chelate ligand

Y = P; X = O, N, S etc., ☐ = ethene coordination site

The ligand



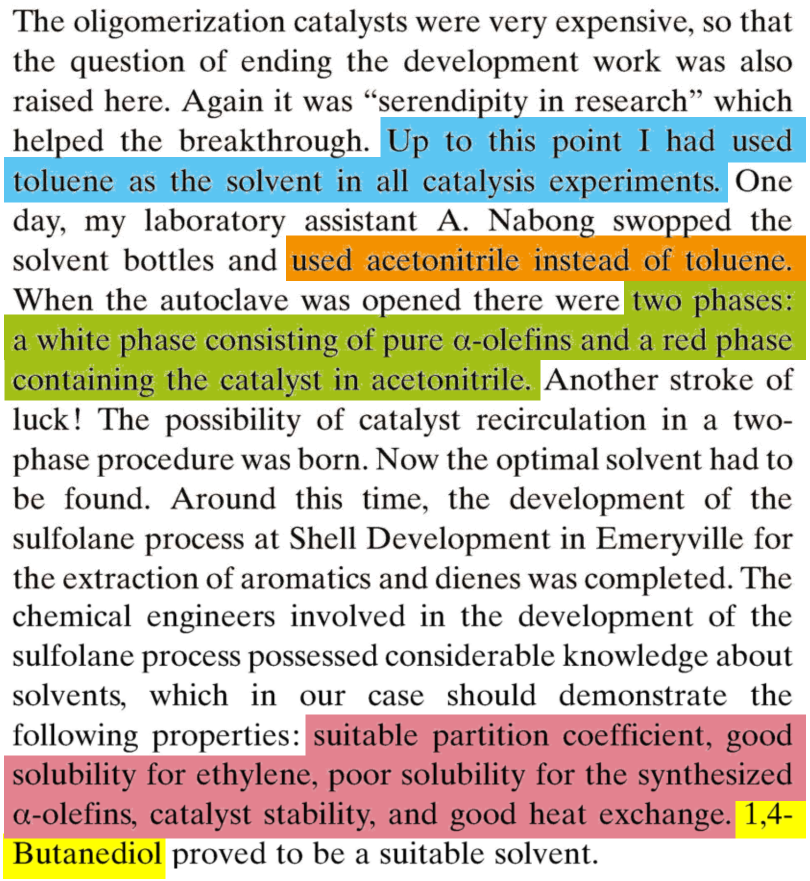
At the same time in our group, T. Shryne pursued the rhodium-catalyzed hydrogenation of sulfolene to sulfolane. He synthesized the ligand Ph_2PCH_2COOH, which had been produced for the first time by K. Issleib. This also seemed to me to be of interest for my work on ethylene oligomerization. Was it the correct proposed model concept (Figure 1)? Was it a stroke of luck ("serendipity in research")? On April 14, 1968 the reaction of Ph_2PCH_2COOH with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) resulted in a red solution, which oligomerized ethylene to linear α-olefins with a Schulz–Flory distribution (geometrical series, Figure 2). Figure 3 shows the first GC analysis of the synthesized olefins.



What is a ‘hemilabile‘ ligand?

…and why is it important for catalysis?

The solvent



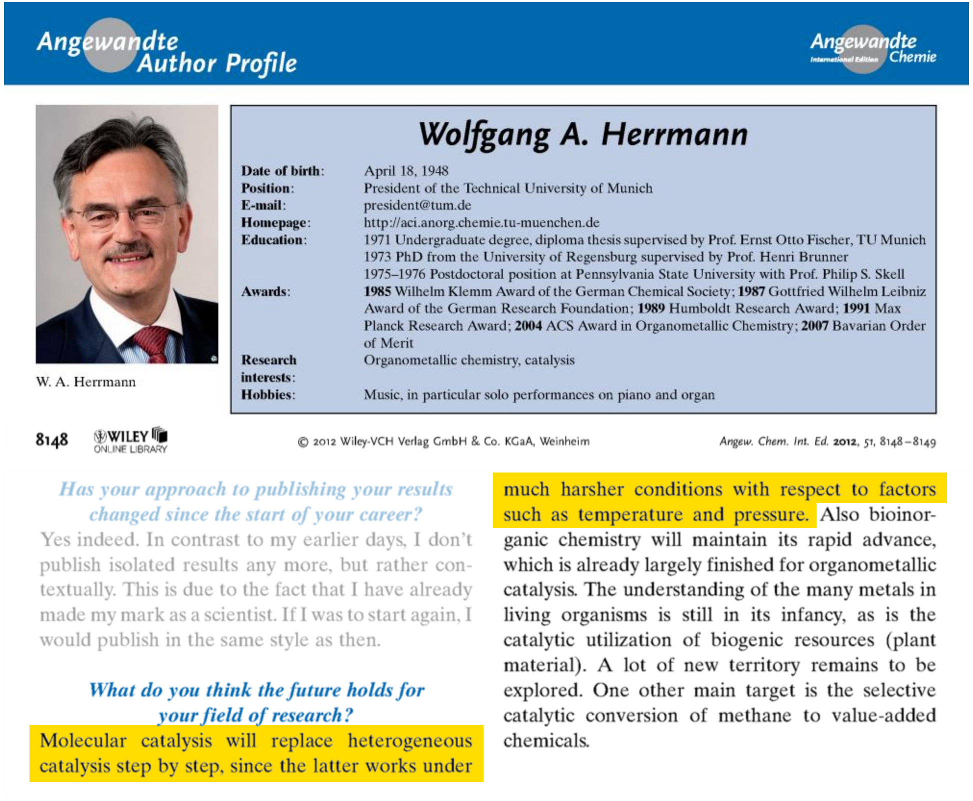
The oligomerization catalysts were very expensive, so that the question of ending the development work was also raised here. Again it was "serendipity in research" which helped the breakthrough. Up to this point I had used toluene as the solvent in all catalysis experiments. One day, my laboratory assistant A. Nabong swopped the solvent bottles and used acetonitrile instead of toluene. When the autoclave was opened there were two phases: a white phase consisting of pure α-olefins and a red phase containing the catalyst in acetonitrile. Another stroke of luck! The possibility of catalyst recirculation in a two-phase procedure was born. Now the optimal solvent had to be found. Around this time, the development of the sulfolane process at Shell Development in Emeryville for the extraction of aromatics and dienes was completed. The chemical engineers involved in the development of the sulfolane process possessed considerable knowledge about solvents, which in our case should demonstrate the following properties: suitable partition coefficient, good solubility for ethylene, poor solubility for the synthesized α-olefins, catalyst stability, and good heat exchange. 1,4-Butanediol proved to be a suitable solvent.

Homogeneous vs. heterogeneous catalysts

Pro’s & con’s

Aspect	Homogeneous	Heterogeneous
Structure/stoichiometry	Defined	Not defined
Active centers	100 %	Small fraction
Diffusion	No problems	Partly high
Reaction conditions	< 150 °C	>> 150 °C
Chemoselectivity	High	Can vary
Stereoselectivity	High	Low
Catalyst separation	Difficult	Easy

Is homogeneous catalysis (industrially) relevant?



Angewandte Author Profile

Angewandte International Edition Chemie

W. A. Herrmann

Wolfgang A. Herrmann

Date of birth:	April 18, 1948
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Homepage:	http://aci.anorg.chemie.tu-muenchen.de
Education:	1971 Undergraduate degree, diploma thesis supervised by Prof. Ernst Otto Fischer, TU Munich 1973 PhD from the University of Regensburg supervised by Prof. Henri Brunner 1975–1976 Postdoctoral position at Pennsylvania State University with Prof. Philip S. Skell
Awards:	**1985** Wilhelm Klemm Award of the German Chemical Society; **1987** Gottfried Wilhelm Leibniz Award of the German Research Foundation; **1989** Humboldt Research Award; **1991** Max Planck Research Award; **2004** ACS Award in Organometallic Chemistry; **2007** Bavarian Order of Merit
Research interests:	Organometallic chemistry, catalysis
Hobbies:	Music, in particular solo performances on piano and organ

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Has your approach to publishing your results changed since the start of your career?

Yes indeed. In contrast to my earlier days, I don't publish isolated results any more, but rather contextually. This is due to the fact that I have already made my mark as a scientist. If I was to start again, I would publish in the same style as then.

What do you think the future holds for your field of research?

Molecular catalysis will replace heterogeneous catalysis step by step, since the latter works under much harsher conditions with respect to factors such as temperature and pressure. Also bioinorganic chemistry will maintain its rapid advance, which is already largely finished for organometallic catalysis. The understanding of the many metals in living organisms is still in its infancy, as is the catalytic utilization of biogenic resources (plant material). A lot of new territory remains to be explored. One other main target is the selective catalytic conversion of methane to value-added chemicals.

Angew. Chem. Int. Ed. **2012**, *51*, 8148.

Molecular catalysts in industry

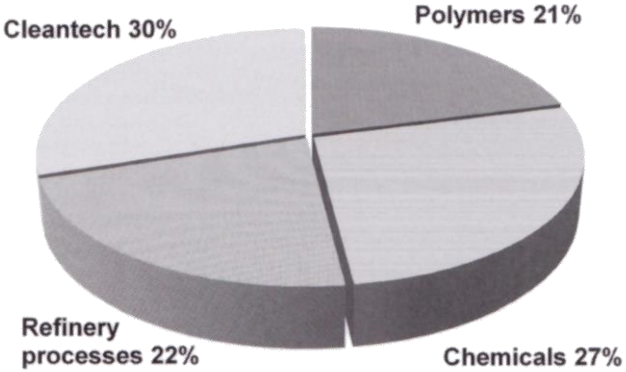


Figure 3.1 Application areas of catalysts (worldwide, 2004).

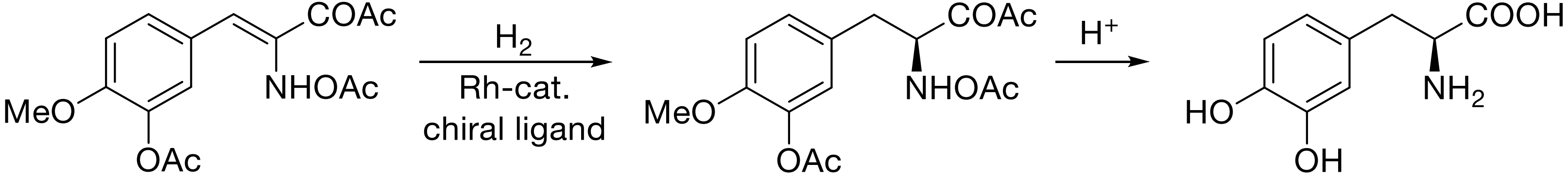
Table 3.1 Worldwide industrial production of chemicals by homogeneous catalysis.

Catalytic process	**Catalyst metal**	**Capacity (1000 t a^{-1})**
Bulk chemicals		
Oxidation processes	Co, Pd, Cr,. . .	18 000
Hydroformylation of alkenes	Rh	>7500
Carbonylation of methanol/methyl acetate	Rh, Ir/Ru	>7000
Hydroformylation of isooctenes/ethylene oxide	Co	>2000
Hydrogenations	Rh, Ru, Ir,. . .	1700
Oligomerization of ethene	Ni	1200
Hydrocyanations	Ni	1000
Olefine polymerizations	Zr, Ti	500
Carbonylation of ethene	Pd	140
Trimerization of ethene	Cr	100
Telomerization of butadiene with methanol	Pd	100
Fine chemicals:		
(*S*)-Metolachlor (hydrogenation)	Ir	10.0
Ibuprofen (carbonylation)	Pd	5.0
Octadienols (telomerization)	Pd	5.0
Citronellal (isomerization)	Rh	1.5
Boscalid (Suzuki-coupling)	Pd	>0.5
Terbafin (Sonogashira-coupling)	Pd/Cu	0.1

Why homogeneous catalysis ?

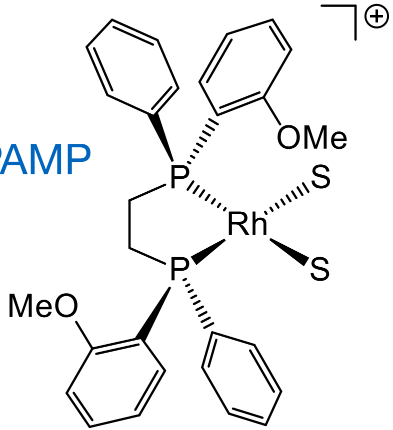
Enantioselective hydrogenation

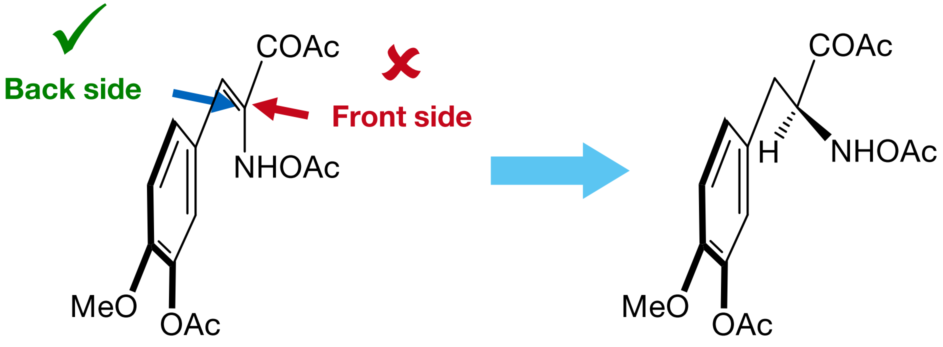
Synthesis of L-Dopa (agent against Parkinson disease)



Knowles, 1968 (Nobel Prize 2001)

(*R*,*R*)-DIPAMP





Nobel Prizes for catalysis research


W. Ostwald
🇩🇪

1909

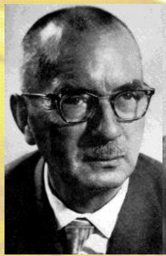

F. Haber
🇩🇪

1918


C. Bosch
🇩🇪

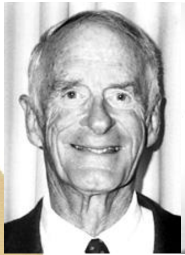

F. Bergius
🇩🇪

1931


K. Ziegler
🇩🇪


G. Natta
🇮🇹

1963


W. S. Knowles
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R. Noyori
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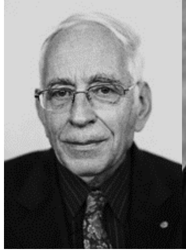
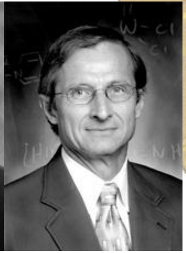
K. B. Sharpless
🇺🇸

2001


Y. Chauvin
🇫🇷


R. H. Grubbs
🇺🇸


R. R. Schrock
🇺🇸

2005


G. Ertl
🇩🇪

2007


R. F. Heck
🇺🇸


E. Negishi
🇺🇸


A. Suzuki
🇯🇵

2010


F. H. Arnold
🇺🇸

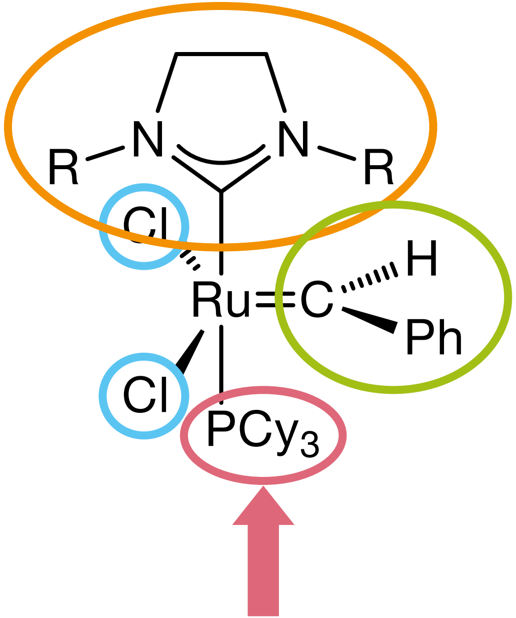
2018

Let‘s get to the basics...

Principles of molecular catalysis

Basics of coordination chemistry

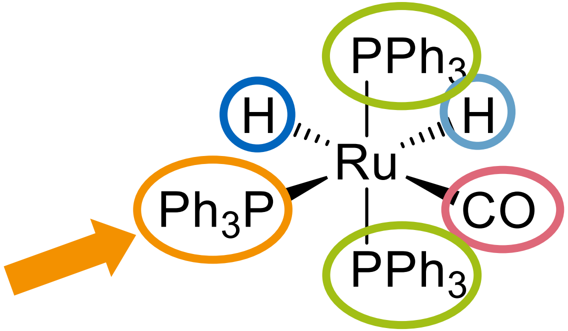
Which ligand will most easily (= quickly) dissociate?



Principles of molecular catalysis

Basics of coordination chemistry

Which ligand will most easily (= quickly) dissociate?



Obviously, the dissociation of a ligand depends on:

⇨ the bond strength (thermodynamics)
⇨ the steric demand
⇨ the charge (→ Coulomb force)
⇨ the effect of the *trans* ligand

Design of molecular catalysts

Parameters for catalyst design

⇨ Free coordination site at the metal is required

⇨ Electronic situation at the metal

Metal is electron poor/rich; late TM (d^8-d^{10}) activate bonds

Ligands; σ-/π-donors increase the electron density at the metal

⇨ Steric demand of ligands – regio- and stereoselectivity

Ligand size

Chirality of the ligand

⇨ Anionic ligands (coordinating vs. non-coordinating)

⇨ Solvents (→ placeholders for vacant coordination sites)

Basics of coordination chemistry

Metal-ligand interaction

Nature of the coordinative bond ⇨ interaction between metal d-orbitals and σ-, π- or π^*-orbitals of a ligand

$M \leftarrow L$

Ligand donates electrons to the metal
σ-symmetry of orbitals
(for π-donors also π-symmetry)
→ σ-donor bond

$M \rightarrow L$

Metal donates electrons to the ligand
π^*-symmetry of orbitals
(for agostic bonds also σ^*-symmetry)
→ π-back bond

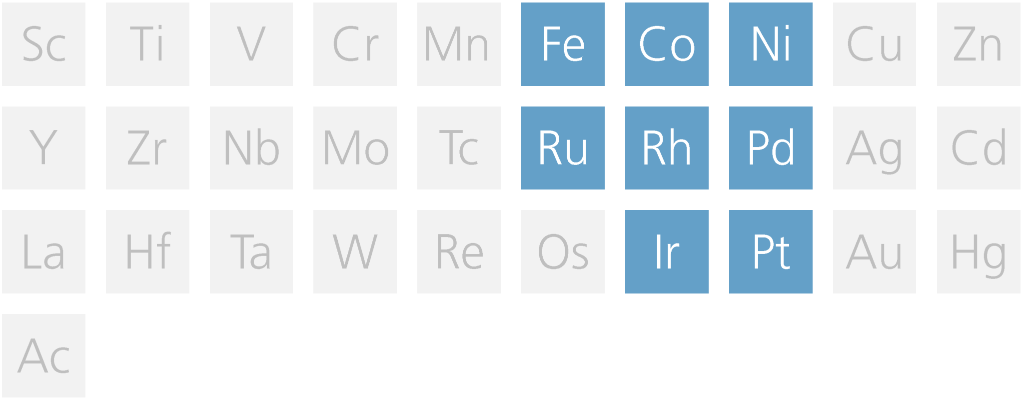
The reactivity of metal complexes depends on subtle effects:

- Each TM exhibits different reactivity, also dependent on the oxidation state
- The ligands vary in binding strength and reactivity

The metals

The metals

Bond activation



Sc	Ti	V	Cr	Mn	**Fe**	**Co**	**Ni**	Cu	Zn
Y	Zr	Nb	Mo	Tc	**Ru**	**Rh**	**Pd**	Ag	Cd
La	Hf	Ta	W	Re	Os	**Ir**	**Pt**	Au	Hg
Ac									

H–H activation

C–H

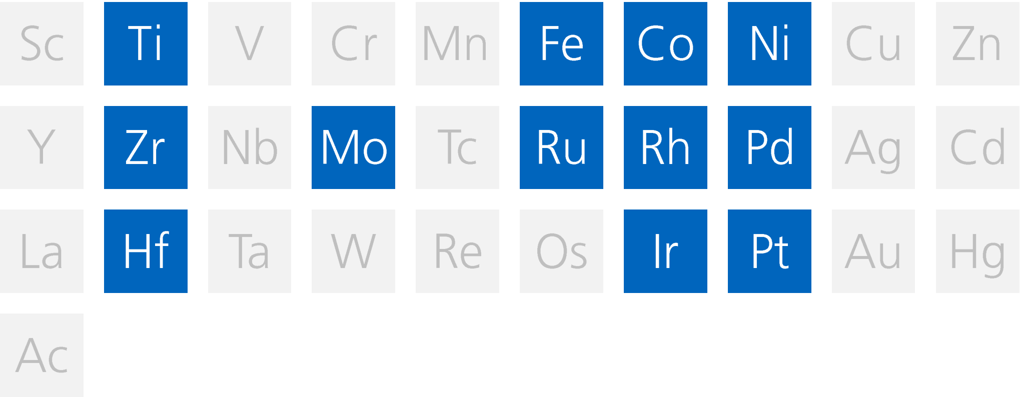
C–O

Reductions

etc….

The metals

C–C bond formation



Sc	**Ti**	V	Cr	Mn	**Fe**	**Co**	**Ni**	Cu	Zn
Y	**Zr**	Nb	**Mo**	Tc	**Ru**	**Rh**	**Pd**	Ag	Cd
La	**Hf**	Ta	W	Re	Os	**Ir**	**Pt**	Au	Hg
Ac									

Hydroformylation

Cross coupling

Olefin metathesis

Olefin polymerization

etc.…

The metals

Oxidation catalysis

Sc	**Ti**	**V**	Cr	**Mn**	**Fe**	Co	Ni	Cu	Zn
Y	Zr	Nb	**Mo**	Tc	Ru	Rh	**Pd**	Ag	Cd
La	Hf	Ta	**W**	**Re**	Os	Ir	Pt	Au	Hg
Ac									

Epoxidations

Wacker-aldehyde

etc….

The metals

Principles of organotransition metal catalysis: the concept

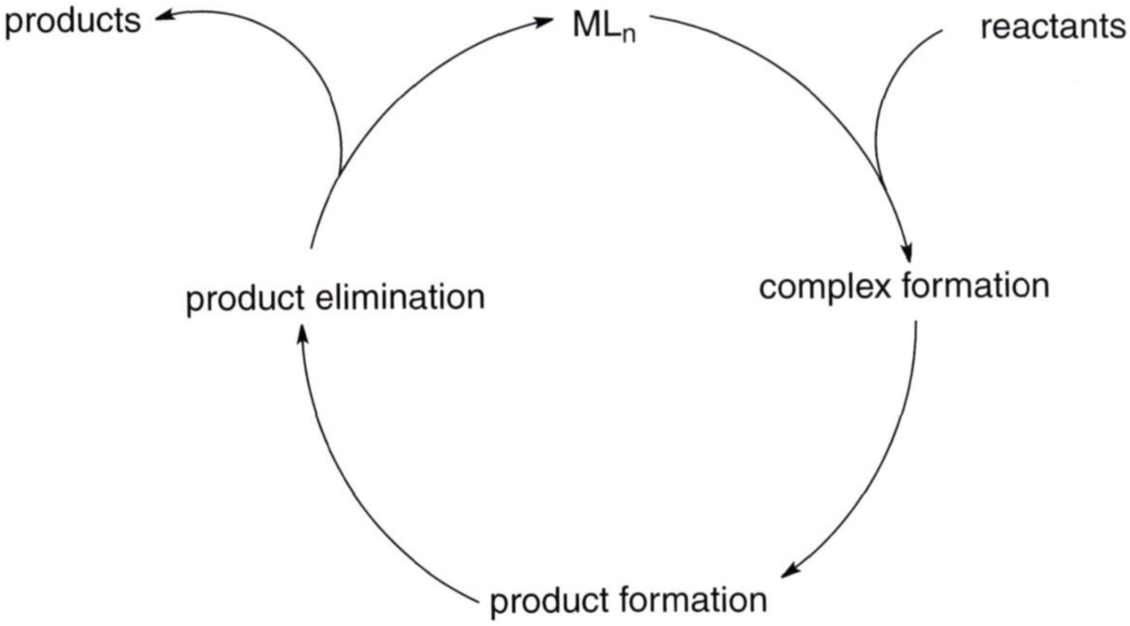
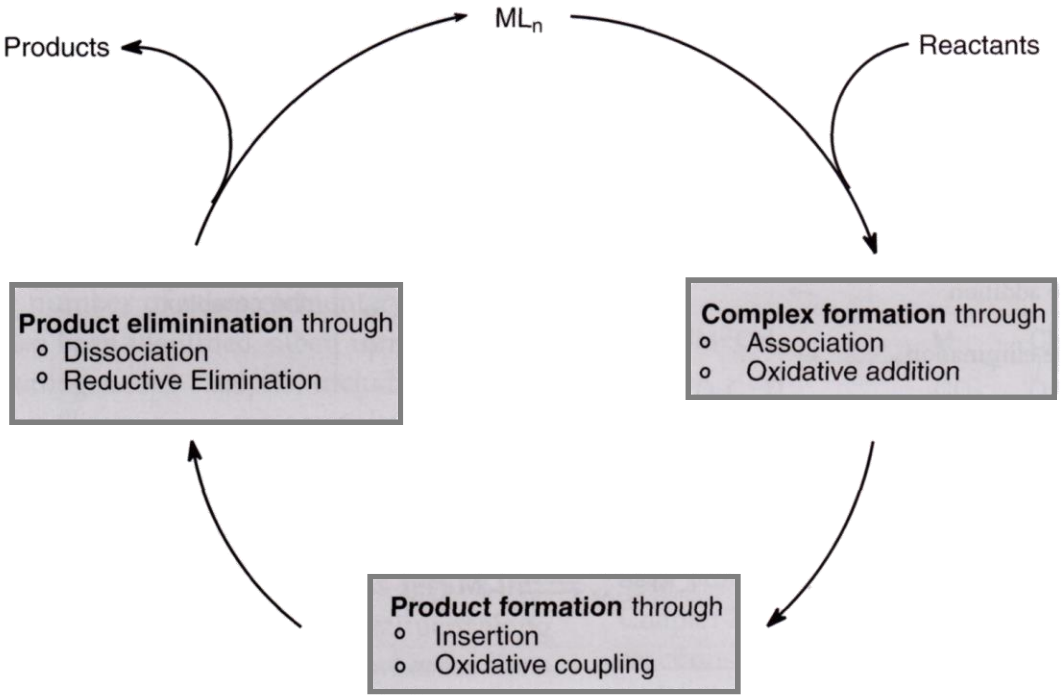


Figure 5.5 General catalytic cycle.

AB, p. 52.

The metals

Principles of organotransition metal catalysis: elementary steps



Product eliminination through
- Dissociation
- Reductive Elimination

Complex formation through
- Association
- Oxidative addition

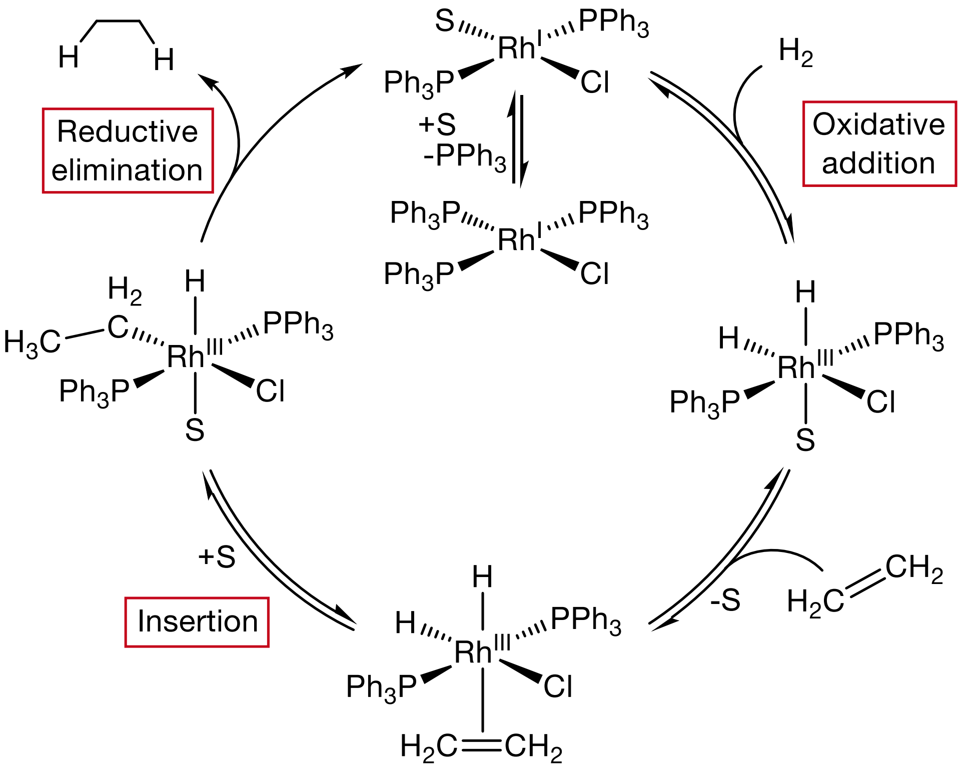
Product formation through
- Insertion
- Oxidative coupling

Figure 5.7 Catalyst cycle with elementary steps.

AB, p. 58.

Example: Catalytic hydrogenation of olefins

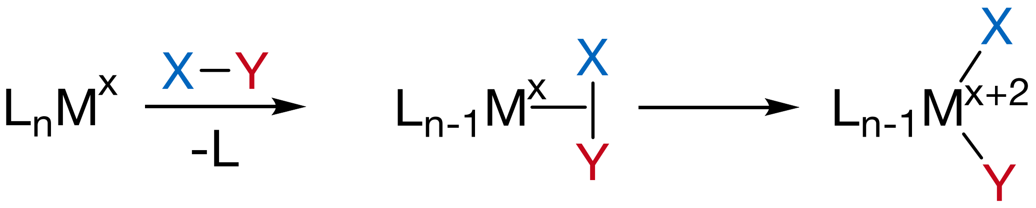
Mechanism by J. Halpern (simplified)



JFH, p. 585 ff.

Oxidative addition

Principle



Preconditions:

- Electron-rich d^8- and d^{10} metals
- Electronically unsaturated 16 VE complexes → free coordination site is required
- Sterically unsaturated complexes

Two different mechanisms:

- Cleavage of apolar bonds (H–H, C–H, C–C, Si–H, …)
- Cleavage of polar bonds (alkyl/aryl halides)

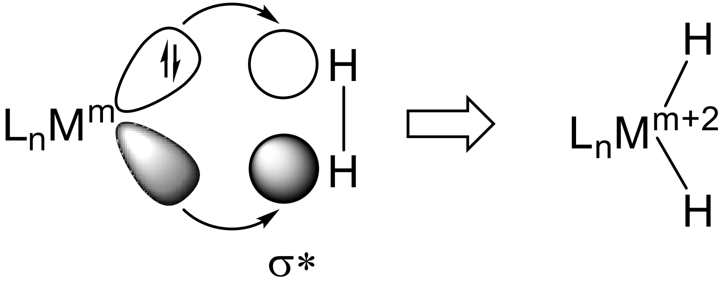
Oxidative addition

Homolytic bond activation – the example of dihydrogen

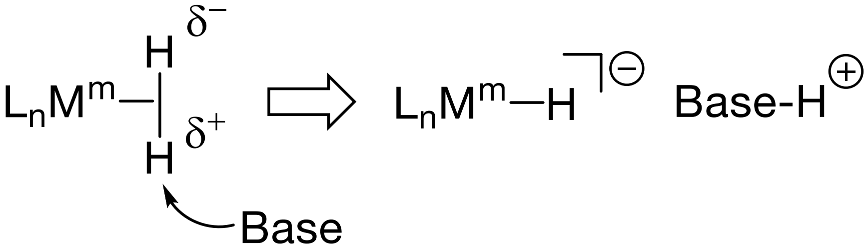
Mechanistic considerations – *cis*-products!

Concerted oxidative addition

Heterolytic dissociation



Backbonding

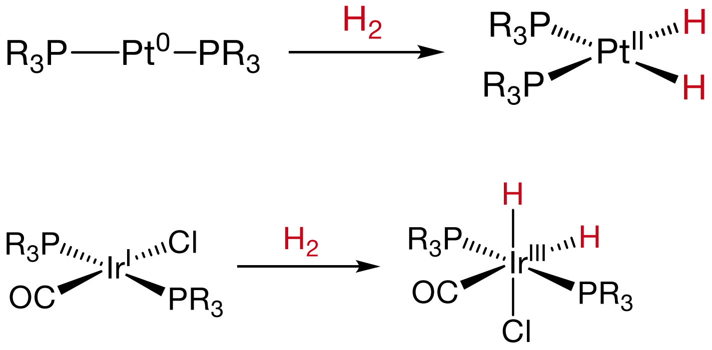


Oxidative addition

Homolytic bond activation – the example of dihydrogen

Mechanistic considerations – *cis*-products!

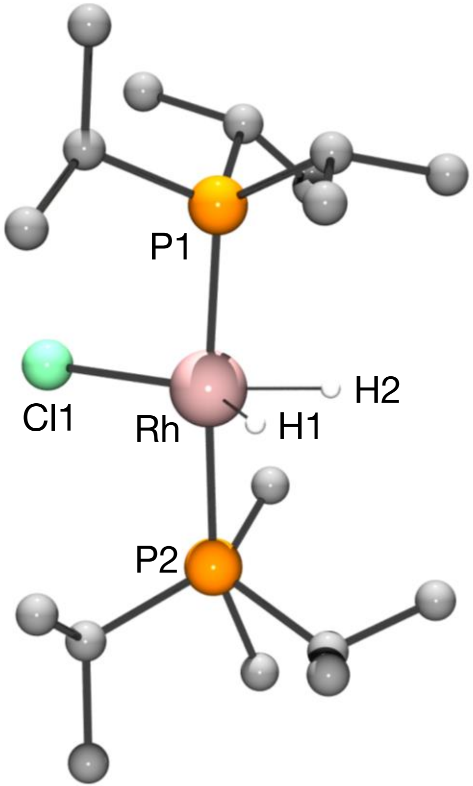
Examples:



Oxidative addition

Homolytic bond activation – the example of dihydrogen

Isolated product of the oxdative addition of H_2 to Rh(I)



Angles

P1-Rh-P2: 175.6°
H1-Rh-H2: 66.2°

Torsion angle

Cl1-H1-H2-Rh: 1.0°

$[(^{i}Pr_3P)_2(H)_2(Cl)Rh]$

R. L. Harlow, D. L. Thorn et al., *Inorg. Chem.* **1992**, *31*, 993.

Oxidative addition

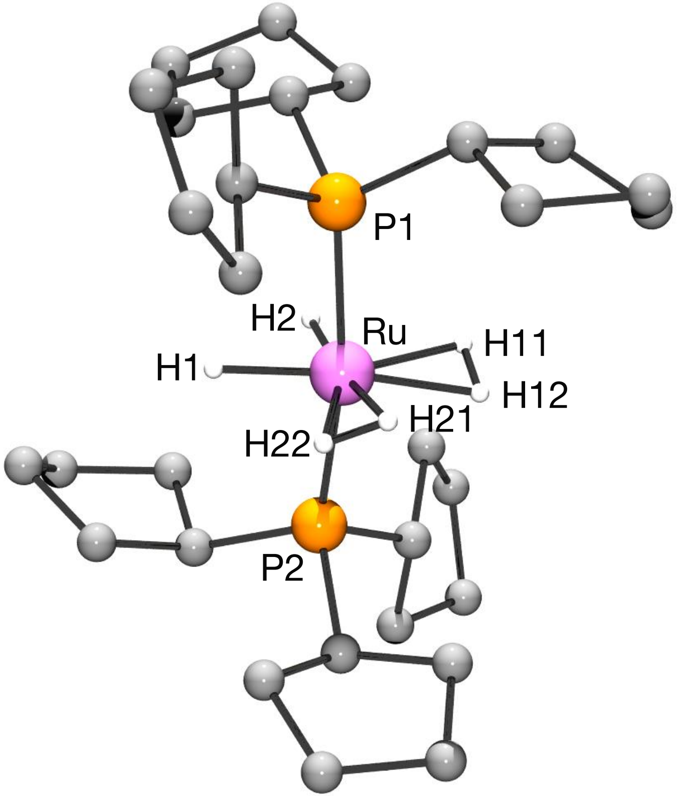
‘Frozen‘ oxidative addition – η^2-dihydrogen ligand

Subtle changes influence the product formation

→Intact H–H bonds
Also detected via ^{1}H-NMR and IR

Neutron diffraction single crystal structure

Distances [pm]:	Angles [°]:
H11–H22: 82.5	H11-Ru-H12: 27.4
H21–H22: 83.5	H21-Ru-H22: 27.5
H1–H2 : 213.2	H1-Ru-H2 : 81.9

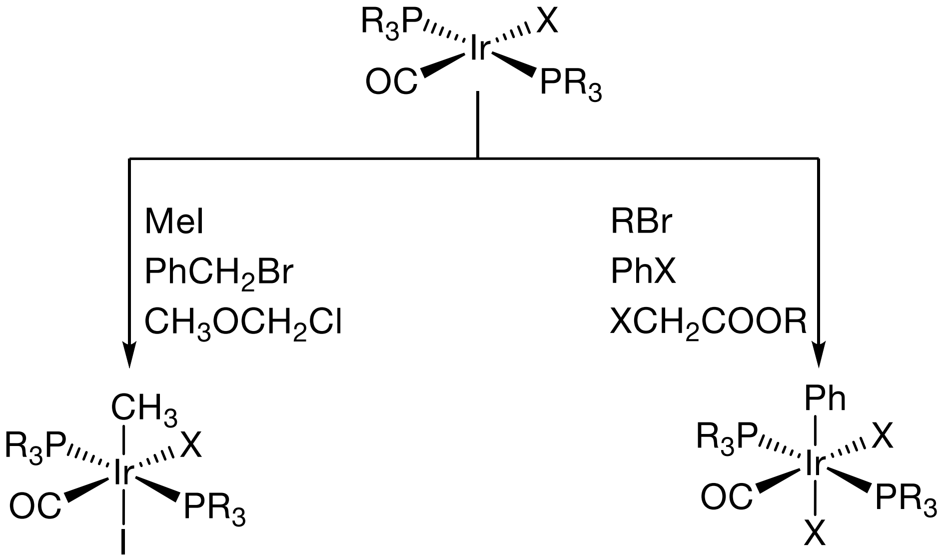


B. Chaudret et al., *JACS* **2005**, *127*, 17592.

Oxidative addition

Heterolytic bond activation of polar bonds

Alkyl- and aryl halides: $S_{N}2$ vs. radical vs. concerted (depend on the substrate and on the metal)



$S_{N}2$

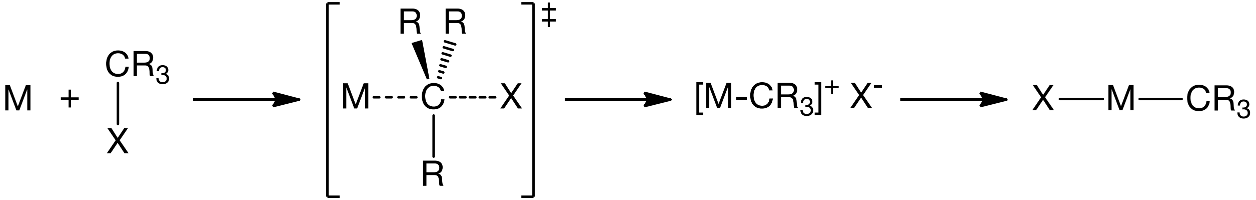
Radical

Oxidative addition

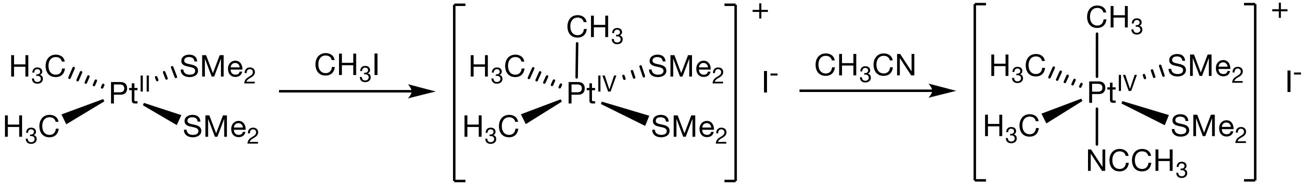
S_{N^2}–type bond activation of polar bonds

Most prominent for alkyl- and aryl halides

S_{N^2} mechanism with a nucleophilic metal center:



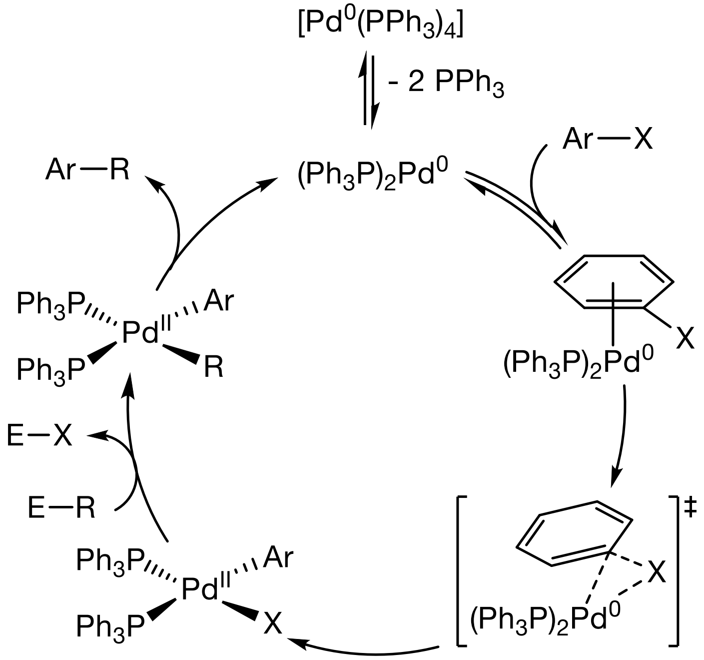
Proof: scavenging of the intermediate



Oxidative addition

Concerted bond activation of medium polar bonds with Pd(0)

Example: C–C cross coupling reactions with Pd(0) complexes

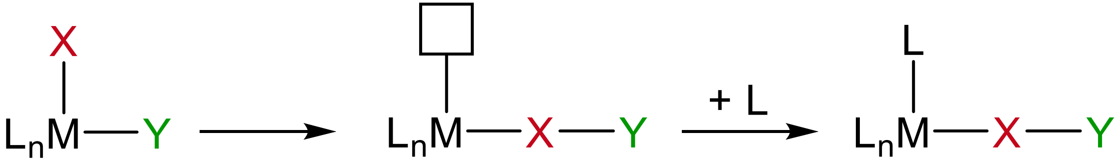


R-E	Name reaction
$R\text{-}BR_2$	Suzuki coupling
R-ZnX	Negishi coupling
R-MgX	Kumuda coupling
$R\text{-}SnR_3$	Stille coupling
Olefins	Heck coupling

Ligand insertion

Principle

Intramolecular insertion (‚migratory insertion‘) → nucleophilic attack



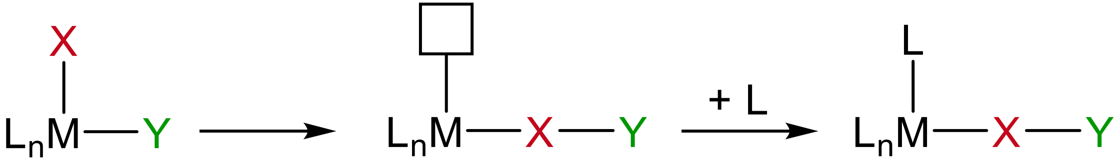
X = nucleophile (H, alkyl, acyl, etc....)
Y = electrophile (CO, olefins, alkynes, (Fischer) carbenes, etc....)

- ⇨ The oxidation state of the metal does not change
- ⇨ X and Y must be in *cis*-position
- ⇨ A free coordination site is created

Ligand insertion

Principle

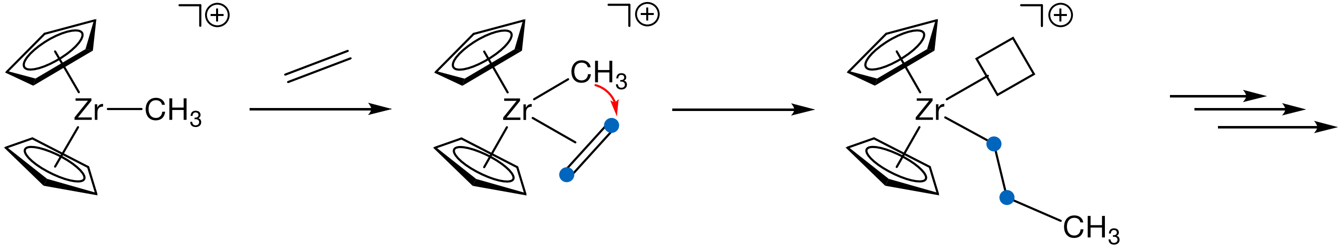
Intramolecular insertion (‘migratory insertion‘) → nucleophilic attack



$$L_n\overset{X}{M}-Y \longrightarrow L_n\overset{\square}{M}-X-Y \xrightarrow{+\,L} L_n\overset{L}{M}-X-Y$$

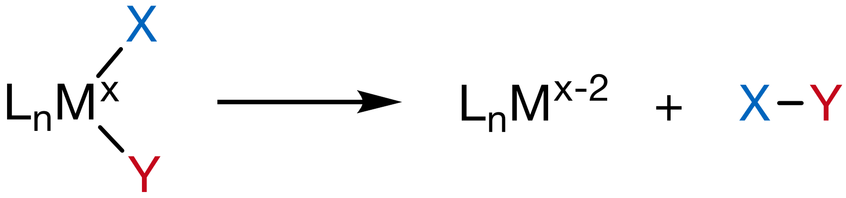
X = nucleophile (H, alkyl, acyl, etc....)
Y = electrophile (CO, olefins, alkynes, (Fischer) carbenes, etc....)

Example:



Reductive elimination

Principle



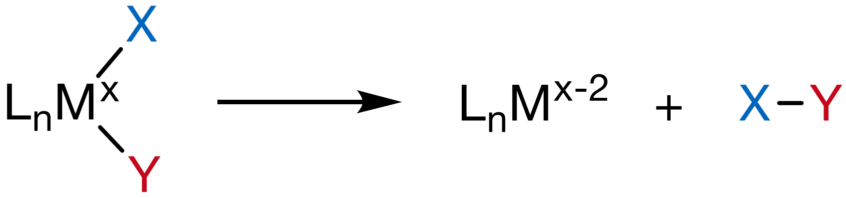
$$L_nM^x(X)(Y) \longrightarrow L_nM^{x-2} + X{-}Y$$

Conditions: - ligands X and Y must stand cis to each other
- the product X–Y must be stable (e.g. by the VE count and oxidation state)
- the metal complex product must be stable

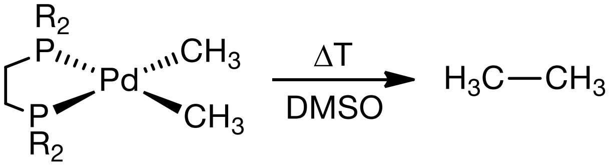
Kinetics:
- X and Y are *trans* to each other → rearrangement slowers RE
- addition of σ-donor ligands accelerates RE
- Large ligands accelerate RE
- 3- and 5-coordinated complexes undergo RE faster than 4- and 6-coordinated complexes

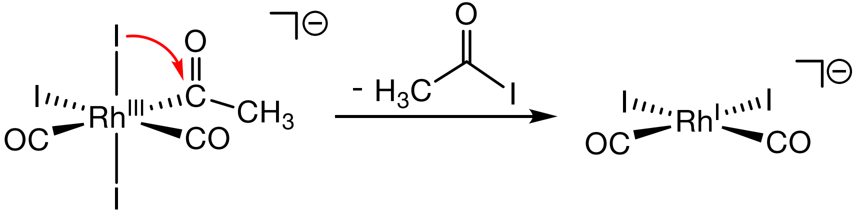
Reductive elimination

Principle



Examples:

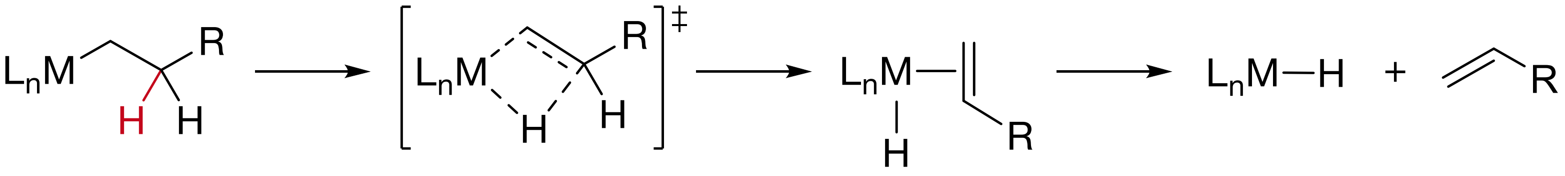




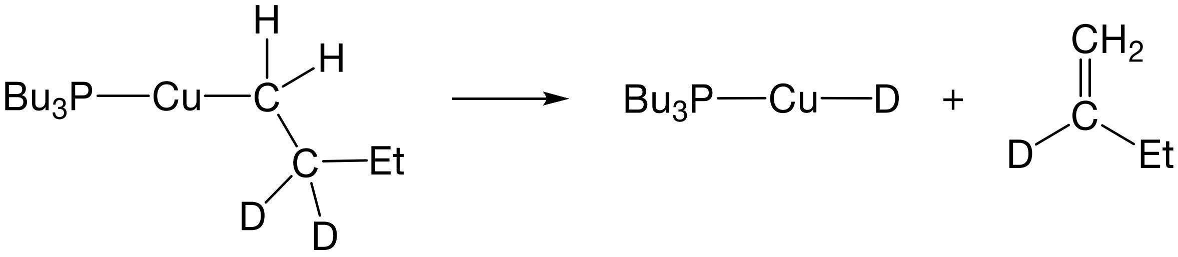
β-Hydride elimination

Alkyl ligands with β-hydrogen atoms are unstable

C–H bond activation by transition metals (especially late TM)



⇨ Experimental proof: deuteration experiments (→ NMR)



The ligands

The ligands

More than meets the eye

⇨ Spectator
Stabilize the complex as such

⇨ Place holder
Help forming a free coordination site

⇨ Charge control
Push/pull of electron density to the metal

⇨ Steric control
Shielding and/or chiral control

⇨ Reactant
React with the substrate to the product

The ligands

Classifications

⇨ coordination over carbon or heteroatoms
⇨ charge: neutral (CO, phosphines, …) or anionic (halides, alkyl, hydroxide, …)
⇨ No. of donating electrons
⇨ bond properties: nucleophile or electrophile? (strong e-donor or e-acceptor?)

Location of e-pair for the σ-bond?

→ free e-pair (phosphines, amines, CO, alkyl, etc…)
→ π-bond (olefins, alkynes, allyl, arenes, Cp and derivatives)
→ σ-bond (e.g. H_2 in dihydrogen complexes)

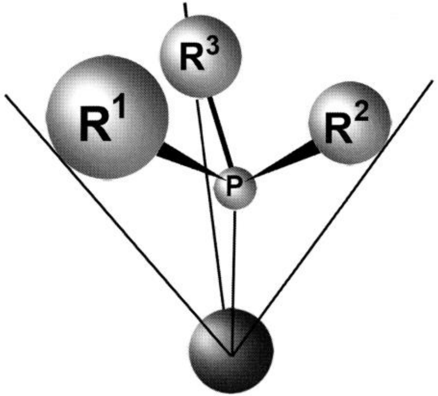
Are there π-interactions?

→ π-donor (e.g. oxo, halide, amido, imido ligands, etc…)
→ no (or weak) π-interactions
→ π-acceptor (e.g. CO, olefins, alkynes, etc…)

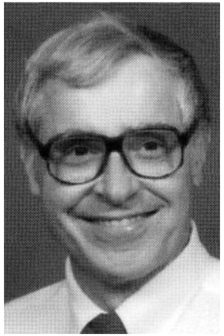
Phosphines

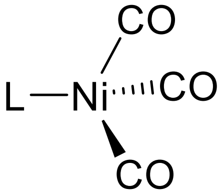
By far most used ligands in organometallic chemistry

- Strong σ-donors
  π-acceptors
- Electronic properties vary with the substituent R



⇨ Studied by Chadwick Tolman





Shift of the CO vibration depends on L

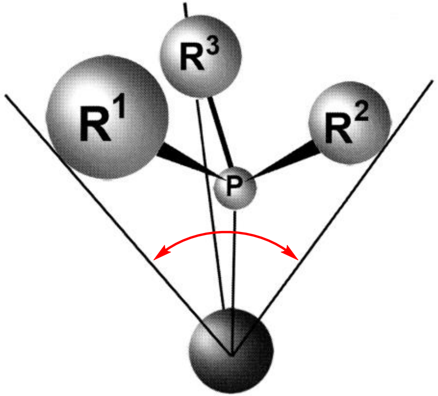
Ligand	$\tilde{\nu}$ (CO) [cm^{-1}]
PMe_3	2064.1
$P(OMe)_3$	2079.5
PEt_3	2061.7
PPh_3	2068.9
$P(OPh)_3$	2085.3
P^iPr_3	2059.2
PCy_3	2056.4
P^tBu_3	2056.1
$P(o\text{-}Tol)_3$	2066.6
$P(Mes)_3$	n.a.

C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

Phosphines

By far most used ligands in organometallic chemistry

- Strong σ-donors
  π-acceptors
- Steric properties vary with the substituent R



Free coordination sites →

$PdL_4 \xrightarrow{-L} PdL_3 \xrightarrow{-L} PdL_2$

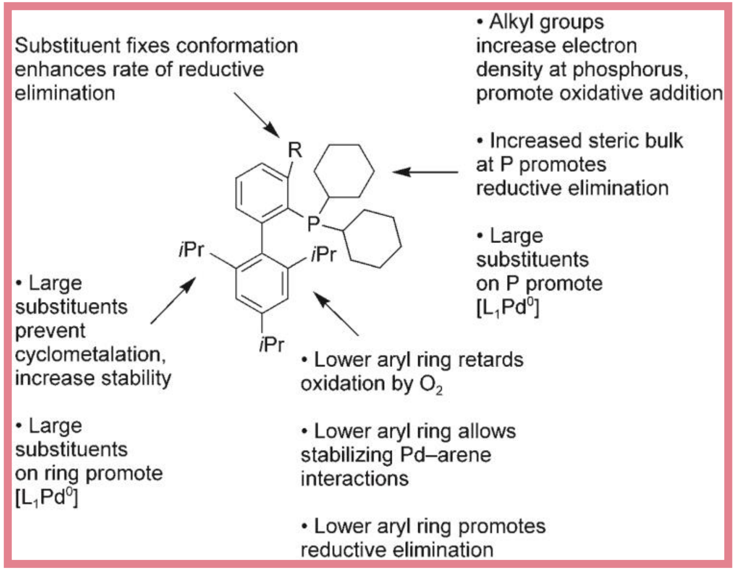
$PMe_3 \sim PMe_2Ph \sim PMePh_2 < PEt_3 \sim PPh_3 < PPr^i_3 < PCy_3 < PPhBu^t_2$

Bulky ligands →

Ligand	Cone angle [°]
PMe_3	118
$P(OMe)_3$	107
PEt_3	132
PPh_3	145
$P(OPh)_3$	128
P^iPr_3	160
PCy_3	170
P^tBu_3	182
$P(o\text{-}Tol)_3$	194
$P(Mes)_3$	212

Dialkylbiarylphosphines

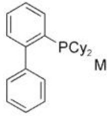
Design influences reactivity and stability of the catalyst



Substituent fixes conformation enhances rate of reductive elimination

- Alkyl groups increase electron density at phosphorus, promote oxidative addition
- Increased steric bulk at P promotes reductive elimination
- Large substituents on P promote [L_1Pd^0]
- Large substituents prevent cyclometalation, increase stability
- Large substituents on ring promote [L_1Pd^0]
- Lower aryl ring retards oxidation by O_2
- Lower aryl ring allows stabilizing Pd–arene interactions
- Lower aryl ring promotes reductive elimination

S. L. Buchwald



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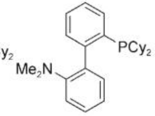
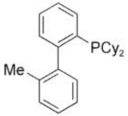
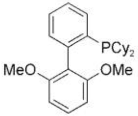


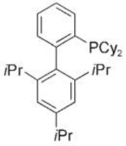
DavePhos



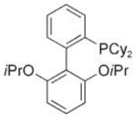
MePhos



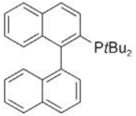
SPhos



XPhos



RuPhos



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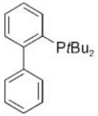
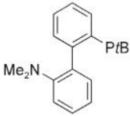


JohnPhos



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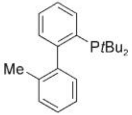

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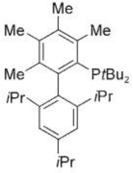

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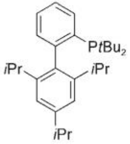

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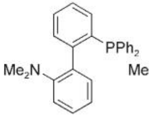

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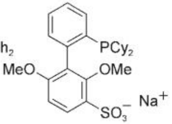
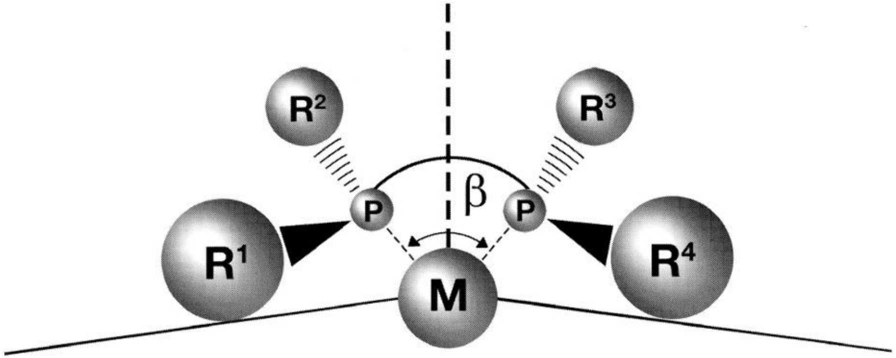


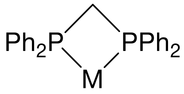
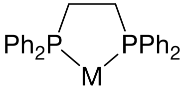
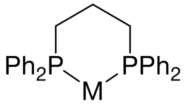
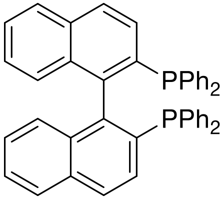
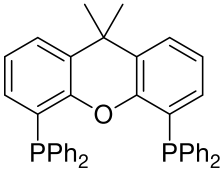
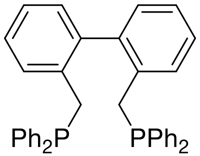
8

Angew. *Chem. Int. Ed.* **2008**, *47*, 6338; *Acc. Chem. Res.* **2008**, *41*, 1461; *Chem. Sci.* **2011**, *2*, 27.

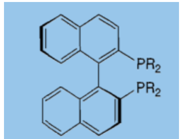
Diphosphines

Chelating ligands – *cis* coordination

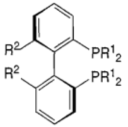


P – P ligand	Bite angle [°]
	72
	84
	86
	92
	112
	113-123

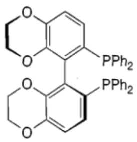
Diphosphines: Chirality



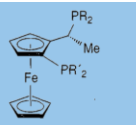
(S)-BINAP: R = Ph
(S)-TolBINAP: R = 4-MeC$_6$H$_4$
(S)-XylBINAP: R = 3,5-(Me)$_2$C$_6$H$_3$



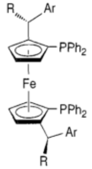
(S)-BICHEP: R^1 = Cy; R^2 = CH$_3$
(S)-BIPHEMP: R^1 = Ph; R^2 = CH$_3$
(S)-BIPHEP: R^1 = Ph; R^2 = OCH$_3$



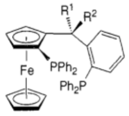
(S)-bisbenzodioxanPhos (SYNPHOS)



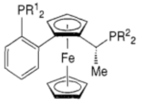
(R)-(S)-Josiphos: R = Cy; R′ = Ph
(R)-(S)-PPF-^{t}Bu$_2$: R = ^{t}Bu; R′ = Ph
(R)-(S)-Xyliphos: R = 3,5-Me$_2$Ph;
R′ = Ph
(R)-(S)-Cy$_2$PF-PCy$_2$: R = Cy;
R = Cy : R = ^{t}Bu; R′ = 4-CF$_3$-Ph



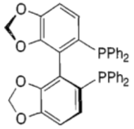
MandyPhos (FERRIPHOS)
R = Me; Ar = Ph
R = Me; Ar = o-Tolyl
R = Me; Ar = 2-Np
R = ^{i}Pr; Ar = Ph
R = N(Me)$_2$; Ar = Ph



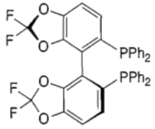
TaniaPhos
R^1 = NMe$_2$; R^2 = H
R^1 = N-pyrrolidyl; R^2 = H
R^1 = Me; R^2 = H
R^1 = ^{i}Pr; R^2 = H
R^1 = H; R^2 = OMe



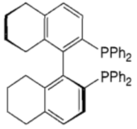
WalPhos
R^1 = Ph; R^2 = 3,5-(CF$_3$)C$_6$H$_3$
R^1 = 3,5-Me$_2$-4-MeOC$_6$H$_2$,
R^2 = 3,5-(CF$_3$)C$_6$H$_3$



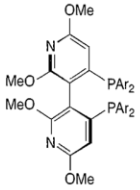
(S)-SEGPHOS



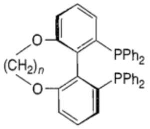
(S)-Difluorphos



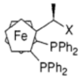
(S)-H8-BINAP



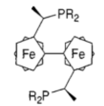
(S)-P–Phos: Ar = Ph
(S)-Tol–P–Phos: Ar = 4-MeC$_6$H$_4$
(S)-Xyl–P–Phos: Ar = 3,5-(Me)$_2$C$_6$H$_3$



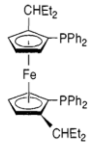
(S)-C$_n$-TunePhos
n = 1–6



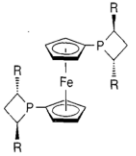
(R,S)-BPPFA: X = NMe$_2$
(R,S)-BPPOH: X = OH
: X = N(H$_3$C)(H$_2$C)$_2$N 



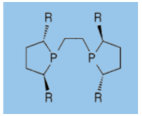
(R,R)-(R,S)-TRAP
EtTRAP; R = Et
PrTRAP; R = Pr
BuTRAP; R = Bu
PhTRAP; R = Ph



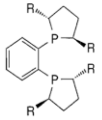
(S,S)-FerroPHOS



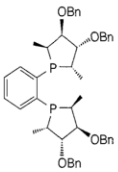
(S,S)-Et-FerroTANE: R = Et



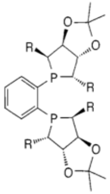
(S,S)-Me-BPE: R = Me
(S,S)-Et-BPE: R = Et
(S,S)-^{i}Pr-BPE: R = ^{i}Pr
(S,S)-Ph-BPE: R = Ph



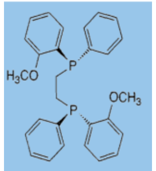
(S,S)-Me-DuPHOS: R = Me
(S,S)-Et-DuPHOS: R = Et
(S,S)-^{i}Pr-DuPHOS: R = ^{i}Pr



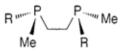
RoPHOS



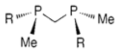
R = Me or Et



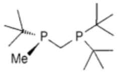
(S,S)-DIPAMP



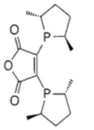
(S,S)-^{t}Bu-BisP*: R = ^{t}Bu
(S,S)-Ad-BisP*: R = 1-adamantyl
(S,S)-Cy-BisP*: R = Cy



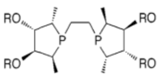
(S,S)-^{t}Bu-MiniPhos: R = ^{t}Bu
(S,S)-Cy-MiniPhos: R = Cy
(S,S)-^{i}Pr-MiniPhos: R = ^{i}Pr



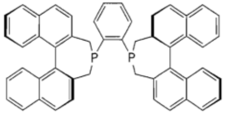
Tri-chicken-foot Phos



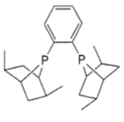
MalPHOS



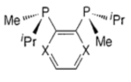
R = Bn
R = ^{t}Bu



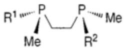
(S,S)-BINAPHANE



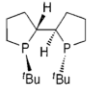
(R,S,R,S)-Me-PennPhos



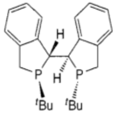
X = CH, N



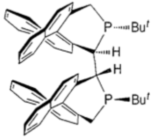
Unsymmetric BisP*
R^1 = 1-Ad; R^2 = ^{t}Bu
R^1 = 1-Ad; R^2 = Cy



(S,S,R,R)-TangPhos



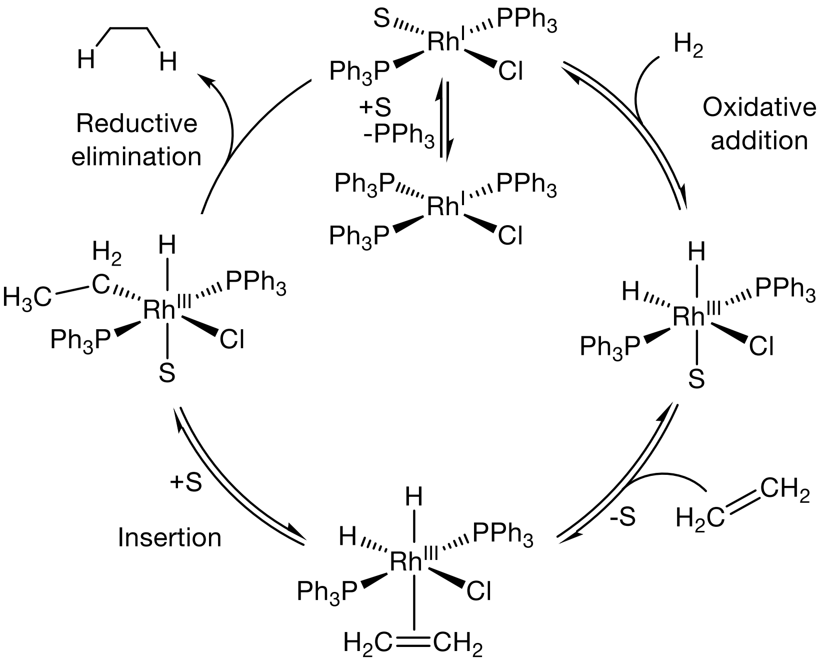
(S,S,R,R)-DuanPhos



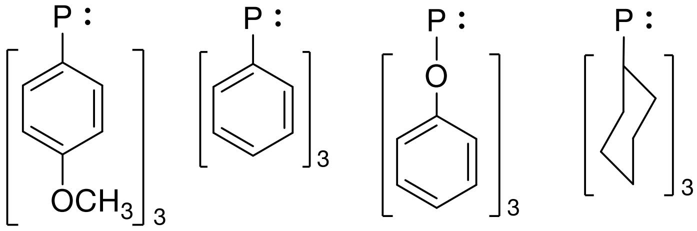
Binapine

The ligand influence

Again: the catalytic hydrogenation of olefins



Relative activity:



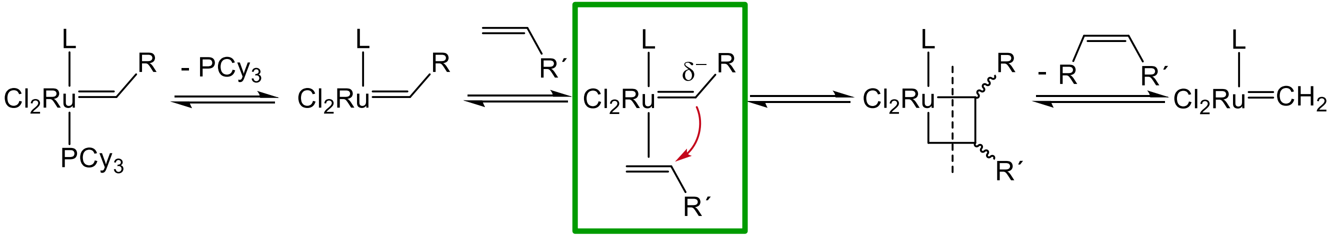
$\tilde{\nu}$ (CO) [cm^{-1}]	2066.1	2068.9	2085.3	2056.4
Cone angle	~ 145	145	128	170

Activity

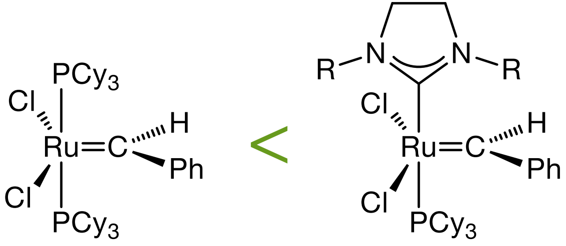
The ligand influence

Example: Grubbs carbenes in olefin metathesis

Mechanism of olefin metathesis with Ru-catalysts



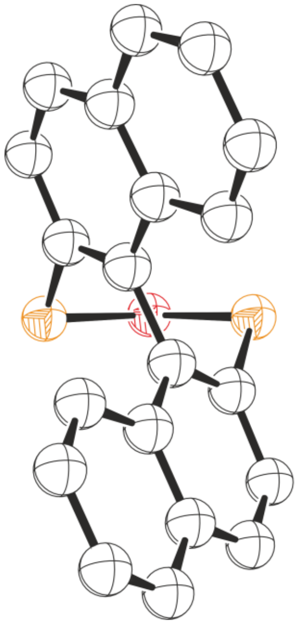
Free coordination site is important
Binding of the substrate is important → *trans*-influence



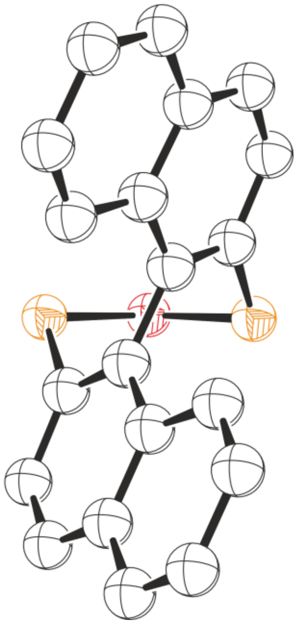
1st generation 2nd generation

The ligand influence

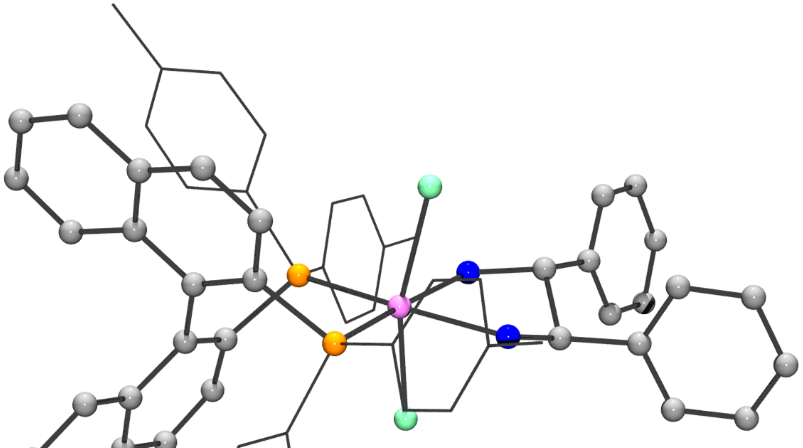
Stereoselectivity with chiral diphosphines



(*S*)-BINAP



(*R*)-BINAP

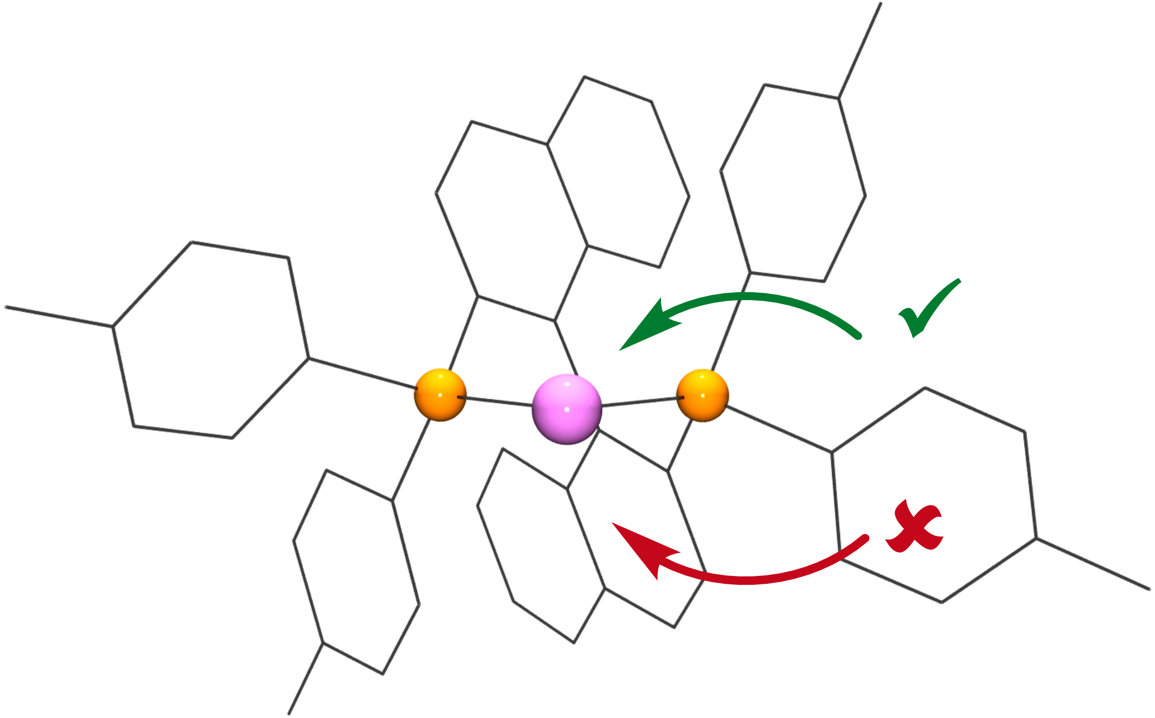


Ryoji Noyori

R. Noyori et al., *JACS* **1995**, *117*, 2675; *Angew. Chem. Int. Ed.* **2002**, *41*, 2008.

The ligand influence

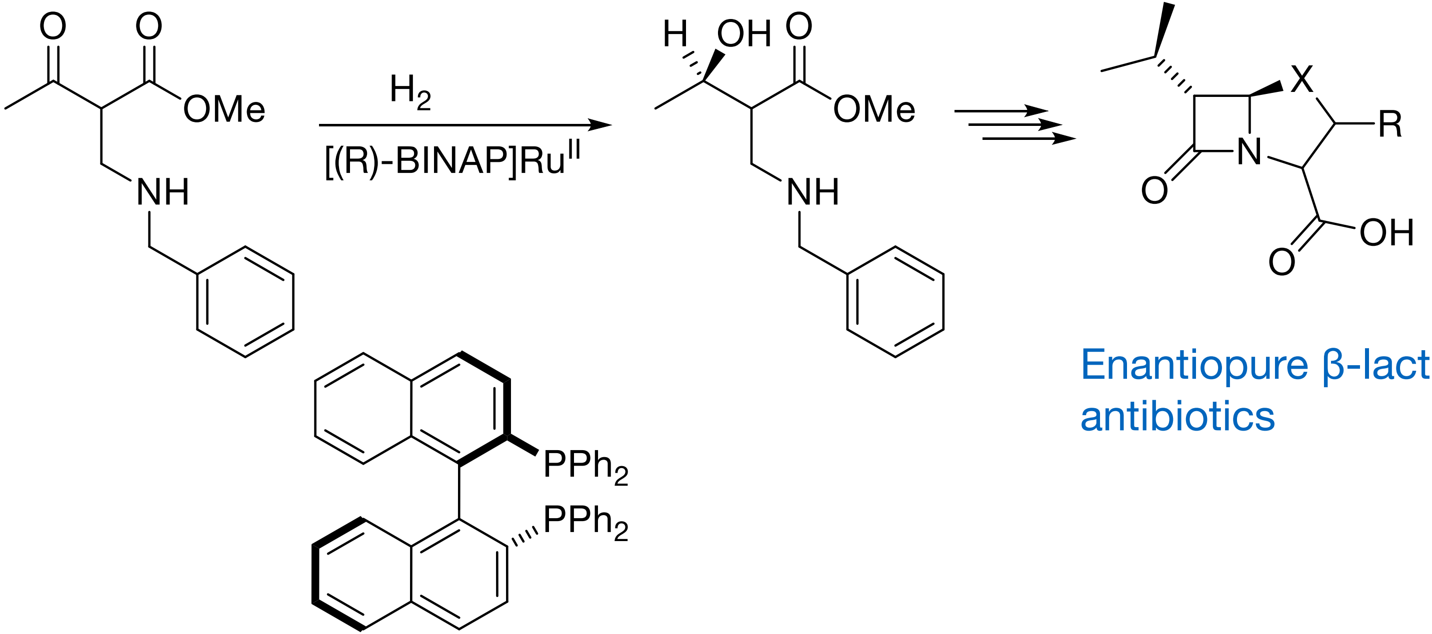
Stereoselectivity with chiral diphosphines



R. Noyori et al., *JACS* **1995**, *117*, 2675; *Angew. Chem.* **2002**, *114*, 2108.

Enantioselective hydrogenation

Synthesis of antibiotics

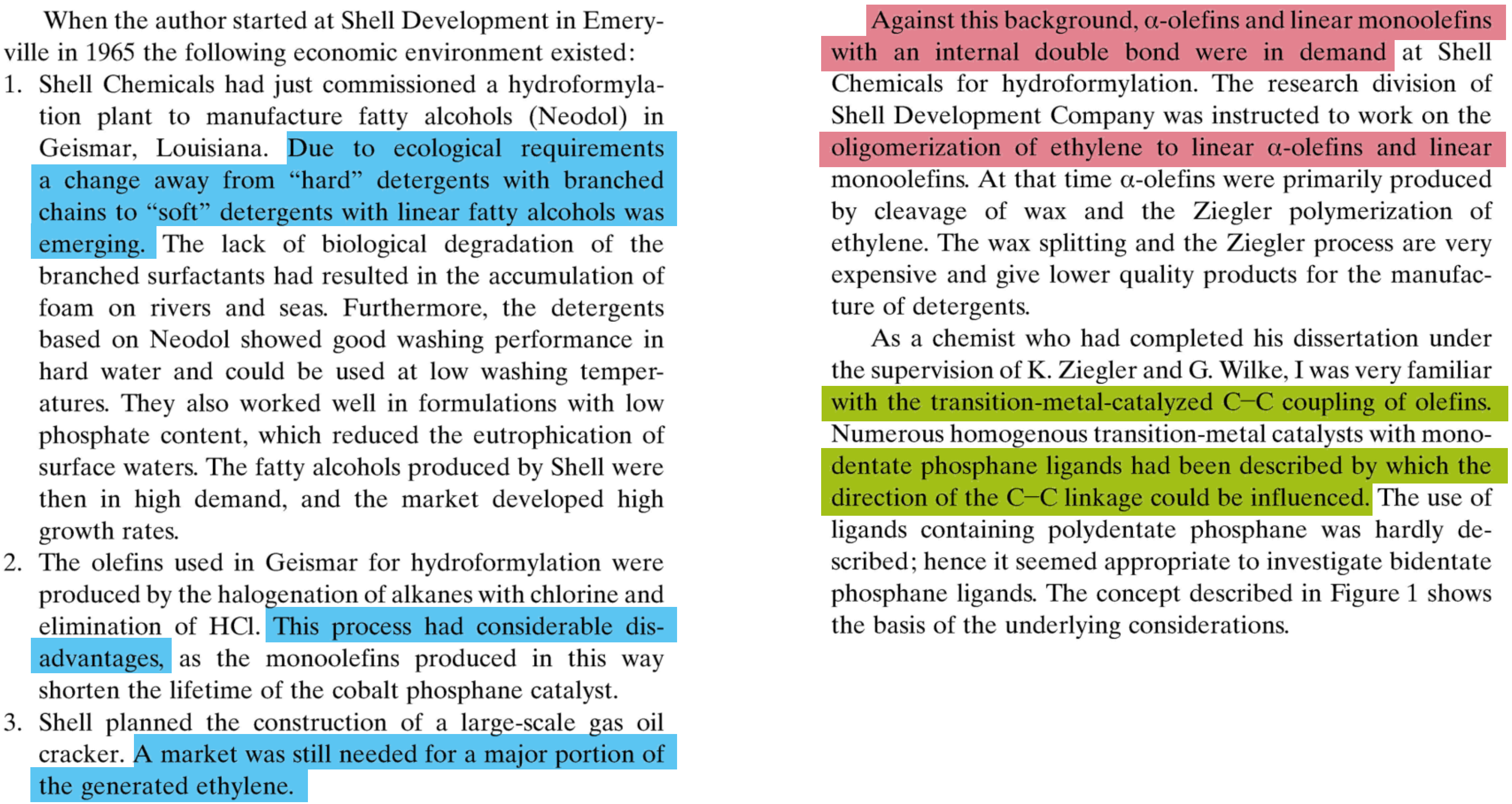


(R)-BINAP

Enantiopure β-lactame antibiotics

Back to the SHOP...

The driving force



When the author started at Shell Development in Emeryville in 1965 the following economic environment existed:

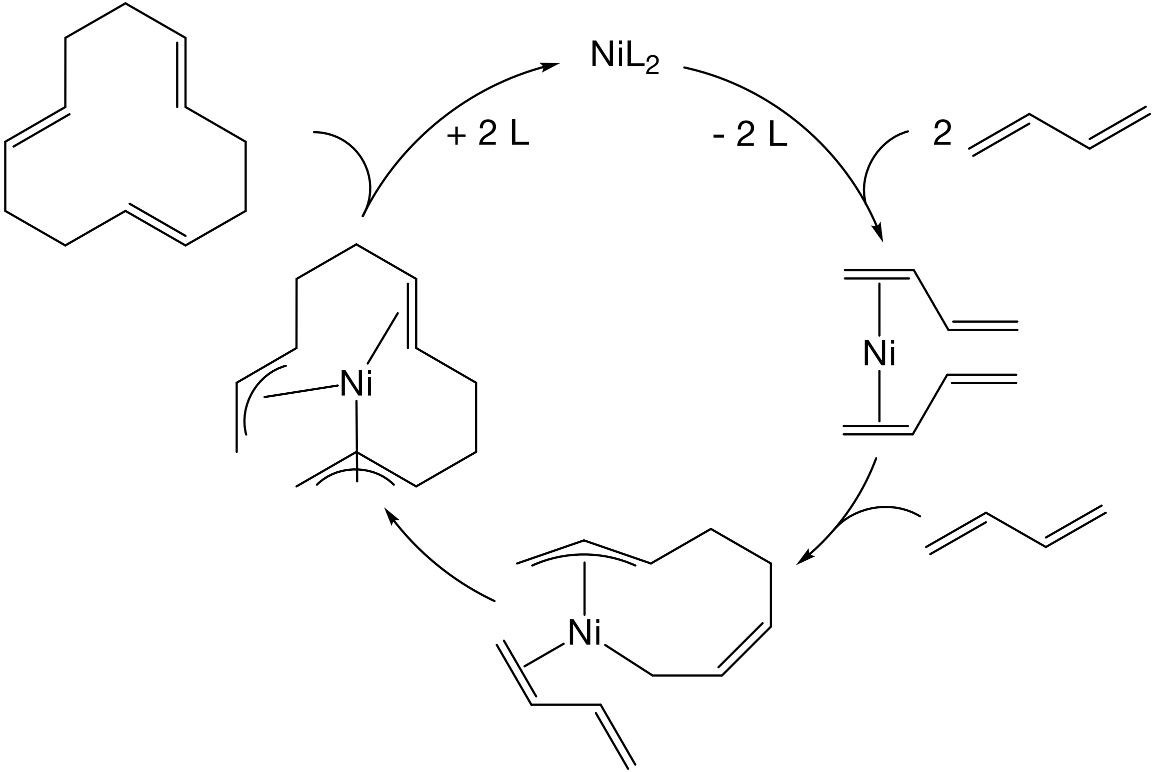
1. Shell Chemicals had just commissioned a hydroformylation plant to manufacture fatty alcohols (Neodol) in Geismar, Louisiana. Due to ecological requirements a change away from “hard” detergents with branched chains to “soft” detergents with linear fatty alcohols was emerging. The lack of biological degradation of the branched surfactants had resulted in the accumulation of foam on rivers and seas. Furthermore, the detergents based on Neodol showed good washing performance in hard water and could be used at low washing temperatures. They also worked well in formulations with low phosphate content, which reduced the eutrophication of surface waters. The fatty alcohols produced by Shell were then in high demand, and the market developed high growth rates.
2. The olefins used in Geismar for hydroformylation were produced by the halogenation of alkanes with chlorine and elimination of HCl. This process had considerable disadvantages, as the monoolefins produced in this way shorten the lifetime of the cobalt phosphane catalyst.
3. Shell planned the construction of a large-scale gas oil cracker. A market was still needed for a major portion of the generated ethylene.

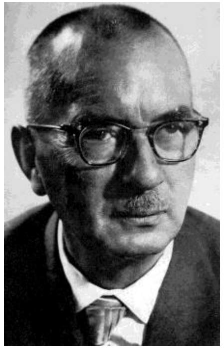
Against this background, α-olefins and linear monoolefins with an internal double bond were in demand at Shell Chemicals for hydroformylation. The research division of Shell Development Company was instructed to work on the oligomerization of ethylene to linear α-olefins and linear monoolefins. At that time α-olefins were primarily produced by cleavage of wax and the Ziegler polymerization of ethylene. The wax splitting and the Ziegler process are very expensive and give lower quality products for the manufacture of detergents.

As a chemist who had completed his dissertation under the supervision of K. Ziegler and G. Wilke, I was very familiar with the transition-metal-catalyzed C–C coupling of olefins. Numerous homogenous transition-metal catalysts with monodentate phosphane ligands had been described by which the direction of the C–C linkage could be influenced. The use of ligands containing polydentate phosphane was hardly described; hence it seemed appropriate to investigate bidentate phosphane ligands. The concept described in Figure 1 shows the basis of the underlying considerations.

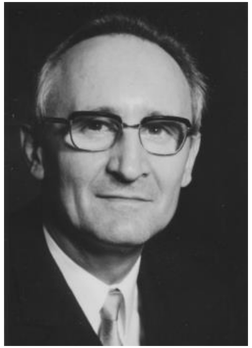
Background

Trimerization of 1,3-butadiene at Ni(0) complexes





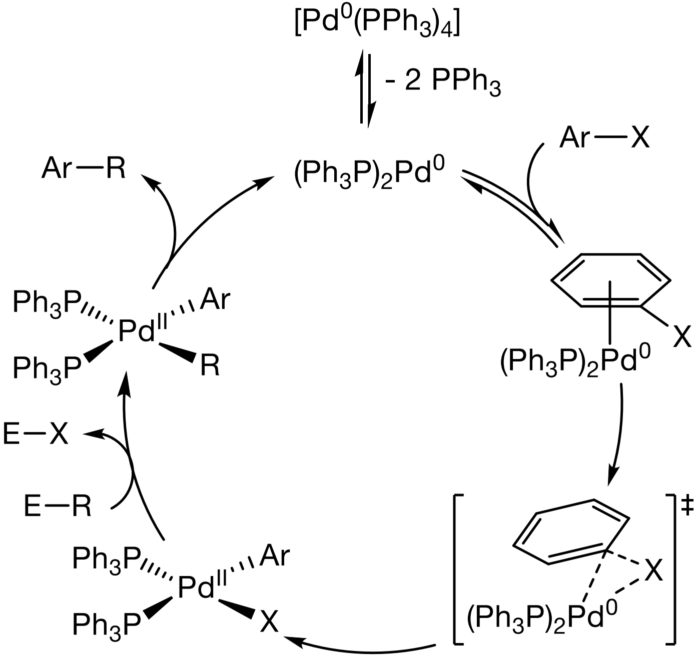
Karl Ziegler
(MPI Mülheim)



Günther Wilke
(MPI Mülheim)

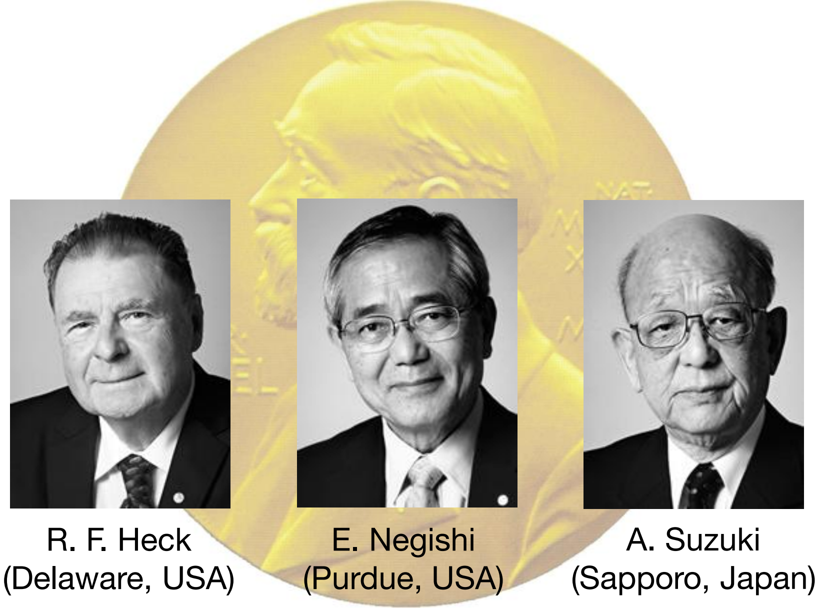
Remember: Pd-catalyzed C–C cross coupling

Discovered in the 1970ies!



Nobel Prize in Chemistry in 2010

‘for palladium-catalyzed cross couplings in organic synthesis’

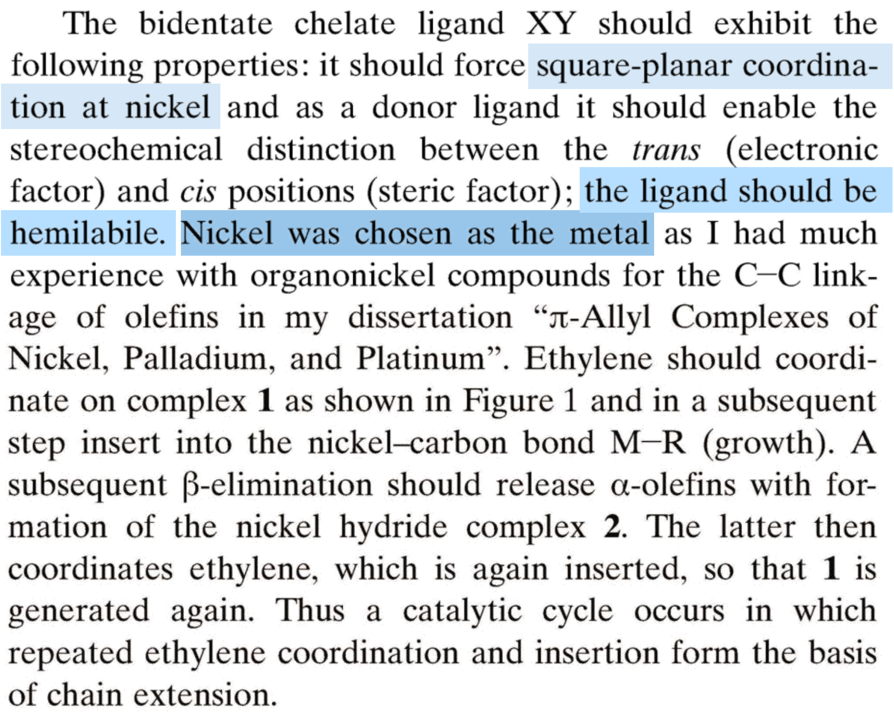


R. F. Heck
(Delaware, USA)

E. Negishi
(Purdue, USA)

A. Suzuki
(Sapporo, Japan)

Designing the catalyst



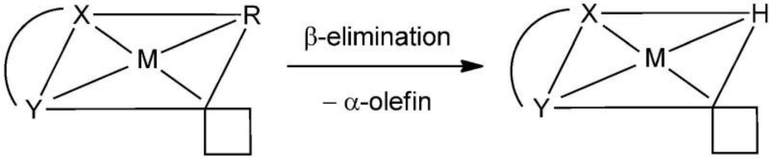
The bidentate chelate ligand XY should exhibit the following properties: it should force square-planar coordination at nickel and as a donor ligand it should enable the stereochemical distinction between the *trans* (electronic factor) and *cis* positions (steric factor); the ligand should be hemilabile. Nickel was chosen as the metal as I had much experience with organonickel compounds for the C–C linkage of olefins in my dissertation "π-Allyl Complexes of Nickel, Palladium, and Platinum". Ethylene should coordinate on complex **1** as shown in Figure 1 and in a subsequent step insert into the nickel–carbon bond M–R (growth). A subsequent β-elimination should release α-olefins with formation of the nickel hydride complex **2**. The latter then coordinates ethylene, which is again inserted, so that **1** is generated again. Thus a catalytic cycle occurs in which repeated ethylene coordination and insertion form the basis of chain extension.

Why square-planar?

Why hemilabile?

Why nickel?

How & why does this catalysis work?



1 **2**

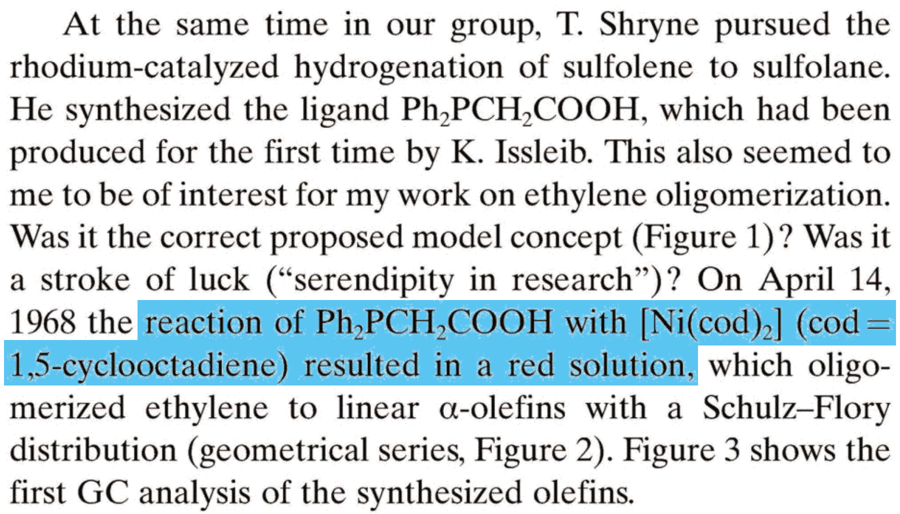
R = growing, linear, ethylene-derived carbon chain

M = nickel

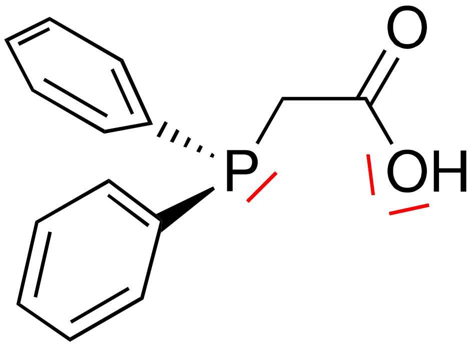
X⌒Y = bidentate chelate ligand

Y = P; X = O, N, S etc., ☐ = ethene coordination site

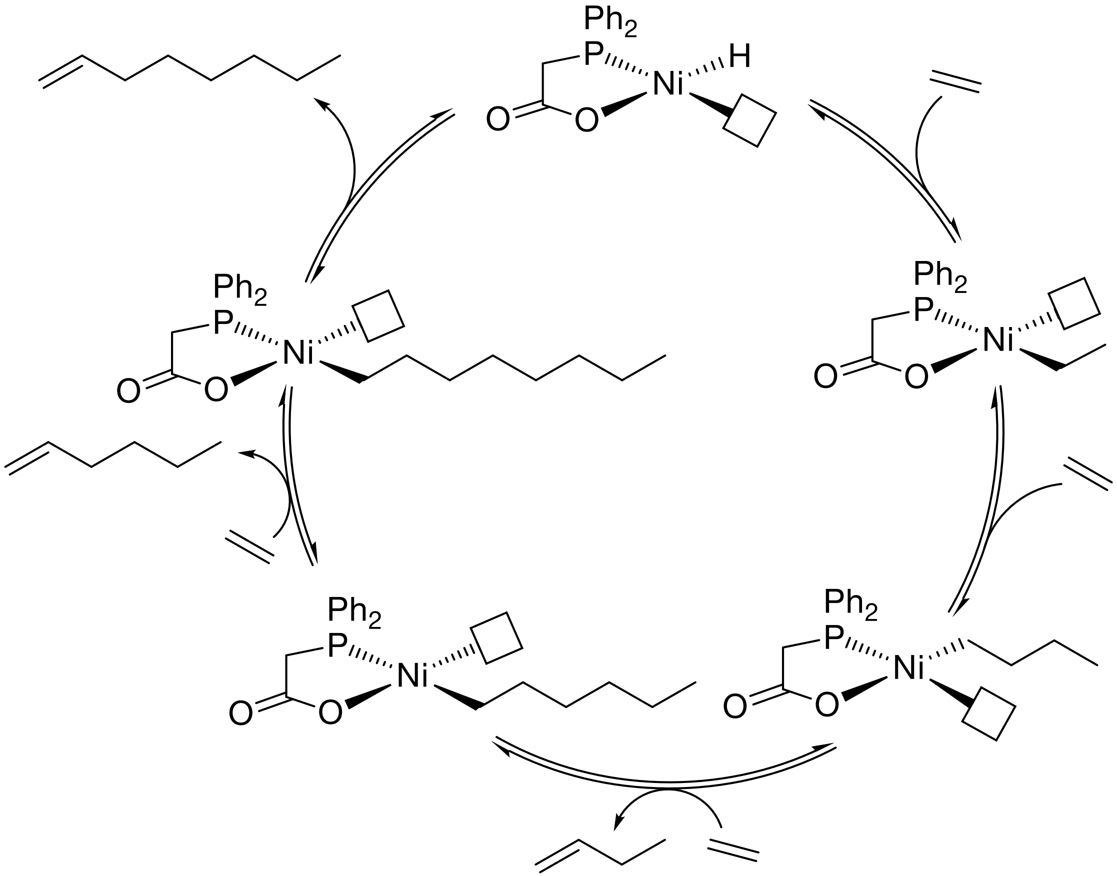
The ligand



At the same time in our group, T. Shryne pursued the rhodium-catalyzed hydrogenation of sulfolene to sulfolane. He synthesized the ligand Ph_2PCH_2COOH, which had been produced for the first time by K. Issleib. This also seemed to me to be of interest for my work on ethylene oligomerization. Was it the correct proposed model concept (Figure 1)? Was it a stroke of luck ("serendipity in research")? On April 14, 1968 the reaction of Ph_2PCH_2COOH with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) resulted in a red solution, which oligomerized ethylene to linear α-olefins with a Schulz–Flory distribution (geometrical series, Figure 2). Figure 3 shows the first GC analysis of the synthesized olefins.



The mechanism of the oligomerization



Sequences of:

- coordination
- ligand migration
- β-H elimination