WORKSHOP HOMOGENE KATALYSE

Materials Valley e.V, Heraeus Holding GmbH, BASF SE Ludwigshafen

P. Hofmann, 23.Januar 2014

Chasing a Dream Reaction Combining Theory and Experiment: The Rhodium-Catalyzed Hydroformylation of Butadiene to Adipic Aldehyde

CaRLa
Catalysis Research Laboratory

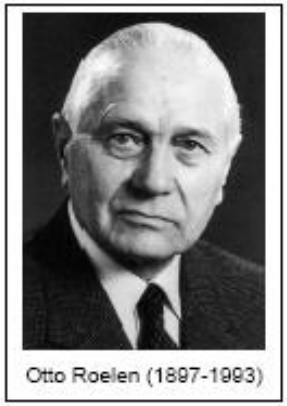
CaRLa – a laboratory incorporated in the University of Heidelberg and supported by BASF

www.carla-hd.de

Heidelberg Collaborative Research Center (2002 – 2013):
Molecular Catalysts: Structure and Functional Design

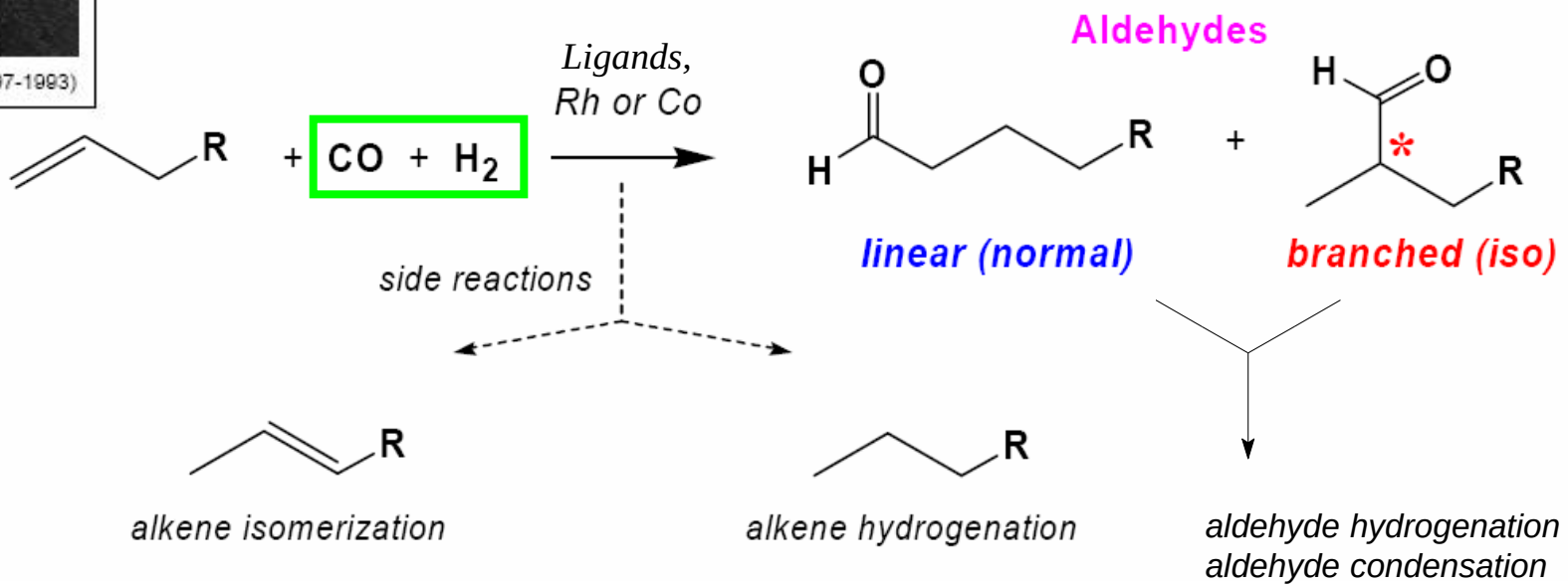
http://www.sfb623.uni-hd.de

University of Heidelberg
Institute of Organic Chemistry


Otto Roelen (1897-1993)

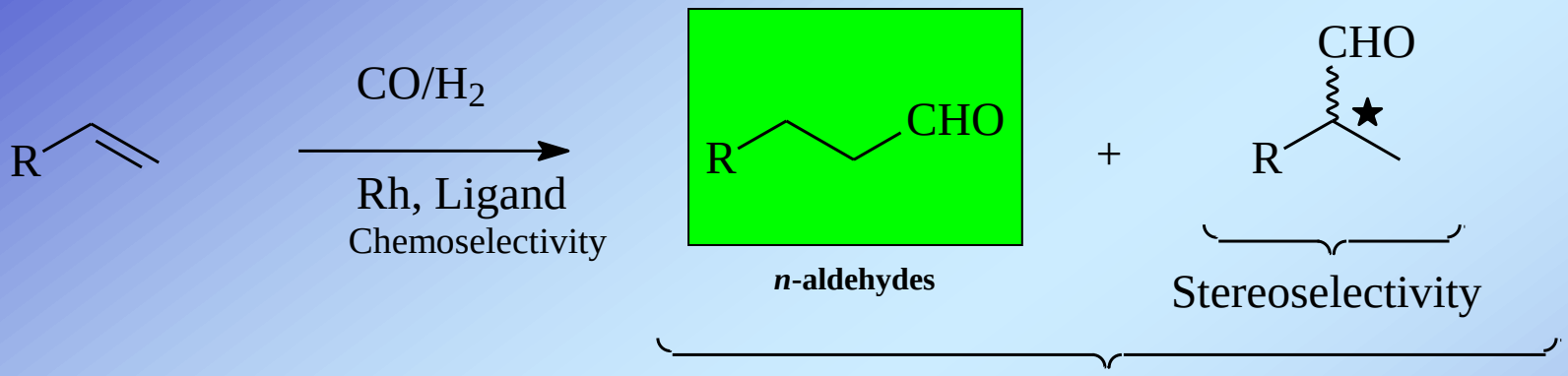
Hydroformylation (The „Oxo-Reaction“)

Discovery: 1938 (O. Roelen) ⟶ 75th Anniversary in 2013



- **Largest homogeneous metal-catalyzed process with single-site catalysts**
- **Perfect atom economy**
- **More than 9 million tons per year of production volume**
- **Over 5 million tons of C_4-oxo products per year**
- **Commercial catalysts metals: Co or Rh without or with ligand systems**
- **Products: aldehydes, alcohols, carboxylic acids, esters, plasticizers, detergents, surfactants, lubricants, solvents, fine chemical intermediates ....**

Rh-Catalyzed Low Pressure *n*-Hydroformylation of 1-Alkenes



Chuck Casey (1997): „*The regioselectivity of hydroformylation is governed by a complex web of electronic and steric effects that have so far defied unravelling*.“

This still holds.

Ligand Design ➡

Research Collaboration with BASF

- **Chemoselectivity (% aldehydes)**
- **Regioselectivity (boosting *n / i - ratio*)**
- **Activity (TOF, TON, [Rh], [L])**
- **Stability (catalyst lifetime)**
- **Accessibility (facile, cheap synthesis)**
- **Structural variability (modular systems)**
- **Product separation, Rh loss aspects …**
- **Engineering aspects**

Typical industrial plant characteristics and requirements:

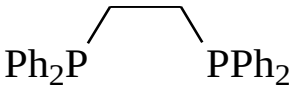
capacity: 250.000 t / a of aldehydes
reactor volumes: 200 – 300 m^3
100 – 300 ppm Rh = kg range of Rh (several mio. €)
phosphine content (e.g. PPh_3) : multi-ton-scale

TOF: above 1000 mol / mol h (at low p, T)
TON: at least 4.000.000 mol product / mol Rh

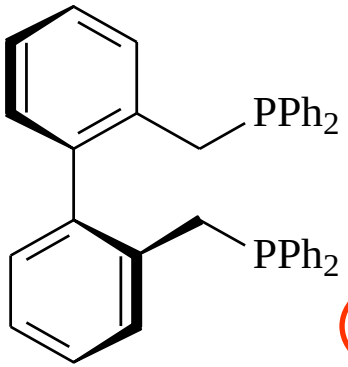
In Search of High Activity and *n*-Selectivity by Ligand Design:

From Triphenylphosphine PPh_3 to Prototypes and Countless Variants of Chelating P-Based Ligands

Prominent Bisphosphine Ligands for Rh

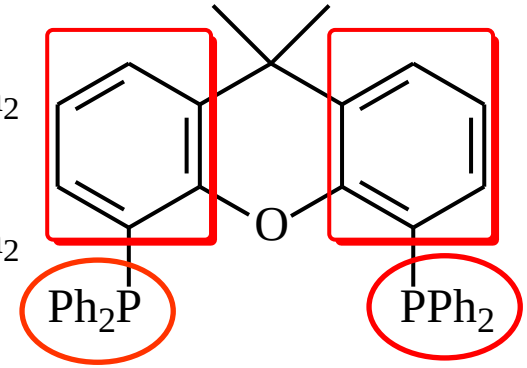


DIPHOS



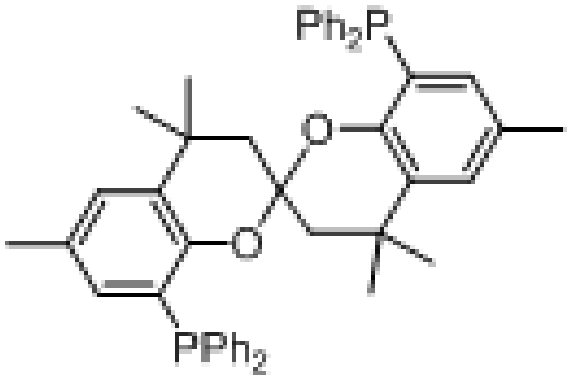
BISBI

DOW, Casey et al.



Xantphos

n / *i* ca. 50



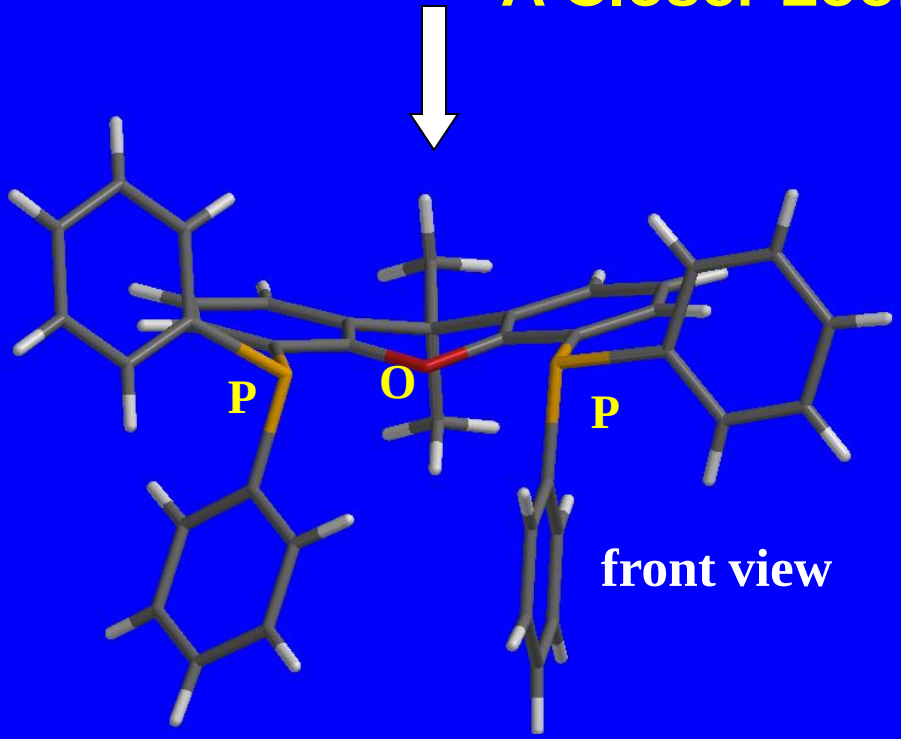
SPANphos

Van Leeuwen et al.

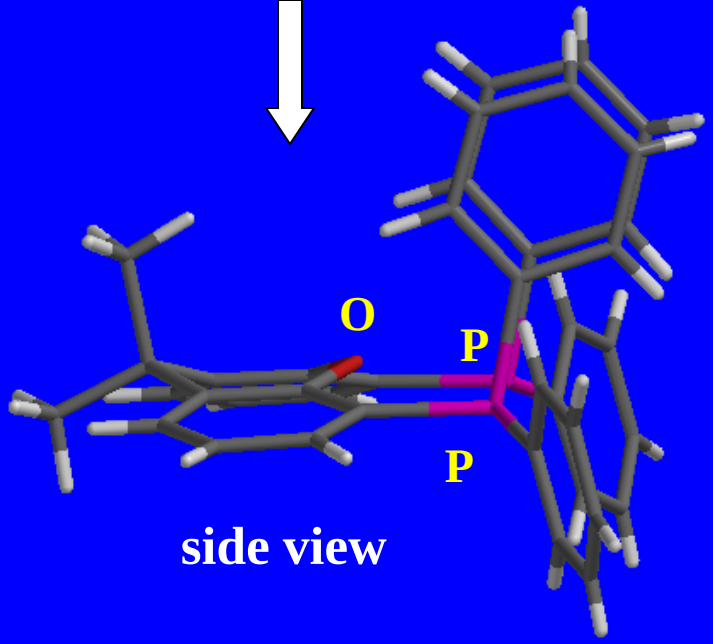
Small / medium bite angles

Wide bite angles

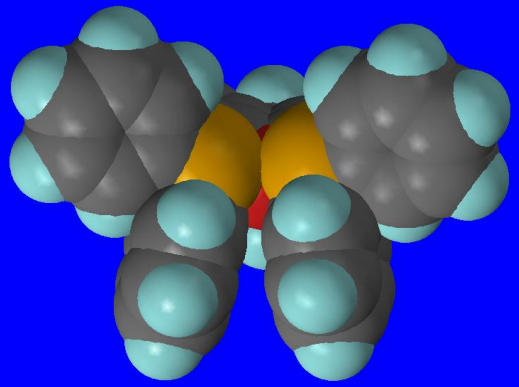
A Closer Look at Xantphos



front view

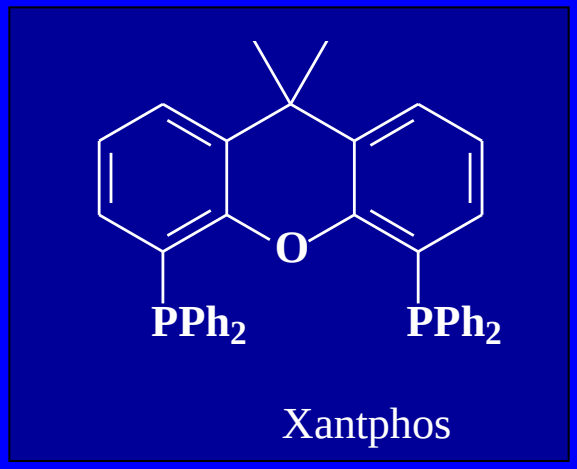


side view

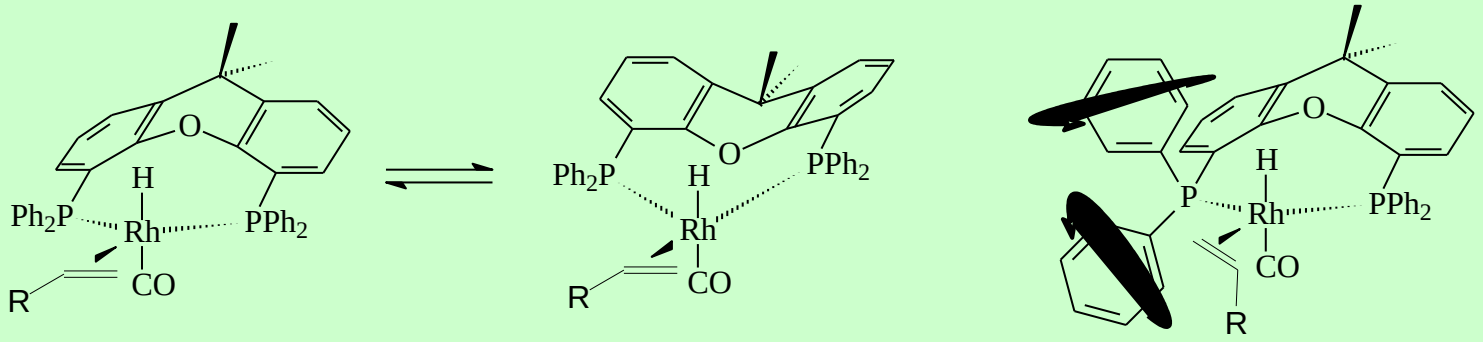


ligand X-ray structure

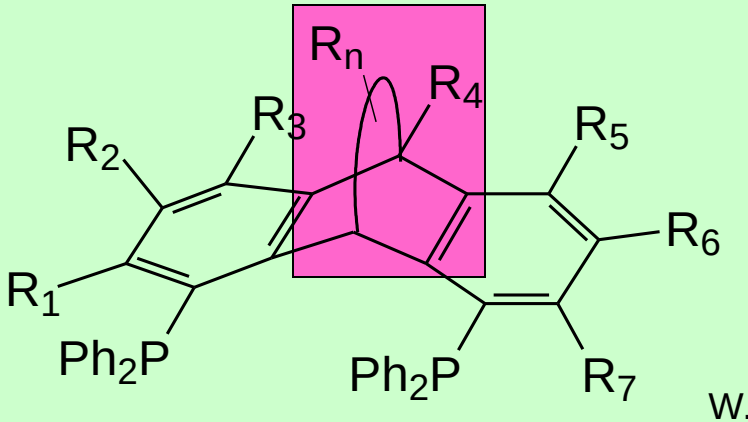
(van Leeuwen et al.)

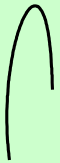


How to hamper facile backbone inversion and free P-substituent rotation ?



Make more rigid structures by bridging



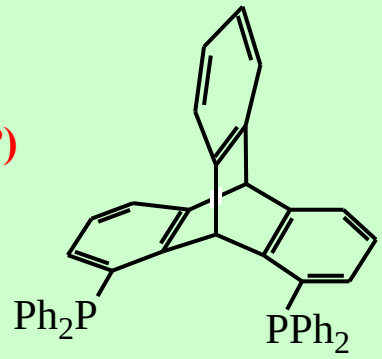


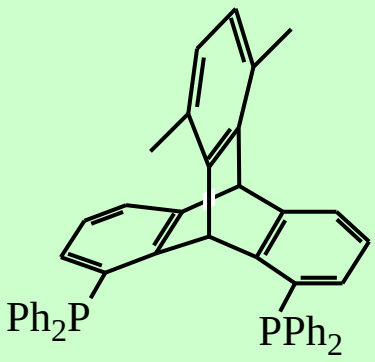
= bridge

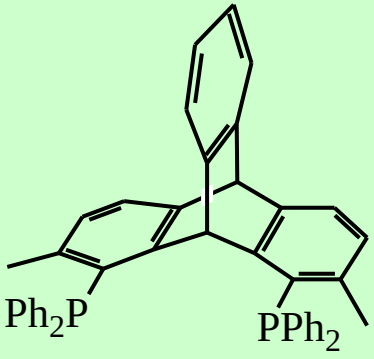
W. Ahlers, M. Röper, P. Hofmann, D.C.M. Warth, R. Paciello,
WO 01/58589, **BASF**

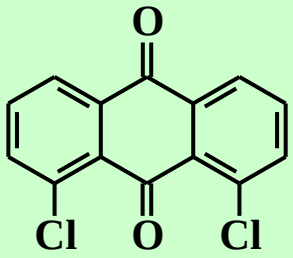
Triptyphos and its Congeners: New Bisphosphane Ligand Systems

„Triptyphos“ (TTP)

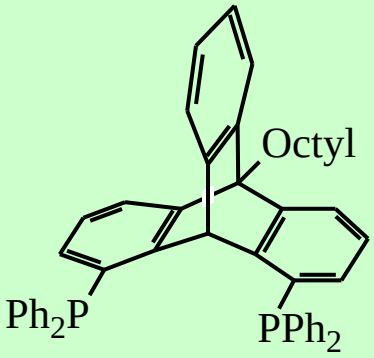


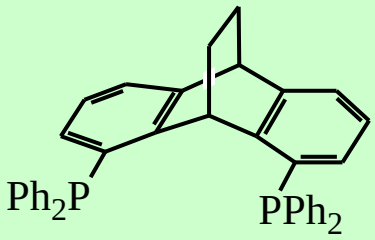


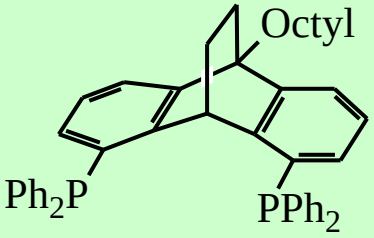


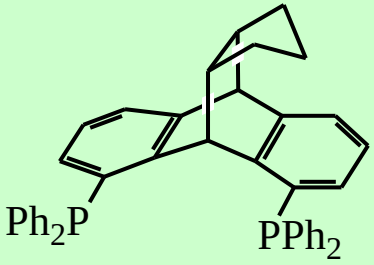


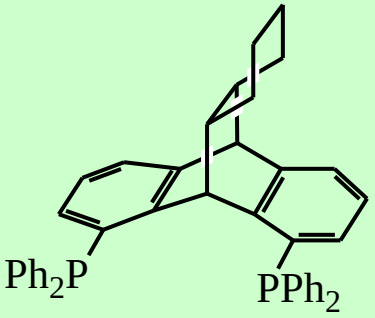
Cheap Precursor

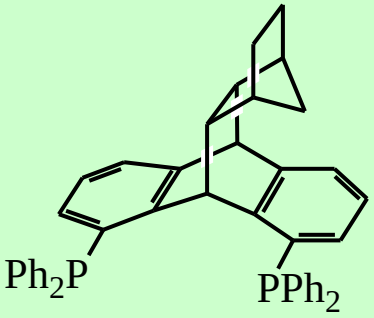








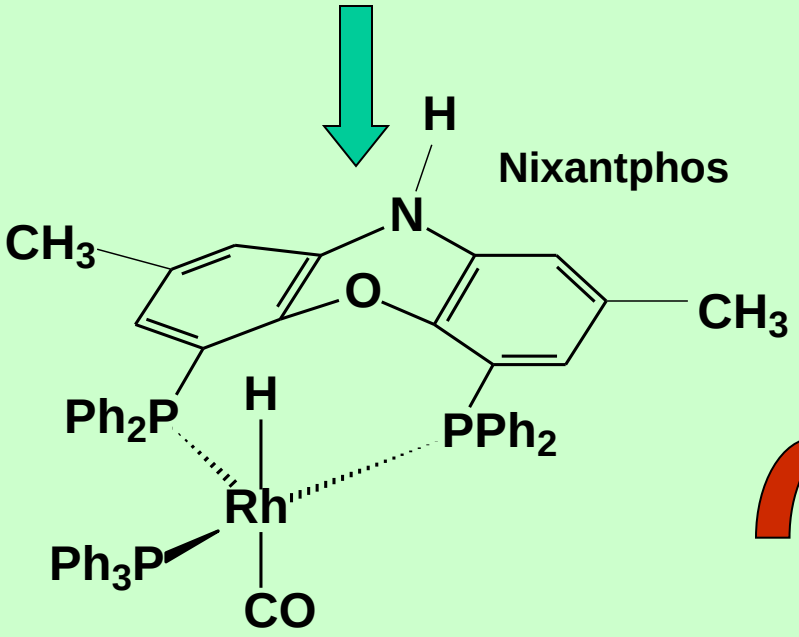




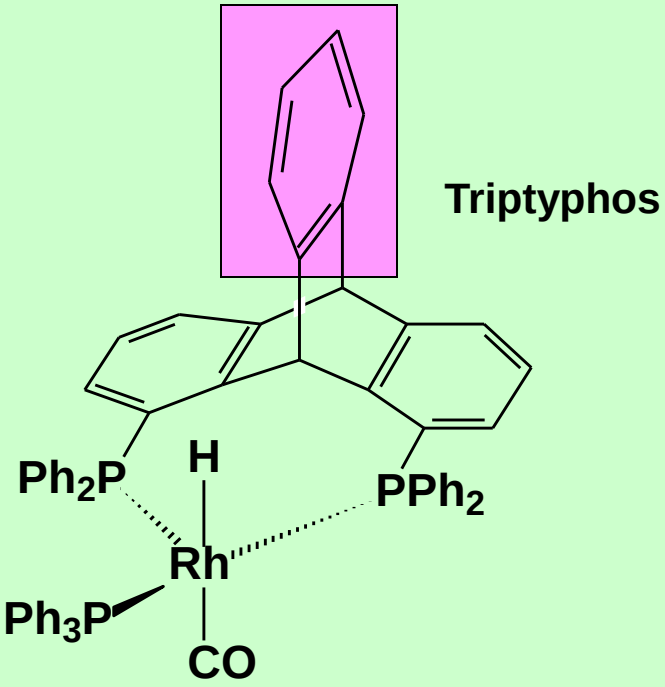
Daniel Warth

All ligands characterized by X-ray

Checking the Structural Concept



Van Leeuwen et al.
X-ray structure



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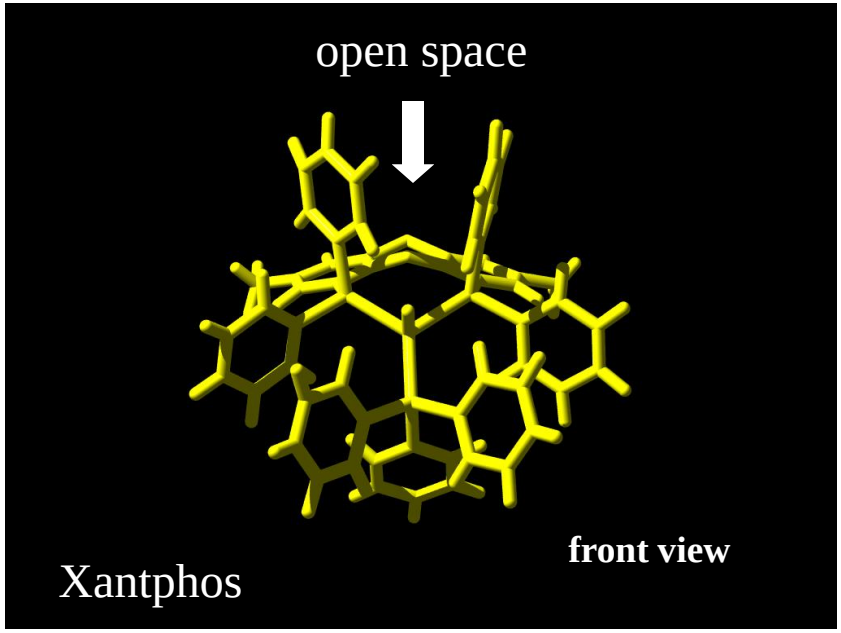
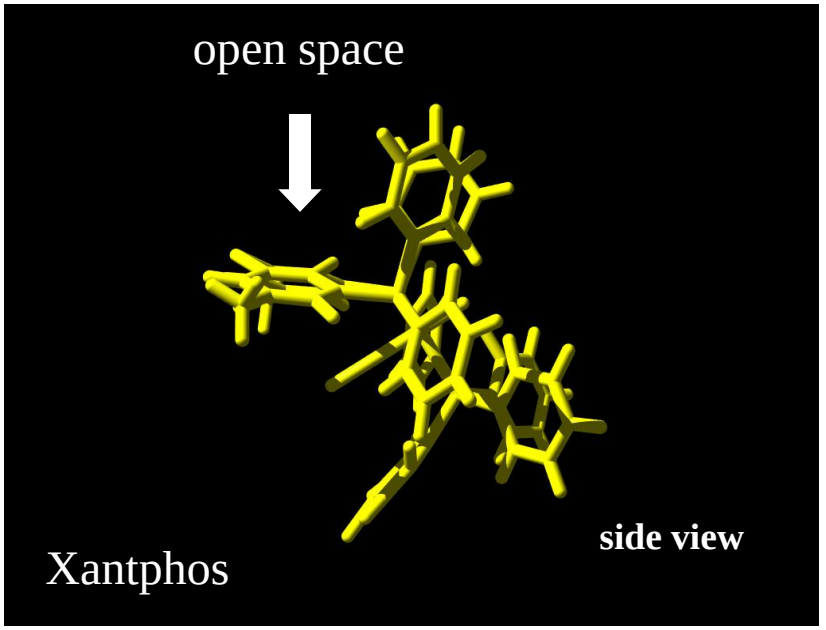
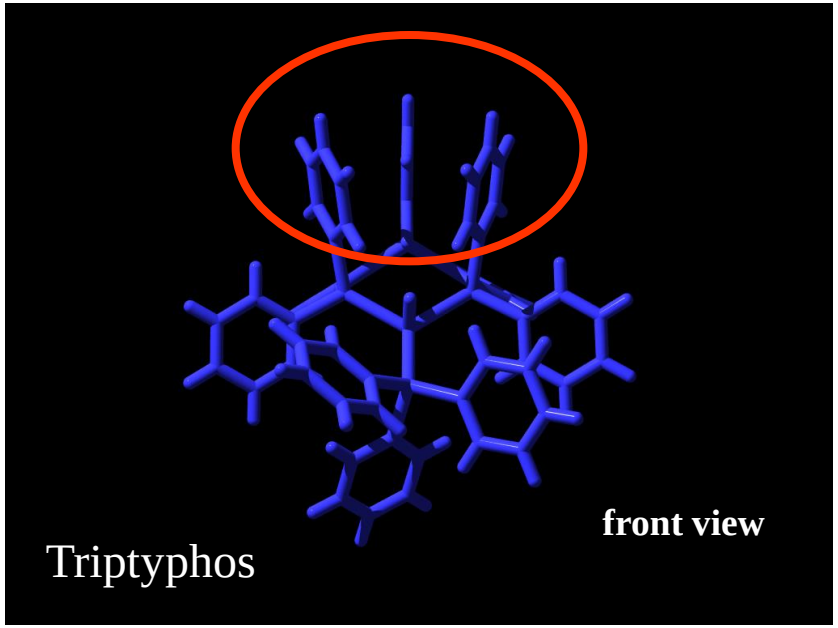
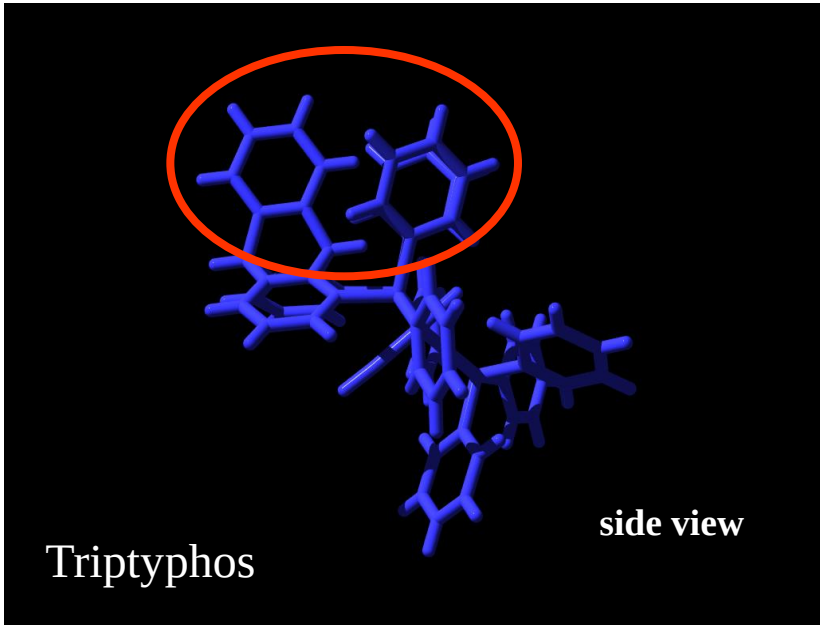
X-ray structure comparison of typical hydroformylation rhodium model complexes (PPh_3 replacing CO, Olefin)

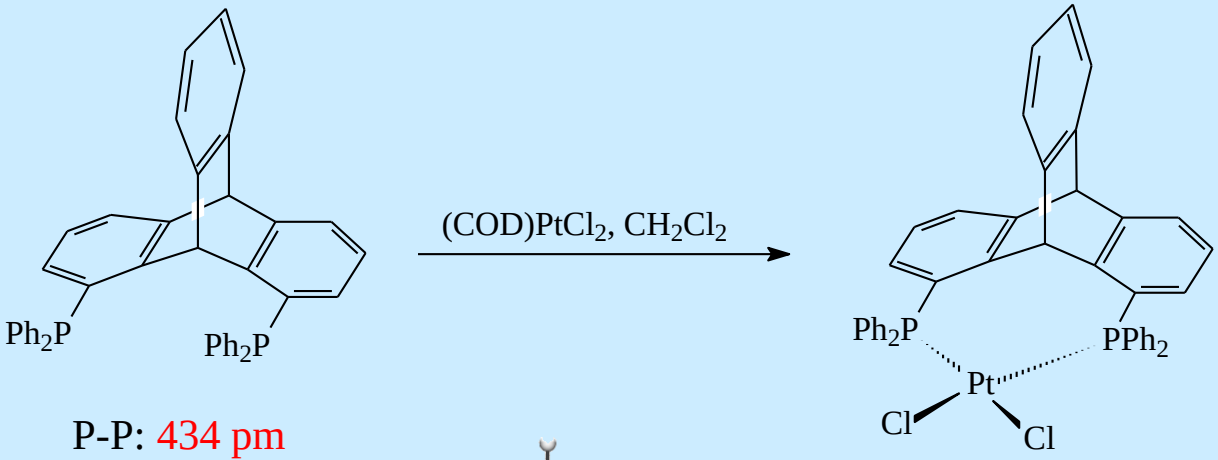

open space
front view
Xantphos


open space
side view
Xantphos

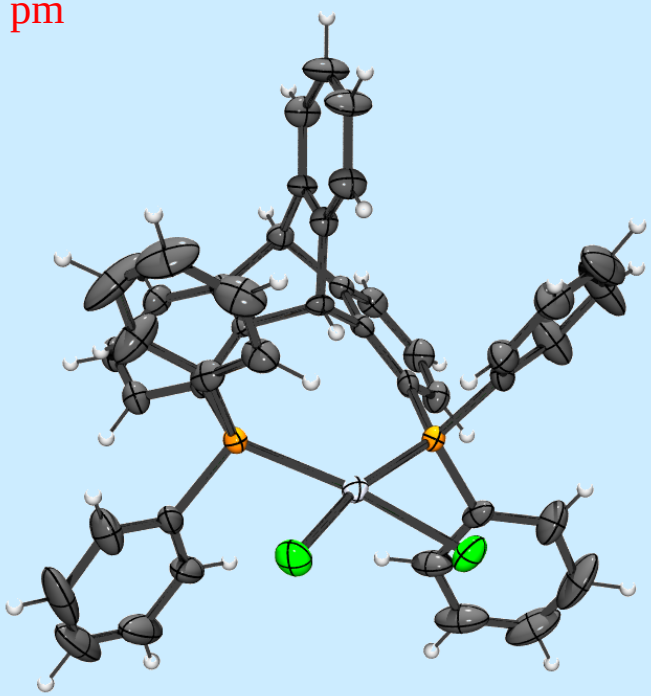

front view
Triptyphos


side view
Triptyphos

Metal Coordination Studies: Probing Accessible Geometries (Pt)



P-P: 434 pm



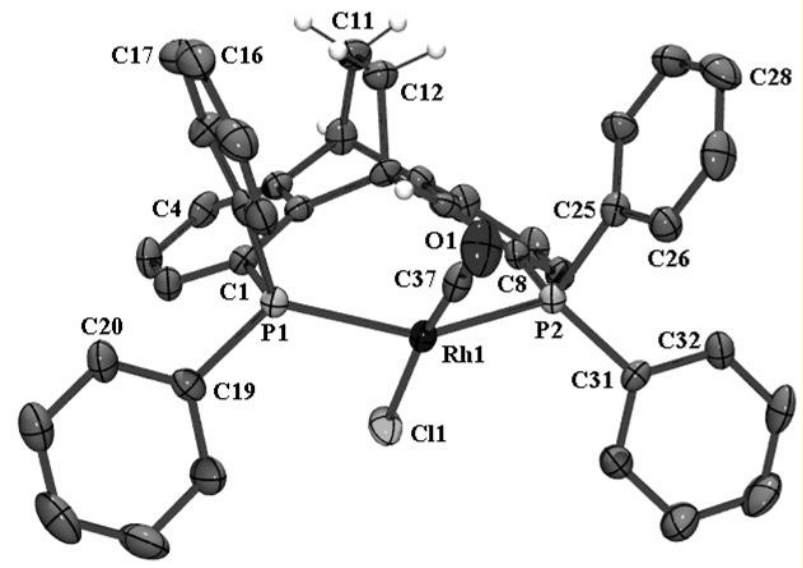
cis, square planar

P ... P = 377 pm
P-Pt-P = 110.8 °

D. Warth

Metal Coordination Studies: Accessible Geometries (Rh)

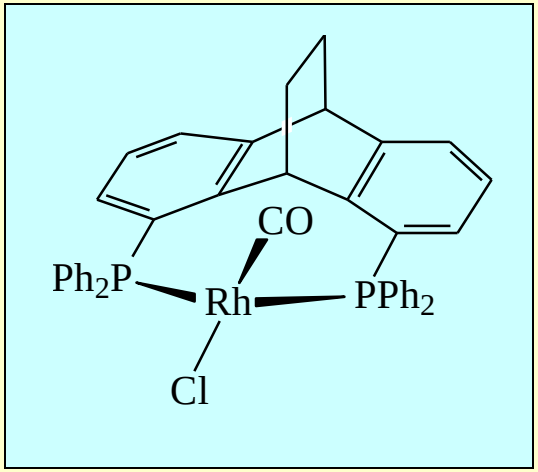
CO „exo“



P ... P = 445.9 pm
P-Rh-P = 147.2°

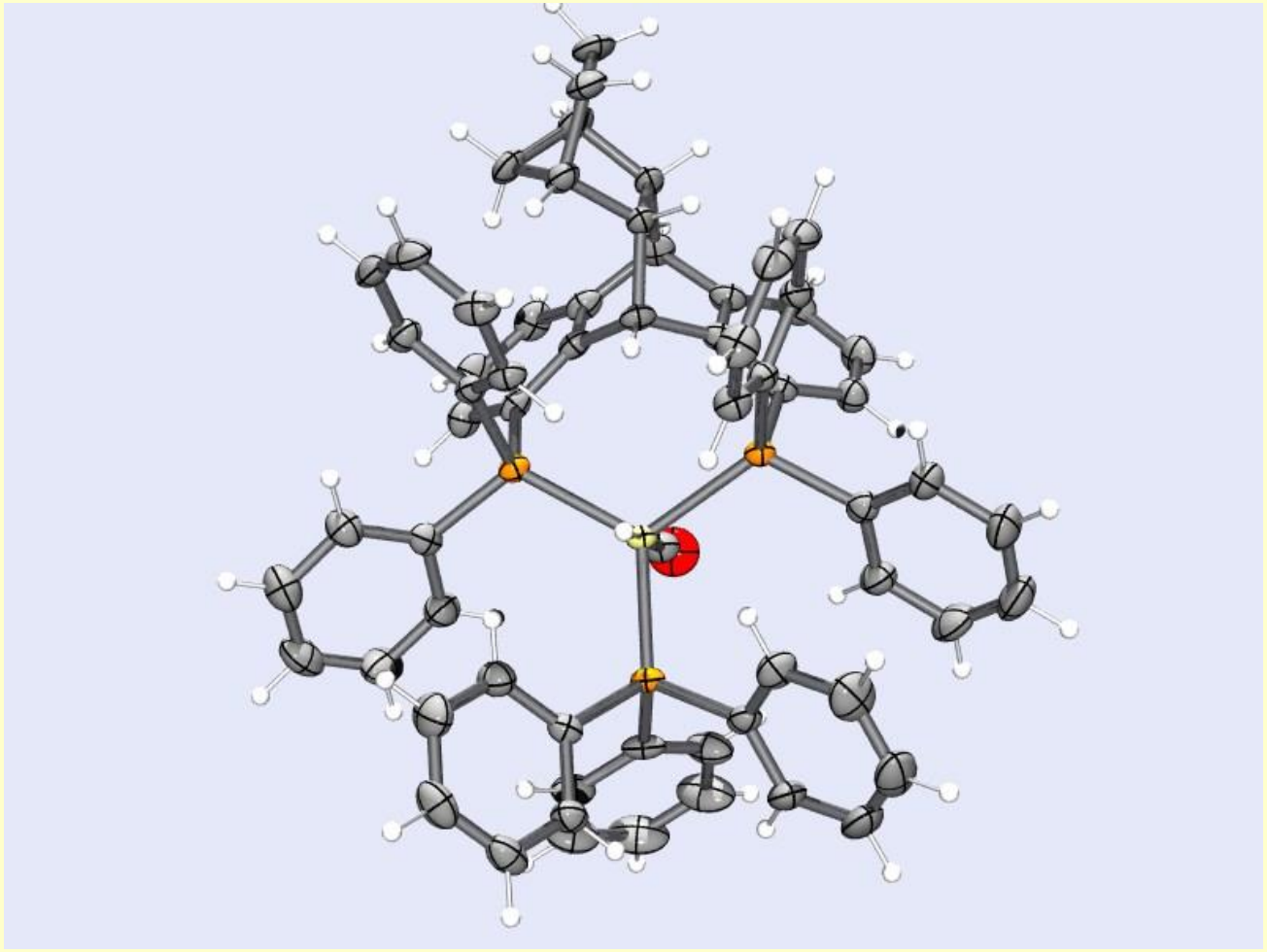
trans, square planar

$[Rh_2(\mu^2\text{–}Cl)_2(CO)_4]$ —(2 Rucaphos, CH_2Cl_2, -2 CO)→

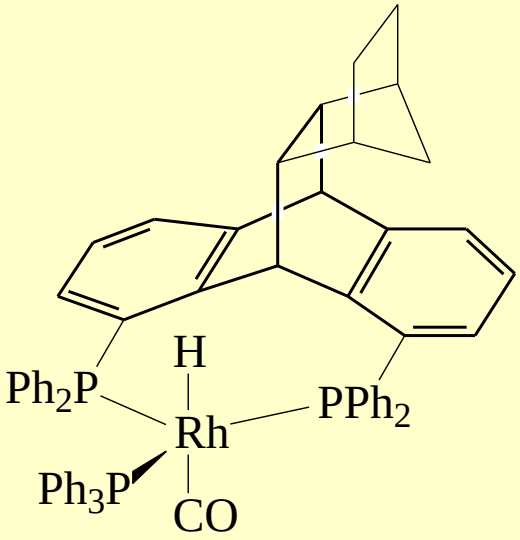


D. Warth

Metal Coordination Studies: Accessible Geometries (Rh)



(Maophos)RhH(CO)(PPh_3)



P ... P : 399.8 pm

Ligand P … P : 480 pm

P-Rh-P = 119.3 °

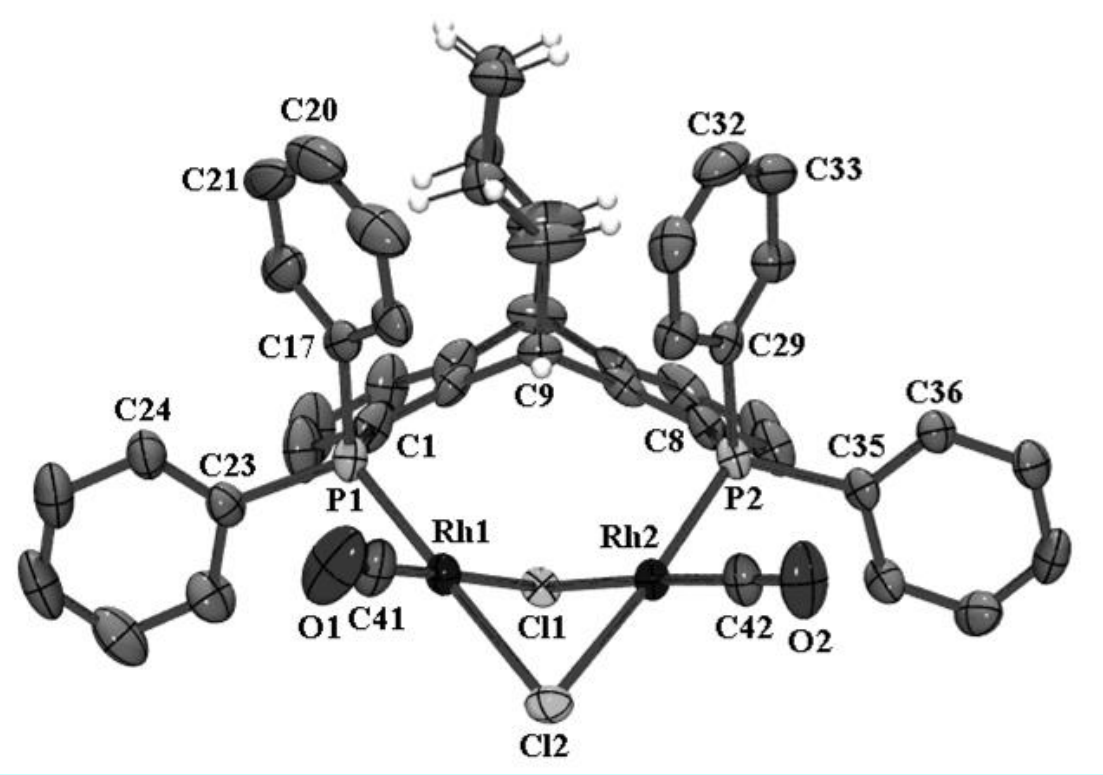
Xray

trigonal bipyramidal

***e,e*-P-coordination**

Sabrina Franz

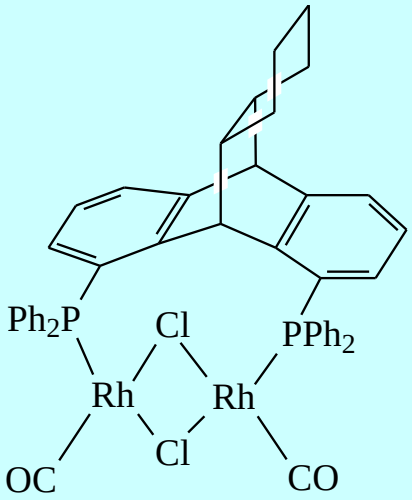
Metal Coordination Studies: Accessible Geometries (Rh)



P … P: 536 pm

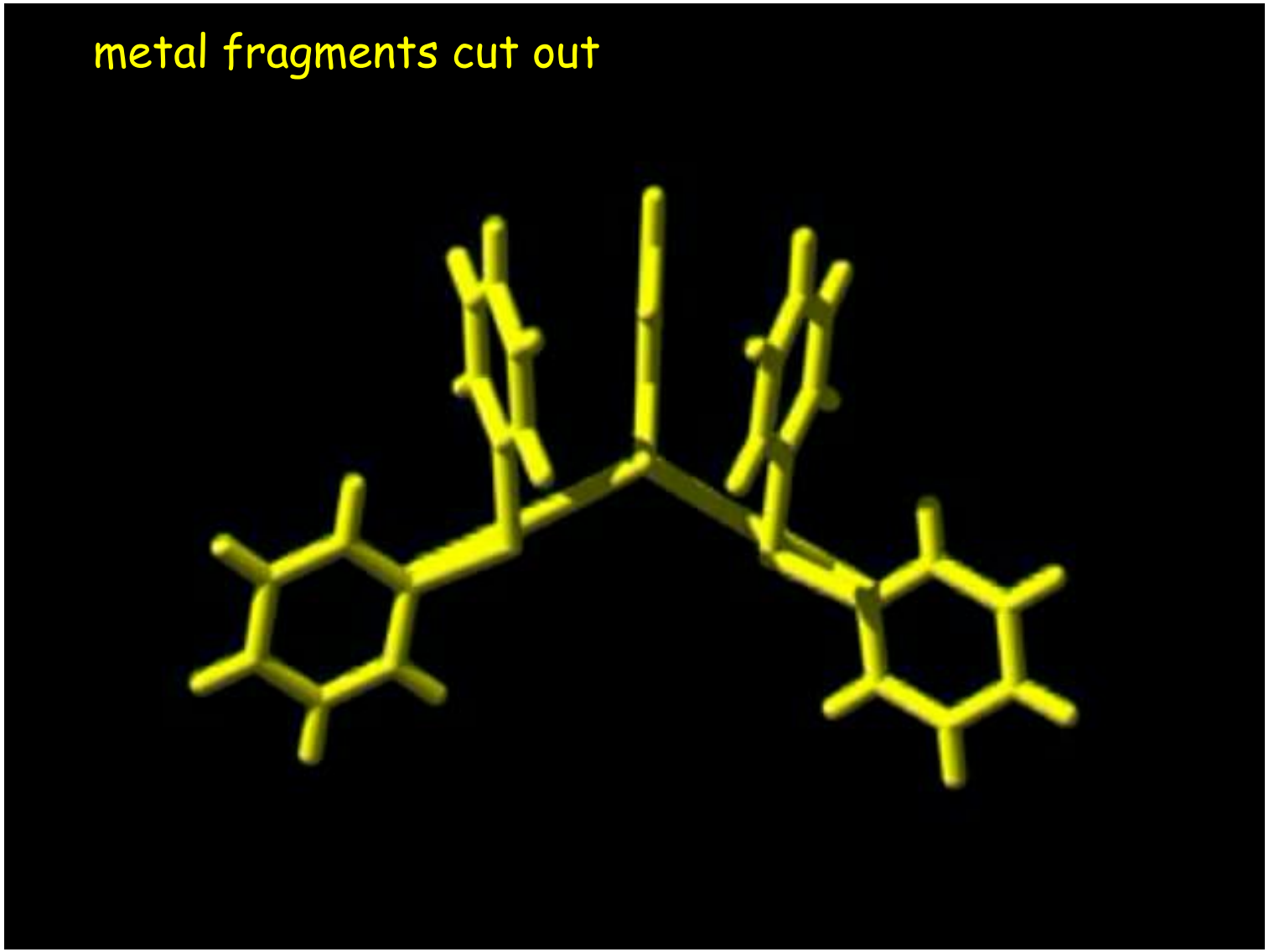
Ligand P … P: 480 pm

dinuclear

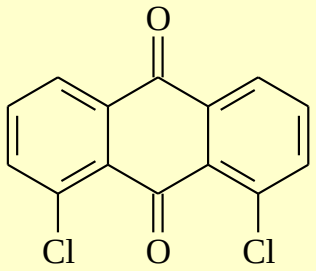


R. Tompers

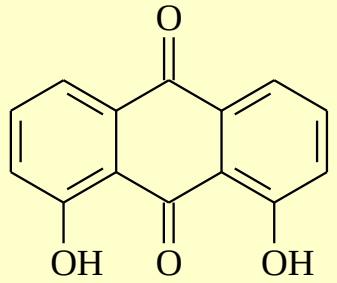
Ligand Flexibility Range from Model Complexes of Triptyphos (X-ray)

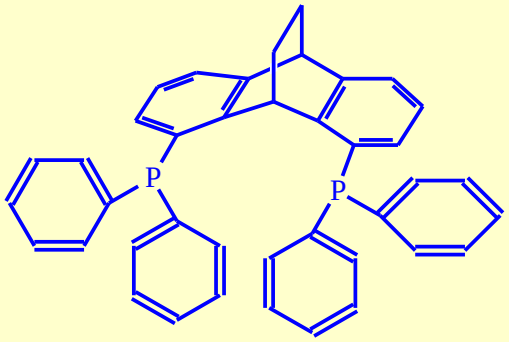


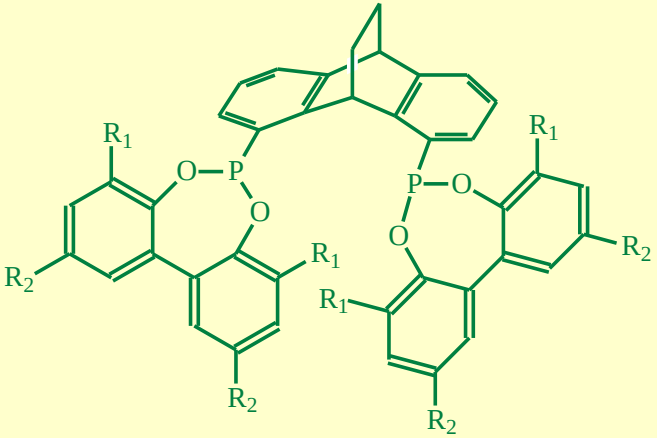
TTP → (TTP)$PtCl_2$ → (TTP)Pd_2Cl_4 → (TTP)Rh(CO)H(PPh_3) → TTP

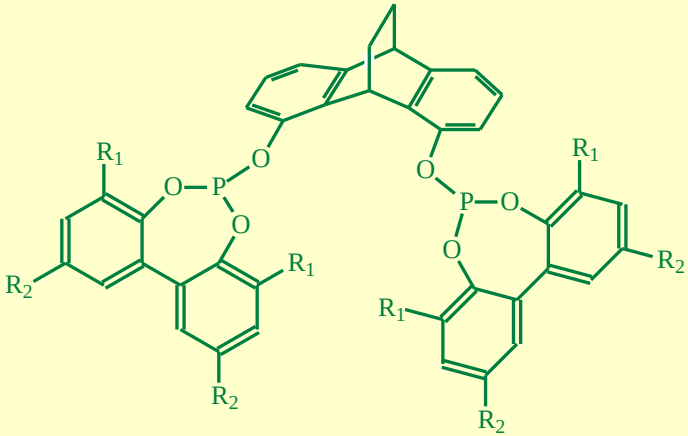


Modular Ligand Synthesis
Rh-Complexation Studies









Bisphosphanes **Bisphosphonites** **Bisphosphites**
Bisphosphoramidites

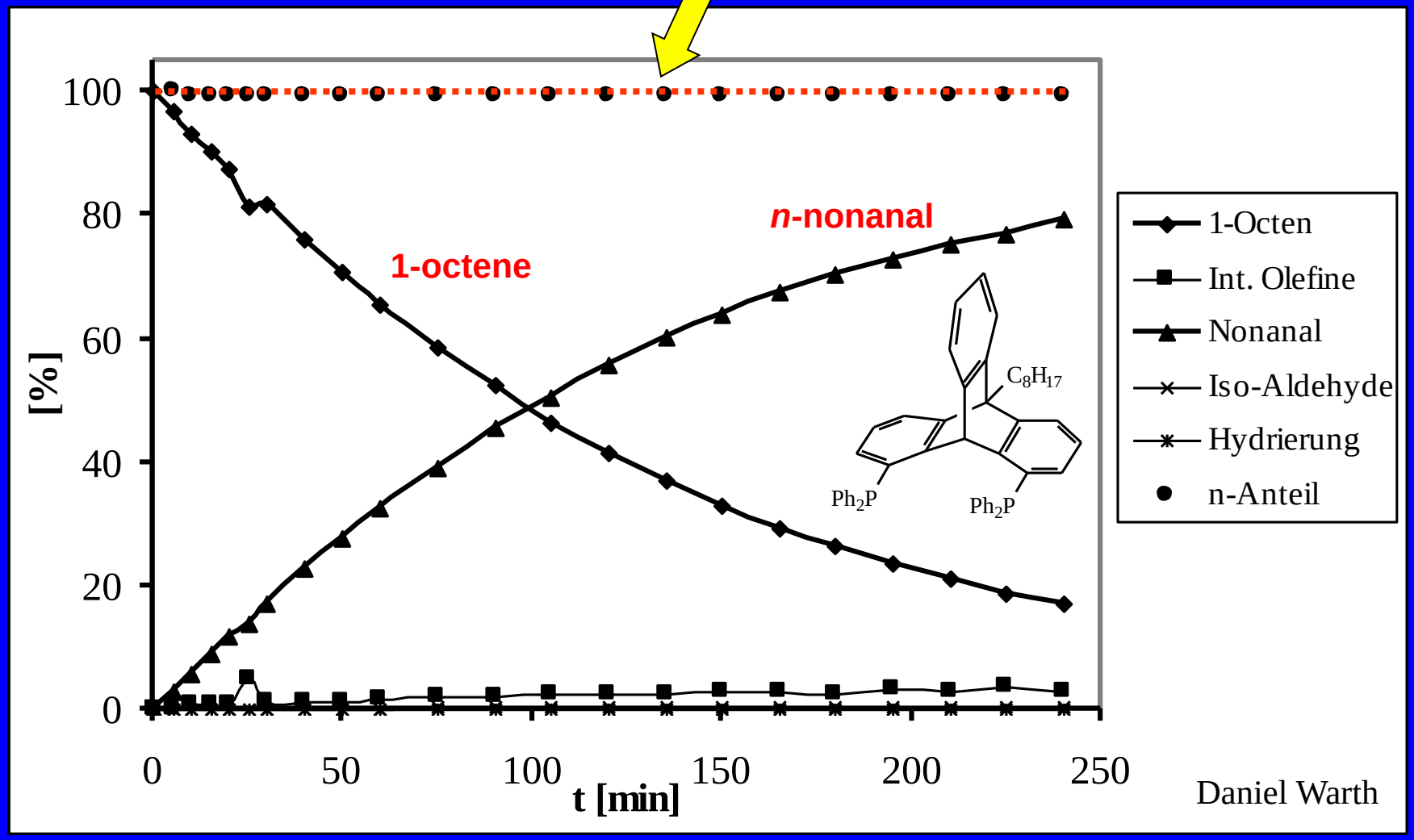
Daniel Warth **Thilo Kaiser** **Tobias Rosendahl**

Ligand Performance, Catalysis: Test Reactions (Batch) → Kinetics

- 80°C / 7 bar H_2/CO (1:1)
- Toluene (THF, 1,4-Dioxane)
- Glass autoclave reactors
- Stirring rate: 1200 rpm
- Substrate: 1-octene
- 50 ppm Rh as $Rh(acac)(CO)_2$
- Preformation: 1 h, 80°C
- Rh:substrate = 1:8000 - 10000
- Automated GC analysis
- Kinetics: 20 samples / 4 h

D. Warth

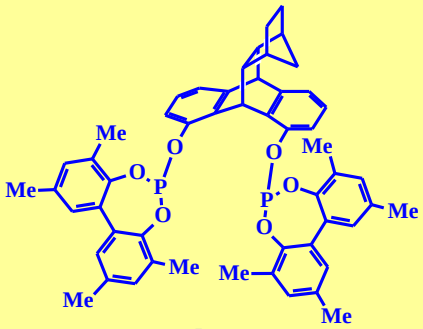
Chemo- and Regioselectivity: above 99% *n*-aldehyde



Kinetics: 7 bar H_2/CO (1:1), 80 °C, 50 ppm Rh, Triptyphos

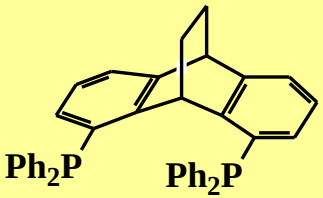
Hydroformylation of 1-Octene, Chemspeed Accelerator

[Rh:Ligand = 1:5, Rh:1-octene = 1:8000, 80°C, 7 bar CO/H_2 (1:1), 4,5h]



1

TOF = 9050
TON = 7800 (4.5 h)



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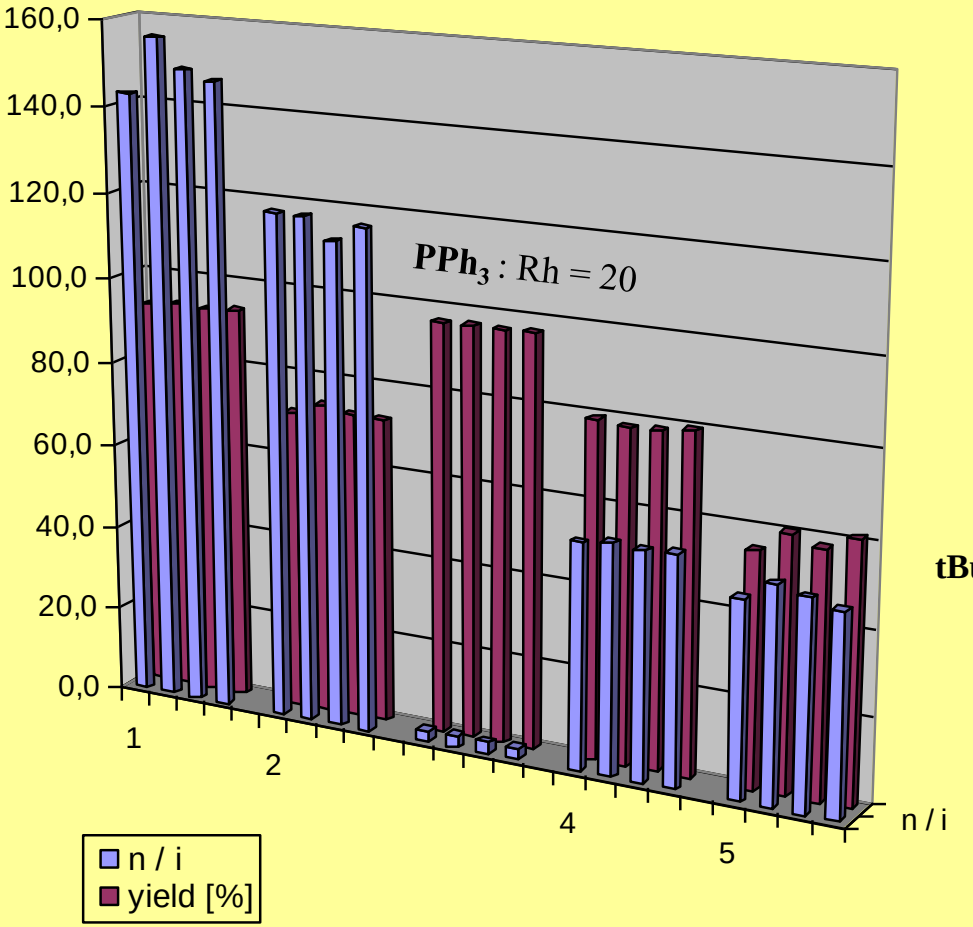

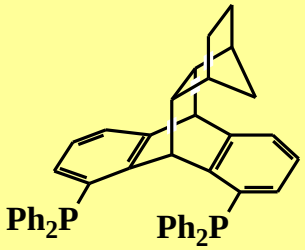

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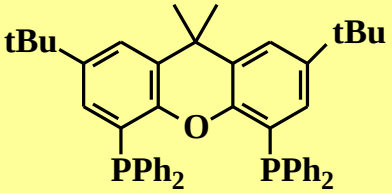


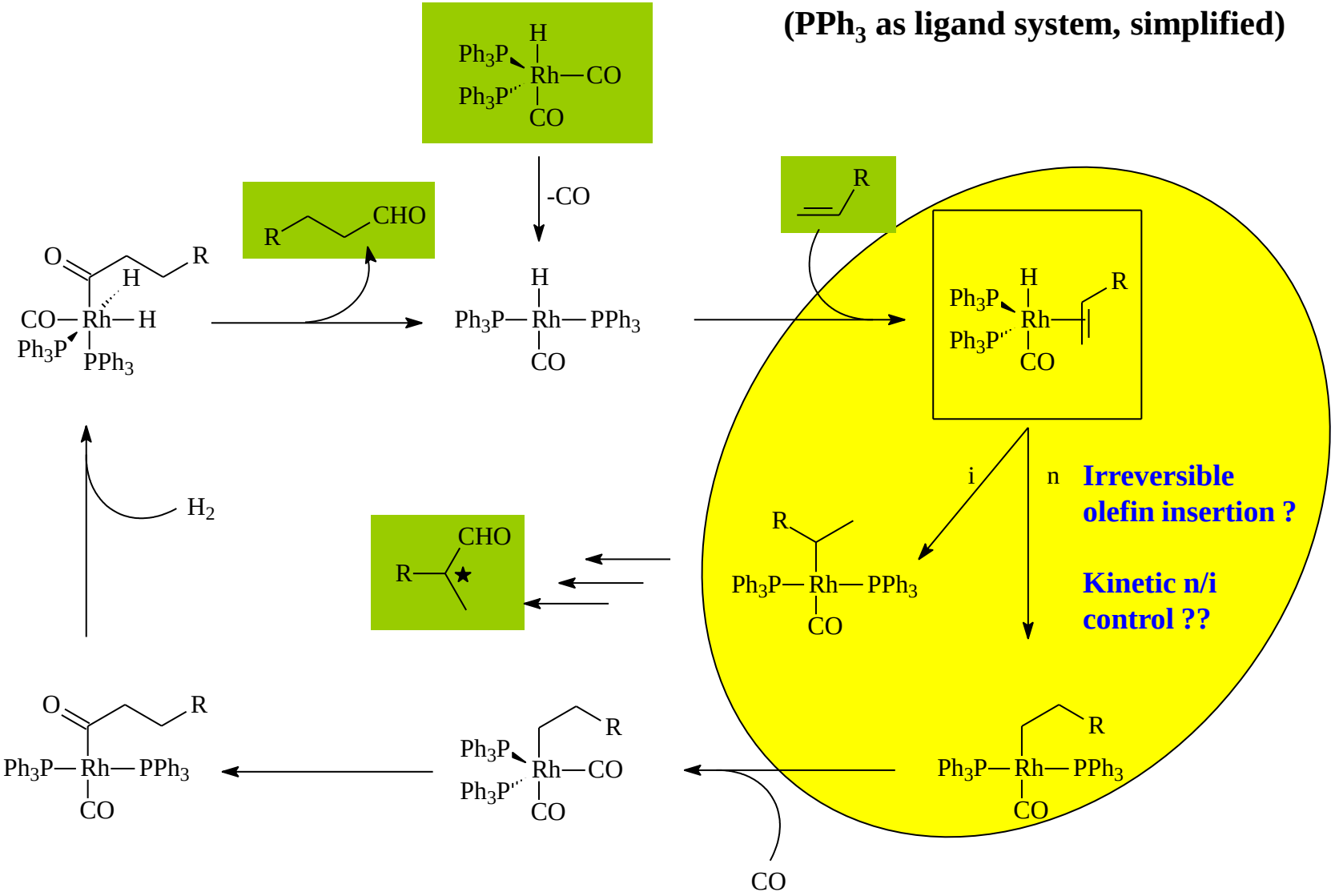
5

	1	1	1	1		2	2	2	2		PPh3 1:20	PPh3 1:20	PPh3 1:20	PPh3 1:20		4	4	4	4		5	5	5	5
n / i	143,1	156,4	149,6	147,5		119,1	119,1	114,1	117,8		2,8	2,7	2,7	2,8		53,4	54,3	53,7	54,1		46,5	50,8	49,2	47,3
yield [%]	92,4	93,3	92,9	93,3		70,9	73,6	72,5	72,1		96,5	96,7	96,6	96,8		79,2	78,3	78,6	79,7		55,1	60,0	57,7	60,9

Activity and Selectivity

Mechanistic Scenario

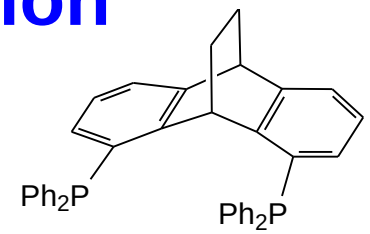
(PPh_3 as ligand system, simplified)



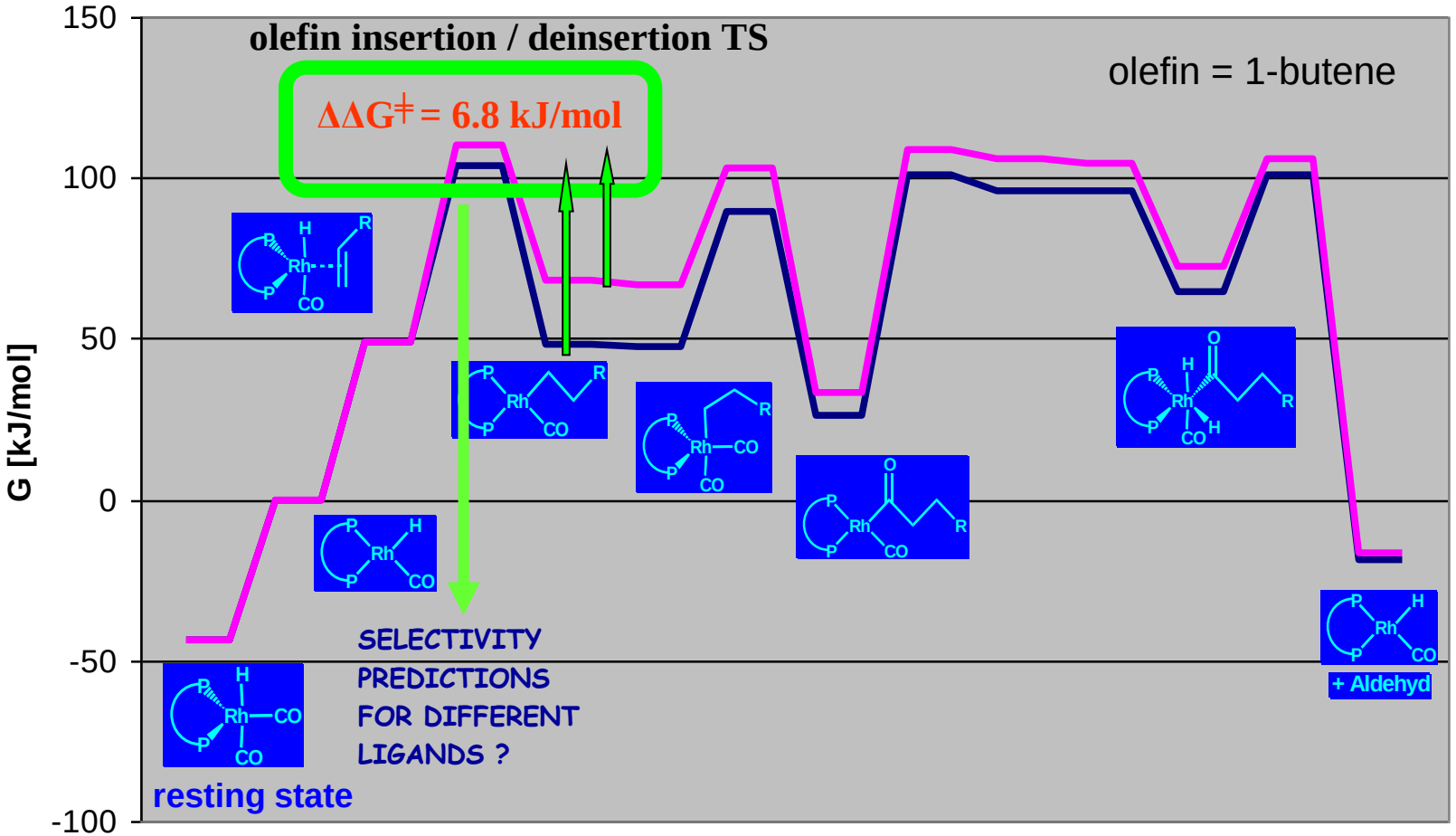
G. Wilkinson, J. D. Evans, J. A. Osborn, *J. Chem. Soc. A*, **1968**, 3133

C. P. Casey, L. M. Petrovich,
J. Am. Chem. Soc., **1995**, *117*, 6007;
S. C. v. d. Slot et al., *Organometallics*, **2001**, *20*, 430

DFT: n- vs. i-Aldehyde Formation



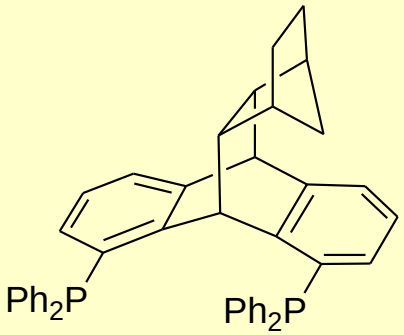
G (100°C,10bar) for n- und i- reaction path



Optimization and molecular vibrations: BP86/SV(P); single point energies: B3LYP/TZVP

P. Deglmann

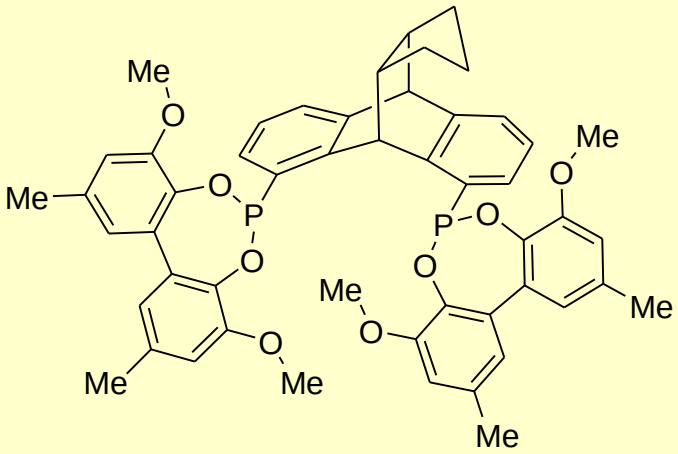
Syngas D_2 / CO: Deuterioformylation – Ligand Set Tested:



Bisphosphane

D. Warth

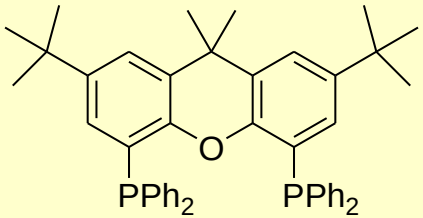
***n*/*i* = 53, TOF = 2239**



Bisphosphonite

T. Kaiser

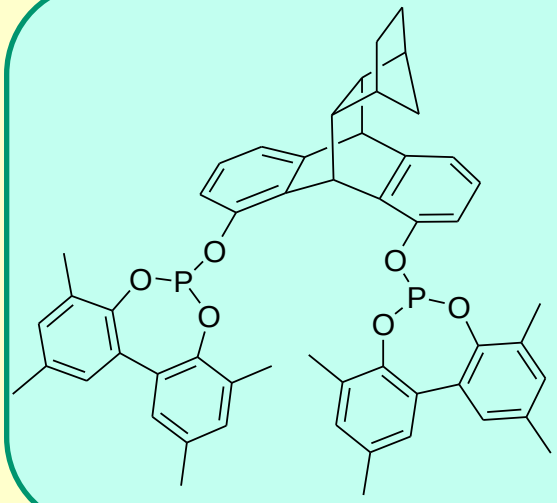
***n*/*i* = 5.5, TOF = 2940**



DitBuXantphos

van Leeuwen

***n*/*i* = 48.6, TOF = 645**



Bisphosphite

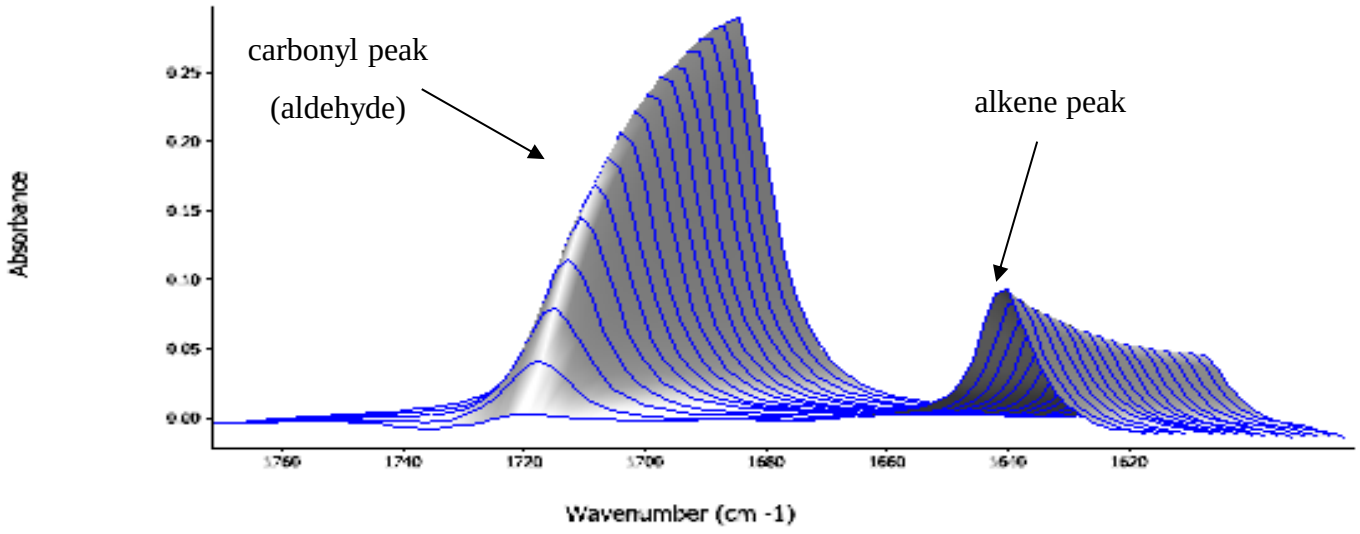
T. Rosendahl

***n*/*i* = 141.5, TOF = 2932**

R. Tompers

Deuterioformylation of 1-hexene – experimental

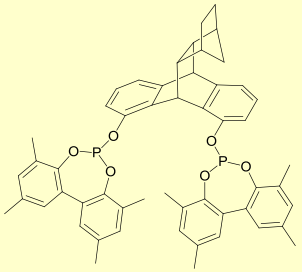
- **Preformation for 2h at 60°C and 7 bar D_2/CO (1:1)**
- **Deuterioformylation with Rh:L = 1:2.5 , Rh:hexene = 1:4000, 60°C, 7 bar D_2/CO (1:1)**
- **Reaction control by *in-situ* IR-spectroscopy**
- **50% Conversion**
- **Distillation of the reaction mixture → hexene, toluene and aldehyde fraction**
- **Quantitative determination of 1-D-hexene, 2-D-hexene as well as α- and β -deuterated heptanals by ^{2}H-NMR**



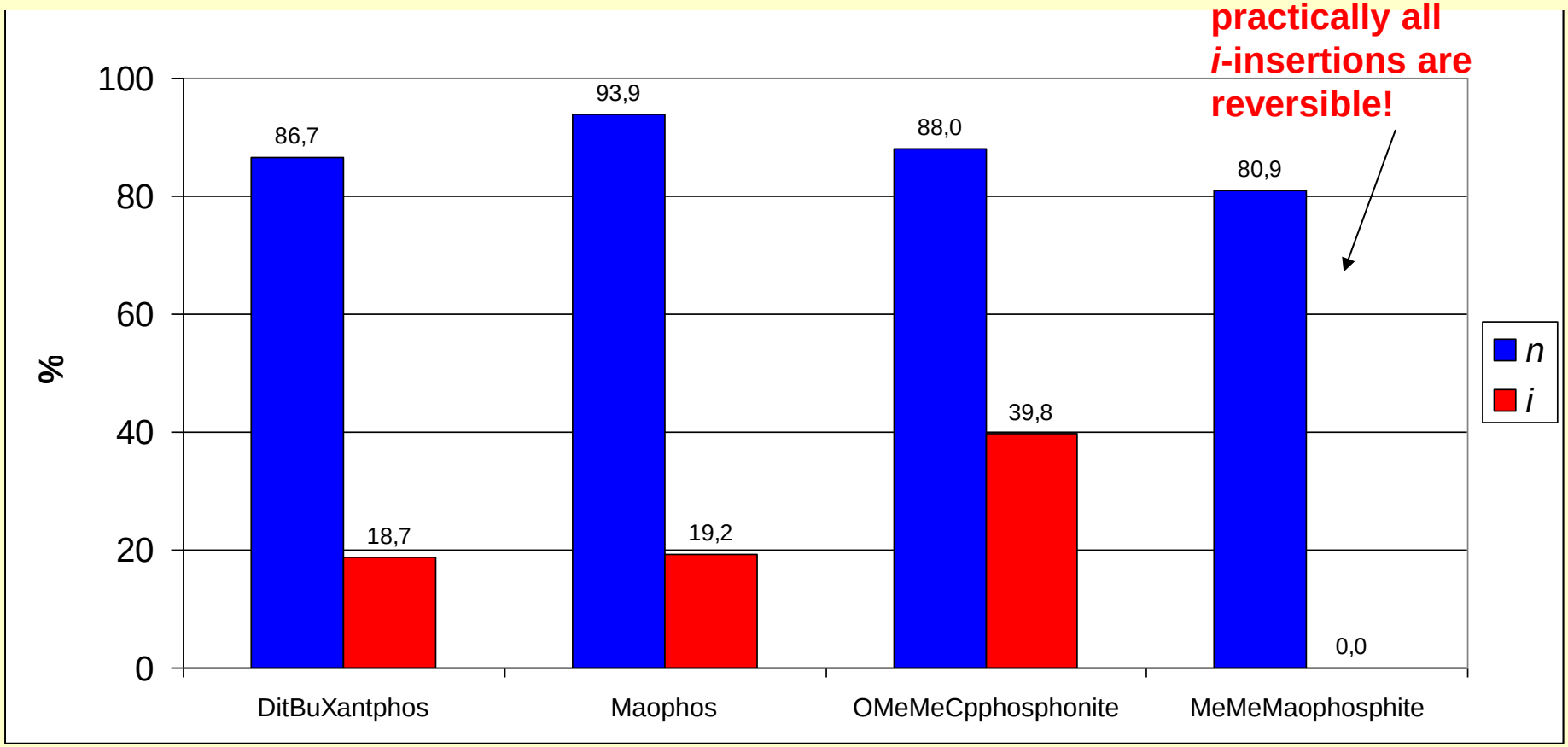
R. Tompers

Deuterioformylation – Results

% irreversible ***n***- and ***i***-insertions

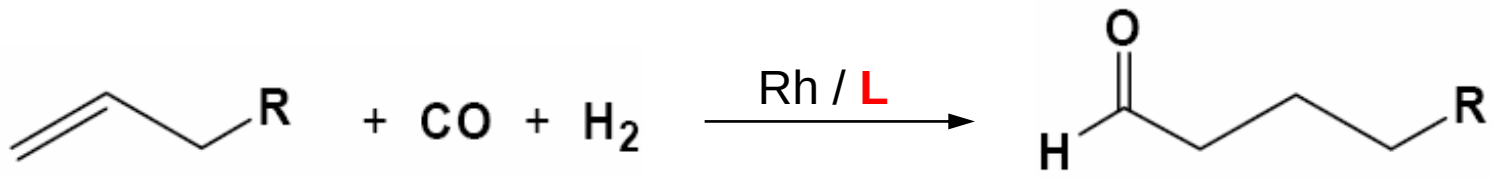


practically all *i*-insertions are reversible!



***n*-selectivity determined by different degrees of reversibility for *n* - and *i* – olefin insertion !**

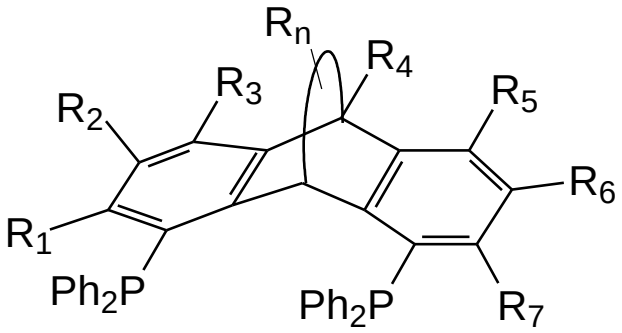
Ligand design for highly *n*-selective and highly active low pressure, low temperature Rh-hydroformylation catalysis of terminal alkenes successfully achieved.



1-alkenes

n-aldehydes

L =



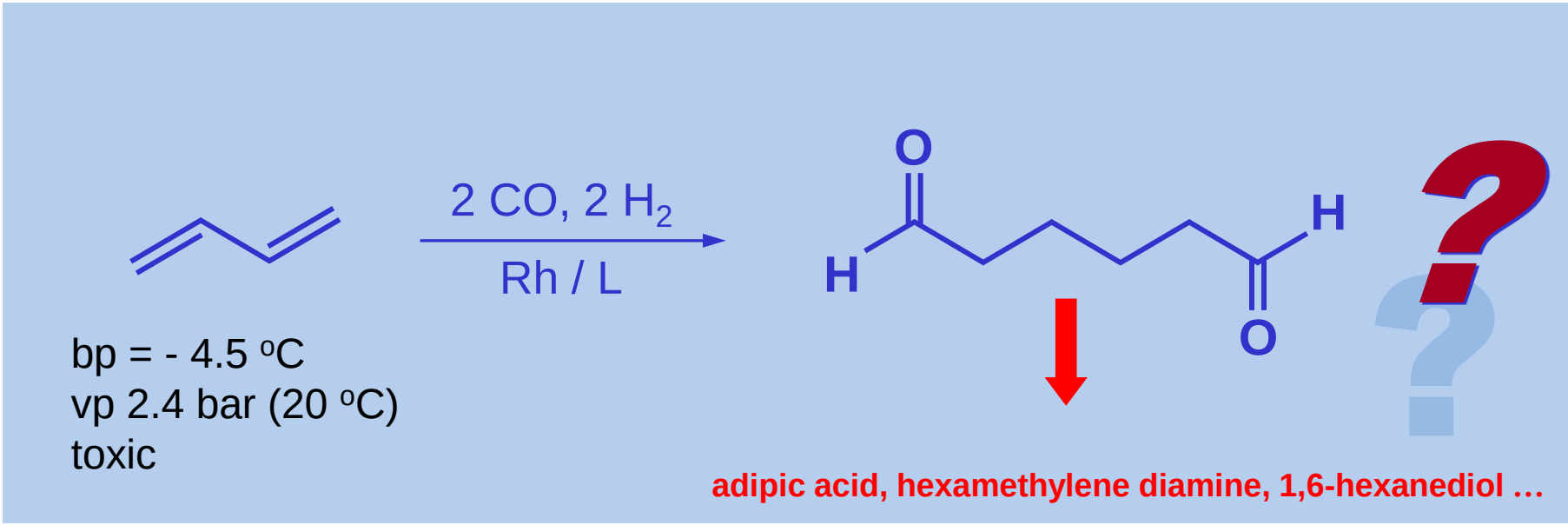
= bridge

Members of the triptyphos ligand family

Further Challenges, Perspectives, Options ?

A „Dream-Reaction“of Oxo-Chemistry

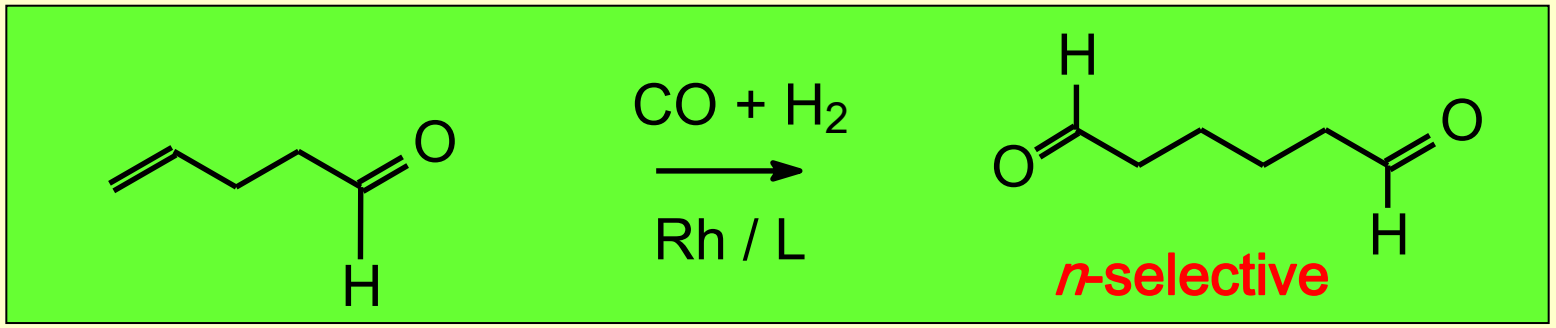
What about Rhodium-Catalyzed Direct Bis-Hydroformylation of 1,3-Butadiene (Steam Cracker Product) to Adipic Aldehyde?



Many unsuccessful (mostly industrial) research efforts since around 1950

„The direct hydroformylation of butadiene to adipic aldehyde is probably the most difficult case with a.o. low reactivity and selectivity“ [P. Arnoldy, Shell Research, cited from van Leeuwen & Claver (Ed.) *Rh-Catalyzed Hydroformylation*, Kluwer, 2000, p.227]

Starting point: **selective *n*-hydroformylation of 4-pentenal, the mono-*n*-hydroformylation product of butadiene, works**

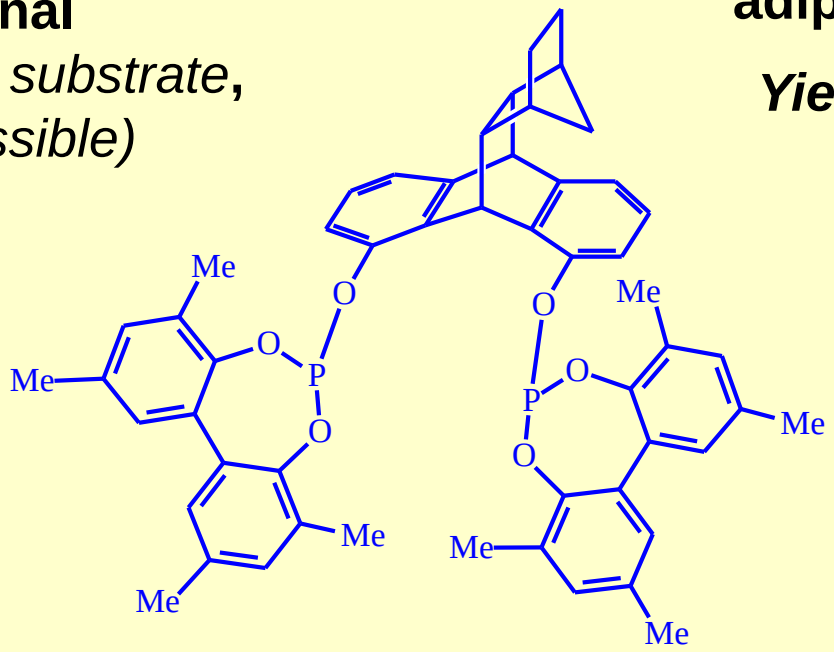


4-pentenal
(itself attractive substrate, easily acessible)

adipic aldehyde

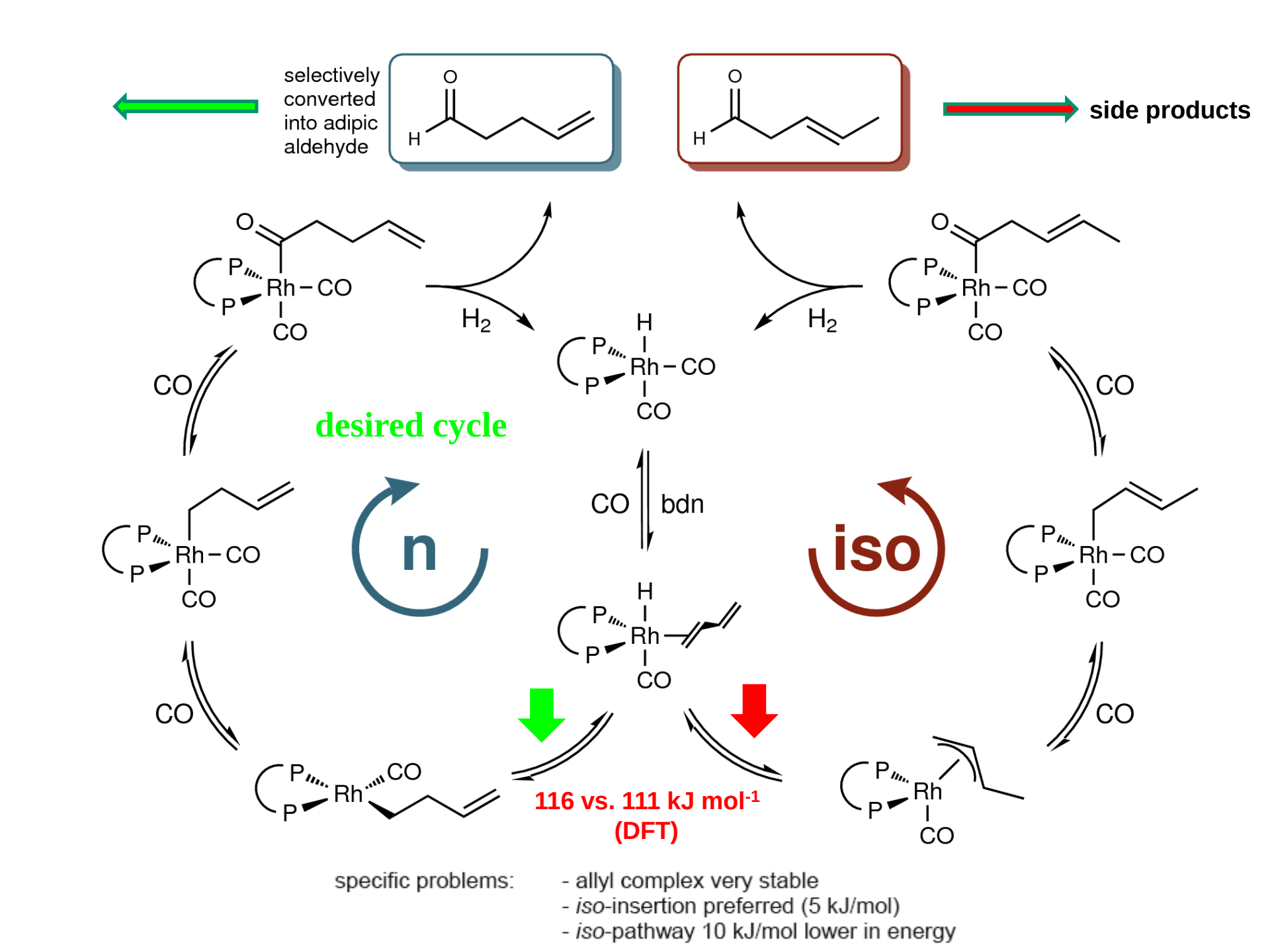
Yield over 95%

L =

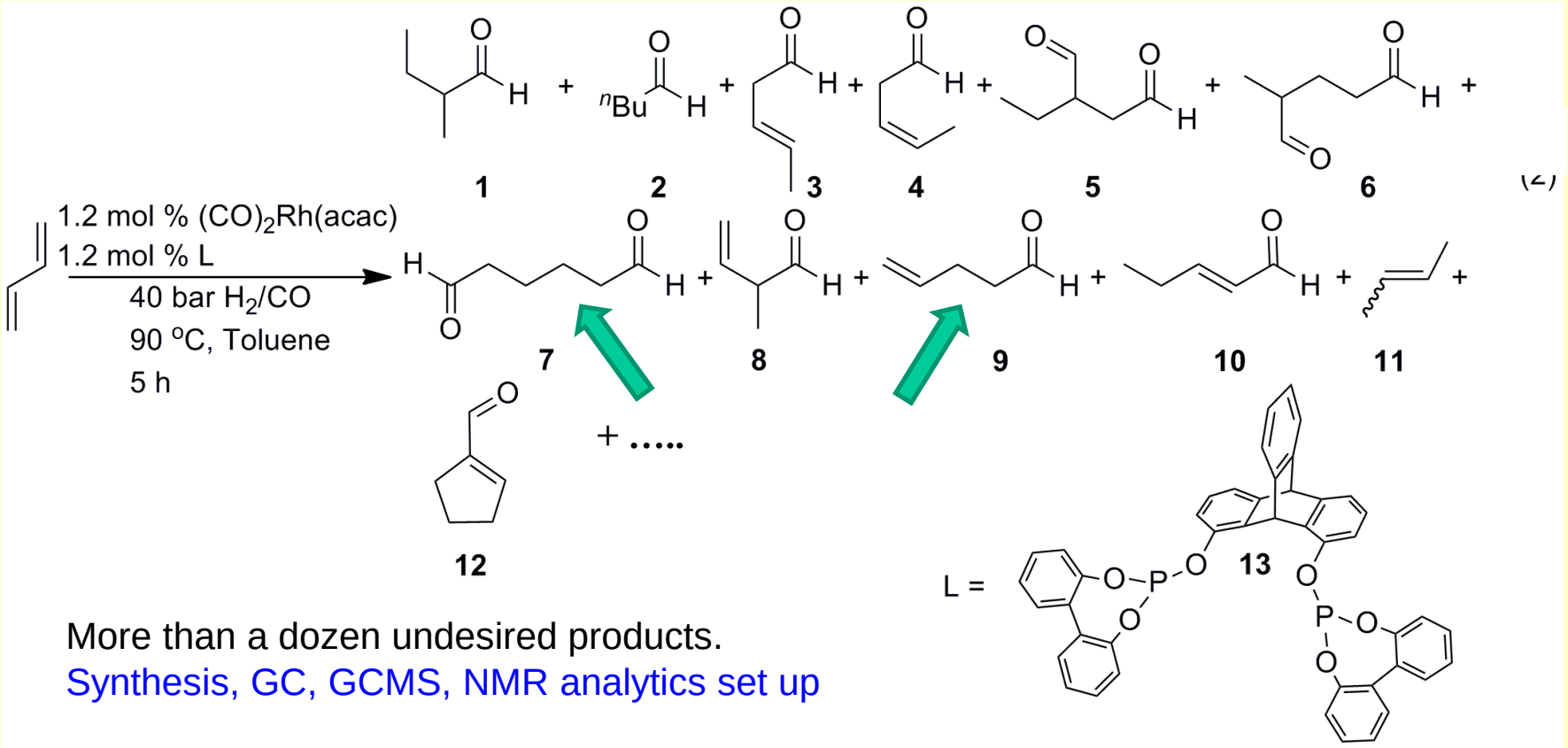


T. Rosendahl

Regioselectivity of first hydroformylation step of butadiene to 4-pentenal is crucial


selectively converted into adipic aldehyde
side products
desired cycle
n
iso
CO
bdn
H2
116 vs. 111 kJ mol-1
(DFT)
specific problems:
- allyl complex very stable
- iso-insertion preferred (5 kJ/mol)
- iso-pathway 10 kJ/mol lower in energy

Product Manifold of Butadiene Hydroformylation from Literature and from Our Own Test Reactions

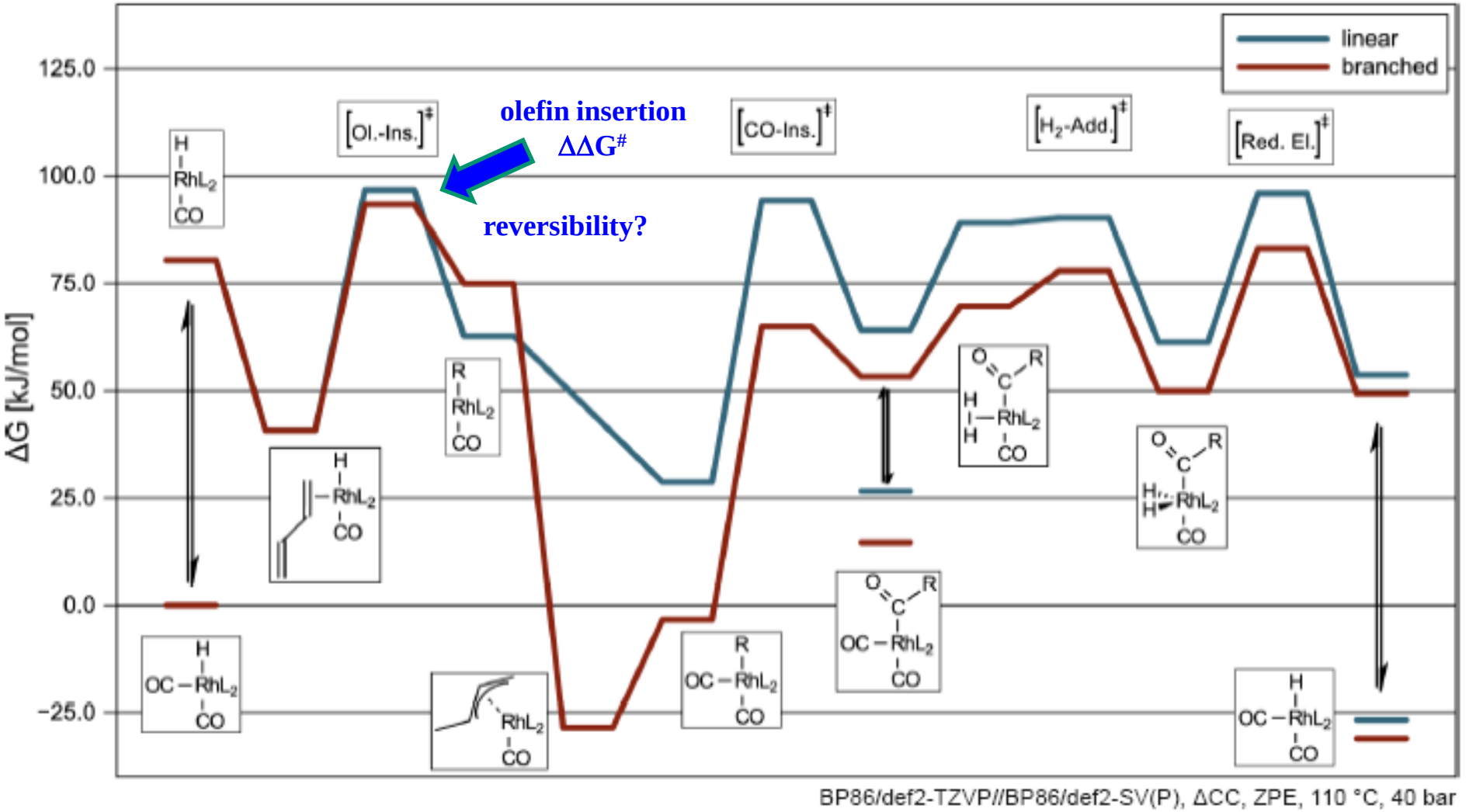


More than a dozen undesired products.
Synthesis, GC, GCMS, NMR analytics set up

Stuart Smith (CaRLa)

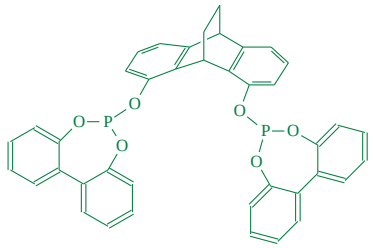
S. E. Smith, T. Rosendahl, P. Hofmann, *Organometallics*, **2011**, *30*, 3643

Catalytic Cycle: 1st Hydroformylation Step, DFT



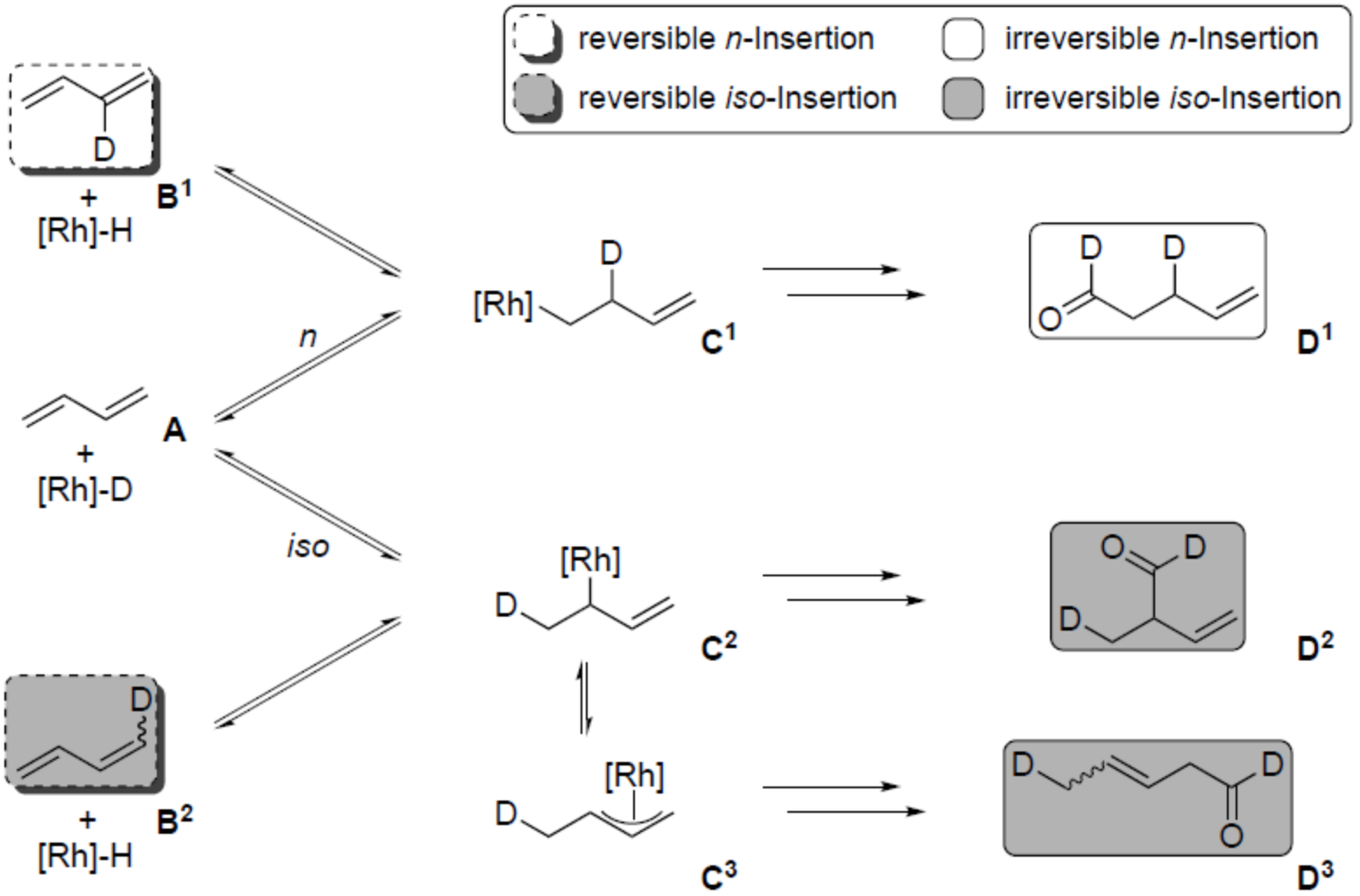
rate determining step?

L_2 =



Sebastian Schmidt

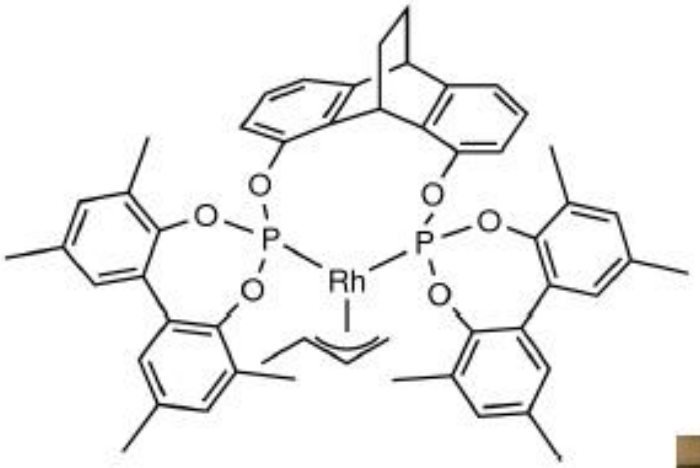
Deuteroformylation Experiment: Insertion Reversibility Found



Sebastian Schmidt

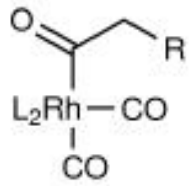
In situ Spectroscopy: IR, NMR

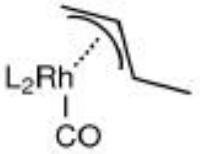
Directly Observable:

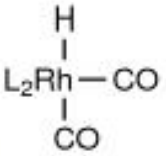


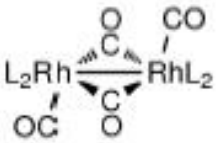
1.) CO
2.) H_2

toluene
60 °C



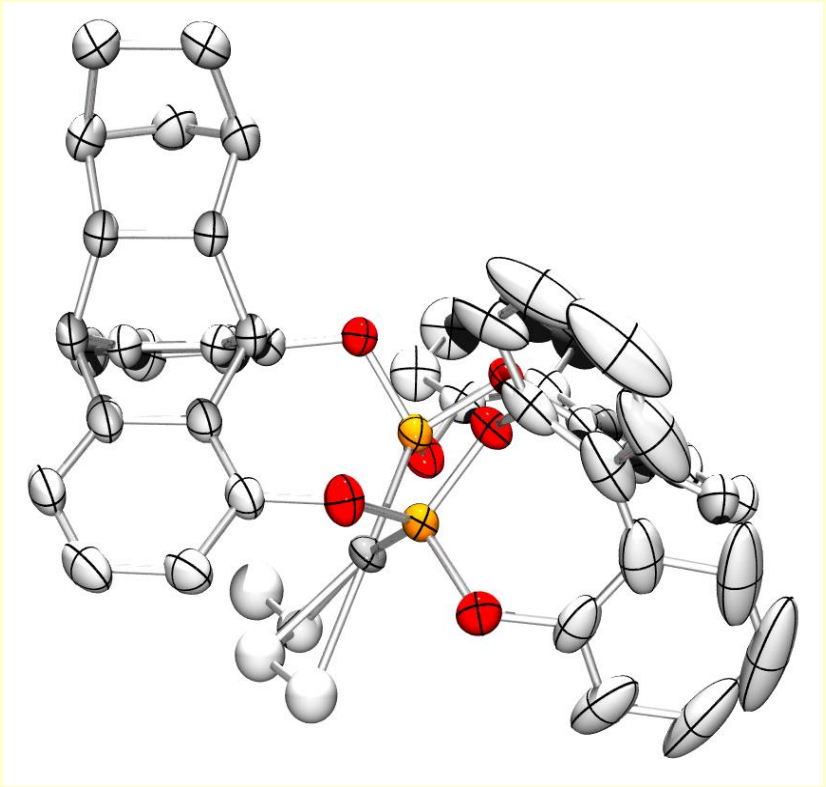


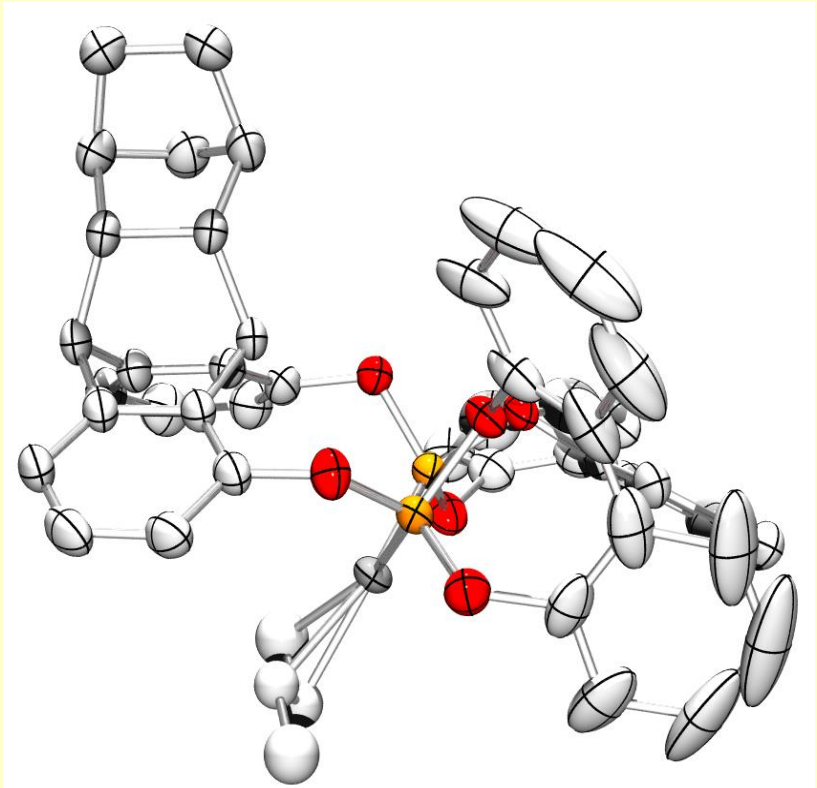


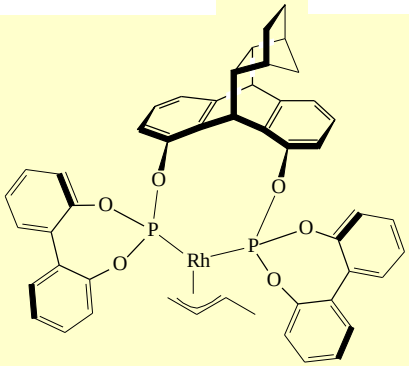


S. Schmidt

Synthesis & X-Ray Structure of (L)Rh-η^3-Methallyl Complexes

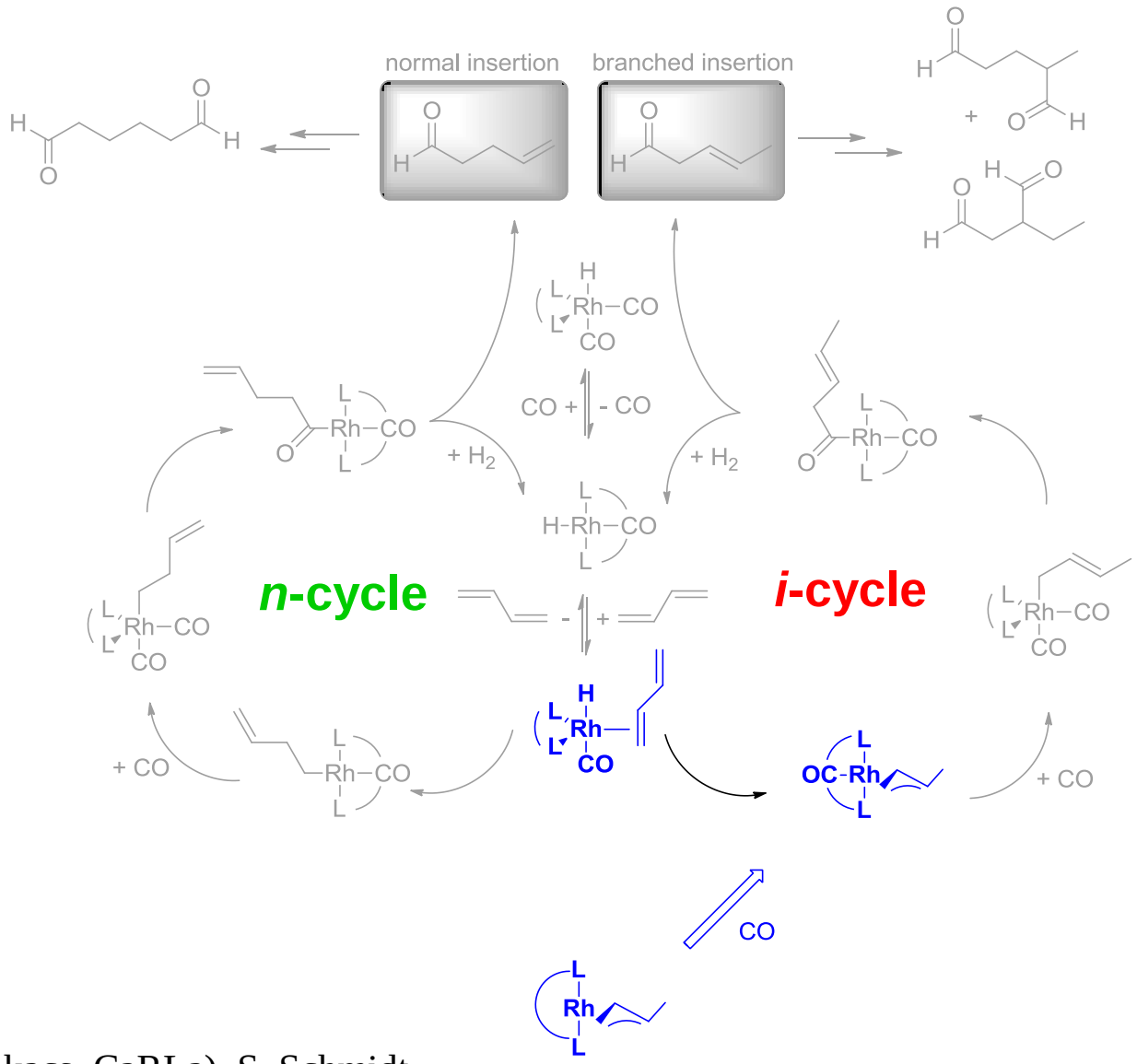






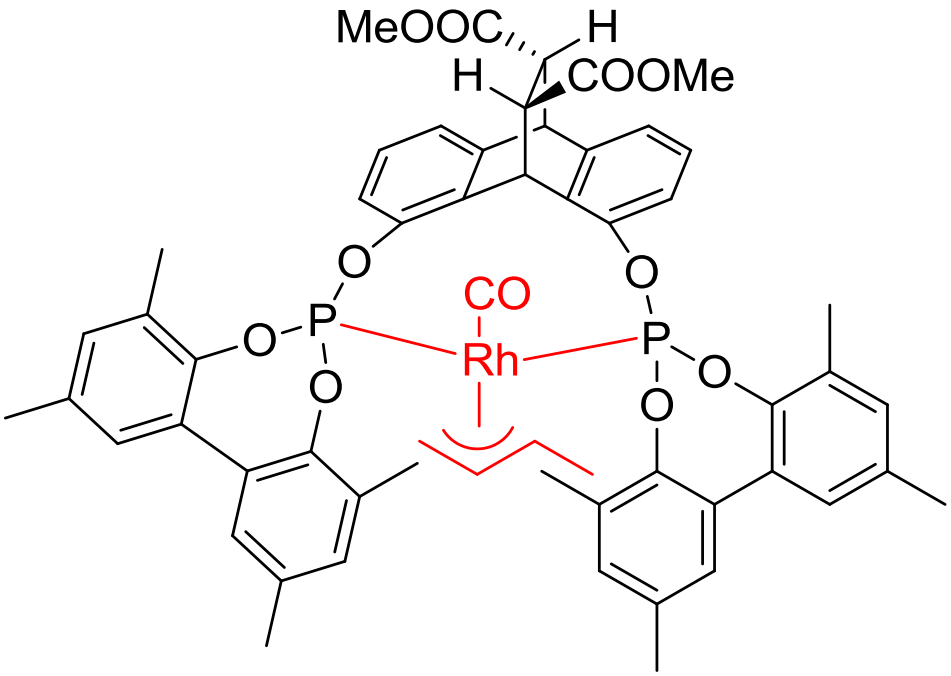
T. Rosendahl

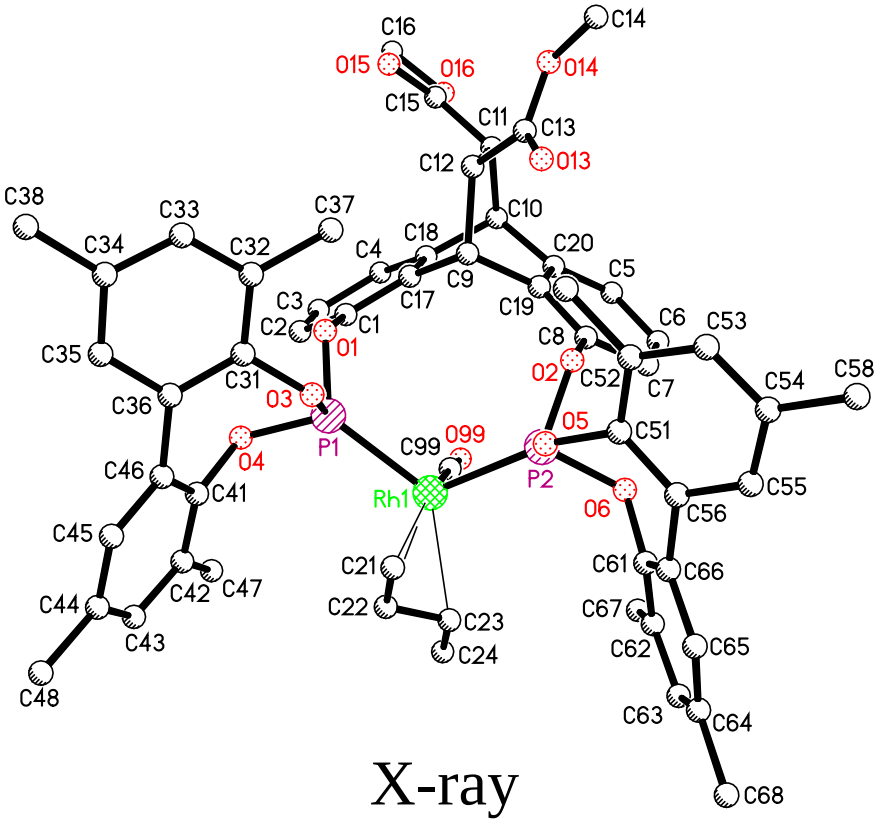
Synthesis of a (L)Rh(η^3-methallyl)(CO) Complex



E. Barath (née Takacs, CaRLa), S. Schmidt

Structure of a Rh(η³-methallyl)(CO) - Complex

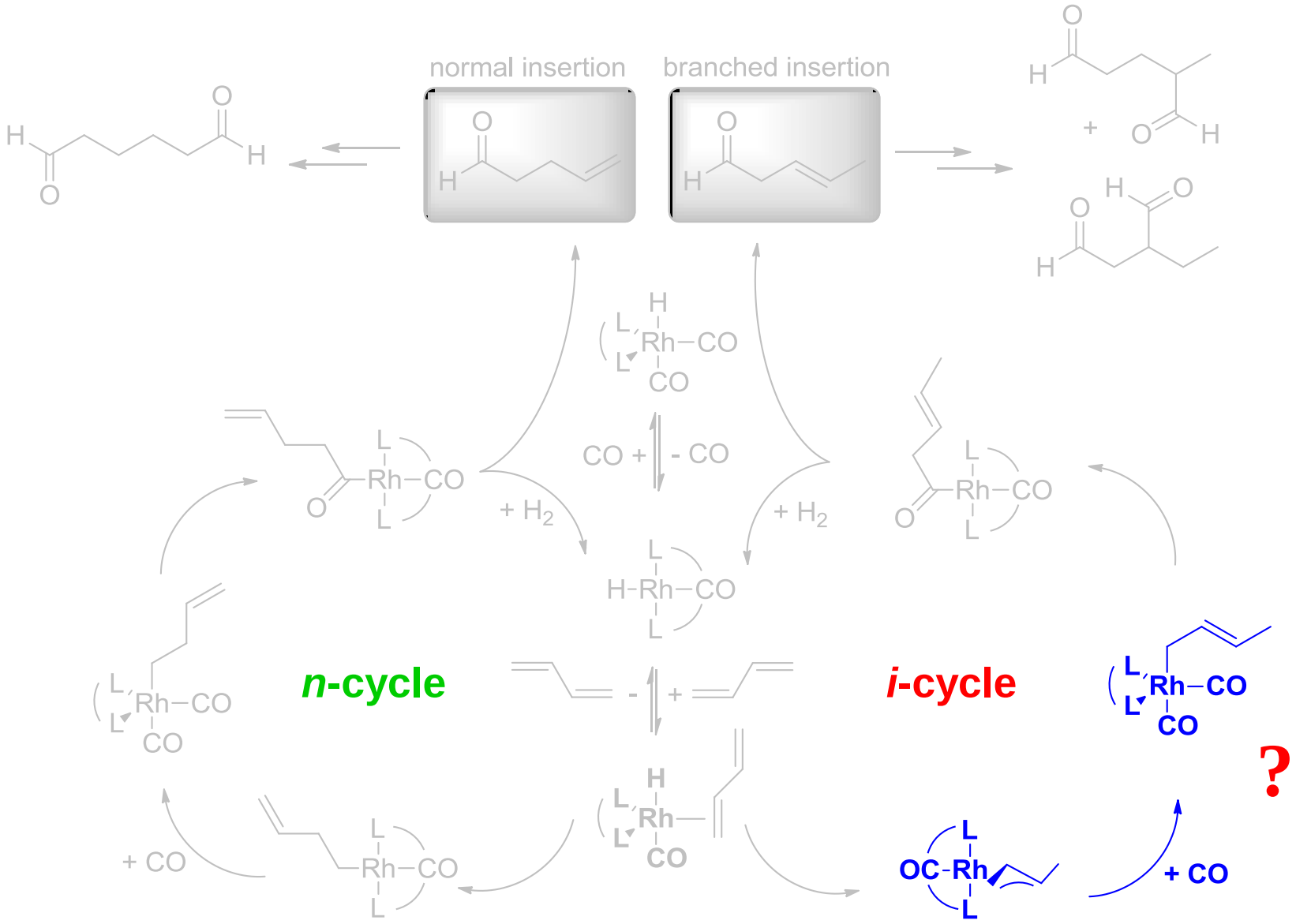




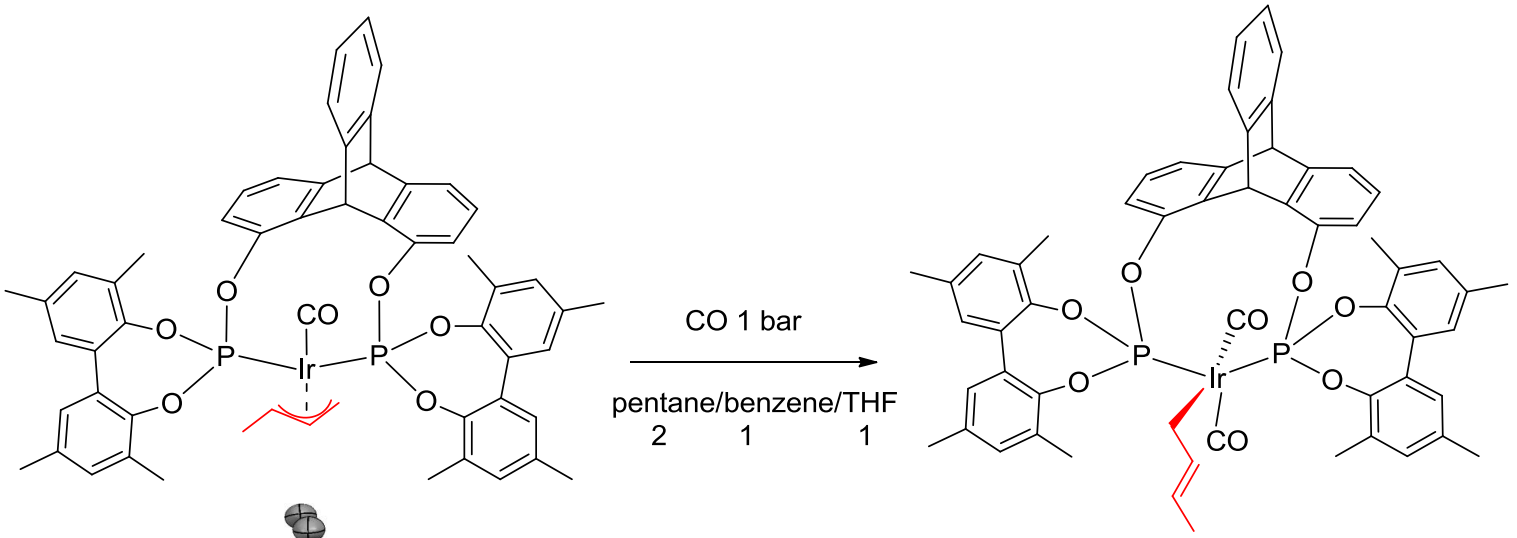
X-ray

Eszter Baráth (née Takács, CaRLa), Sebastian Schmidt

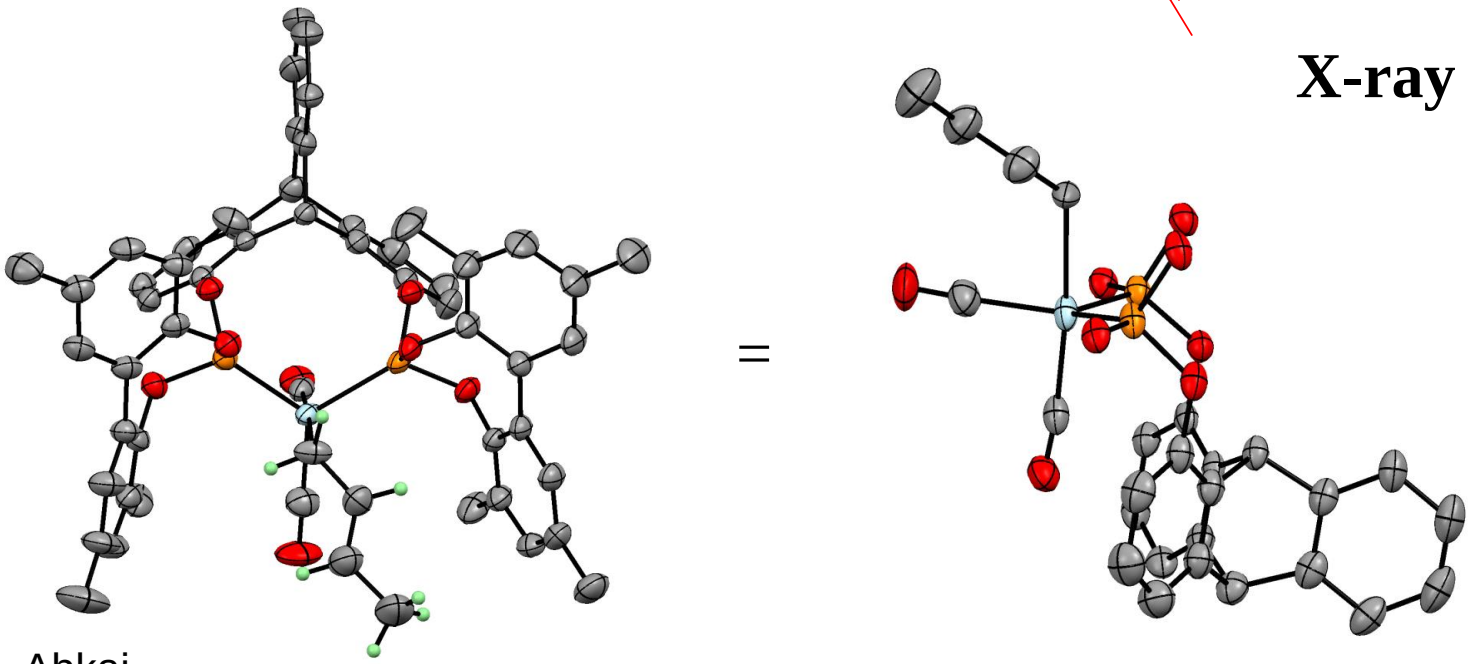
(L)Rh(η³-methallyl)(CO) to (L)Rh(η¹-2-butenyl) Conversion by CO Addition?



Iridium Model Chemistry:
(L)Ir(η³-methallyl)(CO) to (L)Ir(η¹-2-butenyl) Conversion by CO Addition



X-ray

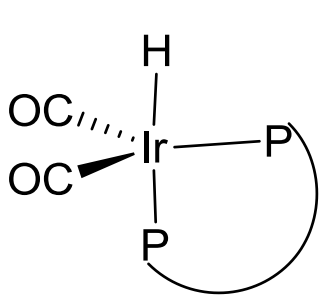


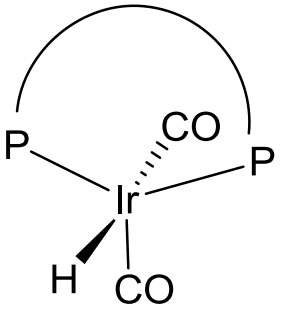
=

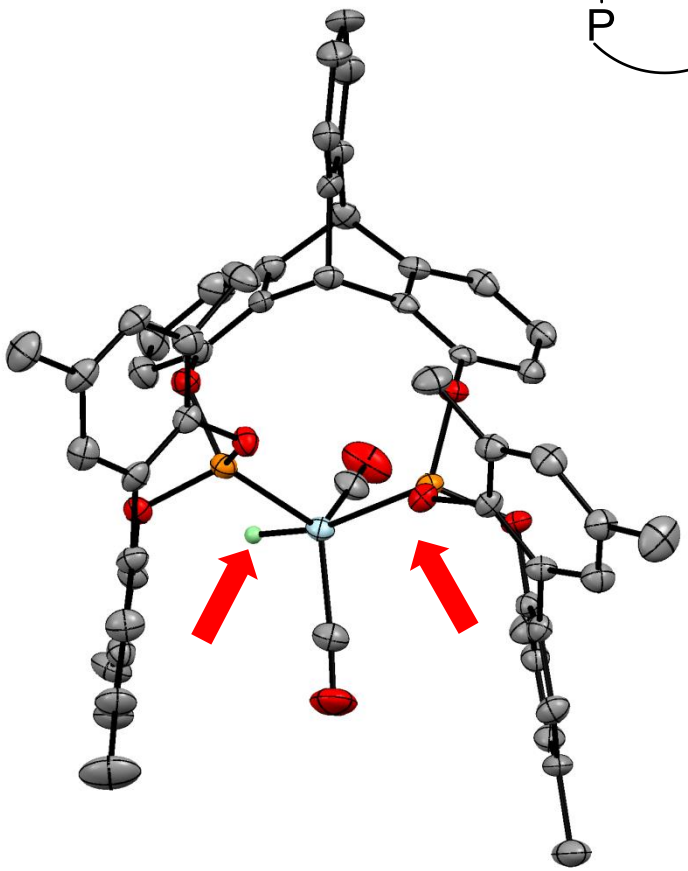
G. Abkai

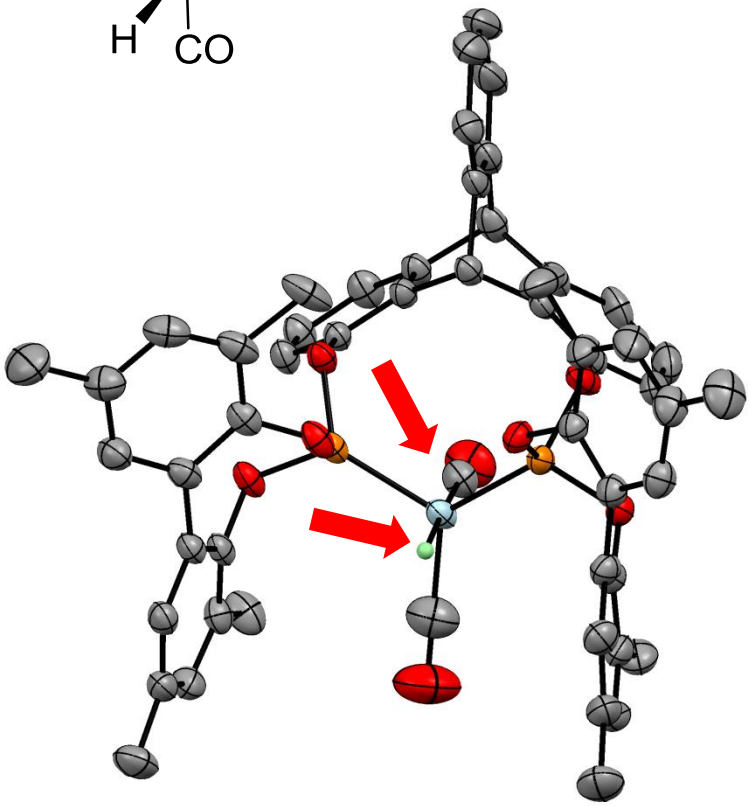
Iridium Model Chemistry: Rh Resting State Analog

Both Stereoisomers (e,a and e,e) Isolated, Characterized by X-Ray, Rapid Interconversion (NMR)





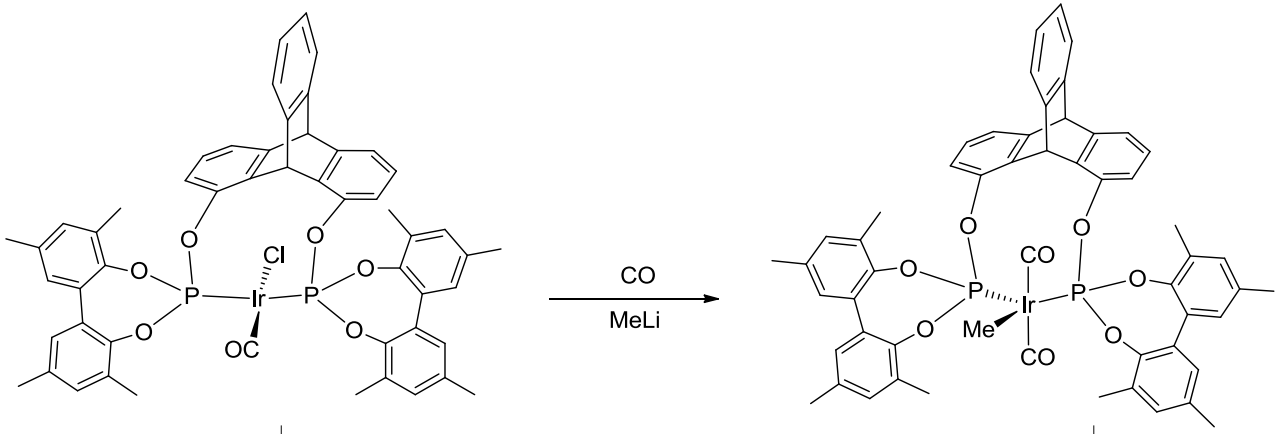




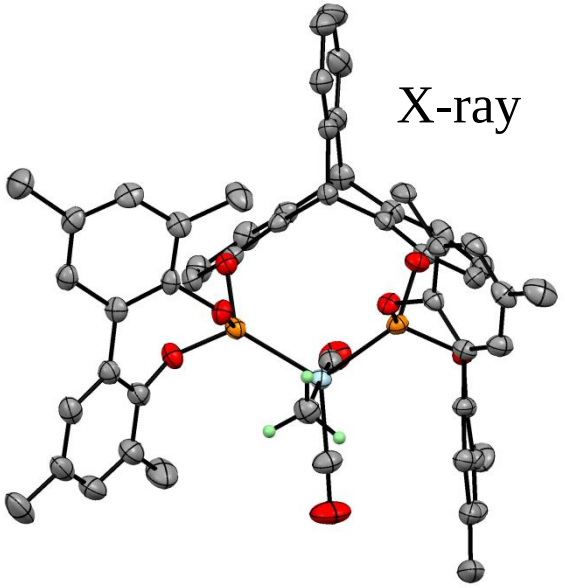
G. Abkai, S.Schmidt

Iridium Model Chemistry:

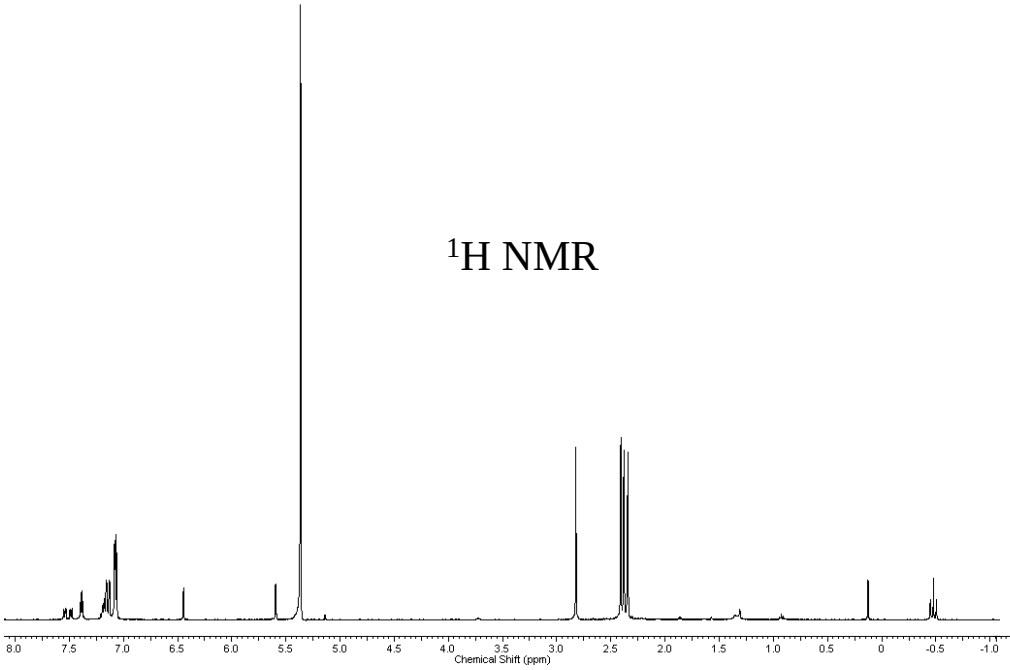
Dicarbonyl Alkyl Iridium Complexes $(L)Ir(CO)_2(R)$, R = Me



X-ray



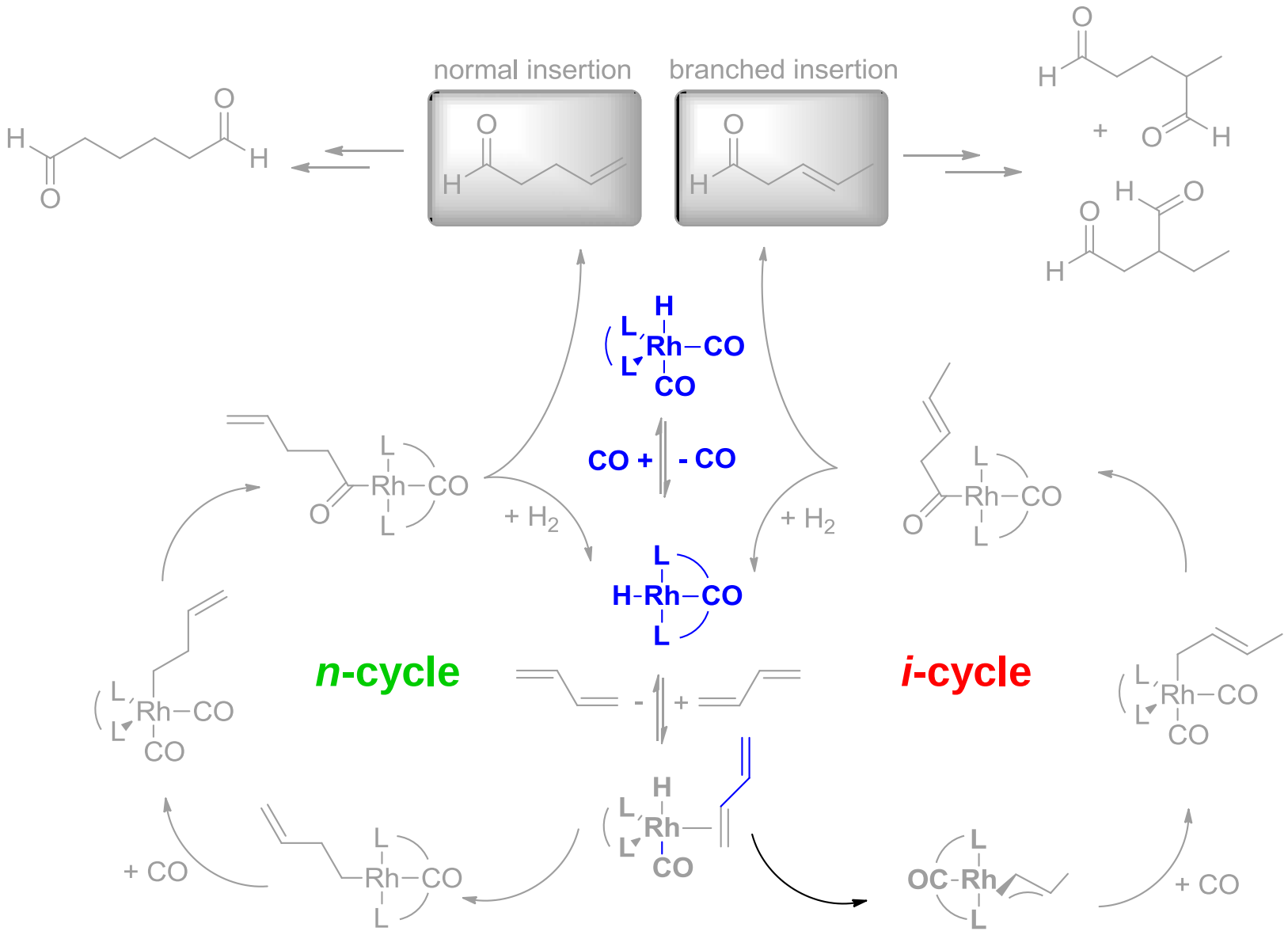
^{1}H NMR



^{31}P NMR

G. Abkai

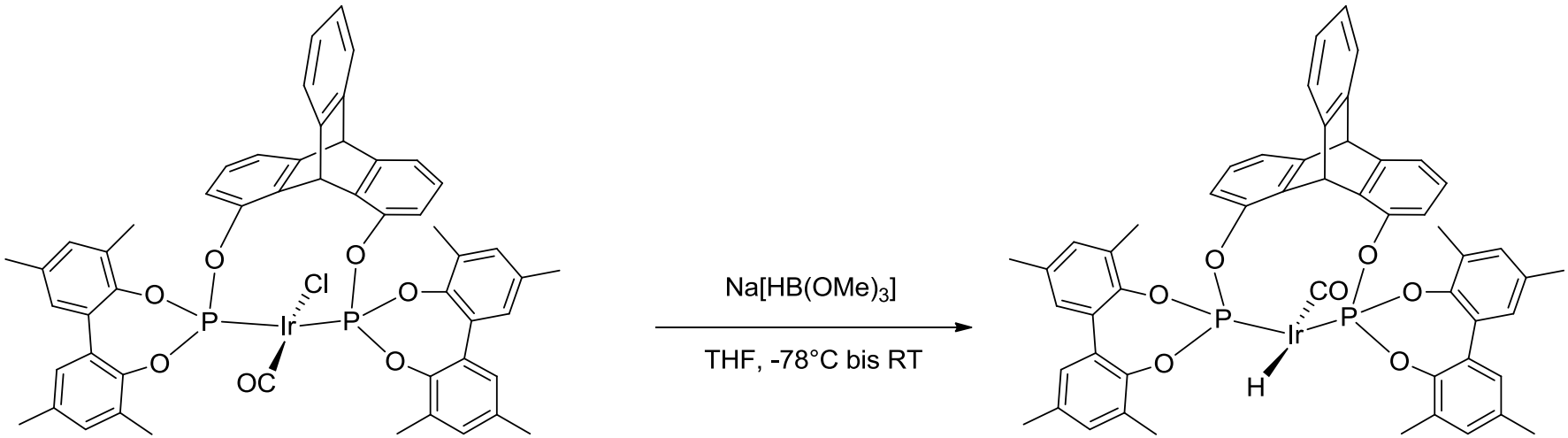
Four-Coordinate 16 VE (L)Rh(CO)H: The Active Species

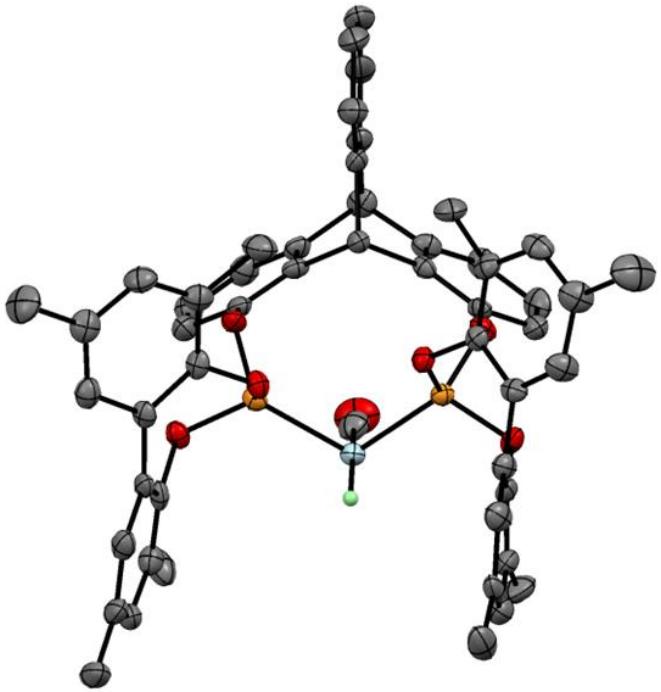


Eszter Baráth (née Takács, CaRLa), Sebastian Schmidt

Iridium Model Chemistry:

Structure of 16 VE (L)Ir(CO)H Analog of Active Rh Species



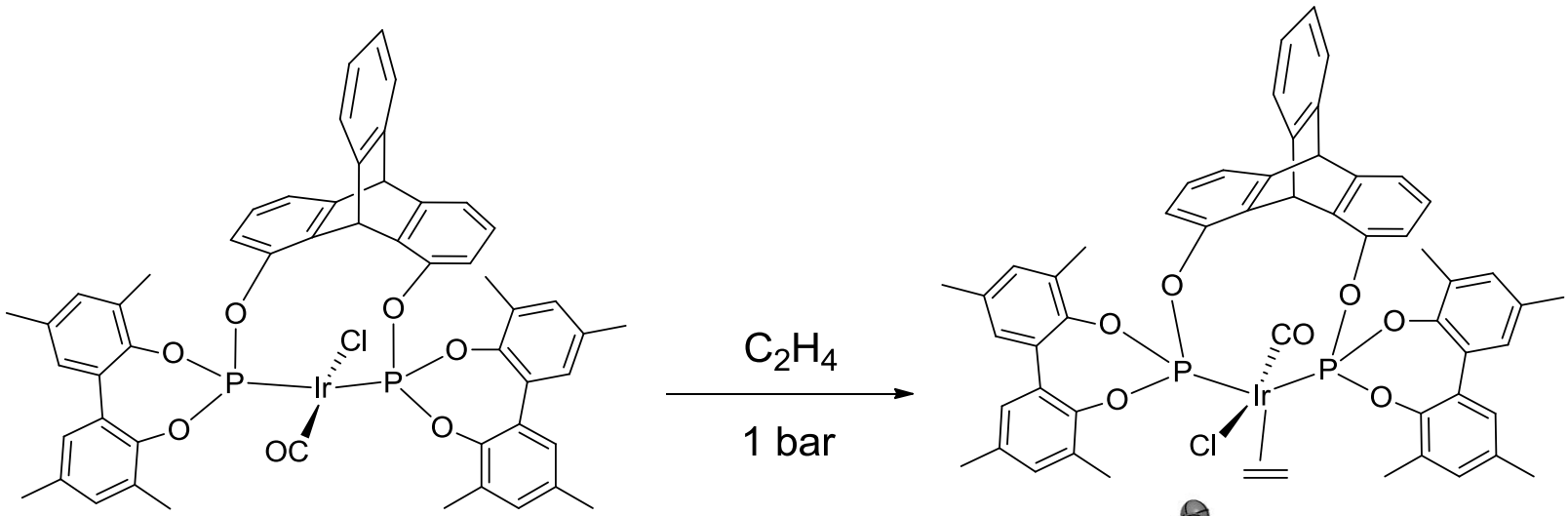


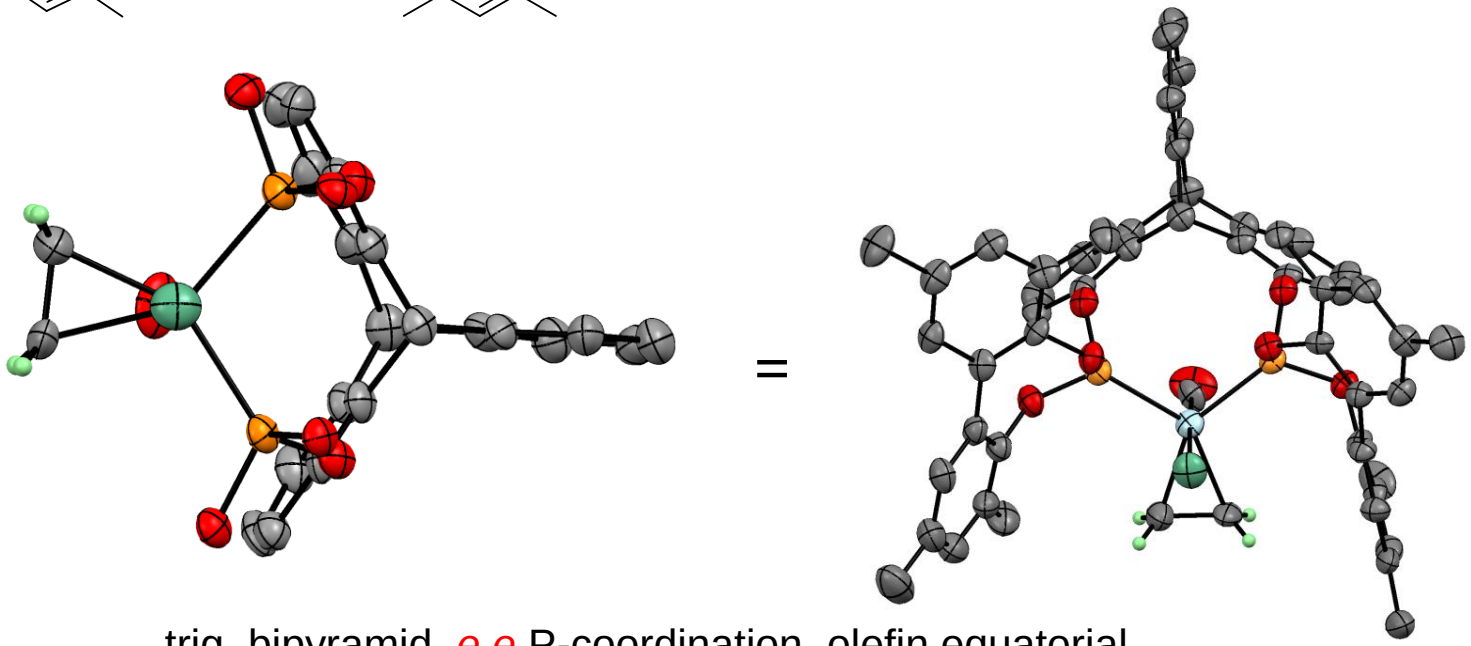
X-Ray

G. Abkai

Iridium Model Chemistry:

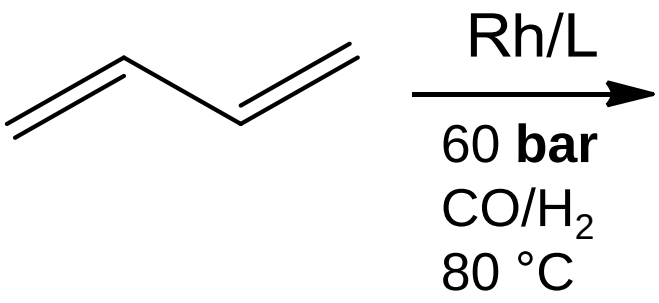
Olefin Coordination of Ethylene (and Other Alkenes, not of Butadiene)





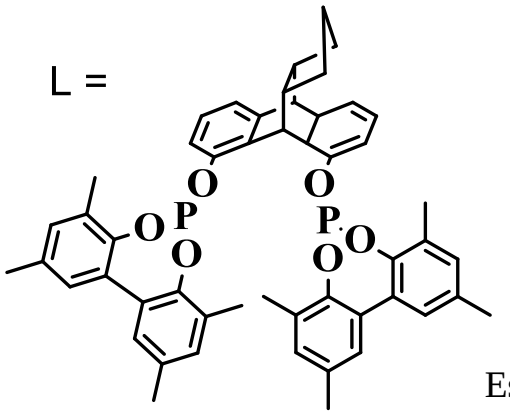
trig. bipyramid, *e,e* P-coordination, olefin equatorial

G. Abkai



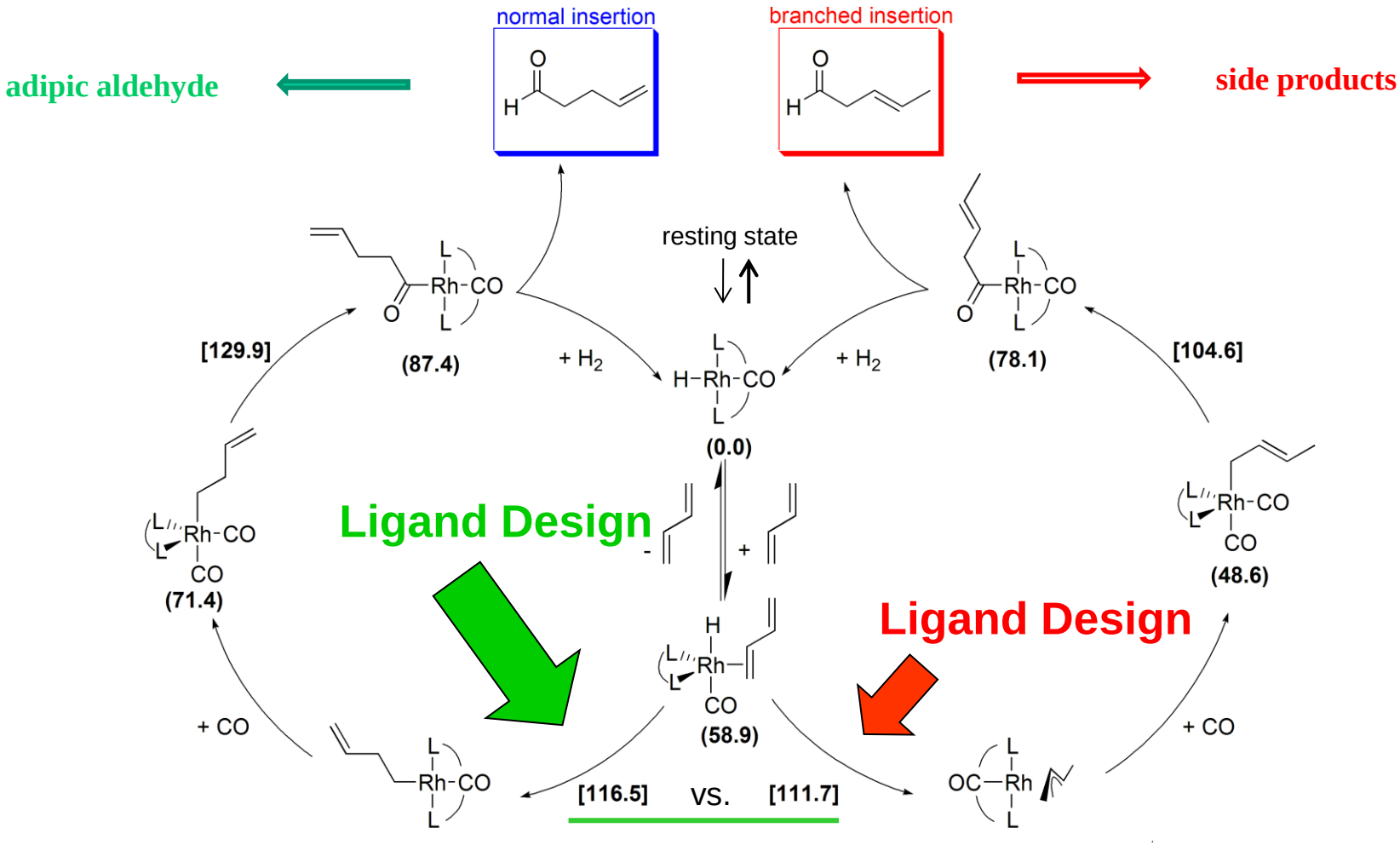
20,9 % 16,8 % 55,5 % 3,7 %

together: 96,9 % aldehyde selectivity



Present status:
close to 60% of desired *n*-insertion for 1st hydroformylation step !

Eszter Baráth (née Takács, CaRLa), Sebastian Schmidt



Strategy: Quantum Chemistry and Experiment
Joint Academia – Industry Research
CaRLa as a Role Model Lab

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