



Progress beyond



Exploring the Impact of Ligand and Catalyst Selection on Petrochemical Applications

Strem Chemicals, Inc.

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Overview



- Solvay Phosphorus Specialties - Strem Chemicals Inc. Partnership
- Chemistry for the Manufacture of Phosphine Ligands
- Applications in Petrochemicals
- Developing Unique Solutions
- Summary and Questions

****Solvay partners with Strem Chemicals for sample distribution***



Strem Chemicals, Inc.

Solvay partners with Strem Chemicals for multi-kilo sample distribution!



Corporate Headquarters
Newburyport, MA USA

European Headquarters
Strasbourg, France

- Established in 1964
- More than 55 years of experience in manufacturing and handling high-quality inorganics and organometallics
- 5,000+ specialty chemicals available
- Laboratory Chemicals for R&D
- cGMP Products Manufactured in Kilo-lab Suites
- High Pressure Materials
- Custom Synthesis Projects
- Customers include:
 - Academic, industrial and government R&D laboratories
 - Commercial scale businesses in the pharmaceutical, microelectronics, chemical & petrochemical industries



Phosphorus Specialties



Solvay:

A Global Leader in Phosphorus Chemistry



Differentiated products and technologies

We offer a wide range of phosphorus-based chemistry to meet precise application requirements



Partnership

We work closely with customers to translate their needs into concrete solutions



Innovation

160 years of know-how and innovation in phosphorus chemistry



Secure and consistent supply source

Stringent quality control standards and timely order fulfillment due to global footprint and supply chain



Scale-up capabilities

From R&D to large scale; largest capacity in the industry

2030 Solvay One Planet Goals

10 ambitious objectives



CLIMATE

Fight against climate crisis



Align **greenhouse gas emissions** with Paris Agreement



Reduce by 26% (-2%/y)

Phase out coal



Achieve 100%

Reduce negative pressure on biodiversity



30% reduction

RESOURCES

Embed circular business



Increase Sustainable Solutions revenues



Achieve 65% vs 50%

Increase circularity



Achieve 15% vs 7%

Reduce non-recoverable industrial waste



30% reduction

Reduce intake of freshwater



25% reduction

BETTER LIFE

Improve quality of life



Safety is a priority



Aim for zero accident

Accelerate Inclusion & Diversity



Parity in 2035 vs 24%
for mid & senior management

Extend maternity leave time and open it to co-parents



16 weeks regardless of the gender in 2021

WE PARTNER WITH CUSTOMERS AND COLLABORATE ACROSS THE VALUE CHAIN TO REDUCE GLOBAL IMPACT

The Markets we Serve



Agriculture

ECO₂FUME® | VAPORPH3OS®

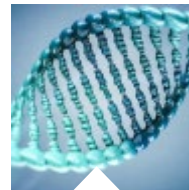
- ✓ Cylinderized phosphine gas fumigants that efficiently eradicate insects at all life stages
- ✓ Used on post-harvest products or storage structures



Textiles

PROBAN® | THPC

- ✓ P-chemistry imparting flame-resistance to textiles & garments
- ✓ THPC for leather treatment applications



Life Sciences

CYTOP® | RhodaPhos®

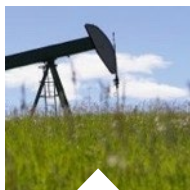
- ✓ Specialty phosphorus compounds for applications requiring stringent purity profiles
- ✓ Catalysis; oligonucleotide synthesis; reagents; intermediates



Electronics

CYPURE® | CYTOP® | CYPHOS® IL

- ✓ High-purity phosphine gases & derivatives used throughout the electronics supply chain
- ✓ Dopants for LED & semi-conductors; capping ligands; solvents; quantum dot materials



Biocides

TTPC | THPS

- ✓ TTPC & THPS for control of microorganisms*
- ✓ Oilfield & industrial wastewater treatment applications



Chemical Processing

CYPHOS® | CYTOP® | RhodaPhos®

- ✓ Phosphine derivatives used in the manufacture of chemical compounds
- ✓ Organic extraction, catalysis, ligands and additives



Plastics, Epoxy & Coating

CYPHOS® | AMGARD® | Albritect®

- ✓ Phosphorus additives optimizing the performance of plastics, epoxy, and coating systems
- ✓ Epoxy resin curing; flame retardant polymers; surface coating treatment; catalysts

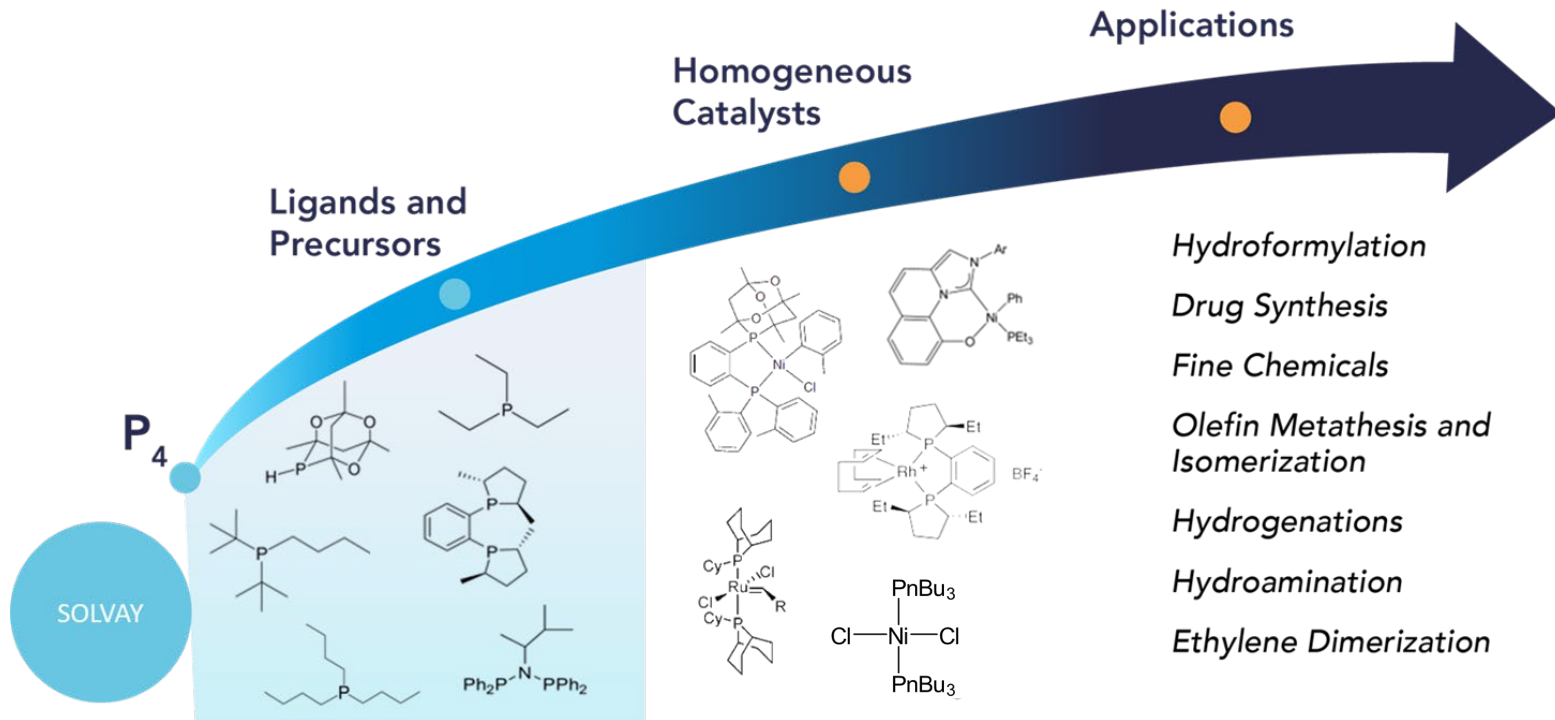


Other

Phos Acid | CYTOP® | CYPHOS® IL

- ✓ Phosphorus-based chemistries for commodity and niche applications
- ✓ Metal extraction & recycling; liquid extractions; ionic liquids; fertilizer; other applications

Solvay in Phosphorus Catalysis



Solvay is the leader in supplying P-based ligands at industrial scale

Chemistry for the Manufacture of Phosphine Ligands



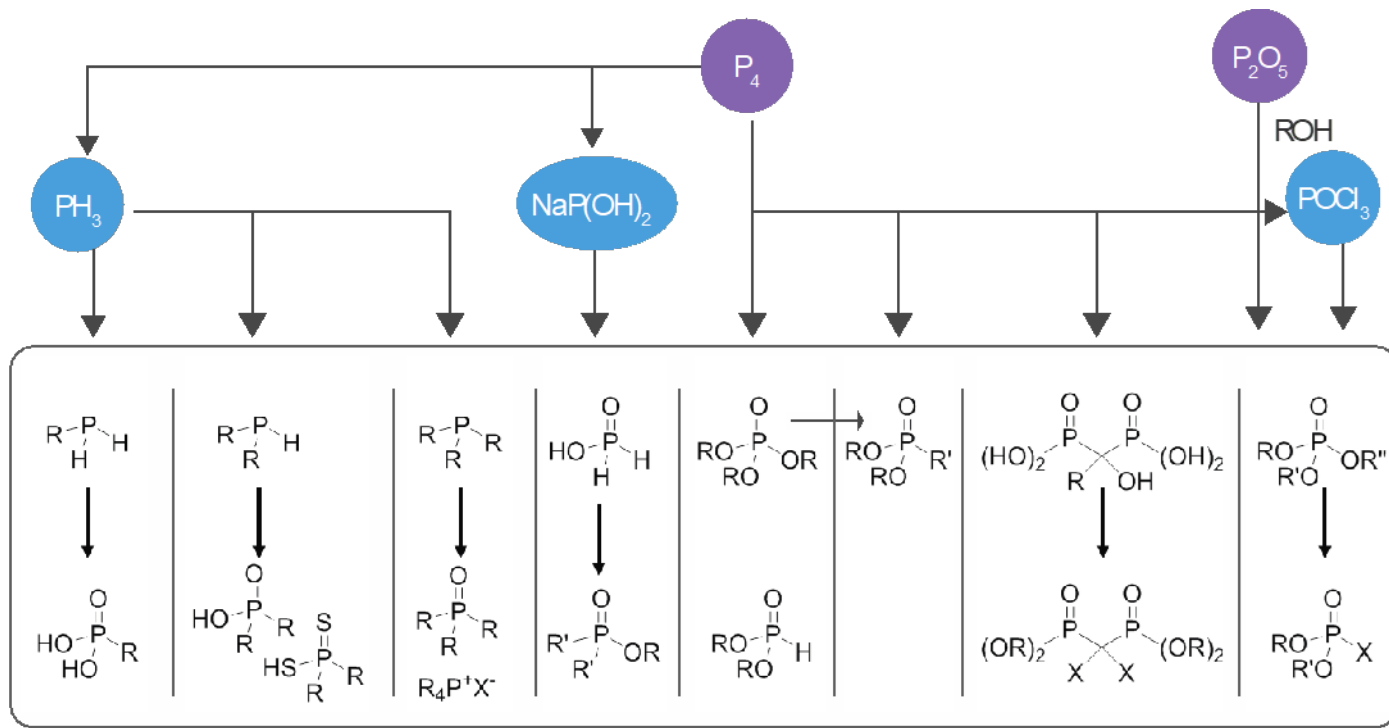
Progress beyond

STREM
CHEMICALS, INC.

Samples available from Strem



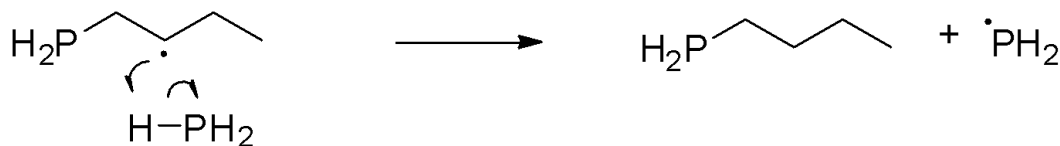
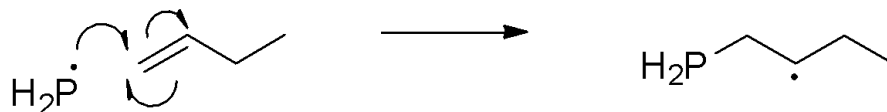
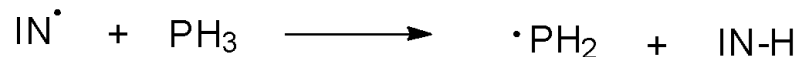
Phosphorus Specialties Product Platform



Foundational Chemistry



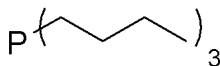
- Free radical addition of PH_3 to olefins is a major component of Solvay's alkylphosphine derivatives technology (alkylphosphine route)



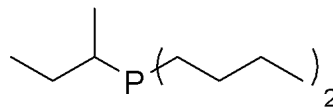
Example – CYTOP[®] 340



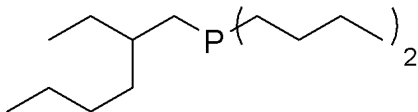
- Product distribution is dependent on the nature of the olefin
- Initiator fragments and some olefin oligomers are formed
- Olefin diversity translates to product diversity



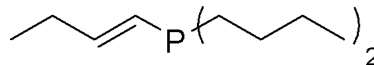
94%



2.5 - 3.0%



0.8%



0.5%

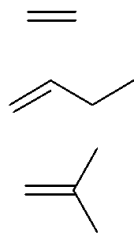
- **CYTOP[®] 340** (Strem: 97-5801)
- Tri(n-butyl)phosphine
- CAS No. 998-40-3

Foundational Chemistry - Olefin Variety

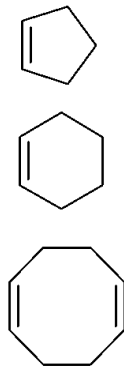


- Product distribution is dependent on the nature of the olefin

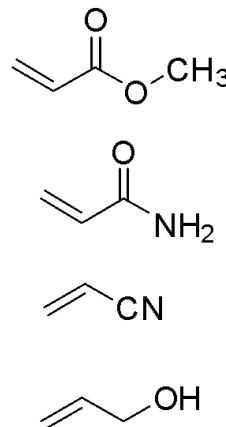
**alpha-olefins,
(linear, branched)**



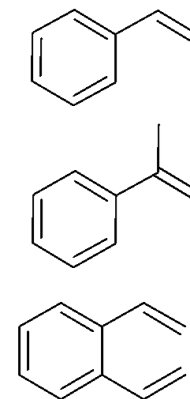
cyclic olefins



**functionalized
olefins**



**aromatic
olefins**

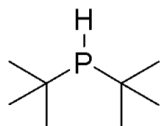
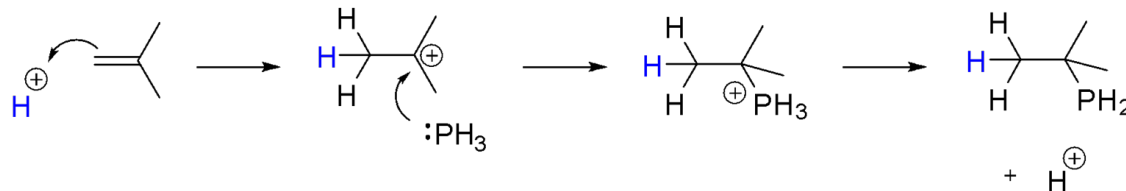


- Reactivity of olefins and the product compositions depend on number of double bonds and positions

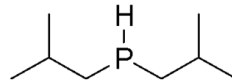
Acid-Catalyzed Addition to Olefins



- Acid-catalyzed addition to olefins allows access to useful products not accessible through free radical routes



vs.



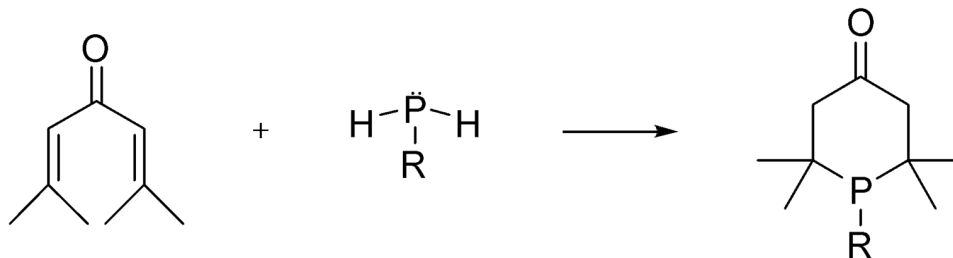
- CYTOP[®] 341** (Strem: 97-5750)
- tri(isobutyl)phosphine
- CAS No. 4125-25-1

- Tri-*tert*-butylphosphine cannot be prepared under acid catalysis
- Tri-*iso*-butylphosphine is readily accessible - **CYTOP[®] 341** (Strem: 97-5750)

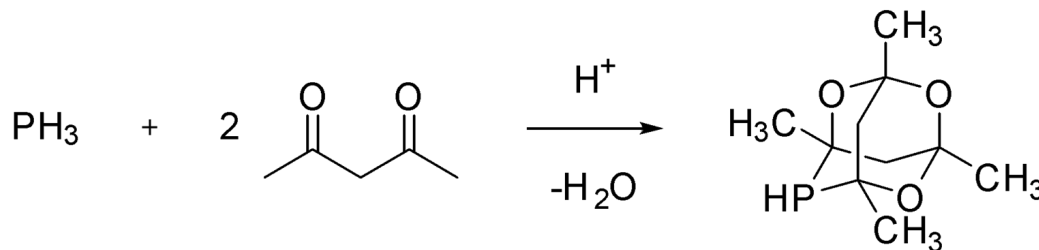
Extensive Toolbox for Synthesis



- Michael Addition to activation olefins



- Addition to 2,4-pentadione



- **CYTOP® 216X** (Strem: 97-1310)
- 1,3,5,7-tetramethyl-2,4,6-trioxa-8-phosphaadamantane
- CAS No. 26088-25-5

Applications in Petrochemical Catalysis



Progress beyond

STREM
CHEMICALS, INC.
Samples available from Strem



Catalysts - A Great Opportunity to Innovate



- Catalysts facilitate the conversion of one molecule to another
- They are essential to industries such as pharma, petro, specialty chemicals, polymers, etc.
- A key enabler to sustainable processes
 - Reduce CO₂ emissions
 - Reduce chemical use
 - Reduce energy input
 - Less waste
 - Higher yields of desired products
- Petrochemical catalysis is critical to basic building blocks in chemistry
- Petrochemical catalysis is valued at greater than \$33 billion USD/year and growing (~25% homogeneous)



Homogeneous catalysts are needed when heterogeneous catalysts cannot provide the desired selectivity, activity, and/or lifetime - many of these require a phosphine ligand at industrial scale

Why the Interest in Phosphorus for Catalysis?



- ***Tunability***: Diversity of structure, steric/electronic effects, thermal and chemical stability, reactivity, selectivity
- ***Key balances*** between P ligands and metals (Cr, Co, Rh, Ni, etc.) critical to ***process efficacy***
- ***Available in multiple forms*** for ease of handling (product stewardship, safety, etc.)
- ***Established manufacturing*** routes, ***Right*** Scale



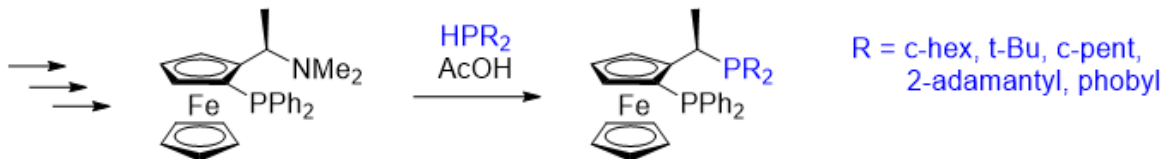
Solvay is a leader in the safe supply of phosphine ligands to the market.

Diverse Ligands Enable Diverse Applications

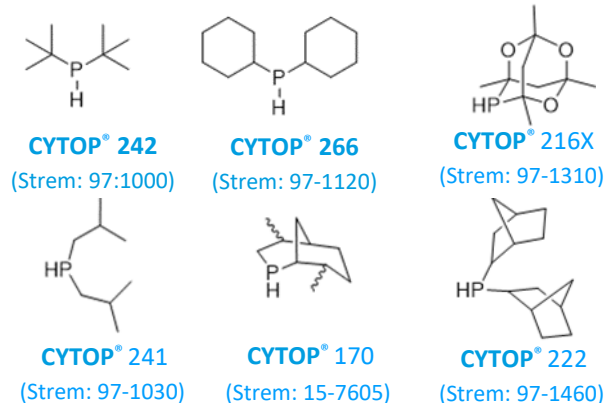
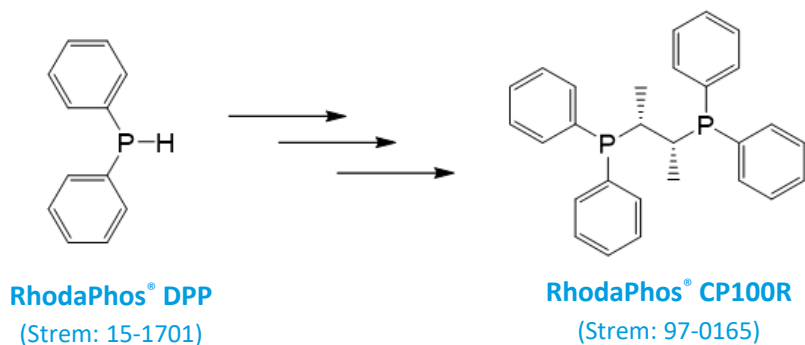
Multifunctional building blocks



- Ability to tune ligand/catalyst properties via changes in composition: a key feature in all successful ligands
- Modularity leads to breadth in applications, i.e., Josiphos™



- Achiral primary and secondary phosphines can be made into chiral motifs for life sciences catalysis

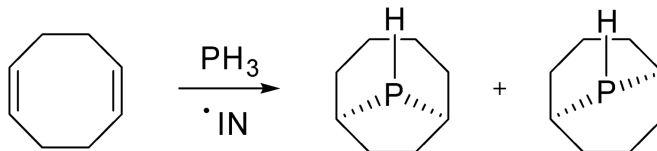


CYTOP[®] 282T – Bulky Phosphine



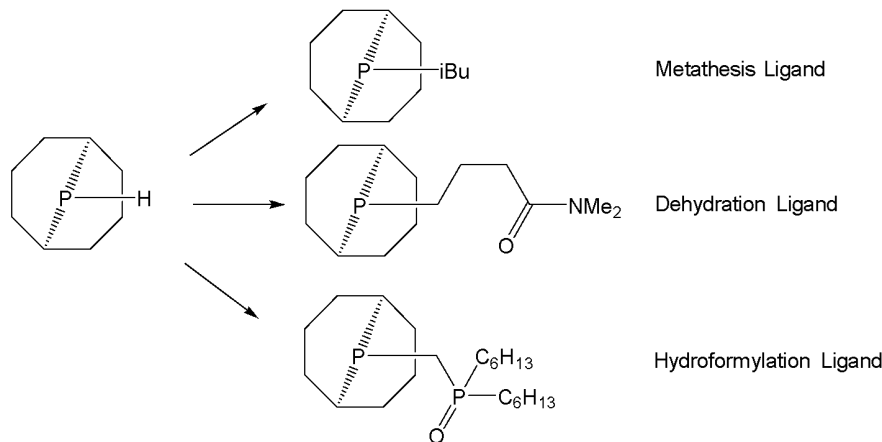
Ligand Precursor

- CYTOP[®] 282T– sterically bulky secondary phosphine
 - Isomers can be separated via selective protonation



- **CYTOP[®] 282T**
(Strem: 15-7535)
- 9-phosphabicyclononane [3.3.1] and [4.2.1]
- CAS No. 13887-02-0/
13396-80-0

- CYTOP[®] 282T is a cost-effective alternative to tertiary-butyl and adamantyl substituents
- Modularity leads to a breadth of applications – Metathesis, Dehydration and Hydroformylation chemistry



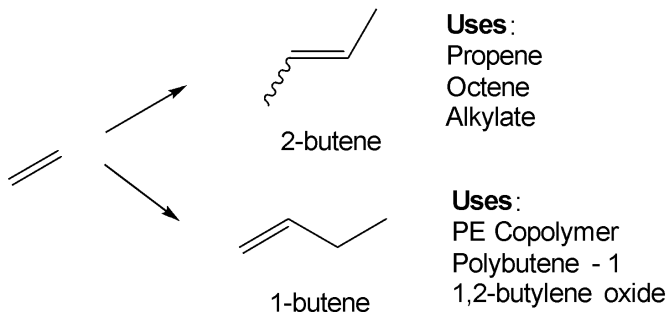
- (1) Pringle, P.G. et al. *Adv. Synth. Catal.*, **2005**, 347, 1345
- (2) Patent, Pringle, P.G. et al. WO2012072594 A1, June 7, 2012
- (3) Patent, Drent, E. et al. US 20080081909 A1, April 3, 2008
- (4) Nolan, S.P. et al. *Chem. Commun.* **2014**, 50, 2205

Ethylene Conversion Applications



Control of conversion is critical

- Ethylene is one of the most important building blocks in chemistry (150+ million tons in 2018)
- Conversion of ethylene to higher value products and different functionalities is critical to a variety of applications
- **Control of this conversion** is key (C4, C6, C8, C10, etc.) and isomers
- Dimerization, oligomerization, oxidation, halogenation, hydroformylation, alkylation, etc. are required

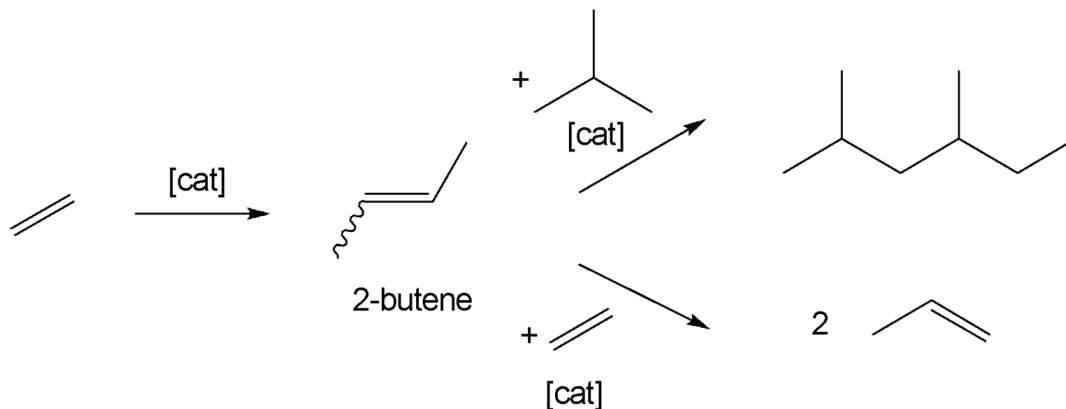


Ethylene to 2-Butene

Key Raw Material for Propylene and Alkylate



- 2-butene is mostly recovered and used in the production of gasoline alkylate
- Increased demand for 2-butene in the production of propylene
- Critical to use the right catalyst for high conversion to 2-butene – maximize productivity and quality



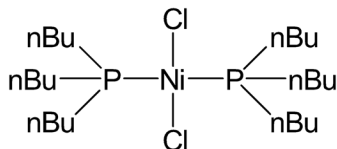
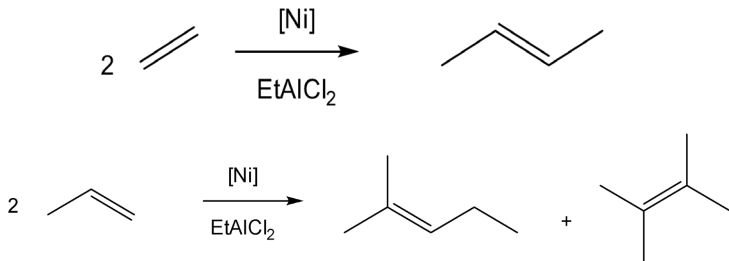
- (1) Chauvin, Y. Einloft, S.; Olivier, H. *ind. & Eng. Chem. Res.* **1995**, 34, 1149
- (2) Behr, A.; Bayrak, Z.; Stochniol, G. et al. *Chem. Eng. & Tech.* **2016**, 39, 263
- (3) WO 2019105844 A1, June 6, 2019
- (4) Hulea, V. *Catal. Sci. & Tech.* **2019**, 9, 4466

Ethylene to 2-Butene

Key Raw Material for Propylene and Alkylate



- RhodaPhos[®] NICAT is a nickel catalyst most commonly employed in dimerizations of olefins of varying lengths (butenes, propenes, ethenes, etc.) – many of these products serve as precursors



RhodaPhos[®] NICAT
(Strem: 28-0075)

- Favors formation of 2-butene in ethylene dimerization
- RhodaPhos[®] NICAT is also applied in processes for polymer formation, cycloadditions of olefins and isomerizations of olefins
- Also employed in dimerization of propylene

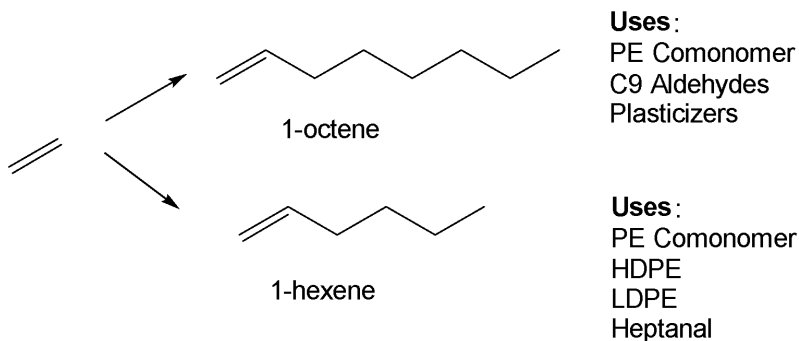
- (1) Chauvin, Y. Einloft, S.; Olivier, H. *ind. & Eng. Chem. Res.* **1995**, *34*, 1149
- (2) Behr, A.; Bayrak, Z.; Stochniol, G. et al. *Chem. Eng. & Tech.* **2016**, *39*, 263
- (3) WO 2019105844 A1, June 6, 2019
- (4) Hulea, V. *Catal. Sci. & Tech.* **2019**, *9*, 4466
- (5) Chemical Week, 20 November 1985, p. 54
- (6) Scott, A. Chemical Week, 3 November 1999, p. 41

Ethylene to 1-Hexene and 1-Octene

Control is key to form desired oligomers

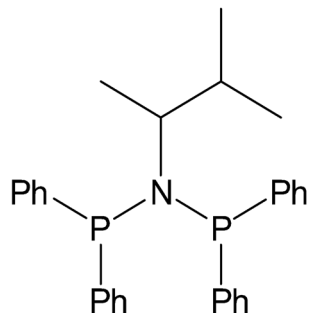


- Control over trimerization vs tetramerization of ethylene is critical
- 1-hexene and 1-octene are BOTH required for different polyester grades (among other applications)
- Control of the ratio of formation is important to simplify purification processes



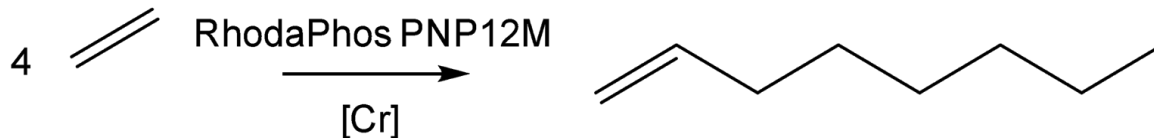
RhodaPhos[®] PNP 12M

Oligomerization of Ethylene



RhodaPhos[®] PNP 12M
(Strem: 15-0745)

- RhodaPhos[®] PNP12M is employed in chromium-catalyzed tetramerization of ethylene
- Selective formation of 1-octene in tetramerization
- High-yielding reaction (1-hexene is second major product)
- Ligand can be modified to include other functional groups at both the phosphorus and the nitrogen atom

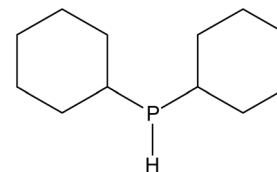
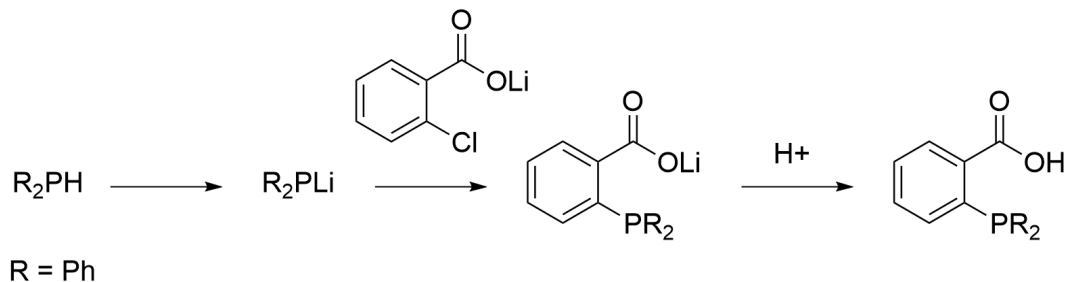


SHOP Process

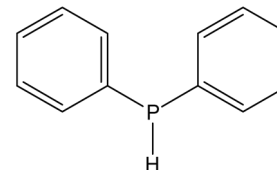


Derivatization of secondary phosphines

- Development of complex and specific ligands is a hallmark of homogeneous catalysis
- SHOP = Shell Higher Olefin Process (1977)
- Ethylene oligomerized to high-purity, even-numbered, linear-alpha olefins followed by isomerization and hydroformylation to make alcohols



CYTOP® 266
(Strem: 97-1120)
Di(cyclohexyl)phosphine
CAS No. 829-84-5



CYTOP® 186TOP
(Strem: 15-1705)
Diphenylphosphine
CAS No. 829-85-6

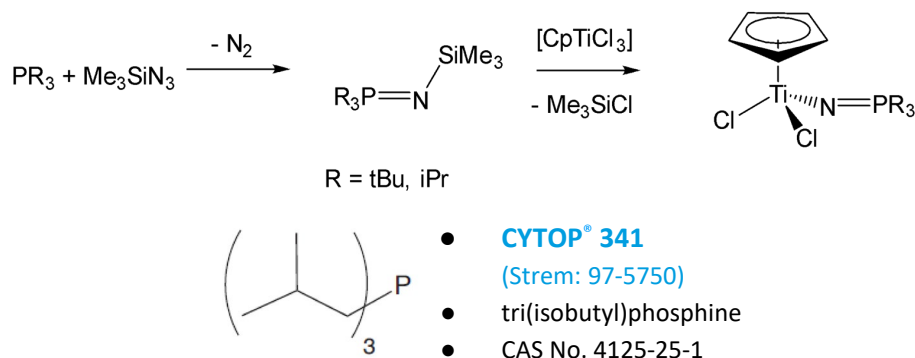
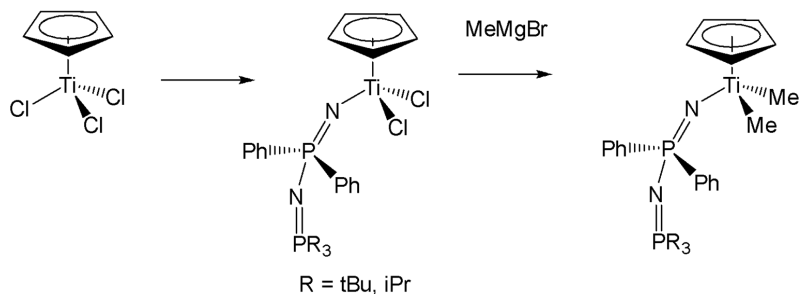
- Process requires industrial quantities of a phosphine ligand

Ethylene Polymerization



Control of Polymer Chain Length

- Ethylene polymerization is a straightforward method to produce high-value polyolefins with properties such as adhesiveness, improved barrier effects, dyeability and printability, among others
- Single-site catalysts effectively control molecular weight and size distribution
- Ti:P complexes offer good control over molecular weight and distribution. They are also relatively stable, easy to handle and easily modified

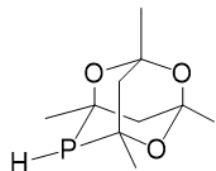
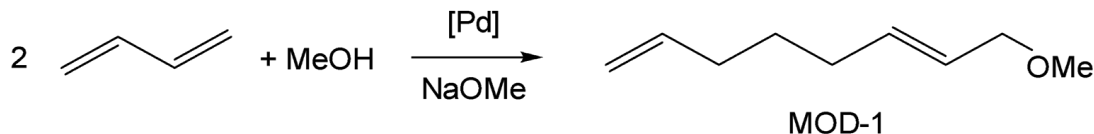


P Ligands for Telomerization of Dienes

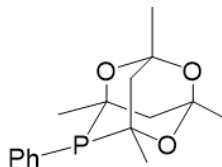
Specialty Chemicals from Petrochemical Feedstocks



- Telomerization of dienes is an industrially relevant process to provide specialty chemicals
- It is 100% atom economical and tolerant to nucleophiles; chemistry requires P ligands
- Current systems (PPh_3) are susceptible to oxidation and have low selectivity
- Replacing with CYTOP® 292:10% increased yield, significant cost improvements at industrial scale



CYTOP® 216
(Strem: 97-1310)



CYTOP® 292
(Strem: 15-5375)

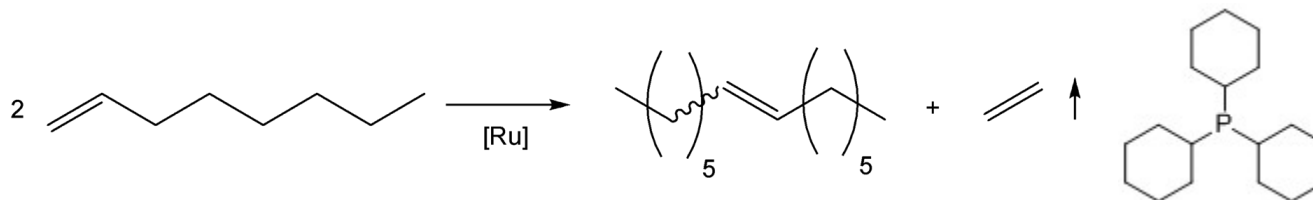
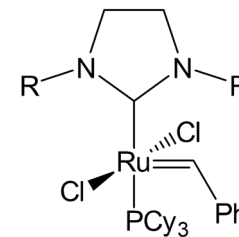
	CYTOP® 292	PPh_3
Conv.	96%	88%
Selectivity	94%	91%
Yield	90%	80%

Production of Alpha Olefins



Metathesis catalysts for 1-octene and methyl oleate

- Metathesis exists predominantly in petrochemical applications as a heterogeneous process
- Highly attractive ruthenium-based catalysts offer an alternative in synthesis of alpha olefins
 - Robustness to air, water and oxygenates
 - High reaction rates and selectivity
- CYTOP® 366 is an effective ligand in the self-metathesis of 1-octene & methyl oleate
 - TON 64,000 – 600,000 with high selectivity (>98%)
 - TOF 3,800/s
 - High activity: combination of bulk and electron donating capabilities of ligand set and stability of catalyst (faster rates than TPP analogues)



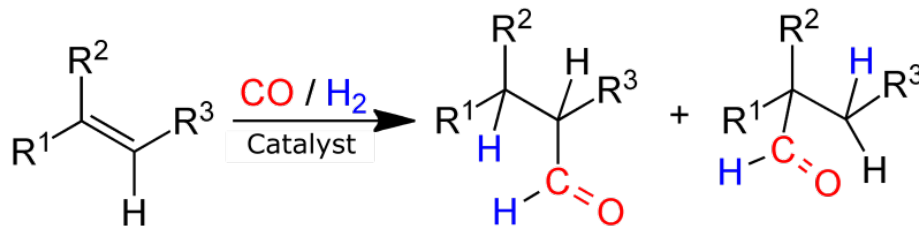
- **CYTOP® 366**
(Strem: 15-6152)
- Tricyclohexylphosphine
- CAS No. 2622-14-2

Hydroformylation

Critical Process for the Production of Aldehydes



- Hydroformylation - the “oxo” reaction - is one of the highest volume homogeneous-catalyzed reactions in the world
- The conversion of alkenes, hydrogen and CO to aldehydes and related products at a rate of over 10 million metric tons/year



- Phosphine-modified versions were discovered initially in the 1960s
- Homogeneous catalysis is dominated by Rhodium and Cobalt systems, many which require a phosphorus-based ligand

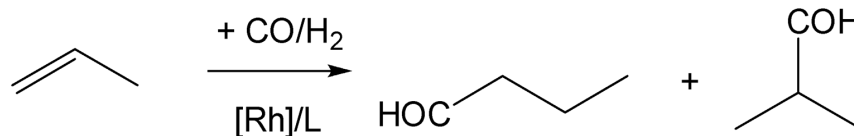
(1) Sluagh, L.H.; Millineaux R.D. J. *Organomet. Chem.* **1968**, 13, 469

Hydroformylation



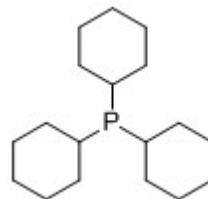
Monodentate phosphines as additives to P-containing catalyst systems

- Many complex, bidentate or chelating ligand systems are known for hydroformylation
- Rh-catalyzed hydroformylation of propylene, addition of phosphines improves activity without impacting branching
- TCHP (tricyclohexylphosphine) shown to substantially increase activity, no change on N/Iso ratio.
- TOP (trioctylphosphine) did not have the same impact but rather decreases activity
- Sterically hindered phosphines enhance activity while non-hindered do not!

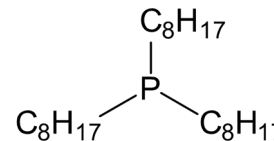


Monodentate Phosphine	Mole ratio $\text{PR}_3:\text{Rh}$	N/Iso Ratio	Activity lb HBu / g Rh · h
none	n/a	2.32	2.78
TCHP	3/1	2.30	4.10
TCHP	6/1	2.31	4.30
TOP	3/1	2.43	2.10
TOP	6/1	2.58	1.05

CYTOP® 366
(Strem: 15-6152)
Tricyclohexylphosphine
CAS No. 2622-14-2

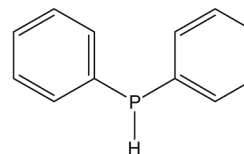


CYTOP® 380
(Strem: 97-6665)
Trioctylphosphine
CAS No. 4731-53-7



Hydroformylation

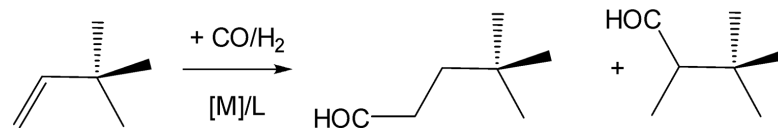
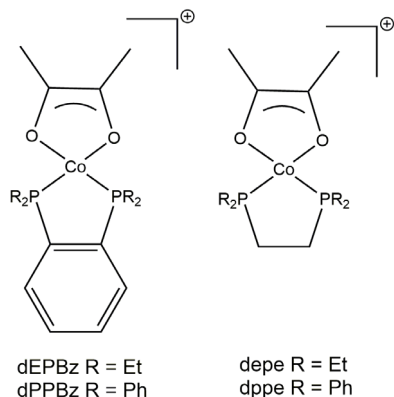
New reactivity for a classic reaction



CYTOP® 186TOP
(Strem: 15-1705)
Diphenylphosphine
CAS No. 829-85-6



- New cationic cobalt supported by phosphines have high reactivity and isomerization activity leading to high L:B selectivities for internal olefins



Catalyst	Temp (°C)	Pressure (bar)	Aldehyde (%)	Aldehyde L:B	Alkane (%)
[Co:DPPBz] ⁺	140	30	60.0	58	0.8
[Co:dppe] ⁺	140	30	64.1	57	1.0
[Co:depe] ⁺	140	30	77.1	54	1.2
[Co:DEPBz] ⁺	140	30	84.8	51	1.2

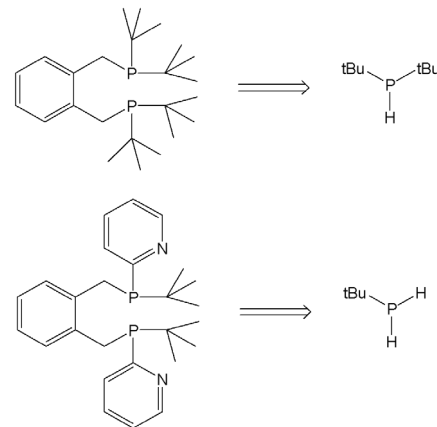
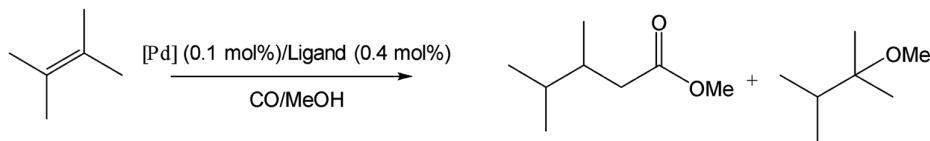
- New ligands offer exceptional stability, high reactivity, and high L:B ratios for internal olefins
- Opens the path to medium-pressure hydroformylation technology
- New efforts make for exciting, industrially relevant discoveries***

Alkoxycarbonylation of Alkenes



Increasing productivity with P-based ligands

- Carbonylation (hydroformylation) of alkene is one of the most important homogeneous industrial processes
 - Can require complex challenges to meet specific needs (improve activity, etc.)
- Recent developments have shown improved routes for sterically hindered and demanding olefins



CYTOP® 242
(Strem: 97-1000)
Di(tert-butyl)phosphine
CAS No. 819-19-2

CYTOP® 142
(Strem: 97-0966)
mono(tert-butyl)phosphine
CAS No. 2501-94-2

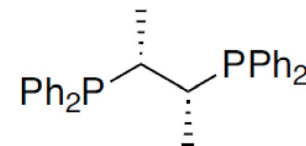
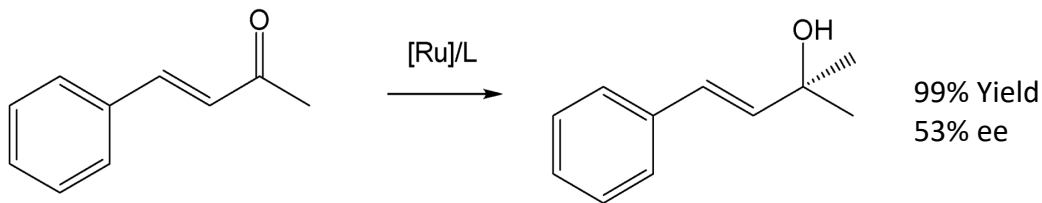
- ***Bulk ethylene can be functionalized with high activity (TON >1,425,000: TOF 44,000/hr) and high selectivity (>99%) with certain P-based ligands***

Hydrogenation



Homogeneous catalysis for asymmetric or symmetric hydrogenations

- Hydrogenation is used to convert alkenes and aromatics into saturated alkanes (paraffins) and cycloalkanes
- Hydrogenation is also used to convert olefins from refining feedstocks to value-added chemicals
- Homogeneous catalysis offers controlled reactivity under milder conditions
- RhodaPhos® CP100R can be employed in the chemoselective production of chiral alcohols



- RhodaPhos® CP100R**
(Strem: 97-0165)
- (2R,3R)-(+)-
Bis(diphenylphosphino)butane
- CAS No. 74839-84-2

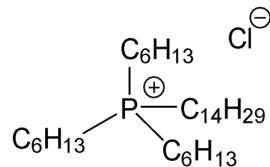
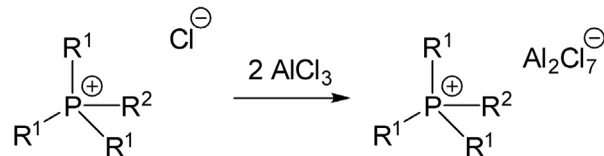
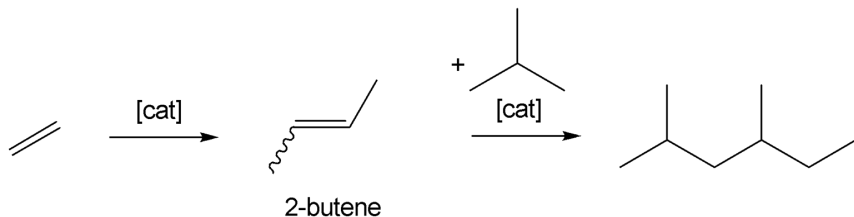
- RhodaPhos® CP100R has also been employed as a bidentate ligand in chromium-based ethylene oligomerizations

Alkylation Chemistry – C8

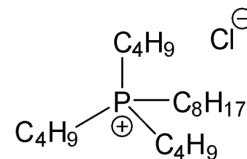
Phosphonium ionic liquids as catalysts



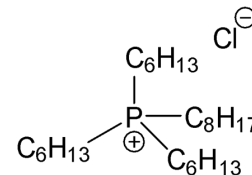
- Alkylation of paraffins with olefins for the production of alkylate for gasoline can use a variety of catalysts
- Many processes involve harsh conditions such as hydrofluoric acid (HF) or sulfuric acid
- Phosphonium ionic liquids can be employed for conversion at near ambient conditions (C8 selectivity >70%)
 - Lewis acidity allows ionic liquid to act as a catalyst



CYPHOS® IL 101
(Strem: 15-6382)
CAS No. 258864-54-9



CYPHOS® IL 253
(Strem: 15-7575)
CAS No. 56315-19-6



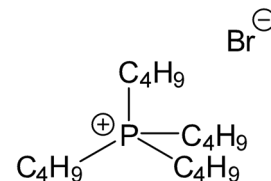
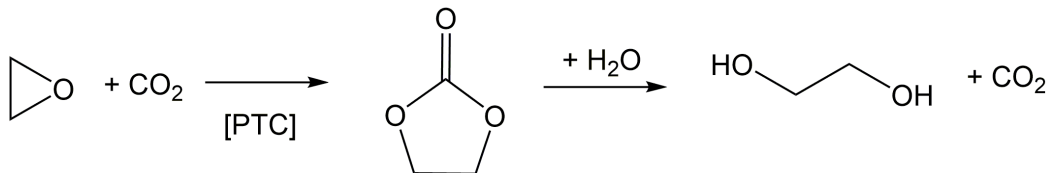
CYPHOS® IL 356
(Strem: 15-7590)
CAS No. 850134-85-9

P Based Phase Transfer Catalysts - PTC



Phosphonium ionic liquids as PTC

- The OMEGA process (Shell) is a catalytic system to produce MEG
 - Applications in manufacture of polyester, antifreeze, dioxanes, etc.
 - MEG is 92% of EG market at about 26.8 MMT (2017)
 - Requires a PTC
- Key advantages of this process are 99% conversion efficiency vs ~90% for traditional methods
- Further advantages include less steam use and less wastewater production
- Chemistry can be catalyzed by P based ionic liquids



CYPHOS® 442

(Strem: 97-1579)

CAS No. 3115-68-2

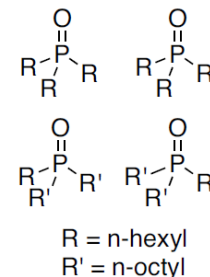
- (1) US Patent 7728164
- (2) US Patent 8735607
- (3) WO Patent 2007104730

Acetic Acid Process

Phosphine oxides as Additives to Reduce Corrosion



- The carbonylation of methanol is a long-established route to acetic acid.
- Rhodium catalysts affect the carbonylation of methanol via addition of CO using added HI or MeI.
- The result is a highly acidic medium that can quickly corrode reactors, process vessels etc.
- CYTOP® 503 has been shown to significantly reduce corrosion while at the same time increasing stability and thus activity of the catalyst system!
 - *Phosphine oxide shown to complex and extract HI very effectively!*



CYTOP® 503
(Strem: 97-1337)

Stabilizer	Molarity	Corrosion (%)
None	n/a	0.516
CYTOP 503	0.25	0.490
CYTOP 503	0.5	0.327
CYTOP 503	1	0.181

Additive	Time (s)	Active Rh(I) (%)	MeI (M)	MeOAc (M)	Feed Conversion (%)
None	912	6	0.008	0.008	44
TPPO	1341	0	0.010	0.010	53
CYTOP 503	1814	36	0.008	0.008	80

316L, 0.5M HI, 3.2 wt% H₂O, HOAc, CO, 70°C, 48hrs

1. Hallinan et al., US 2015/0246866 Sept 3, 2015

Why Work With Solvay?



- **Get the speed, flexibility and intimacy of a small company with strong corporate support**
- Ability to meet demanding purity, supply and scale-up needs, successfully transitioning chemistries from lab quantities to industrial-scale production
- Proven track record of developing innovative and practical routes to market
- Diverse and expanding R&I organization prepared to support today's applications and tomorrow's innovations
- Safe handling and processing of laboratory and large-scale air-sensitive material
- Logistics, registration support, toxicology support

Together, let's unlock the potential of phosphorus chemistry to support your sustainable growth

Custom Solutions - Critical to Sustainability



- Each company has its own feedstocks, equipment, objectives, etc.
- Many situations require a custom ligand or catalyst solution - our specialty
- Solvay has **over 60 years of experience** providing customer-specific ligand solutions
- We have the ability to partner with users and developers to create sustainable, cost-effective and value-added solutions
- Let's talk about your ligand next!



What Does *Your* Future Hold?

Thank You

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Progress beyond

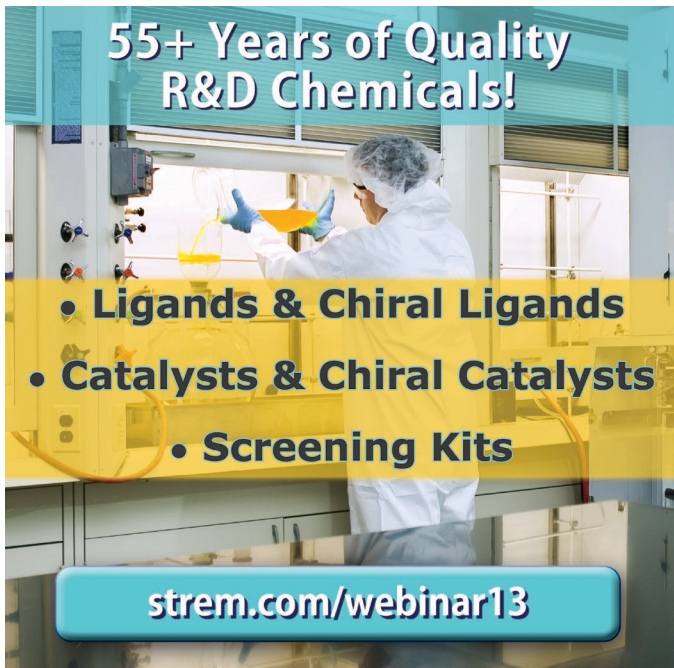


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- **Catalysts & Chiral Catalysts**
- **Screening Kits**

strem.com/webinar13

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Partnership:

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Differentiated products and technologies:

We offer a wide range of phosphorus-based chemistry to meet precise application requirements