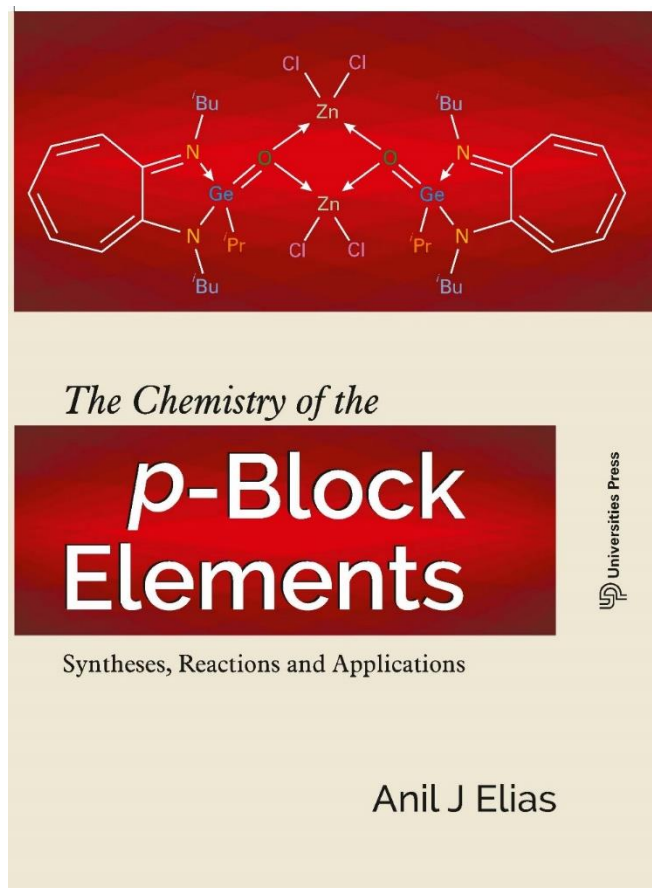


Chemistry of Phosphorus

For more details refer chapter 9 of the book
'The Chemistry of the p-Block elements:
Syntheses, reactions and applications,
2018 Universities Press



- Phosphorus mostly forms tri and penta-valent compounds and the latter in its tetracoordinate form is the most commonly observed oxidation state and geometry.
- **P=O** is one of the strongest double bonds of heavier p block elements (P=O: 544 kJ/mol; P=S 335 kJ/mol) and for many reactions involving phosphorus (III) and phosphorus (V) reagents, the driving force is the formation of the P=O bond (e.g. Wittig reaction)
- Trivalent phosphorus-carbon compounds are excellent ligands with varying steric and electronic properties and are used as spectator ligands in metal complexes for homogenous catalysis
- Phosphates are essential for life processes and many molecules of the living system such as DNA, ATP and phosphacreatine contain phosphate groups. ATP is the universal currency for energy. The average adult's need for phosphorus is about 700 mg per day.
- Phosphorus forms many allotropes of which white phosphorus is the most reactive and ignites in air $\sim 30\text{ }^{\circ}\text{C}$ forming phosphorus pentoxide. This property is used in making phosphorus bombs and smoke screen bombs.
- Since it is one among the three essential plant nutrients (N, P and K), the major use of phosphates are as fertilizers.
- **Diammonium phosphate** along with ammonium sulfate and a red dye is used as an environmentally friendly fire retardant in large quantities to control forest fires by spraying from aeroplanes.
- Phosphorus shows formal oxidation states $-3(\text{Ca}_3\text{P}_2, \text{PH}_3)$, $-2(\text{P}_2\text{H}_4)$, $0(\text{P}_4)$, $+1(\text{H}_3\text{PO}_2)$, $+2(\text{H}_4\text{P}_2\text{O}_4)$, $+3(\text{PCl}_3)$, $+4(\text{H}_4\text{P}_2\text{O}_6)$ and $+5(\text{PCl}_5)$ in its compounds.

- Phosphazenes which are phosphorus-nitrogen double bonded compound with pentavalent tetracoordinate phosphorus find use as inorganic polymers and superbases.
- Organophosphates inhibit the functioning of the enzyme **acetyl cholinesterase** which is the reason for their use in the synthesis of pesticides and nerve gases. Unlike chlorine based pesticides, phosphorus based pesticides degrade rapidly by hydrolysis on exposure to sunlight, air, and soil.
- Herbicides constitute the biggest part of the world pesticide use (40%) and **glyphosate** [*N*-(phosphonomethyl)glycine] is the most widely used herbicide in the world and works by inhibiting a plant enzyme involved in the synthesis of aromatic amino acids.
- Similar to petroleum, the available phosphates in the earth is depleting and this is a looming crisis as before the end of this century, readily available global supplies of phosphorus will start running out.
- Nearly 40% of global reserves of phosphorus as phosphates for future are present in a single country, **Morocco** which has been named the future “Saudi Arabia of phosphorus”.
- Sterically hindered phosphines along with sterically hindered Lewis bases form frustrated Lewis pairs (FLP's).

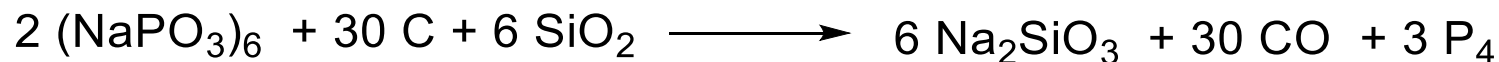
1669



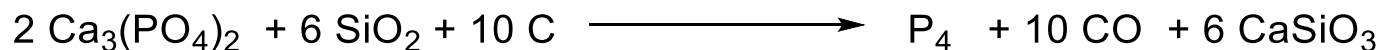
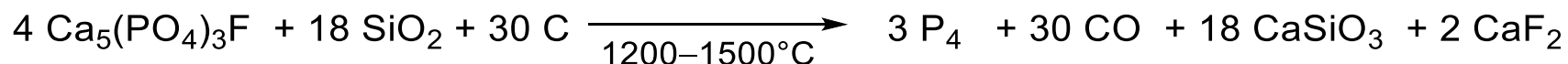
The Alchemist Discovering Phosphorus : a painting
by Joseph Wright ~1750

Hennig Brandt discovers phosphorus from reductive distillation of urine concentrate
by evaporating urine to dryness and distilling the residue with sand.

$\text{Na}(\text{NH}_4)\text{HPO}_4$ in the urine, on heating gets converted to sodium metaphosphate, $(\text{NaPO}_3)_6$



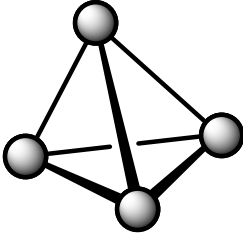
Around 10 lakh tonnes of elemental phosphorus is produced per year, mostly from fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$



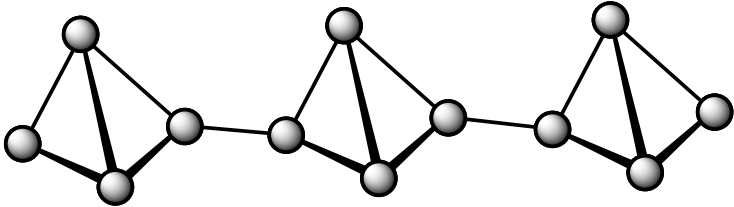
Although about twelve allotropic forms of phosphorus have been reported, the most well established among these are the white, red, violet (Hittorf's) and black allotropes.

Among these, the most sensitive to oxygen is white phosphorus which has a tetrahedral P_4 arrangement of three-membered rings and the lower stability of this allotrope originates possibly from the strain associated with the bond angles of 60° . White phosphorus has to be stored under water to prevent auto-ignition and oxidation to P_2O_5 .

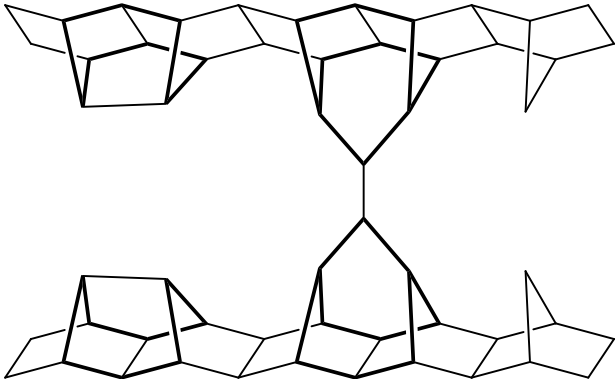
Allotropes of Phosphorus



White



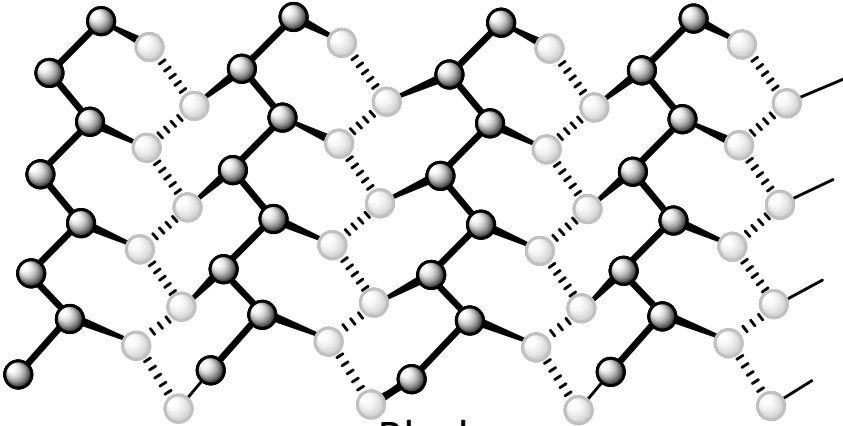
Red



P8

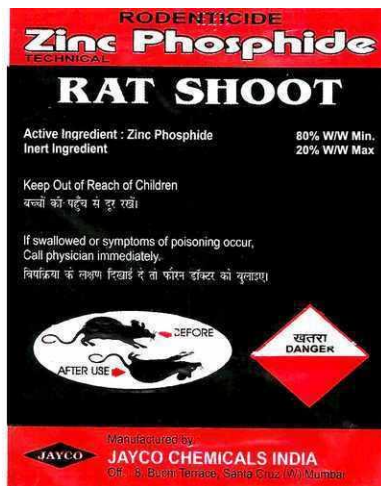
P9

Violet (Hittorf's)



Black

PH_3 ignites in air only at 150°C . However, minor amounts of diphosphine P_2H_4 , if present along with PH_3 will make it catch fire spontaneously on coming in contact with air. PH_3 has the smell of rotten fish and this is one of the reasons aluminium and zinc phosphides are used as rat bait as they slowly release PH_3 upon hydrolysis attracting the pest. Its toxicity is similar to that of cyanide as it inhibits the functioning of cytochrome c oxidase which is part of the electron transport chain in oxidative phosphorylation and ATP synthesis.

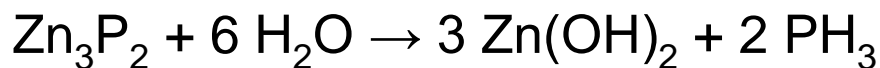


Holmes signal

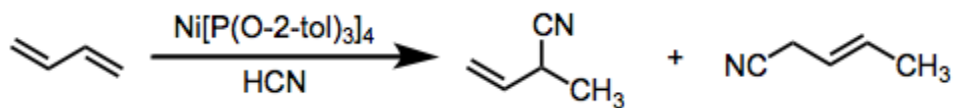


@chemistry_basics

- $\text{CaC}_2 + 2\text{H}_2\text{O} \Rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$
 Calcium carbide Acetylene
- $2. \text{CaP}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Ca(OH)}_2$
 Calcium phosphide Phosphine



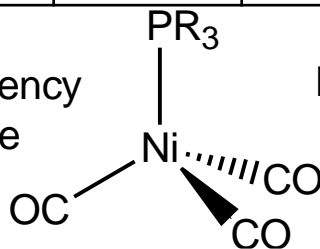
Holmes signal is an age old technique used by sailors for making emergency lighting on the sea surface during night. A can containing both calcium carbide and calcium phosphide is pierced and thrown into the sea.



Tollmann
1977

PR_3	$\nu_{\text{CO}}, (\text{cm}^{-1})$	$\chi(\text{cm}^{-1})$ $\Delta \nu_{\text{CO}}$ wrt $\text{P}(\text{t-Bu})_3$	PR_3	$\nu_{\text{CO}}, (\text{cm}^{-1})$	$\chi(\text{cm}^{-1})$ $\Delta \nu_{\text{CO}}$ wrt $\text{P}(\text{t-Bu})_3$
$\text{P}(\text{t-Bu})_3$	2056.1	0.0	$\text{PPh}_2(\text{C}_6\text{F}_5)$	2074.8	18.7
PCy_3	2056.4	0.3	$\text{P}(\text{OEt})_3$	2076.3	20.2
$\text{P}(i\text{-Pr})_3$	2059.2	3.1	$\text{P}(p\text{-C}_6\text{H}_4\text{-CF}_3)_3$	2076.6	20.5
PEt_3	2061.7	5.6	$\text{P}(\text{OMe})_3$	2079.5	23.4
$\text{P}(\text{NMe}_2)_3$	2061.9	5.8	PH_3	2083.2	27.1
PMe_3	2064.1	8.0	$\text{P}(\text{OPh})_3$	2085.3	29.2
PBz_3	2066.4	10.3	$\text{P}(\text{C}_6\text{F}_5)_3$	2090.9	34.8
$\text{P}(o\text{-Tol})_3$	2066.6	10.5	PCl_3	2097.0	40.9
PPh_3	2068.9	12.8	PF_3	2110.8	54.7
PPh_2H	2073.3	17.2	$\text{P}(\text{CF}_3)_3$	2115.0	58.9

Lowest CO stretching frequency
Most donating phosphine
best σ donor



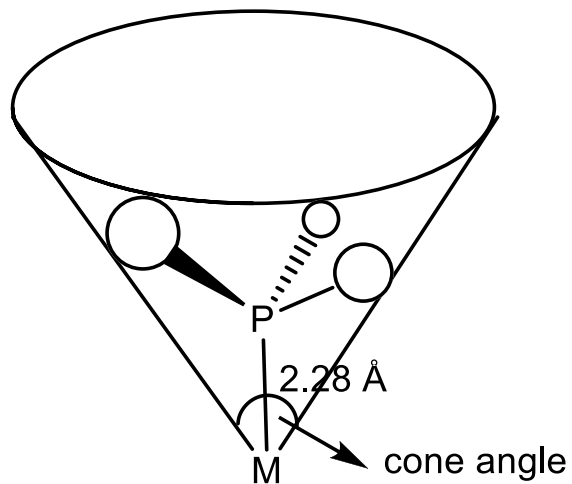
Highest CO stretching frequency
Least donating phosphine
best π acceptor

Tolman's Cone angle

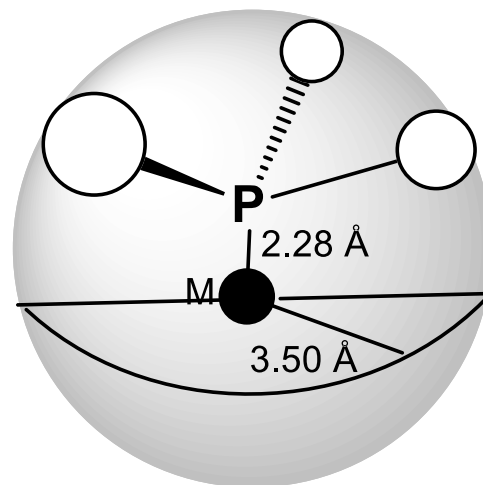
The steric bulkiness of phosphines was first compared by Tolman in 1977 using what is now well known as the cone angle determination. Tolman defined cone angle as the solid angle formed with the metal at the vertex and the ligand substituents at the perimeter of a cone. The distance of 2.28 Å was taken as the average distance between the metal and phosphorus atom of the phosphines.

Nolan's percent buried volume $\%V_{\text{bur}}$

In 2010 Nolan made a comprehensive comparison using around 700 X-ray crystallographic data of phosphines and NHC complexes especially using AuCl as the metal unit and compared the steric properties. He defined $\%V_{\text{bur}}$ simply as the **percent of the total volume of a sphere occupied by a ligand when bound to a metal**. The volume of this sphere represents the potential coordination sphere space around the metal occupied by a ligand/ligand fragment. The sphere has a defined radius (which was fixed at 3.50 Å) and the metal to phosphine distance was fixed at 2.00 Å and 2.28 Å, the latter for a one to one comparison with cone angles. $\%V_{\text{bur}}$ is calculated using crystallographic data and using a dedicated software.



C A Tolman 1977



Percent Buried Volume: %V_{bur}

S P Nolan 2003

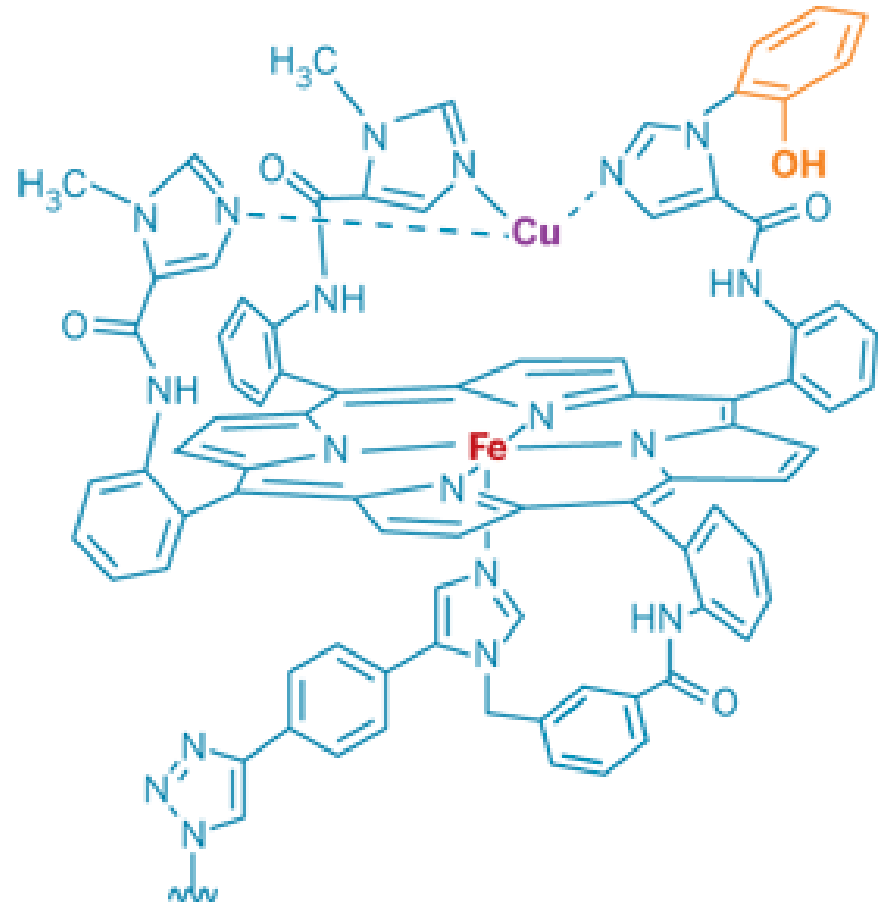
S. No.	Phosphine	Cone Angle (°)	%V _{bur} for R ₃ PAuCl At 2.00 Å (at 2.28 Å)
1	Me ₃ P	118	27.3 (23.3)
2	Et ₃ P	132	31.7 (27.1)
3	Ph ₃ P	145	34.8 (29.9)
4	iPr ₃ P	160	39.1 (24.0)
5	Cy ₃ P	170	38.8 (33.4)
6	t-Bu ₃ P	182	43.9 (38.1)
7	(C ₆ F ₅) ₃ P	184	42.6 (37.3)
8	(o-Tol) ₃ P	194	44.8 (39.4)
9	Mes ₃ P	212	50.5 (45.0)
10	(PhO) ₃ P	128	36.5 (31.9)

Active site of Cytochrome c oxidase

The last enzyme in the respiratory electron transport chain and is located in the mitochondrial membrane. It receives an electron from each of four cytochrome c molecules, and transfers them to one oxygen molecule, converting molecular oxygen to two molecules of water.

The Fe is pentacoordinated and binds O₂ (along with the Cu) before **reducing** it.

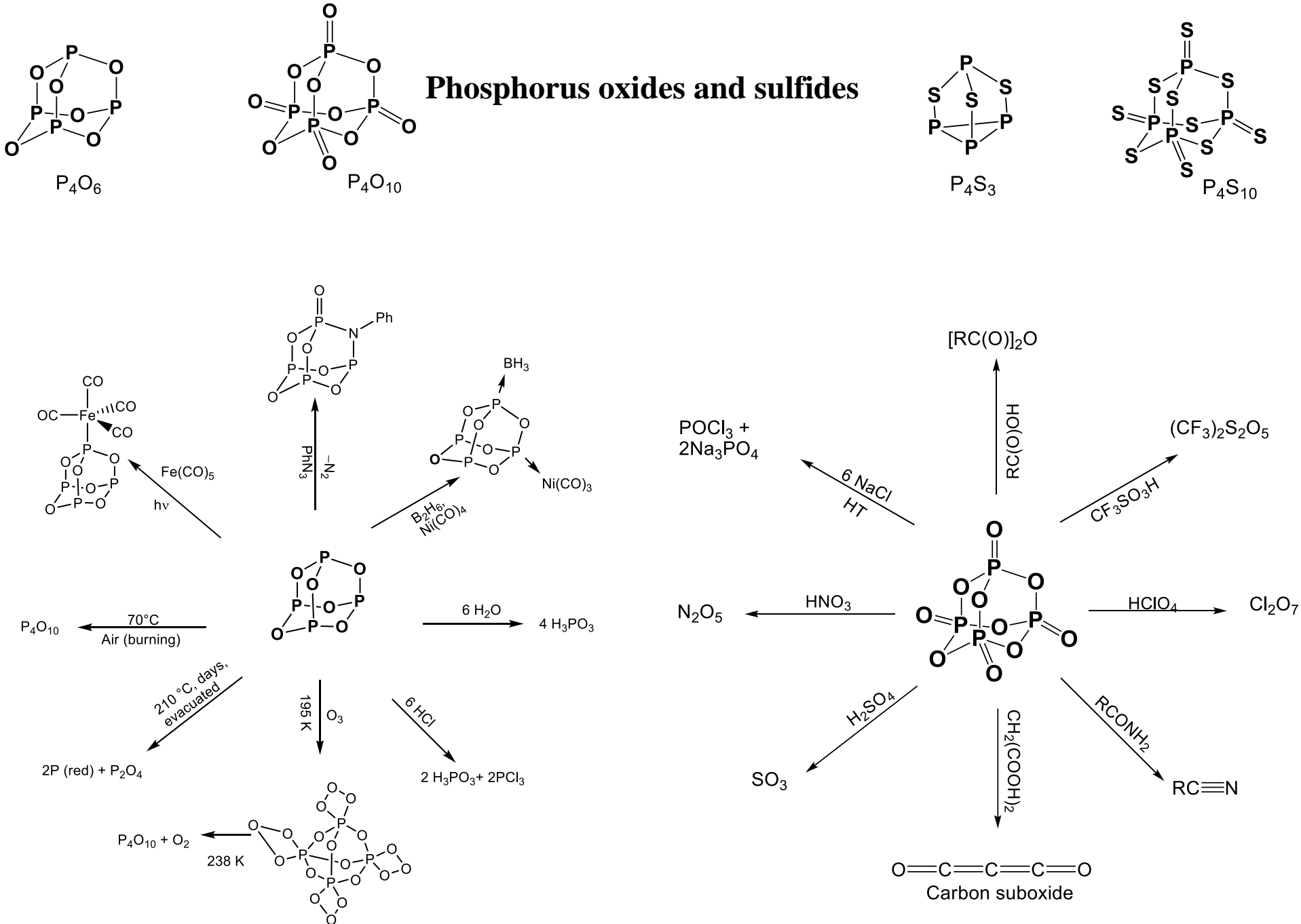
This is also the site which CN⁻ binds during cyanide poisoning [stabilizing the Fe³⁺ state and preventing its redox (Fe²⁺/Fe³⁺) activity] (**Cyanide is a very strong ligand**) also PH₃ from rat poison

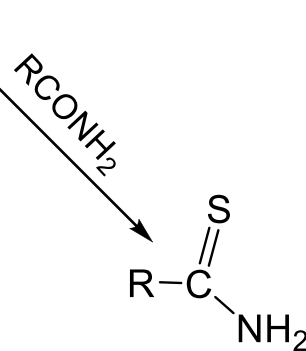
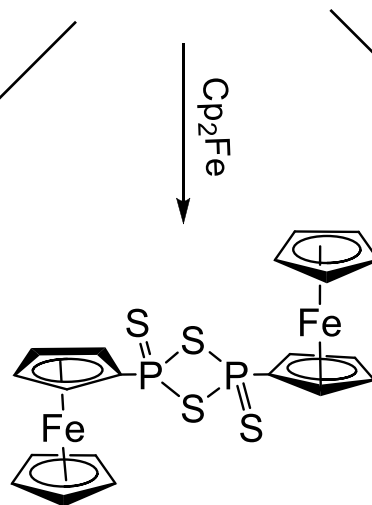
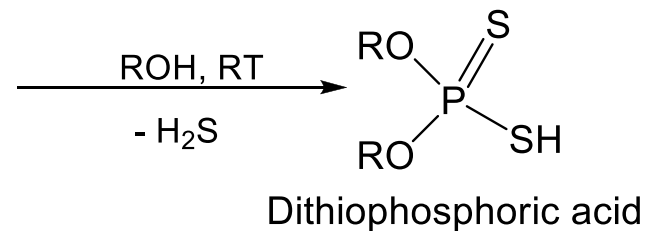
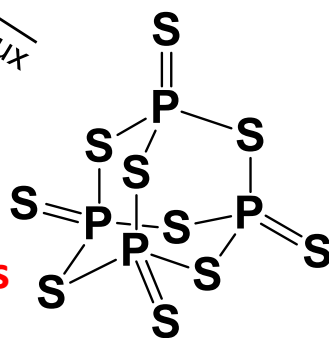
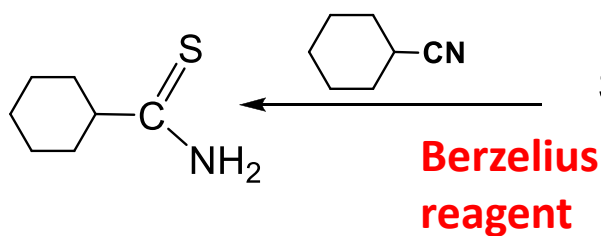
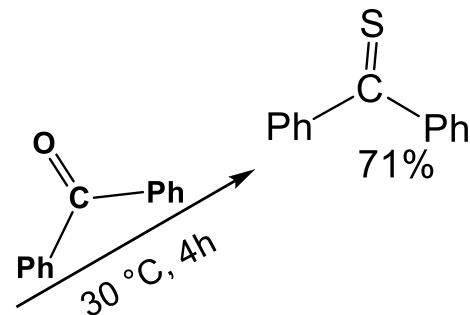
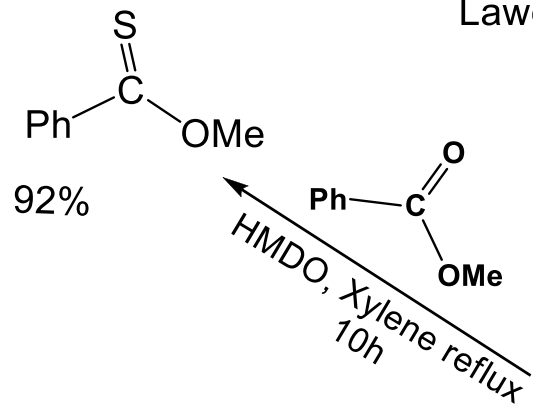
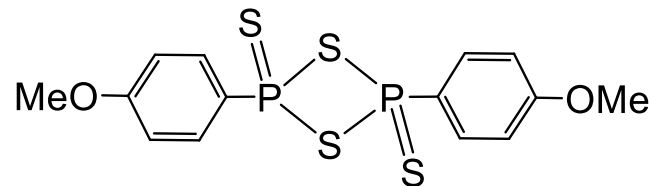


Summary reaction:

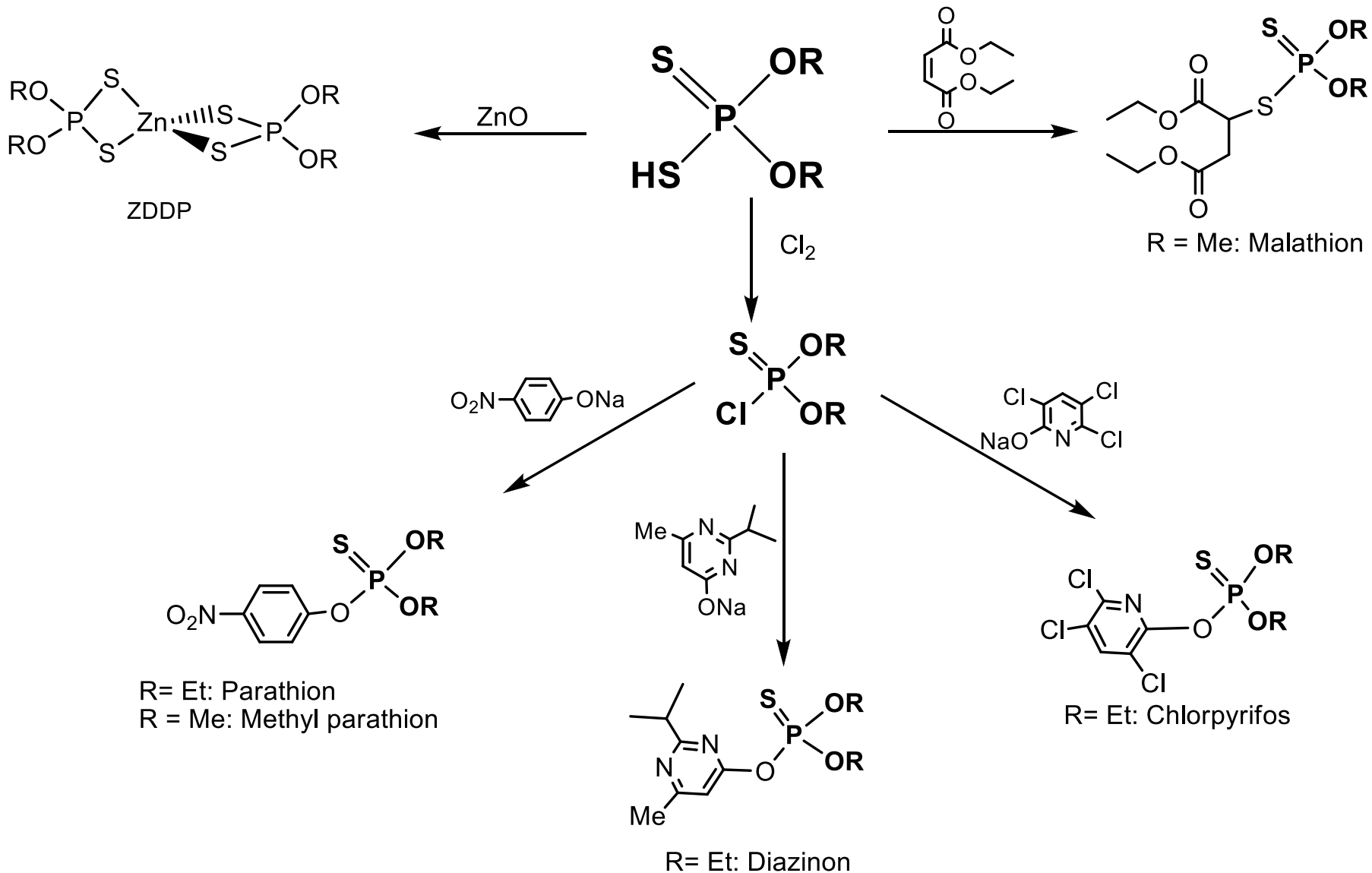


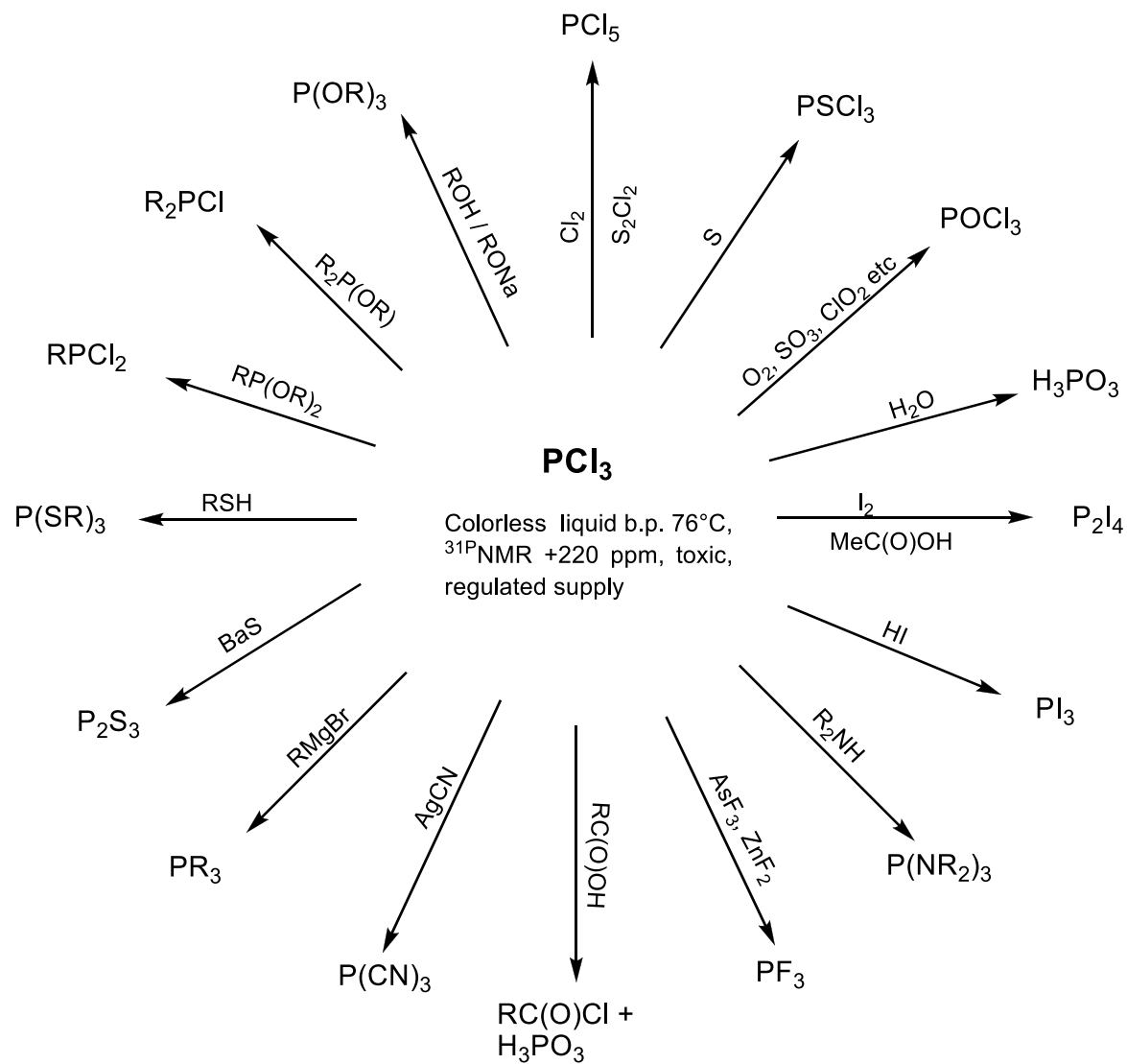
Phosphorus oxides and sulfides





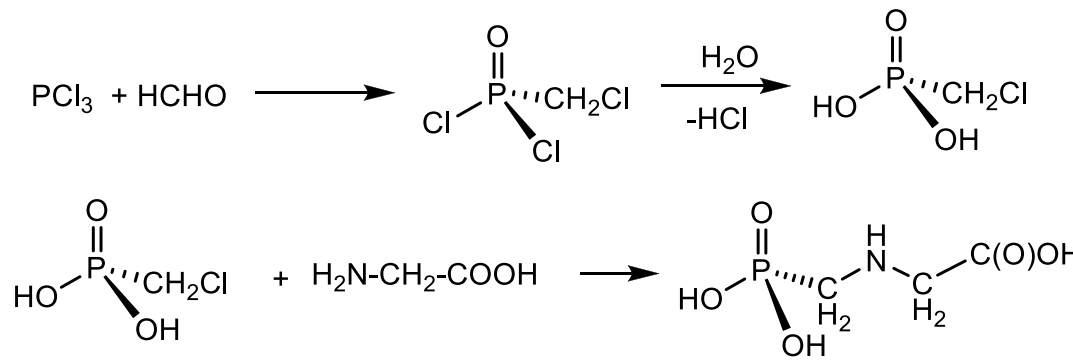
Dithiophosphoric acid: precursor for pesticides





Most widely used herbicide
 2017: 1,065,000 tons

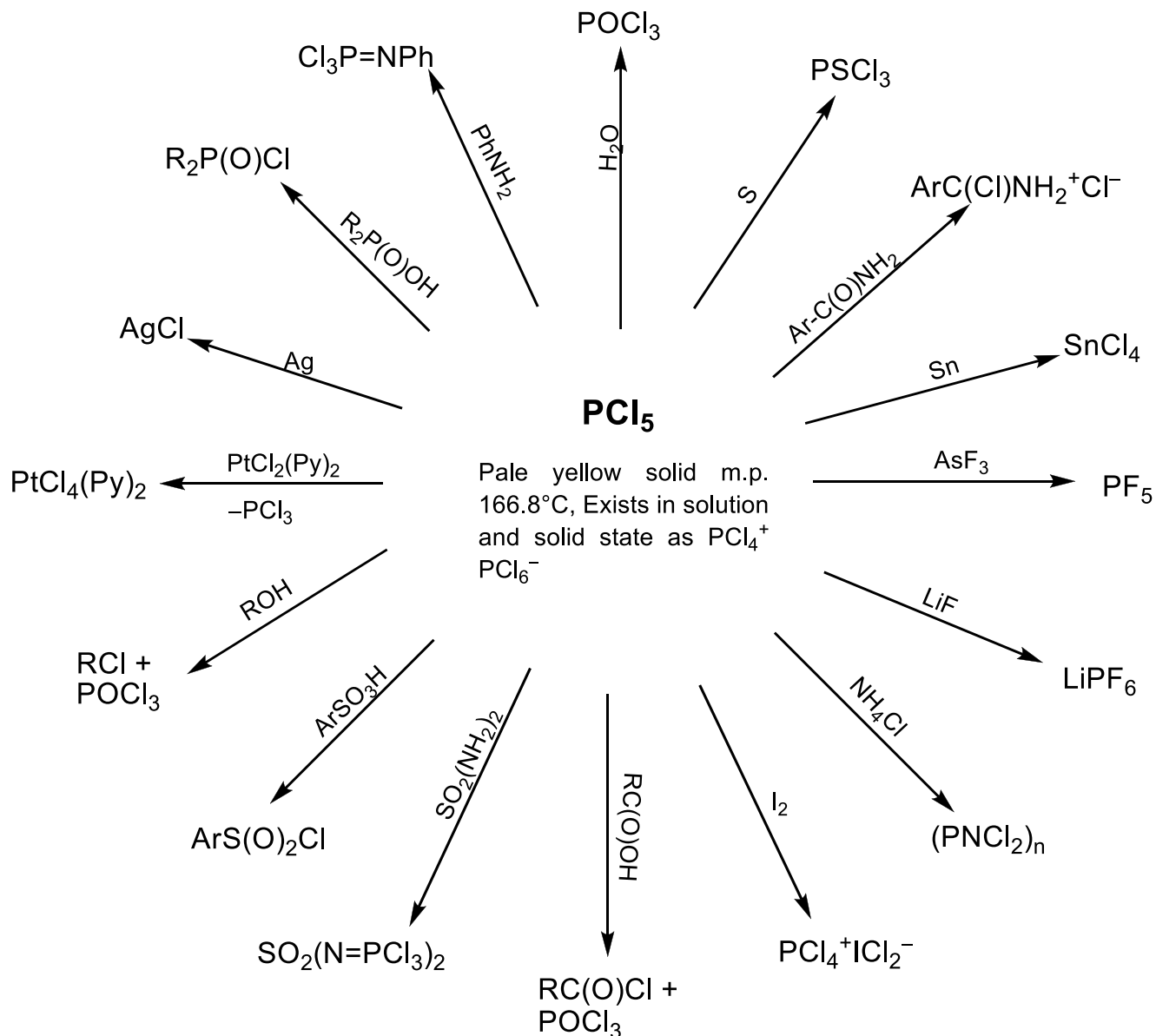
Glyphosate synthesis



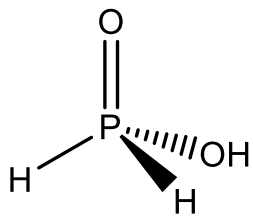


PCl_4^+ and PCl_6^- gives peaks at +86 and -295 ppm respectively with 85% H_3PO_4 as reference

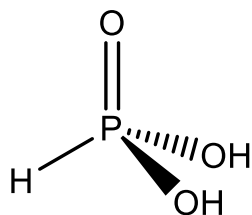
Oxidative chlorination & Substitutive chlorination



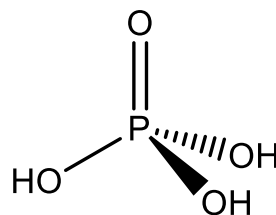
Phosphorus oxyacids



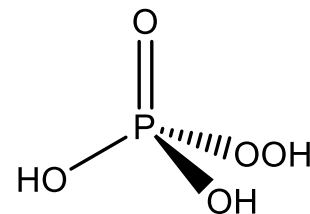
Hypophosphorous acid
(+1)
(Phosphinic acid)



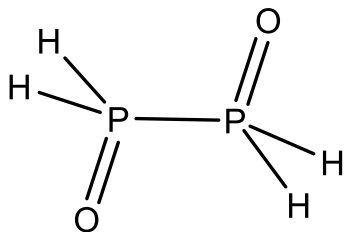
Orthophosphorous acid
(+3)
(Phosphonic acid)



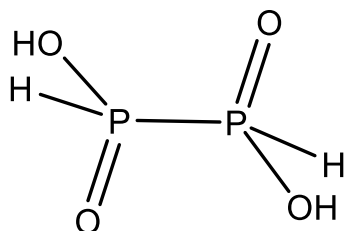
Orthophosphoric acid
(+5)



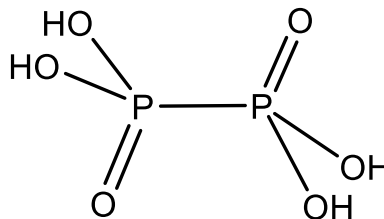
Peroxophosphoric acid
(+5)



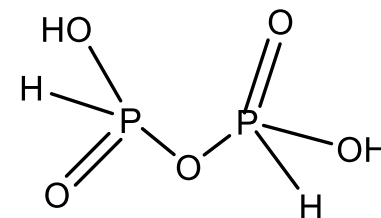
Hypodiphosphorus acid
(0)



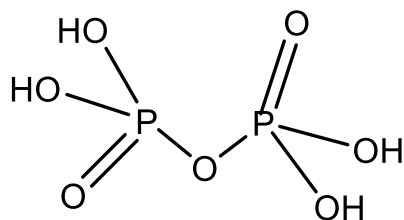
Hypodiphosphonic acid
(+2)



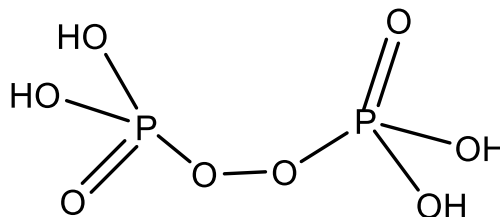
Hypodiphosphoric acid
(+4)



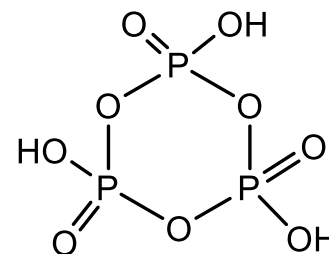
Diphosphonic acid
(+3)



Pyrophosphoric acid
(Diphosphoric acid)
(+5)



Peroxodiphosphoric acid
(+5)

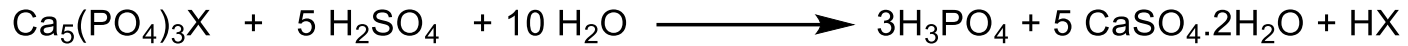


Cyclotrimetaphosphoric acid
(+5)

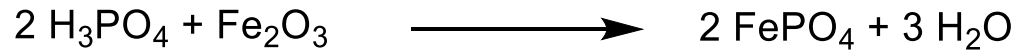
Reaction of white phosphorus with excess of pure O_2 resulted in compound W. Compound W on hydrolysis gave compound X. Compound X on heating about $200-250\text{ }^\circ\text{C}$ gave compound Y. Further heating of X to about $300-400\text{ }^\circ\text{C}$ gave a cyclic compound Z. Identify all compounds and draw structures of compounds Y and Z. The number of phosphorus atoms per molecule in compounds W, X, Y and Z fall in the range 1-4.

H_3PO_2	+3 formal oxidation state of P
H_3PO_3	Presence of P-P bond but not reducing
H_3PO_4	+2 formal oxidation state of P
$H_4P_2O_6$	Sodium tripolyphosphate synthesis
$H_4P_2O_7$	Contains peroxo bond
$H_4P_2O_4$	Electroless nickel plating
	Pyrophosphoric acid

Orthophosphoric acid: synthesis and uses



X= OH ; Hydroxyapatite X=F; Fluorapatite



As arrest remover

dentistry phosphoric acid is used as an etching solution.

It is also used as a solution for anodizing,

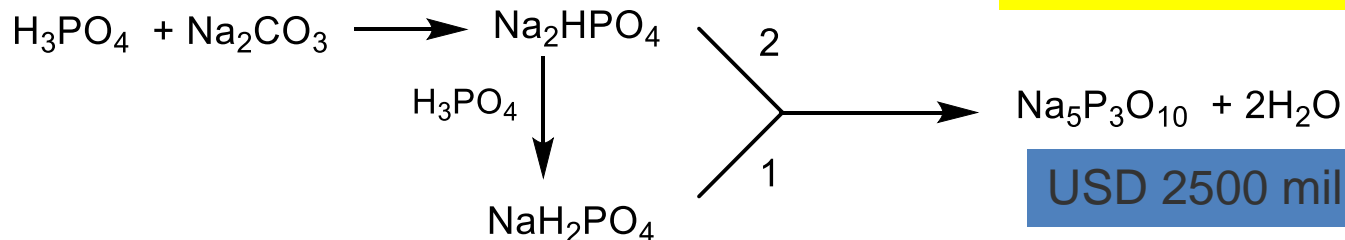
as a buffer agent, as an electrolyte in fuel cells,

as a catalyst in many organic reactions,

a pH adjuster in skin-care products

as a sanitizing agent in dairy and brewery industry

Sodium tripolyphosphate (STPP) is the **most common phosphate additive in detergent powder**



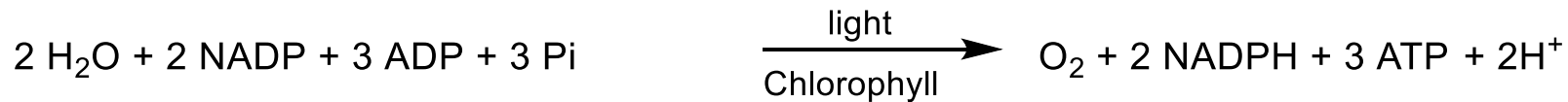
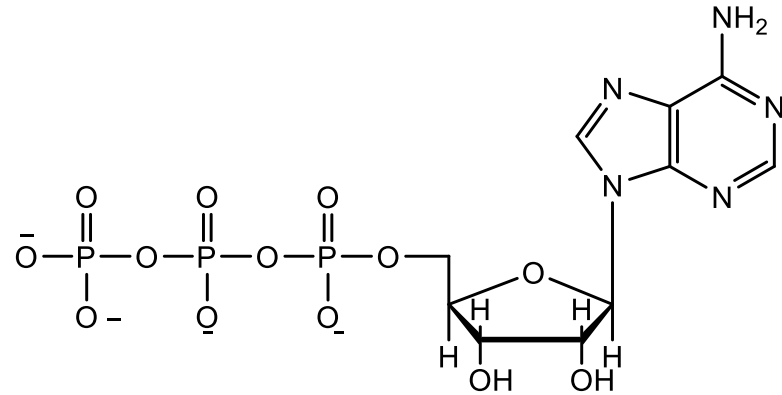
It is a preservative for poultry, meat, and seafood. It is also added to cheese.

USD 2500 million by 2023

Adenosine triphosphate

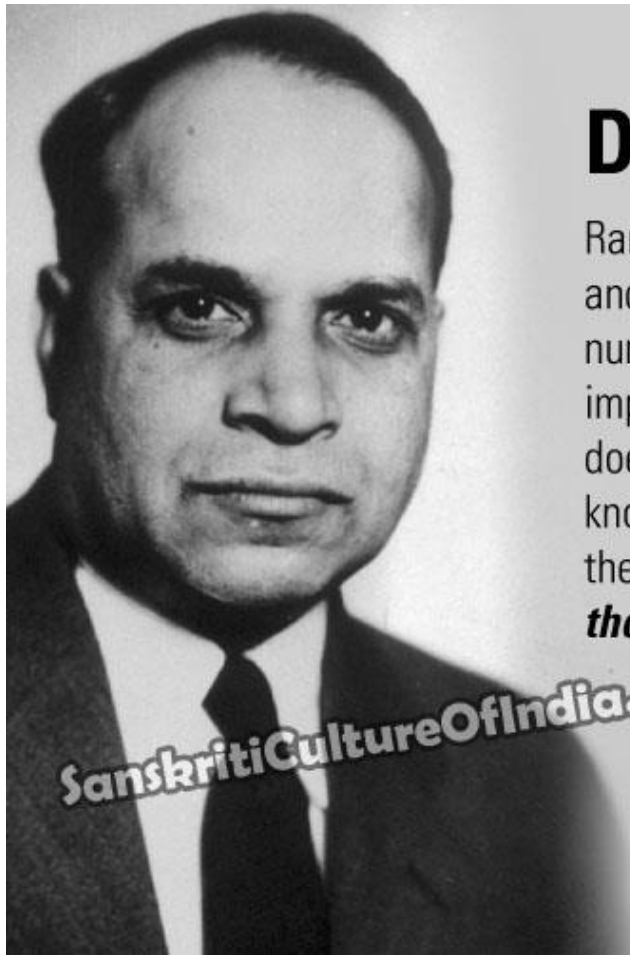
1929 Karl Lohmann: *Naturwissenschaften*

1929 Fiske & Subbarow: *Science*



The energy used by human cells requires the hydrolysis of 100 to 150 moles of ATP on a daily basis. There is only about 5g of ATP in the entire human body. Up to 40 kg equivalent of ATP is used in 24 hours. In human beings ATP molecules are recycled upto 750 times per day.





Dr. Yellapragada Subba Rao

Rarely, extremely rarely, a person comes on the world scene and transforms science and our lives by making a large number of major discoveries in – and otherwise makes important contributions to – more than one basic field and does not only not get a Nobel Prize but does not get to be known by name to most people, including scientists around the world. ***Such an individual is perhaps born once in a thousand years or more.***

SanskritiCultureOfIndia.com

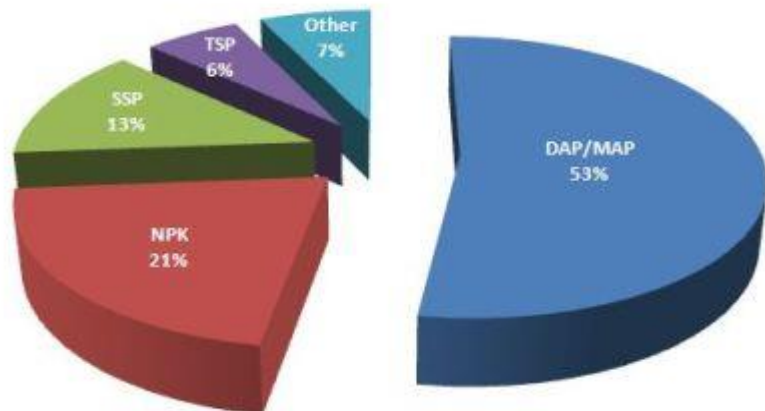
"You've probably never heard of Dr. Yellapragada Subba Rao, yet because he lived you may be well and alive today; because he lived you may live longer".

-American author, Doron K. Antrim

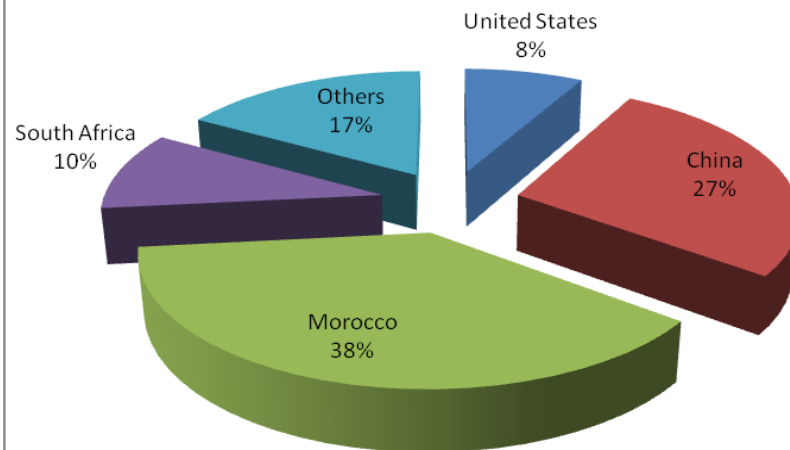
While working with Fiske, his mentor at Harvard Medical School, he made many fundamental and path breaking discoveries other than that of ATP. These include synthesis of phosphacreatine which replenishes ATP while resting, methotrexate the first anticancer drug, folic acid (vitamin B₉), many antibiotics such as aureomycin, the first tetracycline and Hetrazan, the most widely used drug against filariasis which leads to the deformity causing elephantiasis. The Fiske-SubbaRow method of colorimetric estimating phosphorus is still one of the best methods and is in the top 100 cited scientific articles ever with more than 20,000 citations. Died at 53 yrs

Chemical Name (Short form)	Industrial Name	synthesis	Major Uses
Mono ammonium phosphate MAP	Mono ammonium phosphate	$\text{NH}_3 + \text{H}_3\text{PO}_4 \longrightarrow (\text{NH}_4)\text{H}_2\text{PO}_4$	Fertilizer 11-48-00
Diammonium phosphate DAP	Diammonium phosphate	$2 \text{NH}_3 + \text{H}_3\text{PO}_4 \longrightarrow (\text{NH}_4)_2\text{HPO}_4$	Fertilizer 18-46-00
Mono calcium phosphate MCP(TSP)	Triple superphosphate	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 7 \text{H}_3\text{PO}_4 \longrightarrow 5 \text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{HF}$	Fertilizer 00-44-00
Mono calcium phosphate + gypsum SSP	Single superphosphate	$\text{Ca}_3(\text{PO}_4)_2 + 2 \text{H}_2\text{SO}_4 \longrightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2 \text{CaSO}_4$	Fertilizer 00-17-00
	superphosphate	$\text{Ca}(\text{OH})_2 + 2 \text{H}_3\text{PO}_4 \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2 \text{H}_2\text{O}$	Leavening agent
Calcium monohydrogen phosphate	Dicalcium phosphate	$\begin{aligned} \text{CaCl}_2 + \text{H}_3\text{PO}_4 + 2 \text{NaOH} &\rightarrow \text{CaHPO}_4 + 2 \text{NaCl} + 2 \text{H}_2\text{O} \\ \text{H}_3\text{PO}_4 + \text{Ca}(\text{OH})_2 &\rightarrow \text{CaHPO}_4 \end{aligned}$	Dietary, tableting agent, poultry feed

Phosphate Fertilizer Products



Global Reserves (15Gt: R/P=89)



Phosphate Fertilizers - Consumption (millions mt nutrients)

	1970	1980	1990	2000	2010	2020
World	21,117	31,700	35,901	32,472	45,442	57,000
China	949	2,744	5,853	8,610	16,943	22,400
India	541	1,231	3,259	4,215	8,017	14,600
USA	4,346	4,930	3,811	3,862	3,883	3,000
Brazil	417	1,988	1,202	2,338	3,385	4,300
Australia	757	797	579	1,107	946	600
Pakistan	30	226	389	675	757	650
Canada	326	635	578	571	620	500
Turkey	176	619	625	629	515	450
Japan	656	690	690	583	424	400
France	1,809	1,773	1,349	795	295	300
Others	11,108	16,066	17,568	9,088	9,658	9,800

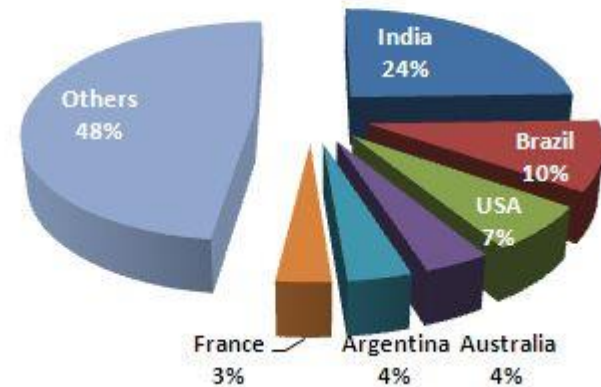
Phosphate Fertilizer Production

2010 = 46 million mt nutrients



Phosphate Fertilizer Imports

2010 = 15 million mt nutrients



Phosphate Fertilizers - Imports (millions mt nutrients)

	1970	1980	1990	2000	2010	2020
World	2,667	6,618	9,835	12,353	15,093	16,000
India	32	452	1,016	423	3,699	4,500
Brazil	215	409	115	1,120	1,528	1,500
USA	257	226	42	196	990	1,100
Australia	16	29	303	661	581	500
Argentina	45	50	43	341	561	100
France	340	647	777	510	481	500
Canada	18	133	248	443	412	250
Pakistan	39	302	253	369	310	300
Italy	133	363	470	402	227	250
China	2	367	1,669	2,212	35	
Others	1,570	3,641	4,901	5,677	6,269	7,000

Phosphate and sulphate based fire retardants



main components of Phos-Chek retardants include ammonium polyphosphate, diammonium phosphate, diammonium sulfate, monoammonium phosphate, attapulgus clay, red dye, and trade secret performance additives



Phosphorus nitrogen compounds

Phosphazenes

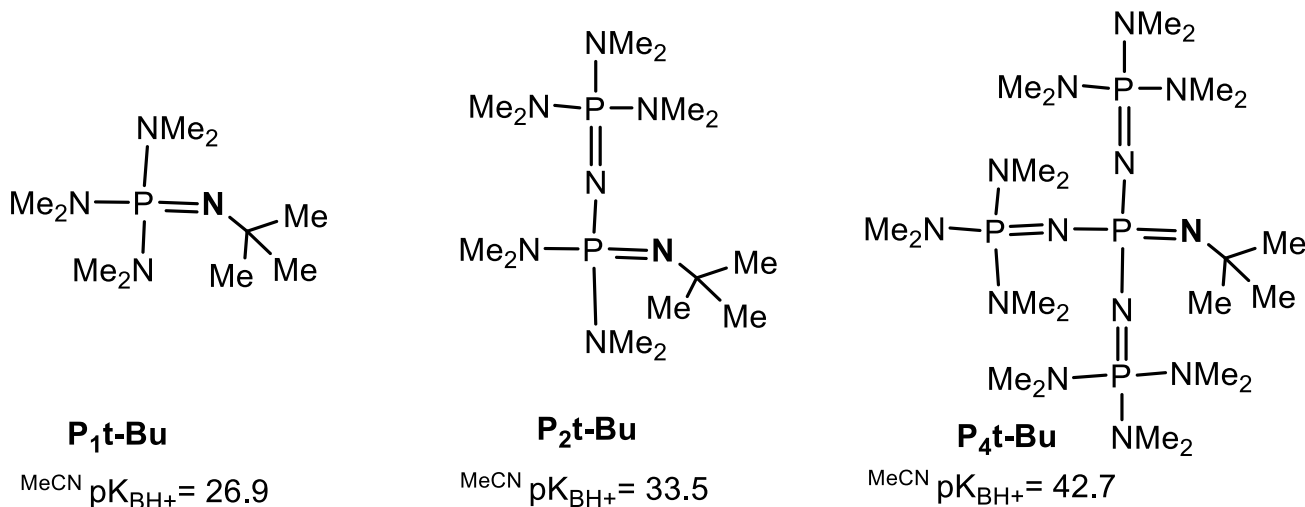


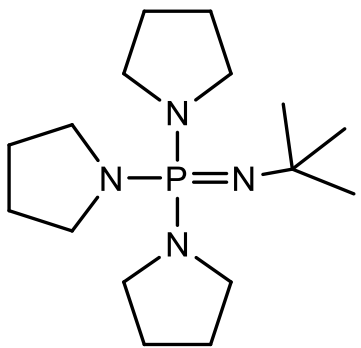
Phosphazenes are compound having pentavalent tetracoordinated phosphorus bound to nitrogen through a double bond. In general, they can be prepared by two different synthetic methods namely the Staudinger method and the Kirsanov method. In the Staudinger method a trivalent phosphorus compound is converted to the phosphazene unit often using an azide. In the Kirsanov method one uses a pentavalent phosphorus halide and react the same with ammonia or primary amines to realize the phosphazene unit.

Phosphazene superbases

Non ionic and non-nucleophilic bases also have an important role in base catalyzed organic reactions. These should be bulky so that the proton can attach to the basic center but no alkylation or complex formation should happen. NaHMDS & KHMDS are examples of alkali-metal based non nucleophilic strong bases. There are also many examples of bulky amines which are non nucleophilic bases such as DBU, Hünigs base (N,N diisopropyl ethyl amine). However, the lesser basicity and the instability of some of these bases toward O₂, hydrolysis, and electrophilic attack (e.g. carbonyls) limit their use

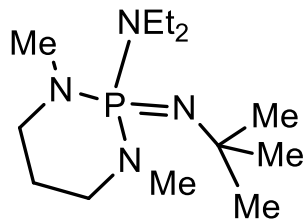
Reinhard Schwesinger in 1987 came out with a set of peralkylated polyamino acyclic phosphazenes, which are extremely strong, uncharged non-nucleophilic bases with a high level of steric hindrance. These compounds, now also known as **Schwesinger bases** or **phosphazene superbases** can be fine tuned to obtain a range of basicities and has been applied to many organic reactions with excellent success.





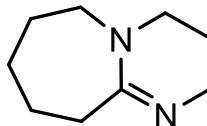
P₁tBu(Pyrr)

MeCN $pK_{BH^+} = 28.4$



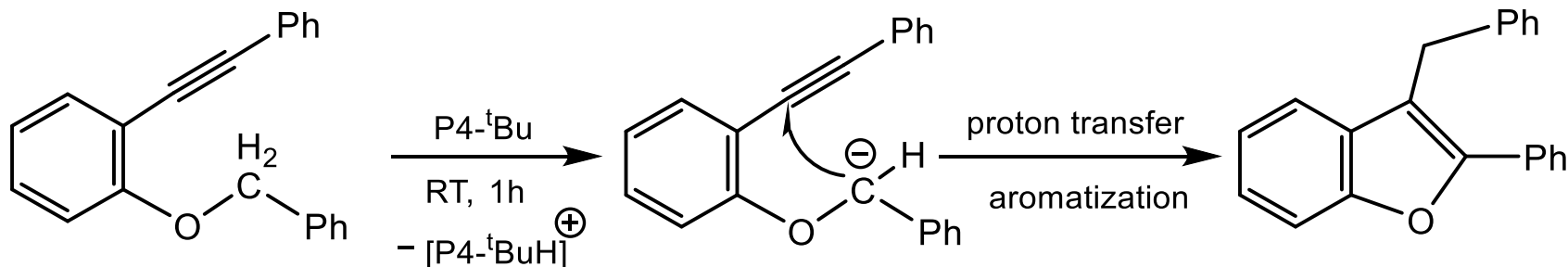
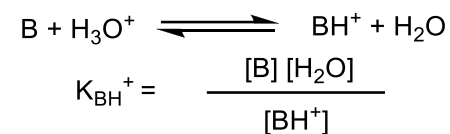
BEMP

MeCN $pK_{BH^+} = 27.6$



DBU

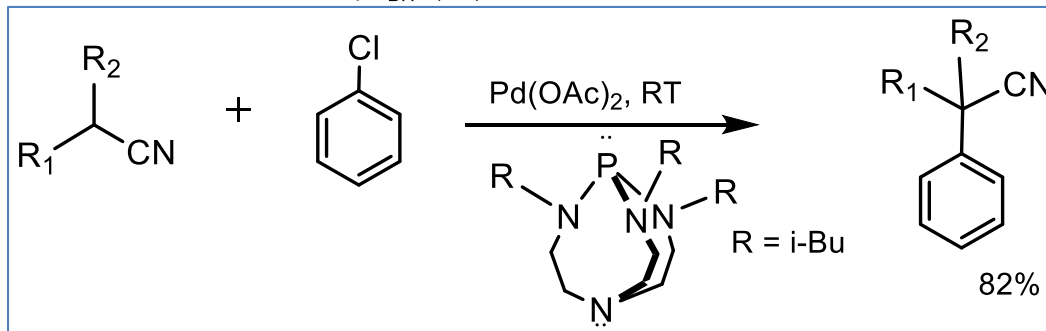
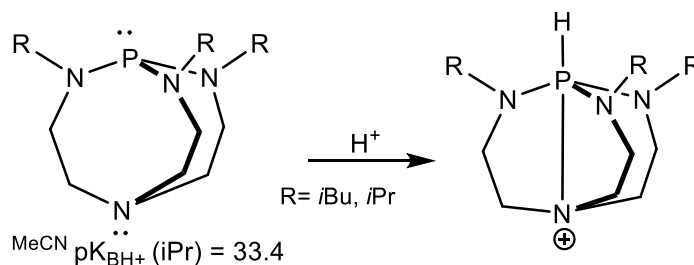
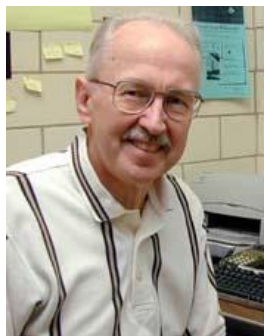
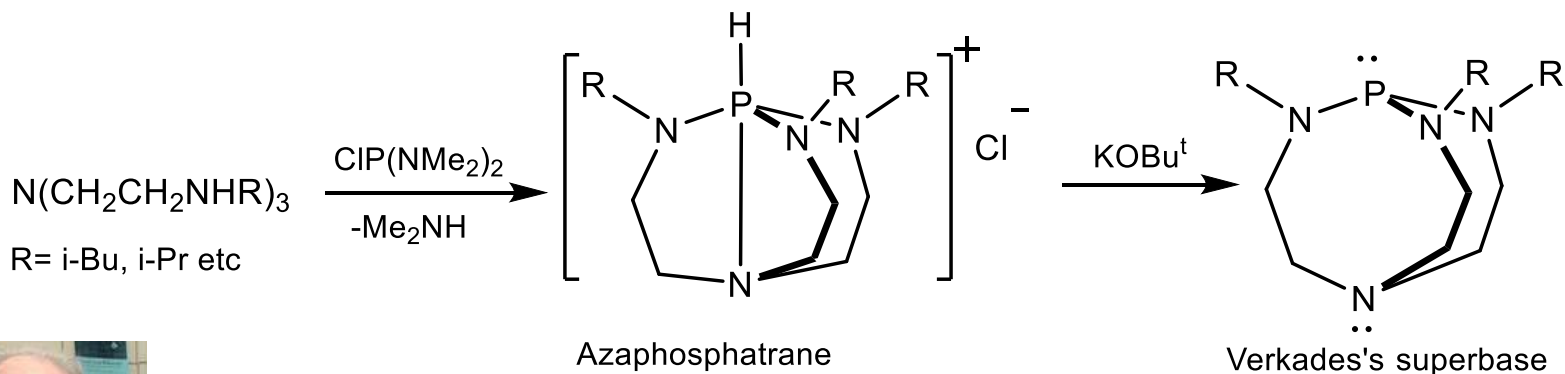
$H_2O pK_a = 13.5$
MeCN $pK_{BH^+} = 24.3$



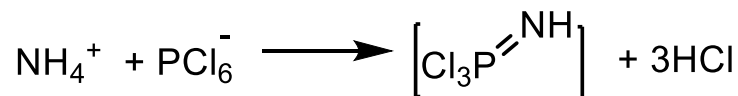
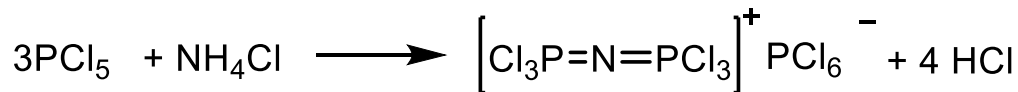
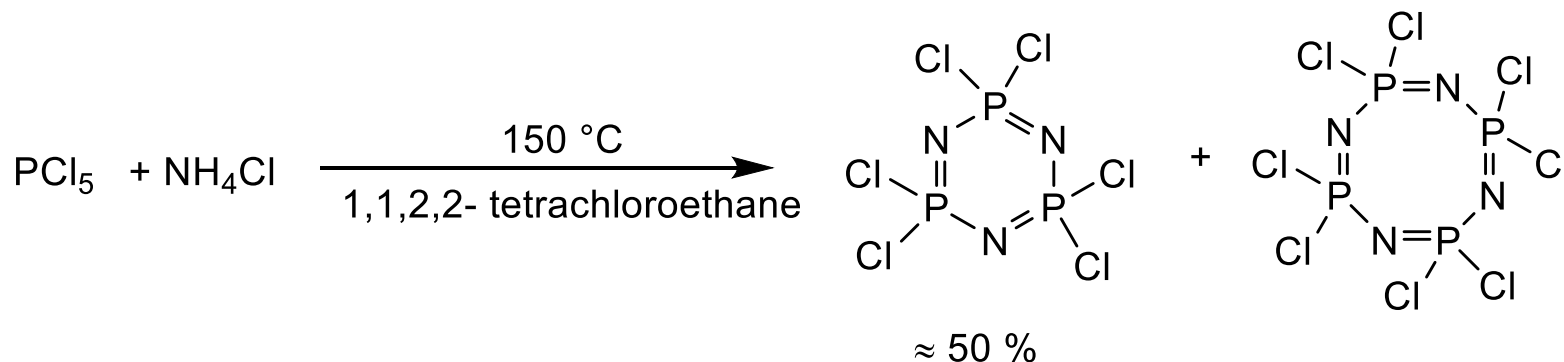
The above reaction does not proceed with n-BuLi, NaOBu^t or P₁-^tBu bases

Verkade's superbases (Proazaphosphatranes)

Verkade's superbases which are ball shaped proazaphosphatranes, are very strong bases due to the extraordinary stability of their protonated forms where the phosphorus center is stabilized by the distal nitrogen as well. Verkade's bases are about 8 orders of magnitude stronger as a Lewis base than any amine known, including the well known diazabicyclo 5,4,0 undecane (DBU) and diazabicyclo 4,3,1 non-5-ene (DBN).

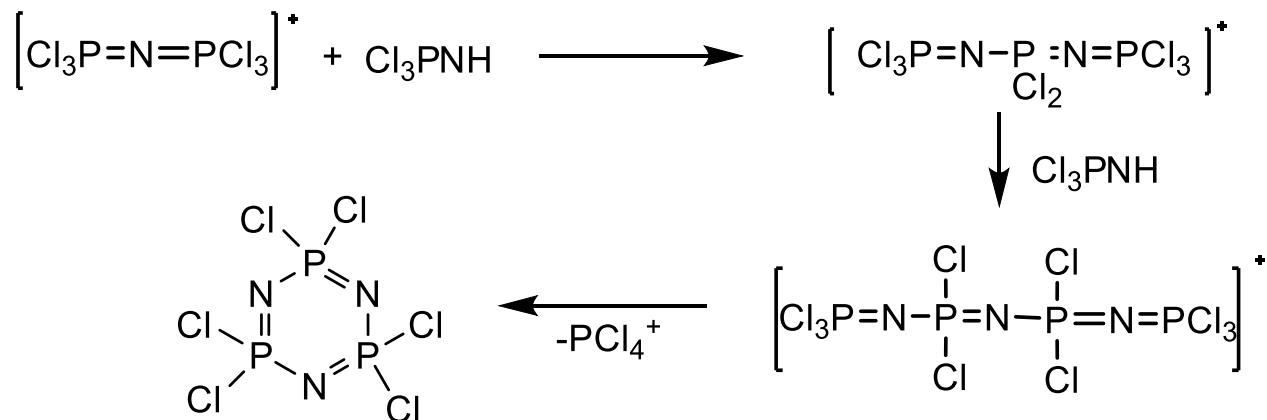


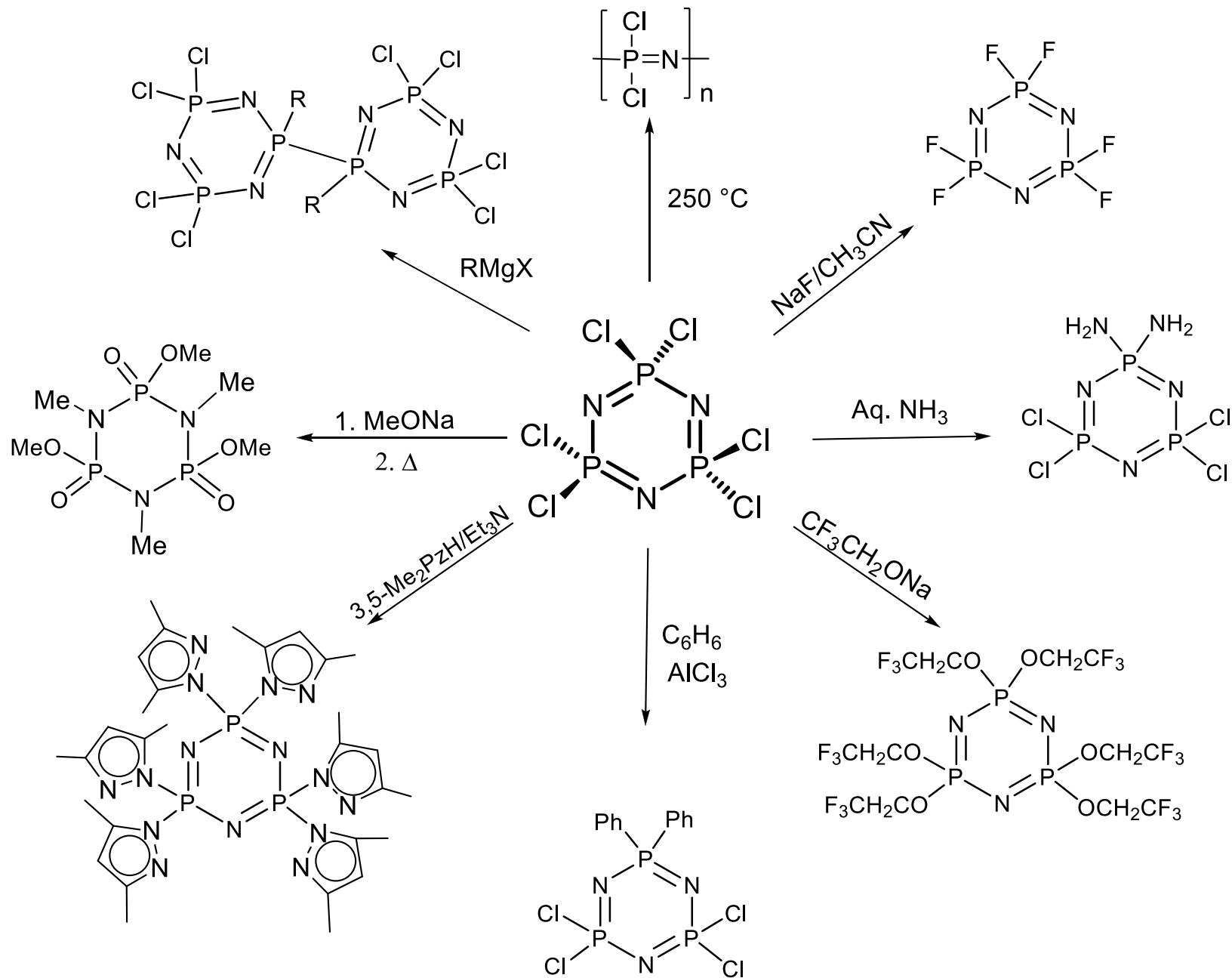
Cyclophosphazenes



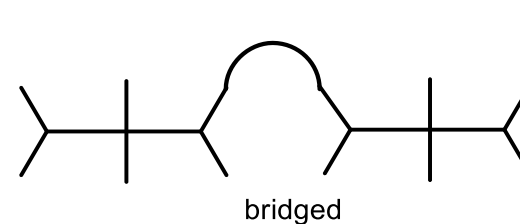
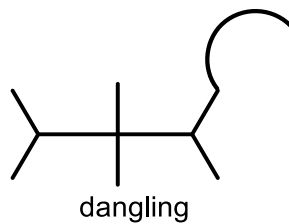
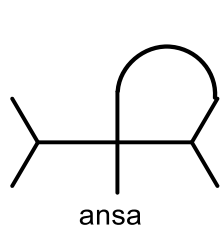
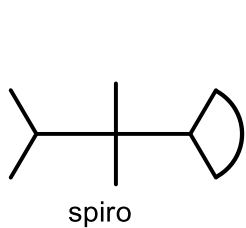
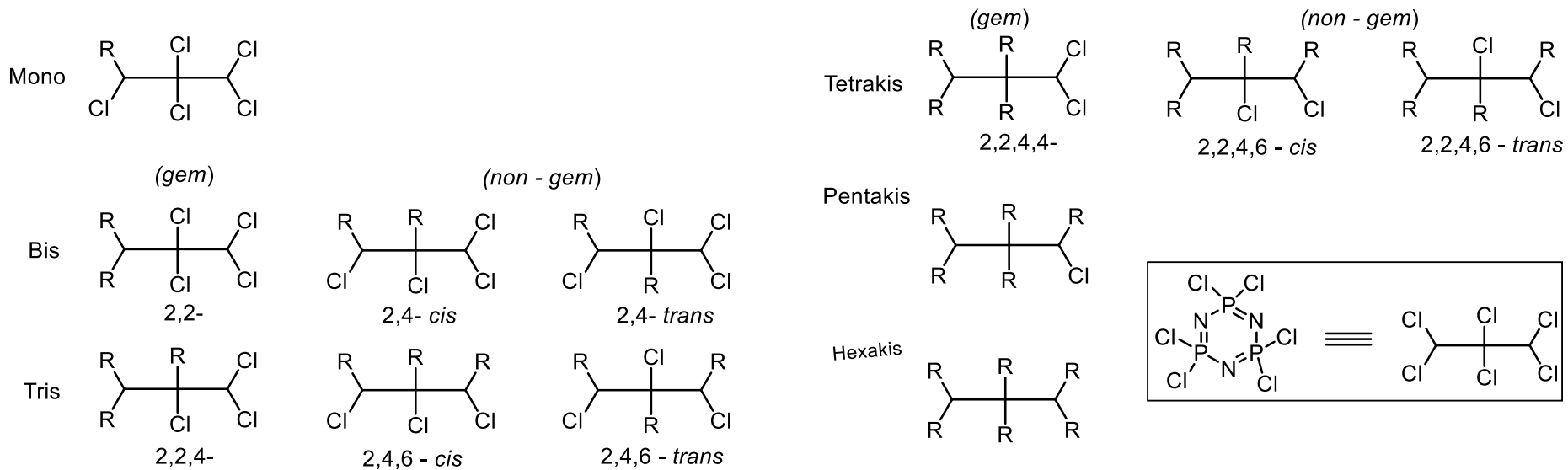
Cl_3PNH has not been isolated but analogous compound

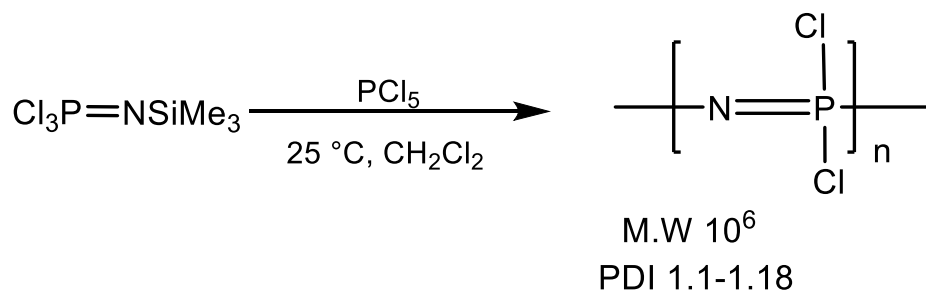
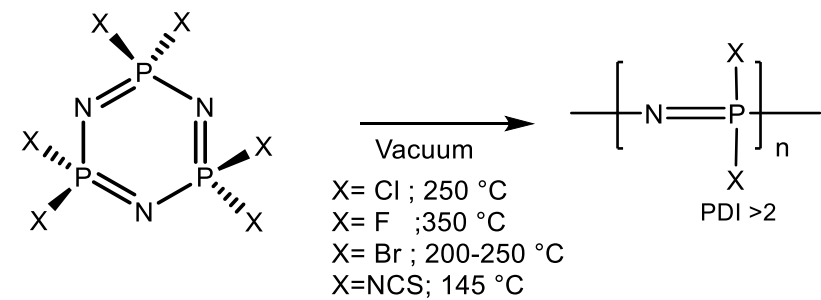
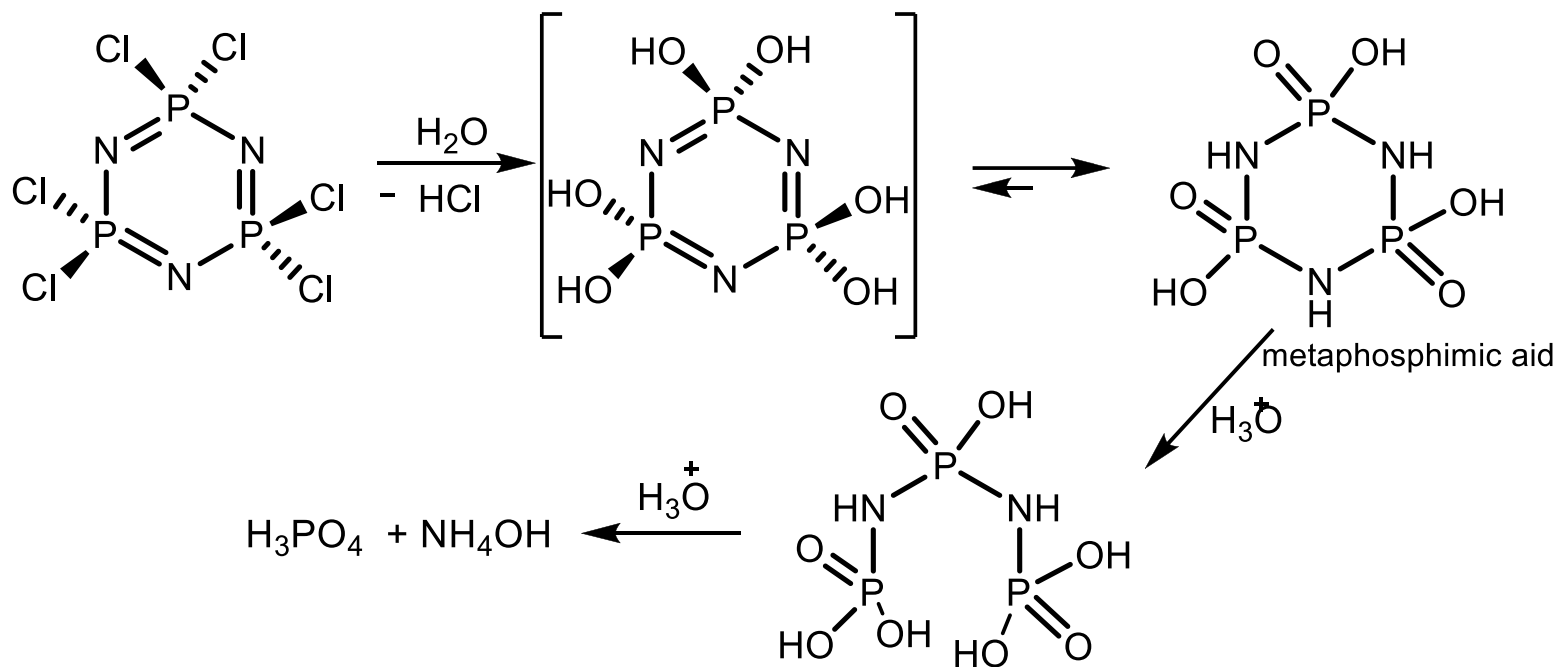
$\text{Cl}_3\text{PNSiMe}_3$ has been made and characterized

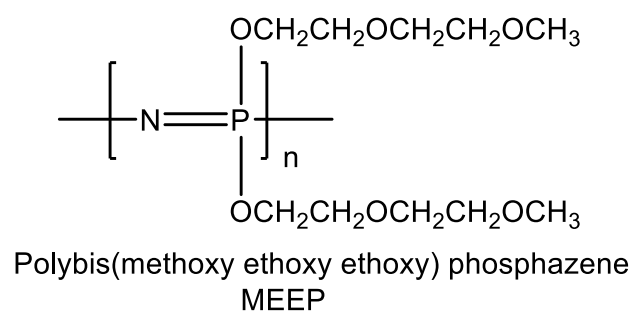
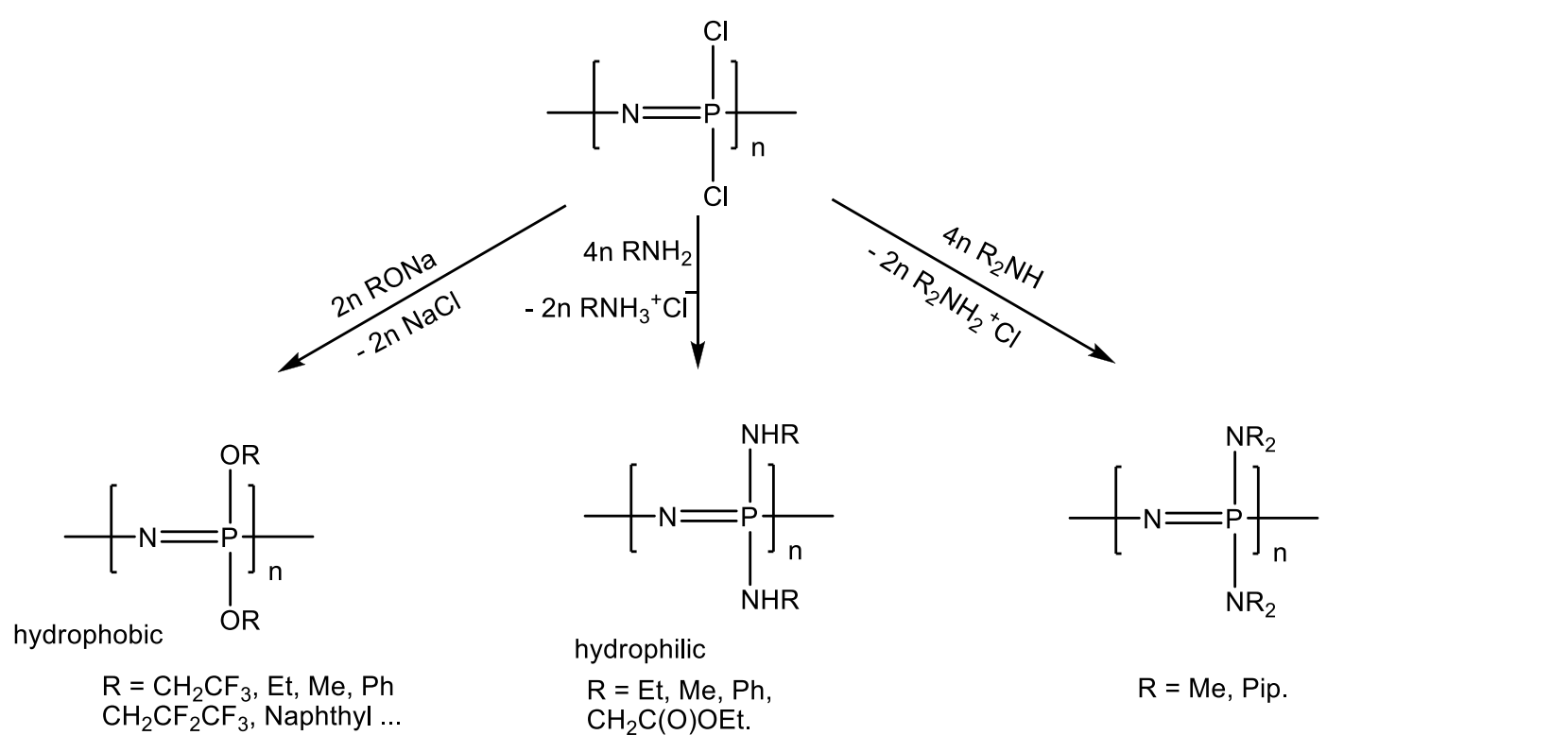




Isomerism in cyclophosphazenes







Polymer electrolyte for lithium batteries

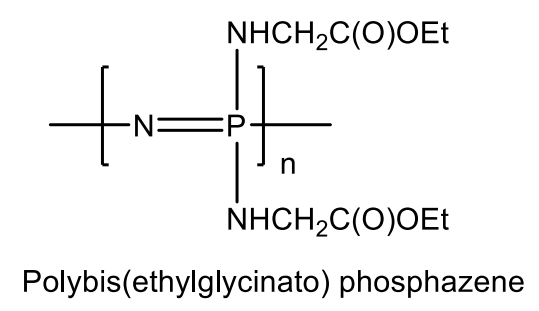
Flexible at low temp (T_g = -83 °C)

Conductivity = 3x10⁻⁵ S/cm at 25 °C

Conductivity higher than poly ethylene oxide

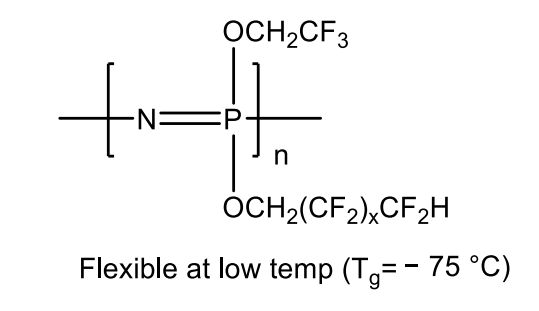
Unlike PEO it is fire resistant

Unlike PEO need not be heated for achieving higher conductivity



Bio erodable polymer

The NH unit bound to P forms hydrogen bonds with water facilitating slow hydrolysis. Products of hydrolysis are non toxic namely EtOH, H₂NCH₂C(O)OH, H₃PO₄ and NH₄OH

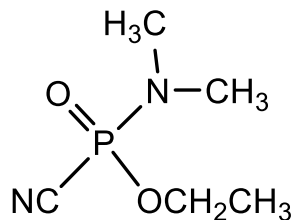


Bio inert polymer

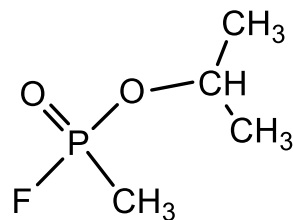
Impenetrable barrier for silicone fluid gels in mammary implants, FDA approved for soft denture lining application. X ray opaque and resistant to bacterial and fungal colonization. For artificial valves for biological use

Nerve gases and their activity

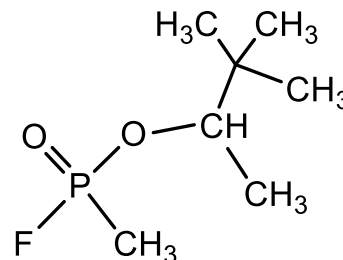
German Origin: G series (Gerhard Schrader, IG Farben)



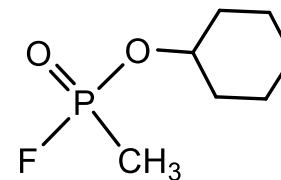
TABUN
GA



SARIN
GB

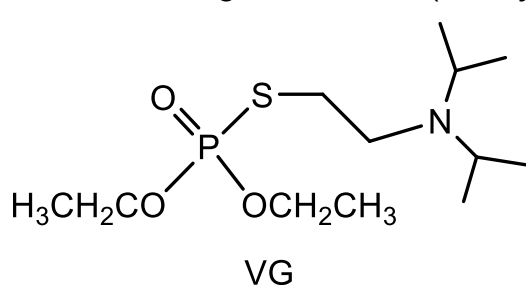


SOMAN
GD

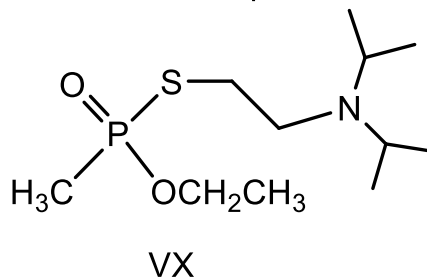


CYCLOSARIN
GF

British Origin: V series (Ranjit Ghosh, ICI, Plant protection lab))

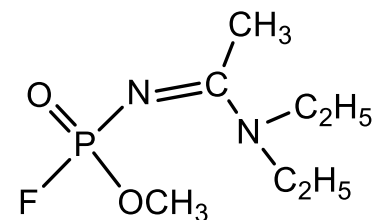


VG



VX

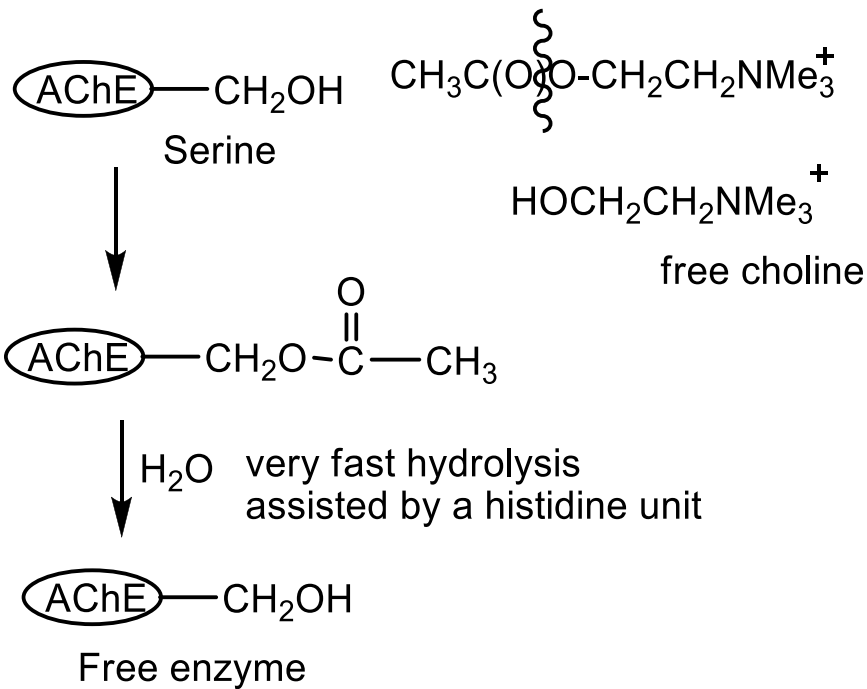
Russian Origin: Novichok



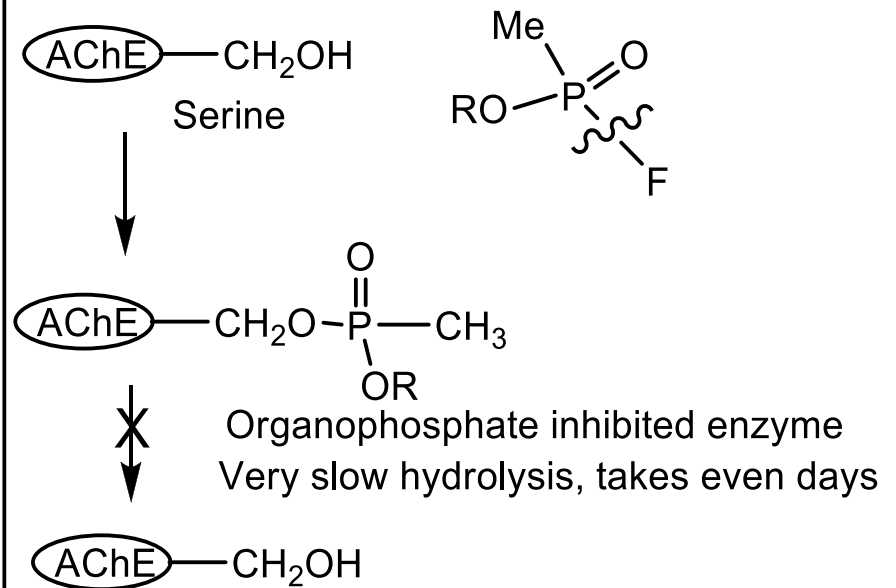
On 4 March 2018, [Sergei Skripal](#), a former Russian military officer and double agent for the UK's [intelligence services](#), and his daughter Yulia Skripal were poisoned in [Salisbury](#), England, with a [Novichok nerve agent](#)

On 30 June 2018, [a similar poisoning](#) of two British nationals in [Amesbury](#), seven miles from Salisbury, involved the same nerve agent. A man found the nerve agent in a perfume bottle, in a litter bin, somewhere in Salisbury and gave it to a woman who sprayed it on her wrist. The woman, Dawn Sturgess, fell ill within 15 minutes and died on 8 July.

Normal Functioning of AChE

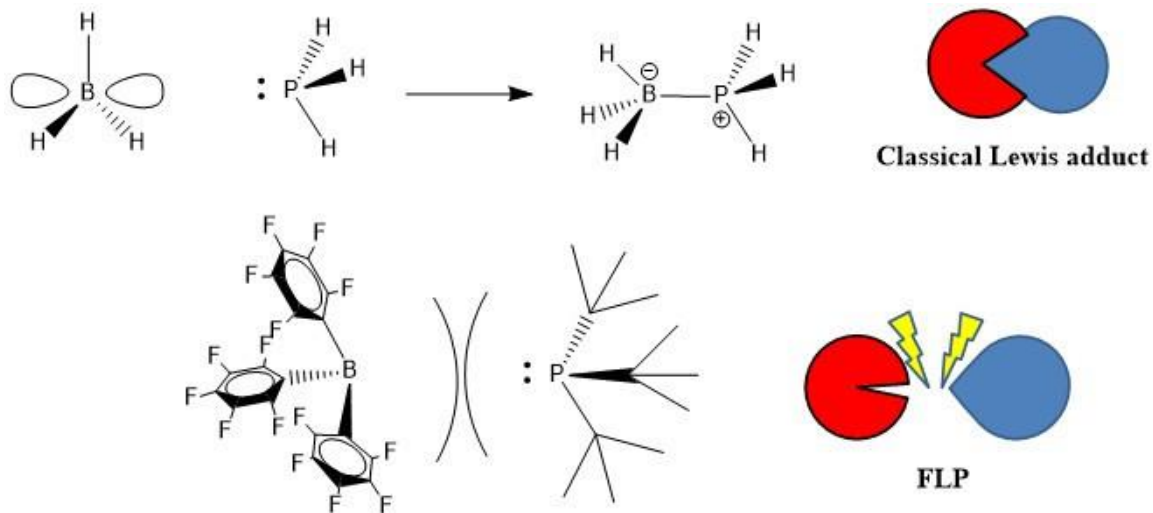


Deactivation of AChE by organophosphate

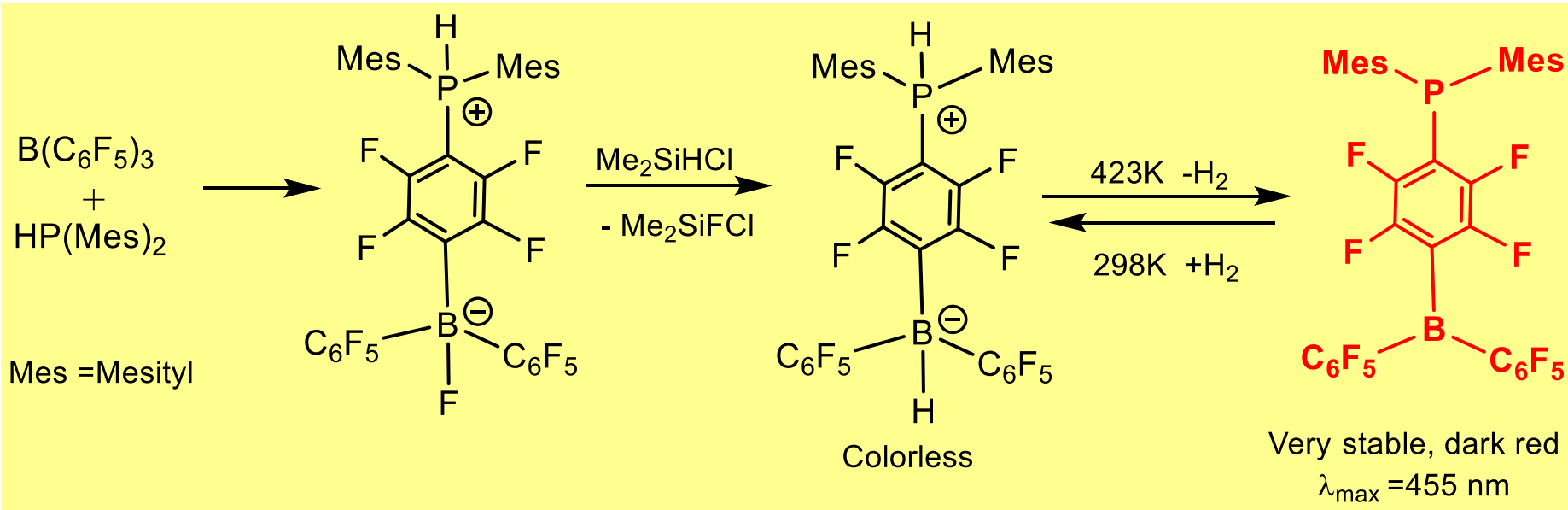


Frustrated Lewis Pairs

Frustrated Lewis pairs (FLP's) are defined as combinations of sterically hindered Lewis acid- Lewis base pairs with unquenched acidity and basicity. Such combinations or pairs have been found to be highly effective in activating small molecules such as H_2 , CO_2 , N_2O , SO_2 , alkenes and alkynes.



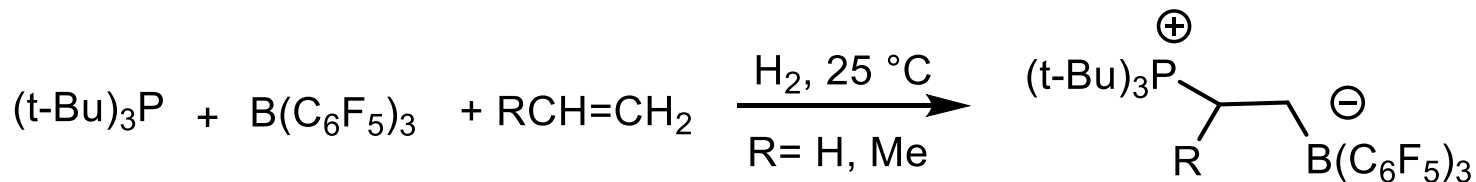
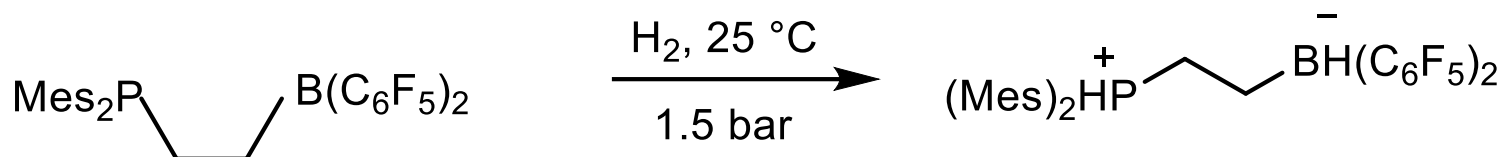
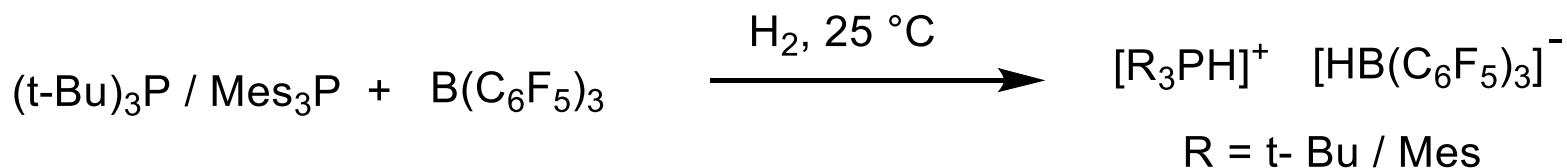
The term 'Frustrated Lewis Pairs' has been first coined by Douglas Stephan of University of Toronto in 2006 when he showed that combinations of sterically encumbered Lewis acid base pairs can be used for reversibly activating hydrogen gas. Among many uses the area shows great promise in the development of the first examples of hydrogenation catalysts where no metal is involved.



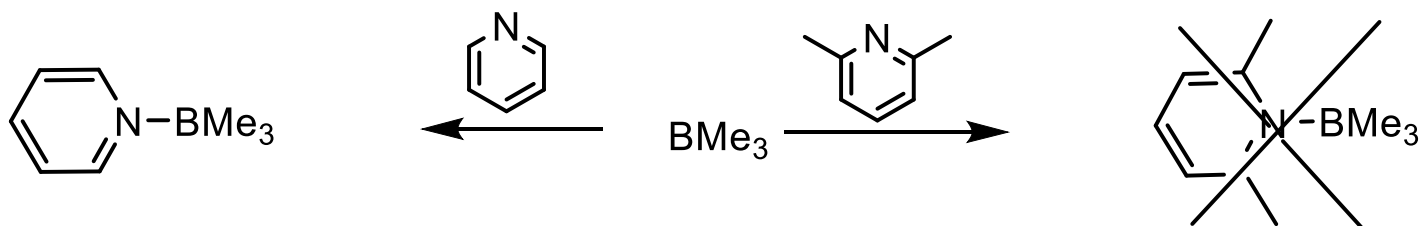
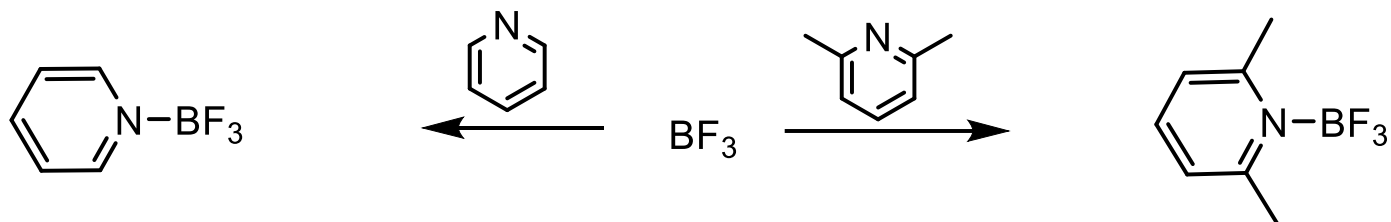
The landmark discovery involved reaction of $B(C_6F_5)_3$ with $HP(Mes)_2$ which resulted in a zwitterionic complex with a hydride unit on the phosphorus and fluoride on the boron. Replacement of the fluoride using Me_2SiHCl resulted in another colorless zwitterionic compound having a hydridic H on the phosphorus and protic H on the boron. A dark red colored aryl linked phosphine-borane species $Mes_2P-C_6F_4-B(C_6F_5)_2$ was obtained on heating this complex around $150^\circ C$ with the release of H_2 . Stephan showed that $Mes_2P-C_6F_4-B(C_6F_5)_2$ heterolytically cleaves H_2 giving back the colorless $Mes_2PH^+-C_6F_4-BH^-(C_6F_5)_2$. They had thus demonstrated the **first reversible metal free hydrogen activation**.

Stephan D W, Reversible, metal-free hydrogen activation, *Science*, 2006 Vol. 314, 1124.

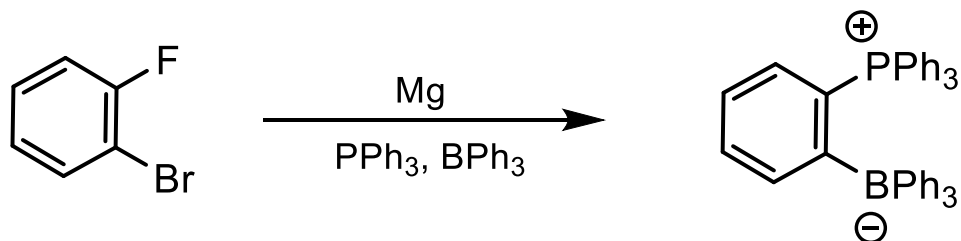
Later on, combinations of a sterically hindered phosphine base and strong Lewis acid or such a pair with a short alkyl chain connecting them were found to be equally good in bringing out the H₂ activation. Also, other molecules such as CO₂ and alkenes were activated by the FLP's



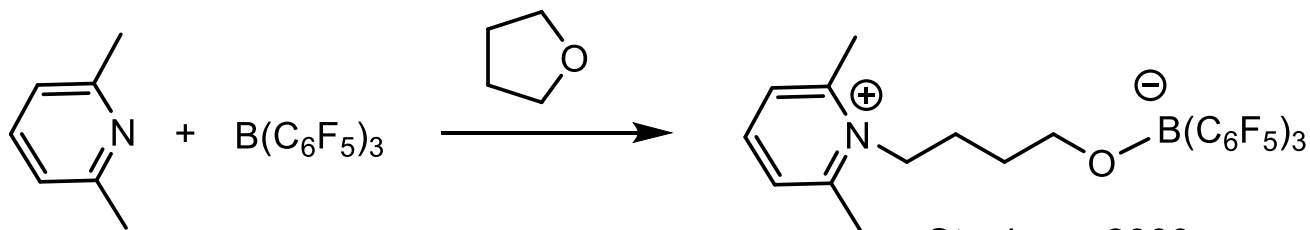
Historical background



H. C. Brown 1942



Wittig, 1959

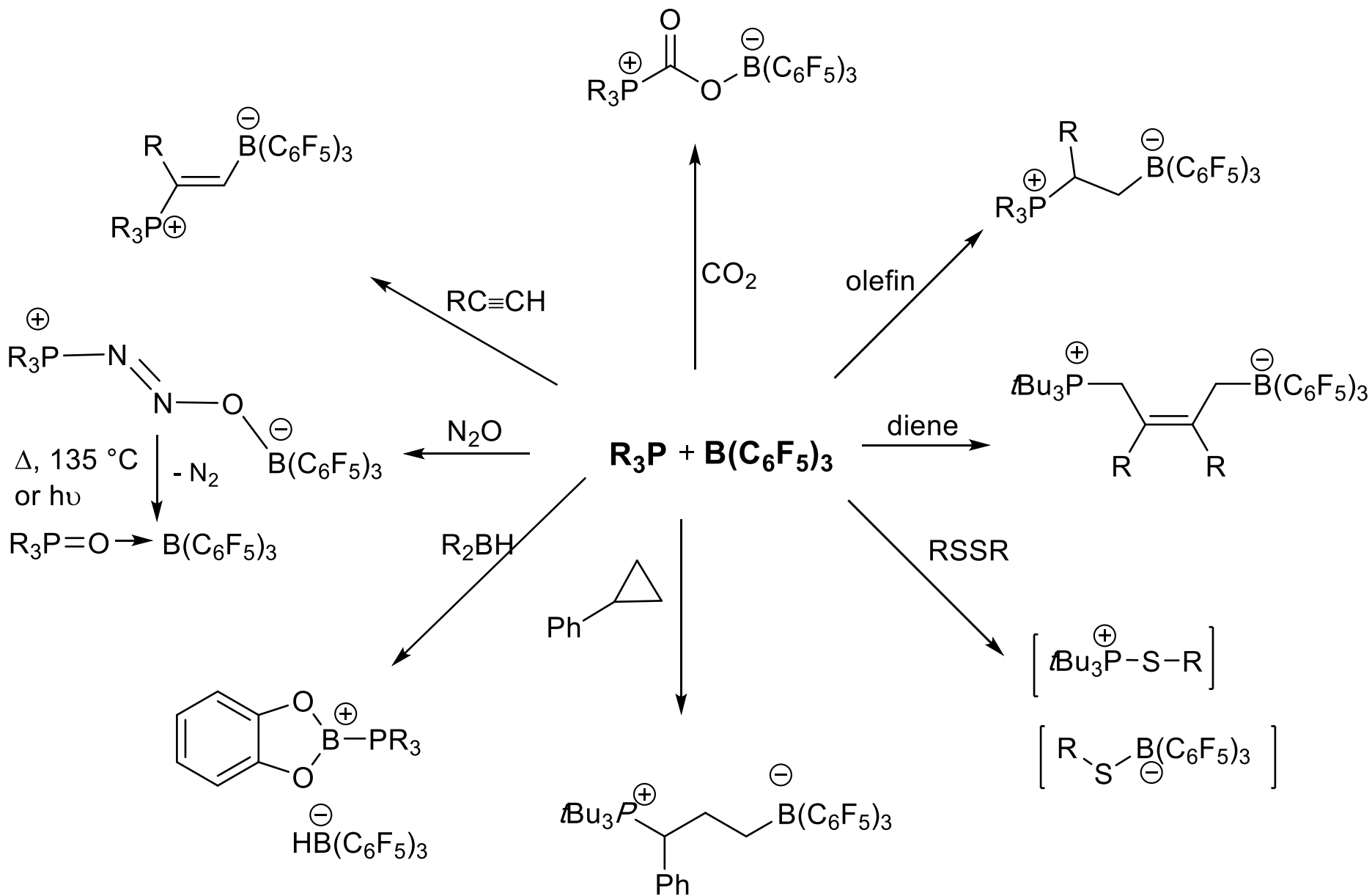


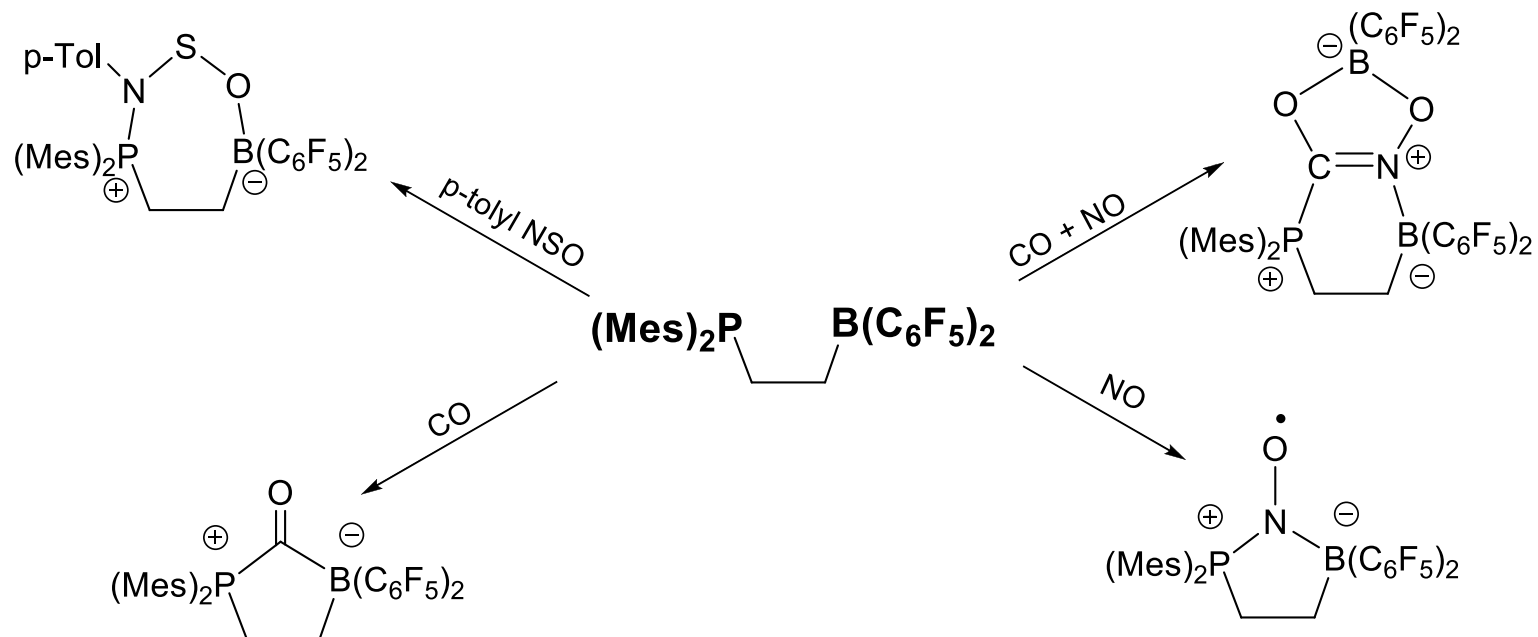
Stephan 2009

A standard and reliable way of measuring Lewis acidity is by using the fluoride ion affinity (FIA) which indicates the strength of a Lewis acid and the energy released when it combines with a fluoride ion. **FIA is defined as the negative of the enthalpy ΔH for the reaction of a Lewis acid (A) with fluoride ion (F^-) giving AF^- , all species in the gaseous form.** FIA values are obtained from quantum chemical calculations in isodesmic reactions. SbF_5 is the strongest conventional Lewis acid that is stable under normal conditions. Molecular Lewis acids which are stronger than monomeric SbF_5 in the gaseous phase are considered as Lewis superacids.

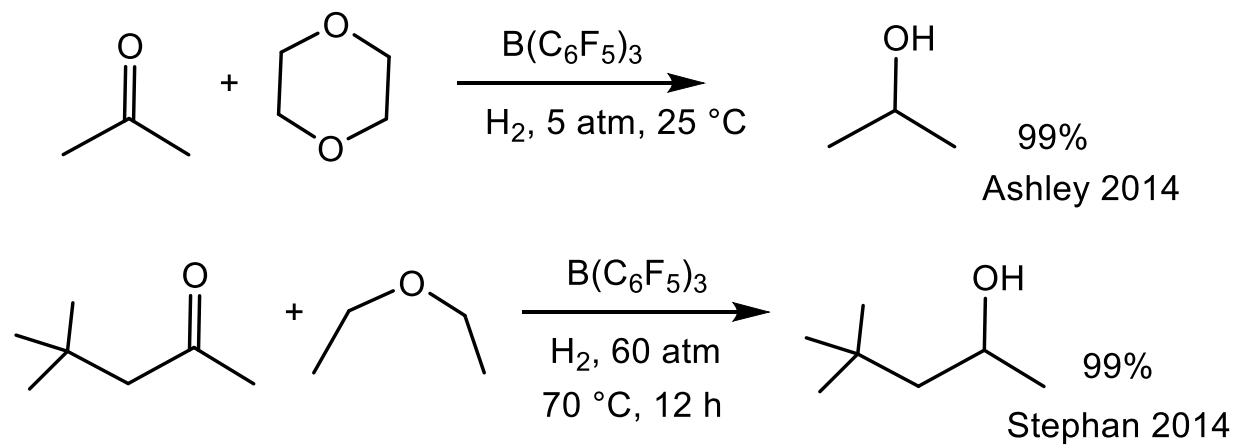
Lewis acid/anion	FIA	Lewis acid/anion	FIA
$CB_{11}F_{11} / CB_{11}F_{12}^-$	716	$Ga(C_6F_5)_3 / [FGa(C_6F_5)_3]^-$	447
$Sb(OTeF_5)_5 / [FSb(OTeF_5)_5]^-$	633	$B(C_6F_5)_3 / [FB(C_6F_5)_3]^-$	444
$B(CF_3)_3 / [FB(CF_3)_3]^-$	552	$BBr_3 / [FBBBr_3]^-$	433
$Al(C_6F_5)_3 / [FAl(C_6F_5)_3]^-$	530	$GaCl_3 / [FGaCl_3]^-$	431
$SbF_5 / [SbF_6]^-$	489	$BCl_3 / [FBCl_3]^-$	405
$AlCl_3 / [FAlCl_3]^-$	457	$PF_5 / [PF_6]^-$	394
$BI_3 / [FBI_3]^-$	448	$BF_3 / [BF_4]^-$	338

Small molecule activation

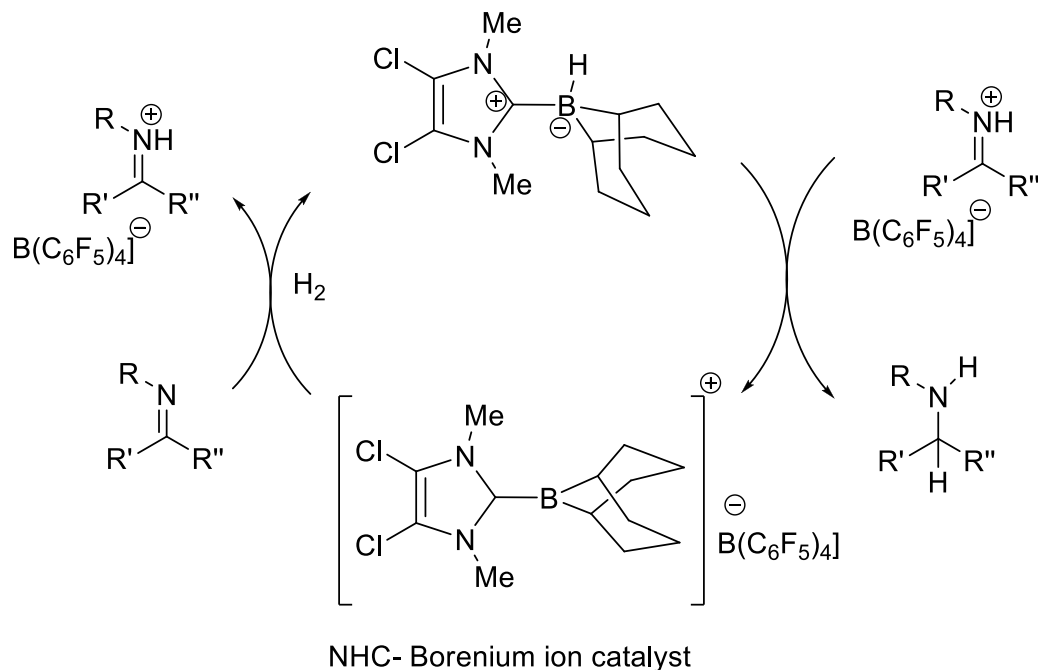




Reduction of ketones

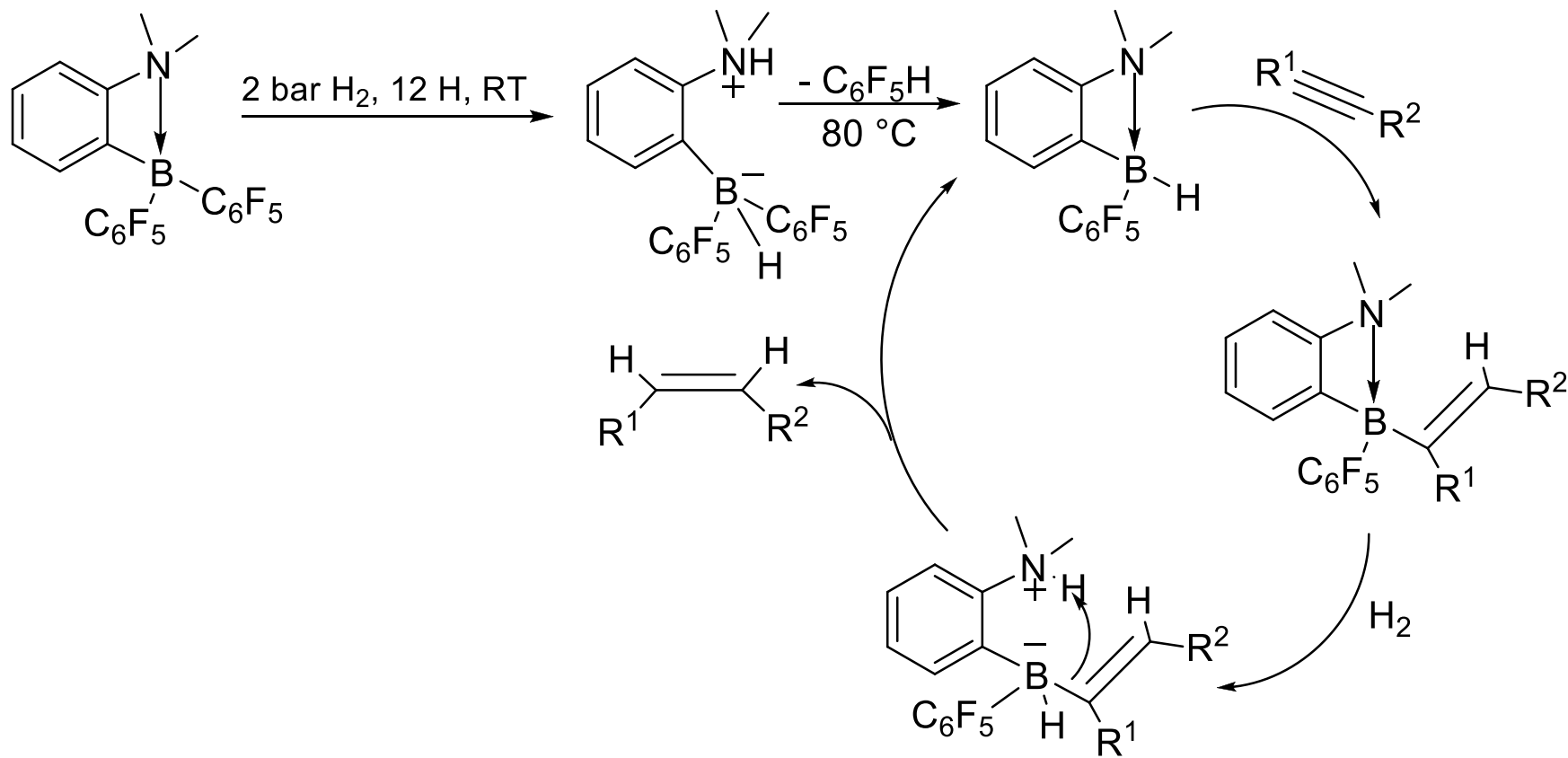


Efficiency as hydrogenation catalysts



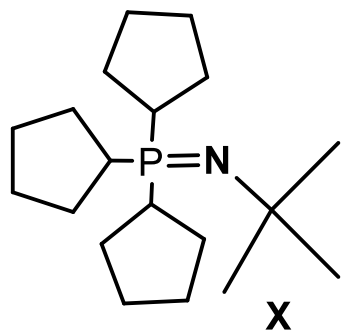
One of the well studied systems is the use of NHC borenium catalysts for metal free hydrogenation of imines as shown in the given catalytic cycle. A maximum turn over frequency (TOF) of 940 h^{-1} has been observed for the archetypal substrate N-benzylidene t-butylamine using the NHC borylenium catalyst having N-methyl and C-chloro substituents on the NHC ring. In comparison with traditional hydrogenation catalysts for hydrogenation of n-hexene, Wilkinson catalyst gave a TOF of 650 h^{-1} and $RuCl(PPh_3)_3$ 9000 h^{-1} . So FLP catalysts for hydrogenation should only be viewed as a complementary hydrogenation methodology that may find applications where trace metals need to be avoided completely

Catalytic alkyne hydrogenation to *cis* alkenes

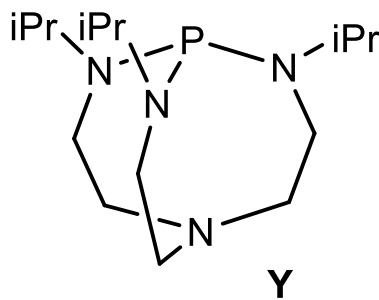
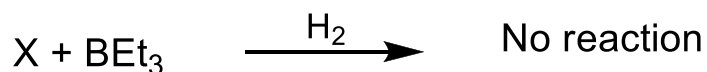
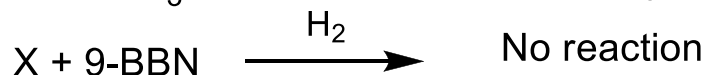
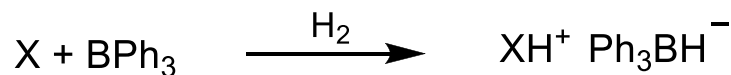


Inverse FLP's

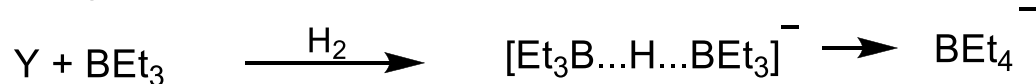
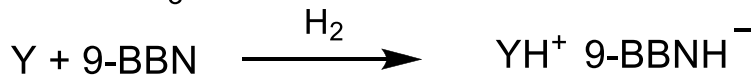
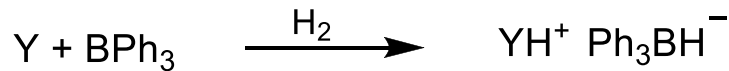
The Lewis acid component of FLP's have been relatively limited to a few strong Lewis acids such as $B(C_6F_5)_3$ while a number of Lewis base amines and phosphines have been tried out. For heterolytic activation of H_2 , it appeared that the Lewis acid partner of the FLP must incorporate strongly electron withdrawing substituents. It was therefore proposed that moderate to weak Lewis acids may be utilized in FLP mediated H_2 cleavage in the presence of sufficiently strong hindered bases. This suggestion was verified by Krempner and coworkers in the design of FLPs with phosphorus based superbases and moderate to weak Lewis acids



MeCN $pK_{BH^+} = 28.4$



MeCN $pK_{BH^+} = 33.4$



Gas phase hydride affinity
kcal/mol

$B(C_6F_5)_3$	-112.0
BPh_3	-74.4
9-BBN	-70.2
BEt_3	-58.5
$B(OMe)_3$	-38.2

What constitutes an FLP?

FLP is a combination of a Lewis acid and a Lewis base that exhibits FLP chemistry !

FLP chemistry involves the concerted action of a Lewis acid and a Lewis base segregated at the transition state of a substrate molecule

Prior segregation of Lewis acid and base is not always required for FLP activity. FLP activity may be accessed by an equilibrium also which gives access to the transiently free Lewis acid and base.

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