

Career of Kit Cummins

14Oct2019

Keita Tanaka

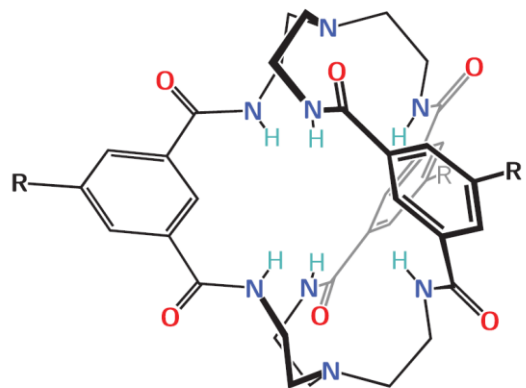


Christopher C. Cummins

- A.B., Cornell University, 1989. (Peter T. Wolczanski)
C–H bond activation and other chemistry of Ti, Zr imide
- Ph.D., MIT, 1993. (Richard R. Schrock)
Coordination chemistry of triamidoamine ligand
- Assistant Professor, MIT (1993-1996)
- Professor, MIT (1996-present)
- Henry Dreyfus Professor, MIT (2015-present)

Research focuses

1. Synthesis and reactivity of three-coordinate TM, metal ligand multiple bond
2. Reactive intermediate & group transfer reaction
3. Sustainable phosphorus chemistry
4. Uranium chemistry (not covered today)
5. Supramolecular chemistry (collaboration with Nocera) (not covered today)



Science **2012**, 335, 450

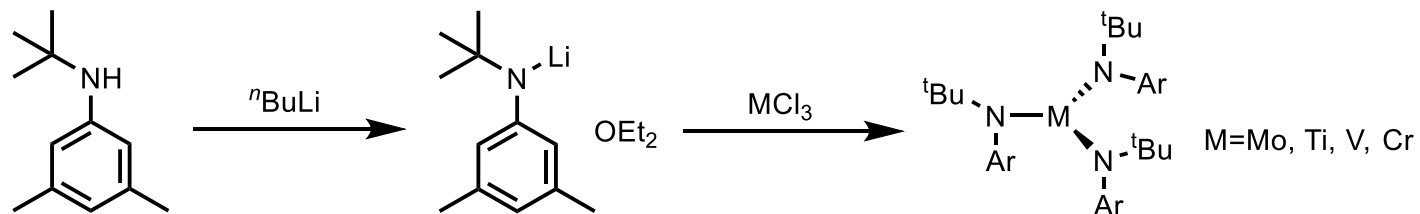
1. Synthesis and reactivity of three-coordinate TM

2. Reactive intermediate & group transfer reaction

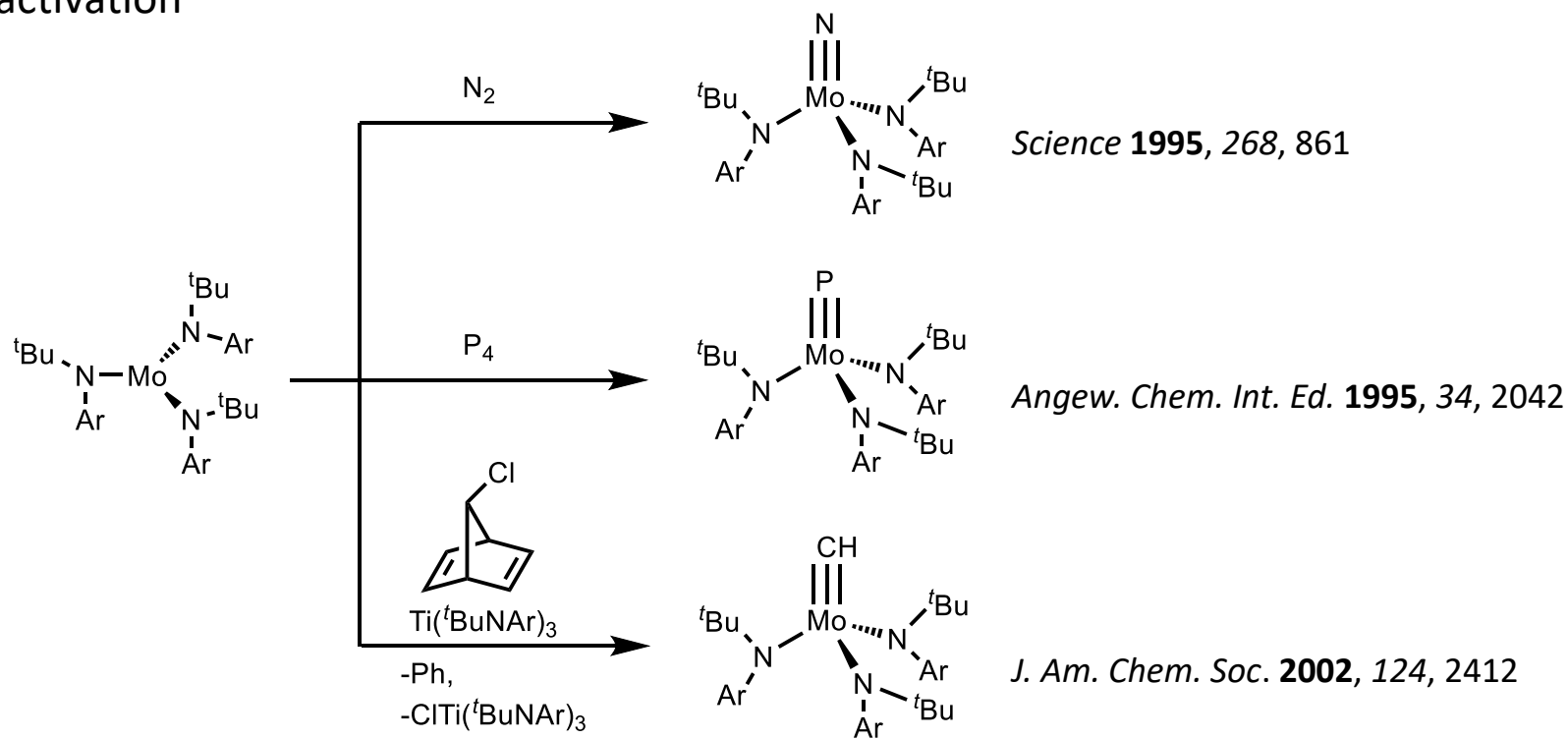
3. Sustainable phosphorus chemistry

Reactivity of three coordinate TM

□ Bulky amide ligand

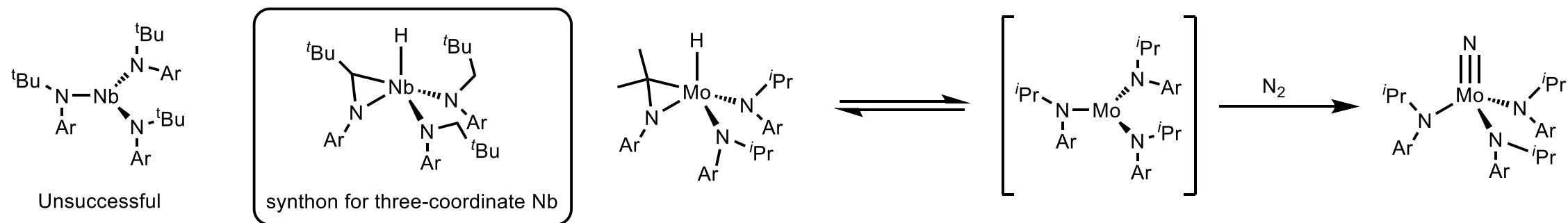


□ Small molecule activation

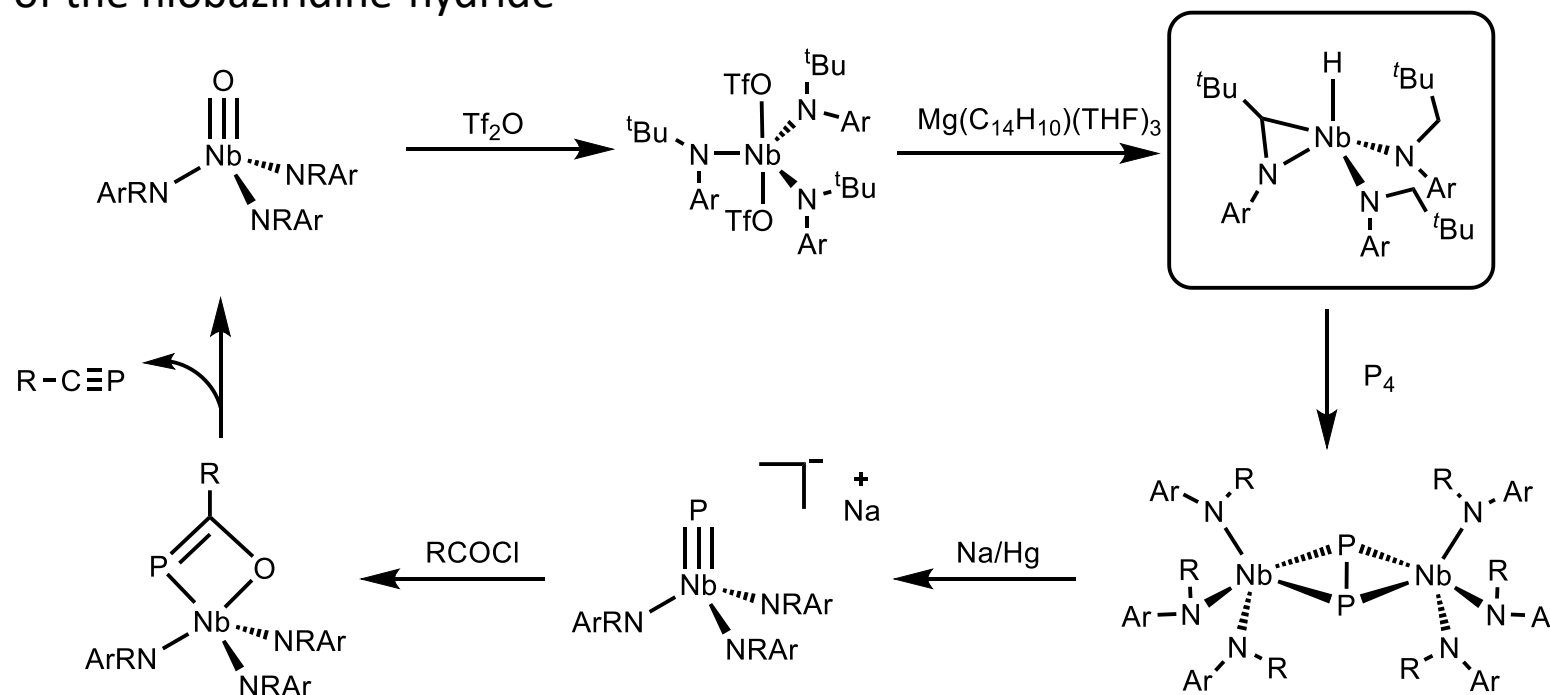


Niobaziridine-hydride

Design of the synthon for tri-coordinate Nb



Reactivity of the niobaziridine-hydride

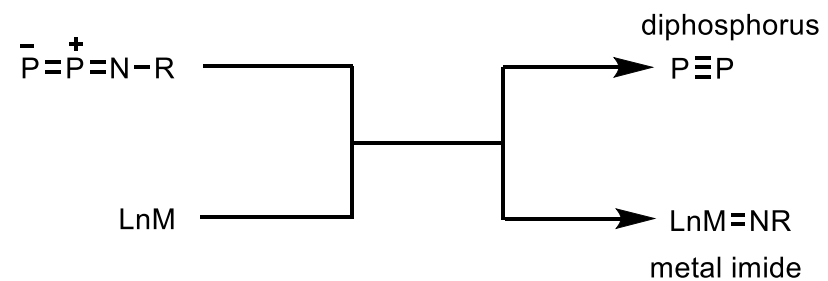
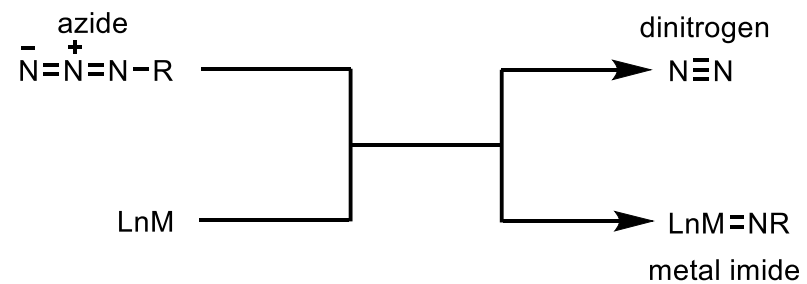


Chemistry of P₂

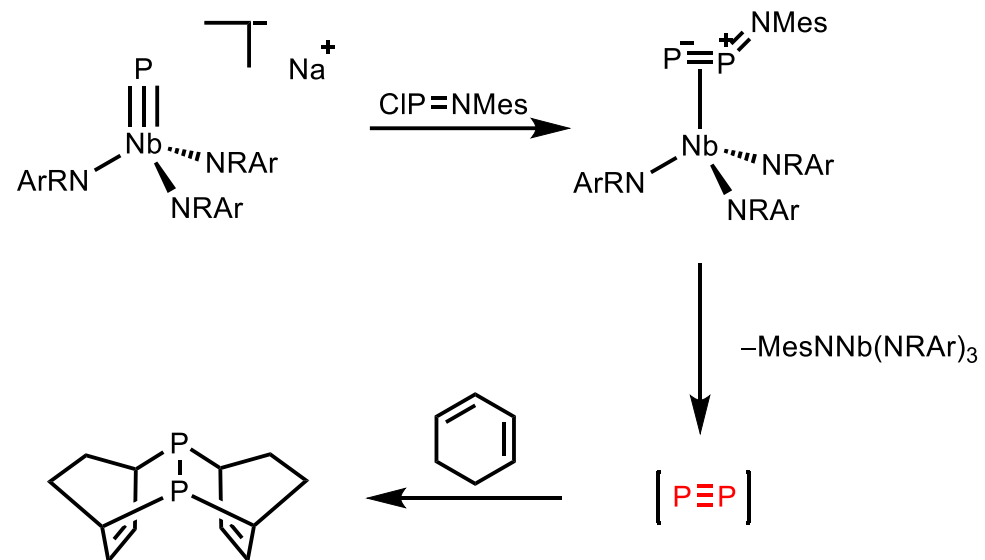
□ P₂

- De = 117 kcal/mol
- Matrix isolation
- P₄ = 2P₂ equilibrium at >1100K
- Reactivity unknown

□ strategy



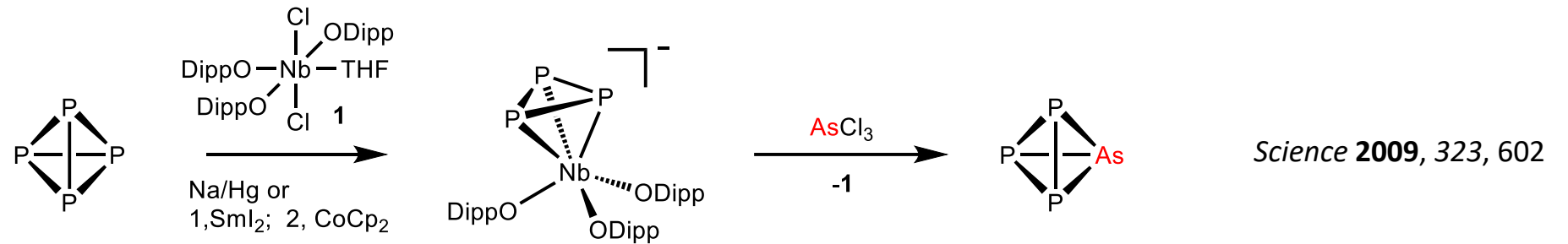
□ Reactivity of P₂



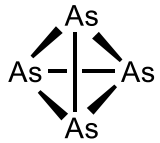
Science 2006, 313, 1276

Chemistry of P₃

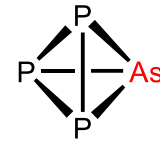
□ Synthesis of AsP₃



□ Comparison of physical property



- thermally unstable
- Photochemically unstable



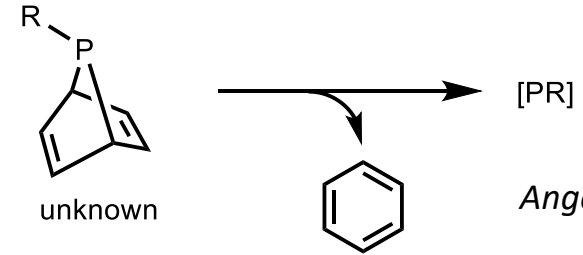
- One of the mixture in the hot (660 °C) vapor of phosphorus and arsenic
- Thermally stable
- Photochemically stable

1. Synthesis and reactivity of three-coordinate TM
- 2. Reactive intermediate & group transfer reaction**
3. Sustainable phosphorus chemistry

Phosphinidene

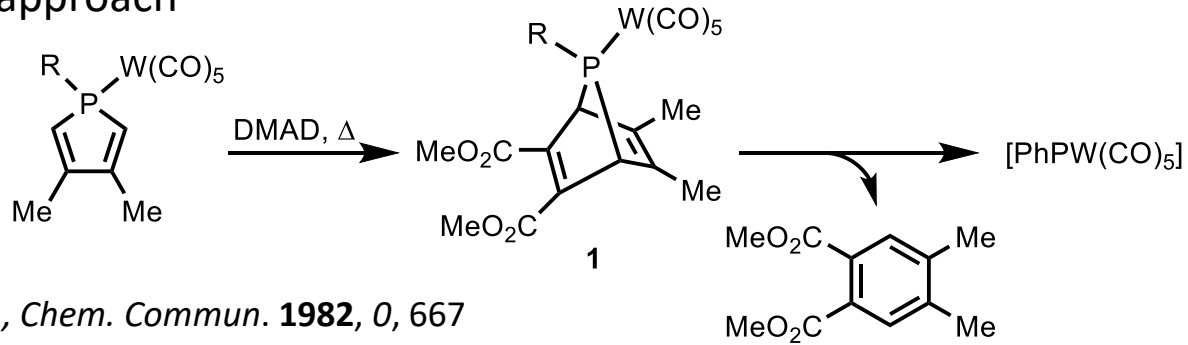
- [PR]
- Phosphorus analogue of carbene, nitrene.
 - Singlet, triplet.
 - Stable, easily accessible precursor needed.

□ target precursor



Angew. Chem., Int. Ed. **1987**, 26, 275

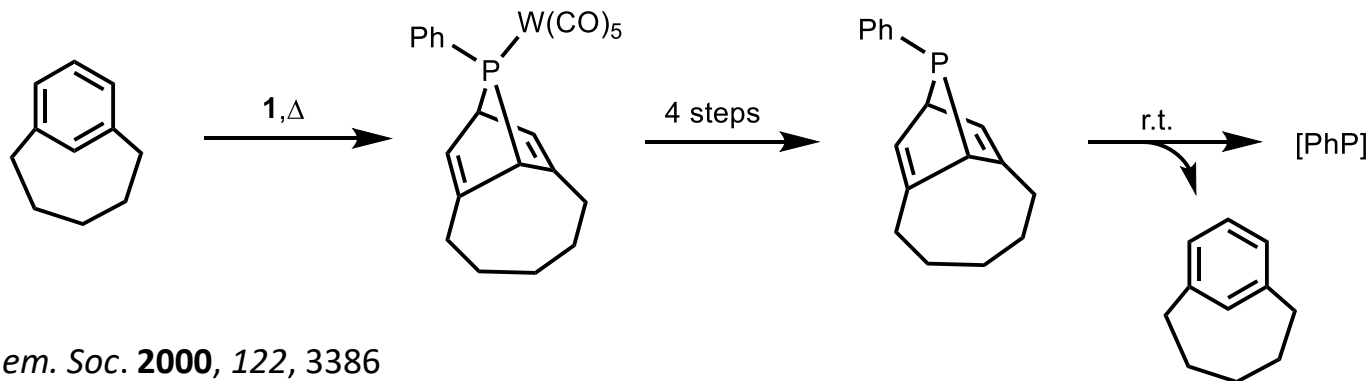
□ Diels-Alder approach



J. Chem. Soc., Chem. Commun. **1982**, 0, 667

- P coordinate to the TM

□ Ring-strain assisted preparation of the first phosphinidene

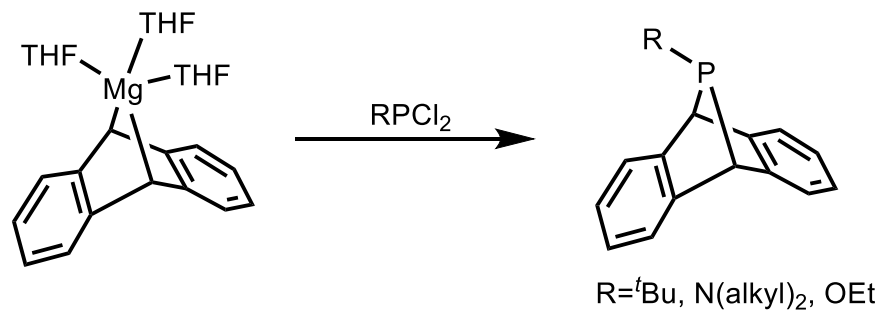


J. Am. Chem. Soc. **2000**, 122, 3386

- multi-step
- unstable at r.t.

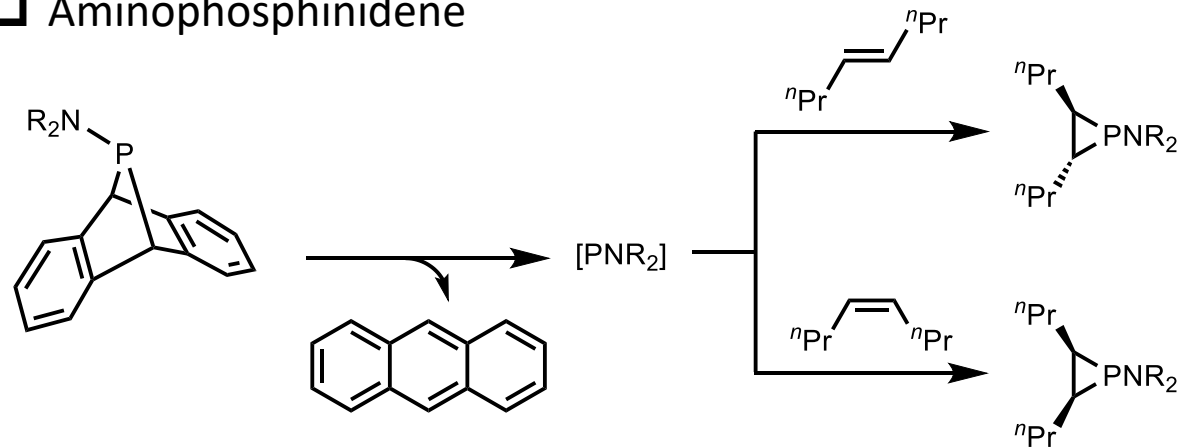
Discovery of Dibenzo-7 λ 3-phosphanorbornadiene Derivatives (RPA)

□ Preparation of RPA

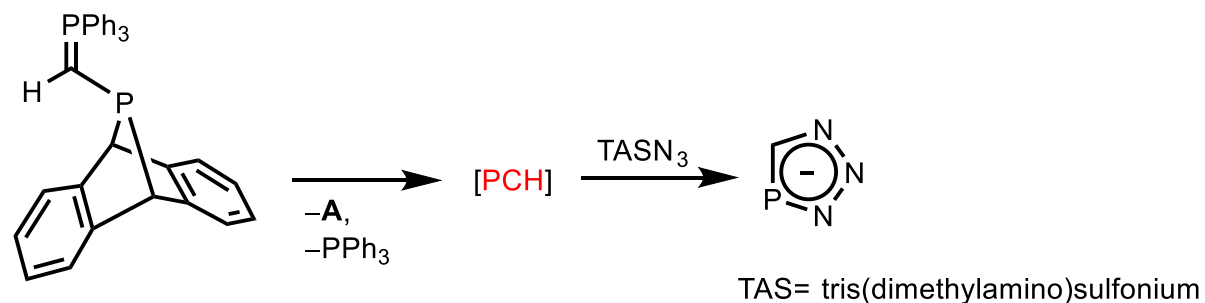


- Facile synthesis
- Stable at r.t.

□ Aminophosphinidene



□ Phosphaethyne



J. Am. Chem. Soc. **2012**, *134*, 13978

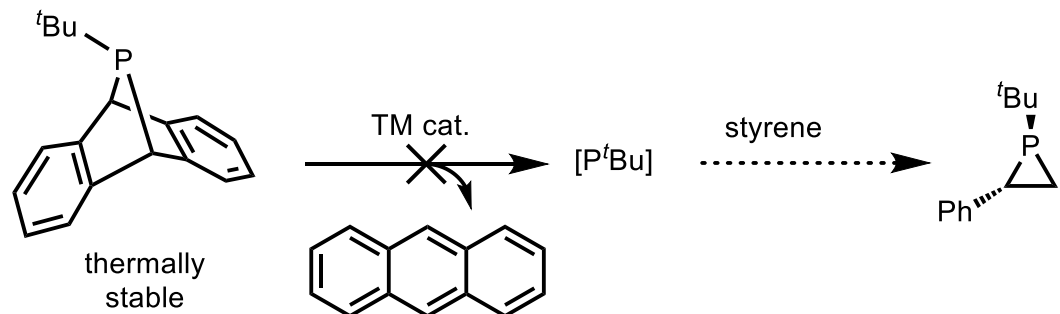
J. Am. Chem. Soc. **2017**, *139*, 10822

J. Am. Chem. Soc. **2016**, *138*, 6731

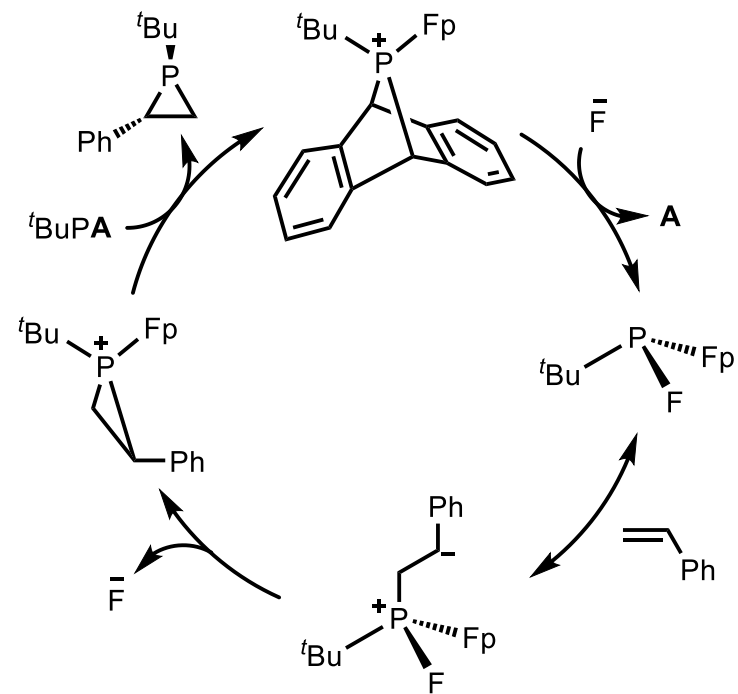
J. Am. Chem. Soc. **2018**, *140*, 17985

Catalytic phosphinidene transfer

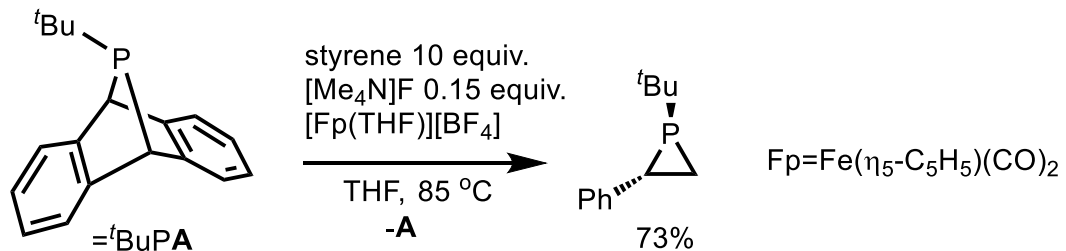
Unsuccessful TM catalyzed PR transfer



Proposed catalytic cycle

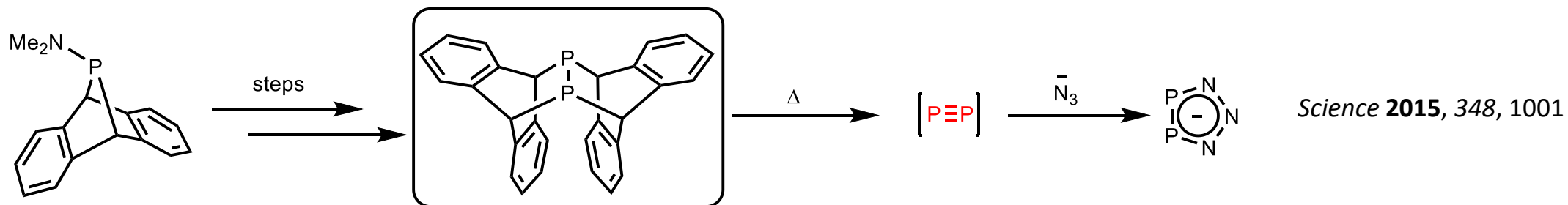


Catalytic PR transfer



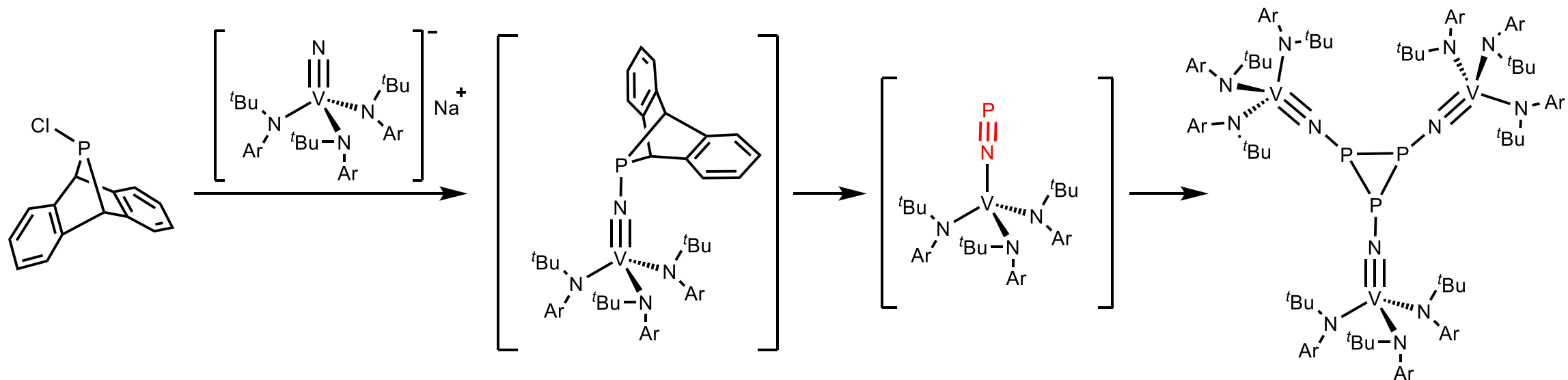
Generation of P₂, PN

□ P₂



J. Am. Chem. Soc. **2014**, *136*, 13586

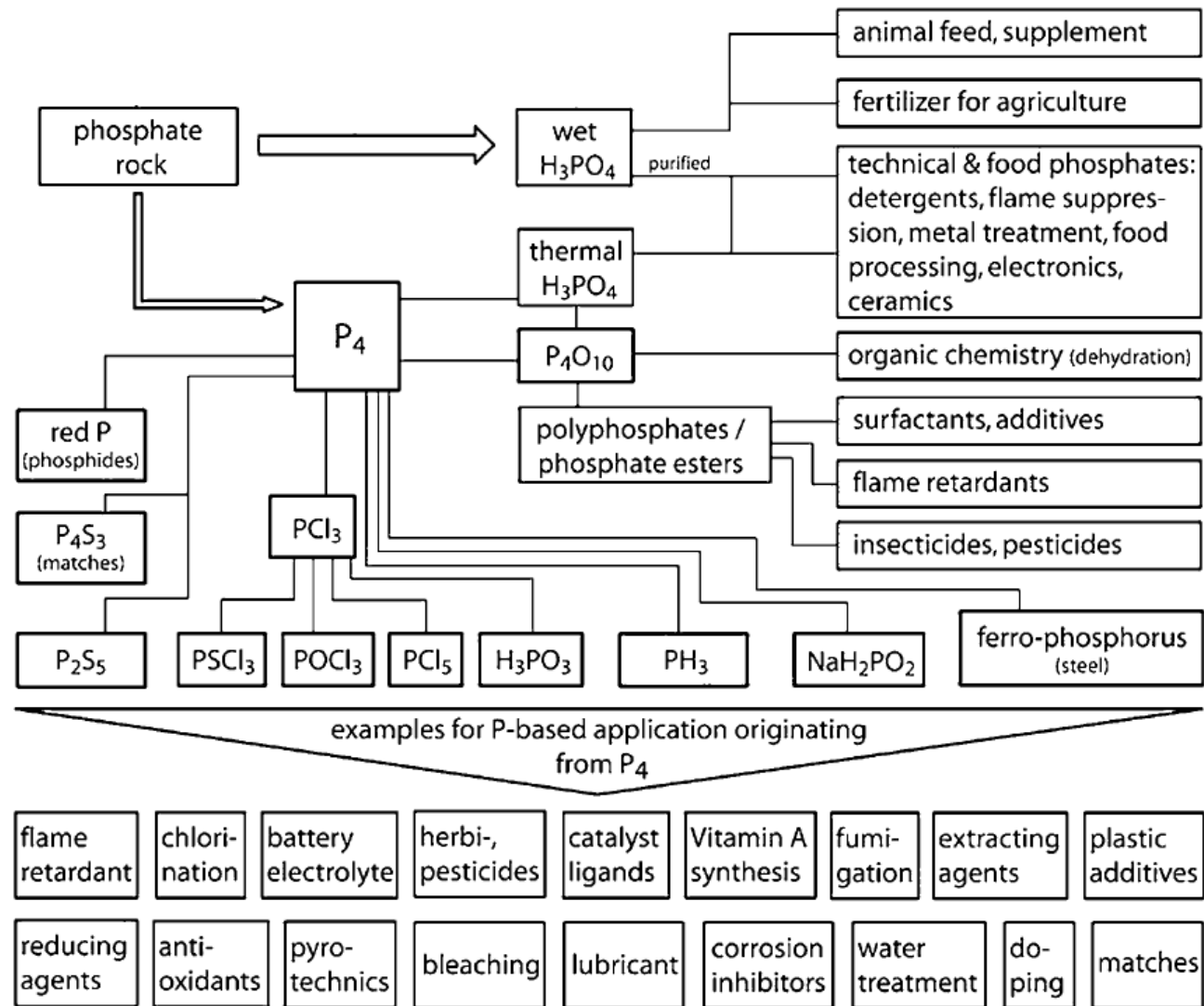
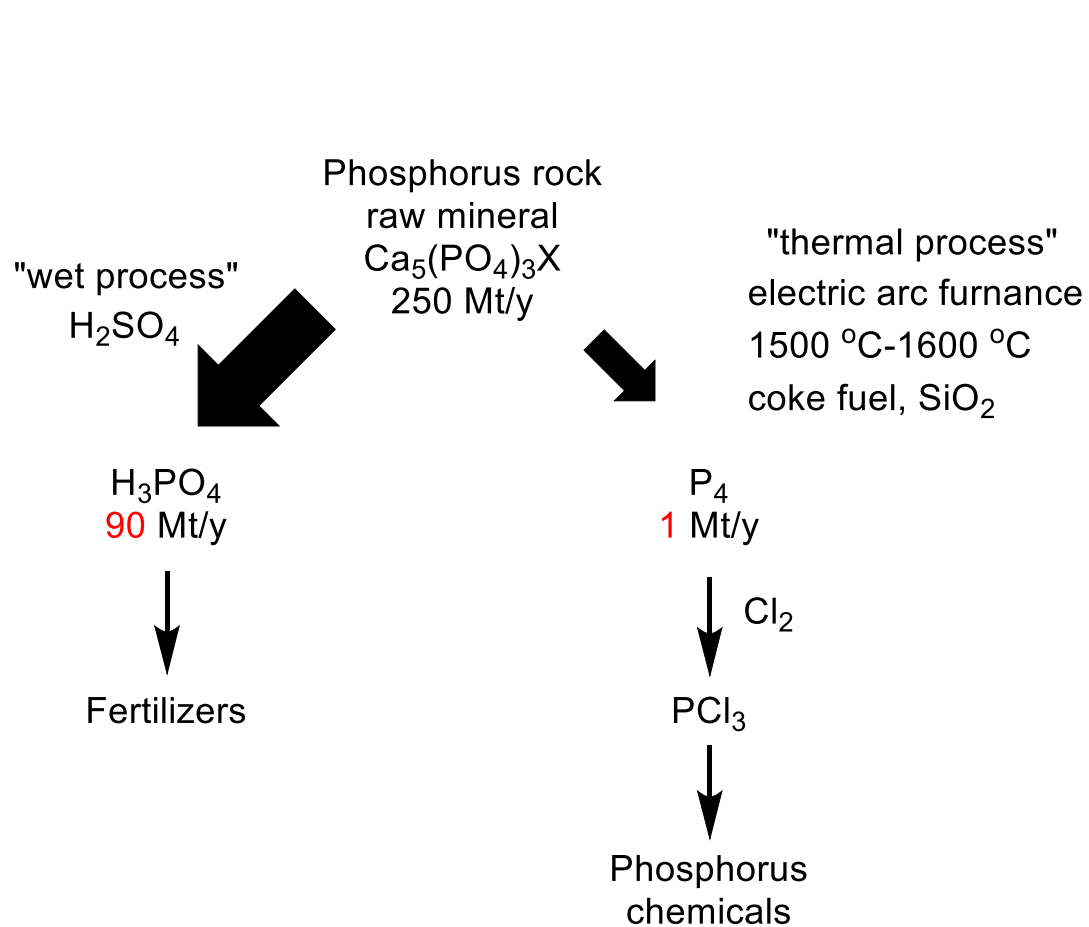
□ PN



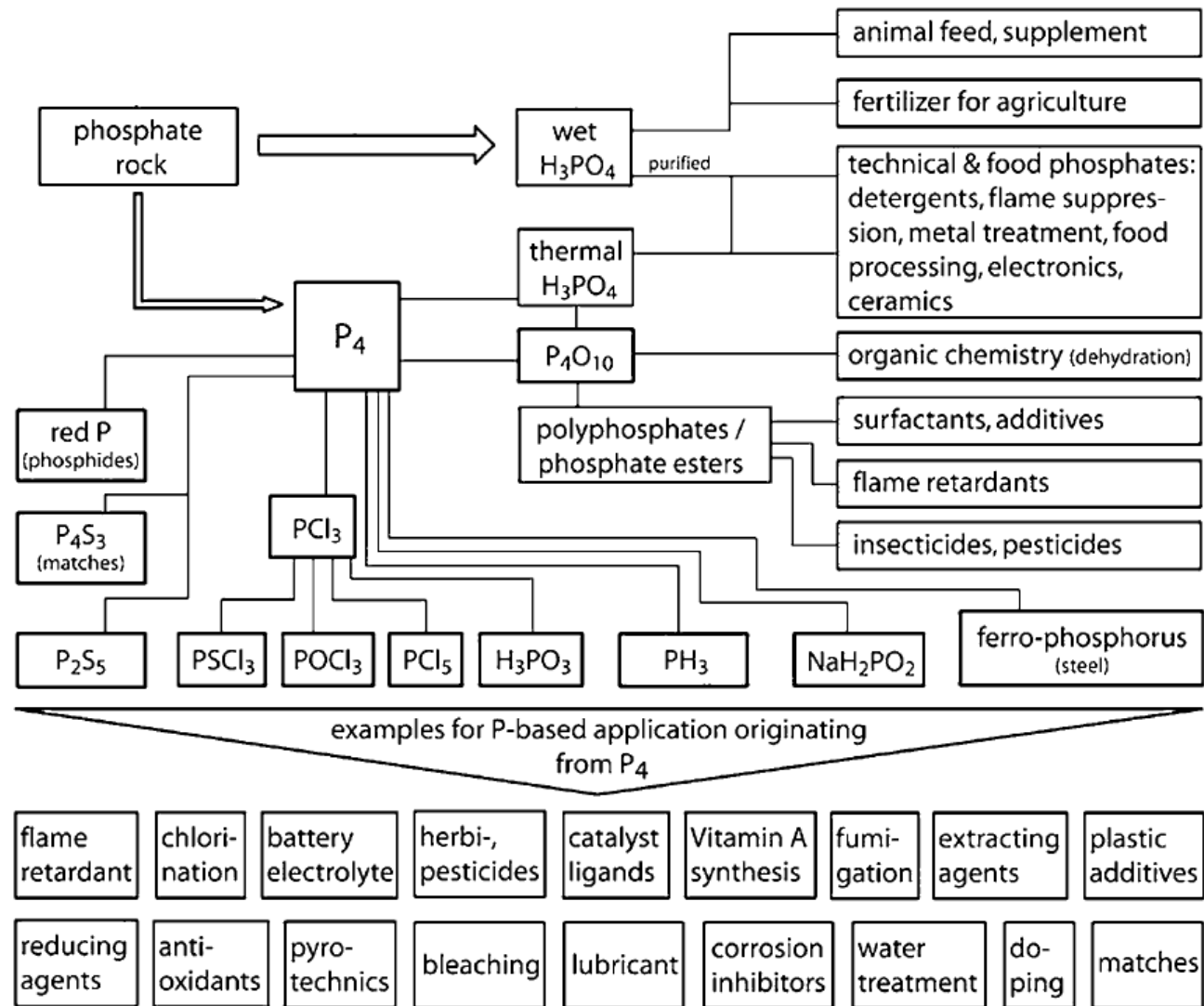
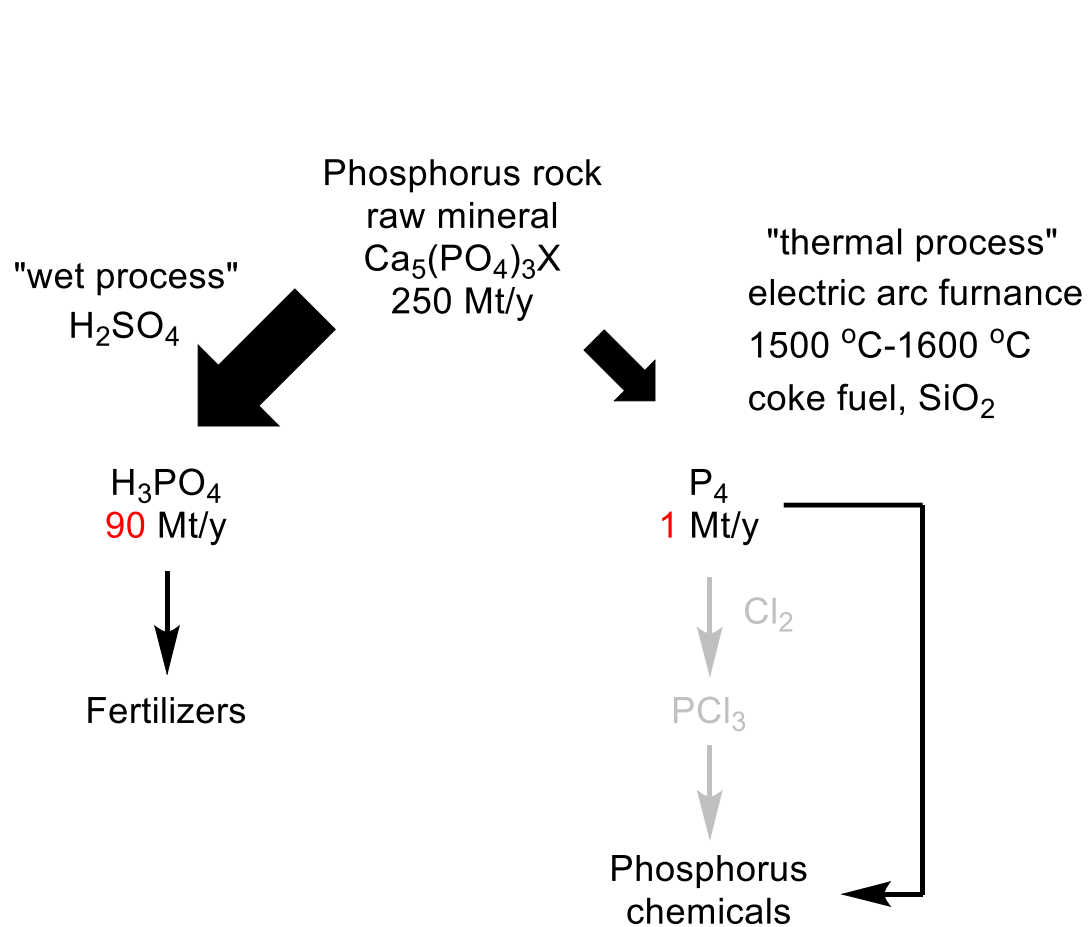
J. Am. Chem. Soc. **2016**, *138*, 16220

1. Synthesis and reactivity of three-coordinate TM
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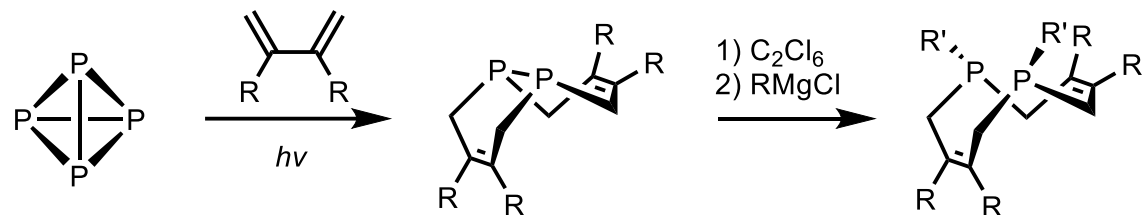
Sustainable phosphorus chemistry



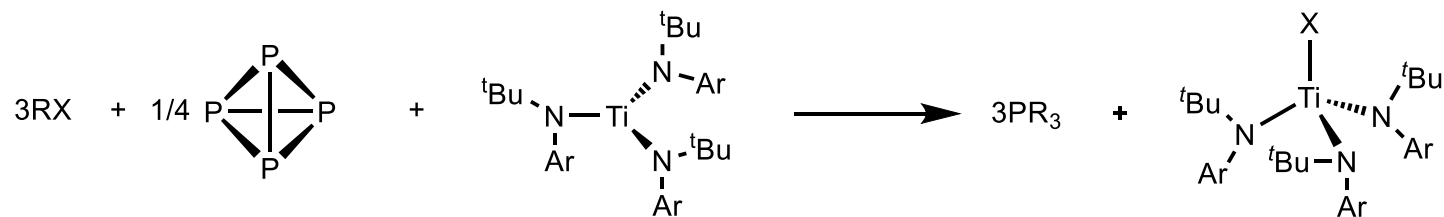
Sustainable phosphorus chemistry



Phosphorus containing compounds from P₄



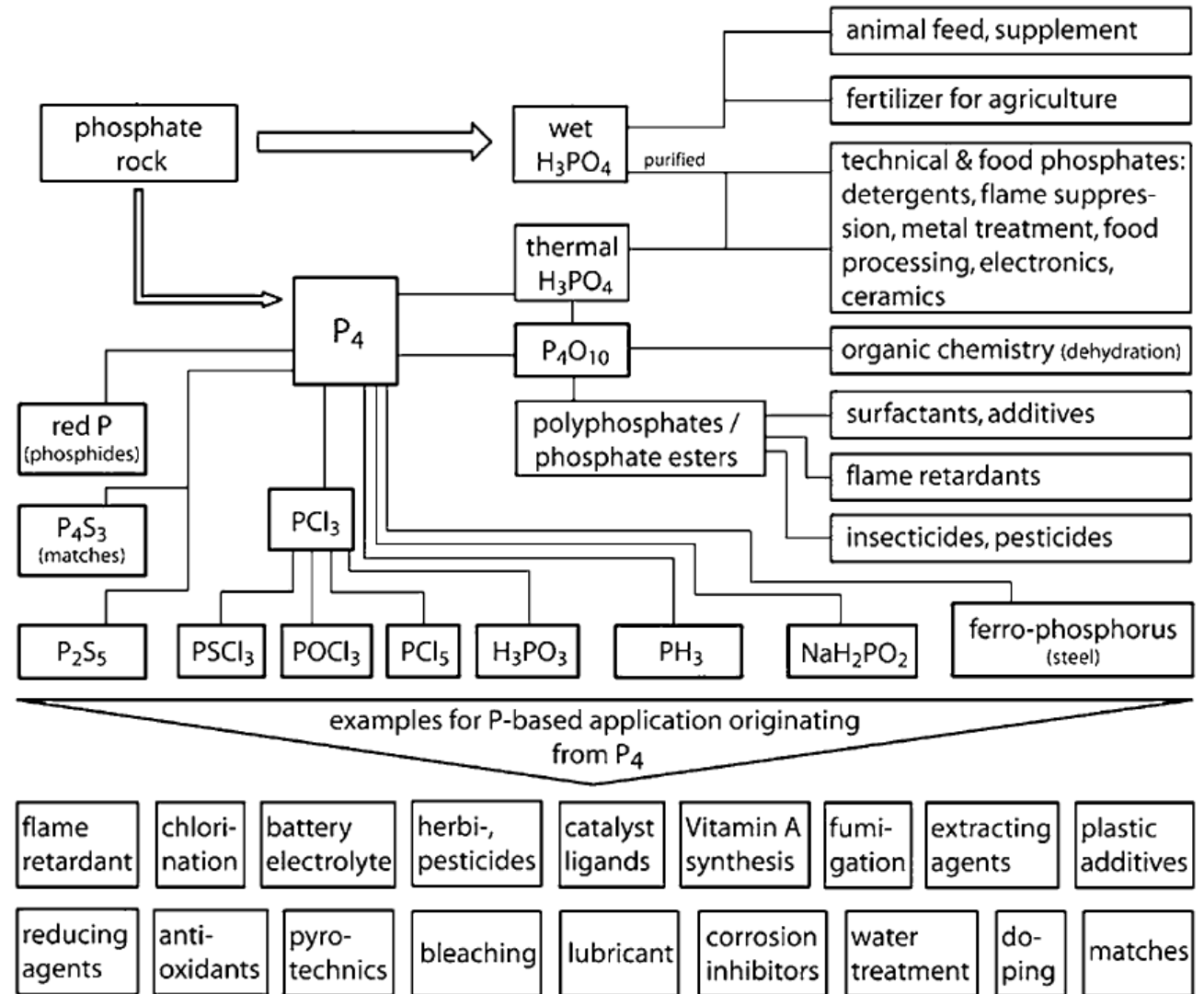
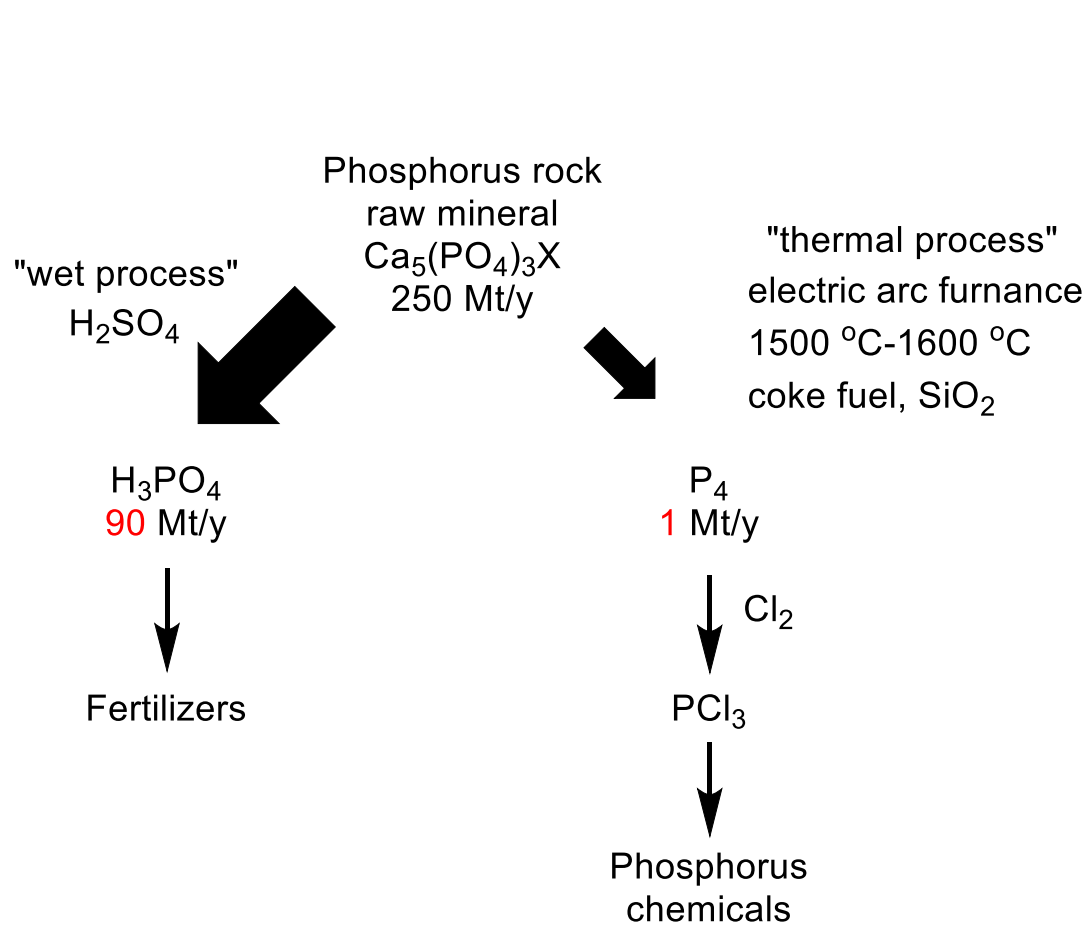
Angew. Chem. Int. Ed. **2010**, *49*, 7516



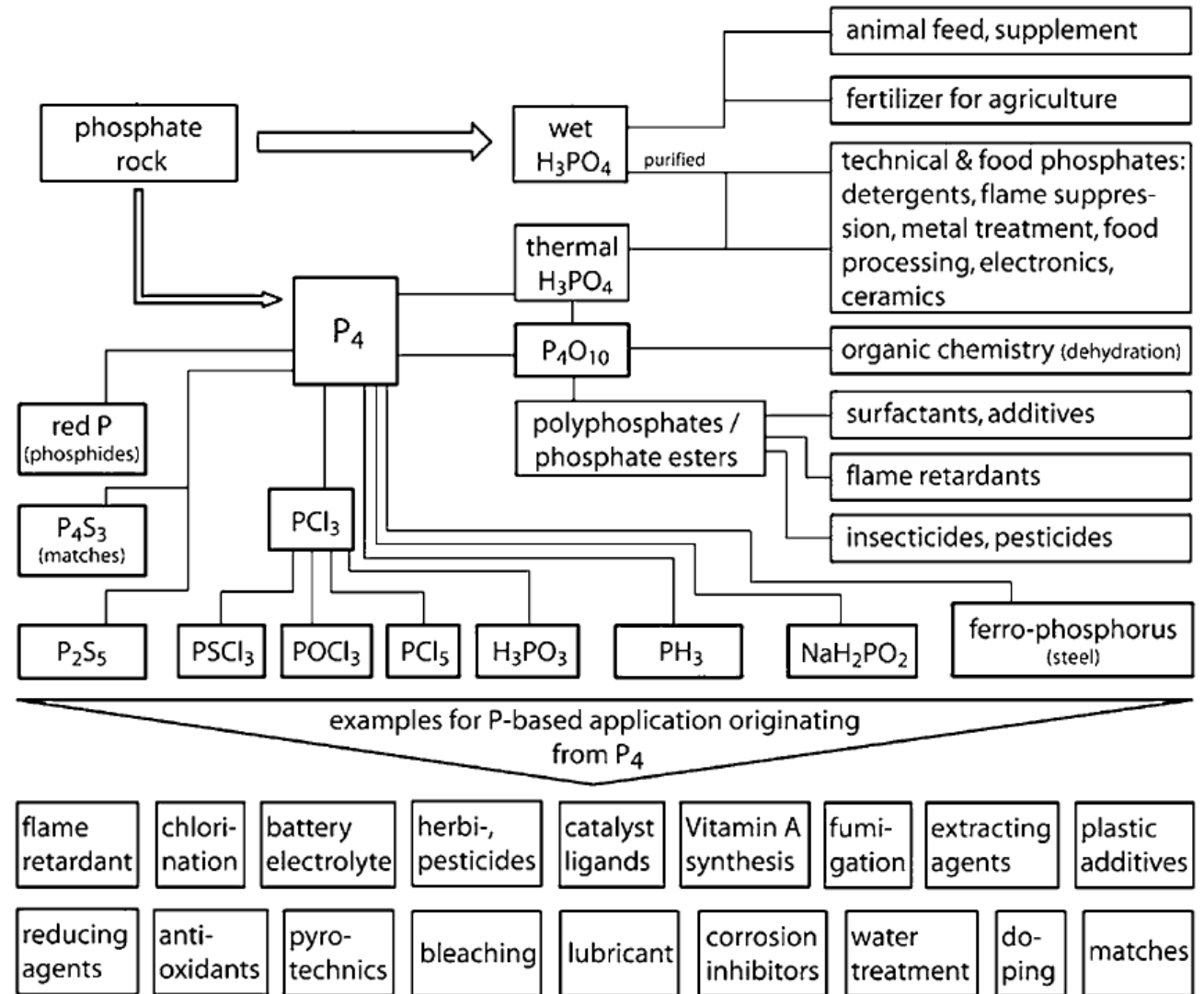
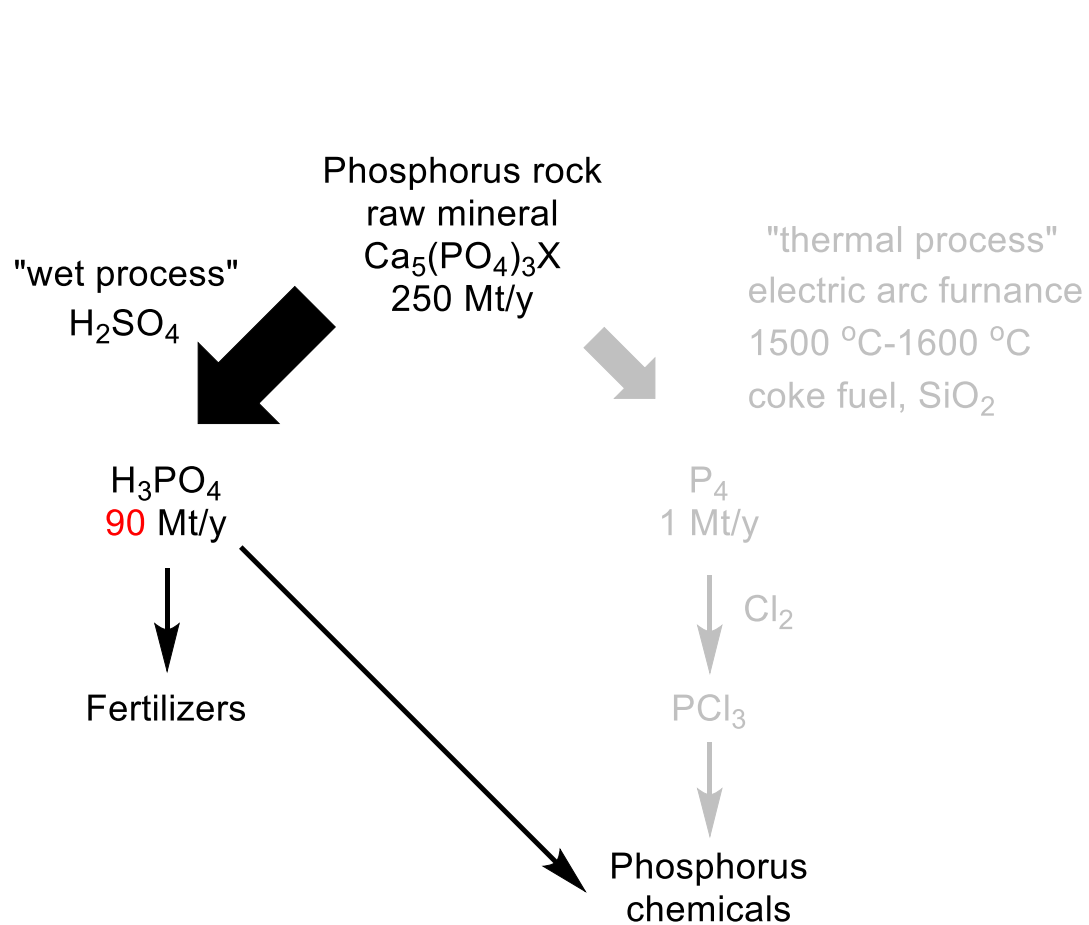
New. J. Chem., **2010**, *34*, 1533

R= Ph, Cy
non-symmetrical phosphine possible
by stepwise addition

Sustainable phosphorus chemistry

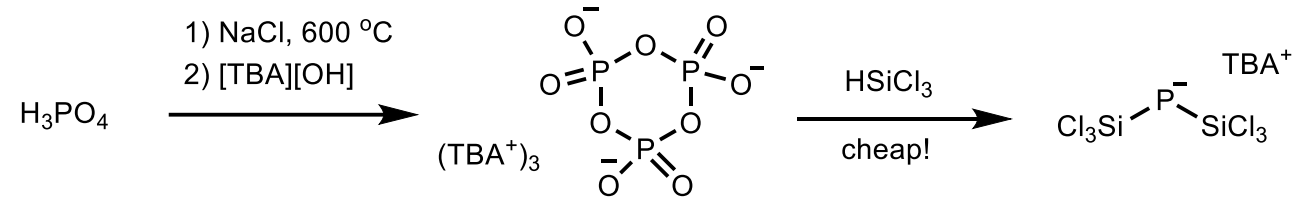


Sustainable phosphorus chemistry



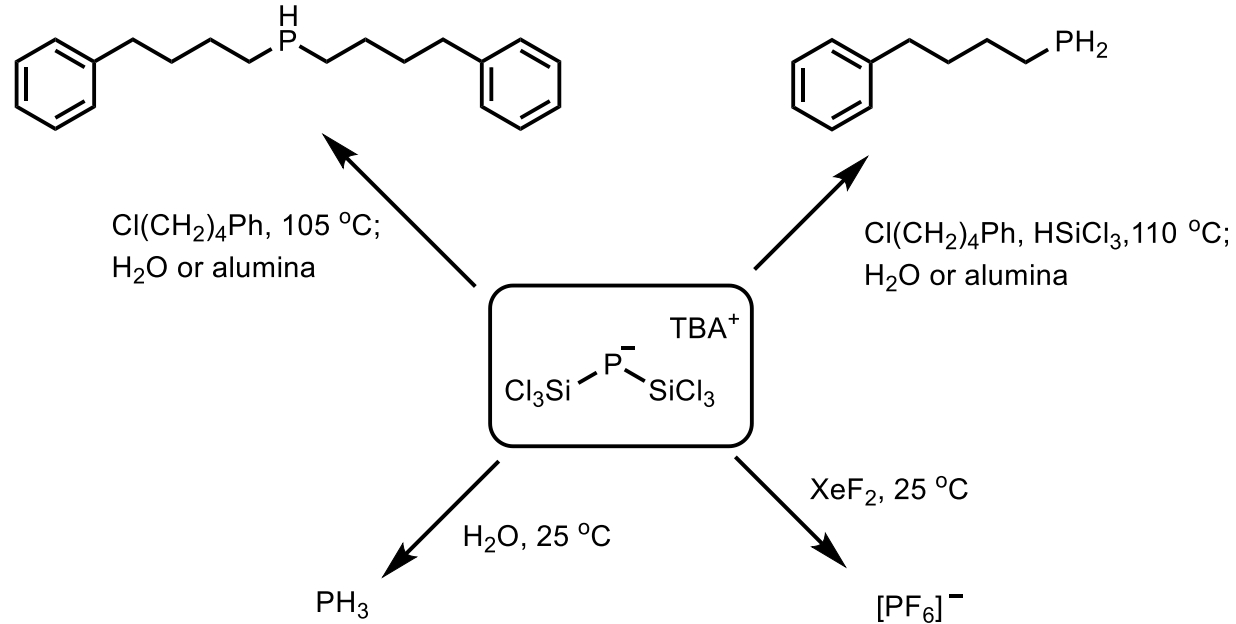
Phosphorus containing compounds from H₃PO₄

□ Preparation 1

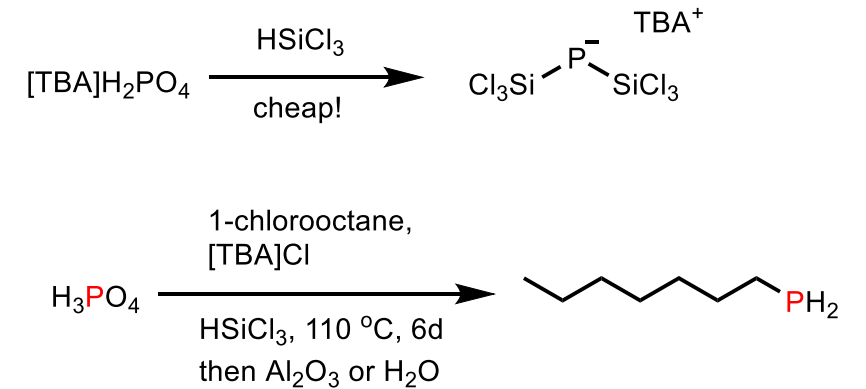


Science **2018**, 359, 1383

□ Synthesis of P containing chemicals

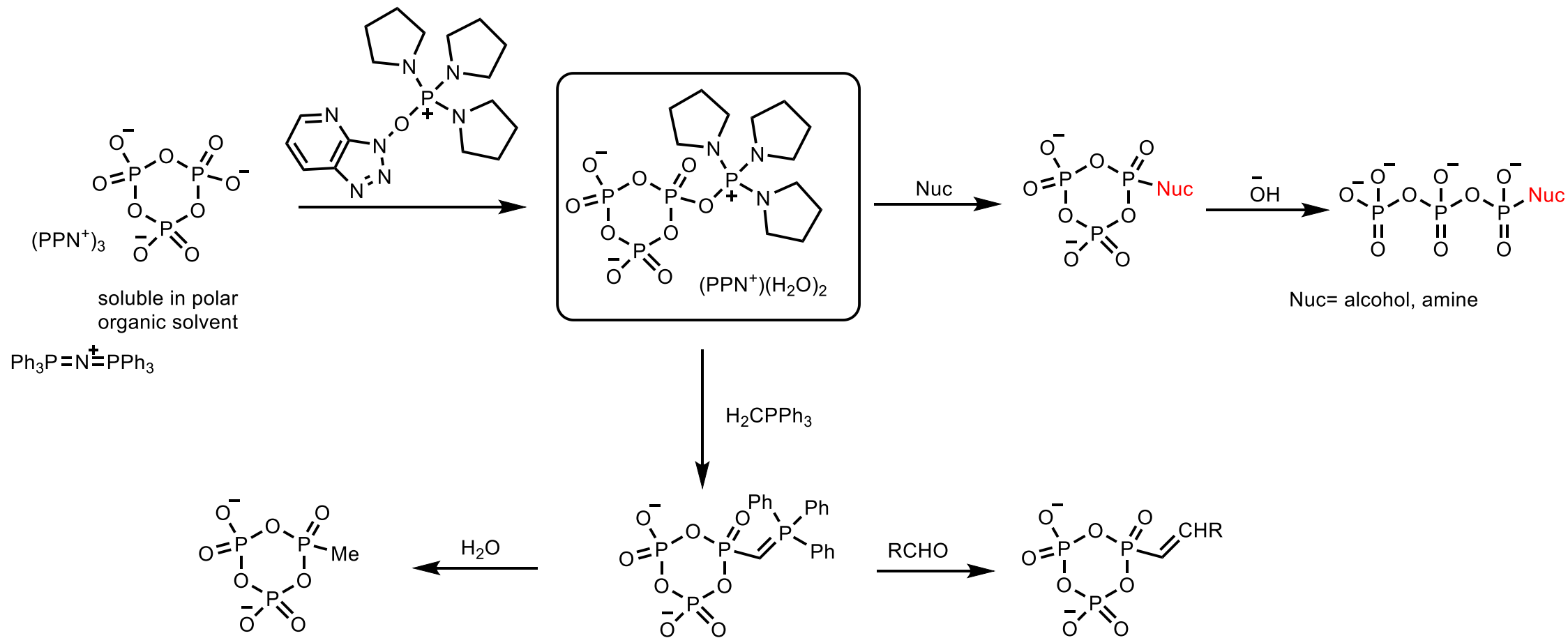


□ Preparation 2

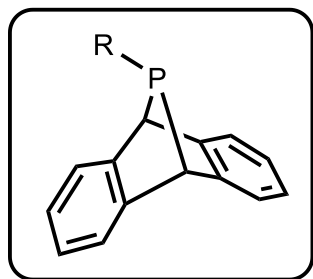


J. Am. Chem. Soc. **2019**, 141, 6375

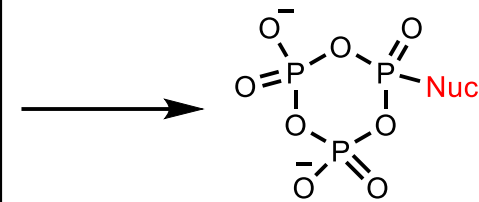
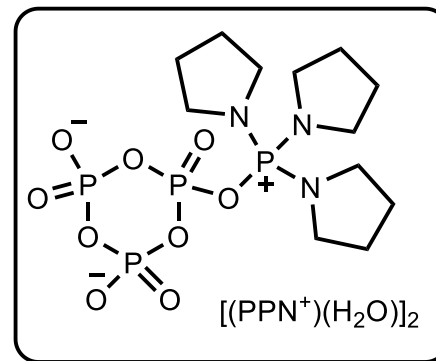
Triphosphorylating reagent



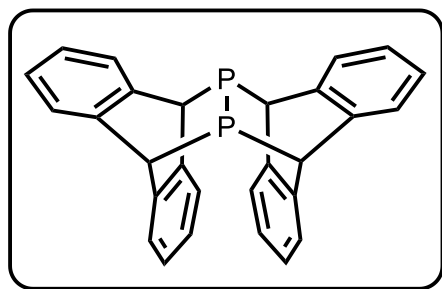
Summary



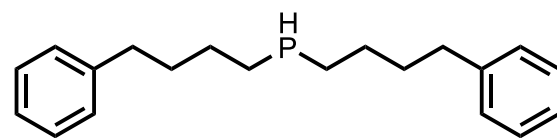
→ PCH
→ PR
→ PN



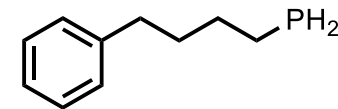
P-element bond formation by new reagent design!



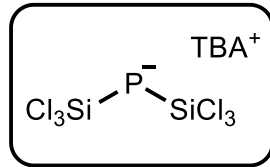
→ P₂



Cl(CH₂)₄Ph, 105 °C;
H₂O or alumina



Cl(CH₂)₄Ph, HSiCl₃, 110 °C;
H₂O or alumina



H₂O, 25 °C

PH₃

XeF₂, 25 °C

[PF₆]⁻