

The Family of Phosphatetrahedranes

Shounak Nath

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Tetrahedranes, a class of molecules with carbon atoms positioned at the vertices of a regular tetrahedron, are highly strained, high-energy species: the unsubstituted tetrahedrane (CH_4) is still an elusive molecule. Tetra-*tert*-butyl tetrahedrane, the first derivative of this class was synthesized in 1978 by Maier and co-workers.¹ The four bulky *tert*-butyl groups impart kinetic stability to this molecule from ring opening bond cleavage, the so called “corset effect”.²

Despite the high energy content of tetrahedranes, the well-known all-phosphorus isostructural analogue, white phosphorus (P_4), is isolable, having significantly reduced angle strain than tetrahedranes. It was first isolated in 1669 by Henning Brandt and still is the only raw material for an industrially practicable way to generate phosphorus-containing fine chemicals.³

Hence a logical way to decrease strain energy in the tetrahedrane core and unlock new reactivity pathways in organophosphorus chemistry is the study of the family of phosphatetrahedranes, with each CH vertex in the parent tetrahedrane systematically substituted by a phosphorus atom. Such species have been investigated extensively in the past by theoretical studies,⁴ but synthesis of these molecules had remained elusive until very recently (Figure 1).

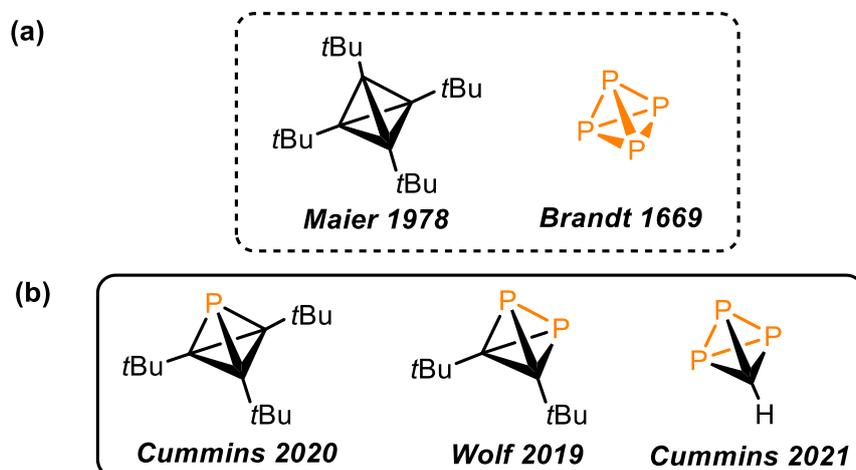


Figure 1. a) Tetra-*tert*-butyl tetrahedrane and white phosphorus b) The family of mixed C/P phosphatetrahedranes.

In 2020, Cummins et al. reported the first synthesis of the tri-*tert*-butylphosphatetrahedrane, $\text{P}(\text{C}t\text{Bu})_3$.⁵ Their approach involved the generation of a 1,2,3-tris(*tert*-butyl)-cyclopropenylphosphinidene which undergoes an intramolecular [2+1]-cycloaddition reaction to afford the target compound. Full characterization of this molecule was performed spectroscopically and confirmation of the tetrahedral PC_3 core was obtained

from single crystal X-Ray diffraction (Figure 2a). The monophosphatetrahedrane has highly acute C-P-C bond angles, but has been found to have incredible thermal stability that has been ascribed to the corset effect of the 9 H-H bonds from the *tert*-butyl groups.

It was almost around the same time that Wolf et al described the synthesis of the first isolable di-*tert*-butyldiphosphatetrahedrane, which is a formal dimer of *tert*-butylphosphaalkyne (*t*BuCP).⁶ The target molecule was obtained from a Ni catalysed reaction of the dimerization of *t*BuCP using [(NHC)Ni(CO)₃] (NHC=1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) and 1,3-bis(2,6 diisopropylphenyl)imidazolin-2-ylidene (IPr)). The structure of this temperature sensitive compound could be assigned unambiguously by spectroscopy and the connectivity of the tetrahedral core was confirmed from an adduct with a silver(I) complex which shows an η^2 coordinated diphosphatetrahedrane unit (Figure 2b). Mechanistic studies were performed experimentally and via DFT calculations to elucidate the mechanism of this Ni catalysed dimerization of *tert*-butylphosphaalkyne.

The last mixed C/P tetrahedrane of this series, the parent triphosphatetrahedrane HCP₃, was synthesized in 2021 by Cummins and co-workers via a completely different methodology involving the transfer of a P₃³⁻ unit from an anionic niobatriphosphatetrahedrane with a carbon centered radical precursor.⁷ The molecule was characterized spectroscopically revealing the three-fold symmetry. HCP₃ was found to be stable in dilute THF solutions for long periods. The cationic Fe(II) adduct of the triphosphatetrahedrane, (dppe)Fe(Cp*)(HCP₃) (dppe = 1,2-bis(diphenylphosphino)ethane, Cp* = η^5 -C₅Me₅) supported the connectivity of the tetrahedral core (Figure 2c).

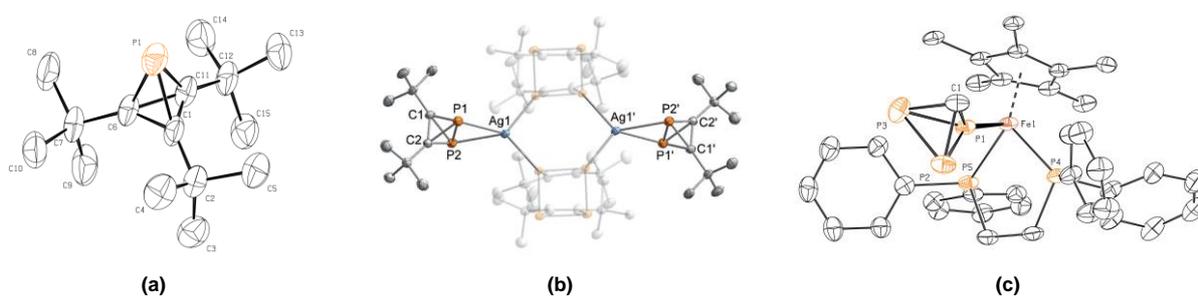


Figure 2. Crystal structures of a) tri-*tert*-butylphosphatetrahedrane⁵ b) Ag(I) complex of di-*tert*-butyldiphosphatetrahedrane⁶ c) Fe(II) complex of triphosphatetrahedrane.⁷

Calculations of strain energies from a series of quantum chemical calculations show that the triphosphatetrahedrane has the least strain among the family of the mixed C/P phosphatetrahedranes, indicating that substituting CH vertices by P atoms in the tetrahedrane core can alleviate the strain energy (Figure 3).

This series of mixed C/P phosphatetrahedranes represent a new class of organophosphorus compounds, which due to their modulated strain energies can access diverse reactivity pathways.⁸⁻¹⁰ With the three completely different approaches to synthesize the three phosphatetrahedranes, pathways to access substituted derivatives will also open up, further providing a handle to modulate the strain energy driven reactivity of these molecules. This

would pave the way towards the synthesis of organophosphorus compounds that have been previously inaccessible via other routes.

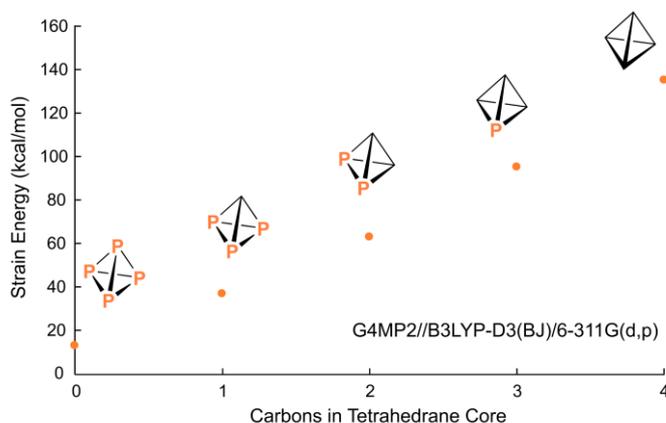


Figure 3. Plot of calculated strain energies of P₄, HCP₃, (HCP)₂, (HC)₃P and (HC)₄ vs number of tetrahedral core carbons.⁷

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