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## Tetrahedranes

## Mixed Phosphatetrahedranes

Andrew R. Jupp\* and J. Chris Slootweg\*

Keywords: phosphorus · strained molecules · tetrahedranes

Tetrahedranes, (CR)<sub>4</sub>, are aesthetically pleasing yet synthetically challenging derivatives of the simplest platonic hydrocarbon.<sup>[1]</sup> They are highly strained and offer potential as high energy-density materials. The parent tetrahedrane, (CH)<sub>4</sub>, is predicted to be isolable<sup>[2]</sup> despite its considerable strain energy (G3(MP2) = 136.8 kcal mol<sup>-1</sup>),<sup>[3]</sup> yet it is still unknown experimentally. In 1978, Maier and co-workers were able to exploit the steric shielding of *tert*-butyl groups on each carbon vertex to access (C*t*Bu)<sub>4</sub> for the first time, and the kinetic stabilization from the bulky substituents was dubbed the “corset effect”.<sup>[4]</sup> The challenging synthesis was ultimately carried out by irradiation of the tetrakis(*tert*-butyl)cyclopentadienone and elimination of CO. The tetrakis(trimethylsilyl)tetrahedrane (C(SiMe<sub>3</sub>)<sub>4</sub>) was later synthesized by isomerization of the cyclobutadiene derivative.<sup>[5]</sup>

The parallels between carbon and phosphorus are well established. Phosphorus has been called the “carbon-copy” since the two elements have similar electronegativities and the CH fragment is isolobal with the P atom.<sup>[6]</sup> This phenomenon has given rise to the field of phospho-organic chemistry, where phosphorus can be conceptually substituted into organic compounds to afford intriguing compounds such as phosphalkenes (R<sub>2</sub>C=PR)<sup>[7]</sup> and phosphalkynes (RC≡P).<sup>[8]</sup>

Tetrahedranes, however, are the one class of molecule where it is more rational to consider them as carbon-based versions of the phosphorus compounds instead of vice versa. P<sub>4</sub> (strain energy: G3(MP2) = 16.0 kcal mol<sup>-1</sup>)<sup>[3]</sup> is the molecular form of elemental phosphorus known as white phosphorus, and was first discovered 350 years ago by the alchemist Hennig Brand.<sup>[9]</sup> The incorporation of CR groups in place of the P atoms on the vertices of the P<sub>4</sub> tetrahedron would give a series of mixed phosphatetrahedranes, as shown in Figure 1 (where R = *t*Bu is used). Although both the all-phosphorus and all-carbon tetrahedral species P<sub>4</sub> and (CR)<sub>4</sub> (R = *t*Bu, SiMe<sub>3</sub>)<sup>[5]</sup> have been known for a long time, the reports highlighted here describe the first examples of mixed P/C tetrahedrane species.

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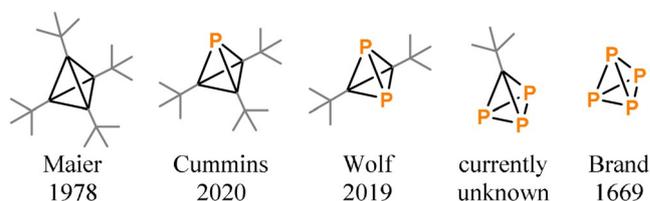
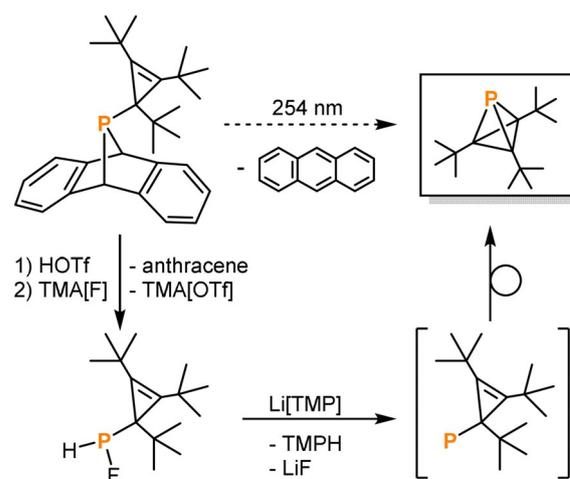


Figure 1. Tetrahedral structures based on carbon and phosphorus vertices.

Cummins and co-workers have successfully synthesized monophosphatetrahedrane P(C*t*Bu)<sub>3</sub>.<sup>[10]</sup> Their approach relied on the generation of the transient 1,2,3-tris(*tert*-butyl)-cyclopropenylphosphinidene (Scheme 1), which undergoes an intramolecular [1+2]-cycloaddition reaction to afford the target product. Initial attempts at phosphinidene generation were based on photolysis of the anthracene-substituted species, which did indeed form a small amount of the phosphatetrahedrane, but also large amounts of unidentified side products. As a change of tack, the authors converted the anthracene derivative to the corresponding secondary phosphine halide by sequential treatment with triflic acid (trifluoromethanesulfonic acid, HOTf) and tetramethylammonium fluoride (TMA[F]). Dehydrohalogenation of this fluorophosphine by the strong base lithium tetramethylpiperidide (Li[TMP]) afforded the desired compound almost exclusively



Scheme 1. Synthesis of tri-*tert*-butylphosphatetrahedrane by Cummins and co-workers. Abbreviations in text.

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by  $^{31}\text{P}$  NMR spectroscopy. The low isolated yield of 19% was attributed to the volatility of the product.

Tri-*tert*-butylphosphatetrahedrane is a waxy colorless solid with a melting point of ca. 31 °C. The  $^{31}\text{P}$  NMR spectrum displays a diagnostic resonance at  $-488.0$  ppm ( $\text{C}_6\text{D}_6$ ), which is typical of highly strained phosphorus compounds ( $\text{P}_4$ :  $\delta^{31}\text{P}\{\text{H}\} = -520$  in  $\text{C}_6\text{D}_6$ ). Single crystals suitable for X-ray diffraction experiments were grown by sublimation, and confirmed the structure as the phosphatetrahedrane with very acute C-P-C bond angles of only  $47.1(4)^\circ$  (average). The product has reasonable thermal stability. No decomposition is observed after heating at 75 °C for 45 minutes in  $\text{C}_6\text{D}_6$ , but 3 hours of heating at 130 °C in  $[\text{D}_8]$ toluene induces partial conversion to a dimeric form with a housene structure.<sup>[11]</sup> Irradiation of the phosphatetrahedrane at 254 nm led to rapid decomposition to a range of products, including the dimer with a diphosphene structure.  $\text{P}(\text{CtBu})_3$  is also susceptible to dimerization in the presence of Lewis acids; for example, the use of 10 mol% triphenylborane afforded a [2+2] dimer of tri-*tert*-butylphosphacyclobutadiene ( $\delta^{31}\text{P}\{\text{H}\} = -47.6$ ) and diphosphahousene ( $\delta^{31}\text{P}\{\text{H}\} = 55.5, -167.0$ ;  $^1J_{\text{PP}} = 171$  Hz)<sup>[11a]</sup> in a 4:1 ratio.

A completely different strategy was employed by Wolf and co-workers for the synthesis of di-*tert*-butyldiphosphatetrahedrane, which was accessed by the nickel-catalyzed dimerization of the corresponding phosphaaalkyne,  $\text{P}\equiv\text{CtBu}$  (Scheme 2).<sup>[12]</sup> The  $\text{P}_2(\text{CtBu})_2$  molecule was isolated as a pyrophoric, yellow oil in up to 55% yield ( $\delta^{31}\text{P}\{\text{H}\} = -468.2$  in  $\text{C}_6\text{D}_6$ ). No single-crystal X-ray structure of the diphosphatetrahedrane was obtained, but a structure of this

species in the coordination sphere of a  $\text{Ag}^{\text{I}}$  cation confirmed the tetrahedral geometry. The pure compound has a melting point of  $-32^\circ\text{C}$ , above which it converts into its known ladderane-type dimer ( $\delta^{31}\text{P}\{\text{H}\} = -23.1$ ; Scheme 2, top).

A thorough mechanistic investigation revealed the formation of  $\text{P}_2(\text{CtBu})_2$ , using  $\text{Ni}^0$  precatalyst **A** bearing three carbonyl ligands and an N-heterocyclic carbene (NHC); specifically 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) or 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr, sometimes abbreviated as IDipp; Scheme 2, bottom)). Displacement of two of the carbonyl ligands by  $\text{P}\equiv\text{CtBu}$  ( $\delta^{31}\text{P}\{\text{H}\} = -68.1$ ) affords the catalytically active nickelaphosphacyclopentene **B** ( $\delta^{31}\text{P}\{\text{H}\} = 92.1$  (IMes) and 93.2 (IPr)). A second phosphaaalkyne reacts with the bound phosphaaalkyne via a head-to-tail dimerization to afford the 1,3-diphosphacyclobutadiene in the coordination sphere of the transition metal (**C**; isolated with  $i\text{Pr}_2\text{Im}^{\text{Me}}$  (1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene),  $\delta^{31}\text{P}\{\text{H}\} = 47.0$ ). Although the four-membered  $\text{P}_2\text{C}_2$  ring has been observed before,<sup>[13]</sup> in this particular system the steric clash of the *tert*-butyl groups with the bulky NHC ligand promotes the isomerization of the four-membered ring into the tetrahedrane derivative (**D**), as supported by DFT calculations. The tetrahedral compound is finally displaced by another equivalent of phosphaaalkyne to afford the product and regenerate **B**. This synthetic protocol could be extended using the adamantyl-substituted phosphaaalkyne  $\text{P}\equiv\text{CAd}$  to afford  $\text{P}_2(\text{CAd})_2$  ( $\delta^{31}\text{P}\{\text{H}\} = -479.8$ ), and even the heterodimer  $\text{P}_2(\text{CtBu})(\text{CAd})$  ( $\delta^{31}\text{P}\{\text{H}\} = -473.8$ ) could be identified.

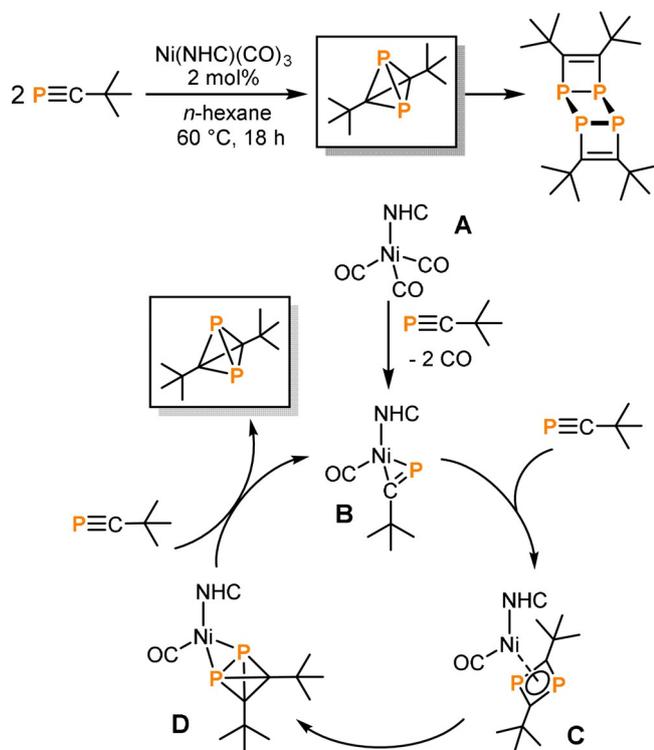
These mixed phosphatetrahedranes  $\text{P}(\text{CtBu})_3$  and  $\text{P}_2(\text{CR})_2$  ( $\text{R} = t\text{Bu}, \text{Ad}$ ), synthesized by completely independent methods, bridge the all-carbon and all-phosphorus tetrahedrane species that have been known for decades. It also raises the tantalizing question of whether the currently unknown combination,  $\text{P}_3\text{CR}$ , can be synthesized. It is noteworthy that the mixed tetrahedrane species  $\text{P}_3\text{As}$  has been previously synthesized by Cummins and co-workers, which features the necessary  $\text{P}_3$  moiety.<sup>[14]</sup> Furthermore, given the incredibly rich activation chemistry of  $\text{P}_4$ ,<sup>[15]</sup> it will be very interesting to see how these strained species are exploited towards the development of new synthetic routes to a wide array of organo-phosphorus compounds in the future.

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## Conflict of interest

The authors declare no conflict of interest.



**Scheme 2.** Synthesis of di-*tert*-butyldiphosphatetrahedrane by Wolf and co-workers. Abbreviations in text.

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