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Tetrahedranes

Mixed Phosphatetrahedranes

Andrew R. Jupp* and J. Chris Slootweg*

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Tetrahedranes, (CR)₄, are aesthetically pleasing yet synthetically challenging derivatives of the simplest platonic hydrocarbon.^[1] They are highly strained and offer potential as high energy-density materials. The parent tetrahedrane, (CH)₄, is predicted to be isolable^[2] despite its considerable strain energy (G3(MP2) = 136.8 kcal mol⁻¹),^[3] 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)₄ for the first time, and the kinetic stabilization from the bulky substituents was dubbed the “corset effect”.^[4] The challenging synthesis was ultimately carried out by irradiation of the tetrakis(*tert*-butyl)cyclopentadienone and elimination of CO. The tetrakis(trimethylsilyl)tetrahedrane (C(SiMe₃)₄) was later synthesized by isomerization of the cyclobutadiene derivative.^[5]

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.^[6] 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 (R₂C=PR)^[7] and phosphalkynes (RC≡P).^[8]

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. P₄ (strain energy: G3(MP2) = 16.0 kcal mol⁻¹)^[3] is the molecular form of elemental phosphorus known as white phosphorus, and was first discovered 350 years ago by the alchemist Hennig Brand.^[9] The incorporation of CR groups in place of the P atoms on the vertices of the P₄ 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 P₄ and (CR)₄ (R = *t*Bu, SiMe₃)^[5] 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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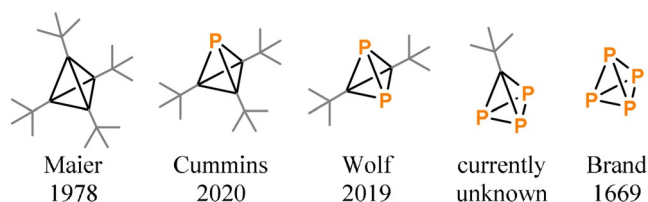
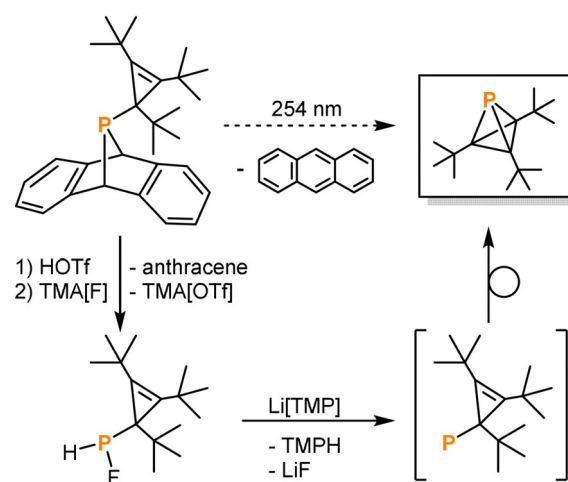


Figure 1. Tetrahedral structures based on carbon and phosphorus vertices.

Cummins and co-workers have successfully synthesized monophosphatetrahedrane P(C*t*Bu)₃.^[10] 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.

by ^{31}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}P NMR spectrum displays a diagnostic resonance at -488.0 ppm (C_6D_6), which is typical of highly strained phosphorus compounds (P_4 : $\delta^{31}\text{P}\{\text{H}\} = -520$ in C_6D_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 C_6D_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.^[11] 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)^[11a] 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).^[12] 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 C_6D_6). No single-crystal X-ray structure of the diphosphatetrahedrane was obtained, but a structure of this

species in the coordination sphere of a Ag^{I} cation confirmed the tetrahedral geometry. The pure compound has a melting point of -32°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 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 P_2C_2 ring has been observed before,^[13] 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.

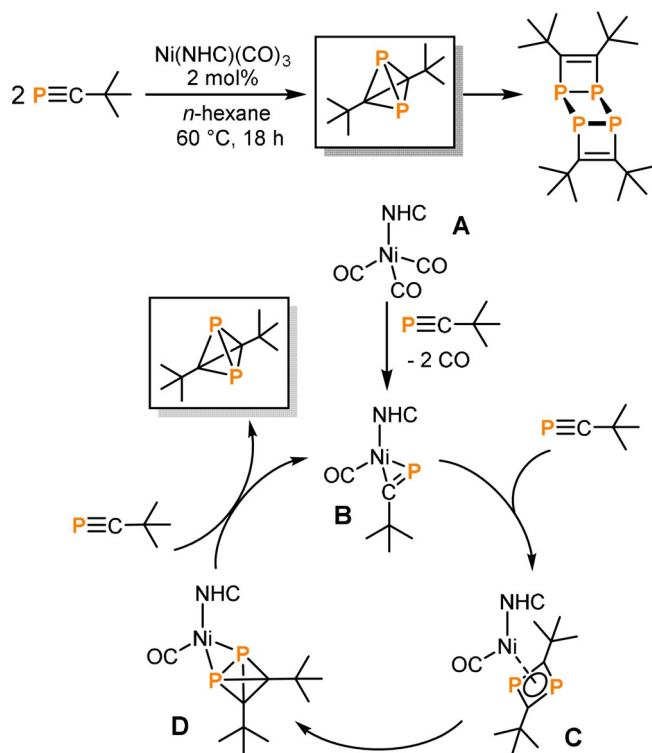
These mixed phosphatetrahedranes $\text{P}(\text{CtBu})_3$ and $\text{P}_2(\text{CR})_2$ ($\text{R} = t\text{Bu}, \text{Ad}$), synthesized by completely independent methods, bridge the all-carbon and all-phosphorus tetrahedrane species that have been known for decades. It also raises the tantalizing question of whether the currently unknown combination, P_3CR , can be synthesized. It is noteworthy that the mixed tetrahedrane species P_3As has been previously synthesized by Cummins and co-workers, which features the necessary P_3 moiety.^[14] Furthermore, given the incredibly rich activation chemistry of P_4 ,^[15] 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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