Mixed Phosphatetrahedranes

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Tetrahedranes, (CR)$_4$, are aesthetically pleasing yet synthetically challenging derivatives of the simplest platonic hydrocarbon. They are highly strained and offer potential as high energy-density materials. The parent tetrahedrane, (CH)$_4$, is predicted to be isolable despite its considerable strain energy (G3(MP2) = 136.8 kcal mol$^{-1}$) 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 (CtBu)$_4$ for the first time, and the kinetic stabilization from the bulky substituents was dubbed the “corset effect.” 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$_3$)$_4$) was later synthesized by isomerization of the cyclobutadiene derivative.

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. This phenomenon has given rise to the field of phospha-organic chemistry, where phosphorus can be conceptually substituted into organic compounds to afford intriguing compounds such as phosphaalkenes (R$_2$C=PR) and phosphaalkynes (RC/P).

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$_4$ (strain energy: G3(MP2) = 16.0 kcal mol$^{-1}$) is the molecular form of elemental phosphorus known as white phosphorus, and was first discovered 350 years ago by the alchemist Hennig Brand. The incorporation of CR groups in place of the P atoms on the vertices of the P$_4$ tetrahedron would give a series of mixed phosphatetrahedranes, as shown in Figure 1 (where R = tBu is used). Although both the all-phosphorus and all-carbon tetrahedral species P$_4$ and (CR)$_4$ (R = tBu, SiMe$_3$) have been known for a long time, the reports highlighted here describe the first examples of mixed P/C tetrahedrane species.

Cummins and co-workers have successfully synthesized monophosphatetrahedrane P(CtBu)$_3$. 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 (TMAF). Dehydrohalogenation of this fluorphosphate by the strong base lithium tetramethylpiperidide (Li[TMP]) afforded the desired compound almost exclusively.

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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 ($P_{E}$: $\delta^1{P}[H] = -520$ 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 $47.1(4)°$ (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 $130^\circ$C in $[D_6]$toluene induces partial conversion to a dimeric form with a house structure.\cite{11a}

Irradiation of the phosphatetrahedrane at 254 nm led to rapid decomposition to a range of products, including the dimer with a diphosphene structure. P(CBu$_3$)$_2$, 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 ($\delta^{31}{P}[H] = -47.6$) and diphosphahousene ($\delta^{31}{P}[H] = 55.5$, $-167.0$; $J_{P-P} = 171$ Hz)\cite{13a} in a 4:1 ratio.

A completely different strategy was employed by Wolf and co-workers for the synthesis of di-tert-butylphosphatetrahedrane, which was accessed by the nickel-catalyzed dimerization of the corresponding phosphaalkyne, P≡CBu ($C_6D_6$) (Scheme 2).\cite{12a} The P$_2$(CBu)$_2$ molecule was isolated as a pyrophoric, yellow oil in up to 55% yield (Scheme 2). The precursor is also susceptible to decomposition to a range of products, including the dimer ($\delta^{31}{P}[H] = -520$) and diphosphahousene ($\delta^{31}{P}[H] = 92.1$ (IMes) and 93.2 (IPr)). A second phosphaalkyne reacts with the bound phosphaalkyne via a head-to-tail dimerization to afford the 1,3-diphosphaacyclobutadiene in the coordination sphere of the transition metal (C; isolated with iPr$_2$Im$^{Me}$ (1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene), $\delta^{31}{P}[H] = 47.0$). Although the four-membered P$_2$C$_2$ ring has been observed before,\cite{13a} 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 tetrahedral derivative (D), as supported by DFT calculations. The tetrahedral compound is finally displaced by another equivalent of phosphaalkyne to afford the product and regenerate B. This synthetic protocol could be extended using the adamantyl-substituted phosphaalkyne P≡CaMe with phosphonium ($P(CBu)_2(CMe)(P≡CaMe)$, $\delta^{31}{P}[H] = -479.8$), and even the heterodimer P$_2$-(CBu,Im)$_2$ (D) ($\delta^{31}{P}[H] = -473.8$) could be identified.

These mixed phosphatetrahedrane P(CBu)$_2$ and P$_2$-(CR)$_2$ (R = Bu, 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$_2$CR, can be synthesized. It is noteworthy that the mixed tetrahedrane species P$_3$As has been previously synthesized by Cummins and co-workers, which features the P$_5$ moiety.\cite{14a} Furthermore, given the incredibly rich activation chemistry of P$_5$,\cite{15a} 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 organophosphorus compounds in the future.

![Scheme 2. Synthesis of di-tert-butylphosphatetrahedrane by Wolf and co-workers. Abbreviations in text.](image)

**Highlights**

- The authors declare no conflict of interest.

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**Conflict of interest**

The authors declare no conflict of interest.


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