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DOI

[10.1002/anie.202004514](https://doi.org/10.1002/anie.202004514)

Publication date

2020

Document Version

Final published version

Published in

Angewandte Chemie, International Edition

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Jupp, A. R., & Slootweg, J. C. (2020). Mixed Phosphatetrahedranes. *Angewandte Chemie, International Edition*, 59(27), 10698-10700. <https://doi.org/10.1002/anie.202004514>

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Tetrahedranes

Mixed Phosphatetrahedranes

Andrew R. Jupp* and J. Chris Slootweg*

Keywords: phosphorus · strained molecules · tetrahedranes

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.

How to cite: *Angew. Chem. Int. Ed.* **2020**, 59, 10698–10700

International Edition: doi.org/10.1002/anie.202004514

German Edition: doi.org/10.1002/ange.202004514

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.

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https://doi.org/10.1002/anie.202004514.

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 $[\text{D}_8]\text{toluene}$ 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 organophosphorus compounds in the future.

Acknowledgements

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.) and a VENI grant (A.R.J.). J.C.S. acknowledges the Alexander von Humboldt Foundation for a Humboldt Research Fellowship for Experienced Researchers.

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.

- [1] H. Hopf, in *Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives*, Wiley-VCH, Weinheim, **2000**, pp. 138–142.
- [2] A. Nemirowski, H. P. Reisenauer, P. R. Schreiner, *Chem. Eur. J.* **2006**, *12*, 7411–7420.
- [3] T. P. M. Goumans, PhD thesis: *Computational Chemistry of Ring Structures and Transition Metal Complexes*, Vrije Universiteit, Amsterdam **2005**.
- [4] G. Maier, S. Pfriem, U. Schäfer, R. Matusch, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520–521; *Angew. Chem.* **1978**, *90*, 552–553.
- [5] a) G. Maier, J. Neudert, O. Wolf, *Angew. Chem. Int. Ed.* **2001**, *40*, 1674–1675; *Angew. Chem.* **2001**, *113*, 1719–1720; b) G. Maier, J. Neudert, O. Wolf, D. Pappusch, A. Sekiguchi, M. Tanaka, T. Matsuo, *J. Am. Chem. Soc.* **2002**, *124*, 13819–13826.
- [6] K. B. Dillon, F. Mathey, J. F. Nixon, in *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*, Wiley, Chichester, **1998**.
- [7] a) G. Becker, *Z. Anorg. Allg. Chem.* **1976**, *423*, 242–254; b) T. C. Klebach, R. Lourens, F. Bickelhaupt, *J. Am. Chem. Soc.* **1978**, *100*, 4886–4888.
- [8] a) M. J. Hopkinson, H. W. Kroto, J. F. Nixon, N. P. C. Simmons, *J. Chem. Soc. Chem. Commun.* **1976**, 513–515; b) G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16–19.
- [9] J. Emsley, in *The 13th Element: The Sordid Tale of Murder, Fire and Phosphorus*, Wiley, New York, **2002**.
- [10] M.-L. Y. Riu, R. L. Jones, W. J. Transue, P. Müller, C. C. Cummins, *Sci. Adv.* **2020**, *6*, eaaz3168.
- [11] a) T. Krachko, A. W. Ehlers, M. Nieger, M. Lutz, J. C. Slootweg, *Angew. Chem. Int. Ed.* **2018**, *57*, 1683–1687; *Angew. Chem.* **2018**, *130*, 1699–1703. For the phosphorus analogue of the cyclopropenylcarbene–cyclobutadiene rearrangement, see: b) V. Lyaskovskyy, N. Elders, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2011**, *133*, 9704–9707.
- [12] G. Hierlmeier, P. Coburger, M. Bodensteiner, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 16918–16922; *Angew. Chem.* **2019**, *131*, 17074–17078.
- [13] A. Chirila, R. Wolf, J. C. Slootweg, K. Lammertsma, *Coord. Chem. Rev.* **2014**, 270–271, 57–74.
- [14] B. M. Cossairt, M.-C. Diawara, C. C. Cummins, *Science* **2009**, *323*, 602.
- [15] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235; c) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; d) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342–1359; e) D. G. Yakhvarov, E. V. Gorbachuk, O. G. Sinyashin, *Eur. J. Inorg. Chem.* **2013**, 4709–4726; f) J. E. Borger, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *Chem. Eur. J.* **2017**, *23*, 11738–11746.

Manuscript received: March 27, 2020

Version of record online: May 11, 2020