Dimerization and Cycloaddition Reactions of Transient Tri-*tert*-butylphosphacyclobutadiene Generated by Lewis-acid Induced Isomerization of Tri-*tert*-butylphosphatetrahedrane

Martin-Louis Y. Riu, André K. Eckhardt, and Christopher C. Cummins*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received August 3, 2021; E-mail: ccummins@mit.edu

Abstract: Tri-*tert*-butylphosphatetrahedrane (**1**) is shown here to act as a synthon of isomeric tri-*tert*-butylphosphacyclobutadiene in the presence of a Lewis acid or transition metal complex. When combined with a substoichiometric amount of triphenylborane, compound **1** forms a ladderane-type dimer of tri-*tert*-butylphosphacyclobutadiene in 72% isolated yield. Trapping of a generated intermediate was achieved by repeating the experiment in the presence of excess styrene (20 equiv) or ethylene (1 atm) and the corresponding [4 + 2] cycloadducts of tri-*tert*-butylphosphacyclobutadiene were isolated in 88% and 74% yield, respectively. The platinum complex $(Ph_3P)_2Pt(C_2H_4)$ also reacts with **1** to form an orange, dihaptic complex of tri-*tert*-butylphosphacyclobutadiene in 80% isolated yield. Additionally, we report a novel method for generating a phosphinidenoid species via fluoride-induced trimethylsilylfluoride elimination, leading to an improved preparative procedure for **1** (182 mg, 33% isolated yield).

Organic tetrahedranes have long captivated the chemistry community because of their unusual bonding properties and reactivity,[1] as well as their potential applications as organic superbases[2,3] and components in high-energy density materials.[4,5] While tetrahedrane is considered the most strained saturated hydrocarbons in terms of Baeyer's strain theory that was first postulated in 1885,[6–8] it was not until 1978 when the first tetrahedrane derivative tetra-*tert*-butyltetrahedrane was successfully isolated.[9] In this seminal study, Maier and co-workers also unveiled the close relationship between tetra-*tert*-butyltetrahedrane and isomeric tetra-*tert*-butylcyclobutadiene, by showing their interconversion through thermolysis and photolysis experiments.[9]

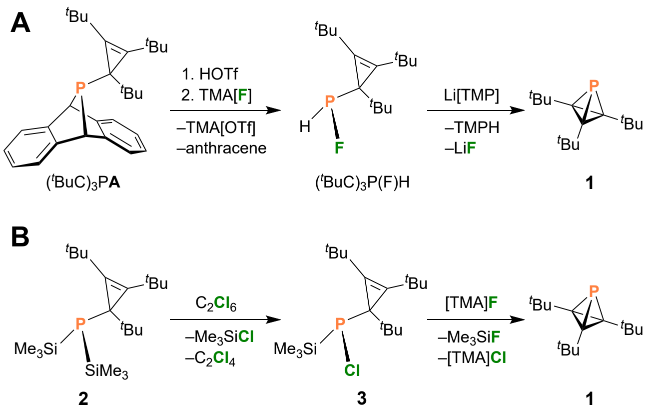
While tetrahedrane-cyclobutadiene isomerization has been shown for a number of tetrahedrane derivatives containing an all-carbon core,[10–15] few examples of the analogous transformation for tetrahedranes containing a mixed-element core exist. Given the recently reported syntheses of *tert*-butyl-substituted mono- and diphosphatetrahedrane derivatives[16–18] and the well known diagonal relationship of carbon and phosphorus,[19] it is conceivable that an uncomplexed phosphacyclobutadiene (pCBD; also known as λ^3-phosphete) ring structure may be accessed. The structures and bonding properties of mono- and diphosphacyclobutadienes have been computationally investigated previously and noted as interesting targets for matrix isolation.[20,21] Here we report that the combination of tri-*tert*-butylphosphatetrahedrane (**1**) and substoichiometric triphenylborane leads to tri-*tert*-butyl-pCBD transfer reactivity. Additionally, we show that treatment of **1** with the reducing transition metal complex $(Ph_3P)_2Pt(C_2H_4)$ produces a dihaptic pCBD complex of platinum under mild conditions.

Our group recently reported the synthesis of **1** via the generation of a cyclopropenyl-substituted phosphinidenoid by dehydrohalogenation of hydro(fluoro)phosphine $(^t\mathrm{BuC})_3\mathrm{P(F)H}$ (Scheme 1A)).[16] However, reactivity studies were hampered by the low isolated yield of **1** (33 mg, 19% yield). Taking into account that anthracene merely acted as a leaving group in the preparation of the hydro(fluoro)phosphine phosphinidenoid precursor, we wondered whether we could obviate the use of $(^t\mathrm{BuC})_3\mathrm{P}\mathbf{A}$ ($\mathbf{A}$ = anthracene, $C_{14}H_{10}$) by preparing **1** from $(^t\mathrm{BuC})_3\mathrm{P(SiMe_3)_2}$ (**2**), which can be prepared on a large scale from $P(SiMe_3)_3$ and $[^t\mathrm{Bu_3C_3}][\mathrm{BF_4}]$ (Scheme 1B).[22] Additionally, Niecke and coworkers previously demonstrated that P–$SiMe_3$ bonds may be cleaved using hexachloroethane to form a P–Cl bond, trimethylsilyl chloride, and tetrachloroethylene.[23] Therefore, we targeted for synthesis $(^t\mathrm{BuC})_3\mathrm{P(SiMe_3)Cl}$ (**3**, Scheme 1), which is analogous to $(^t\mathrm{BuC})_3\mathrm{P}\mathbf{A}$ but with trimethylsilyl chloride in place of anthracene as a neutral leaving group, from **2** using existing methodology.

Accordingly, the combination of **2** and hexachloroethane in thawing diethyl ether led to two new resonance in the ^{31}P NMR spectrum at δ = 100.47 and 100.42 ppm, chemical shifts that are consistent with other reported chloro(trimethylsilyl)phosphines (Scheme 1B).[23,24] Additionally, the signals both exhibit ^{29}Si satellites ($^1J_{\mathrm{PSi}}$ = 64 Hz) and integration of the satellites is consistent with a single Si–P bond for each species (Fig. S.4). Given that the two signals are present in an approximate 3:1 ratio, the upfield ^{31}P NMR resonance is attributed to the ^{37}Cl isotopomer of **3**.[25,26] While we are unable to isolate **3** by crystallization, the crude material obtained from this reaction is fairly clean, as assessed by NMR spectroscopy, and contains only trace amounts of $[^t\mathrm{Bu_3C_3}]$ cation, its counterion, and **2**.

Thermolysis (85 °C, 12 h) of **3** in benzene resulted in a complex mixture of phosphorus-containing products, as assessed by ^{31}P NMR spectroscopy (Fig. S.5). Consequently, we turned our attention to an alternative method of trimethylsilyl chloride extrusion from **3**. Hiyashi, Watanabe, and co-workers previously reported the activation of a P–$SiMe_3$ group by the addition of fluoride to generate a phosphide anion;[27] however, such examples are rare, despite the extensive application of fluoride anion activation of organosilicon compounds.[28,29] Based on this precedent, we wondered whether treatment of compound **3** with fluoride would produce the desired cyclopropenyl-substituted halophosphide anion that could close to form phosphatetrahedrane **1**. This reaction would resemble our dehydrohalogenation route to **1**,[16] in addition to our recent report on organoiron- and fluoride-catalyzed phosphiranation of styrenic olefins, for which a possible intermediate is the iron-

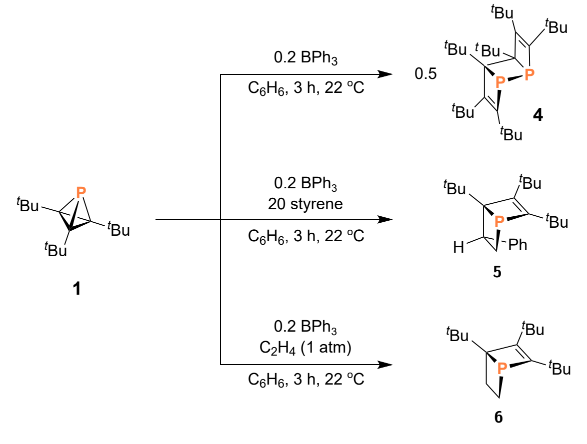
Scheme 1. (**A**) Previously reported synthesis of phosphatetrahedrane **1** starting from (^{t}BuC)$_3$P**A**.[16] (**B**) Improved synthesis of **1** starting from (^{t}BuC)$_3$P(SiMe$_3$)$_2$ (**2**). Abbreviations: TMA, tetramethylammonium; OTf, triflate; TMP, 2,2,6,6-tetramethylpiperidide.



phosphido species FpP(F)(^{t}Bu) (Fp = Fe(η_5-C$_5$H$_5$)(CO)$_2$)) as suggested by our mechanistic investigation.[30]

Indeed, addition of [TMA][F] to a thawing solution of **3** in dichloromethane cleanly forms **1** upon elimination of trimethylsilyl fluoride and tetramethylammonium chloride (Scheme 1). Consistent with formation of Me$_3$SiF, a singlet was observed at $\delta = -157.7$ ppm in the ^{19}F NMR spectrum and a doublet centered at 34.7 ppm ($^1J_{\mathrm{SiF}} = 274$ Hz) was observed in the ^{29}Si NMR spectrum. Crude samples of **1**, obtained as a pale brown oil, were purified by passing a pentane solution of the sample through a plug of acidic alumina, carefully removing volatile materials under reduced pressure from the filtrate, and sublimation of the resulting residue under vacuum (50 mTorr) at 40 °C, allowing for the isolation of **1** as a colorless solid in 33% yield (182 mg). To our knowledge, this is the first example of fluoride-induced generation of a phosphinidenoid from a halo(silyl)phosphine, complementing existing pathways to phosphinidenoids, which are often prepared from dichlorophosphines.[25,26,31–33]

Scheme 2. Triphenylborane-Promoted Reactions of **1**.



With synthetically useful quantities of **1** in hand, we investigated its reactivity with Lewis acids. We previously showed that **1** is highly susceptible to dimerization in the presence of Lewis acids and reacts with tungstenpentacarbonyl tetrahydrofuran to form uncomplexed diphosphahousene.[16] However, when **1** is combined with a substoichiometric amount of triphenylborane (0.2 equiv) in benzene, a new signal, corresponding to a ladderane-type head-to-head dimer of tri-*tert*-butyl-pCBD (**4**), was observed at -47.6 ppm in the ^{31}P NMR spectrum (Scheme 2). Crude **4** was purified by adding pyridine to a pentane solution of **4**, filtering away the precipitated triphenylborane adduct of pyridine, and crystallization at -35 °C. Compound **4** was isolated as colorless crystals in 72% yield and the crystals of **4** were characterized in a X-ray diffraction study (Fig. 1). Due to the close proximity of the *tert*-butyl substituents in **4**, restricted rotation of two *tert*-butyl groups was observed in the ^{1}H NMR spectrum. Coalescence of the broadened *tert*-butyl resonances was observed at elevated temperatures (see section S.1.3.1). Additionally, in an attempt to cleave the P−P bond, **4** was treated with C$_2$Cl$_6$ (1 equiv); however, no reaction was observed.

Interested in trapping a reactive intermediate generated upon the combination of **1** and triphenylborane, the reaction was repeated in the presence of excess styrene (20 equiv). A new signal centered at -27.6 ppm was observed in the ^{31}P NMR spectrum and could be assigned to the cycloadduct **5** (Scheme 2). After removing triphenylborane and excess styrene, crystals of **5** were grown from diethyl ether at -35 °C and the product was isolated in 88% yield. Compound **5** was structurally characterized in an X-ray diffraction study and the molecular structure is depicted in Fig. 1. Remarkably, when this reaction was repeated with ethylene (ca. 1 atm) instead of styrene, clean conversion to the ethylene adduct of tri-*tert*-butyl-pCBD (**6**, Scheme 2) was observed. This [4 + 2] cycloadduct exhibits a resonance centered at 8.3 ppm in the ^{31}P NMR spectrum. Note that examples of phosphorus-containing heterocycles that undergo [4 + 2] cycloaddition to ethylene under mild conditions are exceedingly rare.[34] After removing triphenylborane and filtering a pentane solution of the crude reaction mixture through a plug of silica, compound **6** was isolated as a colorless oil in 74% yield. The product is contaminated with a small amount of **4** and trace amounts of unidentified impurities. However, attempts to further purify the material by crystallization and sublimation were unsuccessful. Additionally, no reaction was observed between the generated intermediate and hydrogen when **1** was combined with triphenylborane in the presence of hydrogen (ca. 1 atm; S.1.6).

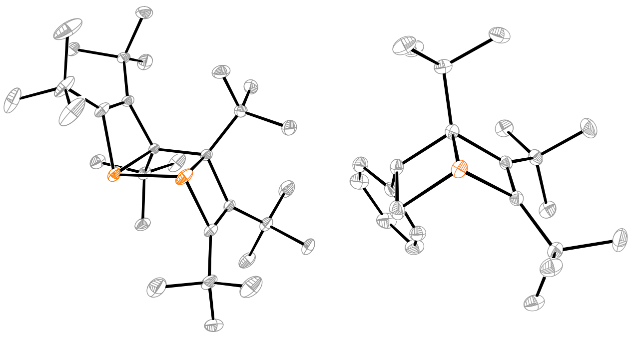


Figure 1. Molecular structure of **4** (left) and **5** (right) shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Orange, phosphorus; gray, carbon.

Extensive literature searching revealed no other examples of 1-phosphabicyclo[2.2.0]hexenes. However, 1- and 2-phosphabicyclo[2.2.0]hexadienes (1- and 2-Dewar phosphinines), classes of heterocycles that are related to **5**, have been prepared by photolysis of phosphinines[35] and by treating kinetically stabilized cyclobutadienes with phosphaalkynes,[36,37] respectively. Additionally, the thermal stability of **5** was investigated by heating a mesitylene solution

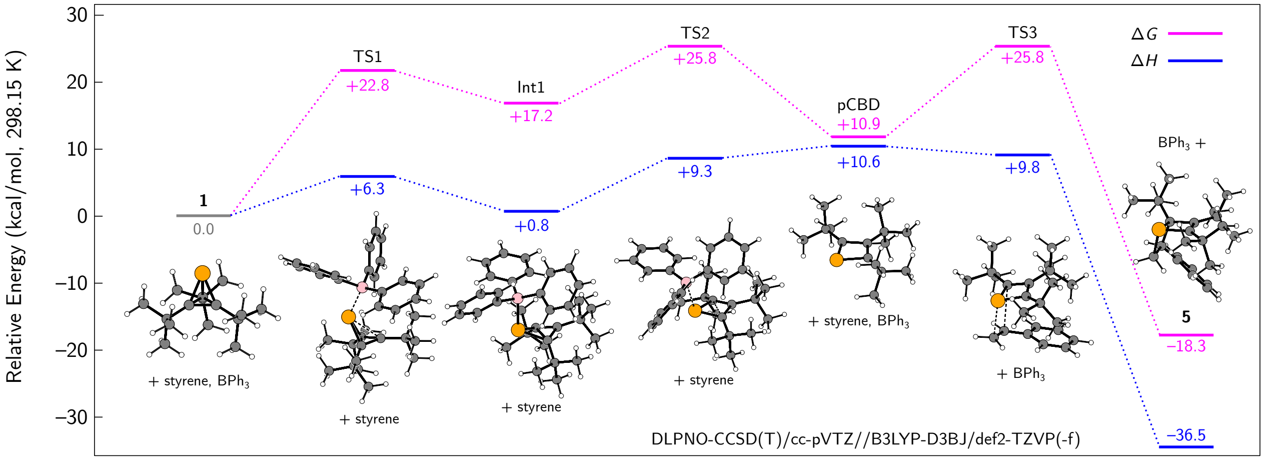


Figure 2. Calculated stationary points and transition states and their relative enthalpies and free energies (298.15 K) involved in the isomerization **1** by triphenylborane (BPh_3) and trapping of tri-*tert*-butylphosphacyclobutadiene by styrene.

of compound **5** to 150 °C, but no changes were observed in the ^{31}P NMR spectrum after 24 h.

The mechanism for the formation of **5** was investigated using quantum chemical calculations (Fig. 2). Geometries were optimized at the B3LYP-D3BJ/def2-TZVP(-f) level of theory and the Gibbs free enthalpies (T = 298.15 K) were obtained using single point energies calculated using the domain-based local pair natural orbital coupled-cluster method with singles, doubles, and perturbative triples excitation (DLPNO-CCSD(T))[38] with the cc-pVTZ basis set[39] and TightPNO settings.[40] The calculations suggest that **1** undergoes C−P bond scission by triphenylborane to give a zwitterionic 2-phosphabicyclo[1.1.0]butane complex (Int1). Note that a similar intermediate has been proposed in the valence isomerization of metal carbonyl-complexed cyclopropenylphosphinidenes.[41] Elimination of triphenylborane and concomitant transannular C−C bond cleavage affords free tri-*tert*-butyl-pCBD, which subsequently undergoes [4 + 2] cycloaddition to styrene. This elimination reaction comprises the rate-determining step for the formation of **5** with a barrier of +25.8 kcal/mol, consistent with the reaction proceeding readily at room temperature. Attempts to locate a pathway involving a direct reaction between styrene and Int1 were unsuccessful. In addition, the formation of other possible isomers of cycloadduct **5** was also explored and we found that the computed pathway to the experimentally observed isomer exhibits the smallest barrier (S.3.2).

The reaction of **1** with a reducing transition metal complex was also explored as it would lead to a transition-metal complex of tri-*tert*-butyl-pCBD. Indeed, the combination of $(Ph_3P)_2Pt(C_2H_4)$ and **1** in thawing tetrahydrofuran cleanly produces **7** (Fig. 3A). Crude **7** was purified by filtration of a diethyl ether solution of the reaction mixture through Celite, removal of volatiles from the filtrate, and trituration of the orange solids using pentane. Complex **7** was isolated in 80% yield and exhibits three inequivalent signals in the ^{31}P NMR spectrum centered at δ 24.9 (dd, $^1J_{\mathrm{PtP}} = 2803.2$ Hz, $^2J_{\mathrm{PP}} = 41.7, 10.2$ Hz), 22.2 (dd, $^1J_{\mathrm{PtP}} = 2564.3$ Hz, $^2J_{\mathrm{PP}} = 10.2$ Hz), −35.6 (dd, $^1J_{\mathrm{PtP}} = 176.7$ Hz, $^2J_{\mathrm{PP}} = 41.7, 10.2$ Hz) ppm.

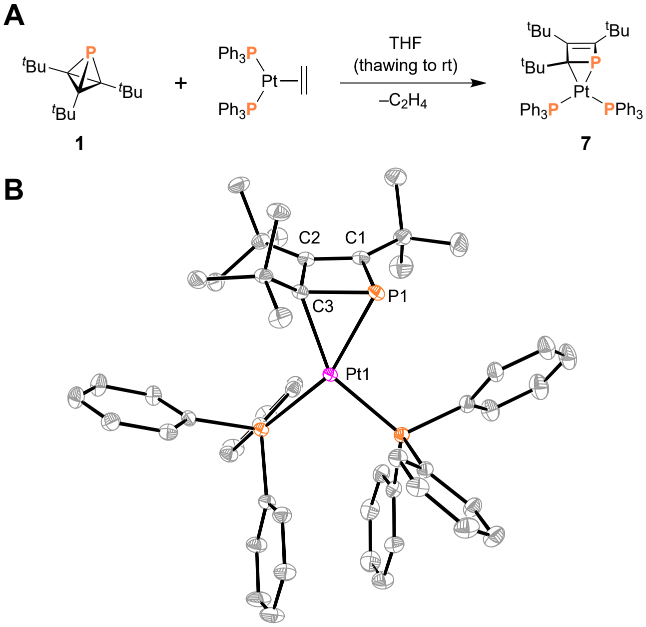


Figure 3. **A)** Synthesis of **7** starting from **1** and $(Ph_3P)_2Pt(C_2H_4)$. **B)** Molecular structure of **7** shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt1−C3: 2.1735(17), Pt1−P1: 2.2867(5), P1−C3: 1.8171(18), C3−C2: 1.569(2), C2−C1: 1.365(3), C1−P1: 1.8831(19). Phosphorus, orange; platinum, fuchsia; carbon, gray.

Crystals of **7** grown from diethyl ether were characterized in an X-ray diffraction experiment and the molecular structure is depicted in Fig. 3B. A notably long bond length of 1.8171(18) was found for P1−C3 (the sum of the single and double bond covalent radii are 1.86 and 1.69 Å, respectively),[42] which is consistent with reduction of the pCBD ligand by the platinum center. Interestingly, the platinum center coordinates to the pCBD in an η^2 fashion in contrast to other reported pCBD complexes.[41,43,44] Likely, steric repulsion between the *tert*-butyl substituents of the pCBD and triphenylphosphine ligands prevents the platinum center from coordinating to the C=C double bond.

The reactions of **1** with triphenylborane and $(Ph_3P)_2Pt(C_2H_4)$ under mild conditions highlight the significant strain energy of **1** and its utility as a synthetic equivalent of tri-*tert*-butyl-pCBD. This investigation was enabled by an improved preparative procedure for **1**, which relied on the generation of a phosphinidenoid by fluoride-induced elimination of $Me_3Si{-}F$ from chloro(silyl)phosphine **3**. This chemistry joins a new and growing body of work on the use of phosphatetrahedranes as building blocks in the synthesis of novel organophosphorus compounds.[45,46]

Acknowledgments: We thank Michael B. Geeson and Feng Zhai for thoughtful discussions and suggestions. **Funding:** This material is based on research supported by the National Science Foundation under CHE-1955612. A.K.E. thanks the Alexander von Humboldt foundation for a Feodor Lynen research fellowship. **Competing interests:** The authors declare no competing interests.

Supporting Information Available

Crystallographic data are available from the Cambridge Structural Database under refcodes 2040155, 2040157, and 2040156. Full synthetic and computational details, including preparative procedures and spectroscopic data for characterization of compounds, are in the supplementary materials.

References

(1) Maier, G. Tetrahedrane and Cyclobutadiene. *Angew. Chem. Int. Ed.* **1988**, *27*, 309–332.

(2) Valadbeigi, Y.; Vianello, R. Is It Possible to Achieve Organic Superbases beyond the Basicity Limit Using Tetrahedrane Scaffolds? *ChemistrySelect* **2020**, *5*, 5794–5798.

(3) Notario, R.; Castaño, O.; Andrés, J. L.; Elguero, J.; Maier, G.; Hermann, C. An Experimental and Theoretical Study of the Basicity of Tetra-*tert*-butyltetrahedrane. *Chem. Eur. J.* **2001**, *7*, 342–346.

(4) Zhou, G.; Zhang, J.-L.; Wong, N.-B.; Tian, A. Computational studies on a kind of novel energetic materials tetrahedrane and nitro derivatives. *J. Mol. Struct* **2004**, *668*, 189–195.

(5) Rayne, S.; Forest, K. A G4MP2 and G4 Theoretical Study into the Thermochemical Properties of Explosophore Substituted Tetrahedranes and Cubanes. *Propellants Explos. Pyrotech.* **2011**, *36*, 410–415.

(6) Baeyer, A. Ueber Polyacetylenverbindungen. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269–2281.

(7) Huisgen, R. Adolf von Baeyer's Scientific Achievements — a Legacy. *Angew. Chem. Int. Ed.* **1986**, *25*, 297–311.

(8) Wiberg, K. B. The Concept of Strain in Organic Chemistry. *Angew. Chem. Int. Ed.* **1986**, *25*, 312–322.

(9) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. Tetra-*tert*-butyltetrahedrane. *Angew. Chem. Int. Ed.* **1978**, *17*, 520–521.

(10) Maier, G.; Born, D. Tri-*tert*-butyl(trimethylsilyl)tricyclo[1.1.0.0^{2,4}]-butane—a Second Tetrahedrane Derivative. *Angew. Chem. Int. Ed.* **1989**, *28*, 1050–1052.

(11) Maier, G.; Neudert, J.; Wolf, O. Tetrakis(trimethylsilyl)cyclobutadiene and Tetrakis(trimethylsilyl)tetrahedrane. *Angew. Chem. Int. Ed.* **2001**, *40*, 1674–1675.

(12) Maier, G.; Neudert, J.; Wolf, O.; Pappusch, D.; Sekiguchi, A.; Tanaka, M.; Matsuo, T. Tetrakis(trimethylsilyl)tetrahedrane. *J. Am. Chem. Soc.* **2002**, *124*, 13819–13826.

(13) Nakamoto, M.; Inagaki, Y.; Nishina, M.; Sekiguchi, A. Perfluoroaryltetrahedranes: Tetrahedranes with Extended σ-π Conjugation. *J. Am. Chem. Soc.* **2009**, *131*, 3172–3173.

(14) Inagaki, Y.; Nakamoto, M.; Sekiguchi, A. Photoisomerization of Perfluoroaryltetrahedranes to Perfluoroarylcyclobutadienes. *J. Am. Chem. Soc.* **2011**, *133*, 16436–16439.

(15) Ochiai, T.; Nakamoto, M.; Inagaki, Y.; Sekiguchi, A. Sulfur-Substituted Tetrahedranes. *J. Am. Chem. Soc.* **2011**, *133*, 11504–11507.

(16) Riu, M.-L. Y.; Jones, R. L.; Transue, W. J.; Müller, P.; Cummins, C. C. Isolation of an elusive phosphatetrahedrane. *Sci. Adv.* **2020**, *6*, eaaz3168.

(17) Hierlmeier, G.; Coburger, P.; Bodensteiner, M.; Wolf, R. Di-*tert*-butyldiphosphatetrahedrane: Catalytic Synthesis of the Elusive Phosphaalkyne Dimer. *Angew. Chem. Int. Ed.* **2019**, *58*, 16918–16922.

(18) Jupp, A. R.; Slootweg, J. C. Mixed Phosphatetrahedranes. *Angew. Chem. Int. Ed.* **2020**, *59*, 10698–10700.

(19) Dillon, K. B.; François, M.; Nixon, J. F. *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-Organic Chemistry*; Wiley, 1998.

(20) Schoeller, W. W.; Busch, T. Aza- versus Phospha-Substitution in Cyclobutadiene: A Theoretical Evaluation of Bonding Properties. *Angew. Chem. Int. Ed.* **1993**, *32*, 617–619.

(21) Schoeller, W. W.; Busch, T.; Haug, W.; Strutwolf, J. Phosphorus in Strained Ring Systems. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *77*, 93–96.

(22) Zurmühlen, F.; Regitz, M. Phosphorverbindungen ungewöhnlicher Koordination: XXV. Cyclopropenylphosphaalkene, Edukte zur Synthese stabiler 2H-Phosphole. *J. Organomet. Chem.* **1987**, *332*, C1 – C5.

(23) Treubel, R.; Niecke, E. Halogen(Silyl)phosphane – Synthese und Eigenschaften. *Chem. Ber.* **1990**, *123*, 1245–1251.

(24) Geier, J.; Frison, G.; Grützmacher, H. Dibenzophosphasemibullvalene. *Angew. Chem. Int. Ed.* **2003**, *42*, 3955–3957.

(25) Nesterov, V.; Schnakenburg, G.; Espinosa, A.; Streubel, R. Synthesis and Reactions of the First Room Temperature Stable Li/Cl Phosphinidenoid Complex. *Inorg. Chem.* **2012**, *51*, 12343–12349.

(26) Schmer, A.; Volk, N.; Ferao, A. E.; Streubel, R. Access and unprecedented reaction pathways of Li/Cl phosphinidenoid iron(0) complexes. *Dalton Trans.* **2019**, *48*, 339–345.

(27) Hayashi, M.; Matsuura, Y.; Watanabe, Y. Fluoride-mediated phosphination of alkenes and alkynes by silylphosphines. *Tetrahedron Lett.* **2004**, *45*, 9167–9169.

(28) Abele, E. Activation of Silicon Bonds by Fluoride Ion in the Organic Synthesis in The New Millenium: A Review. *Main Group Met. Chem.* **2005**, *28*, 45–70.

(29) Abele, E.; Abele, R. Recent Advances in Activation of Silicon Bonds by Fluoride Ion. *Main Group Met. Chem.* **2009**, *32*, 165–194.

(30) Geeson, M. B.; Transue, W. J.; Cummins, C. C. Organoiron- and Fluoride-Catalyzed Phosphinidene Transfer to Styrenic Olefins in a Stereoselective Synthesis of Unprotected Phosphiranes. *J. Am. Chem. Soc.* **2019**, *141*, 13336–13340.

(31) Khan, A. A.; Wismach, C.; Jones, P. G.; Streubel, R. An unconventional route to [(Me$_3$Si)$_2$HCPCl$_2$W(CO)$_5$] and its conversion to the structurally characterized P-chalcogenides (Me$_3$Si)$_2$HCP(X)Cl$_2$ [X = S, Se]. *Dalton Trans.* **2003**, 2483.

(32) Duan, L.; Schnakenburg, G.; Daniels, J.; Streubel, R. P-OR Functional Phosphanido and/or Li/OR Phosphinidenoid Complexes? *Eur. J. Inorg.* **2012**, *2012*, 3490–3499.

(33) Fassbender, J.; Schnakenburg, G.; Ferao, A. E.; Streubel, R. Effects of diminished steric protection at phosphorus on stability and reactivity of oxaphosphirane complexes. *Dalton Trans.* **2018**, *47*, 9347–9354.

(34) Riu, M.-L. Y.; Cummins, C. C. 3,5-Diphenyl-2-phosphafuran: Synthesis, Structure, and Thermally Reversible [4 + 2] Cycloaddition Chemistry. *J. Org. Chem.* **2020**, *85*, 14810–14816.

(35) Blatter, K.; Rösch, W.; Vogelbacher, U.-J.; Fink, J.; Regitz, M. Isomerization Reactions in the System Dewar-Phosphinine/Phosphaprismane/Phosphabenzvalene/Phosphinine. *Angew. Chem. Int. Ed.* **1987**, *26*, 85–86.

(36) Fink, J.; Rösch, W.; Vogelbacher, U.-J.; Regitz, M. 2-Dewar Phosphinines—a New Class of Compounds Containing Two-Coordinate Phosphorus. *Angew. Chem. Int. Ed.* **1986**, *25*, 280–282.

(37) Mack, A.; Pierron, E.; Allspach, T.; Bergsträßer, U.; Regitz, M. Organophosphorus Compounds; 129. Mesitylphosphaacetylene: Synthesis and Reactivity Studies of a New Phosphaalkyne. *Synthesis* **1998**, *1998*, 1305–1313.

(38) Guo, Y.; Riplinger, C.; Becker, U.; Liakos, D. G.; Minenkov, Y.; Cavallo, L.; Neese, F. Communication: An improved linear scaling perturbative triples correction for the domain based local pair-natural orbital based singles and doubles coupled cluster method [DLPNO-CCSD(T)]. *J. Chem. Phys.* **2018**, *148*, 011101.

(39) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(40) Neese, F.; Hansen, A.; Liakos, D. G. Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural orbital basis. *J. Chem. Phys* **2009**, *131*, 064103.

(41) Lyaskovskyy, V.; Elders, N.; Ehlers, A. W.; Lutz, M.; Slootweg, J. C.; Lammertsma, K. Remarkable Metal-Complexed Phosphorus Analogues of the Cyclopropenylcarbene–Cyclobutadiene Rearrangement. *J. Am. Chem. Soc.* **2011**, *133*, 9704–9707.

(42) Pyykkö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1–118. *Chem. Eur. J* **2009**, *15*, 186–197.

(43) Binger, P.; Haas, J.; Herrmann, A. T.; Langhauser, F.; Krüger, C. Cooligomerization of Phosphaalkynes and Alkynes in the Coordination Sphere of Rhodium Complexes. *Angew. Chem. Int. Ed.* **1991**, *30*, 310–312.

(44) Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Richards, A. F.; Francis, M. D.; Dickson, R. S.; Junk, P. C. Novel Dirhodium Complexes Derived from Phosphaalkynes. *Organometallics* **1999**, *18*, 4838–4844.

(45) Hierlmeier, G.; Wolf, R. Activation of Di-*tert*-butyldiphosphatetrahedrane: Access to (tBuCP)$_n$ (n=2, 4) Ligand Frameworks by P−C Bond Cleavage. *Angew. Chem. Int. Ed.* **2021**, *60*, 6435–6440.

(46) Hierlmeier, G.; Uttendorfer, M. K.; Wolf, R. Di-*tert*-butyldiphosphatetrahedrane as a building block for phosphaalkenes and phosphirene. *Chem. Commun.* **2021**, *57*, 2356–2359.