Reactions of Tri-*tert*-Butylphosphatetrahedrane as a Spring-Loaded Phosphinidene Synthon Featuring Nickel-Catalyzed Transfer to Unactivated Alkenes

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Abstract: Cage-opening reactions of the highly strained tri-*tert*-butylphosphatetrahedrane (**1**), shown here to function as a synthon of (tri-*tert*-butylcyclopropenyl)phosphinidene, are described. Treatment of **1** with a base-stabilized silylene led to the corresponding phosphasilene, which was isolated in 72% yield as a red crystalline solid. Phosphinidene transfer was also observed when **1** (2 equiv) was combined with the Wittig reagent Ph_3PCH_2 to form a diphosphirane (50% isolated yield). The reaction is proposed to proceed through a generated phosphaalkene intermediate, which was characterized by NMR spectroscopy. In addition, we report on nickel-catalyzed phosphinidene transfer to styrene, ethylene, neohexene, and 1,3-cyclohexadiene; the corresponding phosphiranes were isolated in 51-64% yield. Computational studies suggest the intermediacy of a nickel phosphinidene species. Treatment of the ethylene-derived phosphirane product with triflic acid delivered elimination of $[^tBu_3C_3]OTf$ and formation of a P−H bond, illustrating the ability of the tri-*tert*-butyl cyclopropenyl group to serve as a protecting group that is removable following phosphinidene transfer.

Carbon-based tetrahedranes are highly strained molecules that possess significant potential energy.[1–3] Given the tetrahedral nature of elemental white phosphorus (P_4), a recent approach to alleviating the strain of these 'fiery'[1] compounds has been the incorporation of phosphorus into the tetrahedrane core, and mono-,[4] di-,[5] and triphosphatetrahedrane[6] derivatives have been successfully synthesized. Despite a reduction in their strain energies, phosphatetrahedranes also exhibit interesting cage-opening reactions and have led to isomeric phosphacyclobutadienes,[7–9] phosphaalkenes,[10] and a novel polymeric material.[6]

Given the spring-loaded nature of its highly strained core (strain energy ca. 96 kcal/mol for $P(CH)_3$),[6] we wondered whether tri-*tert*-butylphosphatetrahedrane (**1**)[4,7] could function as a phosphinidene synthon where two of the three C−P bonds are cleaved to form a new cyclopropene ring and a phosphorus lone pair. Such behavior would be desirable given the utility of singlet phosphinidene synthons in the construction of organophosphorus compounds.[11–16] Moreover, strain energy calculations suggest that monophosphatetrahedranes are the most strained class of phosphatetrahedranes, providing significant driving force for these cage-opening reactions.[6] Herein, we describe the strain-driven phosphinidene reactivity of **1**. In addition to phosphinidene transfer to a base-stabilized silylene, phosphorus ylide, and phosphaalkene, we report on a nickel-catalyzed synthesis of phosphiranes via phosphinidene transfer to alkenes, including unactivated ones. We go on to show

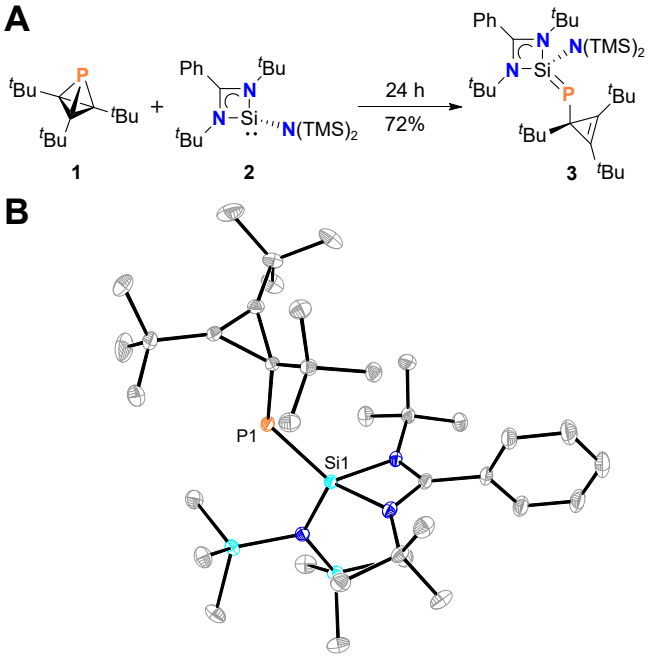


Figure 1. A) Synthesis of phosphasilene **3**. B) Molecular structure of **3** shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Color code: carbon, gray; nitrogen, blue; phosphorus, orange; silicon, teal.

that the $(^tBuC)_3$ substituent of the resulting phosphiranes may be cleaved off using triflic acid to install a P−H bond.

Initial studies were carried out with N-heterocyclic carbenes (NHCs); however, no reaction was observed when **1** was combined with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (IPr) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IMes). The lack of reactivity is consistent with the sluggish cage-opening reactions observed between diphosphatetrahedrane $(^tBuCP)_2$ and bulky NHCs.[10] Consequently, compound **1** was combined with base-stabilized silylene **2** (Fig. 1A), which is known to react with white phosphorus to form a phosphasilene.[17,18] When a benzene solution of **1** was combined with **2**, the solution gradually became dark red over 24 h. NMR analysis of the crude reaction mixture revealed complete consumption of **1** and clean conversion to a new resonance centered at δ −182.3 ppm in the ^{31}P NMR spectrum, consistent with the formation of phosphasilene **3** (Fig. 1A). Additionally, a large $^1J_{PSi}$ coupling constant of 240.4 Hz was observed for **3**, reflecting the presence of a multiple bond between phosphorus and silicon.[19] Given that the silicon center is tetracoordinate, multiple bond character between phosphorus and silicon arises from donation of the phosphorus lone pair into the polarized Si−N antibonds. Formation of

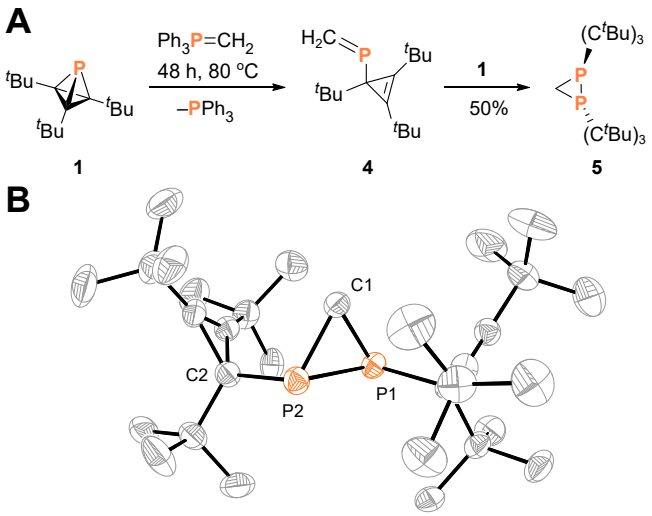


Figure 2. A) Synthesis of **5**, proposed to proceed through phosphaalkene **4**. B) Molecular structure of **5** shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

3 under mild conditions can be attributed to the smaller HOMO-LUMO gap of **2**, relative to those of IPr and IMes.

Crystallization from cold pentane provided **3** in 72% yield as dark red crystals. These crystals were investigated in a single crystal X-ray diffraction experiment, revealing the molecular structure depicted in Fig. 1B. A distance of 2.1341(4) Å was found for P(1)−Si(1) bond, in line with a phosphorus-silicon double bond.[20] The nature of the phosphasilene π-bond was investigated by means of intrinsic bond orbital (IBO) analysis.[21,22] Orbital coefficients of 0.78 and 0.18 were found for phosphorus and silicon, respectively, indicating polarization towards the phosphorus center (S.3.1). This is consistent with the relative electronegativities of phosphorus (2.1) and silicon (1.9),[19] and with a π bond that is on the verge of becoming a phosphorus-based lone pair.

Cage-opening of **1** was also achieved via carbene transfer by heating a benzene solution of **1** with the Wittig reagent Ph_3PCH_2 (Fig. 2A). After 1 h at 80 °C, partial conversion to phosphaalkene **4** (^{31}P NMR δ 347.2 ppm) was observed. Prolonged heating of this mixture resulted in diphosphirane **5** (^{31}P NMR δ −176.3 ppm), consistent with the generated phosphaalkene reacting with a second equivalent of **1**. Therefore, the reaction was repeated using two equivalents of **1** and improved conversion to **5** was observed. Filtration of a pentane solution of the crude material through a plug of silica, followed by removal of all volatile materials from the filtrate under reduced pressure, provided **5** in 50% yield as a colorless solid. Crystals of **5** grown from pentane were analyzed by X-ray crystallography, and the molecular structure is depicted in Fig. 2B.

Given the ease with which **1** reacts with silylene **2** and Ph_3PCH_2, we investigated phosphiranation reactions of alkenes using **1** as the phosphinidene synthon. Note that phosphiranes are interesting targets given their applications as ligands for transition metal catalysts,[23–29] polymer precursors,[30,31] and building blocks for organophosphorus compounds.[32] Multiply-bonded late transition metal complexes are well known tools for forging three-membered rings, such as cyclopropanes and aziridines.[33–35] Moreover, Hillhouse and co-workers demonstrated that phosphinidene transfer to ethylene may be achieved via a nickel phosphinidene com-

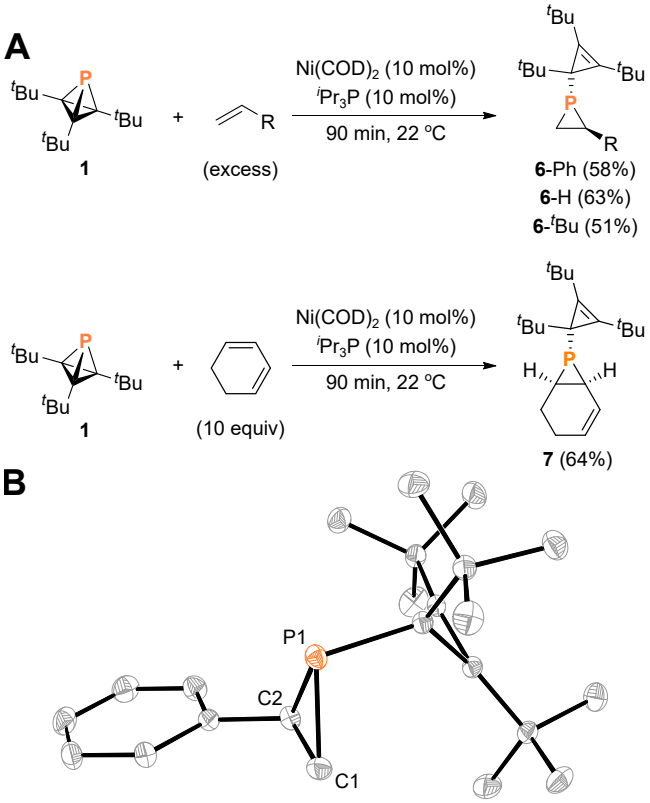


Figure 3. A) Nickel-catalyzed phosphiranation reactions of styrene (10 equiv), ethylene (1 atm), neohexene (10 equiv), and 1,3-cyclohexadiene (10 equiv). B) Molecular structure of **6**-Ph shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

plex;[36] therefore, we employed nickel reagents in our initial investigation.

We found that the combination of **1** with $Ni(COD)_2$ (10 mol %), $^{i}Pr_3P$ (10 mol%), and styrene (10 equiv) resulted in clean phosphirane formation after only 90 min at 22 °C (Fig. 3A). The reaction is stereoselective for the *trans* isomer, as indicated by a single shielded ^{31}P NMR resonance at δ −170.4 (d, $^{2}J_{PH}$ = 19.6 Hz) ppm. Addition of a NMR internal standard followed by quantitative ^{1}H NMR spectroscopy showed 84% conversion, revealing the high efficiency of this reaction. In the absence of $Ni(COD)_2$ or $^{i}Pr_3P$, no reaction was observed, strongly suggesting that the reaction is promoted by a generated nickel catalyst. When the catalyst loading was lowered to <10 mol%, partial conversion to the known [4+2]-cycloadduct of tri-*tert*-butylphosphacyclobutadiene with styrene occurred,[7] and when $^{i}Pr_3P$ was replaced with chelating bis(phosphine) ligands no conversion to the desired phosphirane was observed (S.1.4.1). Conveniently, catalytic phosphiranation (55% conversion) was also observed when $Ni(COD)_2$ was replaced with $Ni(^{4\text{-}tBu}stb)_3$,[37] a commercially available long-term air- and room-temperature-stable Ni(0) source. Additionally, substitution of *cis*-β-deuterostyrene for styrene resulted in stereospecific cycloaddition, leading to a single isomer of deuterium-incorporated phosphirane (S.1.4.6).

To purify phosphirane **6**-Ph, the crude material was taken up in pentane and stirred over charcoal. The slurry was passed through a frit and all volatile materials were removed from the filtrate under reduced pressure, producing pale yellow solids. Crystallization of the solids from cold tetramethylsilane provided **6**-Ph in 58% yield as a beige solid.

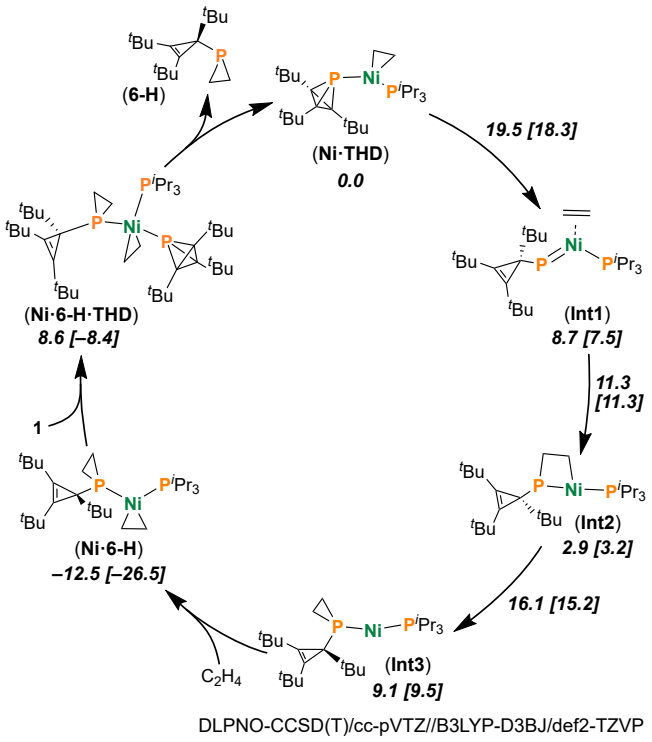


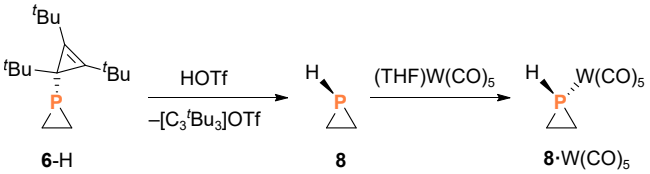
Figure 4. Proposed catalytic cycle leading to the formation of **6**-H. Relative Gibbs free energies and enthalpies (given in brackets) of calculated stationary points and barriers are reported in kcal/mol (298.15 K).

Given the high efficiency of the phosphiranation reaction, incurred losses are attributed to the work up procedure. Crystals of **6**-Ph grown from pentane were analyzed in a single crystal X-ray diffraction experiment, leading to the molecular structure shown in Fig. 3B.

The synthesis of unprotected phosphiranes via catalytic phosphinidene transfer is particularly interesting given the prospect of efficiently preparing *P*-chiral phosphiranes by utilizing optically active ligands. However, examples of such reactions are rare, a circumstance attributable to the paucity of suitable phosphinidene synthons. Only recently, the catalytic phosphiranation of styrenes using RP**A** (R = ^{t}Bu or ^{i}Pr; **A** = $C_{10}H_{14}$, anthracene) reagents was achieved using a substoichiometric combination of Fp^+ (Fp = Fe(η^5-C_5H_5)(CO)$_2$) and tetramethylammonium fluoride.[38] Primary phosphines have also been shown to be competent phosphinidene synthons in the presence of a transition metal catalyst;[39,40] however, transfer to unactivated alkenes to form phosphiranes has yet to be shown.

Remarkably, when catalysis was carried out with ethylene (1 atm) in place of styrene, formation of ethylene adduct **6**-H was observed (Fig. 3A). Consistent with phosphirane formation, a major resonance at δ −220.6 (t, $^2J_{PH}$ = 17.2 Hz) ppm was present in the ^{31}P NMR spectrum. Compound **6**-H was purified by stirring a pentane solution of the crude material over charcoal, followed by filtration. After all volatile materials were removed from the filtrate under reduced pressure, **6**-H was isolated as a waxy, colorless material via sublimation (70 °C, 200 mTorr) in 63% yield. Additionally, *tert*-butyl-substituted phosphirane **6**-^{t}Bu was obtained when neohexene was employed as the olefin (^{31}P NMR δ −205.4 ppm; Fig. 3A). After treating the crude material with charcoal, compound **6**-^{t}Bu was isolated as a colorless oil in 51% yield via distillation (100 °C, 100 mTorr).

Scheme 1. Generation of Phosphirane **8** via the Treatment of **6**-H with HOTf Followed by the Isolation of **8**·W(CO)$_5$.



To probe the chemoselectivity of this reaction, catalysis was carried out with 1,3-cyclohexadiene (10 equiv). Selective formation of vinyl-substituted phosphirane **7** was observed (^{31}P NMR δ −171.9 ppm; Fig. 3A), in contrast to thermal transfer of ^{i}Pr$_2$NP from anthracene to 1,3-cyclohexadiene, which yields the corresponding 7-phosphanorbornene product.[41] The divergent reactivity likely arises from the lowering of the barrier to isomerization to the corresponding 7-phosphanorbornene via π-donation of the ^{i}Pr$_2$N-substituent following [2 + 1]-cycloaddition.[42] After following a purification procedure similar to that employed for **6**-^{t}Bu, compound **7** was isolated as a pale yellow oil in 64% yield. While related transition-metal bound vinyl-substituted phosphiranes have been shown to thermally isomerize to 7-phosphanorbornenes,[43] heating of **7** (mesitylene, 140 °C, 90 min) did not result in its isomerization; rather, compound **7** is thermally stable under these conditions.

The mechanism for the formation of phosphirane **6**-H was investigated using quantum chemical calculations carried out at the DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3BJ/def2-TZVP level of theory plus a Gibbs free energy correction (Fig. 4 and S.82). The calculations suggest that cage-opening of phosphatetrahedrane nickel complex **Ni·THD** to nickel phosphinidene **Int1** proceeds with an activation barrier of 19.5 kcal/mol. Rearrangement of ethylene phosphinidene complex **Int1** results in metallacyclobutane intermediate **Int2** (displacement vectors for the associated transition state are shown in Fig. S.83). Note that a similar species was observed previously by monitoring group transfer from Hillhouse's nickel phosphinidene complex to ethylene using low temperature NMR spectroscopy.[36] Formation of phosphirane-nickel complex **Int3** via the isomerization of **Int2** is uphill by 9.1 kcal/mol and it goes on to react with free ethylene to form complex **Ni·6-H** (−12.5 kcal/mol). Turnover of the catalyst may occur via the formation of a four-coordinate, 18-electron nickel complex (**Ni·6-H·THD**), followed by dissociation of **6**-H. Attempts to observe reaction intermediates by low temperature NMR spectroscopy were unsuccessful (S.1.4.4).

Treatment of isolated **6**-H with HOTf (1.2 equiv) resulted in clean formation of phosphirane (**8**)[44] in 92% yield, as determined by quantitative ^{31}P NMR spectroscopy (S.1.11.2), and the precipitation of [^{t}Bu$_3$C$_3$]OTf, exposing the (^{t}BuC)$_3$ substituent as a cleavable protecting group (Scheme 1). Clean deprotection of phenyl-substituted **6**-Ph was also observed and resulted in a mixture of *cis*- and *trans*-isomers (S.1.12). In order to sequester generated **8** from solution, (CO)$_5$W(THF) was added to the reaction mixture to prepare **8**·W(CO)$_5$ (Scheme 1).[45] Filtration of a pentane solution of the crude material through a plug of silica, followed by the removal of all volatile materials provided a colorless solid. Sublimation of this material delivered a mixture of **8**·W(CO)$_5$ and trace W(CO)$_6$ (43% yield). Attempts to further purify **8**·W(CO)$_5$ were unsuccessful.

The remarkable strain-driven chemistry disclosed herein

sheds light on the rich reactivity phosphatetrahedranes have to offer as building blocks for organophosphorus compounds. In addition to expanding the scope of these reactions and exploring nickel-catalyzed asymmetric phosphinidene transfer by the use of a chiral ligand in place of $^{i}Pr_3P$, we intend to further explore new modes of reactivity enabled by the highly strained core of **1**.

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Supporting Information Available

Crystallographic data are available from the Cambridge Structural Database under refcodes 2102704, 2102709, and 2118437. Full synthetic and computational details, including preparative procedures and spectroscopic data for characterization of compounds, are in the supplementary materials.

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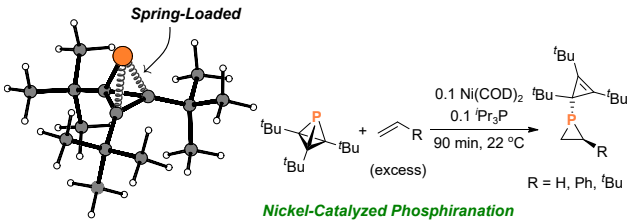
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Nickel-Catalyzed Phosphiranation

TOC Graphic