

# Ph<sub>3</sub>PCN<sub>2</sub>: a stable reagent for carbon atom transfer

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## Abstract:

Precise modification of a chemical site in a molecule at the single-atom level is one of the most elegant yet difficult transformations in chemistry. A reagent specifically designed for chemoselective introduction of monoatomic carbon is a particularly formidable challenge. Here we report a straightforward, azide-free synthesis of a crystalline and isolable diazophosphorus ylide Ph<sub>3</sub>PCN<sub>2</sub>, a stable compound with a carbon atom bonded to two chemically labile groups, triphenylphosphine (PPh<sub>3</sub>) and dinitrogen (N<sub>2</sub>). Without any additives, the diazophosphorus ylide serves as a highly selective transfer reagent for fragments including Ph<sub>3</sub>PC to deliver phosphorus ylide-terminated heterocumulenes and CN<sub>2</sub> to produce multi-substituted pyrazoles. Ultimately, even exclusive C-atom transfer is possible: In reactions with aldehydes, acyclic and cyclic ketones (R<sub>2</sub>C=O), the C-atom substitution forms a vinylidene (R<sub>2</sub>C=C:) en route to alkynes or butatrienes.

## One Sentence Summary:

A new reagent, Ph<sub>3</sub>PCN<sub>2</sub> is described which can be utilized for Ph<sub>3</sub>PC, CN<sub>2</sub> or C-atom transfer.

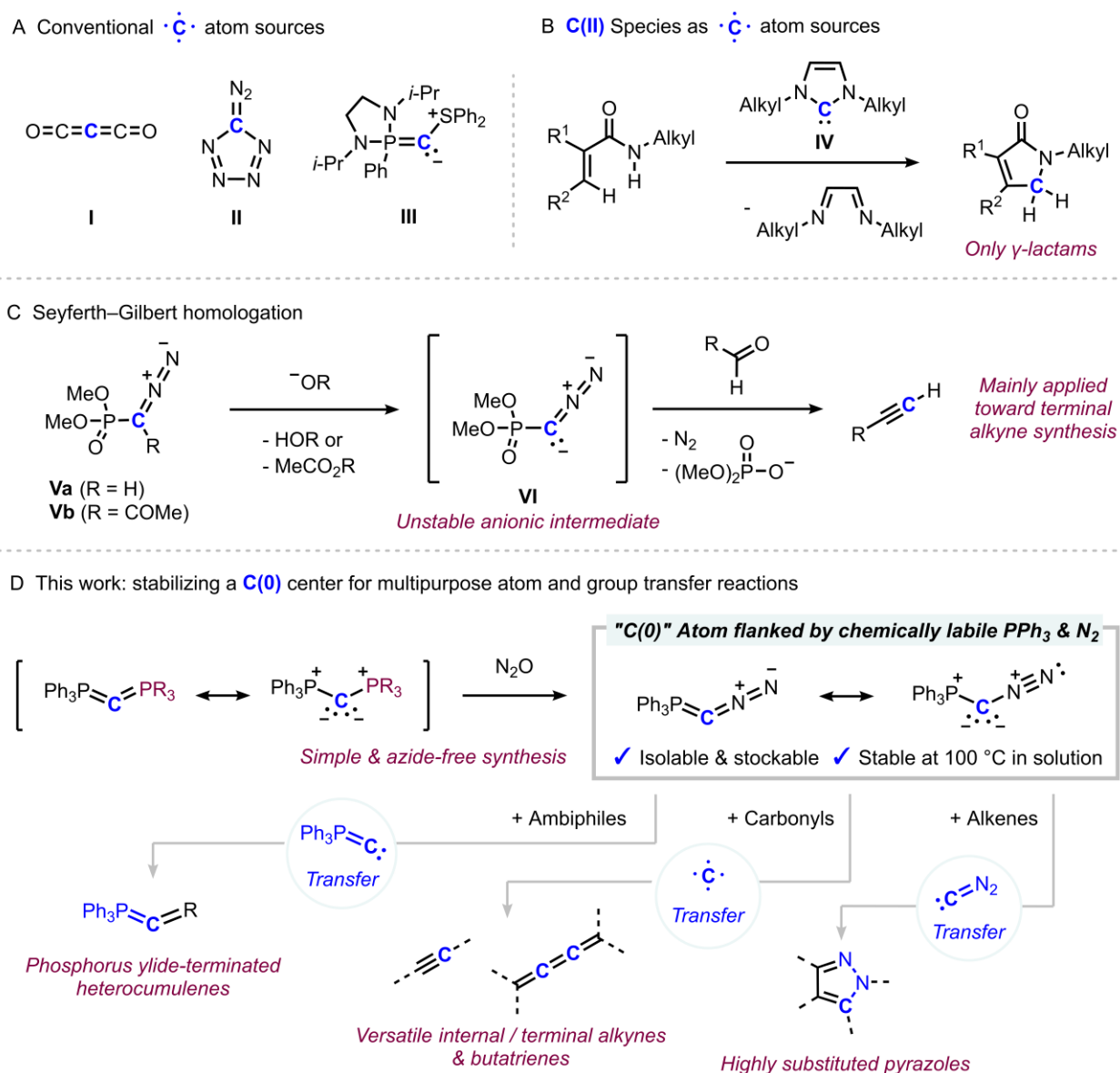
**Main Text:**

Atomic carbon, the simplest building block for the construction of organic molecules as well as carbon allotropes, is known to be an extremely electrophilic species, typically formed by electric discharge of a carbon arc and vaporized into a low temperature matrix for handling (1–3). Electron beam and laser evaporative methods of graphite (1–3), are alternative methods which all require sophisticated equipment and simultaneously produce oligomers of atomic carbon. Molecules such as carbon suboxide (**I**) (4–5) and 5-diazotetrazole (**II**) (2, 6) (Figure 1A) release atomic carbon thermally or photochemically, but the underlying problem that reactions involving atomic carbon are unselective, forming numerous reactive species while the precursors pose serious hazards, has limited their synthetic applications. Limited by the number of available C-atom transfer reagents, Tobisu and co-workers recently reported that the well-established *N*-heterocyclic carbenes (NHC **IV**, Figure 1B) could be utilized as C-atom transfer reagents, however, exclusively to form  $\gamma$ -lactams from  $\alpha,\beta$ -unsaturated amides (7–8).

One of the simplest general ways to conceive of the electrophilic atomic carbon in a stable form, is in its zerovalent [C(0)] form, flanked by two neutral donor groups. The term "carbones" was introduced by Frenking and co-workers to distinguish them from their divalent [C(II)] counterparts, the carbenes (9). Despite numerous reports on the synthesis of carbones, as well as their Lewis-acid complexation reactions (10–11) and small molecule activation (12–13), very few applications to transfer reactions in organic synthesis have been reported. Only the asymmetric P,S-bis(ylide) (**III**) has been reported to act as a carbon source by a multicomponent reaction (14). Just recently, the chemistry of carbene-like compounds such as metalated ylides expanded to reactions at carbon such as  $\text{PPh}_3/\text{CO}$  (15–16) or  $\text{N}_2/\text{CO}$  (17–18) exchange.

The challenges in using carbones as atomic carbon surrogates brought us to envision a C(0)-atom flanked by two simple and labile groups, one of them specifically  $\text{N}_2$ , as the ideal reagent to trigger transfer reactions in synthesis. With this aim, we focused our attention on the Seyferth-Gilbert (S.G.) (19–20) and Bestmann-Ohira (B.O.) (21–24) reagents (**Va** and **Vb**), both of which are widely used in synthetic chemistry to convert aldehydes into alkynes via the diazophosphonyl carbanion intermediate **VI**, which undergoes phosphate and dinitrogen elimination (Figure 1C). Further inspired by the earlier work of Bertrand and co-workers showing that the neutral derivative is indeed synthetically accessible (25–26) we report here the synthesis of a crystalline, isolable and even thermally stable diazophosphorus ylide **1**, a compound with a formal C(0) atom stabilized by triphenylphosphine and dinitrogen. Out of the three possible constitutional isomers with this formula  $\text{Ph}_3\text{PNNC}$  (27), and  $\text{Ph}_3\text{PNCN}$  (28) were both described more than 40 years ago, whereas the target  $\text{Ph}_3\text{PCNN}$  was unknown within the series (for a comparison see Table S2).

Given the precedence of  $\text{N}_2$  (29–31) and  $\text{PPh}_3$  (15–16, 32–36) moieties to be cleavable in organic synthesis, we demonstrate herein that in  $\text{Ph}_3\text{PCN}_2$ , the elimination of the  $\text{PPh}_3$  and  $\text{N}_2$  groups could be selectively controlled, which enables the reagent to act as a  $\text{Ph}_3\text{PC}$ ,  $\text{CN}_2$ , or even a C-atom source all of which are highly relevant in synthesis (Figure 1D).



**Figure 1.** The chemistry of atomic carbon surrogates. (A) Compounds that are capable of transferring a carbon atom to organic molecules (2, 4, 6, 14). (B) Recent C-atom transfer reaction from imidazole-2-ylidenes to form lactams (7–8). (C) Seyferth–Gilbert homologation via diazophosphonyl carbanion **VI** (19–24) and (D) this work.

### Synthesis, structure and electronic properties of diazophosphorus ylide **1**

Hexaphenylcarbodiphosphorane ( $\text{Ph}_3\text{P}=\text{C}=\text{PPh}_3$ , **2a**), already reported in 1961 by Ramirez (37), is a well-studied compound that undergoes a metathesis type reaction with  $\text{CE}_2$  ( $\text{E} = \text{O}, \text{S}$ ) to give heterocumulenes  $\text{Ph}_3\text{P}=\text{C}=\text{C}=\text{E}$  ( $\text{E} = \text{O}, \text{S}$ ) together with the corresponding phosphine chalcogenides (32–34). Kundel and Kästner reported in 1965 that the reaction of phosphorus ylide  $\text{Ph}_3\text{P}=\text{CH}_2$  with  $\text{N}_2\text{O}$  gas could form diazomethane ( $\text{N}_2=\text{CH}_2$ ) in low yields, again with the elimination of triphenylphosphine oxide (TPPO) (35).

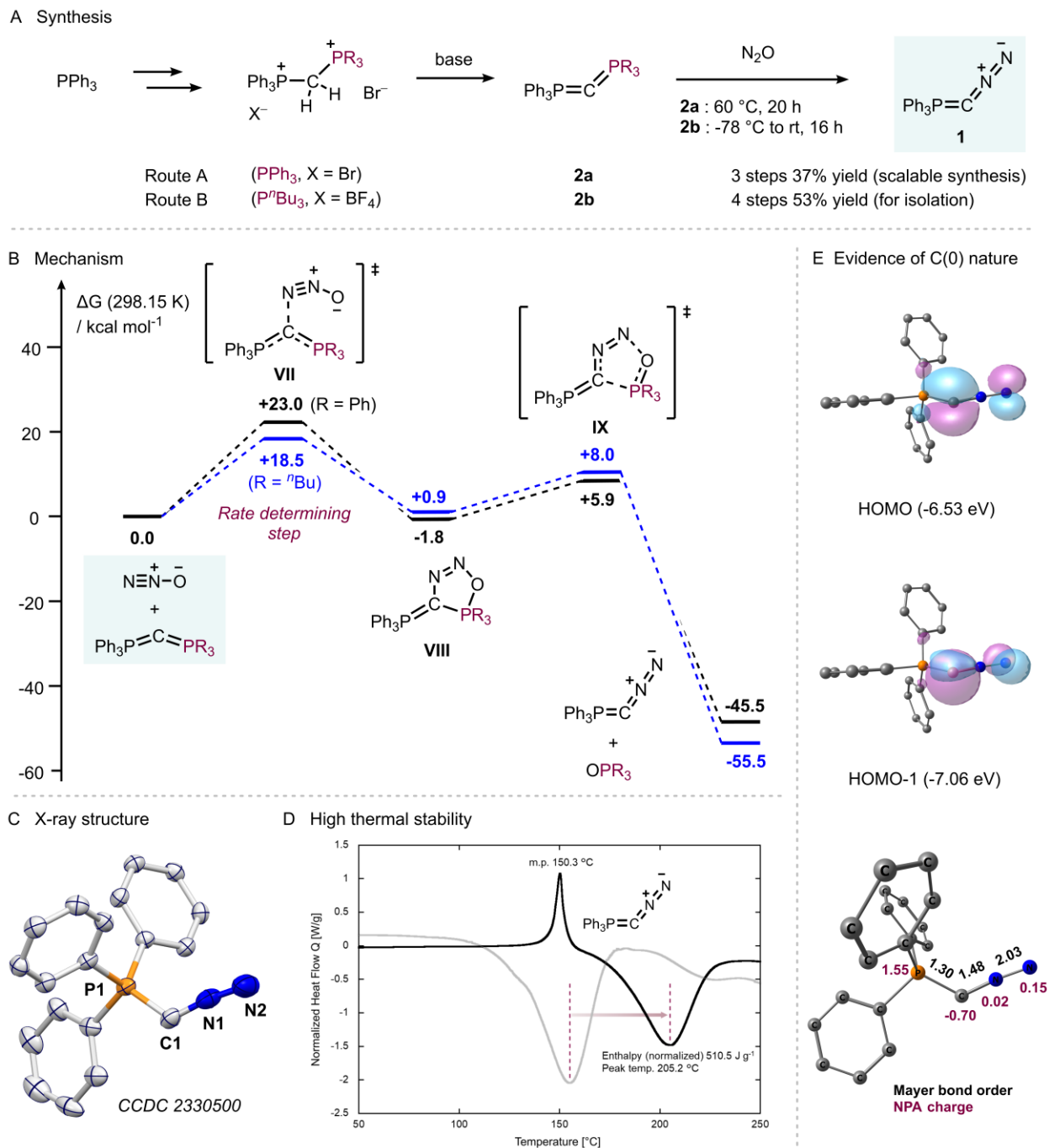
Based on the literature precedent, we envisioned a straightforward, yet unknown, diazo-transfer using carbodiphosphoranes and N<sub>2</sub>O to access our target reagent. The reaction between Ph<sub>3</sub>P=C=PPh<sub>3</sub> (**2a**) and N<sub>2</sub>O only proceeds very slowly at room temperature but slight heating of **2a** at 60 °C under an atmosphere of N<sub>2</sub>O gives selective access to a product with two new <sup>31</sup>P NMR signals at δ = 7.6 ppm and δ = 24.7 ppm (1:1 ratio), the latter (24.7 ppm) assigned to Ph<sub>3</sub>PO (Figure 2A; see Supplementary Materials for the experimental details). Although the characteristic sharp IR band at  $\tilde{\nu} = 1989 \text{ cm}^{-1}$  pointed towards the formation of the targeted phosphorus ylide **1** (**38**) the clean separation from Ph<sub>3</sub>PO proved challenging. Selection of an adequate unsymmetrical carbodiphosphorane **2b** (Ph<sub>3</sub>P=C=P<sup>n</sup>Bu<sub>3</sub>) as the precursor was the key factor for isolating **1** (**39**). Starting from commercially inexpensive PPh<sub>3</sub>, the unsymmetrical carbodiphosphorane containing PPh<sub>3</sub> and P<sup>n</sup>Bu<sub>3</sub> entities (**2b**) was synthesized as a yellow oil in three steps. Exposure of carbodiphosphorane **2b** to N<sub>2</sub>O results in a formal N<sub>2</sub>/P<sup>n</sup>Bu<sub>3</sub> exchange to afford the target diazophosphorus ylide **1** as an off-white solid with the preferential elimination of <sup>n</sup>Bu<sub>3</sub>PO over Ph<sub>3</sub>PO (<sup>n</sup>Bu<sub>3</sub>PO:Ph<sub>3</sub>PO = 7:1). The (3+2) cycloaddition with N<sub>2</sub>O proceeded under milder reaction conditions when <sup>n</sup>PBu<sub>3</sub> was used as the leaving group (Ph<sub>3</sub>P=C=P<sup>n</sup>Bu<sub>3</sub>, -78 °C to rt, overnight; Ph<sub>3</sub>P=C=PPh<sub>3</sub>, 60 °C, 20 h). Computational studies suggested that the formal N<sub>2</sub>/P<sup>n</sup>Bu<sub>3</sub> exchange proceeds via a sequence of (3+2) cycloaddition and retro (3+2) cycloaddition (Figure 2B). The higher electron density at carbon lowers the energy barrier for the nucleophilic attack of carbodiphosphoranes to N<sub>2</sub>O (Ph<sub>3</sub>P=C=P<sup>n</sup>Bu<sub>3</sub>, 18.5 kcal mol<sup>-1</sup> vs Ph<sub>3</sub>P=C=PPh<sub>3</sub>, 23.0 kcal mol<sup>-1</sup>) which agrees with the experimental results. Note, that diazo compounds such as B. O. reagent strictly require azides in their synthesis, while the presented synthesis using N<sub>2</sub>O circumvents the safety hazards associated with the use of azides.

Single crystal x-ray diffraction (sc-XRD) analysis unambiguously determined the bent heterocumulenic structure of **1** (Figure 2C). The P1=C1 bond distance (1.679(3) Å) was slightly longer than that of the precursor, Ph<sub>3</sub>P=C=PPh<sub>3</sub> (**2a**, 1.5998(5)–1.642(1) Å) (**40**) and Bestmann's ketene (Ph<sub>3</sub>P=C=C=O (**5**), 1.671(2) Å) (**41**). The P1–C1–N1 angle was only 121.6(3)°, which was significantly acute compared to other PPh<sub>3</sub> containing heterocumulenes **5** [143.1(1)] (**41**) and **6** [132.09(8)] (Figure 3A). The C1–N1 (1.268(5) Å) and N1–N2 (1.169(5) Å) bonds were in the range of isolable diazoalkenes (C–N: 1.257(7)–1.284(5) Å and N–N 1.147(5)–1.184(7) Å) (**17**, **42–44**).

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, **1** shows a doublet signal at 7.7 ppm (THF-*d*<sub>8</sub>) with a strikingly small coupling to the adjacent <sup>31</sup>P nuclei (<sup>1</sup>J<sub>C,P</sub> = 27.2 Hz), which is assignable to the central C1 atom. The decoupling of this doublet into a singlet signal was confirmed by the <sup>13</sup>C{<sup>31</sup>P}{<sup>1</sup>H} NMR measurements (Figure S30), which together with GIAO calculations (Figure S241) and <sup>13</sup>C-labelling experiments (Ph<sub>3</sub>P<sup>13</sup>CN<sub>2</sub>, Figure S44) support this assignment.

Diazo compounds are often suspected to be hazardous energetic materials. To our delight the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (**45**) showed the surprisingly high thermal stability of **1**. In the DSC plot (Figure 2D), a sharp endothermic peak which is typical for a melting point (m.p.) is observed at circa 150 °C. The melting event is followed by an exothermic decomposition event with an enthalpy of decomposition  $\Delta H_D \sim -511 \text{ J g}^{-1}$  (T<sub>onset</sub> ~ 175 °C). This decomposition is also evident in the TGA plot of **1** (Figure S234), which only shows a 7.3% weight loss at the onset temperature of 189.2 °C close to the weight% loss of the N<sub>2</sub> fragment from **1** (9.3%). In fact, **1** proved to be highly stable under inert atmosphere and even prolonged heating in solution at 100 °C (0.5 M THF solution) does not lead to significant decomposition. These results are in strong contrast with

the liquid B.O. reagent that already exhibits a decomposition event starting around 90 °C (46) also supported by DSC and TGA measurements (Figure 2D); Figure S236–S237).



**Figure 2.** Synthesis, structure and properties of diazophosphorus ylide **1**. (A) Azide-free diazo transfer to symmetrical (**2a**) and unsymmetrical (**2b**) carbodiphosphoranes. Base: KHMDS (for **2a**), NaNH<sub>2</sub> (for **2b**). (B) Mechanistic simulations at the (B3LYP-D3(BJ)/def2-TZVP//BP86-D3(BJ)/def2-SVP (SMD=THF) level of theory for the formal N<sub>2</sub>/P<sup>n</sup>Bu<sub>3</sub> exchange reaction between the carbodiphosphoranes and N<sub>2</sub>O. (C) Molecular structure of diazophosphorus ylide **1** obtained by sc-XRD analysis with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P1–C1 1.679(3), C1–N1 1.268(5), N1–N2 1.169(5), P1–C1–

N1 121.6(3), C1–N1–N2 172.1(4), P1–C1–N1–N2 170(3). (D) Comparison of the differential scanning calorimetry (DSC) measurement of **1** (black) and the B.O. reagent [gray, enthalpy (normalized): 726.6 J g<sup>-1</sup>, peak temperature: 155.5 °C]. (E) Selected Kohn-Sham orbitals of **1** calculated at the (M06-2X/def2-TZVP//BP86-D3(BJ)/def2-TZVP level of theory; isosurface value: 0.04 e<sup>-</sup> au<sup>-3</sup>) and Mayer bond order as well as natural population analysis (NPA) charges of **1** (calcd).

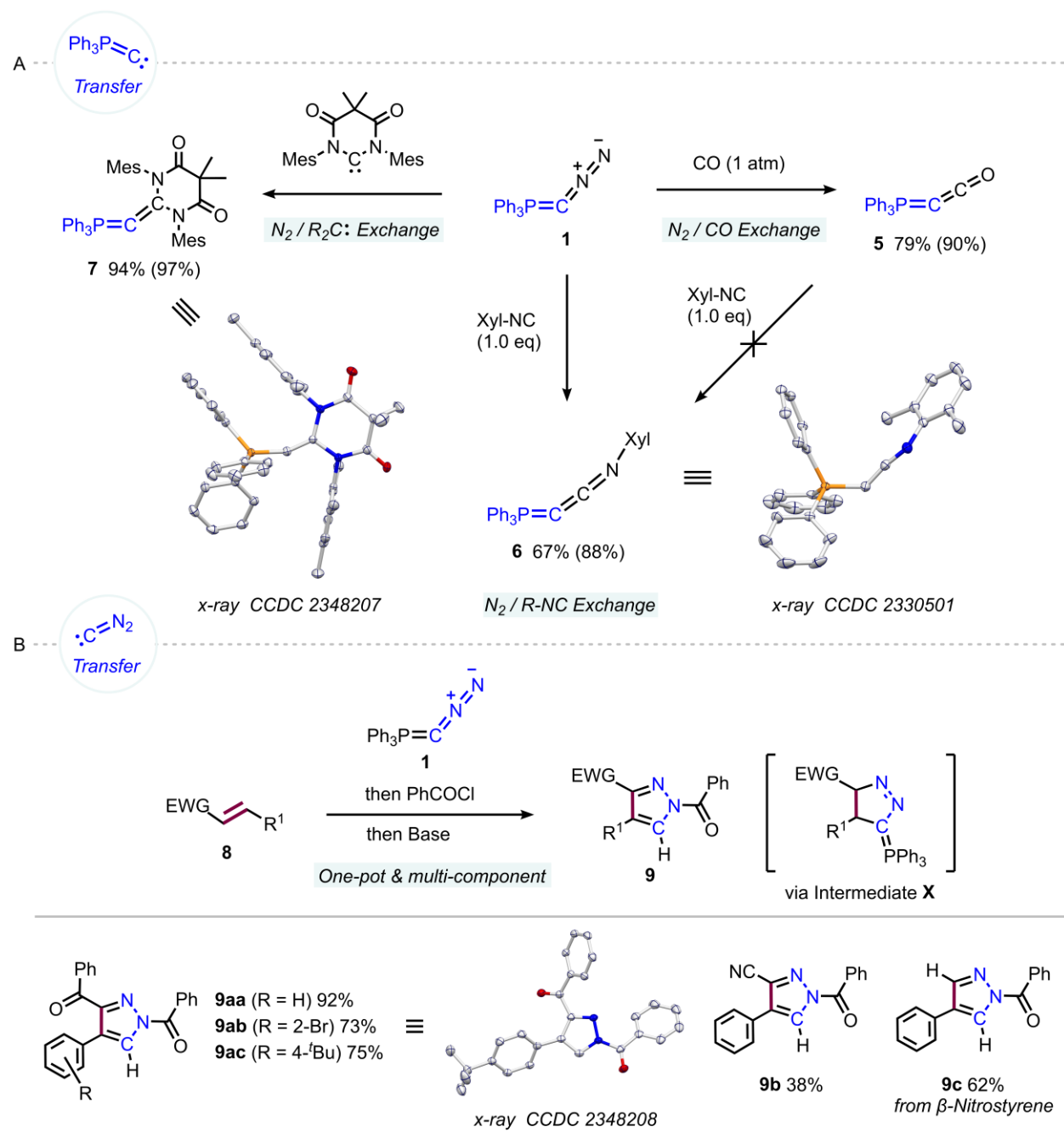
Theoretical calculations were performed to clarify the electronic properties as well as the bonding situation of the stable diazophosphorus ylide. The Kohn-Sham HOMO-1 (-7.06 eV) is a  $\sigma$ -type LP(C1) orbital (LP1) with respect to the P1–C1–N1 plane and the HOMO (-6.53 eV) is a corresponding  $\pi$ -type LP(C1) orbital (LP2) both of which have significant contribution of the  $\pi^*(\text{N1}\equiv\text{N2})$  orbitals (Figure 2E). Furthermore, the natural localized molecular orbital (NLMO) analysis (LP1: P1 4%, C1 78%, N1 7%, N2 8%; LP2: P1 5%, C1 65%, N1 11%, N2 13%, Figure S243), natural population analysis (NPA) charge analysis (P1 1.56, C1 -0.70, N1 0.02, N4 -0.15, Figure 2E) and NBO-based natural resonance theory (NRT) analysis (carbene canonical structure, 36%, Figure S248) all agree with the presence of two lone pairs of electrons on the central carbon atom, and support the interpretation that ylide **1** possesses a "C(0)" atom stabilized by PPh<sub>3</sub> and N<sub>2</sub> (Figure 1E, for details on the electronic properties of **1** and related diazo compounds, see SM) (47).

### Ph<sub>3</sub>PC and CN<sub>2</sub> transfer reactions

The facile synthesis and thermal stability of ylide **1** prompted us to investigate group transfer reactivity. The selective displacement of N<sub>2</sub> enabled the direct coupling of the phosphorus ylide moiety to CO and isocyanides to access heterocumulenes (Figure 3A). Exposure of a THF solution of **1** to carbon monoxide at room temperature afforded the phosphorane ketene **5** (i.e. Bestmann's ketene) selectively in 79% yield. Similarly, the treatment of **1** with xylyl isocyanide at 60 °C gave the phosphorane ketenimine **6** in 67% yield, which was also structurally characterized by sc-XRD analysis. Treatment of the Bestmann's ketene (**5**) with xylyl isocyanide resulted in the full recovery of the starting material even at elevated temperatures highlighting the necessity of the N<sub>2</sub> group to engage in exchange reactions. More importantly, the Ph<sub>3</sub>PC moiety could also be transferred to a stable carbene to give a bent heteroallene terminated by a phosphorus ylide (**7**, 94% yield). The above results could not be achieved with diazoalkane-based molecules (e.g. B.O. reagent) and all would require multi-step synthetic strategies, which emphasizes the advantage of developing a direct Ph<sub>3</sub>PC transfer reaction. Since the product still bears a reactive P-ylide moiety the N<sub>2</sub>/carbene exchange should allow further multi-step processes for instance to access allenes. Note, the combination of PPh<sub>3</sub>/N<sub>2</sub> exchange followed by N<sub>2</sub>/carbene exchange allows overall substitution of a phosphine by a carbene on a carbodiphosphorane.

Selective CN<sub>2</sub> transfer, could also be accomplished chemoselectively toward electron deficient alkenes, also in a multicomponent fashion (Figure 3B). Treatment of **1** with *trans*-chalcone leads to a (3+2) cycloaddition to form the phosphoranylidene pyrazole intermediate **X**, followed by a proton shift (23) and functionalization with electrophiles (in this case, benzoylchloride), PPh<sub>3</sub> elimination with a base (NaH) to eventually afford the highly substituted pyrazole **9a** in 92% yield.  $\alpha,\beta$ -Unsaturated alkenes including *trans*-chalcones with different functionalities (**9ab-9ac**) and cyano alkenes (**9b**) were compatible. In the case of  $\beta$ -nitrostyrene, the nitro group could also be eliminated which allows the synthesis of a pyrazole without an electron withdrawing group on the pyrazole backbone (**9c**). These results open up the potential of ylide **1** to act as a CN<sub>2</sub> surrogate toward unsaturated carbon-carbon bonds enabling access to functionalized *N*-heterocycles. Although carbanion **VI** generated from the B.O. reagent undergoes similar (3+2) cycloaddition reactions with alkenes (23), typically, the phosphonyl moiety cannot be eliminated, which

showcases the advantage of using a neutral  $\text{PPh}_3$  containing reagent. Furthermore, this reagent could circumvent the use of protic solvents which are typical for generating carbanion **VI** and related reactive species which allow multicomponent reactions to synthesize pyrazoles with multiple functionalities.



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**Figure 3.** Group transfer reactions. (A)  $\text{Ph}_3\text{PC}$  transfer toward Lewis bases and (B)  $\text{CN}_2$  transfer toward electron deficient alkenes using diazophosphorus ylide **1**. The NMR yields are in parenthesis. Solvent: THF. Base: NaH (for **9a-9b**), NaOH (for **9c**).

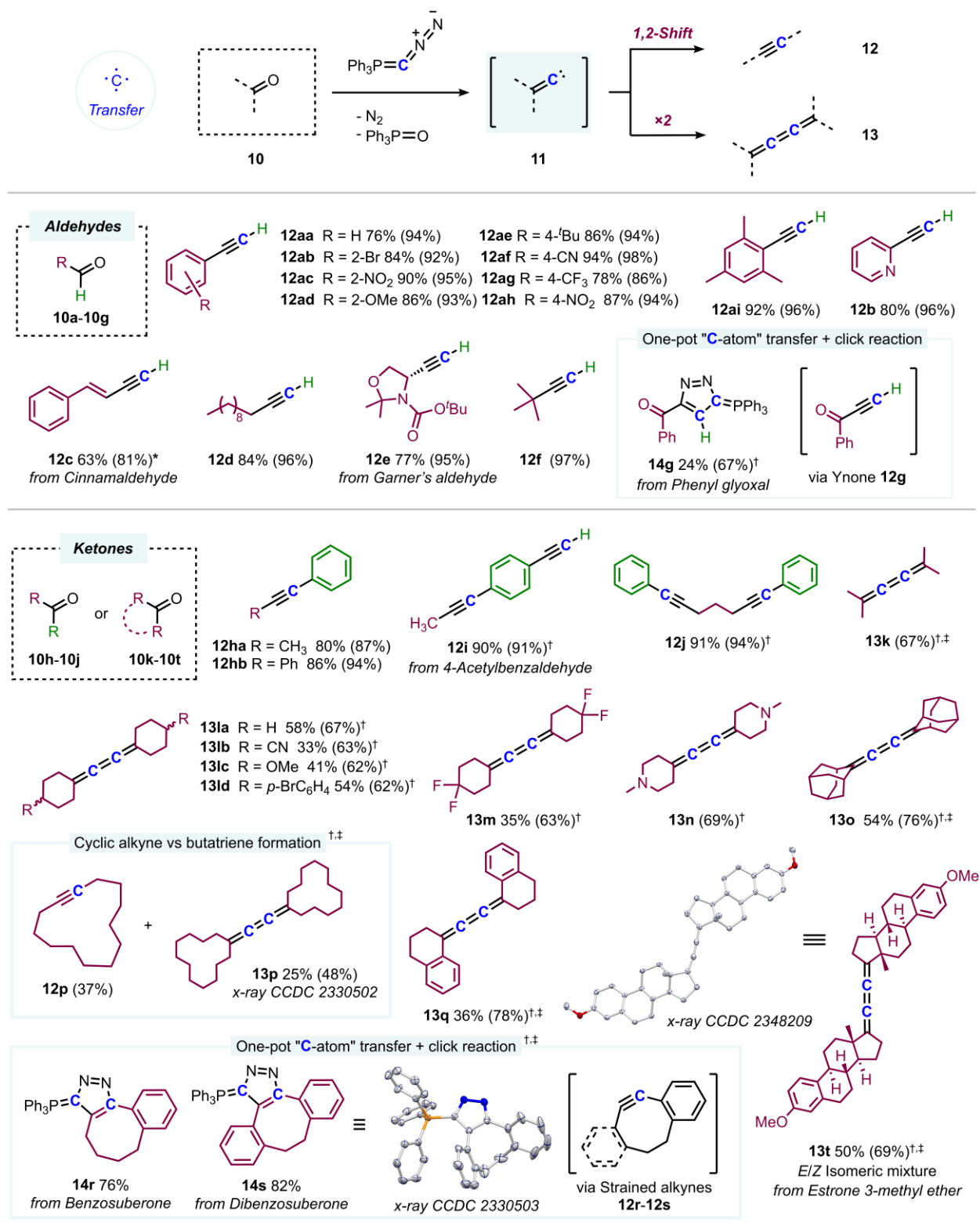
## C-Atom transfer reactions

Compared to the reactive anionic intermediate **VI** (Figure 1C) generated by treating the B.O. reagent with NaOMe, **1** is thermally highly stable and does not require the use of an additional base. Furthermore, **1** is stable in Et<sub>2</sub>O, THF, toluene, benzene and even in CH<sub>3</sub>CN at room temperature, whereas the use of B. O. reagent is restricted to protic solvents such as methanol. We therefore expected a different reaction outcome compared to the B.O. reagent, which was supported not only by the wide functional group compatibility but by the different molecule classes accessible after the O-to-C exchange reaction (Figure 4).

The reaction of aldehydes exclusively gave the corresponding alkynes. Computational studies (Figure S252) support a Wittig-type mechanism to generate transient diazoalkenes, N<sub>2</sub> loss to afford vinylidenes, followed by 1,2-H shift (48). <sup>13</sup>C-labelling experiments using <sup>13</sup>C-labelled benzaldehyde (Figures S122-S123) support a selective 1,2-H over 1,2-aryl shift. Aryl aldehydes with different electronic properties (**12aa**, **12b**), functionalities (-Br, -OMe, -CN, -NO<sub>2</sub> and -CF<sub>3</sub>, **12ab-12ah**) and steric environments (Mes, **12ai**) all afforded the alkynes in excellent yields. Cinnamaldehyde ( $\alpha,\beta$ -unsaturated aldehyde) (**12c**) was also compatible: this transformation is impossible with the B.O. reagent due to the decomposition of the product in MeOH (22) and required substantial optimization of the reagent and additives to ensure selective conversion. Alkyl aldehydes with different functionalities and steric environments (**12d-12f**) and acyclic alkyl(aryl)ketones (**12ha-12hb**) also cleanly afforded the desired alkynes. 4-Acetylbenzaldehyde and 1,5-diphenylpentane-1,5-dione also gave the target dialkynes (**12i-12j**) in high yields demonstrating multiple C-atom transfer events to form multiple internal and terminal alkynes in one-pot. Notably, the  $\alpha$ -ketoaldehyde, phenyl glyoxal, selectively afforded phosphoranylidene pyrazole **14g** similar to the results discussed in the CN<sub>2</sub> transfer section. Formation of **14g** demonstrates a unique one-pot sequence of C-atom transfer and (3+2) cycloaddition to provide densely functionalized pyrazoles directly from an  $\alpha$ -ketoaldehyde. This result allows the following estimation of the relative reaction rates of C-atom transfer and (3+2) cycloaddition reactions: aldehyde-to-terminal alkyne > (3+2) cycloaddition to electron-deficient alkynes > ketone-to-internal alkyne; this matches the results obtained for cinnamaldehyde. Acyclic amides and esters such as *N,N*-dimethylbenzamide and ethyl benzoate resulted in no reaction even at 100 °C, which is reasonable considering the high electron density on the carbonyl carbon atoms.

When dialkyl ketones or cyclic ketones were used as substrates to suppress the tendency of the substituents to undergo 1,2-shift in the vinylidene intermediate, the corresponding butatrienes could be obtained in good yields. For example, when acetone, the simplest ketone, was treated with ylide **1**, only tetramethylbutatriene (**13k**) was selectively obtained, with no sign of 2-butyne. Various cyclic ketones were tested to explore functional group compatibility. Cyclohexanones substituted with -CN, -OMe, -*p*-Br-C<sub>6</sub>H<sub>4</sub>, and -CF<sub>2</sub> groups were compatible (**13la-13m**), which is intriguing considering that this reaction is likely to proceed via a highly reactive vinylidene intermediate. The *N*-heterocyclic ketone piperidinone also selectively afforded butatriene **13n**. The bulkier cyclic ketone 2-adamantanone did not react at room temperature, but the high thermal stability of **1** allowed heating at 90 °C to cleanly form butatriene **13o**. Cyclododecanone, a more geometrically flexible dialkyl ketone, afforded the corresponding butatriene **13p** along with cyclotridecyne (**12p**), a cyclic alkyne. Interestingly, while the cyclic (alkyl)(aryl)ketone, tetralone, selectively gives butatriene **13q**, cyclic arylketones with a larger cycloheptanone core instead gives the corresponding phosphoranylidene pyrazoles **14r-14s**, demonstrating the one-pot synthesis of fused aromatic heterocycles from simple ketones (for NICS values of **14s**, see the SM).





**Figure 4.** C-atom transfer to carbonyl compounds. The NMR yields are in parenthesis. The reaction with benzaldehyde could be conducted in THF, Et<sub>2</sub>O, toluene, benzene, and acetonitrile. Ylide **1** / TPPO mixture obtained from the

reaction of carbodiphosphorane **2a** with N<sub>2</sub>O was used for the synthesis considering the facile synthesis and scalability. \*Ylide **1** was added dropwise. †2.0 equiv. of **1** was used. ‡The reaction was conducted at 60 or 90 °C.

This result shows that less-strained cyclic ketones favor 1,2-shift over dimerization, allowing formation of strained alkynes via C-atom transfer to a cyclic ketone. Finally, a complex steroid derivative, estrone 3-methyl ether was also selectively transformed into the corresponding air-stable butatriene **13t**. From the fact that only a single step is required for the synthesis of butatrienes from easy-to-access ketones avoiding the need for additives including transition metals (Ni, Pd, Cu, Zn) and toxic reducing agents (e.g. SnCl<sub>2</sub>) (49–50), it is reasonable to assume that ylide **1** is advantageous for the synthesis of cumulative doubly bonded species and for the generation of strained alkynes under mild reaction conditions.

We have achieved the synthesis of an isolable and thermally stable diazophosphorus ylide by a simple and straightforward diazo transfer strategy using N<sub>2</sub>O. The chemically labile PPh<sub>3</sub> and N<sub>2</sub> groups allowed the ylide to act as a multipurpose transfer reagent including Ph<sub>3</sub>PC, CN<sub>2</sub> and C-atom transfer reactions. We are confident that further exploration of the reactivity of diazophosphorus ylides should shed light on their application as an atomic carbon surrogate beyond the roles outlined here, for instance to access higher cumulenes or edit the framework of complex molecules.

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#### Author Contributions

T.K. performed the synthesis, initial reactivity studies of  $\text{Ph}_3\text{PCN}_2$ , x-ray analysis and computational studies. T.K. and J.K.Y. performed the reactivity studies of  $\text{Ph}_3\text{PCN}_2$ . T.K. & M.M.H. wrote the manuscript. All authors discussed and approved the final version of the manuscript. M.M.H. managed the project.

#### Competing Interests

The authors declare no competing interests.

**Data and materials availability**

5 The details of the experimental methods, NMR spectra, x-ray analysis, UV-Vis absorption spectra, IR spectra, and computational studies and references are available in the supplementary materials. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2330500 (**1**), 2330501 (**6**), 2348207 (**7**), 2348208 (**9ac**), 2330502 (**13p**), 2348209 (**13t**) and 2330503 (**14s**). These data are provided free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supplementary Materials**

10 Materials and Methods  
Figures S1 to S252  
Tables S1 to S2  
NMR Spectra  
References (51-90)