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Ph₃PCN₂: A stable reagent for carbon-atom transfer

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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, Ph₃PCN₂, a stable compound with a carbon atom bonded to two chemically labile groups, triphenylphosphine (PPh₃) and dinitrogen (N₂). Without any additives, the diazophosphorus ylide serves as a highly selective transfer reagent for fragments, including Ph₃PC, to deliver phosphorus ylide-terminated heterocumulenes and CN₂ to produce multisubstituted pyrazoles. Ultimately, even exclusive carbon-atom transfer is possible. In reactions with aldehydes and acyclic and cyclic ketones (R₂C=O), the carbon-atom substitution forms a vinylidene (R₂C=C:) en route to alkynes or butatrienes.

Atomic carbon, the simplest building block for the construction of organic molecules and carbon allotropes, is known to be an extremely electrophilic species that is typically formed by electric discharge of a carbon arc and then vaporized into a low-temperature matrix for handling (1–3). Electron beam and laser-evaporative graphite methods (1–3) 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) (Fig. 1A) release atomic carbon thermally or photochemically. However, the underlying problem with them is that reactions involving atomic carbon are unselective, forming numerous reactive species while the precursors pose serious hazards, and this 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**; Fig. 1B) could be used as C-atom transfer reagents exclusively to form γ -lactams from α,β -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, which is 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 in a multicomponent reaction (14). Recently, the chemistry of carbone-like compounds such as metalated ylides has been expanded to reactions at carbon such as PPh₃/CO (15, 16) or N₂/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 N₂, 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 through the diazophosphonyl carbanion intermediate **VI**, which undergoes phosphate and dinitrogen elimination (Fig. 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. Of the three possible constitutional isomers with this formula, Ph₃PNNC (27) and Ph₃PNCN (28) were both described more than 40 years ago, but the target Ph₃PCNN was unknown within the series (for a comparison, see table S2).

Given the precedence that N₂ (29–31) and PPh₃ (15, 16, 32–36) moieties are cleavable in organic synthesis, we demonstrate herein that in Ph₃PCN₂, the elimination of the PPh₃ and N₂ groups can be selectively controlled, which enables the reagent to act as a Ph₃PC, CN₂, or even a C-atom source, all of which are highly relevant in synthesis (Fig. 1D).

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

Hexaphenylcarbodiphosphorane (Ph₃P=C=PPh₃, **2a**), which was reported in 1961 by Ramírez *et al.* (37), is a well-studied compound that undergoes a metathesis type reaction with CE₂ (E = O, S) to yield heterocumulenes Ph₃P=C=C=E (E = O, S), together with the corresponding phosphine chalcogenides (32–34). Kundel and Kästner reported in 1965 that the reaction of phosphorus ylide Ph₃P=CH₂ with N₂O gas could form diazomethane (N₂=CH₂) in low

yields, again with the elimination of triphenylphosphine oxide (TPPO) (35). Based on this literature precedent, we envisioned a straightforward, yet unknown diazo transfer using carbodiphosphoranes and N₂O to access our target reagent. The reaction between Ph₃P=C=PPh₃ (**2a**) and N₂O proceeds very slowly at room temperature, but slight heating of **2a** at 60°C under an atmosphere of N₂O gave selective access to two new ³¹P nuclear magnetic resonance (NMR) signals at δ = 7.6 and 24.7 ppm (1:1 ratio), with the latter (24.7 ppm) assigned to Ph₃PO (Fig. 2A; see the supplementary materials for the experimental details). Although the characteristic sharp IR band at $\tilde{\nu}$ = 1989 cm^{−1} pointed toward the formation of the targeted phosphorus ylide **1** (38), the clean separation from Ph₃PO proved challenging. Selection of an adequate unsymmetrical carbodiphosphorane **2b** (Ph₃P=C=P^{*n*}Bu₃) as the precursor was the key factor for isolating **1** (39). Starting from commercially inexpensive PPh₃, the unsymmetrical carbodiphosphorane containing PPh₃ and P^{*n*}Bu₃ entities (**2b**) was synthesized as a yellow oil in three steps. Exposure of carbodiphosphorane **2b** to N₂O results in a formal N₂/P^{*n*}Bu₃ exchange to afford the target diazophosphorus ylide **1** as an off-white solid with the preferential elimination of ^{*n*}Bu₃PO over Ph₃PO (^{*n*}Bu₃PO:Ph₃PO = 7:1). The (3+2) cycloaddition with N₂O proceeded under milder reaction conditions when ^{*n*}Bu₃ was used as the leaving group (Ph₃P=C=P^{*n*}Bu₃, −78°C to room temperature overnight; Ph₃P=C=PPh₃, 60°C for 20 hours). Computational studies suggested that the formal N₂/P^{*n*}Bu₃ exchange proceeds through a sequence of (3+2) cycloaddition and retro (3+2) cycloaddition (Fig. 2B). The higher electron density at carbon lowers the energy barrier for the nucleophilic attack of carbodiphosphoranes to N₂O (Ph₃P=C=P^{*n*}Bu₃, 18.5 kcal mol^{−1} versus Ph₃P=C=PPh₃, 23.0 kcal mol^{−1}), which agrees with the experimental results. Diazo compounds such as B.O. reagent strictly require azides in their synthesis, whereas the presented synthesis using N₂O 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** (Fig. 2C). The P1–C1 bond distance [1.679(3) Å] was slightly longer than that of the precursor, Ph₃P=C=PPh₃ [**2a**, 1.5998(5)–1.642(1) Å] (40), and that of Bestmann’s ketene [Ph₃P=C=C=O (**5**), 1.671(2) Å] (41). The P1–C1–N1 angle was only 121.6(3)°, which was more acute compared with other PPh₃-containing heterocumulenes such as **5** [143.1(1)] (41) and **6** [132.09(8)] (Fig. 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).

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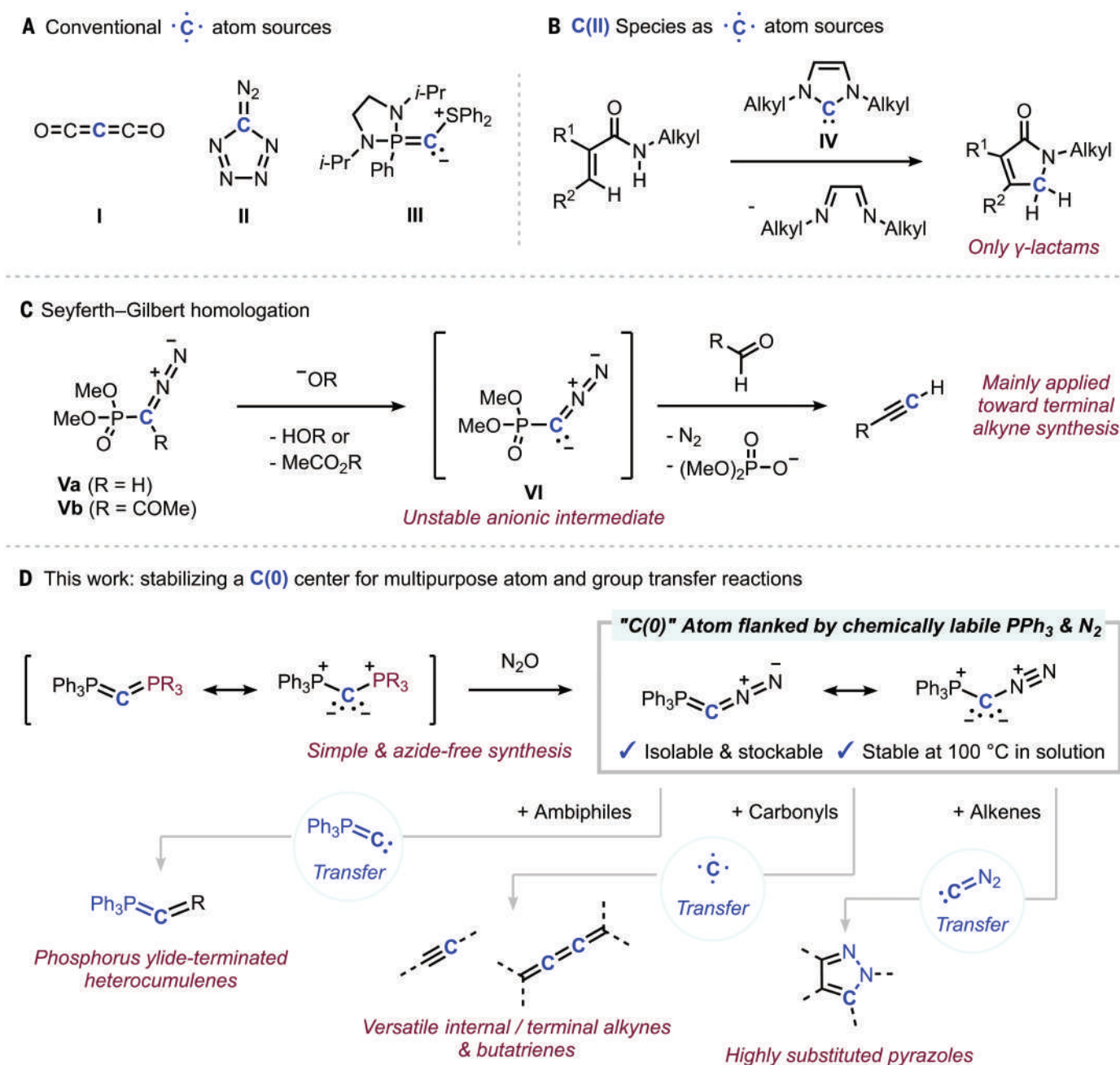


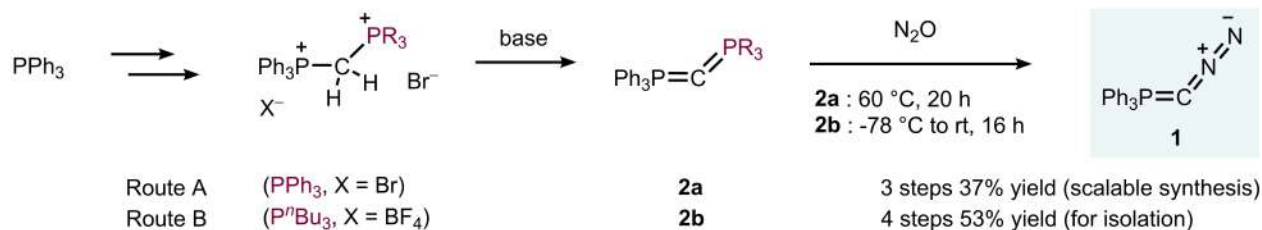
Fig. 1. The chemistry of atomic carbon surrogates. (A) Compounds that are capable of transferring a C atom to organic molecules (2, 4, 6, 14). (B) Recent C-atom transfer reaction from imidazole-2-ylidenes to form lactams (7, 8). (C) Seyferth–Gilbert homologation through diazophosphoryl carbanion **VI** (19–24). (D) Multipurpose transfer reactions with a diazophosphorus ylide.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, **1** showed a doublet signal at 7.7 ppm [tetrahydrofuran- d_8 (THF- d_8)] with a markedly small coupling to the adjacent ^{31}P nuclei ($^1J_{\text{C,P}} = 27.2$ Hz), which is assignable to the central C1 atom. The decoupling of this doublet into a singlet signal was confirmed by the $^{13}\text{C}\{^{31}\text{P}\}\{^1\text{H}\}$ NMR measurements (fig. S30), which together with gauge-invariant atomic orbital (GIAO) calculations (fig. S241) and ^{13}C -labeling experiments ($\text{Ph}_3\text{P}^{13}\text{CN}_2$; fig. S44), supported this assignment.

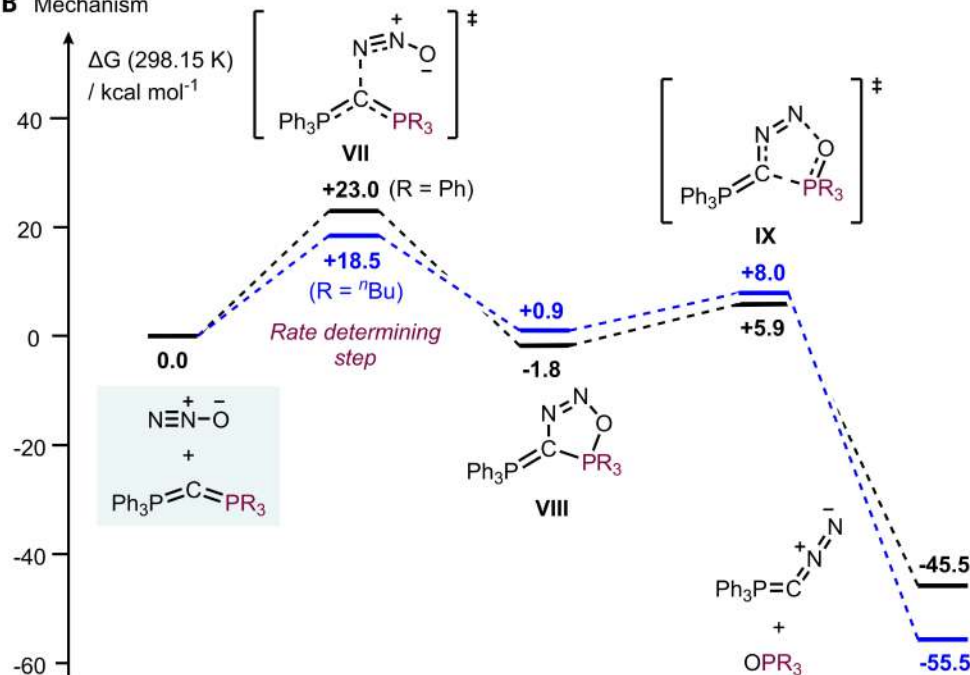
Diazo compounds are often suspected to be hazardous energetic materials. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (45) showed an unexpectedly high thermal stability of **1**. In the DSC plot (Fig. 2D), a sharp endothermic peak typical for a melting point was observed at $\sim 150^\circ\text{C}$. The melting event was followed by an exothermic decomposition event with an enthalpy of decomposition ΔH_{D} of ~ 511 J g $^{-1}$ ($T_{\text{onset}} \sim 175^\circ\text{C}$). This decomposition was also evident in the TGA plot of

1 (fig. S234), which only showed a 7.3% weight loss at the onset temperature of 189.2°C , close to the weight % loss of the N_2 fragment from **1** (9.3%). In fact, **1** proved to be highly stable under an inert atmosphere, and even prolonged heating in solution at 100°C (0.5 M THF solution) did not lead to significant decomposition. These results are in strong contrast to the liquid B.O. reagent, which already exhibited a decomposition event starting at $\sim 90^\circ\text{C}$ (46), an observation also supported by DSC and TGA measurements (Fig. 2D and figs. S236 to S237).

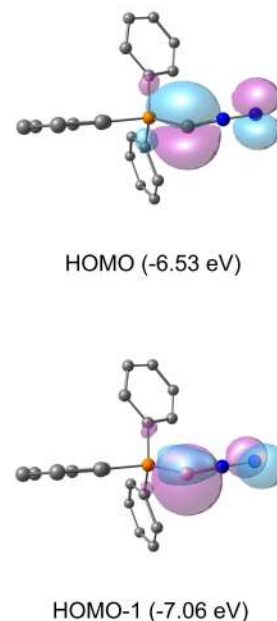
A Synthesis



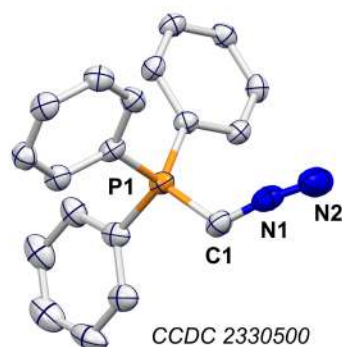
B Mechanism



E Evidence of C(0) nature



C X-ray structure



D High thermal stability

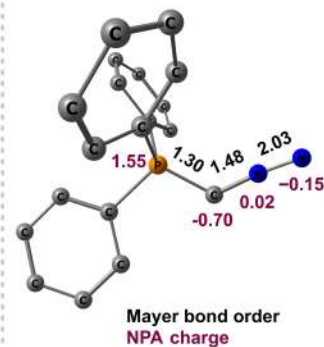
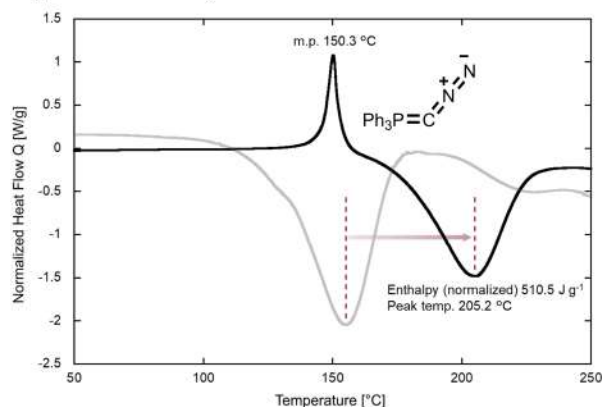


Fig. 2. Synthesis, structure, and properties of diazophosphorus ylide 1.

(A) Azide-free diazo transfer to symmetrical (**2a**) and unsymmetrical (**2b**) carbodiphosphoranes. The base used was KHMDS for **2a** and NaNH_2 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 $\text{N}_2/\text{P}^t\text{Bu}_3$ exchange reaction between the carbodiphosphoranes and N_2O . (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), and P1–C1–N1–N2 170(3). (D) Comparison of the DSC measurement of **1** (black) and the B.O. reagent [gray, enthalpy (normalized): 726.6 J g⁻¹, 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⁻ au⁻³) and Mayer bond order and natural population analysis (NPA) charges of **1** (calculated).

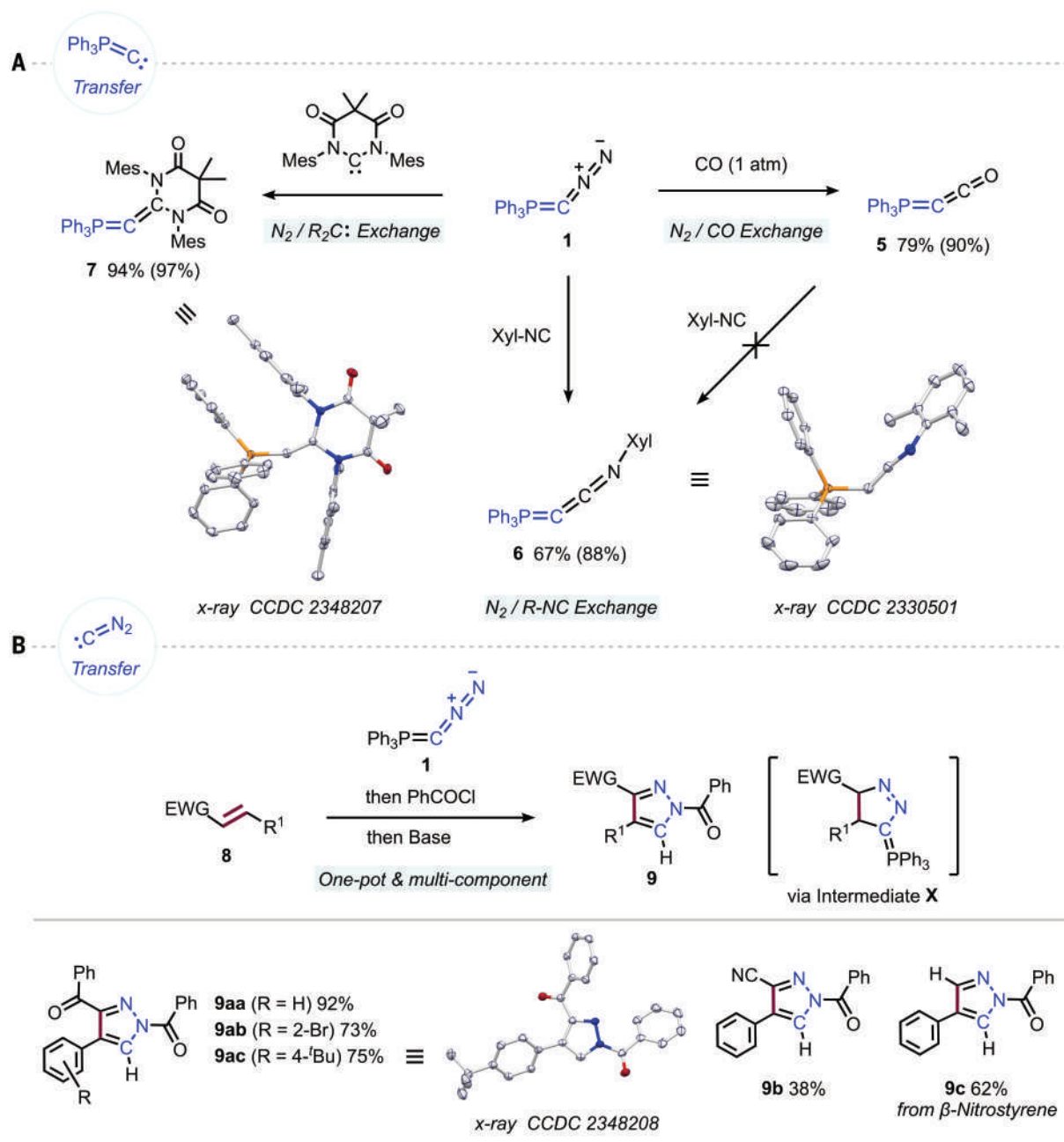


Fig. 3. Group transfer reactions. (A and B) Ph_3PC transfer toward ambiphiles (A) and CN_2 transfer toward electron deficient alkenes (B) using diazophosphorus ylide **1**. The NMR yields are shown in parentheses. The solvent used was THF, and the base was NaH for **9a** and **9b** and NaOH for **9c**.

Theoretical calculations were performed to clarify the electronic properties and the bonding situation of the stable diazophosphorus ylide. The Kohn-Sham highest occupied molecular orbital-1 (HOMO-1) (−7.06 eV) is a σ -type LP(C1) orbital (LP1) with respect to the P1–C1–N1 plane, and the HOMO (−6.53 eV) is a corresponding π -type LP(C1) orbital (LP2), both with a strong contribution from the $\pi^*(\text{N1}=\text{N2})$ orbitals (Fig. 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%; fig. S243), natural population analysis charge analysis (P1 1.56, C1 −0.70, N1 0.02, N4 −0.15; Fig. 2E), and natural bond orbital (NBO)-based natural resonance theory analysis (carbonyl canonical structure, 36%; fig. S248) all agree with the presence of two lone pairs of electrons on the central carbon atom. They also support the interpretation that ylide **1** has a “C(0)” atom stabilized by PPh_3 and N_2 (Fig. 1E; see the supplementary materials for details on the electronic properties of **1** and related diazo compounds) (47).

Ph_3PC and CN_2 transfer reactions

The facile synthesis and thermal stability of ylide **1** prompted us to investigate group transfer reactivity. The selective displacement of N_2 enabled the direct coupling of the phosphorus ylide moiety to CO and isocyanides to access heterocumulenes (Fig. 3A). Exposure of a THF solution of **1** to CO at room temperature afforded the phosphorane ketene **5** (i.e., Bestmann’s ketene) selectively in 79% yield. Similarly, the treatment of **1** with xylal isocyanide at 60°C gave the phosphorane

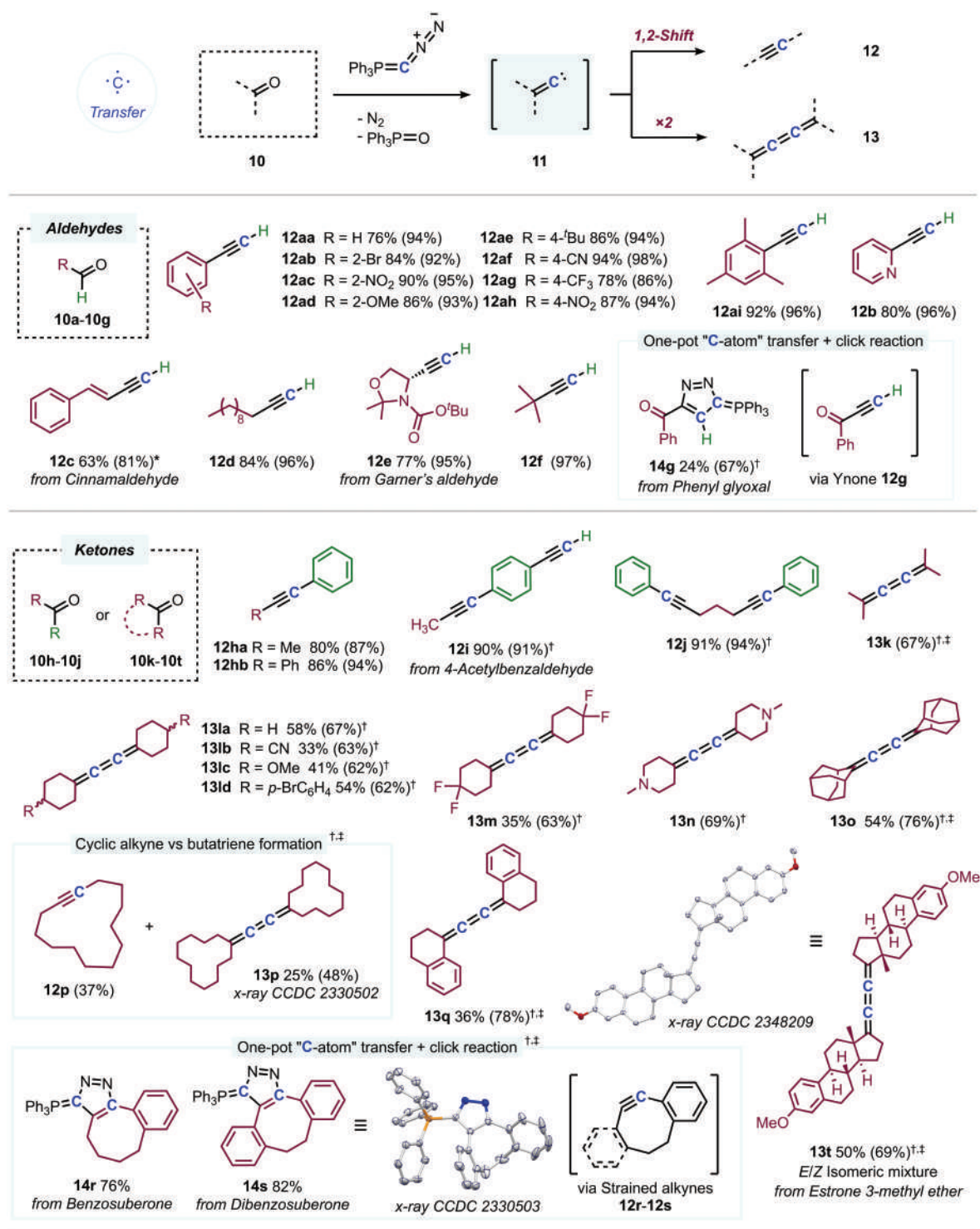


Fig. 4. C-atom transfer to carbonyl compounds. The reaction with benzaldehyde was conducted in THF, Et₂O, toluene, benzene, and acetonitrile. The ylide **1**/TPPO mixture obtained from the reaction of carbodiphosphorane **2a** with N₂O was used for the synthesis considering the facile synthesis and scalability. The NMR yields are shown in parentheses. *Ylide **1** was added dropwise. ‡2.0 equivalent of **1** was used. †The reaction was conducted at 60° or 90°C.

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 tem-

peratures, highlighting the necessity of the N₂ group to engage in exchange reactions. More importantly, the Ph₃PC 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 Ph₃PC

transfer reaction. Because the product still bears a reactive P-ylide moiety, the N₂/carbene exchange should allow further multistep processes, e.g., to access allenes. The combination of PPh₃/N₂ exchange followed by N₂/carbene exchange allows overall substitution of a phosphine by a carbene on a carbodiphosphorane.

Selective CN₂ transfer could also be accomplished chemoselectively toward electron-deficient alkenes, also in a multicomponent fashion (Fig. 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), functionalization with electrophiles (in this case, benzoylchloride), and PPh₃ elimination with a base (NaH) to eventually afford the highly substituted pyrazole **9a** in 92% yield. α,β -Unsaturated alkenes, including *trans*-chalcones with different functionalities (**9ab** to **9ac**) and cyano alkenes (**9b**), were compatible. In the case of β -nitrostyrene, the nitro group could also be eliminated, which allowed 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 CN₂ surrogate toward unsaturated C–C 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), the phosphonyl moiety typically cannot be eliminated, which showcases the advantage of using a neutral PPh₃-containing reagent. Furthermore, this reagent could circumvent the use of protic solvents that are typically used for generating carbanion **VI** and related reactive species, which will allow multicomponent reactions to synthesize pyrazoles with multiple functionalities.

C-atom transfer reactions

Compared with the reactive anionic intermediate **VI** (Fig. 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 Et₂O, THF, toluene, benzene, and even in CH₃CN 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 with the B.O. reagent, which was supported not only by the wide functional group compatibility, but also by the different molecule classes accessible after the O-to-C exchange reaction (Fig. 4).

The reaction of aldehydes exclusively gave the corresponding alkynes. Computational studies (fig. S252) support a Wittig-type mechanism to generate transient diazoalkenes, N₂ loss to afford vinylidenes, followed by a 1,2-H shift (48). ¹³C-labeling experiments using ¹³C-labeled benzaldehyde (figs. S122 and S123) support a selective 1,2-H over 1,2-aryl shift. Aryl aldehydes with different electronic properties (**12aa** and

12b), functionalities (–Br, –OMe, –CN, –NO₂, and –CF₃, **12ab** to **12ah**) and steric environments (Mes, **12ai**) all afforded the alkynes in excellent yields. Cinnamaldehyde (an α,β -unsaturated aldehyde) (**12c**) was also compatible. This transformation is impossible with the B.O. reagent because of the decomposition of the product in MeOH (22) and requires substantial optimization of the reagent and additives to ensure selective conversion. Alkyl aldehydes with different functionalities and steric environments (**12d** to **12f**) and acyclic arylketones (**12ha** and **12hb**) also cleanly afforded the desired alkynes. 4-Acetylbenzaldehyde and 1,5-diphenylpentane-1,5-dione also gave the target dialkynes **12i** and **12j** in high yields, demonstrating multiple C-atom transfer events to form multiple internal and terminal alkynes in one pot. The α -ketoaldehyde phenyl glyoxal selectively afforded phosphoranylidene pyrazole **14g** in a manner similar to the results discussed in the CN₂ transfer section. Formation of **14g** demonstrates a one-pot sequence of C-atom transfer and (3+2) cycloaddition to provide densely functionalized pyrazoles directly from an α -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-terminal 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 a 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 the –CN, –OMe, –*p*-Br-C₆H₄, and –CF₃ groups were compatible (**13la** to **13m**), which is intriguing considering that this reaction is likely to proceed through 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. Although the cyclic (alkyl)(aryl)ketone tetralone selectively gives butatriene **13q**, cyclic arylketones with a larger cycloheptanone core instead give the

corresponding phosphoranylidene pyrazoles **14r** and **14s**, demonstrating the one-pot synthesis of fused aromatic heterocycles from simple ketones (for the nucleus-independent chemical shift values of **14s**, see the supplementary materials). This result shows that less-strained cyclic ketones favor 1,2-shift over dimerization, allowing the formation of strained alkynes through 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**. Because only a single step is required for the synthesis of butatrienes from easy-to-access ketones, avoiding the need for additives such as transition metals (Ni, Pd, Cu, Zn) and toxic reducing agents (e.g., SnCl₂) (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 N₂O. The chemically labile PPh₃ and N₂ groups allowed the ylide to act as a multipurpose transfer reagent, including Ph₃PC, CN₂, 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, e.g., to access higher cumulenes or edit the framework of complex molecules.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Figs. S1 to S252
Tables S1 and S2
References (51–90)
NMR Spectra

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