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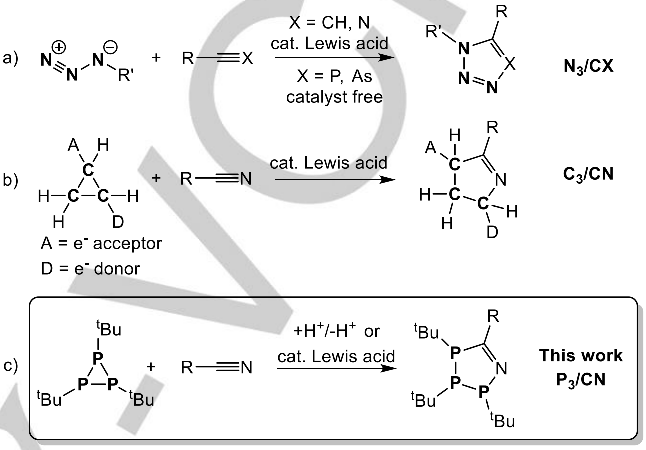
COMMUNICATION

Addition of a Cyclophosphine to Nitriles: An Inorganic "Click" Reaction Featuring Protio-, Organo-, and Main Group Catalysis

Saurabh S. Chitnis,[a] Hazel A. Sparkes,[a] Vincent T. Annibale,[a] Natalie E. Pridmore,[a] Alex M. Oliver,[a] and Ian Manners*[a]

Abstract: We report the addition of a cyclotriphosphine to a broad range of nitriles giving access to the first examples of free 1-aza-2,3,4-triphospholenes in a rapid, ambient temperature, one-pot, high-yield protocol. The reaction produces electron-rich heterocycles (four lone pairs) and features homoatomic σ-bond heterolysis, thereby combining the key features of the 1,3-dipolar cycloaddition chemistry of azides and cyclopropanes. We also report the first catalytic addition of P-P bonds to the C≡N triple bond. The coordination chemistry of the new heterocycles is explored.



Scheme 1. Dipolar additions of N_3, C_3, and P_3 frameworks with CX triple bonds.

Translating the highly-evolved methods of modern organic synthesis to inorganic substrates is interesting from a fundamental perspective and can also reveal atom-efficient protocols for accessing inorganic molecules and materials with unique properties. For example, the transformative role of transition-metal catalysis in organic chemistry has inspired metal mediated homo- and hetero-couplings of other p-block elements,[1a-c] yielding a wealth of interesting inorganic molecules[1d-f] and polymers[1g-j] having properties that are complementary to those accessible with organic analogues.[1k-m] Owing to such examples there is significant interest in the development of new high-yielding, and, in particular, catalytic reactions for assembling complex inorganic frameworks from simple synthons in a modular fashion, as defined by the modern state-of-the-art in organic synthesis.

In this context, the 1,3-cycloaddition of azides with alkynes,[2a] nitriles,[2b] phosphaalkynes,[2c] and arsaalkynes[2d] is a rapid and atom-economic means of assembling heterocycles in a single step (Scheme 1a). The versatility and reliability of such reactions has been recognized as defining the gold-standard for "click" chemistry.[2e] The concept of "click" dipolar cycloaddition translates smoothly from N_3 synthons such as azides to C_3 synthons such as donor-acceptor (DA) cyclopropanes, which add to unsaturated dipoles (ketones, nitriles, aldehydes, etc.) under Lewis acid catalysis to give five-membered organic heterocycles (Scheme 1b).[3] Inspired by the success of the N_3 to C_3 translation, we have now developed a rapid (< 5 mins), ambient temperature, one-pot protocol that enables the click-like addition of a P_3 synthon ($P_3{}^tBu_3$) to the C≡N triple bonds in a broad range of nitriles (Scheme 1c), giving access to a hitherto unisolated class of phosphorus heterocycles in excellent yields. A catalytic variant of the reaction has also been developed, representing the first catalytic addition of P-P bonds to nitriles. These novel P_3/C≡N additions combine the challenging homoatomic σ-bond heterolysis observed in the cycloaddition between the C_3/C≡N pair, with the rich coordination potential of the electron-rich heterocycles obtained from N_3/C≡N cycloadditions.

There is renewed interest[4a-c] in the fundamental chemistry of phosphorus heterocycles due to their potential for applications as optoelectronic materials,[4d] anion sensors,[4e] linkers in supramolecular chemistry,[4f] and metal-free catalysts.[4g,h] As a result, the stoichiometric and catalytic additions of P-P σ bonds to alkenes, alkynes, and ketones is an area of intensive research.[5] Previous work has established that P-P bonds that are polarized by electrophile attachment can also add to nitrile C≡N bonds, but the products in all cases were only isolated in the coordination sphere of a Lewis acid, restricting their further utility.[6] In contrast, the protocols revealed here yields free heterocycles, enabling us to debut a systematic study of their coordination chemistry towards hard and soft, metal and non-metal electrophiles.

Density functional theory (DFT) calculations suggested that the addition of the prototypical cyclotriphosphine $P_3{}^tBu_3$ to MeCN is exothermic by 50 kJ mol^{-1} (see Supporting Information), but no reaction occurred when $P_3{}^tBu_3$ was refluxed in neat MeCN for 24 h (Scheme 2a). When one equivalent of HOTf was added as an electrophilic activator to equimolar mixtures of $P_3{}^tBu_3$ and MeCN in toluene, complete conversion to $[({}^tBuP)_3P({}^tBu)H]^+$ was observed (Scheme 2b), consistent with Weigand's report of Me_3SiOTf-catalyzed conversion of $P_3{}^tBu_3$ to $P_4{}^tBu_4$,[7a,13] and protonation of the latter cyclotetraphosphine with HOTf.[7b] However, when one equivalent of HOTf was added to a solution of $P_3{}^tBu_3$ in either neat RCN or in a 1:1 (by volume) RCN/toluene solution, an immediate reaction took place yielding the N-protonated P_3CN frameworks [**1R**]$^+$ in essentially quantitative

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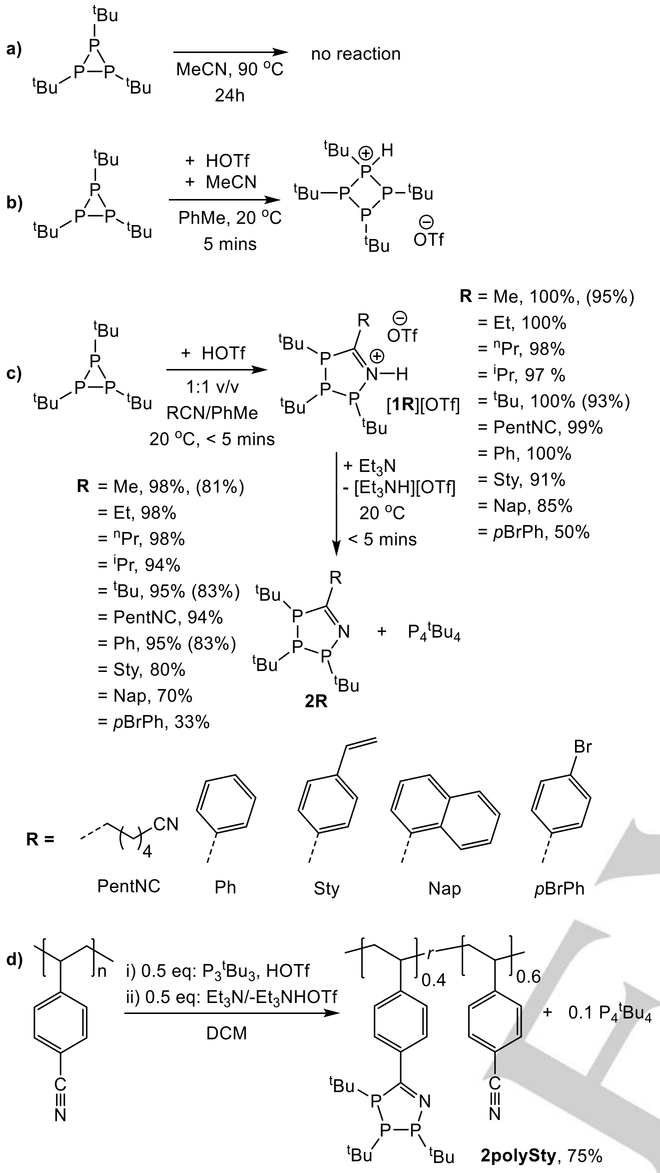


Scheme 2. Reactions of $P_3{}^tBu_3$ with nitriles. Isolated yields are in parentheses. All other yields were determined by ^{31}P NMR spectroscopy.

spectroscopic yield for most derivatives within the time of mixing (Scheme 2c). In situ deprotonation of [**1R**]$^+$ by Et_3N yielded neutral 1-aza-2,3,4-triphospholenes, **2R**, in excellent spectroscopic yield within minutes (Figure S1, Table S1) and >80 % isolated yield for select derivatives following extraction into pentane and recrystallization (Scheme 2c). The material remaining in the mother liquor in each case was $P_4{}^tBu_4$. The reaction scales well, as demonstrated by the successful isolation of **2Me** on a multiple-gram scale. Both aliphatic and aromatic nitriles are suitable substrates. Within aliphatic derivatives, very hindered nitriles are well-tolerated (e.g. ^tBuCN) but within aromatic derivatives, yields were lowered marginally for the bulky naphthalene-1-carbonitrile (**2Nap**, 70%) and significantly for the electron-deficient 4-bromobenzonitrile (**2*p*BrPh**, 33%). While liquid nitriles were better substrates, being used as co-solvents to create the required nitrile excess, solid nitriles could also be used in saturated solutions. For example, poly(4-cyanostyrene) could be functionalized to yield a random copolymer where 40% of the nitrile groups were converted to the corresponding azatriphospholene (Scheme 2d, Figure S7-10, Supporting Information).

Compounds [**1Me**][OTf], [**1^{t}Bu**][OTf], **2Me**, **2^{t}Bu** and **2Ph** have been isolated and characterized by elemental analysis, NMR spectroscopy, and vibrational spectroscopy. The molecular structures of [**1^{t}Bu**][OTf] and **2Me** (Figure 1) were further established by X-ray diffraction and unambiguously show the proposed P_3CN framework. To the best of our knowledge, free azatriphospholenes have not been isolated before, although one example was trapped in 17 % yield between two $W(CO)_5$ fragments. [6c]

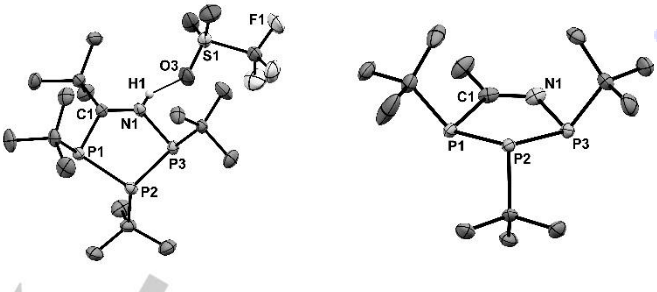
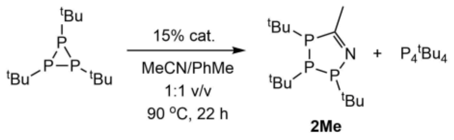


Figure 1. Molecular structure of [**1^{t}Bu**][OTf] (left) and **2Me** (right) in the solid state. Non-essential hydrogen atoms have been omitted for clarity.

To develop an atom-efficient alternative to the above stoichiometric protonation-addition-deprotonation sequence, we hypothesized that transient activation by a catalytic amount of electrophile might also effect the same transformation. Indeed, reactions of azides and DA-cyclopropanes with nitriles are usually catalyzed by added electrophiles.[3] When solutions of $P_3{}^tBu_3$ in 1:1 (v/v) MeCN/PhMe were heated to 90 °C with a variety of electrophiles (15 mol% relative to $P_3{}^tBu_3$), we observed 80-100 % conversion of $P_3{}^tBu_3$ to either $P_4{}^tBu_4$, or a mixture of $P_4{}^tBu_4$ and the desired nitrile-cyclophosphine addition product, **2Me** (Table 1) The observation that Brønsted acids are catalytically active (entries 1 and 2) is particularly interesting considering Baudler's previous report of stoichiometric reactivity between $P_3{}^tBu_3$ and HCl in THF to form the ring-opened linear species $H(^tBu)P{-}P(^tBu){-}P(^tBu)Cl$.[8] The ratio of **2Me** to $P_4{}^tBu_4$ varied significantly between the electrophiles tested. For example, only $P_4{}^tBu_4$ was detected in the case of $B(C_6F_5)_3$ (entry 3). Drawing upon Gabbaï's work on stibonium ion catalysis,[9] $Ph_3SbCl(OTf)$ was also tested and, unexpectedly, provided the best ratio of desired **2Me** to $P_4{}^tBu_4$ (entry 6, Figure S2 for crude ^{31}P NMR spectra). The structure of this novel Sb(V) complex was determined by X-ray crystallography (Figure S3).

Screening a series of nitriles with $Ph_3SbCl(OTf)$ showed that the product distribution shifts towards $P_4{}^tBu_4$ formation with increasing steric bulk at the carbon (Scheme 3a). Given the high yields obtained from stoichiometric routes (Scheme 2c), we conclude that kinetic rather than thermodynamic factors govern the product ratios. Control experiments confirmed that $Ph_3SbCl(OTf)$ (15 mol%) effects the catalytic conversion of $P_3{}^tBu_3$ to $P_4{}^tBu_4$ in the absence of MeCN in 1:1 v/v $MeNO_2$/PhMe in < 5 minutes at 90 °C (Scheme 3b). The choice of $MeNO_2$ as a substitute for MeCN was based on the similar dielectric constants for the two solvents (ε = 37.5 for MeCN and 35.9 for $MeNO_2$). When only one equivalent of MeCN was used relative to $P_3{}^tBu_3$

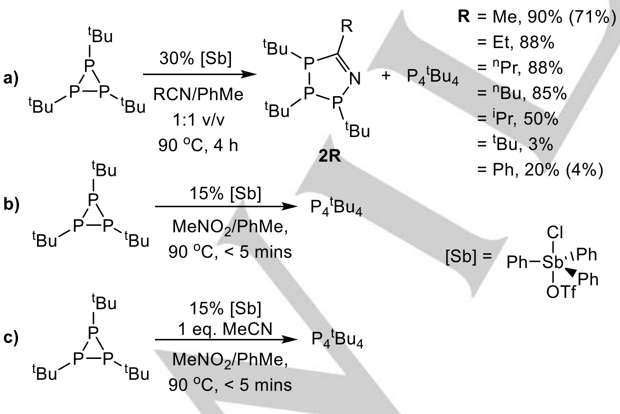
Table 1. Catalyst screening for the addition of $P_3{}^tBu_3$ to MeCN. Yields determined by ^{31}P NMR spectroscopy.



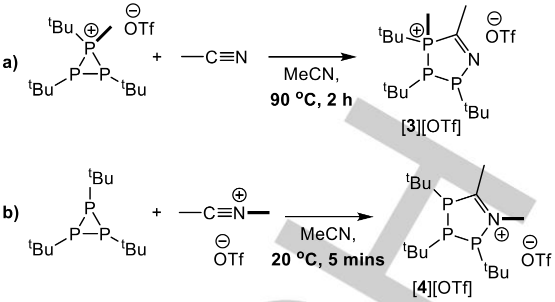
Entry	Catalyst	% Conversion	% **2Me**	% $P_4{}^tBu_4$
1	$[H(OEt_2)_2][B(C_6F_5)_4]$	93	32	68
2	HOTf	100	72	17
3	$B(C_6F_5)_3$	84	0	100
4	$[Ph_3C][B(C_6F_5)_4]$	100	56	44
5	TMSOTf	84	15	85
6	**$Ph_3SbCl(OTf)$**	**96**	**84**	**16**
7	$Ph_3Sb(OTf)_2$	100	80	20

in 1:1 v/v $MeNO_2$/PhMe as solvent, $P_4{}^tBu_4$ was once again the sole product observed, consistent with the formation of $P_4{}^tBu_4$ in reaction of $P_3{}^tBu_3$ with HOTf in the presence of one equivalent of MeCN (cf. Scheme 3c and Scheme 2b).

These experiments suggest that i) formation of **2Me** and $P_4{}^tBu_4$ occurs via separate catalytic cycles, ii) the $P_4{}^tBu_4$ forming cycle is more rapid than the **2Me** forming cycle, and iii) a large excess of MeCN (e.g. when MeCN is the cosolvent) kinetically outcompetes $P_4{}^tBu_4$ formation to yield **2Me** at the expense of $P_4{}^tBu_4$. When only one equivalent of MeCN is used, or when bulky nitriles such as ^{t}BuCN are utilized, the catalytic cycle involving P-P/C≡N addition is sufficiently retarded that the nitrile-free and comparatively faster $P_4{}^tBu_4$ forming catalytic cycle dominates the product distribution.



Scheme 3. Substrate scope and control reactions for the catalytic addition of nitriles to $P_3{}^tBu_3$. Yields were determined by ^{31}P NMR spectroscopy.



Scheme 4. Formation of [**3**][OTf] and [**4**][OTf].

To clarify the role of the electrophile in the above reactions, we prepared isolable triflate salts of $[(^tBuP)_2P(^tBu)Me]^+$ and $[MeCNMe]^+$ as models for the unstable[7a,10] protonated ions $[(^tBuP)_2P(^tBu)H]^+$ and $[MeCNH]^+$. The molecular structure of [MeCNMe][OTf][11] was determined (Figure S11) as symmetric alkylnitrilium cations have not previously been structurally characterized.[12]

Heating a solution of $[(^tBuP)_2P(^tBu)Me][OTf]$ to 90 °C in MeCN for 2 h yielded the P-methylated cationic heterocycle [**3**]$^+$, which was identified spectroscopically (Scheme 4a).[6e] Combining [MeNCMe][OTf] and $P_3{}^tBu_3$ in MeCN at 20 °C resulted in rapid conversion (< 5 minutes) to the N-methylated [**4**]$^+$, which was isolated and characterized crystallographically as its triflate salt (Scheme 4b, Figure S11). These results indicate that the ability to undergo dipolar addition can be unlocked by electrophilic activation of either the cyclophosphine or the nitrile. Based on the above experiments, tentative mechanisms for the electrophile-catalyzed formation of **2R** from $P_3{}^tBu_3$ and RCN are proposed in Scheme S2 (Supporting Information).

With a facile route to the new P_3CN heterocycles **2R** in hand, we assessed their ability to coordinate classical metallic and non-metallic acceptors. The HOMO of **2Me** (Figure 2, left) shows prominent lobes at all pnictogen atoms, foreshadowing a coordinative ambiguity involving these donor sites. The equimolar reaction of **2Me** and **2Ph** with HOTf in DCM yielded [**1Me**][OTf] or [**1Ph**][OTf] quantitatively, indicating protonation of the nitrogen atoms. In contrast, DCM solutions containing **2R** and $[Rh(cod)Cl]_2$ (2:1 stoichiometry) exclusively yielded complexes [Rh(**2R**)(cod)Cl] (R = Me, Ph), featuring Rh-P interactions ($^1J_{PRh}$ ≈ 150 Hz). The structures of [**1Me**][OTf] and both rhodium complexes were established crystallographically (Figure 2 right, and Figure S5).

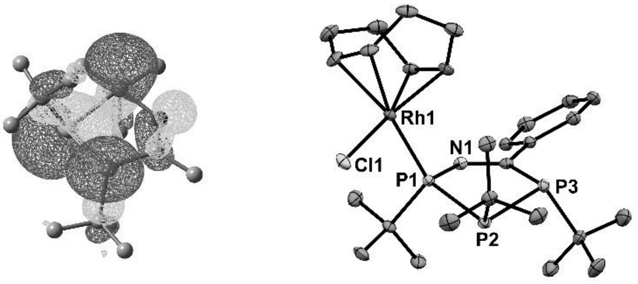


Figure 2. Calculated HOMO of **2Me** (left) and molecular structure of [Rh(**2Ph**)(cod)Cl] (right). Hydrogen atoms have been omitted for clarity.

We interpret these divergent outcomes as being consistent with predictions from hard/soft acid/base (HSAB) theory. The hard, cationic electrophile H^+ coordinates at the hard imine donor site, whereas the soft Rh(I) Lewis acid binds at the soft phosphine donor site. The ^{31}P NMR spectrum of reaction between $GaCl_3$ and **2Me** exhibited three AMX spin systems indicating the presence of three products (Figure S6), which could not be separated. Nevertheless, the formation of multiple $GaCl_3$-**2Me** adducts, presumably by coordination at different sites, evidences the flexible donicity implied by the multi-site HOMO of **2Me**.

In summary, we have disclosed the first stoichiometric and catalytic additions of P-P bonds to the C≡N triple bond giving access to P-C=N-P frameworks free of electrophile stabilization. Using these reactions, the first examples of free azatriphospholenes, **2R**, have been prepared and structurally characterized in good yields with a broad substrate scope in molecular or polymeric nitriles. The reaction presents the P_3/C≡N analogue of the well-established N_3/C≡N and C_3/C≡N dipolar cycloadditions. Due to the simultaneous presence of multiple hard and soft donor sites, the electron-rich heterocycles **2R** exhibit a rich coordination chemistry and may find applications as ligands in heterobimetallic catalysis.

Acknowledgements

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Keywords: phosphorus heterocycles • main group elements • catalysis • click chemistry • cycloaddition

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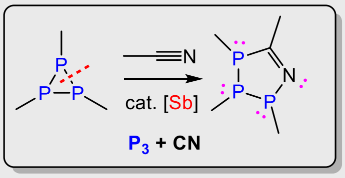
[13] Calculated ΔG_{rxn} for $4P_3{}^tBu_3 \rightarrow 3P_4{}^tBu_4$ is -327 kJ mol^{-1} at the PBE1PBE/6-311+G(d,p) level.

COMMUNICATION

The catalytic cycloaddition of nitriles to a cyclotriphosphine gives the first example of free 1-aza-2,3,4-triphospholenes. This electrophile-mediated reaction is rapid (< 5 mins), and proceeds at ambient temperature in a one-pot, high-yield protocol with a broad scope in nitriles (11 examples), representing a phosphorus analogue of the azide-nitrile and cyclopropane-nitrile "click" [3+2] cycloadditions.



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