On the Ambiphilic Reactivity of Geometrically Constrained Phosphorus(III) and Arsenic(III) Compounds: Insights into Their Interaction with Ionic Substrates

Thomas P. Robinson, Siu-Kwan Lo, Daniel De Rosa, Simon Aldridge, and Jose M. Goicoechea*

Abstract: The ambiphilic nature of geometrically constrained Group 15 complexes bearing the \(N,N\text{-bis}(3,5\text{-di-tert-butyl-2-phenolate})\)amide pincer ligand (ONO\(^{-}\)) is explored. Despite their differing reactivity towards nucleophilic substrates with polarised element–hydrogen bonds (e.g., \(\text{NH}_3\)), both the phosphorus(III), \(\text{P(ONO)}(\text{1a})\), and arsenic(III), \(\text{As(ONO)}(\text{1b})\), compounds exhibit similar reactivity towards charged nucleophiles and electrophiles. Reactions of 1a and 1b with KO\(_2\text{Bu}\) or K\(_2\text{NP}\) afford anionic complexes in which the nucleophilic anion associates with the pnictogen centre \(([(\text{BuO})\text{Pn(ONO)})]^{-}(\text{Pn}=\text{P}(\text{2a}), \text{As}(\text{2b}))\) and \([(\text{Ph}_{3}\text{P})(\text{ONO})]^{-}(\text{Pn}=\text{P}(\text{3a}), \text{As}(\text{3b}))\). Compound 2a can subsequently be reacted with a proton source or benzyl bromide to afford the phosphorus(V) compounds \((\text{BuO})\text{HP(ONO)}(\text{4a})\) and \((\text{BuO})\text{BzP(ONO)}(\text{5a})\), respectively, whereas analogous arsenic(V) compounds are inaccessible. Electrophilic substrates, such as HOTf and MeOTf, preferentially as-sociate with the nitrogen atom of the ligand backbone of both 1a and 1b, giving rise to cationic species that can be rationalised as either ammonium salts or as amine-stabilised phosphonium or arsenium complexes \((\text{Pn}[\text{ONOH}]^{+}(\text{Pn}=\text{P}(\text{6a}), \text{As}(\text{6b}))\) and \((\text{Pn}[\text{ONMe}O])^{+}(\text{Pn}=\text{P}(\text{7a}), \text{As}(\text{7b}))\). Reaction of 1a with an acid bearing a nucleophilic counterion (such as HCl) gives rise to a phosphorus(V) compound HPCI(ONO) (8a), whereas the analogous reaction with 1b results in the addition of HCl across one of the As–O bonds to afford CIAs(III)(ONO) (8b). Functionalisation at both the pnictogen centre and the ligand backbone is also possible by reaction of 7a/7b with KOrBu, which affords the neutral species \((\text{BuO})\text{Pn(ONMe)O}(\text{Pn}=\text{P}(\text{9a}), \text{As}(\text{9b}))\). The ambiphilic reactivity of these geometrically constrained compounds allows some insight into the mechanism of reactivity of 1a towards small molecules, such as ammonia and water.

Introduction

Over the last decade significant advances have been made in the development of main-group species that are capable of activating small molecules.\(^{[21]}\) Most prominent amongst these are alkyl(amine) carbenes (AACs),\(^{[22]}\) low oxidation state compounds of Groups 13 and 14,\(^{[23, 24]}\) and frustrated Lewis pairs (FLPs).\(^{[25]}\) Several of the aforementioned compounds have also shown to be active in catalytic processes, such as the hydrogenation of imines, alkenes and alkynes,\(^{[26]}\) effectively heralding a new era in the chemistry of the p-block elements. It is also worth noting that the substrate scope of such compounds includes molecules such as ammonia, which has historically proven difficult to activate using precious metal catalysts due to the unfavourable coordination/activation equilibrium. New routes resulting in the activation of N–H bonds in ammonia are particularly appealing, because of the dearth of transition-metal systems capable of effecting such a transformation,\(^{[27–29]}\) and the relevance of N–H activation to a number of potentially important industrial processes.\(^{[29]}\)

More recently, geometrically constrained compounds based on phosphorus(III) have also received significant attention in this field. Studies by Arduengo,\(^{[21]}\) Radosevich,\(^{[22–24]}\) Kinjo,\(^{[25]}\) and our own research group have demonstrated that the distorted T-shaped phosphorus(III) compounds pictured in Figure 1 are capable of reacting with polar substrates such as water, alcohols, ammonia and amines.\(^{[26]}\) In the vast majority of cases, these reactions result in a formal oxidative addition of the substrate over the phosphorus(III) centre, although several theoretical studies have subsequently demonstrated that, in all likelihood, these processes involve the ligand backbone.\(^{[27, 28]}\)

We recently reported a phosphorus(III) compound bearing the \(N,N\text{-bis}(3,5\text{-di-tert-butyl-2-phenolate})\)amide ligand (P(ONO)); 1a.\(^{[26]}\) This species was found to react with ammonia and water, activating the E–H bonds in both substrates through a formal oxidative addition to afford the corresponding phos-
phosphorus(V) compounds. Under forcing conditions (heating solid samples under a dynamic vacuum) we were able to show that these processes are reversible. During the course of these studies, we observed that 1a exclusively reacts with nucleophilic species with protic E–H bonds, whereas non-nucleophilic substrates, even those with polar E–H bonds, such as phenylis- lane, fail to react. These observations seemed to indicate that the nucleophilic association of the substrate is necessary prior to any further reactivity taking place. This prompted us to explore the reactivity of 1a towards both nucleophiles and electrophiles in an effort to gain a better understanding of the reaction dynamics. These results, and analogous studies on the heavier arsenic(III) analogue (1b), are reported herein.

Results and Discussion

Structure and bonding considerations for 1a and 1b

As previously reported, 1a exhibits a bent geometry in the solid state with moderate pyramidalization at both the phosphorus and nitrogen atoms ($\Sigma_{\text{angle P}} = 296.1^\circ$; $\Sigma_{\text{angle N}} = 331.6^\circ$), in contrast to planar compound A. Theoretical calculations at the density functional theory (DFT) level revealed that the pyramidal C$_2$ isomer (or electromorph to use the term coined by Arduengo) is the most stable, but relatively close in energy to the C$_6$ symmetric species (within 4 kJ mol$^{-1}$). This energetic difference is within the error of the calculations, and it is worth noting that different computational analyses (varying basis sets and functionals) actually suggest that the planar structure is lower in energy than the C$_2$ isomer (albeit by similarly small values). Therefore, it is highly likely that, in solution, there is a dynamic, and concerted, pyramidal inversion at the phosphorus and nitrogen atoms resulting in a wing-like “flapping” of the ligand backbone. The calculations also revealed that, regardless of the symmetry adopted by 1a, there is an empty, energetically accessible orbital that is largely based on the phosphorus atom, which has anti-bonding character with respect to the P–N and P–O bonds. It is also worth noting that the P–N bond in 1a is significantly polarised, with computed Hirshfeld charges of 0.394 and −0.171 on the phosphorus and nitrogen atoms, respectively. These observations prompted us to explore the reactivity of 1a, and its heavier arsenic analogue (1b), towards nucleophiles in order to establish whether they associate with the phosphorus/arsenic atom.

The arsenic-containing species 1b can be prepared following a similar synthetic methodology to that previously reported for its lighter congener. Reaction of the protonated ligand, N,N-bis(3,5-di-tert-butyl-2-phenyl)amine, H$_2$ONO, with AsCl$_3$ in the presence of three molar equivalents of triethylamine, affords 1b quantitatively, as evidenced by $^1$H and $^{13}$C($^1$H) NMR spectroscopy. The $^1$H NMR spectrum of 1b in CD$_2$Cl$_2$ reveals two equal intensity aromatic resonances at 8.39 and 7.51 ppm as well as two singlets at 1.71 and 1.46 ppm arising from the tert-butyl groups. Cooling of a concentrated pentane solution afforded bright red-orange crystals of the compound in good to high yields.

The structure of 1b (Figure 2) exhibits a planar T-shaped geometry about the arsenic(III) centre (mean deviation from As1/O1/N1/O2 plane is 0.0213 Å) with a near linear O1-As1-O2 angle of 164.39(12)$^\circ$. The O-As-N angles, by contrast, are more acute and approach 90$^\circ$ (82.9(2) and 81.8(2)$^\circ$), giving rise to a sum of bond angles around the arsenic centre ($\Sigma_{\text{angle As}}$) of 329.1$^\circ$. The sum of bond angles around the nitrogen centre, 359.9$^\circ$, is significantly greater than for the lighter phosphorus-containing analogue (331.6$^\circ$). The As–O bond lengths (1.933(4) and 1.933(4) Å) are slightly elongated when compared to the expected values for single bonds (1.84–1.85 Å)\[29, 30\]. By contrast, the As–N bond (1.862(3) Å) is shorter than expected for a single bond (1.90–1.92 Å), indicating a significant degree of π-donation from the nitrogen lone pair to the empty π-orbital on the arsenic centre (and some multiple bond character due to this interaction). The structure and bond metrics for 1b are closely related to the planar 10-As-3 compound 5-aza-2,8-dioxo-l-arsabicyclo[3.3.0]octa-2,4,6-triene previously reported by Arduengo and co-workers\[21\],\[29, 30\] DFT calculations show a good agreement between the optimised geometry of 1b and that determined crystallographically. Interestingly, attempts to optimise the C$_2$ isomer of 1b ultimately converge to the planar (C$_6$) isomer, indicating that in contrast to its phosphorus-containing analogue, the C$_2$ geometry of 1b is not a minimum on the potential energy hypersurface.

Reactivity of 1a and 1b towards nucleophiles

The reactivity of 1a and 1b was explored towards a number of nucleophilic species. In a preliminary report we demonstrated that 1a reacts with nucleophiles with polarised element–hydrogen bonds (NH$_2$, H$_2$O) to give rise to five coordinate phosphorus(V) compounds. By contrast, no reaction is observed between 1b and ammonia, whereas hydrolysis does take place but gives rise to complex reaction mixtures and does not result in any arsenic(V)-containing compounds. Our calculations reveal that this is largely a thermodynamic phenomenon. The reaction between NH$_2$ and 1a is exothermic by 90 kJ mol$^{-1}$, whereas the same reaction between NH$_2$ and 1b is thermodynamically uphill by 86 kJ mol$^{-1}$. This difference in reactivity can be attributed to the increased stabilisation of the “inert pair” on descending Group 15.

No reaction is observed for either 1a or 1b with neutral nucleophiles, such as pyridine or PPh$_3$. In contrast, anionic
nucleophiles do react with both compounds associating with the pnictogen centre. In a typical reaction, the geometrically constrained complexes were reacted with one equivalent of KNu (Nu = Otbu or NPh) in the presence of a cation sequestering agent (either 1,4,7,10,13,16-hexaoxa-2,2-crypt) to aid crystallisation. These reactions yielded the anionic complexes [(tBuO)Pn(ONO)]⁻ (Pn = P (2a) and As (2b)) and [(tBuO)Pn(ONO)]⁻ (Pn = P (3a) and As (3b)) as pictured in Scheme 1.

Reactions involving 1a were monitored by 31P NMR spectroscopy and show quantitative conversion to the desired products, which were observed as singlet resonances at 85.5 and 66.3 ppm for 2a and 3a, respectively. These resonances are shifted upfield with respect to 1a (168.6 ppm), due to the enhanced electron density on the phosphorus centre. Similarly the 1H NMR spectra of both compounds display the requisite number of resonances for a symmetrical N,N-bis(3,5-di-tert-butyl-2-phenolate)amide ligand backbone and for the nucleophilic substituents. Reactions involving 1b similarly give rise to products in which both of the 3,5-di-tert-butyl-2-phenolate arms of the ligand backbone are equivalent as evidenced by 1H and 31C(1H) NMR spectroscopy.

The structures of all four novel anionic complexes were determined by single-crystal X-ray diffraction (Figures 3 and 4). The complexes reveal planar Pn(ONO) moieties (mean deviation from plane for Pn1/O1/N1/O2: 0.0322 Å (2a), 0.0365 Å (2b) 0.0019 Å (3a) and 0.0150 Å (3b)) with the nucleophile orthogonal to the Pn(ONO) core. The planarity of the ligand backbone is also evident in the sum of bond angles around the nitrogen atoms (359.4, 357.4, 359.7 and 360.0° for 2a, 2b, 3a and 3b, respectively). These structures are consistent with lone-pair donation from the nucleophile into the lowest unoccupied molecular orbital (LUMO) of 1a and 2a. DFT calculations reveal that the most significant atomic orbital contribution to this orbital comes from the pnictogen p orbital that is perpendicular to the plane of the molecule (53.75 and 49.97% contributions for the phosphorus and arsenic p orbitals for 1a and 2a, respectively; the z axis is defined as orthogonal to the plane of the molecule). The LUMO of 1a and 2a are also notably pₖ₋ₚ orbitals, antibonding with respect to the Pn–N and Pn–O bonds.

Upon coordination of an anionic nucleophile there is a significant elongation of the Pn–O bonds while the Pn–N bonds remain very similar to those of the parent compound (see Table 1 for a comparison of bond metric data for all complexes). In each of the adducts, the elongation of the Pn–O bonds is not uniform, but rather more pronounced for one of the two aryloxide functionalities of the N,N-bis(3,5-di-tert-butyl-2-phenolate)amide ligand. This significant weakening of the Pn–O bonds strongly suggests that on coordination of a nucleophile, the aryloxide functionalities are susceptible to electrophilic attack. This was probed by reacting 2a and 2b with a pyridinium trifluoromethanesulfonate and benzyl bromide (BzBr).

Reactions of [K(2,2,2-crypt)][2a]·1.5tol with one molar equivalent of pyridinium trifluoromethanesulfonate (PyHOTf) or benzyl bromide afforded the trigonal bipyramidal compounds (rBuO)HP(ONO) (4a) and (rBuO)BzP(ONO) (5a), respectively (Scheme 2). These novel phosphorus(V) compounds display similar structures and 31P NMR chemical shifts (−38.7 and −20.2 ppm for 4a and 5a, respectively) to the E–H activation products that were obtained by reaction of 1a with H₂O or NH₃. In fact, compound 4a can be readily accessed by direct reaction of 1a with HORBu. The reactions proceeded rapidly (before the 31P NMR spectra of the reaction mixtures were recorded) at room temperature affording the compounds in quantitative yields. Consequently, we were unable to ascertain whether electrophilic association of the proton or benzyl functionalities involved the ligand backbone prior to migration of the functional group to the phosphorus centre.

The structures of 4a and 5a were corroborated by single-crystal X-ray diffraction (Figure 5). Both display distorted trigonal bipyramidal geometries as expected for a phosphorus(V)
species with the $N,N$-bis(3,5-di-tert-butyl-2-phenolate)amide ligand occupying two axial and one equatorial positions. For $4a$ the $P$-$O$ distances (1.688(1) and 1.681(1) Å) to the pincer ligand are similar to those observed for related distances in the $H_2O$ and $NH_3$ activation products, whereas for $5a$ these distances are moderately longer (approx. 0.02 Å), presumably due to the greater $\sigma$-donor ability of the benzyl functionality and greater degree of negative hyperconjugation.

Table 1. Comparison of interatomic distances [Å] for compounds 1a–3a and 1b–3b.

|       | 1a          | 2a          | 3a          | 1b          | 2b          | 3b          |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| Pn-N  | 1.757(1)    | 1.759(2)    | 1.749(2)    | 1.862(3)    | 1.891(1)    | 1.874(2)    |
| Pn-O  | 1.659(1)    | 1.830(1)    | 1.852(2)    | 1.933(4)    | 2.028(1)    | 1.995(2)    |
| Pn-Nu | N. A.       | 1.652(1)    | 1.764(2)    | 1.820(1)    | 1.924(2)    |             |

[a] N.A. = not applicable.
Scheme 2. Formation of 4a and 5a from the reaction of [K(2,2,2-crypt)][2a] with pyridinium trifluoromethane sulfonate and benzyl bromide, respectively (E = PyH, X = OTf; E = Bz, X = Br).

When 2b is reacted with an acid such as pyridinium trifluoromethanesulfonate the reaction affords HO\textsubscript{Bu} and 1b, and not the arsenic(V) compound (tBuO)HAs(ONO). Similarly, no reaction between 2b and BzBr takes place even upon heating. These observations illustrate the increased stability of the +3 oxidation state on descending Group 15, and demonstrate that accessing arsenic(V) complexes bearing the ONO\textsuperscript{3-} ligand is synthetically very challenging.

Reactivity of 1a and 1b towards electrophiles

The aforementioned results prompted us to explore the reactivity of 1a and 1b towards electrophilic substrates in an effort to establish whether they too associate with the heavier pnictogen atom centre, or whether they attack the more electro-negative atoms of the ligand backbone. The highest occupied molecular orbital (HOMO) for the pyramidal C\textsubscript{s} isomer of 1a has a significant contribution from the nitrogen atomic orbitals, while the computed Hirshfeld charges reveal significant polarisation of the P–N and P–O bonds, with negative charge accumulating equally over the three atoms of the ligand backbone.

In a typical reaction, one molar equivalent of EOTf (E = H, Me; OTf = trifluoromethanesulfonate) was added to a solution of either 1a or 1b. The reactions were monitored by NMR spectroscopy and reveal quantitative conversion to [Pn{ON(H)O}][OTf] (Pn = P(6a), As (7b)) after heating or sonicating the mixtures (see Experimental Section for full details). The \textsuperscript{31}P NMR spectra of the reactions involving 1a reveal broad resonances, with evidence of weak or non-existent P–H coupling, at 155.5 (\textit{J}_{P-H} = 12 \text{ Hz}) and 149.4 ppm for 6a and 7a, respectively (cf. 168.6 ppm for 1a), indicating that the electrophilic groups do not associate directly with the phosphorus(III) centre. The \textsuperscript{1}H NMR spectra of all four compounds are consistent with two equivalent aryloxide functionalities, which suggest functionalisation at the amide nitrogen atom. The \textsuperscript{1}H NMR resonances for the proton- and methyl-group-functionalised nitrogen atoms were observed at 14.27 and 3.72 ppm for 6a and 7a, respectively. Similarly, reactions involving 1b also reveal clean conversion to the products and the \textsuperscript{1}H NMR resonances of the electrophiles associated with the nitrogen atom were observed at 11.64 and 3.41 ppm for 6b and 7b, respectively.

The structures of all four novel cationic complexes were determined by single-crystal X-ray diffraction (Figures 6 and 7).
Figure 6. Molecular structures of [6a][OTf]·HOTf (left) and [6b][OTf] (right). Thermal ellipsoids pictured at 50% probability level; HOTf/OTf and hydrogen atoms, with the exception of those bonded to N1, omitted for clarity. There are two crystallographically independent molecules of 6b in the lattice, for clarity, only bond metric data for one of them is provided. Selected interatomic distances [Å] and angles [°]: 6a: P1–N1 1.926(2), P1–O1 1.615(2), P1–O2 1.619(2), N1–C6 1.478(3), N1–C20 1.470(3), N1–H1 0.85(3), O1–P1–O2 104.80(10), N1–P1–O1 90.16(8), N1–P1–O2 104.80(10), C6–N1–C20 112.46(17), C6–N1–H1 114(2), C6–N1–P1 105.39(14), C20–N1–H1 111(2), C20–N1–P1 105.20(13), H1–N1–P1 108(2). 6b: As1–N1 2.028(2), As1–O1 1.791(1), As1–O2 1.810(1), N1–C6 1.472(2), N1–C20 1.466(2), N1–H1 0.82(2), O1–As1–O2 98.55(5), N1–As1–O1 87.00(5), N1–As1–O2 85.69(5), C6–N1–C20 114.51(11), C6–N1–H1 109.3(13), C6–N1–As1 105.16(9), C20–N1–H1 111.3(14), C20–N1–As1 105.87(8), H1–N1–As1 110.5(14).

Figure 7. Molecular structures of [7a][OTf] (left) and [7b][OTf] (right). Thermal ellipsoids pictured at 50% probability level; OTf and hydrogen atoms, with the exception of those bonded to C29, omitted for clarity. Selected interatomic distances [Å] and angles [°]: 7a: P1–N1 1.955(2), P1–O1 1.626(2), P1–O2 1.626(2), N1–C6 1.480(2), N1–C20 1.482(2), N1–C29 1.504(2), O1–P1–O2 104.00(7), N1–P1–O1 89.14(6), N1–P1–O2 90.38(6), C6–N1–C20 114.11(12), C6–N1–C29 113.51(12), C6–N1–P1 103.58(9), C20–N1–C29 111.78(12), C20–N1–P1 104.17(9), C29–N1–P1 111.71(10). 7b: As1–N1 2.127(1), As1–O1 1.790(1), As1–O2 1.788(1), N1–C6 1.469(2), N1–C20 1.468(2), N1–C29 1.496(2), O1–As1–O2 100.35(4), N1–As1–O1 85.00(4), N1–As1–O2 83.73(4), C6–N1–C20 112.64(9), C6–N1–C29 111.29(9), C6–N1–As1 104.58(7), C20–N1–C29 114.20(9), C20–N1–As1 103.43(7), C29–N1–As1 109.94(7).
The cationic moieties crystallise alongside a trifluoromethane sulfonate anion, and, in the case of 6a an additional molecule of HOTf. The most striking aspect of the structures is that protonation/methylation has taken place at the nitrogen centre, as evidenced by NMR spectroscopy. All four complexes adopt a distorted tetrahedral geometry around the nitrogen atom and exhibit a significant elongation of the N-Pn bonds (N–P: 1.926(2) and 1.955(2) Å for 6a and 7a, respectively; N–As: 2.028(2) and 2.127(1) Å for 6b and 7b, respectively) relative to 1a (1.757(1) Å) and 1b (1.863(2) Å). The Pn–O bonds experience a moderate contraction on protonation/methylation in the case of the phosphorus containing compounds (0.03 Å), but a much more dramatic contraction (0.13 Å) for the arsenic analogues, which is linked to a change from the planar geometry of 1b to the bent (C2) geometry of both 6b and 7b. This geometric change allows for the aryloxide substituents to get closer to the arsenic centre as the pseudo-axial arrangement of the oxygen atoms in the 10-Pn-3 structure of 1b is lost on functionalisation of the ligand backbone.

Interestingly, all four species exhibit close contacts de inferred from the close proximity distances between the pnictogen(III) centre and trifuoromethanesulfonate anions (6a: 2.790(2) and 2.898(1) Å, 6b: 2.745(2) Å, 7a: 2.760(2) Å, 7b: 2.226(1) Å) indicating a significant degree of positive charge accumulating on the pnictogen centres on functionalisation of the ligand backbone. This is corroborated by DFT calculations which show a large Hirshfeld charges on the pnictogen atoms relative to nitrogen (6a: 0.455 and –0.012, 6b: 0.598 and –0.024, 7a: 0.446 and 0.015, 7b: 0.586 and 0.004, for the heavier pnictogen and nitrogen atoms, respectively). Thus, all four complexes can be thought of as base-stabilised phosphonium or arsenium ions. This bonding formulation has thus previously been proposed for related phosphorus-containing compounds.[32–34]

It is interesting to note that while 1a reacts with HOTf to afford a phosphorus(III) compound with a protonated ligand backbone (6a), the analogous reaction with an acid that has a more nucleophilic counter-ion, such as HCl, affords the phosphorus(V) species HPCI(ONO) (8a). This difference in reactivity suggests that mechanistically, a sufficiently strong nucleophile is required to afford the formal phosphorus(V) oxidative addition product. Reaction of 6a with KOrBu, affords 4a, suggesting that nucleophilic association of the anionic [OtBu moity with the phosphorus centre induces proton migration from the ligand backbone. Similarly, reaction of 6a with tetra-dodecylammonium chloride cleanly affords 8a and the corresponding ammonium trifluoromethane sulfonate salt. Conversely, reactions of 8a with one equivalent of trimethylsilyl trifluoromethane sulfonate show evidence for the formation of 6a, although full conversion was not observed at room temperature with such stoichiometric loadings.

In the aforementioned studies we have established the relative inaccessibility of the arsenic(V) oxidation state for 1b. This is borne out in the reactivity of 1b towards HCl. Whereas 1a reacts with HCl to afford 8a, the reaction of 1b with one molar equivalent of HCl results in the addition of the acid across one of the As–O bonds resulting in the arsenic(III) compound AsCl(H)(ONO) (8b). This was evident from the 1H NMR spectra of these reaction mixtures which reveal the presence of two inequivalent arms of N,N-bis(3,5-di-tert-butyl-2-phenolate)amide pincer ligand on protonation.

The structures of 8a and 8b were both determined by single-crystal X-ray diffraction (Figure 8). While 8a exhibits a distorted trigonal bipyramidal structure consistent with all of the phosphorus(V) complexes we have studied to date, the structure of 8b clearly shows a trigonal pyramidal arsenic(III) centre in which one of the tert-butyl-2-phenolate ligand arms has been protonated and is consequently no longer coordinated to the arsenic centre. The bond metric data for 8a are similar to the other phosphorus(V) compounds reported. The P–O bond lengths to the N,N-bis(3,5-di-tert-butyl-2-phenolate)amide ligand, 1.661(4) and 1.653(4) Å, are slightly shorter than those observed for the aforementioned phosphorus(V) compounds (4a: 1.688(1) and 1.681(1); 5a: 1.721(1) and 1.732(1) Å). The same is also true of the P–N interatomic distance which is 1.699(5) Å in 8a, and 1.720(1) and 1.717(1) Å in 4a and 5a, respectively. The P–Cl bond length is 1.918(2) Å.

The structure of 8b reveals a trigonal pyramidal geometry about the arsenic(III) centre (Σangles[A]=284.8°; Σangles[N]=355.6°) with a relatively obtuse N1-As1-C11 angle due to the steric repulsion of the chloride with the free arm of the N,N-bis(3,5-di-tert-butyl-2-phenolate)amide ligand. The As–N and As–O distances, 1.839(2) and 1.783(2) Å, respectively, are notably shorter than those observed for 1b (As–N: 1.863(2) and As–O: 1.933(4) Å), presumably due to the relaxation of steric strain and the loss of As–N multiple bond character on bending the ligand backbone. It is worth noting that the As–N bond in 8b is still very short and indicative of some multiple bond character.

As mentioned previously, reactions of 6a with KOrBu result in the association of the tert-butoxide anion with the phosphorus(III) centre and migration of the ligand proton to afford the phosphorus(V) product 4a (which can also be accessed by a formal oxidative addition of HOTBu to 1a). The facility with which the proton of the ligand backbone migrates prompted us to carry out related studies with the methylated species 7a and 7b. We hypothesised that methyl migration would not occur and that, consequently novel complexes in which both the nitrogen atom of the N,N-bis(3,5-di-tert-butyl-2-phenolate)amide ligand, and the heavier pnictogen centers could be functionalised. In a typical reaction, 7a or 7b were treated with one molar equivalent of potassium tert-butoxide. These reactions were found to quantitatively afford novel complexes bearing a symmetrical ligand environment and an additional tert-butoxide functionality (as pictured in Scheme 3). Reactions involving 7a reveal an upfield shift in resonance in the 31P NMR spectra from 149.4 to 142.8 ppm. The association of the [OtBu moiety with the phosphorus centre is evident from the appearance of a broad resonance in the 1H NMR spectrum at 1.57 ppm. This resonance is accompanied by two aromatic resonances (7.40 and 7.31 ppm), two resonances arising from the ligand tert-butoxide groups and a doublet due to the methyl group of the ligand backbone. Comparable spectroscopic data were recorded for the arsenic-containing analogue, 9b, although this
sample could not be isolated as a compositionally pure compound due to its relative instability and tendency to decompose.

Compound 9a was characterised by single-crystal X-ray crystallography (Figure 9) and reveals that the nucleophilic O\textsuperscript{tBu} moiety has associated with the phosphorus atom. Both the nitrogen and phosphorus centres exhibit distorted trigonal pyramidal geometries ($\Sigma_{\text{angles}(P)} = 285.2^\circ$; $\Sigma_{\text{angles}(N)} = 345.7^\circ$). That being said, the sum of bond angles around the nitrogen atom is strongly indicative of increased planarity, which we believe to arise due to the lone-pair–lone-pair repulsion arising between the nitrogen and phosphorus centres. The amine and phosphine like character of these centres is evident in the long P–N interatomic distance, 2.573(2) Å, which is notably longer than that observed for 6a and 7a, 1.926(2) and 1.955(2) Å, respectively, and is clearly indicative of the lack of a bonding interaction between the phosphorus and nitrogen centres. The P–O bonds range from 1.627(1) to 1.665(1) Å and are consistent with bond lengths reported for other phosphites.$^{30}$ The N–C bond lengths to the aryl functionalities of the ligand backbone are comparable in magnitude (1.429(2) and 1.440(2) Å) and slightly shorter than that to the methyl functionality 1.464(2) Å, consistent with the reduced covalent radius of a formally $sp^3$-hybridised carbon atom compared to an $sp^3$-hybridised species $\Delta r = (0.03$ Å$)^{29}$.
Conclusion

We have explored the reactivity of the geometrically constrainted Group 15 complexes P(ONO) (1a) and As(ONO) (1b) towards ionic nucleophiles and electrophiles. These studies show that anionic nucleophiles readily associate with the pnictogen(III) centres in both complexes, suggesting that such an association may play an important role in the mechanism for the bond activation of NH₃ and H₂O by 1a. Our studies also reveal that while phosphorus(V) compounds are readily accessible by sequential reactions involving 1a, the corresponding arsenic(V) compounds cannot be synthesised from the heavier analogue 1b.

Reactions involving charged electrophilic substrates give rise to pnictogen(III) compounds in which the electrophile associates with the nitrogen atom of the ligand backbone. Interestingly, when the electrophile in question is a proton, it will associate with the nitrogen atom of the ligand backbone only in the presence of a weakly coordinating counteranion (such as OTf⁻). When a more nucleophilic counter-anion is employed (such as Cl⁻) these reactions result in the generation of a phosphorus(V) compound by proton migration from the ligand backbone to the phosphorus centre. As with previous studies, the analogous arsenic(V) compound was found to be inaccessible.

These studies have helped us probe possible pathways by which 1a is able to activate nucleophilic substrates with polarised E–H bonds. Studies are currently on-going with regard to elucidating a mechanism for such formal oxidative addition reactions.

Experimental Section

General procedures: All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNilab glovebox maintained at < 0.1 ppm H₂O and < 0.1 ppm O₂). ¹H, ³¹P, ¹³C, ¹⁹F NMR spectra were recorded at room temperature using a Bruker AvIII 500 MHz or Bruker AvIII HD NanoBay 400 MHz NMR Spectrometer. ¹H and ¹³C(¹H) spectra are reported relative to tetramethylsilane (TMS) and were referenced to the most downfield residual solvent resonance (¹H NMR spectroscopy: 7.26 ppm (CDCl₃), 7.16 ppm ([D₆]DMSO), 5.32 ppm (CD₂Cl₂) and 3.58 ppm ([D₆]THF); ¹³C(¹H) NMR spectroscopy: 77.16 ppm (CDCl₃), 128.06 ppm ([D₆]DMSO), 53.84 ppm (CD₂Cl₂) and 67.21 ppm ([D₆]THF)). ¹³P NMR chemical shifts were externally referenced to 85.5% solution of H₃PO₄ (aq).

¹¹F NMR chemical shifts were externally referenced to CF₂COOH. Elemental analyses were performed by Elemental analysis Ltd (Devon). EI/Cl mass spectra were obtained on neat samples using a Waters GCT Time of Flight Mass Spectrometer with a temperature programmed solids probe inlet, or an Agilent 7200 Accurate-Mass Q-TOF GCMS with a SIM Direct Inlet probe. ESI mass spectra were obtained from DMF solutions using a Waters LCT time-of-flight mass spectrometer with a Z-spray source (150 °C source temperature, 200 °C desolvation temperature, 2.4 KV capillary voltage and 25 V cone voltage).

Solvents and reagents: Hexane (Sigma–Aldrich, ≥ 97.0%), pentane (Sigma–Aldrich, ≥ 99.0%) and toluene (Sigma–Aldrich, 99.9%) were dried using an MBraun SPS-800 solvent system, THF (Sigma–Aldrich, ≥ 99.9%) was dried over a potassium metal/benzophenone mixture and pyridine was distilled from CaH₂. Cd₁₃ (Aldrich, 99.6%) was dried and stored over activated 3 Å molecular sieves. CdCl₂ (Aldrich, 99.8%), CD₂Cl₂ (Euriso-top, 99.90%) and [D₆]THF (Euriso-top, 99.50%) were each dried over CaH₂, and stored over activated 3 Å molecular sieves. H₂ON and KNPh were synthesised according to a previously reported synthetic procedure.[36,37] 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6, Alfa Aesar, 99.9%) was purified by sublimation and NEt₃ (Sigma–Aldrich, 99.5%) was distilled from CaH₂ prior to use. AsCl₃ (Sigma–Aldrich, 99.99%), KOtBu (Aldrich, ≥ 98%), 4,7,13,16,21,24-hexaoxa-1,10-diazacyclooctadecane (Sigma–Aldrich, 99.99%), [D₆]OTf (Alfa Aesar, 98%), HBr (Sigma–Aldrich, 98%), MeOTf (Apollo, 98%), benzyl bromide (Aldrich, 98%) and HCl (Alfa Aesar, 2 M in EtO) were used as received.

Synthesis of As(ONO) (1b): H₂O (1.00 g, 23.5 mmol) was dissolved in toluene (10 mL). AsCl₃ (198 mL, 2.35 mmol) was added to the stirred solution followed by NEt₃ (1.00 mL, 7.17 mmol), yielding a dark orange solution and white precipitate. The mixture was stirred at room temperature for 3 h. All volatiles were removed under a dynamic vacuum and the product was extracted in pentane (3×10 mL). Removal of volatiles in vacuo yielded 1b as a dark orange solid. Crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated pentane solution at 30 °C. Yield: 880 mg (75%); elemental analysis calcd (%) for Cd₃H₆As(NO₃)₂: C 67.59, H 8.10, N 2.82; found: C 67.15, H 8.09, N 2.93; EI MS: m/z calculated for Cd₃H₆As(NO₃)₂: 497.2275; found: 497.2272; m/z calculated for Cd₅H₁₃As(NO₃)₂: 482.2040; found: 482.1898. ¹H NMR (499.93 MHz, [D₆]DMSO, 298 K): δ = 8.39 ppm (s, 2H; Ar), 7.51 ppm (s, 2H; Ar); 7.11 ppm (s, 18H; tBu), 1.46 ppm (s, 18H; tBu). ¹³C(¹H) NMR (125.72 MHz, [D₆]DMSO, 298 K): δ = 154.0 (Ar), 142.3 (Ar), 137.2 (Ar), 135.9 (Ar), 119.9 (Ar), 111.3 (Ar), 35.7 ([C(CH₃)₃], 35.1 ([C(CH₃)₂] and 30.0 ppm ([C(CH₃)]).

Synthesis of [K(18-crown-6)][(tBuO)P(ONO)] ([K(18-crown-6)] [2a]): Compound 1a (300 mg, 0.661 mmol), KOtBu (74.2 mg, 0.661 mmol) and 18-crown-6 (175 mg, 0.663 mmol) were dissolved in THF (10 mL) at room temperature to give a pale yellow solution. After stirring for 30 min, the solution was filtered through a cannula and all volatiles were removed in vacuo. The residue was washed with toluene (3×5 mL) and the product was dried under a dynamic vacuum. Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a THF solution of the product at room temperature. Yield: 296 mg (54%); elemental analysis calcd (%) for Cd₃H₆As(NO₃)₂: C 67.39, H 8.96, N 1.62; found: C 64.06, H 9.34, N 1.64. ESI MS (−ve mode, DMF): m/z calculated for Cd₃H₆As(NO₃)₂: 526.35; found: 527.01. ¹H NMR (400.17 MHz, [D₆]DMSO, 298 K): δ = 7.39 ppm (d, 4J = 2 Hz, 2H; Ar); 6.57 ppm (d, 4J = 2 Hz, 2H; Ar); 3.40 ppm (s, 24H; 18-crown-6), 1.43 ppm (s, 18H; tBu), 1.34 ppm (s, 9H; tBuO), 1.32 ppm (s, 18H; tBu). ¹³C(¹H) NMR (100.62 MHz, [D₆]DMSO, 298 K): δ = 151.8 (d, 4J = 5 Hz; Ar), 134.5 (d, 4J = 4 Hz; Ar), 134.0 (Ar), 129.4 (d, 4J = 5 Hz; Ar), 121.1 (Ar), 107.0 (d, 4J = 3 Hz; Ar), 72.1 (d, 4J = 11 Hz; OC(CH₃)₃), 70.8 (18-crown-6), 35.0 ([C(CH₃)₃], 34.9 ([C(CH₃)₂] and 30.1 ppm ([C(CH₃)]).

Synthesis of [K(18-crown-6)][(tBuO)As(ONO)] ([K(18-crown-6)] [2b]): Compound 1b (234 mg, 0.470 mmol), KOtBu (52.7 mg, 0.470 mmol) and 18-crown-6 (124 mg, 0.469 mmol) were dissolved in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 30 min after which the solvent was removed under vacuum. The product was crystallised as white solid from hexane. The solution was filtered and the white solid dried in vacuo. Crystals suitable for X-ray diffraction studies were grown by
slow diffusion of hexane into a THF solution of the product at room temperature. Yield: 355 mg (86%); elemental analysis calc'd (%) for C₆H₆AsNO₃: C 60.42, H 8.42, N 1.60; found: C 60.52, H 8.54, N 1.44. ESI MS (+ve mode, DMF): m/z calcd for C₆H₆AsNO₃ [M⁺]: 357.29; found: 356.24; m/z calcd C₆H₆AsNO₃ 513.22; found: 513.61.

'H NMR (400.17 MHz, D₂ [THF, 298 K]): δ = 7.54 (d, Jₚₓ₋ₚₓ = 2 Hz, 2H; Ar), 6.56 (d, Jₚₓ₋ₚₓ = 2 Hz, 2H; Ar), 3.38 (s, 24H; 18-crown-6), 1.44 (s, 18H; tBu), 1.33 (s, 18H; tBu), 1.26 ppm (s, 9H; tBu).

Synthesis of [K(18-crown-6)][(Ph₃P)ONOP(5)] ([K(18-crown-6)][3a]): A preparative synthesis of [K(18-crown-6)][3a] was not possible due to extremely high sensitivity of the product, which upon manipulation readily decomposes to [(Ph₃P)ONOP(5)]. However, evidence for the formation of 3a can be observed by NMR tube scale reactions. In a typical reaction, 1a (20.0 mg, 0.0440 mmol), KNPH₃THF₅₁₅₁ (9.6 mg, 0.0441 mmol) and 18-crown-6 (11.6 mg, 0.0439 mmol) were added to an NMR tube equipped with a J. Young airtight tap and the mixture dissolved in D₂ [THF] to give a pale yellow solution. 'H NMR (400.20 MHz, D₂ [THF, 298 K]): δ = 7.07 (d, Jₚₓ₋ₚₓ = 2 Hz, 2H; Ar), 6.90–6.85 (m, 4H; NPh), 6.79–6.73 (m, 3H; NPh), 6.52–6.47 (m, 2H; NPh), 6.51 (d, Jₓ₋ₓ = 2 Hz, 2H; Ar), 3.49 (s, 24H; 18-crown-6), 1.28 (s, 18H; tBu), 1.26 ppm (s, 18H; tBu); [13C]NMR (100.63 MHz, D₂ [THF, 298 K]): δ = 151.2 (d, Jₓ₋ₓ = 5 Hz; Ar), 149.4 (d, Jₓ₋ₓ = 8 Hz; NPh), 135.0 (Ar), 134.8 (d, Jₓ₋ₓ = 3 Hz; Ar), 129.8 (d, Jₓ₋ₓ = 5 Hz; Ar), 127.6 (s), 125.5 (brs; NPh), 120.0 (brs; NPh), 112.4 (Ar), 106.7 (d, Jₓ₋ₓ = 4 Hz; Ar), 70.8 (s; 18-crown-6), 34.9 (C(CH₃)₃), 24.8 (C(CH₃)₂), 32.5 (C(CH₃)₂), 30.2 ppm (C(CH₃)₂); [31P]NMR (162.00 MHz, D₂ [THF, 298 K]): δ = 66.3 ppm (s); [31P]H NMR (162.00 MHz, D₂ [THF, 298 K]): δ = 66.3 ppm (s).

Synthesis of [K(2,2,2-crypt)][(Ph₃P)ONOP(3)] ([K(2,2,2-crypt)][3b]): Compound 1b (160 mg, 0.322 mmol), KNPH₃THF₅₁₅₁ (70.1 mg, 0.322 mmol) and 2,2,2-crypt (121 mg, 0.322 mmol) were dissolved in THF (10 mL) resulting in a yellow solution. The mixture was stirred at room temperature for 15 min after which the solution was concentrated to 0.5 mL in vacuo. Crystals of the product were obtained by slow diffusion of hexane into the THF solution and were isolated by filtration. Yield: 245 mg (71%); elemental analysis calc'd (%) for C₇₅H₆₁AsNO₃: C 64.42, H 8.02, N 5.18; found: C 63.48, H 7.84, N 5.23. ESI MS (+ve mode, DMF): m/z calcd for C₇₅H₆₁AsNO₃ [(H[NiAs]ONOP(3)⁺): 513.24; found: 513.97; [13C]NMR (400.17 MHz, D₂ [THF, 298 K]): δ = 7.07 (d, Jₚₓ₋ₚₓ = 2 Hz, 2H; Ar), 6.90–6.85 (m, 4H; NPh, 6.79–6.73 (m, 3H; NPh), 6.52–6.47 (m, 2H; NPh), 6.51 (d, Jₓ₋ₓ = 2 Hz, 2H; Ar), 3.49 (s, 24H; 18-crown-6), 1.28 (s, 18H; tBu), 1.26 ppm (s, 18H; tBu); [31C]NMR (100.63 MHz, D₂ [THF, 298 K]): δ = 151.2 (d, Jₓ₋ₓ = 5 Hz; Ar), 149.4 (d, Jₓ₋ₓ = 8 Hz; NPh), 135.0 (Ar), 134.8 (d, Jₓ₋ₓ = 3 Hz; Ar), 129.8 (d, Jₓ₋ₓ = 5 Hz; Ar), 127.6 (s), 125.5 (brs; NPh), 120.0 (brs; NPh), 112.4 (Ar), 106.7 (d, Jₓ₋ₓ = 4 Hz; Ar), 70.8 (s; 18-crown-6), 34.9 (C(CH₃)₃), 24.8 (C(CH₃)₂), 32.5 (C(CH₃)₂), 30.2 ppm (C(CH₃)₂); [31P]NMR (162.00 MHz, D₂ [THF, 298 K]): δ = 66.3 ppm (s); [31P]H NMR (162.00 MHz, D₂ [THF, 298 K]): δ = 66.3 ppm (s).
0.217 mmol) was added, resulting in a pale pink solution and the formation of a white precipitate. The mixture was stirred at room temperature for 15 min after which the solid was isolated by filtration. Yield: 64 mg (46%); elemental analysis calc (%) for C$_{35}$H$_4$AsF$_5$NO$_3$: C 53.78, H 6.38, N 2.16; found: C 54.33, H 6.80, N 2.21. CI MS (CH$_4$ carrier gas): m/z calcd for C$_{35}$H$_4$AsF$_5$NO$_3$: 498.2353; found: 498.2426; m/z calcd C$_{35}$H$_4$AsF$_5$NO$_3$: 482.2027; found: 482.2133; $^1$H NMR (400.17 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 11.64 (br, 1H, NH), 7.84 (d, $J_{NH}$ = 2 Hz, 2H; Ar), 7.25 (d, $J_{NH}$ = 2 Hz, 2H; Ar), 1.36 (s, 18H; Bu); $^{13}$C[H] NMR (100.62 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 151.8 (Ar), 145.5 (Ar), 137.9 (Ar), 131.3 (Ar), 124.5 (Ar), 117.7 (Ar), 35.2 (C(CH$_3$)$_3$) 34.9 (C(CH$_3$)$_3$), 31.4 (C(CH$_3$)$_3$), 29.3 ppm (C(CH$_3$)$_3$); $^{19}$F[H] NMR (376.54 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -78.3 ppm.

Synthesis of [PON(Me)][OTf] (7a)[OTf]: Compound 1a (100 mg, 0.220 mmol) was dissolved in toluene (5 mL) and MeOTf (24.9 $\mu$L, 0.220 mmol) was added. The solution was heated at 70°C for 24 h resulting in the growth of colourless needle-shaped crystals. The supernatant was removed by cannula filtration and the crystals washed with toluene (3 x 5 mL) and dried in vacuo. Yield: 85 mg (60%); elemental analysis calc (%) for C$_{35}$H$_4$F$_5$NO$_3$: C 58.33, H 7.02, N 2.27; found: C 58.50, H 7.10, N 2.35; CI MS (NH$_4$ carrier gas): m/z calcd C$_{35}$H$_4$F$_5$NO$_3$: 468.3375; found: 468.3151; $^1$H NMR (499.93 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 7.60 (brs, 2H; Ar), 7.39 (d, $J_{NH}$ = 2 Hz, 7H; Ar), 7.13 (s, 18H; Bu), 1.33 ppm (s, 18H; Bu); $^{13}$P[H] NMR (99.93 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -3.72 ppm (s, 3H; NCH$_3$) all other resonances as above; $^{13}$C[H] NMR (125.71 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 149.3 (Ar), 147.0 (d, $J_{CH} = 12$ Hz; Ar), 139.2 (Ar), 134.0 (d, $J_{CH} = 3$ Hz; Ar), 126.2 (Ar), 114.8 (Ar), 47.6 (d, $J_{CH} = 26$ Hz, NCH$_3$), 35.6 (C(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$), 29.4 ppm (C(CH$_3$)$_3$); $^{19}$F[N] NMR (161.99 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 149.4 ppm (brs); $^{13}$P[N] NMR (161.99 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 149.4 ppm (brs); $^{13}$F[N] NMR (376.54 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -78.7 ppm.

Synthesis of [AsO(Me)][OTf] (7b)[OTf]: Compound 1b (705 mg, 1.417 mmol) was dissolved in toluene (15 mL) and MeOTf (160 $\mu$L, 1.457 mmol) was added to the solution, which was stirred at 80°C for 3 days, resulting in the precipitation of a white/pink solid. The solid was isolated by filtration and dried in vacuo. Yield: 733 mg (78%); elemental analysis calc (%) for C$_{35}$H$_4$F$_5$NO$_3$: C 54.46, H 6.63, N 2.12; found: C 54.40, H 6.48, N 2.08; $^1$H NMR (466.2030; found: 466.2202; m/z calcd for C$_{35}$H$_4$AsF$_5$NO$_3$: 512.2528; found: 512.2520; $^1$H NMR (400.17 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 7.31 (d, $J_{CH} = 2$ Hz, 2H; Ar), 7.28 (d, $J_{NH} = 2$ Hz, 2H; Ar), 3.41 (s, 3H; NCH$_3$), 1.40 (s, 18H; Bu), 1.31 ppm (s, 18H; Bu); $^{13}$C[H] NMR (100.62 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 149.4 (Ar), 145.6 (Ar), 139.7 (Ar), 135.0 (Ar), 124.5 (Ar), 114.8 (Ar), 46.2 (NCH$_3$), 35.5 (C(CH$_3$)$_3$), 34.9 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_3$), 29.4 ppm (C(CH$_3$)$_3$); $^{19}$F[N] NMR (376.54 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -77.9 ppm (brs).

Synthesis of HPCl(O)NO (8a): Compound 1a (200 mg, 0.441 mmol) was dissolved in Et$_2$O (5 mL) and HCl (220 $\mu$L, 2.27 mmol) was added. The colourless solution was stirred for 30 min after which all volatiles were removed in vacuo. The colourless solid was extracted into hot hexane (3 mL) and the solution filtered. Colourless crystals of 8a grew upon standing at room temperature, which were isolated by filtration. A further crop could be isolated by concentrating the mother liquor solution. Yield: 139 mg (64%); elemental analysis calc (%) for C$_{35}$H$_4$Cl$_5$NClO$_5$: C 68.63, H 8.43, N 2.86; found: C 68.86, H 8.49, N 2.92; $^1$H NMR (400.20 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 8.97 (d, $J_{CH} = 967$ Hz, 1H; Ph), 7.66 (s, 2H; Ar), 7.11 (d, $J_{NH} = 2$ Hz, 2H; Ar), 1.45 (s, 18H; Bu); 1.41 ppm (s, 18H; Bu); $^{13}$P[H] NMR (400.20 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 8.97 ppm (s, 1H; Ph), all other resonances as above; $^{13}$C[H] NMR (100.63 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = 144.2 (Ar), 139.4 (d, $J_{CH} = 9$ Hz; Ar), 133.9 (d, $J_{CH} = 6$ Hz; Ar), 124.6 (d, $J_{CH} = 24$ Hz; Ar), 116.6 (Ar), 1064 (d, $J_{CH} = 17$ Hz; Ar), 34.6 (C(CH$_3$)$_3$), 34.1 (C(CH$_3$)$_3$), 31.1 (C(CH$_3$)$_3$), 29.0 ppm (C(CH$_3$)$_3$); $^{1}$H NMR (261.99 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -31.3 ppm (d, $J_{NH} = 967$ Hz); $^{1}$P[H] NMR (161.99 MHz, CD$_2$Cl$_2$; 298 K): $\delta$ = -31.3 ppm (s).
X-ray diffraction: Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N2 cooling device.[43] Data were collected at 150 K using mirror monochromated Cu Kr radiation (\(\lambda = 1.5418\) Å; Oxford Diffraction Supernova). Data were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[44] Structures were subsequently solved using direct methods or using the charge flipping algorithm as implemented in the program SUPERFLIP[45] and refined on \(F^2\) using the SHELXL 2013-4 package.[46]

The Grimme3 empirical dispersion correction was applied to all calculations.[47] A single polarisation functions, was used to describe all phosphorus, arsenic, nitrogen and oxygen atoms while a DZ basis set was used for all remaining atoms. Geometry optimisations were performed using the Becke88 exchange functional with Perdew86 local correlation functional.[48,49] The Grimme3 empirical dispersion correction was applied to all calculations.[41] All structures were optimised using the gradient algorithm of Versluis and Ziegler.[50]

CCDC 1489274 (1b), 1489275 ([(K2,2-2,2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-
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Received: June 30, 2016
Published online on September 15, 2016