Reactivity studies of an imine-functionalised phosphaalkene; unusual electrostatic and supramolecular stabilisation of a $\sigma^{2}\lambda^{3}$-phosphorus motif via hydrogen bonding†

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A P–C heavy-alkene analogue that is unreactive towards the addition of strong acids on its double-bond is presented; instead, a strategically located imine nitrogen on the periphery forms protonated adducts displaying hydrogen bonding interactions. These materials are significantly more stable than the parent species, demonstrating an unprecedented approach towards the stabilisation of a multiple-bonded heavy main group fragment, in this case, a phosphaalkene. An HCl adduct self-assembles with H$_2$O into a dimeric network displaying a discrete quadrilateral hydrogen-bonded arrangement.

The study of molecular systems incorporating multiple-bonded heavy p-block elements has challenged chemists for decades. The high reactivity exhibited by heavy multiple bonds (E=P, As; E: third to sixth-row element from group 13) renders these species increasingly interesting at the fundamental and applied level.1

Early on, breaking of the double-bond rule with reports on the synthesis of stable species containing P=–C, P=–N, Si=–C, Si=–Si, As=–C, and other multiple bonds, were accompanied by studies with small molecules (e.g. HCl, H$_2$O, O$_2$, Br$_2$, MeOH, Mel) to confirm the sensitivity and reactivity of the multiple bonds.2 For example, the addition of HX (X: Hal) to P=–C compounds (Scheme 1) is an archetypical example showcasing their increased reactivity. For other species, similar pathways (hydrolysis, oxidation, addition) lead to decomposition products in most reactions with small molecules.3 In sporadic cases, a multiple-bonded fragment is kept upon reaction with small molecules via rearrangement,4 substitution/addition reactions,5 or due to increased stability of the unusual bonding by other means (e.g. aromaticity in phosphinine).6 For example, dicoordinate phosphorus species display increased stability to small molecules in some examples, which is expressed in the ability to avoid protonation or alkylation.5,7

The initially suggested instability of these species led to a naturally apparent dichotomy in which efforts have focused on either the stabilisation and isolation of the exotic motif as final materials (e.g. polymer chemistry and materials science), or their utilisation as highly-reactive synthons that can act as intermediates in driving unique chemical transformations (e.g. small-molecule activation,10 unique reactivity,11 catalysis,12 polymer-precursors,13 high-spin materials14). Regarding the former direction, finding ways to stabilise systems featuring multiple bonding to heavier elements are among the crucial goals in the modern main group community; increased stability to small molecules should broaden the scope of applying these fascinating materials in catalysis and optoelectronic materials.

In here, we explore the reactions of the imine containing phosphaalkene (1)15 with a variety of strong acids (Scheme 2). Despite being a sensitive compound under atmospheric conditions, when 1 reacts with hydrogen chloride (HCl), trifluoromethanesulfonic acid (HTF$_3$), and hexafluorophosphoric acid (H$_3$PO$_4$) under inert conditions, the P=–C bond remains unchanged. The resulting protonated derivatives are significantly stabilised in comparison to 1 as demonstrated by simple decomposition experiments followed via $^{31}$P-NMR spectroscopy. Remarkably, reacting 1 and HCl with subsequent...
exposure to the atmosphere, leads to a hydrogen-bonded dimer (2-H$_2$O) as verified by X-ray diffraction, FTIR, NMR and elemental analysis, offering an example of a multiple bonded heavier main group compound (RP$^{+}$=CR$_2$) involved in supramolecular chemistry via hydrogen bonding (i.e. HB) interactions.$^{16}$ The reaction of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) with Mes*PCI$_2$ (Mes* = 2,4,6-tri-tert-butylphenyl) leads to phosphaalkene 1, previously reported based on spectroscopic data.$^{17}$ Despite potential stabilisation of 1 via π-conjugation and charge delocalisation, (Fig. S1†), the P=C bond is highly air/moisture sensitive, and decomposition products are spectroscopically visible after a few minutes of exposure to atmospheric conditions (Fig. S2†).

After several attempts, single-crystals of 1 were obtained by diffusion of hexanes into dichloromethane (DCM) under inert conditions (Fig. 1). The crystal structure of 1 displays bond lengths reflecting P1=C3, N1=C2 double bonds and N2=C2, C2–C3 single bonds, the latter is somewhat long for two singly bonded C$_{sp2}$ centres (1.494(4) Å), thus the bicyclic torsional strain frustrates the possibility to achieve electronic delocalization across the P=C to N=N=C-N pathway. The P=C bond length (1.676(3) Å) and low-field $^{31}$P-NMR ($\delta$ = 254 ppm) indicate 1 is a "classically polarised" phosphaalkene (P$^2$C$^=\!$) with a proximal, but non-conjugated imine functionality. The π-accepting nature of the sp$^2$ hybridised P and N atoms as well as their proximity renders 1 interesting as an ancillary ligand as reported for other systems (vide infra). The reactivity of 1 with anhydrous HCl was tested, and a downfield shift of ~60 ppm in the $^{31}$P-NMR spectrum was observed (Fig. S2†); such perturbation is not related to bond length changes (vide infra) on the environment around the phosphorus. We were unable to obtain single crystals of 2 under inert conditions, but only when left crystallising under ambient conditions, resulting in the hydrated form 2-H$_2$O (Fig. 2A). Structural analysis of 2-H$_2$O shows the formation of a dimeric hydrochloride hydrate salt, which self-assembled from 2 + H$_2$O. The crystallisation was attempted twice again with slight variations of the conditions, and yet, the same crystal structure was obtained, which indicated the motif is energetically preferential. The reproducibility is interesting from a crystal-engineering perspective where the desire for the rational design of systems leading to discrete structures prevails.$^{19}$ The molecular structure of 2-H$_2$O was solved in the monoclinic space group C2/c. Heavy atoms were refined anisotropically, and hydrogen atoms were placed at geometric positions with fixed C–H distances, except for the N–H and water hydrogen atoms, which were located on the electron difference map. The asymmetric unit consists of the cationic fragment [1 + H]$^+$, as well as a hydrogen bonded chloride anion and a water molecule.

As a hydrogen-bond network, (Fig. 2A & S3†) the quadrilateral centred ring (~0.11 nm$^2$) with the two peripheral iminium hydrogen donors is leading to a significant stabilisation as rationalised by the repeated crystallisations. A search on the Cambridge Structural Database (CSD) of the Cl···(H$_2$O)$_2$···Cl arrangement without constraints, yielded 1512 hits; restricting the search to the isolated dimeric motif observed in 2-H$_2$O (a ring; with two chloride anions as HBA from three donors each, and two H$_2$O molecules as doubly HBD each) gave no results. A few isostructural arrangements, but with slightly different hydrogen bond coordination numbers on the HB network exist (see Fig. S3†). The discrete nature of the central HB motif in 2-H$_2$O epitomises the small-limit of such water/chloride hydrogen-bonded cluster, in this case, embedded in a hydrophobic environment.$^{21}$ Regardless of the interpretation, the study of hydrate and chloride containing rings and other topological arrangements is fundamentally important due to the ubiqui-

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2** Simplified synthetic procedures: (A) 1; THF, –78 °C. (B) 2; (i) anhydrous HCl (2 M, THF), THF, –78 °C. (C) 6; (ii) [Pd(MeCN)$_2$Cl$_2$], DCM, rt. (D) 3; (iii) CF$_3$SO$_3$H (neat), THF, –78 °C. (E) 4; (iv) HPF$_6$ (60% aq.), MS (3 Å), THF, –78 °C. (Fig. S1)
and other weak electrostatic interactions such as London dispersion may assist in stabilising HB interactions (Fig. S5†). Solution NMR experiments were performed (pages S18–S22†) to demonstrate the prevalence of HB in 2 and $2 + \text{H}_2\text{O}$ (not exclusively of the dimer). For example, titration of 2 (Fig. 2B) with a stoichiometric amount of deoxygenated water, resulted in downfield shifts of the N–H and H$_2$O signals strongly suggesting that a hydrogen bonded equilibrium is cooperatively established. Additional experiments (e.g. concentration dependency) in which specific experimental conditions led to expected chemical shift changes of the N–H, and the appearance of minor species in $^{31}\text{P}-\text{NMR}$ from complex equilibria (ion-pairs, hydrogen-bonded adducts, and others), validated the presence of HB in solution (see ESI†). The same type of evidence has been consistently used to demonstrate the presence of HB in the past.24

The HB situation of 2 was further studied via infrared spectroscopy (Fig. 3C and Fig. S6 and S7†). The anhydrous form of 2 (red curve) lacks any –OH stretches at >3300 cm$^{-1}$. On the other hand, measurements obtained from a dilute sample of 2 in DCM (0.5% H$_2$O), shows the arising of a discrete band at ∼3384 cm$^{-1}$, which corresponds to a HB –OH vibrational mode (blue curve). A three-fold concentration increase of 2 (i.e. more likely to participate in HB) to yield an approximate equimolar 2/H$_2$O mixture, led to the black spectrum featuring two, well-resolved discrete bands at 3490 and 3421 cm$^{-1}$. These vibrations occur at approximately 250 cm$^{-1}$ lower wavenumbers than the –OH stretches of free H$_2$O in CCl$_4$, indicating HB interactions. The two –OH resonances separated by only 69 cm$^{-1}$ from the other reliably confirm the self-assembly of the dimeric motif in solution (Fig. S6 and S7† for details)25 and correlate well with solid-state IR-data. Theoretically, QTAIM molecular graphs (Bader analysis) verifies the HB interactions of this cluster (Fig. S8†). Examples of hydrogen bonding in compounds containing unsaturated/multiple bonded heavy main group motifs are rare.16,28–31

Intrigued by the stability of 1 after the reaction with HCl, its reactivity with TIOH (previously used to yield phosphinium cations from phosphaalkenes)28 and HPF$_6$ (60% aq.), acids orders of magnitude stronger than HCl, were tested. The $^{31}\text{P}-\text{NMR}$ spectra of 3 and 4 exhibited low-field shifts typical of phosphaalkenes >300 ppm and were confirmed crystallographically (Fig. 3). Dicoordinate phosphonium cations also

![Fig. 2 ORTEP representation of $2\text{H}_2\text{O}$. Ellipsoids are plotted at 50% probability levels. (B) $^1\text{H}$-NMR spectra of 2 and $2 + \text{H}_2\text{O}$. Top: Anhydrous. Bottom: H$_2$O titrated 2. Red and blue box: N–H signal; green box: H$_2$O signal shifted due to the presence of HB. Bottom integrals assume a dimeric species. (C) FTIR: –OH region expansion of 2 and $2 + \text{H}_2\text{O}$ experiments (ESI/Fig. S6†).](image1.png)

![Fig. 3 ORTEP representations of (A) 3 (B) 4 (only one of the two independent molecules is displayed; see the asymmetric unit in Fig. S11†). Ellipsoids are plotted at 50% probability levels.](image2.png)
exhibit strongly deshielded $^{31}$P NMR resonances and a $\Delta \delta^{31}$P of 70 ppm and higher compared to their corresponding parent phosphaalkenes, as stated before for 1 (Fig. S1f), a resonance structure with a cationic phosphorus centre is plausible. However, the observed geometric parameters in the solid-state structures of 2-H$_2$O, 3, and 4 (vide infra) suggest that the charge delocalisation mainly occurs via the nitrogen atoms (Fig. S8f). Despite the pronounced effect on the $^{31}$P chemical shifts for all adducts, we believe that the observed species are typical of customarily polarised phosphaalkene units. The solid-state structures of 3 and 4 (Table S1f) show similar geometric parameters for the P═C unit in comparison to 2-H$_2$O. The N1-C2--N2 motif displays similar bond lengths, whereas the P═C distances are slightly longer in 3 (1.689(4) Å) and 4 (1.695(5)/1.688(5) Å) in comparison to 2-H$_2$O and 1. In both cases, strong HB interactions between the cationic iminium and the anion are observed. The donor–acceptor distances are in the range of 2.932(7)–3.097(3) Å, thus significantly shorter than in the DBU-HCl adduct (5) (3.156(6) Å, Table S2f). DBU salts together with other adduct derivatives and its parent compound DBU are widely relevant in various areas such as catalysis, ionic liquids, organic synthesis, and others; however, the single crystal structure of this organic hydrochloride salt was reported for the first time (Fig. S9f). These hydrogen bonds are fundamentally interesting because they lie at the Brönsted acid/base and HB interface.

Additionally, single crystals of the Pd(n) complex (6) from the reaction of 1 with [PdCl$_2$(MeCN)$_2$] were obtained (Fig. S10f); as previously observed, the resulting P═C bond length shortened upon metal coordination (1.648(7) Å), and as a result of the formation of the square planar complex, the torsion angle between the P═C and N═C is reduced (6: 12.3(7)$^\circ$) with respect to the other species (52–57$^\circ$) (Table S1f). The relative donor strengths of the N and the P binding sites are reflected by the Pd–Cl distances of 2.296(2) and 2.335(2) Å to the trans-chlorides, respectively suggesting stronger P binding.

In summary, a broad set of fascinating P═C containing systems obtained from the reactions of 1 with very strong acids and a Pd(n) precursor (1, 2-H$_2$O, 3, 4, 6), as well as the structurally unreported hydrochloride salt of DBU (5), are presented. The protonated derivatives are significantly stabilised towards decomposition of their phosphaalkene in comparison to 1, proving a vital role of both the anionic fragments and HB interactions in suppressing undesired processes. The HCl adduct self-assembles into a dimeric species selectively, and exhibits a novel HB type of quadrilateral arrangement stabilised by two HB donor-only water molecules and two triply HB accepting chloride anions as the smallest water–chloride cluster of that type. The potential use of these systems as supramolecular precursors, in catalysis, and other applications may be envisioned. The introduction of this concept incentivises the use of rational design towards compounds that incorporate formidable multiple bonding to heavier p-block elements by strategically positioning saviour atoms on the periphery of the main group scaffold.

Conflicts of interest
There are no conflicts to declare.

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Notes and references

