Hydride Abstraction and Deprotonation – an Efficient Route to Low Co-ordinate Phosphorus and Arsenic Species

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Abstract

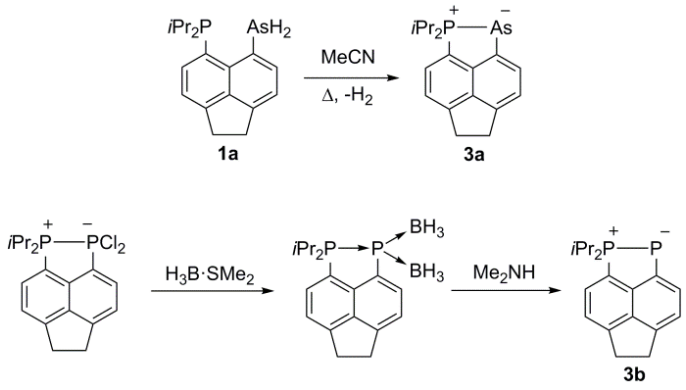
Treatment of Acenap(P*i*Pr$_2$)(EH$_2$) (Acenap = acenaphthene-5,6-diyl; **1a**, E = As; **1b**, E = P) with Ph$_3$C·BF$_4$ resulted in hydride abstraction to give [Acenap(P*i*Pr$_2$)(EH)][BF$_4$] (**2a**, E = As; **2b**, E = P). These represent the first structurally characterised phosphino/arsino-phosphonium salts with secondary arsine/phosphine groups, as well as the first example of a Lewis base stabilised primary arsenium cation. Compounds **2a** and **2b** were deprotonated with NaH to afford low co-ordinate species Acenap(P*i*Pr$_2$)(E) (**3a**, E = As; **3b**, E = P). This provides an alternative and practical synthetic pathway to the phosphanylidene-σ^4-phosphorane **3b** and provides mechanistic insight into the formation of arsanylidene-σ^4-phosphorane **3a**, indirectly supporting the hypothesis that the previously reported dehydrogenation of **1a** occurs via an ionic mechanism.

Introduction

Alkylidene-σ^4-phosphoranes (R$_2$C=PR$_3$), more commonly known as Wittig reagents, are widely used intermediates in the formation of C=C double bonds. The arsenic and phosphorus equivalents, arsanylidene-σ^4-phosphoranes (RAs=PR$_3$) and phosphanylidene-σ^4-phosphoranes (RP=PR$_3$), are rare by comparison. Transition metal stabilised phosphanylidene-σ^4-phosphoranes (R$_3$P=P(R)→ML$_n$) were first synthesised by Mathey and co-workers in 1990[1] and have received attention as "phospha-Wittig" reagents for the generation of P=C bonds, in which they act as phosphinidene (R–P) transfer reagents.[2–6] Free phosphanylidene-σ^4-phosphoranes are rather reactive species, with only a handful of published examples where the compound is stabilised by extremely electron withdrawing substituents,[7,8] steric shielding,[9–11] or the combination of a rigid backbone and steric shielding.[12]

Low co-ordinate arsenic chemistry is significantly less studied than that of phosphorus, with most attention being focused on arsaalkenes (R$_2$C=AsR'), diarsenes (RAs=AsR),[13–16] and phosphine- and carbene-stabilised cationic species.[17–19] Until recently, the only semi-isolable arsanylidene-σ^4-phosphorane to be reported was 2,6-Trip$_2$C$_6$H$_3$As=PMe$_3$ (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$)[20] which, despite extensive steric shielding, decomposes to the diarsene at room temperature.

In previous work by our group, an arsanylidene-σ^4-phosphorane (**3a**) and phosphanylidene-σ^4-phosphorane (**3b**) have been synthesised and isolated as vividly red solids (Scheme 1).[21–23] These compounds display exceptional thermal stability which, in contrast to previous examples, stems from *peri*-substitution stabilisation. The pnictogen centres were mounted on a rigid acenaphthene backbone, which forces the phosphine moiety into close proximity with the phosphinidene/arsinidene group. This results in significant stabilisation and hence compounds which are bottleable while remaining sterically unhindered. Compound **3a**, therefore, represents the first isolable arsanylidene-σ^4-phosphorane and **3b** a rare example of a stable phosphanylidene-σ^4-phosphorane with a sterically accessible two coordinate phosphorus centre. These two compounds, although structurally similar, were synthesised by wildly different routes. Compound **3a** was obtained via a dehydrogenation reaction of the primary arsine **1a**[23] while **3b** was synthesised by deprotection of an intermediate bis(borane) adduct (Scheme 1).[21]

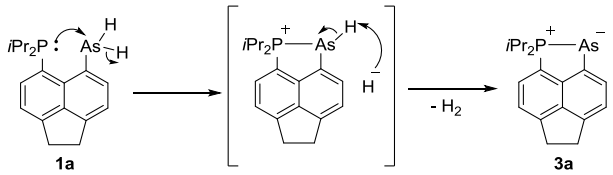


Scheme 1: Original synthetic routes to the arsanylidene-σ^4-phosphorane (**3a**) and phosphanylidene-σ^4-phosphorane (**3b**).

Since the dihydrogen elimination in the synthesis of **3a** represents a novel pathway to low coordinate pnictogen species, we decided to study the mechanism of this transformation in more detail. The results of this investigation are presented in this paper.

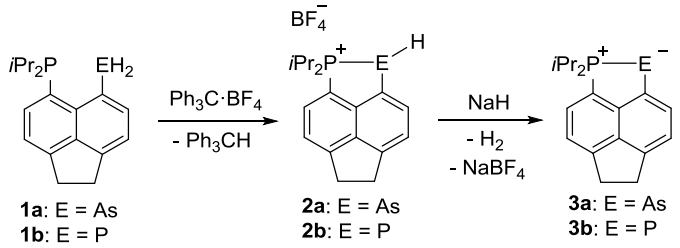
Results and Discussion

We have observed that the elimination of hydrogen from **1a**, shown in Scheme 1, is significantly faster in polar solvents. Standing of a solution of **1a** in acetonitrile at room temperature gives full conversion to **3a** in 7 days, whilst a solution in benzene takes approximately 5 weeks. This led us to suggest that hydrogen evolution occurs via a highly polar or ionic-related mechanism. It can be envisaged that this may involve elimination of a hydride from the arsenic centre, which is facilitated by synchronous electron transfer from the lone pair of the proximal phosphine to an empty σ*(As–H) orbital, thus weakening the As–H bond. This could result in an arsino-phosphonium salt, which is deprotonated by the hydride to give H_2 and **3a** (Scheme 2).



Scheme 2: Proposed mechanism for the dehydrogenation of **1a** via an arsino-phosphonium intermediate.

To test the plausibility of this mechanism, we decided to mimic this pathway chemically. To this end, we treated the primary arsine with the hydride abstractor triphenylcarbonium tetrafluoroborate ($Ph_3C{\cdot}BF_4$), which yielded an isolable arsino-phosphonium salt **2a** (Scheme 3). Deprotonation of this salt to afford **3a** was performed with sodium hydride (i.e. a hydride source) to most closely mimic the mechanism shown in Scheme 2.



Scheme 3: Two step synthesis of arsanylidene/phosphanylidene-σ^4-phosphoranes **3a** and **3b** through hydride abstraction, followed by deprotonation.

Synthesis of arsanylidene-phosphorane 3a

Treatment of **1a** with 1 equivalent of $Ph_3C{\cdot}BF_4$ in THF led to the rapid formation of **2a** in the form of a white precipitate, which was collected by filtration and washed with diethyl ether (69% yield). A very distinctive doublet of doublets was observed in the ^{1}H NMR spectrum of **2a** (δ_H 4.88, $^2J_{H,P}$ = 13.7 Hz, $^4J_{H,H}$ = 1.3 Hz) corresponding to the arsenic bound hydrogen. It is interesting to note that the $^2J_{H,P}$ through-bond coupling in this compound is significantly smaller than the, formally ^5J, through-space coupling observed in the primary arsine **1a** ($^5J_{H,P}$ = 59.7 Hz).[23] The $^{31}P\{^1H\}$ NMR spectrum of **2a** shows a singlet at δ_P 74.9, very similar to the signal observed for the arsanylidene-phosphorane **3a** (δ_P 75.3).

Single crystal X-ray diffraction confirmed the identity of the arsino-phosphonium salt **2a** (Figure 1, Table 1). The compound displays minimal distortion of the acenaphthene backbone, with a P9–C9···C1–As1 torsion angle of only 6.3(2)°. The P–As distance of 2.325(1) Å is consistent with a P–As single bond[24] and is somewhat longer than that found in **3a** (2.262(2) Å),[23] consistent with the higher bond order in the arsanylidene-phosphorane. The bond angles about arsenic are all rather acute, suggesting that the lone pair at arsenic has significant s-character. In addition to X-ray diffraction, ^{1}H and $^{31}P\{^1H\}$ NMR; **2a** was fully characterised by ^{31}P, $^{13}C\{^1H\}$ and ^{11}B NMR spectroscopy, as well as Raman spectroscopy, Electrospray Ionisation Mass Spectrometry (ES MS) and elemental analysis.

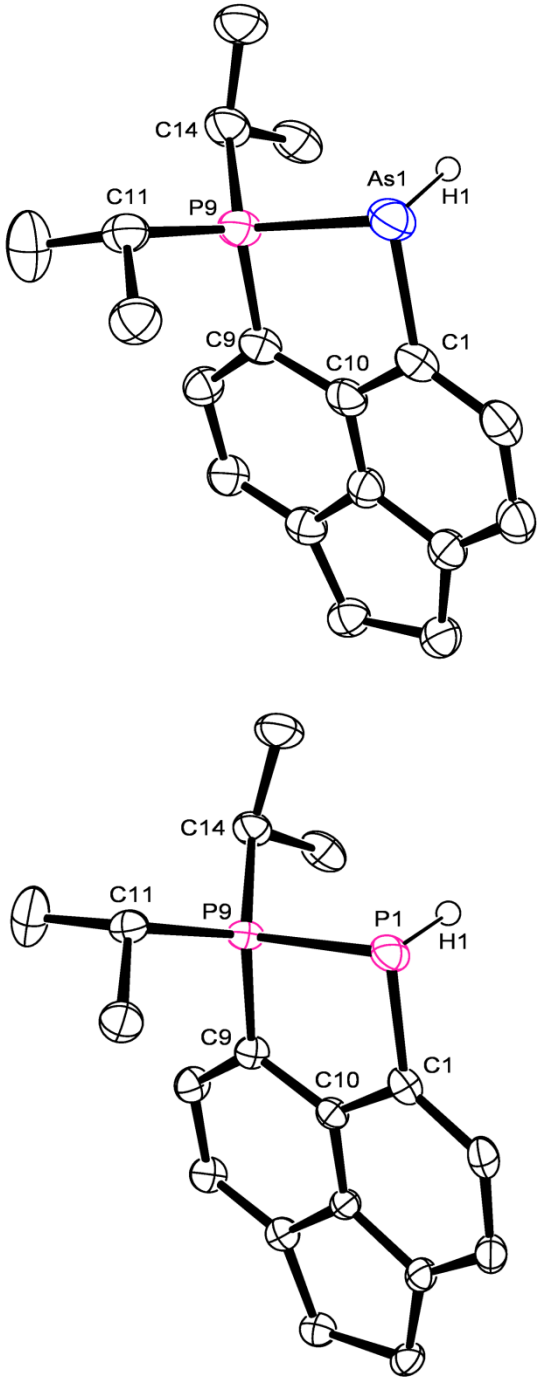
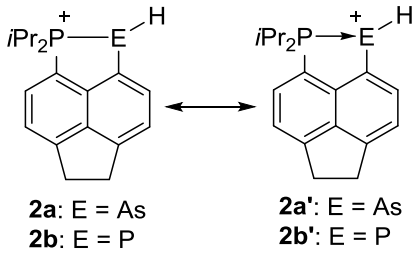


Figure 1: Structure of the cations of **2a** (top) and **2b** (bottom) in the solid state. Carbon bound hydrogen atoms and counterions (BF_4^-) omitted for clarity.

The bonding in compound **2a** can be described using either zwitterionic (**2a**) or dative forms (**2a'**) (Scheme 4). Neither model is completely accurate and the debate over which is more appropriate can be a contentious issue[25,26] which we will not delve into here. For the sake of consistency, we will by default refer to and draw the compound as the arsino-phosphonium form, **2a**, unless the phosphino-arsenium form is to be discussed specifically.



Scheme 4: Alternate resonance forms of compounds **2a** and **2b**; E = As, P.

Compared to their phosphorus counterparts, arsino-phosphonium salts (general formula $[R_3P^+–AsR_2]X^–$) are rare. Only a few instances of such compounds exist in the literature, with some representative examples shown in Figure 2.[27–29] Of these compounds, there are no examples containing a secondary arsine moiety (i.e. As–H motif). Compound **2a**, therefore, represents the first such species to be synthesised and characterised.

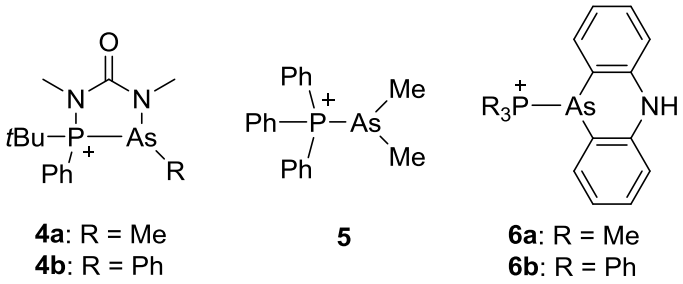


Figure 2: Examples of previously synthesised arsino-phosphonium cations.

More generally, if compound **2a** is considered in its (dative) phosphino-arsenium form ($R_3P→AsHR^+$, **2a'**, see Scheme 4), it represents the first example of a base stabilised primary arsenium cation ($HRAs^+$) to be published in the literature.

Compound **2a** was subsequently treated with 1 equivalent of sodium hydride in THF at −78°C (Scheme 3). On addition of NaH, the reaction mixture was observed to transition from a white suspension to pale pink, which gradually darkened to a deep red-purple on warming to room temperature. Extraction with toluene (to remove the $NaBF_4$ salt byproduct) afforded the arsanylidene-phosphorane **3a** as a deep red solid in good yield (87 %) and purity. The identity and purity of the compound was determined by ^1H, $^{13}C\{^1H\}$, ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy.

Synthesis of phosphanylidene-phosphorane 3b

Primary phosphine **1b**, which was recently synthesised by our group,[30] was subjected to heating in both acetonitrile and toluene to determine if **3b** could be formed directly. However, it was found that hydrogen evolution does not occur and no **3b** was detected after prolonged heating. Subjecting **1b** to sequential hydride abstraction and deprotonation, however, seemed a viable route to **3b**. This is due in part to the success of these reactions on the arsenic congener, but also on account of an $[M - H]^+$ peak observed in the ES+ MS spectrum of compound **1b**[30], suggesting that loss of hydride from **1b** is facile. Treatment of **1b** with $Ph_3C{\cdot}BF_4$ under the same conditions as **1a** led to the formation of phosphino-phosphonium salt **2b** as a white precipitate in high yield (75%) and purity. The reaction was slower than the corresponding transformation with **1a**, with 40 minutes elapsing before the first signs of precipitate formation.

The $^{31}P\{^{1}H\}$ NMR spectrum of **2b** shows two doublets at δ_P 74.2 (iPr$_2$P) and −132.0 (PH) with a coupling constant of $^{1}J_{P,P}$ = 242 Hz. This is somewhat lower in magnitude than that seen with similar phosphino-phosphonium salts, where the phosphorus-bound hydrogen is substituted for a phenyl ($^{1}J_{P,P}$ = 303 Hz) or ferrocenyl group ($^{1}J_{P,P}$ = 311 Hz).[31] In the ^{31}P NMR spectrum, the signal at δ_P −132.0 splits into a doublet of doublets with $^{1}J_{P,H}$ = 208 Hz. This $^{1}J_{P,H}$ coupling constant is comparable to that observed in the primary phosphine **1b** ($^{1}J_{P,H}$ = 204 Hz).[30] Similar to the arsenic analogue **2a**, the $^{2}J_{H,P}$ through-bond coupling of the phosphorus-bound hydrogen, as observed in the ^{1}H NMR spectrum ($^{2}J_{H,P}$ = 9.3 Hz), is actually considerably smaller than the related through-space coupling in compound **1b** ($^{5}J_{H,P}$ = 47.8 Hz).[30]

The crystal structure of **2b** is shown in Figure 1 and Table 1. Once again, the compound shows a relatively relaxed acenaphthene backbone, with a P9–C9···C1–P1 torsion angle of only 4.0(1)°. The P1–P9 distance of 2.229(1) Å is typical of a P–P single bond[24] and is very similar to that observed in previously published *peri*-substituted phosphino-phosphonium salts.[31] In addition to X-ray diffraction, ^{1}H, ^{31}P and $^{31}P\{^{1}H\}$ NMR; **2b** was further characterised by $^{13}C\{^{1}H\}$ and ^{11}B NMR spectroscopy, Raman spectroscopy, ES MS and elemental analysis.

Phosphino-phosphonium salts are relatively well known in the literature, with a very significant contribution by the Burford group to this area of chemistry.[32–35] Although phosphino-phosphonium salts of the form $R_2HP^+–PR_2$ have been synthesised previously,[36] and a few related triphosphine-1,3-diiums $R_3P^+–PH–PR_3^+$ have also been reported,[37] compound **2b** is the first example of a phosphino-phosphonium salt containing a secondary phosphine group.

As with compound **2a**, **2b** can alternatively be considered as a phosphenium cation stabilised by a (phosphine) Lewis base (**2b'**, see Scheme 4). Free primary phosphenium cations (HRP^+) are currently unknown in the literature. The first example of a base-stabilised form was published earlier this year by Bertrand[38] and was stabilised by NHC co-ordination. Thus, compound **2b** represents a new and radically different entry into this very narrow field of compounds.

The presence of a relatively reactive E–H bond in both compounds (**2a** and **2b**) is exciting, as it opens up the possibility of using these compounds as efficient synthons. For example, it may be possible to utilise dehydrocoupling reactions to build up catenated dicationic species with potentially interesting electronic and structural characteristics.

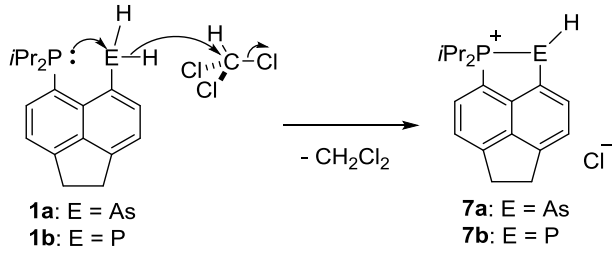
The described hydride abstraction route represents a fundamentally new method of phosphino-phosphonium generation, its main distinguishing feature being the utilisation of a primary phosphine as a starting material. As mentioned recently by Burford,[39] only a small number of preparative methods exist for cationic pnictogen species. The vast majority of these utilise halide abstraction/displacement as an entry point and hence are limited to the pnictogen halides as starting materials.

Compound **2b** was found to react analogously to **2a** on treatment with NaH (Scheme 3), forming a pink suspension that darkened to a deep red on warming to room temperature. Working up the reaction in the same manner as **2a** afforded phosphanylidene-phosphorane **3b** as a crimson solid in 81% yield. The identity and purity of the compound was determined by ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P and $^{31}P\{^{1}H\}$ NMR spectroscopy.

It should be noted that although NaH was used as a base, so as to mimic the proposed mechanism in Scheme 2, the deprotonation of both **2a** and **2b** is rather facile and can be achieved with relatively weak bases. Addition of triethylamine (1.5 eq) to NMR samples of **2a** and **2b** resulted in a bright red solution and the formation of **3a** and **3b** as detected by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. This result is somewhat surprising, as one might expect compounds **3a** and **3b** to be strongly basic given the pnictido-like character of the two coordinate P/As atoms, possessing two lone pairs and a (formally) negative charge.

Reaction with chloroform

As an interesting aside, it was found that both the primary arsine **1a** and primary phosphine **1b** react with chloroform. A solution of **1a** in $CDCl_3$ showed decomposition to a mixture of products (by $^{31}P\{^{1}H\}$ NMR spectroscopy) within minutes, whilst **1b** showed no decomposition initially and decomposed to a complex mixture (albeit less complex than in the case of **1a**) over 3 days. In both cases crystals were obtained from the solutions and found, by X-ray diffraction, to be analogues of the salts **2a** and **2b** with chloride counterions (**7a** and **7b**). While the amount of isolated crystals of **7a** was small and the crystallisation was difficult to reproduce, in the case of **7b** the crystals collected were of analytical purity and complete characterisation by multinuclear NMR, ES MS, elemental analysis and Raman spectroscopy was possible. A plausible mechanism for this transformation is shown in Scheme 5.



Scheme 5: Proposed mechanism for the reaction of **1a** and **1b** with chloroform to give chloride salts **7a** and **7b**.

This reactivity demonstrates the relative ease with which compounds **1a** and **1b** will give up a hydride, even to relatively weak hydride acceptors such as chloroform. This can be attributed to the proximal phosphine lone pair, which promotes the reaction. The fact that the arsino/phosphino-phosphonium salt forms so readily lends further indirect support to the hypothesis that an arsino-phosphonium salt is the intermediate formed during dehydrogenation of **1a**.

The solid state structures of compounds **7a** and **7b** are very similar to those of the tetrafluoroborate salts **2a** and **2b** and so are reproduced in the supporting information (SI). Structural parameters are shown in Table 1.

Computational studies

The elimination of dihydrogen from compound **1a** was further probed by computational methods. It is, however, difficult to assess whether or not the proposed ionic pathway (Scheme 2) is followed during the reaction with our computational protocol. Two alternative pathways with corresponding transition states have been located and examined at the M06-2X/6-311+G**//B3LYP/6-31G*(*) level of density functional theory (DFT). However, in both cases, the kinetic barriers calculated for these two pathways are incompatible with the observed rate of dihydrogen elimination from **1a**.

For the isolated molecule a transition state was located corresponding to a concerted, unimolecular dissociation of H_2 (**TS13a**, Figure 3). This transition state describes a synchronous elongation of both As–H bonds (from ca. 1.5 Å in **1a** to 1.7 Å), assisted by the onset of P–As bonding (note the decrease of the P···As distance from ca. 3.2 Å to 2.9 Å on going from **1a** to **TS13a**). Despite this assistance, the computed barrier is very high, $\Delta H^{\ddagger}$ = 150.6 kJ·mol^{-1} relative to **1a** in the gas phase. Immersion in a polarisable continuum reduces this barrier slightly, by up to 5 kJ·mol^{-1} using the parameters of acetonitrile. The dissociation process is facilitated by entropy, but this amounts to just a few kJ·mol^{-1} at the transition state. The final estimated $\Delta G^{\ddagger}$ in acetonitrile is 139.4 kJ·mol^{-1} at room temperature (Figure 4), too high to be compatible with the rate of reaction observed under these conditions (and assuming that tunnelling is not the major pathway at this temperature). No charge separation between the two dissociating H atoms is apparent in **TS13a**, both have close to zero charge in a Mulliken population analysis (MPA) and also in the polarisable continuum. From this we conclude that the evolution of hydrogen from **1a** most likely does not occur via this concerted mechanism.

Interestingly, in a recent mechanistic study[40] of room temperature hydrogen elimination from an organotin trihydride, assisted by a nitrogen base, a similar transition state to **TS13a** was located on the reaction coordinate computationally. However, similar to **TS13a**, its associated $\Delta G^{\ddagger}$ was too high for a reaction occurring at room temperature, and an alternative polar mechanism was suggested to account for the difference.

Looking into a more polar pathway, one such possibility was explored, in which one hydrogen atom is first transferred from the As atom to the P atom. This was seen as a plausible pathway, as the phosphonium centre generated after hydride removal from **1a** is Lewis acidic and hence capable of stabilising the “free” hydride by forming a hypervalent five-coordinate intermediate (**8a**, Figure 3). This intermediate is fairly high in energy, more than 110 kJ·mol^{-1} above **1a** in the gas phase.[41] However, the transition state connecting both (**TS18a**, Figure 3) is lower in energy than **TS13a**. Because **TS18a** is very polar (computed dipole moment exceeds 8 D in the gas phase) it is stabilised in a polarisable continuum, to the extent that **TS18a** becomes lower than **8a** in acetonitrile (Figure 4) indicating that **8a** would not be a stable intermediate in this solvent. H_2 elimination from **8a** via **TS83a** has a large activation barrier, more than 120 kJ·mol^{-1}, thus raising the total activation barrier from **1a** to **TS83a** to more than 230 kJ·mol^{-1} (Figure 4). This is far too high to be overcome under ambient conditions.

TS83a is a "zwitterionic" transition state, as the H atoms leaving from P and As have noticeable negative and positive charges (ca. −0.2*e* and +0.1*e*, respectively, according to MPA). In other words, these H atoms have significant hydridic and protic character, as seen in transition states for H_2 activation by frustrated Lewis pairs.[42] Stabilisation from the bulk solvent is not very pronounced, however, leaving **TS83a** prohibitively high in energy. Transfer of an H atom to P followed by H_2 elimination is, therefore, an unlikely pathway for this reaction.

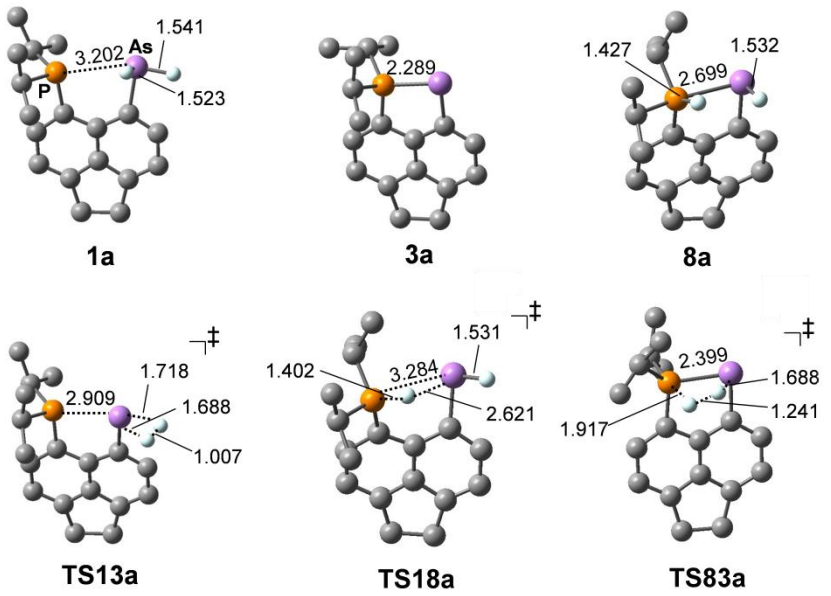


Figure 3: Stationary points involved in the unimolecular dissociation of H_2 from **1a**, including key distances in Å (B3LYP-optimised); carbon-bound H atoms omitted for clarity.

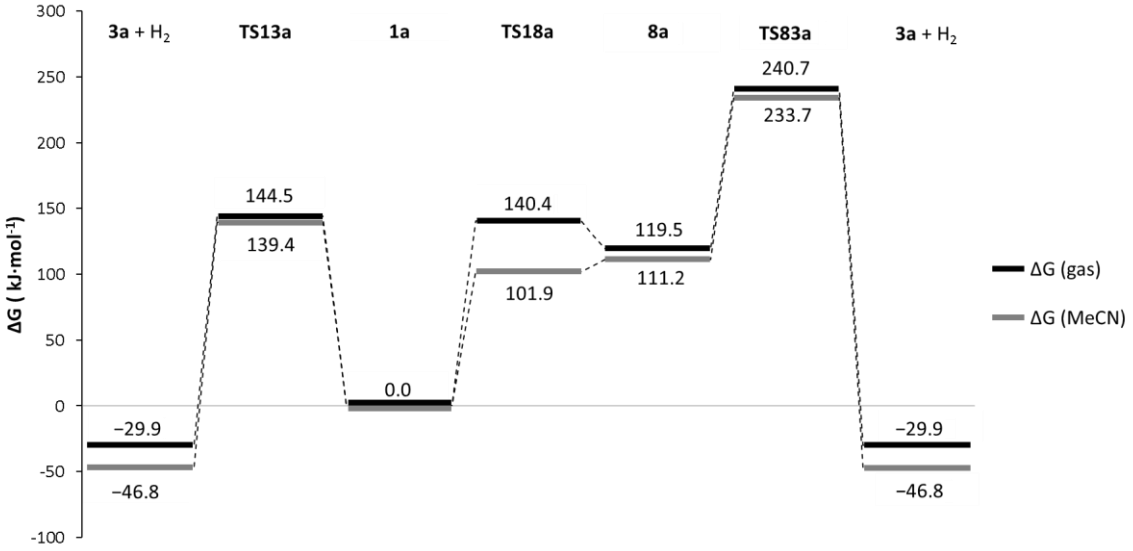


Figure 4: Computed free energies (Δ*G*) for selected stationary points in the gas phase and in a continuum modelling acetonitrile (denoted MeCN), in kJ·mol^{-1} relative to **1a**. Energies computed at the M06-2X/6-311+G**//B3LYP/6-31G*$^{(*)}$ level.

Given the accessibility of ionic **2a**, and the fact that both pathways computed above are kinetically prohibited, a hydridic elimination pathway remains the most plausible explanation for the dehydrogenation of **1a**. One can envisage a transition state in which the P lone pair donates into the σ*(As–H) orbital, lengthening the As–H bond and conferring more electron density to the H atom (Figure 5). This atom then may or may not fully dissociate from the As, before using its electron density to remove the residual proton and leaving as H_2. Given the ionic nature of this mechanism, and the high likelihood of strong solvent interactions, such a transition state is difficult to compute. Searches for such an "asymmetric dipolar" transition state were unsuccessful and always afforded

TS13a, even in the presence of a polarisable continuum during optimisation (which would serve to stabilise such zwitterionic structures). Explicit inclusion of reaction partners that could stabilise the forming hydride appears to be necessary, but a detailed study of all possible pathways that might be followed is beyond the scope of the current study.

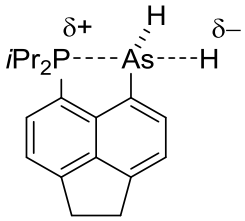
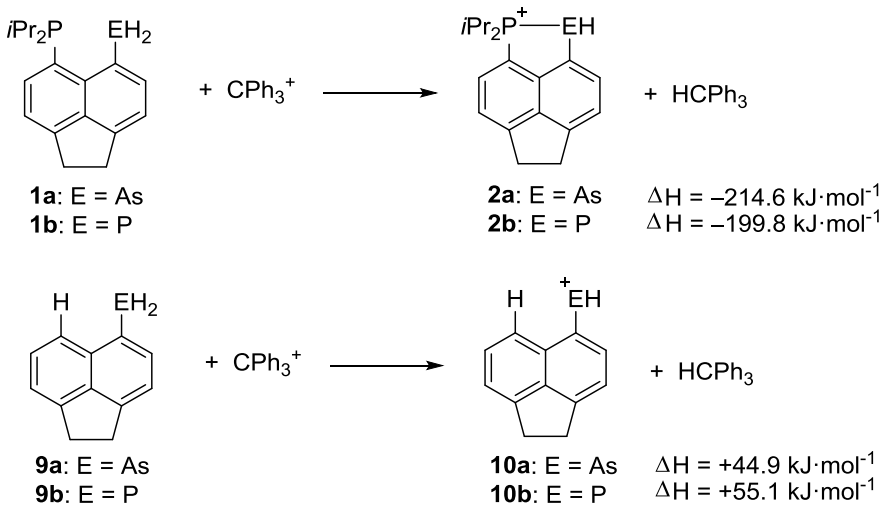


Figure 5: Tentative zwitterionic transition state for elimination of H_2 from **1a**.

Finally, we have also computed the driving forces for the hydride abstraction reactions according to Scheme 6. The formation of the cations **2a/2b** from **1a/1b** is predicted to be strongly exothermic in the gas phase, with ΔH = −214.6 kJ·mol^{-1} and −199.8 kJ·mol^{-1} respectively (no counterions included).



Scheme 6: Hydride abstraction reactions with calculated reaction enthalpies in the gas phase.

Immersion in a polarisable continuum with the parameters of THF increases these driving forces slightly, to −219.9 kJ·mol^{-1} and −204.8 kJ·mol^{-1} respectively. Notably, these calculations indicate that the driving force for the formation of **2b** is smaller than that of **2a**.

The stabilising effect of the diisopropylphosphine group was assessed through simple model calculations, in which this group was replaced with a hydrogen atom in the reactants and products (Scheme 6, **9a/9b** → **10a/10b**). The computed driving force changed from −214.6 kJ·mol^{-1} to +44.9 kJ·mol^{-1} for the arsine, and from −199.8 kJ·mol^{-1} to +55.1 kJ·mol^{-1} for the phosphine. As expected, the presence of the P*i*Pr$_2$ moiety in **1a/1b** strongly promotes hydride abstraction from the adjacent EH_2 group (E = P, As). However, the extent to which these cations are stabilised (more than 250 kJ·mol^{-1} in the gas phase) is rather impressive.

Conclusions

It has been shown that hydride abstraction from the bis(phosphines) **1a** and **1b** affords arsino/phosphino-phosphonium salts **2a** and **2b** in good yields and purity. Both of these salts can be deprotonated to yield low co-ordinate species **3a** and **3b**. This reaction sequence provides a new and high-yielding route to **3a** and **3b**. In addition, although reaction partners where chosen so as to favour an ionic pathway, these transformations provide indirect support for the ionic mechanism proposed in Scheme 2, wherein hydride is eliminated from **1a** to give an arsino-phosphonium salt which is deprotonated to form **3a**. Compounds **2a** and **2b** are interesting in their own right, serving as the first examples of arsino-phosphonium and phosphino-phosphonium salts to contain a secondary arsine/phosphine moiety. Furthermore, compound **2a** can also be considered as the first base stabilised primary arsenium cation. The presence of a reactive E–H bond in these compounds opens up the possibility of using these species as a starting point for further reactions, such as dehydrocoupling.

Hydride abstraction from **1a** was computed to be more strongly exothermic than in **1b** (by ca 15 $kJ{\cdot}mol^{-1}$), and **1a** reacts more rapidly with both $Ph_3C{\cdot}BF_4$ and chloroform. This is in line with the observation that **1a** undergoes spontaneous hydrogen elimination to give compound **3a**, while compound **1b** does not. Given the stability of the hydride abstraction product **2a**, and the relative ease of its formation, an ionic mechanism as proposed in Scheme 2 remains the most likely pathway for this reaction.

Table 1: Selected bond lengths (Å), angles (°) and out-of-plane displacements for **2a**, **2b**, **7a** and **7b**. CCDC 1419683-1419686 contain the supplementary crystallographic data for these structures.

2a			
C1–As1	1.969(4)	C9–P9	1.794(5)
As1–P9	2.325(1)		
out-of-plane displacement (As1)	0.162	out-of-plane displacement (P9)	0.083
C1–As1–P9	87.0(1)	C1–As1–H1	96(2)
P9–As1–H1	94(2)	splay angle[a]	−6.5(10)
2b			
C1–P1	1.844(3)	C9–P9	1.801(3)
P1–P9	2.229(1)		
out-of-plane displacement (P1)	0.118	out-of-plane displacement (P9)	0.048
C1–P1–P9	90.4(1)	C1–P1–H1	93(1)
P9–P1–H1	93(1)	splay angle[a]	−9.0(7)
7a			
C1–As1	1.964(6)	C9–P9	1.797(5)
As1–P9	2.350(2)		
out-of-plane displacement (As1)	0.137	out-of-plane displacement (P9)	0.163
C1–As1–P9	86.6(2)	C1–As1–H1	106(4)
P9–As1–H1	94(4)	splay angle[a]	−5.5(13)
7b			
C1–P1	1.795(6)	C9–P9	1.838(6)
P1–P9	2.230(2)		
out-of-plane displacement (P1)	0.148	out-of-plane displacement (P9)	0.154
C1–P1–P9	90.2(2)	C1–P1–H1	111(4)
P9–P1–H1	92(4)	splay angle[a]	−8.9(14)

[a] Splay angle = P9–C9–C10 + C9–C10–C1 + C9–C1–E1 – 360; E = P, As

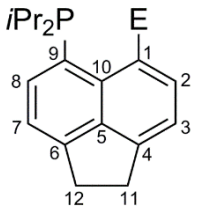
Experimental Section

General Procedures

All experiments were carried out in standard Schlenk glassware under an inert atmosphere or in a glove box unless otherwise stated. Solvents were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. Compounds **1a** and **1b** were synthesised according to literature procedures.[23,30] Where possible, new compounds were fully characterized by ^{31}P, $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR, including measurement of $^{1}H\{^{31}P\}$, H−H DQF COSY, H−P HMQC, H−C HSQC, and H−C HMBC experiments. The NMR numbering scheme is shown in Scheme 7.

Instrumentation

All NMR spectra were recorded using a JEOL GSX Delta 270 or a Bruker Avance 300 spectrometer at room temperature. 85% H_3PO_4 was used as an external standard in ^{31}P, $BF_3{\cdot}OEt_2$ in $CDCl_3$ was used as an external standard in ^{11}B, and TMS was used as an internal standard in ^{1}H and ^{13}C NMR. Measurements were performed at 25 °C unless otherwise indicated. All Raman spectra were obtained in the range 4000–300 cm^{-1} on a Perkin-Elmer System 2000 NIR Fourier transform spectrometer. Mass spectra were acquired by the National Mass Spectrometry Facility (NMSF) in Swansea on a Thermo Scientific LTQ Orbitrap XL, or by Mrs Caroline Horsburgh at the University of St Andrews on a Micromass LCT. Elemental analysis (C, H and N) was performed by Mr Stephen Boyer at London Metropolitan University.



Scheme 7: NMR numbering scheme for all compounds in the experimental section.

[Acenap(P*i*Pr$_2$)(AsH)][BF$_4$] **2a**

A solution of **1a** (412 mg, 1.19 mmol) in THF (10 mL) was added dropwise to a stirred suspension of $Ph_3C{\cdot}BF_4$ (389 mg, 1.19 mmol) in THF (10 mL) and stirred at room temperature for 1 h. The resultant white precipitate was collected by filtration, washed with diethyl ether (10 mL) and dried in vacuo to afford **2a** (355 mg, 0.82 mmol, 69%) as a fine white powder. Crystals suitable for single crystal X-ray diffraction were grown from slow diffusion of diethyl ether into a concentrated solution of **2a** in $CDCl_3$. **M.p.** 167–168 °C. **ELA** $C_{18}H_{23}AsBF_4P$ (432.08) calcd. C 50.04, H 5.37; found C 50.12, H 5.30. **Raman** (glass capillary): $\tilde{\nu}$ = 3060 (m, ArH), 2979 (m) and 2938 (s, CH), 2131 (m, AsH), 1604 (s), 1574 (w), 1454 (s), 1421 (s), 1381 (vs), 1349 (s), 1219 (w), 1106 (w), 887 (w), 836 (w), 768 (w, BF), 723 (w), 645 (w), 589 (vs), 551 (m), 526 (m), 395 (m) cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.25 (dd, $^{3}J_{H,P}$ = 9.6 Hz, $^{3}J_{H,H}$ = 7.3 Hz, 1H, 8-H), 7.90 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H, 2-H), 7.66 (ddt, $^{3}J_{H,H}$ = 7.4 Hz, $^{4}J_{H,P}$ = 2.6 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 1H, 7-H), 7.52 (dt, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, 3-H), 4.88 (dd, $^{2}J_{H,P}$ = 13.7 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H, AsH), 3.62–3.47 (m, 5H, 11-H, 12-H, *i*Pr CH), 3.37–3.14 (m, 1H, *i*Pr CH), 1.46–1.30 (m, 9H, 3 × *i*Pr CH_3), 1.22 (dd, $^{3}J_{H,P}$ = 19.4 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, *i*Pr CH_3). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.7 (d, $^{4}J_{C,P}$ = 2.8 Hz, qC-6), 148.7 (s, qC-4), 142.6 (d, $^{2}J_{C,P}$ = 20.7 Hz, qC-10), 139.7 (d, $^{3}J_{C,P}$

= 12.4 Hz, qC-5), 135.3 (d, $^{2}J_{C,P}$ = 3.1 Hz, C-8), 134.7 (d, $^{3}J_{C,P}$ = 6.5 Hz, C-2), 124.5 (s, qC-1), 122.4 (s, C-3), 122.2 (d, $^{3}J_{C,P}$ = 10.7, C-7), 115.8 (d, $^{1}J_{C,P}$ = 53.0 Hz, qC-9), 31.4 (s, C-11/C-12), 30.8 (s, C-11/C-12), 25.2 (d, $^{1}J_{C,P}$ = 14.6 Hz, *i*Pr CH), 24.8 (d, $^{1}J_{C,P}$ = 22.0 Hz, *i*Pr CH), 18.3 (s, *i*Pr CH_3), 17.9 (s, *i*Pr CH_3), 17.6 (d, $^{2}J_{C,P}$ = 3.3 Hz, *i*Pr CH_3), 17.0 (d, $^{2}J_{C,P}$ = 3.3 Hz, *i*Pr CH_3). **^{31}P NMR** (121 MHz, $CDCl_3$): δ = 74.9 (m). **^{31}P{^{1}H} NMR** (109 MHz, $CDCl_3$): δ = 74.9 (s). **^{11}B NMR** (96 MHz, $CDCl_3$): δ = −0.9 (s). **MS (ES+)** 377 (100) $[M - BF_4 + 2O]^+$. **HRMS (ES+)** calcd. for $C_{18}H_{23}O_2AsP$ $[M - BF_4 + 2O]^+$ 377.0646; found 377.0646.

[Acenap(P*i*Pr$_2$)(PH)][BF_4] **2b**

A solution of **1b** (600 mg, 1.98 mmol) in THF (10 mL) was added dropwise to a stirred suspension of $Ph_3C{\cdot}BF_4$ (655 mg, 1.98 mmol) in THF (10 mL) and stirred at room temperature for 2 h. The resultant white precipitate was collected by filtration, washed with diethyl ether (10 mL) and dried in vacuo to afford **2b** (580 mg, 1.49 mmol, 75%) as a fine white powder. Crystals suitable for single crystal X-ray diffraction were grown from slow diffusion of diethyl ether into a concentrated solution of **2b** in $CDCl_3$. **M.p.** 163–166 °C. **ELA** $C_{18}H_{23}BF_4P_2$ (388.13) calcd. C 55.70, H 5.97; found C 55.65, H 6.08. **Raman** (glass capillary): $\tilde{\nu}$ = 3063 (m, Ar–H), 2936 (s, C–H), 2318 (m, P–H), 1613 (vs), 1454 (s), 1423 (s), 1387 (s), 1349 (m), 1108 (m), 768 (m, B–F), 725 (m), 596 (vs), 562 (m), 535 (m), 465 (m), 426 (m), 367 (m) cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.36 (dd, $^{3}J_{H,P}$ = 9.3 Hz, $^{3}J_{H,H}$ = 7.3 Hz, 1H, 8-H), 7.92 (≈ td, $^{3}J_{H,P}$ = 7.1 Hz, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1H, 2-H), 7.74–7.66 (m, 1H, 7-H), 7.52 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{H,P}$ = 2.2 Hz, 1H, 3-H), 4.97 (ddd, $^{1}J_{H,P}$ = 207 Hz, $^{2}J_{H,P}$ = 9.3 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1H, PH), 3.71–3.61 (m, 1H, *i*Pr CH), 3.60–3.50 (m, 4H, 11-H, 12-H), 3.35–3.22 (m, 1H, *i*Pr CH), 1.47–1.33 (m, 9H, 3 × *i*Pr CH_3), 1.21 (dd, $^{3}J_{H,P}$ = 19.6 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, *i*Pr CH_3). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.7 (d, $^{4}J_{C,P}$ = 2.8 Hz, qC-6), 149.2 (s, qC-4), 141.6 (dd, $^{2}J_{C,P}$ = 20.6 Hz, $^{2}J_{C,P}$ = 2.6 Hz, qC-10), 139.0 (d, $^{3}J_{C,P}$ = 12.5 Hz, qC-5), 135.1 (d, $^{2}J_{C,P}$ = 3.6 Hz, C-8), 134.8 (dd, $^{2}J_{C,P}$ = 26.6 Hz, $^{3}J_{C,P}$ = 7.8 Hz, C-2), 122.6 (d, $^{3}J_{C,P}$ = 11.5 Hz, C-7), 122.4 (d, $^{3}J_{C,P}$ = 9.5 Hz, C-3), 120.1 (dd, $^{1}J_{C,P}$ = 20.1 Hz, $^{2}J_{C,P}$ = 2.5 Hz, qC-1), 114.0 (dd, $^{1}J_{C,P}$ = 58.6 Hz, $^{2}J_{C,P}$ = 4.6 Hz, qC-9), 31.7 (s, C-11/C-12), 31.0 (s, C-11/C-12), 24.9 (m, *i*Pr CH), 24.4 (m, *i*Pr CH), 17.7 (d, $^{2}J_{C,P}$ = 1.1 Hz, *i*Pr CH_3), 17.4 (d, $^{2}J_{C,P}$ = 2.8 Hz, *i*Pr CH_3), 17.2 (dd, $^{2}J_{C,P}$ = 5.6 Hz, $^{3}J_{C,P}$ = 2.0 Hz, *i*Pr CH_3), 16.5 (dd, $^{2}J_{C,P}$ = 4.7 Hz, $^{3}J_{C,P}$ = 3.5 Hz, *i*Pr CH_3). **^{31}P NMR** (109 MHz, $CDCl_3$): δ = 74.2 (dm, $^{1}J_{P,P}$ = 242 Hz, *i*Pr$_2$P), −132.0 (dd, $^{1}J_{P,P}$ = 242 Hz, $^{1}J_{P,H}$ = 208 Hz, PH). **^{31}P{^{1}H} NMR** (109 MHz, $CDCl_3$): δ = 74.2 (d, *i*Pr$_2$P), −132.0 (d, PH), $^{1}J_{P,P}$ = 242 Hz. **^{11}B NMR** (96 MHz, $CDCl_3$): δ = −0.9 (s). **MS (ES+)** 301 (100) $[M - BF_4]^+$. **HRMS (ES+)** calcd. for $C_{18}H_{23}P_2$ $[M - BF_4]^+$ 301.1270; found 301.1270.

Acenap(P*i*Pr$_2$)(As) **3a**

A suspension of NaH (16 mg, 0.68 mmol) in THF (10 mL) was added dropwise over 30 minutes to a stirred suspension of **2a** (294 mg, 0.68 mmol) in THF (15 mL) at −78 °C. The reaction was allowed to warm to room temperature overnight, with stirring, to afford a deep red solution. Solvents were removed in vacuo and the resulting solid dissolved in toluene (30 mL) and filtered to remove insoluble salts. Volatiles were removed in vacuo to afford arsanylidine-phosphorane **3a** as a dark red solid (204 mg, 0.59 mmol, 87%). ^{1}H, ^{13}C{^{1}H}, ^{31}P and ^{31}P{^{1}H} NMR spectra were in good agreement with previously published data.[23] Full NMR assignments for this compound can be found in the SI.

Acenap(P*i*Pr$_2$)(P) **3b**

A suspension of NaH (28 mg, 1.14 mmol) in THF (10 mL) was added dropwise over 30 minutes to a stirred suspension of **2b** (446 mg, 1.14 mmol) in THF (20 mL) at −78 °C. The reaction was allowed to warm to room temperature overnight, with stirring, to afford a deep red solution. Solvents were removed in vacuo and the resulting solid dissolved in toluene (50 mL) and filtered to remove

insoluble salts. Volatiles were removed in vacuo to afford phosphanylidene-phosphorane **3b** as a crimson solid (276 mg, 0.92 mmol, 81%). ^{1}H, ^{13}C{^{1}H}, ^{31}P and ^{31}P{^{1}H} NMR spectra were in good agreement with previously published data.[21] Full NMR assignments for this compound can be found in the SI.

[Acenap(P*i*Pr$_2$)(AsH)][Cl] **7a**

A solution of **1a** (100 mg, 0.23 mmol) in chloroform (1 mL) was left to stand in an NMR tube for 2 days. A very small number of colourless crystals of **7a**·3CHCl$_3$ deposited on the side of the NMR tube and were analysed by single crystal X-ray diffraction. An insufficient amount of material was obtained for further analysis.

[Acenap(P*i*Pr$_2$)(PH)][Cl] **7b**

A solution of **1b** (100 mg, 0.33 mmol) in chloroform (1 mL) was left to stand in a sealed vial for 3 days. Colourless crystals of **7b**·3CHCl$_3$ deposited on the walls of the vial, which were collected by decantation, washed with small amount of CHCl$_3$ and dried in vacuo. Yield 55 mg (0.079 mmol, 24%). **ELA** $C_{18}H_{23}ClP_2$·2.4$CHCl_3$ (619.09) calcd. C 39.31, H 4.11; found C 39.18, H 4.47. **Raman** (glass capillary): $\tilde{\nu}$ = 3062 (m, Ar–H), 2970 (m) and 2931 (s) and 2870 (m, C–H), 2298 (m) and 2193 (m, P–H), 1611 (s), 1387 (s), 647 (vs), 367 (vs), 261 (vs) cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.59 (dd, $^{3}J_{H,P}$ = 9.0 Hz, $^{3}J_{H,H}$ = 7.3 Hz, 1H, 8-H), 7.99–7.92 (m, 1H, 2-H), 7.66–7.60 (m, 1H, 7-H), 7.46 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{H,P}$ = 1.9 Hz, 1H, 3-H), 5.29 (ddd, $^{1}J_{H,P}$ = 216 Hz, $^{2}J_{H,P}$ = 9.2 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, PH), 4.56–4.27 (m, 1H, *i*Pr CH), 3.96–3.67 (m, 1H, *i*Pr CH), 3.58–3.45 (m, 4H, 11-H, 12-H), 1.55–1.28 (m, 9H, 3 × *i*Pr CH_3), 1.18 (dd, $^{3}J_{H,P}$ = 19.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 3H, *i*Pr CH_3). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.0 (d, $^{4}J_{C,P}$ = 2.6 Hz, qC-6), 148.4 (s, qC-4), 135.5 (d, $^{2}J_{C,P}$ = 3.1 Hz, C-8), 134.3 (dd, $^{2}J_{C,P}$ = 25.5 Hz, $^{3}J_{C,P}$ = 7.8 Hz, C-2), 122.1 (m, C-3, C-7), 31.6 (s, C-11/C-12), 30.9 (s, C-11/C-12), 26.2 (m, 2 × *i*Pr CH), 18.4 (m, 2 × *i*Pr CH_3), 18.0 (d, $^{2}J_{C,P}$ = 2.2 Hz, *i*Pr CH_3), 17.3 (m, *i*Pr CH_3). **^{31}P NMR** (121 MHz, $CDCl_3$): δ = 72.8 (dm, $^{1}J_{P,P}$ = 248 Hz, *i*Pr$_2$P), −128.8 (dd, $^{1}J_{P,P}$ = 248 Hz, $^{1}J_{P,H}$ = 216 Hz, PH). **^{31}P{^{1}H} NMR** (121 MHz, $CDCl_3$): δ = 72.8 (d, *i*Pr$_2$P), −128.8 (d, PH), $^{1}J_{P,P}$ = 248 Hz. **MS (ES+)** 301 (100) $[M - Cl]^+$.

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Keywords

phosphorus; arsenic; low co-ordinate; peri-substitution; base-stabilisation.

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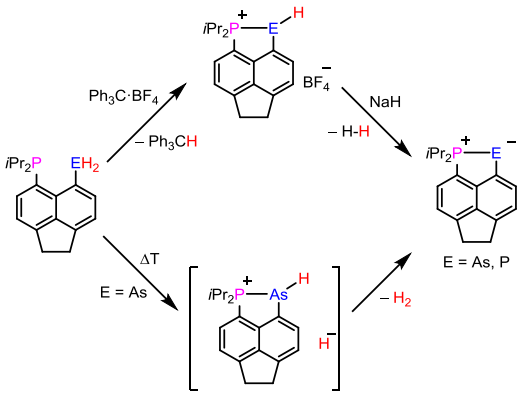

Key topic: dihydrogen elimination

Hydride abstraction from a primary phosphine/arsine affords the first examples of secondary phosphino/arsino-phosphonium salts. Subsequent deprotonation provides a novel and high yielding route to phosphine-stabilised phosphinidene/arsinidene. These investigations indirectly support ionic mechanism for the spontaneous dehydrogenation of the primary arsine.

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