Exploring the reactivity of donor-stabilised phosphenium cations: Lewis acid catalysed reduction of chlorophosphanes by silanes

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ABSTRACT: Phosphane-stabilised phosphenium cations react with silanes to effect either reduction to primary or secondary phosphanes, or formation of P-P bonded species depending upon counter-anion. This operates for in situ generated phosphenium cations, allowing catalytic reduction of P(III)-Cl bonds in the absence of strong reducing agents. Anion and substituent dependence studies have allowed insight into the competing mechanisms involved.

Introduction

Organophosphorus species find use as optoelectronic materials,[1] pharmaceuticals,[2] ligands,[3] and many other applications, and have historically been prepared primarily by reaction of organometallic nucleophiles with chlorophosphane electrophiles.[4] Complimentary routes have been developed exploiting phosphane reaction with electrophiles,[5] transition metal catalysed cross-coupling,[6] or hydrophosphination of unsaturated species.[7] These processes all rely on the presence of a P-H bond for later functionalisation but P-H species are not generally commercially available for any but the simplest derivatives. P-H species are accessible by reductive cleavage of P-C bonds using alkali metals (Na/NH_3 or Li/THF) followed by aqueous workup.[8] This approach shows poor functional group tolerance and selectivity in heteroleptic phosphanes, however, so is typically used only with simple, homoleptic phosphane precursors. It has been reported that P-Cl bonds may be reduced under milder conditions using Zn metal.[9] P-H species are instead typically synthesised by the milder reduction of phosphorus-halogen, phosphorus-oxygen, or phosphorus-nitrogen bonds using stoichiometric reduction by main group metal hydrides, with a single reference in the literature reporting Pd-catalysed reduction of P-Cl bonds under H_2;[10] P=O moieties are resistant to Pd catalysed hydrogenation.[11] Aluminium hydride reducing agents are effective at reducing a wide range of P-X bonds (X = halide, OR, O), with reductive coupling to form P-P bonds a common side reaction.[12] The most common such reagent, $LiAlH_4$, is pyrophoric and its use is made hazardous by the exothermic aqueous work-up which releases dihydrogen as a byproduct. Reductive coupling can be avoided by using the milder reagent DIBAL, but with a significant increase in cost and retention of the hazardous workup.[13] $NaBH_4$ has been reported to reduce secondary chlorophosphanes to directly form the protected secondary phosphane-borane adduct,[14,15] which may then be deprotected if required, but does not reduce other P-X bonds (X = OR, O).[16] Borane itself, BH_3, does not reduce P-Cl bonds, instead forming chlorophosphane-borane adducts which may then be cleanly reduced to P-H species with the protecting group intact.;[17,18] a mixture of $LiAlH_4$ and $NaBH_4$ may also be used to form phosphane-borane adducts, generating the required BH_3 in situ.[19]

Silanes have been extensively used as mild reducing agents, with and without catalysts, [20,21,22] for the reduction of P=O bonds to convert phosphane oxides to phosphanes, a reaction driven by the formation of strong Si-O bonds.[23] This has been used not just in phosphane synthesis, but to develop variations of the Wittig,[11] Mitsunobu[24] and Appel[25] reactions which are catalytic in phosphane. Investigation has shown at least two competing mechanisms for this process,[26,27] both of which rely on the nucleophilicity of the terminal oxygen to drive the reaction. For this reason, more Lewis acidic halosilanes (e.g. $HSiCl_3$, Si_2Cl_6, $PhSi(Cl)H_2$) are in general more effective reducing agents rather than the more hydridic species as might be expected.[28] Unhalogenated silanes therefore require extended reaction times and higher temperatures for less nucleophilic phosphine oxides.[25] These silanes are insufficiently reducing, however, to directly reduce P-Cl bonds due to the combined low nucleophilicity of the unactivated Si-H moiety and the reduced thermodynamic driving force of Si-Cl bond formation.

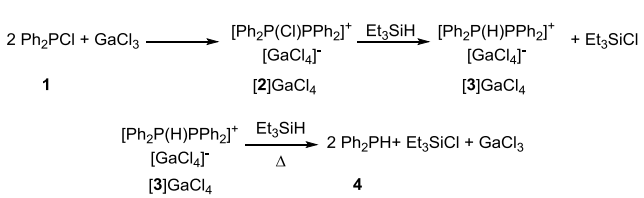
We reasoned that unactivated hydrosilanes should nevertheless react with a sufficiently electrophilic P(III) centre; Vidović[29] and Stephan[30] recently reported analogous reaction of P(III) dications with silanes. Whilst ligand exchange reactions about donor-stabilised phosphenium cations have been studied in the past,[31,32] and they have been investigated as ligands in transition metal complexes,[33,34] comparatively little is known about their other reactivity, in part due to their perceived instability and high Lewis acidity.[35]The principle exceptions to this are the N-heterocyclic phosphenium cations where chelation and nitrogen π-donor ligands stabilise the resultant cations to give catalytically useful species.[36,37,38] For phosphane-stabilised phosphenium cations, the empty p orbital on phosphorus is quenched by donation of a lone pair from a second phosphane. These species may also be regarded as phosphino-phosphonium species[39] but as they remain electrophilic at the three-coordinate phosphorus centre due to the low-lying and minimally hindered P-P σ* orbital, the phosphane-

phosphenium nomenclature is used herein as a better representation of the observed reactivity.

Results and Discussion

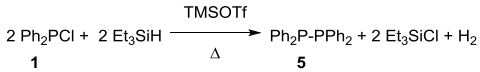
To our delight, on reaction of the known adduct of the weak donor ligand **1**, $[Ph_2(Cl)P\text{-}PPh_2]GaCl_4$,[**2**]$GaCl_4$,[39] with one equivalent of Et_3SiH in PhCl (Scheme 1), the ^{31}P NMR showed immediate P-H bond formation and, after heating at 60 °C for 1 hour, clean conversion to $[Ph_2(H)P\text{-}PPh_2]GaCl_4$, [**3**]$GaCl_4$ with transformation of Et_3SiH to Et_3SiCl. No immediate reaction was observed on addition of a second equivalent of Et_3SiH, but further heating at 60 °C overnight lead to almost complete conversion to Ph_2PH, **4**, with trace formation of $Ph_2P\text{-}PPh_2$, **5**; all Et_3SiH was converted to Et_3SiCl with $GaCl_3$ liberated overall. We subsequently tested the more stable $[Ph_3P\text{-}PPh_2]GaCl_4$[39] with Et_3SiH and, while this required 2 hours at 60 °C to go to completion, **4** and **5** were formed in 49:1 ratio. When **1** and Et_3SiH were reacted with 25 mol% $GaCl_3$ (i.e. a catalytic loading) in PhCl, immediate formation of [**3**]$GaCl_4$ was evident, and heating overnight at 100 °C gave complete conversion to **4**, implying catalytic behaviour.

Scheme 1: Successive hydride transfer from silane to phosphorus centre.



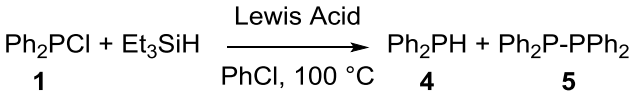
A range of Lewis acids, silanes, and halophosphanes were screened to probe the scope of this potentially useful catalytic reactivity. The Lewis acids were screened by reaction of **1** and Et_3SiH with an initial 25% loading of Lewis acid and heated for up to 7 days at 100 °C, with daily monitoring (Table 1). The exception to this was $FeCl_3$, for which a 5% loading was initially tested to avoid issues with paramagnetic broadening in the NMR. Of these results, $GaCl_3$ was found to be the optimal Lewis acid for P-H bond formation, giving essentially quantitative yields even at 5% catalyst loading. The use of Weakly Coordinating Anions (WCAs) resulted in very different reactivity from that observed for $GaCl_3$ and $AlCl_3$. Me_3SiOTf is an insufficiently strong halide abstraction agent to form [**2**]OTf but, reasoning that a small thermal population may be formed on heating, was nevertheless tested as a potential Lewis acid. Prolonged heating at 100 °C lead to clean conversion to a sharp singlet at δ-15.3 ppm, indicating the formation of $Ph_2P\text{-}PPh_2$, **5**, and growth of a peak at 4.5 ppm in the ^1H NMR corresponding to the formation of H_2, for an effective dehydrocoupling reaction (Scheme 2).

Scheme 2: Reductive coupling in the presence of TMSOTf, leading to overall dehydrocoupling



In comparison, at elevated temperatures both $NaBAr^F$ and $NaBAr^{Cl}$ (BAr^F= tetrakis(3,5-trifluoromethylphenyl)borate, BAr^{Cl}= tetrakis(3,5-dichlorophenyl)borate) give simultaneous dehydrocoupling and P-H bond formation, in direct contrast to the behaviour of OTf, coupled with anion decomposition, either by hydrodehalogenation(BAr^F) or protodeboronation (BAr^{Cl}). On heating at 100 °C, the BAr^F anion undergoes fluoride abstraction, leading to the formation of partially fluorinated phosphane centres and Et_3SiF, confirmed by ^{11}B, ^{19}F and ^{29}Si NMR, but no change in the final ^{11}B NMR spectrum is observed on addition of excess pyridine, indicating an absence of free 3° boron species. In contrast, the BAr^{Cl} system showed almost complete loss of signal intensity in the ^{11}B NMR, indicating protodeboronation and formation of BAr_3 species. Together, these confirm the presence of anion-dependent reaction mechanisms.

Table 1: Screening Lewis acids for catalytic efficacy



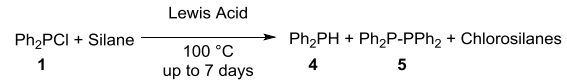
			Conversion[a]	
Lewis Acid	**Loading**	**Time**	**4**	**5**
$GaCl_3$	5%	7 days	> 99%	-
	10%	5 days	> 99%	-
	25%	1 day	> 99%	-
$AlCl_3$	25%	7 days	61 %	-
	100%	1 day	92 %	8%
$FeCl_3$	5%	7 days	-	7 %
TMSOTf	25%	5 days	-	82 %
	100 %	7 days	-	> 99%
$NaBAr^{F}$ [b]	25%	1 day	68 %	26 %
$NaBAr^{Cl}$ [b]	25%	1 day	62 %	38 %

[a]. NMR conversion by relative ^{31}P NMR intensity (see ESI for full details). [b]. Anion decomposition observed.

Having identified a suitable Lewis acid and loading, several commercially available silanes were screened as hydride donors (Table 2). At a 5% catalyst loading, Et_3SiH proved the most effective donor, but increasing the catalyst loading could be used to improve yield of **4** with other, cheaper silanes. For Et_3SiH to PHMS, the trend in reactivity follows that predicted by Mayr's nucleophilicity index,[40,41] but this trend is reversed for Ph_3SiH to $PhSiH_3$. This may indicate that the steric hindrance about Si is such that the assumptions about rate of reaction in Mayr's scale are not valid for the very hindered phosphenium electrophiles, as seen for other bulky electrophiles.[42]

Screening some simple aryl-alkyl and alkyl-alkyl chlorophosphanes revealed significant influence of steric bulk and electron donating substituents on reduction (Table 3). Surprisingly, Ph(^{t}Bu)PCl was reduced more efficiently than the less bulky Ph(^{n}Bu)PCl, which even after 7 days at 100 °C with an increased 25% catalyst loading showed only a complex, unresolved dynamic mixture in the ^{31}P NMR which is attributed to free and rapid exchange between the many diastereomeric possibilities of [Ph(^{n}Bu)(H)P-P(^{n}Bu)Ph]$^+$ and [Ph(^{n}Bu)P-P(^{n}Bu)Ph-P(^{n}Bu)Ph]$^+$.

Table 2: Screening silanes as hydride donors



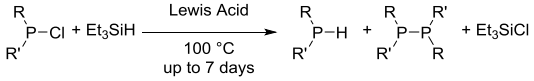
			Conversion[a]	
Silane	**Catalyst**	**Time**	**4**	**5**
Et_3SiH	$GaCl_3$ (5 %)	7 days	> 99%	-
$PhMe_2SiH$	$GaCl_3$ (5 %)	7 days	40%	34 %
	$AlCl_3$ (100 %)	5 days	87 %	13 %
$Me_2Si(H)$-O-$Si(H)Me_2$	$GaCl_3$ (5 %)	7 days	31 %	42 %
$Me_2Si(H)$-O-$Si(H)Me_2$	$GaCl_3$ (25 %)	7 days	97 %	-
PHMS	$GaCl_3$ (5 %)	7 days	20 %	32 %
	$AlCl_3$ (100 %)	7 days	85 %	12 %
Ph_3SiH	$GaCl_3$ (5 %)	7 days	19 %	18 %
Ph_2SiH_2	$GaCl_3$ (5 %)	7 days	51 %	26 %
$PhSiH_3$	$GaCl_3$ (5 %)	7 days	82 %	18 %

a. NMR conversion by relative ^{31}P NMR intensity.

Addition of excess base at this point caused the spectra to resolve to cleanly give exclusive formation of the rac- and meso- P-P coupled species, indicating that whilst transfer of the first hydride to form the protio-phosphane-stabilised phosphenium is easily achieved, the transfer of the second is not. Repetition at 50% $GaCl_3$ loading (i.e. preforming the halophosphane-phosphenium) did give a small yield of Ph(^{n}Bu)PH (see ESI) but the dimers remained the dominant product. To probe the influence of anion, the reduction of both Ph(^{t}Bu)PCl and Ph(^{n}Bu)PCl was repeated in the presence of 25 % TMSOTf, and the same phenomena were observed. The reduction of P-N and P-O bonds using a 5% loading of $GaCl_3$ does proceed but much more slowly and with unwanted side reactions. For the reduction of $Ph_2PN^iPr_2$, the consumption of Et_3SiH is coupled with the formation of Et_3SiCl rather than $Et_3SiN_iPr_2$, indicating consumption of the $GaCl_3$ and the formation of less Lewis acidic gallium amido species – this ultimately is not therefore a catalytic reaction, and a different mechanism may be in play, driven by the relative difference in Si-N vs Ga-N bond strengths. On reaction of Ph_2POEt with Et_3SiH in the presence of 5% $GaCl_3$, slow formation of 4 and 5 is observed, along with $Ph_2P(O)Et$ and Ph_2PEt and a number of unknown by-products, indicating simultaneous competing Arbuzov-type reactivity.

Reduction of primary dichlorophosphanes by Et_3SiH in the presence of catalytic Lewis acid is also achievable, with cyclic species and the rac- and meso-R(H)P-P(H)R products of incomplete reduction as side products; no R(Cl)P-P(Cl)R were observed. Use of a higher loading of Lewis acid leads to improved yield of primary phosphane and, as before, use of TMSOTf provides only reductive coupling products. PCl_3 reacts rapidly with effervescence and a marked exotherm on introduction of the $GaCl_3$ to produce a red precipitate, with PH_3 and P_4 the sole observable species in solution; the red solid was confirmed as a polymeric phosphorus species by chemical testing (see ESI for details). Given the stability of P-N bonds under these reaction conditions, we attempted the reduction of the heteroleptic species Ph(^{i}Pr$_2$N)PCl.Slow cyclisation was observed with a 5% $GaCl_3$ loading, but increasing the loading to 50% (i.e. preforming the phosphane-phosphenium) lead to rapid reaction at room temperature to form [(^{i}Pr$_2$N)Ph(H)-PPh(N^{i}Pr$_2$)]$^+$ as the dominant species with small quantities of rac- and meso-(^{i}Pr$_2$N(Ph)P)$_2$, and cyclic byproducts. On heating to 100 °C, however, the protio-phosphane-stabilised phosphenium decomposed into a complex mixture and no Ph(^{i}Pr$_2$N)PH was observed.

Table 3: Reduction of secondary P-Cl, P-O, and P-N bonds



			Conversion[a]	
Substrate	**Catalyst**	**Time**	**R_2PH**	**R_2P-PR_2**
Ph_2PCl	none	3 days	-	trace
Ph_2PCl	$GaCl_3$ (5 %)	7 days	> 99 %	-
Ph(^{n}Bu)PCl	$GaCl_3$ (25 %)	7 days	-	> 99%
Ph(^{n}Bu)PCl	$GaCl_3$ (50 %)	7 days	26 %	74 %
Ph(^{n}Bu)PCl	TMSOTf (25 %)	7 days	3 %	95 %
Ph(^{t}Bu)PCl	$GaCl_3$ (5 %)	7 days	84 %	16 %
Ph(^{t}Bu)PCl	TMSOTf (100 %)	9 days	23 %	34 %
^{t}Bu$_2$PCl	$GaCl_3$ (5 %)	7 days	66 %	-
^{t}Bu$_2$PCl	TMSOTf (25 %)	7 days	8 %	-
Ph_2POEt[b]	$GaCl_3$ (5 %)	7 days	3 %	10 %
$Ph_2PN^iPr_2$	$GaCl_3$ (5 %)	7 days	15 %	5 %

a. NMR conversions by relative ^{31}P NMR intensity. b. Other products observed. See ESI for details.

The potential utility of silane/Lewis acid reduction of chlorophosphanes to practical synthesis was explored by the reduction of **1** on a 2 mmol scale using $AlCl_3$ and PMHS as the reductive system. Following work-up with $Me_2S.BH_3$, the desired product, $Ph_2P(BH_3)H$, was isolated in unoptimised 59% yield. This augurs well for the potential future application of this reactivity, given the comparatively mild reaction conditions and cheap, easily handled reagents, but the yield remains low and reaction times long compared to other reductive approaches to this compound (e.g. $LiAlH_4$, $NaBH_4$). Additional work on optimisation of reaction conditions and Lewis acid are required before this can be considered a generally useful method for primary and secondary phosphane synthesis.

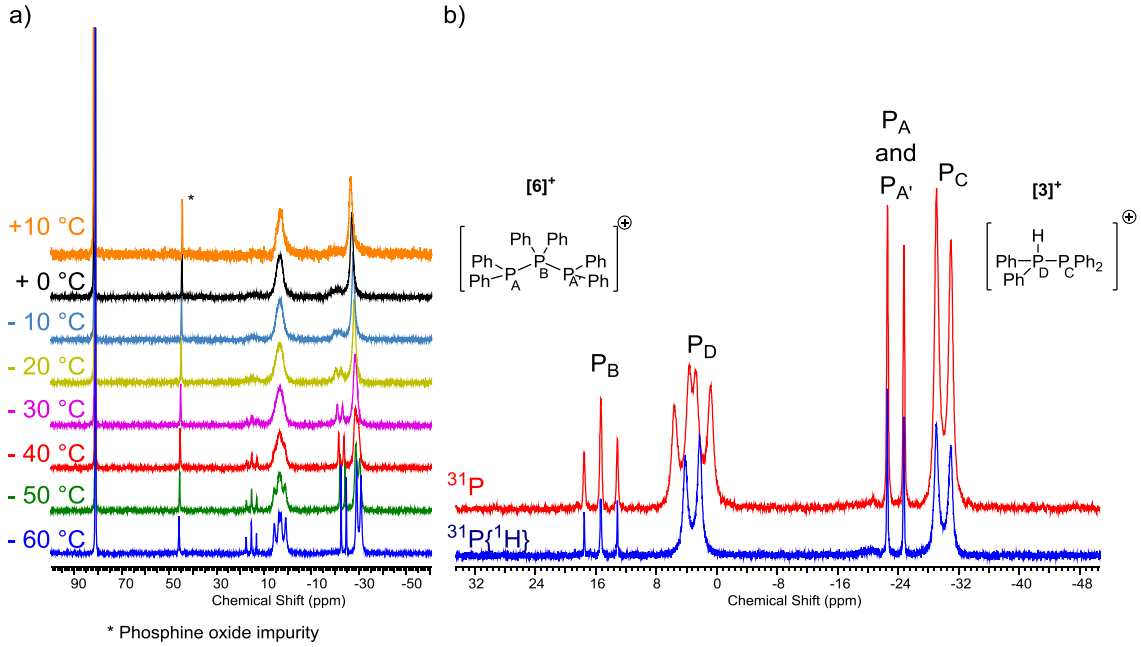
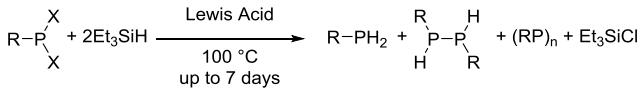


Figure 1 – Variable Temperature NMR Studies. a) VT studies on reaction mixture showing decoalescence on cooling. B) Comparison of ^{31}P and $^{31}P\{^{1}H\}$ NMR at -60 °C showing clean formation of [**3**]$^{+}$ and [**6**]$^{+}$



			Conversion[a]		
Substrate	**Catalyst**	**Time**	**RPH_2**	**R(H)P-P(H)R**	**$(RP)_n$[b]**
$PhPCl_2$	$GaCl_3$ (5 %)	7 days	65 %	23 %	10 %
$PhPCl_2$	TMSOTf (25 %)	7 days	-	-	86 %
$PhPCl_2$[c]	$NaBAr^{Cl}$ (100 %)	~ 5 minutes	42 %	13 %	45 %
$^{t}BuPCl_2$	$GaCl_3$ (5 %)	7 days	18 %	-	44 %
$^{t}BuPCl_2$	$GaCl_3$ (25 %)	7 days	30 %	8 %	62 %
PCl_3[c]	$GaCl_3$ (5 %)	~ 5 minutes	23 %	-	77 %

a. NMR conversions by relative ^{31}P NMR intensity. b. cyclic systems including $(RP)_4$, and larger rings. See ESI for details c. Proceeds at ambient temperature.

Table 4: Reduction of primary chlorophosphanes and PCl_3

Mechanistic Concerns

Given the dramatic influence on anion and substituents on reaction products, we sought a deeper understanding of the mechanisms involved. During reductions with substoichiometric Lewis acid, the ^{31}P NMR shows a number of broad product signals, indicative of multiple exchanging species. Reductions were performed with a 25% Lewis acid loading ($GaCl_3$ and TMSOTf) and heated at 60 °C to allow the reactions to proceed, after which variable temperature NMR studies were used to freeze out the exchange processes and identify the intermediates.

For the $GaCl_3$ catalysed reaction, on cooling to -30 °C the ^{31}P spectra resolve to show [**3**]$GaCl_4$ and the known adduct $[Ph_2P\text{-}P(Ph_2)\text{-}PPh_2]GaCl_4$, [**6**]$GaCl_4$,[43] as the exchanging species (see Figure 1); the TMSOTf reaction mixture does not fully resolve to show $^{1}J_{P\text{-}P}$ coupling even down to -70 °C but the unresolved peaks do correspond to those seen for $GaCl_3$, confirming the formation of phosphenium intermediates in this reaction, and that transient M-H bond formation is not required for Si-to-P hydride transfer.

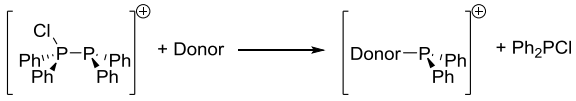
Given the difference in reactivity observed for the $[GaCl_4]^{-}$ and TfO^{-} salts, and the anion degradation observed when catalytic loadings of $NaBAr^{F}$ and $NaBAr^{Cl}$ were used to initiate reduction, we synthesised [**2**]BAr^{F} and [**2**]BAr^{Cl} to preform the phosphenium cation with a WCA. In both cases, on addition of Et_3SiH, formation of [**3**]$^{+}$ occurred rapidly at ambient temperature. Reaction stopped at that stage for the BAr^{F} salt, and [**3**]BAr^{F} was isolated in 60% yield as a colourless crystalline solid. Although [**3**][$B(C_6F_5)_4$] is known in the literature,[44] this is the first crystallographically characterised salt of this cation. The cation is disordered about an inversion centre, and the proton could not be located in the difference map, but the proton position can be assigned by comparison to calculated geometry (See ESI for details). The P-P bond length is short at 2.176 (3) Å, compared to that of [**2**]$GaCl_4$ and $[Ph_3P\text{-}PPh_2]OTf$ (2.205(4) Å[31] and 2.230 (1) Å[39] respectively) as expected with the reduction in steric demand. In contrast, the BAr^{Cl} salt continued to react, with slow formation of [**6**]BAr^{Cl} seen over 19 days. This was accompanied by loss of intensity in the ^{11}B spectrum. On addition of excess pyridine, a new signal formed at δ0.5 ppm in the ^{11}B NMR, indicating the formation of a four-coordinate boron species and thus that the protio-phosphane-stabilised phosphenium is sufficiently acidic to cause protodeboronation of the BAr^{Cl} anion even at ambient temperature.

Since ambient temperature reaction of the BAr^{Cl} salts with silanes leads to dehydrocoupling whilst **4** is observed when the reaction mixture is heated, a different mechanism is implicated. When a reaction in which BAr^{Cl} had thermally degraded

was recharged with **1** and Et_3SiH and further heated at 100 °C, preferential reduction to form **4** was observed (see ESI for details). Ingleson has shown that tris(3,5-dichlorophenyl)borane is a competent Lewis acid for activating silanes via FLP chemistry,[45] and it is therefore plausible that a borohydride intermediate is involved in this process. Similar behaviour is implicated in the $NaBAr^{Cl}$-induced reduction of $PhPCl_2$. When $PhPCl_2$ and Et_3SiH are premixed before $NaBAr^{Cl}$ addition, rapid reaction ensues giving $PhPH_2$ as the major product; addition of pyridine confirmed anion degradation and the formation of a py-Ar_3 species in situ.

The source of the hydride was confirmed to be the silane by isotopic labelling. Reaction of **1** with catalytic (25%) $GaCl_3$ in the presence of Et_3SiD gave clean formation of Ph_2PD and a 1:1:1 triplet in the ^{31}P NMR, ruling out solvent activation. An analogous experiment combining **1**, 25% Me_3SiOTf and 1:1 mixture of Et_3SiH and Et_3SiD on heating at 100 °C cleanly formed **5** in addition to H_2, HD and D_2 as seen in the ^1H and ^2H NMR, confirming hydrogen formation and overall dehydrocoupling. The necessity for phosphenium formation for reduction was confirmed by heating **1** with Et_3SiH at 100 °C in the absence of Lewis acid – no reduction was observed after 3 days. To rule out the possibility that $[GaCl_4]^-$ might be acting as a soluble Cl- source interacting with Et_3SiH to form a 5-coordinate activated silane, the combination of **1** and Et_3SiH were heated at 100 °C with 10 % $[BnNEt_3]Cl$ – after 7 days, 3% of the **1** had reacted to form **5** as the sole product. The observation of **6**$[GaCl_4]$ in the variable temperature studies indicated the formation of **5** as an intermediate, but this is not seen under equivalent catalyst loadings at higher temperatures, implying that reduction of the P-P bond may also occur under these conditions. A control reaction of **5** with 25% $GaCl_3$ and Et_3SiH showed that Lewis acid mediated cleavage of the P-P bond to form **4** does occur, but that it is slow (47% conversion after 3 days at 100 °C) relative to the formation of **4** from **1** (near quantitative conversion after 1 day at 100 °C), indicating that it is a minor pathway.

Table 5: Relative donor strengths of phosphanes as evaluated by donor exchange.

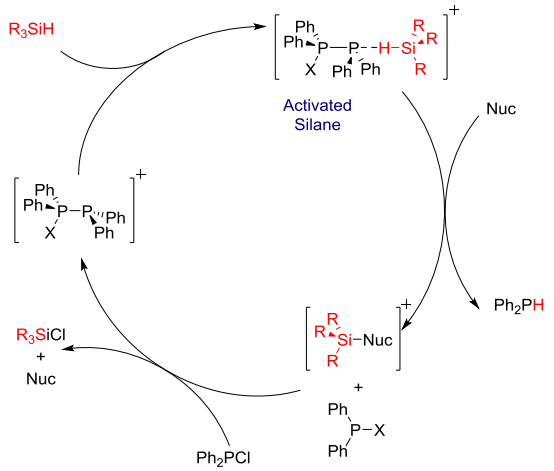


Donor	Relative Stability / kCalmol^{-1}
Ph_2PCl	0.00
Ph_2PH	-5.95
Ph_2P-PPh_2	-10.45
Ph_3P	-11.83
Ph(^{n}Bu)PCl	-0.74
Ph(^{n}Bu)PH	-8.50
Ph(^{t}Bu)PCl	-1.80
Ph(^{t}Bu)PH	-8.18
Ph(^{i}Pr$_2$N)PCl	-0.51
Ph(^{i}Pr$_2$N)PH	-10.91

All calculations were performed at the M06-2X/6-311g(d,p) level with PCM(Dichloromethane) solvent model. See ESI for details.

Both radical and Lewis acid hydride abstraction were considered as potential mechanisms of hydride transfer. However, as $^tBu_2P$-P^tBu_2 is a known species accessible via single electron reduction and is not formed under these reaction conditions, this argues strongly against a radical mechanism for P-P coupling in these species.[46] For all stoichiometric reactions, formation of protio-phosphane-stabilised phosphenium cations is rapid (minutes to hours at ambient temperature) whereas subsequent hydride transfer requires extended heating. Furthermore, the observation of $[\mathbf{2}]^+$ and $[\mathbf{3}]^+$, and $[\mathbf{3}]^+$ and $[\mathbf{6}]^+$ simultaneously, in conjunction with free **1**, giving well resolved signals in the ^{31}P NMR indicates that there is a significant increase in donor strength at each stage of the process. A quantitative assessment of relative donor strength was obtained by DFT evaluation of ligand exchange about $[\mathbf{2}]^+$ for a selection of relevant donors involved in the reactions observed, as shown in Table 5, where a more negative value indicates an increasingly stable adduct relative to $[\mathbf{2}]^+$. The results are in agreement with the experimental observation that Ph_3P displaces Ph_2PCl from $[\mathbf{2}]^+$,[39] and the qualitative observation that the rate of hydride transfer to phosphenium (of the order $[\mathbf{2}]^+ > [\mathbf{3}]^+ > [\mathbf{6}]^+ \approx [Ph_3P\text{-}PPh_2]^+$) correlates well with the calculated donor strengths of the phosphanes. Furthermore, it can be seen that in each instance the secondary phosphane is a stronger donor than the corresponding secondary chlorophosphane and that the alkyl-substituted phosphanes are stronger donors than diphenylphosphane derivatives. This may in part explain the increased formation of P-P coupled products in these cases as reduced electrophilicity at phosphorus favours competitive deprotonation instead.

Scheme 3: Proposed Catalytic Cycle for Halophosphane Reduction



From these results, it can be seen that anion participation is not required for the transfer of hydride from silane to phosphorus for the halo-phosphenium but that phosphenium stabilisation (or lack thereof) and thus Lewis acidity is important. We therefore propose a Piers-Oestreich type-transfer mechanism,[47,48] whereby the Si-H bond coordinates to the Lewis acidic site at phosphorus followed by attack of a donor centre (solvent, anion, or one of the many phosphanes in solution) generating a transient silylium cation intermediate. This silylium intermediate can then abstract a halide from another equivalent of chlorophosphane or tetrahalogallate, closing the catalytic cycle (Scheme 3). After formation of protio-phosphane-phosphenium, subsequent reaction could then either proceed via a second equivalent of silane reacting at P,

forming a second P-H bond, or reaction with a base to deprotonate the intermediate, forming a diphosphane. This step would appear to be strongly anion dependent. The proposed mechanism is likewise consistent with the less successful reduction of P-N and P-O bonds in the presence of Lewis acid and silane due to the reduced lability of these bonds relative to P-Cl systems, and with the decomposition of the BAr^F anion as $ArCF_3$ groups are known to react with silylium species.[49]

Conclusions

We have investigated the reactivity of phosphane-stabilised phosphenium cations with hydrosilanes and shown that they undergo facile hydride transfer to form protio-phosphane-stabilised phosphenium species. These can then further react through two, anion-dependent reaction pathways; deprotonation effects reductive concatenation with the formation of P-P bonds, whilst hydride transfer to the less electrophilic, protio-phosphane-stabilised phosphenium centre leads to primary or secondary phosphanes. These transformations can be made catalytic in Lewis acid, and can be extended using cheap Lewis acids and silanes potentially offering a mild, operationally simple reduction protocol without reactive M-H bonds. Further catalytic applications of these donor-stabilised phosphenium cations are currently under investigation.

ASSOCIATED CONTENT

Supporting Information.
Complete synthetic details, multinuclear NMR data, computational results and Cartesian coordinates of all optimised species are available in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data have been submitted to the Cambridge Crystallographic Database (Deposit number: 1846580).

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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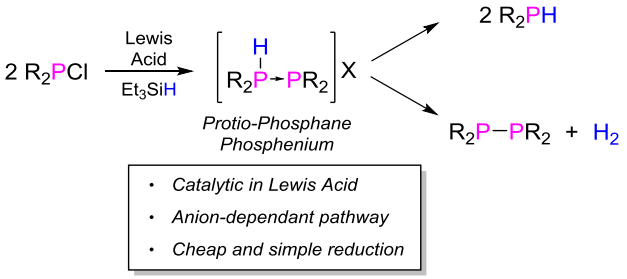

Phosphane-stabilised phosphenium cations react with hydrosilanes in an anion-dependent process leading either to secondary phosphanes, or reductive coupling to diphosphanes and liberation of H_2. Studies into the mechanism of the transformation are reported, and catalytic-in-Lewis-acid variants explored.